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# Charge-discharge process of MnO<sub>2</sub> supercapacitor

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Abstract: Mechanochemical synthesis of  $\alpha$ -MnO<sub>2</sub> was carried out with KMnO<sub>4</sub> and Mn(CH<sub>3</sub>COO)<sub>2</sub> in 1:1 mole ratio. The electrochemical performance of MnO<sub>2</sub> electrode was investigated by cyclic voltammograms and alternating current impedance. The charge-discharge process of MnO<sub>2</sub> supercapacitor in 6 mol/L KOH was studied within 1.2 V at 200 mA/g, suggesting that it displays double-layer capacibility in low potential scope and pseudo-capacitance properties in high potential scope. It is found that Mn<sub>3</sub>O<sub>4</sub>, an electrochemical inert, mainly forms in the initial 40 charge-discharge cycles. During cycling, the pseudo-capacitance properties disappear and the discharge curves are close to ideal ones, indicating double-layer capability. The maximum capacitance of MnO<sub>2</sub> electrode is as high as 416 F/g, and retains 240 F/g after 200 cycles. The equivalent series resistance increases from 17 to 41  $\Omega$ .

Key words: manganese dioxide; supercapacitor; pseudo-capacitance; double-layer capability; charge-discharge process

## **1** Introduction

Compared with traditional capacitor, supercapacitor has higher capacitance, more energy density and power density, which makes it widely used in many kinds of fields from mobile equipment to electric vehicles[1]. Noble metal oxides such as  $RuO_2$  have high pseudocapacitance, but the application is limited by its high cost. However, some cheap metal oxides, such as  $Co_3O_4$ , NiO and  $MnO_2$ , also have pseudocapacitance [2–3], and  $MnO_2$  has become hotspot in recent research for its abundant resource and good electrochemistry performance[4–5]. Studies on the preparation of  $MnO_2$ are always carried out with hydrothermal method[6], sol-gel method[7], circumfluence cooling method[8], etc. Nevertheless, the reports about mechanochemical synthesis of  $MnO_2$  are really few.

In this study,  $MnO_2$  was prepared mechanochemically with  $KMnO_4$  and  $Mn(CH_3COO)_2$  in 1:1 mole ratio, and level-loaded to a supercapacitor. The structure of as-prepared  $MnO_2$  was investigated by XRD and IR. Galvanostatic tests, cyclic voltammograms, and alternating current(AC) impedance were used, aiming at researching the performance of supercapacitor during charge-discharge cycling in 6 mol/L KOH.

#### 2 Experimental

#### 2.1 Reagents and instrument

Main reagents of KMnO<sub>4</sub> (AR, Xiangke, Changsha), Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (AR, Xilong, Shantou), polytetrafluoroethylene(PTFE) (5%, mass fraction) and acetylene black (Chelong, Shanxi) were used.

Main instruments of ND6-2L planetary ball-miller (Nadatianzun, Nanjing), D-500 X-ray diffractrometer (Siemens, Germany), CHI660 electrochemistry workstation (Chenhua, Shanghai)and Land battery tester (Jinnuo, Wuhan) were employed.

#### 2.2 Experimental procedure

KMnO<sub>4</sub> and Mn(CH<sub>3</sub>COO)<sub>2</sub> were mixed in a stainless steel vessel in 1:1 mole ratio. After milling at 260 r/min for 9 h (the mass ratio of ball to power was 10:1), the product was pickled in 0.1 mol/L H<sub>2</sub>SO<sub>4</sub>, then stirred by magnetic force at 200 r/min for 2 h to remove K<sup>+</sup>. Subsequently, it was washed until neutral with distilled water to remove the redundant Mn(CH<sub>3</sub>COO)<sub>2</sub>. Then, it was dried at 120 °C to constant mass, mixed with acetylene black and PTFE (5%, mass fraction) at the mass ratio of 75:15:10, dried to subarid, rolled to electrode with 0.3 mm in depth, 10 mm × 10 mm in area

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(stainless steel current collector). At last, it was dried at 120  $^{\circ}$ C and level-loaded to a symmetrical supercapacitor (Fig.1), using 6 mol/L KOH as the electrolyte.



Fig.1 Schematic diagram of supercapacitor

The structure of as-prepared MnO<sub>2</sub> was investigated using a Siemens D-500 X-ray diffractometer (Cu K<sub> $\alpha$ </sub> radiation, 0.154 18 nm) in a  $\theta/2\theta$  geometry (XRD). Qualitative analysis of Mn—O and other functional groups were carried out with a FTIR (AVATAR360, Nicolet Corp, USA). Galvanostatic tests were performed on a Land CT2001A battery tester at 200 mA/g within 1.2 V, and manipulated by LANDdt 4.2 software. The cyclic voltammetry (CV, -0.60-0.65 V) and AC impedance (0.001 Hz-10 kHz) were operated in a three-electrode cell configuration. A Hg/HgO and a 2 cm×2 cm platinum gauze were used as reference and counter electrodes, respectively. In these studies, all electrodes were tested in 6 mol/L KOH solution.

# **3** Results and discussion

## 3.1 Structure characterization

The X-ray diffraction patterns of the MnO<sub>2</sub> electrodes are shown in Fig.2. As can be seen from Fig.2 that the characteristic peaks of electrode material before charging appear at 12.78°, 36.94°, 37.52°, 41.22°, 41.9°, 49.8° and 69.7°, involving no peaks of other valent state manganese. All the peaks for the sample can be indexed to a pure tetragonal phase (space group *I*4/*m* (No.87)) of  $\alpha$ -MnO<sub>2</sub> (JCPDS 44-0141). The broaden terrace and low intension peaks indicate the MnO<sub>2</sub> prepared is weak-crystalline[9–10]. After 200 charge-discharge cycles, the characteristic peaks at 32.41°, 36.04°, 44.37°, 58.76° as well as 37.52°, 41.9°, illuminate that MnO<sub>2</sub> is turned into Mn<sub>3</sub>O<sub>4</sub>, leading to irreversible deep discharge.

## **3.2 IR characterization**

Fig.3 shows the IR pattern of the material. Peaks at about 3 374  $\text{cm}^{-1}$  and 1 637  $\text{cm}^{-1}$  correspond to the stretching and bending vibration of hydroxide in

adsorbed water, and the ones at 1 383 cm<sup>-1</sup> and 522 cm<sup>-1</sup> indicate Mn—O bond characteristically[11]. Additionally, no other functional groups are involved.



**Fig.2** X-ray diffraction patterns of MnO<sub>2</sub>: (a) Before chargedischarge; (b) After 200 charge-discharge cycles

![](_page_1_Figure_13.jpeg)

Fig.3 IR pattern of synthesized MnO<sub>2</sub>

#### 3.3 Cyclic voltammograms and AC impedance

Typical cyclic voltammograms and AC impedance plots are shown in Figs.4 and 5, respectively.

At the beginning of scanning, a tiny oxidation peak appears at 0.57 V, and the corresponding reduction peak comes up at 0.41 V. With increasing number of scanning times, the redox peaks move positively. After 200 times

![](_page_2_Figure_2.jpeg)

Fig.4 CV curves of MnO<sub>2</sub> electrode at scan rate of 40 mV/s

![](_page_2_Figure_4.jpeg)

Fig.5 Nyquist plots for MnO<sub>2</sub> electrode

of scanning, the oxidation peak moves to 0.62 V and the reduction one moves to 0.42 V, respectively. The dispersion is relevantly increased from 0.16 to 0.20 V, showing the irreversibility of electrode reaction. Meanwhile, the redox peaks disappear gradually, and the peak current diminishes gently. Mn<sub>3</sub>O<sub>4</sub>, an electrochemistry inert, is the main cause of such phenomenon.

As shown in Fig.5, after 20 and 200 cycles, the AC impedance plots exhibit semi-circularities in the range of 0.001-10 kHz, indicating that the electrode processes are controlled by electrochemistry polarization, namely the proton embedding and disembodying interfacially. When the cycling numbers increase from 20 to 200, the semicircle diameter increases from 12 to 30  $\Omega$ , showing that the electrode reaction resistance increases. Besides, the exchange current can be calculated to be 430 mA/g and 172 mA/g respectively according to Ref.[12]. This is mainly caused by the production of Mn<sub>3</sub>O<sub>4</sub> electrochemistry inert material that reduces the surface catalytic activity of electrode.

Below 0.1 Hz, the biases are not ideally perpendicular to the coordinates, indicating that the diffusion approach determines the electrode process, and the concentration dispersion polarization leads to the impedance. The slope may reflect the electric double-layer forming speed: the precipitous slope denotes fast electric double-layer forming speed. Fig.5 indicates that along with the increase of the cycle numbers, the formation speed of electric double-layer gets slower and slower, leading to the decline of electrode specific capacity.

## 3.4 Galvanostatic testing

Galvanostatic tests were carried out in 1.2 V potential window at 200 mA/g. Discharge curves after 2, 80 and 200 cycles are shown in Fig.6. Owning to the existence of equivalent series resistance( $R_{ESR}$ ), the voltage decreases suddenly at the beginning of discharging (Fig.6).  $R_{ESR}$  consists of the electrode/ solution, active material/current collector interface resistance and the electrochemistry reaction resistance.

Supercapacitor shows different discharge characteristics in various voltage ranges. For example, the second discharge process experiences three steps (Fig.6(a)). The special linearity characteristic of electrochemistry double-layer capacitor displays in the low potential range of 0-0.6 V (the third step), as well as in high potential range of 0.95–1.15 V (the first step); but in the high potential range of 0.60-0.95 V (the second step), the flexural curve reflects minishing discharge rate. This is caused by the redox reaction occurred on the electrode, which can be represented as pseudocapacitance. Nevertheless, in the 20th discharge process, the high potential range for the redox reaction is diminished by 0.25 V, and the pseudocapacitance also decreases. The 200th discharge curve is close to ideal one, for the redox process died away in high potential area, which is in accord with the vanishment of redox peaks in Fig.4.

It is inferred that the reaction occurred on the electrode is the redox process  $Mn(IV) \longrightarrow Mn(III)$ . At the same time, a few formed MnOOH combines with  $MnO_2$  irreversibly. But when discharging more deeply, the crystal lattices are destroyed, leading to irreversible electrode processes. As a result, the electrode resistance and the reaction resistance increase. The reactions could be considered as[13]

 $MnOOH+e^{-} \rightarrow HMnO_{2}^{-}$ (2)

$$MnOOH+HMnO_{2}^{-} \rightarrow Mn_{3}O_{4}+H_{2}O+OH^{-}$$
(3)

#### 3.5 Equivalent series resistance and capacitance

The capacitance of electrode and equivalent series

![](_page_3_Figure_3.jpeg)

**Fig.6** Discharge curves of  $MnO_2$  supercapacitor: (a) After 2 cycles; (b) After 80 cycles, (c) After 200 cycles

resistance can be calculated by [14]

 $C=4It/(mV) \tag{4}$ 

 $R_{\rm ESR} = \Delta V/I \tag{5}$ 

where C is the capacitance of electrode, F/g; I is the discharge current, A; t is the discharge time, s; m is the mass of active material, g; V is the discharge voltage, V.

 $R_{\rm ESR}$  is the equivalent series resistance of supercapacitor,  $\Omega$ ;  $\Delta V$  is the initial transitory voltage dispersion, V. The results are shown in Figs.7 and 8, respectively.

![](_page_3_Figure_10.jpeg)

Fig.7 Discharge capacitance of MnO<sub>2</sub> electrode

![](_page_3_Figure_12.jpeg)

Fig.8 R<sub>ESR</sub> of MnO<sub>2</sub> supercapacitor

It can be found that during the first 40 chargedischarge cycles, the maximum capacitance of electrode is 416 F/g, declining 4.5 F/g per cycle; the minimum  $R_{\rm ESR}$  is 17  $\Omega$ , ascending 0.36  $\Omega$  per cycle. This is mainly caused by the formation of Mn<sub>3</sub>O<sub>4</sub> (Figs.2 and 4). Whereas, the capacitance tends to be steady during the next 160 cycles: the capacitance declines 0.3 F/g per cycle, reaches 240 F/g or so finally, while the  $R_{\rm ESR}$ ascends 0.06  $\Omega$  per cycle, reaches about 36  $\Omega$  at the end.

# **4** Conclusions

1) The supercapacitors are of various capacitance characteristics in different discharge potential ranges, namely showing electrochemistry double layer capability in low potential range and pseudocapacitance in high potential range. 2) The electrochemistry inert  $Mn_3O_4$  is mainly formed during the first 40 charge-discharge cycles, which makes the redox peaks in cyclic voltammograms disappear, and reduces the pseudocapacitance in high potential scope.

3) The maximum capacitance of capacitor electrode is 416 F/g and retains 240 F/g after 200 cycles; the  $R_{ESR}$ increases from 17 to 41  $\Omega$  during the charge-discharge cycles in 1.2 V discharge window at 200 mA/g.

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