

An effective Pd-Ni₂P/C anode catalyst for direct formic acid fuel cell

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(([†]J.F Chang and L.G. Feng contributed equally to this work))

Abstract. Direct formic acid fuel cell is an emerging energy conversion device for which palladium (Pd) is considered as the state-of-the-art anode catalyst. In this communication, we show that the activity and stability of palladium for formic acid oxidation can be significantly enhanced using nickel phosphide (Ni₂P) nanoparticles as a co-catalyst. X-ray photoelectron spectroscopy (XPS) reveals a strong electronic interaction between Ni₂P and Pd. A direct formic acid fuel cell incorporating the best Pd-Ni₂P anode catalyst exhibits a power density of 550 mW/cm², 3.5 times of that of an analogous device using a commercial Pd anode catalyst.

Direct formic acid fuel cells are considered as a promising power source for portable electronic devices. The development of active anode catalysts for the oxidation of formic acid is therefore an active area of research.^[1] Pd-based catalysts have recently drawn attention because they can catalyze the oxidation of formic acid by a direct path which reduces the poisoning effect associated with conventional Pt catalysts.^[2] Increasing the activity of Pd can lead to a lower usage of this rare and costly metal. Several nanostructure Pd catalysts exhibited a high performance for formic acid oxidation; however, these catalysts were synthesized under harsh conditions and required cumbersome post-treatments.^[2b, 3] Addition of Ni, Co, Fe, P or N to Pd is reported to enhance the latter's catalytic activity.^[4] Unfortunately the dissolution or instability of the promoter elements resulted in a rapid decay of catalytic performance.

Herein, we demonstrate Ni₂P as a stable co-catalyst for Pd-catalyzed formic acid oxidation. The Pd-Ni₂P/C anode system shows remarkable catalytic activity and stability. When

integrated in a direct formic acid fuel cell, the hybrid catalyst gives a superior power density and discharge stability than several state-of-the-art catalysts.

The Ni₂P/C particles were synthesized by a solid phase reaction. Pd was deposited onto Ni₂P/C by a microwave-assisted ethylene glycol reduction method (see the Supporting Information for details). The Raman spectra of Ni₂P/C particles display two very distinctive D and G bands at 1331 and 1589 cm⁻¹, respectively (Figure S1). The D band arises from structural defects in the graphitic plane, while the G band is related to the E_{2g} vibrational mode of the sp² bonded graphitic carbons. In the XRD pattern of the Ni₂P/C, the diffraction peaks due to Ni₂P are visible (Figure S2). These peaks are not observed in the XRD pattern of Pd-Ni₂P/C. However, the presence of Ni₂P was confirmed by EDS (Figure S3g) and the element distribution maps (Figure S3a-f). Typical TEM images of Ni₂P/C and Pd-Ni₂P/C (30 wt% of Ni₂P on C) are shown in Figure 1. The Ni₂P nanoparticles can be observed with a finger lattice of 0.221 nm corresponding to its (111) lattice (Figure 1a).^[5] After deposition of Pd, the Pd nanoparticles were uniformly distributed on the Ni₂P/C hybrid support with a narrow size distribution; the average particle size of Pd is about 3.5 nm (Figure 1b and d), which is an optimal particle size for formic acid oxidation.^[1g, 2e, 6] Finger lattices of Ni₂P and Pd can be both observed (Figure 1c). The particle size of Pd in other samples where the wt% of Ni₂P on C varied was also about 3.5 nm (FigureS4).

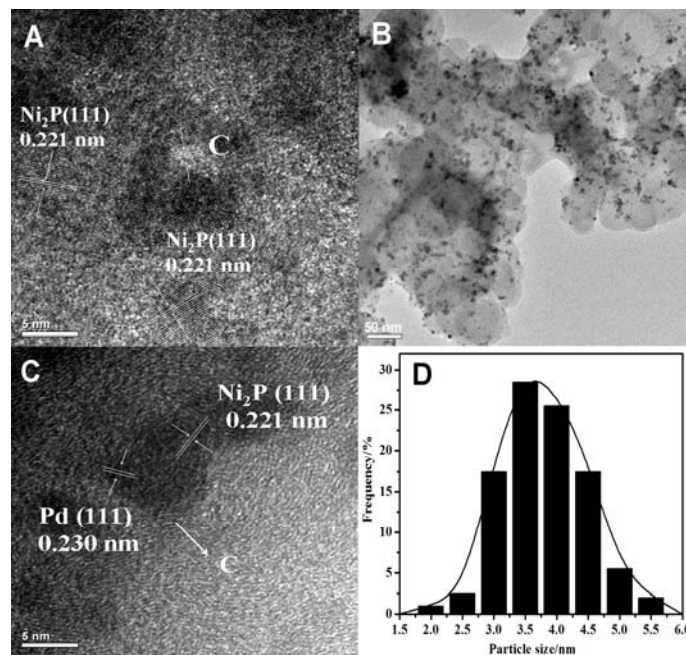


Figure 1 (A) A HRTEM image of Ni₂P/C where the (111) lattice of Ni₂P can be observed; the carbon support is also visible. (B) A TEM image of Pd-Ni₂P/C catalyst. (C) A HRTEM image of Pd-Ni₂P/C catalyst; both Pd(111) and Ni₂P(111) lattices can be observed and the carbon support is visible.; (D) The size distribution of Pd-Ni₂P/C catalyst.

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Typical Pd electrochemical behaviors for all Pd-Ni₂P/C samples were observed in 0.5 M H₂SO₄ (Figure S5). The Pd-Ni₂P/C (30 wt% of Ni₂P on C) catalyst shows the largest electrochemical surface areas (ECSA) according to the area of the hydrogen desorption peaks (Table S1). The more accurate ECSA obtained from CO-stripping experiments (Figure S6) were used to calculate the specific activity for all catalysts. The peak potential of the adsorbed CO is commonly used as a tool to compare the anti-poisoning ability.^[1b, 1e] The Pd-Ni₂P/C (Ni₂P-30 wt%) catalyst has the most negative peak potential (Table S1) indicating this material has the best anti-poisoning ability.

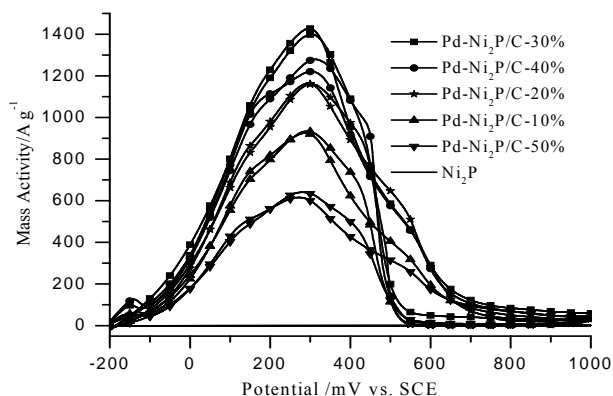


Figure 2 Cyclic voltammograms of Ni₂P and Pd-Ni₂P with different amounts of Ni₂P in 0.5 M H₂SO₄ solution containing 0.5 M HCOOH at 50 mV s⁻¹.

The activity of Pd-Ni₂P/C catalysts with different wt% of Ni₂P was compared (Figure 2 for mass activity; Figure S7 for specific activity; Table S2 for overall comparison). Ni₂P alone has almost no catalytic activity, but it has a strong influence on the activity of Pd. The optimized loading is 30% Ni₂P on C. The Pd-Ni₂P/C-30% catalyst has the best catalytic stability according to chronoamperometric (CA) measurements (Figure S8). Electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) were applied to investigate the influence of Ni₂P loading. According to EIS (Figure S9), it is hypothesized that more formic acid is oxidized around the peak potential at the Pd-Ni₂P/C-30% catalyst, probably due to a reduced passivation at Pd. In the XPS spectra, a shift of Pd binding energy was observed (vide infra); this shift was the same among all samples with different Ni₂P loadings (Figure S10). Thus, the optimal loading of Ni₂P likely arises from a balanced interaction between the Pd and Ni₂P, but not simply from an optimal electronic effect which would have been detected by XPS.

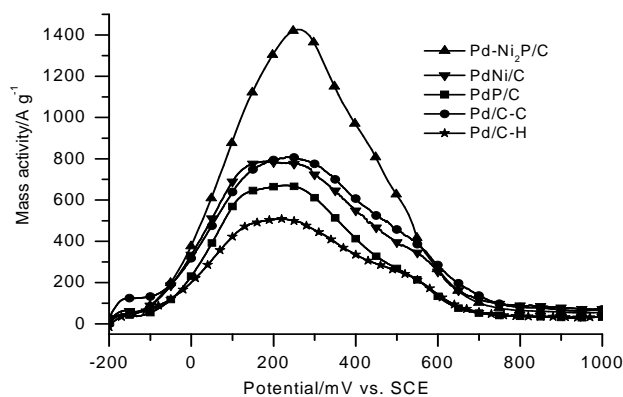


Figure 3 Linear sweep voltammograms of Pd-Ni₂P-30%, PdNi/C, PdP/C, Pd/C-C and Pd/C-H in 0.5 M H₂SO₄ solution containing 0.5 M HCOOH at 50 mV s⁻¹.

The Pd-Ni₂P/C-30% catalyst was compared with state-of-the-art commercial Pd/C (Pd/C-C) catalyst, home-made Pd/C (Pd/C-H), PdNi/C and PdP/C catalysts by linear sweep voltammetry (Figure 3 for mass activity and Figure S11 for specific activity). Among all these catalysts, the Pd-Ni₂P/C-30% exhibits the best activity for formic acid oxidation. Pd-P/C and Pd-Ni/C perform slightly better than Pd/C-C, but are largely inferior than Pd-Ni₂P/C. The promotional effect of Ni₂P is therefore much larger than P or Ni alone. The Tafel slopes of these catalysts were also compared (Fig S12), and Pd-Ni₂P/C-30% has the smallest Tafel slope (Table S3), which is advantageous for practical applications. Furthermore, the specific activity of Pd-Ni₂P/C-30% compares favorably with other recently reported catalysts (Table S4). The stability of catalysts was probed by chronoamperometric measurements with stationary and rotating disk electrodes (Figure S13). The Pd-Ni₂P/C-30% catalyst exhibits the best stability for formic acid oxidation, with the highest stable currents.

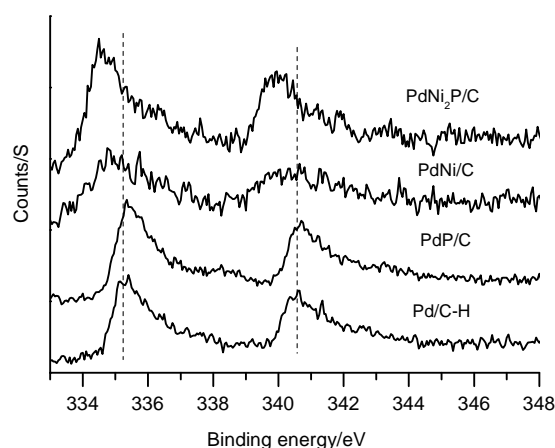


Figure 4 XPS spectra of Pd 3d region for Pd-Ni₂P/C-30%, PdNi/C, PdP/C, and Pd/C-H.

XPS was applied to probe the origin of the promotional effect of Ni₂P. From Pd to Pd-Ni₂P/C (Figure 4), the Pd 3d peaks are shifted significantly, by about 1 eV, to a lower binding energy. This shift might be attributed to a partial electron transfer from Ni₂P to Pd; this would increase the electron density of Pd and enhance the penetration of outer-layer electron to the

inner layer.^[7] This results in higher shielding of the nuclear charge and weakens the binding of 3d electrons. On the other hand, the Pd 3d peaks are not substantially shifted from Pd to PdNi/C and PdP/C. These results suggest that the enhanced activity and stability of Pd-Ni₂P/C might be attributed to a strong electronic interaction between Pd and Ni₂P. In addition to the electronic effect, Ni₂P might directly participate in formic acid oxidation. Recently, Ni₂P was found to be an effective hydrogen evolution catalyst.^[8] Hydrogen adsorption might be facile on Ni₂P, which might accelerate the formic acid oxidation similar to the hydrogen spill-over effect.^[9] Ni₂P might also activate water, producing -OH_{ads} to oxidize CO and other poisoning intermediates adsorbed at adjacent Pd sites through the so-called bi-functional mechanism.^[1g, 10] More work is required to testify these mechanistic hypotheses.

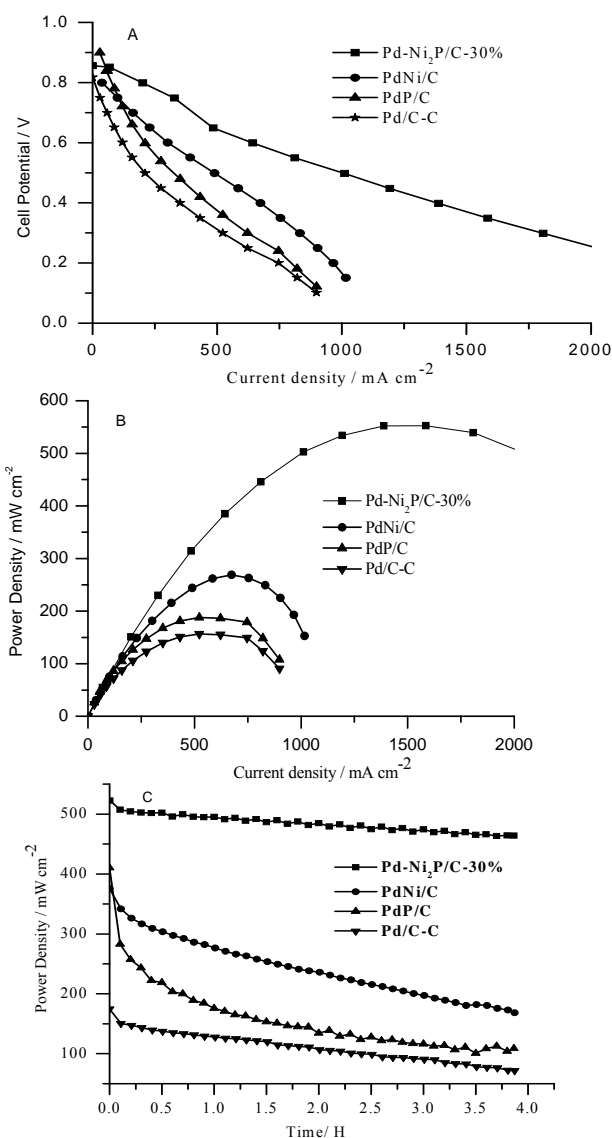


Figure 5. (A) Steady-state polarization, (B) power-density curves and (C) discharge curves at 0.35V for Pd-Ni₂P-30%, PdNi/C, PdP/C and Pd/C-C as anode catalysts for direct formic acid fuel cell with 3 M formic acid at 30 °C. The flowing rate of formic acid was 200 mL min⁻¹ and the flowing rate of O₂ was 500 mL min⁻¹.

To demonstrate the potential of the Pd-Ni₂P/C catalyst in a direct formic acid fuel cell, the catalyst was integrated at the

anode of a home-made fuel cell. The steady-state polarization and power-density curves of several catalysts were compared (Figure 5a and 5b). Consistent with the results from electrochemical measurements, the Pd-Ni₂P/C-30% catalyst exhibits the highest power density. This power density of 550 mW/cm² is about 2 times of that of PdNi/C, 3 times of that of PdP/C, and 3.5 times of that of state-of-the-art Pd/C commercial catalyst. Moreover, the Pd-Ni₂P/C catalyst also shows the most stable discharge ability at 0.35 V (Figure 5C). These results confirm the promising activity of Pd-Ni₂P/C for direct formic acid fuel cell.

In summary, a novel Pd-Ni₂P/C electrocatalyst was developed for formic acid oxidation. The catalyst exhibited excellent activity and stability, and was successfully integrated into a direct formic acid fuel cell, showing superior performance than state-of-the-art Pd/C catalyst. The work is a significant step towards the development of more active and practical catalysts for direct formic acid fuel cell.

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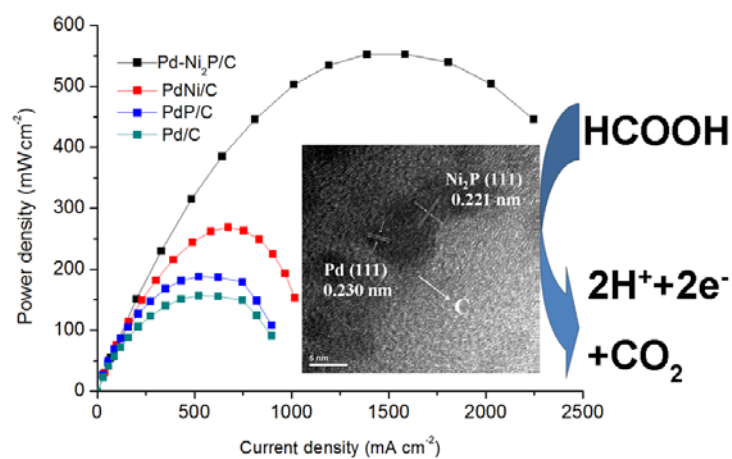
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Electrocatalysis

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A novel Pd-Ni₂P/C electrocatalyst was developed for formic acid oxidation. A direct formic acid fuel cell integrating this catalyst showed superior power density and discharge stability than state-of-the-art commercial Pd/C catalyst.