Fabrication and the electrochemical activation of network-like MnO$_2$ nanoflakes as a flexible and large-area supercapacitor electrode

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Abstract

Porous network-like MnO$_2$ thick films are successfully synthesized on a flexible stainless steel (SS) mesh using a simple and low-cost electrodeposition method followed by an electrochemical activation process. Morphology, chemical composition and crystal structure of the prepared electrodes before and after the activation process are determined and compared by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) analyses. The results show that the implementation of the electrochemical activation process does not change the chemical composition and crystal structure of the films, but it influences the surface morphology of the MnO$_2$ thick layer to a flaky nanostructure. Based on the electrochemical data analysis, the maximum specific capacitance of 1400 mF (381 F g$^{-1}$) and 3700 mF (352 F g$^{-1}$) are measured for small (2.6 cm$^2$) and large (10 cm$^2$) surface area electrodes, respectively. In addition, a flexible symmetric MnO$_2$/MnO$_2$ solid state supercapacitor shows a capacitance of 0.3 F with about 98% retention at different bending angles from 0° to 360°.

Keywords: Supercapacitor, MnO$_2$, electrochemical activation, nanostructure, flexible
Introduction

In recent years, great efforts have been devoted for exploring the flexible and wearable energy storage devices, such as flexible displays, artificial skins, and portable electronic equipments [1-3]. Among the energy storage devices, supercapacitors (SC) which fill the gap between batteries and conventional capacitors have attracted attention due to their ability to supply more power, long cycle life, and fast dynamic of charge propagation. There are two basic mechanisms for storing energy in supercapacitors including electric double layer capacitance (EDLC) originating from pure electrostatic charge accumulation at the interface between the electrolyte and the electrode e.g. carbon-based materials [2], and the pseudo-capacitance due to the fast and reversible surface redox reactions of various electroactive materials, e.g. metal oxides and conductive polymers [4-7].

MnO\textsubscript{2} is one of the most attractive candidates because of its plausible advantages such as having a high theoretical specific capacitance ($C_{Th}^{MnO_2}$=1370 F g\textsuperscript{-1}) combined with natural abundance, low-cost, and being environmentally benign [17-23]. However, the poor electrical conductivity and low ion diffusivity of MnO\textsubscript{2} has remained a major challenge that limits the rate capabilities for high power performances [24]. Many strategies have been proposed to mitigate these limitations including the increase of the specific surface area of the electrode material [25], using conductive additives, and the deposition of manganese oxide nanostructures on a highly conductive porous substrate [26,27].

In general, the overall activation processes for both EDLCs and faradic-based supercapacitor electrodes influenced the morphology, chemical composition or crystallinity of the active materials (Fig. 1). In MnO\textsubscript{2}-based SC electrodes, it seems that the electrochemical activation process could affect the nature of the porous MnO\textsubscript{2} active material.

In this work, to address the above mentioned issues, a porous layer of MnO\textsubscript{2} was synthesized on a flexible stainless steel substrate to fabricate SS/MnO\textsubscript{2} electrode. Then, the electrochemical activation process was conducted on the fabricated electrode to investigate the effects of activation process on the chemical composition, crystal structure and the surface morphology of the MnO\textsubscript{2} thick layer in detail. Finally, the electrochemical and
supercapacitive behavior of the activated SS/MnO$_2$ electrode was studied as well. The maximum electrochemical capacitance of 381 F g$^{-1}$ was obtained at constant discharge current density of 0.1 A g$^{-1}$ for MnO$_2$-based electrode. Moreover, the synthesis process as well as the scalability and bendability of the prepared MnO$_2$ electrodes show the potential applications in future flexible energy storage devices.

**Experimental**

**Preparation of manganese dioxide film**

Manganese oxide film was prepared by using the electrochemical deposition in a three-electrode electrochemical cell consisted of a cleaned stainless steel (SS) mesh substrate (1.6×1.6 cm$^2$), a platinum sheet (1.5×1.5 cm$^2$) and an Ag/AgCl (KCl 3.0 M) electrodes as working, counter and reference electrodes, respectively. The anodic electrodeposition of the manganese dioxide film was performed at a constant current density of 2.2 mA cm$^{-2}$ in a solution containing 0.10 M of Mn(CH$_3$COO)$_2$.4H$_2$O and 0.10 M of Na$_2$SO$_4$ in different deposition times of 50, 150, 500, 1000 and 2000 s (Scheme 1). During the electrodeposition, the solution was agitated with a magnetically driven Teflon coated stirring bar. Then, the electrodeposited electrodes were washed out with deionized water several times followed by annealing at 200 °C for 30 min in an ambient atmosphere with a heating rate of 4 °C min$^{-1}$. After the heat treatment, the prepared electrodes were electrochemically activated by potential cycling at a scan rate of 50 mV s$^{-1}$ in a potential window from 0 to +1 V for 300 cycles in 1.0 M Na$_2$SO$_4$ aqueous electrolyte (activation process in Scheme 1). The mass loading was determined separately by measuring the mass of the electrodes before and after electrodeposition/activation process by using semi-micro analytical balances (GR-202) with the accuracy of 0.02 mg.

**Scheme 1**

**Electrochemical analysis**

The electrochemical properties of the samples were analyzed by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD using an electrochemical analyzer (AUTOLAB PGSTAT 302N) in 1.0 M Na$_2$SO$_4$ aqueous solution. CV measurements were carried out at different scanning rates in the potential range of 0 to +1.0 V. The GCD tests were conducted within the same potential window at various current densities from 0.10 to 2.0 A g$^{-1}$. 

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Results and Discussion

Fabrication and characterization

**Fig. S1** (Supplementary material) shows the potential-time curves during the galvanostatic electrodeposition of manganese dioxide for different time intervals. The equilibrium electrode potential reached to +0.7 V. The first peak is associated with the initial nucleation of the manganese dioxide on SS mesh [33]. Mass loading of the MnO$_2$ on the SS mesh was controlled by varying the electrodeposition time. **Fig. S2** shows the loaded mass of electrodeposited MnO$_2$ as a function of the electrodeposition time.

**Fig. 2a** shows the CV curves of the SS/MnO$_2$ electrodes before and after the electrochemical activation process. The obvious increase in the surface area under the CV curve can be attributed to four different physicochemical scenarios: (i) change in the morphology, (ii) change in the chemical composition, (iii) crystal structure transition, and (iv) wetting of the porous electrodeposited layer.

XRD analysis indicates that the activation process had no significant effect on the crystal structure of the electrodeposited film (**Fig. 2b**). All the diffraction peaks except that for the SS substrate had low intensity, which can be explained by the incomplete crystallinity of MnO$_2$ [34]. However, it clearly shows four distinct diffraction peaks at 2$\theta$=19.1°, 37.2°, 44.7°, and 65.8° which is indexed to the diffractions from the (111), (311), (400) and (440) crystal planes of the MnO$_2$, respectively (JCPDS card no. 00-042-1169). According to FTIR spectra analysis (**Fig. 2c**), it further supports our XRD results, i.e. activation process causes no significant change in chemical composition. In addition, the peaks at around 3400 and 1600 cm$^{-1}$ are assigned to the stretching vibration and scissors bend of the H-O-H bond, and another peak at around 530 cm$^{-1}$ corresponds to characteristic vibrations of Mn−O bonds [35].

The morphology of the MnO$_2$ films was investigated by FE-SEM (**Fig. 2d**). It is obvious that the MnO$_2$ layer was uniformly grown on the SS mesh (see the cross-sectional images, **Fig. S3**). It was found that the morphology of the smooth surface was changed to a porous network-like structure (nanoflakes) during the activation process (**Fig. 2e**). The thickness of nanoflakes and spaces between them were measured about 30±5 and ~100 nm [36,14]. Therefore, the electrolyte can also cause wetting of the porous layer during the activation process. The crystalline structure and the chemical composition of MnO$_2$ nanostructure have not been changed during the activation process. So, the main reason for the improved capacitance of activated SS/MnO$_2$ electrode is the change in the morphology of the electrode
surface, as confirmed by FE-SEM images. On one hand, the morphology change can cause the capacitance of the electrode, and on the other hand, besides the morphology change, the wetting of the electrode surface can also affect the capacitance of the electrode.

**Fig. 2**

The electrochemical properties of the MnO$_2$ electrodes for different electrodeposition time were also investigated using CV measurement. **Fig. 3a** and **b** show the normalized CV curves to the active mass and the geometric surface area of the MnO$_2$ electrodes, respectively. The sample prepared with deposition time at 1000 s was chosen as the optimized electrode for further studies.

**Fig. 3**

**Fig. 4a** demonstrates the CV curves of the optimized electrode at various scan rates from 10 to 100 mV s$^{-1}$ in the potential range from 0 to +1.0 V. CV curves show a good rectangular shape which is due to redox reactions. The GCD curves of the electrode were obtained at various discharge currents (**Fig. 4b**). The GCD curves show nearly triangular shape with low IR drop at various current densities confirming the ideal capacitive properties with good electrochemical reversibility. Calculated specific and real capacitances as a function of current density are shown in **Fig. 4c**. The specific capacitance was measured to be 381 F g$^{-1}$ and 176 F g$^{-1}$ at the current density of 0.1 and 2.0 A g$^{-1}$, respectively.

To further study the application potential of MnO$_2$/SS electrode, an electrode with larger area (at about 10 cm$^2$) was also prepared, which demonstrates the scalability of the prepared samples. The electrochemical results showed that the specific (and real) capacitance of the fabricated electrode was about 353 F g$^{-1}$ (and 3.7 F) at the current density of 0.10 A g$^{-1}$ (**Table S2**).

**Fig. 4**

In continuing the work, a flexible (**Fig. S4**) and symmetric cell was prepared to investigate and evaluate the actual performance of the MnO$_2$ as an electrode material for supercapacitor
device. Symmetric and relatively packed capacitor, MnO$_2$//MnO$_2$, was assembled with a filter film as a separator. **Fig. 5a** and **b** represents the CV curves of the solid state MnO$_2$//MnO$_2$ device at different cell voltages ranging from +0.4 V to +1.0 V at different scan rates. The specific (and real) capacitance of the symmetric system was calculated of about 43 F g$^{-1}$ (and 0.3 F) according to the GCD curves based on the total active mass in both electrodes at the different current densities as shown in **Fig. 5c** and **d**. As illustrated in **Fig. 5d**, the symmetric system presents rate capability retention of about 63%.

After 1000 cycles, specific capacitance of the device still remains 80% of its initial specific capacitance. These results suggested that the structure exhibited an outstanding flexibility, **Fig. 5e**, (with about 98% retention in capacitance at different bending angles from 0° to 360°), which indicated that the prepared device possesses a good performance when compared with similar symmetric MnO$_2$ based supercapacitors such as MnO$_2$/graphene, graphene/MnO$_2$/CNT, MnO$_2$, MnO$_2$ nanowire/graphene, MnO$_2$/TiO$_2$, MnO$_2$/CNT [41-46].

**Conclusions**

In summary, we have fabricated a supercapacitor electrode based on MnO$_2$ nanostructure using a two-step electrochemical method: electrodeposition and activation process. By loading different amount of MnO$_2$ on SS mesh, an optimized electrode (based on electrochemical performance) has been prepared. This flexible, high mass, and large area electrode has demonstrated the capacitance of 381 F g$^{-1}$ or 533 mF cm$^{-2}$ with relatively low ohmic resistance and fast charge transfer kinetics. The effect of activation process on surface morphology and capacitance of the MnO$_2$ electrodes was modelled by a semi-empirical approach (supporting Information, SI). Finally, the prepared MnO$_2$//MnO$_2$ solid state symmetric device can be introduced as a low price and flexible supercapacitor in energy storage realm.

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**Figure and Scheme Captions**

**Fig. 1.** The general physicochemical effects of the activation process on EDLCs and faradic-based SCs (metal oxides/hydroxides and conducting polymers)
**Scheme 1.** Schematic illustration of the electrodeposition and activation processes of the MnO$_2$/SS electrode (the inset scale bar is 500 nm for all SEM images). The surface morphology of the MnO$_2$ film was changed to porous and flaky nanostructures by activation process.

**Fig. 2.** CV curves (a), XRD patterns (b), and FTIR spectra of the MnO$_2$ electrodes before and after the electrochemical activation process (c). Substrate peaks of the SS in XRD patterns identifies by “*“. FE-SEM images of MnO$_2$ electrodes before (d) and after (e) the electrochemical activation process. Insets are the magnified FE-SEM images. (f) A typical photograph of the prepared large area and flexible electrodes.

**Fig. 3.** Normalized CV curves to the active mass (a) and geometric surface area (b) of MnO$_2$ electrodes for different electrodeposition time at $\nu=50$ mV s$^{-1}$ in 1.0 M aqueous Na$_2$SO$_4$ electrolyte. (c) The areal and specific (gravimetric) capacitance of the prepared electrodes versus electrodeposition time at $\nu=50$ mV s$^{-1}$. The dash lines show the linear behaviour of the capacitance as a function of the electrodeposition time (or thickness of the porous layer) before the effect of dead masses become dominant. Note: in the present semi-empirical model, the effect of dead mass is not considered.

**Fig. 4.** CV curves at various scan rates between 10 and 100 mV s$^{-1}$ (a) and GCD curves at different current densities ranging from 0.10 to 2.0 A g$^{-1}$ (b) of the optimum electrode. (c) Total real and specific capacitance of the optimized MnO$_2$ electrode at different current densities. This electrode shows a good rate capability with retention at about 46%.

**Fig. 5.** (a) CV curves of the assembled symmetric supercapacitors in different potential windows at a scan rate of 50 mV s$^{-1}$, (b) CV curves at scan rates between 10 and 100 mV s$^{-1}$ in the potential window of 0.0 to +1.0 V. (c) galvanostatic charge/discharge curves at current densities ranging from 0.1 to 2 A g$^{-1}$ in the potential window of 0.0 to +1.0 V. (d) variation of the specific capacitance with current density. (e) Cycle lifetime of the full cell at 2.5 A g$^{-1}$ and (f) CV curves obtained at a scan rate of 50 mV s$^{-1}$ at different bending angles. It shows very well flexibility.
Fig. 1

Activation Process

EDLCs
- Wetting

Faradic-Based SCs
- Wetting
- Morphology Change
- Chemical Change
- Crystal Structure Transition

Scheme 1

SS → Electrodeposition → MnO$_2$/SS → Activation → MnO$_2$/SS
Fig. 2
Fig. 3

Fig. 4
Fig. 5