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Manganese dioxide-supported silver bismuthate as an efficient electrocatalyst for oxygen reduction reaction in zinc-oxygen batteries

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ABSTRACT

In this paper, we present a new efficient composite electrocatalyst, manganese dioxide-supported silver bismuthate ($Ag_4Bi_2O_5/MnO_2$), for oxygen reduction reaction (ORR) in alkaline media. The new electrocatalyst was characterized with scanning electron microscope (SEM), powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Electrochemical measurements indicate that the $Ag_4Bi_2O_5/MnO_2$ composite is a very efficient electrocatalyst for ORR in alkaline media. The physical and electrochemical characterization results suggest that the high activity is ascribed to the support effects from MnO_2 and the synergetic effects among $Ag_4Bi_2O_5$ and MnO_2. The analysis of rotating disk electrode (RDE) results shows that the ORR occurs via a four-electron pathway on the surface of the $Ag_4Bi_2O_5/MnO_2$ electrocatalyst. This electrocatalyst was further tested in a designed zinc–oxygen ($Zn–O_2$) battery. This battery can offer a discharge time of 225 h at $120\,mA\,cm^{-2}$, increasing by more than 492% as compared with pure MnO_2 electrocatalyst. It demonstrates that this inexpensive $Ag_4Bi_2O_5/MnO_2$ electrocatalyst is a viable alternative to platinum electrocatalyst for energy conversion devices.

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1. Introduction

Fuel cells, zinc oxygen ($Zn–O_2$) and lithium oxygen ($Li–O_2$) batteries are considered to be the promising power sources for electric vehicles and bikes [1–6]. However, the oxygen reduction reaction (ORR) at the cathodes of these electrochemical devices is very sluggish so that the usage of highly active electrocatalysts is indispensable. Platinum (Pt)-based materials are commonly used as the electrocatalysts for ORR due to their high catalytic activity and durability in both acidic and alkaline media. But the high cost and scarcity of Pt seriously hinder its widespread application in the field of electric vehicles [7–9]. Therefore, there is a great need for the development of Pt-free electrocatalysts towards ORR. The carbon-supported non-precious metals and transition metal oxides (Ag/C, CoO_x/C, MnO_x/C) have been investigated extensively as electrocatalysts to catalyze ORR in alkaline media [10,11]. Among these materials, manganese oxides have been proposed as the most potential candidates for cathode electrocatalysts due to their low price, environmentally friendly nature and Pt-like

behavior towards ORR [12,13]. Nevertheless, this application is limited because MnO_2 has moderate catalytic activity towards ORR and is easy to transform into relatively electrochemical inert Mn_3O_4, which reduces its electrochemical activity, particularly at high overpotential [14,15].

Recently, it has been found that doping $Ag_4Bi_2O_5$ nanoparticles with MnO_2 can significantly improve the discharge specific capacity and electrochemical stability of MnO_2 cathode materials for alkaline secondary batteries [15]. The remarkable improvement may result from the better synergistic effects of the Ag–Bi as compared with the existing single element dopant [16–19]. It is expected that nano-$Ag_4Bi_2O_5$ supported by MnO_2 may have superior catalytic activity towards ORR. In the present paper, we report a new efficient electrocatalyst, manganese dioxide-supported silver bismuthate ($Ag_4Bi_2O_5/MnO_2$) composite, for ORR in alkaline media. The $Ag_4Bi_2O_5/MnO_2$ composite electrocatalyst was obtained by the deposition of $Ag_4Bi_2O_5$ nanoparticles onto the surface of MnO_2 particles. Its catalytic activity towards ORR is far superior to that of the existing pure MnO_2 electrocatalyst. This enhancement might benefit from the activity of $Ag_4Bi_2O_5$, the support effects from MnO_2, and the stabilization of MnO_2 by the synergetic effects among Ag, Bi and Mn.

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2. Experimental

2.1. Synthesis of $Ag_4Bi_2O_5/MnO_2$ electrocatalyst

The manganese dioxide (MnO_2) (Jianchen Electrolytic Manganese Industry Company, China) was pretreated with a planetary ball mill for 1 h, and then selected using a 300-mesh 304 stainless steel screen. The obtained 18 g 300-mesh MnO_2 (90 wt.% of the total catalyst) was added to a base solution containing 50 mL 4 mol L^{-1} KOH, which was denominated as solution A. In addition, 1.16 g Ag_2O and 1.17 g Bi_2O_3 (AR, Fuchen Special Chemical Industry, China) were dissolved in 50 mL 1 mol L^{-1} HNO_3 (denoted as solution B). 11.87 g KOH was dissolved in deionized water to obtain 50 mL 9 mol L^{-1} KOH (denoted as solution C). Under the conditions of 45 °C and a strong agitating at 800 rpm, 50 mL solution B and 50 mL solution C were pumped into the base solution A by two peristaltic pumps at a flow rate of 0.2 mL min^{-1}, respectively. The $Ag_4Bi_2O_5$ was then generated and precipitated on the surface of MnO_2 to form the $Ag_4Bi_2O_5/MnO_2$ electrocatalyst.

2.2. Morphological and structural characterizations

The morphology of the synthesized samples was examined by a field-emission scanning electron microscope (FSEM, S4700, Hitachi, Japan). The energy-dispersive X-ray (EDX, Oxford EDS Inca Energy Counter 300, operated at 10 kV) microanalysis was conducted to validate the element compositions and contents. The phase structures of the prepared electrocatalysts were analyzed using a Rigaku D/max2500VB2+/PCX X-ray diffractometer (XRD)

with a Cu anticathode (40 kV, 200 mA) at a scanning rate of 10° min^{-1} and a scanning angle (2θ) from 10° to 90°. X-ray photoelectron spectroscopy (XPS) was carried out on a ULVAC-PHI Quantera SXM. The data were corrected on the basis of the binding energy of C (286.4 eV).

2.3. Electrochemical tests

The rotating disk electrode (RDE) tests were carried out with an electrochemistry workstation (PARSTAT 2273) in a three-electrode system at room temperature. A Pt wire and a saturated calomel electrode (SCE) were used as the auxiliary electrode and the reference electrode, respectively. The well-dispersed catalyst ink (5 mg mL^{-1}) was prepared by adding 0.02 g electrocatalyst (MnO_2, $Ag_4Bi_2O_5$ or $Ag_4Bi_2O_5/MnO_2$) and 0.005 g acetylene black (battery level, Hangzhou Juychem) into a solution of 1.85 g deionized water, 0.15 g Nafion (5 wt.%, D520 DuPont) and 1 mL isopropanol under a sonication process for 30 min. 10 μL of the catalyst ink was taken by a Toppette Pipettor and dripped onto the surface of a polished glassy carbon rotating disk electrode (φ = 5 mm, Pine Instrument). The solvent was completely evaporated at room temperature. The catalyst loading on the working electrode was 0.2 mg cm^{-2}.

The cyclic voltammetry (CV) test was carried out to study the electrochemical activity and stability of the electrocatalysts in ultra-high purity argon or oxygen-saturated 0.1 mol L^{-1} KOH solution at room temperature. The CV was tested in the potential range from −1.0 to 0 V vs. SCE at a scanning rate of 50 mV s^{-1}. The ORR activity of an as-prepared electrocatalyst was evaluated by linear sweep voltammetry (LSV) in ultra-high purity

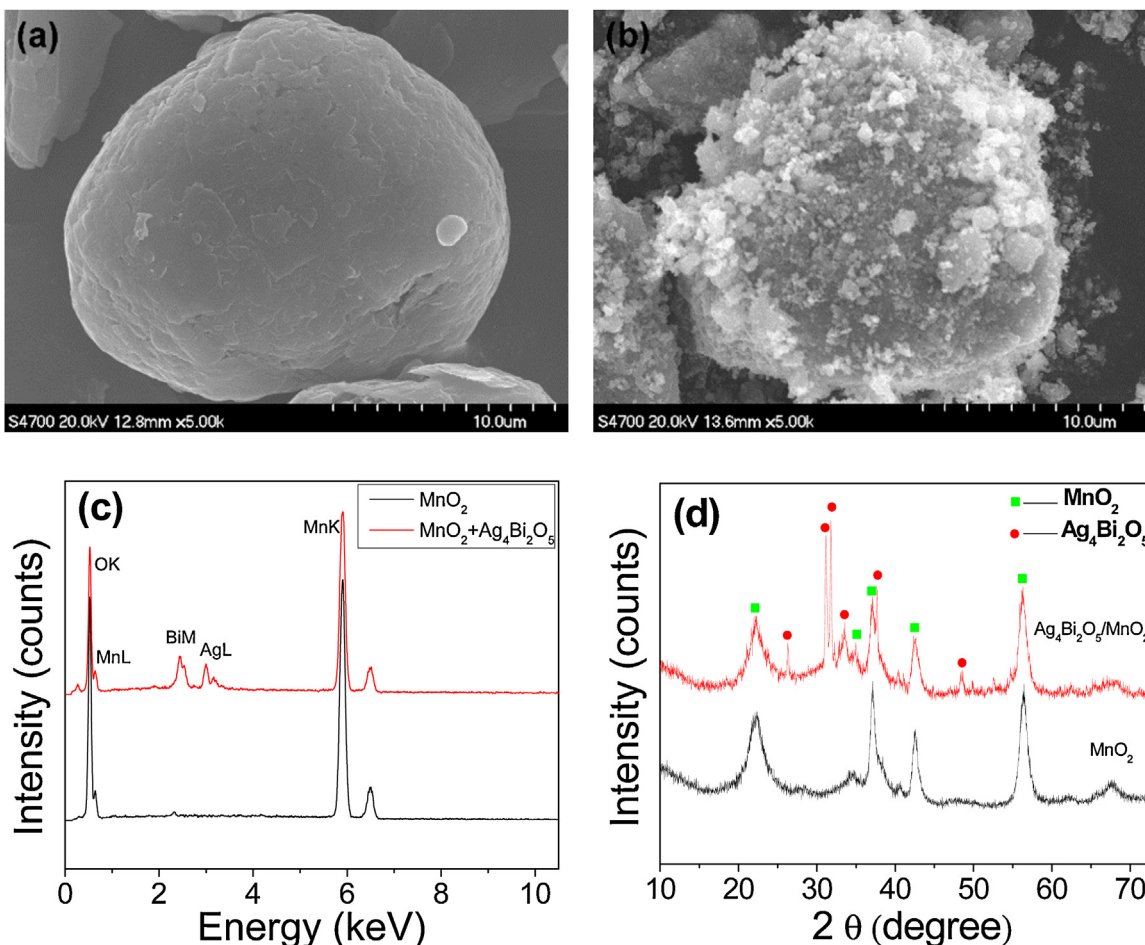**Fig. 1.** FSEM images of (a) MnO_2 and (b) $Ag_4Bi_2O_5/MnO_2$, (c)EDS spectra, and (d) XRD patterns of the MnO_2 and $Ag_4Bi_2O_5/MnO_2$ samples.