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Effects of surface modification on electrochemical performance of MnO_2 ①

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Abstract: The MnO_2 samples coated with $Ca(OH)_2$ were prepared by a liquid-phase surface treatment method. The physical properties of the samples were examined by SEM, EDAX and chemical analysis, and their electrochemical performances were investigated by means of galvanostatic charge-discharge, cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The SEM results show that the samples coated with $Ca(OH)_2$ display a porous surface structure. The electrochemical experiments indicate that the surface modification decreases the polarization of MnO_2 electrodes and improves their discharge potentials and discharge capacities.

Key words: manganese dioxide; surface modification; cyclic voltammetry; electrochemical impedance spectroscopy
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1 INTRODUCTION

MnO_2 is widely used as electrode materials in primary batteries due to its low cost, environmentally friendly nature and good electrochemical performance[1-4]. As the main cathode material of alkaline batteries, the properties of MnO_2 are crucial to the electrochemical performance of the batteries. MnO_2 has attracted numerous attentions of researchers since its early discovery as a cathode material in Leclanché type dry cell[4, 5]. In order to overcome the drawbacks of MnO_2, such as the bad reversibility and easy overcharge, the researchers have extensively investigated the effects of various additives such as Fe, Ti, Bi, Ba, Pb, Ni, Co, and V[6-12] on the electrochemical performance of MnO_2. It has been found that Bi, Ba and Pb can improve the reversibility of MnO_2, and the additions of Co and Ni are advantageous to avoiding the overcharge of MnO_2 electrodes. Although the electrochemical performance of MnO_2 has been greatly improved in the past several decades, its rate capability and electrochemical reversibility need to be further improved to meet the actual increasing requirements.

The surface modification is a novel method to improve the properties of materials[13, 14]. Wu's results[13] showed that the electrochemical performance of $Ni(OH)_2$ powder was obviously improved by the surface treatment. However, few studies have been carried out in the surface modification of MnO_2.

In this paper, the effects of the surface modification using $Ca(OH)_2$ on the physical properties and electrochemical performance of MnO_2 were investigated.

2 EXPERIMENTAL

2.1 Preparation of samples

With continual stirring, the $Ca(NO_3)_2$ solution (0.25 mol/L) and KOH solution (0.2 mol/L) were slowly added to the well-sealed reaction vessel with 20 mL ammonia solution (6.47 mol/L), 0.5 mol commercial MnO_2 and appropriate amount of Tween-20. The reaction temperature was controlled at (40 ± 1) ℃, and the pH value of the reaction solution was held at (12.50 ± 0.1). After the reaction had been undertaken for certain time, the reaction product was aged in the mother solution for 2 h at (40 ± 1) ℃. The product was filtered off, rinsed several times using deionized water, and dried at 60 ℃ in air.

When the addition amount of Ca^{2+} was 0.1, 0.05, 0.033 and 0.025 mol, the corresponding product obtained was labeled with A, B, C, and D, respectively. Commercial MnO_2 was designated as E.

2.2 Physical characterization of samples

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The MnO_2 contents in samples were determined by the ferrous sulphate reduction method[2]. The morphologies and surface compositions of the samples were examined by scanning electron microscopy (SEM) and EDAX with an FEI SIRION system and Link-Isis analyzer.

2. 3 Preparation of electrodes and their electrochemical measurements

The pasted manganese electrodes were prepared as follows: 160 mg of MnO_2 and 80 mg of graphite powder were thoroughly mixed with a certain amount of 5% (mass fraction) PTFE solution. The paste obtained was incorporated into a nickel foam (2 cm × 2 cm × 1. 1 mm) with a spatula. The pasted electrodes were dried at 60 ℃ and then roll-pressed to a thickness of 0. 5 mm. Thereafter, the electrodes were soaked in 9 mol/L KOH for 8 h before being coupled with Ni electrodes on either side as the counter electrodes and an Hg/HgO electrode as reference.

Galvanostatic charge-discharge studies were conducted with BT-2000 Arbin battery testing instrument. The primary discharge was undertaken from open-circuit potential to − 1. 0 V (vs Hg/HgO) at constant currents of 62. 5 mA/g and 250 mA/g, respectively. In the charge-discharge experiments the pasted manganese electrodes were galvanostatically discharged to − 0. 2 V at rate of 62. 5 mA/g, and then charged to 0. 5 V at rate of 31. 25 mA/g. Electrochemical impedance spectroscopy (EIS) measurement was performed with a Potentiosta/Galvanostat Model 273 in conjunction with a model 5210 lock-in amplifier. The frequency range was from 120 kHz to 5 mHz, and the excitation amplitude was 10 mV.

Cyclic voltammetry experiment was performed with a Potentiosta/Galvanostat Model 273 potentiosta within a potential range from − 1. 0 V to 0. 6 V (vs Hg/HgO) at a rate of 0. 5 mV/s. The working electrode was cavity microelectrode described in the literature[15]. The counter electrode and the reference electrode were just the same as the above experiments. All the electrochemical measurements were performed at room temperature.

3 RESULTS AND DISCUSSION

3. 1 Physical properties of samples

The SEM images of the samples are illustrated in Fig. 1. The morphology of MnO_2 sample is obviously altered by the surface treatment. Compared with the untreated sample (E), the treated sample (B) shows more regular shape and porous surface, which is advantageous to improving the electrochemical activity of MnO_2. The results of EDAX show that the surface of Sample B consists of manganese, oxygen and calcium. This indicates that $Ca(OH)_2$ is coated on the surface of MnO_2 during the treatment process of MnO_2 in the Ca-containing alkaline solution.

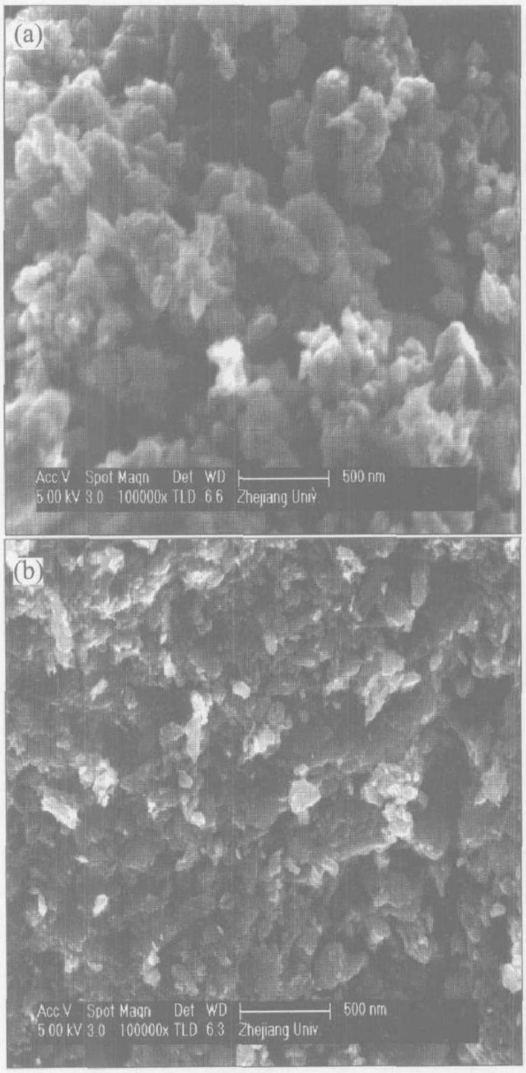

Fig. 1 SEM images of samples
(a) —Sample B; (b) —Sample E

The MnO_2 contents in various samples are displayed in Table 1. It can be seen that as the addition amount of Ca^{2+} in the treatment solution increases, the MnO_2 content in the samples decreases. This implies that the amount of $Ca(OH)_2$ coated on the surface of MnO_2 increases with the increasing content of Ca^{2+} in the treatment solution.

Table 1 MnO_2 contents in samples

Sample	$x(MnO_2)/\%$
A	85. 72
B	88. 22
C	88. 73
D	89. 34
E	91. 12

3.2 Electrochemical performance of samples

The primary discharge curves of the samples at different rates are displayed in Fig. 2. It can be seen that the samples coated with $Ca(OH)_2$ show larger discharge capacity and higher discharge potential at both low and high rates than the untreated sample, and relatively higher calcium content is advantageous to improving the electrochemical performance of the MnO_2 samples. The beneficial effects of the surface modification using $Ca(OH)_2$ on the electrochemical performance of the samples can be attributed to the formation of the porous surface structure, which can enhance the diffusion of electrolyte within the porous electrodes.

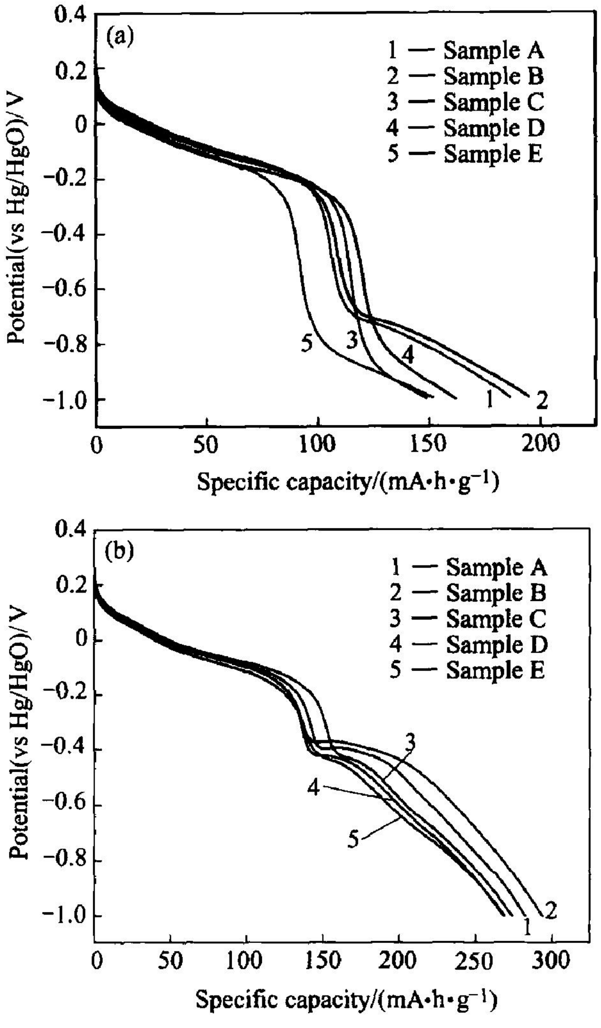

Fig. 2 Discharge curves of samples at different rates

(a) —250 mA/g; (b) —62.5 mA/g

The cyclic behaviors of the manganese electrodes with the treated (B) and untreated (E) surface are illustrated in Fig. 3. In accordance with Ref. [16], the discharge capacities of both Sample B and Sample E have a relatively large deterioration rate during the whole cycle, but Sample B has larger discharge capacity than Sample E at all cycles. The data in Table 2 indicate that the surface modification using $Ca(OH)_2$ markedly increases the open-circuit potential and accumulative discharge capacity of MnO_2 sample.

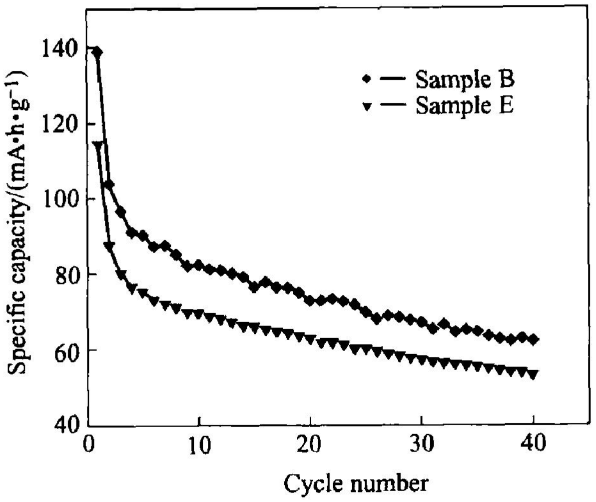

Fig. 3 Cyclic performance of samples

Table 2 Open-circuit potentials and accumulative specific capacities of electrodes

Sample	Open-circuit potential/mV	Accumulative specific capacity/(mA · h · g^{-1})			
		10 cycles	20 cycles	30 cycles	40 cycles
B	196	981.7	1 787.4	2 496.4	3 124.8
E	141	789.7	1 445.9	2 042.0	2 592.6

Cyclic voltammetry measurement results are displayed in Fig. 4. During the cathodic sweep, the first cathodic peak (− 0.2 V) represents the one electron reduction of Mn(Ⅳ), which corresponds to the homogeneous reaction in the solid phase of Mn(Ⅳ) → Mn(Ⅲ). The second strong cathodic peak (− 0.44 V) represents the reduction of the Mn(Ⅲ), which corresponds to the heterogeneous phase reaction[8]. The curves of samples B and E are similar. The similar position and shape of peaks imply that the surface modification does not change the electrochemical reaction mechanism of MnO_2. It can be found from Fig. 4 that Sample B exhibits higher cathodic peak current than Sample E, indicating that the sample coated by $Ca(OH)_2$ has higher electrochemical activity.

In order to investigate the effects of $Ca(OH)_2$ treatment on the kinetic process of MnO_2 electrodes, electrochemical impedance spectroscopy (EIS) of the electrodes was measured at open-circuit potentials. The Nyquist plots of samples B and E are displayed in Fig. 5(a). The plots show a semicircle in high-frequency region due to the charge transfer resistance parallel with the double layer capacitance; and a straight line in low-frequency region. The radius size of the semicircle reflects the magnitude of the charge-transfer resistance; and the straight line generally originates

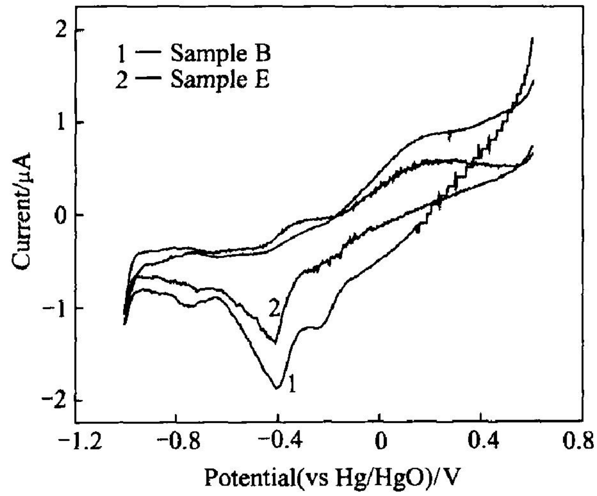

Fig. 4 Cyclic voltammograms of Sample B and Sample E

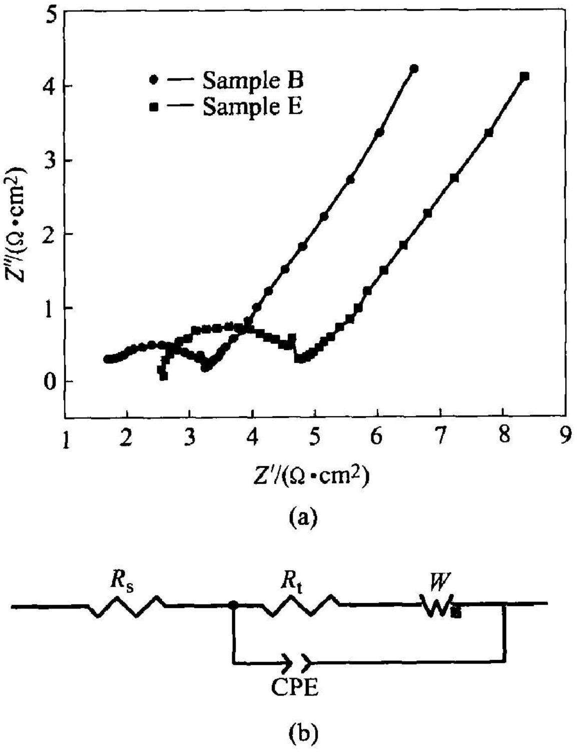

Fig. 5 Nyquist plots for Samples B and E at open-circuit potentials(a) and corresponding equivalent circuit(b)

from solid phase proton diffusion, which reflects the capability of proton diffusion. This system can be depicted by the equivalent circuit shown in Fig. 5(b), where R_s is the total ohmic resistance of the electrode system, CPE the constant phase element related to the double layer capacity, R_t charge-transfer resistance, W the Warburg impedance (Z_w) of the solid phase diffusion[17, 18]. Table 3 lists the fitting parameters (R_s, R_t, W_{s-R} and W_{s-T}) of EIS, where $W_{s-T} = L^2/D$, L is the effective diffusion thickness and D the effective diffusion coefficient. It can be seen from Table 3 that R_s, R_t, W_{s-R} and W_{s-T} values of the sample coated with $Ca(OH)_2$ decrease. This indicates that the ohmic, electrochemical and diffusion polarizations of MnO_2 electrodes are all decreased by the surface modification with $Ca(OH)_2$. Therefore, the MnO_2 samples with $Ca(OH)_2$ coating have higher electrochemical activity, larger discharge capacity and relatively better electrochemical reversibility.

Table 3 Simulation results for EIS of electrodes

Sample	R_s/ (Ω • cm²)	R_t/ (Ω • cm²)	W_{s-R}/ (Ω • cm²)	W_{s-T}/ s
B	1.488	1.900	4.834	187.5
E	2.404	2.573	5.967	202.2

4 CONCLUSIONS

1) The MnO_2 samples coated by $Ca(OH)_2$ are obtained by a liquid-phase surface modification method. The results of SEM show that the samples coated by $Ca(OH)_2$ have more regular shape and porous surface structure.

2) The electrodes of MnO_2 coated by $Ca(OH)_2$ display lower ohmic, electrochemical and diffusion polarizations. This results in higher electrochemical activity, larger discharge capacity and relatively better electrochemical reversibility of the MnO_2 samples coated with $Ca(OH)_2$.

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