Preparation of porous manganese hydroxide film and its application in supercapacitors

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Preparation of a manganese hydroxide film by electrochemically induced deposition method is reported here. The morphology and crystal structure of the film have been investigated by scanning electron microscopy and X-ray diffraction, respectively. The possible deposition mechanism of the film is also discussed. Moreover, the capacitive properties of the film have been evaluated by cyclic voltammetry and galvanostatic charge-discharge method. The results indicate that the morphology of the deposits depends on the amount and size of evolved H₂ bubbles, which can be adjusted by changing the composition of electrolyte and deposition current density. The capacitive properties of film are affected by the deposition parameters. The film prepared under the optimum deposition conditions shows excellent capacitive properties: high specific capacitance (493 F g⁻¹ in 0.1 M Na₂SO₄ aqueous solution from 0 to 1 V at a current density of 1 mA cm⁻²), high electrochemical reversibility and excellent long-term charge-discharge cycle stability (2.2% loss of the specific capacitance observed at the 2000th cycle under the charge-discharge current density of 10 mA cm⁻²).

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Electrochemical supercapacitors are attracting increased interest in power-source applications such as hybrid electric vehicles, short-term power sources for mobile electronic devices, etc.¹ Electrochemical supercapacitors can be divided into two catalogues according to different energy storage mechanism: electrochemical double-layer capacitors and redox supercapacitors²,³. In the former, energy storage arises mainly from the separation of electronic and ionic charges at the interface between the electrode materials and the electrolyte solution. In the latter, fast Faradic reactions take place at the electrode materials at characteristic potentials like in batteries, and give rise to pseudo-capacitors.

For supercapacitive materials, there are three main kinds: carbon with high specific surface, electroactive materials with several redox states or structures and electronically conducting polymer. The excellent performance of supercapacitors usually results from the high specific surface area as well as the high reversible redox reactions of the electrode materials⁴. Hence, developing the electroactive materials with high specific surface area, low cost and high reversible redox reactions are of importance to the electrochemists. Manganese oxide is a promising pseudocapacitive electrode material as it has good capacitance performance and is cost-effective. Recently, manganese oxide thin films prepared by various methods, such as sol-gel, electrochemical and chemical deposition, and redox deposition, have been applied widely in supercapacitors and exhibit capacitive behavior⁵-¹². However, to the best of our knowledge, few papers have reported the capacitive properties of manganese hydroxide.

We report here the preparation of a porous manganese hydroxide thin film by electrochemically induced deposition method. The film morphology has been optimized by adjusting the components of electrolyte and deposition parameters. The capacitive properties of the manganese hydroxide thin film have been investigated by cyclic voltammetry and galvanostatic charge-discharge method. The effects of deposition parameters on the capacitive properties of the manganese hydroxide thin film have also been investigated.

Materials and Methods

Preparation of manganese hydroxide thin film

The manganese hydroxide film was deposited directly onto graphite substrate (1.3×0.5×0.4 cm³). The graphite substrate was polished with ultra-fine emery paper, washed with acetone and double-
distilled water, then sealed using silicone sealant with an exposure area of 0.65 cm², and finally immersed into 30 wt.% HNO₃ for 3 h to activate the surface. The graphite substrate pretreated with above procedure was used as the cathodic electrode during deposition of manganese hydroxide. Another graphite substrate (4x4x0.5 cm³) with a small hole (Φ 0.5 cm) was used as anodic electrode. The corresponding schematic diagram of the electrolytic cell is shown in Fig. 1. The electrolyte used was 0.1 M Na₂SO₄ + 5 g/L polyglycol; 150 mL of the electrolyte solution was used for the deposition of manganese hydroxide. The deposition of manganese hydroxide was performed by the galvanostatic method at different current densities. A supplied solution consisting of 0.25 M Mn(CH₃COO)₂ and 0.1 M Na₂SO₄, was gradually added into the electrolyte through the feed-in hole with a definite time interval. After the completion of the deposition process, the cathodic electrode with manganese hydroxide deposits was rinsed with double-distilled water and then dried in air at room temperature overnight. The loading mass of manganese hydroxide was obtained by measuring the weight difference of the electrode before and after the deposition using a microbalance with an accuracy of 10 µg (Sartorius CP 225D, Germany).

Morphology, crystal structure and capacitive properties of manganese hydroxide films

The morphology and crystal structure of the deposits were investigated by scanning electron microscopy (SEM) (JSM 5600LV) and X-ray diffraction (XRD) (D/MAX-RA). The capacitive properties of the manganese hydroxide film were investigated by cyclic voltammetry and galvanostatic charge-discharge method in 0.1 M Na₂SO₄ aqueous solution on a CHI 660B electrochemical working station (CH Instrument, Inc). A typical three-electrode cell was employed and a platinum foil was used as the counter electrode. The experiments were carried out at room temperature using a saturated calomel electrode (SCE). All chemicals were of analytical grade. Double-distilled water was used throughout.

Results and Discussion

The morphology and deposition mechanism of manganese hydroxide film

The effect of the electrolyte composition on the morphology of manganese hydroxide film was investigated. Figure 2a shows that the size of deposits is not uniform and some big flakes exist. When the

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**Fig. 1**—The schematic diagram of the electrolytic cell for the preparation of manganese hydroxide.

**Fig. 2**—SEM images of microporous manganese hydroxide thin film prepared at 23 mA cm⁻² current density: (a) 0.1 M Na₂SO₄; (b) 0.1 M Na₂SO₄ + 5 g/L polyglycol (The supplied mass and rate of deposition solution are 1.25 mL and 16.7 µL min⁻¹, respectively).
electrolyte solution is changed from 0.1 M Na$_2$SO$_4$ to 0.1 M Na$_2$SO$_4$ + 5g/L polyglycol aqueous solution, the micrograph of the deposits varies. In Fig. 2b, the deposits with a uniform and small size are observed. Compared with Fig. 2a, it is observed from Fig. 2b that the porosity of the film increases and the texture size of the film decreases. It results from the important role of polyglycol, which is used as a surfactant and bubble stabilizer to adjust the amount and size of the evolved hydrogen (H$_2$) bubbles during the deposition process.

In order to investigate the crystal structure of the film, the deposits were scraped from the surface of graphite electrodes and XRD analysis was carried out using Cu target at an angle ($\theta$) speed of 4° min$^{-1}$. The corresponding XRD pattern is shown in Fig. 3. The peaks at $d=3.3573$ and 2.1359 are the characteristic of graphite, which should arise from graphite substrate. According to X-ray diffraction standard cards, the rest peaks (denoted as ■) demonstrate that the deposits exist as manganese hydroxide (Mn(OH)$_2$). Thus, a possible deposition mechanism of the manganese hydroxide film can be deduced. When a suitable current density is applied, a lot of H$_2$ bubbles evolve from the surface of graphite cathode and hydroxyl ions are generated. When the supplied solutions are added gradually into the electrolyte, manganese cations meet hydroxyl ions to yield manganese hydroxides, which are deposited onto the surface of graphite cathode to form a thin film. Meanwhile, the H$_2$ bubbles act as dynamic templates during deposition process which results in a porous film. The mechanism implies that the morphology of the deposits can be adjusted by the amount and size of H$_2$ bubbles, which can be controlled by changing the composition of electrolyte and the deposition parameters during the deposition process of manganese hydroxide film.

The effect of deposition current density, which will result in a change of size and amount of H$_2$ bubbles, on the morphology of Mn(OH)$_2$ porous film was also investigated. Figure 4 shows the SEM images of manganese hydroxide film deposited from 0.1 M Na$_2$SO$_4$ + 5g/L polyglycol aqueous solution at different deposition current densities. The figure shows that the morphology of film is dependent on the deposition current density. At lower (10 mA cm$^{-2}$) and higher (46 and 69 mA cm$^{-2}$) deposition current densities, the films are composed of bigger size Mn(OH)$_2$ deposits and show lower porosity. It is noteworthy that the film with the highest porosity and uniformity can be observed at the deposition current density of 23 mA cm$^{-2}$. It implies that the film obtained at the deposition current density of 23 mA cm$^{-2}$ has the highest specific surface area which is closely related with its capacitive properties.

**Capacitive properties of the Mn(OH)$_2$ film electrode**

The typical cyclic voltammograms (CVs) of the graphite and Mn(OH)$_2$/graphite electrodes measured in 0.1 M Na$_2$SO$_4$ aqueous solutions at 50 mV s$^{-1}$ are shown in Fig. 5a. The CVs of Mn(OH)$_2$ film electrode have a rectangular-like and symmetric shape (Fig. 5a, curve 2). Moreover, its capacitive current is much larger than that of graphite electrode (curve 1). It implies that the porous Mn(OH)$_2$ film electrode has good capacitive performance. According to curve 2, the specific capacitance of the Mn(OH)$_2$ film electrode at 50 mV s$^{-1}$ can be calculated as 450 F g$^{-1}$.

A rectangular-shaped CV over a wide range of scan rate is very important for practical capacitive applications. That provides a higher energy density because the usable potential range is wide. In addition, a higher power density is expected as the critical scan rate increases. The power characteristics of the Mn(OH)$_2$ film electrode are examined by changing the scan rate and the corresponding results are shown in Fig. 5b. The figure shows that all the CVs of the Mn(OH)$_2$ thin film electrode remain a rectangular-like with symmetric shape, even at a high scan rate of 200 mV s$^{-1}$. It shows that the Mn(OH)$_2$ thin film electrode has excellent power characteristics.

It is well known that high power characteristics should arise from high electrochemical reversibility of an electrode. The electrochemical reversibility of the Mn(OH)$_2$ thin film electrode was also investigated by examining the current-potential ($i$-$E$) responses with
the different upper and lower potential limits of CVs. The corresponding results indicate that whatever on the positive or negative sweeps, all i-E responses almost follow the same pattern. In addition, a rapid rise/decay in current is clearly found as the sweep direction of CV is changed. These imply that the Mn(OH)₂ thin film electrode has high electrochemical reversibility which results in excellent power characteristics.

The charge-discharge properties of the Mn(OH)₂ thin film electrode were investigated by chronopotentiometry in 0.1 M Na₂SO₄ aqueous solution from 0 to 1 V at a current density of 1 mA cm⁻². For comparison, the chronopotentiogram of the graphite electrode is also measured under the same conditions. The results show both charge-discharge curves have a linear and symmetrical feature. This implies that both electrodes have excellent electrochemical reversibility and capacitive characteristics. Moreover, the Mn(OH)₂ thin film electrode has much larger charge-discharge interval than that of the graphite electrode which should be attributed to the pseudocapacitive behaviour of Mn(OH)₂. The specific capacitance of the Mn(OH)₂ thin film electrode can be evaluated by chronopotentiograms according to the relation.  

Fig. 4—SEM images of manganese hydroxide film prepared at different deposit current densities in 0.1 M Na₂SO₄ + 5 gL⁻¹ polyglycol aqueous solution: (a) 10; (b) 15; (c) 23; (d) 31; (e) 46; and (f) 69 mA cm⁻².
where $C_s$ is the specific capacitance of the electrode based on the mass of Mn(OH)$_2$ thin film, $I$ is the charge-discharge current, $t$ is discharge time, $\Delta V$ is potential window of charge-discharge, $m$ is the mass of Mn(OH)$_2$ thin film. According to Eq. (1), the specific capacitance of the Mn(OH)$_2$ thin film electrode in 0.1 M Na$_2$SO$_4$ aqueous solution from 0 to 1 V at a current density of 1 mA cm$^{-2}$ can be calculated and equals to 493 F g$^{-1}$.

**Fig. 5**—(a) CVs of the graphite (curve 1) and manganese hydroxide film (curve 2) electrodes at a scan rate of 50 mV s$^{-1}$ in 0.1 M Na$_2$SO$_4$ aqueous solution; (b) CVs of manganese hydroxide film electrode in 0.1 M Na$_2$SO$_4$ aqueous solution at different scan rates: (1) 10; (2) 25; (3) 50; (4) 75; (5) 100; (6) 150; (7) 200 mV s$^{-1}$ (The loading mass of Mn(OH)$_2$ is 0.18 mg cm$^{-2}$).

Effects of the preparation conditions on the capacitive properties of the Mn(OH)$_2$ film electrode

The capacitive properties of hydrous manganese oxides are dependent on not only reversible redox states but also their synthesis conditions. In order to obtain the best capacitive properties, the optimum deposition conditions of Mn(OH)$_2$ film in 0.1 M Na$_2$SO$_4$ + 5g/L polyglycol aqueous solution were investigated. Note that for an ideal capacitor, the CV has a rectangular-like shape and the capacitance can be evaluated from its CV current density. Hence, we estimate the capacitances of Mn(OH)$_2$ films by their CV anodic current densities at 0.5 V at a scan rate of 50 mV s$^{-1}$ in 0.1 M Na$_2$SO$_4$ aqueous solutions. The effects of the deposition current density ($i_D$), supplied mass (SM) and supplied rate (SR) of the supplied solution on the CV anodic current density ($i_A$) of deposit film have been investigated and the corresponding results indicate that the optimum deposition conditions for Mn(OH)$_2$ film are: $i_D$ = 23 mA cm$^{-2}$, SM = 1.25 mL and SR = 16.7 µL min$^{-1}$.

The long-term cycle stability of the Mn(OH)$_2$ film electrode

The long-term cycle stability of the Mn(OH)$_2$ thin film electrode was examined by the galvanostatic charge-discharge method at a current density of 10 mA cm$^{-2}$ in 0.1 M Na$_2$SO$_4$ aqueous solution. The results show that only a decrease of 2.2% of the specific capacitance of the Mn(OH)$_2$ thin film electrode is observed at the 2000th cycle. This implies that the Mn(OH)$_2$ thin film electrode has excellent long-term cycle stability.

Conclusions

The porous manganese hydroxide film has been prepared successfully by electrochemically induced deposition method. The Mn(OH)$_2$ film electrode prepared under the optimum deposition conditions has a specific capacitance as high as 493 F g$^{-1}$ in 0.1 M Na$_2$SO$_4$ aqueous solution from 0 to 1 V at a current density of 1 mA cm$^{-2}$. The Mn(OH)$_2$ film, prepared by low-cost environment-friendly method, exhibits excellent power characteristics, high electrochemical reversibility and long-term charge-discharge stability, and can be a promising supercapacitive electrode material.

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