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Electrocatalytic activity and stability of Ag-MnO_x/C composites toward oxygen reduction reaction in alkaline solution

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ABSTRACT

Ag-MnO_x/C composites were prepared using $AgNO_3$ and $KMnO_4$ as the precursors and Vulcan XC-72 as the support. The physical properties of the Ag-MnO_x/C composites were investigated via X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The activity and the stability of the series of Ag-MnO_x/C composites toward the oxygen reduction reaction (ORR) in alkaline media were investigated through the electrochemical techniques. The results show that the main species MnO_2 and Ag_2O in the fresh sample convert into Mn_3O_4 and Ag(0), respectively, after the heat treatment in N_2 at 300 °C (Ag-MnO_x/C-300). The Ag-MnO_x/C-300 sample shows the highest activity toward the ORR, with the half-wave potential of the ORR shifting negatively only 0.035 V compared to that on the commercial 40 wt. % Pt/C (JM). The electron transfer number during the ORR on the Ag-MnO_x/C composite increases with the value close to four after the heat treatment at 300 °C, which is mainly attributed to the formation of Ag(0), rather than Mn_3O_4. The heat treatment brings about a better catalytic stability of the composite, and no obviously negative shift takes place for the half-wave potential of the ORR on the Ag-MnO_x/C-300 composite after 1000 cycles accelerated aging test. The maximum power density of the zinc-air battery with the Ag-MnO_x/C-300 air electrode reaches up to 130 mW cm^{-2}, higher than those based on the Pd/C and Pt/C cathode catalysts, which shows that the Ag-MnO_x/C-300 composite is a promising candidate as the catalyst for the air electrode.

1. Introduction

With the increasingly environmental pollution, it is strongly expected to develop clean energy techniques, such as fuel cells and metal-air batteries, to meet the ever-increasing demands of power sources for both portable electronics and electrical vehicles. Oxygen reduction reaction (ORR), as the main cathode reaction for these clean energy technologies, brings about the main voltage-drops because of its slow kinetics and high over-potential. At present, the widely used catalysts for the ORR are still Pt-based catalysts due to their relatively high activity and stability. However, the scarcity of Pt, associated its high cost make the necessary to replace Pt with the non-Pt electrocatalysts.

Among the numerous non-Pt electrocatalysts candidates for the ORR, manganese oxides have gained intensive attention due to their relatively high ORR activity, attractive cost and environmentally friendly [1–7]. Early work focusing on manganese oxides as the ORR catalysts in alkaline media produced a wide range of conclusions about the effect of the chemical composition, crystallographic structure and the morphology on the catalytic activity [8–10]. For example, the orders of the ORR activity of different manganese oxides are as follows: $Mn_5O_8 < Mn_3O_4 < Mn_2O_3 <$ MnOOH [10], β-MnO_2 < λ-MnO_2 < γ-MnO_2 < α-MnO_2 ≈ δ-MnO_2 [11], as well as α-MnO_2 nano-spheres and nano-wires outperform their counterpart in the morphology of microparticles [4], and so on. On the other hand, silver, as the less expensive noble metal, has also been extensively reported for its relatively high activity toward the ORR [12–14], with the ORR overpotential being about 50-100 mV negative shift compared to that on Pt/C [12,14,15]. Besides, the superior ORR activity at high pH, coupled with the better long-term stability of Ag in alkaline media make it competitive with Pt as an oxygen cathode catalyst [16–18]. However, though the widely acknowledged four electron pathway during the ORR on Ag is predominant, peroxide could still be produced as an intermediate [12,19]. Interestingly, manganese oxides are the best candidates for their excellent activity for peroxide decomposition [20,21]. Therefore, recent researches have been carried out to combine the advantages of Ag and MnO_x into one Ag-MnO_x/C catalyst [22–26], and found that a synergistic effect may exist among Ag and MnO_x [25].

Among the several methods for the preparation of the Ag-MnO_x/C composites, $AgMnO_4$ pyrolysis is the first choice due to the

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relatively higher activity of the Ag-MnO_x/C composite toward the ORR than the others [23–25], however, the only drawback of this method is that the atomic ratio of Ag/Mn could not be altered and the preparation of the $AgMnO_4$ is relatively cumbersome [25]. In this paper, the Ag-MnO_x/C composite was prepared using $KMnO_4$ and $AgNO_3$ as the precusers, then heat treated in N_2 at different temperature. The conditional experiments shows the optimum Ag/Mn atomic ratio and the precious metal (Ag) loading in the composite, which shows the comparable activity toward the ORR compared with that for the sample prepared by $AgMnO_4$ pyrolysis, are only 0.4 and 10 wt. %, respectively, much lower than the values (1 and 22 wt. %) in reference [25], and the detail discussion about these are not present here. The ORR activity and stability of the composite with the optimized Ag/Mn atomic ratio and the Ag loading before and after the heat treatment were investigated in detail, meanwhile the possibility of the composite as the catalyst in the air electrode was evaluated in real zinc-air battery.

2. Experimental

2.1. Chemicals and materials

The carbon support (Vulcan@ XC-72, $S_{BET} = 250\ m^2\ g^{-1}$) was purchased from Cabot Corporation. The 40 wt. % Pt/C was purchased from Johnson Matthey, denoted as JM. All the other chemicals are analytic reagents and used as received without any further treatment.

2.2. Synthesis of catalysts

The preparation precess for the Ag-MnO_x/C composite with the mass loadings of 10 wt. % Ag and 20 wt. % MnO_x (MnO_2 supposed as the active material) was as follows: firstly, 145.4 mg $KMnO_4$ (0.92 mM) and 63 mg $AgNO_3$ (0.37 mM) were added into the homogeneous aqueous suspension of 288 mg carbon black (XC-72) in 92 mL of H_2O, then stirred ultrasonicly at room temperature for 10 minutes to ensure the total dissolution of $KMnO_4$ and $AgNO_3$. Later, the suspension was transferred to a flask and stirred mangnetically for 30 minutes at 80 °C. The resultant precipitate was filtrated, washed by DI water, and dried at 70 °C in vacuum. The filtrate was detected by X-ray fluorescence and the results showed that silver and manganese were completely deposited onto the carbon surface. Carbon works partially as the reducing agent via the reaction: $4KMnO_4 + 3C + 2H_2O \rightarrow 4MnO_2 + 3CO_2\uparrow + 4KOH$ and partially as the support for Ag and MnO_x. The prepared sample is denoted as Ag-MnO_x/C-fresh. Then, a certain amount of the composite prepared above, about 100 mg, was transferred to a quartz boat which was then placed in a tube furnace. The tube furnace was heated to the aimed temperature with a heating rate of 5 °C min^{-1} after flowing highly-purified N_2 into the furnace to replace the air thoroughly, and then kept at the aimed temperature for 2 h. After that, the composite was naturally cooled down to room temperature in highly-purified N_2. The sample treated at 200, 300 and 400 °C are denoted as Ag-MnO_x/C-200, Ag-MnO_x/C-300 and Ag-MnO_x/C-400, respectively.

For comparison, the 30 wt. % MnO_x/C composite was synthesized by a process described as follows: the homogeneous aqueous suspension of carbon (146 mg) and $KMnO_4$ (109 mg) was stirred mangnetically for 30 minutes at 80 °C, then filtrated, washed, and dried at 70 °C in vacuum. The procedure of the heat treatment for the MnO_x/C composite is same as that for the Ag-MnO_x/C composite. On the other hand, 20 wt. % Pt/C and 20 wt. % Pd/C were also prepared with $NaBH_4$ and ethylene glycol as the reducing agent [27], respectively, and used as the cathode catalysts for the zinc-air batteries for comparison.

The 30 wt. % Ag/C was synthesized according to reference [12]. 823 mg of sodium citrate and 95.2 mg of $AgNO_3$ were dissolved in 69 mL of DI water, and then 75.7 mL of $NaBH_4$ solution (7.4 mM) was added dropwise under vigorous stirring to obtain a yellowish-brown Ag colloid. Later, the aqueous suspension with 140 mg carbon (XC-72) was added into the Ag colloid, after stirred for 8 h, the suspension was filtered, washed and dried in vacuum at 70 °C.

2.3. Physical characterization of the catalysts

The crystalline structure of the prepared catalysts were analyzed by X-ray diffraction (XRD) recorded on a Rigaku X-2000 diffractometer using Cu Kα radiation with a Ni filter. The tube voltage and the tube current were kept at 40 kV and 100 mA, respectively. The 2θ angular was scanned from 10^o to 90^o with the scan rate being $5^o\ min^{-1}$. The elemental valence on the surface of the composites was analyzed by X-ray photoelectron spectroscopy (XPS) performed on Thermo Fisher Scientific K-Alpha (UK) using an Al-Kα radiation (1486.6 eV). The power was 72 W (12 kV, 6 mA) and the binding energies were regulated according to C1s peak at 284.8 eV from the samples. The morphology of the samples was recorded by JEOLJEM-2011EM microscope operated at 120 kV.

2.4. Electrochemical measurements

The activity of the catalysts toward the ORR was evaluated by the rotate disk electrode (RDE) and the rotating ring-disk electrode (RRDE) techniques according to the reference [25]. RDE and RRDE techniques were performed on an electrochemical workstation (CHI 760D, Chenhua Company) and a bipotentiostat (Pine Instrument), respectively. Briefly, a glassy carbon disk electrode covered with a catalyst film was served as the working electrode, while a Pt-wire and a Hg/HgO electrode used as the counter and the reference electrodes, respectively. The working electrode was prepared as follows: 5.0 mg of catalyst was mixed with 2 mL of absolute ethanol and 40 μL of Nafion solution (5 wt. %, DuPont, USA), then formed a homogeneous suspension ultrasonically. 20 μL of the prepared catalyst suspension was deposited on the RDE (Φ5 mm) or the disk of the RRDE (Φ5.7 mm), and then the solvent was evaporated at room temperature. For the RRDE measurements, the ring potential was fixed at 0.20 V (vs. Hg/HgO), which is high enough to oxidize the HO_2^- produced on the working electrode. The collection efficiency of the RRDE (N) is 0.38. The HO_2^- yields and the electron transfer numbers(n) of the ORR were calculated by the equations $X_{HO2-} = (2I_{ring}/N)/(I_{disk} + I_{ring}/N)$ and $n = 4\text{-}2 \times X_{HO2-}$, respectively. All the potentials in this paper refer to the Hg/HgO in 0.1 M NaOH aqueous solution unless otherwise stated.

In order to evaluate the short-term catalytic stability of the composites toward the ORR, accelerated aging tests (AAT) were performed. The cyclic voltammetry (CV) curves in N_2-saturated 0.1 M NaOH solution and the linear scanning voltammetry (LSV) curves in O_2-saturated 0.1 M NaOH solution were recorded before and after each certain cycles running between -0.500 and 0.200 V with the scan rate of 0.100 V s^{-1} in O_2-saturated 0.1 M NaOH solution at room temperature.

2.5. Zinc-air battery tests

A homemade zinc-air single battery with the zinc foil and the air electrode as the anode and cathode electrodes, respectively, was fabricated to evaluate the possibility of the composite used as the cathode catalyst. The 32 cm^2 air electrodes with different catalysts were prepared as follows: a certain amount of activated carbon, acetylene black, catalyst as well as 40 wt. % poly(tetrafluoro- ethylene) (PTFE) and DI water were mixed to form homogeneous slurry. The slurry was brushed onto the Ni-foam with the back covered