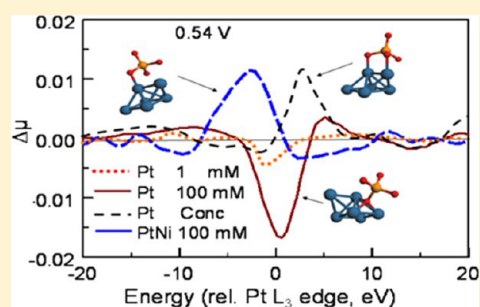


Mitigating Phosphate Anion Poisoning of Cathodic Pt/C Catalysts in Phosphoric Acid Fuel Cells

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S Supporting Information

ABSTRACT: The effect of phosphate anion poisoning of cathodic Pt-based catalysts in phosphoric acid fuel cells was investigated by observing the kinetics of the oxygen reduction reaction (ORR) in the presence of varied concentrations of H₃PO₄. In an attempt to reduce phosphate anion poisoning, a Pt-based Ni alloy catalyst was synthesized. Detailed electrochemical and X-ray absorption spectroscopy investigations have been carried out on both Pt and PtNi electrocatalysts under in situ conditions. It was found that the phosphate poisoning effect on the ORR is much less severe on PtNi/C than on Pt/C. The $\Delta\mu$ X-ray absorption near-edge spectroscopy analysis suggests that the adsorbed phosphate anions actually remain to higher potential on PtNi than on Pt, and this inhibits OH adsorption from water activation and the conversion from OH to O, thus allowing more sites for the ORR. Due to the presence of phosphate anions on the atop sites of PtNi/C, OH cannot occupy such sites now either due to steric hindrance or just lower availability of atop sites, and thus, it appears to keep the remaining sites (2-fold and 3-fold) free for molecular oxygen to undergo the ORR.



1. INTRODUCTION

Phosphoric acid fuel cells (PAFCs) that utilize aqueous phosphoric acid as electrolyte have been commercialized successfully and used for many stationary applications.¹ However, further improvements are necessary in order to retain their current position in the market as one of the most widely used fuel cell types for stationary power.² The most favored cathodic material for the oxygen reduction reaction (ORR) in PAFCs is still carbon supported Pt in high-surface-area form. Over the years, extensive studies have been devoted to improving the catalysts, such as making the smallest possible Pt particles to increase the dispersion,³ preparing patterned platinum surfaces with cyanide to enhance the ORR,⁴ or preparing Pt-MO₂/C (M = Ce, Zr, Pr, Ce_{0.9}Zr_{0.1}) electrocatalysts with significantly enhanced stability,^{5,6} and so on. However, the performance of PAFCs is still limited primarily by the strong adsorption and poisoning of the Pt sites by the phosphate anions.⁷

In aqueous solution with a large range of pH, the phosphate anions may compete with hydrogen, oxygen, and hydroxide species for platinum adsorption sites, which in turn impacts the ORR negatively.⁸ The adsorption of phosphate anions on Pt presents an additional complication in the sense that phosphoric acid has polyprotic properties with three proton dissociation constants. Thus, the species and mode of phosphate anion adsorption on Pt is highly dependent on the pH, but also on the potential, and the morphology and crystal orientation of the Pt, and so on.^{8–10} Further, it has been

clarified that the high sensitivity of the ORR performance to the structure of the catalyst stems primarily from the structure-sensitive adsorption of the phosphate anions.^{11,12}

Tanaka et al. proposed that phosphate anions adsorb with three oxygen atoms on a Pt(111) surface in a 3-fold site, but with only one or two oxygen atoms involved on Pt(100) and Pt(110) surfaces.¹³ This is consistent with the most pronounced poisoning effect by phosphate anions observed on Pt(111) surfaces, as compared to that on Pt(100) and Pt(110) surfaces.¹² From these results, it is reasonable to deduce that the adsorption of phosphate anions on Pt could be suppressed in part by altering the crystalline facets on the surface. In another approach to overcoming the phosphate anion poisoning problem, Pt(111)Sn has shown the tendency to mitigate anion adsorption on Pt in acid media by freeing more active sites via an apparent electronic or ligand effect, but this is yet to be fully understood.¹² In either case, the addition of a second atom type has been shown to help free Pt sites from phosphate anions, thereby enhancing the ORR.

Following this line of reasoning, a study of the extent of phosphate anion poisoning of a Pt/C catalyst alloyed with Ni in a PAFC is explored in this work. A wide array of electrochemical techniques [cyclic voltammetry (CV), ORR Tafel plots, CO stripping] were performed in 0.1 M HClO₄

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