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Co₃O₄ supported on N, P-doped carbon as a bifunctional electrocatalyst for oxygen reduction and evolution reactions

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ABSTRACT

Noble metals, such as platinum, ruthenium and iridium-group metals, are often used as oxygen reduction or evolution reaction (ORR/OER) electrocatalysts. To reduce the cost and provide an application of bifunctional catalysis, in this work, cobalt oxide supported on nitrogen and phosphorus co-doped carbon (Co₃O₄/NPC) was fabricated and examined as a bifunctional electrocatalyst for OER and ORR. To prepare Co₃O₄/NPC, NPC was pyrolyzed from melamine and phytic acid supported on carbon, followed by the solvothermal synthesis of Co₃O₄ on NPC. Linear sweep voltammetry was used to evaluate the activity for OER and ORR. For OER, Co₃O₄/NPC showed an onset potential of 0.54 V (versus the saturated calomel electrode) and a current density of 21.95 mA/cm² at 0.80 V, which was better than both Co₃O₄/C and NPC. The high activity of Co₃O₄/NPC was attributed to a synergistic effect of the N, P co-dopants and Co₃O₄. For ORR, Co₃O₄/NPC exhibited an activity close to commercial Pt/C in terms of the diffusion limited current density (−4.49 vs −4.76 mA/cm² at −0.80 V), and Co₃O₄ played the key role for the catalysis. Chronoamperometry (current versus time) was used to evaluate the stability, which showed that Co₃O₄/NPC maintained 46% current after the chronoamperometry test for OER and 95% current for ORR. Overall, Co₃O₄/NPC exhibited high activity and improved stability for both OER and ORR.

1. Introduction

Metal-air batteries have attracted considerable interest because of their many advantages, such as environmental friendliness, high conversion efficiency, quick start-up and high energy density. However, improvements in the cathode catalysts are still the challenge for their application [1]. Bifunctional catalysts play key roles in metal-air batteries for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Platinum and its alloys are often used as mono-functional cata-

lysts for ORR [2–6]. Ruthenium or iridium-group metals remain the best known catalysts for OER but show poor performance for ORR [7,8]. Therefore, a cheap and bifunctional catalyst should be developed to meet the application.

Heteroatom-doped carbon has been much studied for ORR. The introduction of a heteroatom changes the local charge density as well as asymmetry spin density of the carbon lattice, which creates catalytic sites for ORR [9–20]. Doped carbon has been explored as a bifunctional oxygen catalyst. Zhang et al. [21], Li et al. [22] and Ma et al. [23], respectively, explored ni-

trogen and phosphorus co-doped carbon as a bifunctional oxygen catalyst. With N, P co-doped carbon, OER is facilitated by N, P co-doped graphene, and the active site for ORR is the N dopant and it is enhanced by the P dopant [21,22].

Efforts to obtain bifunctional catalysts have resulted in cobalt-based catalysts supported on heteroatom-doped carbon. The cobalt-based catalysts have variable valence states for ORR and OER, but are hindered by a low electrical conductivity, which can be improved by its being hybridized with heteroatom-doped carbon. Liang et al. [24] designed Co_3O_4 hybridized with N-doped reduced graphene oxide (rGO) as a bifunctional oxygen catalyst, in which the N species enhanced ORR activity and Co_3O_4 catalyzed OER. Cobalt and N-doped carbon nanotubes showed high performance in a wide pH range for ORR and OER because of the combination of the embedded structure and doped nitrogen [25]. Co_3O_4 on N-doped carbon nanoweb has a large specific surface area and abundant active sites for catalyzing ORR and OER [26]. $MnCo_2O_4$ hybridized with N-rGO exhibited enhanced ORR reactivity [27,28]. Liang et al. [27] demonstrated that the substitution of Co^{3+} sites by Mn^{3+} increased the ORR reactivity compared with the pure Co_3O_4, but decreased the OER activity, which was attributed to Co^{2+} as the active sites for ORR [29] and Co^{3+} for OER [27]. $NiCo_2S_4$ supported on N- and S-doped rGO has high ORR activity because of a synergistic effect. The doped rGO served as a synergist while $NiCo_2S_4$ was critical for OER reactivity [30]. $CoFe_2O_4$ supported on N- and S-doped rGO has enhanced activity for ORR and OER because of a similar synergistic effect [31]. Jin et al. [32] developed a one-pot method to prepare cobalt-cobalt oxide/N-doped carbon hybrids for OER, which showed excellent activity because of the variable valence states of cobalt, carbon-encapsulated structure and nitrogen dopant.

There are still few studies on cobalt-based catalyst supported on N, P co-doped carbon. Here, Co_3O_4 supported on N, P co-doped carbon (Co_3O_4/NPC) was fabricated as a bifunctional catalyst for ORR and OER. Co_3O_4/NPC was prepared by two steps. First, NPC was pyrolyzed from melamine and phytic acid supported on carbon particles. Then Co_3O_4/NPC was synthesized by the solvothermal method followed by oxidization in air. The activity of Co_3O_4/NPC for OER was enhanced due to a synergistic effect between Co_3O_4 and NPC, and the stability was improved mainly by Co_3O_4. For ORR, even though the activity was enhanced by the P dopant in NPC, the N, P co-dopants have little effect on the activity of Co_3O_4/NPC and Co_3O_4 played the key role. Because of its overall oxygen electrode activity and stability, Co_3O_4/NPC will be useful as a bifunctional electrocatalyst for OER and ORR.

2. Experimental

2.1. Catalyst preparation

To prepare NPC, 0.55 g melamine, 0.2 g Vulcan XC-72, 32 mL deionized water and 4 mL formaldehyde solution (37%) were heated and stirred at 70 °C for 5 min to form a homogeneous ink. Then phytic acid amine solution, which contained 2 mL phytic acid solution (50%), 8 mL deionized water and 2.5 mL ammonia solution (25%) was added and the solution was stirred for another 10 min. The mixture was transferred into a 100 mL autoclave and heated at 160 °C for 4 h with a heating rate of 10 °C/min. After cooling, the powder was collected by filtration, washed, and dried. The dried powder was heated at 750 °C for 1.5 h under Ar. N-doped carbon (NC) was prepared without phytic acid amine solution and the other conditions were the same.

To prepare Co_3O_4/NPC, 0.09 mmol $Co(OAc)_2 \cdot 4H_2O$ and 0.18 mmol urea were added into 10 mL ethylene glycol solution under continuous magnetic stirring. After the metal salt was dissolved, 0.075 g NPC was added and stirring continued for 30 min to form a homogeneous suspension. The mixture was transferred to a 25 mL autoclave and heated at 180 °C for 4 h. After cooling, the product was collected by centrifugation, washed with deionized water and dried overnight. The product was calcined in air at 350 °C for 2 h. Co_3O_4/C was prepared using Vulcan XC-72 as the support instead of NPC.

Pt/C (20 wt% Pt on Vulcan XC72) was purchased from Sigma-Aldrich.

2.2. Sample characterization

The sample was pressed into a powder for X-ray diffraction (XRD) detection on a Rigaku UltimaIV X diffractometer using nickel filtered Cu K_α radiation ($\lambda = 0.15406$ nm). Transmission electron microscope (TEM) images were taken by a Tecnai G2 F20 microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250Xi with a monochromic Al X-ray source.

2.3. Electrochemical measurements

All electrochemical tests were carried out on a Princeton Parstat 2273 electrochemical work station with a three-electrode cell. A platinum wire was employed for the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. A glassy carbon electrode (5 mm in diameter) coated with catalyst was used as the working electrode and as the rotating disk electrode. The working electrode was modified with the catalyst by dropping catalyst ink on the glassy carbon surface. The catalyst ink consisted of 1.31 mg of catalyst, 0.9 mL deionized water and 0.1 mL Nafion solution (5 wt%) mixed by sonication. The catalyst ink (0.015 mL) was added dropwise onto the glassy carbon surface. The catalyst loading was about 0.1 mg/cm².

Cyclic voltammetry (CV) experiments were done with a scan rate of 50 mV/s in N_2 or O_2-saturated KOH solution (0.1 mol/L). Linear sweep voltammetry (LSV) experiments with a rotating disk electrode were carried out with a scan rate of 10 mV/s at various rotating rates in O_2-saturated KOH (0.1 mol/L). The stability of the samples was evaluated by chronoamperometry (current versus time) in O_2-saturated KOH (0.1 mol/L). Electrochemical impedance spectra (EIS) were recorded in the frequency range from 100 kHZ to 10 mHZ with an AC signal amplitude of 5 mV. To ensure O_2 saturation, the gas was bubbled into the electrolyte prior to the start of each experiment and