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Effects of temperature and concentration of sulfuric acid on the electrodeposition of grainy electrolytic manganese dioxide

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Abstract: The effects of temperature and the concentration of sulfuric acid on the cell voltage, the anode current efficiency of electrodeposition and the particle size of grainy electrolytic manganese dioxide (EMD) were investigated. The structure, particle size and appearance of grainy EMD were determined by powder X-ray diffraction, laser particle size analysis and scanning electron micrograph measurements. As the concentration of sulfuric acid increases, both the cell voltage and the average anode current efficiency decrease. With the increase of electrolysis temperature in the range of 30-60°C, the cell voltage, average anode current efficiency and particle size decrease. The optimum temperature of 30°C and concentration of sulfuric acid of 2.5 mol/L for electrodeposition of the grainy EMD were obtained. XRD patterns show that the grainy EMD electrodeposited under the optimum conditions consists of γ-MnO_2 and has an orthorhombic lattice structure. According to the results of SEM, the grainy EMD has a spherical or sphere-like appearance and a narrow particle size distribution with an average size of about 7 μm. The grainy EMD is a promising cathode of rechargeable alkaline batteries for high energy density and a prospective precursor for production of the $LiMn_2O_4$ cathode of lithium ion batteries.

Key words: alkaline batteries; electrolytic manganese dioxide; temperature; sulfuric acid; electrodeposition

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1 Introduction

Electrolytic manganese dioxide (EMD) is used as a major cathode material in rechargeable alkaline manganese dioxide batteries [1-2]. Synthesis of the EMD with high energy density and electrochemical reactivity is one of the key problems in the production of rechargeable alkaline manganese dioxide batteries. Thus, many attempts have been made to improve the structure and performances of EMD [3-5].

On the other hand, manganese dioxide is also a main raw material for the production of spinel $LiMn_2O_4$, which is attractive for the cathode of lithium ion batteries because of a favorable combination of electrochemical performances, cost, safety and non-toxicity[7-11].

EMD is generally produced by anodic deposition using acidified aqueous solutions of manganese (II)-sulfate as the electrolyte. Blocky EMD is deposited on the anode and removed from the electrode mechanically. After being washed, neutralized and dried, the deposits are ground into powders [12-13]. The EMD consists of cornered and rough surface particles, which are unfavorable to improve the density and performances of EMD and those of $LiMn_2O_4$.

In our previous study [14], spherical grainy EMD was synthesized by electrodeposition and an optimum current density of 30 A/dm^2 was obtained. The aim of this work is to further investigate the effects of temperature and concentration of sulfuric acid on the deposition of grainy EMD.

2 Experimental

The cell consisted of two lead electrodes (an anode and a cathode) was fixed in a PP (polypropylene) electrolytic bath. The electrodes were immersed vertically in the bath. Electrolysis was conducted at an anode current density of 30 A/dm^2 in 300 mL of 0.9 mol/L $MnSO_4$ solution with different contents of sulfuric acid. Stirring was adopted to circulate the electrolyte during deposition experiments and the process took 4 h. The grainy EMD deposits in the bath were collected by filtration. After repeated washing with deionized water, the grainy EMD was dried in a vac-

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uum atmosphere at 80°C.

Powder X-ray diffraction (XRD) measurements were made with a Rigaku diffractometer equipped with Cu K_α radiation. Scanning electron micrographs (SEM) were obtained with a JEOL JSM-5600LV scanning electron microscope. The average particle diameter was measured using a Malven microplus particle size analyzer.

3 Mechanism of grainy EMD deposition

The electrode reactions of grainy EMD deposition can be described as follows [15].

Anode:

$$Mn^{2+}+2H_2O \rightarrow MnO_2+4H^++2e \quad (1)$$

$$2H_2O \rightarrow O_2+4H^++4e \quad (2)$$

Cathode:

$$2H^++2e \rightarrow H_2 \quad (3)$$

Overall:

$$Mn^{2+}+2H_2O \rightarrow MnO_2+H_2+2H^+ \quad (4)$$

Water electrolysis:

$$2H_2O \rightarrow O_2+2H_2 \quad (5)$$

In fact, the deposition of manganese dioxide at the anode is complicated, which takes place through several intermediate steps. A reasonable mechanism of the electrodepositing reaction of grainy EMD is as follows [15].

$$2Mn^{2+} \rightarrow 2Mn^{3+}+2e^- \quad (6)$$

$$2Mn^{3+} \rightarrow Mn^{2+}+Mn^{4+} \quad (7)$$

$$Mn^{4+}+4H_2O \rightarrow Mn(OH)_4+4H^+ \quad (8)$$

$$Mn(OH)_4 \rightarrow MnO_2 \cdot 2H_2O \quad (9)$$

4 Results and discussion

4.1 Effects of the concentration of sulfuric acid on grainy EMD deposition

The effects of the concentration of sulfuric acid ($C_{sulfuric\text{-}acid}$) on the cell voltage for grainy EMD deposition are shown in **figure 1(a).** Decreasing the cell voltage is a consequence of an increase in $C_{sulfric\text{-}acid}$. It is well known that the cell voltage (V) is determined by the anodic potential *(E_a),* cathodic potential (E_c) and the resistance of electrolyte *(R)* as follows:

$$V=E_a-E_c+IR \quad (10)$$

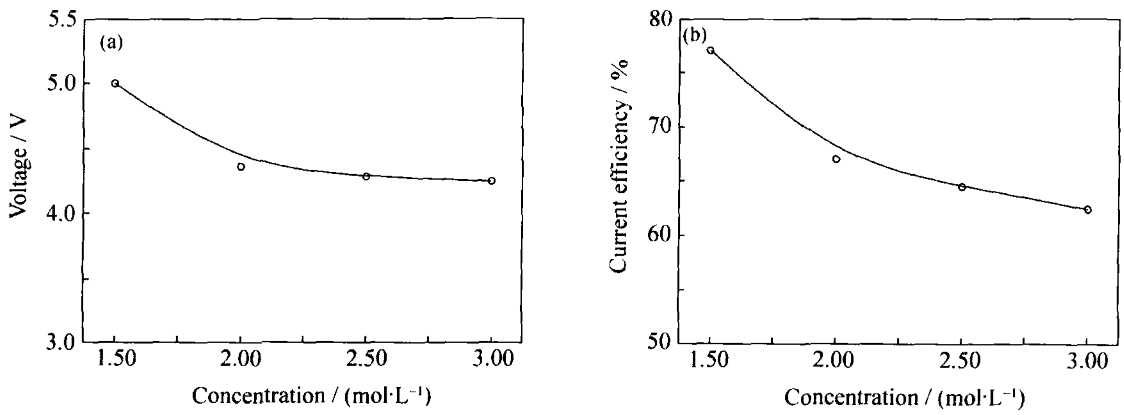

Figure 1 Effects of the concentration of H_2SO_4 on the cell voltage (a) and the average anode current efficiency (b) for EMD deposition at 30°C.

With the enhancement of $C_{sulfuric\text{-}acid}$, the concentration of H^+ and SO_4^{2-} increases, which causes an obvious increase of ion conductivity, so the resistance of the electrolyte decreases. The large concentration of H^+ also causes high cathodic potential and anodic potential according to the electrode reactions of grainy EMD deposition. As a synthetic result of those factors, the cell voltage decreases with the increase of $C_{isulfuric\text{-}acid}$ **in this work. Figure 1(b) shows the effects of $C_{isulfuric\text{-}acid}$ on the average anode current efficiency for** grainy EMD deposition. With the increase of $C_{isulfuric\text{-}acid}$ in the range of 1.5-3.0 mol/L, the average current efficiency for grainy EMD deposition decreases from 77.0% to 62.4%. According to the mechanism of the electrodeposition reaction of grainy EMD, the increase of H^+ in the electrolyte will hinder the hydrolyzation of Mn^{4+}, which hampers the disproportionation of Mn^{3+} (equation (7)) consequently and causes the increase of Mn^{3+} in the electrolyte. The large amount of Mn^{3+} may be transferred to the cathode and reduced to Mn^{2+}, so the average current efficiency decreases. Furthermore, both profiles in figures 1(a) and (b) show a decreasing change rate with the increase of $C_{sulfuric\text{-}acid}$. It may be attributed to the lower ionization ratio of sulfuric acid in the electrolyte with a higher $C_{sulfuric\text{-}acid}$.

The $C_{sulfuric\text{-}acid}$ has a complicated influence on the particle size of grainy EMD as shown in **figure 2.** The grainy EMD has the largest average particle diameter at a $C_{sulfuric\text{-}acid}$ of about 2.4 mol/L. The particle size of grainy EMD is related to the development of crystals and agglomeration of crystals and primary particles. The development of crystals involves nucleus formation and the growth of crystals. Usually, the rate of nucleus formation is enhanced with the increase of H^+ and SO_4^{2-} , wihch facilitates developing small size crystals. It may account partly for the decrease of particle diameter with an increase of $C_{sulfuric\text{-}acid}$ in the range of 2.4-3.0 mol/L. As to the low $C_{sulfuric\text{-}acid}$ of 1.5-2.4 mol/L, the particle size increases with the enhancement of $C_{sulfric\text{-}acid}$. It is possibly because the agglomeration of crystals and particles dominates the particle size of grainy EMD deposits, yet the mechanism of agglomeration is still unknown and much work has to be done.

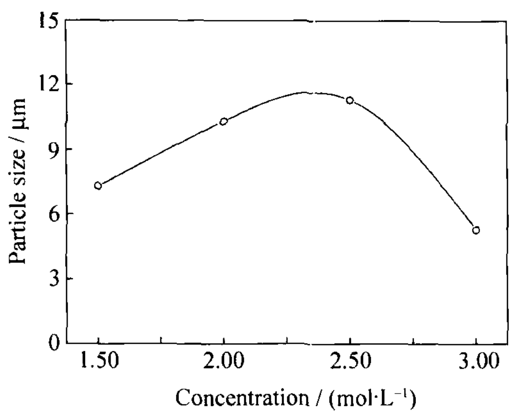

Figure 2 Effect of the concentration of H_2SO_4 on the particle size of EMD deposited at 30°C.

4.2 Effects of temperature on grainy EMD deposition

To investigate the effects of temperature on grainy EMD deposition, a $C_{sulfuric\text{-}acid}$ of 2.5 mol/L was adopted according to the results of section 4.1. As shown in **figure 3,** an increase in temperature results in decreasing the cell voltage and average anode current efficiency, and the lowest cell voltage and current efficiency is obtained when the temperature is highest. As it is expected, with the increase of temperature, the viscosity of the solution decreases and the speed of thermal movement of molecules is enhanced, which results in better conductivity and a lower cell voltage. In addition, the decrease of polarization at an enhanced temperature also contributes to the decrease of the cell voltage. According to the electrode reactions described in the third section, besides the reaction of grainy EMD deposition, oxygen evolution may also take place at the anode. And the application of a higher temperature during the deposition of grainy EMD can lead to the formation and incorporation of soluble 6- and 7-valent manganese species. As the temperature of electrolysis increases, the rate of competitive reactions increases drastically and results in the decrease of current efficiency for grainy EMD deposition. It is consistent with the phenomena that larger amount of gas evolution and deep color of solution is observed at a higher temperature.

As shown in **figure 4,** the average particle diameter of EMD decreases with the increase of temperature of the electrolyte. Although both the rate of nucleus formation and that of crystal growth increase with the enhancement of temperature, the former increases more drastically usually. So it facilitates developing small size crystals. Furthermore, higher crystallinity is resulted from improved temperature, which is disadvantageous for the agglomeration of the crystals and primary particles. Therefore, the grainy EMD of small size is obtained at an enhanced electrolysis temperature.

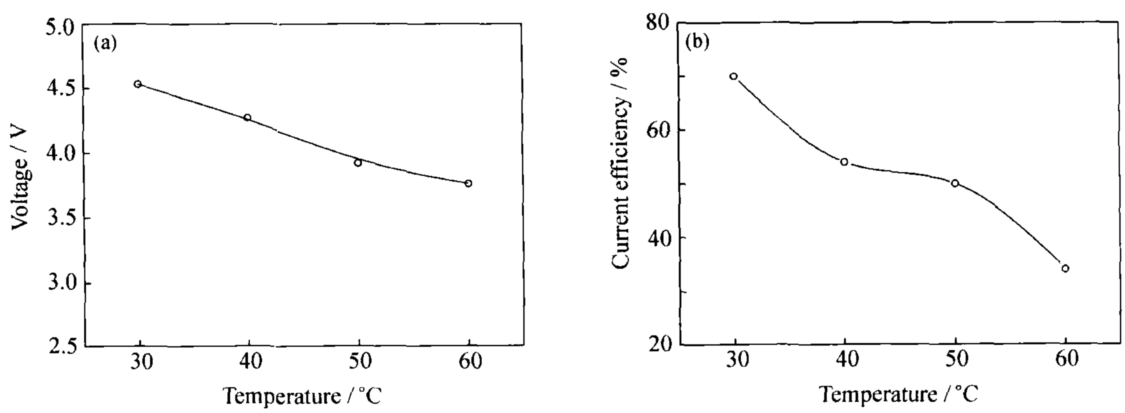

Figure 3 Effects of temperature on the cell voltage (a) and the average anode current efficiency (b) for EMD deposition.

According to the effects of temperature and the concentration of sulfuric acid on the cell voltage, anodic current efficiency and particle size, a temperature of 30°C and a $C_{sulfric\text{-}acid}$ of 2.5 mol/L are considered as the optimum conditions for the electrodeposition of grainy EMD.

4.3 Characterization of grainy EMD

The grainy EMD deposited under the optimum conditions was characterized by XRD and SEM measurements. XRD patterns of manganese dioxide shown in **figure** 5 are in good agreement with those of PDF (powder diffraction file) sample No.14-0644, which indicates the deposits consist of γ-MnO_2 and can be indexed as orthorhombic lattice. The sharp peaks in the XRD patterns suggest the grainy EMD be of well developed crystalline.

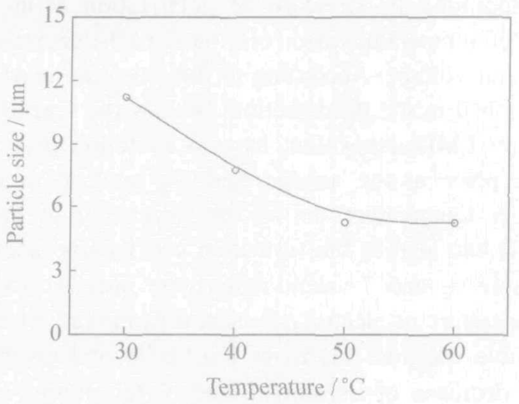

Figure 4 Effect of temperature on average particle diameter of EMD.

The appearance of the grainy EMD is shown in **figure 6.** The grainy EMD sample consists of spherical or sphere-like particles as shown in figures 6(a) and (b). The sample has a narrow particle size distribution with an average size of about 7 *μm*. The particles are the agglomeration of little spheres of 1-3 μm. Some narrow cracks are observed among the little spheres. As shown in figure 6(c), the individual spheres are composed of many tiny primary grains whose size ranges from 20 to 100 nm.

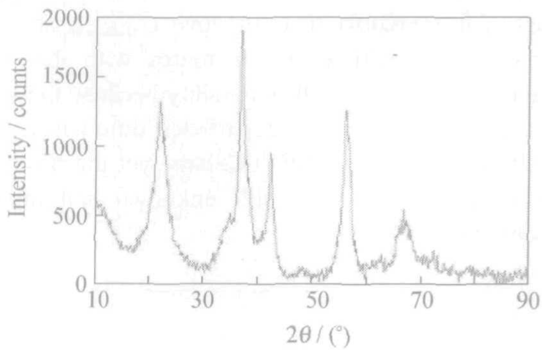

Figure 5 XRD patterns of grainy EMD.

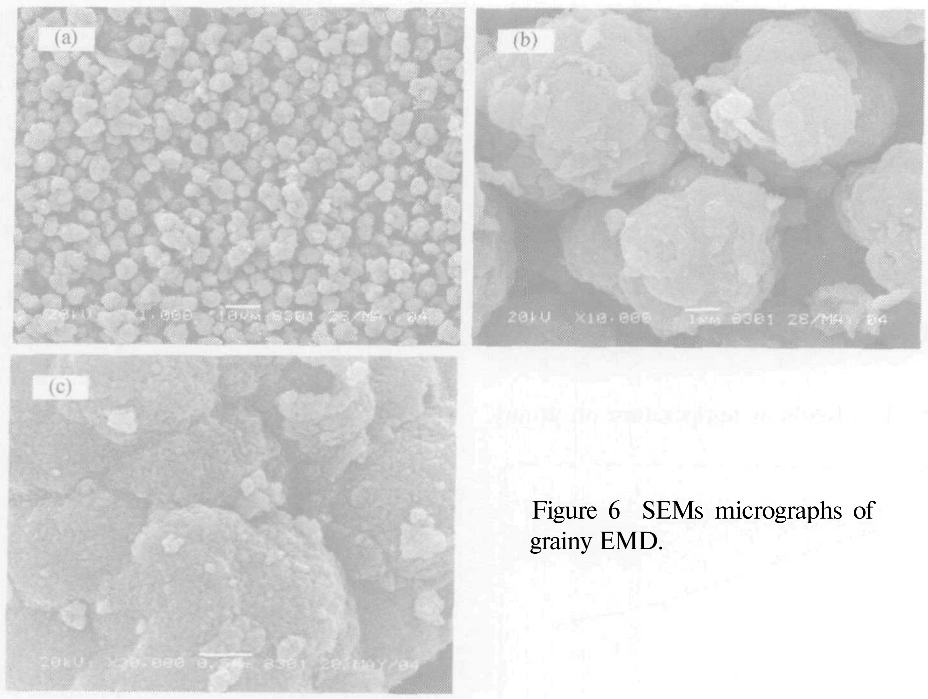

Figure 6 SEMs micrographs of grainy EMD.

5 Conclusions

(1) As the concentration of sulfuric acid increases, both the cell voltage and the average anode current efficiency decrease, and the particle size of grainy EMD increases firstly and then decreases with the maximum at a $C_{sulfuric\text{-}acid}$ of about 2.4 mol/L.

(2) With the increase of electrolysis temperature in the range of 30-60°C, the cell voltage, average anode current efficiency and particle size decrease.

(3) The grainy EMD electrodeposited under the optimum conditions (30°C, 2.5 mol/L H_2SO_4) consists of γ-MnO_2 and has an orthorhombic lattice structure. It has a spherical or sphere-like appearance and a narrow particle size distribution with an average particle diameter of about 7 μm, which is expected for an in-

dustrial product.

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