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Enhanced electrochemical properties of manganese dioxde doped with Ag_3BiO_x

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Abstract In this work, Ag_3BiO_x was prepared and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical properties of electrolytic manganese dioxide (EMD) cathodes doped with Ag_3BiO_x were studied by galvanostatic charge/discharge and cyclic voltammetry. The results indicated that the electrochemical performance of EMD electrode was effectively improved by doping of Ag_3BiO_x. EMD electrode doped with Ag_3BiO_x possessed remarkably higher discharge voltage, larger capacity and better reversibility than that of pure EMD electrode.

Keywords: Manganese dioxide, Ag_3BiO_x, Dopant, Electrochemical properties

1. INTRODUCTION

The alkaline Zn/MnO_2 cell provides a major advance on most conventional battery types in portable power sources [1,2].However, due to the low discharge capacity on heavy load and poor rechargeability for the existing alkaline Zn/MnO_2 cells, lots of attempts have been made to improve manganese dioxide through adding other elements. In order to improve the performances of manganese dioxide electrodes, many studies on the addition of bismuth oxide (Bi_2O_3) [3–10], Pb-oxide [11] and other materials [12–18] were carried out. On the basis of these studies, these materials improve the utilization and cycling property of MnO_2 electrode. However, there is no significant effect on discharge performance in the high voltage region above 1.0V [19, 20]. This is very important because most digital products demand the good discharge property in this region.

In order to overcome these disadvantages, in this work, a new material, Ag_3BiO_x, was firstly used as dopant in the manganese dioxide. The physical properties and electrochemical performances of the synthesized products have been investigated in detail. The results have indicated that it can improve the performance of high voltage discharge and cycling ability for manganese dioxide.

This study focused on the chemical preparation of high purity Ag_3BiO_x and the improvement to the discharge performance and rechargeability by incorporating Ag_3BiO_x to manganese dioxides electrodes.

2. EXPERIMENTAL PART

2.1. Chemical synthesis of Ag_3BiO_x

Silver nitrite ($AgNO_3$) and bismuth nitrite ($Bi(NO_3)_3$) were weighed to obtain an Ag/Bi mol ratio of 3. The $AgNO_3$ and $Bi(NO_3)_3$ were added under stirring to an aqueous solution (1.5 liter) containing 10 mol of dissolved KOH per mol of the two nitrites combined, thereby producing a neutralized precipitate in the solution. The neutralized precipitate suspension obtained was heated to 90 ^{0}C, and subjected to oxidation treatment by, under stirring, adding potassium peroxodisulfate ($K_2S_2O_8$) as oxidizing agent to the suspension at the ratio of 1:1 Ag and Bi. After the oxidation treatment, the oxidized precipitate was ripened by holding it at a temperature of 90 ^{0}C for 60 min; the precipitate was recovered by filtering, washed with water and dried at 100 ^{0}C. The oxidation treatment is a treatment for raising the valence of the Ag and Bi in the neutralized precipitate, e.g, a treatment for oxidizing Ag^{+1} to Ag^{+2}, Bi^{+3} to $Bi^{+3.5}$or Bi^{+5}.

$$3AgNO_3 + Bi(NO_3)_3 + 6NaOH \rightarrow Ag_3BiO_3 + 6NaNO_3 + 3H_2O$$

$$\left[Ag^{(+1)} \rightarrow Ag^{(+1.8)} \text{ and } Bi^{(+3)} \rightarrow Bi^{(+3.5)} \text{ oxidation reaction} \right][21]$$

$$\begin{aligned} &Ag_3BiO_3 + (0.8\times3 + 0.5)/2\ K_2S_2O_8 + (0.8\times3 + 0.5)NaOH \rightarrow \\ &Ag_3BiO_{(1.8\times3+3.5)/2} + (0.8\times3 + 0.5)\ K_2SO_4 + (0.8\times3 + 0.5)/2\ H_2O \end{aligned}$$

2.2. Morphological and structural characterization

The morphology and granularity of Ag_3BiO_x were observed by means of SEM (LEO 1430VP, Germany). The crystalline structure of Ag_3BiO_x sample was characterized by powder X-ray diffractometry (XRD) on a MAC M18Xce Diffractometer with Cu Kα radiation source.

2.3. Electrochemical measurements

Electrolytic manganese dioxide (EMD) powders (Xiangtan Electrochemical Technology Co., Ltd) were doped with various ratios of Ag_3BiO_x powders. Both powders were well mixed until homogenization in an agate mortar for about 30 min. The prepared product was physically modified EMD (Ag_3BiO_x-EMD). As comparision, pure EMD was used which has a theoretical capacity of 308 mAh• g^{-1} in regard to one-electron discharge step. The working electrode was manufactured from the mixture of cathode active material with expansive graphite and acetylene black as conductive additive and polytetrafluoroethylene (PTFE) as binder. The electrode performance was measured by a three-electrode configuration. The working electrode was composed of a 5:2:1 mixture of Ag_3BiO_x, graphite and acetylene black. The mixture was milled in an agate mortar and then pressed into nickel foam current collector, forming a 1.0mm thick pellet. Platinum foil was used as an auxiliary electrode. Hg/HgO electrode was used as a reference electrode and was separated from the working electrode by a Luggin capillary. Experiments were performed in 9 M KOH electrolyte at room temperature. The gavanostatic discharge was performed using a BT2042 battery tester at different constant current densities to a voltage of -1.0 V. The cyclic voltammograms were recorded in the potential envelope of +0.4 and -1.0 V vs Hg/HgO at a scan rate of 0.5 mV/s. The cycling experiments were carried out under constant current in the range of -0.4 and +0.35 V vs. Hg/HgO with discharge and charge rates of C/2 and C/4, respectively.

3. RESULTS AND DISCUSSION

3.1. Surface morphology and structural characterization

The morphology of Ag_3BiO_x was observed with scanning electron microscope (seen from Fig.1). The particles of Ag_3BiO_x sample were distributed uniformly and had regular crystal shapes. Such kind of morphology is very important to excellent electrochemical performance of the materials.

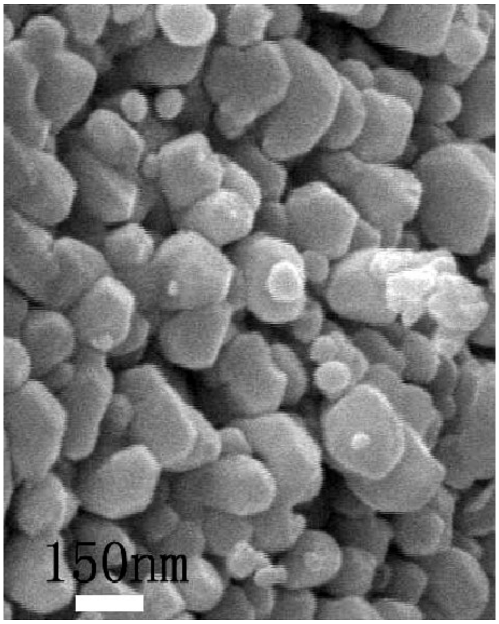

Figure1. SEM of Ag_3BiO_x

Fig. 2 showed the XRD pattern of Ag_3BiO_x. The powder particles are clearly composed of crystals having many peaks but different from those of Bi_2O_3, Ag_2O and AgO. The new peaks composed of the three elements Ag, Bi and O [21].

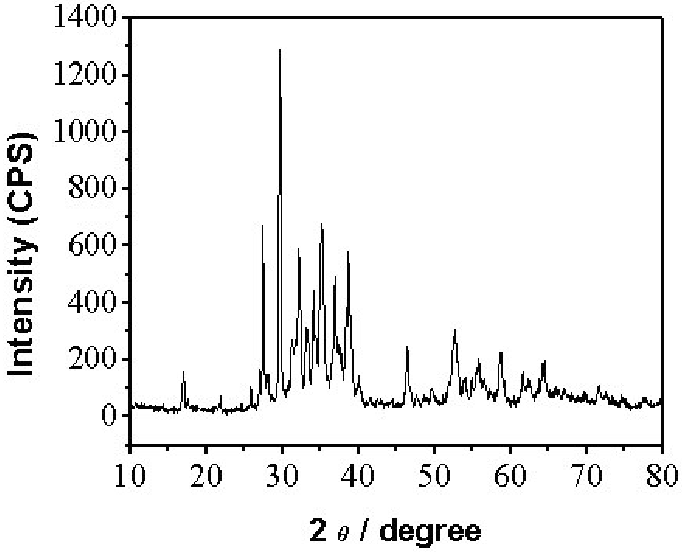

Figure 2. XRD pattern of Ag_3BiO_x

3.2. The electrochemical performance of Ag_3BiO_x -EMD electrodes

3.2.1. Discharge of Ag_3BiO_x -EMD electrodes

Both Ag_3BiO_x-EMD and EMD electrodes were studied with platinum foil as counter electrodes and Hg/HgO as reference electrodes under the same test condition. Fig.3 showed the galvanostatic discharge curves of the EMD electrodes doped with various contents of Ag_3BiO_x. The electrodes were discharged up to -1.0 V under a constant current of 50 mAg^{-1}.

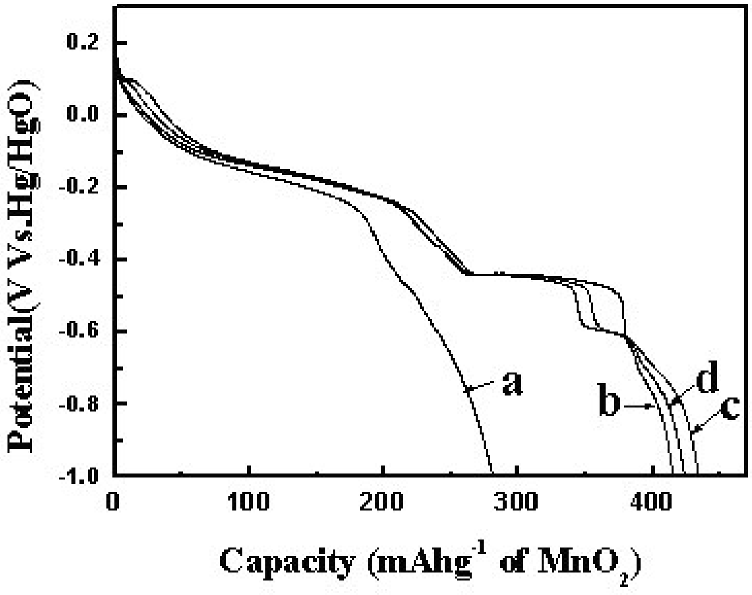

Figure3. Discharge curves of Ag_3BiO_x-EMD electrodes with different contents of Ag_3BiO_x: EMD+ Ag_3BiO_x (wt.) %: (a) 0; (b) 2; (c) 5; (d) 9.

It can be seen from Fig.3, the discharge property of the EMD doped by Ag_3BiO_x was obviously superior to that of pure EMD, as indicated by the higher discharge voltage and capacity of Ag_3BiO_x-EMD. The capacity of Ag_3BiO_x -EMD increased up to 30% (above -0.4 V) and to 54.5% (down to -1.0 V) as compared with pure EMD electrode. The doping of Ag_3BiO_x enhanced the activity of MnO_2 and decreased the cathodic polarization of MnO_2 so as to raise the discharge voltage of Ag_3BiO_x -EMD. It appeared a wide discharge platform at -0.15 and -0.43V for Ag_3BiO_x-EMD, while no discharge platform for EMD.The considerable increase in discharge capacity was due to the discharge capacity of the second electron of MnO_2. That can be expressed by the following reaction:

$$MnOOH + H_2O + e^- \rightarrow Mn(OH)_2 + OH^-$$

From the results, it was also observed that the activity of MnO_2 was enhanced with the doping content of Ag_3BiO_x up to a certain level ((optimum doping of Ag_3BiO_x) and then decreased. This indicated that the extra doping caused a decrease in relative amount of MnO_2, thus decreased the discharge capacity of Ag_3BiO_x-EMD electrode. The result showed that an optimum doping dosage is 5%.

3.2.2. Cyclic voltammetry

Fig. 4A and 4B were the first five cycle voltammetric curves of the MnO_2 electrode and 5% Ag_3BiO_x doped MnO_2 electrode. It can be seen that the pure MnO_2 electrode has two reduction peaks in the range of -0.1-0.6V, corresponding to Mn(IV)→Mn(III)(-0.2V, versus Hg/HgO) and Mn(III)→Mn(II) (-0.52 V). The two corresponding anodic peaks also occur in the reverse scan process. Additionally, Fig. 4a showed the gradual decrease in peak current in the cycling process of MnO_2. The reason is that Mn(III) is partially dissolved to form $[Mn(OH)_4]^-$, causing decrease in active material on the one hand, and the electrochemically inert material Mn_3O_4 is formed in this range[7–10] on the other hand. Yu and his co-workers [22, 23] have also observed the peak of Mn_3O_4 on the CV curve for MnO_2 electrode and remark that Mn_3O_4 has no electrochemical activity. For the first cycle of the doped sample, the relatively lower reduction peak probably comes from the coreduction process of Ag_3BiO_x and MnO_2, namely, Bi(V)Mn(IV)→Bi(III)Mn(III). Besides, the formation peak for Mn_3O_4 does not appear during the reduction process. Therefore, it can be concluded that the doping of Ag_3BiO_x prevented the formation of Mn_3O_4. If Bi(III) was present, the formation of Mn_3O_4 did not occur [22, 23]. In the same way, the reduction peak at -0.6V corresponded to Bi(III)Mn(III) →Bi(III)Mn(II).

Fig. 4 also demonstrated that the doped MnO_2 electrode had two reduction peaks, obviously greater than that of pure MnO_2 electrode, respectively. That indicated that Ag_3BiO_x -EMD electrode had much higher electrochemical activity than EMD electrode.

In the reverse process of cyclic voltammetry, the oxidation peak of the doped sample at -0.5 V possibly corresponds to Bi(0)→Bi(III) and the two oxidation peaks at -0.05 and 0.15 V correspond to the successive oxidation of Bi(III)Mn(II)→ Bi(III)Mn(III) →Bi(III)Mn(IV) [24]. The oxidation peak of the doped sample (-0.05 V) moves to the negative direction. That is attributed to the increase in reversibility of EMD electrode due to Ag_3BiO_x doping. From the first five cycles of cyclic voltammetry, it can be seen that the peak current of MnO_2 electrode (-0.1 V) gradually decreased down to zero. Comparatively, the oxidation peak of Ag_3BiO_x-EMD gradually and slightly moved to the positive direction (-0.05→0.03 V), but the peak current gradually increased to a stable value. It was apparent that Ag_3BiO_x doping made the oxidation or reduction process easier and increased the reversibility of MnO_2.

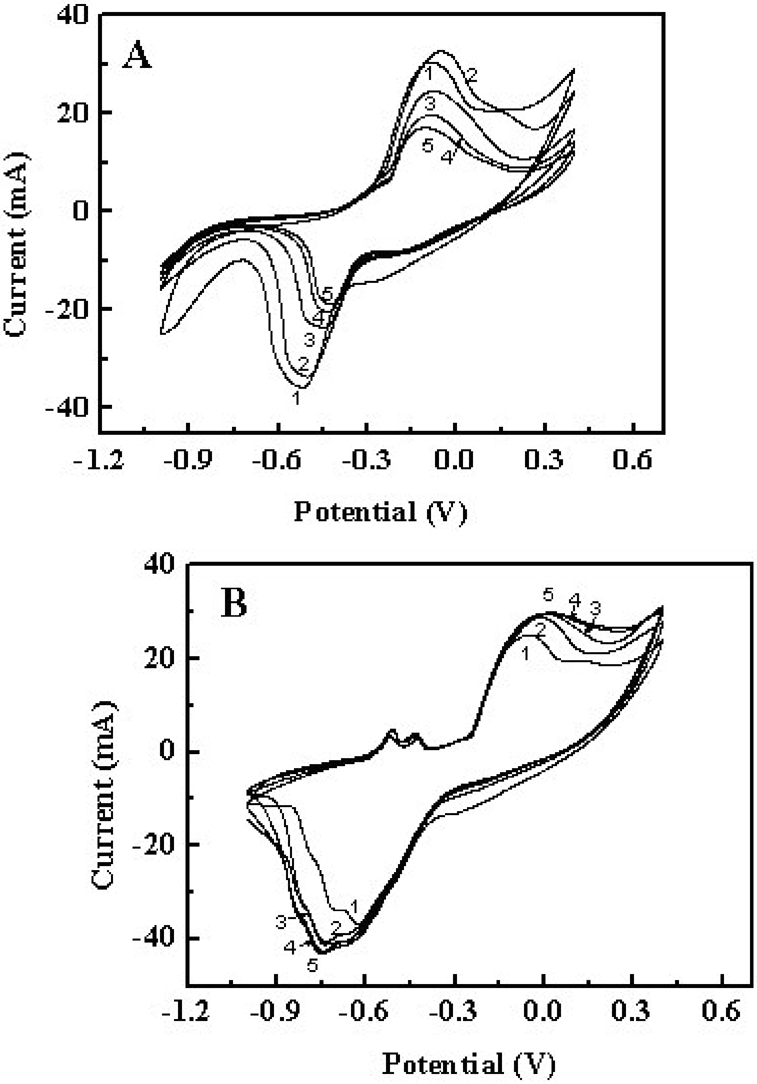

Figure 4. Cyclic voltammogram of EMD (A), Ag_3BiO_x-EMD (B). Mixture ratio: 95% EMD+5% Ag_3BiO_x

3.2.3. Cyclability

Fig. 5 illustrated the capacity of single electron versus cycling numbers following the regime that Ag_3BiO_x-EMD (doped with 5% Ag_3BiO_x by weight), 5 % Bi_2O_3-EMD and pure EMD electrodes were discharged down to -0.4 V at C/2, followed by galvanostatical charging up to 0.35 V at C/4[25].

Although the voltage was fading during the cycles, the Ag_3BiO_x-EMD electrode showed the higher capacity and longer cycling life than 5 % Bi_2O_3-EMD and pure EMD electrodes. During the first 10 cycles, the average cycling capacity of Ag_3BiO_x-EMD electrode was up to 135 mAh• $g^{-1}$and greater than that of EMD electrode. Obviously, the improvement of cycling property benefited from the doping of Ag_3BiO_x. Thus, Ag_3BiO_x offered an important benefit of good long-term cyclability compared to the Bi_2O_3 additive.

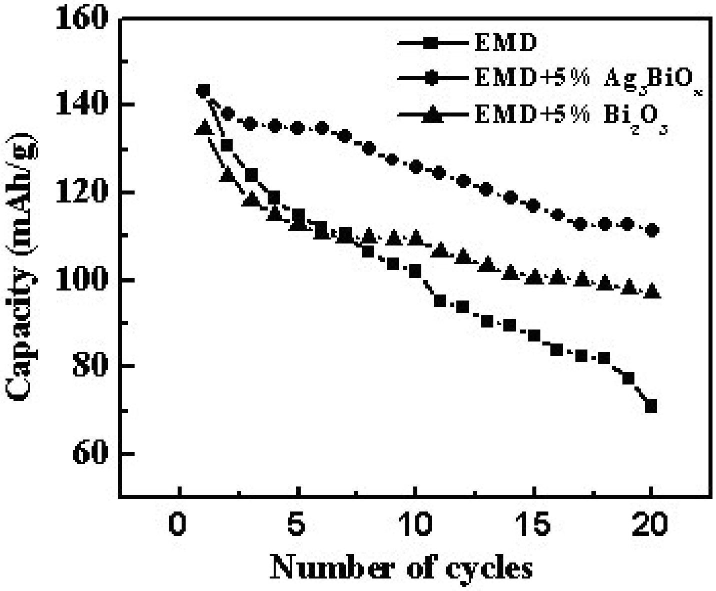

Figure 5. Cycle life curves of EMD, Ag_3BiO_x-EMD and Bi_2O_3-EMD electrodes

4. CONCLUSIONS

Ag_3BiO_x has been synthesized by a chemical oxidization method. The results indicated that the doping of Ag_3BiO_x can increase the discharge capacity and rechargeability considerably in the one-electron region compared to that doped with Bi_2O_3. The doping of Ag_3BiO_x put a new way to enhance the commercial feasibility of alkaline manganese dioxide cells.

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