Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp1077-1078

Morphology Tailoring of Manganese Oxide by Electrodeposition for Supercapactior Application

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Abstract

In this study, a DC electrodeposition technique has been applied for the morphology tailoring of manganese dioxides (MnO_x). The morphology of MnO_x can be controlled by a selection of precursor. Thin film of MnO_x was synthesized by using potassium permanganate ($KMnO_4$), while a vertical sheet of MnO_x was synthesized by using manganese sulfate ($MnSO_4$) solutions. Furthermore, the hybrid structure of MnO_x was successfully fabricated by the two-step electrodeposition. It was found that the hybrid structure of MnO_x shows the highest specific capacitance of 279.03 ± 39.38 F/g.

1. Introduction

Supercapacitor or electrochemical capacitor (EC) is one kind of energy storage devices that become importance recently because its longer life time and fast charge/discharge compared to battery. Most of ECs were made from carbon materials such as carbon nanotubes, graphene and activated carbon. Working mechanism of this kind of EC is based on electrostatic charges between electrode material and electrolyte, so that it is also called as electric double layer capacitor (EDLC). However, there is also another type of ECs called pseudocapacitor which made from metal oxide or conductive polymers. Among metal oxide materials for pseudocapacitor, manganese oxide (MnO_x) is gained more attentions because its high energy density, low cost and natural abundance [1]. However, the electrochemical properties of MnO_x strongly depend on its morphology and structure [2].

In this research, MnO_x with different structures were synthesized using electrodeposition techniques with different precursors and their morphology and electrochemical properties were investigated.

2. Experimental

Stainless steel 304 (SS304) was used as a substrate for electrodeposition. SS304 was cleaned by using ultrasonication for 15 min with acetone, ethanol, deionized (DI) water, respectively. For electrodeposition, two types of precursors were used; 0.1 M manganese permanganate ($KMnO_4$) and 0.1 M manganese sulfate ($MnSO_4$) prepared in DI. 0.1 M of each precursor was prepared in DI. Three types of MnO_x were synthesized. The first sample was synthesized by using $KMnO_4$ solution for 10 min (hereafter referred to as Mn-K10). The second sample was synthesized by using $MnSO_4$ solution for 10 min (hereafter referred to as Mn-S10). The third sample is a hybrid structure of MnO_x prepared by two-step electrodeposition using $KMnO_4$ solution and subsequently $MnSO_4$ solution with a deposition time of 5 min for each solution (hereafter referred to as Mn-KS5/5). A deposition area was 1×1 cm^2. The SS304 sheet and graphite rod were connected as anode and cathode electrodes, respectively. The morphology of MnO_x was characterized by scanning electron microscope (SEM).

Electrochemical measurements of samples were carried out in a three-electrode cell (Metrohm, AUTOLAB PGSTAT 302). The fabricated sample was used as a working electrode. Pt and Ag/AgCl were used as counter and reference electrodes, respectively. 1 M Na_2SO_4 aqueous solution was used as electrolyte. The electrochemical properties were characterized by galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS). The specific capacitance (C_S) was calculated from CD curves according to the following eq. (1);

$$C_S = \frac{I \times \Delta t}{\Delta V \times m} \quad (1)$$

where I is a discharge current (A), Δt is a discharge time (s), ΔV is a voltage change after a full charge or discharge and m is a mass of active materials (g).

3. Results and Discussions

Figs. 1(a)-1(c) show SEM images of Mn-K10, Mn-S10 and Mn-KS5/5, respectively. The morphology of Mn-K10 and Mn-S10 were completely different. Mn-K10 shows a dense film, while Mn-S10 shows a vertical sheet stacking on the surface of substrate. The Mn-KS5/5 shows a mix of two morphologies of dense film and vertical sheet structures. These results show that morphology of MnO_x can be controlled by a selection of precursor. Furthermore, the hybrid structure of MnO_x was successfully fabricated by the two-step deposition.

Fig. 2(a) shows CD curves obtained from Mn-K10, Mn-S10 and Mn-KS5/5 at a current of 1 mA. A relatively symmetric triangular shapes were obtained, implying a good capacitive behavior. From the CD curves, C_S of Mn-K10, Mn-S10 and Mn-KS5/5 were calculated to be 228.49 ± 19.52, 252.11 ± 27.64, and 279.03 ± 39,38 F/g, respectively.

Fig. 2(b) shows a Nyquist plots of Mn-K10, Mn-S10 and Mn-KS5/5 at a frequency range between 0.01 Hz to 100 kHz. All samples show resemble semicircle curves with different diameters. This implies the different electrochemical properties of each sample. The intrinsic resistance (R_S) and the charge transfer resistance (R_{CT}) of each sample can be determined from the offset on the x-axis and the diameter of the semicircle, respectively. The values of R_S of Mn-K10, Mn-S10 and Mn-KS5/5 are 8, 5 and 5 Ω, respectively. Similarly, the values of R_{CT} of Mn-K10, Mn-S10 and Mn-KS5/5 are 41, 7 and 11 Ω, respectively.

From the above electrochemical results show that the hybrid MnO_x material, Mn-KS5/5, show the highest specific capacitance, implying a potential use as an electrode of supercapacitor. The highest capacitance of Mn-KS5/5 may contribute to the combination of the structure of the film and vertical sheet. From our previous results, it was shown that in the case of the vertical sheet, if the deposition time is 5 min, the sheet is less dense and not perfectly coated over the substrate, resulting in a penetration of an electrolyte ions to a current collector and a current leakage [3]. In the hybrid structure, the vertical sheet structure provides a high surface area of electrode material, while a film also acts a buffer between a vertical sheet and a current collector.

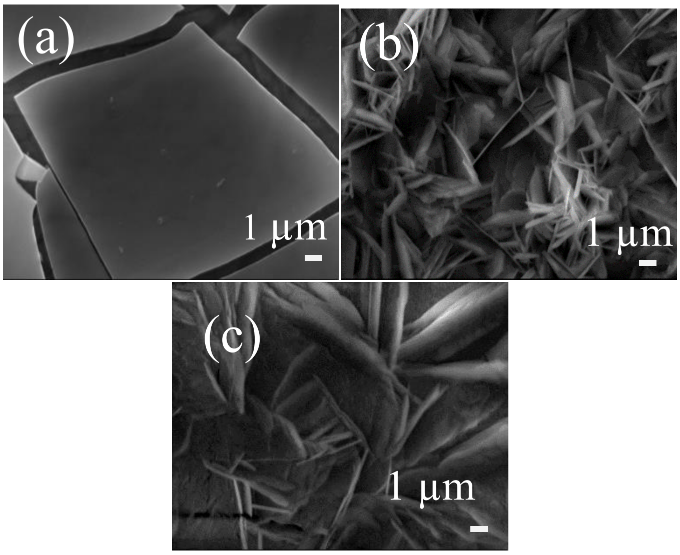

Fig. 1 SEM images of (a) Mn-K10, (b)Mn-S10, and (c) Mn-KS5/5.

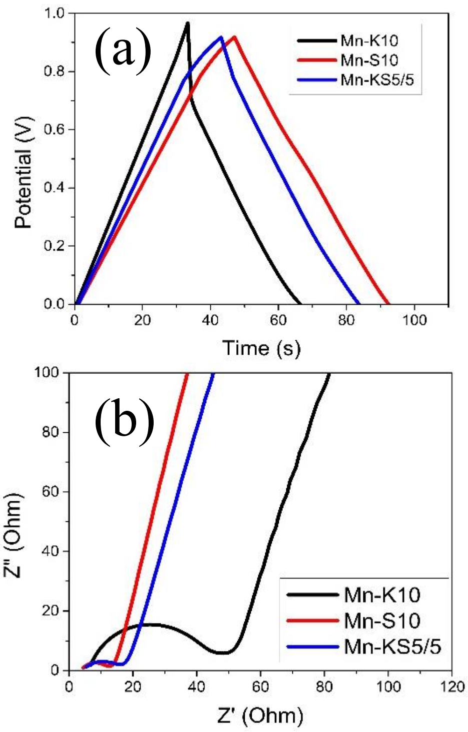

Fig. 2 (a) galvanostatic charge-discharge curves and (b) electrochemical impedance spectra of Mn-K10, Mn-S10 and Mn-KS5/5.

4. Conclusions

Morphology tailoring of MnO_x was demonstrated by a DC electrodeposition technique. The morphology of MnO_x can be controlled by a selection of precursor. Thin film of MnO_x was synthesized by using $KMnO_4$, while a vertical sheet of MnO_x was synthesized by using $MnSO_4$ solutions. Moreover, the hybrid structure of MnO_x between thin film and vertical sheet was successfully fabricated by the two-step electrodeposition. It was found that the hybrid structure of MnO_x shows the highest specific capacitance of 279.03 ± 39.38 F/g.

Acknowledgements

We acknowledge the financial support from the Thailand Graduate Institute of Science and Technology (TGIST).

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