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Influence of phosphoric anions on oxygen reduction reaction activity of platinum, and strategies to inhibit phosphoric anion adsorption

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ABSTRACT

Nafion-membrane-based proton exchange fuel cells (PEMFCs) typically operate at below 100 °C. However, H₃PO₄-doped polybenzimidazole (PBI)-based PEMFCs can operate at 100–200 °C. This is advantageous because of accelerated reaction rates and enhanced tolerance to poisons such as CO and SO₂, which can arise from reformed gas or the atmosphere. However, the strong adsorption of phosphoric anions on the Pt surface dramatically decreases the electrocatalytic activity. This study exploits the “third-body effect”, in which a small amount of organic molecules are pre-adsorbed on the Pt surface to inhibit the adsorption of phosphoric anions. Pre-adsorbate species inhibit the adsorption of phosphoric anions, but can also partially occlude active sites. Thus, the optimum pre-adsorbate coverage is studied by correlating the oxygen reduction reaction (ORR) activity of Pt with pre-adsorbate coverage on the Pt surface. The influence of the pre-adsorbate molecule length is investigated using the organic amines, butylamine, octylamine, and dodecylamine, in both 0.1 mol/L HClO₄ and 0.1 mol/L H₃PO₄. Such amines readily bond to the Pt surface. In aqueous HClO₄ electrolyte, the ORR activity of Pt decreases monotonically with increasing pre-adsorbate coverage. In aqueous H₃PO₄ electrolyte, the ORR activity of Pt initially increases and then decreases with increasing pre-adsorbate coverage. The maximum ORR activity in H₃PO₄ occurs at a pre-adsorbate coverage of around 20%. The effect of molecular length of the pre-adsorbate is negligible, but its coverage strongly affects the degree to which phosphoric anion adsorption is inhibited. Butylamine adsorbs to Pt at partial active sites, which decreases the electrochemically active surface area. Adsorbed butylamine may also modify the electronic structure of the Pt surface. The ORR activity in the phosphoric acid electrolyte remains relatively low, even when using the pre-adsorbate modified Pt/C catalysts. Further development of the catalyst and electrolyte is required before the commercialization of H₃PO₄-PBI-based PEMFCs can be realized.

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1. Introduction

Nafion-membrane-based proton exchange fuel cells (PEM-

FCs) typically operate at below 100 °C. However, H₃PO₄-doped polybenzimidazole (PBI)-based PEMFCs can operate at 100–200 °C, so are known as high-temperature PEMFCs* Corresponding author. Tel: +86-411-84379603; E-mail: sunshine@dicp.ac.cn# Corresponding author. Tel: +86-411-84379063; E-mail: gqsun@dicp.ac.cn

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(HT-PEMFCs). This is advantageous because of accelerated reaction rates and enhanced tolerance to poisons such as CO and SO₂, which can arise from reformed gas or the atmosphere. The higher operation temperature also simplifies water management of the single phase. HT-PEMFCs are highly efficient and environmentally benign power generators, so have extensive application prospects in power stations and potable power sources [1]. Phosphoric acid-doped PBI is a “state-of-the-art” electrolyte in HT-PEMFCs as it possesses high conductivity and superior stability at temperatures as high as 200 °C [2–6]. H₃PO₄ is doped into the PBI and also added to the catalyst layer to facilitate proton transfer. Unfortunately, H₃PO₄ also tends to adsorb on the Pt surface, which occludes Pt active sites and degrades its catalytic activity [7]. There is an ~38–93-mV loss in the half-wave potential of the cathodic oxygen reduction reaction (ORR) of Pt in the presence of H₃PO₄ compared with that in pure HClO₄ electrolyte. The exact loss depends on the dominant exposed facet of the Pt, and occurs at H₃PO₄ concentrations as low as 1 mmol/L [8].

In the past, phosphoric anion adsorption on the Pt surface has attempted to be mitigated by modifying the electronic structure [9] or tuning the geometric configuration of Pt [10]. Pt alloys such as PtNi and PtCo exhibit a d-band center that is down-shifted compared with that of Pt. This down-shift results in weaker adsorption of phosphoric anions and hydroxide anions [11]. The situation is different for PtAu alloys, in which the d-band center of the Pt is up-shifted. Nevertheless, better ORR activity of PtAu was observed in H₃PO₄ electrolyte compared with Pt. This was explained by the geometric effect, where phosphoric anions preferentially adsorb at “three-fold sites” on the Pt surface [8,12,13]. The presence of such sites is lower on the PtAu alloy surface because Pt atoms are isolated by Au atoms [14].

Another strategy was recently proposed to suppress phosphoric anion adsorption. This involves pre-adsorbing CN⁻ and other molecules on the Pt surface. This decreases the availability of three-fold sites on the Pt surface and thus suppresses phosphoric anion adsorption. This has been referred to as the “third-body effect” [15,16]. Pre-adsorbates suppress the adsorption of phosphoric anions, but sacrifice partial Pt active sites. Thus, the catalytic activity of Pt depends on the pre-adsorbate coverage. Markovic et al. [17] investigated poisoning of the Pt(111) surface by sulfuric anions, and correlated the pre-adsorbate surface coverage (θ_{CNad}) with the ORR activity in 0.05 mol/L H₂SO₄. A small change in θ_{CNad} had a dramatic effect on the ORR activity and peroxide production. When the electronic and ensemble effects of adsorbed spectators were balanced, the ORR activity exhibited a bell-shaped dependence on coverage, at a θ_{CNad} of 0.3 ML (atomic monolayer). As well as acting as a third body, electron-donating pre-adsorbates reportedly modify the electronic structure of Pt in Pt alloys, thus improving the catalytic activity [9,18–21].

Amine functional groups readily bond with Pt and their N atoms can potentially donate electrons to transition metals [9,22–24]. In the current study, butylamine (BA) is used as a pre-adsorbate. The influence of BA coverage on the ORR activity of a smooth Pt bulk electrode is investigated in 0.1 mol/L

HClO₄ and 0.1 mol/L H₃PO₄. The influence of the length of the pre-adsorbate molecule on the ORR activity of a Pt/C catalyst is then investigated in 0.1 mol/L HClO₄ and 0.1 mol/L H₃PO₄. A series of organic amines, BA, octylamine (OA), and dodecylamine (DA) is used for this purpose.

2. Experimental

2.1. Preparation of working electrode

2.1.1. Modification of the smooth Pt bulk electrode

Before modification, the Pt bulk electrode (diameter of 5 mm, geometric surface area of 0.196 cm²) was polished using 50 nm Al₂O₃ paste, and then cleaned consecutively in concentrated sulfuric acid and sodium hydroxide. Two μ L of BA solution (0.01 mmol/L in ethanol) was pipetted onto the Pt surface. Evaporation of the ethanol yielded the BA-modified Pt bulk electrode.

2.1.2. Modification of the Pt/C catalyst

Fifty mg of Pt/C catalyst (Johnson Matthey, HISPECTTM4000, 40 wt% Pt) was wetted by distilled water, and then dispersed in ethanol to form a uniform ink of concentration of 1 mg/mL. Four μ L of BA was then dissolved in ethanol, and was added dropwise to the catalyst ink under ultrasonication. The ink was then filtered, washed with ethanol, and dried under vacuum. The obtained sample was denoted as BA-Pt/C. Replacing BA with OA or DA yielded OA-Pt/C and DA-Pt/C, respectively.

2.1.3. Preparation of the thin film electrode

The preparation of the thin film electrode is described elsewhere [25,26]. Briefly, the catalyst powder was dispersed in a water/5 wt% Nafion-ionomer/ethanol solution (1:1:100, v/v/v), to form a uniform ink of concentration of 2.5 mg/mL. A glassy carbon rotating disc electrode (diameter of 5 mm, geometric surface area of 0.196 cm²) was polished and cleaned. Ten μ L of ink was then pipetted on the glassy carbon electrode and allowed to dry, to form a thin uniform catalyst film. The Pt loading on the working electrode was 25 μ g/cm².

2.2. Determination of BA coverage on Pt bulk surface, and measurements of ORR activity

2.2.1. Electrochemical apparatus

Electrochemical measurements were conducted on a CHI 760B instrument, using a typical three-electrode cell, with a Pt wire as a counter electrode and saturated calomel electrode (SCE, 0.302 V vs. reversible hydrogen electrode (RHE) in 0.1 mol/L HClO₄, 0.327 V vs. RHE in 0.1 mol/L H₃PO₄) as a reference electrode. A salt bridge was used to prevent contamination of the electrolyte and Pt catalyst by Cl⁻. All potentials stated in this study have been converted into potentials vs. RHE.

2.2.2. Determination of BA coverage on Pt surface

The modified Pt bulk electrode was first electrochemically cleaned in N₂-saturated 0.1 mol/L HClO₄ by cycling in the potential window 0.05–1.05 V (a safe window for BA) at a scan

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