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Article (Special Issue on Electrocatalysis Transformation)

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

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ARTICLE INFO

Article history:

Received 23 April 2016

Accepted 23 May 2016

Published 5 July 2016

Keywords:

Platinum

Phosphoric anion poisoning

Oxygen reduction reaction

Modified electrode

H₃PO₄-PBI based fuel cells

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

This work is supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA09030104), the National Basic Research Program of China (973 Program, 2012CB215500), and the Key Program of the Chinese Academy of Sciences (KGZD-EW-T08).

DOI: 10.1016/S1872-2067(16)62472-5 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 37, No. 7, July 2016

(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

rate of 100 mV/s. This removed ethanol and other contaminants. BA molecules gradually desorbed or were electrochemically oxidized when the potential was higher than +1.1 V. After cleaning, the electrode was experienced potential scanning from 0.05 to 1.1 V to desorb BA molecules gradually by increasing the sweep cycles. The BA coverage was determined by comparing the charge of the underpotential adsorption-desorption of atomic hydrogen (Q_H) in the potential window of 0.05–0.42 V in the background cyclic voltammetry (CV) curve of the modified Pt bulk electrode with that of a clean Pt bulk electrode. A constant of 0.21 mC/cm²Pt ($\theta_{BA} = Q_H/Q_H^0$) was assumed.

2.2.3. Measurement of ORR activity

Electrodes were first electrochemically cleaned in N₂-saturated 0.1 mol/L HClO₄ by cycling from 0.05 to 1.05 V at a scan rate of 100 mV/s. Background CV curves and ORR polarization curves were collected at a scan rate of 10 mV/s in N₂-saturated 0.1 mol/L HClO₄ (statistic), O₂-saturated 0.1 mol/L HClO₄, and 0.1 mol/L H₃PO₄, at a rotation rate of 1600 r/min. The specific activity was evaluated from the kinetic current at 0.9 V vs. RHE, using the Koutecky-Levich equation:

$$1/i = 1/i_k + 1/i_{lim}$$

where i and i_{lim} are the measured ORR current at 0.9 V and limiting current collected at 0.4 V, respectively, in ORR polarization curves.

3. Results and discussion

3.1. CV curves and ORR polarization curves over the smooth Pt surface in HClO₄ and H₃PO₄ electrolytes

CV curves and ORR polarization curves were recorded over the smooth Pt surface in HClO₄ and H₃PO₄ electrolytes, and are shown in Fig. 1. The CV curves of the smooth Pt surface (Fig. 1(a)) in both electrolytes can be divided into three regions: the underpotential adsorption-desorption of hydrogen region (0.05–0.4 V vs. RHE), double-layer region (0.4–0.6 V vs. RHE), and Pt oxidation region (0.6–1.05 V vs. RHE). The most significant difference in the CV curve recorded in H₃PO₄ compared with that recorded in HClO₄ occurs in the underpotential ad-

Table 1

Comparison of integrated H_{ad/de} charges (Q_{Hupd}), ORR onset potentials (E_0), half-wave potentials ($E_{1/2}$), and kinetic current densities at 0.9 V ($j_k@0.9V$) normalized to the geometric surface area of the electrode over the smooth Pt surface in 0.1 mol/L HClO₄ and 0.1 mol/L H₃PO₄.

Solution	Q_H (μC)	E_0 (mV vs. RHE)	$E_{1/2}$ (mV vs. RHE)	$j_k@0.9V$ (mA/cm ²)
0.1 mol/L HClO ₄	83.5	1012	795	0.81
0.1 mol/L H ₃ PO ₄	80.0	990	606	0.14

sorption-desorption of hydrogen region. In HClO₄, two distinct peaks are observed at 0.13 and 0.22–0.4 V, which are attributed to Pt(110) and Pt(111), respectively. In H₃PO₄, the peak at 0.13 V is weaker, while the peak at 0.27 V is sharper, compared with in HClO₄. The sharp current peak at 0.27 V may result from the adsorption of phosphoric anions on the reconstructed Pt surface; i.e. at potential induced stepped faces and oriented terraces from the low index facet. This is similar to observations of Au surfaces [8,27]. The integrated charge of the hydrogen region in H₃PO₄ is therefore unreliable for determining the active surface of Pt, although this approach is suitable for Pt in the HClO₄ electrolyte. The potential of OH⁻ adsorption shifts to more positive values compared with the Pt oxidation region in HClO₄. This indicates suppressed adsorption of OH⁻ species on the Pt surface and the delayed formation of platinum oxide in H₃PO₄. This is probably due to the competitive adsorption of phosphoric anions and OH⁻ species at 0.4–0.87 V [13].

ORR polarization curves over the smooth Pt surface in HClO₄ and H₃PO₄ electrolytes are shown in Fig. 1(b). The onset potential and half-wave potential of the ORR polarization curves of the Pt bulk surface in H₃PO₄ exhibit large shifts to more negative potentials compared with those in HClO₄. The charge of hydrogen underpotential adsorption-desorption (denoted Q_H), onset potential, half-wave potential, and geometric kinetic current density are listed in Table 1. The ORR kinetic current density of the clean Pt bulk electrode in H₃PO₄ is 17% of that in HClO₄. This confirms the poisoning of Pt by phosphoric anions [8]. The maximum ORR current in the diffusion controlled region in H₃PO₄ (0.9 mA) is less than that in HClO₄ (1.1 mA) under the same rotation rate. This may partly result from the decrease in Pt active sites because of the strong ad-

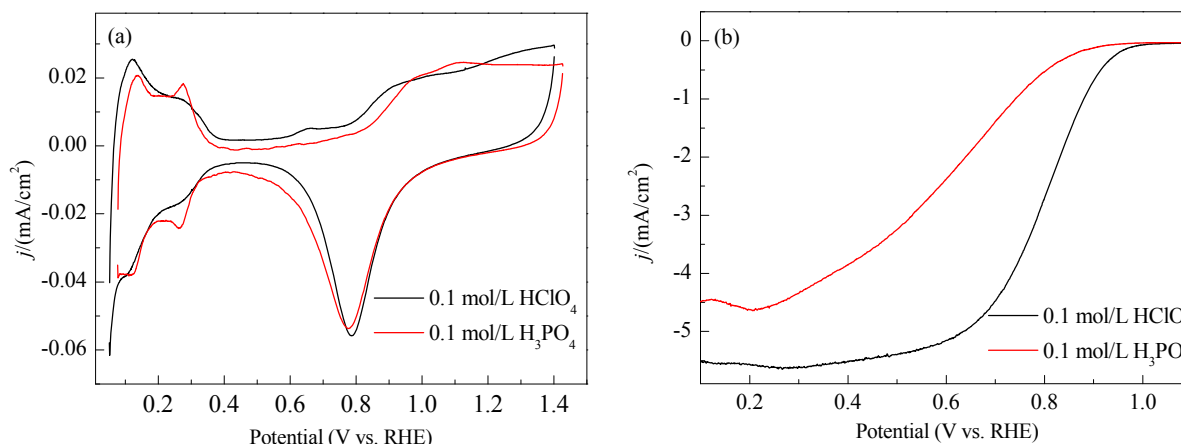


Fig. 1. CV curves (a) and ORR polarization curves (b) of clean Pt bulk electrodes in 0.1 mol/L HClO₄ and 0.1 mol/L H₃PO₄.

sorption of phosphoric anions, and more significantly to the 2e⁻ ORR pathway at < 0.3 V [17,28].

3.2. Influence of BA coverage on the ORR activity of BA-modified Pt

The underpotential adsorption-desorption of hydrogen regions of CV curves for the modified Pt bulk electrode with var-

ying BA coverage is shown in Fig. 2. CV curves recorded in HClO₄ and H₃PO₄ are shown in Fig. 2(a) and (b), respectively. The notation “CX BA-Pt” bulk indicates the CV curve collected after X cycles from 0.05 to 1.1 V. From C1 BA-Pt bulk to C7 BA-Pt bulk (i.e. with increasing potential cycles as described in Section 2.2), the hydrogen underpotential adsorption-desorption current gradually increases, and peaks of the respective Pt crystal facet become more distinct. This is evidence for the con-

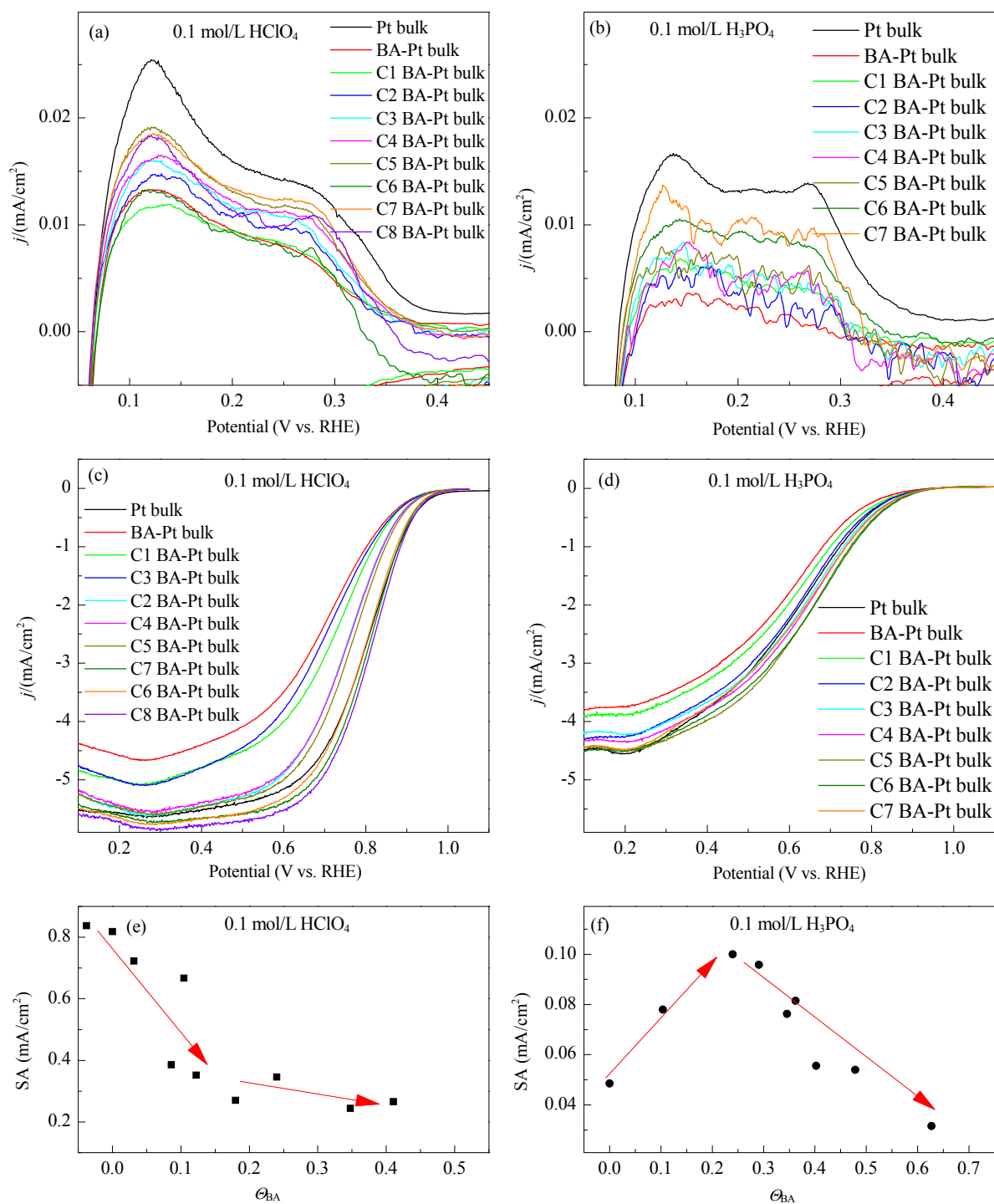


Fig. 2. CV curves (a, b), ORR polarization curves (c, d), and geometric specific activity (kinetic current density at 0.9 V) (e, f) of bulk Pt with varying coverages of BA, in 0.1 mol/L HClO₄ and 0.1 mol/L H₃PO₄.

tinuous desorption of BA from the Pt surface, and thus the decrease in BA coverage. ORR polarization curves of the modified Pt bulk surface in HClO_4 and H_3PO_4 electrolytes are shown in Fig. 2(c) and (d), respectively. The derived ORR kinetic current density at 0.9 V (in the mixed kinetic-diffusion controlled region) as a function of BA coverage is shown in Fig. 2(e) and (f). The ORR activity of the modified Pt bulk surface progressively decreases with increasing BA coverage in HClO_4 , as shown in Fig. 2(e). BA molecules inevitably occupy partial Pt active sites, which decreases the electrochemically active surface area. Adsorbed BA may also modify the electronic structure of the Pt surface. Previous studies have investigated the electronic adjustment of Pt by polyvinylpyrrolidone (PVP). N atoms of adsorbed PVP accepted electrons from the Pt atoms of particles larger than 20 nm, or even bulk Pt. Pt atoms accepted electrons from the N atoms of PVP for Pt nanoparticles smaller than 7 nm [18]. In the current study, bulk Pt may donate electrons to BA. The electron density of the modified Pt bulk surface is likely to be lowered, and the *d*-band center shifted to more positive potential, which is detrimental to ORR activity.

In H_3PO_4 electrolyte, the Pt surface is partially covered by phosphoric anions. Pre-adsorbing BA on the Pt surface suppresses the adsorption of phosphoric anions, relative to that of unmodified Pt. Fig. 2(f) shows that the ORR activity of the smooth bulk Pt electrode exhibits a bell-shaped profile with BA coverage. The highest ORR activity is obtained at a BA coverage of ~20%. The specific ORR activity of the modified Pt surface is lower than that of the clean bulk Pt electrode, until the BA coverage becomes higher than 50%. The bell-shaped profile in ORR activity is reasonable considering the co-adsorption of BA and phosphoric anions on the Pt surface. Phosphoric anions preferentially adsorb on the Pt surface in face-centered cubic (fcc) or fcc-inverted form, occupying three-fold sites [8,12,13]. BA prefers to occupy the “atop” sites of Pt [22], as shown in Fig. 3. The selective adsorption of BA decreases the availability of three-fold sites, which suppresses the adsorption of phosphoric anions. A BA coverage of 20% results in the minimum co-coverage of BA and phosphoric anions, and thus the highest ORR activity as shown in Fig. 3.

3.3. Effect of molecular length of pre-adsorbate on suppression of phosphoric anion adsorption

BA, OA, and DA have similar molecular structures, but dif-

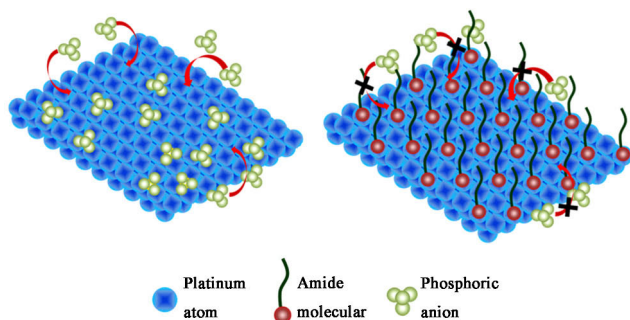


Fig. 3. Strategy to suppress the adsorption of phosphoric anions via the third-body effect.

ferent chain lengths of ~0.6, 1.2, and 1.8 nm, respectively. These amines are used as pre-adsorbates to investigate the effect of molecular length on the suppression of phosphoric anion adsorption on the Pt surface, and thus on ORR activity.

Background CV curves, ORR polarization curves, and ORR-specific activities of BA-Pt/C, OA-Pt/C, and DA-Pt/C catalysts in H_3PO_4 and HClO_4 electrolytes are shown in Fig. 4. Compared with pristine Pt/C, the Q_H is lower for the BA-Pt/C, OA-Pt/C, and DA-Pt/C catalysts in both 0.1 mol/L HClO_4 and 0.1 mol/L H_3PO_4 , as shown in Fig. 4(a) and (b), respectively. In 0.1 mol/L HClO_4 , with increasing pre-adsorbate length, the Q_H values are DA-Pt/C (28.4 μC) \approx OA-Pt/C (28.8 μC) > BA-Pt/C (24.8 μC). In H_3PO_4 , the Q_H values are BA-Pt/C (32.1 μC) > OA-Pt/C (27.6 μC) > DA-Pt/C (26.2 μC). In H_3PO_4 , the “apparent” underpotential hydrogen adsorption-desorption current contains contributions from the adsorption-desorption of hydrogen and that of phosphoric anions. Thus, the Q_H is unreliable for calculating the electrochemically active surface area in H_3PO_4 , as is usually done when using HClO_4 .

ORR polarization curves over the modified Pt/C electrodes in HClO_4 and H_3PO_4 electrolytes, and derived Tafel plots, are shown in Fig. 4(c) and (d). For the HClO_4 electrolyte, ORR currents (at 0.9 V) in the Tafel plots (insets in Fig. 4(c) and (d)) are normalized to the electrochemically active surface area (ECSA) and Pt mass. For the H_3PO_4 electrolyte, they are only normalized to the Pt mass, as shown in Fig. 4(e) and (f). The ECSA cannot be calculated from the hydrogen region because of the influence by phosphoric anion adsorption on the Pt surface in H_3PO_4 . In HClO_4 , the lower ECSA of BA/OA/DA-Pt/C due to coverage by the pre-adsorbate has little influence on the specific ORR activity. This is evidenced by their near overlapping ORR curves in Fig. 4(c), and their similar ORR-specific currents in Fig. 4(e).

The modified Pt/C catalyst exhibits better ORR activity in phosphoric acid compared with the unmodified Pt/C catalyst. This is shown in Fig. 4(d) and (f). The half-wave potential shifts by 35 mV to more positive potential. The Pt mass-specific activities of the BA-Pt/C, OA-Pt/C, and DA-Pt/C catalysts are 1.67, 1.72, and 1.9-fold that of the Pt/C catalyst, respectively. This suggests that pre-adsorbates suppress the adsorption of phosphoric anions, as is observed on the smooth Pt surface. The molecular length of the pre-adsorbate has little influence on the adsorption of phosphoric anions, in contrast to pre-adsorbate coverage. Compared with the HClO_4 electrolyte, the ORR activity in the phosphoric acid electrolyte remains relatively low, even when using the pre-adsorbate-modified Pt/C catalysts. This is because HClO_4 only weakly adsorbs to Pt. Further development of the catalyst and electrolyte [7,29–31] is required to overcome phosphoric anion poisoning before the commercialization of H_3PO_4 -PBI-based PEMFCs can be realized.

4. Conclusions

This study aimed to mitigate the poisoning of Pt by phosphoric anions using the third-body effect. This involved pre-adsorbing a small amount of organic molecules on Pt to inhibit the adsorption of phosphoric anions. In aqueous HClO_4

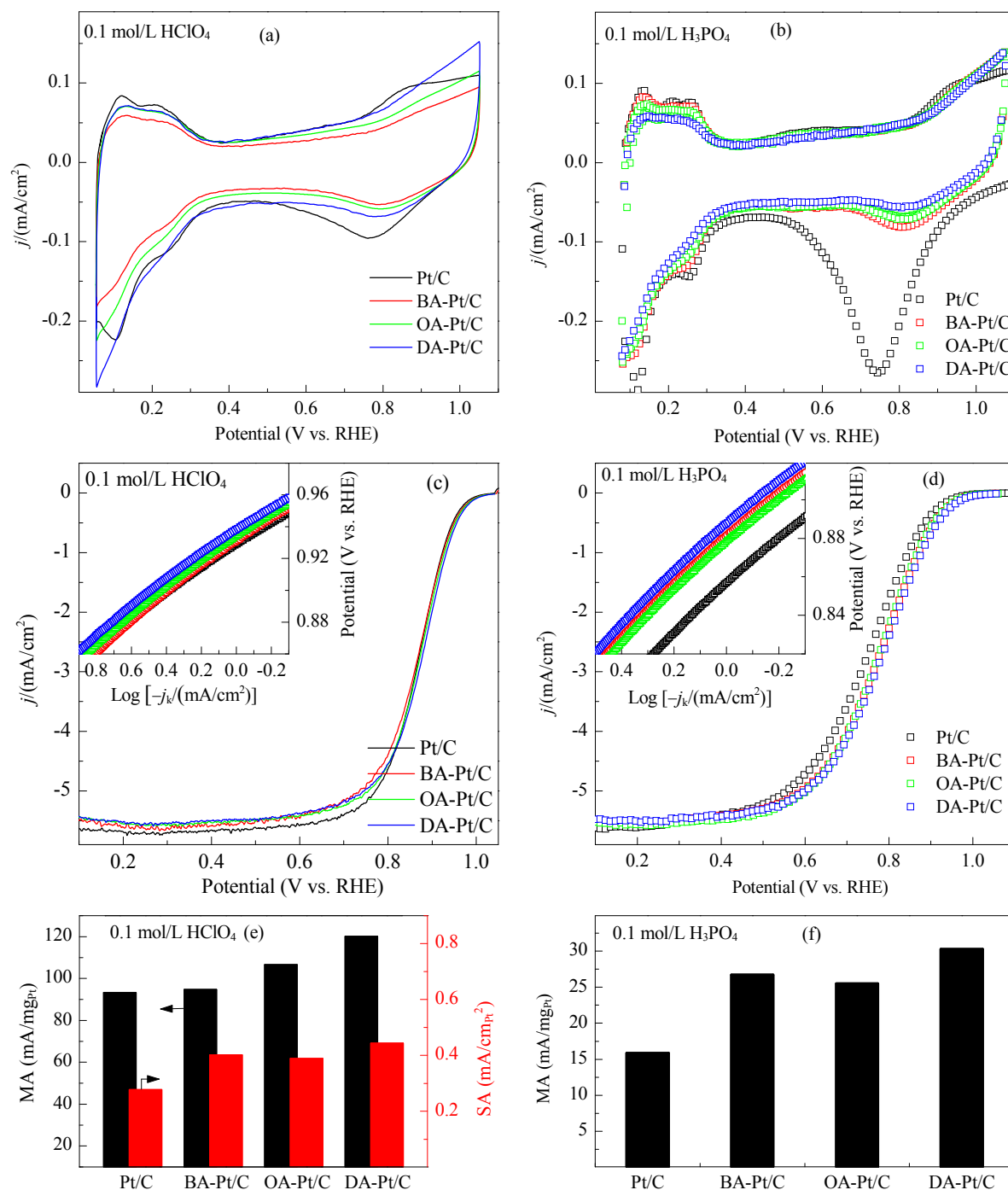


Fig. 4. CV curves (a, b), ORR polarization curves (c, d), and specific activities (kinetic current densities) at 0.9 V (e, f) of BA-modified, OA-modified, and DA-modified Pt/C in 0.1 mol/L HClO₄ and 0.1 mol/L H₃PO₄.

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, with the optimum coverage observed at ~20%. The molecular length of the pre-adsorbate has a negligible effect on the ORR activity, but its coverage strongly affects the inhibition of phosphoric anion adsorption. The ORR activity of the modified Pt/C remains relatively low in phosphoric acid compared with in the absence of

phosphoric acid. Further development is required to improve the ORR activity of Pt-based catalysts in phosphoric acid.

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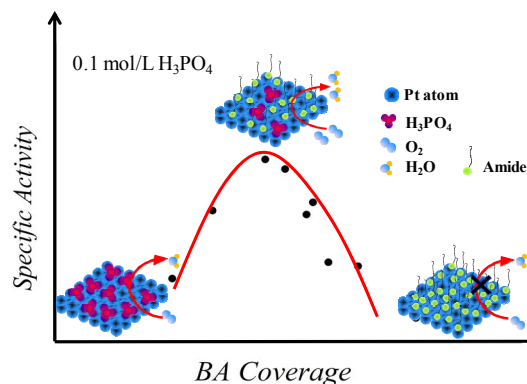
Graphical Abstract

Chin. J. Catal., 2016, 37: 1134–1141 doi: 10.1016/S1872-2067(16)62472-5

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

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Pre-adsorption of amide molecules on Pt surface effectively suppresses the phosphoric anion adsorption, resulting to a “volcanic” profile of the ORR activity as a function of the BA coverage on Pt surface in phosphoric acid electrolyte.



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