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Technical Communication

Cobalt oxyphosphide as oxygen reduction electrocatalyst in proton exchange membrane fuel cell

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ABSTRACT

The cobalt oxyphosphides supported on carbon black were prepared using incipient wetness method and characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The possibility of their application as the electrocatalyst for oxygen reduction reaction (ORR) in proton exchange membrane fuel cell (PEMFC) was investigated and the electrocatalytic activities were evaluated by the electrochemical measurements and single cell test, respectively. The electrocatalyst presents attractive catalytic activity towards ORR and good stability in acid media and exhibits an onset potential for oxygen reduction as high as 0.69 V (RHE) in H₂SO₄ solution. The maximum power density obtained in a H₂/O₂ PEMFC is 57 mW cm⁻² with Co₄P₂O₉/C loading of 1.13 mg cm⁻². No significant performance degradation is observed over 50 h of continuous fuel cell operation. The combination of heteroatom P with nanostructured oxides with high stability, excellent functionality and low cost which are prerequisites for large-scale applications, probably provide a new solution for the critical challenge of finding effective cathode materials for PEMFC.

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1. Introduction

As an alternative power source for residential and transportation application, proton exchange membrane fuel cell (PEMFC) has drawn much attention because of their advantages such as high efficiency, near-zero emission, etc. [1]. Up to date, although the PEMFC has been successfully demonstrated in many fields, there are still many key issues, such as durability, reliability, cost and operation flexibility, still need to be addressed. A significant fraction of the fuel cell cost comes from the high cost of electrocatalysts. Considering the activity and stability, platinum-based catalysts are still the

best catalysts for PEMFC, especially for the oxygen reduction reaction (ORR) occurring at the cathode [2]. However, the high price and the limited resources of the noble metal Pt hamper its final commercial application [3]. Thus, the design of inexpensive, stable, and catalytically active materials, which can substitute for the Pt-based catalysts, is urgently required to make PEMFC economically viable.

Since Jasinski's [4] discovery of the catalytic properties of Co phthalocyanines in 1964, many researches on non-Pt catalysts have been widely conducted such as transition metal chalcogenides (e.g., Co₉S₈/C and Co₉Se₈/C) [5–8], transition metal oxides, nitrides and carbides (e.g., Mo₂N/C, TiO_x/C, Fe–C–N

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and MnO_x/C [9–13] et al. and the macrocycles complexes (e.g., transition metal N_4 -macrocycles and Co-PPY-C) [14–17]. Among these non-Pt catalysts, nanostructured catalysts doped with heteroatom such as N, P, B [18–20] have been garnered great attentions because of their high activity under acid conditions.

Recently, Gong et al. [21] have developed a nitrogen-containing carbon nanotubes (VA-NCNTs) catalyst, which can act as a metal-free electrode with a much better electrocatalytic activity, long-term operation stability, and tolerance to crossover effect than platinum for oxygen reduction in alkaline fuel cells. Subramanian et al. [22] has synthesized a new nitrogen-modified carbon-based catalyst, which shows an onset potential at around 0.78 V (RHE) and the amount of H_2O_2 generated during oxygen reduction was approximately 1–3% at 0.5 V (RHE). It is believed that the addition of heteroatom atom has improved the activity and stability of the metal, oxides and carbon-based materials [19–23]. Oxyphosphides, containing heteroatom P and oxygen, exhibit promising properties such as high stability. It has been reported that oxyphosphides can enhance the stability of the Pt-based catalysts in PEMFC as the support [24]. Moreover, the oxyphosphides are also believed to theoretically reduce the complexity of the three phase boundary, which can potentially satisfy two of these electrode requirements, catalysis and proton conductivity in one moiety and in results contribute to the high activity of the catalysts. However, there are no articles related to the investigation of the ORR activity of the oxyphosphides, which act as a main active component for the electrocatalysts. In this article, the cobalt oxyphosphide as a promising ORR catalyst is investigated. The results show that the cobalt oxyphosphide electrocatalyst exhibits attractive catalytic activity for the ORR in PEMFC. It is expected to be a promising Pt-free electrocatalyst for the alternative of platinum-based catalyst in PEMFC.

2. Experimental

2.1. Catalyst preparation

Cobalt oxyphosphides supported on the Vulcan XC-72 (Cabot Corp, BET 235 $\text{m}^2 \text{g}^{-1}$, denoted as C) were prepared by incipient wetness method. A mixed aqueous solution of cobalt nitrate and ammonium phosphate was added to the XC-72 carbon black at room temperature. After impregnated for 12 h, the samples were agitated and dried in a water bath at 80 °C until the water had been evaporated, subsequently transferred into an oven to dry at 120 °C for 1 h. The samples were finally calcined at 500 °C for 3 h under nitrogen atmosphere. The molar ratio of Co to P of the catalysts is controlled in 1/1, 1/2 and 2/1, respectively.

2.2. Characterizations of the catalysts

XRD characterizations of cobalt oxyphosphides were carried out on a Rigaku diffractometer (D/max-2400X) using Cu K α source ($\lambda = 1.542 \text{ \AA}$) with a Ni filter. The XRD spectra were recorded between 20° and 90° at a scan rate of 10°/min⁻¹. The particle size of the catalyst was evaluated by applying the

Scherrer equation [25]. Transmission electron microscopy (TEM) measurement was performed on a JEOL JEM-2000EX operating at 120 kV. Two hundred particles were applied to calculate the catalyst average particle size.

The electrochemical measurements were carried out using a Princeton applied research VMP3 electrochemical analyzer and a three-electrode test cell at room temperature. The working electrode was a thin layer of Nafion bonded catalyst cast on a glassy carbon (GC) electrode. A Pt foil and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The electrolyte was a solution of 0.5 M H_2SO_4 . High pure oxygen or nitrogen was bubbled into the electrolyte to maintain an oxygen or oxygen-free atmosphere near the working electrode. The preparation of the working electrodes has been described in our previous article [9]. The Linear sweep voltammetry (LSV) curves were obtained in the potential range of 0.94–0.24 V vs. RHE with a scan rate of 2 mV s^{-1} after oxygen bubbling for 30 min.

The single cell test of the 30 wt% $\text{Co}_4\text{P}_2\text{O}_9/\text{C}$ as the cathode electrocatalyst was conducted in a 5 cm^2 single PEMFC. The anode electrode adopted 47.6 wt% Pt/C (T.K.K. Corp.) with Pt loading of 0.3 mg cm^{-2} and Nafion-212 (DuPont) was used as the membrane. The preparation of cathode electrode and membrane electrode assembly (MEA) has been described in our previous article [9]. The $\text{Co}_4\text{P}_2\text{O}_9/\text{C}$ loading in the electrode was about 0.49 mg cm^{-2} and 1.13 mg cm^{-2} , respectively. Fuel cell polarization measurement was carried out with the cell operating temperature of 80 °C and the fuel (H_2) and the oxidant (O_2) humidified by passing through water at temperature of 90 °C and 85 °C, respectively. The gas pressures were all kept at 0.2 MPa at both electrodes. Performance data were recorded in the steady state and the polarization curves were uncorrected for internal resistance (IR) losses. Short time stability test of single cell with $\text{Co}_4\text{P}_2\text{O}_9/\text{C}$ as cathode electrocatalyst was also carried out at a constant current density of 100 mA cm^{-2} with the same operating condition.

3. Result and discussion

3.1. X-ray diffraction (XRD) characterizations

Fig. 1 shows the XRD patterns of the cobalt oxyphosphides with different Co/P ratios. The patterns all show broad peaks at $2\theta \approx 26.3^\circ$ corresponding to the characteristic peaks of C (0 0 2). Peaks corresponding to three different phases are observed in the diffraction patterns of the cobalt oxyphosphide catalysts. The XRD pattern of the sample (a) with the higher P content (Co/P = 1/2) shows four characteristic peaks at 28°, 29.7°, 31.1° and 37.6°, which are signed to CoP_2O_6 (3 1 0), CoP_2O_6 (–2 2 2), CoP_2O_6 (0 1 3) and CoP_2O_6 (2 2 2) plane, respectively. The XRD pattern of the sample (b) with the Co/P molar ratio of 1/1 shows two characteristic peaks at 29.7° and 35.2°, which are signed to $\text{Co}_2\text{P}_2\text{O}_7$ (1 2 –2) and CoP_2O_6 (1 3 0) plane, respectively. This indicates that the pattern of our synthesized samples match well with the standard crystallographic pattern of CoP_2O_6 phase (PDF 27-1120) and $\text{Co}_2\text{P}_2\text{O}_7$ phase (PDF 39-709). Finally, the sample (c) with the lowest P content (Co/P = 2/1) has no obvious diffraction peaks corresponding to cobalt oxyphosphide compounds, indicating this

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