Nanoalloys as catalysts for fuel cell application: A combined theoretical and experimental study

Daojian Cheng[1]

[1] *State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, P.R. China*

Presenting author: chengdj@mail.buct.edu.cn

With respect to the catalysts in fuel cells, Pt-based alloy surfaces and nanoalloys have been employed to prevent the CO poisoning and to improve the oxygen reduction reaction (ORR) catalytic activity of pure Pt electrocatalysts [1,2]. In addition, Pd-based nanoalloys show higher formic acid oxidation (FAO) activity than commercial Pd/C. Here, molecular simulation, first principles density functional theory (DFT) calculations and experiments have been used to study the oxygen reduction reaction (ORR) and formic acid oxidation (FAO) activity of transition metal alloy surfaces and nanoalloys [3-5].

For alloy surfaces [3], it is found that the Pt(111) with subsurface Ni, which is modeled by replacing the subsurface layer of Pt(111) with a single layer of Ni, displays the best CO tolerance and highest oxygen reduction reaction (ORR) activity, compared with the other Pt-Ni surfaces. Similar results are also found for other alloy surfaces, such as Pt(111) with subsurface Co, Fe, Mn, Sc, or Ti.

For nanoalloys [4], the composition-dependent search process shows that, among the 55-atm Pd-Pt nanoalloys with different composition, the three-shell onion-like structure Pd-Pt nanoalloy (TS-cluster) exhibits the highest stability and ORR activity. Moreover, computer screening of composition, structures, and new elements alloying with Pt is used to design new nanoalloys for the ORR.

In experiments [5], shape-controlled snthesis of PdCu nanocrystals (NCs) for FAO was studied, and the mass activities of these carbon-supported NCs follow the order of sphere PdCu/C > sphere-like PdCu/C > cubic PdCu/C. In addition, we synthesize Cu@CuPt core@shell nanowires (NWs) with 1D nanostructure by using Cu NWs as templates in organic solvent medium. The ORR mass activity and specific activity of PtCu NWs are 3.1 and 3.7 times larger than that of the commercial Pt/C catalyst. Theoretical studies suggest that the electronic effect of the Cu substrate on the Pt monolayer could be the main reason for the higher activity of PtCu NWs than that of the commercial Pt/C catalyst. In addition, a core-shell Cu@Pd nanowire with enhanced activity and stability for formic acid oxidation (FAO) was prepared by decorating Pd shell on the surface of Cu nanowire. The catalytic activity of Cu@Pd/C toward FAO is about 4 times higher than that of the commercial Pd/C. The enhanced activity of the catalyst may mainly result from the synergetic effect of Cu and Pd, which was confirmed by DFT calculations.

References:

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