

Data analysis preparation and characterization of porous manganese oxide films for super capacitor by cathodic electrode position

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Abstract. Porous manganese oxide film for electrochemical supercapacitors is electrodeposited directly onto a nickel sheet by cathodic electrodeposition in a KMnO_4 aqueous solution. The obtained film is characterized by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), cyclic voltammetry (CV) and galvanostatic charge/discharge test. The SEM images showed the formation of porous structure on the surface of nickel substrate. The CV curves are tested in a Na_2SO_4 aqueous solution, showing double layer capacitive behavior in the potential window of $-0.2 \sim 1.0$ V versus SCE. The highest specific capacitance is 165.7 F g^{-1} with a scan rate of 1 mV s^{-1} .

Introduction

Supercapacitor is a new energy storing device [1-2] between chemical power source and electrostatic condenser. Supercapacitor has the advantage of high power density, rapid charging/discharging, longer service time and good temperature characteristics. Therefore, it is a new kind of efficient and practical energy storage device.

Currently, much attention is paid on power density, energy density and cycling performance, which are the key parameters for energy storage devices, since the demand for power sources delivering energy in the high-power or pulse-power form has increased [3]. The previous study of electrochemical capacitor is mostly involved in the two aspects: electrode materials and electrolyte solutions, which are the main factors determining the performances of electrochemical capacitor.

Many materials have been used as electrode materials. They can be divided into three categories: carbon materials [4-8], conductive polymers [9-10] and transition metal compounds [11-14]. As electrochemical capacitor electrode materials, metal oxides produce electrode potential to charge the capacitance, mainly by highly reversible chemical suck and take off redox reaction [15].

Manganese is a kind of transition metals due to its ion exchange, molecular adsorption, catalytic, electrochemical and magnetic properties [16-17]. Manganese element can be presented in three different valence states and its oxides are highly complex. Manganese dioxide is a material with the advantage of high specific capacitance, wide use as catalysts and molecular-sieves, and low cost of raw materials. Therefore, the research of manganese oxide has been the hot point.

In the present paper, the manganese oxide films for electrochemical supercapacitors were obtained by cathodic electrodeposition from a KMnO_4 aqueous solution, controlling the deposition time and the current density. The as-prepared films were characterized by energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Moreover, the electrochemical performances were also detected by cyclic voltammetry (CV) and galvanostatic charge/ discharge test.

Experiment

Preparation of MnO_2 film

Prior to the deposition, nickel sheet used as the substrate was polished in an acidic solution, containing concentrated HNO_3 , H_3PO_4 and glacial acetic acid with a volume ratio of 2:6:3. The electrolyte of electrodeposition was prepared with analytical pure KMnO_4 and was adjusted the pH value to 1 by adding concentrated H_2SO_4 .

The MnO₂ films were electroplated directly onto 1 × 3 cm² nickel sheet by cathodic electrodeposition from the 0.2 M KMnO₄ aqueous solution at a current density of 0.2 A dm⁻² and 90°C by the galvanostatic method. Moreover, the anode was a flat-plate carbon, and the deposition time was 5 minutes. The as-deposited films were thoroughly washed with deionized water.

Apparatus

A PS-3005D power supply (Zhaoxin Electronic Equipment & Instrument Corporation Shenzhen, China) was used to electrodeposit MnO₂ films. The specific capacitance of the sample was detected by cyclic voltammetry and galvanostatic charge/discharge test in an electrochemical workstation (CHI-660D, Chenhua Instrument, China). During the measurement of electrochemical performances, a standard three-electrode system was employed, including a platinum wire (1 mm diam), a Hg/Hg₂Cl₂ electrode (SCE, saturated KCl, 0.214 V vs NHE at 25 °C), a prepared MnO₂ film as counter electrode, reference electrode and working electrode, respectively. All the electrodes were immersed in electrolyte. And the measurement process was finished in a 1 M Na₂SO₄ aqueous solution, at room temperature and normal pressure. The data were collected by the electrochemical workstation.

Results and discussion

Fig. 1(a) shows the XRD patterns of the sample, in which only diffraction peaks of MnO₂ and substrate can be observed, indicating that only the MnO₂ film is formed on nickel substrate. The distinctive diffraction peaks for the sample is located at 37.9°, 65.1° and 77.8°, respectively. These peaks can be indexed to ramsdellite MnO₂ (PDF#42 - 1316), and the corresponding crystalline faces are (111), (020) and (313). Moreover, the lattice contents are a=9.531 Å, b=2.864 Å, c=4.7 Å and α=β=γ=90°. According to the Scherrer formula, the grain size is calculated to be 24.3 nm.

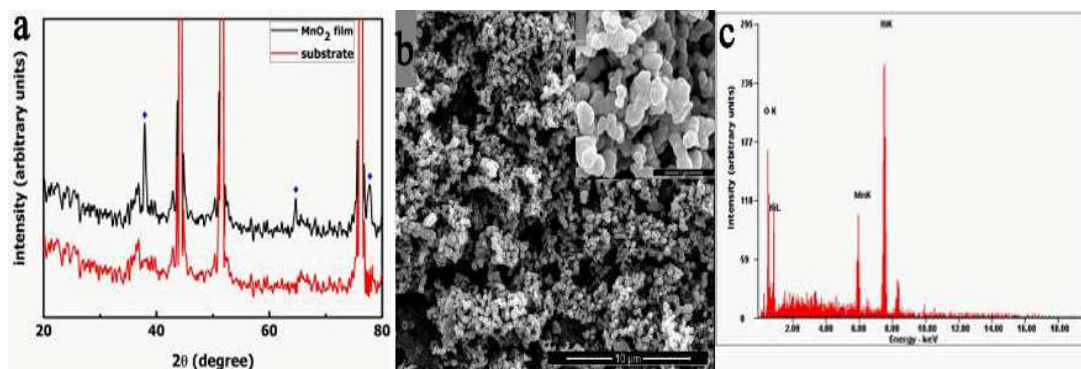


Fig. 1: (a) XRD pattern of the as-prepared MnO₂ film; (b) SEM images with different magnification of the MnO₂ film; (c) EDS spectrum of the MnO₂ film.

The morphologies of the MnO₂ films can be observed in Fig. 1(b). The clusters appear as interleaving sheets or flakes. These clusters arrange in order to form porous structure. The reason for the formation of the porous structure may be as follow. On the cathode, the current efficiency is very low in the conversion of the metal ions valence from high to low. Because the electrolyte is acidic, hydrogen ions in the solution are reduced to hydrogen atoms and hydrogen, which are adsorbed on the substrate surface to prevent the deposition of MnO₂. However, the surface of the substrate does not been completely occupied by hydrogen atoms and hydrogen. There is still MnO₂ deposit growing heterogeneously to form the porous structure as shown. The size of the deposit is about 217 nm, consisting of several crystal grains.

To analyse the detail component of the sample, the EDS measurement is carried out. The EDS data show that the film contains O, Mn and Ni elements in Fig. 1(c). The image gives further evidence to the composition of the product. The surface of the film consists of small nanoparticles and the deposit is a very thin layer on the substrate. Therefore, the intension of Ni is higher than Mn and O.

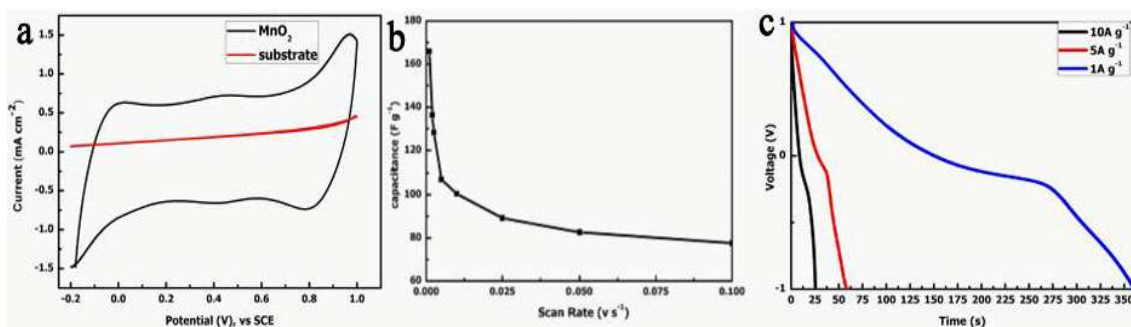


Fig. 2: (a) The cyclic voltammograms of the obtained film and nickel substrate; (b) Capacitance vs scan rate for a sample; (c) Typical discharge curves for the as-prepared MnO₂ film in the potential range of -1.0 ~ 1.0 V.

Fig. 2(a) explains that the cyclic voltammogram of the MnO₂ film tested in the 1 M Na₂SO₄. The image shows double layer capacitive behavior within the potential range of -0.2 ~ 1.0 V versus SCE. The highest specific capacitance is 165.7 F g⁻¹ with a scan rate of 1 mV s⁻¹. In Fig. 2(a), the voltammogram of the substrate in red line is also tested in the same system as the obtained films. The voltammogram exhibits the ideal capacitive characteristics and displays voltammetric current remains nearly constant.

Fig. 2(b) displays the specific capacitance values with different scan rates and summarizes the effect of scan rate on specific capacitance. The image shows a decrease of specific capacitance with increasing scan rate following a logarithmic correlation. The specific capacitance is 77.56, 82.62, 89.18, 100.47, 107.08, 128.27, 136.36 and 165.85 F g⁻¹ with the potential scan rate of 100, 50, 25, 10, 5, 2.5, 2 and 1 mV s⁻¹, respectively.

Galvanostatic charge/discharge experiment is performed at current densities of 10, 5 and 1 A g⁻¹. The discharge curves of MnO₂ film are shown in Fig. 6, indicating a good capacitive behavior. Fig. 2(c) exhibits the discharge time at different current densities to calculate specific capacitance values. The specific capacitance value is 181 F g⁻¹ with the scan rate of 1 A g⁻¹. The specific capacitance value is larger than that obtained in the cyclic voltammetry. The reason may be that the ions and electrons have enough time to deliver on the interface and surface of the film during the faradic redox reaction.

Conclusion

Porous manganese oxide films have been obtained by cathodic electrosynthesis from the KMnO₄ aqueous solution. The results of XRD, EDS, CV, SEM and galvanostatic charge/discharge test indicated the formation of porous manganese oxide films. SEM showed the porosity of as-prepared film. The XRD patterns of the samples demonstrated that the film is the ramsdellite MnO₂ with a grain size of 24.3 nm. Cyclic voltammetry of the obtained film shows that the high specific capacitance (SC) is 165.7 F g⁻¹ with a scan rate of 1 mV s⁻¹, while the result of galvanostatic charge/discharge test is 181 F g⁻¹. And the double layer capacitive behavior is in the larger voltage window of -0.2 ~ 1.0 V versus SCE. The obtained samples showed the high power-energy characteristics and have a potential application in electrode materials of the supercapacitor.

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