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Materials

Electrochemical characterization of MnO_2 as the cathode material for a high voltage hybrid capacitor

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Abstract: Manganese dioxide (MnO_2) was prepared using the ultrasonic method. Its electrochemical performance was evaluated as the cathode material for a high voltage hybrid capacitor. And the specific capacitance of the MnO_2 electrode reached 240 $F \cdot g^{-1}$. The new hybrid capacitor was constructed, combining Al/Al_2O_3 as the anode and MnO_2 as the cathode with electrolyte for the aluminum electrolytic capacitor to solve the problem of low working voltage of a supercapacitor unit. The results showed that the hybrid capacitor had a high energy density and the ability of quick charging and discharging according to the electrochemical performance test. The capacitance was 84.4 μF, and the volume and mass energy densities were greatly improved compared to those of the traditional aluminum electrolytic capacitor of 47 μF. The analysis of electrochemical impedance spectroscopy (EIS) showed that the hybrid capacitor had good impedance characteristics.

Key words: manganese dioxide; hybrid capacitor; high voltage; high energy density

1. Introduction

Compared with traditional capacitors, supercapacitors have higher capacitances and larger energy densities, which make them widely used in many kinds of fields from mobile equipment to electric vehicles [1-3]. Supercapacitors are usually divided into two types: double-layer capacitors and electrochemical capacitors. The former depend on the mechanism of double electric layers, which is a result of the separation of charges at the interface between the electrode surface of activated carbon or carbon fiber and the electrolyte. The latter depend on the fast Faraday redox reactions.

Because of the limitation of the breakdown potential of the electrolyte, the working voltage of an electrochemical capacitor is usually lower than 3 V. Increasing the number of cells in series will reduce the total capacitance and increase equivalent series resistance.

Based on the high working voltage of electrolytic capacitors, the concept of hybrid capacitors was proposed [4-5]. The hybrid supercapacitor combines the anode of an electrolytic capacitor with the cathode of an electrochemical capacitor, so it possesses the following features: high working voltage from an electrolytic capacitor; high specific capacitance and high energy density from an electrochemical capacitor. The capacitor can work at a high voltage without connecting many cells in series. The electrochemical-electrolytic hybrid capacitor was first introduced by the Evans Capacitor Company [6]. They combined Ta/Ta_2O_5, which was the anode of a tantalum electrolytic capacitor, with RuO_2, which was the cathode of an electrochemical capacitor, to make a series of hybrid capacitors.

However, the prices of Ta and RuO_2 are very expensive, so the application of the hybrid capacitor is limited by its high cost in some new satellite phones, space area, and military engineering [7]. As is known to all of us, Al and MnO_2 are much cheaper compared to Ta and RuO_2, so with the concept of hybrid capacitors, we tried to combine Al/Al_2O_3 with MnO_2 to make a new hybrid capacitor. The Al/Al_2O_3 foil used in an aluminum electrolytic capacitor has been studied as the anode of a hybrid capacitor to increase the working voltage in recent years [8-9]. MnO_2 was prepared by the ultrasonic method, which has the advantage of reactant dispersing in comparing with other methods, such as the sol-gel method [10-11], hydrothermal synthesis [12], liquid deposition [13-14] and

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so on. It can produce local high-temperature and high-pressure during collapsing, which promotes the solicitation of chemical reactions. Then electrochemical properties of MnO_2 were investigated in the electrolyte for an aluminum electrolytic capacitor. Finally, a hybrid capacitor sample was constructed and its electrochemical performances were studied.

2. Experimental

2.1. Synthesis of MnO_2

Aqueous solutions of $KBrO_3$ (analytical reagent, A.R.) and $MnSO_4$ (A.R.) in the molar ratio of 1:3 was irradiated by ultrasound for 4 h. The working frequency was 40 kHz. The temperature was held constant at 50°C during the sonication. The reaction equation is described as

$$KBrO_3+3MnSO_4+3H_2O\rightarrow 3MnO_2\downarrow+KBr+3H_2SO_4.$$

All the solutions were made from doubly-distilled water. After the reaction was completed, the resulting black solid product was filtered, washed until neutral with distilled water to remove by-products, then dried at 80°C for 4 h, and subsequently characterized as described below.

2.2. Structure and morphological characterization

The crystallographic structure of the powder was examined by X-ray diffraction (XRD) using a diffractometer (M21XVHF22, Japan). Surface morphology of the sample was observed using a scanning electron microscope (SEM) (JSM-6480LV, Japan).

2.3. Electrochemical measurement

(1) Preparation of MnO_2 electrodes.

The powder was mixed well with acetylene black and poly vinylidene fluoride (PVDF) at the mass ratio of 70:20:10 to obtain a paste. The paste was coated onto an aluminum foil of 20 mm×20 mm, dried at 80°C for 4 h, and then pressed at 10 MPa for 1 min to assure a good electronic contact.

(2) Measurement of MnO_2 electrodes in the electrolyte for an aluminum electrolytic capacitor.

The electrochemical properties of MnO_2 electrodes were measured in a beaker type electrochemical cell, which consisted of MnO_2 as the working electrode, a graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A Luggin capillary was used to minimize errors due to the *IR* (current intensity×resistance) drop in the electrolyte.

The prepared electrodes were measured in the electrolyte for the aluminum electrolytic capacitor by cycle voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) tests. The frequency range was from 10 kHz to 10 mHz, with an amplitude of 5 mV.

(3) Test of the hybrid electrolytic-electrochemical capacitor.

The hybrid capacitor was constructed by combining Al/Al_2O_3 (35 V, Nanguang Electronic Materials Company, Tianjin, China) as the anode of the aluminum electrolytic capacitor, with the prepared MnO_2 as the cathode of the electrochemical capacitor. The two electrodes were separated by a membrane. Both the anode size and the cathode size were 20 mm×20 mm. Then the hybrid capacitor was injected with the electrolyte for an aluminum electrolytic capacitor, and after 12 h electrochemical measurements were conducted.

The hybrid capacitor was also measured by cycle voltammetry, galvanostatic charge-discharge, and EIS tests. The frequency range was from 10 kHz to 10 mHz, with an amplitude of 5 mV.

All of the above electrochemical performances were investigated with the VMP2 Multichannel Potentiostat (Princeton Applied Research, USA).

3. Results and discussion

3.1. Structure and morphological characterization

X-ray diffraction patterns of MnO_2 are shown in Fig. 1. The diffraction peaks correspond to the (120), (131), (230), (300), (002), (160), (242), (421), and (003) planes from left to right, respectively. All these peaks can be indexed to pure orthorhombic γ-MnO_2 (JCPDS card 14-644, a=0.636 nm, b=1.015 nm, c=0.409 nm). Some little impurity peaks are observed such as α-MnO_2. Fig. 2 shows the SEM images of MnO_2. It can be seen that the particle is spherical, and the particle size is about 1-5 μm.

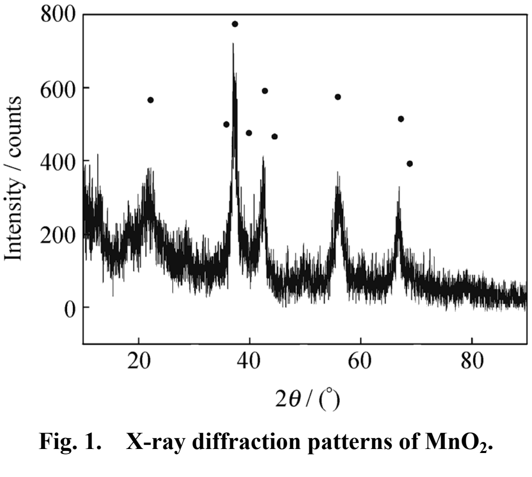

Fig. 1. X-ray diffraction patterns of MnO_2.

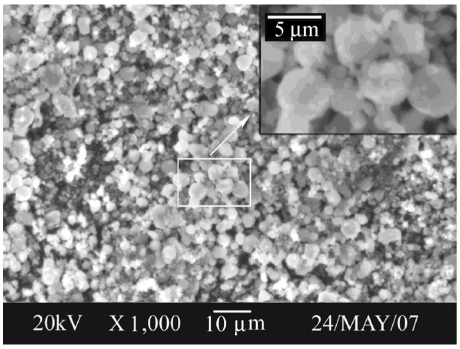

Fig. 2. SEM images of MnO_2 prepared by ultrasound.

3.2. Electrochemical performance of MnO_2 electrodes in the electrolyte for an aluminum electrolytic capacitor

Cyclic voltammetry is considered to be a suitable tool to characterize the capacitive behavior of electrode materials. A large-current, rectangular-type cyclic voltammogram and symmetry in anodic and cathodic directions are the indications of the ideal capacitive behavior of electrode materials [15]. Fig. 3 shows the CV curves of MnO_2 electrodes in the electrolyte for an aluminum electrolytic capacitor at the scan rate of 5, 10, and 20 $mV \cdot s^{-1}$, respectively, in the voltage range of 0.0-0.8 V *versus* SCE. The CV curves have no sharp redox peaks and the anodic and cathodic directions are symmetric. The CV current density increases gradually with the increase in the scanning rate of CV, even at 20 $mV \cdot s^{-1}$, the symmetrical characteristic of the curve is still good. The CV curves indicate that MnO_2 electrodes exhibit good capacitive behavior in the electrolyte for the aluminum electrolytic capacitor.

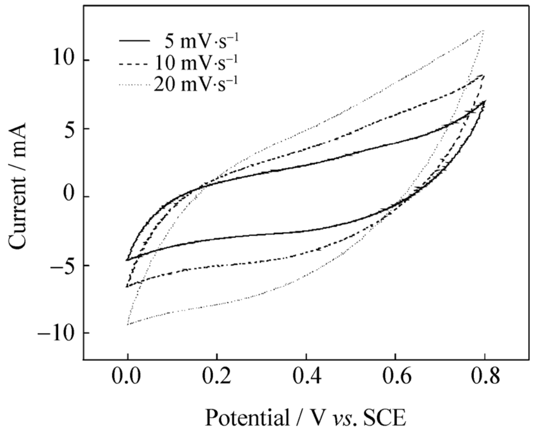

Fig. 3. Cyclic voltammograms of the MnO_2 electrode at different scan rates.

Fig. 4 shows the charge and discharge behaviors of the MnO_2 electrode at the current density of 1 $A \cdot g^{-1}$. At the beginning of discharge, a potential drop can be observed which could be termed as the *IR* drop. The specific capacitance of the MnO_2 electrode was calculated according to the formula $C=(i \cdot \Delta t)/(\Delta V \cdot m)$, where C is the specific capacitance, i the applied current, Δt the discharge time, m the mass of the active material, and ΔV the applied potential range. It can be seen that the voltage changes pseudo-linearly with time during discharge. The specific capacitance of MnO_2 electrodes in the electrolyte for an aluminum electrolytic capacitor reaches 240 $F \cdot g^{-1}$ and the discharge efficiency is about 60%.

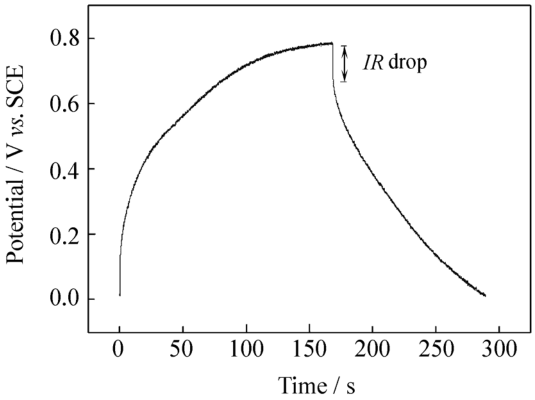

Fig. 4. Galvanostatic charge/discharge plot for the MnO_2 electrode at 1 $A \cdot g^{-1}$.

According to the results of Evans Company, the capacitance of RuO_2 cathode with four electrolytes used in the aluminum electrolytic capacitor ranged from 14% to 36% that of the sulfuric acid electrolyte [6]. The typical value of the capacitance of RuO_2 in sulfuric acid is about 760 $F \cdot g^{-1}$, so the capacitance of RuO_2 in four electrolytes for the aluminum electrolytic capacitor ranged from 106 to 273 $F \cdot g^{-1}$. As we mentioned above, RuO_2 is much more expensive than MnO_2. Now although the cheaper material MnO_2 is used instead of RuO_2, the capacitance achieves 240 $F \cdot g^{-1}$. It provides the possibility of using MnO_2 to make the Al_2O_3-MnO_2 hybrid capacitor.

Usually there have been two mechanisms proposed for the charge storage in MnO_2-based electrodes through pseudocapacitive processes [16]. The first one is based on the concept of intercalation of H^+ or alkali metal cations such as K^+ in the electrode during reduction and deintercalation upon oxidation.

$MnO_2+H^++e \Leftrightarrow MnOOH$

or

$MnO_2+C^++e \Leftrightarrow MnOOC$,

$(MnO_2)_{surface}+C^++e \Leftrightarrow (MnO_2^-)_{surface}$.

The second mechanism is based on the surface adsorption of electrolyte cations (C^+) on MnO_2, where $C^+=Na^+, K^+, Li^+$.

The electrolyte used in the experiment contains some organic acid and some ammonium salts, such as ethylene glycol, oxalic acid, resorcinol, sebacic acid, and ammonium formate. So it may be proposed that both the mechanisms are suitable for the electrolyte we used. Both the intercalation of H^+ and NH_4^+ and the surface adsorption of NH_4^+ contribute to the capacitance, as shown below. Those may be the main reason why the capacitance of MnO_2 electrodes in the electrolyte for the aluminum electrolytic capacitor can achieve 240 $F \cdot g^{-1}$.

$MnO_2+H^++e \Leftrightarrow MnOOH$,

$MnO_2+NH_4^+ +e \Leftrightarrow MnOONH_4$,

$(MnO_2)_{surface}+NH_4^+ +e \Leftrightarrow (MnO_2^- NH_4^+)_{surface}$.

Fig. 5 is the Nyquist plot for the MnO_2 electrode. The ac impedance plot exhibits arc shape in high frequency range and nearly a 45° line in low frequencies. The arc shape in high frequency indicates that the electrochemical polarization exists, namely the proton or metal cations embedding and disembodying interfacially. The nearly 45° line in low frequencies indicates that the controlling process in low frequencies is a diffusion process. This is consistent with the mechanism discussed above. The internal resistance is about 4.6 Ω from Fig. 5. The resistance of the electrochemical reaction is a little higher (29 Ω) due to the low conductivity of the MnO_2 electrode material. In addition, there may be some side reactions caused by impurities in the electrolyte at the end of charge. So the discharge efficiency is only 60% in Fig. 4. Decreasing the contact resistance between the electrode and current collector, modifying the MnO_2 electrode material, increasing the conductivity of the electrolyte and purifying the electrolyte can reduce the resistance and enhance the discharge efficiency.

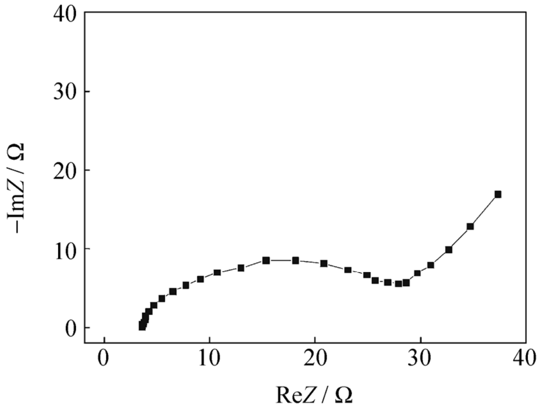

Fig. 5. Nyquist plot for the MnO_2 electrode.

3.3. Electric characteristics of hybrid capacitor

Fig. 6 shows the charge and discharge curve of the hybrid capacitor (0.0-10.0 V). It can be seen that the discharge voltage of the capacitor changes linearly with time, and the behavior of charge/discharge is quite perfect. It also can be seen that the anode takes on most of the capacitor voltage during the charge-discharge period, because the dielectric layer of Al_2O_3 can bear a much higher voltage. This keeps the voltage drop at the cathode/electrolyte interface below the breakdown potential of the electrolyte. That is why the hybrid capacitor can work in such a high voltage.

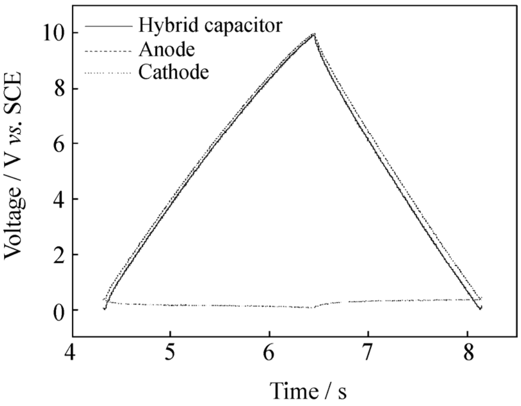

Fig. 6. Galvanostatic charge/discharge profiles for the hybrid capacitor (*I*=1 mA).

The capacitance of the hybrid capacitor is about 84.4 μF, and the discharge efficiency is about 80%. The energy stored can be calculated according to the equation $E=1/2 \cdot CV^2$, where E is the storage energy of the capacitor, J; C the capacitance of the hybrid capacitor, F; and V the work voltage, V. The energy density can be expressed in two ways, the energies of per unit mass and per unit volume, as shown in Table 1. Electrical properties of the sample capacitor prepared were compared with other two commercial aluminum electrolytic capacitors. The volume energy density of the hybrid super-capacitor is almost 6 times more than that of the aluminum electrolytic capacitor I. The mass energy density is almost 3 times more than that of the aluminum electrolytic capacitor I. Both the mass and volume energy densities are nearly equal to those of the aluminum electrolytic capacitor II. The specific capacitance of the sample capacitor is also improved.

Electrochemical impedance spectroscopy (EIS) measurement was used for the hybrid capacitor. Fig. 7 is the Nyquist plot for the sample hybrid capacitor. The impedance behavior of the hybrid capacitor is nearly ideal. The ESR (equivalent serial resistance) of the hybrid supercapacitor is about 1.70 Ω at 1 kHz. It is a little higher than other two aluminum electrolyte capacitors because of the low conductivity of MnO_2. Although ESR is a little high, the time constant *RC* (resistance×capacitance) is still in millisecond. The

RC value of the capacitor is listed in Table 1.

Table 1. Property comparison of three types of capacitors

Capacitor	Capacitance / μF	Mass specific capacitance / (mF·g^{-1})	Volume specific capacitance / (mF·cm^{-3})	Mass energy density / (J·g^{-1})	Volume energy density / (J·cm^{-3})	ESR / Ω	*RC* / ms
Sample	84.4	0.288	0.485	0.176	0.297	1.70	0.08
I	47	0.079	0.079	0.048	0.048	0.58	0.03
II	1000	0.278	0.377	0.170	0.231	0.07	0.07

Note: *RC* is the constant time, I and II are two commercial aluminum electrolytic capacitors. All the working voltages of the capacitors are 35 V.

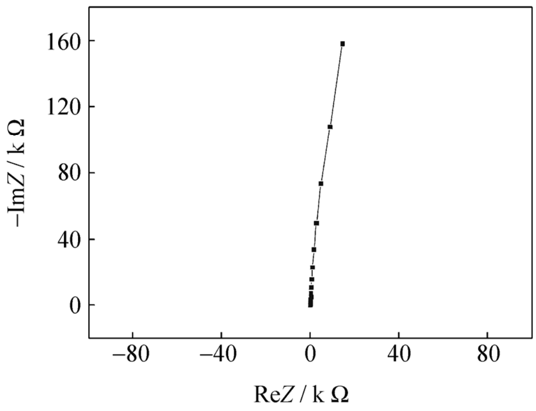

Fig. 7. Nyquist plot for the hybrid capacitor.

4. Conclusions

A new hybrid capacitor with a new structure, using Al/Al_2O_3 as the anode, MnO_2 as the cathode, was prepared. The electrochemical performances of MnO_2 electrodes in the electrolyte for an aluminum electrolytic capacitor were investigated firstly. The experiment results showed that the capacitance of MnO_2 could achieve 240 F·g^{-1}, near to 260 F·g^{-1}, which is the capacitance of RuO_2 in the electrolyte for an aluminum electrolytic capacitor. The sample capacitor could work at high voltages and achieve a higher energy density of 0.297 J·cm^{-3}. And the specific capacitance of the sample capacitor was also improved. The analysis of EIS showed the sample capacitor had a good impedance behavior. The opportunity to develop a high voltage capacitor with low cost and new structure was presented in this paper.

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