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Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

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Silver supported on Co₃O₄ modified carbon as electrocatalyst for oxygen reduction reaction in alkaline media



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ARTICLE INFO

Article history: Received 19 December 2012 Received in revised form 12 March 2013 Accepted 12 March 2013 Available online 20 March 2013

Keywords: Silver Cobalt oxide Oxygen reduction reaction Alkaline media

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 resource 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 (Co₃O₄) 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 friendship [8]. The active sites of Co³⁺ ions on the Co₃O₄ play a determinant role

1388-2481/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.elecom.2013.03.017

ABSTRACT

The electroreduction of oxygen was firstly studied on Ag/Co_3O_4 –C in alkaline media prepared by depositing Ag on Co_3O_4 modified carbon (Co_3O_4 –C). The Ag/Co_3O_4 –C composite not only displayed relatively large electrochemical active surface area (ESA), high catalytic activity towards oxygen reduction reaction (ORR), but also exhibited good methanol tolerance and stability in alkaline media. Ag/Co_3O_4 –C could be a valuable catalyst for ORR and be applied to alkaline fuel cells and metal–air batteries.

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in the performance for ORR [9]. Xu et al. [10] synthesized carbonsupported Co_3O_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 Co₃O₄, we firstly synthesized Ag/Co₃O₄–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 Co₃O₄–C catalysts. Compared to Pt/C, the Ag/Co₃O₄–C composite showed better methanol tolerance and stability in alkaline media.

2. Experimental

The Ag/Co₃O₄–C catalyst was prepared by two-step procedure. In the first step, the Co₃O₄ 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 NH₄OH (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 Co₃O₄–C was washed, dried and collected. In the second step, 39 mg KBH₄ and 272 mg trisodium citrate were dissolved into 100 mL distilled water, then 50 mL of 2 mM AgNO₃ was added dropwise into the solution to obtain a yellowishbrown silver colloid. Next, 200 mg Co₃O₄–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/Co₃O₄–C. For

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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 on a CHI 660A electrochemical workstation system with a conventional three electrode cell. A Pt wire and Hg/HgO electrode were used as counter electrode and reference electrode, respectively. The catalyst loading on the electrode was calculated as 402 µg cm⁻². The onset potential is determined by the point of intersection of two tangent lines, one drawn parallel to the baseline (*i.e.*, from 0.1 to 0 V), and the other parallel to the linearly increasing portion of the oxygen-reduction curve [13]. Kinetic currents were calculated by $i_k = i/(1 - i/i_d)$, where *i* is the measured current and i_d is the diffusion limited current at -0.5 V.

3. Results and discussions

Fig. 1a shows the FTIR spectra of Co_3O_4 –C. Two bands of around 565 and 663 cm⁻¹ are assigned to OB3 (B denotes the Co^{3+} in an octahedral hole) vibration and the ABO3 (A represents the Co^{2+} in a tetrahedral hole) vibration in the spinel lattice, respectively [14], suggesting the formation of Co_3O_4 . In Fig. 1b. The peaks at about 31.3°, 36.8°, 59.4° and 65.2° can be obviously observed, which means the formation of cubic structure Co_3O_4 (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 image of Co_3O_4 –C, the Ag particles with around 15 nm were well dispersed

on Co_3O_4 –C. For Ag/C, Ag particles tended to aggregate, resulting in the large undispersed Ag particles (25 nm). This indicates that Co_3O_4 hinders the aggregation of Ag particles.

Fig. 2a displays the cyclic voltammogram (CV) curves for Ag/C Co_3O_4 -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, 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/mg_{Ag + Co3O4}, which was higher than those of Ag/C (5.14 mA/mg_{Ag}) and Co_3O_4 -C (15.3 mA/mg_{Co3O4}). 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 welldispersed smaller Ag particles. The smaller the Ag particles, the higher the Ag actual surface area, which can also be 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/ Co_3O_4 –C. 2) The interaction between metal and transition metal oxide can change the electronic structure of metal and cause the shift of



Fig. 1. (a) FTIR spectra for Co₃O₄-C sample. (b) XRD pattern of Ag/Co₃O₄-C sample. (c), (d) and (e) TEM images of Ag/Co₃O₄-C, Ag/C and Co₃O₄-C.



Fig. 2. (a) CV curves of Ag/C and Ag/Co₃O₄–C samples in N₂-saturated (black curve) and O₂-saturated 1 M KOH solution. (b) Comparison of the polarization curves for ORR on Co₃O₄–C, Ag/C, Ag/Co₃O₄–C and Pt/C in O₂-saturated 1 M KOH solution at 1600 rpm. (c) Comparison of electrochemical surface area and specific activity at -0.1 V. The inset shows CV for Pb UPD for Co₃O₄–C, Ag/C, Ag/Co₃O₄–C. (d) The Koutecky–Levich plots at -0.15 V. The inset presents polarization curves for ORR on Ag/Co₃O₄–C catalyst in O₂-saturated. (e) Linear potential scan curves of Ag/Co₃O₄–C and Pt/C in aqueous 1 M KOH solution containing 1 M methanol. (f) Chronoamperometric responses of Ag/Co₃O₄–C and Pt/C at -0.2 V in oxygen saturated 1 M KOH solution.

d-band center [19]. Lin et al. reported gold–cobalt oxide binary catalyst (Au/CoO_x) for ORR. They found cobalt oxide changed the electronic structure of gold [20]. So there may be an electronic effect between Ag and Co₃O₄ leading to an increased binding energy to the adsorbed oxygen, which facilitates the O—O bond splitting, and increases the catalytic activity [16]. 3) Co₃O₄ is oxidized by bonding with dissolved oxygen and is reduced again as it supplies adsorbed oxygen to Ag. As a result, it increases the rate of oxygen transport to Ag. 4) Co_3O_4 has activity for ORR in alkaline media, so the addition of Co_3O_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 Ag/RGO catalyst recently reported by Lim et al. [7],

Table 1

Kinetic	parameters for	r catalytic reduction	of oxygen at Ag	$g/C, Co_3O_4-C, A$	g/Co ₃ O ₄ -C and Pt/C electrocataly	ysts.
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Potential (V)	Ag/C		C0 ₃ 0 ₄ -C		Ag/Co ₃ O ₄ -C		Pt/C	
	n	$k \times 10^3 (\mathrm{cm/s})$	n	$k \times 10^3 (\mathrm{cm/s})$	n	$k \times 10^3 (\text{cm/s})$	n	$k \times 10^3 \text{ (cm/s)}$
-0.05	2.7	0.09	3.1	0.11	3.8	0.15	3.9	3.6
-0.1	2.6	0.39	3.3	0.75	3.8	1.7	4.0	16.0
-0.15	2.8	3.5	3.1	7.0	4.0	7.8	3.9	29.0
-0.2	2.8	13.0	3.3	12.0	3.8	16.0	3.9	33.0

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/Co_3O_4 –C was found to have better electrocatalytic activity towards ORR in alkaline solution than Ag/C and Co_3O_4/C . The specific activity of Ag/Co_3O_4 –C was measured as being 2.7 times that of Ag/C. As compared to Pt/C, Ag/Co_3O_4 –C showed better methanol tolerance and stability in alkaline media.

Acknowledgments

This work was supported by the Science and Technology Pillar Program of Gansu Province, PR China (1104GKCA041).

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