Silver supported on Co$_3$O$_4$ modified carbon as electrocatalyst for oxygen reduction reaction in alkaline media

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1. Introduction

The oxygen reduction reaction (ORR) plays an important role in electrochemical technologies, including fuel cells and metal-air batteries. Previous researches have reported that Pt-based materials are the most efficient catalysts for ORR [1]. However, the high cost and shortage of Pt limit its wide application in electrochemical technologies, so some non-Pt catalysts should be explored to replace it [2–5].

Among these options, Ag is a promising catalyst for replacing Pt because of its low cost, relatively high activity for ORR, high methanol tolerance and stability. Tammeveski et al. reported Ag nanoparticle/multi-walled carbon nanotube (AgNP/MWCNT) prepared by sputter deposition of Ag catalyst on the surface of MWCNT. It revealed AgNP/MWCNT catalyst had a high electrocatalytic activity for ORR and the specific activity was similar to that of bulk Ag [6]. Very recent work by Lim et al. [7] described highly dispersed Ag nanoparticles on a reduced graphene oxide (RGO) via a simple surfactant-free synthetic process at low temperatures. This catalyst (Ag/RGO) had a large surface area of active sites for ORR and demonstrated high activity compared to Ag/C. However, compared to Pt/C, the activity of silver for ORR is still not satisfactory and need to be improved.

Cobalt oxides (Co$_3$O$_4$) have been investigated as non-precious ORR catalysts and applied in metal-air batteries in terms of their low cost, low electrical resistance and environmental friendliness [8]. The active sites of Co$^{3+}$ ions on the Co$_3$O$_4$ play a determinant role in the performance for ORR [9]. Xu et al. [10] synthesized carbon-supported Co$_3$O$_4$ catalyst by the solvent-mediated morphological control method. It was found that the activity of such catalyst can be modified by tailoring the number of surface-exposed Co$^{3+}$ ions and it exhibited higher current density than Pd-based catalyst.

Considering the effective catalytic activity for ORR and the low cost of Ag and Co$_3$O$_4$, we firstly synthesized Ag/Co$_3$O$_4$–C composite by a two-step process and investigated their catalytic activity for ORR in alkaline media. It exhibited higher ORR activity than Ag/C and Co$_3$O$_4$–C catalysts. Compared to Pt/C, the Ag/Co$_3$O$_4$–C composite showed better methanol tolerance and stability in alkaline media.

2. Experimental

The Ag/Co$_3$O$_4$–C catalyst was prepared by two-step procedure. In the first step, the Co$_3$O$_4$ on carbon (Vulcan XC-72R, Cobot Corp.) was prepared through hydrothermal method as described by Liang et al. [11]. Briefly, 5.7 mL 0.2 M Co(OAc)$_2$ aqueous solution was added to 50 mL carbon black ethanol solution, followed by the addition of 1.5 mL NH$_4$OH (30% solution). After stirred for 10 h at 80 °C, the solution was transferred to autoclave for hydrothermal reaction at 150 °C for 3 h. Finally, the prepared Co$_3$O$_4$–C was washed, dried and collected. In the second step, 39 mg KBH$_4$ and 272 mg trisodium citrate were dissolved into 100 mL distilled water, then 50 mL of 2 mM AgNO$_3$ was added dropwise into the solution to obtain a yellowish-brown colloid. Next, 200 mg Co$_3$O$_4$–C was dispersed into the above colloid. After the suspension was stirred for 12 h, the black precipitate was filtered, washed, and dried at 80 °C for 12 h. The Ag/C catalyst was prepared through the same steps as Ag/Co$_3$O$_4$–C.
comparison, the Pt/C catalyst was prepared by ethylene glycol (EG) method [12].

Fourier transform infrared spectroscopy (FT-IR) transmission data were collected with a Nicolet 5700 FT-IR. Phase identification was performed using X-ray diffraction (XRD, Siemens D/max-RB powder X-ray diffractometer). The morphology was examined by using JEM-1022EX transmission electron microscopy (TEM). To quantify the actual loading amount of every composite, Atomic Absorption Spectrometer (AAS, ContrAA700) was carried out, in which the Ag loadings of every catalysts was 5 wt.% and the mass loading of Ag and Co3O4 on carbon was 9 wt.%

Rotating disk electrode (RDE) measurements (ATA-1B, Jiangfen Electroanalytical Instruments, Jiangsu, 3 mm diameter) were performed using X-ray diffraction (XRD, Siemens D/max-RB powder X-ray diffractometer). The morphology was examined by using JEM-1022EX transmission electron microscopy (TEM). To quantify the actual loading amount of every composite, Atomic Absorption Spectrometer (AAS, ContrAA700) was carried out, in which the Ag loadings of every catalysts was 5 wt.% and the mass loading of Ag and Co3O4 on carbon was 9 wt.%.

Results and discussions

Fig. 1a shows the FTIR spectra of Co3O4–C. Two bands of around 565 and 663 cm⁻¹ are assigned to OB3 (B denotes the Co³⁺ in an octahedral hole) vibration and the ABO3 (A represents the Co²⁺ in a tetrahedral hole) vibration in the spinel lattice, respectively [14]. The peaks located at 31.3°, 36.8°, 59.4° and 65.2° can be obviously observed, which means the formation of cubic structure Co3O4 (PDF#43-1003). According to the powder diffraction file (PDF#65-2871), the peaks located at about 38.1°, 44.3°, 64.4° and 77.5° were attributed to the Ag (111), Ag (200), Ag (220), and Ag (311), respectively. The result indicates the formation of Ag/Co3O4–C. Fig. 1c, d and e shows TEM images of Ag/Co3O4–C, Ag/C and Co3O4–C. Comparing with the TEM image of Co3O4–C, the Ag particles with around 15 nm were well dispersed on Co3O4–C. For Ag/C, Ag particles tended to aggregate, resulting in the large undispersed Ag particles (25 nm). This indicates that Co3O4 hinders the aggregation of Ag particles.

Fig. 2a displays the cyclic voltammogram (CV) curves for Ag/C Co3O4–C and Ag/Co3O4–C catalysts in N2-saturated and O2-saturated 1 M KOH solution. For Ag/C and Ag/Co3O4–C catalysts, in the potential range of 0–0.5 V vs. Hg/HgO, the anodic peaks were related to the formation of Ag₂O layers, and the cathodic peak was assigned to the reduction of Ag₂O to Ag [15]. For the Ag/Co3O4–C catalyst, the reduction peak of Ag₂O shifted to a negative potential compared to Ag/C, indicating there is a stronger interaction between adsorbed oxygenated species on Ag/Co3O4–C [16,17]. In O2-saturated media, an extra reduction peak was observed due to the ORR. It was evident that for the Ag/Co3O4–C, the peak potential had a positive shift compared to Ag/C and Co3O4–C, which reflects a better catalytic activity for ORR on Ag/Co3O4–C than Ag/C and Co3O4–C.

To further investigate the catalytic activity for ORR, LSV measurements on a RDE were carried out in O2-saturated 1 M KOH solution (Fig. 2b). For Ag/Co3O4–C catalysts, the positive shift on the onset potential and more positive half-wave potential indicate that Ag/Co3O4–C has better electrocatalytic activity than pure Ag/C and Co3O4–C catalysts. In order to characterize the intrinsic electrocatalytic performance of catalysts, the mass activity, specific activity (SA) and electrochemical surface area (ESA) of catalysts should be calculated. For Ag/Co3O4–C, the mass activity at −0.1 V was 17.6 mA/mgAg + Co3O4, which was higher than those of Ag/C (5.14 mA/mgAg) and Co3O4–C (15.3 mA/mgCo3O4). The ESA of Ag catalysts can be determined by Pb underpotential deposition (Pb UPD) using the theoretical value of 0.26 mC cm⁻² for a monolayer of Pb on Ag surface [6]. According to the Fig. 2c, the ESA of Ag/Co3O4–C was larger than that of Ag/C. The addition of Co3O4 inhibits the aggregation of Ag particles, leading to the presence of well-dispersed smaller Ag particles. The smaller the Ag particles, the higher the Ag actual surface area, which can be also seen in Ref. [18]. The SA value of the Ag/Co3O4–C was measured as being 2.7 times that of Ag/C catalyst at −0.1 V. The increased activity for Ag/Co3O4–C could be attributed to the following reasons. 1) The larger ESA resulted from the smaller particle size of Ag leads to the increased activity for Ag/Co3O4–C. 2) The interaction between metal and transition metal oxide can change the electronic structure of metal and cause the shift of
d-band center [19]. Lin et al. reported gold–cobalt oxide binary catalyst \( \text{Au/CoO}_x \) for ORR. They found cobalt oxide changed the electronic structure of gold [20]. So there may be an electronic effect between \( \text{Ag and Co}_3\text{O}_4 \) leading to an increased binding energy to the adsorbed oxygen, which facilitates the \( \text{O}--\text{O} \) bond splitting, and increases the catalytic activity [16]. 3) \( \text{Co}_3\text{O}_4 \) is oxidized by bonding with dissolved oxygen and is reduced again as it supplies adsorbed oxygen to \( \text{Ag} \). As a result, it increases the rate of oxygen transport to \( \text{Ag} \). 4) \( \text{Co}_3\text{O}_4 \) has activity for ORR in alkaline media, so the addition of \( \text{Co}_3\text{O}_4 \) may also increase the activity for ORR. Therefore, the actual active site for this increased performance for ORR is not clear. The corresponding catalytic reaction mechanism for the improved performance will be considered to be studied in our next work. Compared to the \( \text{Ag/RGO} \) catalyst recently reported by Lim et al. [7],
Table 1  
Kinetic parameters for catalytic reduction of oxygen at Ag/C, Co3O4/C, Ag/Co3O4/C and Pt/C electrocatalysts.

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Ag/C n x 10^3 (cm/s)</th>
<th>Co3O4/C n x 10^3 (cm/s)</th>
<th>Ag/Co3O4/C n x 10^3 (cm/s)</th>
<th>Pt/C n x 10^3 (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−0.05</td>
<td>2.7 0.09</td>
<td>3.1 0.11</td>
<td>3.8 0.15</td>
<td>3.9 3.6</td>
</tr>
<tr>
<td>−0.1</td>
<td>2.6 0.39</td>
<td>3.3 0.75</td>
<td>3.8 1.7</td>
<td>4.0 16.0</td>
</tr>
<tr>
<td>−0.15</td>
<td>2.8 3.5</td>
<td>3.1 7.0</td>
<td>4.0 7.8</td>
<td>3.9 25.0</td>
</tr>
<tr>
<td>−0.2</td>
<td>2.8 13.0</td>
<td>3.3 12.0</td>
<td>3.8 16.0</td>
<td>3.9 33.0</td>
</tr>
</tbody>
</table>

though the Ag/RGO catalyst showed high catalytic activity for ORR, the Ag/Co3O4/C catalyst with uncomplicated preparation method and low cost will be a valuable catalyst for ORR in alkaline media.

The kinetics of the ORR catalyzed by Ag/Co3O4/C was further studied via RDE experiments. Fig. 2d shows the Koutecky–Levich plots of catalysts obtained from the current density under the mixed diffusion/kinetic controlled region at the potential of − 0.15 V, and the ORR kinetic parameters were summarized in Table 1. For Ag/C and Co3O4/C, the low metal and metal oxide loading may result in a high contribution of the carbon support [17]. The ORR occurs mainly through 2-electron process in the Vulcan carbon [21], so more peroxide was produced on the Ag/C and Co3O4/C. For Ag/Co3O4/C, the combination of Ag and Co3O4/C reduced the effect of carbon, following 4-electrons pathway, which suggests a complete reduction of O2 to OH− in alkaline media. By comparison of the kinetic rate constant (k), it is found that the k values of Ag/Co3O4/C are slightly larger than those of Ag/C and Co3O4/C, resulting in a faster reaction rate.

The influence of methanol on ORR activity over the Ag/C, Ag/Co3O4/C and Pt/C catalysts was evaluated in an O2-saturated 1 M KOH + 1 M CH3OH solution (Fig. 2e). Obviously, a shoulder at − 0.2 V can be observed during the methanol-containing ORR for Pt/C catalyst, indicating the occurrence of methanol oxidation reaction [22]. In contrast, ORR curves for Ag/Co3O4/C and Ag/C catalysts were almost overlapped in the absence and presence of methanol, which signifies the Ag catalyst is inert to methanol. According to the short-term stability test in alkaline media (Fig. 2f), the ORR current generated by Ag/Co3O4/C decreased by 9% over 5000 s of continuous operation at − 0.2 V, whereas a decrease of 20% in current is observed for Pt/C, demonstrating Ag/Co3O4/C has a good catalytic stability for ORR in alkaline solution.

4. Conclusion

Novel hybrid catalyst Ag/Co3O4/C was found to have better electrocatalytic activity towards ORR in alkaline solution than Ag/C and Co3O4/C. The specific activity of Ag/Co3O4/C was measured as being 2.7 times that of Ag/C. As compared to Pt/C, Ag/Co3O4/C showed better methanol tolerance and stability in alkaline media.

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References