Long-term evolution of solid oxide fuel and electrolysis cell 3-D microstructure

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Solid oxide fuel cells (SOFC) are highly efficient electrochemical conversion devices for the production of electricity that combine fuel flexibility with low emissions of pollutants. The reverse operation in electrolysis mode (SOEC) allows storing electrical energy into fuels, such as hydrogen and synthetic methane. This technology is of particular interest nowadays, since the energy sector is undergoing profound transformations towards production from renewable sources. Increased system flexibility and availability is consequently needed to cope with the variability and uncertainty in both the supply and the demand. Despite the advantages provided by solid oxide cell (SOC) devices, improvement in their lifetime must be demonstrated for widespread market implementation, especially in electrolysis mode. The mitigation of the detrimental microstructural alterations upon long-term operation requires the understanding of the phenomena causing the changes and of the effects on the electrochemical performance. The standard electrodes fabrication procedure involves the sintering of randomly mixed powders, which results in an interconnected microstructure characterized by relatively high initial density of three phase boundaries (TPB) sites. However, this configuration is prone to significant rearrangement, due to material mobility at high temperature. Coarsening, interdiffusion and formation of secondary phases are commonly observed. Moreover, although the performance is known dependent upon the density of connected TPBs, the effects of the nearby morphology are yet to be clarified, as well as the dependence upon the operation mode. The objective of the present Thesis is to clarify and discern the causes of degradation induced by microstructural rearrangement in SOFC and SOEC modes. The study is therefore focused on two main areas of focus: (i) the characterization of the morphology near the TPB sites to investigate the surfaces available for diffusion and the effect on performance and (ii) microstructural evolution in the cell upon long-term operation, i.e., up to 15000 h, with the emphasis placed on the Ni-yttria-stabilized zirconia (YSZ) cermet and the interface between the gadolinia-doped ceria (GDC) compatibility layer and YSZ electrolyte. A set of quantification methods based on 3-D imaging was developed to improve the understanding of selected issues observed for these heterogeneous
Abstract

The time evolution analysis was performed on a series of samples imaged by focused ion beam-scanning electron microscopy (FIB-SEM) serial sectioning and extracted from stacks operated under different conditions and for varying operation times. The evolution of microstructural properties was tracked using existing and newly-developed algorithms, to advance the capability to describe quantitatively fine alterations of the microstructure. The focus was on measurements that directly relate to the expected driving forces for material alterations or electro-catalytic properties of the TPB sites, such as dihedral angle, curvature, estimate of the internal energy and the available length, a concept proposed within this Thesis for the characterization of surfaces available for diffusion near the electrochemical reaction sites.

The available lengths in two electrode microstructures produced by distinct manufacturing routes (Ni-YSZ and lanthanum strontium manganite (LSM-YSZ)) were investigated. The subset in Ni-YSZ and in particular in LSM-YSZ shorter than the extension of diffusion profiles reported in the literature was found non-negligible, indicating that the corresponding fraction of TPBs may be limited. The analysis was extended with an elementary kinetic numerical model, which accounts for heterogeneous chemistry and transport. It confirms that such limitation causes a flattening of the spatial distribution of surface coverages, hindering reaching the equilibrium at the limit of the domain. The study also suggests that the selection of the elementary steps is of importance, due to their impact on the diffusion gradients and because performance limitations depend principally on the coverage of the “active” species.

The analysis of the evolution of the Ni-YSZ microstructure after up to 15000 h of operation distinguished two regimes, which under the treated conditions are mainly related to the relocation of the Ni phase. The first one is as expected a rapid reduction of TPB density caused by the coarsening of the Ni phase driven by minimization of the mean curvature. The second one proceeds once Ni competitive growth is constrained by the YSZ phase. It is therefore subtler and more difficult to detect, but of high practical relevance for the long-term stability. The results indicate that the microstructural evolution indeed continues, even though significant concurrent modifications of the YSZ could not be ascertained. The minimization of the Ni/Pore interface proceeds further, together with the reduction of the spread of dihedral angle distributions. SOEC operation leads also to a specific evolution of the Ni-YSZ microstructure near the electrolyte, characterized by the migration of Ni towards the inner part of the electrode and a localized diminution of total and connected TPBs. The analysis of interfacial curvature and dihedral angles confirmed differences in the driving force observed during SOFC operation. The difference has been analyzed in the light of electrowetting, which relates alterations of Ni wettability to the magnitude and direction of polarization. It is a possible explanation, which is complicated to ascertain because of the difficulties in the measurements of dihedral angles. Lastly, accumulation of SrZrO$_3$ at the interface between the GDC barrier layer and the YSZ electrolyte is detected in all the 3-D reconstructed Volumes. Although the secondary phase is initially generated during the sintering process of the strontium-based electrode, the investigated dataset indicates a continuous accumulation at the interface during aging, which is more pronounced in SOEC mode.
The investigations and capabilities developed within this Thesis for the understanding of the relations between differences in the morphology and topology of heterogeneous microstructures and degradation mechanisms are expected relevant for supporting future improvements of the design and operation of solid oxide electrodes.

Keywords
Solid oxide cells, fuel cell, electrolysis, electro-catalytic sites, 3-D electron microscopy, degradation, surfaces available for diffusion, interfacial curvature.
Les piles à combustible à oxyde solide (SOFC), ou piles à oxyde solide, sont des dispositifs électrochimiques très efficaces pour la production d’énergie qui garantissent de faibles émissions de polluants et l’utilisation d’une grande variété de combustibles. L’opération inverse - électrolyse (SOEC) - permet de stocker de l’énergie électrique sous forme de combustibles, tels que l’hydrogène ou le méthane. Cette technologie présente aujourd’hui un intérêt particulier, car le secteur de l’énergie s’oriente progressivement vers une production accrue à partir de sources renouvelables. Une meilleure flexibilité du système est donc nécessaire pour faire face à la variabilité et à l’incertitude de la relation entre la demande et la consommation d’électricité. Malgré les nombreux avantages offerts par les cellules à oxyde solide (SOC), une amélioration générale de la durabilité doit être garantie pour permettre sa diffusion sur le marché, en particulier pour les applications d’électrolyse.

Afin d’atténuer les modifications préjudiciables de la microstructure survenant lors d’un fonctionnement sur le long terme, il est nécessaire de comprendre les causes spécifiques de la dégradation et les effets sur la performance électrochimique. Le procédé de fabrication des électrodes implique le frittage de poudres de différentes tailles préalablement mélangées, produisant une microstructure interconnectée initialement caractérisée par une densité élevée de sites de réaction électrochimiques (TPB). Cependant, cette microstructure est soumise à une altération importante due à la mobilité des matériaux causée par la température de fonctionnement élevée. Par conséquent, il est courant d’observer l’agglomérations des phases dans les matériaux hétérogènes, ainsi que la diffusion et la formation de phases secondaires au propriétés indésirables. De plus, les effets réels sur les performances électrochimiques dus à la morphologie des surfaces de contact et au mode opératoire restent à clarifier.

L’objectif de cette Thèse est l’étude des causes de dégradation induites par l’altération de la microstructure dans les modes SOFC et SOEC. Par conséquent, la présente étude se concentre sur deux domaines d’intérêt principaux : (i) la caractérisation des surfaces disponibles pour le transport des espèces chimiques près des sites de réaction électrochimiques et (ii) l’analyse de l’évolution de la
Résumé

La microstructure lors d’essais à long terme (jusqu’à 15000 heures), portant en particulier sur le cermet Ni-YSZ et sur l’interface YSZ/GDC. Afin de mieux comprendre les phénomènes de dégradation, l’analyse a été réalisée sur une série d’échantillons testés dans les deux modes de fonctionnement et pour différentes durées de fonctionnement. Les images 3-D ont été prises en utilisant la technique du faisceau ionique focalisé – microscopie électronique à balayage (FIB-SEM), puis reconstruites spécifiquement. L’évolution des propriétés de la microstructure a été caractérisée par une combinaison d’algorithmes existants et spécifiquement développés, afin de détecter quantifier de manière adéquate les altérations plus fines. L’accent a été mis sur les mesures concernant les mécanismes responsables des altérations des matériaux et des propriétés électro-catalytiques des sites de réaction électrochimiques, tels que les angles dièdres, la courbure des surfaces et l’énergie interne. En particulier, le concept de longueurs disponibles pour la diffusion a été développé et proposé dans cette Thèse.

L’extension de ces longueurs a été mesurée dans deux électrodes différentes (respectivement Ni-YSZ et LSM-YSZ). Les résultats obtenus (en particulier pour l’électrode LSM-YSZ) indiquent qu’une fraction non négligeable des longueurs est inférieure à l’extension des profils de diffusion rapportée dans la littérature. Par conséquent, les sites de réaction électrochimiques correspondants peuvent avoir des limitations de performances. L’analyse a été étendue à l’aide d’un modèle numérique de cinétique élémentaire, afin de décrire les réactions chimiques individuelles et le transport par diffusion des espèces adsorbées. Ces limitations entraînent un aplatissement général de la distribution spatiale des concentrations, générant des conditions qui dévient de l’équilibre sur tout le domaine de la longueur considérée. L’étude souligne également l’importance de la sélection de mécanismes électrochimiques élémentaires, en raison de leur impact sur les gradients de diffusion spécifiques et sur la concentration d’espèces considérées comme "actives". L’évolution de l’électrode Ni-YSZ après 15000 heures de fonctionnement comporte deux étapes distinctes, principalement dues au repositionnement de la phase métallique. Au cours de la première étape, une réduction rapide de la densité de sites de réaction électrochimique est provoquée par l’agglomération progressive du Ni et entraînée par la minimisation de la courbure moyenne d’interface. La seconde débute une fois la croissance compétitive de la phase nickel est contrainte par la phase céramique (YSZ). Bien que plus difficile à détecter, ce deuxième régime est d’intérêt fondamental pour la stabilité à long terme. Les résultats indiquent en effet comment l’évolution se poursuit tout au long de la durée des tests effectués, même s’il n’a pas été possible de détecter des altérations significatives de la phase YSZ. La minimisation de l’énergie associée à l’interface entre le Ni et la phase poreuse continue sans cesse, parallèlement à la réduction de l’amplitude des distributions des angles dièdres. Le fonctionnement en électrolyse provoque également une altération spécifique de la microstructure à l’interface avec l’électrolyte, caractérisée par la migration du Ni en direction de la partie interne de l’électrode et par une diminution localisée des sites de réaction électrochimiques. L’analyse de la courbure et des angles dièdres a confirmé que l’altération est due à une force non présente dans le mode pile à combustible. L’explication a été discutée sur la base de l’effet "électromouillage", qui décrit l’altération de la mouillabilité du nickel en fonction de la direction et de l’intensité de la
polarisation appliquée.
Enfin, l’accumulation de SrZrO$_3$ à l’interface entre l’électrolyte GDC et YSZ a été détectée dans
tous les échantillons analysés. Bien que la phase secondaire se soit formée pendant le frittage de
l’électrode à base de strontium, les volumes étudiés ont montré que l’accumulation se poursuit
pendant l’opération et est accentuée en mode électrolyse.
Les méthodes développées dans cette thèse constituent une avancée pour la quantification des
altérations morphologiques et topologiques fines de microstructures, et la compréhension des
mécanismes de dégradation, par conséquent pour le support du développement d’électrodes à
oxyde solide plus durables et performantes.

**Mots-clés**

Cellules à oxyde solide, piles à combustible, électrolyse, sites de réaction électrochimiques, micro-
scopie électronique 3-D, dégradation, surfaces disponibles par diffusion, courbure des surfaces.
Le solid oxide fuel cells (SOFC), o pile ad ossido solido, sono dispositivi elettrochimici altamente efficienti per la produzione energetica che garantiscono basse emissioni di agenti inquinanti ed l’utilizzo di un’ampia varietà di combustibili. L’operazione in modalità inversa - elettrolisi (SOEC) - consente di immagazzinare energia elettrica sotto forma di combustibili, come idrogeno e metano. Questa tecnologia è di particolare interesse al giorno d’oggi, dal momento che l’intero settore energetico si sta progressivamente indirizzando verso una maggiore produzione da fonti rinnovabili. Una migliore flessibilità del sistema è dunque richiesta per fronteggiare la variabilità e l’incertezza del rapporto fra domanda e consumo di energia elettrica. Nonostante i numerosi vantaggi offerti dalle pile ad ossido solido (SOC), un generale miglioramento della durabilità deve essere garantito per permetterne la diffusione nel mercato, specialmente in elettrolisi.

Per poter mitigare le dannose alterazioni della microstruttura che avvengono durante il funzionamento a lungo termine, è necessario comprendere le specifiche cause della degradazione e gli effetti sulla performance elettrochimica. Il processo di fabbricazione degli elettrodi prevede la sintetizzazione di polveri di diversa dimensione precedentemente mescolate, producendo una microstruttura interconnessa inizialmente caratterizzata da un’alta densità di siti di reazione elettrochimica (TPB). Tuttavia, tale microstruttura è soggetta ad una significativa alterazione a causa della mobilità dei materiali dovuta all’alta temperatura di funzionamento. Di conseguenza, è comune osservare la formazione di agglomerati di materiale, insieme all’interdiffusione e formazione di fasi secondarie. Inoltre, i reali effetti sulla performance elettrochimica dovuti alla morfologia delle superfici di contatto ed alla specifica modalità operativa devono ancora essere chiariti.

Questa Tesi pone come obiettivo l’investigazione delle le cause di degradazione indotte dall’alterazione della microstruttura in entrambe le modalità SOFC e SOEC. Pertanto, il presente studio si focalizza su due principali aree di interesse: (i) caratterizzazione dell’estensione delle superfici disponibili per la diffusione di specie chimiche in prossimità dei siti di reazione elettrochimica ed (ii) analisi dell’evoluzione della microstruttura in seguito a test di lunga durata (fino a 15000 ore),
Riassunto

focalizzandosi in particolare sul cermet Ni-YSZ e sull’interfaccia YSZ/GDC. Al fine di migliorare la comprensione dei fenomeni di degradazione, l’analisi è stata eseguita su una serie di campioni testati in entrambe le modalità d’operazione e per diversi tempi di funzionamento. Le immagini 3-D sono state prelevate tramite la tecnica a fascio ioni-co focalizzato (FIB-SEM) ed in seguito appositamente ricostruite. L’evoluzione delle proprietà della microstruttura è stata quindi caratterizzata tramite una combinazione di algoritmi esistenti ed appositamente sviluppati, per poter adeguatamente descrivere e quantificare le alterazioni più fini. L’attenzione è stata posta sulle misurazioni riguardanti i meccanismi che provocano le alterazioni dei materiali e delle proprietà elettro-catalitiche dei siti di reazione elettrochimica, come ad esempio angolo diedro, curvatura delle superfici ed energia interna. In particolare, il concetto di lunghezze disponibili per la diffusione è stato sviluppato e proposto nella presente Tesi.

L’estensione di tali lunghezze è stata misurata in due differenti elettrodi (rispettivamente Ni-YSZ e LSM-YSZ). I risultati ottenuti (in particolare per l’elettrodo LSM-YSZ) indicano come una frazione non trascurabile di tali lunghezze sia inferiore rispetto all’estensione dei profili di diffusione riportati in letteratura. Pertanto, i corrispondenti siti di reazione elettrochimica potrebbero presentare delle limitazioni nelle prestazioni. L’analisi è stata estesa utilizzando un modello numerico cinetico elementare, per poter descrivere le singole reazioni chimiche ed il trasporto per diffusione delle specie adsorbite. Tali limitazioni infatti provocano un generale appiattimento della distribuzione spaziale delle concentrazioni, ostacolando il raggiungimento dell’equilibrio sull’intero dominio della lunghezza considerata. Lo studio inoltre evidenzia l’importanza della selezione dei singoli meccanismi elettrochimici, a causa del loro impatto sugli specifici gradienti di diffusione e sulla concentrazione delle specie considerate “attive”.

L’evoluzione dell’elettrodo Ni-YSZ dopo 15000 ore di funzionamento è contraddistinta da due differenti stadi, causati principalmente dal riposizionamento della fase metallica. Durante il primo stadio si assiste ad una rapida riduzione della densità di siti di reazione elettrochimica, causata dalla progressiva agglomerazione del Ni e guidata dalla minimizzazione della curvatura superficiale media. Il secondo invece ha luogo dal momento in cui la crescita competitiva del nichel è vincolata dalla fase ceramica (YSZ). Sebbene risulti maggiormente difficile da rilevare, il secondo stadio assume un’elevata rilevanza per quanto riguarda la stabilità di lungo termine. I risultati infatti indicano come l’evoluzione continui durante l’intera durata dei test condotti, anche se non è stato possibile accertare significative alterazioni del YSZ. La diminuzione dell’interfaccia tra Ni e la fase porosa procede ulteriormente, insieme alla riduzione dell’ampiezza delle distribuzioni degli angoli diedri. L’operazione in elettrolisi provoca inoltre una specifica alterazione della microstruttura all’interfaccia con l’elettrolita, caratterizzata dalla migrazione del Ni verso la parte interna dell’elettrodo, ed a una diminuzione localizzata siti di reazione elettrochimica. L’analisi della curvatura e degli angoli diedri ha confermato come l’alterazione sia dovuta ad una forza agente che non è presente in modalità pila a combustibile. La spiegazione è stata discus in base all’effetto “electrowetting”, ovvero l’alterazione della bagnabilità del nichel dipenderebbe dalla direzione ed intensità della polarizzazione applicata.
Infine, l’accumulo di SrZrO$_3$ all’interfaccia tra GDC ed’elettrolita YSZ è stato rilevato in tutti i campioni analizzati. Sebbene la fase secondaria si formi durante il processo di sinterizzazione dell’elettrodo a base di stronzio, i volumi investigati hanno evidenziato come l’accumulo continui durante l’operazione e sia accentuato in elettrolisi.

I metodi sviluppati nella presente Tesi forniscono un utile strumento di quantificazione delle alterazioni morfologiche e topologiche, favorendo la comprensione dei meccanismi di degradazione e di conseguenza lo sviluppo di elettrodì ad ossidi solidi maggiormente duraturi e performanti.

**Parole chiave**
Celle ad ossidi solidi, celle a combustibile, elettrolisi, siti di reazione elettrochimica, microscopia elettronica 3-D, degradazione, superfici disponibili per diffusione, curvatura delle superfici.
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<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>ASR</td>
<td>area specific resistance</td>
</tr>
<tr>
<td>BOP</td>
<td>balance of plant</td>
</tr>
<tr>
<td>CHP</td>
<td>combined heat and power</td>
</tr>
<tr>
<td>EDM</td>
<td>electrical discharge machining</td>
</tr>
<tr>
<td>EDS</td>
<td>energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
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<tr>
<td>EsB</td>
<td>energy selective backscatter</td>
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<td>FE</td>
<td>finite-element</td>
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<td>FIB-SEM</td>
<td>focused ion beam-scanning electron microscopy</td>
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<td>FU</td>
<td>fuel utilization</td>
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<tr>
<td>GDC</td>
<td>gadolinia-doped ceria Gd$_2$O$_3$-CeO$_2$</td>
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<td>gas-diffusion layers</td>
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<td>interfacial shape distributions</td>
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<td>LHV</td>
<td>lower heating value</td>
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<tr>
<td>LSC</td>
<td>lanthanum strontium cobaltite La$<em>x$Sr$</em>{x-1}$CoO$_3$</td>
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<td>lanthanum strontium manganite La$<em>x$Sr$</em>{x-1}$MnO$_3$</td>
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<td>MEA</td>
<td>membrane electrode assembly</td>
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<td>MIC</td>
<td>metallic interconnectors</td>
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<td>MIEC</td>
<td>mixed ionic and electronic conductor</td>
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<td>orthogonal collocation of finite element</td>
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<td>pzC</td>
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<td>RU</td>
<td>repeating unit</td>
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<td>RWGS</td>
<td>reverse water gas shift</td>
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<td>SAED</td>
<td>selected area electron diffraction</td>
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<tr>
<td>TPB</td>
<td>three phase boundary</td>
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<tr>
<td>TSA</td>
<td>total surface area</td>
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<tr>
<td>UAV</td>
<td>unmanned aerial vehicles</td>
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<tr>
<td>WGS</td>
<td>water gas shift</td>
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<tr>
<td>YSZ</td>
<td>yttria-stabilized zirconia $\text{Y}_2\text{O}_3\cdot\text{ZrO}_2$</td>
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## Latin Letters

<table>
<thead>
<tr>
<th>Symbol</th>
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<td>$A_{ij}$</td>
<td>interfacial surface among each couple of particles</td>
<td>$\mu m^2$</td>
</tr>
<tr>
<td>$A_n$</td>
<td>Arrhenius pre-exponential coefficient</td>
<td>$cm^x mol^{-x} s^{-x}$</td>
</tr>
<tr>
<td>$C_D$</td>
<td>Stern double layer capacity</td>
<td>$F$</td>
</tr>
<tr>
<td>$C_H$</td>
<td>Helmholtz double layer capacity</td>
<td>$F$</td>
</tr>
<tr>
<td>$C_d$</td>
<td>Gouy-Chapman double layer capacity</td>
<td>$F$</td>
</tr>
<tr>
<td>$D_i^{diff}$</td>
<td>diffusion coefficient of surface species</td>
<td>$cm^2 s^{-1}$</td>
</tr>
<tr>
<td>$D_i^0$</td>
<td>Arrhenius pre-exponential coefficient for diffusion</td>
<td>$cm^2 s^{-1}$</td>
</tr>
<tr>
<td>$D$</td>
<td>dielectric constant</td>
<td>$F m^{-1}$</td>
</tr>
<tr>
<td>$E_{iact}$</td>
<td>activation energy</td>
<td>$kJ mol^{-1}$</td>
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<tr>
<td>$E_{int}$</td>
<td>interfacial specific energy</td>
<td>$J$</td>
</tr>
<tr>
<td>$F_H$</td>
<td>Helmholtz free energy</td>
<td>$J$</td>
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<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>$96487 C mol^{-1}$</td>
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<tr>
<td>$H_V$</td>
<td>total curvature per unit of volume</td>
<td>$m^{-1} m^{-3}$</td>
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<tr>
<td>$H$</td>
<td>mean curvature</td>
<td>$\mu m^{-1}$</td>
</tr>
<tr>
<td>$I$</td>
<td>current</td>
<td>$A$</td>
</tr>
<tr>
<td>$J^{diff}$</td>
<td>surface Fickian diffusive flux</td>
<td>$cm s^{-1}$</td>
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<tr>
<td>$K_{LSW}$</td>
<td>Lifshitz–Slyozov–Wagner constant</td>
<td>$s^{-1}$</td>
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<td>$K$</td>
<td>gaussian curvature</td>
<td>$\mu m^{-2}$</td>
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<tr>
<td>$L_A$</td>
<td>available length</td>
<td>$\mu m$</td>
</tr>
<tr>
<td>$M$</td>
<td>grain boundary mobility</td>
<td>$m^2 s^{-1} kg^{-1}$</td>
</tr>
<tr>
<td>$N_V$</td>
<td>number of grains per unit of volume</td>
<td>$m^{-3}$</td>
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<tr>
<td>$N_i$</td>
<td>number fraction of the solid phase</td>
<td>-</td>
</tr>
<tr>
<td>$N_{vox}$</td>
<td>number of neighboring voxels with different phase</td>
<td>-</td>
</tr>
<tr>
<td>$O^X_{O(YSZ)}$</td>
<td>oxygen on YSZ vacancy</td>
<td>-</td>
</tr>
<tr>
<td>$P_g$</td>
<td>driving pressure for grain growth</td>
<td>$Pa$</td>
</tr>
<tr>
<td>$P_Z$</td>
<td>pinning pressure</td>
<td>$Pa$</td>
</tr>
<tr>
<td>$Q_e$</td>
<td>charge density on the metal surface</td>
<td>$cm^{-2}$</td>
</tr>
<tr>
<td>$R_{pol}$</td>
<td>polarization resistance</td>
<td>$ohm$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td>Units</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
<td>------</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
<td>$8.314 J mol^{-1}K^{-1}$</td>
</tr>
<tr>
<td>$S_{AV}$</td>
<td>total surface per unit of volume</td>
<td>$m^2 m^{-3}$</td>
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<tr>
<td>$S_{ij}$</td>
<td>estimated specific surface of the spherical particles</td>
<td>$\mu m^2$</td>
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<tr>
<td>$S_{V}$</td>
<td>surface-to-volume ratio</td>
<td>$\mu m^2 \mu m^{-3}$</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>$K$</td>
</tr>
<tr>
<td>$U_{Nernst}$</td>
<td>Nernst potential</td>
<td>$V$</td>
</tr>
<tr>
<td>$U_{losses}$</td>
<td>polarization losses</td>
<td>$V$</td>
</tr>
<tr>
<td>$U_{el,eq}$</td>
<td>equilibrium potential</td>
<td>$V$</td>
</tr>
<tr>
<td>$U_{el}$</td>
<td>potential difference between electrode and electrolyte</td>
<td>$V$</td>
</tr>
<tr>
<td>$U_{op}$</td>
<td>operating voltage</td>
<td>$V$</td>
</tr>
<tr>
<td>$U_{tn}$</td>
<td>thermoneutral voltage</td>
<td>$V$</td>
</tr>
<tr>
<td>$V_{m}$</td>
<td>molar volume</td>
<td>$m^3 mol^{-1}$</td>
</tr>
<tr>
<td>$V_{O(YSZ)}$</td>
<td>oxygen vacancies on YSZ</td>
<td>-</td>
</tr>
<tr>
<td>$W(r_i)$</td>
<td>fraction of phase volume associated to each discrete distribution bin of ray length</td>
<td>-</td>
</tr>
<tr>
<td>$Z_C$</td>
<td>propensity for mean curvature decrease</td>
<td>$\mu m^{-1}$</td>
</tr>
<tr>
<td>$Z_{PSD}$</td>
<td>propensity of particles’ growth</td>
<td>$\mu m^{-1}$</td>
</tr>
<tr>
<td>$Z_{E}$</td>
<td>Zener factor</td>
<td>$\mu m^{-1}$</td>
</tr>
<tr>
<td>$Z_{ii}$</td>
<td>intra-phase coordination number</td>
<td>-</td>
</tr>
<tr>
<td>$Z_{ij}$</td>
<td>inter-phase coordination number</td>
<td>-</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>coordination number for the solid phase</td>
<td>-</td>
</tr>
<tr>
<td>$\bar{Z}$</td>
<td>average coordination number of all solid particles</td>
<td>-</td>
</tr>
<tr>
<td>$(Z_r)$</td>
<td>surface Zr sites on YSZ</td>
<td>-</td>
</tr>
<tr>
<td>$a$</td>
<td>activity</td>
<td>-</td>
</tr>
<tr>
<td>$b$</td>
<td>elementary number of charges</td>
<td>-</td>
</tr>
<tr>
<td>$c_i$</td>
<td>surface species concentration</td>
<td>$mol cm^{-2}$</td>
</tr>
<tr>
<td>$c_q$</td>
<td>charges concentration in the diffuse double layer</td>
<td>$cm^{-3}$</td>
</tr>
<tr>
<td>$d_50$</td>
<td>median phase size diameter</td>
<td>$\mu m$</td>
</tr>
<tr>
<td>$d$</td>
<td>distance between points</td>
<td>voxel</td>
</tr>
<tr>
<td>$e$</td>
<td>electron</td>
<td>-</td>
</tr>
<tr>
<td>$f_{i,t}$</td>
<td>Cartesian coordinate of point $i$ over axis $t$</td>
<td>-</td>
</tr>
<tr>
<td>$g(t)$</td>
<td>number of particles per unit volume at time $t$</td>
<td>$m^{-3}$</td>
</tr>
<tr>
<td>$i$</td>
<td>current density</td>
<td>$A cm^{-2}$</td>
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<tr>
<td>$k_{fr}$</td>
<td>forward and backward kinetic constants</td>
<td>$cm^2 mol^{-x} s^{-x}$</td>
</tr>
<tr>
<td>$l_{TPB}$</td>
<td>area-specific TPB line</td>
<td>$m^{-1}$</td>
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<tr>
<td>$l_{vox}$</td>
<td>voxel size</td>
<td>$nm$</td>
</tr>
<tr>
<td>$n_i^V$</td>
<td>number of particles per unit volume</td>
<td>$\mu m^3$</td>
</tr>
<tr>
<td>$P_{tot}$</td>
<td>total pressure</td>
<td>$atm$</td>
</tr>
<tr>
<td>$q_n$</td>
<td>net production rate of surface species at the TPB</td>
<td>$mol cm^{-1} s^{-1}$</td>
</tr>
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### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{Cr}$</td>
<td>critical radius at which the grain neither grows nor shrinks</td>
<td>$\mu m$</td>
</tr>
<tr>
<td>$r_C$</td>
<td>critical maximum grain radius</td>
<td>$\mu m$</td>
</tr>
<tr>
<td>$r_i$</td>
<td>radius of the particle or phase</td>
<td>$\mu m$</td>
</tr>
<tr>
<td>$\dot{s}_i$</td>
<td>chemical reactions source term</td>
<td>$mol \ cm^{-2} \ s^{-1}$</td>
</tr>
<tr>
<td>$P_n$</td>
<td>sticking probability</td>
<td>-</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>$s$</td>
</tr>
<tr>
<td>$w_n$</td>
<td>molecular weight</td>
<td>$g \ mol^{-1}$</td>
</tr>
<tr>
<td>$z$</td>
<td>number of electrons involved in the electrochemical reaction</td>
<td>-</td>
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</tbody>
</table>

### Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G^0_R$</td>
<td>Standard Gibbs energy of reaction</td>
<td>$J \ mol^{-1}$</td>
</tr>
<tr>
<td>$\Delta G_R$</td>
<td>Gibbs energy of reaction</td>
<td>$J \ mol^{-1}$</td>
</tr>
<tr>
<td>$\Delta H_R$</td>
<td>enthalpy of reaction</td>
<td>$J \ mol^{-1}$</td>
</tr>
<tr>
<td>$\Gamma_i$</td>
<td>total number of active surface sites</td>
<td>$mol \ cm^{-2}$</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>volume-weighted sphericity</td>
<td>-</td>
</tr>
<tr>
<td>$\Theta_i$</td>
<td>surface coverage</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_{a/c}$</td>
<td>symmetry anodic and cathodic coefficients of the charge transfer mechanism</td>
<td>-</td>
</tr>
<tr>
<td>$(\xi)$</td>
<td>surface $\chi$ sites on YSZ</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$</td>
<td>dimensionless concentration</td>
<td>-</td>
</tr>
<tr>
<td>$\epsilon_{el}$</td>
<td>electrical efficiency</td>
<td>-</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>applied potential at the interface between electrode and electrolyte</td>
<td>$V$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>overpotential</td>
<td>$V$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>interfacial surface energy</td>
<td>$Jm^{-2}$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>curvature</td>
<td>$\mu m^{-1}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>chemical potential</td>
<td>$V$</td>
</tr>
<tr>
<td>$\nu_i$</td>
<td>stoichiometric factor of the reaction</td>
<td>-</td>
</tr>
<tr>
<td>$\omega$</td>
<td>coefficient in Appendix D</td>
<td>-</td>
</tr>
<tr>
<td>$\phi_i$</td>
<td>volume fraction</td>
<td>-</td>
</tr>
<tr>
<td>$\psi_i$</td>
<td>solid volume fraction</td>
<td>-</td>
</tr>
<tr>
<td>$\rho$</td>
<td>structural gradient</td>
<td>$m$</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>number of surface sites occupied by each molecule</td>
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</tr>
<tr>
<td>$\tau$</td>
<td>coefficient in Appendix D</td>
<td>-</td>
</tr>
<tr>
<td>$\theta$</td>
<td>dihedral angle</td>
<td>°</td>
</tr>
<tr>
<td>$\upsilon$</td>
<td>coefficient in Appendix D</td>
<td>-</td>
</tr>
<tr>
<td>$\xi$</td>
<td>dimensionless coefficient</td>
<td>-</td>
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</table>
Introduction

Context

The nations and global organizations dealing with energetic and environmental problems agree that CO$_2$ emissions from human activities are a fundamental contribution to the climate change. As ratified during the “Paris Agreement” in 2016 [27], the goal is to limit the average temperature increase to 1.5 °C above pre-industrial period levels, which is considered a threshold to significantly alleviate the risks and impacts of climate change. For this reason, the reduction of greenhouse gas emissions is one of the most important challenges that a large share of the nations is trying to face.

Nevertheless, such agreement has to contend with the prediction of the U.S. Energy Information Administration, which forecasts that the world energy consumption will rise by 28% between 2015 and 2040 [28]. As also mentioned in the World Energy Outlook by the IEA in 2017 [29], the share of renewables will reach 40% of the total power generation, capturing two-thirds of the global investments in the realization of new power plants. However, the growing energy consumption will still be mainly covered from fossil fuels, accounting for 77% of the energy use by 2040. This implies that global carbon emissions are set to keep rising, from 33.9 billion metric tons in 2015 to 39.3 in 2040.

Oil and gas prices will likely be key factors, while the spread of renewable technologies (such as solar photovoltaics) and the electrification of the transportation will be mainly led by China and India, which will ultimately influence the contributions to the total energy production. In this regard, the implementation of policies will continue to support the production and the adoption of renewable electricity worldwide through competitive auctions and carbon taxes.

A limitation in the carbon emissions can be achieved by combining electricity generation with increased efficiency compared to traditional solutions with a sturdy spread of renewables. In this regard, the most common renewable sources such as wind and solar are intermittent in their nature, presenting challenges concerning the energy storage and the network load balance. Energy systems
will most likely face a radical transition from load-following production to production-following consumption. In this context, the power-to-gas concept has gained significant attention in recent years, to convert the excess electrical power into fuel to store electrical power for long periods of time and with very low energy losses [30]. It ultimately allows a better regulation of both short term and seasonal storages, ensuring higher flexibility and responsiveness of the whole energy system and lower congestion of the power transmission grid. In this framework, a replacement of the petroleum-based hydrocarbons with CO$_2$-recycled synthetic liquid fuels would improve the sustainability of transportation, representing a valid complement to the electrification of vehicles [31]. In particular, carbon dioxide can be separated from the outlet exhaust gases of traditional power plants and dissociated afterwards with water using renewable or nuclear energy. This strategy would allow a step towards a neutral carbon emission while maintaining the existing infrastructure of vehicles and fuel distributors.

Given the above-mentioned prospects, high temperature solid oxide cells solid oxide cells (SOC) provide concrete and viable solutions. This technology guarantees superior electrical efficiency, fuel flexibility and the possibility of reversible operation as a power production device (fuel cell mode - SOFC) as well as hydrogen or syngas generator (electrolysis mode - SOEC).

The fuel cell market has been increasing steadily in recent years. In particular SOFC shipments raised by about 50% every year, with 24 MW shipped in 2017 (in total 55.9 MW from 2013 to 2017) [32]. The global installed SOFC capacity reached 76.4 MW in 2017, accounting for 11.4% of the total fuel cell market. The growth is driven by the higher demand of combined heat and power CHP units in Europe and the Japanese Ene-Farm deployment project [33]. In addition, portable and unmanned aerial vehicle unmanned aerial vehicles (UAV) applications in the military sector have contributed to the increase of the demand. The SOEC market is in comparison nascent, partly because stack durability and lifetime have to be improved to reach a large-scale commercial distribution.
Intermediate-temperature solid oxide cells

Basic principles

Intermediate-temperature solid oxide cells are electrochemical conversion devices composed by two electrodes separated by an electrolyte that operate in a range of temperatures between 700°C and 850°C. This provides an intrinsic thermodynamic advantage with respect to lower temperature fuel cell technologies by ensuring faster electrochemical kinetics and improving the electrical conversion efficiency.

In fuel cell mode, the electrochemical device converts the chemical energy in the fuel into electrical power and heat. \( \text{H}_2 \) or CO molecules are directly oxidized by the oxygen ions from the electrolyte, forming \( \text{H}_2\text{O}/\text{CO}_2 \) and releasing electrons. The electrolysis mode instead offers an alternative method to store electrical energy into chemical fuels with high energy density. The operating conditions are the opposite, with \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) molecules reduced forming \( \text{H}_2 \) and CO. The outlet gases can then be converted into synthetic natural gas or liquid fuels through technologically mature systems such as methanol and Fisher-Tropsch synthesis [34]. In the latter case, oxygen or enriched air can be an added value [35], while fuel cell operation requires oxidant consumption. Results on hydrogen production by SOEC were reported more than three decades ago [36] but the interest on this research topic has increased drastically during the last ten years, triggered by the knowledge from SOFC research and the growing need for novel and efficient energy storage solutions. A representation of the two operating modes is displayed in Fig. 2.

The electrochemical reactions involve gas species, ions and electrons. These reaction sites are therefore the triple phase boundaries (TPB) in heterogeneous materials, which in a cermet are
Introduction

Figure 2 – Working principles of fuel cell and electrolysis operation modes in the case of H₂/H₂O reactions. The four visible layers are the fuel electrode, the electrolyte, a compatibility layer and the oxygen electrode (respectively from left to right).

Located at the junctions of the ceramic, the metallic and the pore phases. As indicated by the red points in the schematic in Fig. 3A, the three phase boundarys (TPBs) define the zones where the gas species are consumed and generated, and the oxygen ions and electrons are transported. The effective electro-catalytic properties of the TPBs are therefore key for the performance. A limiting case occurs when the TPB does not have connection with the exterior throughout one of the three phases, which results in an isolated and thus inactive TPB (points represented with the light blue color). Since the transport of the oxygen ions in ceramic materials is the dominant contribution to the ohmic losses, the electrochemically-active TPBs are close to the electrolyte, where the transport distance for ions is smaller. In state-of-the-art SOC electrode microstructure, the TPB are 3-D lines that are the focus of several chapters in the thesis.

Eqs. 1-2 are the two half reactions in the case of H₂O/H₂, while Eq. 3 is the total reaction. The direction of the arrows defines the operation mode (fuel cell toward the right, electrolysis toward the left). Similarly, the oxidation of CO and the reduction of CO₂ can also take place when hydrocarbons are present at the fuel inlet, as shown by Eq. 4.

\[ \text{H}_2 (\text{gas}) + \text{O}^{--} \Leftrightarrow \text{H}_2\text{O} (\text{gas}) + 2\text{e}^- + \text{e} \]  

\[ \frac{1}{2}\text{O}_2 (\text{gas}) + 2\text{e}^- \Leftrightarrow \text{O}^{--} \]  

\[ \frac{1}{2}\text{O}_2 (\text{gas}) + \text{H}_2 (\text{gas}) \Leftrightarrow \text{H}_2\text{O} (\text{gas}) + 2\text{e}^- \]  

\[ \text{CO} (\text{gas}) + \text{O}^{--} \Leftrightarrow \text{CO}_2 (\text{gas}) + 2\text{e}^- \]
Because of the inverse direction of the electronic current, the two operation modes also differ in terms of heat generation, with implications for the thermal management of the device: contrarily to the exothermic fuel cell situation, the splitting of the water (or CO₂) molecules requires electrical and thermal energy, making the electrolysis an endothermic process. As described by Fig. 4, the heat generated by the ohmic losses is equivalent in the two cases and essentially scales with the square of the current density. The sum of this term with the heat of reaction provides the net heat source term, which in the fuel cell case is always positive and therefore has to be removed from the system. Excess air is therefore usually required for thermal management. On the other hand, in electrolysis the heat flux is negative in the range between the open circuit voltage point (OCV) the so-called thermal neutral voltage ($U_{tn}$), where the internal losses equal the heat of the reaction. In fact, by increasing the current density, the heat generated by ohmic losses progressively compensates that required by the reaction. This heat can be provided from high temperature sources, such as nuclear or concentrated solar. It is worth mentioning that the electrical efficiency in SOEC mode can exceed 100% when the operating voltage ($U_{op}$) is lower than the thermoneutral [2], as visible in Eq. 5. Typical values of the thermoneutral voltage for steam and CO₂ electrolysis at 800°C are respectively 1.29 V and 1.45 V, and they slightly rise with temperature. For larger values of operating voltage, the ohmic losses cover the totality of the required thermal energy and consequently the electrical efficiency is inferior to 100%.

\[
\epsilon_{el(SOEC)} = \frac{\Delta H_R}{2R} \frac{1}{U_{op}} = \frac{U_{tn}}{U_{op}}
\]
Introduction

On the other hand, in SOFC mode, the electrical efficiency is the ratio between the electrical power produced and the chemical energy consumed, and it is practically in the range of 50%-70% based on the lower heating value (LHV) [37]. Operating with CH$_4$ results in higher electrical efficiency with respect to pure H$_2$, because of the inferior entropy losses. In particular, the maximum thermodynamic efficiency is defined as the ratio between the total Gibbs free energy $\Delta G_R$ and the enthalpy of reaction $\Delta H_R$ (for the CH$_4$ and H$_2$ reactions, thermodynamic efficiency is approximately 100% and 80%, based on the LHV at 800°C [38]). Such yields exceed the performance of traditional power production systems, even large scale ones, since the electrochemical conversion is not restricted by the thermodynamic limitations of the Carnot cycle. For the same reason, the SOC technology releases less polluting and particle emissions, since there is no direct combustion.

The facilitated kinetics at high temperature provides flexibility in terms of catalyst materials and fuels, which allows operation with different hydrocarbons as fuel feed [39]. Ni is commonly used as an electro-catalyst for hydrogen conversion in the fuel electrode. When methane is the fuel in SOFC mode, the production of H$_2$ is promoted by the steam reforming (SR) reactions and the water gas shift (WGS). Although the oxidation of carbon monoxide is possible, under the operation conditions of practical interest for power production, it is mainly indirectly converted through the WGS reactions.

In SOEC mode, CO$_2$ electrolysis can however occur in the case of mixed inlet compositions, even if the reduction of steam usually dominates, because the two reactions have similar total enthalpy of

Figure 4 – Comparison of the thermal contributions in fuel cell and electrolysis. Image from [2].
Intermediate-temperature solid oxide cells

reaction (approximately 250 k J/mol for H₂O electrolysis vs 280 k J/mol for CO₂ electrolysis at 800°C [40]). Furthermore, the reverse water gas shift (RWGS) reaction (Eq. 6) is shifted toward H₂ and CO₂ consumption and H₂O and CO production at temperatures higher than 700°C [41]. Compared to the single electrolysis of H₂O or CO₂, co-electrolysis is therefore more complex since the CO production can occur simultaneously via chemical and electrochemical reactions. This solution however allows to perform the conversion reactions in a single device, without the need for an external RWGS reactor. According to the study by S. Kim et al [42], CO₂ reduction is dominated by the RWGS reaction, which is the predominant conversion pathway at temperatures higher than 800°C and at high CO₂ concentrations. Among the two electrochemical conversion mechanisms, the authors concluded that steam is the dominant reactant in co-electrolysis, tentatively attributed to the lower activation energy.

\[
CO₂_{(gas)} + H₂_{(gas)} \rightleftharpoons CO_{(gas)} + H₂O_{(gas)} \quad (6)
\]

A SOC can in principle operate in both SOFC and SOEC modes due to the reversibility of the electrochemical reactions. The main practical difficulty is the design of the system balance of plant, since the requirements on the auxiliary components differ for each functioning mode. For instance, in electrolysis an evaporator is needed in all cases to heat-up the steam, while in SOFC mode a pre-reformer may be needed.

Polarization losses

The Nernst potential \( U_{Nernst} \) corresponds to the reversible potential at open-circuit. The expression is the ratio between the total Gibbs free energy of the reaction and the product of the Faraday constant \( F \) and the number of exchanged electrons \( z \) (Eq. 7). In the case of a H₂/H₂O binary gas mixture, the expression can be recast in terms of the activity of each gas species \( a \), \( \Delta G_R^0 \) is the standard Gibbs free energy and \( R \) the universal gas constant.

\[
U_{Nernst} = \frac{\Delta G_R}{zF} = \frac{\Delta G_R^0}{2F} + RT \log \frac{a_{H₂O}}{a_{H₂}a_{O₂}^{0.5}} \quad (7)
\]

Given the dependence to the activities of the gas species, the fuel molar fraction and total pressure affect the value of the Nernst potential. It varies over the active area of a cell under current, because the gas compositions change from the inlet to outlet of the gas stream induced by the consumption of reactants and generation of reaction products. When current is applied, the potential varies from the OCV value, increasing in SOEC mode while decreasing in SOFC mode. This variation is associated to several losses, which depend on the selected cell materials (composition and morphology), design
configuration and operation conditions.

The values of the measured potential under polarization is commonly estimated as the difference between the Nernst potential (or OCV) and the sum of the losses $U_{losses}$, which are commonly classified into three main categories as explained hereafter.

$$U_{op}(i) = U_{Nernst} - \sum U_{losses}$$ (8)

- **Activation** losses relate to charge transfer at the TPBs, and they depend on the excess energy required to overcome the rate-limiting reaction steps. As covered in 4, these losses can be described in multiple ways with differing degrees of complexity. The Butler-Volmer formalism is the most common.

- **Ohmic** losses arise from the resistance to the transport of ions and electrons. It is in most cases dominated by ion conduction in the electrolyte, hence the need for reduction of its thickness. Because most SOC materials have comparatively high electron conductivity, the potential losses can become significant in the case of loss of percolation or long transverse current paths because of the design of the interconnection system. However, significant losses can also occur at the interfaces of the various layers, where oxide scales or secondary phases might grow, as is the case for instance with metallic interconnectors (MIC).

- **Concentration**: under polarization, a gradient in composition develops throughout the thickness of the porous electrode, because of the concurrent generation and consumption of gas species at the TPBs. Thus, the gas concentration in the gas channel differs from that in the active zone next to the electrolyte. The consequent difference in potential from the theoretical values estimated based on gas channel composition is commonly referred to as concentration overpotential. It is a useful concept to compare electrode performance, even though it does not correspond to a physical voltage drop. Gas phase transport results in a limiting current density under high current, even under negligible fuel depletion in the channel. It is further relevant for practical applications under mild overpotential where operation at high conversion is usually sought. The multi-component diffusion problem inside the porous media is usually described by Fick’s or dusty-gas models. Both mass transport equations account for the Knudsen diffusion, molecular diffusion and the effect of a finite pressure gradient [43].

Even if the Nernst potential varies locally over the cell under polarization, the operation potential is practically considered uniform in most planar designs, because an equipotential develops in the metallic interconnects, because of its very high in-plane electronic conductivity.
SOC materials

Solid oxide cell are multilayers of materials with contrast in their electrochemical, thermal and mechanical properties. The high temperature of operation requires the use of ceramic materials for stability reasons. Besides electro-catalytic and transport properties, chemical compatibility and stability in oxidizing and/or reducing atmospheres, attention must be placed on the minimization of the mismatches in thermal expansion as well, because of their brittleness, the high sintering temperature and joints with the other stack components, i.e., MIC and gas-diffusion layers (GDL). Therefore, compared to other technologies, improper material selection, stack design and operation can exacerbate dramatically the vulnerability of SOCs to thermal cycling and load following. The latter is theoretically limited by the electrochemistry or residence times, rather than the thermal response, which is a potential future advantage of the technology.

Fuel electrode

The main functions of the solid oxide fuel electrode are to provide sites available for the electrochemical reaction together with gas, ions and electron transport, from the gas channel and current collection to the active sites. In the case of anode-supported cells, the layer must also guarantee the mechanical stability of the whole membrane electrode assembly (MEA). Under operation with hydrocarbons, sufficient catalytic activity for reforming is also desirable to limit the size, cost and complexity of fuel pre-processing [44].

The most widely used fuel electrode is a composite made of Ni and yttria-stabilized zirconia Y$_2$O$_3$-ZrO$_2$ (YSZ). Nickel is a relatively cheap metal that provides high electro-catalytic and catalytic activity at SOC operation temperature. YSZ is usually ZrO$_2$ doped with 8% mol of Y$_2$O$_3$ (referred to as 8YSZ) to stabilize the cubic structure that has the highest ionic conductivity. In the case of a supporting material, 3YSZ is sometimes preferred for higher strength because of the toughening mechanisms induced by stress-induced tetragonal to monoclinic transformation, at the cost of lower conductivity. The standard manufacturing route consists in mixing sub-micron sized powders of NiO and YSZ (including a pore-former, depending on the desired properties) tape-casted and sintered at temperatures around 1400°C forming a cermet. The electrolyte can be co-casted to limit manufacturing steps and obtain directly a bilayer. In the case a distinction is made between the supporting and electrochemically active layer to improve specifically their properties, the latter is commonly screen-printed before the electrolyte. Upon the first exposure to H$_2$ at high temperature, the NiO is reduced. The concurrent shrinkage of the NiO/Ni phases results in a reticulate porous microstructure. The kinetics for Ni reduction/reoxidation are fast at operation temperature. For these reasons, Ni reoxidation is a critical event. Whether in SOFC or SOEC mode, it is necessary to inject a minimal quantity of H$_2$ (~ 10% in practice) and control fuel depletion to guarantee a reducing atmosphere in the whole fuel compartment. In the current generation, the size distribution
and composition of the powders, the sintering temperature and reduction conditions are selected to maximize the density of TPBs and ion conduction, while maintaining sufficient mechanical stability. Since the electrochemically-active region does in most cases not extend beyond 20 µm away from the electrolyte [45], the electron conduction necessitates the percolated metallic phase from the TPBs to the current collectors. The total thickness of the Ni-YSZ layers in anode-supported electrodes ranges from around 200-1500 µm and their gas-phase transport properties must be tailored accordingly.

Several fuel electrodes with low or no metallic content have been investigated mainly to obtain redox-stable materials. Most candidate materials have a perovskite structure, such as lanthanum chromates and strontium titanites [46–49]. Such materials exhibit a good electrochemical performance, a superior stability to redox cycles and excellent tolerance to impurities such as sulphur and carbon. In this regard, ceria-based oxides are optimal electro-catalysts in the case of CH₄ gas mixtures [50, 51]. The electronic conductivity is in general inferior compared to the traditional Ni-YSZ electrodes, even if it can be improved by combining with metals. The principal drawbacks compared to Ni-YSZ are the higher costs of the raw materials and increased complexity of production. The performance is usually lower, and the long-term stability still need to be fully proven, which requires a review of the actual benefits in terms of revenue.

Another route is the impregnation of a skeleton ceramic support (scaffold) by a liquid phase containing the component selected for deposition. This manufacturing technique permits to achieve higher resistance to pollutant agents while guaranteeing equal or even superior power density [52]. The main advantage consists in the relative simplicity of implementation, which translates into lower cost of fabrication.

**Electrolyte**

This layer must selectively transport oxygen ions, provide minimum electronic conductivity and be gas phase impervious over a wide range of oxygen chemical potential. It must be chemically inert and thermo-mechanically compatible with the joined cell materials. The conductivity of the material enhances with temperature, leading to a consequent decrease of the ohmic polarization.

The standard electrolyte is a dense layer of cubic 8% mol-YSZ, much less often 3% mol-YSZ with a thickness in the range of 5 to 20 µm, in the anode-supported case. The first crystal structure provides better conductivity, while the second has a superior mechanical strength because of the tetragonal to monoclinic transformation. The YSZ electrolyte is usually screen printed or co-cast on the Ni-YSZ support.

Gadolinia-doped ceria Gd₂O₃-CeO₂ (GDC) has been considered as well because of the better ionic conductivity and similar mechanical properties, at least in air. It can therefore operate at lower
temperatures while maintaining sufficient ionic conductivity [53]. However, the drawbacks of single-layer GDC electrolytes are a non-negligible electronic conductivity and chemical expansion in reducing atmosphere. Samaria-doped ceria (SDC) electrolytes also offer similar advantages [54]. In fact, an inferior temperature of operation would be highly beneficial to reduce the cost of the stack components (in particular the interconnects and sealings), and the balance of plant complexity [55].

**Oxygen electrode**

The requirements for the oxygen electrode are similar to those for the fuel electrode, i.e., good electron and oxygen ion conductivity, good chemical stability and good catalytic properties for oxygen molecule dissociation and reduction. Gas-phase transport is usually less critical in the case of anode-supported cells, because of the limited thickness. This electrode can suffer high degradation, because of the high polarization losses associated with the oxygen reduction reaction (ORR) [44].

For this reason, the selection of materials for oxygen electrodes has been the subject of extensive research in the last decades, resulting in a variety of materials and combinations. Composite electrodes and single solid phase mixed ionic and electronic conductor (MIEC) were developed and correspond to the current generation (in particular lanthanum oxides), since commercially viable metals cannot be implemented due to the oxidizing atmosphere. Lanthanum strontium manganite La$_x$Sr$_{x-1}$MnO$_3$ (LSM) has been historically first used for high temperature designs, then combined with YSZ to increase the TPB density and the effective ionic conductivity. Lanthanum strontium cobaltite ferrite La$_x$Sr$_{x-1}$Co$_y$Fe$_{y-1}$O$_3$ (LSCF) as well as lanthanum strontium ferrite La$_x$Sr$_{x-1}$FeO$_3$ (LSF) and lanthanum strontium cobaltite La$_x$Sr$_{x-1}$CoO$_3$ (LSC) single solid phase or composites were investigated afterwards and are currently widespread, in particular LSCF-based materials.

A mixed electronic/ionic conductor allows for the bulk transport of oxygen, as long as the concentration of oxygen vacancies is sufficient, which may not be always the case in SOEC. Hence the reaction sites in an e.g. LSCF-based composite are not only the TPB regions but also the whole MIEC-pore interface. LSCF has a higher thermal expansion than LSM, typically resulting in channel cracking upon sintering. This was a reason for the development of LSCF-GDC composites, as well as the further improvement of the effective ionic conductivity. A drawback of LSCF, LSF or LSC based oxygen electrodes is the chemical reaction with the YSZ electrolyte. A GDC compatibility layer is commonly placed in between the electrode and the YSZ electrolyte, to limit the formation of a SrZrO$_3$ secondary phase with poor conductivity at the interface. A study of this phenomenon is exposed in Chapter 7.

A slurry of LSCF and GDC or LSM and YSZ powders is commonly screen printed on top of the electrolyte or compatibility layer and sintered at approximately 1100°C. The average thickness is comprised between 20 and 50 $µm$. In the case of anode-supported cells, an additional current
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collection layer is deposited on top of the electrode and to reduce the ohmic losses that can arise from in-plane electronic current constrictions.

Stack design

Different stack configurations were considered during the years, with the tubular and planar being common. The first one is more expensive but requires less attention to compartment sealing since at least the tube is intrinsically gas-tight. The second is often favoured because the current collection is simpler, which typically results in superior energy density, and the potential for fabrication cost reductions is higher.

Among planar configurations, a further distinction is made depending upon the type of supporting layer (i.e. anode-, electrolyte- or cathode-supported). The functional layers of the MEA are applied on the thicker supporting one, which guarantees the mechanical stability of the assembly. Anode/-fuel electrode supported cells are the most adopted nowadays, because it allows the reduction of the electrolyte thickness to lower the ohmic losses, compared to electrolyte supported cells (often referred to as the “first generation” of solid oxide cells). As mentioned before, the thickness, typically in the range of about 200-2000 $\mu$m, causes higher gas diffusion losses, which places requirements on the porosity of the cermet. For this reason, a thin “active layer”, characterized by a finer microstructure to increase the number of sites available for electrochemical reaction is often placed between the thicker and “coarser supporting layer” and the thin electrolyte.

Three arrangements of the fuel and air gas flow can be implemented in planar designs, namely co-, counter- or cross-flow. Each flow configuration results in differences in the spatial distribution of current density and overpotentials, which in turn affect that of temperature and the gas. The first typology is usually adopted since it guarantees lower thermal gradients across the cell length. In a co-flow stack, the position of the highest current density in SOFC mode is controlled by the trade-off between higher temperature and fuel rich regions, near the outlet and inlet, respectively. In counter-flow, the two conditions are near the fuel inlet, with some variation in the case of operation with low fractions of pre-reformed methane.

Degradation mechanisms

A minimum lifetime target in the range of 40 $kh$ has been defined for the commercial viability of the SOC technology. The degradation rate of the state-of-the art is just above the threshold for widespread market entry. In order to increase the long-term stability and consequently the economic viability, the degradation rate needs to be reduced below 0.5% $kh^{-1}$. An alternative emerging approach is production at lower costs with the possibility of replacement.

The morphological and chemical alterations are difficult to detect and quantify, since they depend
upon local geometrical and compositional features within the complex microstructures, as well as on the spatial variation of local conditions present in a SOC stack during operation [56]. The performance and durability of SOC materials is therefore expected to be highly influenced by 3-D characteristics of their microstructure, such as the density of electrocatalytic sites and their accessibility, among others. A simplified view of the complex physics of SOC degradation is that phenomena provoke a diminution of these qualities. The possibilities are numerous and the following list is not exhaustive: cracking, microstructural coarsening (intrinsic or enhanced by contamination), contaminant (endogenous or exogenous) deposition at the electrocatalytic sites or in the pores, phase transformation, interdiffusion and segregation at grain boundaries with the formation of secondary phases or solid solutions, reoxidation or decomposition in reducing atmosphere because of gas leakages and parasitic combustion, etc. Moreover, because cells in a stack are connected in-series, the malfunctioning of a single cell usually lead fairly rapidly to the complete failure of the device, with limited possibilities for recovery.

**SOFC operation**

On the fuel electrode side, the microstructure of the Ni-YSZ anode is known to evolve over time. Due to the high temperature, the metallic phase has sufficient mobility for relocation driven by energy minimization, which consists at a first appraisal in the increase of the average size of the larger particles at the expenses of the smaller ones. This coarsening process can imply a reduction of the TPB density as well as a loss of percolation and a consequent decrease of the effective electronic conductivity.

The Ni-YSZ cermet is sensitive to a few exogenous pollutants that can be present in the fuel or released by other stack components. The most common is sulphur, which has been studied the most but is practically mitigated by an up-stream filter in most systems. Chlorine and siloxane are also of interest [57], but H₂S remains the most dangerous. The contamination mechanisms differ for each volatile species, but in general compounds are adsorbed on the Ni surface, interfering first the electrochemical and chemical reactions. Prolonged exposure to higher levels can cause phase formation such as NiCl₂ and Ni₃S₂ in the fuel electrode and SrSO₄ in the oxygen electrode [58]. In the case of synthetic coal gas, even a small phosphorus concentration (< 1 ppm) caused the formation of bulk Ni phosphide phases, which afterwards combine affecting the whole electrode percolation [59]. Degradation by carbon deposition on the catalyst has similar effects and occurs when a partially pre-reformed stream of hydrocarbon is fed into the stack outside from the thermodynamic safe window of conditions, because of e.g. the failure of a system component. Silicon on the other hand, can be generated from the sealing material applied to isolate the electrode from the metallic interconnects. Thus, ensuring acceptable thresholds for the partial pressure of volatile species is key, in particular for operation with natural gas and becomes somewhat more complex in the case of biofuels. The research on materials that are tolerant to the above-listed contaminants continues.
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Because tolerance is usually achieved at the cost of performance and/or increased production costs, novel materials are not yet widely implemented in stacks.

Another cause of critical degradation is the reoxidation of Ni, when the nickel undergoes a partial or complete reoxidation accompanied by strong volume expansion (up to 70% [60]). The reoxidation typically leads to the formation of internal porosity, therefore, a reoxidized NiO phase occupies a larger volume than after sintering, leading to stress in the YSZ scaffold and electrolyte, among others. The phenomenon begins to occur at oxygen partial pressures greater than $10^{-14}$ atm at 800°C [61].

Standard cells degrade rapidly and usually fail mechanically after a few reduction/reoxidation cycles[62]. Such expansion induces cracks and delamination, either in the electrode or at the interface with the electrolyte. The presence of a critical oxygen partial pressure is usually the result of a sealing leakage and/or of high fuel utilization. The steam partial pressure positively favours this process, as well as higher temperatures (below 525°C the kinetics is slow). Another possible cause is the lack of a proper utilization of protective gas (H$_2$) during the shutdown and start-up phases. The expansion of Ni results in significant mechanical stresses in the YSZ scaffold. In the specific case of the fuel electrode supported cell, the shielding compressive design stress in the thin brittle electrolyte is released and turns into high tensile stress that provokes channel cracking of the electrolyte [63].

Similar to the contaminant case, Ni-based electrodes insensitive to redox cycling are challenging to design and examples of their implementation in stacks remain limited. This is because providing space in the YSZ scaffold to accommodate expansion and limit tensile stress, high TPB density and constraint to effectively limit Ni mobility in the long-term, are opposite requirements. Increased redox tolerance is currently typically achieved at the cost of performance and stability with unclear commercial benefits. As described by Faes [60], the tolerance may be increased by fabricating more porous electrodes (> 50%), although this arrangement would however reduce the electrochemical properties of the cell.

As described in the previous section, several candidate materials for the oxygen electrode were tested during the last years to ensure good electrocatalytic properties without compromising the stability. Lanthanum oxides such as LSM or LSC tend to react with other materials (YSZ) forming a low conductivity phase of La$_2$Zr$_2$O$_7$ or SrZrO$_3$ [64]. This process can already occur during sintering of the cathodes at high temperatures, and can be mitigated by A-site deficiency [65], but operation at high overpotential, potentially promoted by Cr contamination can also result in the formation of these secondary phases. Similarly, LSCF electrodes also react with YSZ. A GDC or YDC compatibility layer that acts as a barrier for the diffusion of strontium towards the electrolyte is almost systematically implemented. Their densification is however not straightforward and the formation of a solid solution (of YSZ and GDC) of lesser conductivity is difficult to avoid.

Morphological changes of the cathode materials under polarization were reported [66]. In the case
of LSM, the start of the operation is characterized by an activation phenomenon during the first hours of operation, which stems from a compositional and morphological change of the interface with YSZ improving oxygen dissociative adsorption or surface diffusion. After prolonged operation, an increase of losses is related to the incorporation of oxygen in the crystal lattice in LSM grains near the LSM/YSZ interface. LSM particles hence detach from the electrolyte forming crater- shaped basins [67], resulting in a diminution of TPBs and contact area. This phenomenon also causes the formation of secondary insulating phases such as zirconate.

Chromium is practically the most critical pollutant for oxygen electrodes. Depending upon the geometry, it either migrates from the interconnect plates or Cr-volatile species are released from the balance of plant (BOP) components or MICs and transported in the gas stream to form deposits that block the electrocatalytic sites. In the case of LSC, LSCF or LSCF-based electrodes, the chromium is not deposited selectively near the TPB but rather uniformly over the MIEC-pore interface. The detrimental effect on the performance is supposed less than for LSM, which does however not necessarily mean that the amount of captured chromium is lower. Therefore, protective coatings are applied on the MIC and critical stack and balance of plant components to mitigate chromium volatilization.

**SOEC operation**

The literature on the degradation in electrolysis mode indicates that the degradation rate is higher than during SOFC operation. It was initially based on the testing of materials developed for SOFC operation, which were simply operated in reverse mode.

The main difference compared to SOFC operation is the different inlet gas composition, which in steam electrolysis can reach up to 90% of water content affecting the Nernst potential (which lowers to 0.84 V at 800°C). On the other hand, depending on the applied current density and the nominal gas flow rate, the outlet region of a SOFC instead presents comparable humidity content. The high steam content requires the implementation of an evaporator. This is also required for SOFC operation with internal reforming, but from the standpoint of electrochemical button-cell tests to investigate intrinsic cell material degradation, it adds significant complexity. The inappropriate mixing of H₂ and H₂O gases causes fluctuations in the measured potential, and can practically lead in the worst case to local Ni reoxidation. The inlet steam flux may transport impurities present in the water or accumulated from the metallic walls of the evaporator and the connecting pipes. In addition, SOEC operation requires an additional heat source when operated at potentials inferior to \( U_{i,n} \), since the ohmic losses cannot fully balance the endothermic reaction. Since the process generates a lower amount of heat compared to the SOFC case, the thermal gradient across the cell is reduced. Lastly, the concentration of oxygen vacancies in the LSCF composite strongly depends on the operation mode, increasing under cathodic polarization [68] with implications on
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the degradation mechanisms.

The number of published results on the long-term testing of SOEC stacks is increasing but remains limited compared to SOFC [69–71]. A larger increase rate of area specific resistance (ASR) is commonly detected during the first hours of operation [72, 73]. The initial passivation can originate from the deposition of impurities on the active sites, such as silica and chromium on Ni in the Ni-YSZ electrode similarly to the SOFC case [74]. The long term ASR degradation rate reported for steam electrolysis ranges from 2 to 4 % $k h^{-1}$, while the addition of CO$_2$ causes a more severe decrease in performance, in the range of 6 – 25 % $k h^{-1}$ [73–77]. Similar results were confirmed by internal experimental tests. The reasons of the higher degradation may be ascribed to the impurities contained in the CO$_2$ (mainly sulphur), which can favour carbon deposition in the active electrode [78].

Delamination near the interface between the oxygen electrode and electrolyte was observed in several single cell experiments, possibly due to the higher partial pressure. Inter-grain fracture initiates in the electrolyte layer and propagates parallel to the oxygen electrode/electrolyte interfaces. The formation of closed porosity in the electrolyte was tentatively explained by Mawdsely et al. [79], asserting that any defect present at the interface can act as a nucleation point where the oxygen partial pressure may progressively surge. This would be due to the mismatch between the good ability of zirconia to release oxygen and the inferior capability of the electrode material to transport the ions away toward the bulk region. Furthermore, Virkar [80] analysed the impact of the chemical potential, since electrons conduction in the electrolyte must be considered for determining the local distribution of oxygen chemical potential within the electrolyte. This phenomenon is often accompanied with the formation of intermediate phases at the interface, which inevitably induce mechanical stresses and/or weakening contributing to the delamination of the electrolyte.

Ni depletion in approximately the first 10 $\mu$m next to the interface between the electrolyte and the Ni-YSZ electrode is also detected, and usually associated to a re-agglomeration in the inner electrode further away from the interface. This first modifies the spatial distribution of connected TPBs and, in a simplified view, the thickness of the electrolyte grows increasing the ohmic resistance [81]. Another frequent degradation phenomenon promoted under SOEC operation is the formation of SrZrO$_3$ next to the electrolyte, despite the presence of the GDC compatibility layer [82]. In co-electrolysis and CO$_2$ reduction, carbon deposition seems to appear at high voltage and this formation indicates a highly reducing atmosphere at the active TPB sites [76, 83].

Thesis objectives

The present thesis is articulated around the investigation of physical phenomena that cause electrochemical performance degradation through microstructural alterations in the cell layers of SOECs.
The several degradation mechanisms that can compromise the commercial viability of SOC devices are identified and often mitigated empirically. The understanding remains incomplete and often described by oversimplified scaling relations that convey little quantitative information about their dependence on the variety of conditions in a SOC stack, i.e. have limited practical use for SOC design and operation.

Based upon the literature survey presented in this Introduction, the emphasis is placed on the characterization of the electrochemically-active zone in regards of the role of heterogeneous electrochemistry and on the alteration of the microstructure stability over time. In the specific, the first objective is to quantify the effect of the extension of the surfaces available for diffusion, i.e. the local morphology near TPBs, on the charge transfer mechanism. This approach relates the overall electrochemical performance to the quality of the active sites rather than the quantity, by considering the morphology in proximity to the TPBs. The second focus is on the transport of the cell electrode constituents leading to a spatial redistribution of the solid phases and/or interdiffusion of the chemical elements. In this case the analysis aims at understanding to what extend these processes are caused by microstructure rearrangements largely independent on the polarization or the electrochemical operation mode.

Because SOC cell layers are made of heterogeneous interconnected materials, their degradation is believed dependent upon their 3-D microstructure. Therefore, a specific objective of the present thesis is to provide a set of analytical tools based on 3-D imaging to improve the understanding of selected frequent failures that limit the lifetime of solid oxide cells. It comprises a refined comprehension of how microstructural features impact the electro-catalytic activity, which presents remaining unknowns, despite studies for decades. The analysis has been performed on a series of samples extracted from stacks operated under different conditions and for varying operation times. The evolution of morphological and topological parameters have been tracked using existing and newly-developed algorithms, allowing to describe qualitatively as well as quantitatively the alteration of the microstructure. Specific topics were selected in this Thesis to guide the tool developments and test their practical applicability and relevance:

1. Quantitative characterization of the morphology near the TPBs in composite SOC electrodes and study of the electro-catalytic surfaces reactions associated to the individual charge transfer steps.
2. Evolution in the bulk of the Ni-YSZ electrode after SOFC and SOEC operation.
3. Changes localized at the Ni/YSZ interface after SOFC and SOEC operation, where the depletion of Ni in the region next to the electrolyte has been observed in electrolysis operation.
4. Study of the stability of the YSZ/GDC/LSCF interface, comprising the quantification of the detrimental effects of the SrZrO$_3$ secondary phase.

However, the developed characterization methods, models and understanding are relevant to the
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study of other degradation mechanisms in SOC, specifically those requiring the 3-D characterization of the morphology.

Thesis outline

The Thesis is organized into seven chapters, which are summarized hereafter. The description of the current understanding and challenges in this Introduction provides a general overview. Expanded literature surveys specific to the treated problematic are given in the introduction Section of each chapter.

- **Chapter 1** starts with an overview of the electron microscopy and segmentation procedures and standard methods for 3-D property measurements. The second part of the chapter lists the samples analysed in the Thesis, including the description of the test conditions and measured performance and degradation.
- **Chapter 2** provides a post-test analysis of a stack tested for 10.7 $kh$ in SOEC conditions. This was a case study at the start of the Thesis, which guided the following investigations and defined the list of priorities among the individual degradation mechanisms.
- **Chapter 3** presents first an algorithm capable of quantifying the extension of the surface available for surface diffusion at each TPB in the heterogeneous microstructure, which were defined as “available lengths”. The algorithm has been applied on two different electrode microstructures, i.e. Ni-YSZ and LSM-YSZ. The information about the electrode microstructure provided by the developed measurement was then investigated to better understand the relation between the size and shape of TPB regions and the measured available lengths.
- **Chapter 4** studies the effect of the available length on the electrochemical performance. A detailed heterogeneous electrochemistry model has been implemented to describe the dependence of the surface coverage profiles on the extension of the available lengths and applied overpotential. Two numerical models respectively referred to the $H_2/H_2O$ and $CO/CO_2$ electro-chemical reactions were implemented.
- **Chapter 5** examines the microstructural changes in Ni-YSZ cermet samples operated under SOFC and SOEC conditions up to 15 $kh$, by measuring and analysing metric and topological properties using methods developed in this Thesis.
- **Chapter 6** is focused on the alteration of the Ni/YSZ interface after SOFC and SOEC operation. The tested hypothesis was that the observed differences are influenced by the electrowetting phenomenon, using the 3-D imaging dataset and developed characterization methods.
- **Chapter 7** is a quantification of the strontium migration at the GDC/YSZ interface after SOFC and SOEC operations. The interface of several samples was first reconstructed and analysed with developed routines. The detrimental effect of the formed SrZrO$_3$ secondary phase was estimated by transport analysis.
Contributions to the presented study

The outcome of the research performed in this thesis is highlighted in the Conclusion chapter, together with considerations for the improvement of microstructures and the operation of fuel and electrolysis cells.

A goal of a Thesis is to advance the knowledge and capabilities of a research group. The candidate therefore naturally benefits from the status existing at the start of his Thesis and collaborations with colleagues and contacts from the group. The details of such contributions are provided hereafter. In addition, the present thesis does not include the experimental work on button cells performed by the candidate to support the research on co-electrolysis in the group. An example of this activity [84].

The main collaborations with employees of the Group of Energy and Material (GEM) of Dr. Jan Vanherle at EPFL are:

- Dr. Arata Nakajo – fundamental contributions in Chapters 3, 5, 6 and 7 (co-author). He provided code as the starting point for improvements or to assist the developments performed in this Thesis, as well as several of the 3-D focused ion beam – scanning electron microscopy datasets.
- Dr. Stephan Diethelm – provided support in the analysis of the experimental results in Chapter 2.
- Dr. Priscilla Caliandro – provided the experimental data for the measurement of the capacitance in Chapter 6.
- The technical staff of GEM-EPFL (Nicola Accardo, Steve Joris and David Constantin) – provided great help in the experimental activity of the whole research group, participated to the assembly and operation of the long-term stacks tests presented in this work and the preparation of the samples.

The scanning electron microscopy (SEM), TEM and FIB-SEM serial sectioning measurements were performed at the Interdisciplinary Center for Electron Microscopy (CIME) at EPFL. The candidate performed the 2-D SEM/EDS experiments on a FEI Teneo microscope located in the campus in Sion.

- Dr. Emad Oveisi – performed the transmission electron microscopy (TEM) measurements, including energy-dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED) presented in Chapter 2.
- Dr. Marco Cantoni, Dr. Pierre Burdet and Dr. Lucie Navratilova performed directly or provided active assistance for the 3-D FIB-SEM measurements used in this Thesis.
Collaborations with contacts outside from the EPFL were:

- Prof. Wilson K. S. Chiu (University of Connecticut) – provided extended advices for Chapter 4.
- Peter Damian and Matt B. DeGostin (University of Connecticut) – generated the artificial packed spheres Volumes used in Chapter 4.
- SOLIDpower SpA (Italy) and SOLIDpower SA (Switzerland): provided the tested cells, stacks as well as samples investigated in this work. The long-term segmented-cell tests were also performed at their facilities at Yverdon-les-Bains.
- European Institute for Energy Research (EIFER), Technical Research Centre of Finland (VTT) – performed each one SOEC long-term short stack experiment. The detailed list is presented in Chapter 1).
Experimental and methodology

This Chapter describes the procedures for 3-D electron microscopy measurements. The list of analyzed Volumes and SOFC/SOEC testing conditions is then presented together with a brief overview of the methods for the quantification of the metric and topological properties.

1.1 Focused ion beam-scanning electron microscopy - FIB-SEM

A FIB-SEM serial sectioning dataset consists of a stack made of slices that provide a 3-D representation of the imaged sample Volume. Measurements of pristine and aged samples can help understanding (i) the processes responsible for modifications of the morphology and topology of the materials upon operation and (ii) the effects on the electrochemical performance. The schematic in Fig. 1.1 illustrates the standard arrangement for FIB-SEM serial sectioning measurements. The microscope is equipped with an electron and a Ga ion column in a “cross-beam” arrangement. The electron column is usually in vertical position, whereas the second ion column is at an angle around 50°. 90° arrangements for 3-D imaging also exist but they provide less flexibility, in particular for the preparation of TEM lamellae. For 3-D imaging, the sample is therefore placed at the eucentric location and tilted to orient its surface perpendicular to the ion beam (FIB). Trenches are first milled to uncover a face from which the imaging run starts. They are oversized to provide space to accommodate for re-deposition during the acquisition to limit shadowing effects and allow for the escape of x-rays in the case of 3-D EDS measurements. During the acquisition, the face of the sample is sequentially ion polished at a shallow angle and imaged. Interlaced milling and imaging provide increased throughput. The software correction of electron images acquired at an angle is usually enabled by default during the acquisition.

Porous samples such as SOC material layers must be impregnated with resin to fill the voids that otherwise would be penetrated by electrons, showing through the actual current slice, and limit un-
Figure 1.1 – Schematic of the cross-beam arrangement for FIB-SEM serial sectioning. The ion beam (in red) sequentially mills slices of material. The electron beam (in green) interacts with the material resulting in the emission of electrons as well as characteristic x-rays that are collected by the detectors. Image taken from [3].

Chapter 1. Experimental and methodology

even milling promoting curtaining effects and re-deposition. In contrast to x-ray nanotomography, FIB-SEM serial sectioning is a “destructive method” since each slice is irreversibly milled during the imaging process. This is a drawback that prevents in-situ imaging and places constraints for correlative analyses. The samples are polished mechanically with sandpaper up to 0.5 \( \mu m \) and gold coated, in order to obtain a close to flat external surface that provides sufficient electron conduction to avoid charging effects, limit artifacts of the deposited/milled fiduciary marks for tracking and the risks that the underneath imaged volume is damaged by the sample preparation.

Upon raster scanning of the section, the electron beam excites the specimen up to a depth that depends mainly on the energy of the incident electrons and material composition. The size of this interaction volume therefore impacts the spatial resolution in 3-D imaging. Other practical limitations are the accurate measurement and control of the thickness of the slices, which requires tracking to dynamically position the ion beam, and the reliability of autofocus and autostigmation during the acquisition.

The FIB milling rate is controlled using fiduciary marks milled on top of the Volume of interest before the acquisition. It consists in a set of two V-groves milled on a Pt-deposit at a known in-plane angle and covered with carbon coating for protection and enhanced grayscale contrast. The grooves are imaged every slice and processed by software to compute and adjust the progression rate during the imaging run with a precision in the range of 1 nm. The fiduciary marks include a set of three additional parallel groves for the alignment of the slice and, if needed depending upon the sample, for auto-focus and stigmation performed typically every 60 and 180 minutes, respectively. In the present study, tracking was set to obtain isometric voxels to prevent artificial anisotropy in the datasets. The accuracy of the tracking was as expected, but always resulted inVolumes slightly larger than the target size (for 10 nm voxel size, less than 10%).
The same detectors as for standard 2-D SEM are usually available for a 3-D imaging run. The signals include therefore backscattered electrons as well as secondary electrons detectors, i.e., those re-emitted from an outer atomic shell after absorption of the incident electron and characterized by lower energy (<50 eV). EDS detectors are commonly installed in cross beam microscopes, but the imaging conditions for adequate contrast and spatial resolution in the electron images differ most of the time from the higher energies required for microanalysis [85]. The implementation of automatic switching of the acceleration voltage is nowadays commercially available, once the complications due to communication between proprietary software were solved [86].

Most of the 3-D reconstructions analyzed in this Thesis were acquired with a ZEISS crossbeam 540 and part with a Zeiss NVision 40 microscope. Both are characterized by an angle of 54°, working distance of 5.2 mm for 3-D imaging and equipped with energy selective backscatter (EsB), In-Lens and Everhart-Thornley (hereafter referred to as secondary electron secondary ion (SESI)) secondary detectors. Automatic switching of the acceleration voltage is available only on the crossbeam 540. The combination of signals from different detectors increases the capability to discriminate the material phases, providing for instance Z and surface electrical properties contrast. Topological contrast from secondary electrons are usually of lower relevance for 3-D imaging, but may cause artifacts. The relevance of the information conveyed by signal for the present study is expanded hereafter:

- **In-Lens located in the electron column**: collects the low energy secondary electrons from the upper region of the interaction volume within a narrow collection angle, and provides contrast depending on the surface electrical properties, as well as channeling contrast that is visually clear but proved however challenging to use for the 3-D segmentation of grains.
- **Everhart-Thornley mounted on the wall of the chamber facing the specimen laterally**: detects secondary electrons with less sensitivity to charging, compared to the In-Lens detector.
- **EsB located in the electron column**: detects the high-energy backscattered electrons and provides Z contrast. Hence, the phases of the sample characterized by higher atomic number exhibit higher brightness. An energy filter allows further contrast adjustments.

Microscope electronics and software allow dual channel acquisition (any two of EsB and In-Lens or SESI). A good contrast with sufficient peak separation in the grayscale histogram is needed for the correct identification of the phases, which is usually facilitated by combining images acquired by different detectors.

Most of the electron imaging was performed at 1.5 kV, 1.6 nA and 1 µs dwell time, with variations on selected Volumes of up to 1.8 kV, 2.0 nA and 4 µs, respectively. The signal from the in-column secondary electron (in-lens) and EsB detectors were recorded to obtain adequate contrast depending on the imaged material layer and facilitate the removal of artifacts before segmentation.

FIB-SEM serial sectioning can be coupled with other imaging techniques to improve the capability
Chapter 1. Experimental and methodology

for chemical mapping or retrieve crystallographic information beyond the In-lens channeling contrast mentioned above. For instance, EDS can be implemented to provide additional chemical information such as the presence of impurities or formed secondary phases. During a FIB-SEM/EDS run, electron images are acquired under the same conditions as standard FIB-SEM, i.e. at low acceleration voltage to limit the interaction volume and improve the 3-D spatial resolution. Every 10 slices, the acceleration voltage is automatically switched from 1.5-1.8 kV to 10 kV for EDS acquisition. The voltage of 10 kV allows for the mapping of the main relevant elements present in the sample investigated in this study. The 3-D EDS maps are then resampled and registered on the electron image dataset for segmentation. Additional information concerning 3-D electron and EDS elemental mapping imaging can be found in the whitepaper [86].

As mentioned before, the tracking of the section being imaged is a dynamic process, hence the slices in the raw FIB-SEM dataset are not perfectly aligned. Post-run alignment and stacking of the slices form a 3-D reconstruction of the structure, which can be segmented (labelled) for quantitative microstructural analyses. The Volumes of interest considered in this Thesis were imaged at a baseline isometric voxel size of 10 nm, with selected acquisitions at 7 nm. As explained later in Chapter 3, such high magnification is essential to perform accurate quantification of the available TPB length. Features of comparable or smaller size cannot be adequately identified under such conditions. Because of resolution limitations caused by the interaction volume, an additional improvement cannot be achieved by simply further diminishing the voxel size. The potential for improvements for the materials investigated in the present study is likely limited, but a systematic study is yet to be performed. Other practical considerations such as the quality of impregnation and the resistance of the resin to the electron dose will likely prove relevant as well.

1.2 3-D segmentation

The segmentation consists in partitioning a digital image by assigning a label to each pixel, such that subsets with the same label share common characteristics. The 3-D grayscale reconstruction obtained by alignment of the slices using the three central groves must be processed to remove imperfections and artifacts that can hamper the correct identification of the material phases. This is the reason why a set of images that exhibit an equilibrated histogram with high signal to noise ratio expedites the whole reconstruction process [87].

Due to the physical complexity of the FIB-SEM acquisition process, the final images may contain several artifacts, or in the worst case, the dataset is not of sufficient quality for 3-D quantitative analyses. The inspection of the orthogonal slices in the image stack and measured slice thicknesses reveals improper 3-D control of the FIB and if the subvolume imaged with accurate tracking remains sufficient. Since the detectors are tilted with respect to the imaged specimen surface and milling enormous trenches penalizes throughput, a mild in-plane gradient in brightness is often observed,
particularly in the in-lens secondary electron detector images. In addition, a surface with uneven and non-flat topography may lead to imperfect ion milling, with a “curtaining effect” resulting in the formation of striations across the milling face. The resin impregnation does not always completely fill the voids, especially in the case of very narrow regions. The image processing of these limited zones is complicated, in particular in the case of charging (when a fraction of the emitted electrons remains trapped in the specimen resulting in very bright spots). Similar issues are due to the closed porosity in the solid phases that cannot be filled by resin.

Three softwares were used for the image processing: the open source package “Fiji” [88] was used to align and pre-filter the stack of acquired images, while the corrections for artefacts are performed using Matlab routines in combination with Avizo package [89, 90]. The secondary electron and the backscattered electron datasets are both processed with the same workflow before merging. The main steps are summarized hereafter:

1. Slice alignment: as mentioned before, the fiducial marks milled and embedded in a coating deposited on the material are used to precisely align slices in the stack.
2. Background correction to compensate for non-uniform illumination: a shadowing correction is applied by histogram spreading applied to each pixel individually using white and black references.
3. Stripes removal: in the case of vertical stripes due to curtaining effects that arise when the milling becomes less stable, a filter detecting and removing the vertical patterns using Fourier and wavelet analysis is applied [91].
4. A 3-D bilateral filter is temporarily applied to remove noise while preserving edges, in preparation of the following step.
5. Artifacts removal: in the present study, most are due to imperfect impregnation or decomposition of the resin because of the electron dose, in particular during imaging at the smallest voxel sizes. Tests suggest that this workflow step is likely significantly lighter when imaging at 15-20 nm voxel size. Masks are generated by combining the signal from EsB and InLens detectors. The artifacts are detected by morphological operations, including opening and closing using a spherical structuring element, and simple procedures for object recognition based on local thickness distribution and dimensions of the bounding box. The mask generation is implemented to stay away as much as possible from the expected phase interfaces. Manual corrections are also included whenever necessary. The masks are inspected visually for other artifacts or alteration of the expected interfaces, before removal from the datasets after application of the stripe removal filter (step 3). A 3-D bilateral filter is then applied followed by a mild 3-D median filter.
6. Marker-based watershed segmentation is performed to assign to each voxel a label value corresponding to the phase identified.

The last step 6 is hereafter described in further details. The common analogy for describing the
Chapter 1. Experimental and methodology

watershed algorithm is the identification of “watershed lines” from the inundation of a topographic map [87]. The practical application of watershed-based segmentation comprises several steps. A main purpose for multi-phase segmentation is to avoid a “coating” of phase of intermediate grayscale at the interface between the darker and brighter phases. It arises because the grayscale gradient at such interface in the data is not infinite. The first step is the generation of markers for each phase based on grayscale values for which the assignment to a phase is unambiguous. Here, automatic methods for thresholding such as Otsu are used as a first guess, refined afterwards by visual inspection of the histogram and directly of multiple sections oriented in all 3 directions. Manual corrections are implemented whenever needed. The image gradient is then generated, thresholded and subtracted to the labelled markers. The watershed algorithm afterwards fills the masked and unassigned regions from the markers. Segmentation results are systematically inspected visually to verify the homogeneity in the three directions and seldom remove artifacts manually. An example of segmentation result and corresponding EsB image is shown in Figs. 1.2A-B.

Figure 1.2 – (A) LSCF-GDC electrode EsB electron image, (B) segmented image. (Black: pore, grey: LSCF, white: GDC).

Caution is needed for the application of the filtering and correction steps, because they can irreversibly affect the measurement of topological properties on the reconstructed domain, compared to the actual ones. Tests showed that variations within reasonable limits in the filtering and artifact removal parameters do not influence standard properties such as the TPB density or phase size distribution to a larger extent than differences observed between Volume samples. However, the question remained open before this Thesis for the measurement of properties that are sensitive to the local morphology, such as the available length (Chapter 3) or the dihedral angles (Chapters 5 and 6). Intuitively, the impact on tiny features is expected proportional to the number and intensity of applied filters. Appendix E provides a first estimate of the variability in the measurements presented in this Thesis.
1.3 List of sample Volumes and corresponding electrochemical dataset

This section presents the nine Volumes that are investigated in the following Chapters. Samples from experiments available at GEM-EPFL were selected to cover a wide range of long-term tests in SOFC and SOEC modes. Table 1.1 provides an overview, discussed in further details below.

<table>
<thead>
<tr>
<th>Number</th>
<th>Operation mode</th>
<th>Operation time [kh]</th>
<th>Type of cell/stack</th>
<th>Current density [A cm(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pristine</td>
<td>-</td>
<td>Ref. cell</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Pristine</td>
<td>-</td>
<td>Ref. cell</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Pristine</td>
<td>-</td>
<td>Ref. cell</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>SOFC Thermal aged</td>
<td>1.9</td>
<td>Seg. cell (3x4)</td>
<td>OCV + EIS</td>
</tr>
<tr>
<td>5</td>
<td>SOEC</td>
<td>2</td>
<td>6-cells stack</td>
<td>-0.775</td>
</tr>
<tr>
<td>6</td>
<td>SOFC</td>
<td>4.7</td>
<td>6-cells short stack</td>
<td>0.4</td>
</tr>
<tr>
<td>7</td>
<td>SOEC</td>
<td>10.7</td>
<td>6-cells short stack</td>
<td>0.6 until 2 kh, 0.5 after</td>
</tr>
<tr>
<td>8</td>
<td>SOFC</td>
<td>15</td>
<td>Seg. cell (3x4)</td>
<td>0.3</td>
</tr>
<tr>
<td>9</td>
<td>SOFC Thermal cycles</td>
<td>2.6 (124 thermal cycles)</td>
<td>6-cells short stack</td>
<td>OCV + IV curves</td>
</tr>
</tbody>
</table>

Table 1.1 – Summary of the analyzed experiments and operation conditions. The oxygen electrodes of all the samples were fed with compressed air.

The first LSM-YSZ sample was selected for the study in Chapter 3, to allow the comparison of the available length in microstructures produced by distinct manufacturing routes. Otherwise, the cell samples for evolution analyses are all from the same SOLIDpower anode-support, electrolyte and barrier layer technology, without variations of the cell manufacturing route. Because of the contingency in long-term stack testing, a set based on a same production batch was however not available. The six aged samples are from short stack or segmented cell experiments, for operation conditions as close as possible to those of practical interest for SOFC or SOEC applications. If not specifically mentioned, the FIB-SEM reconstructions include the Ni-YSZ hydrogen electrode, YSZ electrolyte, GDC compatibility layer and LSCF-based oxygen electrode. Different locations were also sampled to detect variations along and across the flow path.

Short stacks usually comprise 6 planar cells (Fig. 1.3A), with fuel/feed and air fed in co-flow configuration. The manifold, interconnection and sealing design is that currently commercialized by SOLIDpower, except for samples 6 (SOFC 4.7 kh) and 7 (SOEC 10.7 kh). The active area in the case
of segmented-cell experiments (Fig. 1.3B, C and D) is divided into 20 elements (5 along the flow path by 4). The cell support and total footprint area of the current collection design is the same as the current SOLIDpower design (80 cm²), but the effective active area is slightly smaller because of the segmentation. It enables the control of the testing conditions for each segment individually, such as applied potential, current and gas compositions, within the constraints in the polarization of upstream segments [92]. Electrochemical impedance spectroscopy (EIS) measurements are performed on each individual segment, which provide a spatial mapping of the degradation. During EIS, only the segment being measured is polarized with the remaining of the active area usually left at OCV.

Figure 1.3 – (A) SOLIDpower 6 cell stack design. Footprint view of (B) segmented cell, (C) MIC, cell with segment numbering convention and (D) setup installed at SOLIDpower.

1. **Pristine LSM-YSZ**: this composite LSM-YSZ oxygen electrode was produced by Hexis [93] for the EU project SOFCLife and available before the start of this Thesis [94]. The initial purpose was a degradation study of the total conductivity, but only a pristine sample after sintering was considered in this Thesis. The ink comprising LSM and YSZ powders in equal volumetric quantity was screen-printed on a 3YSZ substrate. After sintering, the thickness of the LSM-YSZ layer was approximately 50 µm. The Volume was extracted underneath the surface of the sample.

2. **Reference A**: the sample was extracted from an anode-supported pristine cell after reduction in a short stack at 800°C.
3. Reference B: the sample was extracted from an anode-supported pristine cell after reduction at 800°C and cooldown.

4. SOFC 1900 h: the sample was extracted from segment 6 (inlet) in a segmented-cell held at OCV and 750°C under dry H₂ diluted with N₂ (respectively 3.6 and 2.4 NmL min⁻¹ cm⁻²) and air (92.5 NmL min⁻¹ cm⁻²) for most of the time. The periodic EIS measurements allowed quantifying the evolution of the contributions to the ASR. In particular, that of charge-transfer in the Ni-YSZ electrode measured at a DC bias of 0.9 A raised from 47 to 74 mΩ cm² during the first 50 h and then stabilized at 66 mΩ cm² [92].

5. SOEC 2000 h: 6-cell stack tested under steam electrolysis conditions (90% H₂O, 10% H₂ at 12 NmL min⁻¹ cm⁻² as well for the air side), at 750°C and 0.775 A cm⁻² (steam conversion (SC) 50%). The average potential degradation rate during constant current density polarization was almost null, with the first 1500 h characterized by an even slight reduction of the measured voltage (-0.7 % kh⁻¹). The available electrochemical data does however not allow precise conclusions about the cell degradation. The measured improvement may be due to an improvement of the electrical contact, that can further partially mask the electrode and or cell degradation. Indeed, segmented-cell experiments often exhibit such variability in the electrical contact over this time span, even though direct comparison with stack results on this aspect is delicate.

6. SOFC 4700 h: 6-cell short stack tested for 4700 h at 760°C, 0.4 A cm⁻² under dry H₂ diluted with N₂ (respectively 6.2 and 4.1 NmL min⁻¹ cm⁻² – 45% fuel utilization (FU)) and air flow of 62.5 NmL min⁻¹ cm⁻², with an active area of 48 cm². The average voltage degradation rate measured by IV characteristics at 0.4 A cm⁻² (80% FU) was in the range of 0.9 (+/-0.05) % kh⁻¹. Two regions of interest were imaged, respectively near the gas inlet and at the outlet regions (6A and 6B in Fig. 1.4).

7. SOEC 10700 h: 6-cell short stack tested for 10700 h at 720°C with a feed made of 90% H₂O and 10% H₂ molar fraction for a total feed flow of 9.3 NmL min⁻¹ cm⁻² (12 NmL min⁻¹ cm⁻² on the air side) and an active area of 48 cm². The current density was 0.6 A cm⁻² (SC 50%) for the initial 3250 h and lowered to 0.5 A cm⁻² (SC 40%) for the remaining of the test. The degradation during the initial 2000 h was characterized by a voltage increase of 4% kh⁻¹, subsequently stabilizing below 0.5% kh⁻¹. During the test, four water interruption incidents occurred, and the test was stopped after the last one. Details are provided in Chapter 2, which is dedicated to the post-test analysis of this experiment [95].

8. SOFC 15000 h: a segmented-cell experiment of 15000 h performed by SOLIDpower under dry H₂ diluted with N₂ (respectively 3.6 and 2.4 NmL min⁻¹ cm⁻², 95 NmL min⁻¹ cm⁻² on the air side) at 750°C. The segments were first polarized for 800 h, then left at OCV until 4500 h, beside short-term tests for setup developments. Potentiostatic control was applied for a large share of the remaining test time (cumulated time under polarization exceeding 8500 h) to ensure equipotential conditions over the cell, representative of stack operation for this design. The potential was set at 0.8 V, corresponding to an average current density of 0.3
A cm$^{-2}$ (58% FU). However, the current density dropped for segments 6 and 7 located at the inlet of the second row of segments (Fig. 1.3C). EIS measurements confirmed higher ohmic losses at these locations, presumably due to contact alterations that may be related to thermomechanical issues. In particular, from 4000 to 10000 h of operation, the central part along the symmetry axis showed a larger increase in ohmic losses, while after 14500 h a rise is observed on segments located near the gas inlet. The polarization losses measured by EIS presented a limited time evolution, reaching mostly stabilization after approximately 5000 h of operation (between 5000 and 10000 h of operation). Analysis based on the distribution of relaxation times (DRT) revealed that the charge transfer resistance on the hydrogen electrode side is larger in the inlet area of the repeat-elements, suggesting a higher degradation in this zone. The measurements exhibited a slight diminution at 10000 h, followed by an increase after 15000 h of accumulated testing time. In this case two Volumes were extracted, respectively from segments 12 and 19 referring to Fig. 1.3 (Volumes 8A and 8B in Fig. 1.4).

9. SOFC thermal cycling: 124 deep thermal cycles (up to RT) performed with a 6-cells short stack over 2600 h (including heating and cooling ramps), fed with dry H$_2$ diluted by N$_2$ (3.6 NmL min$^{-1}$ cm$^{-2}$ and 2.4 NmL min$^{-1}$ cm$^{-2}$) and air (62.5 NmL min$^{-1}$ cm$^{-2}$). Between each cycle an I-V curve was recorded up to 0.4 A cm$^{-2}$ (FU=80%). The measured OCV decreased from 1.19 (+/-0.03) V to 1.03 (+/-0.027) V in average after 105 cycles, corresponding to a decrease of 6.4% kh$^{-1}$. The increase of leakages that was more severe in three cells was likely caused by mechanical damage of the sealing due to the thermal cycles.
1.4 Methods for the quantification of standard morphological and topological properties

The set of quantification methods used in the present Thesis to aid the comprehension of the evolution of the microstructure over time is a combination of existing and algorithms developed on purpose, which are summarized below. All the property measurement methods listed hereafter require segmented Volumes and were implemented in Matlab.

- **Volume fraction**: the procedure is a straightforward voxel counting with a label mask; the sum of counts for a given label over the total sample Volume provides the volume fraction of the corresponding phase. This computation is performed either over the whole Volume or slice-by-slice to detect potential spatial variations along the three directions.

- **Contiguity**: the algorithm provides the volume of the components that connect two opposite faces of the Volume, such as detailed in [96]. In the present study, identical information was retrieved using the available “bwconncomp” Matlab function for black and white Volumes. Each phase is first individually thresholded and the domain labelled by “bwconncomp”, which is a sequence of search for unvisited voxels followed by flood filling, repeated until the whole phase domain has been visited. A 6-neighborhood definition was used for the flood filling. Each region of connected voxels is therefore assigned a distinct label. The inspection of labels

![Figure 1.4 – location of the extracted Volumes.](image)
touching the boundaries of the sample Volume allows computing the fraction of the phase label that connects different faces. Calculations are performed by default for each three pairs of faces. In the Volumes investigated in this Thesis, a region connecting a pair of opposite faces also connects the others. Therefore, the provided fractions correspond to regions connected in all directions. The reported isolated fractions correspond to regions that do not connect any pair of opposite faces.

• **TPB length**: each unit of TPB length corresponds to the interfacial line formed by three adjacent voxels of different phases, in blocks instead of data points representation (Fig. 1.5). As described in [97], the Volume is scanned in the three directions using a 4 voxel window. The sum of the retrieved lengths in the three directions provides the total TPB length. The index list of four voxels forming a TPB line of unit length is stored to retrieve the corresponding position for analyzing the distribution of TPBs along specific directions or generate binary Volumes for topological analyses based on skeletonization. The subset of TPBs that resides on regions with connection to the exterior of the sample Volume is identified by combination with the labelling procedure described above, except that the connection of TPBs must be analyzed in six directions. For instance, TPB on small isolated Ni inclusions are disconnected from the rest of the metallic interconnected network. Analogously, the fraction of isolated TPB can be quantified as well.

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**Figure 1.5** – Schematic of lines and interfaces among voxels in a cubic representation. On the left, example of detected TPB lines of unit length (in red). On the right, the interfacial surface areas (ISA) among different phases. Each grayscale level refers to a phase.

• **Interfacial surface areas (ISA)**: are measured for each pair of phases (i.e. Ni/YSZ or Pore/YSZ for Ni-YSZ). The routine simply scans the Volume for jumps in voxel labels, which are afterwards assigned to each interface from the inspection of the voxel labels before/after the jump. The procedure is executed in the three directions. Such face counting is known to overestimate the surface area compared to the real microstructure, due to the block representation. The results are adjusted by multiplying for the coefficient “π/6”, assuming close to spherical
1.4. Methods for the quantification of standard morphological and topological properties

shapes. Moreover, the sum of the ISAs related to a certain phase provides its total surface area (TSA).

• Phase size distribution (PSD): the definition of a geometrical concept for measuring the size distributions of reticulate phases is not straightforward [17]. Two methods were considered. They convey different information about the microstructure, intuitively from the standpoint of either a network of channels or packed particles, which for the studied material are partially arbitrary and suppositional.
  - Filling by overlapping spheres: each portion of the selected phase can be filled with overlapping monosized spheres of a given radius [98]. By incrementally reducing the radius, the fraction of the visited phase volume increases and is tabulated to generate a cumulative size distribution. The median phase size diameter ($d_{50}$) is often reported for comparing microstructures.
  - Ray tracing: the method is that proposed by Grew at al. [97, 97]. It is based on tracing of rays within the measured phase following a 3-D 19-direction vector set with local zero at the voxel center. Each outer voxel at the interface with the measured phase is examined to serve as a launch point for rays along the normal directions. The rays traverse the structure until another interface is reached and their lengths are tabulated. The process is repeated for all the voxels belonging to the ISA of the phase. The calculation of number-weighted ray length probability density function is straightforward. Volume-weighted distributions are more relevant for the present study (with unit of $\mu m^{-1}$). They are constructed based upon the estimation of (i) the number of phase paths (channels) of a given diameter in the structure based on the relationship between the channel cross-section perimeter and number of rays traversing a channel centerline voxel, which depends upon a geometric constant and (ii) the corresponding phase volume. The geometric constant can be practically obtained by integration for normalization and the comparison with the theoretical value for square cross-sections ($\approx 0.25$) provides a verification of the underlying assumptions in the derivation of the phase size distribution. The details of the development can be found in [97].

The methods listed above form the basis of standard 3-D microstructural analyses and were available before the start of the Thesis. Methods were developed or adapted specifically in this Thesis to advance the characterization capabilities at GEM-EPFL for finer investigations of microstructural alterations. They are listed below and the rationale as well as their detailed description are provided in the respective Chapters.

• Surface available for diffusion at TPBs, referred to as “available length” (Chapter 3).
• Curvature analysis of the interfaces (Chapter 3).
• Dihedral angles at TPBs (Chapters 5).
• Interfacial specific energy density (Chapter 6).
Chapter 1. Experimental and methodology

- Finite-element (FE) transport analysis (Chapter 7).
This Chapter describes a post-test analysis performed on a short stack composed of 6 solid oxide cells that has been tested for more than 10000 hours in steam electrolysis mode. The outcome of the analysis serves as a starting point for the detailed investigations that will be presented in the following Chapters.  

2.1 Durability test

A 6-cells SOE short-stack realized by SOLIDpower has been tested in electrolysis mode by EIFER [99] in steam electrolysis mode for 10700 h (refer to sample number 7 in Chapter 1).

Fig. 2.1 displays the six I-V curves associated to each cell and confirmed that the performance was analogous to other experiments conducted in similar conditions [73]. Voltage evolution with time is reported in Fig. 2.2. In the first 3250 h a current density of -0.6 A cm\(^{-2}\) was applied (corresponding to a steam conversion SC of 50%). Marked initial degradation can be observed in the first 2000 h, with a voltage increase of up to 8%. A similar behavior during the initial operating phase has been reported in [72, 76]. After a water supply interruption incident at 3250 h where all cell voltages rose above 1.7 V for about 15 min, the current density was reduced to -0.5 A cm\(^{-2}\) (SC 42%). The incident caused the OCV to permanently decrease from 0.88 V to 0.86 V, which could be related to the formation of small leakages through the sealing or cracks in the electrolyte. Therefore, the stack suffered an irreversible, but far from fatal, degradation through this important feed interruption. Even under these extreme conditions of steam starvation, the stack could withstand operation for some time.

1Part of the content was also presented at the 12th European SOFC & SOE Forum that took place in Lucerne (Switzerland) on the 5th-8th July 2016 and published as G. Rinaldi, S. Diethelm, E. Oveisi, P. Burdet, J. Van herle, D. Montinaro, Q. Fu, A. Brisse, “Post-test analysis on a Solid Oxide Cell stack operated for 10,700 hours in steam electrolysis mode”, Fuel Cell 17 (2017), 541-549 [95].

Personal contribution: post-test analysis of the operated stack through SEM-EDS and TEM-EDS characterization.
(<100 h) thanks to the electronic conduction through the YSZ electrolyte [100]. It was observed that a continuous temperature drop occurred during the test (-1 $K h^{-1}$), interpreted as due to the improving contact of one current pickup endplate. Progressive recovery of all the repeating unit (RU) took place between 3500 – 5000 h of operation, followed by a slight degradation lower than 0.5% $kh^{-1}$; cooling due to the temperature drift is partially responsible for this observed voltage increase, i.e. intrinsic temperature-corrected degradation would still be lower. After more than 10000 h of test, other feed interruption incidents provoked further degradation and the stack was operated partially in SOFC mode. Overall, this experiment demonstrated an as yet reasonable stack robustness.

Figure 2.1 – I-V curves of the 6 repeating units (RUs).
2.2 Post-test analysis

Two of the six repeated units were selected (RU 1 and RU 4) in order to examine the effects of position in the stack. RU1 was chosen as a stack-border cell that showed a slightly higher loss than the opposite border cell RU6; and RU4 was chosen as a stack-center cell that showed an average behavior among the 6 RUs. These two RUs were prepared and examined for post-test analysis. Both RUs were cut in eight parts, as shown in Fig. 2.3. RU 4 was embedded in resin and cut by a circular saw and the surfaces of samples were then polished to obtain flat cross sections. RU 1 was instead cut with an electrical discharge machining (EDM); pieces were then fractured by hand in order to examine the surface morphology. The results of the analysis reported in the following were acquired at the center of each RU (in the region highlighted by the green rectangle in Fig. 2.3). It was verified that no appreciable differences were observed between gas inlet and outlet regions (locations 1 and 2 in Fig. 2.3). The post-test analysis was conducted by SEM [101]; atomic percentages of the various elements were quantified with energy-dispersive X-ray spectroscopy [102] at an acceleration voltage of 15 kV. The interaction volume in this case is around 1 µm³ and the minimum significative threshold of atomic percentage considered is around 1% (values below are considered attributable to signal noise). A sample of the first cell (location 3 in Fig. 2.3) was FIB polished. A lamella belonging to RU 1 (location 4 in Fig. 2.3) was extracted and examined with a TEM [103] at an acceleration

![Figure 2.2 – Voltage and temperature evolution of the SOE stack with time.](image-url)
voltage of 200 kV combined with EDS and selected area electron diffraction SAED. In the following, results from the post-test analysis of the electrodes and electrolyte are discussed.

**Figure 2.3 – Schematic of the two RUs cut for post-test analysis. The green rectangle represents the region where the main investigation has been conducted. Additional sample positions examined are indicated by squares numbered 1–5.**

### 2.2.1 Fuel electrode – cathode

The hydrogen/steam electrode exhibits a progressive nickel depletion in the proximity of the electrolyte in both repeating units. To understand the extent of this phenomenon, an analysis was conducted in two different regions of RU4, respectively in the cell center (Figs. 2.4 A, C and E) and on the cell edge below the sealing layer (Figs. 2.4 B, D and F). This second area (corresponding to location 5 in Fig. 2.3) was subjected to a similar thermal history, but without the electrochemical reactions. Figs. 2.4 A and B display part of the Ni-YSZ electrode of the RU4, which provides a clear picture of the regions in the proximity of the electrolyte. Distribution maps reported in Fig. 2.4 C and D qualitatively exhibit the depletion zone at the interface (the dashed line indicates the edge of the electrolyte). Moreover, the increase in oxygen and zirconium percentage indicates that YSZ is not affected by depletion. Spatial evolution of the atomic percentage for each element has been evaluated with four vertical line scans. In Figs. 2.4 E and F the arithmetic averages have been reported (continuous lines). A steep decrease in Ni composition can be observed in the first case (Fig. 2.4 E), occurring mainly in the first 5 µm at the interface with the electrolyte (the oxygen electrode was delaminated in this RU). In the second case (Fig. 2.4 F), the transition of the elements at the interface appears to be sharper. This depletion caused also a slight relocation of Ni in the following 30 µm, as described in [74, 81, 104]. In particular, Holzer et al. [17] analysed the effect of humidity for a H₂O/H₂ mixture in fuel cell mode. The coarsening of Ni would cause a displacement of nickel particles from the TPB to the inner part of the electrode through surface migration or volatilization of Ni(OH)₂. Lastly, this implies a growth of the effective electrolyte thickness and a reduction of electrochemically active TPB, which leads to an inactive Ni-YSZ region [105, 106].
2.2. Post-test analysis

A small content of impurities was measured, including Fe, Al and Na, even if the average atomic percentage measured for these elements is around 1% (not significant enough to draw a conclusion). Such impurities are likely introduced during the preparation of the samples. Si is the only element that presents a higher concentration, in particular at the electrolyte/hydrogen electrode interface (Fig. 2.5B). Silicon in fact is the main constituent of the sealing that seals the active area of the cell from the exterior. In presence of high steam content, it reacts forming volatile Si(OH)$_4$ at atmospheric pressure [107]. Hauch et al. [74] also reported a similar accumulation of Si, which crosses the electrode through the pores and tends to stick on the available TPBs in the form of SiO$_2$. According to Kreka et al. [108], under cathodic polarization to potentials below -1.8 V silica may be reduced.

Figure 2.4 – (A) Ni-YSZ electrode with 4 line scans located at the center of RU 4, (B) Ni-YSZ electrode with 4 line scans located at the edge of RU 4 (under the sealing), (C), (D) EDS quantification analysis (1 µm minimum region of confidence) for the two cases, (E), (F) EDS Ni atomic percentage distribution maps for the two cases.
2.2.2 Electrolyte

Several detachments between electrolyte and GDC compatibility layer were observed (Figs. 2.4 A, 2.6 and 2.8) in RU 4, similarly to what was presented by J. R. Mawdsley et al. [79]. This was probably induced during the preparation process of the samples, expanding the cracks already present in the microstructure. Otherwise, such an extended delamination would have produced voltage drops that were not observed during the experiment. High magnification pictures of FIB-polished samples (Figs. 2.6 A and 2.6 B) clearly outline the formation of small cavities along the YSZ grains and, in proximity of the GDC layer, also inside the grains (approximately in the last 1 $\mu m$). In fact, the intergranular fractures propagate along the YSZ grain boundaries and link up to voids (diameter < 100 $nm$) that generate cracks followed by widespread delamination [72]. This phenomenon is enhanced in electrolysis mode and can be the result of the formation of high internal oxygen pressure due to cation diffusion in the electrolyte, as stated in [80]. According to the author, this phenomenon would be triggered by the relatively small electron opposite conduction in the
2.2. Post-test analysis

electrolyte. In fact, a higher electronic resistivity would comport a more likely formation of cavities. Similar occurrence has been described in [109, 110], where an analogous horizontal orientation of the voids was identified. In case of SOFC operation, the oxygen pressure inside the electrolyte is inferior with respect to the fuel electrode and consequently there would not be a risk of delamination [111].

![Figure 2.6](image)

**Figure 2.6** – (A) YSZ electrolyte and Ni-YSZ electrode, (B) focus on YSZ electrolyte (RU 4).

Figs. 2.7 A and B show fractured YSZ grains belonging to RU 1. The void structures on the detached grains surface are highlighted by black arrows. An explanation of this phenomenon has been given by Tietz et al. [82], who proposed that the voids are probably generated from the mass transport of species with different diffusion coefficient due to the electrochemical potential. In addition, also the orientation of the YSZ grains seems to have a certain influence on the depth of these void formations, which also implies a different contact resistance. The portion of electrolyte material detached from these voids migrated and re-deposited in form of a dense layer at the interface with the GDC layer.

Finally, TEM observation (Fig. 2.10 A) displays a vast detachment at the YSZ/GDC interface generated by an extended pores formation (approximately 500 nm) at 0.7 μm from the edge of the YSZ electrolyte. The EDS analysis along the vertical line scan (Fig. 2.10 B) reveals that the atomic percentage of the various elements across the crack is not significantly changing, thus no chemical changes occurred.
Figure 2.7 – (A), (B) YSZ grain surface with fractured grain boundary at high magnification (RU 1).
2.2. Post-test analysis

2.2.3 Oxygen electrode – anode

The oxygen electrode unveils several cracks between the different layers in both the RUs (Fig. 2.8 A). Similarly to the electrolyte, these detachments, generated from a weakening of the interface, have been enhanced during the manipulation of the samples. These cracks can favor the accumulation of impurities that may infiltrate more easily in the inner part of the electrode. This is the case described in Figs. 2.8 B – D, where a vertical line of sulphur combined with Sr (coming from the LSC layer) probably in the form of SrSO$_4$ formed during operation. As explained in [112] the formation of such a compound occurs when the LSC electrode is exposed to SO$_2$. Even if the environmental compressed air was cleaned with filters, some oil particles in ppb range may be transported by the inlet feed flow. Moreover, a typical SO$_2$ content of 10 ppb is present in urban air [113]. After 10000 h of functioning the accumulation can be significant and the presence of these cracks could locally enhance the gas transport compared to other diffusion paths, favoring the accumulation of such impurities. On the other hand, the overall distribution of S in the two RUs was barely detectable.

![Figure 2.8](image)

Figure 2.8 – (A) cracks on the oxygen electrode (RU 4), (B) crack with SrSO$_4$ inclusion on the oxygen electrode (RU 4), (C) (D) S and Sr EDS maps.
Fig. 2.9 A shows a cross section of the cell with the formation of a dense mixed layer between YSZ electrolyte and GDC compatibility layer for RU 4. The mixed layer is highlighted in the FIB polished picture (Fig. 2.9 B) and is approximately 1 µm thick. The darker tone of grey represents strontium inclusions. In particular, Sr from the LSC layer is transported through the GDC pores by surface diffusion or gas transport and combines with YSZ, forming SrZrO$_3$. The formation of this compound occurs first during the sintering process, but the operation in electrolysis may enhance this process, as also presented in [82]. Moreover, the presence of SrZrO$_3$ hinders the $O^-$ current and such extended formation, like the one in Fig. 2.9 B, can locally obstruct the ions flux. The et al. [81] supposed that the driving force for this degradation is the chemical potential gradient of SrZrO$_3$ formation. The shape of the Sr inclusions follows a dendritic pattern similar to what has been proposed in [114], where a Monte Carlo simulation approach was used to reproduce the solid/solid interfaces evolution in cation-conducting crystalline solids with different conductivity. These inclusions may ultimately lead to the complete obstruction of the current passage in some regions. On the other hand, the ions flux could be forced to cross smaller sections increasing locally the heat generated due to ohmic losses.

The EDS line scan in Fig. 2.10 B highlights the presence of the SrZrO$_3$ inclusions between 2.2 and 2.6 µm along the vertical direction. This presence is confirmed by the atomic percentage of Sr and Zr that is almost equal in this region. The line scan also exhibits a distributed diffusion of Ce through the YSZ layer until the crack. This solid solution between the GDC and YSZ elements most likely happened due to the high temperatures during the sintering process [115]. In addition, element distribution maps (Figs. 2.10C - E) reveal a tangible Zr diffusion which also matches with the Sr inclusions. As described in [116], at first Zr diffuses into the GDC layer during the sintering process, and then the Sr particles reach the Zr sites when the LSC electrode is applied forming the SrZrO$_3$ inclusions. The study also confirms that the operation under polarization enhances this
phenomenon. SAED analyses performed on the inclusions (Fig. 2.10 F) certify the SrZrO$_3$ formation. In fact, the experimental SAED pattern corresponds to the [-111] zone axis of SrZrO$_3$, which at room temperature exhibits an orthorhombic structure (Pbnm) [117]. Lastly, the diagonal pores structure visible in the bottom part of Fig. 2.10A looks similar to intermixed Ni and ZrO$_2$ microstructure described in the work of Hansen [118].
Chapter 2. Post-test analysis on a SOC stack operated for 10700 hours in steam electrolysis mode

Figure 2.10 – A) Cross-sectional TEM micrograph of YSZ-GDC interface (RU 1), (B) line scan quantification analysis, (C), (D), (E) EDS Zr, Ce and Sr atomic percentage distribution maps, (F) SAED pattern identified as SrZrO$_3$ (RU 1).
Quantitative EDS analysis has been applied on the oxygen electrode of RU 4 to calculate the average atomic concentration along line scans (Figs. 2.11A - C). Strontium migration through the GDC pores is evident, with a value corresponding to 4% (± 2%) at the interface with the YSZ electrolyte and 8% (± 1.5%) in the LSC electrode (at% of Sr in La$_{0.6}$Sr$_{0.4}$Co O$_3$ is 8%). Also Zr and Y from the electrolyte are present in the first 2 $\mu$m of the GDC layer and the peaks of Sr appear to be in concomitance with the diminution of Ce, which confirms the hypothesis of the formation of SrZrO$_3$ at the YSZ/GDC interface, as mentioned before. Moreover, in Figs. 2.11B and C it is possible to notice an increase in chromium concentration along the GDC layer with an atomic percentage around 2% (± 1%) and the peak at 3 $\mu$m from the electrolyte interface. On the other hand, the electrochemical active sites do not appear to be covered. In addition, a few bulk particles of Cr can be observed, as f.ex. in Fig. 2.11D (red arrow). According to Schuler et al. [112] these formations are typical in LSC-based electrode material and, in particular, are due to the high Sr activity that leads to the generation of bulky SrCrO$_4$ grains.
Figure 2.11 – (A) GDC-LSC oxygen electrode (RU 4), (B), (C) EDS line scans quantification analysis (1 µm minimum region of confidence), (D) EDS Cr atomic percentage distribution maps.
2.3 Conclusions

The 10700 h steam electrolysis stack test, after initial degradation and a severe incident, exhibited remarkable stability at \(-0.5\, \text{A cm}^{-2}\) between 4000 h and 10000 h of operation although the long-term operation caused several changes in the cell microstructure:

1. Ni depletion at the interface with the electrolyte (to a depth of 5 \(\mu m\))
2. void formation in the electrolyte along and inside the YSZ grain boundaries, especially in proximity of the GDC layer
3. formation of a dense layer at the interface between YSZ electrolyte and GDC compatibility layer filled by SrZrO\(_3\) inclusions
4. accumulation of Si in the fuel electrode at the interface with the electrolyte and of Cr in the GDC compatibility layer
5. sulphur inclusion along cracks in the oxygen electrode

Even if delamination was found in RU 4, they were probably caused by the sample manipulation since the voltage remained stable until the end of experiment. Ni depletion and the accumulation of voids in the electrolyte created an overall weakening of the structure to cause the possible initiation of cracks. These alterations are expected to lead to a decrease in performance, lowering the available TPB sites in the cathode and obstructing the passage of oxygen ions because of the accumulation of SrZrO\(_3\) at the YSZ/GDC interface. The degradation mechanisms discovered are in line with the ones presented in analogous studies on single cells [81, 82], even if the different structure of the stack led to accumulation of impurities. For this reason, further analysis will be conducted to understand whether the low atomic concentration of contaminants discovered (Si and Cr overall) could have a noticeable impact on global performance.
Characterization of the morphology near triple-phase boundaries in solid oxide cell electrodes

The post-test analysis presented in Chapter 2 indicates that several degradation phenomena may provoke a reduction of the overall density of sites available for electrochemical reaction, in particular in the proximity to the electrolyte. Changes in morphology near the sites with consequences on the performance are also expected. The present Chapter is dedicated to the second aspect and proposes a method for electrochemical performance characterization, focused on the measurement of the surfaces available for diffusion at each TPB. In the first part, the developed spilling algorithm is described and tested against real Ni-YSZ and LSM-YSZ Volumes and artificially generated packed-spheres structures. The second part investigates the relation between the extension of the available length and the size of TPB regions. The developed methodology will be also used in Chapter 5 as an improved capabilities for the quantification of the Ni-YSZ microstructure evolution.

3.1 Introduction

The electrochemical performance of SOC electrodes depends on the density and activity of their TPB sites, which are the geometrical intersections between the pore and solid phases in heterogeneous materials. Intuitively, two aspects are relevant for the quality of the sites. First, the transport of oxygen anions, gas species and electrons through the electrode material from the electrolyte, gas channel and electron current collector to the TPB sites must be efficient. Second, the morphology near the sites influences locally the supply of products and reactants that diffuse through the porous composite.

A variety of composite materials has been developed to obtain efficient transport, electro-catalytic properties and chemical and mechanical compatibility with adjacent layers and stack components.

1Personal contribution: development of spilling algorithm and percolation model, realization of the morphological analysis.
Chapter 3. Characterization of the morphology near triple-phase boundaries in solid oxide cell electrodes

While the Ni-YSZ cermet is the most widely used fuel electrode material, on the oxygen side, several ceramic materials were investigated to achieve adequate performance. In the case of Sr-doped LaMnO$_3$, the elementary steps of oxygen reduction occur near the TPBs. Indeed, in the condition of practical interest for the operation of SOC stacks, the transference number is dominated by electron and ion transport in LSM and YSZ, respectively [119].

In a first approximation, the electrode performance scales with the density of connected TPBs. Further analyses show that the local morphology and network topology play a role for the accessibility mainly by the transport of oxygen ions, which can be affected by narrow necks and tortuous pathways [94], which relates to the connected TPB density. The present study extends the analysis to the characterization of the morphology near the TPB sites.

The linear relationship between the TPB density and the polarization resistance of Ni-YSZ has been established using patterned electrode experiments [120], in which the details of the reaction kinetics were qualitatively analyzed [121]. This setup geometry eliminates gas transport limitations that can occur in porous electrodes and facilitates the accurate measurement of the total TPB length. Nevertheless, few studies attempted to analyze specifically the impact of surface-diffusion processes associated to each elementary step on the overall performance. In the case of controlled TPB geometries, this effect is not noticeable, but as stated by Bessler et al. [122] among others, the morphology close to the TPBs is expected to impact the performance, limiting the diffusion of surface species under polarization. For this type of calculations, the TPB is not treated as a geometrical line but a region with a size that represents the extent of the reaction zone [123].

Few studies attempted to investigate the spatial variation of surface coverages under polarization on patterned Ni-YSZ electrodes as a function of “available length”, which corresponds in a 2-D geometry to the width of ribbons on the Ni and YSZ phases. In a reticulate microstructure, such a length relates to the ISA between the pore and solid phases surrounded by TPB lines. The outcome of the analyses mentioned above suggests an extension ranging from a few nm to 100 nm on the Ni surface and from 100 nm up to a few µm on the YSZ surface. One such seminal mechanistic study of the hydrogen oxidation and reduction on patterned Ni-YSZ anodes was performed by Vogler et al. [5]. Hydrogen-spillover was identified as the most likely rate-limiting step. Simulations under polarization showed almost no gradient on the Ni surface, while on the YSZ side, surface diffusion profiles were in the range of 100 nm. The difference is principally due to the fast diffusivity of hydrogen on Ni and, in general, it can be stated that adsorption/desorption kinetics are faster than surface diffusion. Goodwin and co-workers [4] adopted a similar approach to that of Vogler et al., but implemented the splitting of the YSZ surface sites into two groups, surface oxygen and zirconium sites. The results were qualitatively similar, with however a higher extension of the diffusion profiles on the YSZ sites reaching up to 2 µm due to the smaller surface diffusion coefficients. Hanna et al. [6] also developed numerical and analytical models for the oxidation of CO. In this case, the simulations indicate a gradient of CO coverage extends up to 10 nm from the TPB at an applied
3.1. Introduction

An analogous approach can be applied to investigate the oxygen reduction reaction in LSM-YSZ microstructures. Even though other materials with higher ionic conductivity were adopted in the last years, LSM remains relevant mainly for high temperature applications, because of its mechanical and chemical stability. A significant body of literature is available on the regimes in the contributions of the surface and bulk reaction pathways [124]. Below 700-800°C and for overpotentials lower than 0.2 V, oxygen is adsorbed on the LSM surface and diffuses toward the TPBs. For higher overpotentials, the electrochemical reaction occurs directly on the LSM sites and the bulk transport of oxygen ions toward the YSZ electrolyte becomes predominant. Bertei et al. [9] recently calculated a diffusion length of 224 nm at 800°C based on the estimation of parameters such as kinetic constants and diffusion coefficients from electrochemical impedance spectroscopy data. Fu and co-workers [10] attempted to measure the length available for surface diffusion as the interface length between LSM and pores on 2-D SEM images. The median length divided by two was around 290 nm. Another approach was adopted by Van Heuveln [125], which estimated the extent of the physical TPB width on YSZ as 50±20 nm assuming a circular particle in contact with the electrolyte. Horita et al. [7, 8] characterized the reaction sites for O₂ reduction at the LSM/YSZ interface by tracer experiments and secondary-ion mass spectrometry (SIMS). The high concentration of ^{18}O at the TPB region indicates that the electrochemical reaction occurs mostly near the geometrical TPBs even though O₂ can diffuse through LSM under cathodic polarization higher than 0.336 V. This is due to the formation of oxygen vacancies in the LSM electrode [126]. In this case, the diffusion length was estimated smaller than 0.95 µm. Further, transmission electron microscopy and atomic force microscopy (AFM) studies by Jiang et al. [127, 128] and Backhaus-Ricoult [129] show that the morphology and composition of the interface between LSM and YSZ near the TPBs evolves under polarization. In particular, the formation of convex rings characterized by an average width of 150±50 nm indicates activity over such length and may afterwards slightly modify the diffusion path of the oxygen atoms toward the electrolyte phase.

At a first appraisal, the references discussed above would suggest a limited effect of surface transport, based on the inspection of indirect and averaged measurements of the available length. The actual impact on the overall electrochemical performance remains however still unclear, because the complexity of heterogeneous electrodes microstructures may result in local limitations in the case of insufficiently extended surfaces at the TPBs. The references discussed previously suggest that the diffusion length under polarization is more extended in LSM-YSZ compared to Ni-YSZ.

The advance of x-ray and electron microscopy methods for the 3-D imaging of SOC electrodes enabled the direct measurement of properties such as connected TPB density and ISA [3]. Hence, the ratio between the measured ISA (between pore and each solid i) and total TPB density provides
Chapter 3. Characterization of the morphology near triple-phase boundaries in solid oxide cell electrodes

Table 3.1 – Total TPB and interfacial surface area for pristine Ni-YSZ and LSM-YSZ from the literature and computed average available length \( (L_{A,av}) \). ISA values were adjusted by multiplying for the factor \( \pi/6 \) to estimate the actual surface area from the digitized Volume assuming close to spherical shapes.

<table>
<thead>
<tr>
<th></th>
<th>TPBTot [( \mu\text{m}/\mu\text{m}^3 )]</th>
<th>ISAPoreNi-LSM [( \mu\text{m}^2/\mu\text{m}^3 )]</th>
<th>ISAPoreYSZ [( \mu\text{m}^2/\mu\text{m}^3 )]</th>
<th>( L_{A,av}\text{Ni-LSM} ) [( \mu\text{m} )]</th>
<th>( L_{A,av}\text{YSZ} ) [( \mu\text{m} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-YSZ</td>
<td>9.04</td>
<td>0.53</td>
<td>1.51</td>
<td>0.06</td>
<td>0.17</td>
</tr>
<tr>
<td>Ni-YSZ [131]</td>
<td>6.79</td>
<td>0.35</td>
<td>0.84</td>
<td>0.05</td>
<td>0.12</td>
</tr>
<tr>
<td>LSM-YSZ</td>
<td>37.5</td>
<td>1.47</td>
<td>3.26</td>
<td>0.04</td>
<td>0.09</td>
</tr>
</tbody>
</table>

a first estimate of the average available length \( (L_{A,av}) \) in reticulate SOC microstructures (Eq. 3.1).

\[
L_{A,av} [\mu\text{m}] = \frac{\text{ISA}_{\text{Pore}}}{{TPB}_{\text{tot}}}
\]  

(3.1)

This calculation is expected to underestimate the actual available diffusion length. In a voxelized representation, it indeed assumes that each ISA unit element is assigned to a single TPB unit length, whereas in the reticulate electrodes’ microstructure the surfaces available for diffusion are expected to overlap. Examples of average available length computed respectively for Ni-YSZ and LSM-YSZ microstructures are listed in Table 3.1. The data is from 3-D FIB-SEM studies of pristine materials presented in previous publications. The Ni-YSZ Volume presents a voxel size of 7 \( \text{nm} \) and a total reconstructed volume of \( 17 \times 10 \times 19 \, \mu\text{m}^3 \) [130]. In the case of LSM-YSZ, the isometric voxel size is 10 \( \text{nm} \) and the volume size \( 15 \times 10 \times 10 \, \mu\text{m}^3 \) [94]. Additional values from the study by Joos et al. [131] on Ni-YSZ were added for comparison.

In the Ni-YSZ Volumes the average available length on Ni ranges from 50 to 60 \( \text{nm} \) for the two cases considered. The references discussed above do not suggest a limitation for the surface transport of species. In contrast, the average available length on YSZ is larger, between 120 and 170 \( \text{nm} \). In this case, a limitation may occur since the diffusion profile computed by Goodwin et al. [4] is of similar or larger dimension. For the LSM-YSZ Volumes, the average available length on YSZ is also larger with respect to LSM, the average available length of which falls within the order of magnitude reported in literature.

The average available length computed in Table 3.1 does not account for the complexity of the reticulated Ni-YSZ and LSM-YSZ microstructures. In reality, a distribution of available length is expected. Visual inspection of 3-D reconstructions suggests that the subset of available length much smaller than the computed average may not be negligible. Consequently, charge transfer may be locally limited at these sites, affecting the overall electrode performance.

The purpose of this study is the 3-D characterization of the distribution of the available length on the solid phases. An algorithm capable of measuring lengths related to each TPB has been
3.2. Materials and methods

The Ni/YSZ and LSM/YSZ Volumes investigated in the present study are respectively referred to the pristine samples 3 and 1 described in Chapter 1. The related size is 17x10x19 $\mu m^3$ for the pristine Ni-YSZ and 15x10x10 $\mu m^3$ for the pristine LSM-YSZ, with isometric voxel sizes of 7 and 10 nm. The ESB and in-lens detector data were combined to facilitate the removal of artifacts due to minor resin impregnation and decomposition. A 3-D bilateral filter was applied before segmentation using Matlab routines with calls to Avizo for image gradient and watershed transform computations.

The interfacial surface area, volume fractions, total and connected TPB density were computed using the methods described in [96, 97]. The phase size distributions were calculated based on the phase volume that can be filled with overlapping spheres of a given size e.g. [17, 98] and the coordination number was calculated after skeleton-based partitioning of each phase [94, 132]. Besides the two real samples obtained by FIB-SEM serial sectioning, artificial packed spheres Volumes were generated with controlled particle radii, volume fraction and particle neck sizes, as described in ref. [133].

A method was developed to locally measure the available length on the two solid phases associated to each TPB in the segmented 3-D FIB-SEM reconstructions. Fig. 3.1 provides an overview of the method. The algorithm scans the reconstructed segmented Volumes (Figs. 3.1A-B) slice by slice along the 3 directions (X, Y, Z) (Fig. 3.1C). In this two-dimensional digitized representation, each TPB of unit length is a point and each diffusion surface on a solid phase is a line, defined as the available length $L_A$. This stereological approach is valid under the assumption that all portions of the structure and all directions of measurement are equally represented (uniformity and isotropy) [3, 134]. Moreover, the developed measurement relies on the simplification that in a 3-D structure the diffusion of surface species driven by the electrochemical reaction occurs perpendicularly to the considered TPB of unit length. The real situation is expected to be more complex in particular in narrow regions, where the diffusion gradients may develop following directions where the density of free sites is higher.

An example of the available length detected on a section in the 3-D dataset is displayed in Fig. 3.1D, in blue and red. TPBs (in green) are recognized when all the three phases are present in four adjacent voxels (e.g. Fig. 3.1C). The validity of a TPB is treated following a set of rules and the consistency of
paths along the solid-pore interfaces with two-dimensional 4-neighborhood, applied first on the four voxels forming the TPB, then an expanded window of 16 voxels.

- In the case two voxels of the same solid phase (white or dark grey in Fig. 3.1C) are located diagonally, the TPB is not valid because the pore is not connected directly with the remaining solid phase. On the contrary, in the case of two diagonal pores voxels, two distinct TPBs are documented.
- A valid TPB may be discarded if the surrounding voxels do not form a consistent pathway. A 4 by 4 screening window comprising the 12 neighboring voxels to the TPB element is inspected to ensure that the TPB has 4-neighborhood connection with the exterior of the window through both the solid and pore phase voxels in the dataset throughout the potential start of the path. The pore neighboring voxels located in the four corners are discarded if adjacent only to perpendicular solid phases voxels.
- The initial solid voxel connected to the TPB from which the spilling starts must be then
3.2. Materials and methods

identified. In the case of non-unique possibilities, the voxels connected to the pore voxels and with 4-neighborhood connectivity with the solid voxels of the TPB are kept.

- Finally, pore voxels are discarded if not connected to the solid phase at TPB and to its exterior continuation. In the case of diagonal pore voxels intersected by two diagonal solid voxels, only one is considered valid based on its position.

Once the solid voxels outside the TPB have been identified, the discrete values are assigned for the initial pathway length depending on the possible geometrical combinations within the 4 by 4 window (values equal to 1, 2, 1.707 or 2.707 voxels). This procedure was implemented in an attempt to reduce measurement noise for low lengths, but did not significantly affect the measurements for the structures considered in this study.

The spilling then proceeds over each solid phase along the interface with pore to follow the evolution of the morphology while guarantying the 8-connectivity of the solid and pore phases pathways. The grey line in Fig. 3.1E (“I”) illustrates how the proposed algorithm proceeds along the pore-solid interface considering 1 voxel in the case of a linear path and \( \sqrt{2} \) voxel for a diagonal path. The accuracy provided by methods differing in terms of assumptions and implementation complexity is compared in Fig. 3.1F. The length measured by the implementation selected for the present study (grey “I” in Fig. 3.1E) lies in-between simple voxel counts (blue in Fig. 3.1F) and voxel edge count (red in Fig.1f), which respectively underestimate and overestimate the length. It provides similar accuracy for the present test case as the method “R” (green in Fig. 3.1E), which is expected to be more rigorous but more complex to implement.

The measurement procedure verifies that each voxel belonging to the considered solid phase is in contact with at least one pore voxel to guarantee the consistency of the followed path. The spilling algorithm stops when either another TPB or the exterior of the Volume is reached, as visible in Fig. 3.1D. In the latter case, the measured lengths were documented but not included in the presented results. This also implies that the available length for each TPB is only part of the associated length measured by the spilling algorithm, which can be considered as half in a first approximation (assumption of symmetry in all cases). In addition, the algorithm guarantees consistent behavior when complex bifurcations possibilities are met. In fact, a single length can in rare cases be shared by three different TPBs in the case of singularities or remaining errors from the segmentation process.

In the Volumes considered in the present study, approximately 1-2% of the detected TPBs did not comply with the validity and initial 4-neighborhood conditions. 6-13% of the measured lengths were touching the boundary of the Volumes and therefore documented but discarded for the analyses. The percentage of lengths that could not be tracked because of bifurcation problems was less than 1%. The list of valid measured lengths is used to generate by binning an estimate of the probability density function for each pore-solid interface, considering either the full list corresponding to the total TPB or the subset of connected TPBs. The common logarithm of the available length was used
Chapter 3. Characterization of the morphology near triple-phase boundaries in solid oxide cell electrodes

as independent variable.

Curvature analysis was performed to investigate the relation between available length and local morphology. A triangular surface mesh of the three-phase Volumes is generated using Avizo's implementation of the marching cube algorithm with smoothing. The surface mesh for each individual phase is then reconstructed using Matlab post-processing routines. The principal curvatures $\kappa_1$ and $\kappa_2$ at each mesh patch of the reconstructed meshes are measured by Avizo based on a local quadratic surface fit and four repetitions of averaging among patches sharing common mesh edges (two layers of neighbor patches were considered). The subsets of principal curvatures corresponding to each inter-phase surfaces in the full mesh dataset is finally retrieved using Matlab routines and weighted by the corresponding subset of triangle areas to generate interfacial shape distributions (ISD) [135]. The bi-variate ISD plots can be divided into four distinct regions, respectively bumps ($\kappa_1$ and $\kappa_2 > 0$), saddles of the first type ($\kappa_1 > -\kappa_2$), saddles of the second type ($\kappa_1 < -\kappa_2$) and dimples ($\kappa_1$ and $\kappa_2 < 0$). Surfaces that lay on the 45° diagonal with positive slope have a spherical shape, while those on the two axes have cylindrical shape. In the case of negative $\kappa_2$, those surfaces surround the void at the interior. The origin of the plot represents a planar surface. The zones $\kappa_1 < \kappa_2$ are not populated, because of the principal curvature definition. A more exhaustive description is given in Appendix B.

3.2.1 Validation

A comparison of the measurements performed in the three directions indicates the isotropy of both the considered pristine Ni-YSZ and LSM-YSZ Volumes in terms of available length (not shown). The measured probability densities are spread over about two orders of magnitude and are further characterized by larger noise at lower lengths. As anticipated, the digitized Volume representation can be a limitation for the proposed measurement, which does not allow the features of the microstructure close to the spatial resolution of the dataset to be characterized accurately. This is illustrated in Fig. 3.2A with the probability density distribution of the available length on Ni measured on the Volume sample with the native 7 nm isometric voxel size (solid line) and after resampling at 10 nm (dashed line). The difference is small for lengths >20 nm and does not severely affect the global trend in the shape of distribution, but it becomes unstable for smaller lengths. The corresponding thresholds assigned after visual inspection is indicated by the vertical dashed lines. Below this limit, the data is considered statistically unreliable, even though the general trend may still convey qualitative information. Fig. 3.2A also compares the distributions obtained with the spilling algorithm and the simplest approach in Fig. 3.1E and F based on the counting of the voxels in the considered solid phase that form the interface with pores (dashed blue line in Fig. 3.2A). The trend is qualitatively similar, but the spilling algorithm provides increased stability for lengths smaller than 150 nm, which is much larger than the threshold of 20 nm discussed previously.

The algorithm was tested on a series of artificially-generated randomly-dispersed packed spheres
3.2. Materials and methods

Figure 3.2 – (A) Computed distribution of available length on Ni in a Ni-YSZ sub-Volume with 7 nm voxels and after resampling at 15 nm with the measurement method “R” and voxel counting in Fig. 3.1. The vertical dashed black line corresponds to a threshold under which the measurement is unstable for the standard 7 nm measurement. (B) Comparison of the available length ratios ($L_{Ni,LSM}/L_{Ni,YSZ}$) computed by the percolation theory-based model (y-axis) and measurements with the spilling algorithm ($L_{Ni,LSM}/L_{Ni,YSZ}$) on the y-axis) for the packed spheres (points 1-7) and Ni-YSZ and LSM-YSZ Volumes imaged by FIB-SEM serial sectioning (points 8-9).

structures, produced with the in-house code described in Ref. [133]. The computed means of the measured available length distributions ($\overline{L_A}$) were compared with predictions from a percolation theory-based model. Indeed, the artificially-generated Volumes are intuitively expected to comply best with the assumptions of percolation theory, which is based on a representation of the structure as spheres [136]. The details of the model derivation are reported in Appendix A.

The artificial structures were generated by imposing solid volume fractions and fixed particle diameters for the two solid phases (Table 3.2). A single variation of the intra-phase neck size was also tested (median of the neck size distribution of 0.21 and 0.26 $\mu m$). The first five structures have the same combinations of particle sizes but different volume fractions, while the sixth and the seventh were generated using input values that are close to the measurements on the Ni-YSZ and LSM-YSZ Volumes (Section “Experimental” and corresponding measured properties later in Table 3.3). The parameters used for the artificial Volume generation were used as input to the model based on percolation theory. The computed mean of the available length distribution ($\overline{L_A}$) and the calculation by the percolation theory model are listed in Table A.1.

The comparison between the available length (i) measured on the artificial packed sphere and 3-D
Chapter 3. Characterization of the morphology near triple-phase boundaries in solid oxide cell electrodes

<table>
<thead>
<tr>
<th>Particles diameter [µm]</th>
<th>Volume fraction [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YSZ</td>
</tr>
<tr>
<td>1 &quot;Small necks&quot;</td>
<td>0.51</td>
</tr>
<tr>
<td>2 &quot;Large necks&quot;</td>
<td>0.51</td>
</tr>
<tr>
<td>3 &quot;Intermediate Ni/LSM vol. frac.&quot;</td>
<td>0.51</td>
</tr>
<tr>
<td>4 &quot;High Ni/LSM vol. frac.&quot;</td>
<td>0.51</td>
</tr>
<tr>
<td>5 &quot;Low Ni/LSM vol. frac.&quot;</td>
<td>0.51</td>
</tr>
<tr>
<td>6 &quot;High Ni/LSM diameter&quot;</td>
<td>0.47</td>
</tr>
<tr>
<td>7 &quot;Small Ni/LSM diameter&quot;</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 3.2 – Input parameters for the generation of the artificial packed spheres Volumes and calculations with the percolation theory model (description in Appendix A).

electron microscopy Volumes and (ii) computed by the percolation model is summarized in Fig. 3.2B. The ratios of the mean of the available length distributions (\(\bar{L}_{A, Ni/LSM} / \bar{L}_{A, YSZ}\)) measured on the packed spheres and real structures are reported on the x-axis. The ratios of the available length computed with the model described in Appendix A lies on the y-axis. The overall alignment along the 45 degrees dashed line highlights the qualitative agreement between the two approaches for the artificial structures, as well as for the investigated Ni-YSZ and LSM-YSZ SOC electrode materials.

Analyzing the artificial structures with same diameter (corresponding to circles 1 to 5 in Fig. 3.2B), points 1 and 2 are almost adjacent on the chart despite the differences in neck size among particles. The ratio seems to increase monotonically with that of the volume fraction of the second phase (Ni or LSM, points 1-5). Points 6 and 7 also follow this trend in the available length measurement dataset, despite the differences in diameter. The black circles 8 and 9 referring to the real Ni-YSZ and LSM-YSZ structures are characterized by lower ratios. In this case, the input diameters for the percolation model were selected by choosing the median of the phase size distribution measured by the code described in Section “Methodology”, while the ratios on the y-axis were retrieved from the available length distributions discussed later in Figs. 3.3.

The available length computed with the percolation theory-based model depend on the estimated specific surface of the spherical particles (\(S_{i,j}\)) and the inter-phase coordination number (\(Z_{i,j}\)), as expressed in Eq. A.11. This is in line with the observed dependence on the volume fraction, which is reflected on the magnitude of the ratios of measured ISAs (4: \(\text{ISA}_{\text{Pore}/\text{Ni}-\text{LSM}} / \text{ISA}_{\text{Pore}/\text{YSZ}} = 1.46\) and 5: 0.59, see Table A.1). In fact, the phases are complex and reticulate in the real Ni-YSZ and LSM-YSZ structures (points 8 and 9), resulting in lower ratio (0.35 and 0.45, respectively), compared to the more homogeneous packed sphere Volumes generated with similar volume fraction and mean phase diameter. This implies a lower ratio in Fig. 3.2B.
3.3 Results and discussion

3.3.1 Ni-YSZ and LSM-YSZ structures

The qualitative agreement between the available length measured by the spilling algorithm on artificial structures and model predictions indicates that the developed measurement captures from a Volume-averaged perspective the expected dependence on the variation of standard microstructural parameters, such as volume fractions and particle sizes. The results also suggest that the percolation-based model can capture trends for the real Ni-YSZ and LSM-YSZ structures. The model does however not inform about the distribution of the available length, which is a limitation for the precise analysis of the size and shape of TPB regions. The detailed analysis of the Ni-YSZ and LSM-YSZ real structures in this section is therefore performed using the developed spilling algorithm.

As described in Section “Methodology”, the detected available length that touch the boundary with the exterior are discarded for the analysis. The differences in the percentages reported in Table 3.3 between the solid phases in a same material occur because larger $L_A$ are more likely to touch the external border. However, because of the relatively large size of the two analyzed Volumes compared to the measured available length, still 87-94% are considered valid, which is not expected to affect the relevance of the study. The total TPB counts, i.e. half of the spilling iterations were approximately $4 \times 10^6$ and $6 \times 10^6$ for Ni-YSZ and LSM-YSZ, respectively. The results listed in Table 3.3 also highlight a limitation of the model based on percolation theory. As discussed previously, the ratio is correctly captured, but not the absolute value. The discrepancy is comparatively less for the packed-sphere Volumes (Table A.1), which indicates that SOC electrode microstructures significantly differs from a representation by mono-sized phase particles.

<table>
<thead>
<tr>
<th></th>
<th>$d_{50}$ [$\mu m$]</th>
<th>Volume fraction [-]</th>
<th>Mean $L_A$ [$\mu m$]</th>
<th>$L_A$ touching border [%]</th>
<th>$L_A$ from percolation [$\mu m$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-YSZ</td>
<td>0.37</td>
<td>0.45</td>
<td>0.28</td>
<td>0.43</td>
<td>0.29</td>
</tr>
<tr>
<td>LSM-YSZ</td>
<td>0.16</td>
<td>0.28</td>
<td>0.39</td>
<td>0.30</td>
<td>0.31</td>
</tr>
</tbody>
</table>

*Table 3.3 – Median phase size ($d_{50}$), volume fraction and mean available length ($L_A$) measured on the Ni-YSZ and LSM-YSZ FIB-SEM Volumes.*

The measured distributions of the available length for Ni-YSZ and LSM-YSZ are shown in Figs. 3.3C and E. The sixth packed spheres Volume generated using properties similar to the Ni-YSZ FIB-SEM reconstruction is reported for comparison in Fig. 3.3I. In each plot, the distributions corresponding to the total (connected + unconnected) and effective (connected only) TPBs are displayed with a continuous curve and a dotted curve, respectively. The vertical lines indicate the mean of the distribution ($\overline{L_A}$) in the case of total TPBs. The comparison of the ISA and integral of the non-normalized available length distribution informs about the portion of ISA between the pore and
the solid phases that is visited by spilling from the TPB, i.e. that relevant for the electrochemical performance, without however considering overlap among directions.

Figure 3.3 – (A), (D) and (G): cropped 2-D sections respectively from the Ni-YSZ, LSM-YSZ and 6th packed spheres Volume. (B), (E) and (H): view of the corresponding detected available length lines (blue for Ni/LSM, red for YSZ). (C), (F) and (I): available length distributions obtained with the spilling algorithm measurements. The vertical lines indicate the mean and the left portion of the distribution shown in grey correspond to the threshold of 4 times the voxel size.

The distributions of $L_A$ on YSZ in both electrode materials are shifted toward larger lengths compared to Ni and LSM. This qualitatively depends on the more reticulate YSZ microstructure as illustrated in Figs. 3.3A-B and D-E, where examples of cropped cross-sections in the Ni-YSZ and LSM-YSZ 3-D dataset are displayed with related color coded available length. In particular, the lengths on Ni (Fig. 3.3B) are on average shorter and visually less tortuous with respect to YSZ (Fig. 3.3E). This
3.3. Results and discussion

trend complies with the ratios of the ISA reported in Table 3.1, the \( \text{ISA}_{\text{Pore/YSZ}} \) in Ni-YSZ being approximately three times larger than \( \text{ISA}_{\text{Pore/Ni}} \). Hence, the shift between the distribution for Ni and YSZ as well as the computed mean values indicated by the vertical lines follow the expected trend. This observation is valid also for the LSM-YSZ case, where \( \text{ISA}_{\text{Pore/YSZ}} \) is about twice larger than \( \text{ISA}_{\text{Pore/LSM}} \). This is visually observed in Figs. 3.3D-E by the finer YSZ structure compared to the particle-like LSM phase, which may further explain the higher distribution peak in Fig. 3.3E.

The mean values of the available length distributions \( L_A \) measured for both microstructures are higher than the estimated averaged available length \( L_{A,av} \) presented in Table 3.1. A reason is that Eq. 3.1 assumes that each ISA unit element is assigned to a single TPB unit length, whereas the spilling algorithm can visit a ISA unit element several times. Assuming that each available length is shared by two TPBs, the computed mean of the available length distributions corresponds to sufficient values that allow a developed diffusion profile of the surface species up to close to the equilibrium, according to the literature data discussed in the “Introduction”. The difference between the available length distributions for the total and effective TPB density is limited in terms of shape and is slightly more pronounced for Ni-YSZ. The slight shifts of the distributions toward longer lengths indicate that the available length associated to isolated TPBs are on average slightly smaller than the average values.

The visual inspection of Fig. 3.3A and D indicates that the morphology of the YSZ phase in LSM-YSZ and Ni-YSZ differs significantly. This is due to the different mixture of starting powders and sintering temperature, around 1100°C and 1400°C for LSM-YSZ and NiO-YSZ, respectively. Further, the as sintered NiO-YSZ material is reduced before the first use. The effect on the available length on YSZ is significant, yielding a mean available length on YSZ in the LSM-YSZ electrode about half of that in the fuel electrode. These results indicate that the available length \( L_A \) in heterogeneous materials is influenced by the manufacturing route, which will be discussed in further details in the Section “Microstructural analysis”. The available length distributions computed on the artificial structures generated to mimic the Ni-YSZ microstructure (number 6 in Table 3.3) are provided in Fig. 3.3I for comparison. Because the structure is made of interconnected spheres, an available length measured by the spilling algorithm can spread over more than one spherical particle, which is not accounted for in the percolation model based on reasoning at the particle scale. There is a correspondence with Figs. 3.3C, including the mean values. The shape of the distribution for Ni is however better captured than that for YSZ, as could be anticipated because the latter structure visually deviates more from a packed sphere representation. The measurements also show increased variability for lengths below approximately 4 voxels, for the same reasons as discussed previously in the Section “Validation”.

The distributions in Fig. 3.3C, F and I indicate that the subset of available length smaller than the diffusion profiles discussed in the Introduction is not negligible. Figs. 3.4A and B provides the cumulative distribution of available length together with the estimated extensions of the diffusion
profiles under polarization reported in the literature for Ni-YSZ and LSM-YSZ (vertical dashed lines and shaded area). For such lengths, a limitation on the spillover reaction may occur, consequently of performance at these electrocatalytic sites, even if the TPB is connected and highly accessible. The percentage of measured available length lower than indicative thresholds are respectively 3-43% and 21-99% for Ni and YSZ, and 92-100% and 22% for LSM and YSZ. The vertical bars indicate the lower value together with the range of variation in transparency, showcasing that a strong uncertainty on the exact percentage remains.

Figure 3.4 – Cumulative distribution of the available length measured on Ni-YSZ (A) and LSM-YSZ (B). The vertical dashed lines and horizontal coloured bars (in transparency) indicate the range of diffusion profile length reported in the literature (Goodwin et al. [4], Vogler et al. [5], Hanna et al. [6], Horita et al. [7, 8], Bertei et al. [9], Fu et al [10], Van Heuveln et al. [4]).

For the Ni-YSZ, the morphology of the Ni phase does not appear critical for the performance, contrarily to that of the YSZ phase. In particular, according to Goodwin [4], the surface diffusion profile on YSZ may exceed 2 $\mu$m, which would be problematic for most of the TPB sites detected in the present Ni-YSZ material. Similarly, but opposite in terms of phases, the length of the oxygen diffusion paths measured by Horita et al. [7] is larger than the majority of the measured lengths on LSM. Estimations from other studies from the literature [9, 10] also suggest that the analyzed microstructure may not be optimal. Therefore, the results indicate that a diffusion limitation on LSM may occur for most of the TPBs, which may modify the contributions of the bulk and surface reaction pathways.

It is worth mentioning that microstructural changes during operation are expected to modify the available length. Ni-YSZ and LSM-YSZ are affected by degradation phenomena during aging that typically lead to an increase of the electrode polarization resistance. On the fuel side, Ni agglomeration is considered as the main reason for the reduction of TPB density [16, 63, 137, 138]. The decrease proceeds initially rapidly because of the fast rearrangement of the pore and Ni phases.
and then coarsening is slower typically after a few hundred hours [139]. The average available length on Ni is intuitively expected to increase, while not significantly improving the electro-catalytic activity of the TPB. A specific analysis on the effects of Ni-YSZ microstructural evolution is presented in Chapter 5. A coarser Ni phase may result in longer available length on YSZ as well, but a detailed analysis will be required. For LSM-YSZ, Liu et al. [140] reported that degradation strongly depends on the oxygen partial pressure, which can promote under high overpotential the formation of secondary phases at the interfaces such as lanthanum zirconate (La$_2$Zr$_2$O$_7$) and strontium zirconate (SrZrO$_3$). In both electrodes, impurities, e.g. chromium, silicon, and sulfur may form deposits or cause phase transformation that reduce the number of connected TPBs as well as the available length.

### 3.3.2 Microstructural analysis

In this section, the microstructural information provided by the developed available length measurement is analyzed in further details, in particular with regards to the morphology near the TPBs. A first extension of the analysis provided in Section “Ni-YSZ and LSM-YSZ structures” is to analyze each couple of available length at a same TPB together instead of separately. Indeed, the electro-catalytic activity of a TPB can be limited by the morphology of one of the two surfaces or both, as illustrated in Fig. 3.5A for Ni-YSZ. Therefore, the percentage of potentially limited TPBs provided in the previous Section may be inaccurate, depending upon the microstructure.

The occurrence of the combined limitation is investigated by generating the bi-variate probability density of the available length shown in Figs. 3.5C and D. The trends for Ni-YSZ and LSM-YSZ are different. The results indicate a correlation between the available length on Ni and YSZ, e.g. TPBs with a large available length on Ni also benefit from a larger available length on YSZ. The contrary is less clear, which suggests that the local extent of the $ISA_{\text{Pore}/\text{YSZ}}$ does not necessarily influence that of $ISA_{\text{Pore}/\text{Ni}}$. Further, the bi-variate distribution is almost not populated below the 45° line, indicating that the Ni reduction results in a microstructure that yields local $L_{A,\text{YSZ}} > L_{A,\text{Ni}}$. There is in contrast no evidence of a correlation between $L_{A,\text{YSZ}}$ and $L_{A,\text{LSM}}$ at the TPBs.

The observed difference between the two composite electrodes may arise from their manufacturing route. The synthesis of the Ni-YSZ cermet starts with the sintering of the NiO and YSZ powders at around 1400°C, followed by the reduction of NiO around 800°C, which results in an increase in porosity from typically 8% to 27-29% for the studied Ni-YSZ material [130] together with a reorganisation of the Ni phase. The production of LSM-YSZ does not in contrast comprise such chemical change and the temperature-dependence of the sintering of two ceramic phases is relatively similar [141]. This, together with the lower sintering temperature implies a less significant relocation of the microstructure compared to the Ni-YSZ case, resulting in a closer relationship between the produced electrode microstructure and the random distribution obtained by the powder mixing.
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Figure 3.5 – (A), (B) Example of combinations of Ni and YSZ available length (blue and red) at selected TPBs (green circles), showcasing situations where the available length on either one (I) or two (II) solid surfaces, or neither (III) may affect performance. (C), (D) Bi-variate available length distributions associated to same TPB respectively in Ni-YSZ and LSM-YSZ. The regions below the threshold under which the data is considered statistically unreliable is shaded in grey.

The available length data was projected on the 3-D sample Volume to visually appreciate the relation between the shape of the TPB lines and the local morphology. For each solid phase, the data retrieved by scanning in the three directions was merged into a single Volume for display and object-based analysis. Each TPB elements, i.e. the 4 voxels forming a TPB of unit length was assigned a value corresponding to the measured available length (rescaled over 16 bits), keeping the higher value in the case of voxels forming TPBs oriented in different directions. The rationale for this simplification is that the electrochemical reaction is less or not limited at all if the length in one direction is sufficient. For verification, the procedure was also performed by assigning the average value for shared TPB voxels. The results were qualitatively similar and pointing to the same conclusions (not shown).
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The TPB lines were identified as distinct objects in the 3-D dataset to further quantitatively investigate the potential correlation between their shape and available length. For this purpose, labelling and skeletonization were combined, for the separation into TPB objects and their classification, respectively. The number of disconnected spatial graphs are approximately 12000 and 68000 for Ni-YSZ and LSM-YSZ. For each solid phase, the arithmetic average of the available length on each TPB line was computed. The skeletonized TPB regions were further classified into two categories defined as “loops” and “open lines”. As the names suggest, the first corresponds to a mildly tortuous circular path without starting or ending points. In principle, all the TPB regions should form a closed path or traverse the full electrode Volume. In the present case, the “open lines” therefore reach the boundary of the Volumes with the exterior. However, a discontinuity in the TPB line was seldom induced because of the low percentage of TPBs identified as not valid by the spilling algorithm (Section “Methodology”).

Figs. 3.6A-E show the reconstructed TPB lines with color-coded available length in Ni-YSZ and LSM-YSZ. Selected sub-Volumes instead of the full data are shown for visualization purpose. The higher TPB density in LSM-YSZ (Figs. 3.6D and E) is evident given the edge dimension of the sub-volume is half of that of Ni-YSZ and, as discussed before, the available length are on average shorter compared to Ni-YSZ. A clear association between the shape of TPB lines and range in $L_A$ in the color scale is difficult to assess for LSM in LSM-YSZ, as well as YSZ. At most, TPB loops formed by small LSM particles seem to correspond to small lengths, such as illustrated in the insert in Fig. 3.6E. The inspection of Figs. 3.6B and C suggests in contrast qualitative relationships for Ni in Ni-YSZ. The TPB loops of lower length seem to correspond to smaller $L_A$ (Fig. 3.6B). Further, the Ni available length in the longer and less tortuous open lines or loops correspond to larger available length.
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Figure 3.6 – Regions of interest showing TPB lines with color coded available length in Ni-YSZ (A-C) and in LSM-YSZ (D, E). $L_A$, YSZ in Ni-YSZ (A) and $L_A$, YSZ in LSM-YSZ (D) comprise both TPB open lines and loops. Available length on Ni in Ni-YSZ corresponding to the subset of closed loops (B, note that part of the loops connect outside from the region of interest) and open lines (C).

An analysis of the TPB lines is shown in Figs. 3.7 and 3.8 for Ni-YSZ and LSM-YSZ, respectively. The bi-variate distributions were generated from the 3-D object dataset: the lengths of the TPB line objects are on the y-axis and the corresponding average available length on the x-axis. The fraction of TPB objects that are open lines are 29% and 69% in Ni-YSZ and LSM-YSZ, respectively. The plots for Ni interestingly reveal a pronounced correlation between the size and available length, especially for the TPB loops smaller than approximately 100 nm (Fig. 3.7B.I.). A similar but much less pronounced pattern is observed for the Ni open lines (Fig. 3.7B.II.). The distribution for YSZ is very different and a clear correlation is not observed (Fig. 3.7A). The solid phases in LSM-YSZ show a similar pattern as YSZ in Ni-YSZ (Fig. 3.8), except for a more pronounced trend for TPB loops and available length below approximately 100 nm (Fig. 3.8A.I., Fig. 3.8B.I.). It is here worth mentioning that the shortest TPB open lines correspond to fragments near the sample Volume boundaries.
3.3. Results and discussion

Figure 3.7 – Bi-variate distribution of available length $L_A$ and corresponding TPB object lengths for YSZ (A) and Ni (B) in Ni-YSZ. (A.I.) and (B.I.) correspond to the subset of TPB line objects forming loops, whereas (A.II.) and (B.II.) refer to that of open-lines.

---

a.i.

YSZ in Ni-YSZ

b.i.

Ni in Ni-YSZ

---

a.ii.

YSZ in Ni-YSZ

b.ii.

Ni in Ni-YSZ

---

Density (•)
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Figure 3.8 – Bi-variate distribution of available length $L_A$ and corresponding TPB object lengths for YSZ (A) and LSM (B) in LSM-YSZ. (A.I.) and (B.I.) correspond to the subset of TPB line objects forming loops, whereas (A.II.) and (B.II.) refer to that of open-lines.
The analysis therefore highlights a relation between the size of TPB regions and their average Ni available length, which is not observed for neither YSZ or LSM. This indicates that the Ni phase after the reduction has a distinct morphology, compared to the ceramic phases. Fig. 3.9 suggest that the shape of the TPB lines is predominantly controlled by the spatial distribution of Ni, likely because in a first approximation only the Ni phase is mobile and redistributes upon reduction, which is qualitatively supported by the sharper and wedgier microstructure observed in Fig. 3.3A. Consequently, the relocation of the Ni phase characterized by higher mobility and lower melting temperature must adapt to the morphology of the YSZ. A Ni particle (in red, translucency) constrained in the YSZ structure (light grey) is shown in Fig. 3.9A with a TPB line (red, loop). The location complies with the expected dihedral angles (≈ 150°) [16]. The available length on Ni in this specific configuration is dependent upon the radius of the particle in each slice considered, and therefore on the Ni morphology. This is illustrated qualitatively in Fig. 3.9B where a larger Ni particle is shown. YSZ lengths on the other hand do not exhibit a clear dependence in both cases. The Ni particle displayed in Fig. 3.9A is isolated and does not percolate with the other Ni regions, thus the TPB is not connected. Indeed, shorter closed TPB rings have a higher probability to be related to the junction of an isolated small inclusion and a much larger region of the opposite phase. This qualitative analysis however seems to hold for larger inclusions such as shown in Fig. 3.9B and C, for convex and concave Ni shapes.

Figure 3.9 – Selected close-up views in the Ni-YSZ dataset showing TPB loops (red) and open lines (blue) near isolated Ni particles (A, B: red, translucency) and connected regions (C).

Lastly, a curvature analysis was performed to extend the above qualitative analysis to the variety of shapes in the heterogeneous Ni-YSZ and LSM-YSZ microstructures. Figs. 3.10A-E report the ISD plots of the three ISA interfacial areas combinations for both composite electrode, following the approach described in Section “Methodology” and in Appendix B. It is worth mentioning that inverted phases (i.e. Ni/YSZ vs YSZ/Ni) would correspond to similar plots reversed over the diagonal line $\kappa_1 = -\kappa_2$ (where the mean curvature is null), e.g. a predominance of dimples is mirrored by a prevalence of bumps in the complementary ISA set. The fraction of the surface corresponding to each of the four main shape categories is indicated in white. The diagonal dashed lines with negative slopes correspond to constant mean curvature $(\kappa_1 + \kappa_2)/2$. In particular, the line that separates
the two saddles regions is characterized by null mean curvature. The parabolic dashed lines show constant Gaussian curvature, $\kappa_1 \kappa_2$ and is null in the origin.

Figure 3.10 – ISD plots related to the three interfacial surfaces. The percentages indicate the fraction of the surface area corresponding to the four zones. (A): Ni-YSZ Volume, respectively Pore/YSZ, Pore/Ni and Ni/YSZ interfaces. (B): LSM-YSZ Volume, respectively Pore/YSZ, Pore/LSM and LSM/YSZ.

At first, the distribution of YSZ shapes is similar for the Pore/YSZ (Fig. 3.10A) and Ni/YSZ (Fig. 3.10C) subsets, with ISDs mostly populated in the second and third regions corresponding to saddle shapes. This is in line with the hypothesis that the ceramic phase would act as a matrix limiting the Ni relocation. The Ni surface facing pore (mirror of Fig. 3.10) appears comparatively shifted toward saddles of the second type and dimples. This is visually confirmed by Figs. 3.3A and 3.4B, which indicate that the interface between Ni and pore is mostly slightly concave. This specific arrangement of Ni after reduction differs from a packed sphere representation. It is intuitively controlled by the large Ni dihedral angle ($\sim 150^\circ$) [16] and minimization of surfaces area with highest energy ($\gamma_{Pore/Ni} > \gamma_{Ni/YSZ} > \gamma_{Pore/YSZ}$) within the constraint imposed by the YSZ scaffold. In this regard, the results indicate that the Ni surface enclosed between two YSZ regions has a slightly concave, rather than convex shape, where the kinetics of Ni reduction may play a role. The relationship between formed TPB lines and $L_A$ illustrated in Fig. 3.9 can also apply in a simplified view to Ni hourglass shapes constrained by YSZ. Indeed, narrow necks in slender shapes are likely to pinch-off and therefore populate the “bump” region in the ISD. The fraction with cylindrical shapes is also significant for the
3.4 Conclusions

The electrochemical performance of solid oxide cell electrode composite materials is known to be dependent upon the density of TPBs and their accessibility by the transport of gas species, electrons and ions. This study investigates the additional potential effect of the local morphology near the TPBs. It is focused on the characterization of the extension of the surface on the two (Ni resp. LSM, and YSZ) solid phases at each TPB, because a narrow or restricted surface may limit the diffusion of the surface species involved in the charge-transfer mechanism and therefore affect the electrochemical performance.

A spilling algorithm was developed to measure the available length, a property to quantify the extension of regions available for surface diffusion on 3-D reconstructions obtained by e.g. x-ray nanotomography or focused-ion beam – scanning electron microscopy. The current approach is stereological and consists in scanning the 3-D Volumes slice by slice in 3 directions, where TPBs are points and each diffusion surface a line. The available length was first measured in a set of artificially-generated packed sphere structures with controlled properties for validation. The results were successfully compared with a percolation theory-based model, which expresses the dependence of the available length on the interfacial surface areas and coordination number of the solid phases expected for such structures.

The distributions of available length measured on real Ni-YSZ and LSM-YSZ electrodes imaged by FIB-SEM indicate a spread over about 2 orders of magnitude. In both LSM-YSZ and Ni-YSZ, the available length was larger on YSZ than in LSM and Ni, which is a trend opposite to the phase Ni/YSZ interfaces, which is in line with the need for the Ni phase to accommodate a location on YSZ where the dihedral angle condition is fulfilled.

In LSM-YSZ, the ISDs for Pore/YSZ (Fig. 3.10D) and Pore/LSM (Fig. 3.10E) are both characterized by the predominance of saddles and dimples. Hence, the two solid phases exhibit a pronounced convex shape that corresponds to an intuitive representation of sintered spherical particles, as discussed previously. The interface between the two solid phases is instead distributed roughly around zero mean curvatures. Moreover, the spread of the distribution is larger and associated to larger values of Gaussian curvature compared to Ni-YSZ, which implies smaller radii of curvatures. The inspection of Fig. 3.10D shows that the larger LSM regions are not embedded in YSZ like Ni in Ni-YSZ, but rather surrounded by multiple YSZ particles. Moreover, the multitude of small ceramic particles are interconnected through necks that cause a very extended surface area over which the available length develops. Hence, the resulting intricate TPB network (Figs. 3.6) does not allow to relate the size of the particle (and consequently with the available length) with the extension of TPB lengths, since it derives from the junction of particles of different size.
Chapter 3. Characterization of the morphology near triple-phase boundaries in solid oxide cell electrodes

diameter. The subset of TPBs with electrochemical performance potentially affected by the local morphology may not be negligible, 3-43% and 21-99% for Ni and YSZ, and 92-100% and 22% for LSM and YSZ, based on the estimated lengths of the diffusion profiles from the literature.

The relations between the two available length at each TPBs, as well as the size of the TPB regions were investigated with the support of interfacial shape distributions computed by curvature analysis. The results highlighted a very clear difference between LSM-YSZ and Ni-YSZ, which cannot be identified by the inspection of standard metric and topological properties. Evident relationships were not observed for neither phases in LSM-YSZ, likely because the latter composite sintered at a lower temperature around 1100°C retains a closer link to the mixed starting powders. In contrast, the sintering temperature is higher for NiO-YSZ and the synthesis involves the reduction of Ni. It results in a microstructure where the relocation of Ni yields a clear relationship between the phase size, available length, extension and shape of the TPB regions, mostly for Ni. In particular, TPBs with a large available length on Ni also benefit from a larger available length on YSZ. Further, small available length often beneficially correspond to isolated TPBs, as expected from the relationship with the local Ni phase size.

The study indicates first that design in the view of the maximization of the TPB density may not be optimal for all composite electrodes. Differences in the elementary steps in the reactions and surface transport properties should be accounted specifically for each phase. Second, the clear difference observed between Ni-YSZ and LSM-YSZ suggests possibilities for tailoring the available length by adjustments of the manufacturing route, sintering properties and material dihedral angles. The effects of microstructural evolution upon prolonged operation are investigated in Chapter 5. Further, the sensitivity of the available length measurement to differences in the microstructure that could not be anticipated by standard metrics may help to better describe the degradation of the Ni-YSZ microstructure and the impact on performance after aging.
Effect of available length on the electrochemical performance (Ni-YSZ electrode)

This Chapter investigates the dependence of the surface coverage profile near TPB under polarization on the available length metric developed in Chapter 3. Two elementary kinetic reaction-diffusion numerical models are adapted from the literature to assess the influence on the $\text{H}_2/\text{H}_2\text{O}$ and $\text{CO}/\text{CO}_2$ electrochemical reactions. A sensitivity analysis is performed by varying the extension of available length, gas composition and magnitude of diffusion coefficients.

4.1 Introduction

The electrode performance depends on the density of connected TPBs and the transport properties of the phases [130], as well as on the morphology in the electrochemically active regions. A gradient of adsorbed species is likely present on the Ni and YSZ surfaces under polarization. The size and morphology of the surfaces available for diffusion can locally differ in the complex and reticulate Ni-YSZ microstructure, potentially leading to a limitation of electrochemical performance whenever the diffusion gradient is constrained within a region that is not sufficiently extended. As previously shown in Fig. 3.4, a non-negligible fraction of the detected available length is lower than values reported in the literature.

Macroscopic computational models that describe the electrochemical reactions using Butler-Volmer equation with apparent dependencies on the partial pressure of gas species are limited for the analysis of the effect of the morphology near TPBs. The parameters that depend on local conditions would be lumped into the exchange current density, which is fitted with experimental data in most of the cases. A more detailed approach consists in considering a selection of charge transfer mechanisms, which depends on the concentration of the chemical species adsorbed on the surface.

---

1 Personal contribution: adaptation and implementation of the numerical models, generation and analysis of the results.
of the electrode and the electrolyte near the TPB. The species diffuse because concentration gradients
generated by polarization [122]. A continuum numerical model based on elementary kinetics with a
one-dimensional spatial discretization of the surfaces near the TPB is adopted to investigate the
relation between the available length and the electrochemical performance.

As explained in [4], the approach allows to separate the contribution of each individual chemical
and electrochemical step in the reactions along the discretized domain. The implementation of
parallel charge-transfer pathways can inform about the dependence on the local concentrations
of reactants and products on both the SOFC and SOEC operation modes (oxidation or reduction).
The reversibility of the proposed mechanisms requires a set of thermodynamically consistent
properties. The OCV is then an outcome of the model, obtained when the net electronic current of
the electrochemical pathways is null. Hence, this approach does not require an explicit definition
of the Nernst potential (which can be computed only in the case of chemical equilibrium), nor of
the activation overpotential. A-priori assumptions on rate-determining step is not needed and the
contribution of each process can be independently evaluated.

4.1.1 Selection of mechanisms

The implementation follows the approach by Goodwin et al. [4] for H₂/H₂O gas species (Eq. 4.1)
and by Hanna et al. [6] for CO/CO₂ reactions (Eq. 4.2).

\[ H_2 \text{gas} + O^X_{O(YSZ)} \Leftrightarrow H_2O_{gas} + V^2_O(YSZ) + 2e^-_{(Ni)} \]  

\[ CO_{gas} + O^X_{O(YSZ)} \Leftrightarrow CO_2 \text{gas} + V^2_O(YSZ) + 2e^-_{(Ni)} \]  

In the first case, the authors quantitatively described the hydrogen oxidation and reduction by
comparing alternative electrochemical charge-transfer mechanisms with the experimental data
obtained by Mizusaki et al. [120] on patterned anodes. Although no mechanism could be unam-
biguously discarded, most studies adopted the H₂ spillover [5, 121, 142–144], because of the best
agreement with the experimental data. Atomic hydrogen, first adsorbed on the Ni surface, crosses
over the TPB reacting with oxygen ions O²⁻_{O(YSZ)} combining in form of hydroxyl ions OH⁻ (Eq. 4.3).
The OH⁻ ions then react with additional H_{(Ni)} generating H₂O_{(Ni)} (Eq. 4.4). In electrolysis, the
process is reversed.

\[ H_{(Ni)} + O²⁻_{(YSZ)} \Leftrightarrow OH^-_{(YSZ)} + (Ni) + e^-_{(Ni)} \]  

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4.2 Modeling approach

\[ H_{(Ni)} + OH_{(YSZ)}^{-} \Leftrightarrow H_2O_{(Ni)} + (YSZ) + e^{-}_{(Ni)} \] (4.4)

However, other authors [145] considered that the oxygen migration pathway is dominant. Bulk diffusion of \( H \) in Ni could also occur under certain conditions [146, 147], but such possibilities are not further examined in the present work.

As mentioned in Chapter 3, Vogler et al. [5] adopted a similar approach consisting in combining detailed chemical and electrochemical elementary steps with the spatial variation of surface coverages under positive and negative polarization. Among the compared mechanisms, \( H_2 \) spillover yielded agreement with the experimental data set compiled by Bieberle et al. [121]. The main difference concerns the adsorption and desorption of \( H_2O \) from the YSZ surface implemented in the charge transfer mechanism [142]. The approach by Goodwin and co-workers consists instead in splitting the YSZ sites into the types (\( \chi \)) and (\( Z_r \)), referring to chemisorbed \( H_2O \) in the form of \( OH_{(\chi)}^{-} \) and \( OH_{(Z_r)}^{-} \) respectively [148].

In the case of the CO/\( CO_2 \) electrochemical reaction, less literature is available. A reason is that CO oxidation is believed to be slower than \( H_2 \) by at least one order of magnitude and consequently often neglected [149, 150]. The mechanism used in this study was proposed by Hanna et al. [6], where CO surface species are directly involved in the charge-transfer steps and \( CO_2 \) molecules are produced or consumed at the TPBs without further surface diffusion (Eq. 4.6).

\[ O_{O,(YSZ)}^{-} + (YSZ) \Leftrightarrow O_{(YSZ)}^{-} + V_{O,(YSZ)}^{-} + e^{-}_{(Ni)} \] (4.5)

\[ O_{(YSZ)}^{-} + CO_{(Ni)} \Leftrightarrow CO_{2, gas} + (YSZ) + (Ni) + e^{-}_{(Ni)} \] (4.6)

The first of the two charge-transfer reaction (Eq. 4.5) consists in a single electron transfer from the surface \( O_{(YSZ)}^{-} \) across the TPB, generating the intermediate \( O_{(YSZ)}^{-} \). This approach was firstly proposed by Yurkiv et al. [151, 152], where the outcome of the model was validated against the experimental data by Lauvstad et al. [153]. In this case, the intermediate \( O_{(YSZ)}^{-} \) spills over the TPB to form \( O_{(Ni)} \), which then interacts with \( CO_{(Ni)} \) and \( CO_2_{(Ni)} \) forming the gas species corresponding to the direction of the electrochemical reaction.

### 4.2 Modeling approach

The assumptions of the one-dimensioned spatial discretization model are following:
As explained previously, a stereological approach was adopted for the available length measurements (Chapter 3), whereas in the real microstructure the species diffuse on irregular surfaces on 2-D space. Hence, TPB lengths and diffusion surfaces are respectively considered as points and 1-D lines in the model.

- Material properties are assumed uniform.
- Steady-state conditions are enforced, even if the surface transport equation (Eq. 4.7) contains a dynamic term.
- Temperature and pressure are assumed constant.
- The 1-D surface diffusion is perpendicular to the TPB.
- The concentration of the gas domain is constant, hence the production and consumption of species do not affect the gas molar fraction.
- Electron conduction and gas phase transport are not considered.

The governing equation for the conservation of surface species $i$ is Eq. 4.7, where $c_i$ [mol/cm$^2$] is the concentration. The dimensionless surface coverage $\Theta_i$ is the ratio between concentration and the number of available sites $\Gamma_i$ [mol/cm$^2$] on both metal and electrolyte surfaces (Eq. 4.8), assuming a Langmuir-Hinshelwood pathway. Moreover, the term $\sigma_i$ embodies the number of sites occupied by each molecule of the $i$th species, which is always equal to 1 for all the gases considered. Since the model described in the present study is for Steady-state conditions, the time dependence is set equal to zero (left hand side of Eq. 4.7).

$$\frac{\partial c_i(x, t)}{\partial t} = -\frac{\Gamma_i}{\sigma_i} \frac{\partial J_{i, \text{diff}}(x, t)}{\partial x} + \dot{s}_i(x, t)$$ (4.7)

$$\Theta_i = \sigma_i c_i / \Gamma_k$$ (4.8)

The term $\dot{s}_i$ [mol/cm$^2$/s] (right hand side of Eq. 4.7) expresses the chemical source term, which embodies all the elementary steps (Eq. 4.9). The terms $k_{f,r}$ [cm$^2$/mol$^x$/s$^x$] are the forward and backward specific kinetic constants, which must be thermodynamically consistent and are expressed in Arrhenius form. The coefficients $v_i$ are the stoichiometric coefficient of the reactions.

$$\dot{s}_i(x) = \sum_m v_{i,m} \left( k_{f,m} \prod_{j \in \text{Reac}, m} c_{j,m}^v(x) - k_{r,m} \prod_{j \in \text{Prod}, m} c_{j,m}^v(x) \right)$$ (4.9)

The second term in Eq. 4.7 accounts for the spatial variation of the Fickian diffusion flux $J_{i, \text{diff}}$ [cm/s] under polarization (Eq. 4.10). This means that at OCV condition, the diffusion flux is null and the surface coverage of all the species is constant along the available length. The mobility of the adsorbed
species toward the neighbor free sites is expressed by the diffusion coefficient $D_{i}^{diff}$ [cm$^2$/s].

$$J_{i}^{diff}(x) = -D_{i}^{diff} \frac{\partial \Theta_{i}(x)}{\partial x} \tag{4.10}$$

As shown in the drawing reported in Fig. 4.1, the variation of surface coverages at the TPB is equal to the net production rate of species $q_n$ [mol/cm/s] depending on the $n_{th}$ charge-transfer mechanism (Eq. 4.11). The sign depends on the direction of the electrochemical reaction (production or consumption). Electrons and oxygen ions are transported through the metal and the electrolyte respectively.

$$J_{i}^{diff}(x = 0) = -D_{i}^{diff} \frac{\partial \Theta_{i}(x)}{\partial x} \bigg|_{x=0} = \pm \frac{q_n}{\Gamma_k} \tag{4.11}$$

At the edge of the considered available length, the symmetry boundary condition is enforced by imposing a null surface coverage variation (Eq. 4.12). Therefore, only the chemical source term is active.

$$J_{i}^{diff}(x = L_{Ni} | L_{YSZ}) = 0 \Rightarrow \frac{\partial \Theta_{i}(x)}{\partial x} \bigg|_{x=L_{Ni} | L_{YSZ}} = 0 \tag{4.12}$$
Chapter 4. Effect of available length on the electrochemical performance (Ni-YSZ electrode)

Figure 4.1 – Interactions among gas and surface species on Ni and YSZ surfaces. Point (A): at the TPB, the diffusion flux is null and the spatial variation of surface coverages is equal to the production or consumption rate of each charge-transfer mechanism (Eq. 4.12). Point (B): along the available length both terms presented in Eq. 4.7 are contributing. Point (C): the spatial gradient of surface coverages is null at the end of the considered available length (Eq. 4.11). Hence, the chemical source term is the only contributing. In the model, the surfaces of diffusion are considered flat.
4.2. Modeling approach

The conservation of the number of adsorption sites on Ni and YSZ is enforced by Eq. 4.13. In the present study, the amount of free sites \( \Theta_{(-)} \) is computed as the remaining fraction of the sum of the surface coverages. Goodwin and workers [4] instead defined a diffusivity coefficient also for Ni, omitting Eq. 4.13. This coefficient was obtained from a study by Mogensen et al. [154], in which the authors attempted to measure the diffusion of nickel on a Ni-H\(_2\) system. The mobility of Ni (even if inferior to that of H\(_2\)) suggests that a reorganization of the microstructure may occur during operation. Alternatively, Vogler and workers [5, 122, 151, 152] included the free sites term \( \Theta_{(-)} \) in the diffusion flux \( J_{diff} \) (Eq. 4.10). Moreover, the diffusion coefficient for the YSZ free sites remains undocumented in the literature. This aspect represents an uncertainty in the presented approach and, in the case of low surface coverage of free sites (due to high currents) the extension of available lengths may differ. As an example, the expression of the coverage rate of the spatial distribution of adsorbed hydrogen on Ni surface is shown in Eq. C.1 in Appendix C.

\[
\Theta_{(-)} = 1 - \sum \Theta_i
\]  
(4.13)

The production rate of species \( q_n \) is defined as the difference between the forward and reverse terms (Eq. 4.14). The sign of this balance is reversed for reactants \( (A, B) \), while it is positive for the products of the reaction \( (C, D) \). The local faradaic current therefore is defined as the sum of all the production rates of the parallel pathways \( i_{tot} = F \sum_n q_n \ [A/cm] \).

\[
q_n = q_{f,n} - q_{r,n}
\]  
(4.14)

The two terms in Eqs. 4.15-4.16 depend on the product of the charge transfer kinetic constants \( k \ [cm^x/mol^y/s^z] \), with the activities of reactants \( a_{A,B} \) and products \( a_{C,D} \), and with the exponential term which includes the symmetry coefficients \( \beta_{alc} \) and the difference in electro-static potential between electrode and electrolyte \( U_{el} \ [V] \).

\[
q_{f,n} = k_{f,n} a_{A} a_{B} \exp \left( \frac{\beta_{a,n} F U_{el}}{RT} \right)
\]  
(4.15)

\[
q_{r,n} = k_{r,n} a_{C} a_{D} \exp \left( -\frac{\beta_{c,n} F U_{el}}{RT} \right)
\]  
(4.16)

The kinetic constants of the reaction rates are expressed in Arrhenius form and mainly depend on temperature. The activities of the involved species are defined as surface concentrations in the case of surface species \( c_{i,surf} = \Theta_i \Gamma_k [mol/cm^2] \) or as gas concentrations in the case of gas species.
Chapter 4. Effect of available length on the electrochemical performance (Ni-YSZ electrode)

c_i, gas (mol/cm^3). Moreover, the activity of bulk species is evaluated as the molar fraction of the bulk phase. The symmetry coefficients are formally specific to each electrochemical step and the two branches (anodic and cathodic) must fulfill the constraint \( \beta_a + \beta_c = 1 \). Lastly, the difference between the potential \( U_{el} \) and the equilibrium potential \( U_{el,eq} \) defines the overpotential \( \eta \) (Eq. 4.17). At equilibrium every charge transfer reaction should have a null production rate of species (constrained by the Nernst equation). On the other hand, if a single branch does not satisfy the equilibrium condition, a common value of \( U_{el,eq} \) cannot be defined.

\[
\eta = U_{el} - U_{el,eq}
\]  

(4.17)

In this study, the potential \( U_{el} \) is imposed and varied to investigate the diffusion profile for specified available lengths.

The kinetic constants of the chemical and electrochemical reactions are described in Arrhenius form (Eq. 4.18).

\[
k_n = A_n e^{-E_{act}^n/RT} T^\beta
\]  

(4.18)

In the case of absorption of gas molecules, forward kinetic constants are defined by the sticking probabilities \( P_n \) (Eq. 4.19), where \( w_n \) is the molecular weight.

\[
k_{f,n} = P_n \sqrt{\frac{RT}{2\pi w_n}}
\]  

(4.19)

If not explicitly reported, the coefficients related to the backward constants are computed in a thermodynamically consistent way from the Gibbs reaction enthalpy (Eq. 4.20) and are reported in Appendix C.

\[
k_{b,n} = k_{f,n} e^{-\Delta G_n/RT}
\]  

(4.20)

Similarly, also diffusion coefficients of surface species \( D_{i, diff} \) (cm/s) are expressed in Arrhenius form (Eq. 4.21).

\[
D_{i, diff} = D_i^0 e^{-E_{act}^i/RT}
\]  

(4.21)
4.2. Modeling approach

The heterogeneous steps coupled with the surface transport form a system of non-homogeneous partial differential equations (PDE). The model was implemented in the software package gPROMS [155], which provides PDE solvers. A logarithmic spatial discretization for Ni and YSZ domains with orthogonal collocation of finite element (OCFEM) was used for better capturing gradients near the TPB point. The dimensions of the domains were varied for analysis, which are specified in the following Section.

4.2.1 H₂ and H₂O model parameters

As mentioned previously, the H₂/H₂O model is mainly derived from reference [4]. The hydrogen spillover reactions in Eqs. 4.3-4.4 are implemented. The specificities of the approach adopted by Goodwin et al. is the splitting of the YSZ sites in two parallel subsets "χ" and "Zr".

Moreover, Zr sites are not explicitly involved in the charge transfer mechanism, therefore they do not play a relevant role in the determination of the diffusion profile.

Therefore, the surface coverages of Ni and YSZ surface sites are expressed as:

\[ \Theta_{(Ni)} = 1 - \Theta_H - \Theta_{H_2O} - \Theta_{OH} - \Theta_O \]  
(4.22)

\[ \Theta_{(\chi)} = 1 - \Theta_{OH_{(\chi)}} - \Theta_{O_{(\chi)}} \]  
(4.23)

\[ \Theta_{(Zr)} = 1 - \Theta_{OH_{(Zr)}} - \Theta_{H_{(Zr)}} \]  
(4.24)

The considered forward and backward chemical and electrochemical reactions are listed in Table 4.1, together with the Arrhenius coefficients \( A_n \) and the activation energies \( E_{act}^n \). The reaction \( 1_{f, YSZ} \) relates the equilibrium between the perpendicular bulk transport of vacancies \( V_O^- \) through the electrolyte and the surface oxygen ions concentration \( O_O^- \) (reference is made to Fig. 4.1). Depending on the direction of polarization, \( O^- \) are produced or consumed at the TPB by the charge transfer mechanism \( 1_{f, CT} \). The approach adopted in the present model relies upon the hypothesis of faster bulk transport compared to surface diffusion. Therefore, the surface concentration and surface coverage are considered constant along the available length and they do not directly depend on the applied overpotential.

Several simplifications, compared to the reality, are worth a mention. In the majority of cases the transport of vacancies is not perfectly perpendicular to the TPB, but it rather follows the shortest path to the electrolyte [147] (as visible in Fig. 4.2). In addition, limitations may arise in narrow YSZ regions (Fig. 4.2, red arrows), but most TPBs should not be strongly concerned because of the average YSZ dihedral angle of approximately 100° (see Chapter 5). The contribution of grain
diffusion is also neglected.

The oxygen ion activity $a_{O^2-}$ and the oxygen vacancy activity $a_{V_O^2}$ are assumed material properties for YSZ, and are reported in Table 4.2 together with additional parameters used as input for the simulations. Table 4.3 instead lists the diffusion coefficients of each surface species. Due to the large uncertainty, the values were selected from two different references.
### 4.2. Modeling approach

<table>
<thead>
<tr>
<th>Number</th>
<th>Reactions</th>
<th>$A_n$ [cm$^3$/molF$/s^*]$</th>
<th>$E_{n act}^{\text{act}}$ [kJ/mol]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$_f$, Ni</td>
<td>$H_2 + 2(Ni) \Rightarrow 2H(Ni)$</td>
<td>1e-2</td>
<td>-</td>
<td>[156]</td>
</tr>
<tr>
<td>1$_t$, Ni</td>
<td>$2H(Ni) \Rightarrow H_2 + 2(Ni)$</td>
<td>2.54e+19</td>
<td>81.21</td>
<td>[156]</td>
</tr>
<tr>
<td>2$_f$, Ni</td>
<td>$H_2O + (Ni) \Rightarrow H_2O(Ni)$</td>
<td>1e-1</td>
<td>-</td>
<td>[156]</td>
</tr>
<tr>
<td>2$_t$, Ni</td>
<td>$H_2O(Ni) \Rightarrow H_2O + (Ni)$</td>
<td>3.73e+12</td>
<td>60.79</td>
<td>[156]</td>
</tr>
<tr>
<td>3$_f$, Ni</td>
<td>$H(Ni) + O(Ni) \Rightarrow OH(Ni) + (Ni)$</td>
<td>5e+22</td>
<td>97.90</td>
<td>[156]</td>
</tr>
<tr>
<td>3$_t$, Ni</td>
<td>$OH(Ni) + (Ni) \Rightarrow H(Ni) + O(Ni)$</td>
<td>1.78e+21</td>
<td>36.09</td>
<td>[156]</td>
</tr>
<tr>
<td>4$_f$, Ni</td>
<td>$H(Ni) + OH(Ni) \Rightarrow H_2O(Ni) + (Ni)$</td>
<td>3e+20</td>
<td>42.70</td>
<td>[156]</td>
</tr>
<tr>
<td>4$_t$, Ni</td>
<td>$H_2O(Ni) + (Ni) \Rightarrow H(Ni) + OH(Ni)$</td>
<td>2.27e+21</td>
<td>91.76</td>
<td>[156]</td>
</tr>
<tr>
<td>5$_f$, Ni</td>
<td>$2OH(Ni) \Rightarrow H_2O(Ni) + O(Ni)$</td>
<td>3e+21</td>
<td>100</td>
<td>[156]</td>
</tr>
<tr>
<td>5$_t$, Ni</td>
<td>$H_2O(Ni) + O(Ni) \Rightarrow 2OH(Ni)$</td>
<td>6.37e+23</td>
<td>210.86</td>
<td>[156]</td>
</tr>
</tbody>
</table>

#### Table 4.1 – Kinetic constants of the chemical surface and charge-transfer reactions referred to the H$_2$/H$_2$O model (* sticking probability $P_n$). The coefficients related to the backward constants of charge-transfer and surface reactions on the YSZ sites are not reported and were computed in a thermodynamically consistent way from the Gibbs reaction enthalpy (Eq. 4.20).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>973 K</td>
</tr>
<tr>
<td>Total pressure</td>
<td>$p_{tot}$</td>
<td>1 atm</td>
</tr>
<tr>
<td>Total (Ni) active sites</td>
<td>$\Gamma_{Ni}$</td>
<td>1.7e-9 mol/cm$^2$</td>
</tr>
<tr>
<td>Total ($\chi$) and (Zr) YSZ active sites</td>
<td>$\Gamma_{\chi}, \Gamma_{Zr}$</td>
<td>1.25e-9 mol/cm$^2$</td>
</tr>
<tr>
<td>Faraday</td>
<td>$F$</td>
<td>96485 C/mol</td>
</tr>
<tr>
<td>Universal gas constant</td>
<td>$R$</td>
<td>8.314 J/mol/K</td>
</tr>
<tr>
<td>Oxygen ion activity</td>
<td>$a_{O^2-}$</td>
<td>0.9626</td>
</tr>
<tr>
<td>Oxygen vacancy activity</td>
<td>$a_{O^-}$</td>
<td>0.0374</td>
</tr>
<tr>
<td>Anodic symmetry factor Eq. 4.3</td>
<td>$\beta_{a,1}$</td>
<td>0.5</td>
</tr>
<tr>
<td>Anodic symmetry factor Eq. 4.3</td>
<td>$\beta_{a,2}$</td>
<td>0.3</td>
</tr>
<tr>
<td>Cathodic symmetry factor Eq. 4.4</td>
<td>$\beta_{c,1}$</td>
<td>0.5</td>
</tr>
<tr>
<td>Cathodic symmetry factor Eq. 4.4</td>
<td>$\beta_{c,2}$</td>
<td>0.7</td>
</tr>
</tbody>
</table>

#### Table 4.2 – Global parameters of the H$_2$/H$_2$O model.

<table>
<thead>
<tr>
<th>Surface species</th>
<th>$A_n$ [cm$^3$/molF$/s^*]$</th>
<th>$E_{n act}^{\text{act}}$ [kJ/mol]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H(Ni)$</td>
<td>2.5e-3</td>
<td>14.65</td>
<td>[4]</td>
</tr>
<tr>
<td>$H_2O(Ni)$</td>
<td>6e-3</td>
<td>28</td>
<td>[122]</td>
</tr>
<tr>
<td>$O(Ni)$</td>
<td>6.3e-3</td>
<td>61.3</td>
<td>[122]</td>
</tr>
<tr>
<td>$OH(Ni)$</td>
<td>6e-3</td>
<td>30.5</td>
<td>[122]</td>
</tr>
<tr>
<td>$OH(\chi)$</td>
<td>5e-8</td>
<td>-</td>
<td>[4]</td>
</tr>
<tr>
<td>$O(\chi)$</td>
<td>5.85e-11</td>
<td>49</td>
<td>[4]</td>
</tr>
<tr>
<td>$OH(Zr)$</td>
<td>5e-8</td>
<td>-</td>
<td>[4]</td>
</tr>
<tr>
<td>$H(Zr)$</td>
<td>5e-8</td>
<td>-</td>
<td>[4]</td>
</tr>
</tbody>
</table>

#### Table 4.3 – Diffusion coefficients in the H$_2$/H$_2$O model.
4.2.2 CO and CO$_2$ model parameters

This model is simpler compared to the H$_2$/H$_2$O one, since only the surface coverages of four species are computed [6]:

\[
\Theta_{(Ni)} = 1 - \Theta_{CO}
\]  \hspace{1cm} (4.25)

\[
\Theta_{(YSZ)} = 1 - \Theta_{O^-}
\]  \hspace{1cm} (4.26)

On the metallic surface, CO$_2$ is assumed to immediately adsorb or desorb after consumed or produced (Eq. 4.6). Hence, its surface coverage (that would be constant along the Ni available length) is neglected because much smaller compared to CO and Ni. The associated kinetics constant of the chemical and electrochemical reaction are listed in Table 4.4. On the ceramic side, the spatial coverage of $O^-$ is constant and it depends on the applied overpotential. For this reason, the diffusion coefficient can be neglected in Steady-state condition. The input parameters are presented in Tables 4.5 and 4.6. Given the higher simplicity of this model, the simulations were performed at fixed CO partial pressure ($p_{CO}$).

<table>
<thead>
<tr>
<th>Number</th>
<th>reactions</th>
<th>$A_n$ ( \text{[cm}^2 \text{mol}^{-1} \text{s}^{-1}] )</th>
<th>$E_{act}^{ct}$ ( \text{[kJ/mol]} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$\text{f, Ni}$</td>
<td>( CO + \text{(Ni)} \Rightarrow CO(\text{Ni}) )</td>
<td>( 5e^{-1}$ )</td>
<td>-</td>
<td>[156]</td>
</tr>
<tr>
<td>1$\text{r, Ni}$</td>
<td>( CO(\text{Ni}) \Rightarrow CO + \text{(Ni)} )</td>
<td>( 3.563e+11 )</td>
<td>( 111.3 - 50 \Theta_{CO} )</td>
<td>[156]</td>
</tr>
<tr>
<td>1$\text{f, CT}$</td>
<td>( O_{\text{YSZ}}^\alpha \text{(YSZ)} + \text{(YSZ)} \Rightarrow O_{\text{YSZ}}^\alpha \text{(YSZ)} + \text{O}^{-} \text{(YSZ)} + e^{-}\text{(Ni)} )</td>
<td>( 2.099e+2 )</td>
<td>-</td>
<td>[6]</td>
</tr>
<tr>
<td>1$\text{r, CT}$</td>
<td>( O_{\text{YSZ}}^- \text{(YSZ)} + e^{-}\text{(Ni)} \Rightarrow O_{\text{YSZ}}^\alpha \text{(YSZ)} + \text{O}^{-}\text{(YSZ)} )</td>
<td>( 3.704e+6 )</td>
<td>-</td>
<td>[6]</td>
</tr>
<tr>
<td>2$\text{f, CT}$</td>
<td>( O_{\text{YSZ}}^- \text{(YSZ)} + CO\text{(Ni)} \Rightarrow CO_2 \text{gas} + \text{(YSZ)} + \text{(Ni)} + e^{-}\text{(Ni)} )</td>
<td>( 1.32e0 )</td>
<td>-</td>
<td>[6]</td>
</tr>
<tr>
<td>2$\text{r, CT}$</td>
<td>( CO_2 \text{gas} + \text{(YSZ)} + \text{(Ni)} + e^{-}\text{(Ni)} \Rightarrow O_{\text{YSZ}}^- \text{(YSZ)} + CO\text{(Ni)} )</td>
<td>( 4.498e+4 )</td>
<td>-</td>
<td>[6]</td>
</tr>
</tbody>
</table>

* sticking probability $P_n$.

Table 4.4 – Kinetic constants of chemical surface and charge-transfer reactions in the CO/CO$_2$ model.
4.3 Results

4.3.1 Effects of the extension of available lengths

4.3.1.1 \( \text{H}_2/\text{H}_2\text{O} \) model

A sensitivity analysis was first conducted by varying the available lengths and the concentration of the gas mixture in the \( \text{H}_2/\text{H}_2\text{O} \) case. As visible in Fig. 4.3, two lengths were selected for Ni (10 nm and 100 nm), and a range from 100 nm to 10 \( \mu \text{m} \) for YSZ. It is important to remark that the gas concentration is fixed in each simulated current-voltage curve. On the other hand, the Tafel plots inform about the behavior of the electrochemical performance at different specific regions of the cell’s active area: in fuel cell operation for instance, the plot with 99% of \( \text{H}_2 \) would correspond to the inlet zone, while that with 10% to the outlet, where most of the fuel is depleted (and vice-versa in electrolysis mode).

The Tafel plots are surprisingly not influenced by variation of lengths, except at high overpotential in fuel cell mode and in particular at low \( \text{H}_2 \) molar fraction. Under these conditions, only the shorter Ni available lengths (continuous yellow line and dashed orange line) appear to influence the displayed trends. In electrolysis mode, no significant variations are observed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>( T )</td>
<td>1023 K</td>
</tr>
<tr>
<td>Total pressure</td>
<td>( p_{tot} )</td>
<td>1 atm</td>
</tr>
<tr>
<td>CO Partial pressure</td>
<td>( p_{CO} )</td>
<td>0.323 atm</td>
</tr>
<tr>
<td>Total (Ni) available sites</td>
<td>( \Gamma_{Ni} )</td>
<td>2.66e-9 mol/cm(^2)</td>
</tr>
<tr>
<td>Total (YSZ) available sites</td>
<td>( \Gamma_{YSZ} )</td>
<td>1.3e-9 mol/cm(^2)</td>
</tr>
</tbody>
</table>

Anodic symmetric factor Eq. 4.5
Cathodic symmetric factor Eq. 4.5
Anodic symmetric factor Eq. 4.6
Cathodic symmetric factor Eq. 4.6
area-specific TPB line

\( \beta_{a,1} \) 0.5  
\( \beta_{c,1} \) 0.5  
\( \beta_{a,2} \) 0.5  
\( \beta_{c,2} \) 0.5  
\( l_{TPB} \) 2.03e+4 1/m

Table 4.5 – Parameters in the CO/CO\(_2\) model.

<table>
<thead>
<tr>
<th>Surface species ( \text{CO}_{(Ni)} )</th>
<th>( A_n ) ([cm^2/mol^x/s^y])</th>
<th>( E_n^{act} ) ([kJ/mol])</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_{(Ni)} )</td>
<td>1.2e-5</td>
<td>28.87</td>
<td>[157]</td>
</tr>
</tbody>
</table>

Table 4.6 – Diffusion coefficient in the CO/CO\(_2\) model.
Chapter 4. Effect of available length on the electrochemical performance (Ni-YSZ electrode)

Figure 4.3 – Comparison of Tafel curves for variation of gas concentrations and the Ni and YSZ available lengths (H₂/H₂O model).

The spatial distribution of surface coverages of the species involved in the two charge transfer reactions (Eq. 4.3 and 4.4) are reported in Fig. 4.4 (50% H₂ - 50% H₂O gas molar fractions), to comprehend the reasons for such discrepancy between operation modes. Applied potential was varied from +0.5 V (red - fuel cell mode) to -0.5 V (blue – electrolysis mode). The TPB is placed on the left portion of the plots. The 10 nm YSZ length is also included for comparison. Due to the limitation of the number of discretization points in the numerical model, in the cases of 10 µm YSZ length the coverage plots display an inferior extension of the diffusion profile (starting at 30 nm instead of 3 Å). The difference in the case of shorter available length is evident, emphasized at high positive potentials. In fact, the shortest diffusion path does not allow the diffusion profile to reach equilibrium. This would lead to a stronger consumption/production of gas species, provoking a further limitation by shifting the gas mixture. In accordance to the Tafel plots presented in (Fig. 4.3), TPB coverage is much more affected at high positive potentials.
4.3. Results

Figure 4.4 – Spatial distribution of surface coverage for varying the extensions of the Ni and YSZ available lengths and applied potential (blue - electrolysis, green - OCV, red - fuel cell). Gas composition of 50% $H_2$ - 50% $H_2O$. (A)-(F): six surface species involved in the charge transfer mechanisms (Eqs. 4.3 and 4.4).
Furthermore, the gradients on (χ) sites extend up to 10 \( \mu m \). Even if this value is much larger compared to the average available lengths measured in the previous chapter, surface coverages at TPB are not significantly affected by shorter lengths (and therefore the charge transfer kinetics are not affected). In the Ni case, the coverage values at TPB are slightly more influenced, in particular by large potentials.

Surface H and Ni exhibit an opposite trend, since the surface coverage balance (Eq. 4.22) can be approximated as \( \Theta_{(Ni)} \approx 1 - \Theta_H \). Moreover, these two species have a limited impact on the charge transfer reactions, since they are placed in the opposite branches of the first electrochemical reaction (Eq. 4.3) and their contribution is partially balanced. Therefore, the H\(_2\)O surface coverage at the TPB is more relevant for the overall reactions. Lastly, the surface coverage plots indicate a non-linear relationship between the two operation modes. In particular stronger negative potentials do not cause a large deviation from values obtained at OCV.

Fig. 4.5 shows the four Faradaic current production rates (Eqs. 4.15 and 4.16) that are involved in the hydrogen spilling mechanism and that respectively belong to the first and the second half of the two charge transfer branches (Eqs. 4.3 and 4.4). The rates were computed for each couple of available lengths (refer to Fig. 4.4), hence they almost perfectly overlap. As an example, the term \( q_1 \) can be expressed by Eq. 4.27.

\[
q_1 = k_{f,1\text{ct}} \Gamma_{Ni} \Theta_{H(Ni)} \Gamma_{x} \Theta_{OH^-} \exp \left( \frac{\beta_{a1} F U_{el}}{RT} \right) \]  
(4.27)

Although the terms \( q_1 \) and \( q_2 \) show a perfectly identical trend, \( q_3 \) and \( q_4 \) exhibit an opposite behavior which slightly varies at + 0.5 V for smaller Ni length. Such tiny discrepancy provokes the differences previously described in the Tafel plots (Fig. 4.3). Since \( q_1 \) and \( q_2 \) are almost identical for every applied potential, the resulting current is null (Eq. 4.14). This implies that the second charge transfer mechanism (Eq. 4.4) is limiting in both operation modes. Therefore, the surface coverage of H\(_2\)O controls in a simplified view the overall electrochemical reaction for the selected mechanisms.

In the present model, the symmetry condition is not explicitly enforced, but is rather governed by the Neumann boundary condition related to \( \Theta_{OH^-} \). Such expression is described in Eq. 4.28.

\[-D_{OH^-}^{diff} \Gamma_{x} \frac{\partial \Theta_{OH^-}(x)}{\partial x} \bigg|_{x=0} = I_{CT, 1} - I_{CT, 2} \equiv (q_1 - q_2) - (q_3 - q_4)\]  
(4.28)

Since the derivative of \( \Theta_{OH^-} \) appears to be null at the TPB (Fig. 4.4C), the two currents must be identical.
4.3. Results

Figure 4.5 – Faradaic current production rates of the two charge transfer mechanisms (Eq. 4.3 and 4.4). The gas composition is 50% $H_2$ - 50% $H_2O$. The rates were computed for each couple of available lengths described in Fig. 4.4. The terms $q_1$ (in blue) and $q_2$ (in black) overlap.

4.3.1.2 CO/CO$_2$ model

Given the lower complexity with respect to the previous model, only the variations of extension of the Ni available length are assessed at fixed gas composition ($p_{CO} = 0.323$ atm and $p_{CO_2} = 0.032$ atm). In fact, the YSZ available length has no influence on the spatial coverage of oxygen ions $O^{-}$ under the selected transfer reactions (Eqs. 4.5 and 4.6).

The Tafel plots comparison in Fig. 4.6A indicates essentially a negligible variation, apart for the case with length of 2 nm (in blue) where the difference in performance is barely noticeable. Unlike the $H_2/H_2O$ model, a limited difference also occurs in electrolysis mode.

The spatial distributions of CO coverage in Fig. 4.6B show consistent trends with the previous descriptions. In the case of 2 nm length, the coverage cannot reach the equilibrium value already for small applied potentials. Moreover, the extension of the gradient in fuel cell mode is more pronounced, probably due to the high CO coverage at OCV ($\approx 0.95$) that limits a further adsorption.
Chapter 4. Effect of available length on the electrochemical performance (Ni-YSZ electrode)

Figure 4.6 – (A): Comparison of Tafel plots for different available length on Ni simulated with the CO/CO$_2$ model ($p_{CO} = 0.323$, $p_{CO_2} = 0.032$). (B): Spatial distribution of the CO surface coverage for varying Ni and YSZ available lengths and applied potential (blue - electrolysis, orange - fuel cell).
4.3.2 Effect of the gas concentration in the H\textsubscript{2}/H\textsubscript{2}O case

Fig. 4.7 are reports the spatial distribution of the coverage of the six surface species involved in the charge transfer mechanisms for three different gas molar fractions. While the species on the YSZ \( \chi \) sites do not vary significantly (apart from high overpotential values), differences are observed for the Ni sites. H and H\textsubscript{2}O surface coverages vary proportionally to the respective gas molar fractions. In particular, it is interesting to notice in Fig. 4.7F that smaller coverages yield more pronounced gradients that however develop over similar extension. In reality, the magnitude of the gradient is strictly related to the gas production/consumption rate via the surface chemical reaction. In the case of H\textsubscript{2}O for instance, the strong positive potential causes a net production of surface species at the TPB that have to be transported away.
Figure 4.7 – (A)-(F): Spatial surface coverage distribution plots of the species involved in the charge-transfer mechanisms for different $H_2/H_2O$ molar fractions and applied potentials.
4.3.3 Effect of the diffusion coefficients

The effect of the diffusion coefficients on the overall transport mechanism is assessed by their lowering or increasing by several orders of magnitude.

4.3.3.1 $\text{H}_2/\text{H}_2\text{O}$ model

As mentioned in [5], an uncertainty of 2–3 orders of magnitude is expected, since no interactions between adsorbates have been accounted, in particular in the case of high coverages. As discussed in the list of the assumptions, Ni self-diffusion was not considered. However, the adsorbed species on a metallic atom could be also transported by its relocation. Lastly, the diffusion coefficients may significantly increase along grain boundaries.

The Tafel plot were computed for variation of the diffusion coefficients over $\pm 3$ orders of magnitude. Contrarily to the variation of available lengths, the impact is evident for both positive and negative applied potentials. As expected, the diminution comports a progressive degradation of the performance caused by transport limitation. On the other hand, larger coefficients do not yield a noticeable benefit for the baseline conditions treated here, since the available lengths are sufficiently extended.

The variation of the polarization resistance is also shown (Fig. 4.8B) and is expressed as the ratio between voltage and current derivatives (Eq. 4.29).

$$R_{pot} = \frac{dU}{dI}$$  \hspace{2cm} (4.29)

The changes are not reduced upon lowering of at a coefficient by one order of magnitude, but deviation starts to occur at high potential. It is interesting to notice the initial rise of the polarization resistance in electrolysis followed by decrease after -0.1 V. Such behavior was already identified in the PhD thesis of P. Caliandro [20], in which a net difference between the two operation modes was observed in electrochemical impedance spectroscopy measurements.
Chapter 4. Effect of available length on the electrochemical performance (Ni-YSZ electrode)

Figure 4.8 – (A) Comparison of Tafel plots computed for variations of the diffusion coefficients ($H_2/H_2O$ model). (B) Polarization resistances comparison.

The corresponding spatial distributions of surface coverage are displayed in Fig. 4.9. The cases with baseline values of diffusion coefficients are represented with a continuous thicker line. The reduction caused a strong expansion of the gradients at large potentials, especially on Ni. Contrarily, larger coefficients contributed to reduce the extension of the gradients by flattening the coverage distribution even at higher potential. In the latter case, shorter available lengths would not affect the electrochemical performance.
4.3. Results

Figure 4.9 – (A)-(F): Spatial distribution of the surface coverage of species involved in the charge-transfer mechanisms for variation of diffusion coefficients and applied potentials ($H_2/H_2O$ model).
4.3.3.2 CO/CO$_2$ model

The results are qualitatively similar to those of the H$_2$/H$_2$O model, with a progressive degradation of the performance for smaller diffusion coefficients (Fig. 4.10). In case of a diffusion coefficient 3 orders of magnitude smaller, the curve appears almost flat at high potentials, which signifies a nearly complete limitation of the electrochemical reaction.

![Tafel plots comparison by varying the diffusion coefficients (CO/CO$_2$ model).](image)

Since CO is the only active species, the diffusion coefficient has a direct impact on the concentration at the TPB and, therefore, on the current density. The two plots in Figs. 4.11 display how a smaller diffusion coefficient causes an increase in the magnitude of the gradient and a concurrent spatial widening. Inversely, a larger coefficient induces the flattening of the profile and the shift of the gradient extension, comporting a more uniform gas exchange rate profile along the available length.
4.3. Results

Figure 4.11 – (A)-(B): CO spatial surface coverage distribution plots varying the different diffusion coefficients and the applied potentials.

4.3.4 Effect of the reduction of free Ni sites

Two of the most typical impurities that can be found during operation are sulfur and carbon, in particular in SOFC mode. Such compounds occupy the free available sites of the metallic surface hindering the adsorption of the gas species and consequently interfering with the chemical and electrochemical reactions.

Carbon deposition is formed when hydrocarbons are present in the gas fed, and it concerns single atoms that directly create a bond with catalyst sites. The reduction of CO is the most common source of carbon deposition, which may ultimately lead to formation of C nanofibers [75, 158]. Moreover, high conversion rates and current density favor accumulation on the metallic surface [76]. Studies by Li et al. [83] indicate that the deposition rate would be higher in SOEC mode with the highest carbon content near the TPB. Nonetheless, this mechanism is typically prevented by ensuring a sufficiently steam-to-carbon ratio [159].

Traces of sulfur are instead often present in the fuels (in particular biofuels [160]) and they combine with hydrogen forming $H_2S$. Even if the sensitivity of nickel to poisoning decreases at high temperatures [51], sulfur starts to deposit on the metallic sites even at very low quantities (about 1 ppm) in form of nickel sulfide [161, 162]. In general, the adsorption on nickel is reversible only in the case of low concentrations (< 10 ppm), whereas the transport to the bulk region (sulfidation) irreversibly damages the catalyst for concentrations larger than 50 ppm [51, 163, 164].

Besides to situations leading to severe chemical and crystallographic alterations, the microstructure is not significantly altered and the performance degradation is related to the concentration of impurities. This leads to an augmentation of the activation polarization resistance because of the longer path the oxygen ions have to follow to reach the available active sites [20]. In case of complete
coverage of the free sites, the TPB is passivated.

In this regard, Hansen [165] related the sulfur coverage ($\Theta_S$) to the loss of performance using an empirical expression which depends on the temperature and the ratio $p_{H_2S}/p_{H_2}$. A rise of the cell's resistance would be detectable starting from chemisorbed $\Theta_S$ higher than 0.7-0.8. They concluded that the adsorbed H near the TPB does not actively participate in the electrochemical reaction. This statement holds in the case of charge transfer mechanisms different from those used in the present analysis (for instance oxygen spillover [5]).

The effect of the contamination of Ni free sites by impurities is assessed by progressively increasing a coverage $\Theta_{Imp}$ until 0.7 (Eq. 4.30) under the assumption of equally distributed concentration among the surface of the metallic phase. The simulations were performed with the $H_2/H_2O$ model only.

$$\Theta_{Ni} = 1 - \sum\Theta_{species} - \Theta_{Imp}$$ (4.30)

Fig. 4.12A indicates a progressive shift of the Tafel plots with the rise of $\Theta_{Imp}$, while there is no evident difference between the two operating modes. This behavior is explicit in the polarization resistance plots (Fig. 4.12B), where the logarithmic difference between each step appears constant until the last case ($\Theta_{Imp} = 0.7$) which exhibits a further increase. It is here worth to mention that Hansen [165] considered a minimum sulfur coverage of 0.5 as the threshold to provoke a loss of performance.

The plots of surface coverage distribution displayed in Figs. 4.13A-C provide a better view of the influence of impurities on the concentration of the other species. In this case, only Ni species are considered because YSZ sites are assumed not affected by impurities. Consequently, only the Ni side is a bottle neck for the overall charge transfer mechanism. The increase of $\Theta_{Imp}$ comports a diminution of the coverage of all the other species, independently on their magnitude. The drop in the surface concentrations at $\Theta_{Imp}$ equal to 0.7 would comport a net reduction of the current density at the TPB because of the reduction of the activities of the species that actively participate in the electrochemical reactions (Eqs. 4.15 and 4.16). This suggests that at very high impurities coverage the polarization resistance would rise at a higher rate. Moreover, the profiles’ extension do not vary with coverage, hence it is expected that a variation of the available lengths on Ni would have effects similar to those discussed in the previous sections.
4.3. Results

Figure 4.12 – (A) Tafel plots comparison by progressively increasing the sulfur surface coverage (50% H₂ - 50% H₂O, 100 nm Ni, 1 µm YSZ). (B) Polarization resistances comparison.
Chapter 4. Effect of available length on the electrochemical performance (Ni-YSZ electrode)

Figure 4.13 – Surface coverage distribution plots of the species on Ni sites (50% H₂ - 50% H₂O, 100 nm Ni, 1 µm YSZ).
4.4 Conclusion

A sensitivity analysis was performed with two models, a first for \( \text{H}_2/\text{H}_2\text{O} \) and another for CO/CO\(_2\). The effect of the available lengths is mild under the conditions and hypothesis considered in this study. Even if a shortening of the lengths produce a flattening of the diffusion gradients, the impact on the electrochemical performance is moderate. The analysis highlighted a significant limitation only at high applied potential, since the magnitude of the gradients is larger.

The selection of the elementary charge transfer elementary steps modifies the extension of the gradients, since the concentrations of species at the TPB influences the kinetics. As shown by the \( \text{H}_2/\text{H}_2\text{O} \) model, the "\( \chi \)" sites on YSZ are characterized by very large gradients that are not influenced by shortening of lengths. However, the same cannot be considered a-priory valid for any species and/or materials.

An important consideration is the uncertainty on the actual values of the diffusion coefficients. Surface species with higher \( D_{\text{eff}} \) would present shorter profiles and consequently lower sensitivity to length shortening. Inversely, transport of less mobile species may be more affected by the morphology near the TPB. In the Ni case, chemical kinetics is much faster compared to surface diffusion. The results indicate that a more precise estimation of these coefficients will be required for future analysis, since one order of magnitude of variation can sensibly change the results. Even if the accumulation of impurities causes a serious limitation of the electro-catalytic activity, the model suggests that the extensions of the diffusion profile are not influenced and therefore shorter available lengths may not cause an additional detrimental effect in this case.
Degradation of the Ni-YSZ electrode after long-term operation

This Chapter presents a study of the evolution of the Ni-YSZ electrode material considered in this Thesis during operation in SOFC or SOEC mode. A set of samples aged for different conditions and operation times up to 15 \( kh \) are used for evolution analysis. Microstructural changes are characterized in 3-D by the measurement of standard metric and topological properties as well new as concepts and procedures developed within this Thesis. The rationale for 3-D is a better understanding of the electrode degradation in the long-term, which proved complicated using the quantification methods available at GEM-EPFL at the start of this Thesis [63, 138] because the microstructural changes are becoming ever subtler upon material improvements.  

5.1 Introduction

The agglomeration of Ni is the most visible alteration of the \( H_2 \) electrode microstructure, due to the high Ni mobility and low wettability to the YSZ surface, which relates to interfacial surface tensions at material interfaces. It could be appreciated clearly by visual inspection of 2-D micrographs of mechanically-polished sections in the Ni-YSZ electrode of a previous cell generation [63]. The changes are much subtler in the current SOLIDpower electrode, which is characterized by a more homogeneous microstructure. These significant improvements complicate the detection and quantification of the degradation, consequently the understanding of the degradation regimes relevant for long-term operation.

The evolution of the metallic phase in Ni-YSZ electrodes has been commonly studied in the literature

\(^1\)A first version of the concepts and analyses discussed in this Chapter was presented in the proceedings “G. Rinaldi, A. Nakajo, M. Cantoni, W.K.S. Chiu, J. Van herle, ”Characterization of the local morphology at triple-phase boundaries after SOFC/SOEC operation” presented at the 13th European SOFC & SOEC Forum that took place in Lucerne (Switzerland) on the 3rd-6th July 2018.

**Personal contribution:** adaptation and development of quantification methods, analysis of the results.
in the light of competitive growth, where regions with larger characteristic sizes tend to grow at the expense of the smaller ones [17, 137]. The next two sub-sections provide first a general overview of standard coarsening theories and then of the alterations commonly observed in the Ni-YSZ microstructure.

5.1.1 Overview on coarsening theories

Coarsening theories were developed to describe the evolution of the size and shape of ensembles of particles or grains. In a two-phase material, the reduction of the second phase particles’ number and concurrent growth of the average size yields a decrease of the total interfacial surface area, hence of the system total energy. Such a process driven by energy minimization is referred to as Ostwald ripening or coarsening [11]. In the case of second phase particles of different sizes in a matrix, the growth is competitive [13]. Fig. 5.1 shows the evolution of Sn particles dispersed in a PbSn eutectic liquid (at temperature > 183°C). This is an example of a material with a stress-free matrix, the evolution of which is well described by coarsening theory.

![Figure 5.1](image.png)

*Figure 5.1 – Micrographs of Sn solid particles embedded in a Pb-Sn matrix after increasing aging time, illustrating coarsening. Image reproduced from [11], p. 117.*

The starting point for the derivation of coarsening governing equations is that microstructural evolution is driven by the minimization of the excess free energy associated to the presence of interfaces. The total volume of the solid phases is essentially conserved during this process [166, 167]. Material migrates from regions characterized by high to low chemical potential ($\mu$), when the mobility is sufficient compared to the time scale of the observation. A driving force for the transport of atoms is therefore the difference of chemical potential generated by variations in local surface curvature [168]. This dependence is expressed by Eq. 5.1, where the variation in potential between an atom on a curved surface ($\mu$) and another on a flat surface ($\mu_0$) is proportional to the mean
5.1. Introduction

Surface curvature ($H$).

$$\mu - \mu_0 = V_m \gamma (\kappa_1 + \kappa_2) = V_m \gamma (2H)$$  \hspace{1cm} (5.1)

where “$V_m$” is the molar volume, “$\gamma$” the interfacial free energy (isotropic) and “$\kappa$” the curvature. Therefore, a diminution of mean curvature comports a reduction of the chemical potential. From a thermodynamic system perspective and assuming that all the material has the same properties as in the bulk, the presence of interfaces contribute to the system’s Gibbs energy following Eq. 5.2 [11, 168].

$$G - G_0 = \gamma TSA$$ \hspace{1cm} (5.2)

Under the assumption of constant interfacial free energy along the surface, a reduction of the total surface area (TSA) therefore comports a reduction of the Gibbs free energy. Eqs. 5.1 and 5.2 are similar in essence; they inform about the same driving force but they refer to different length scales (atomic and bulk, respectively). Thus, surfaces with higher curvature tend to disappear over time and the characteristic size of the dispersed second phase tends to increase. The system evolves to lower as much as possible the surface energy.

The Lifshitz–Slyozov–Wagner (LSW) theory was a stepping stone in understanding microstructural evolution under Ostwald ripening [169, 170]. The analysis for the derivation of governing equations is based upon several assumptions. The medium consists in an ensemble of spherical second-phase particles (characterized by radii “$r_i$”) dispersed into a supersaturated matrix; both first and second phases are fluids. The volume fraction of the dispersed phase is infinitesimally small (infinitely diluted system), but the number of particles is sufficient for treating the material as a continuum. Therefore, interactions among the particles are not important and the coarsening rate of a particle does not depend upon its neighborhood. Because exact threshold values are not provided, arbitrariness remains on the validity of these assumptions to a given material. The particles are also assumed fixed in space and nucleation or coalescence are not considered significant.

The derivation of the governing equations comprises three main components: a kinetic equation providing the size change rate of particles as a function of radius, a continuity equation for the particle size distribution and mass conservation [13]. The first is derived using the quasi-stationary assumption. The continuity equation for the size distribution is given with Eq. 5.3, with “$g(t)$”
defined as the number of particles per unit volume at time \( t \).

\[
\frac{\partial g}{\partial t} = \frac{\partial}{\partial r} \left( g \cdot \frac{dr}{dt} \right)
\]  

(5.3)

This yields a diffusion problem described by the Laplace equation with boundary conditions provided by the linearized Gibbs-Thomson equation and a particle size varying in relation to a mean field concentration \( \lim_{r \to \infty} \delta(r) = \delta_m \), where \( \delta(r) = 1/r \) and \( \delta_m \) stands for the supersaturation of the matrix \( (\delta_m \ll 1) \) [13, 168]. It provides, under the requirement of flux conservation at the matrix-particle interface and of pure solute particle, the rate of the growth or dissolution of an isolated spherical domain into a supersaturated medium:

\[
\frac{dr}{dt} = \left( \frac{\delta_m - 1}{r} \right)
\]  

(5.4)

The mass conservation equation under the assumption of a zero source term is reported in Eq. 5.5, where \( \delta_0 \) is the bulk alloy composition, \( \xi = 4\pi/(3V_m c_{\infty}) \) ("\( c_{\infty} \)" is the solute concentration in the matrix at a flat interface) and \( g_3(t) = \int_{0}^{\infty} g(r, t) dr \).

\[
\delta_0 = \delta_m(t) + \xi g_3(t)
\]  

(5.5)

The well-known power law Eq. 5.6 is obtained by asymptotic analysis, that is, it holds for \( t \to \infty \) and describes the coalescence at long times. The evolution of the mean radius depends upon a constant \( "K_{LSW}" \) (related to the thermophysical properties of the system) [22]:

\[
\langle \bar{r}(t) \rangle^3 - \langle \bar{r}(t = 0) \rangle^3 = K_{LSW} t
\]  

(5.6)

Eq. 5.6 predicts that the coarsening of particles reduces their total interfacial surface area and results in unconstrained growth over time. The system reaches an asymptotic state independent of the initial conditions and that can be computed. The corresponding particle size distribution scaled by the average radius does not change over time, hence the theory predicts self-similar evolution at long time. In the standard LSW formulation \( g_3 \to \delta_0/\xi \) at infinite time, yielding the coefficient \( "K_{LSW}" \) equal to \( 4/9 \).

There are however several caveats to the application of Eq. 5.6. The mean field approximation to
describe competitive growth as a function of the mean particle size does not account for effects induced by interactions with neighboring particles. In particular, regimes where the migration by diffusion is dominated by short-range effects between contacting particles may not be precisely described. As an intuitive example, a particle surrounded exclusively by larger neighbors evolves identically as if it was surrounded by smaller ones. Theories were therefore developed to cope with the intrinsic limitation of the unrealistic null volume fraction of the second phase, such as Ardell [171] and Marqusee and Rose [172]). The henceforth obtained variations of Eq. 5.6 usually express the coarsening rate as monotonic increasing function of the second phase volume fraction, leading to different size distributions. Their applicability to Ni-YSZ microstructural changes is not discussed specifically in this Thesis. Besides the questionable application to coarsening of a two-solid phase material with contrast in properties, an inspection of the time-independent distributions shows that they are asymmetrical with a marked tail at small relative radii [13], which does not correspond to the measurements (see Section 5.3).

The effect of secondary phases on the motion of interfaces in multi-phase materials is of considerable technological interest. The most natural applications relate to the control of the grain size in a material. A well-known outcome of the seminal work by Smith and Zener [173] is the so-called Zener equation [15, 174], which describes the pinning of a grain boundary in the presence of a secondary phase. The analysis is based upon the equilibrium between the pinning pressure ($P_Z$) due to the drag force exerted by particles on grain boundaries and the driving pressure for grain growth derived from Eq. 5.1 ($P_g$) in the material. The Zener equation obtained by expressing the equilibrium for spherical secondary particles (or cylindrical, in 2-D) as well as grain boundaries provides a critical grain radius after which further growth is not expected. The inaccuracies due to the assumption of maximum pinning force at each inclusion and for the estimation of the surface density of inclusions on the grain boundaries are expected to compensate. In the equilibrium equation originally proposed Eq. 5.7, “r” and “\(\phi\)” are the radius and the volume fraction of the secondary inclusions (YSZ in this case).

\[
P_Z = \gamma \frac{3\phi}{4r} \equiv P_g = \frac{\gamma}{r_{C}} \quad (5.7)
\]

The Zener factor $Z_F$ is defined as the inverse of the critical (maximum) grain radius $r_{C}$ (Eq. 5.8). The maximum drag force exerted by spherical inclusions depends upon the dihedral angles at the interface. The original Eq. 5.8 holds for incoherent spherical particles (grain boundary perpendicular to the spherical inclusion surface). A modification in angles due to the nature of the particle changes the maximum drag force and corresponding position. The maximum pinning drag can be twice larger [14], resulting in half of the critical radius expression proposed in Eq. 5.8.

\[
Z_F = \frac{3\phi}{4r} \equiv \frac{1}{r_{C}} \quad (5.8)
\]
The application of the Zener equation is formally limited to the cases of randomly distributed monosized spherical particles. Evident practical limitations are that the interfacial tension between the two phases is not considered, as well as the precise shape of the interface, and that the effect of size distributions is not included. For this reason, several refinements to the formulation of the pinning pressure were proposed, for instance by adding a factor that accounts for the different particles’ size. Revised dependencies on volume fraction were also proposed, leading to exponents in the range of 1/3 to 1 in Eq. 5.8. As for the LSW theory, a systematic comparison of the experimental results for Ni-YSZ and predictions by modified Zener equations will not be performed in this Chapter. The above discussion however highlights that the imprecision on the critical radius estimated by a Zener-type equation is expected to be large (see Section 5.3).

Hillert [12] expanded upon the analysis by Lifshitz and Slyozov to study grain growth regimes, including pinning by a secondary phase. The expression for grain growth rate is derived using a mean field approximation as well. Eq. 5.9 corresponds to the case of spherical particles, where "$M$" is the mobility of the grain boundary and "$r_{Cr}$" the critical radius at which the grain neither grows nor shrinks. In the absence of pinning, analytical developments indicate that $r_{Cr}$ corresponds to the average size $\overline{r}$ for 2-D analysis, and $9/8\overline{r}$ for 3-D.

\[
\frac{dr}{dt} = My \left( \frac{1}{r_{Cr}} - \frac{1}{r} \pm Zf \right) \tag{5.9}
\]

The Z term acts against the movement of the boundaries, thus small particles complying to the condition $1/r > 1/r_{Cr} + Zf$ shrink, whereas large grains further expand when $1/r < 1/r_{Cr} - Zf$. 2-D and 3-D steady-state distributions were computed for parabolic grain growth in a single-solid phase. In the case of Zener pinning, the analysis shows that the size distribution cannot remain constant and growth will proceed until the average size reaches the Zener limit. Hillert [12] also treated grain growth from the viewpoint of topological rules, leading to a so-called defect model. The analysis for a 2-D system with an average coordination number among grains of 6 allowed discussing the limits for growth regimes. Normal growth corresponds to the case of relatively uniform grain sizes, whereas in the case of abnormal growth, some significantly larger grains grow rapidly increasing the differences in size. Normal growth is expected to proceed until Eq. 5.10 is reached. Abnormal growth is then expected to initiate if some grains are larger than the average until the second limit Eq. 5.11, which corresponds to the 2-D Zener equation. The analysis therefore suggests that for such a system under the regime of normal growth, the critical radius estimated by the Zener equation is an upper limit for the average size.

\[
r_{Cr} = \frac{1}{3Zf} = \frac{4r}{9\phi} \tag{5.10}
\]
As illustrated by Hillert’s defect model, the coarsening behavior of a region is expected to be dependent upon its surrounding. The concept of communicating neighbor surface elements and the local diffusion length scale were introduced by DeHoff [166, 175] as an attempt to circumvent limitations of the LSW theory. It addresses the prediction that as the volume fraction approaches zero, the distance between particles increases and consequently the coarsening rate drops, which is not accounted for in the LSW theory. In the simplest case of spherical particles, DeHoff’s theory yields a particle size distribution independent of the volume fraction and coarsening rates in general lower than predicted by standard mean field theories.

Sintering problems are in contrast traditionally treated from the standpoint of topology, where the evolving medium is viewed as networks of contacting particles and of pores represented by spatial graphs, i.e., vertices and edges [176]. In the simplest case of a single solid phase, three stages are expected: (i) adjustments in local morphology and inter-particle distance to minimize internal energy, as discussed previously, (ii) decrease in topological connectivity, followed by (iii) breakdown of the pore network [177]. We here note that the description corresponds to densification and that a constraint of constant volume fraction may also lead to a decreased connectivity of the solid phase.

An approach for the analysis of sintering is to assume that the rules that control the topological evolution in the second regime mirror those observed during grain evolution [176–178]. Topological changes consist in the switching or disappearance of an edge, which can yield the disappearance of a whole grain [178]. As defined by Rhines and DeHoff [176], the “topological transformations occur when the Euclidean dimensions of some part of the system chance to pass through zero”. As an example, the average grain volume increases linearly with time (Eq. 5.12 - \( N_V \) is the number of grains per unit of volume) and is proportional to the mobility, surface tension and the structural gradient \( \rho \). The latter parameter is constant in steady state growth (Eq. 5.13), and it depends on the curvature \( (H_V) \) and total surface per unit of volume \( (SA_V) \) since the grain shapes do not change. The linear dependence with time of the average grain volume visible in Eq. 5.12 recalls the LSW theory expression reported in Eq. 5.6, where the average volume of the particle (i.e. sphere) is proportional to the cubing of the average radius.

\[
\frac{1}{N_V} = Kt
\]

\[
\rho = \frac{H_VSA_V}{N_V} = const
\]
Chapter 5. Degradation of the Ni-YSZ electrode after long-term operation

Zöllner et al. [178] showed that during self-similar coarsening, the edge and grain reduction events are proportional to $t^{-1.5}$, and in general the evolution of the microstructure involves the loss of a grain face (even for shrinking events).

The applicability of such scaling laws to microstructural changes in Ni-YSZ is unclear, since it is defined in terms of objects, among others. A set of properties upon which the analogy between material sintering and grain growth is built is however of interest [177]. The genus, which is commonly illustrated as the number of handles, as well as the edge density, are expected to decrease. Concurrently, the coordination number of the vertices in the network tends towards a value of three and higher coordination numbers correspond to intermediate states; as a result, the average edge length increases.

5.1.2 Knowledge on the evolution of the Ni-YSZ microstructure upon SOC operation

Several of the above-mentioned assumptions for the derivation of coarsening governing equations partially apply to the Ni-YSZ electrode. The latter indeed comprises two solid phases and is porous. The contrasts in properties are significant, in particular those relevant for the mobility (750°C corresponds to 59% and 34% of the Ni and YSZ melting point, respectively), whereas those in volume fractions or characteristic phase size are usually below a factor of two. Both solid phases have complex morphologies, yielding a reticulated network where they mutually constrain. This description deviates from a representation as a suspension of spherical particles or few small inclusions in a matrix used for the derivation of coarsening governing equations presented in the previous Section. Further, a key objective in the design of SOC electrodes is to maintain the percolation of each phase separately [138], thus the microstructural alterations under the regimes relevant over long operation time are expected to be mild.

According to Holzer et al. [17], two transport mechanisms are possible in the Ni-YSZ electrode: surface diffusion and gas-phase transport of volatile species. The first mechanism derives from the difference in surface curvature between regions, and in particular it is generated by the vacancies diffusion between particles of different size [179]. In the Ni-YSZ cermet, transport of Ni by surface diffusion is expected to dominate due to the much larger mobility compared to YSZ. Two pathways, on the solid-pore interfaces and along the grain boundaries may contribute. Vassen et al. [179] estimated an effective Ni free sites diffusion coefficient of $1.3 \, \mu m^2 \, s^{-1}$ at 800°C by fitting a theoretical scaling law for growth to experimental data.

Similarly, gas-phase transport is expected to be dominated by Ni volatile species, in particular Ni(OH)$_2$($g$), because of the presence of steam during SOC operation. The equilibrium partial pressure of Ni(OH)$_2$($g$) varies in the range of $10^{-8} - 10^{-11}$ (see Fig. 6.1 in Chapter 6). Despite the small values, the anticipated effect of the steam partial pressure on the coarsening dynamics of Ni-based electrodes is often mentioned, but clear evidences are to our knowledge limited in the literature,
except under selected conditions of very high surface-specific gas flow rates on thin electrodes [17]. Simple calculations based on equilibrium partial pressure and estimated gas phase flux however suggest that the amount of material transported by long-range gas-phase transport is limited.

The detrimental effects of Ni coarsening for SOC electrodes are a decrease of the effective TPB density as well as of the connectivity of the Ni phase, causing a progressive decrease of performance [137, 180]. A consequent reduction of the interfacial surface area with pores and YSZ is also commonly observed. According to Davis et al. [181], the propensity for agglomeration in the Ni-YSZ microstructure is in part due to high Ni dihedral angles (∼117°), which ultimately leads to a depletion of connected electrochemical sites, mainly due to the loss of percolation. In general, the growth of the metallic phase characterized by phase size measurements mainly occurs during the first 500 hours of operation [16, 63, 138]. The initial growth is followed by a decrease of the growth rate up to an apparent stabilization, which corresponds to the expected and desirable constrained normal growth behavior.

At the present stage of development of the SOC technology, the degradation observed during the first thousand hours may not be critical if it stabilizes and remains within acceptable limits. From a practical standpoint, it boils down to a constraint for the appropriate sizing of a stack. The actual difficulty with such mild apparent degradation is to assess the performance degradation over periods corresponding to the current lifetime target of SOC devices. Therefore, questions still remain on the evolution and possible degradation regimes in the long-term, in which the initial rearrangement of the microstructure may also play a role.

The YSZ phase is often considered close to static, since the diffusion coefficient of Zr⁴⁺ is seven orders of magnitude lower than that of Ni [181]. This first simplification may require clarifications for long-term analyses. Indeed, studies attempted to give a better description of the microstructural evolution in Ni-YSZ, where the interaction between the YSZ phase and the evolution of Ni particles follows Zener pinning, mirroring grain growth in polycrystalline materials [15, 16]. As described in the previous Section, the rearrangement of Ni is subject to constraints and reaches stabilization when the equilibrium between the pinning pressure exerted by the YSZ particles and the curvature-driven motion of the Ni-pore interface is reached. From this perspective, the morphology of the YSZ scaffold is most likely key for the durability of the Ni-YSZ electrode and it may place requirements for identifying SOC operation strategies to guarantee its stability.

Microstructural changes of YSZ have been studied by performing accelerated tests at high temperature (>1100°C) [182], or by phase-field numerical models [183, 184]. Cronin et al. [180] mentioned that YSZ might have a limited mobility indicated by the slight decrease in specific interfacial area. Moreover and along the lines of first predictions using the Zener equation derived for spherical particles (Eqs. 5.7-5.8), Chen-Wiegart et al. [185] observed that a lowering of the YSZ volume fractions yields faster Ni relocation and agglomeration. It is here worth mentioning that this requirement is
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opposite to the intuitive recommendations for improved redox cycling tolerance.

The long-term stability of Ni-YSZ materials of the present generation has been achieved using the current knowledge on the effects of the initial microstructural properties on Ni coarsening, such as volume fractions, phase size distributions and interfacial surface areas. Besides the aforementioned analyses based upon Zener pinning, Tanasini et al. [138] used continuum modelling combined with percolation theory to identify the critical regimes leading to the loss of percolation of the Ni phase. A limitation of the study is that a complete rearrangement of the cermet microstructure is assumed at each time step. Therefore, refinements in the analysis level are needed to improve the current generation of materials.

Abdeljawad et al. [184] simulated the evolution of artificial packed sphere structures using phase-field modelling. In the case of an initially coarse Ni phase, the reduction of connected TPBs comports a net diminution of the electrochemical performance, despite improved gas-phase transport provided by a growth of the pore size. In the case of finer Ni particles, the increase of the average pore radius may sufficiently facilitate gas transport to partially compensate for the diminution of TPB density, stabilizing the degradation over time. Although all the configurations undergo a decrease of performance due to coarsening, finer Ni particles on average maintain a higher maximum power density after aging. Pecho et al. [186] mention that anodes sintered with finer particles have better conductivity, which they attributed to lower tortuosity and higher connectivity. However, initial coarser Ni particles improve the tolerance to redox cycling, because a larger pore size distribution helps to accommodate rearrangement. On the other hand, a coarser and less sintered YSZ phase would be more fragile because of narrower necks.

Testing parameters, i.e., mainly temperature, but also gas composition, current density and/or overpotential, are expected to influence the severity of microstructural alterations. For instance, a diminution of 100°C of the operation temperature can sensibly slow down the coarsening kinetics [187]. Local increases of temperature due to non-uniform electrochemical reactions in a stack or repeated transients during load following may therefore influence the mobility of the Ni phase, directly or indirectly by mild changes of the YSZ phase. Results from the literature however indicate that establishing unambiguous relationships between Ni-YSZ microstructural alterations and controlled operation conditions is not straightforward. The effects of the uneven spatial distribution of current density in a stack (which in co-flow and SOFC is higher at the inlet despite the lower temperature, due to the larger reactants concentration) is unclear. The effects on the alteration of the interface with the electrolyte are specifically discussed in Chapter 6.

The objective of the present Chapter is to better comprehend how the driving forces for microstructural alterations evolve upon operation and the consequences for the long-term stability of Ni-YSZ electrodes. An evolution analysis is performed using eight reconstructions from samples tested in SOFC and SOEC modes. Samples aged under close to stack operation conditions that became avail-
able at GEM-EPFL during the course of this Thesis are favored, to determine whether unexpected behavior and/or contamination may practically prevail over the studied time span. An emphasis is placed on 3-D characterization, because the changes to detect and quantify are known subtler in the current generation of Ni-YSZ materials than the previous one. In a first step, standard metric and topological properties are evaluated and the results analyzed in terms of established theories described previously, i.e., LSW, topological coarsening and Zener constrained growth. In a second step, the available length, dihedral contact angles and interfacial curvature are measured in an attempt to assess directly the driving force terms in the coarsening governing equations, e.g. with less strong geometrical simplifications than applied in several past analyses.

5.2 Experimental

Table 5.1 lists the eight Volumes imaged by FIB-SEM serial sectioning and used for the evolution analysis of microstructural changes in the SOLIDpower Ni-YSZ electrode material. The exhaustive description of the sample test conditions as well as of the image processing methods for reconstruction is available in Chapter 1. A short summary is provided hereafter. Pristine Volume A is selected as Volume 1. Volume 2 was operated for 1.9 kh in a segmented-cell kept at OCV for most of the time, besides periodic I-V and EIS measurements (segment 6 in Fig. 1.3). Volume 3 was polarized in SOEC mode for 2 kh. Volumes 4 and 5 belong to the same short stack operated for 4.7 kh in SOFC and they were extracted from the gas inlet and outlet regions of the cell, respectively. Volume 6 was tested in SOEC mode for 10.7 kh and corresponds to the case study expanded in Chapter 2. Volumes 7 and 8 are from a segmented cell operated for 15 kh in SOFC mode. The former comes from a segment located in the inlet region (segment 12), while the latter comes from the middle and close to the external border in contact with the sealing (segment 19 - Fig. 1.3). The reconstructed Volumes are from regions next to the interface with the electrolyte.

<table>
<thead>
<tr>
<th>Volume</th>
<th>Denomination</th>
<th>Dimensions [µm]</th>
<th>Voxel size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pristine A</td>
<td>17.1-10.0-18.5</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>SOFC 1.9 kh – Seg. 6</td>
<td>16.7-10.7-16.7</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>SOEC 2 kh</td>
<td>17.0-11.5-15.0</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>SOFC 4.7 kh - Inlet</td>
<td>21.0-12.0-19.5</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>SOFC 4.7 kh - Outlet</td>
<td>9.1-18.2-7.4</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>SOEC 10.7 kh</td>
<td>9.7-9.7-9.7</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>SOFC 15kh – Seg. 12</td>
<td>17.0-10.7-14.6</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>SOFC 15kh – Seg. 19</td>
<td>14.0-11.0-14.0</td>
<td>10</td>
</tr>
</tbody>
</table>

*Table 5.1 – List of analysed Volumes.*
5.3 3-D Characterization of microstructural evolution

5.3.1 Standard properties

In this section, the data is analyzed following approaches common in the literature. Parameters including volume fractions, median phase diameters (measured by overlapping spheres ($d_{50,s}$) and ray tracing ($d_{50,r}$)), total and connected TPB density, interfacial surface areas (ISA), total surface areas (TSA) and contiguity were computed on the 3-D reconstructions with in-house implementations of existing methods (Chapter 1, [96, 130]). The surface to volume ratio ($S_v$) was computed by dividing the total surface areas by the corresponding volume fractions. The measured topological properties are reported in Table 5.2 and Figs. 5.2A-F.

<table>
<thead>
<tr>
<th>Metric</th>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
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<tr>
<td>Vol. frac. [µm$^3$/µm$^3$]</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pore</td>
<td>0.28</td>
<td>0.25</td>
<td>0.29</td>
<td>0.31</td>
<td>0.30</td>
<td>0.30</td>
<td>0.28</td>
<td>0.27</td>
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<td>0.44</td>
<td>0.42</td>
<td>0.43</td>
<td>0.43</td>
<td>0.44</td>
<td>0.43</td>
</tr>
<tr>
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<td>0.30</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.28</td>
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</tr>
<tr>
<td>$d_{50,s}$ [µm]</td>
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<td></td>
<td></td>
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<td>TPB [µm/µm$^3$]</td>
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<td></td>
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<td></td>
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<td></td>
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<td>6.9</td>
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<td>4.7</td>
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</tr>
</tbody>
</table>

Table 5.2 – Metric and topological properties measured on the pristine and aged Ni-YSZ Volumes. The average standard deviation is reported in the last column. ISA values were adjusted by multiplying with the factor $\frac{\pi}{6}$ to estimate the actual surface area from the digitized Volume assuming close to spherical shapes (Chapter 1).

The coarsening of the Ni phase is as expected clearly indicated by the increase of the Ni median diameter $d_{50}$ (approximately 33% after 2 kh in SOEC and 4.7 kh in SOFC operation). The measurements also suggest a slight increase of the YSZ median diameter with respect to the pristine Volume, which however cannot be ascertained statistically with the present dataset. Volumes 2 and 3 exhibit a significant difference in Ni $d_{50}$, despite a similar testing time of 1.9 kh and 2 kh, respectively.
Figure 5.2 – Evolution of measured topological properties (data referred to Table 5.1): (A) total surface areas, (B) interfacial surface areas, (C, D): median phase diameter measured by overlapping spheres (C) and ray tracing (D), density of total and connected TPB (E) and their ratio (F). Measurements on Volumes aged under SOFC and SOEC are shown in red and blue, respectively. The trend lines and error bars are provided as a guide for the eye; the latter were estimated based on measurement of sub-volumes with a size of $9^3 - 10^3 \, \mu m$. 

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Therefore, the difference may be due to polarization and or gas composition effects, since Volume 2 was polarized in SOEC, whereas Volume 3 was at OCV under SOFC gas and temperature conditions for most of the time. The discussions on their comparison will be based on this difference, even though additional measurements will be needed to ascertain that variations in Ni and pore volume fractions due to sampling a peculiar zone do not play a role. The dataset does not highlight a clear pattern in the variation of the pore size, confirming that the rearrangement of the solid phases does in the present case not involve loss of material (i.e. densification or gas-phase transport).

The diminution of total and connected TPB density also follows expected trends (Fig. 5.2B). Significant differences are not observed between the 6 directions for measuring TPB connectivity (not shown), therefore the values in Table 5.2 and Fig. 5.2B correspond to the measured average. The ratio $\text{TPB}_{\text{eff}}/\text{TPB}_{\text{tot}}$ overall decreases upon SOFC operation. It is a consequence of a reduction in Ni connectivity, likely because of necking followed by pinch-off, which will be discussed later. The evolution in SOEC mode exhibits slight differences. The initial drop after 2 kh is more severe but then stabilizes, yielding a lower TPB reduction after 10.7 kh compared to SOFC Volumes 7 and 8, despite their longer exposure to operation temperature (15 kh), as well as Volumes 4 and 5 (4.7 kh). The decrease in connected TPB density after 4.7 kh, followed by an increase (15 kh), seems to just exceed the limits for statistically significance. Unambiguous conclusions about the reasons cannot be drawn at this point, because a clear trend on whether it arises from differences in e.g. porosity because of sampling and/or polarization could not be identified.

The evolution of the phases’ total surface areas (Fig. 5.2C) is similar in SOFC and SOEC and characterized by monotonic decrease until 4.7 kh and 2 kh in SOFC and SOEC mode, respectively. It is therefore consistent with the faster increase in $d_{50}$ in SOEC. Although the Ni phase experiences the most obvious variation (~36%), the measurements suggest a decrease larger than the estimated standard variation for YSZ as well (~9%). The trend for YSZ after normalization ($S_v$) is however less clear. Because the Ni mobility is highest and the ranking in interfacial surface energy estimated from dihedral angle measurements is $\gamma_{\text{Ni/Pore}} > \gamma_{\text{Ni/YSZ}} > \gamma_{\text{YSZ/Pore}}$ (see later Eq. 5.17), microstructural re-arrangement in terms of interfacial surface area is dominated by the two Ni ISAs. The ISA Pore/YSZ remains in contrast mainly unaffected after SOFC operation. In this regard, a slight surge that counterbalances the net diminution of ISA Ni/YSZ is even observed in the two SOEC Volumes.

It is worth mentioning that clear differences were observed within the SOEC samples when comparing the regions next to the electrolyte and further away. The depletion of Ni close to the interface resulted in a finer but less connected Ni microstructure, resulting in higher total TPB but lower connected TPB density and accessibility [130]. This indicates possible differences in the Ni transport mechanism between SOFC and SOEC conditions. The present Chapter is not focused on these aspects, which are discussed in Chapter 6. The FIB-SEM dataset for Volumes 3 and 6 comprise the interface with the YSZ electrolyte. Both Volumes 3 and 6 used for the present analyses were extracted 6 $\mu$m away from the interface. The properties scans presented in Chapter 6 qualitatively suggest
that average measurements from this offset are not largely affected.

The volume fractions measured in the dataset present a non-negligible difference between the maximum and the minimum values in Table 5.2, respectively 17%, 7% and 9% for pore, YSZ and Ni. In particular, Volumes 4 and 5 aged in SOFC mode for 4.7 kh exhibit the highest pore volume fraction, but consistent trends with respect to operation time, mode and location on the cell are not observed. Therefore, the observed differences may be rather due to sampling different regions with variability arising from manufacturing, than be directly related to a degradation phenomenon. They were somewhat unexpected based upon rapid convergence studies on individual imaged Volumes. They therefore suggest stochastic longer-range variability in the SOLIDpower Ni-YSZ electrode, even when considering only regions next to the electrolyte. In this regard, an attempt of quantification is proposed in Appendix E, in which the measured properties obtained from sampling two locations within a same segment are compared. The results indicate a difference in volume fraction of ±3.5%, which is comparable to the standard deviation reported in Table 5.2 (0.01 μm$^3$μm$^{-3}$)

The first analysis based on the measurement of standard properties highlights a net reduction of the total and connected TPB density during approximately the first 2 kh of operation in SOEC and up to 4.7 kh in SOFC. This study is focused on the longer-term behavior and additional measurements are required for an accurate estimation of the time constant. The trends in the evolutions of the interfacial surfaces, in particular Ni/Pore, and size distributions are overall similar. Therefore, an apparent plateau in standard properties is then reached, suggesting that long-term operation does not further negatively alter the Ni-YSZ microstructure. The exceptions are a subtle evolution of YSZ that cannot be ascertained with the present dataset, and the monotonic decrease in Ni contiguity. Unambiguous trends related to the position, i.e., local operation conditions could not be identified: the detected variations between Volumes 4 and 5 (4.7 kh SOFC), as well as 7 and 8 (15 kh SOFC) are within the statistical variation estimated in Appendix E.

The first results are in line with EIS measurements performed on the 15 kh segmented-cell. Spectra were analyzed by the distribution of relaxation times (DRT) to measure the contribution to the ASR of charge transfer and gas-phase transport in the Ni-YSZ (refer to Chapter 1. The two segments displayed a similar evolution of the charge transfer resistance under a bias of 0.2 or 0.5 A cm$^{-2}$, which slightly diminished from 4000 to 10000 h of operation (from ~0.09 to ~0.08 Ω cm$^{-2}$, bias of 0.5 A cm$^{-2}$, EIS measurements not available before) and then increased until 15000 h up to the value at 4000 h. A notable evolution of the contribution of gas-phase transport was also not observed for both segments. The initial decay measured by DRT occurred in contrast faster [92]: the ASR of charge transfer in Ni-YSZ surges of about 40% in the first 50 hours of operation, reaching then an apparent stabilization for the remaining of the measurement campaign (1200 h). The magnitude of the decay is similar to that of the connected TPB density between the pristine state and that after apparent stabilization. Indeed, complementary have shown that the accessible TPB is not significantly affected by SOFC operation up to 4700 h [130], henceforth of the effects of the transport
properties on performance.

The phase size distributions are measured by the ray tracing method developed by Grew et al. [96] and filling by overlapping monosized spheres introduced in Chapter 1. Volume instead of number weighted probability density functions were computed. The ray tracing and overlapping spheres methods for measuring size distributions probe the microstructure using distinct geometrical concepts. They intuitively correspond to a representation as a network of channels and particles, respectively. They are therefore complementary and the ray tracing method appears at a first appraisal more suitable for characterizing in particular the visually highly-ricetulated ceramic phase. In the present study, both however indicate similar trends, which also illustrates their discrimination limits.

As anticipated from the $d_{50}$ measurements, the most evident alteration concerns the Ni phase (Fig. 5.3C). The inspection of the size distribution provides additional information compared with the apparent stabilization in Fig. 5.2A. Sizes larger than 1 $\mu m$ seem to proceed slightly but still continuously over time, and a net discrepancy between the pristine and the aged Volumes is observed below approximately 0.7 $\mu m$. The disappearance of Ni regions characterized by smaller size is in line with competitive growth. The size distributions of YSZ mostly overlap. A clear trend could not be identified to confirm the evolution of the ISA (Fig. 5.2C). The variations in the pore size distributions are also observed, but the trend is complicated: the density of sizes smaller than the average first increases (SOFC 1.9 kh), followed by a drop (SOFC 4.7 kh) and finally stabilization close to the pristine case. The evolution in the SOEC case is milder. This trend actually follows that of the pore volume fraction and might therefore be an artifact, that size distribution measurements cannot resolve.

The measured standard properties do not highlight an evident effect of the position along the gas flow. Volumes 4 and 5 (SOFC 4.7 kh, from the inlet and outlet, respectively) and Volumes 8 and 9 (SOFC 15 kh, extracted from the inlet and center close to the external edge) do not differ notably, even though the current density and hydrogen to steam ratio are higher at the inlet. This first analysis based on two pairs of Volume suggests that the gas composition does not notably impact the evolution of the microstructure under practical SOFC operation conditions. A stronger effect during the initial operation cannot be excluded, but the relevance for long-term stability does not seem critical.
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Figure 5.3 – Phase size distributions measured by ray tracing. Evolution during SOFC (A, C, E) and SOEC (B, D, F) operation.
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A first comparison between the measured evolution and that predicted by LSW and Zener theories can be carried out based upon the standard property measurements presented previously. A further analysis of the applicability of the theories requires the inspection of topological properties, in particular for topological coarsening. The discussion below starts with the evolution of the median phase sizes $d_{50}$ and ISAs, followed by the comparison of the size distributions with the steady-state ones discussed in the Introduction. An important comment based upon the derivation of the coarsening equations is that the following comparison implies that the morphology is dominated by close to spherical shapes. The curvature analysis provided in Chapter 3 indicated that this representation of the Ni-YSZ microstructure is questionable.

The agreement with competitive growth following Ostwald ripening (Eq. 5.6) is tested qualitatively in Figs. 5.4A and B. In the former, the inverse of the surface to volume ratio ($S_v$) rather than an average or median radius is plotted against the cubic root of time [22], because this characteristic length is not directly related to an a priori assumption on the morphology. A linear trend is expected [167]. The measured data suggest that the relationship may imprecisely apply for YSZ under SOFC conditions, but not for Ni. Fig. 5.4B provides a comparison between the steady-state dimensionless distributions predicted by the LSW theory as well as those for 2-D and 3-D unconstrained grain growth by Hillert et al. [12] and the measured Ni size distributions scaled by the median diameter. The distribution shapes are clearly different and the same applies to all shown in Fig. 5.3. A tail at larger, rather than at smaller diameters is observed in the pristine sample, as well as after 1900 h in SOFC before the plateau of the median phase diameter growth is reached. Therefore, the comparison in Fig. 5.4 cannot ascertain whether or not the coarsening of the YSZ phase occurs to a noticeable extent in the conditions treated here. Further, even if standard coarsening may be applicable, the regime they treat may not have been reached yet.

Nelson et al. [16] observed a good agreement between the critical Ni diameter predicted by the 2-D version of the Zener equation [15]. The comparison in Fig. 5.4C shows that the median diameter measured by ray tracing is bounded by the 2-D limit for normal growth from Hillert et al [12] and the 3-D Zener equation. The 2-D Zener equation seems to provide a better estimate of an upper limit, but the offset is non-negligible. The agreement is in contrast good for the phase size diameters measured by overlapping spheres, the geometrical concept of which is closer to the derivation of the Zener equation (Fig. 5.4D). The interfacial shape distributions (ISD) presented in Chapter 3 (pristine Ni-YSZ) and Appendix F do also not allow to justify unambiguously the choice of the 2-D over the 3-D version, even though the subset of YSZ cylindrical shapes is fairly high in the Ni/YSZ interface. The standard Zener equation applies to an incoherent interface (dihedral angle of 90°). A derivation following the one described in e.g. [14] and assuming the average Ni dihedral angle of 140° computed later in this Section leads to pinning pressure about twice higher, which is in good agreement with the measurements. The range between the predictions from the considered versions of the Zener equation in Figs. 5.4C-D is large. Limitations in terms of volume fraction are
5.3. 3-D Characterization of microstructural evolution

\[ r_{cr} = \frac{1}{3}Z_f = \frac{4r}{9\phi} \quad \text{Eq. 5.10} \]

\[ r_{cr} = \frac{2r}{3\phi} \quad \text{Eq. 5.11} \]

\[ r_{cr} = \frac{4r}{3\phi} \quad \text{Eq. 5.8} \]

\[ r_{cr} = \frac{4r}{3\phi}(1 + \cos(\pi - \theta_{Ni})) \quad \text{Eq. 5.8 modified [14]} \]

Figure 5.4 – Comparison of the measured evolution with LSW and Zener theory. (A) Inverse of the $S_V$ ratio plotted against the cubic root of operation time. (B) Dimensionless steady-state size distributions predicted by LSW and unconstrained grain growth theories [12, 13] and measured dimensionless Ni size distribution. (C,D) Evolution of critical diameters predicted by Zener equations [12, 14, 15] and median phase diameter measured by ray tracing (C) and filling with overlapping spheres (D).
also reported in the literature and they are not treated here: they lead to exponents on the volume fraction “φ” in Eq. 5.8 ranging from approximately 1/3 to 1 [15].

5.3.2 Available length on Ni and YSZ

The analysis based on standard properties presented above is extended with the measurement of “available length” \( L_A \) introduced in Chapter 3. The goal is to analyze how the morphology of the surface near the TPB evolves in operation and infer the potential consequences for electrochemical performance, as well as test further whether or not microstructural changes still proceed in the long-term. The previous section showed that properties such ISA, PSDs and TPB density partially inform about these aspects. Moreover, the \( L_A \) measurement permits to relate the size of the Ni regions with the extension of the surface available for diffusion, as discussed in Chapter 3. Two qualitative trends are expected. The available length on YSZ at a TPB is larger than the one associated on Ni (see Fig. 3.5). The effect of the decrease in Ni/Pore interfacial surface area is also expected to be balanced by that of the TPB density. Chapter 3 further highlighted a relationship between available length on Ni and the length of TPB lines (see Fig. 3.7). Hence, the disappearance of small Ni regions should be reflected predominantly on shorter Ni available lengths. It is however not possible to anticipate the effect on the available length on YSZ.

The calculations of the average available length \( (L_A, av) \) in Table 5.3 indicate a nearly constant value for Ni and as expected an increase for YSZ. The averaged measurements do not indicate a risk of drastic changes in the local electrocatalytic properties of the TPB.

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*Table 5.3 – computed average available lengths \( (L_A, av) \) from the ratio between ISA and TPB values listed in Table 5.2.*

The measured number-weighted distributions of available length on Ni and YSZ are provided in Figs. 5.5A and 5.6A. The vertical black dashed lines on the leftward part of the plots correspond to the threshold below which the measurement is considered statistically unreliable (Chapter 3). The vertical dashed colored lines refer to the computed mean available length. In addition, the inserts (Figs. 5.5B and 5.6B) are multiplications by the total TPB density reported in Table 5.2, to facilitate the visual appreciation of how the \( L_A \) measurement population evolves upon aging. Integration therefore yields the corresponding TPB\(_{Tot}\).

The two solid/pore interfaces exhibit differences in their evolution: the spread of the available length on Ni slightly decreases, resulting in a gathering toward the peak values, causing a progressive diminution of lengths larger than approximately 0.2 \( \mu m \). The mean for Ni is practically constant,
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Figure 5.5 – (A) Evolution of the available length distribution on Ni. The black vertical dashed lines correspond to the approximate threshold of 4 voxels (here 40 nm) below which the data is considered statistically unreliable. The vertical dashed lines are the mean of the distributions. (B) Distributions weighted by the density of total TPBs.

Figure 5.6 – (A) Evolution of the available length distribution on YSZ. The black vertical dashed lines correspond to the approximate threshold of 4 voxels (here 40 nm) below which the data is considered statistically unreliable. The vertical dashed lines are the mean of the distributions. (B) Distributions weighted by the density of total TPBs.
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with a slight decrease upon SOEC operation. The results indicate in contrast a shift toward larger lengths for YSZ with operation time. Volumes 6 and 8 aged for the longest periods (SOFC 15 kh) however exhibit slightly inferior mean values compared to Volumes 3-5 (SOEC 2 kh, SOFC 4.7 kh). The mode of the YSZ distributions progressively shifts from approximately 0.4 to 0.6 μm, while in the Ni case it stays close to constant around a smaller value of 0.15 μm, except for the Volumes operated for more than 10 kh.

The trends of the mean available length \( \bar{L}_A \) comply with the average \( L_A \) calculations discussed previously (about 3 times larger), but the differences in the available length distribution on Ni upon aging are more significant than those observed for the PSD (Figs. 5.3) and standard properties (Table 5.2). The inspection of the Ni available length distribution weighted by TPB suggests two regimes (Fig. 5.5B): in the first stage (0 h to 4.7 kh), the decrease in ISA Ni/Pore and total TPB density results in an only mildly size-dependent diminution of the \( L_A \) population. The maximum decrease of the central portion of the distribution (approximately from 0.05 - 0.3 μm) proceeds until 4.7 kh. The second regime is observed for Volumes 6-8 operated for more than 10 kh. The shape of the distribution is modified, with further reductions of the tails resulting in clustering around the peak slightly shifted towards smaller length (around 0.15 μm). The distribution of available length on YSZ weighted by the total TPB density mostly varies for lengths smaller than approximately 1 μm. This is most likely the consequence of the relocation of the Ni phase, since the ISA Ni/YSZ reported in Table 5.2 does not significantly vary.

The available length measurement therefore suggests that microstructural changes proceed further between 4.7 kh and 15 kh. A reasoning mirroring competitive growth does not apply to the distributions. Indeed, both populations of shorter and longer available lengths decrease. As suggested by Fig. 5.4B, this behaviour does not imply shrinkage of larger regions, but it relates to the diminution of TPBs associated to larger Ni regions (characterized by longer \( L_A \)), which indeed does not seem to stop after prolonged testing time. It is however not possible to determine whether or not a stable state has been reached, since for both phases, the Volumes aged for more than 10 kh exhibit noticeably different features compared to 2 kh (SOEC) and 4.7 h (SOFC). The measured trends would not comport a detrimental impact on the surface-diffusive reactions involved in the charge-transfer mechanisms, since the shorter lengths (right tails of the distributions) tend to diminish in both cases.

5.3.3 Dihedral angles

The measurement of dihedral angles at TPBs informs about interfacial energies, which are material properties. It consequently allows quantifying the wettability at material interfaces. Higher wettability, i.e. lower dihedral angle and interfacial surface energy results in higher adhesion work between the two adjacent phases, whereas large angles indicate that relocation of the interface
is less constrained. In a first simplification, contact angles are considered fixed properties of the materials and drastic variations are not expected upon operation time. They may be practically altered because of e.g. impurities that alter the local composition, different operation temperature and possibly quenching of the sample; heat-up usually results in a decrease of the contact angle and increase in wettability. A dedicated analysis of these effects is outside the scope of the Thesis. The purpose of the developed measurements is to detect potential anomalies and identify the need for targeted investigations.

A force equilibrium between interfacial surface tensions exists at the TPBs Eq. 5.14, as illustrated in Fig. 5.7A, which yields the relation between the dihedral angles and interfacial tension vectors $\overrightarrow{\gamma}$ Eq. 5.16. The ranking in energy is therefore Eq. 5.17.

$$\overrightarrow{\gamma}_{Ni/Pore} + \overrightarrow{\gamma}_{Ni/YSZ} + \overrightarrow{\gamma}_{YSZ/Pore} = 0 \quad (5.14)$$

$$\theta_{Pore} + \theta_{YSZ} + \theta_{Ni} = 360^\circ \quad (5.15)$$

$$\frac{\gamma_{Ni/YSZ}}{\sin(\theta_{Pore})} = \frac{\gamma_{Ni/Pore}}{\sin(\theta_{YSZ})} = \frac{\gamma_{YSZ/Pore}}{\sin(\theta_{Ni})} \quad (5.16)$$

$$\gamma_{Pore/Ni} > \gamma_{Ni/YSZ} > \gamma_{YSZ/Pore} \quad (5.17)$$

The dihedral angle measurement implemented in this Thesis is stereological, mirroring that of the available length (Chapter 3). The reconstructed Volume is scanned slice by slice. Starting from the 4-voxels forming a TPB, the routine detects the interfacial voxels in each phases (blue, yellow and red in Fig. 5.7B). The midpoint between each couple of interfacial voxels defines the location of the interface (green, orange and magenta in Fig. 5.7B). The dihedral angles are computed from the hypothetical triangles drawn with the coordinates of two interfacial points and the center of the TPB (Eq. 5.18).

$$\theta_{A0B} = \cos^{-1} \left( \frac{f_{AO}^2 + f_{OB}^2 - f_{AB}^2}{2f_{OA}f_{OB}} \right) \quad (5.18)$$

For each TPB in the reconstruction, the procedure is repeated considering first the closest triad of interfacial points, then expanded until an user-specified number of triads is reached. The computed
average is tabulated as the dihedral angles at the TPB. A sensitivity analysis was performed to assess how the measurement is influenced by the specified number of points for averaging. A value of six was selected since it provides a dispersion that cannot be further ameliorated by adding additional points, and corresponding approximately to a radius of 40-60 nm around the TPB. The fifth Euclid postulate (Eq. 5.15) is guaranteed in all cases. The algorithm also ensures the correct recognition of angles larger than 180°, which cannot be directly computed by Eq. 5.18. Supplementary information on the measurement procedure is provided in Appendix D.

The average standard deviation of the Ni dihedral distribution is the lowest (below 23°) and it tends toward a slight decrease over time (see Table 5.4). This is presumably due to the higher Ni mobility together with the larger Ni angle value (~140°) compared to YSZ (~95°) and pore (~125°), practically leading to higher accuracy. The standard deviations of the dihedral angle distributions are highest in the two SOEC Volumes, for Ni and especially YSZ. As investigated further in Chapter 6, it may indicate the presence of another driving force for the displacement of TPBs and/or nearby morphology. YSZ dihedral angles have in general the highest standard deviation. The reason is not necessarily physical but it may be because the grayscale of YSZ is intermediate in the SE In-lens electron images and the precise identification of its morphology at the TPBs may be more affected by artifacts or slight variations during watershed-based segmentation. Comparison with another imaging technique or artificially-generated grayscale data may be needed for an unambiguous confirmation.

The probability density functions of dihedral angles are shown in Figs. 5.8. Similar to the convention adopted for the available length measurements, the vertical dashed lines indicate the distribution.
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<table>
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<tr>
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</table>

Table 5.4 – Average dihedral angles measured from Figs. 5.8. The average standard deviation is reported in parentheses.

mean. The black lines correspond to the averaged values measured by Nelson et al. on reconstructions from differential absorption contrast x-ray nanotomography data [16], applying a similar stereological approach based on spline fitting on a dataset with a spatial resolution in the range of 25 nm. As mentioned previously, the dihedral angles at TPBs relate to interfacial surface energies and are therefore material properties. Large variations are consequently not expected, except in the case of e.g. contamination by impurities. Stereological measurements of randomly dispersed sintered particles however yield a distribution, with the mean corresponding to the theoretical values. In the present case, the Ni-YSZ microstructure is not completely stable after sintering and foremost the reduction of Ni. Therefore, slight variations may be initially observed and the measurements may be then also partly influenced by pinning effects upon aging. A lingering evolution can therefore not be excluded upon aging, resulting in gradual distribution peaking until the majority of the angles stabilize at their theoretical values.

Figs. 5.8 indicate peaking of the distributions upon aging in SOFC. The measurement is not able to ascertain that variations in mean and modal values are significant (±6% in Appendix E). A pattern is observed in the evolution of $\theta_{Ni}$ and $\theta_{Pore}$, which seems dominated by the subset of angles lower and higher than the mean, respectively. From a geometrical standpoint, a change in the dihedral angles can be achieved upon displacement of TPB. For instance, the shift of a TPB region promoted for reaching a close to equilibrium Ni dihedral angle will also affect the YSZ and/or pore angle, leading in turn to potential deviation from their mean value. Therefore, displacement related to the minimization of mean curvature and surface area that lead to configurations where the three dihedral angles are closer to their theoretical values are intuitively favored.

The distribution of pore dihedral angle displays a coherent evolution with time for angles larger than approximately 120-125° in SOFC. Accordingly, the related smaller (more wettable) Ni and/or YSZ angles would be naturally prone to increase upon aging. The accretion of the left portion of the $\theta_{Pore}$ distribution is less manifest and is associated to an expansion of Ni and/or YSZ dihedral angles. In this case, less wettable solid phases may have lower tendency to relocate because of the smaller curvature at the three phase junctions, comporting a net shift toward smaller values of the average pore angles.

The SOEC aged Volumes (Volume 6 in particular) display a noticeable difference in the $\theta_{Ni}$ and $\theta_{YSZ}$ distributions in term of skewness and modal values. The YSZ phase presents the largest variability.
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Figure 5.8 – Evolution of the YSZ (A), Ni (B) and pore (C) dihedral angle distributions upon operation. The vertical dashed color lines are the mean of the distributions, while the black ones are the values measured by Nelson et al. [16], respectively 97°, 151° and 111°.

These results suggest that a specific force may be acting at the TPB level, since ISAs and $L_A$ seem qualitatively less affected by the difference in operation.

The available length and dihedral angle measurements inform both on the morphology near the TPBs. The available lengths depend on morphology and dihedral angles are material-dependent properties, but it is difficult to identify a-priori their relationship. The linear correlation between the two metrics is assessed, by computing the Pearson correlation factor of each couple, i.e., three angles and two available lengths. The results for the pristine Volume reported in Table 5.5 confirm a strong negative linear correlation between the three dihedral angles and a positive correlation between available length of the two phases, as already discussed in Chapter 3. $\theta_{Ni}$ value shows a smaller linear correlation with $\theta_{Pore}$. The absence of a linear correlation suggests that the two play a role at a different scale (as assumed for the derivation of the Zener equation for a coherent
5.3. 3-D Characterization of microstructural evolution

Figure 5.9 – Linear correlation factors between dihedral angles and available lengths.

Table 5.5 – Correlation matrix of dihedral angles and available lengths for Volume 1 pristine.

The evolution upon operation of the linear correlation factors is shown in Fig. 5.9. That between the two available lengths does not vary drastically. A reason is that a change in the position of a TPB yields an augmentation or diminution of the associated YSZ length that depends upon the displacement of the neighbouring Ni/Pore interface. The close to constant value of approximately +0.2 suggests that the microstructural changes near the TPB would not change drastically in terms of regime and/or do not proceed with strong asymmetry on the interfaces. The correlation between the Ni and pore dihedral angle becomes less strong upon aging, whereas it is the opposite for the pore and YSZ dihedral angles. This result suggests that the displacement of TPBs and/or localized changes in the morphology favor the rearrangement of the Ni dihedral angles over that of YSZ, comporting a further diminution in the $\theta_{Ni}$ vs. $\theta_{Pore}$ negative correlation. Overall, SOFC and SOEC Volumes present similar evolution, while an evident difference is noticeable between Volumes 2 (SOFC 1.9 kh) and Volume 3 (SOEC 2kh).
5.3.4 Evolution of the topology of the Ni and pore phases

A set of measurements were performed to discuss the evolution of the phase network topology. They consist in phase size distribution using filling by overlapping mono-sized spheres as described in Chapter 1 (Methodology) and skeletonization of TPB regions as provided in Chapter 3 and, following identical procedures, of the Ni phase Volume. Fig. 5.10A displays the difference between the size distribution of the domain of Ni and pore together, and that obtained by using the Ni Volume as a mask upon each filling step. The difference therefore provides an indication of how Ni occupies the Ni and pore domain, i.e., the corresponding size distribution in the YSZ scaffold. As expected under the assumption of a close to static YSZ phase, Ni locates preferentially in regions of largest sizes within the YSZ scaffold. Upon operation, the Ni phase further fills the largest Ni and pore regions. The difference between the pristine sample and after aging is however limited, owing to the significant growth of the Ni phase in Figs. 5.3E and F. The process seems stabilized after 1900 h, even though Volumes operated for 10.7 kh (SOEC) and 15 kh (SOFC) yield the distributions most shifted towards the left. Therefore, the size of regions within the YSZ scaffold occupied by Ni does not seem to vary significantly upon operation.

The size distribution of closed TPB lines measured by skeletonization following the approach from Chapter 3 shifts as expected towards larger length, with a continued disappearance of smaller TPB lines from 4.7 to 15 kh (SOFC), but an apparent re-appearance after 10.7 kh of SOEC operation (Fig. 5.10B). The detection capability of the approach used for Figs. 5.10A and B is however likely limited and evolution analysis on a same sample using non-destructive imaging methods will be required for confirmation.

The distribution of the length of skeleton branches after skeletonization of the Ni phase, using the same routine as for the TPB lines, is shown in Fig. 5.10C. An increase in branch (or spatial graph edge) length is observed, as discussed in the section “Overview of coarsening theories” but for the pore network upon topological coarsening. It is associated to the pinch-off of necks of about the size of the median Ni phase size in the pristine sample (Fig. 5.10D). The neck size distribution is a complementary measurement to that of the size distribution. It is obtained by applying the labelling procedure used for standard contiguity measurement at each sequential filling by spheres of the diameter being considered. The number of necks corresponding to this size is counted by tracking how separate regions connect upon decreasing of the sphere size.

The densities of “handles” in the Ni and pore phase are computed from the Euler characteristics, number of objects and cavities. It informs about the number of redundant connections. It decreases significantly in the Ni network (Fig. 5.10E), whereas that of the pore phase stays either constant (SOFC) or increases (SOEC). The trends shown in Figs. 5.10 (A, C, D, E) seem to stabilize after 4.7 h (SOFC) and 2 h (SOEC), which corresponds to the time at which most standard properties discussed previously reach their plateau. The measurement of coordination number does however not indicate
5.3. 3-D Characterization of microstructural evolution

Figure 5.10 – Evolution of the topology of the phases. (A) Phase size distribution measurement providing the difference between a standard phase measurement by filling the domain of pore and Ni together by overlapping spheres and of the pore and Ni domains together and by considering the same domain but retrieving only the subset for the Ni phase. (B) Size distribution of TPB lines (subset of closed loop). (C) Size distribution of edge length in the Ni phase. (D) Neck size probability distribution normalized with respect to the pristine (0 h) Volume. (E) Evolution of the density of handles density from genus in the Ni and pore phases measurement. (F) Evolution of the fraction of skeleton vertices in the Ni phase with a coordination number “Z” of 1, 3 and 4; the fraction for \( Z_{\text{Ni-Ni}} = 4 \) is multiplied by 10 for display purposes.
clearly that the partial breakdown of the Ni phase follows rules for the disappearance of grain edges such as identified during grain growth. Most of the network vertices have a coordination number of one (“dead-end”) or of three (Fig. 5.10F). The fraction with a coordination of four (and larger) is very low (approximately 4% in the pristine sample). It still seems to decrease upon both SOFC and SOEC operation until 1.9-2 kh.

5.3.5 Curvature analysis

The distribution of mean and Gaussian curvatures inform about the evolution of interfacial shapes during aging. As seen in Eq. 5.1, the difference in mean curvature represents the driving force for the modifications of the interfaces and consequently of the microstructural changes. Negative mean curvature corresponds to a concave shape of the first phase (e.g. concave Ni shape for the Ni/YSZ interface), which is useful to interpret the results, even though the inverse is not necessarily true. Curvature measurements are commonly presented using scaling by $S_\nu$, for two phase materials following self-similar evolution. This yields for a growing sphere in a matrix a size-independent ISD. In the present study, the evolutions of each subset of the interfaces, e.g. Ni/Pore and Ni/YSZ are investigated, rather than the whole phase surface. The results are hereafter presented using curvatures with dimension of $\mu m^{-1}$. The processing of curvature measurements into bivariate ISDs is also provided in Appendix F.

The distributions of the mean and Gaussian curvature shown in Figs. 5.11 are ranked according to Eq. 5.17, i.e., from the highest (A,B) to the lowest (C,F) interfacial surface energy. As anticipated from phase transport properties and interfacial energy considerations, the most striking changes upon aging concern the Ni/Pore interface, followed by Ni/YSZ and YSZ/Pore. The modes of the Gaussian curvature distributions are located slightly away from the null value and are likely associated to the mean distributions peaks. A condition of null mean and Gaussian curvatures cannot be reached in a 3-D space since all the surfaces would be completely flat. This such distance instead represents the inflection point that separates the positive (bumps or dimples) from negative Gaussian curvatures (saddles type 1 or 2, see Appendix B).

Figs. 5.11C and F suggest that the evolution of the Ni/Pore interface comprises two phases. The mode of the $H_{\text{Ni/Pore}}$ distribution is smaller than zero in the pristine sample, and it shifts towards zero and even slightly positive values upon SOFC operation until 4.7 kh (Fig. 5.11C). Afterwards, peaking of the $H_{\text{Ni/Pore}}$ distribution is observed, characterized by the disappearance of shapes with $H$ higher than approximately 2.5 $\mu m^{-1}$. The Gaussian curvature of the Ni/Pore interface (Fig. 5.11F) indicates that concave shapes dominate initially (see also Chapter 3). The evolution of its distribution is characterized by monotonic peaking upon SOFC operation, without a clear change in the mode. In particular, the surface area with positive Gaussian curvature larger than 4 $\mu m^2$ noticeably decrease upon aging (Figs. 5.11E-F), because competitive growth results in the disappearance of such bumps.
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Figure 5.11 – Probability density distributions of mean (left) and Gaussian (right) curvature at the interfaces: YSZ/Pore interface (A, D), Ni/YSZ interface (B, E), Ni/Pore interface (C, D). The distributions are displayed in ascending order of the interfacial energy (refer to Table 6.2 in Chapter 6).
or dimples characterized by high curvature. The ISDs (Appendix F) confirm that overall a transition from concave to convex shape occurs for the Ni/Pore interface.

The Ni/YSZ interface evolves to a lesser extent than the Ni/Pore interface; the same applies for the YSZ/Pore interface, where only variations in $K_{YSZ/Pore}$ are detected. This is in a first approximation the consequence of the rearrangement of the Ni/Pore concave interfacial shapes. A trend towards peaking is also observed, with a decrease in density for $H_{Ni/YSZ}$ larger than approximately 5 $\mu m$, but without distribution shift. A subtle decrease in the density of positive Gaussian curvature over time occurs, but for values larger than 30 $\mu m^2$ (out of the displayed range in $K_{Ni/Pore}$ in Figs. 5.11), which results from the higher stability of the YSZ phase.

As observed for the dihedral angles distributions (Figs. 5.8), the trends for Volume 6 (SOEC 10.7 kh) deviate from the others, especially for the two Ni interfaces. As visible in Figs. 5.11D and F, the peaks of the Gaussian curvature distributions are similar to those of the pristine Volume, further suggesting that the additional contribution of another force affected the microstructure after 10.7 kh of SOEC operation.

The curvature measurements do not allow identifying an effect of the position of the sample along the gas flow direction. Although inlet samples (Volumes 4 and 7) appear to have lower Gaussian peak values for the Ni/Pore interface (Fig. 5.11F), this is not reflected in the mean distributions (Fig. 5.11E). Considering only the two Volumes tested for 4.7 kh in SOFC mode, the outlet sample (Volume 5) appears to have experienced more pronounced changes, which relates to higher steam partial pressure and slightly increased temperature, but lower current density, which may both facilitate Ni migration and consequently the minimization of curvature.

Lastly, an attempt to highlight variation of the whole YSZ surface was made by merging the mean and Gaussian curvatures distributions of the YSZ/Pore and YSZ/Ni interfaces (respectively Figs. 5.11A-B and Figs. 5.11E-F). The results are displayed in Figs. 5.12. The rise of the peak values in both plots is evident for the SOFC long-term tested Volumes (with the exception of sample SOFC 4.7 kh inlet). With respect to the pristine case, the mean curvature distributions of the aged Volumes appear to slightly shift from concave to convex shape, even though contrarily to the Ni case the modal values remain unaffected (Fig. 5.11C). Moreover, the Gaussian plot exhibits a net increase of both negative and positive values with time. Although greatly influenced by the relocation of the metallic phase, Figs. 5.12 demonstrate the consistent alteration of the ceramic surface, which cannot be considered static.
5.3. 3-D Characterization of microstructural evolution

Figure 5.12 – (A, B): Probability density distributions of mean and Gaussian YSZ curvatures.

5.3.6 Propensity for microstructural evolution

The available length, dihedral angles and curvature analysis indicate that the microstructural evolution proceeds after 4700 h, even though the connected TPB density and Ni phase size distribution reach an apparent plateau. The inference of how microstructural changes may further proceed by the inspection of the probability density functions of mean and Gaussian curvature or ISD (Appendix F) is however particularly difficult and is expected to require advanced modelling [135]. Nelson et al. [16] derived an expression for quantifying the propensity of particles’ growth “Z_{PSD}” based upon the difference in chemical potential between particles of a given size with respect to the average phase size (Eqs. 5.19 and 5.20). The analysis stems from Eq. 5.1 and follows a representation of the microstructure as spherical particles, i.e., interfacial shapes are described by one radius of curvature. The computed propensity for growth therefore indicates that regions smaller than the average tend to disappear by agglomeration into larger ones. The computed propensity has the unit dimension of $\mu m^{-1}$, since the chemical potential difference $\Delta \mu_i$ is normalized by the partial molar volume of the two solid phases ($V_i$) and by the interfacial tension $\gamma_{Ni/YSZ}$.

$$Z_{PSD_{Ni}}(r_i) = \frac{\Delta \mu_{Ni}(r_i)}{\gamma_{Ni/YSZ} V_{Ni}} = 2W(r_i) \frac{\sin(\theta_{YSZ})}{\sin(\theta_{Pore})} \left( \frac{1}{r_m} - \frac{1}{r_i} \right)$$ (5.19)

$$Z_{PSD_{YSZ}}(r_i) = \frac{\Delta \mu_{Ni}(r_i)}{\gamma_{Ni/YSZ} V_{YSZ}} = 2W(r_i) \frac{\sin(\theta_{YSZ})}{\sin(\theta_{Pore})} \left( \frac{1}{r_m} - \frac{1}{r_i} \right)$$ (5.20)

The coefficients “$W(r_i)$” account for the fraction of phase volume associated to each discrete distribution bin of ray length. The application of Eqs. 5.19 and 5.20 to the present dataset is shown in Figs. 5.13. The size distributions computed by ray tracing (Figs. 5.3) are used as the radii “$r_i$”, with
CHAPTER 5. DEGRADATION OF THE Ni-YSZ ELECTRODE AFTER LONG-TERM OPERATION

Figure 5.13 – (A, B): propensity of growth of Ni and YSZ regions $Z_{PSD}$. The vertical dashed lines indicate the average radii $r_m$ (Eqs. 5.19 and 5.20).

The average radii $r_m$ (indicated by the vertical dashed lines). The sign describes the competitive growth as follows: positive (negative) values indicate a propensity for growth (shrinkage) of the regions of corresponding characteristic size. The average dihedral angles listed in Table 5.4 are used for the calculations. As expected, the propensity of Ni for growth/shrinkage is the highest in the pristine state, in particular for sizes below approximately 0.5 $\mu$m and then progressively weakens upon operation. Ni regions of smaller characteristic size undergo significant volume loss initially, followed by stabilization after approximately 4.7 kh. The evolution of YSZ regions smaller than the average is limited, despite the computed $Z_{PSDYSZ}$, which indicates propensity for disappearance. In contrast, the trend suggests that the propensity for accretion of the larger ones decreases upon SOFC operation. This result is in line with the standard analysis, which suggested a subtle evolution of the YSZ phase. However, the larger standard deviation in the measured YSZ dihedral angles may contribute to increased variability in the computed propensity, compared to Ni, which will warrant further investigations.

The representation of the YSZ and Ni phases as spherical particles has limitations, as highlighted in Chapter 3. The derivation proposed by Nelson et al. [16] can be applied using directly the relationship between chemical potential and mean curvature (Eq. 5.1) to relax the assumption of spherical shape. Hence, the propensity for mean curvature decrease $Z_C$ can be described as an evolution tendency towards mean curvature reduction (Eqs. 5.21 and 5.22). The choice of a zero mean curvature for $H_m$ is intuitive, because it yields to an interface velocity of zero. However, as
5.3. 3-D Characterization of microstructural evolution

mentioned previously, a 3-D shape cannot result in a Dirac distribution and the equivalent in Eqs. 5.19 and 5.20 is an infinite radius. The modes of the mean curvature distributions in Figs. 5.11 are here instead used for estimating “\(H_m\)” as a first arbitrary guess, which is expected to progressively tend to zero with aging. The weights “\(W(H_i)\)” are here the total area of the mesh patches within mean curvature of class “\(i\)”

\[
Z_{\text{Ni/Pore}}(H_i) = 2W(H_i) \frac{\sin(\theta_{\text{YSZ}})}{\sin(\theta_{\text{Pore}})} |H_m - H_i|
\]  

(5.21)

\[
Z_{\text{YSZ/Pore}}(H_i) = 2W(H_i) \frac{\sin(\theta_{\text{Ni}})}{\sin(\theta_{\text{Pore}})} |H_m - H_i|
\]  

(5.22)

The results are shown in Figs. 5.14. A larger area of the interface between Ni and pore has initially a concave shape (negative values). The two regimes discussed previously in the curvature analysis are observed during SOFC operation. The first part of the Ni/Pore interface evolution proceeds by the diminution of concave shapes together with a shift of the distributions toward the null mean curvature, until the height of the positive and negative peaks reach a similar value. After approximately 4.7 kh their reduction proceeds afterwards symmetrically. Oppositely, the heights of the two peaks in the YSZ/Pore distribution are initially similar and an imbalance develops upon operation. The augmentation of concave surfaces is likely associated to the reduction of the concave Ni/YSZ curvatures (Fig. 5.11B). The evolution of the Ni/YSZ interface is milder than for the Ni/Pore interface and, besides the peaks’ height imbalance, the significance of the trend cannot be determined a priori (see differences between the two SOFC 15 kh samples). Interestingly, the propensity for curvature decrease reaches zero for negative mean curvature lower than approximately \((-20 \mu m^{-1})\), whereas it tends towards stabilization for large positive mean curvatures at the Ni/Pore interface. The behaviour is in line with the observation that large concave Ni interfaces are minimized from the beginning of operation. The diminution of surfaces with convex shapes is instead milder, intuitively because such arrangement of the microstructure is favoured by the low wettability of Ni and minimization of the Ni surface to volume ratio.

Clear differences between the computed propensities are not identified between SOFC and SOEC operation, even though Volume 6 (SOEC 10.7 kh) has overall larger values of propensity with respect to Volumes 4 and 6 (SOFC 4.7 kh, i.e., operated for about half of the time). In particular, mean curvatures higher than 15 \(\mu m^{-1}\) do not appear reduced, in contrast to the negative ones.
Figure 5.14 – (A, B): Propensity of mean curvature minimization ($Z_C$) for the YSZ/Pore and Ni/Pore interfaces.
5.4 Overview of observed microstructural alterations

The evolution of the Ni-YSZ electrode microstructure under operation has been investigated by analyzing the metric and topological properties measured on 3-D FIB-SEM reconstructions. The standard analysis highlights the competitive growth of the Ni phase up to 4.7 kh of SOFC and 2 kh of SOEC operation. The increase in $d_{50}$ and decrease in Ni total surface area cause as expected a diminution of the total and connected TPB density. Significant changes in phase volume fraction are not observed. A stabilization is afterwards observed, except for the Ni contiguity upon SOFC operation, which also leads to a further decrease in the ratio $TPB_{eff}/TPB_{tot}$. The results are in line with the stability of the contributions of Ni charge-transfer and gas-phase transport to the total ASR measured by EIS in SOFC mode. Further, the accessible TPB analysis available until 4.7 kh suggests that a large degradation of the transport properties does not occur during this time span. The standard metrics do however not provide sufficient sensitivity to determine whether or not a stable state has been reached. The Ni median diameter measured by filling by overlapping monosized spheres is close to the limits predicted by the 2-D or 3-D version of the Zener equation for incoherent or coherent interfaces, respectively. The agreement suggests that the constrained growth has reached a nearly stable state, but the uncertainty on the applicability limits showcased by the large differences between predictions from the 2-D and 3-D versions and geometrical assumptions remain too large for assessing the stability in the long-term. Further, significant differences with the expected size distributions are observed, showcasing the difficulties to analyze the long-term microstructural evolution of Ni-YSZ using governing equations for systems dominated by spherical shapes. The measurements also suggest a subtle evolution of the YSZ phase, which warrants further investigations.

The measurement of available length, dihedral angles and interfacial curvature indicate that the microstructure continues to evolve after 2 kh (SOEC) and 4.7 kh (SOFC). It further suggests the presence of two stages in particular in SOFC mode. The distribution of available length associated to each TPB displays a reduction of the spread in the Ni case. That is, a progressive decrease of the shorter and larger lengths and a concurrent accumulation towards the peak values ($\mu m$) are observed, even though the ISA Pore/Ni initially decrease (up to 4.7 kh) followed by apparent stabilization. The modification of the Pore/YSZ interface is mainly the consequence of the movement of the metallic phase. The measured available lengths on YSZ shift with operation time towards larger values, even if the total ISA Pore/YSZ does not significantly evolve. The detrimental effect on the performance of the measured changes in the available length on Ni and YSZ is likely low.

The evolution of the microstructure after 2 kh and 4.7 kh in SOEC and SOFC, respectively, and presence of two steps are confirmed by mean curvature measurements. That of the Ni/Pore interface is also characterized by a first step during which the predominant convex interfacial shapes reduce to approach the null mean curvature. Then, both convex and concave surfaces gather toward the
null mean curvature. Despite the greater mobility of the metallic phase, the YSZ surface appears to relocate according to the same principles of mean curvature minimization. Dihedral angles distributions also exhibit a continuous shift and gathering toward the henceforth assumed average values. The evolution after 10.7 kh of SOEC operation however apparently differs from that after 15 kh of SOFC operation in particular for the Ni and YSZ dihedral angles and curvature at the interfaces with the pore phase. The trend in the evolution between 2 kh and 10.7 kh is however difficult to identify clearly with the two available Volumes.

From a network topology standpoint, the genus of the Ni phase decreases notably. The edge length increases and necks initially smaller than the median diameter concurrently disappear. The measured vertices’ coordination number indicates that the evolution does likely not follow common topological rules for edge disappearance observed for grain growth. The evolution of the Ni phase may therefore not be dominated by edge contraction and disappearance, but the result of direct edge pinch-off, which seems to stabilize after 2 kh and 4.7 kh in SOEC and SOFC. However, the reason for the further decrease afterwards in the ratio between effective and total TPB remains unclear.

The available length, dihedral angles, interfacial curvature, as well as analysis of the propensity for growth do however not allow determining whether or not the Ni-YSZ microstructure has reached a stable state. A reason is the coarse discretization in the evolution analysis. Volume 6 (SOEC 10.7 kh) may in particular evolve further, because of the difference with Volumes 7-8 (SOFC 15 kh).

The size distribution of the regions where the Ni phase resides in the porous YSZ scaffold varies less than could have been anticipated. A possibility under the assumption that changes in the YSZ phase are subtle at most, is that the observed Ni coarsening can be achieved to a non-negligible extent by displacement of the interfaces, without complete relocation, at least after 1.9 kh in SOFC mode. A tentative of representation of such microstructure alteration is provided in the 2-D sketches in Fig. 5.15. The drawing on the left illustrates a region after the reduction process. The Ni dihedral angles at the TPBs contribute to accentuate concave interfaces with pore. Although relocation tends to reduce both mean and Gaussian curvatures, a concave arrangement seems favored after reduction, to which pinning of the Pore/Ni interface upon Ni reduction may contribute. The detected reduction of TPB density could be in part the consequence of a rearrangement such as shown in Fig. 5.15, because of the illustrated local shift of the three-phases junctions (red arrows). Changes in dihedral angles, available length and curvature after 2 kh (SOEC) and 4.7 kh (SOFC) may indicate that there is still a driving force and such local adjustments form most of the long-term evolution. This is in line with the dependency between Ni available lengths and TPB extension discussed in Chapter 3. Under the hypothesis of constant volume fraction, the convex Ni/Pore ISAs would be less extended with respect to the previous concave shape.

From the analyzed data, concepts from topological coarsening theory may better describe the observed microstructural changes, with a first stage characterized by the breakdown of the connectivity
5.4. Overview of observed microstructural alterations

Figure 5.15 – 2-D schematic of the difference between concave and convex Ni/Pore interface.

of the Ni phase, driven by the tendency towards average null mean curvature of the interfacial surfaces and concurrently resulting in a decrease in TPB density. Once this condition is reached, large changes in particles location does not proceed further, while the relocation continues toward the diminution of the larger absolute value of curvatures. Under these assumptions of mild adjustments of interface positions, the TPB density may not further diminish strongly, even though a stable state has not been reached yet. Nevertheless, the rearrangement of the dihedral angles’ distributions (Figs. 5.8) does not exclude a further shift of TPB position with the consequent decrease of TPB density.

The YSZ phase is central for the stability of the cermet, which acts as a matrix constraining the relocation of the more mobile Ni phase. A first look at the Zener equation informs that higher volume fraction and fine microstructure is desirable. Whenever the constraining function would be altered by e.g. repeated temperature excursions upon transients during load following, Ni relocation would be triggered with the risk of a consequent decrease of electrochemical active sites. The analysis in the view of pinning and the lowest YSZ dihedral angles however suggests that a significant share of the morphological features allowing an efficient constraint of the Ni phase are fine and henceforth potentially affected first by YSZ coarsening. Another practical related open question is whether the close to equilibrated state is dependent only upon the YSZ microstructure, which would allow the screening of a-priori redox-tolerant microstructures.

An important aspect outside the scope of the Thesis is the relationship between the coarsening of grains and that of the phase. An analysis would require first the measurement of the grain size evolution itself. As described by Zoller et al. [178], the grain evolution in alloys in essentially divided into an early non-self-similar coarsening, which depends on the initial displacement of the microstructure. This phase is then followed by self-similar evolution, characterized by a progressive loss of grain edges and vertices that usually follows specific scaling laws. Significant variations in grain size distributions may then warrant a specific study of their effect on the displacement and
pinning of the interfaces.
Effects of polarization on the microstructural changes at the YSZ/Ni-YSZ interface

This Chapter extends the analysis presented in Chapter 2 (Section 2.2.1) by investigating Ni migration near the interface with the electrolyte. The study involves the quantification of the spatial variation of the metric and topological properties along the direction perpendicular to the interface with the YSZ electrolyte, including TPB density, volume fraction, dihedral angles, interfacial curvature and interfacial energy distribution. In the last part of the Chapter, the results are tentatively discussed in the light of the “electrowetting” theory. ¹

6.1 Introduction

Electrolysis involves the reduction of \( \text{H}_2\text{O} \) (and \( \text{CO}_2 \) in the case of co-electrolysis) instead of the oxidation of \( \text{H}_2 \) in fuel cell mode. As presented in Chapter 2, a specific feature of the degradation under steam electrolysis conditions is the depletion of Ni in the electrode region adjacent to the YSZ electrolyte. This phenomenon is well documented in the literature [74, 81, 95, 104, 106] and is observed typically under cathodic polarization at high current density during extended periods. Localized detachments at the interfaces between Ni and YSZ occur in the region near the electrolyte and are combined to an accumulation of Ni in the Ni-YSZ electrode further away from the electrolyte. The YSZ volume fraction remains in contrast almost unaffected. Tao et al. [106] also observed the formation of nanopores near the Ni/pore surface within the depletion zone. The loss of contact between the Ni and YSZ phases is believed to lead to localized reduction of TPB density, which together with the decrease in Ni connectivity leads to an interface region with poor or passivated electro-catalytic activity. Oxygen ions must be transported further away within the Ni-YSZ electrode through the YSZ scaffold, which results in an increase of the apparent electrolyte thickness, hence of the ohmic losses.

¹ *Personal contribution: development of quantification methods and analysis of the results.*
The current understanding has been established using mainly 2-D representations of the microstructure, such as those provided in Chapter 2. Although the phenomenon is nowadays well documented, few studies available in the literature were specifically performed on 3-D reconstructions, which mainly focused on the quantification of the reduction of volume fraction and TPB density in proximity to the electrolyte. Recently, Trini and co-workers [188] performed 3-D FIB-SEM serial sectioning measurements of a 25 cells stack tested for 9000 hours in steam electrolysis, which exhibited a Ni depletion of up to 5% compared to the bulk Ni volume fraction. Similar studies conducted on single cells after testing for 1000-2000 hours detected only a limited Ni depletion at the interface [189, 190]. Degradation rates were however significantly higher in electrolysis than in fuel cell operation even if the study concluded that the different polarization conditions did not necessarily accelerate the alteration of the Ni-YSZ cermet. On the other hand, all the studies listed above showed a clear correlation between Ni growth and temperature and consequently diminution of connected TPB density (∼ 12% of reduction after 9000 h at 750°C vs ∼ 30% after 2000 h at 850°C [190]). The GEM group [130] extended the post-test analysis of the short stack operated in SOEC mode for 10700 h provided in Chapter 2 and ref. [95]. 3-D FIB-SEM serial sectioning combined with 3-D EDS elemental mapping allowed the measurement of metric and topological properties. The Ni depletion at the interface with YSZ electrolyte was quantified and a decrease of connected and accessible TPB density up to approximately 2.5 µm away from the YSZ electrolyte was observed. In this region, the Ni phase also exhibited a smaller size compared to that further away in the bulk of the electrode.

Despite the number of studies that detected the phenomenon and quantified the extension of the depletion, the understanding of the degradation mechanisms remains incomplete. The difference in behavior between SOFC and SOEC intuitively stems from the contributions of electrochemical potential. Candidates in terms of apparent operation conditions are at a first appraisal polarization and/or steam partial pressure. The predominance of the latter is discussed first, in the light of enhanced transport by the contribution of Ni volatile species. The humidity content varies within the cells depending upon the feed gas composition, the operation mode, the position in the electrode and along the flow path. At first, Jiang at al. [143] measured a larger average dimension of Ni particles after sintering in humid compared to dry atmosphere. This difference was tentatively discussed in the light of increased Ni mobility due to the presence of H2O. Holzer et al. [17] reported a difference in aging of Ni-GDC between dry and high steam partial pressure under relatively high inlet surface specific gas flow, leading to different degradation pathways. Under humid atmosphere, the formation of a continuous GDC layer surrounding the Ni particles was observed, which contributed to hinder further Ni relocation. The authors also detected a reduction of the Ni volume fraction, due to volatilization. The equilibrium partial pressure of Ni(OH)2(g) exceeds by several orders of magnitude that of pure gaseous nickel Ni(g), and can further vary by more than two orders of magnitude within the window of common SOFC or SOEC operation conditions (Fig. 6.1) [18]. Hence, even though surface diffusion is considered the dominant Ni transport mechanism (with a free surface diffusion coefficient of 1.3 µm² s⁻¹ at 800°C [179]), the evaporation and consequent
6.1. Introduction

precipitation of Ni(OH)$_2$ may therefore still contribute [191].

Figure 6.1 – Dependence of the partial pressure of Ni(OH)$_{2.4}$ and Ni$_{4.1}$ on the steam partial pressure in the gas mixture. Image reproduced from [17] and referred to the calculations published in [18].

The schematics in Figs. 6.2A-B are provided for a qualitatively discussion of the differences in the spatial distribution of gas composition between SOFC and SOEC and the potential effects on the microstructural changes. In a first approximation, the overpotential distribution throughout the electrode thickness (Fig. 6.2A) is opposite between SOFC and SOEC operation modes, with a magnitude that tends to zero after the initial “active length”. The latter length depends upon the ratio of the effective transport properties of mainly the YSZ phase and connected TPB density. It is typically of 5-10 µm for most Ni-YSZ composites. The oxygen ion current follows a similar profile, while the electronic current density is null at the electrolyte and maximum at the interface with the current collector. Thus, the production and consumption of species occur in a narrow stripe next to the electrolyte, resulting in gas-phase transport fluxes to or from the gas channel that depend on the magnitude of the applied potential.

Fig. 6.2B depicts the estimated distribution of H$_2$ and H$_2$O partial pressure along the flow path, with inlet compositions of 100% H$_2$ in fuel cell mode and 90% H$_2$O -10% H$_2$ in electrolysis mode. For illustration purposes, the considered fuel utilization/steam conversion are of about 50%, which yields similar outlet compositions. Therefore, if the main reason for Ni depletion at the interface in SOEC mode were enhanced Ni volatilization due to a larger steam partial pressure, significant differences would have been expected in SOFC mode as well, especially between the inlet and outlet in tests at high fuel utilization, which has so far not been observed during the testing of SOLIDpower cells at GEM-EPFL. Moreover, contrarily to what is observed, Ni(OH)$_x$ is expected to move down the H$_2$O partial pressure ($p_{H_2O}$) [74], suggesting transport towards, rather than away from the electrolyte in SOEC conditions. This simple analysis suggests that the depletion of Ni observed during SOEC operation is specific to this operation mode. An effect induced by the overpotential
Chapter 6. Effects of polarization on the microstructural changes at the YSZ/Ni-YSZ interface

Figure 6.2 – comparison between SOFC and SOEC. (A) Example of local overpotential distribution along the electrode thickness. (B) Example of H₂ and H₂O molar fractions distribution along the electrode length (100% H₂ in SOFC mode, 90% H₂O -10% H₂ in SOEC mode). Inlet and outlet respectively correspond to x = 0 and x = 1.

appears therefore more likely. Tao et al. [106] reported that Ni migration in SOEC mode was not detected in a previous work [192] characterized by the same feed gas composition but lower current density.

The tentative explanation for Ni migration away from the electrolyte provided by Mogensen et al. [19] indicates that the degradation proceeds following two phases. In the first one, the Ni regions near the electrolyte start to lose contact with YSZ as well as intra-phase connectivity. This process may be triggered by the partial reduction of YSZ in the case of very high overpotential and by the reduction of impurities such as SiO₂. According to the proposed mechanism, the negative polarization may also change the Ni/YSZ and Ni/Pore interfacial energy yielding a shift from “wetting (negative) to de-wetting (positive)” values, consequently inducing a rounding of the Ni surface shapes. The spheroidization of the surface facilitated by transport enhanced by the high temperature and the steam partial pressure, is expected to alter the percolation of the Ni phase. It may also contribute to the fast reduction of connected TPBs at the Ni/YSZ in the first ≈ 100 hours reported in literature in SOEC mode.

The second phase develops after the loss of percolation of the Ni phase near the electrolyte, which results in the growth of a passivated gap because of the depletion of connected TPB and where the p₇H₂O is approximately constant (Fig 6.3). A difference in electrochemical potential difference consequently establishes between non-connected and active metallic inclusions at the TPB, since in the first case the potential depends essentially on the gas composition. The induced driving force then promotes the diffusion towards the active TPBs, where the Ni particles precipitate forming a denser layer. Under this hypothesis, the migration of Ni(OH)₃ species away from the electrolyte
could happen also in SOFC mode, favored by the potential gradient and by the lower concentration of H$_2$O in the electrode. The recent study by Hauch et al. [78] highlighted the presence of a similar depletion region after dry CO$_2$ electrolysis. Since only CO$_2$ and CO are present in the gas mixture, this suggests that the dominant parameter is the negative overpotential rather than the H$_2$O partial pressure.

6.1.1 Visual observations of micrographs from tested single cells and stacks

The previous discussion suggests that the transport of Ni away from the electrolyte accompanied by localized detachment and spheroidization is mainly sensitive to the polarization. The occurrence of affected Ni/YSZ interface and distinct Ni morphology is further supported by the qualitative visual inspection of micrographs.

Figs. 6.4A-C show three SE in-lens electron images from the FIB-SEM grayscale dataset, where tiny features are easier to observe than after segmentation. Fig. 6.4A clearly shows localized detachments at the interface between the YSZ and the Ni phase (highlighted by the yellow arrows) in the sample aged in SOEC for 10.7 kh. Similar features were not found in the 3-D dataset of the pristine cell (Fig. 6.4B) and segmented-cell test for 15 kh in SOFC mode (Fig. 6.4C).
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Figure 6.4 – (A) SE electron image in the FIB-SEM dataset showcasing localized detachment of Ni from the YSZ electrolyte interface after 10.7 kh of SOEC operation (black - Pore, grey - YSZ, white/light grey - Ni). (B), (C): Comparison with pristine and 15 kh SOFC data.

Micrographs of cross-sections from a fractured unpolished sample subjected to extreme cathodic polarization are shown in Figs. 6.5A and C with corresponding Ni EDS map (Fig. 6.5B). The sample was extracted from a single cell tested for approximately 600 hours in co-electrolysis at 0.79 $A cm^{-2}$. In the last hundred hours, the voltage surged up to 2 $V$ due to an accidental water shortage, which irreversibly damaged the cell. A layer of approximately 8 $\mu m$ depleted in Ni is clearly seen in Fig. 6.5A with an apparent concurrent agglomeration zone highlighted by the red arrows. Higher magnification reveals small and possibly isolated Ni particles near the YSZ electrolyte (Fig. 6.5C). The 2-D micrograph suggests a quasi-spherical shape, in line with the above discussion. Indeed, the microstructural modifications tend towards minimization of internal energy, leading to a decrease in total surface area and mean curvature (and consequently also of Gaussian - Appendix B). The location of the arrows on the YSZ surface that were initially contact regions can be further inferred (yellow arrows).

The expected threshold for the reduction of zirconia is around -1.8 $V$ under common SOEC gas composition and temperature and the presence of Ni further decreases the stability and favours the formation of Ni-Zr intermetallic nanoparticles infiltrated within the Ni phase [108, 118]. The specific analysis of these aspects is outside the scope of the Thesis. 2-D imaging of mechanically polished cross-sections does not allow the detection of such features. In contrast, the gray inclusions observed in Ni in Fig. 6.4A warrant dedicated TEM analyses.
Figure 6.5 – Micrograph of a single cell tested in co-electrolysis that exhibits a severe alteration of the interface between the YSZ electrolyte and Ni-YSZ electrode. The red arrows indicate a thin Ni agglomeration layer. (B): Ni atomic percentage estimate (1 µm minimum region of confidence). (C): Spherical Ni particles at the interface with the YSZ electrolyte. The single cell was operated for 600 hours in co-electrolysis mode (25% CO₂, 65% H₂O, 10% H₂) at 0.79 A cm⁻² and 750°C. In the last 100 hours, a water shortage caused a surge in the voltage up to 2 V, which irreversibly damaged the cell.
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6.2 Experimental

The microstructural alterations near the electrolyte were studied using six reconstructions, which are listed in Table 6.1. The detailed description is provided in Chapter 2. A brief summary is provided hereafter. The sample Volumes were selected to measure and compare the evolution of the interface between different testing conditions. The first one is the pristine sample (B in Chapter 2), while the second and the third are from SOEC tests of 2 kh and 10.7 kh, respectively. The fourth was exposed to 124 thermal cycles. Sample Volumes 5 and 6 belong to the same segmented cell operated in SOFC mode for 15 kh. The first is from segment 12 (second along the flow path, one of the two middle rows) and the second from segment 19 (outlet region, row next to the sealing). Compared to the results presented in Chapter 6, the interface with the electrolyte is included in the volume of interest for the specific analysis of its microstructure (the left side in Figs. 6.4).

<table>
<thead>
<tr>
<th>Number</th>
<th>Volume</th>
<th>Dimension [µm]</th>
<th>Voxel size [nm]</th>
<th>Electrolyte portion [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reference B</td>
<td>21 – 10.5 - 15</td>
<td>10</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>SOEC 2kh - Center</td>
<td>18.3 – 11.5 - 15</td>
<td>10</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>SOEC 10.7 kh</td>
<td>14.76 – 9.97 - 10.5</td>
<td>10</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>Thermal aging</td>
<td>20.3 - 14.7 - 12.2</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>SOFC 15kh Seg. 12</td>
<td>22 - 9.3 - 14.6</td>
<td>10</td>
<td>1.3</td>
</tr>
<tr>
<td>6</td>
<td>SOFC 15kh Seg. 19</td>
<td>21.8 - 10.6 -12.9</td>
<td>10</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*Table 6.1 – list of Volumes with electrolyte inspected.*

6.3 Microstructural analysis of the interface

The presentation of the results is organized following two sections. First, the variations of properties such as volume fractions, TPB density and dihedral angles are analyzed by scans along the direction perpendicular to the interface with the YSZ electrolyte. In particular, the measurement of dihedral angles is expected to be relevant to assess directly the effect of overpotential on the alteration of the interface. The second is a curvature and interfacial energy analysis, which informs specifically on the driving force terms for Ni relocation.

6.3.1 Variations of the volume fraction, TPB density and dihedral angles along the electrode thickness

In a first one-dimensional continuum approximation, the gradient in overpotential in the Ni-YSZ electrode develops along the Z direction (see Fig. 6.2A), and is limited along the other two directions within planes parallel to the electrolyte. Dihedral angles measured by scanning planes parallel and perpendicular to the electrolyte are therefore compared. A schematic of the measurement procedure is shown in Fig. 6.6. In the case of measurements performed in directions perpendicular to the
6.3. Microstructural analysis of the interface

Figure 6.6 – Drawing representing the computation of the dihedral angles in the directions on the plane parallel to the electrolyte (case A and B) and perpendicular to the electrolyte (case C).

Electrolyte (YSZ)

axonometric view

The results for Volume 3 (SOEC 10.7 kh) are shown in Fig. 6.7. Fig. 6.7A provides scans of the total and connected TPB density (continuous and dashed black lines, respectively) and of the volume fractions (red, blue and green for pore, YSZ and Ni, respectively). Fig. 6.7B provides the dihedral angles of the three phases (red, blue and black for YSZ, Ni and pore, respectively) measured in the YZ and XY planes at total, as well as connected TPBs. As mentioned previously, dihedral angle measurements in the XZ plane are not displayed, since the results are similar to those in plane YZ. The reconstructions are aligned with respect to the estimated interface position, based on the location where the YSZ volume fraction reaches 70% (orange arrow in Fig. 6.7), since the microstructural alterations are expected to be low for this phase. The vertical dashed line at around \( z = 1 \ \mu m \) (magenta arrow) is a threshold, below which the rapid decrease of the TPB density affects the statistical reliability of the measured dihedral angles. Hence, the portion of electrode below this threshold is not considered and not displayed in the subsequent figures.
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Figure 6.7 – Scans along the z direction (perpendicular to the electrolyte) of (A) surface specific TPB counts and volume fractions and (B) dihedral angles in Volume 3 (10.7 kh, SOEC).

Chapter 5 showed that the stereological measurement of dihedral angles has limitations, even though the computed average values are in line with those reported by Nelson et al. [16]. The present analysis is based mainly on the Ni dihedral angles, which has the lowest standard deviation. A reason may be that the watershed segmentation possibly affects more severely the YSZ phase with intermediate grayscale value and the pore dihedral angles. Appendix E also indicates that the averaged dihedral angles measured on two reconstructions from nearby regions (same fragment of segment) can differ by approximately 6%. Consequently, the present analysis is focused on trends observed within each sample Volume, rather than the comparison of measured absolute values. The results are therefore presented in terms of \( \bar{\theta} / \bar{\theta} \), where \( \bar{\theta} \) is the average measured in the corresponding reconstruction. The discussion in the Introduction indicates that differences can be expected between dihedral angles measured at connected or isolated TPBs, which cannot be confirmed with the present dataset. Therefore, the trends are discussed based on the dihedral angles measured at the total TPBs.

The results are provided in Figs. 6.8-13 and discussed below:

- **TPB density**: The distribution along the electrode thickness is close to constant in the pristine and SOFC Volumes (Figs. 6.8, 6.11-13). In contrast, the two SOEC Volumes show a decrease near the electrolyte, with stabilization reached at a position around \( z = 5 - 6 \ \mu m \) (Figs. 6.9-10). In the two latter cases, the difference between total and connected TPB density increases near
6.3. Microstructural analysis of the interface

the electrolyte, denoting an increase of isolated TPBs and therefore of Ni regions. The thermal cycling Volume surprisingly also displays a small diminution near the interface.

- **Volume fraction**: The depletion of Ni is observed in the two SOEC Volumes (Figs. 6.9-10), whereas the Ni volume fraction stays approximately constant in all the others (Figs. 6.8, 6.11-13). It corresponds well to the observed locations of decreased TPB density and is approximately mirrored by an increase of porosity. The peak of the latter at the interface in the 10.7 kh SOEC sample may not necessarily indicate that severe Ni depletion occurred upon SOEC operation, since it corresponds to a valley in the YSZ volume fraction (see also Figure 6.7). Further inspection however indicates that a local minimum in YSZ volume fraction is also observed next to the interface in Volumes 1, 5 and 6, i.e. Pristine and SOFC 15 kh, and approximately corresponds rather to a Ni volume fraction local maximum. Therefore, the apparent accumulation of Ni next to the electrolyte is present already after the NiO-YSZ sintering and reduction and is likely not a consequence of SOFC operation.

- **Dihedral angles**: The data suggest that $\theta_{Ni}$ in the YZ plane decreases subtly at the interface after SOEC operation, while $\theta_{YSZ}$ and to a lesser extent $\theta_{Por}$ exhibit an opposite trend. The diminution is highest in the 10.7 kh SOEC Volume (by ~ 8%). Care is however needed with the present dataset, because the statistical variability is also the highest for this Volume sample due to the smaller foot print area. The evolution at the interface of the XY plane dihedral angles instead does not show the same decrease as for the YZ direction. This trend is in line with the hypotheses discussed in the Introduction, since strong gradients in overpotential along directions parallel to the electrolyte are not expected. As will be discussed later, large uncertainty remains on the expected magnitude of modifications in dihedral angles. It can at present not be excluded that they are subtle and possibly even below the detection limits of stereological measurements.
Figure 6.8 – Scans along the z direction (perpendicular to the electrolyte) of (A) surface specific TPB counts and volume fractions and (B) dihedral angles in Volume 1 (0 h).

Figure 6.9 – Scans along the z direction (perpendicular to the electrolyte) of (A) surface specific TPB counts and volume fractions and (B) dihedral angles in Volume 2 (2 kh, SOEC).
6.3. Microstructural analysis of the interface

Figure 6.10 – Scans along the z direction (perpendicular to the electrolyte) of (A) surface specific TPB counts and volume fractions and (B) dihedral angles in Volume 3 (10.7 kh, SOEC).

Figure 6.11 – Scans along the z direction (perpendicular to the electrolyte) of (A) surface specific TPB counts and volume fractions and (B) dihedral angles in Volume 4 (Thermal cycling, SOFC).
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Figure 6.12 – Scans along the z direction (perpendicular to the electrolyte) of (A) surface specific TPB counts and volume fractions and (B) dihedral angles in Volume 5 (15 kh, SOFC, segment 12).

Figure 6.13 – Scans along the z direction (perpendicular to the electrolyte) of (A) surface specific TPB counts and volume fractions and (B) dihedral angles in Volume 6 (15 kh, SOFC, segment 19).
6.3. Microstructural analysis of the interface

6.3.2 Curvature analysis

Differences in interfacial shapes along the direction perpendicular to the YSZ electrolyte are investigated by division of each sample Volume into four sub-regions of identical size, as illustrated in Fig. 6.14. The curvature measurements follow the approach described in Chapter 3 and Appendix B to investigate the spatial variation of mean ($H$) and Gaussian ($K$) curvature. The Volumes are resampled at 15 nm isometric voxel size to reduce the size of the large curvature dataset. The principal curvatures are measured on the triangle patch of smoothed multi-label meshes generated by a marching cube, with four averaging passes applied over a patch neighborhood of two layers. The probability density of the median and Gaussian curvatures are computed from the measured principal curvature at each patch and patch areas for distribution weighting. Averaging between the two specular interfaces is applied, i.e., Ni/YSZ and YSZ/Ni.

As seen in Fig. 6.14, Region 1 (in blue) contains a portion of the electrolyte region. The associated values of the distributions are affected and can deviate from the others (in particular for the YSZ/Pore and YSZ/Ni interfaces). Therefore, even though the Ni-YSZ/YSZ layers are produced by co-casting, differences in morphology can exist between the phase interfaces within the Ni-YSZ and with the YSZ electrolyte, to which differences in YSZ grain size (see Fig. 6.4), hence sinterability may contribute. The clarification of the reasons is outside the scope of the Thesis, but such aspects should be considered for future studies, since the analysis of the effect of polarization in commercial Ni-YSZ microstructure are consequently complicated.

The mean and Gaussian curvature results are presented in Figs. 6.15 and 6.16, respectively and discussed hereafter. The mean and Gaussian curvatures are related by Eqs. B.4 and B.5 and the diminution of one corresponds to that of the other. Therefore, the trends in Figs. 6.16 overall follow those of the mean curvature (6.15).

- $H_{\text{YSZ/Pore}}$ (Fig. 6.15A) The mode is similar in Regions 2-4 in all Volumes and close to null mean curvature. Region 1 that contains the electrolyte is slightly shifted towards negative mean curvature and presents a higher peak, including in the pristine Volume. The subset of YSZ shapes that belong to the YSZ electrolyte therefore slightly differs from that in the Ni-YSZ composite, which is not surprising. A small decrease of the peak height is observed in Regions 2-4 of Volume 3 (SOEC 10.7 kh). Such a variation could be due to Ni relocation from the interface to the inner regions. The lower peak height and larger spread of mean curvatures could be associated to the initial position of the Ni particles after sintering, the migration of which towards the inner part of the electrode leaves extra porosity at the electrolyte interface. A significant share of the YSZ features at which Ni initially resides is expected to remain because of the low YSZ mobility.

- $H_{\text{Ni/YSZ}}$ (Fig. 6.15B) As for the $H_{\text{YSZ/Pore}}$ distribution, the peak height is highest in Region 1 associated to YSZ concave shapes, which can be appreciated also visually in Fig. 6.4. The
Chapter 6. Effects of polarization on the microstructural changes at the YSZ/Ni-YSZ interface

Figure 6.14 – 2-D representation of the partitioning of 3-D Volume into four sub-regions for curvature measurements to investigate variations in shapes along the direction perpendicular to the YSZ electrolyte (in grey). The cross-section is from Volume 1 (10.7 kh, SOEC).

other Regions are characterized by approximately the same mode and height, with a slight shift to \( H = 0 \). The results suggest that Volumes 4-6, i.e. without exposure to SOEC conditions exhibit a slightly larger difference between region 1 and the others. They also suggest a slight shift towards negative mean curvature for the two SOEC Volumes, which would be expected for spheroidization.

• \( H_{Ni/Pore} \) (Fig. 6.15C) A notable increase of the peak height from Region 1, 2 and 3 is observed for Volume 3 (SOEC 10.7 kh) and associated to a decrease in the distribution density for approximately \( H < 6 \mu m^{-1} \). The trend stems from the relocation of Ni, since Volume 1 does not display any difference among the four regions. Further, differences between Regions 1-4 are not observed in the pristine sample as well as after thermal cycling, and ascertaining the statistical significance of those in the 15 kh samples will require additional data. Variations may also occur after 2 kh of SOEC operation, but the trend is surprisingly opposite to that in the 10.7 kh SOEC Volume. The curvature results suggest that a driving force specific to electrolysis mode alters the curvature near the electrolyte lowering the distribution peak. This may trigger the relocation of Ni, towards re-balancing and minimization of the mean curvature (in a similar way as identified for the long-term evolution of the cermet presented in Chapter 5). The Regions’ distribution peaks are lower in the 10.7 kh than in the 15 kh Volumes, which would suggest that the evolution away from the YSZ interface also differs in SOEC and SOFC mode.

• \( K_{YSZ/Pore} \) (Fig. 6.16A) The difference between Region 1 and the others is more pronounced
for Volumes 2-3 (SOEC 2 kh and 10.7 kh), which relates to the share of the Ni/YSZ interface converted into YSZ/Pore interface upon Ni relocation.

- $K_{\text{Ni/YSZ}}$ (Fig. 6.16B) The peaks are lower and compensated by an increased density of negative Gaussian curvature in Volume 3, compared to the pristine and SOFC samples. The distributions of Gaussian curvature in Region 3 and 4, further differ from those in Volumes 5 and 6 (SOFC 15 kh).

- $K_{\text{Ni/Pore}}$ (Fig. 6.16C) An increase of the peak height in Volume 3 is observed between Regions 1-2 and 3-4. Significant variations among Regions 1-4 in terms of $K_{\text{Ni/Pore}}$ are not observed for the other sample Volumes, while Volumes 5 and 6 are characterized by the highest peak value.

In general, each distribution presents peak values that substantially depend on the mobility of the interface, with largest values for the Ni/Pore interface and smallest for YSZ/Pore. A correspondence with the operation time is overall observed, since the minimization of mean curvature is a driving force for the microstructural evolution in all cases. In fact, Volumes 5 and 6 after 15 kh in SOFC usually exhibit higher peak values compared to the others. In contrast, a broadening of the mean (and Gaussian) distributions is observed for Volume 3, despite the 10.7 kh of operation, in particular for the Ni/Pore interface. The reasons why the trends in Region 4 after 10.7 kh of SOEC operation are qualitatively closer to e.g. Region 1 than Region 4 after 15 kh of SOFC operation remain at this point unclear, owing to the spatial distributions of volume fractions, dihedral angles and TPB density. Large overpotentials are indeed not expected in Region 4, which warrant further investigations to first confirm the results obtained on the smaller Volume 3 and then understand the reason. The results are nevertheless in overall agreement with those reported in Chapter 5, which further showcase the relatively small variability of the curvature measurements within the Volumes and the clear sensitivity to e.g. the YSZ electrolyte.
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Figure 6.15 – Probability density of mean curvature: (A) YSZ/Pore interface. (B) Ni/YSZ interface. (C) Ni/Pore interface.
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Figure 6.16 – Probability density of Gaussian curvature distribution plots. (A) YSZ/Pore interface. (B) Ni/YSZ interface. (C) Ni/Pore interface.
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6.3.3 Computation of the interfacial energy distribution along the fuel electrode thickness

Curvature analysis provides part of the information for assessing the interfacial energy density within the 3-D microstructure. Computational approaches applicable directly on voxel representations were proposed and are straightforward to implement, e.g. [193]. Each voxel at the interface is provided with an interaction energy, which depends on the phases of the neighboring voxels using commonly 8- and 26-neighborhood definitions in a 2-D square lattice and 3-D, respectively. The total interfacial energy of each voxel is computed as the sum of the interaction energies of its neighbors [194]. The procedure to compute the interfacial energy "\( E_{\text{int}} \)" for each voxel of phase "\( u \)" is shown in Eq. 6.1, where "\( \gamma_{u,v} \)" and "\( \gamma_{u,w} \)" are the interfacial tensions, while "\( N_{\text{vox}} u,v \)" and "\( N_{\text{vox}} u,w \)" are the number of neighboring voxels with different phase (\( v \) and \( w \) in the example). The neighboring surfaces between voxels of the same phase are not counted, hence the "internal" ones are characterized by null interfacial energy. Moreover, to each neighboring voxel of different phase is assigned \( 1/26 \) of the hypothetical spherical surface inscribed in the cubic voxel, with diameter equal to the voxel size "\( l_{\text{vox}} \)" (10 nm for all the six Volumes). The contributions from the 26 neighboring voxels are therefore equally weighted.

\[
E_{\text{int}} = \frac{\pi l_{\text{vox}}^2}{26} (N_{\text{vox}} u,v \gamma_{u,v} + N_{\text{vox}} u,w \gamma_{u,w}) \quad (6.1)
\]

The parameter used for the estimation of the interfacial energy at each voxel forming a material interface in the 3-D dataset is computed using the values reported in Table 6.2. The interfacial tension between Ni and YSZ is obtained from the literature [195], while the others are computed by Eq. 5.16.

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_{\text{Ni}} ) [( ^\circ )]</td>
<td>140</td>
<td>Mean from reference Volume (Table 5.3)</td>
</tr>
<tr>
<td>( \theta_{\text{YSZ}} ) [( ^\circ )]</td>
<td>95</td>
<td>Mean from reference Volume (Table 5.3)</td>
</tr>
<tr>
<td>( \theta_{\text{Pore}} ) [( ^\circ )]</td>
<td>125</td>
<td>Mean from reference Volume (Table 5.3)</td>
</tr>
<tr>
<td>( \gamma_{\text{Ni/YSZ}} ) [( Jm^{-2} )]</td>
<td>2</td>
<td>[195]</td>
</tr>
<tr>
<td>( \gamma_{\text{Ni/Pore}} ) [( Jm^{-2} )]</td>
<td>2.43</td>
<td>Computed (Eq. 5.16)*</td>
</tr>
<tr>
<td>( \gamma_{\text{YSZ/Pore}} ) [( Jm^{-2} )]</td>
<td>1.57</td>
<td>Computed (Eq. 5.16)</td>
</tr>
</tbody>
</table>

Table 6.2 – Computed interfacial surface tensions from Eq. 5.16. * For comparison, a value of 2 [\( Jm^{-2} \)] is computed at 750°C from reference [26].

The approach combines the information from the morphology and interfacial tensions values, which allows to relate the computed interfacial energy with the curvatures in a discrete (pixelized) space. Intuitively, voxels with a higher number of neighbors belonging to different phases correspond to regions of higher curvature and present higher interfacial energy. Moreover, the Ni/Pore interface has on average higher energy, because of the larger interfacial tension (2.43 [\( Jm^{-2} \)]) - Table 6.2. In
6.3. Microstructural analysis of the interface

Figure 6.17 – Interfacial specific energy density distribution along the electrode normalized by the footprint area (XY plane). (A) YSZ/Pore interface. (B) Ni/YSZ interface. (C) Ni/Pore interface.

addition, the voxels near the TPBs exhibit the greatest values of interfacial energy, in particular in the case of low dihedral angles (high wettability). The accuracy of the calculation depends on the voxel size, which was not tested here and left for future work.

The energy associated to the voxels in each Volume is computed by applying Eq. 6.1. There are several possibilities of graphical representation. Figs. 6.17 display the interfacial footprint surface specific energy spatial distributions along the electrode thickness (parallel to the XY plane). The energies of the subset of voxels belonging to each one of the three interfaces in the XY plane are summed and then normalized by the reconstruction footprint area to account for the dimensions of the examined Volumes. This measurement permits the visualization of the alteration of the interfacial energy caused by the polarization mode.

The results in Figs. 18 therefore indicate a decrease of Ni/YSZ interfacial energy from approximately 6 µm, until the YSZ interface, which is more pronounced in Volume 3 (SOEC 10.7 kh) compared to Volume 2 (SOEC 2 kh). This trend will be discussed in the next Section under the light of electrowetting, which associates alterations of the Ni/YSZ interface to changes in applied potential. The trend is opposite for the YSZ/Pore interface, with a gradual increase of the associated interfacial energy towards the interface, which likely stems from the interfacial area left after migration of Ni. On the other hand, the energy associated to the Ni/Pore interface appears constant along the z direction, likely due to the subsequent re-arrangement of the Ni phase.
Moreover, an overall diminution of the interfacial energy upon operation time is noticeable in all the cases, which is systematically lowest in Volume 5. The footprint area specific energy of the Ni/Pore interface is on average also lower (refer to Table 6.2) and evolves more significantly upon operation time due to the larger mobility of Ni. In particular, the mild yet net evolution of the YSZ/Pore interface is confirmed by the decrease of interfacial energy of Volume 6. These considerations are in line with energy minimization discussed in Chapter 5.

6.4 Discussion on the driving forces that affect the stability of the electrode/electrolyte interface

6.4.1 Effects of the applied overpotential on the dihedral angles

This Section examines the possibility that the applied polarization influences interfacial surface tensions in the Ni-YSZ electrode. The electrowetting phenomenon is investigated as a candidate mechanism for the observed difference between SOFC and SOEC operation. The theory predicts a modification in wettability (hence of the dihedral angles) upon the application of a difference in electrostatic potential between an electrode and electrolyte (usually liquid). This phenomenon is commonly studied by measuring variations in dihedral angles at the interfaces formed by liquid drops on flat solid surfaces [25, 196, 197]. A description of electrowetting theory is provided in Appendix G.

Under this hypothesis, apparent modifications in the Ni dihedral angle are anticipated, following a trend similar as the liquid drop in Fig. G.4 in Appendix G. Indeed, the Ni mobility is the highest, which may allow over extended periods re-arrangement resembling those observed for liquid systems. Because of its significantly lower mobility (Chapter 5), strong variations in the YSZ dihedral angle are less likely and may be also a consequence of Ni, rather than YSZ mobility. Therefore, the modification of the Ni/YSZ interface may be detected by that of the Ni dihedral angle, which inversely alters the pore dihedral angle. The magnitude of the Ni/Pore and Ni/YSZ interfacial tensions would not change. The relation between interfacial surface tensions and dihedral angles is discussed in Chapter 5 (Eqs. 5.14-17).

In an electrical double layer, a relationship between the Ni dihedral angle and the variation in applied potential ($\epsilon$) is obtained by combining the solution of the differential Lippmann-Helmholtz equation (Eq. G.5) with Eq. 5.16, which yields to Eq. 6.2, where “$\theta_{Pore}$” and “$\theta_{Ni}$” refer to the dihedral angles at the potential of zero charge or zero zeta potential (pzc) (where the Ni-YSZ surface
tension is maximum at potential $\epsilon_{\text{max}}$, while “$C_D$” is the so-called "double layer” capacitance.

$$\sin(\theta_{Ni}(\epsilon)) = \frac{\gamma_{YSZ/Pore} \sin(\theta_{Pore})}{\gamma_{YSZ/Pore} \sin(\theta_{Pore_0}) - C_D(\epsilon) \frac{2}{(\epsilon - \epsilon_{\text{max}})^2}}$$

(6.2)

In the present study, the dependence of the Ni dihedral angle on the applied potential is estimated by combining parameters from the literature and measurements from single cell experiments (Table 6.2). For this first analysis, the values of dihedral angles measured on the pristine Volume are selected (Table 5.4). The parameters “$\theta_{Pore}$” and “$\theta_{Ni_0}$” are imposed equal to “$\theta_{Pore_0}$” and “$\theta_{Ni_0}$”.

The dependence of the capacitance on the applied overpotential is estimated from the PhD Thesis of P. Caliandro [20], which includes an electrochemical impedance spectroscopy study of the same SOLIDpower cell material as considered here. The physical processes contributing to the measured spectra were identified by sensitivity analyses and processing using the DRT method. The dataset used for the present study is a set of EIS measurements on a single cell, where the current density is varied from 0.7 $A \ cm^{-2}$ (SOFC mode) to -0.7 $A \ cm^{-2}$ (SOEC mode) at 800°C (corresponding to an overpotential range from +0.05 to -0.05 $V$). The inlet gas composition was 50-50% $H_2/H_2O$. The measured evolution of the capacitance for charge transfer in the Ni-YSZ electrode (characteristic frequency ranging from $6 \times 10^3$ to $10^4 \ Hz$) is provided in Fig. 6.18. The computed values of the capacitance are approximately one order of magnitude higher than those estimated by e.g. Doppler et al. [198], who applied EIS on Ni pattern electrodes of different geometries. The minimum of the capacitance is 9.6 $F \ m^2$ at 0.009 $V$ and it corresponds to the pzc and is used as $\epsilon_{\text{max}}$ in Eq. 6.2.

The variation in $\theta_{Ni}$ with applied potential (Eq. 6.2) is shown in Fig. 6.19. For comparison, the capacitance values were also diminished and augmented by one order of magnitude (shaded area). Since the potential is raised to the power of two, the curve is parabolic with the maximum angle at the pzc. It is worth mentioning that the minimum capacitance is not reached at OCV condition, thus the value of $\theta_{Pore_0}$ is slightly larger, inducing a small vertical shift of the curve. A high accuracy is however not required for the present estimation, since the objective is to support a qualitative discussion of the possible effects of electrowetting during long-term operation, in particular regarding differences between SOEC and SOFC operation. The estimation of $\epsilon_{\text{max}}$ is in contrast important, since it determines the shift along the overpotential axis. In fact, Fig. 6.19 indicates that the estimations performed in this Thesis yield a slight increase of the angle until the pzc point followed by decrease upon increasing anodic overpotential (SOFC), whereas in electrolysis mode the expected decrease is monotonic. As mentioned by Mogensen [19], the pzc potential should be however similar to the OCV. The evolution of the capacitance in Fig. 6.18 is also the reason for the larger diminution of the Ni dihedral angle under electrolysis.
Chapter 6. Effects of polarization on the microstructural changes at the YSZ/Ni-YSZ interface

Figure 6.18 – Dependence of the capacitance for the charge transfer process on polarization, from the PhD Thesis of P. Caliandro (pag. 93) [20]. The data come from measurements on a single cell test with a fuel composition of 50-50% H₂/H₂O at 800°C. The minimum measured capacitance is 9.6 F m² at 0.009 V, which corresponds to the pzc.

Figure 6.19 – Computed variation of θ_Ni under polarization. The maximum value corresponds to 140°. Negative values comport a decrease of the angle therefore higher wettability. The shaded area displays the variation of ± 1 order of magnitude of the capacitance values.
6.4. Discussion on the driving forces that affect the stability of the electrode/electrolyte interface

The computed difference in dihedral angle is slightly inversely correlated with the magnitude of $\gamma_{YSZ/Pore}$ (a 20% increase of interfacial energy corresponds to a $\theta_{Ni}$ diminution of -0.43% at -0.43 V, with respect to -0.52% visible in Fig. 6.19). On the other hand, the magnitude of the capacitance has a direct effect on the alteration of the Ni dihedral angle (-0.63% at -0.43 V for a 20% increase in the capacitance values). Thus, the data measured by Doppler et al. [198] would comport an even milder alteration of $\theta_{Ni}$. Fig. 6.19 indicates that changes in dihedral angle may be challenging to detect directly by stereological measurements; an increase in the capacitance values in Fig. 6.18 by one order of magnitude yields a diminution of $\theta_{Ni}$ of ~ 6% at -0.4 V (lower bound of the shaded area), which is in the range of the detection limit suggested by Appendix E. Therefore, experimental methods for improved accuracy of capacitance should be considered as part of the efforts for further investigations of electrowetting in the Ni-YSZ electrode.

6.4.2 Schematic description of observed microstructural changes

The analysis of the 3-D microstructure clearly identified the migration of Ni away from the interface and the progressive diminution of the TPB sites in the region next to the electrolyte in SOEC mode. The augmentation of mean and Gaussian curvatures in this zone (highlighted by the diminution of peak values and the broadening of the distributions) may have promoted the transport of Ni towards the inner region of the electrode, in order to rebalance the overall curvature minimization of the Ni/Pore surface. The diminution of internal specific energy at the Ni/YSZ interface is in part compensated with the augmentation in the YSZ/Pore interface. Such a variation was not observed after thermal cycling and SOFC operation, confirming the relation of the process with electrolysis operation.

This Section discuss how the electrowetting phenomenon may contribute to the rearrangement of the microstructure where the negative applied potential forms part of the driving force. The observed changes are illustrated qualitatively in the 2-D schematics displayed in Figs. 6.20. This simplified view assumes that the YSZ scaffold regions occupied by Ni do not change drastically, which complies with the result from Chapter 5, at least after 2 kh of SOEC operation. For the sake of simplicity, the interface between the YSZ electrolyte and the Ni particle is flat and not slightly concave as measured in Fig. 6.16A. The description distinguishes three steps, which are described below. Nevertheless, depending on the morphology of the 3-D microstructure, the local evolution metallic phase may sensibly differ compared to that used for illustration in the drawings. For example, the Ni/YSZ interface may be perpendicular to the electrolyte, hence subjected to more complex overpotential distribution.

1. As discussed in Chapter 5, the pristine state deviates from a stable configuration, resulting in a higher spread in the dihedral angle distribution. Further, a large share of the Ni/Pore interface has a concave shape. However, the initial stage of coarsening occurs fairly rapidly
and therefore the starting point for the discussion is that shown in Fig. 6.20A. The dihedral angles of the Ni phase adjacent to the YSZ electrolyte do not differ from those in the bulk of the electrode (Fig. 6.20A). The ISD plot F.3 in Appendix F also indicates that the share of Ni/YSZ cylindrical or “bumpy” shapes is higher than their convex counterparts.

2. Upon SOEC polarization, electrowetting would comport a diminution of the Ni/YSZ interfacial surface tension, causing a decrease of the Ni dihedral angle and increased Ni wettability on YSZ. As schematized by the green arrows in Fig. 6.20B, this process would promote Ni migration away from the interface, comporting also a shift towards cylindrical shapes, which may lead to higher mean curvature in this region. Such shapes are expected to evolve towards necking and pinch-off because of Rayleigh instability. Thus, the volume of the particles adjacent to the electrolyte would be subjected to clenching because of the increased wettability, thus favouring the migration of part of the Ni. The accumulation of material away from the electrolyte would also cause an increase in the Ni size at this location, which would further promote competitive growth at a local scale. Further, the pinning force exerted on the Ni/Pore interface is also expected to change, significantly in the case of displacement of the TPB position, unlike illustrated in Fig. 6.20B. We emphasize that this description remains hypothetical at this point. It indeed depends upon the magnitude of the dihedral angle changes, which proved challenging to estimate from EIS measurements and ascertain directly by stereological measurement. In this regard, a lateral shift of the TPB position (maintaining the same angle) would however lead to a pinch-off from the inner inclusions.

3. Once the instability is established, competitive growth is expected to lead to either the complete absorption of the regions with smaller characteristic size in contact with the electrolyte or to their detachment (Fig. 6.20C). In the latter case, the TPB formed by the isolated particle is inactive, and consequently the Ni dihedral angles would restore their nominal size. This might be a reason why ascertaining a change in dihedral angle proved to be complicated. As mentioned in Section 6.3.1, attempts to measure separately angles at connected and isolated TPBs did not highlight specific trends. This second alteration of the metallic angles can favour the detachment of the Ni inclusions from the electrolyte, leaving a gap beside as seen in Fig. 6.4A. In order to minimize the surface energy (in particular the surface-to-volume ratio) and restore the lower wettability, part of the material would relocate from the external edges, eventually towards spheroidization (Figs. 6.5). Moreover, in this case, further transport of Ni towards the inner region could occur only through volatilization.

The calculation in Fig. 6.19 indicates that a similar effect could be also induced after a prolonged fuel cell operation, but in the case of overpotentials significantly higher than in SOEC mode. For small overpotentials, $\theta_{\text{Ni}}$ may slightly rise or remain almost unchanged compared to OCV conditions.

Furthermore, additional considerations can be made:

- As roughly illustrated in Fig. 6.20C, the reestablishment of the nominal wettability is likely
6.4. Discussion on the driving forces that affect the stability of the electrode/electrolyte interface

Figure 6.20 – Drawing of the evolution of the Ni/YSZ interface after long term SOEC polarization. (A): At reference condition (see text for explanation), the amplitude of $\theta_{Ni}$ corresponds to its nominal value. (B): after SOEC polarization, the decrease of $\gamma_{Ni/YSZ}$ by electrowetting would yield a diminution of $\theta_{Ni}$, promoting migration of Ni away from the TPB. (C): The process may ultimately induce the necking of the Ni particles or disappearance (not shown). In the former case, the TPBs at the isolated material are inactive and $\theta_{Ni}$ would expand again to restore the nominal wettability.

To provoke a modification of YSZ dihedral angles, since the reduction of the volume of the isolated metallic particle would be associated to a displacement of TPB. This may explain the increase of $\theta_{YSZ}$ exhibited in Fig. 6.10. Moreover, the larger discrepancy in the SOEC Volume between the first slice and the others regarding the YSZ/Pore interface in Figs. 6.15 and 6.16, could be linked to this portion of Ni/YSZ surface that has been lost after the Ni migration. This effect could also explain the increase of YSZ/Pore interfacial specific energy towards the interface of the two SOEC Volumes in Fig. 6.17. On the other hand, Ni/Pore interfacial energy remains almost constant along the electrode thickness, likely due to the greater mobility of the Ni phase. In fact, the migration of material towards the inner part of the electrode counterbalances the reduction of the curvatures (Figs. 6.15C and 6.16C).

- A high electrostatic field occurs at locations where the radius of curvature of material is small [199]. Smaller dihedral angles (in particular YSZ for the Ni-YSZ) may provoke an increase of the local electric field, which can further contribute to enhance instability. Indeed, the field from a curved surface is computed as the ratio between the applied electronic potential and the radius of curvature [200].

- For smaller applied positive potentials (SOFC mode), the Ni dihedral angle could slightly increase. This possibility depends on the value of the applied potential at the pzc. In this regard, the peak in Ni volume fraction near the electrolyte in Figs. 6.12-13 may indicate an accumulation of material, compared to the thermal cycling sample (Fig. 6.11). However, the
Chapter 6. Effects of polarization on the microstructural changes at the YSZ/Ni-YSZ interface

relevance of such an effect cannot be ascertained with the present dataset.

The hypothesis of liquid Ni needs clarification, which is required for the rigorous application of the electrowetting phenomenon, since its effect would be almost negligible on solid/solid interfaces. The melting temperature of metals is known to be dependent upon the dimension of the particle [201]. Further, Smirnov [202] highlights the possibility in the case of gold for fusion of the particle shell at temperatures lower than the melting point, whereas the bulk remains solid. In this regard, the difference in temperature between regions nearby TPBs and the electrode average under polarization is of interest, but difficult to assess. A higher temperature is intuitively expected, in particular in the Ni layers in contact with the YSZ phase where ohmic losses occur. Because of the low wettability of Ni on YSZ, the applied potential can alter the dihedral angles due to the high mobility of the metallic superficial atoms under these conditions. On the other hand, low wettable surfaces (characterized by small angles) may hinder this phenomenon.

6.4.3 Effect of oxygen partial pressure

Jiao et al. [21] investigated the evolution under polarization of a patterned Ni-film anode sputtered on a YSZ substrate, detecting a strong relocation of Ni due to the increase in wettability. The difference in partial pressure of the oxygen adsorbed on the Ni surface near the TPB, due to the generation and consumption of surface species (as described in Chapter 4) was discussed as a tentative explanation. The increase of oxygen activity on the adsorption sites would lead to the reduction of surface tension (and reduction of the Ni dihedral angle). The oxygen activity is related to the H_{2}O partial pressure in the gas phase near the TPB, which differs from the bulk value according to the applied current density. The above-mentioned relationships described in [21] are displayed in Figs. 6.21. Variations of $p_{H_{2}O}$ below 0.8 atm would not strongly modify the Ni angle, while a greater humidity would cause a surge of wettability.

![Figure 6.21 – (A) Dependence of $a_{O_{2}}\text{(Ni)}$ with Ni surface tension and $p_{H_{2}O}\text{(gas)}$. (B) Dependence of Ni dihedral angle with $a_{O_{2}}\text{(Ni)}$ at 800°C. Images obtained from [21].](image-url)
Figure 6.22 – oxygen surface coverage distribution on Ni sites for varying bulk gas molar fraction and applied potentials.

The computation of adsorbed species on Ni sites described in Chapter 4 can provide a first estimate of the values of oxygen surface coverage for different gas concentrations and applied potentials. As shown in Fig. 6.22, operation in SOFC (SOEC) mode comports an increase (decrease) of oxygen coverage. However, according to Jiao et al. [21] the diminution of surface tension and angle becomes significant for steam partial pressures higher than 0.8 atm, which can be met only near the cell inlet in SOEC mode or at the outlet in SOFC mode, under a practical fuel utilization of 80%.

A series of clear practical consequences are expected from a direct dependence between wettability and steam partial pressure as shown in Fig. 6.21. The maximum variation in Ni dihedral angle and of the consequences would be observed under SOEC OCV conditions, while a strong negative potential would reduce the $p_{H_2O}$ (re-establishing the standard surface tension). Nevertheless, the reported experimental work confirms a relation between wetting angle and applied potential.

Saiz et al. [203] investigated the dependence of the interfacial tension in metal/oxide systems (i.e. pure metal/Al$_2$O$_3$) on the partial pressure of oxygen. The work of adhesion (defined as the work needed to reversibly separate the interface) is related to the oxygen activities, following non-linear dependency. Under high $p_{O_2}$, the surface tension and in particular the dihedral angle diminish likewise with oxygen activity, causing an overall augmentation of the work of adhesion. In case of intermediate $p_{O_2}$, interfacial tension depends on the oxygen activity and the work of adhesion is similar to the nominal value for pure surfaces. Lastly, under lower $p_{O_2}$, a direct dependence between dihedral angle and oxygen activity is observed, but the effect on the adhesion work could
Chapter 6. Effects of polarization on the microstructural changes at the YSZ/Ni-YSZ interface

not be quantified, due to experimental limitations. In the light of the study by Saiz et al., the effects of oxygen partial pressure could lead to the alteration of the interface and in particular of the dihedral angles under electrolysis condition. In the case of high $pO_2$ (Fig. 6.22), $\theta_{Ni}$ would diminish proportionally to the oxygen activity (influenced by the rate of consumption of species, i.e. the local current density).

6.5 Conclusion

The evolution of the interface between Ni and YSZ was examined in 3-D with a focus on the variation of microstructural properties along the direction perpendicular to the electrolyte plane upon SOFC and SOEC polarization. As expected from the literature, the migration of the Ni phase away from the electrolyte was detected in the SOEC Volume, leading to a reduction of connected TPB density near the electrolyte that is detrimental for the performance. Changes were observed approximately in the first 6 $\mu$m for the two SOEC Volumes. The lower peak values of mean and gaussian curvatures distributions at the Ni/Pore interface indicate that a driving force other than discussed in Chapter 5 and dependent upon the operation mode contribute to Ni migration.

Patterns of degradation due to the electrowetting phenomenon were searched for in the 3-D reconstruction and first calculations performed to estimate the effects of applied overpotential on the surface tension between YSZ and Ni. High uncertainties on the magnitude of the expected changes in dihedral angles remain and further, the degradation seems to differ in SOEC mode not only near the YSZ interface, but also to some extent further away. However, the estimate indeed suggests a dissimetry between SOFC and SOEC. A qualitative description of the degradation was provided for regions subjected to SOEC overpotential.

The observed increase in general mean curvature near the interface may arise from a diminution of the Ni dihedral angle (and increase in wettability). The latter can in turn promote the transport of Ni towards the bulk of the electrode to reduce the mean curvature of the surface in contact with porosity. The phenomenon proceeds until the passivation of the region, by either pinch-off or disappearance of small regions by competitive growth, resulting in apparent detachments.

The central difference between the two operation modes would be the value of the potential at the point of maximum interfacial Ni/YSZ surface tension (pzc). Since the dependence of the Ni dihedral angle with overpotential is parabolic, a positive shift of the pzc compared to the OCV causes a stabilization of the angle under SOFC polarization and a net decrease in electrolysis mode. However, for high applied potential, larger than those of practical relevance, the dihedral angles should decrease in all cases.

A straightforward recommendation to mitigate degradation in SOEC mode is to operate the cell at low overpotentials. It can be achieved by an increase of temperature to facilitate charge transfer,
6.5. Conclusion

which would however also increase the surface diffusion coefficient of Ni. A dependence upon overpotential, i.e. position in the cell is expected but additional reconstructions and experiments will be needed for confirmation. Possibilities for mitigation may be also achieved qualitatively by a finer YSZ microstructure next to the electrolyte to limit competitive growth. A finer YSZ electrolyte side may also provide additional sites for pinning the Ni/Pore interface. A complementary approach is the modifications of the dependence between dihedral angle and overpotential, which may be achieved by doping.

The confirmation of the trend discussed in this Chapter requires further investigation of the effects of polarization on the wettability of Ni over YSZ, and a better understanding of the effects of partial pressure of oxygen on the interfacial tension and dihedral angles. In this case, the hypothesis described in Section 6.4.2 would not be substantially affected, since Ni relocation is likely rather promoted by an alteration of $\theta_Ni$. Nevertheless, if variations of $p_{O_2}$ comport a reduction of the interfacial tension, the gas composition would be the key factor controlling the wettability of the metallic phase.
Strontium Migration at the GDC-YSZ Interface of Solid Oxide Cells in SOFC and SOEC Modes

This Chapter extends the analysis presented in Chapter 2 (Section 2.2.3) by investigating the detrimental effect of the strontium migration from the oxygen electrode to the interface between the electrolyte and interlayer in SOFC and SOEC modes. The operation in SOFC mode caused a limited decrease of the conductivity, while the effects on the performance are more significant for SOEC operation. ¹

7.1 Introduction

One contribution to performance degradation arises from the chemical interaction between the oxygen electrode (typically lanthanum-cobalt-iron-strontium oxides with perovskite structure) and its environment [205]. As seen in the case study presented in Chapter 2, Sr evaporates in the form of hydroxide and/or migrates by surface, solid or gas-phase diffusion [116]. In the case of YSZ electrolytes, Zr can also diffuse, and react with Sr forming a secondary SrZrO₃ phase at the interface, along with closed porosities [206].

Zirconate formation is known to occur during the fabrication sintering of the cell layers (above 1000°C) with a critical effect on the initial cell performance. Hence, a gadolinium-doped-ceria layer is inserted between the electrolyte and oxygen active electrode to prevent the formation of this secondary phase without compromising the transport of oxygen ions. In commercial cells, the GDC layer is often screen-printed for costs reasons. Full densification is difficult to achieve

¹The content was included in the conference paper “G. Rinaldi, A. Nakajo, J. Van herle, P. Burdet, E. Oveisi, M. Cantoni, Strontium Migration at the GDC-YSZ Interface of Solid Oxide Cells in SOFC and SOEC Modes, ECS Transactions, 78 (1) 3297-3307 (2017)” [204] presented at the 15th International Symposium on Solid Oxide Fuel Cells (SOFC-XV) that took place the 23rd -28th July 2017 in Hollywood (FL).

Personal contribution: co-developed the morphological properties detection routines and the finite element simulation, performed the analysis.
with this deposition method, resulting in a partially porous microstructure. Therefore, only part of the thickness of the blocking layer efficiently limits cation diffusion and SrZrO$_3$ can be found also in pristine cells [207]. Furthermore, several studies reported enhanced accumulation upon operation in SOEC mode [81, 82]. The mechanism remains however only partially understood and the knowledge on the evolution during operation and the effect on the performance is limited. The conductivity of this phase is about five orders of magnitude inferior to the one of the pure electrolyte (1.87e-4 S/m for SrZrO$_3$ and 5.4 S/m for YSZ at 800°C [208, 209]). For this reason, SrZrO$_3$ inclusions partially obstruct the oxygen ion conduction paths and force transport through smaller sections, increasing the effective ohmic resistance and local ohmic heating. They are located within an interdiffusion region between the YSZ and ceria-based layer, which forms during the sintering process already. The solid-state reaction results in the formation of a thin and convoluted interaction zone, which is most extended in the electrolyte and exhibits an ionic conductivity lower by two orders of magnitude compared to YSZ [206]. Zr migration also results in the formation of closed porosities along the YSZ grain boundaries leading to a mechanical weakening of the interface [72]. The presence of voids combined with thermal cycles may provoke delamination of the interface.

The purpose of this Chapter is a quantitative 3-D characterization of the evolution of the zirconate secondary phase during operation in both SOFC and SOEC modes and of the effect on the effective conductivity of the interface.

### 7.2 Experimental

The cells analyzed under SOFC conditions were all composed by a Ni-YSZ support electrode on the fuel feed side, a YSZ electrolyte, a GDC compatibility layer and a LSCF-based oxygen electrode. The SOEC aged sample comprised instead a LSC-based oxygen electrode. Table 7.1 lists the footprint area and GDC thickness for the four Volumes examined. The results of the analysis were normalized by the footprint area because of the different reconstructed Volumes. The effective thickness of the GDC layer was estimated as the distance in the Z direction between the position of the first SrZrO$_3$ when scanning from the YSZ side and the location where the volume fractions of pores and GDC are equal (Figs.7.1A and B). The testing conditions of the four analyzed samples are summarized hereafter (detailed information on the testing conditions was provided in Chapter 1):

- **V1**: pristine cell A, after Ni reduction.
- **V2 (SOFC-mode)**: segmented cell exposed for 1.9 $kh$ to air and H$_2$.
- **V3 (SOFC-mode)**: short stack operated for 4.7 $kh$ with dry H$_2$ at 0.4 A/cm$^2$ and 780°C for most of the time (inlet region).
- **V4 (SOEC-mode)**: 6-cell short stack tested for 10.7 $kh$ at 0.6 A/cm$^2$ for the first 3250 h and at 0.5 A/cm$^2$ afterwards, at 720°C (feed flow composition of 90% H$_2$O and 10% H$_2$).
7.2. Experimental

<table>
<thead>
<tr>
<th>Volumes list</th>
<th>Footprint area [µm²]</th>
<th>Estimated GDC layer thickness [µm]</th>
<th>Voxel size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1: pristine A</td>
<td>71.54</td>
<td>5.7</td>
<td>7</td>
</tr>
<tr>
<td>V2: SOFC, 1.9 kH</td>
<td>41.71</td>
<td>3.8</td>
<td>7</td>
</tr>
<tr>
<td>V3: SOFC, 4.7 kH inlet</td>
<td>45.16</td>
<td>3.8</td>
<td>10</td>
</tr>
<tr>
<td>V4: SOEC, 10.7 kH</td>
<td>106.58</td>
<td>3.1</td>
<td>10</td>
</tr>
</tbody>
</table>

*Table 7.1 – Dimensions of the reconstructed Volumes.*

3-D EDS elemental mapping was performed for the sample V4 only, by changing the acceleration voltage automatically every 10 sections to 10 kV, which allowed the detection of La, Sr, Co, O, Gd, Ce, Zr and Y (Fig. 7.2A). 3-D EDS also enabled to confirm that features with a distinct grayscale and located at the YSZ/GDC interface contain Sr and Zr. The measurements did not reveal a clear continuous Sr-gradient across the GDC compatibility layer (Fig. 7.2A). Previous post-test analysis of the SOEC V4 sample (Chapter 2) by TEM-EDS with selected area electron diffraction confirmed the presence of a SrZrO₃ secondary phase [95] at the interface between the YSZ electrolyte and GDC layer, which corresponds to the grayscale features in the FIB-SEM dataset. In the V4 case, delamination just below the YSZ/GDC interface was observed over large areas at several locations, in both 2-D and 3-D analyses (see Figs. 7.2A and B).

The segmentation, which consists in assigning to each voxel belonging to a same material phase the
Chapter 7. Strontium Migration at the GDC-YSZ Interface of Solid Oxide Cells in SOFC and SOEC Modes

Figure 7.2 – (A) Electron image and corresponding EDS map from a section in the 3-D serial sectioning dataset of the sample aged in SOEC mode for 10,700 h, including the YSZ electrolyte, the GDC compatibility layer and oxygen electrode. (B) Reconstruction of the full dataset (grayscale electron images and segmented Volume).

same label, was based on the grayscale electron images using Matlab routines with calls to Avizo for image gradient and watershed transform computations. Further descriptions of the methods used for image processing and quantitative 3-D analyses are provided in [94]. Figs. 7.1A and 7.2B show overall and close-up 3-D views of the aligned grayscale and segmented datasets. The Sr inclusions can be identified because of their darker level of grey. For the present study where 3-D EDS elemental mapping was not performed systematically, YSZ and GDC phases were treated as a single phase, because of their similar grayscale levels.

7.3 Analysis

A series of metric and topological properties of the detected strontium zirconate phase was measured to identify the mechanisms of formation and to comprehend whether or not a detrimental evolution occurs in the long-term. The evolution after SOFC and SOEC operation was examined by measuring the volume fractions, interfacial surface areas, 3-D phase size distribution and connectivity. For the purpose of this analysis, the region of interest is limited to the GDC layer and its interface with the
YSZ electrolyte.

7.3.1 Volume Fraction

Fig. 7.3 displays scans of the volume fraction of the SrZrO$_3$, YSZ/GDC and pore phases, measured slice by slice along the perpendicular Z-direction. The Sr-inclusions were detected already in the pristine sample (V1), with a maximum in the slice volume fraction of 3.5%. The scans clearly indicate that the inclusions are located at the beginning of the GDC layer, at the start of the pores phase. The GDC layer is thicker in the pristine sample. This does however not seem to impede the diffusion process more efficiently, since the sample after 1.9 kh of SOFC exposure (V2) exhibits a similar volume fraction profile, despite a thinner GDC layer. The amount of secondary phase is higher after 4.7 kh in SOFC short stack operation (V3) and is the highest in the sample operated in SOEC mode for 10.7 kh, with a peak in the slice volume fraction reaching 25%, and a wider spread across the interface with respect to the other cases (approximately 1.6 µm instead of 0.8 µm). As a general trend, the accumulation seems to scale with test duration under polarization.

Figure 7.3 – Volume fraction scans along the Z direction, perpendicular to the interface. The peak values of the SrZrO$_3$ volume fraction are listed in the legend.
Chapter 7. Strontium Migration at the GDC-YSZ Interface of Solid Oxide Cells in SOFC and SOEC Modes

7.3.2 Interfacial Surface Areas

The interfacial surface areas (Table 7.2) provide further information about the morphology and location of the inclusions within the YSZ/GDC interface. The second column lists the volume of detected SrZrO$_3$ per interface footprint area. The data confirms that the secondary phase quantity increases during operation. In the third and fourth column are the ISA between Sr and pores and YSZ/GDC, respectively. The subset of the interfacial surface area in contact with GDC/YSZ appears to increase with time, contrarily to that with pores. The trend is more clearly observed in the ratio (column 5 in Table 7.2). This indicates that the Sr zirconate phase tends to become further included in the microstructure during operation, up to being mostly embedded in the V4 case.

<table>
<thead>
<tr>
<th>Volumes list</th>
<th>Specific vol. $SrZrO_3$ [µm$^3$/µm$^2$]</th>
<th>$ISA_{Sr-pore}$ [µm$^2$/µm$^3$]</th>
<th>$ISA_{Sr-GDC}$ [µm$^2$/µm$^3$]</th>
<th>Ratio$(Sr-GDC/Sr-pore)$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>0.011</td>
<td>26.9</td>
<td>47.4</td>
<td>1.8</td>
</tr>
<tr>
<td>V2</td>
<td>0.016</td>
<td>15.6</td>
<td>41.1</td>
<td>2.6</td>
</tr>
<tr>
<td>V3</td>
<td>0.048</td>
<td>15.7</td>
<td>42.2</td>
<td>2.7</td>
</tr>
<tr>
<td>V4</td>
<td>0.168</td>
<td>1.6</td>
<td>52.0</td>
<td>32</td>
</tr>
</tbody>
</table>

*Table 7.2 – Dimensions of the reconstructed Volumes.*

7.3.3 Phase Size Distribution

The phase size distribution measurements shown in Fig. 7.4 indicate that the morphology of the secondary phase differs in the samples aged in SOFC and SOEC, as anticipated by the decrease in total interfacial surface area (Table 7.2). The pristine case is characterized by a smaller size with a peak at 0.1 µm. The size of the inclusions is larger in the samples aged in either SOFC or SOEC mode (see decrease in the 0.1 µm peak and increase in the 0.3-0.5 µm range of the distributions in Fig. 7.4). While the two SOFC cases have similar size distributions despite the different operational time, the SOEC Volume (V4) presents a further accretion. The volume fraction, ISA and phase size distribution measurements suggest that the secondary phase is initially dispersed, small and in contact with the pore phase. The decrease of the total surface to volume ratio is linked to an increase of the size distribution and a decrease of the share in contact with the pore phase, suggesting a shift towards a dendritic-like pattern. After 10.7 kh of SOEC operation, the amount of secondary phase is significant enough to result in a change in morphology.
7.4 Characterization of Individual Sr Zirconate Inclusions

The analysis of the individual SrZrO$_3$ regions detected in each sample was conducted to study further differences in morphology. The segmented SrZrO$_3$ regions were first labelled, then each individual region characterized. The regions smaller than 8 voxels were not included in the analysis (Table 7.3).

![Graph showing phase size distribution](image)

**Table 7.3 – Number-based analysis of detected SrZrO$_3$ regions.**

<table>
<thead>
<tr>
<th>Volumes list</th>
<th>Number of SrZrO$_3$ regions per footprint area</th>
<th>Fraction considered for the analysis</th>
<th>Percentage totally enclosed in GDC [%] - corresponding fraction of SrZrO$_3$ vol. [%]</th>
<th>Average inclusion vol. [$\mu m^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>1.6</td>
<td>0.97</td>
<td>0.9 - 0.3</td>
<td>0.0071</td>
</tr>
<tr>
<td>V2</td>
<td>1.5</td>
<td>1.00</td>
<td>12.5 - 1.1</td>
<td>0.0107</td>
</tr>
<tr>
<td>V3</td>
<td>5.4</td>
<td>0.45</td>
<td>16.3 - 0.1</td>
<td>0.0197</td>
</tr>
<tr>
<td>V4</td>
<td>14.5</td>
<td>0.99</td>
<td>68.8 - 2.7</td>
<td>0.0117</td>
</tr>
</tbody>
</table>

The density function of the region size resembles that of a Pareto distribution, the majority with relatively small dimension and, on the other hand, a few much larger. As shown in Table 7.3, all the
individual regions in the pristine sample (V1) are in contact with the pore phase. After SOFC and SOEC aging, about 12-16% and 69% of the inclusions are embedded in the GDC phase, respectively, but they represent a small portion of the total volume. After operation in SOEC mode (V4), the SrZrO$_3$ secondary phase is present as many small and more convoluted regions (which lower the number weighted average volume compared to the V3 case), but most of the volume forms largely extended and connected regions.

Fig. 7.5A displays the volume-weighted sphericity (\(\Sigma\)) distribution of the inclusions. This parameter informs on how close the shape of a particle approaches that of a perfect sphere (\(\Sigma \leq 1\)). The shape deviates gradually from a sphericity of 0.15-0.35 (V1, pristine) down to 0.02-0.05 (V4, SOEC). Fig. 7.5B provides the distribution of the ratio of the interfacial surface area of SrZrO$_3$ between GDC and pores, similarly to the fifth column of Table 7.2, but here for each inclusion. These two plots suggest that the regions grow towards the YSZ electrolyte depending on the operation time, with a severe alteration after SOEC aging. Fig. 7.5C shows the volume of each particle sorted from the largest (x=1) to the smallest and displayed in logarithmic scale. The most extended regions are therefore reported on the leftward part of the plot, while increasing x values refer to ever smaller individual inclusions. V4 SOEC Volume contains both the largest and the smallest inclusion, even if their number is one order of magnitude higher than in the other Volumes. Fig. 7.5C indicates that the size of the largest particle increases monotonically with operation duration.
7.4. Characterization of Individual Sr Zirconate Inclusions

Figure 7.5 – Volume weighted sphericity (A) and surface area to volume ratio (B) distribution of the detected individual SrZrO$_3$ inclusions. (C) Volumes of the individual inclusions sorted from the largest ($x=1$) to the smallest.
7.5 Transport Analysis

The conductivity of SrZrO$_3$ is four orders of magnitude lower than that of GDC (respectively $1.87 \times 10^{-6}$ S/cm at 800°C and 0.087 S/cm at 750°C) [206, 209]. Finite-element (FE) transport simulations were performed to quantify the effect of the detected inclusions alone on the effective ionic conductivity of the YSZ electrolyte/GDC compatibility layers together. The performance degradation was assessed by comparing two cases. The transport analysis was first performed by implementing the ratio of the ionic conductivity values mentioned above. Then, an ideal limiting case was simulated by treating the Sr-inclusions as GDC/YSZ, i.e. with the same conductivity. The ratio of the two cases was then computed to obtain a global increase in resistivity. This simplified analysis does not distinguish the difference in the detrimental effect on transport between the subset of the secondary phase enclosed in the GDC and that located mostly on the external surface.

The simulations were performed in Abaqus with periodic boundary conditions imposed across the Z-direction and no-flux boundary conditions on the other x and y directions. The four Volumes considered were aligned on the peak of the Sr volume fraction and cropped at 2.1 µm further along the Z-direction. The footprint areas are those listed in Table 7.1. An additional GDC/YSZ layer of 0.9 µm (reaching a total length of 3.0 µm) was added for imposing the periodic boundary conditions on corresponding pairs of points on opposing surfaces [210]. The computational domains were generated by converting the voxels into 1st order brick elements. The Volumes were resampled by a factor of 4 in each direction to keep the RAM memory requirements below 256 GB in all cases. Simulations on test Volumes with a size of 3.5 µm$^3$ showed that the resampling results in an increase of the effective conductivity of 0.9%.

The effect of the SrZrO$_3$ on the simulated distribution of current is shown in Figs. 7.6A-B. The presence of extended regions may further hinder the ionic current, leading to a significant local increase of flux. Whether or not the additional ohmic losses can cause noticeable local increases of the temperature with detrimental consequences on the mechanical stability of the interface remains an unclarified question.
7.5. Transport Analysis

Figure 7.6 – Simulated distribution of the ionic current in the V3 sample (SOFC, 4700 h). (A) SrZrO$_3$ treated as part of the GDC/YSZ ion-conducting phase, (B) as close to insulating, as in the real microstructure.

The increase in resistivity computed for each Volume is provided in Table 7.4. The effect of the zirconate phase is the highest for the V4 Volume (SOEC), leading to an increase in the effective resistivity of 13%. Fig. 7.7 suggests at first appraisal a close to linear dependence on the operation time, which is however most likely misleading. The estimates of the rate of increase in resistivity and specific Sr- volume are 0.6 % $k h^{-1}$ and 1.1 % $k h^{-1}$ in SOFC and SOEC mode, respectively. The inclusions detected in the pristine Volume V1 and formed during the sintering process have a limited effect on the performance, estimated to 1.5%. After 1900 h at OCV (V2), the increase in resistivity is similar to the pristine case (V1). The degradation of the effective conductivity is more significant after 4700 h in SOFC mode (V3). In general, there is a clear correlation between the surface specific volume of SrZrO$_3$ and the decrease in effective conductivity.
Chapter 7. Strontium Migration at the GDC-YSZ Interface of Solid Oxide Cells in SOFC and SOEC Modes

<table>
<thead>
<tr>
<th>Volumes</th>
<th>Increase in resistivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td>1.49</td>
</tr>
<tr>
<td>V2</td>
<td>1.50</td>
</tr>
<tr>
<td>V3</td>
<td>4.13</td>
</tr>
<tr>
<td>V4</td>
<td>12.91</td>
</tr>
</tbody>
</table>

Table 7.4 – Results of the transport analysis.

![Graph showing increase in effective resistivity after aging](image)

Figure 7.7 – Increase in effective resistivity after aging.

7.6 Conclusion

Differences in the morphology and topology of the SrZrO$_3$ secondary phase detected in the interface region between the YSZ electrolyte and GDC blocking layer were analyzed in cell samples in pristine state and after aging in SOFC mode for 1,900 $h$ and 4,700 $h$, and after 10.7 kh of operation in SOEC conditions. The measurement of metric and topological properties indicates not only accumulation during operation, clearly predominant in SOEC conditions, but also changes in the microstructure. The size distribution of the secondary phase increases with operation time, resulting in the formation of a reticulated network after 10,700 $h$ in SOEC mode and the subset of the interfacial surface area in contact with the pore phase significantly decreases.

The effect on the effective conductivity of the interface, i.e. the cell performance, has been quantified by 3-D finite-element simulations. The effect of the SrZrO$_3$ alone is limited in the pristine cell (1.5 %), but it increases by up to 13 % after 10,700 $h$ in SOEC mode.
The study does not clarify whether or not the strong accumulation in the V4 case is mainly ascribable to the extended operation duration or to the conditions in electrolysis mode. For this purpose, 3-D analysis including additional Volumes of interest is required to comprehend the differences in microstructural alterations.
Conclusions and Outlook

The commercial viability of the solid oxide cell technology can be improved by material modifications for longer lifetime and/or adequate strategy for stack replacement. Both complementary approaches require improved understanding of the long-term degradation, which is dependent upon the stability of the cell microstructure. The mitigation of the detrimental effect of material migration and inter-diffusion (particularly in electrolysis mode) requires the precise understanding of the underlying physics and of their relationships with the electrochemical reactions, i.e., in terms of (i) driving force for material degradation and (ii) consequences on the effective electro-catalytic properties. The objective of this Thesis was to develop the capability to quantify and investigate these two aspects. A set of characterization techniques is developed to advance the capability that were available at the start of this Thesis, hence the comprehension of the underlying physics. The focus is on selected state-of-the-art solid oxide cells, but the approaches and methods are relevant for electrode microstructures with different materials and/or morphologies, consequently for other technological applications as well, where electrochemical reactions occurs in heterogeneous microstructures that evolve upon operation.

This concluding Chapter provides the synthesis of the two main areas of focus of the present work divided into two sections: a) characterization of the morphology near the TPB sites to investigate the surfaces available for diffusion and b) microstructural evolution in the cell, with the emphasis placed on the Ni-YSZ cermet upon long-term operation and the formation of secondary phases at the GDC/YSZ interface. Recommendations for future work and a discussion on the relevance of the results of this Thesis for the improvement of SOC microstructures are then provided in separate sections.

Surface available for diffusion near TPBs

The investigation of the effects of the morphology near TPBs on the effective electro-catalytic properties of SOC electrodes is based on the idea that performance does not only relates to the density
Conclusions and Outlook

of active sites. Since charge transfer involves species adsorbed on nearby surfaces, it is expected also dependent on the extension of the interfacial surfaces near the TPBs where the reactions occur. The relevance of the study was warranted by the visual inspection of 3-D reconstructions and first estimates of the length of diffusion profiles reported in the literature. The concept of available length based on stereological measurements was therefore developed to examine in Chapters 3 and 4 how the quality of TPBs may depend upon the nearby surfaces available for diffusion, besides considerations on the mere TPB density. Despite the stereological nature of the measurement procedure, the problematic is treated from a 3-D and microstructural property perspective, which is to our knowledge the novelty of the present work. As visible in the example reported in Fig. 1, two available lengths relate to each TPB (case A). A limitation may occur when one or both the associated available lengths are shorter than the diffusion gradient, hence not sufficiently extended (cases B and C respectively).

Figure 1 – Close-up view in a Ni-YSZ cross-section with TPBs highlighted in red and surfaces for LA measurements by spilling algorithm in blue (Ni) and green (YSZ). Case A: both available lengths are sufficiently extended. Case B: $L_A$ on Ni is short and may limit performance, while $L_A$ on YSZ is sufficiently extended. Case C: the $L_A$ on both surfaces are short and may affect the performance.

The test performed with artificially-generated packed spheres structures informed about the validity of the developed method and confirmed as expected a correspondence between the available length and the measured ISA in contact with the pore phase. The analysis performed on Ni-YSZ and
LSM-YSZ composite electrodes reveals that a non-negligible portion of the measured available length ($L_A$) is lower than the diffusion profiles reported in the literature (respectively 3-43% and 21-99% for Ni and YSZ, and 92-100% and 22% for LSM and YSZ). In particular, the average value measured for LSM was lower than 200 nm, potentially affecting the supply of oxygen to TPBs. In the Ni-YSZ electrode, the $L_A$ on YSZ is on average longer than on Ni and it matches the fraction between Ni/Pore and YSZ/Pore ISAs. However, the diffusion of surface species on Ni sites does not appear particularly affected, since the developed profiles reported in the literature are shorter than 20 nm. A critical assessment of the actual impact of the YSZ side will however require further efforts, because the comprehension of the charge transfer mechanisms and of the catalytic properties remains incomplete. In general, the percentage values provided in Chapter 3 are subject to large uncertainty because the actual impact of regions available for diffusion smaller than needed for fully developed diffusion profile on the effective polarization resistance is imprecisely known.

A model was developed to study the impact of the available length on the electrochemical performance in Chapter 4. Two elementary kinetic reaction-diffusion numerical models were implemented respectively for $\text{H}_2$-$\text{H}_2\text{O}$ and CO-CO$_2$ reactions for Ni-YSZ, following formalisms reported in the literature. The models allowed to perform a sensitivity analysis to assess the effect of the $L_A$ extension depending upon different gas compositions, species surface diffusion coefficients and presence of contaminants. The results highlighted that a shorter available length causes a flattening of the spatial distribution of surface coverages with the consequence that the diffusion profile cannot develop fully, i.e., surface species coverage cannot reach the equilibrium. However, the predicted effect on the performance was found limited for the two studied cases, except for very high applied potentials. The numerical study suggests that the selection of the elementary steps in the charge transfer mechanisms is of importance, since only the surface coverage of the “active” species have a real impact on the current density for a given potential. For instance, in the H spillover case, the spatial distributions of the $H_{(Ni)}$ and Ni free sites are severely affected by shortened available length, but the apparent effect is small since the two are placed on the two sides of the mechanism, and thus their impact cancels out. A potential limitation arises then mainly from adsorbed $\text{H}_2\text{O}_{(Ni)}$.

The surface diffusion coefficients of species reported in the literature for Ni-YSZ spread over six orders of magnitude, but they play a central role within the investigated range. The variation mainly influences the magnitude of the gradients (and consequently the currents), but not the spatial extension of the profile. The presence of contaminants that partially cover the available free sites has a detrimental impact on the performance, but the influence on the extension of the diffusion profile is very limited.

Besides electro-catalytic properties, the microstructural information conveyed by the available length measurement were studied in Chapter 3 for pristine materials with differences in their manufacturing route. A relationship between available length and the size of TPB lines was observed for Ni-YSZ, together with a general correspondence with the size of the inclusions. A likely reason is the
Conclusions and Outlook

shrinkage of the NiO/Ni phase upon reduction. Moreover, TPBs with a large $L_A$ on Ni are associated to larger $L_A$ on YSZ, while small available lengths often beneficially correspond to isolated TPBs, as expected from the relationship with the local Ni phase size. On the other hands, the fabrication of LSM-YSZ is completed after sintering, thus the stronger link to the stochastic arrangement of the starting powders does not result in clear a relation between the size of phase regions and TPBs.

Evolution of the Ni-YSZ microstructure

The evolution of the Ni-YSZ microstructure after SOFC and SOEC operation was investigated on 3-D reconstructions obtained by 3-D electron microscopy. A series of quantification methods were applied to identify and assess how the driving forces for microstructural changes during the lifetime of the cells.

The study in Chapter 5 is focused on the long-term evolution of the Ni-YSZ microstructure, with as a main objective the comprehension of how the driving forces place intrinsic limitations on the lifetime of the electrode. The investigation of the standard volume averaged metric and topological properties indicates a flattening of the TPB density and Ni median diameter after approximately 4.7 kh of operation, confirming as expected coarsening but without specific information about the potential for further rearrangement of the microstructure.

The measurement of available lengths, dihedral angles and distribution of interfacial curvatures hence served to investigate further the stability of the interfaces. Among the three interfaces, Ni/Pore presents the highest interfacial tension, followed by Ni/YSZ, which is also reflected on the magnitude of the dihedral angles. The low wettability combined to the large diffusion coefficient at the temperature of operation strongly promotes the relocation of the Ni phase. The results indicate that the evolution proceeds further after the plateau in TPB density and Ni size detected by the standard measurements. Over the investigated test period of 15 kh, two regimes were observed, which mainly concern the relocation of the Ni phase.

The first stage results in the rapid reduction of the TPB density and of the Ni/Pore ISA. In parallel, the peak of the mean curvature distributions shifts from concave to null (or slightly positive). This is likely the consequence of a rearrangement of the Ni phase (in particular the smaller regions) driven by minimization of the mean curvature. This first stage does not dominate after 4.7 kh in SOFC and 2 kh in SOEC, even though additional Volumes will be required to precisely identify the limit. The performed analysis confirmed that the evolution of the Ni-YSZ cermet cannot be explained simply by competitive growth in the light of Ostwald ripening. The evolution during the first part exhibits also characteristics of topological coarsening. The genus of the Ni phase decreases notably and the analysis of the skeleton branches of the solid phases confirmed overall elongation and necking upon aging. The measurement of skeleton vertices coordination numbers does however not indicate that
the evolution of the microstructure follows the topological edge contraction and disappearance rules as known for grains.

The physics controlling the first regime is complex and yet to be fully understood. From a practical standpoint, the consequences are well-known and are nowadays accounted in the sizing of SOC stacks. The second regime (including its development depending upon the first one) is much subtler and difficult to detect, but of higher practical interest at the present stage of development of the technology for achieving extended lifetime. It is associated to vanishing of the smaller but also shrinkage of the larger Ni regions, causing an augmentation of the share of Ni available lengths between 0.05 and 0.2 \( \mu m \). Such evolution is associated to the decrease of the larger values of mean curvature and the concurrent rise of the peaks’ magnitude. In addition, positive Gaussian curvature values larger than 4 \( \mu m^2 \) decrease upon time. This indicates that bumps or dimples shapes characterized by high curvature are prone to reduction because of their lower stability. Furthermore, it is not possible to ascertain whether the cermet has reached stabilization, since the Volumes aged for more than 10 kh exhibits a different behavior.

The measurements performed in Chapter 5 indicate that despite minor changes in connected TPB density, surface relocation proceeds further to minimize curvature, and it is not possible to determine using the available experiments whether or not it slows down. Extensive relocation of Ni regions does not seem to occur in the second stage, but the aging process still involves the rearrangement of the surfaces.

A known function of the YSZ matrix is to constrain the growth of the Ni phase. The results suggest that the YSZ phases exhibits a small but noticeable relocation compared to the pristine case, highlighted by the alteration of the interfacial curvatures and the slight rise in median diameter. Although such results need further validation, they are of particular interest for the microstructural evolution after 15 kh. The measured Ni median diameter is close to the limits predicted by the 2-D or 3-D version for coherent interface of the Zener equations, suggesting that the constrained growth has reached a nearly stable state. The measurement of dihedral angles however indicates long-term evolution, as either further changes in surface curvature or displacement of TPB lines, i.e., until equilibrium conditions for pinning are reached locally.

Thus, if the YSZ backbone is not significantly altered upon times within the target operation window of SOC systems, strong degradation of the properties most relevant for the electrochemical performance are not expected. An alteration of the YSZ stability may however allow further Ni re-arrangement. In this regard, Ni reduction-oxidation cycles characterized by strong volume changes can cause a redistribution of Ni hence of shapes and pinning position on YSZ. Similarly, repeated temperature excursions during load following may also be detrimental for the integrity of the ceramic phase.

Surface diffusion is expected to dominate the transport of Ni, thus isolated or narrow regions can in
Conclusions and Outlook

A first approximation not evolve further if they are surrounded or constrained by the YSZ phase. For these reasons, the total and effective TPB density cease to evolve significantly after a few thousands of hours, but the minimization of mean curvature proceeds further and leads to a gathering of the Ni available length distribution toward the peaks. The distribution of available length on YSZ shifts toward larger values during operation, which is linked to the motility of Ni, as confirmed by the different evolution of the YSZ/Pore and Ni/YSZ interfacial curvatures. In general, the available length on Ni and in particular YSZ increases over time, even if such growth is associated to a diminution of the density of active sites.

The second part of the study was focused on the effect of the applied potential. Despite the specific selection of sample extraction locations, a clear difference between inlet and outlet regions of the cell could not been ascertained. This is probably due to the relatively low fuel utilization during the experiments (< 0.5) and the statistical variability in the measured properties, which remains too high for such a study using commercial electrode materials.

The study however revealed trends in the evolution of the measured microstructural properties amongst SOFC and SOEC modes. Variations in the driving forces for evolution are observed at the interface between the Ni-YSZ electrode and YSZ electrolyte, where the electrochemically-active sites are located. A diminution of total and connected TPB is detected in such region, associated to a depletion of Ni (more severe after 10 kA of SOEC operation). Evidences of depletion are not observed after SOFC operation, rather the measurements suggest a slight accumulation of Ni at the interface. Curvature analysis confirmed a change for the Ni/Pore interface after 10 kA in SOEC mode, exhibiting lower peak height of mean and Gaussian curvature distributions in correspondence of the electrolyte interface. The Ni phase hence migrates toward the bulk of the electrode to minimize its curvature that has been reduced by another driving force related to polarization. The stereological quantification of the dihedral angles perpendicular and parallel with respect to the electrolyte proved complicated. Because the length scale approaches the voxels size and the orientation of the interfaces are 3-D in reality, the low statistical validity did not allow the clear identification of an alteration. On the other hands, the quantification of the Ni/YSZ interfacial specific energy exhibited a net diminution in the first 6 µm in proximity to the electrolyte for the two SOEC Volumes.

The results were analyzed in the light of the electrowetting theory, which relates the alteration of interfacial tension (and contact angles) with the applied potential. The maximum angle is associated to the point of maximum surface tensions (at pzc), while the interfacial surface tension diminishes by applying a different value of potential. Therefore, the Ni dihedral angle would accordingly reduce gaining wettability. The pzc potential does not necessarily correspond to the OCV value depending on the materials and the gas compositions, leading to different impact on the surface tension under SOFC and SOEC modes. These two aspects were estimated using capacitance values from EIS measurements on single cells, but their relevance for the analysis warrants further fundamental studies of the interface properties. In the first case, an increase of applied potential would comport
SrZrO$_3$ secondary phase at the GDC/YSZ interface

The interface between the GDC barrier layer and the YSZ electrolyte has been already investigated in the literature, but mostly in 2-D. The 3-D analysis presented in Chapter 7 allowed identifying finer changes in the microstructure. The transport pathway was identified by assessing the presence of Sr in the closed porosities. The detrimental geometrical impact of the SrZrO$_3$ secondary phase on the effective conductivity of the interface was quantified by finite-element transport simulations.

The 3-D characterization is not straightforward in the case of the SOLIDpower cell. The size of the inclusions is in the range of 0.05 – 0.4 $\mu$m, which requires low voltage imaging for increasing the spatial resolution of the 3-D dataset. After confirming by 2-D SEM EDS, TEM EDS and SAED that distinct grayscale features correspond to the SrZrO$_3$ secondary phase (in Chapter 2), segmentation with manual assistance is needed to properly separate the grey scale values compared to the surrounding GDC and YSZ layers and capture their small and complex shapes.

The SrZrO$_3$ secondary phase is known to form already after the sintering process and the results indicate that accumulation proceeds further during aging in both operation modes. Although the phenomena is clearly promoted by SOEC operation resulting in the formation of a reticulated network rather than dispersed inclusions, an additional number of Volumes are required to ascertain the statistical significance of the SOFC measurements. Moreover, the study does not clarify whether or not the strong accumulation is mainly ascribable to the extended operation duration or to the operational mode. Nevertheless, the increase in resistivity comports a consequent augmentation of the ASR that most likely endures with aging.

The post-test analysis presented in Chapter 2 also identified the additional interdiffusion phase between GDC and YSZ, that was instead investigated by Szasz et al. [211] using differences in grayscale contrast in electron images under different imaging conditions. In the present study, 3-D EDS was also used for a Volume and it should be generalized for systematic future studies of the interdiffusion zone. With a thickness proportional to the sintering temperature, it is characterized by a conductivity lower than YSZ (2%-8%), which generates additional ohmic losses. On the other
Conclusions and Outlook

hand, this layer prevents the accumulation of SrZrO$_3$, hence depending on the thickness, its initial formation may be beneficial for long-term operation. The correct identification of this phase would allow to perform a more detailed transport analysis of the ionic current and to compute the eventual detrimental impact on performance.

The implementation of a dense GDC layer would further mitigate the formation of SrZrO$_3$ during sintering, even if diffusion paths via defects or grain boundaries would however likely still result in an alternation of the interface with the electrolyte. Denser layers can be obtained by physical vapor or pulsed laser deposition, which are expensive fabrication routes. The proposed estimation of the detrimental effect of zirconates on the effective conductivity is focused on geometrical effects. The predicted degradation is limited, but it does not include the effects of compositional changes in the inter-diffusion region. Hence, further analyses are required to quantify the detrimental effect in term of performance degradation and to quantify the benefit in terms of cost using more complex fabrication techniques.

Recommendations for future works

The recommendations for future work identified from the research and results performed in this Thesis are summarized below:

- Although the elementary kinetic reaction-diffusion models highlighted a limited dependence of the performance on the available lengths in Ni-YSZ, a different charge transfer mechanism (e.g. oxygen spillover) may lead to other conclusions due to the transport properties of the selected active species. In addition, the quantification of the diffusion coefficients of the surface species must be refined (in particular for YSZ), since the large uncertainty in the data available in the literature is reflected on the computed extension of the diffusion gradients.

- The available length measurement is expected of interest for other microstructures where the electrochemical reaction involves the surface diffusion of species from or to the active electrochemical sites (i.e. not only fuel cell, but also batteries). In the case of Ni-YSZ and LSM-YSZ composites polarized within ranges corresponding to stack operation, the contrast in bulk transport properties is large and surface diffusion over large length scales is not expected. The complexity is likely further increased in composites with MIEC bulk material properties such as Ni-GDC or impregnated electrodes.

- The study on the Ni-YSZ microstructural evolution requires extension to a larger number of volumes. Model experiments may also facilitate reducing the statistical variability in the measurements and/or accelerated testing help the confirmation of hypotheses. In the case of the Ni-YSZ electrode, samples exposed to multiple long operation times (> 15 kh) are essential to understand the remaining deviation from the most stable configuration. The effects of redox and polarization cycling on the Ni distribution and YSZ backbone is also a matter of
Recommendations for future works

The study highlighted that for several properties, the length scale of interest is close to the spatial resolution of 3-D electron microscopy. This complicates their measurement; an example that warrants further investigations concerns the dihedral angles. The quantification routine scans the closest voxels to the TPB, which are more prone to errors and inaccuracies that may occurring during stack cooldown, sample preparation, imaging and segmentation. It cannot be discarded that the correct measurement of angles may require information up to the atomic level. As a first step, a benchmark using TEM and SEM on a lamella could be performed with attention paid on the interface orientation. For validation purposes, samples with known geometry would help to reduce the intrinsic variability in stereological measurement.

Concerning the alteration of the electrode/electrolyte interface, specific tests such as performed by Jiao et al. [21] would help to quantify the dependence between applied potential and wettability. In addition, the effect of gas composition and specifically of the local $p_{O_2}$ warrants clarifications. A sensitivity analysis with an extended range comprising the variation of gas compositions and applied potential in both operation modes is needed. Model experiments could be designed to investigate specifically the wettability and tendency for relocation of Ni, using e.g. layer deposited on top of other materials with known properties. In the case the mentioned hypotheses are confirmed experimentally, improved accuracy in the determination of the interface capacitance is needed, which may involve EIS measurements on defined geometries (i.e. pattern electrodes) to remove imprecisions in standard single cells tests.

3-D imaging with phase mapping based on grayscale contrast in BSE and SE electron images are useful for analyzing subtle changes and explore new possible design. However, it does not allow the measurement of all the microstructural properties considered relevant for improving the performance and durability of SOC electrodes. Thus, an analysis that encompasses the effect of the phase grain size would be beneficial for improving further the understanding of the observed microstructural changes. As observed in the electron image in Fig. II, the surface curvature seems to exhibits local changes at the interfaces with the grain boundaries (highlighted by the red arrows). Automatic 3-D segmentation using channeling contrast in the secondary electrons InLens dataset did not prove straightforward. Dedicated efforts will be required to adjust the imaging condition for improved contrast, assess the feasibility and accuracy that can be achieved using segmentation methods. The expected evolution of the grains comports a progressive diminution of edges and vertices, with larger concave cells growing at the expenses of smaller convex ones [178]. Hence, the diminution of the total interfacial mean curvature is related to the evolution of the grains. Consequently, the complete stabilization of the interfaces may be reached after prolonged time if the number of grains is minimized, but a discrete event such as a redox cycle may reset the whole process. The presented study on the morphology near the TPB is focused on geometrical aspects, but
information at the grain scale is also anticipated relevant for studying the relation between surface effective transport properties and charge transfer. Indeed, surface transport may depend upon the size and the orientation of grains near the TPB. Quantitative measurements of grain size and orientation would require x-ray or electron diffraction experiments.

![Image](image-url)

**Figure II** – SE electron image in a FIB-SEM dataset showing localized variations in curvature of the Ni/Pore interface at the intersection with grain boundaries (sample operated for 15 kh in SOFC mode).

- As mentioned in the previous Section, the characterization of the interdiffusion zone at the YSZ/GDC interface would allow to perform a more detailed transport analysis of the ionic current and to compute the detrimental impact on performance. Sufficient contrast required for facilitated segmentation seems to necessitate a higher acceleration voltage in SEM measurements (4 kV were used in [209]), which also affects the spatial resolution. Part of the data presented in Chapter 7 was from FIB-SEM combined with automatic tension switching for EDS, which could be used systematically.

**Comments for improved SOC electrode microstructures**

The targets that the design of SOC electrodes must achieve were a background thread throughout this Thesis: stability of the materials over time in stack environment, adequate effective electrochemical performance and low production costs (Fig. III). The sintering of dispersed particles commonly adopted leans toward the first one. It typically results in a close to randomly-arranged microstructure with sufficient density of reaction sites, transport properties and thermo-mechanical stability. The effective transport and electrochemical properties, such as TPB density, can be adjusted indirectly by the selection of the fraction of each solid phase, the properties of the starting powders’ particles, the sintering conditions within the limits allowed by available sintering aids and, for Ni-based
electrodes, the reduction conditions. The porosity can be also adjusted using pore formers or sacrificial phases. The problematic is schematized in Fig. III, which refers to TPBs in terms of a combination of material properties rather than a geometrical point, to encompass the case of a single-solid phase mixed ionic and electronic conductor. Connected TPBs can be electrochemically active, but the effective-electrocatalytic properties of a subset may be limited by the morphology and/or topology of the electrode structure, instead of by bulk material properties.

![Diagram](image)

**Figure III** – *Left: the three main targets for the design of SOC electrodes. Right: illustration of the classification of TPBs.*

From this standpoint, the state-of-the-art Ni-YSZ electrode material has several advantages, as discussed in the Introduction. The microstructure is subject to significant rearrangement during operation, but as highlighted by the results in this Thesis, the efforts over more than two decades achieved sufficient stabilization. The SOFC experience indicates indeed that lifetimes approaching the targets for commercial viability can be reached if the cell materials are adequately protected from detrimental events such as mechanical failures, reoxidation/reduction, contamination or voltage drops (or surges in SOEC).

In this regard, the reduction of the mobility of the solid phases and the mitigation of the overpotential must be adequately guaranteed throughout the lifetime, depending on the operating mode. The results presented in Chapters 5-6 indicate that long-term SOFC operation does not cause a further diminution of the performance of the Ni-YSZ electrode, since the overall TPB density remains almost unaffected after 4700 h. Nevertheless, the study demonstrated that the microstructure continues to evolve, hence a lower temperature of operation may allow to reduce phase migration. On the other hand, low overpotential is central in SOEC mode to mitigate Ni depletion at the interface with the electrolyte. In this case, a higher temperature would contribute to diminish the overpotential for a given current. Ni migration would be also favored, but the detrimental component of the driving force that relates to overpotential is expected less. The control of these two parameters ultimately affects the total power density.
Conclusions and Outlook

In a simplified view, the requirements for highest (i) density and (ii) effective electro-catalytic properties of the TPB sites are opposite and an adequate balance must be found. The second encompasses the effective transport properties and, as discussed specifically in this Thesis, morphological and material properties close to the TPB. Random microstructures have however limitations for such adjustments of properties and the question arise of whether or not design should be targeted at TPB properties rather than quantity. Fabrications routes that allow introducing in-purpose anisotropy are therefore being developed for a few years to improve mainly the effective transport properties. Examples include freeze casting or orientation by a magnetic field, which showed benefits for both fuel and oxygen electrodes despite the overall diminution of TPB density [212, 213]. The complementary area of investigation focuses on the diverse functionality of the particles, i.e. that generating more current compared to the fraction responsible for the transport. As described by Bertei et al. for the Ni-ScSZ structure [214], the two typologies are mutually exclusive. Ongoing research is therefore confirming a trade-off between transport of species in general and number of actives sites. This is in line with the discussions in Chapter 3. The results indicate that differences in the elementary steps in the reactions and surface transport properties should be accounted specifically for each phase. Here, the clear difference observed between Ni-YSZ and LSM-YSZ suggests possibilities for modifying separately the available length by adjustments of the manufacturing route, sintering properties and dihedral angles, if possible without detrimental effect on the bulk material properties. As mentioned in Chapter 4, a remaining significant hurdle for using the available length as a target design is the uncertainty discussed previously on the electrochemistry of even standard materials, besides grain size and orientation considerations.

The density of TPBs is inversely proportional to the average available length. The accurate selection of the particle’ size of the starting powders should consider the extension of the diffusion gradient associated to the charge transfer mechanisms. Indeed, a high initial TPB density could be inadequate in case of long gradients, since part of the active sites may be limited (as measured for the LSM/YSZ electrode). On the contrary, the overall TPB density can be maximized in the case of relatively short diffusion gradients.

The mobility of Ni can be reduced by implementing a finer constraining phase with increased volume fraction. An overall refinement may not be needed, if there are sufficient and adequate placement of locations for the pinning of the interfaces. A finer structure also comports an augmentation of TPB sites, even though their accessibility may be reduced. Moreover, smaller particles are characterized by lower surface-to-volume ration and higher surface curvature, increasing the risks of alteration upon aging. Indeed, the active layer casted between the electrolyte and the standard electrode would be intrinsically unstable, since the smaller Ni features will be more prone to relocated toward the inner portion of the electrode characterized by coarser regions. On the other hand, coarser/denser inclusions comport an inferior initial TPB density, but a likely more stable structure less prone to relocation. In particular, in the case of electrolysis operation the use of “active” layers with coarser...
Ni particles may help to hinder the migration, by competitive growth due to the large volume of material. Indeed, a more uniform distribution of particle size in the powders would be reflected in a reduced fraction of small and large regions after sintering, hence less prone to relocation from competitive growth.

Yet, even though the focus was not on changes of the fine surface morphological features, degradation experiments outside the scope of this Thesis demonstrated their performance stability. A higher wettability on the mobile phase (translating into smaller contact angle) is also expected to slow down the migration (see also the cellular automata numerical model in Wang et al. [215]). As an example, a larger wettability of Ni on YSZ can be reached with the addition of titanium [216]. Moreover, the hypothesis stated in Chapter 6 needs to be explored further, even though the relation between applied potential and relocation has been highlighted. If the hypothesis proves correct, the choice of the wettability properties would be of primary importance. The control of these properties may then permit the production of a more stable microstructure that would not undergo the more rapid degradation in the first part of operation.

Manufacturing routes for the next generation of electrodes also include infiltration/impregnation methods, which involve a relatively cost effective application of a thin coating or a dispersion of nanoparticles on a pre-sintered backbone. Nanosized particles have very high surface energy and therefore limiting the propensity for coarsening during operation is key. Care is here needed in the direct application of the above recommendations for current generation materials. A scaffold sufficiently fine to constrain the competitive growth and prevent abnormal growth may not be in line with the requirement of highest ionic conductivity. Further, at this scale, the relevance of wettability considerations may play an increasingly important role, with a stronger relationship with surface curvature. Increased attentions may be then required on the related questions discussed previously, such as whether or not dihedral angle measurements require information up to the atomic scale and the effects of grain size on the curvature.
The approach used in this study to estimate the mean available length (Fig. 3.2B) is based upon percolation theory and the measurement of interfacial surface areas in 3-D Volumes. The data for the artificial structures and electrode microstructures imaged by FIB-SEM in this study are reported in Table A.1. Percolation theory relies on the prediction of coordination numbers, i.e., number of contacts among neighboring spherical particles. Hence, the number fraction of the solid phase “i” in the binary mixture containing solid phases “i” and “j” is defined in Eq. A.1. For the sake of brevity, equations only for the phase “i” are provided in the following description.

\[
N_i = \frac{\psi_i}{\psi_i + \psi_j} \times \frac{r_i^3}{r_i^3 + r_j^3}
\]  

(A.1)

where \(\psi_i\) and \(r_i\) are the solid volume fraction and the radius associated to the each phase.

The total coordination number for the solid phase “i” \((Z_i)\) is computed according to Eq. A.2 [136]. The value of the overall average coordination number of all solid particles \(\bar{Z}\) is often set equal to 6, based on estimation from synthetic packed spheres structures [217, 218]. It was set equal to 5.3 for the Ni-YSZ and LSM-YSZ, which corresponds to measurements performed for electrode materials such as investigated in this study in ref. [94] using a discrete representation of the microstructure provided by skeleton edge and vertices-based partitioning.

\[
Z_i = 3 + \frac{\bar{Z} \times r_i^2}{N_i \times r_i^2 + N_j \times r_j^2}
\]  

(A.2)
Appendix A. Percolation theory-based model for available length calculations

The intra and inter-phase coordination numbers are expressed in Eqs. A.3 and A.4, respectively.

\[ Z_{i/i} = \frac{Z_i \times \psi_i}{r_i} \times \frac{\psi_i}{r_i} + \frac{\psi_j}{r_j} \]  

(A.3)

\[ Z_{i/j} = \frac{N_i \times Z_i \times Z_j}{Z} \]  

(A.4)

The number of particles per unit volume \( n_i^V \) is computed as the ratio between the volume fraction \( \phi_i \) and the spherical volume of the solid phases “i” (Eq. A.5). Even if the estimated values for hard spheres is expected inferior than the actual number of particles present in artificial packed spheres Volumes, because of the overlap to manipulate the neck size, they can be considered valid as long as the contact angles among particles do not exceed 30° [219].

\[ n_i^V = \frac{\phi_i}{4/3\pi r_i^3} \]  

(A.5)

A stereological simplification passing from a 3-D to a 2-D representation shown in Fig. A.1 is adopted to compare the direct measurement of the available length by spilling algorithm with estimation from the percolation model for mono-sized particles.

Figure A.1 – Schematics of the type of sphere arrangements considered in the percolation model.

The interfacial surface areas \( ISA_{TOT} \) per unit of volume in the artificial structures presented in Table 208
A.1 were measured using the standard methods described in the section "Methodology". Division by \( n_i^V \) provides the amount of surface shared by the "i" particle with pores and with the particles of opposite phase (Eq. A.6).

\[
S_{\text{Pore}/i} = \frac{ISA_{\text{TOT}i}}{n_i^V}, \quad S_{i/j} = \frac{ISA_{\text{TOT}ij}}{n_i^V}
\] (A.6)

The shared surface among each couple of particles can be approximated by dividing the coordination number (Eq. A.7). As mentioned previously, this assumption formally holds in the case of small contact angles.

\[
A_{i/j} = \frac{S_{i/j}}{Z_{i/j}} \equiv A_{j/i} = \frac{S_{j/i}}{Z_{j/i}}
\] (A.7)

As shown in Fig. A.1 with dashed red lines, the TPB circumferences at inter-phase contacts are computed with Eq. A.8, and the related radius with Eq. A.9.

\[
TPB_{i/j} \equiv TPB_{j/i} = 2\pi \sqrt{\frac{A_{i/j}}{\pi}}
\] (A.8)

\[
r_{TPB_{i/j}} \equiv r_{TPB_{j/i}} = \sqrt{\frac{A_{i/j}}{\pi}}
\] (A.9)

The available length \( L_{Ai} \) is computed by gradually expanding a hypothetical annulus (with external radius \( r_{MAX} \)) until the contact surface \( S_{\text{Pore}/i} \) is fully covered (Eq. A.10). Therefore, the ratio between the area of the annulus (with external radius \( r_{MAX} \) and internal radius \( r_{TPB_{i/j}} \)) and the perimeter of the TPB yields the expression for the available length Eq. A.11.

\[
S_{\text{Pore}/i} - \pi \left(r_{MAX}^2 - r_{TPB_{i/j}}^2\right)Z_{i/j} = 0
\] (A.10)

\[
L_{Ai} = \frac{\pi \left(r_{MAX}^2 - r_{TPB_{i/j}}^2\right)}{2\pi r_{TPB_{i/j}}} = \frac{\left(r_{MAX}^2 - r_{TPB_{i/j}}^2\right)}{2r_{TPB_{i/j}}}
\] (A.11)
Appendix A. Percolation theory-based model for available length calculations

<table>
<thead>
<tr>
<th>Volume size [voxel(^3)]</th>
<th>Voxel size [nm]</th>
<th>ISA [(\mu m^2/\mu m^3)]</th>
<th>Ni/LSM-Pore</th>
<th>YSZ-Pore</th>
<th>Ni/LSM-YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 &quot;Small necks&quot;</td>
<td>420x420x420</td>
<td>14</td>
<td>2.32</td>
<td>2.10</td>
<td>0.38</td>
</tr>
<tr>
<td>2 &quot;Large necks&quot;</td>
<td>420x420x420</td>
<td>14</td>
<td>1.93</td>
<td>1.91</td>
<td>0.66</td>
</tr>
<tr>
<td>3 &quot;Medium Ni/LSM vol. frac.&quot;</td>
<td>420x420x420</td>
<td>14</td>
<td>1.93</td>
<td>2.43</td>
<td>0.53</td>
</tr>
<tr>
<td>4 &quot;High Ni/LSM vol. frac.&quot;</td>
<td>420x420x420</td>
<td>14</td>
<td>2.59</td>
<td>1.77</td>
<td>0.53</td>
</tr>
<tr>
<td>5 &quot;Low Ni/LSM vol. frac.&quot;</td>
<td>420x420x420</td>
<td>14</td>
<td>1.62</td>
<td>2.74</td>
<td>0.53</td>
</tr>
<tr>
<td>6 &quot;High Ni/LSM diameter&quot;</td>
<td>270x270x270</td>
<td>23</td>
<td>1.33</td>
<td>2.38</td>
<td>0.71</td>
</tr>
<tr>
<td>7 &quot;Small Ni/LSM diameter&quot;</td>
<td>270x270x270</td>
<td>10</td>
<td>2.74</td>
<td>5.28</td>
<td>1.07</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mean (L_A) [(\mu m)]</th>
<th>(L_A) from percolation [(\mu m)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/LSM</td>
<td>YSZ</td>
</tr>
<tr>
<td>1 &quot;Small necks&quot;</td>
<td>0.32</td>
</tr>
<tr>
<td>2 &quot;Large necks&quot;</td>
<td>0.26</td>
</tr>
<tr>
<td>3 &quot;Medium Ni/LSM vol. frac.&quot;</td>
<td>0.25</td>
</tr>
<tr>
<td>4 &quot;High Ni/LSM vol. frac.&quot;</td>
<td>0.30</td>
</tr>
<tr>
<td>5 &quot;Low Ni/LSM vol. frac.&quot;</td>
<td>0.23</td>
</tr>
<tr>
<td>6 &quot;High Ni/LSM diameter&quot;</td>
<td>0.21</td>
</tr>
<tr>
<td>7 &quot;Small Ni/LSM diameter&quot;</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table A.1 – Properties measured on the artificial packed spheres Volumes.
The shape of each patch in a surface mesh is characterized by two radii \((r_1\) and \(r_2\)) intersecting the normal vector at this location (Fig. B.1). The principal curvatures \(\kappa_1\) and \(\kappa_2\) are defined as the inverse of these radii (Eq. B.1).

\[
\kappa_1 = \frac{1}{r_1}, \quad \kappa_2 = \frac{1}{r_2},
\]

(Eq. B.1)

Two metrics are of interest for the characterization of 3-D shapes, i.e., to describe and study variations upon aging: the mean curvature “\(H\)”, defined as the average of the two principal curvatures (Eq. B.2) and the Gaussian curvature “\(K\)”, the product of the two (Eq. B.3).

\[
H = \frac{1}{2} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) = \frac{\kappa_1 + \kappa_2}{2}
\]

(Eq. B.2)

\[
K = \frac{1}{r_1 r_2} = \kappa_1 \kappa_2
\]

(Eq. B.3)
Appendix B. Interfacial curvature

Figure B.1 – Surface portion with the relative radii of curvature $r_1$ and $r_2$ (in this case they have equal sign).

The pair of principal curvatures measured on a meshed material interface (see Chapter 3 for a description of the measurement procedure) are commonly processed to generate a bivariate interfacial shape distribution (ISD), which provides a graphical representation of the interface morphology (Fig. B.2). Thereby, pairs of curvatures (on the two axes) define regions that correspond to distinct shapes and the distribution density provides the probability of finding such a shape in the microstructure.

respectively bumps ($\kappa_1$ and $\kappa_2 > 0$), saddles of the first type ($\kappa_1 > -\kappa_2$), saddles of the second type ($\kappa_1 < -\kappa_2$) and dimples ($\kappa_1$ and $\kappa_2 < 0$). Surfaces that lay on the 45° diagonal $\kappa_1=\kappa_2$ with positive slope have a spherical shape, while those on the two axes have cylindrical shape. In the case of negative $\kappa_2$, those surfaces surround the void at the interior. The origin of the plot represents a planar surface. The zones $\kappa_1 < \kappa_2$ are not populated, because of the principal curvature definition. Surfaces on the diagonal line $\kappa_1=-\kappa_2$ have null mean curvature, while the origin of the plot represents a planar surface (null mean and Gaussian curvatures).
A same interface can be measured from two opposite directions perpendicular to the surface, i.e., from the “inside” and the “outside”, e.g. Ni/Pore and Pore/Ni. In the case of perfect measurement, complementary ISDs are symmetrical with respect to the diagonal line $\kappa_1 = -\kappa_2$.

The evolution of the microstructure is driven by minimization of the mean curvature. The Gaussian curvature is relevant to uniquely characterize the surface shape. Indeed, a saddle surface characterized by inverse radii ($r_1 = -r_2$) has null mean curvature, but is not planar. The relation between the two quantities is Eq. B.4 [220], therefore the modification of one comports that of the other (Eq. B.5).

\[
\frac{H^2 - K}{K^2} = \text{const} \tag{B.4}
\]

\[
\frac{\partial}{\partial t} \left( \frac{H^2 - K}{K^2} \right) = \frac{2H}{K^2} \frac{dH}{dt} - \left( \frac{2H^2}{K^3} - \frac{1}{K^2} \right) \frac{dK}{dt} = 0 \tag{B.5}
\]

Intuitively, the mere minimization of the mean curvature would be insufficient to correctly describe...
the microstructure evolution: for instance, a saddle surface characterized by inverse radii \((r_1=-r_2)\) yields a null mean curvature, even though such an interface is not planar.
Further data of the heterogeneous kinetic reaction-diffusion H$_2$/H$_2$O model

As an example, the complete spatial surface coverage rate for the hydrogen adsorbed on Ni is visible in Eq. C.1. In particular, each forward and backward kinetic constant with the associated stoichiometric coefficient are multiplied by the surface concentrations of the species that are involved in the same reactions (in this case number 1, 4 and 5). Since a steady-state condition was enforced, the overall time dependent expression is null. The two boundaries conditions are displayed in Eq. C.2 and Eq. C.3.

\[
\frac{\partial \Theta_{H_{2}(Ni)}(x,t)}{\partial t} = D_{H_{2}(Ni)}^{eff} \frac{\partial^2 \Theta_{H_{2}(Ni)}}{\partial z^2} + \left[ 2k_{1,f}c_{H_{2}(Ni)}\Theta_{2(Ni)}^2 - 2k_{1,r}c_{H_{2}(Ni)}^2 c_{(Ni)} - k_{4,f}c_{H_{2}(Ni)} c_{O_{(Ni)}} + k_{4,r}c_{OH_{(Ni)}} c_{(Ni)} - k_{5,f}c_{H_{2}(Ni)} c_{OH_{(Ni)}} + k_{5,r}c_{H_{2}O_{(Ni)}} c_{(Ni)} \right] \Gamma_{Ni}^{-1}
\]

\[
-D_{H_{2}(Ni)}^{eff} \frac{\partial \Theta_{H_{2}(Ni)}}{\partial x} \bigg|_{x=0} = -\frac{q_{1} - q_{2}}{\Gamma_{Ni}}
\]

\[
\frac{\partial \Theta_{H_{2}(Ni)}(x)}{\partial x} \bigg|_{x=L_{Ni}} = 0
\]

Moreover, the Gibbs reaction enthalpy term is adopted to compute the thermodynamically consistent
Appendix C. Further data of the heterogeneous kinetic reaction-diffusion $H_2/H_2O$ model

backward kinetic rates of reactions "$m$" (Eq. 4.20). The expression is displayed through Eq. C.4, where "$\nu^f$" and "$\nu^r$" are the forward and reverse stoichiometric factors. The related molar enthalpy and molar entropy coefficients of the $i$-th species are showed Table C.1.

$$\Delta G_m = \sum v^f_{i,m}(h_i - TS_i) - \sum v^r_{i,m}(h_i - TS_i)$$  \hspace{1cm} (C.4)

<table>
<thead>
<tr>
<th>Species</th>
<th>$h_i$ [kJ/mol]</th>
<th>$s_i$ [J/molK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{2(g)}$</td>
<td>19.9</td>
<td>165.3</td>
</tr>
<tr>
<td>$H_2O(g)$</td>
<td>-217.8</td>
<td>231.5</td>
</tr>
<tr>
<td>$O_{2(g)}$</td>
<td>21.8</td>
<td>242.3</td>
</tr>
<tr>
<td>$(Ni)$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$H_{(Ni)}$</td>
<td>-32.7</td>
<td>39.6</td>
</tr>
<tr>
<td>$H_2O_{(Ni)}$</td>
<td>-281.6</td>
<td>122.5</td>
</tr>
<tr>
<td>$OH_{(Ni)}$</td>
<td>-199.7</td>
<td>99.6</td>
</tr>
<tr>
<td>$O_{(Ni)}$</td>
<td>-228.7</td>
<td>32.4</td>
</tr>
<tr>
<td>$V_O$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$O_O^{2-}$</td>
<td>-85.6</td>
<td>148.4</td>
</tr>
<tr>
<td>$(\chi)$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$O^{2-}_{(\chi)}$</td>
<td>-85.6</td>
<td>139.6</td>
</tr>
<tr>
<td>$OH^{2-}_{(\chi)}$</td>
<td>-173.8</td>
<td>124.5</td>
</tr>
<tr>
<td>$(Zr)$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$OH_{(Zr)}$</td>
<td>-208.8</td>
<td>124.5</td>
</tr>
<tr>
<td>$H_{(Zr)}^{-}$</td>
<td>90.3</td>
<td>37.0</td>
</tr>
</tbody>
</table>

*Table C.1 – Standard-state thermodynamic properties for $Ni$, $\chi$ and $Zr$ species at 700°C [4] ($H_2/H_2O$ model).*
Dihedral angles were calculated by measuring the angles between the segments that connect two interfacial points and the center of the four-voxels TPB (hereafter subscript “O”) (Chapter 6). As an example, Eq. D.1 expresses the relationship for the Ni dihedral angle \( \theta_{Ni} \), which depends on the three edges of the triangle defined by the three interfacial points.

\[
\theta_{Ni} = \cos^{-1}\left(\frac{d_{O-Ni/Pore}^2 + d_{O-Ni/YSZ}^2 - d_{Ni/YSZ-Ni/Pore}^2}{2d_{O-Ni/Pore} d_{O-Ni/YSZ}}\right)
\] (D.1)

where the distance “\( d_{i-O} \)” between each \( i-th \) point and the center “O” is computed from their Cartesian coordinates \( f_{i,t} \) (respectively “\( f_{i,x} \)” and “\( f_{i,y} \)”).

\[
d_{Ni-Pore} = \sqrt{\left(f_{Ni/Pore,x} - f_{O,x}\right)^2 + \left(f_{Ni/Pore,y} - f_{O,y}\right)^2}
\] (D.2)

Since this formulation does not allow the correct recognition of angles larger than 180°, a geometrical correction is implemented. In the case the TPB point lays outside the triangle, the largest angle must be corrected. At first, the coefficients \( \tau \) and \( \upsilon \) are computed by Eqs. D.3 and D.4:

\[
\tau = \frac{\omega}{|\omega|} \left( f_{Ni/YSZ,y} f_{Ni/Pore,x} - f_{Ni/YSZ,x} f_{Ni/Pore,y} + (f_{Ni/Pore,y} - f_{Ni/YSZ,y}) f_{O,x} + (f_{Ni/YSZ,x} - f_{Ni/Pore,x}) f_{O,y} \right)
\] (D.3)
Appendix D. Computation of dihedral angles

\[ v = \frac{\omega}{|\omega|} \left( f_{YSZ/Pore,y} f_{Ni/Pore,x} - f_{YSZ/Pore,x} f_{Ni/Pore,y} ight) \\
\quad + (f_{Ni/Pore,y} - f_{YSZ/Pore,y}) f_{O,x} \\
\quad + (f_{YSZ/Pore,x} - f_{Ni/Pore,x}) f_{O,y} \]  \hspace{1cm} (D.4)

And the coefficient \( \omega \) is defined as:

\[ \omega = \frac{1}{2} \left( - f_{YSZ/Pore,y} f_{Ni/YSZ,x} + f_{Ni/Pore,y} (- f_{YSZ/Pore,x}) \\
\quad + f_{Ni/YSZ,x} + f_{Ni/Pore,x} (f_{YSZ/Pore,y} - f_{Ni/YSZ,y}) \\
\quad + f_{YSZ/Pore,x} f_{Ni/YSZ,x} \right) \]  \hspace{1cm} (D.5)

The TPB point lays outside the triangle if one of the three statement Eq. D.6 is not valid. The largest computed angle is then adjusted by substitution with its reciprocal, with respect to 360°.

\[ \tau > 0, \quad v > 0, \quad (\tau + v) < 2 \frac{\omega^2}{|\omega|} \]  \hspace{1cm} (D.6)
Estimation of the variability in the measurements – test case on 15 kh SOFC sample (segment 12)

The results of first attempts to quantify the variability in the measurements are presented in this Appendix, by (i) estimating the convergence of the properties within a Volume and (ii) comparing the results from reconstructions of different regions within a same segment.

Measurements by dividing the pristine sample into 9 sub-Volumes of 6.375$^3 \mu m^3$ and 4 of 9.75$^3 \mu m^3$ do not differ largely, and are further similar to the values computed on the full Volume (mean of TPB, $d_{50}$, ISA and connectivity and volume fraction). The standard deviations are lower in measurements performed on the 4 larger Volumes, even though they are in general low. The maximum ratio of the standard deviation over the mean among the properties listed above occur for TPB measurements. They are 0.041 and 0.017 for the 6.375$^3 \mu m^3$ and 4 of 9.75$^3 \mu m^3$ subdivision, respectively. Further, the analysis performed for the measurements of the thermo-elastic properties on the same pristine Volume showed convergence around 9.3$^3 \mu m^3$ [221].

The variability in the measurements has been estimated further by comparing the properties measured from sampling a segment at two different locations (15 kh SOFC segment 12, both close to the YSZ electrolyte). The first of the two Volumes has been presented in Chapter 5 (Volume 8). Moreover, two smaller Volumes (10 $\mu m^3$) extracted from Seg. 12 were also analyzed for comparison (respectively Region 1 closer to the electrolyte and Region 2 to the inner part of the electrode). The values and differences in percentage respect to Seg. 12 are listed in Table E.1.
Appendix E. Estimation of the variability in the measurements – test case on 15 kh SOFC sample (segment 12)

Table E.1 – The values in brackets are the percentage difference with the Volume 7 reported in Chapter 5 (SOFC 15 kh segment 12).

<table>
<thead>
<tr>
<th></th>
<th>Seg. 12 (A)</th>
<th>Seg. 12 (B)</th>
<th>Seg. 12 (A) Region 1</th>
<th>Seg. 12 (A) Region 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dimensions [µm]</strong></td>
<td>-</td>
<td>17-10.7-14.6</td>
<td>17.8-11.5-14</td>
<td>10-10-10</td>
</tr>
<tr>
<td><strong>Vol. frac. [µm^3/µm^3]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore</td>
<td>0.26</td>
<td>0.27 (3.54%)</td>
<td>0.26 (0.89%)</td>
<td>0.25 (-3.99%)</td>
</tr>
<tr>
<td>YSZ</td>
<td>0.46</td>
<td>0.45 (-3.33%)</td>
<td>0.46 (-1.27%)</td>
<td>0.48 (2.76%)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.28</td>
<td>0.29 (2.25%)</td>
<td>0.28 (1.28%)</td>
<td>0.28 (-0.90%)</td>
</tr>
<tr>
<td><strong>d_{50} [µm]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ</td>
<td>0.42</td>
<td>0.40 (-4.76%)</td>
<td>0.41 (-2.24%)</td>
<td>0.42 (0.01%)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.62</td>
<td>0.63 (1.61%)</td>
<td>0.61 (-1.59%)</td>
<td>0.61 (-0.79%)</td>
</tr>
<tr>
<td><strong>Total TPB [µm/µm^3]</strong></td>
<td>-</td>
<td>6.5</td>
<td>6.6 (1.65%)</td>
<td>6.5 (0.62%)</td>
</tr>
<tr>
<td><strong>Connected TPB [µm/µm^3]</strong></td>
<td>-</td>
<td>4.8</td>
<td>4.9 (2.22%)</td>
<td>4.7 (-2.14%)</td>
</tr>
<tr>
<td><strong>ISA [µm^2/µm^3]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ/Pore</td>
<td>1.52</td>
<td>1.56 (2.33%)</td>
<td>1.53 (0.70%)</td>
<td>1.51 (-0.68%)</td>
</tr>
<tr>
<td>Ni/Pore</td>
<td>0.35</td>
<td>0.35 (1.13%)</td>
<td>0.35 (0.78%)</td>
<td>0.34 (-2.23%)</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>1.04</td>
<td>1.09 (4.62%)</td>
<td>1.05 (1.05%)</td>
<td>1.07 (2.56%)</td>
</tr>
<tr>
<td><strong>TSA [µm^2/µm^3]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ</td>
<td>2.56</td>
<td>2.65 (3.26%)</td>
<td>2.59 (0.84%)</td>
<td>2.58 (0.64%)</td>
</tr>
<tr>
<td>Ni</td>
<td>1.39</td>
<td>1.44 (3.75%)</td>
<td>1.40 (0.98%)</td>
<td>1.41 (1.36%)</td>
</tr>
<tr>
<td><strong>Contiguity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore</td>
<td>0.97</td>
<td>0.99 (1.81%)</td>
<td>0.98 (0.77%)</td>
<td>0.97 (0.43%)</td>
</tr>
<tr>
<td>YSZ</td>
<td>1.00</td>
<td>1.00 (0.00%)</td>
<td>1.00 (0.00%)</td>
<td>1.00 (0.00%)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.93</td>
<td>0.91 (-2.30%)</td>
<td>0.89 (-4.50%)</td>
<td>0.87 (-5.67%)</td>
</tr>
<tr>
<td><strong>S_v [µm^-1]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore</td>
<td>7.28</td>
<td>7.18 (-1.38%)</td>
<td>7.27 (-0.17%)</td>
<td>7.51 (3.15%)</td>
</tr>
<tr>
<td>YSZ</td>
<td>5.54</td>
<td>5.92 (6.81%)</td>
<td>5.66 (2.14%)</td>
<td>5.42 (-2.07%)</td>
</tr>
<tr>
<td>Ni</td>
<td>4.96</td>
<td>5.03 (1.46%)</td>
<td>4.95 (-0.29%)</td>
<td>5.08 (2.29%)</td>
</tr>
<tr>
<td><strong>Dihedral angles [°]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore</td>
<td>119.3</td>
<td>126.8 (6.26%)</td>
<td>119.3 (-0.04%)</td>
<td>119.7 (0.35%)</td>
</tr>
<tr>
<td>YSZ</td>
<td>96.4</td>
<td>97.1 (0.74%)</td>
<td>96.3 (-0.14%)</td>
<td>96.3 (-0.14%)</td>
</tr>
<tr>
<td>Ni</td>
<td>144.3</td>
<td>136.1 (-5.67%)</td>
<td>144.5 (0.13%)</td>
<td>143.9 (-0.22%)</td>
</tr>
</tbody>
</table>

In general, the measured properties between segments A and B differ within a range from 2% to 4%, above 6% for a few cases. The difference in volume fractions (±3.5%) is higher than anticipated and indicate that the microstructure is characterized by mild heterogeneity across distance larger than the typical ROIs in electron microscopy. It is expected to also pass on the analysis of volume-normalized properties, such as TPB and surface area densities.

As discussed in Chapter 5, dihedral angles are measurements of local features that may be more sensitive to the segmentation process, and they consequently present the highest volatility. It is interesting to notice that a reduction of the Ni angles comports a reciprocal increase of the pores angle, with YSZ remaining almost unchanged. Such difference is not due to a mismatch in the detected TPBs, since the total and effectively connected values display a good similarity (<2% difference). In fact, the position of the interfacial voxels surrounding the TPBs are determined by the watershed algorithm. In this regard, a better accuracy of the dihedral angles may be achieved by diminishing the voxel size. Among the ISA values, Ni/YSZ interface presents the higher difference (>4%). The variability of volume fractions and ISA values is combined in the surface-to-volume ratios, corresponding to difference higher than 6% in the YSZ case.
Lastly, the measured properties of the smaller regions 1 and 2 on average exhibit smaller difference with respect to segment 12 B, even though the variability in volume fractions does not change (up to 4% for Pore). The average values of dihedral angles are similar to segment 12 A (0.35% of maximum difference), suggesting the effect of the reconstruction process on the morphology near the three phases junctions.
ISD plots of the Volumes presented in Chapter 5

The ISDs of the eight Volumes presented in Chapter 5 are provided below. The diagonal dashed lines with negative slopes indicate constant mean curvature. The parabolic dashed lines instead refer to constant gaussian curvature.
Figure F.1 – YSZ/Pore interface ISD plots. The numbers are associated to the Volumes respectively presented in Chapter 5.
Figure E2 – Ni/Pore interface ISD plots. The numbers are associated to the Volumes respectively presented in Chapter 5.
Appendix F. ISD plots of the Volumes presented in Chapter 5

Figure F.3 – Ni/YSZ interface ISD plots. The numbers are associated to the Volumes respectively presented in Chapter 5.
The present Appendix firsts provides a brief overview on the theory of the electrical double layer. The second section describes the concept of “electrocapillarity”, or the dependency of the interfacial surface energy on the applied potential in case of an electrolytic solution. Lastly, focus is placed on the effects on the wettability (i.e. on the dihedral angles), defined as “electrowetting” phenomenon.

**G.1 Electrical double layer model**

At the boundary between a metallic electrode and an electrolyte, a double layer develops upon the application of a potential. It is characterized by the presence of positive and negative charges at equal distance in two liquid phases. Helmholtz described this layer as a parallel plate condenser of approximately 3 to 8 Å where a linear drop in potential occurs [199]. Gouy and Chapman expanded the concept by considering a subsequent and larger region where the charge distribution of ions decreases as a function of the distance from the metal surface [23]. In this case, the distribution of charges is described by the Poisson equation with a space charge density following the Boltzmann distribution. It decreases exponentially away from the surface. The difference between the Helmholtz and Gouy-Chapman models is illustrated in Fig. G.1. Hence, Stern integrated the two concepts into an extended model, in which few ions adhere to the electrode as suggested by Helmholtz (known as internal Stern layer), while the remaining form a Gouy-Chapman diffuse layer [222].

The capacity quantifies the charge stored between the two conducting surfaces separated by a dielectric. Grahame [24] defines the associated capacity of the Stern double layer ($C_D$) as a series
Figure G.1 – Distribution of charges and potential in a double layer, following Helmholtz (A) and Gouy and Chapman (B) descriptions, from [23]. \( \xi \) is along the direction perpendicular to the electrolyte.

The assembly of the Helmholtz capacity \( (C_H) \) and the Gouy-Chapman capacity \( (C_d) \):

\[
\frac{1}{C_D} = \frac{1}{C_H} + \frac{1}{C_d} \tag{G.1}
\]

Here, the non-linear Gouy-Chapman capacity (differential capacity) is provided by Eq. G.2, where "\( D \)" is the dielectric constant, "\( c_q \)" the concentration of charges in the diffuse double layer, "\( b \)" the elementary number of charges and "\( Q_e \)" the charge density on the metal surface:

\[
C_d = -\frac{dQ_e}{d\xi} \equiv bF \sqrt{\frac{Dc_q}{2\pi RT}} \frac{bF}{2RT} \cosh \frac{bF}{2RT} \xi \tag{G.2}
\]

"\( \xi \)" is defined as the zeta potential across the slipping plane in the diffusive double layer. In other words, it embodies the difference between the dispersion medium and the stationary layer attached to each dispersed particle. In the case of H\(_2\)/H\(_2\)O reactions, the zeta potential can be expressed as the natural logarithm of the ratio between the surface and the bulk concentration of ions (H\(^{+}\) or OH\(^{-}\)), hence as the pH of the medium.
G.2 Effects of applied potential on the interfacial surface tension - electrocapillarity

In the case of uncharged state, the surface tends to be minimized, while the presence of electrical charges has an inverse effect of repulsion [23]. The interaction between the excess charges comports a reduction of the potential energy of the charged species at the interface, and thus a consequent diminution of the interfacial tension. Therefore, such phenomenon contrasts the effects of the surface tension, and is independent of the direction of the applied potential.

The electrocapillarity theory predicts that the surface tension ($\gamma$) at the interface between electrode and electrolyte is a function of the applied potential ($\epsilon$) generated by the repulsion forces of the charges at the double layer, which is provided by the Lippmann-Helmholtz equation (Eq. G.3):

$$\frac{d\gamma}{d\epsilon} = -Qe$$  \hspace{1cm} (G.3)

The dependence between the interfacial tension and the applied potential is parabolic (Fig. G.2). The point of maximum interfacial tension (defined as the electrocapillarity maximum) signifies that the excess charge is zero both on the metal and on the electrolyte. At this point, the corresponding potential is defined as the pzc, where the electrical charge density on a surface is zero ($d\gamma/d\epsilon = -Qe = 0$) [222]. The experimental results shown in Fig. G.2 interestingly indicate that the pzc does not necessarily coincide with a potential of zero. Thus, the interfacial tension can either increase or decrease upon small applied potential, depending upon polarization direction. For sufficiently large applied potentials, the theory predicts a net diminution of tension.

![Figure G.2 – Dependence between applied potential and the interfacial tension of mercury in contact with different aqueous solutions. Image from [24].](image-url)
Upon polarization, the surface-specific energy required to charge the double layer of capacity “$C_D$” is subtracted from the original surface tension. The relationship between the two quantities is:

$$\frac{d^2\gamma}{d\epsilon^2} = C_D$$

(G.4)

Under the assumption of constant capacity, the surface tension can be therefore expressed by Eq. G.5, assuming a parabolic shape with the vertex at the maximum interfacial energy ($\gamma_{\text{max}}$) which corresponds to the maximum electrocapillary potential ($\epsilon_{\text{max}}$), defined as the pzc.

$$\gamma = \gamma_{\text{max}} - \frac{1}{2}C_D(\epsilon - \epsilon_{\text{max}})^2$$

(G.5)

In reality, this relationship is not perfectly parabolic (see Fig. G.2), and the differential capacity instead depends on the applied potential (Fig. G.3). In particular, close to the pzc, the Gouy-Chapman capacity ($C_d$) dominates for low concentrations, whereas the Helmholtz capacity ($C_H$) is predominant for large surface charge density (Eq. G.1).

Figure G.3 – Differential capacity $C_D$ of mercury at different electrolyte concentrations as a function of the applied potential. The value “$\epsilon_{\text{max}}$” corresponds to the pzc. Image from [23].
G.3  Effects of applied potential on wettability - electrowetting

The dihedral angle between the external surface of the particle and the interface with the adjacent particle or layer quantifies the wettability of the materials, as illustrated in Fig. G.4 where a liquid drop lays on a flat solid surface. The relation between the dihedral angle “θ” and the three interfacial tensions “γ_i” [223] is described by the Young equation applied to a flat solid surface (Eq. G.6). The interfacial tensions are expressed by Eq. G.7, where “F_H” is the Helmholtz free energy, “ISA_i” the area between the two phases and “μ” the chemical potential of the components.

\[
γ_{SV} - γ_{SL} = γ_{LV} \cos(θ) \quad (G.6)
\]

\[
γ_i = \left( \frac{F_H}{ISA_i} \right)_{T,H_j} \quad (G.7)
\]

The dihedral angle in the case of non-spreading liquid is higher than 0° and lower than 180°. A smaller angle indicates higher wettability, which in other words defines the adhesion of the particle to the surface. The same concept can be applied to solid-solid interfaces, where the wettability depends on the materials.

As mentioned in the previous Section “Effects of applied potential on interfacial surface tension – electrocapillarity”, the interfacial tension between electrode and electrolyte is affected by the applied potential, because of the presence of a double layer. Hence, it is possible to modify the dihedral angle by applying a voltage difference between a liquid droplet and solid electrode covered by a dielectric layer. This phenomenon was confirmed experimentally and referred to as “electrowetting” [25, 196, 197]. Under this assumption, only the tension γ_{SL} can be varied, while the other two remain unaffected, which results in a direct dependence with the dihedral angle (Eq. G.6). The combination Eq. G.5 and Eq. G.6 and assumption of constant capacity (C) yields Eq. G.8, where θ_0 is the angle in
Appendix G. Electrocapillarity

the case of $\epsilon_{\text{max}}$ (or pzc) \[224\].

\[
\cos(\theta(\epsilon)) = \cos(\theta_0) + \frac{1}{\gamma_{LV}} \int_{\epsilon_{\text{max}}}^{\epsilon} C \epsilon \, d\epsilon = \cos(\theta_0) + \frac{C(\epsilon - \epsilon_{\text{max}})^2}{2\gamma_{LV}} \tag{G.8}
\]

The reason for Eq. G.8 is schematized in Figs. G.5. The dihedral angle is maximum in the case of maximum interfacial tension $\gamma_{SL0}$ (Fig. G.5A). It is indeed a measure of the ratio between the electrostatic energy per unit area of the parallel plate capacitor and the surface tension of the liquid drop \[225\]. Deviation from that condition results in a decrease of the dihedral angle (Fig. G.5B), until the minimum value $\theta_{\text{min}}$ in the extreme case of $\gamma_{SL} = 0$ (Fig. G.5C). It is important to note that the dihedral angle cannot be larger than the maximum value $\theta_0$ because the potential is raised to the power of two in Eq. G.8.

\[
\cos(\theta_{\text{min}}) = \frac{\gamma_{SV}}{\gamma_{LV}} \tag{G.9}
\]

Figure G.5 – Saturation model (solid phase in grey, liquid droplet in pink and vapor in white). (A): maximum dihedral angle $\theta_0$ related to the maximum interfacial energy $\gamma_{SL0}$ (at pzc). (B): decrease of both $\theta$ and $\gamma_{SL}$ upon applied potential. (C): point of minimum angle $\theta_{\text{min}}$ in the case of $\gamma_{SL} = 0$. Image adapted from \[25\].
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Education

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- Thesis title: "Long-term evolution of solid oxide fuel and electrolysis cells 3-D microstructure".

Oct 2011 – Mar 2014
M.Sc., Energy and Nuclear Engineering, Politecnico di Torino (Torino, Italy).
Thesis: Study of the $CO_2$ sequestration in a molten carbonate fuel cell tri-generation plant
Supervisor: Prof. Massimo Santarelli, Dr. Andrea Lanzini, Prof. Jack Brouwer

Sep 2008 – Oct 2011
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List of publications

May 2017
Strontium migration at the GDC-YSZ interface of solid oxide cells in SOFC and SOEC modes.

Feb 2017
Post-test analysis on a Solid Oxide Cell stack operated for 10700 hours in steam electrolysis mode.

Jul 2015
Steam and co-electrolysis sensitivity analysis on Ni-YSZ supported cells.
G. Rinaldi, S. Diethelm, J. Van herle, ECS Transactions, 68 (2015), 3395 - 3406

Feb 2015
Study of the $CO_2$ sequestration in a molten carbonate fuel cell tri-generation plant.

Experiences

Business Concept, CTI Entrepreneurship (Lausanne, Switzerland).
The course provides the practical tools to transform an idea into a strong business project

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Mechatronic manager, Bosch (Milano, Italy).
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Tools

Languages  Matlab, Python
           OS  Windows, Linux, MacOS
           CAD  Solid Works, AutoCad, DraftSight
           CFD  Comsol, gPROMS
           Office  Word, Excel, Power Point

Languages

Italian  Mother tongue
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French  Level: B2