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One-pot synthesis of Ag–CoFe₂O₄/C as efficient catalyst for oxygen reduction in alkaline media

Ying Wang ^{a,c,*}, Qing Liu ^a, Limin Zhang ^a, Tianjun Hu ^b, Wenjing Liu ^c,
Nan Liu ^c, Fangyue Du ^c, Qing Li ^c, Yixiao Wang ^c

^a School of Chemistry and Material Science, Shanxi Normal University, Linfen, 041004, China

^b Shanxi Normal University, Linfen, 041004, China

^c Modern College of Arts and Sciences, Shanxi Normal University, Linfen, 041004, China

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ABSTRACT

Ag–CoFe₂O₄/C with one-pot solvothermal synthesis is described as an electrocatalyst for the oxygen reduction reaction (ORR) in alkaline solution. Compared to Ag/C and CoFe₂O₄/C, the Ag–CoFe₂O₄/C catalyst shows better activity for ORR in term of half-wave potential. The ORR on Ag–CoFe₂O₄/C mainly favours 4e[−] reaction pathway. Compared to Pt/C, Ag–CoFe₂O₄/C exhibits good methanol tolerance and durability for ORR in alkaline solution. Furthermore, the Ag–CoFe₂O₄/C also displays high catalytic activity for OER.

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Introduction

Oxygen reduction reaction (ORR) plays an important role in electrochemical technologies, including metal-air batteries and fuel cells. However, the sluggish kinetics of the ORR limits the efficiency [1], so the development of catalyst for ORR is very vital. Pt-based materials have been recognized as the most efficient ORR catalysts. However, the high cost and scarcity hamper their large scale commercialization [2,3]. Therefore, it is important to develop highly active catalyst based on non-Pt materials for ORR.

Up to date, many non-Pt materials have been investigated as ORR catalysts, such as metal oxides [4–6] and carbon-base materials [7,8]. Among these, spinel oxides as efficient

catalysts have attracted much attention because of low cost, environmental friendship and stability [9]. For example, Chen and co-workers reported highly active Co_xMn_{3-x}O₄ spinels by a rapid room-temperature synthetic method. It was found that the Co_xMn_{3-x}O₄ nanoparticles manifested a remarkable high activity towards the ORR/OER as a result of their high surface area and numerous defects [10]. Moreover, Co₃O₄ [11,12], CoFe₂O₄ [13], ZnCo₂O₄ [14], MnFe₂O₄ [15] have been reported as efficient catalysts for ORR. It is known that the activity of spinel oxides is limited by their low conductivity [10]. So supporting the spinel oxides on carbon based materials is an effective approach [16,17]. The carbon materials have high electrical conductivity and large surface area, and some functional groups on carbon such as oxygen and nitrogen functional groups are beneficial for anchoring metal

* Corresponding author. School of Chemistry and Material Science, Shanxi Normal University, Linfen, 041004, China.

E-mail address: wangyme@163.com (Y. Wang).

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oxides [18], which makes them good substrate for spinel oxides. Recently, Yang et al. reported a hybrid of CoFe_2O_4 supported on N/S dual-doped graphene as an efficient catalyst for ORR. This graphene structure not only facilitated the mass transfer of O_2 but also was beneficial for engineering the covalent coupling between CoFe_2O_4 and graphene which decreased the resistance of ORR process [19].

Compared to spinel oxides, Ag catalyst has good electron conductivity and is a kind of promising catalysts for ORR [20,21]. So far, there are many methods reported to improve the catalytic activity of Ag, such as alloying with metal [22], structure control [23], and compositing with metal oxides [24–27]. Among these, Ag/metal oxides has been studied the most [28,29]. Park et al. investigated the difference in ORR activities between $\text{Ag}/\text{Mn}_3\text{O}_4/\text{C}$ and Ag/C in alkaline solution and found that $\text{Ag}/\text{Mn}_3\text{O}_4/\text{C}$ showed higher activity than Ag/C due to the electronic effect between Ag and Mn_3O_4 [30].

Considering the low cost of CoFe_2O_4 and conductivity of Ag, we firstly investigated the electrocatalytic activity of $\text{Ag}-\text{CoFe}_2\text{O}_4/\text{C}$ composite for ORR in alkaline media. To the best of our knowledge, the $\text{Ag}-\text{CoFe}_2\text{O}_4/\text{C}$ composite as ORR catalyst has never been reported. The results suggested that this catalyst exhibited higher activity than Ag/C and $\text{CoFe}_2\text{O}_4/\text{C}$, and better methanol tolerance and durability than Pt/C in alkaline solution.

Experimental

Catalyst preparation

The $\text{Ag}-\text{CoFe}_2\text{O}_4/\text{C}$ was prepared through solvothermal method as described by Ma et al. [31] with some modifications. Typically, 0.6 g carbon black (Vulcan XC-72R) was dispersed in 60 mL of anhydrous ethanol by ultrasonication. 0.1181 g AgNO_3 , 0.0929 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2579 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 20 mL of anhydrous ethanol and added dropwise to carbon black ethanol solution. After 1.6 g CH_3COONa was added to the above mixture under continuous stirring, the solution was transferred to autoclave for hydrothermal reaction at 180 °C for 12 h. The product was washed with ethanol and distilled water several times, and dried in an oven at 80 °C for 12 h. The Ag/C and $\text{CoFe}_2\text{O}_4/\text{C}$ were synthesized through the same method as $\text{Ag}-\text{CoFe}_2\text{O}_4/\text{C}$.

Characterization

The phase structure of the composite oxides was determined by room-temperature X-ray powder diffraction (XRD) using an X-ray diffractometer (Bruker D8 Advance) with filtered $\text{Cu K}\alpha$ radiation. The morphology was examined by using JEM-2100 transmission electron microscopy (TEM). The X-ray photoelectron spectroscopy (XPS) was with $\text{Mg K}\alpha$ radiation recorded by VG ESCALAB 210 instrument. The actual loading was analyzed by Atomic Absorption Spectrometer (AAS, ContrAA700). The Ag and CoFe_2O_4 loading on every catalyst was about 7.2 wt.% and 9.6 wt.%, respectively.

Electrochemical measurements

The electrochemical measurements were performed on a CHI 660E electrochemical workstation system in a three electrode system. Hg/HgO electrode and a Pt wire were used as reference electrode and counter electrode, respectively. In briefly, 10 mg of catalyst was ultrasonically suspended in 1 mL ethanol and 50 μL 5 wt.% Nafion solution for 30 min, then 6 μL slurry was coated on the surface of glassy carbon (GC) electrode, resulting in a catalyst loading of 0.455 mg cm^{-2} . Commercial 20 wt.% Pt/C (Johnson Matthey) was used for comparison with the same powder loading.

The cyclic voltammetry (CV) tests were performed over the potential range of 0.5 to -0.8 V vs. Hg/HgO at a scan rate of 100 mV s^{-1} . Rotating disk electrode (RDE) measurements were carried out in O_2 -saturated 0.1 KOH solution at a scan rate of 10 mV s^{-1} , with the electrode rotating at 400, 900, 1600 and 2500 rpm. The ORR polarization curves were corrected by subtracting background current measured under N_2 atmosphere. The transferred electron number was calculated from the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_d} = \frac{1}{J_k} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6}$$

Where J is the measured current density, J_k and J_d are the kinetic and diffusion limited current densities, respectively; F is the Faraday constant, n is transferred electron number, C_0 is the saturated concentration of oxygen, D_0 is the diffusion coefficient of oxygen and ν is kinematic viscosity of the electrolyte [13]. For the OER test, the working electrode was scanned from 0 to 1.0 V vs. Hg/HgO at a scan rate of 10 mV s^{-1} in N_2 -saturated 0.1 KOH with the electrode rotated at 1600 rpm.

Results and discussion

Fig. 1a shows the XRD patterns for $\text{Ag}-\text{CoFe}_2\text{O}_4/\text{C}$, Ag/C and $\text{CoFe}_2\text{O}_4/\text{C}$. For all samples, there was a broad peak at about 25.0° , which is attributed to the graphite (002) of carbon [32]. Similar to the $\text{CoFe}_2\text{O}_4/\text{C}$ sample, the synthesized $\text{Ag}-\text{CoFe}_2\text{O}_4/\text{C}$ exhibits five weak broad peaks located at 30.1° , 35.4° , 43.1° , 56.9° and 62.6° , which are indexed to the (220), (311), (400), (511) and (440) crystal facets of cubic spinel CoFe_2O_4 (PDF#22-1086). Moreover, the composite catalyst also exhibits other sharp diffraction peaks located at 38.1° , 44.3° , 64.4° and 77.5° , respectively. The positions of these peaks were coincident with those of the pure Ag/C , implying the presence of Ag phase in the material simultaneously. It can be found that the position and intensity of peaks for CoFe_2O_4 in the composite are similar to those of $\text{CoFe}_2\text{O}_4/\text{C}$. Only the intensity of peak recorded at 43.1° decreased (Fig. 1b). It may be attributed to the overlap of diffraction peaks of CoFe_2O_4 and Ag. The results indicate that the material is composed of both Ag and CoFe_2O_4 .

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