

Studies on the Reduction Mechanism of Oxygen on Ag/C Catalysts in Alkaline Solutions

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Carbon-supported silver (Ag/C) catalysts with different Ag contents are prepared using the Ag (I) coordination polymer, $[Ag(C_7H_6NO_2)(C_6H_{12}N_4)(H_2O)]_n$. The mechanism and activity of the oxygen reduction reaction (ORR) on these Ag/C catalysts are investigated by the cyclic voltammetry and the rotating ring disk electrode (RRDE) in alkaline solutions. The test results indicate that, under the same Ag crystallite sizes, the activities increase with increasing Ag contents from 5 to 20 wt.% and the ORR proceeds by a four-electron pathway on Ag/C catalysts, but with decreasing Ag contents, the ORR is catalyzed via the four-electron pathway and the two-electron pathway simultaneously. [DOI: 10.1115/1.4025055]

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1 Introduction

Silver has a very high catalytic activity for O_2 reduction in alkaline electrolyte [1–4]. Furthermore, it is a good catalyst for perhydroxyl ion decomposition [4,5]. The key to using Ag as catalyst lies in raising the specific surface area of Ag and making Ag particles well distributed on the carrier as far as possible [6,7].

Although the studies of Ag/C catalysts for ORRs in alkaline media have been reported in many literatures, the effects of silver particle sizes and metal contents on ORR mechanism are not well explained; results and findings from different papers are inconsistent, and no definite conclusions can be drawn from them. Lima et al. [8] reported a 2.3-electron ORR on 20-wt.% Ag/C (47.7-nm Ag particle size), while the result of Demarconnay et al. [9] showed a 3.6-electron ORR on 20-wt.% Ag/C (close to 15-nm Ag particle size). Coutanceau et al. [10] investigated the influence of metal contents on Ag/C catalyst activity in a half cell. They found that the optimum was around 20 wt.%. Guo et al. [11] found the number of electrons transferred for ORRs on Vulcan XC-72 and 10-, 20-, 40-, and 60-wt.% Ag/C (around 15-nm Ag particle size) catalysts were calculated to be 1.93, 3.63, 3.83, 3.83, and 3.77, respectively. Except for the 10-wt.% Ag/C catalyst, all other Ag/C catalysts show the ORR via a four-electron transfer pathway and the ORR proceeded by the two-electron pathway mechanism on the Vulcan XC-72 carbon. Yang et al. [12] reported that oxygen reduction on Ag particles is a structure-sensitive reaction: four-electron reduction seems to occur at crystalline plane sites and two-electron reduction at edge and corner sites. The size of Ag particles affects the different catalytic activity for the four-electron and two-electron reduction of oxygen.

In the previous work, Ag/C catalysts were prepared with the $[Ag(L)(bbi)]$ [13]. The electrocatalytic activity of the Ag/C catalysts was significantly enhanced compared with that of Ag/C catalysts prepared by the conventional method [14]. The rotating disk electrode method and the cyclic voltammetry were used to study the kinetics and mechanism of O_2 reduction on Ag/C catalysts [15]. The test results indicated that the ORR proceeded by the four-electron pathway mechanism on larger 20-wt.% Ag/C particles (174 nm) and the ORR proceeded by the four-electron

pathway and the two-electron pathway mechanisms on finer 0.5-wt.% Ag/C particles (4.1 nm) simultaneously.

In this paper, Ag/C catalysts with the different metal contents were prepared with the coordination polymer of $[Ag(C_7H_6NO_2)(C_6H_{12}N_4)(H_2O)]_n$ ($C_7H_6NO_2 = 4$ -aminobenzoate, $C_6H_{12}N_4 =$ hexamethylenetetramine). The effect of Ag/C catalysts with the different Ag contents on ORR was studied.

2 Experimental

2.1 Preparation of Catalysts. The coordination polymer of $[Ag(C_7H_6NO_2)(C_6H_{12}N_4)(H_2O)]_n$ was synthesized according to the method provided in Ref. [16]. Five-, ten-, and twenty-weight percent Ag/C catalysts were prepared by the steps described in Ref. [14] with the polymer.

2.2 Physical Characterization. The morphologies of Ag/C catalysts were observed using scanning electron microscopy (SEM) (XL30 ESEM FEG, Philips). The X-ray diffraction data of Ag/C catalysts were recorded by X-ray diffraction (XRD) (Siemens D5005, SIEMENS, Germany) using $CuK\alpha$ ($\lambda = 1.5418 \text{ \AA}$) as radiant; the tube voltage was 40 kV and the tube current 40 mA.

2.3 Preparation of Electrodes. Two hundred milligrams of Ag/C catalysts were weighed and added to 0.5 ml of 10-wt.% polytetrafluoroethylene (PTFE) solution (Cabot, USA); the mixture was mixed fully and pressed into a round sheet of 2.0 cm in diameter. The nickel net was pressed onto one side of the round sheet, and a thin layer of PTFE was coated evenly on another side. Ag/C electrodes prepared were dried in a vacuum drying oven at 40 °C for 72 h.

The RRDE with a glassy carbon electrode (5-mm diameter) was used. Four milligrams of Ag/C catalysts was dispersed in 20 μ l of 10-wt.% PTFE solution, and resultant suspension was agitated in an ultrasonic bath for 30 min. The suspension was coated on the glassy carbon electrode, which was air dried for 1 h.

2.4 Electrochemical Characterization. The reduction of O_2 from air was studied in a three-electrode cell that contained a Pt counter electrode, an Hg/HgO/1.0 mol I^{-1} OH^{-} reference electrode (0.107 V), and an Ag/C electrode as a working electrode. The electrolyte was 1.0-mol I^{-1} KOH aqueous solution. Cyclic

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voltammograms were conducted with a CHI660A electrochemical workstation system (Shanghai Chenhua).

The electron transfer number of oxygen reduction was studied in O₂-saturated 1.0-mol l⁻¹ KOH solution in a three-electrode cell using the Ag/C glassy carbon electrode as the working electrode, Hg/HgO/1.0 mol l⁻¹ OH⁻ electrode as the reference electrode, and platinum spiral wire as the auxiliary electrode. The electrochemical measurements were performed by the CHI660A electrochemical workstation system, and the rotation rates were controlled by the AFMSRXB Model Analytical Rotator (Pine Instrument Company, USA).

3 Results and Discussions

3.1 Physical Characterization. Figure 1 shows SEM images of Ag/C catalysts prepared. Although the Ag metal contents vary from 5 to 20 wt.%, the distribution and the mean particles sizes of the Ag/C catalysts are almost identical, which implies that the metal content does not have a significant effect on the Ag metal dispersion in these three catalysts. From the SEM images, the mean particle size of Ag/C catalysts is around 10.0 nm.

The structures of three Ag/C catalysts with different Ag metal contents were further characterized by XRD and are shown in Fig. 2. The peaks located at about 38.2 °C, 44.4 °C, 64.6 °C and 77.6 °C are attributed to the (111), (200), (220), and (311) crystal-line planes of Ag with a face-centered cubic structure according to the silver powder diffraction file (JCPDS No. 01-1167). The mean crystallite sizes of Ag particles calculated using Scherrer's equation were 9.1, 9.5, and 8.7 nm for 5, 10, and 20-wt.% Ag/C catalysts, respectively, which agrees well with the results obtained by the SEM.

3.2 Electrochemical Characterization. Figure 3 shows the cyclic voltammetric curves of three Ag/C catalysts at three

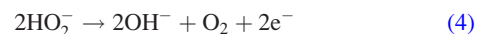
different metal contents in a 1.0-mol l⁻¹ KOH solution. The reduction of O₂ in alkaline electrolytes can proceed by two pathways [10], namely, direct O₂ reduction to OH⁻ ions, which is called four-electron pathway (Eq. (1)),



or oxygen reduction to HO₂⁻ ions, which is called two-electron pathway (Eq. (2))



with subsequent reduction of peroxide ion to OH⁻ ions (Eq. (3)) or the decomposition of peroxide ion (Eq. (4)). The concentration of HO₂⁻ ions is quite low; thus, the current produced by HO₂⁻ ions is very difficult to test.



There is one cathodic peak observed at -0.09 V in Fig. 3(a), and the reduction peak supports the four-electron pathway mechanism. One wider cathodic peak exists at -0.3 ~ 0.1 V in Fig. 3(b), and the reduction peak is attributed to the four-electron pathway and two-electron pathway as well. There are two cathodic peaks observed in Fig. 3(c), and the reduction peaks at 0.06 V and at -0.21 V support the four-electron pathway and the two-electron pathway mechanisms, respectively.

As it can be seen from Fig. 3, under the same Ag crystallite sizes, the peak intensities increase with increasing Ag contents from 5 to 20 wt.%, and the ORR is catalyzed via the two-electron pathway and the four-electron pathway simultaneously, with decreasing Ag contents. Because the mean particles sizes of Ag/C

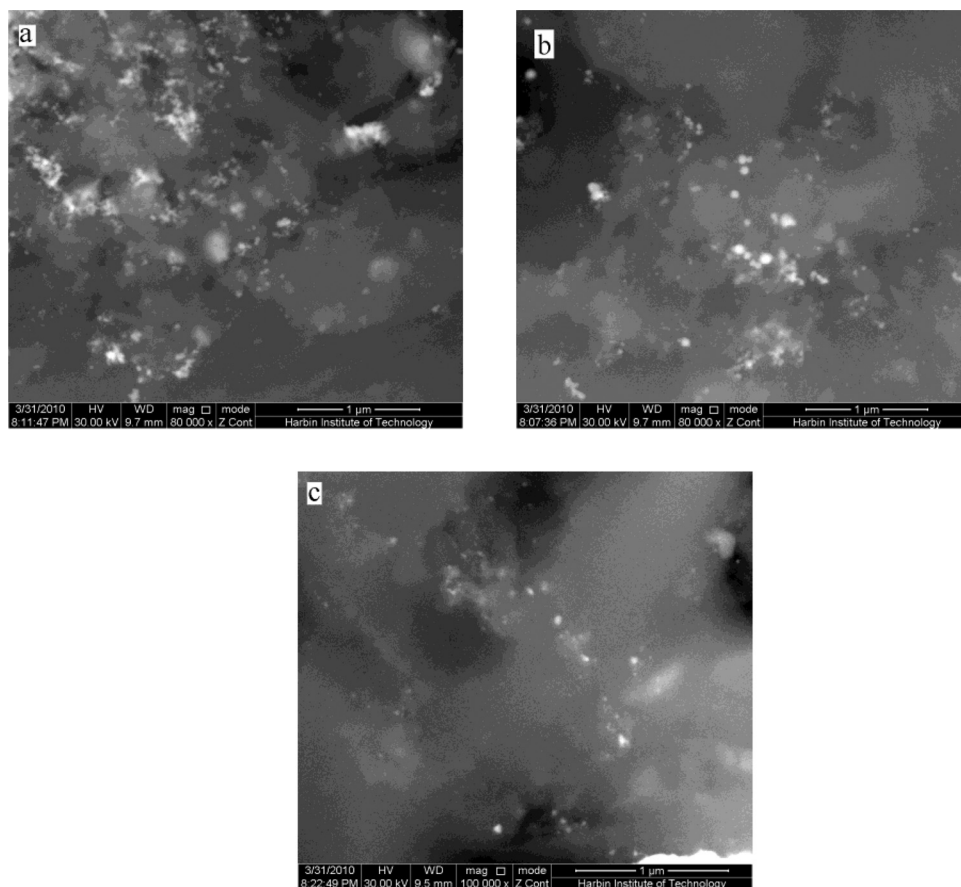


Fig. 1 SEM images of (a) 20-, (b) 10-, and (c) 5-wt.% Ag/C catalysts

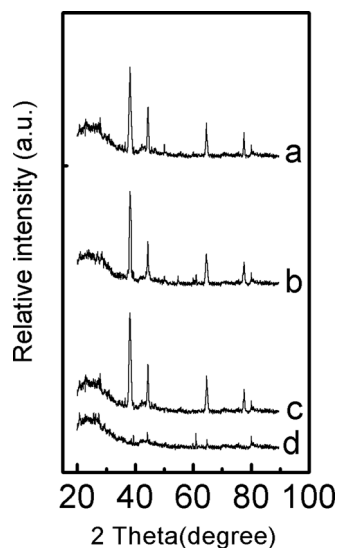


Fig. 2 XRD patterns of (a) 20-, (b) 10-, and (c) 5-wt.% Ag/C catalysts and (d) Vulcan-XC 72R carbon

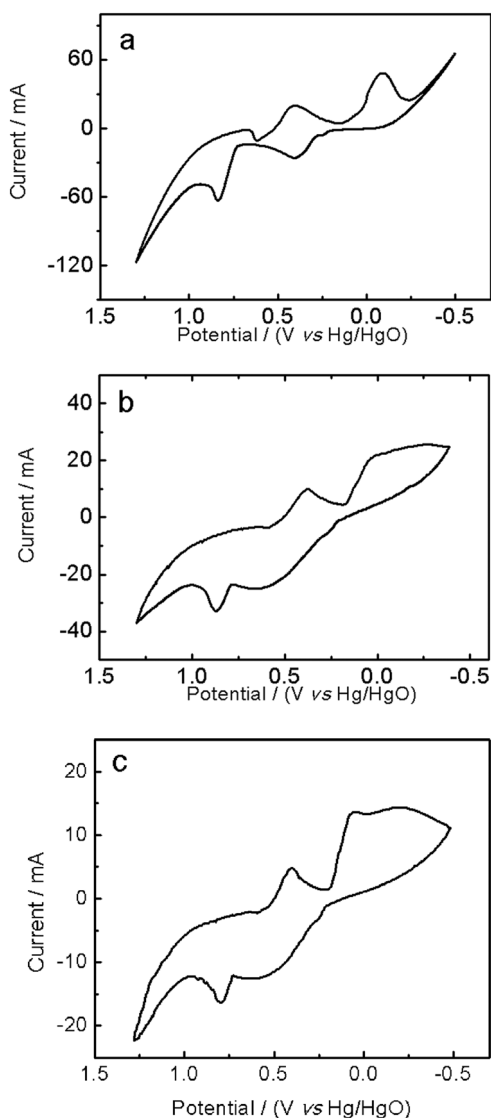


Fig. 3 Cyclic voltammograms of (a) 20-, (b) 10-, and (c) 5-wt.% Ag/C catalysts

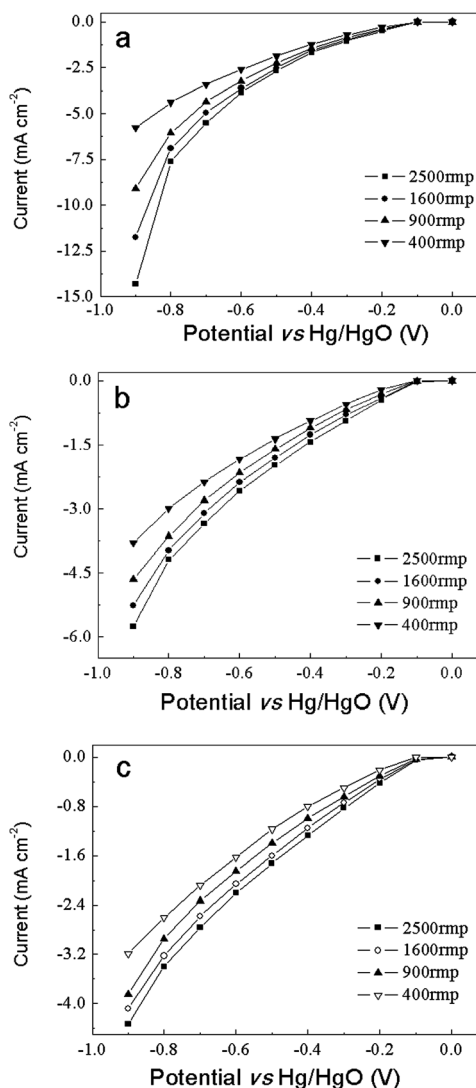


Fig. 4 Polarization curves of the oxygen reduction on (a) 20-, (b) 10-, and (c) 5-wt.% Ag/C catalysts

catalysts with different Ag contents are identical, the ORR should proceed by the same pathway either on 20-wt.% Ag/C catalysts or on 5-wt.% Ag/C catalysts. Thus, the two-electron peak observed in Fig. 3(c) is attributed to be catalyzed by the Vulcan XC-72 carbon via the two-electron pathway.

To further verify the ORR mechanism on the Ag/C catalysts, the RRDE measurements were carried. Figure 4 shows the curves of the current potential for O₂ reduction on Ag/C catalysts with different Ag contents at different rotation rates.

The limiting currents at different rotation speeds are used to construct the Levich plots for different Ag/C catalysts, as shown in Fig. 5, which is derived according to Koutecky–Levich equation,

$$i_L = 0.620 n F A D_0^{2/3} \omega^{1/2} \nu^{-1/6} C_0$$

where i_L (A) is the limiting current for the electrode reaction of reactive species by the diffusion-controlled process, n (mol⁻¹) is the electron transfer number per mole of reactive species, F (C mol⁻¹) is Faraday constant, A (cm²) is electrode area, D_0 (cm² s⁻¹) is the diffusion coefficient of O₂ in 1-mol l⁻¹ KOH solution, ω (s⁻¹) is rotation rate, ν (cm² s⁻¹) is kinetic viscosity of water, and C_0 (mol l⁻¹) is the concentration of O₂ in 1-mol l⁻¹ KOH solution at 25 °C [17].

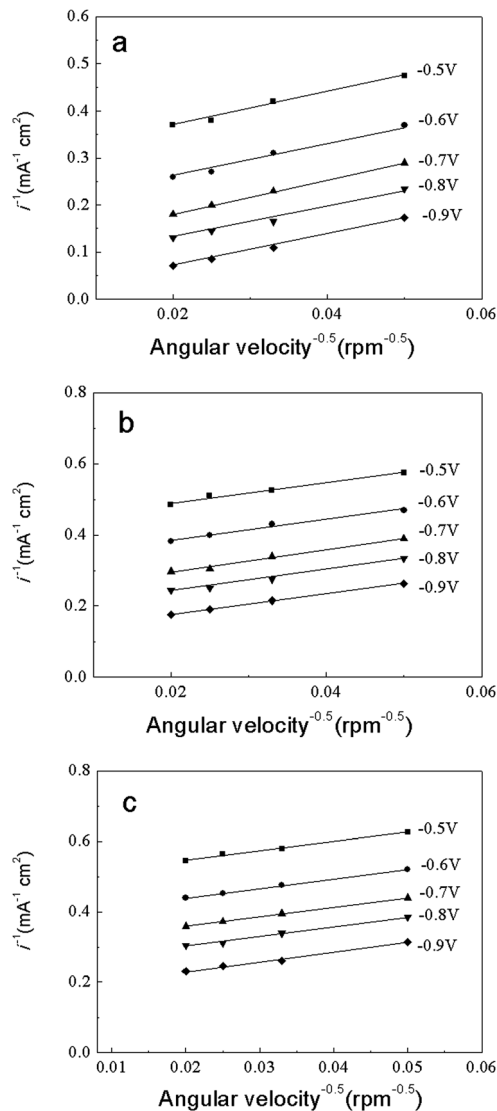


Fig. 5 Levich plots of the oxygen reduction on (a) 20-, (b) 10-, and (c) 5-wt.% Ag/C catalysts

From the slopes shown in Fig. 5, the number of electrons transferred on 5-, 10-, and 20-wt.% Ag/C were calculated to be 3.29, 3.56 and 3.88, respectively. The 20-wt.% Ag/C catalysts show that the ORR is catalyzed via a four-electron pathway. The fact that less than four electrons is transferred on 5- and 10-wt.% Ag/C indicates the ORR is catalyzed by the Vulcan XC-72 carbon via the two-electron pathway as well, which agrees with the results obtained by the cyclic voltammetry. In our previous work [15], the ORRs are found to proceed by a four-electron pathway on 20-wt.% Ag/C catalysts with larger Ag particles (174 nm).

4 Conclusion

The factors that influence the ORRs on the Ag/C catalysts have been investigated in alkaline solutions. From the results obtained by the cyclic voltammetry and the RRDE, the ORRs are found to proceed by a four-electron pathway either on Ag/C catalysts with larger Ag particles or on Ag/C catalysts with finer Ag particles. The pathway of the ORR has nothing to do with Ag particle sizes and Ag contents, but the ORR catalyzed by the Vulcan XC-72 carbon via the two-electron pathway is clear gradually, besides catalyzed by the Ag/C via the four-electron pathway with constantly decreasing Ag contents.

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