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Electrochemical Properties of Electrodeposited MnO_2 Nanoparticles

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Abstract. The present study shows the electrodeposition of MnO_2 from $KMnO_2$ solution and its electrochemical studies. XRD analysis shows the electrodeposited MnO_2 has nano-sized particle of 18 nm. The electrochemical properties have been investigated using the cyclic voltammetry, galvanostatic charge/discharge and impedance techniques. The electrodeposited MnO_2 shows good electrochemical behavior with high specific capacitance value of ca. 306 F g^{-1}. Moreover, it shows high capacitance stability of 90% over 1000 charge/discharge cycles. Impedance result shows low solution resistance and charge transfer resistance, an indication of the conductive nature for the electrodeposited film.

Introduction

Different types of materials have been reported for supercapacitor applications including metal oxides, polymers, carbon and hybrid materials [1-4]. MnO_2 has an excellent capacitive performance in the aqueous electrolytes so it is widely used as electrode material for supercapacitor applications [5]. Many preparation methods had been proposed to prepare MnO_2 thin films such as spray pyrolysis, RF sputtering, sol gel, hydrothermal and electrodeposition [6-8] methods. Among of these methods, electrodeposition is simple and economical method to produce high quality MnO_2. Moreover, many manganese precursors can be used for electrodeposition process such as $KMnO_4$, $Mn(CH_3COO)_2$, $Mn(NO_3)_2.4H_2O$, $MnSO_4$ [5,9]. Different MnO_2 film morphologies were obtained such as nanoflakes, nanorods, nanosheets, nano-nests, nanowires, and nanopetals [8,9]. These morphologies render facile electrolyte penetration and better surface utilization of the active material for Faradaic reactions. In this paper, MnO_2 thin film was obtained from $KMnO_4$ solution by low cost, fast and environmental friendly chronopotentiometry electrodeposition and it was characterized by different chemical and electrochemical techniques.

Experimental procedures and techniques

MnO_2 was electrodeposited from 0.5 M $KMnO_4$ solution by chronopotentiometry using stainless steel (SS) electrodes as working electrode. The electrodeposition was performed by applying 0.15 A cm^{-2} for 30 minutes. The electrodeposition process can be illustrated using equation (1) [10]. It involves MnO_4^- reduction and the deposition rate is governed by diffusion–electromigration kinetics.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4\,OH^- \quad (1)$$

Phase identification was performed using a Rigaku Miniflex II X-ray diffractometer employing Cu-K_α radiation (λ = 0.15406 nm). Infrared spectrum was measured using a Perkin Elmer FTIR spectrometer, Spectrum 100. The electrochemical properties were measured in 1 M Na_2SO_4 as electrolyte using a 3-electrode configuration system (the prepared MnO_2 as a working electrode, Ag/AgCl as a reference electrode and Pt wire as a counter electrode). The data were collected using an electrochemical workstation (Autolab/PGSTAT M101, Netherlands).

Results and discussion

1. Structural and morphological analyses

Fig. 1(a) shows the XRD pattern for electrodeposited MnO_2. The detected peaks show formation of ramsdellite MnO_2 phase according to ICCD card (00-0050331). In addition, two peaks related stainless steel substrates are observed. The MnO_2 crystallite size was calculated using Scherrer formula and it was found to be 18 nm. The nanostructure MnO_2 was confirmed by FESEM study in our recent publication [2]. Fig. 1(b) shows FTIR spectrum for MnO_2. The absorption bands at 510, 620 and 765 cm^{-1} are assigned to the pairing mode between Mn−O stretching modes of tetrahedral and octahedral sites in MnO_2. The absorption bands at 1090 cm^{-1} is attributed to O–H bending vibrations combined with Mn atoms. It is obvious that the absorption bands at 3440 and 1635 cm^{-1} belong to the absorbed water.

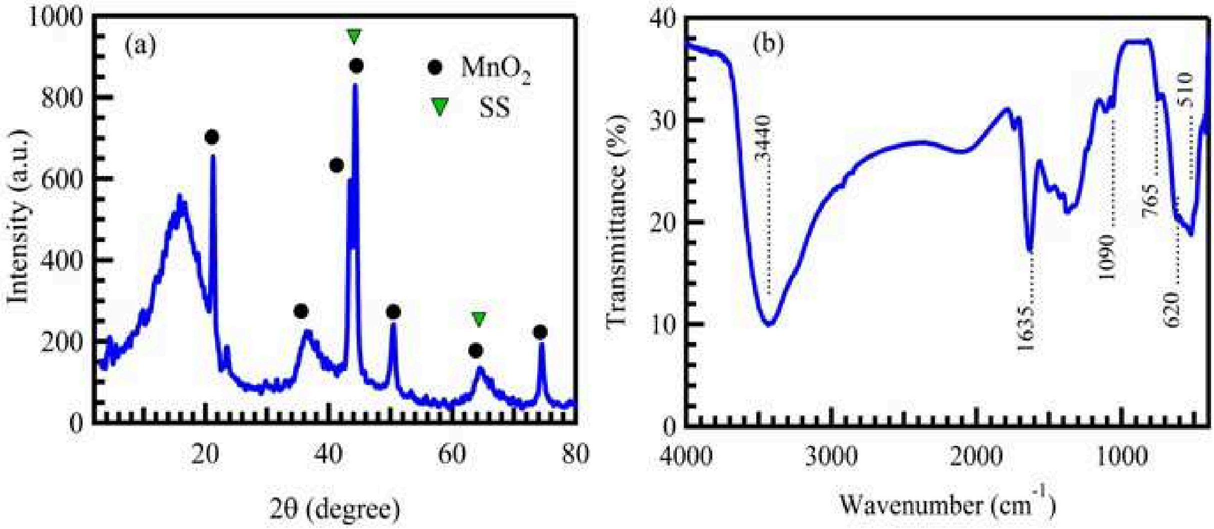

Fig. 1 XRD profile (a) and FTIR spectrum (b) of electrodeposited MnO_2.

2. Electrochemical measurements

Cyclic voltammetry and galvanostatic charge/discharge. Figure 2(a) shows the CV curve of electrodeposited MnO_2 at 10 mV s^{-1}. The CV for electrodeposited MnO_2 shows almost rectangular shape that reveals the ideal capacitive behaviour. The specific capacitance (C_{cv}) was calculated from the area under CV curve. The C_{cv} values decrease with increasing of scan rate (306, 265 and 227 F g^{-1} at 10, 50 and 100 mV s^{-1}, respectively) as shown in Fig. 2(a). The electrodeposited MnO_2 film has fine particles which lead to high electroactive surface area and easy accessibility of Na^+ ions which provides higher specific capacitance values. Electrodeposited MnO_2 film shows specific capacitance value higher than that reported for MnO_2 film (116 F g^{-1} at 50 mV s^{-1}) [5]. The proposed mechanism for charge storage on MnO_2 is based on the intercalation/deintercalation of Na^+ in the electrode material and the adsorption of Na^+ on the MnO_2 electrode surface as represented by the equations (2) and (3) [9]. The charge/discharge curves of MnO_2 at the voltage window of 0–1 V are displayed in Fig. 2(b) at 1 A g^{-1}. The curves are almost linear with neglected iR drop indicating reversibility of the electrode with good conductivity.

$$\mathrm{MnO_2 + M^+ + e^- \leftrightarrows MnOOM} \qquad (\mathrm{M^+ = Na^+ \text{ or } H_3O^+}) \qquad (2)$$

$$\mathrm{(MnO_2)_{surface} + M^+ + e^- \leftrightarrows (MnOOM)_{surface}} \qquad (\mathrm{M^+ = Na^+ \text{ or } H_3O^+}) \qquad (3)$$

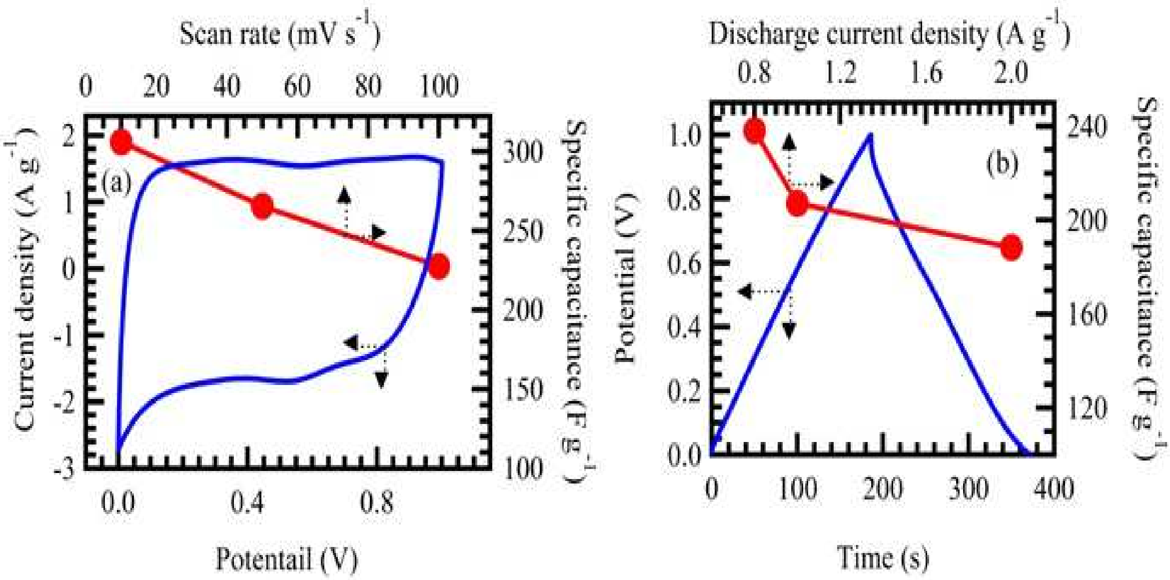

Fig. 2. Cyclic voltamogram at 10 mV s^{-1} and variation of specific capacitance as a function of scan rate (a) and galvanostatic charge/discharge at 1 A g^{-1} and variation of specific capacitance as a function of current densities (b) for electrodeposited MnO_2.

The specific capacitance (C_{cdc}) can be calculated from charge/discharge using the equation reported elsewhere [8]. The C_{cdc} values were 238, 207 and 188 F g^{-1} at 0.8, 1, and 2 A g^{-1}, respectively. These values are higher than those reported for MnO_2 nanoparticles (201 F g^{-1} at 1 A g^{-1}) [11].

Life stability and impedance studies. The stability test of electrodeposited MnO_2 was performed using galvanostatic charge/discharge at 3 A g^{-1}. The electrodeposited MnO_2 shows high stability of more than 90% over 1000 cycles (Fig. 3(a)). This is higher than that obtained by other studies [8]. This is a good evidence for the stable nature of MnO_2 electrode which suggests it as a good candidate for supercapacitor applications. The electrochemical impedance spectroscopy (EIS) was done in the frequency range of 0.01 Hz–50 kHz. *Nyquist* plot for electrodeposited MnO_2 is shown in Fig. 3(b), the inset shows the zoomed view at high frequency region. A small semicircle at the high frequency region and a straight line at the low frequency region can be seen. MnO_2 nanoparticles shows low solution resistance (R_s) of 1.52 Ω and charge transfer resistance (R_{ct}) of 1.30 Ω, indicating high electrical conductivity of the MnO_2 materials. The vertical linear section at the low frequency region demonstrates a pure capacitive behaviour. EIS measurement indicates that the electrodeposited MnO_2 has good capacitive performance.

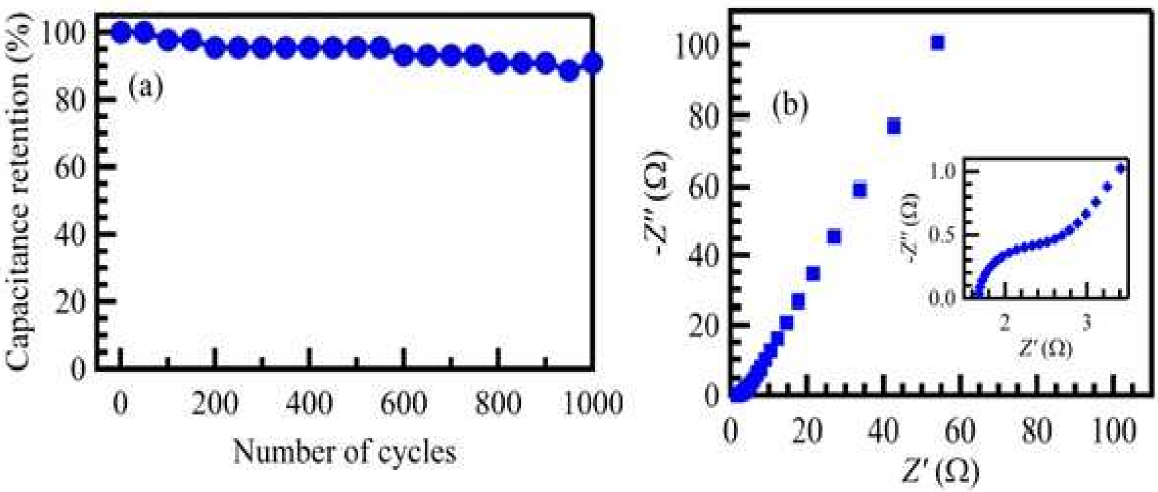

Fig. 3 Cycling stability (a) at 3 A g^{-1} and *Nyquist* plot (b) of MnO_2 at open circuit potential; Inset shows the magnified *Nyquist* plot at high frequency region.

Conclusion

MnO_2 nanoparticles has been successfully obtained by electrodeposition process from $KMnO_4$ solution. Fine aggregate of MnO_2 particles (18 nm) are confirmed by XRD analysis. MnO_2 nanoparticles shows very high specific capacitance values calculated from CV and charge-discharge data of 306 F g^{-1} and 238 F g^{-1} at 10 mV s^{-1} and 0.8 A g^{-1} respectively. Electrodeposited MnO_2 shows long cycle life of 90% over 1000 cycles. The low R_s and R_{ct} values obtained from impedance studies indicate that the good electrochemical performance of electrodeposited MnO_2 electrode.

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