Cathodic Potentiostatic Electrodeposition and Capacitance Characterization of Manganese Dioxide Film

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Abstract—MnO₂ film was obtained on stainless steel surface by cathodic potentiostatic electrodeposition method in KMnO₄ aqueous solution in a three-electrode electrochemical cell. The specific capacitance of MnO₂ film was studied by cyclic voltammetry method in 0.1M Na₂SO₄. The results indicated that the film electrolyzed 1.5h under 0.55V voltage in 0.4M KMnO₄ solution with pH value of 12 had the largest specific capacitance of 232.94 F·g⁻¹.

Keywords—electrodeposition; KMnO₄; MnO₂; cyclic voltammetry; capacitance

I. INTRODUCTION

Electrochemical capacitors (ECs) are becoming attractive energy storage systems for their potential applications such as power sources for camera flash equipment, cellular phones, batteries and fuel cells. The energy stored in the ECs is either capacitive or pseudocapacitive in nature. The capacitive (nonfaradaic) process is based on charge separation at the electrode/electrolyte interface, whereas the pseudocapacitive (faradaic) process relies on redox reactions that occur in the electrode materials [1]. Transition-metal oxides have been identified as possible electrode materials for ECs. Among the many transition-metal oxide materials, the amorphous phase of RuO₂·xH₂O formed by the sol-gel method at low temperatures shows excellent pseudocapacitive behavior with a large specific capacitance of as high as 720 F·g⁻¹ and excellent reversibility [2]. However, the high cost of ruthenium and the environmental problems associated with the use of strong acidic electrolytes have limited its commercial use. Therefore, it is urgent to investigate alternate transition-metal oxides, which are cheap, available in abundance, nontoxic, and environmentally friendly. Manganese dioxide has attracted much attention because it has these favorable properties and manganese oxide electrode materials have been prepared by various synthetic methods [3-6]. Manganese dioxide was in various structures prepared with different methods or conditions. Different structure and morphology had different affect on their capacitive property [7, 8]. In this article the manganese dioxide film electrodes were obtained by cathodic electrodeposition method with the potassium permanganate as precursor material. The capacitance of the manganese oxide films were investigated by cyclic voltammetry (CV) in 0.1 M Na₂SO₄ alkaline solution. The articles related to the preparation of manganese dioxide with the potassium permanganate as original material were focus on several methods such as hydrothermal synthesis method [9-11], redox reaction method [12-14] or decomposition method [15,16]. Cathodic electrodeposition method has not been reported as far as we know.

II. EXPERIMENTAL

A. The pretreatment of stainless steel electrode
The stainless steel slice was cut into the size of 1cm×1cm and then taken as working electrode. First, it was burnished with coarse sand paper, Second, ultrasonic oscillation for 5 min in 0.1M NaOH aqueous solution, 0.1M oxalic acid aqueous solution and acetone respectively. Third, it was dried in infrared fast drying oven. Finally it was weighed.

B. The preparation and characterization of manganese dioxide film electrode
The electrochemical measurements were carried out using a CHI660B in a three electrode electrochemical cell, in which the stainless steel slice electrode was used as the working electrode, a platinum plate as the counter, and a saturated calomel electrode (SCE) as the reference electrode. The manganese dioxide films were obtained by cathodic potentiostatic electrodeposition method under 0.55V voltage with potassium permanganate aqueous solution as precursor material. The working electrode was weighed before and after the deposition, in order to calculate the weight of the deposit. Cyclic voltammetry was performed to determine the electrochemical properties and specific capacitance of the manganese oxide film electrodes in 0.1M Na₂SO₄ (pH =6) at room temperature. The average specific capacitance (C) was calculated from the following equation

$$C = \frac{q}{2ΔV M} \quad(1)$$

where q is the voltammetric charge, M is the mass of manganese oxide, and ΔV is the potential range. The XRD patterns were determined by D/Max-IIIC (Rigaku, Japan) at room temperature with Cu Kα radiation. Morphology and Energy Dispersive Spectrometry (EDX) were obtained using a JEM-2000EX (JEOL, Japan). Infrared spectra of the samples were recorded on a FT-IR (Nicolet Impact 410, USA) by KBr disk method.

III. RESULTS AND DISCUSSION

A. The comparison experiment
Cyclic voltammetry was performed to compare the electrochemical properties of the stainless steel electrode and
MnO\textsubscript{2} film electrode in 0.1M Na\textsubscript{2}SO\textsubscript{4} at a scan rate of 5mV.s\textsuperscript{-1}. The results are shown in Fig. 1. It is obvious that the capacitance of MnO\textsubscript{2} film electrode is far larger than that of stainless steel electrodes, so the influence error of stainless steel can be ignored.

B. Capacitance characterization of the manganese oxide film electrodes

The cyclic voltammograms and specific capacitance of MnO\textsubscript{2} film electrodes prepared at pH values of 8.44, 11.93, 12.31, 13.71 were obtained in Fig. 2. The specific capacitance of MnO\textsubscript{2} film electrodes was largest at the pH values of 11.93 and 12.31. It maybe because that the MnO\textsubscript{2} film electrode that prepared in the strong alkali solution contain some OH\textsuperscript{-} group among the lattice units, the following reaction will occur during the charging discharging process:

\[ \text{MnO}_2 + \text{H}_2\text{O} + \text{e}^- = \text{MnOOH} + \text{OH}^- \]  

(2)

Thus it would aggregate lots of Mn\textsuperscript{3+} in the lattices and produce cationic spaces, as a result, the transfer rate of proton and alkali metal ion among these cationic spaces will be increased. But if the solution is in a more strong alkali condition, the number of the Mn\textsuperscript{3+} in the lattices will be reduced and the cationic spaces decreased either. So the specific capacitance decreased. In Fig. 3 the relation of electrolyze time and specific capacitance were represented.

For the film that prepared at 0.55V voltage, pH value equals to 12, the concentration of KMnO\textsubscript{4} solution equals to 0.1M, there is a maximum on the curve of specific capacitance on the electrolyze time, this mean that there are two contrast factors determine the specific capacitance. At the beginning of the electrodeposition, both the specific capacitance and the amount of active material (MnO\textsubscript{2}) increased with the time. With time extension the amount of MnO\textsubscript{2} increased but the thickness of the electrode also increased, the latter one would increase the resistance of the electrode. So the specific capacitance decreased after electrolyze 1.5h. In Fig. 4 the cyclic voltammograms of MnO\textsubscript{2} film electrode and the relation of concentrations of KMnO\textsubscript{4} on the specific capacitance were obtained. On the conditions of voltage equal to 0.55V, pH value is 12, and electrolyze time is 1.5h, the specific capacitance increased with the concentration of KMnO\textsubscript{4} solution. This may because the amount of active MnO\textsubscript{2} increase with the concentration of KMnO\textsubscript{4} solution. The exact reason needs the further investigation.
C. 3.3 Structure characterization of the manganese oxide film electrodes

The X-ray diffraction pattern of the manganese oxide film (prepared at 0.55V voltage, pH value equals to 12, the concentration of KMnO$_4$ solution equals to 0.4M, electrolyze 1.5h) is shown in Fig. 5. It is an amorphous structure. Fig. 6 is the scanning electron micrograph of the same manganese oxide film. From the images we observed the film is flat rough, it mainly contains Mn and O elements. The S and Na elements may come from the Na$_2$SO$_4$ solution. Fig. 7 shows the FTIR spectra of MnO$_2$ film, the regions from 800 – 500 cm$^{-1}$ correspond to the Mn–O stretching and bending vibrations. The absorption of around 1700 and 1400 cm$^{-1}$ in the spectrum is the H–O bending vibrations. The regions from 2800 – 3700 cm$^{-1}$ correspond to the H–O stretching vibration [17].

IV. CONCLUSION

In summary, MnO$_2$ film can be obtained on stainless steel surface by cathodic potentiostatic electrodeposition method at 0.55V voltage in KMnO$_4$ aqueous solution. The capacitance property of MnO$_2$ film was quite well in 0.1M Na$_2$SO$_4$. The film electrolyzed 1.5h under 0.55V voltage in 0.4M KMnO$_4$ solution with pH value of 12 had the largest specific capacitance of 232.94 F.g$^{-1}$. The X-ray diffraction pattern shows that the film is an amorphous structure.

REFERENCES


