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Pd-based Bimetallic Core-Shell Catalysts for Direct Formic Acid Fuel Cells

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Direct formic acid fuel cell (DFAFC) is a potential power generator for portable electronic devices. DFAFCs have many advantages over H_2 proton exchange membrane (PEM) fuel cells and direct methanol fuel cells (DMFCs) due to its non-toxicity, easy to store and transport, and low crossover flux through membrane [1, 2]. Among all anode catalysts, Pd has attracted a lot of attention due to its superior catalytic activity towards formic acid electro-oxidation. However, it is expensive and shows a poor long-term stability due to surface poisoning caused by intermediate species that form during the oxidation reaction [3]. To minimize the poisoning, improve the performance and lower the cost, Pd-based bimetallic catalysts are investigated.

We found that a change in the electronic structure of the Pd surface significantly alters the activity and stability of Pd towards formic acid electro-oxidation, as well as the hydrogen desorption energy, for flat layered Pd-based bimetallic catalysts that is about 5 nm Pd film deposited on various metals, such as Co, Cu, Au, and Ag (see Figure 1).

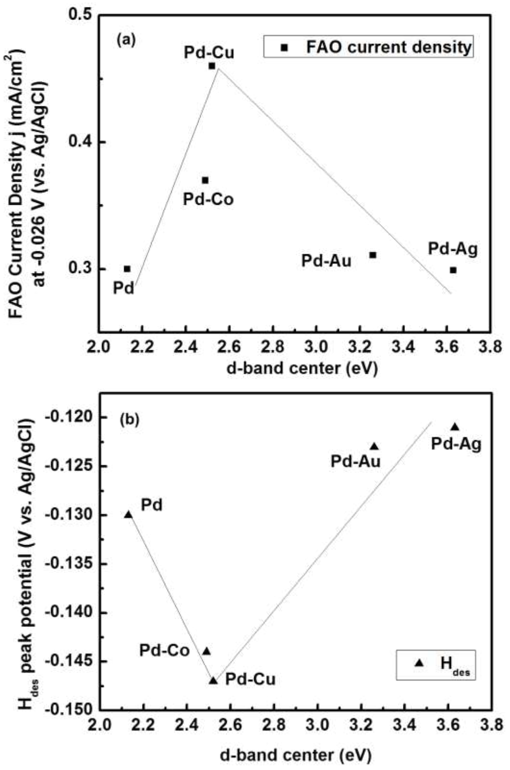

Figure 1: Relationship between the formic acid oxidation (FAO) current density and d-band center (a), and the hydrogen desorption potential and d-band center (b), for flat layered Pd, Pd-Co, Pd-Cu, Pd-Au, and Pd-Ag bimetallic samples.

In this study, M-Pd (M = Au, Ru, Cu, etc.) bimetallic core-shell nanoparticles with Pd as the shell are prepared. The particles (size and shape) are characterized by TEM. X-ray photoelectron spectroscopy (XPS) analysis shows a binding energy (BE) shift of Pd peaks to a higher binding energy, while M peaks shifts to an opposite direction compared to their pure metal states. Those opposite binding energy shifts indicate that there is charge transfer from Pd to M (M = Au, Ru, Cu, etc.). In addition, a change of the valence band shape and shift of the d-band center away from the Fermi level are also observed in the XPS valence bands for the M-Pd samples with the different core M metals. This electronic perturbation of M-Pd system results in an alteration of the interaction between the intermediate species and the Pd surface. As a result, changes in current density and stability of formic acid electro-oxidation are observed in cyclic voltammetry (CV) and chronoamperometry (CA) tests for the bimetallic systems compared to pure Pd nanoparticles. For this paper, the binding energy shift of Pd peaks and d-band center shift of the M-Pd nanoparticles are correlated to their activity and stability toward formic acid electro-oxidation.

References

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