

The synthesis and electrochemical characterization of mesoporous carbon based on MF resin and MnO₂ composite

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To improve the electrical conductivity of MnO₂, the composite material of mesoporous carbon and MnO₂ was synthesized. The mesoporous carbon was prepared by a polymerization-induced colloid aggregation method (PICA) using melamine formaldehyde resin as the carbon precursor and fumed silica (14 nm) as a hard template. The composite of mesoporous carbon and MnO₂ was prepared by a redox reaction between KMnO₄ and oxygen on the surface of carbon. The synthesized mesoporous carbon has a high specific surface area (~1500 m²g⁻¹) and an average pore size as large as 7 nm. Electrochemical properties of the mesoporous carbon-MnO₂ composite were elucidated by cyclic voltammograms and galvanostatic charge-discharge in 1.0 M Na₂SO₄ electrolyte. A specific capacitance of 128 Fg⁻¹ was obtained at a current density of 0.1 Ag⁻¹.

Keywords: Pseudocapacitor, Supercapacitor, Porous carbon materials, MnO₂ composite.

Introduction

Electrochemical capacitors (ECs) have been known for many years, but only recently are emerging as an attractive energy-storage/conversion device for future use in hybrid electric vehicles in combination with rechargeable batteries or fuel cells [1]. The ECs are classified into two types according to their charge storage principle [2]. The first is an electrical double-layer capacitor (EDLC) using activated carbon (AC) with a high surface area and the other is a pseudocapacitor using metal oxides and conducting polymers.

Various metal oxides, such as RuO₂, IrO₂, NiO₂, CoO_x, SnO₂, and MnO₂, were used as electrode materials [3-7]. Among these materials, amorphous hydrated ruthenium oxide exhibits ideal pseudocapacitive behavior, remarkably high specific capacitance (as high as 700 - 1000 F/g [3]), and excellent reversibility. However, the high cost and the toxicity to the environment have limited its practical application. Therefore, much attention has been increased for the demand on the relatively cheap and environmentally friendly materials.

MnO₂ appears to be a promising material due to its superior electrochemical performance, environmentally benign nature, and low cost [8, 9]. However, the relatively low electrical conductivities of pristine MnO₂, to a great extent, limit their high rate performance [10, 11, 20]. The intrinsic MnO₂ is generally decorated with conducting

agents, such as carbons and conducting polymers, in order to enhance their electrical conductivities.

In this work, the composite material of mesoporous carbon (MC) and MnO₂ was prepared to improve the electrical conductivity of MnO₂. Melamine formaldehyde resin was used in order to obtain MC with a facile mesoporous structure through a polymerization-induced colloid aggregation (PICA) method. MC/MnO₂ composite was prepared by a redox reaction between KMnO₄ and oxygen-containing groups on MC surface. The system of electrochemical capacitors consists of the composite material (MC/MnO₂) as the positive electrode and AC as the negative electrode. The microstructure and electrochemical properties of the synthesized MC and MC/MnO₂ were evaluated.

Experimental

Materials preparation

The MC was prepared by a polymerization-induced colloid aggregation (PICA) method [12], using melamine as a carbon precursor and fumed silica as a hard template. In the typical synthesis of melamine formaldehyde resin (MF)/silica composites, 3.15 g melamine and 5.0 ml formaldehyde (36 wt%) were first added into 12.5 ml deionizer water and stirred for 20 minutes at 75 °C to obtain a clear solution. The resulting precursor solution was cooled to 40 °C and poured into 30 ml fumed silica colloid solution (5.0 wt%) under stirring at 40 °C and then the pH value of the mixtures was adjusted to 4.5 using 2 M HCl solution; the mixtures were kept for 3 hours to obtain the MF/silica composites. These composites were collected by filtration, washed

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with water, and dried in air at 60 °C. The composites were firstly cured in air at 180 °C for 24 hours and then carbonized under a high purity nitrogen atmosphere up to 800 °C for 2 hours. Subsequently, 20 wt% HF solution was used to etch the silica in the resulting carbon/silica composites for 24 hours. Finally, after washing, the products were dried in air at 120 °C for 2 hours.

MC/MnO₂ composite

0.2 g of KMnO₄ was dissolved in 30 ml of distilled water, and then 0.3 g of MC was added to it and heated to 70 °C under stirring for 4 h. The suspension was filtered, washed several times with distilled water, and dried at 100 °C for 24 hours in a vacuum oven.

Structure characterizations and electrochemical tests

The morphology of MC/MnO₂ composite was examined using scanning electron microscope (FE-SEM, Jeol JSM-6700F). The crystalline phases were analyzed with X-ray diffraction (XRD, Rigaku D/Max-2500/PC). The Brunauer, Emmett, and Teller (BET) method was used to measure the surface areas and pore volumes of samples (Belsorp-Mini II, Belsorp, Japan). The carbon content of MC/MnO₂ composite was determined by a thermogravimetric analysis (TGA).

The electrochemical properties of the active material were examined using a coin cell (CR 2032). The positive electrode was made by coating the slurry of active material (MC + MnO₂). The positive electrode was prepared by mixing the composite material, Super-P carbon black, and polyvinylidenefluoride (PVDF) in a mass ratio of 80 : 10 : 10. After stirring the mixtures for 1 h in N-methylpyrrolidone, the resulting slurry was coated on a titanium disc current collector. The negative electrode used MSP20 (Kansai Coke & Chemicals, Japan, resin) activated carbon as an active material. The separator and electrolyte were TF 4035 (NKK, Japan, Cellulose, 35 μm) and a 1.0 M Na₂SO₄ solution, respectively. Galvanostatic charge and discharge tests of the cell were carried out at current densities of 0.1 ~ 1 Ag⁻¹ between 0.05 V and 0.85 V. Cyclic voltammetry (CV) was carried out at a scan rate of 2 ~ 20 mVs⁻¹ between 0.05 V and 0.85 V. Electrochemical impedance spectroscopy (EIS) was recorded by applying a low amplitude voltage of 5 mV root mean square to the system at its open circuit potential at frequencies from 100 kHz to 0.01 Hz. Galvanostatic charge and discharge, EIS, and CV were characterized using a potentiostat (EC-Lab, France).

Results and Discussion

Analysis of carbon content and structures

The SEM image of the as-synthesized MC is shown in Fig. 1(a). The MC seems to be porous, with pore sizes ranging from micrometer to nanometer range. The presence of nanoporosity was confirmed by BET

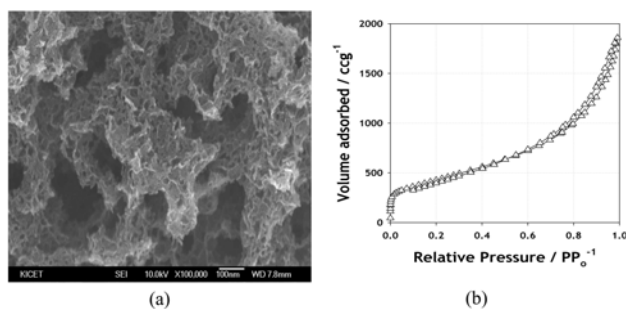


Fig. 1. FE-SEM image (a) and N₂ adsorption/desorption isotherm (b) of the MC.

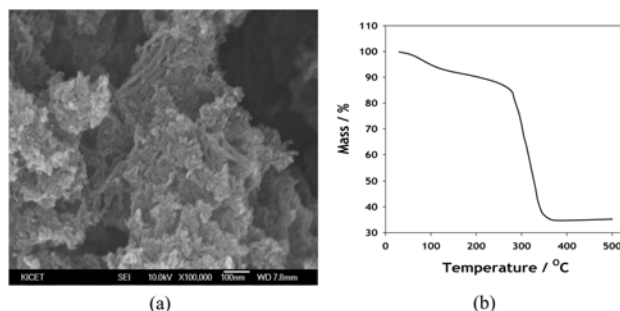


Fig. 2. FE-SEM image (a) and TGA curve (b) of the MC/MnO₂ composite.

measurements and N₂ adsorption data (Fig. 1(b)). The pore sizes of this sample calculated from desorption branch is mainly concentrated near 7.4 nm. Its BET surface area and total pore volume are 1531 m²g⁻¹ and 2.85 cm³g⁻¹, respectively.

The SEM image of the as-synthesized MC/MnO₂ composite is shown in Fig. 2 (a). This MnO₂ powder consists of many agglomerated nano-particles (size : about 10 nm) in the MC. The carbon content of the product was determined by a thermogravimetric analysis (TGA) in oxygen at 500 °C. The TGA curve of the prepared powder is illustrated in Fig. 2 (b). The weight loss from room temperature to 250 °C can be attributed to the dehydration of physically adsorbed and chemically bonded water molecules. The weight loss between 250 °C and 400 °C is assigned to the oxidation of carbon. TGA result confirms that the weight fraction of carbon in the prepared composite is about 50 wt%.

Fig. 3 illustrates the XRD pattern of the synthesized MC/MnO₂. The broad peaks indicate that the sample is composed of nano-particles. Peaks at 2θ = 26, 37, and 65 ° are observed. Among the peaks, the peaks at 2θ = 26 and 37 ° are assigned to be α-MnO₂ and 65 ° to α'-MnO₂ [13, 14], which indicates that the sample is a mixture of α- and γ-MnO₂. MnO₂ exists in various crystallographic forms, such as α, β, γ, δ, λ, etc., depending on how MnO₆ octahedra subunits are inter-linked. Among these different crystallographic forms, α- and δ-forms of MnO₂ are found to be more suitable than the rest, because of the availability of sufficient gap in the structures for doping/undoping of cations [15]. Also, γ-MnO₂ is known to exhibit considerable

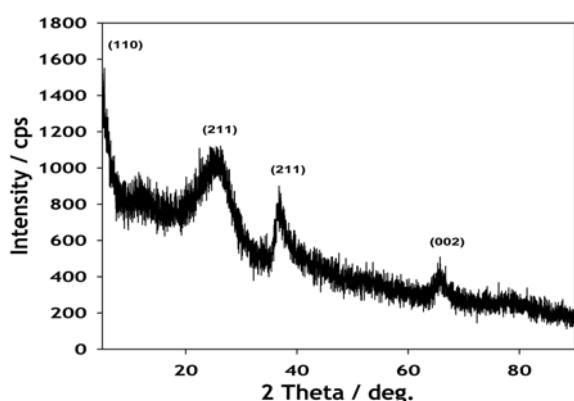


Fig. 3. The XRD pattern of MC/MnO₂ composite.

electrochemical performance [16].

Electrochemical characteristics

The carbons containing nitrogen were effective in adsorbing acidic materials such as H₂SO₄, H₂S, and HCl [17]. Therefore, the MC based on melamine resin is almost not electrochemically active in neutral electrolyte. However, mesoporous structured carbon can be easily prepared from melamine formaldehyde resin. Therefore, the MC is only used to improve the electrical conductivity of MnO₂ without any contribution to capacitance.

The capacitance behavior of MnO₂ is identified by reversible redox process, involving Mn⁴⁺ followed by surface insertion/deinsertion of cations:



where Mⁿ⁺ represents a cation [18].

Fig. 4(a) shows respective CV curves of the prepared MC/MnO₂ composite measured at a scan rate ranging from 2 to 10 mVs⁻¹ between 0.05 and 0.85 V in 1.0 M Na₂SO₄ electrolyte solution. It can be clearly seen that there are no obvious redox peaks in the working potential range and the CV curves obtained at different scan rates present quite good mirror images with respect to the zero-current line and symmetric I-E

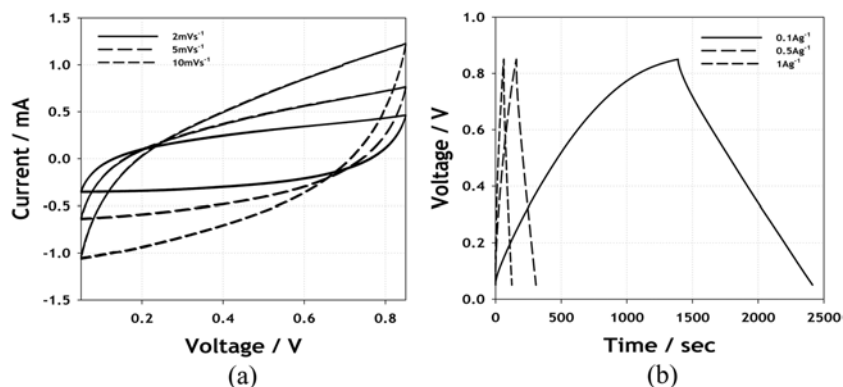


Fig. 4. Cyclic voltammograms (a) with different scan rates and galvanostatic charge-discharge curves (b) of MC/MnO₂ composite.

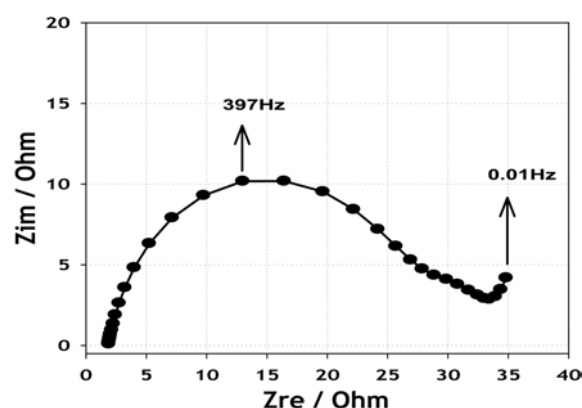


Fig. 5. Nyquist plots of MC/MnO₂ composite (100 kHz - 0.01 Hz).

response. As the oxide is mainly amorphous with a short range ordering, it is likely that the insertion of cations takes place dominantly at the surface of the MnO₂ particles. The assumption of surface process is supported by CV, without diffusion controlled redox current peaks [19].

In addition, galvanostatic constant current charge-discharge curves at various current densities were performed from 0.05 V to 0.85 V; respective curves are shown in Fig.4 (b). Specific capacitance was calculated by [9]:

$$C = I \cdot (\Delta T) / (\Delta V) \cdot (X) \quad (2)$$

where I, T, V and X denote current density, discharge time, potential range in discharge, and the weight of the active material, respectively. The specific capacitance of MC/MnO₂ composite is 128, 93, and 77 Fg⁻¹ at 0.1, 0.5, and 1 Ag⁻¹, respectively.

Fig. 5 shows the Nyquist plots of the experimental impedance data. All the measured impedance spectra are similar in shape, with a semicircle at the higher-frequency region and a spike at the lower-frequency region. The semicircle represents the charge transfer resistance (RCT) (i.e., the kinetic resistance to charge transfer at the electrode - electrolyte interface). The spike in the lower-frequency region represents the

Warburg impedance (Z_w) associated with the diffusion of cations into the particles. The RCT values are found to be 33 ohm for the MC/MnO₂. Other papers that conducted this experiment with MnO₂ only show more than 100 ohm of the RCT value for the resistance measurement. [19] Therefore, the electrochemical analysis demonstrated that MC/MnO₂ composite had good capacitive behavior due to the electrical conductivity improvement by mesoporous carbon.

Conclusions

The MC with average pore size of 7 nm, pore volume of 2.85 cm³g⁻¹, and BET specific surface area of 1531 m²g⁻¹, have been successfully synthesized by PICA method. The MnO₂ of MC/MnO₂ composite was identified by X-ray diffraction to be a mixture of α - and γ -MnO₂. MnO₂ powder consists of many agglomerated nano-particles dispersed in the MC. Electrochemical properties of MC/MnO₂ composite were studied by CV, galvanostatic charge/discharge in 1.0 M NaSO₄ aqueous solution. The CV curves obtained at different scan rates present roughly good mirror images with respect to the zero-current line and symmetric I-E response. The specific capacitance of MC/MnO₂ composite is 128, 93, and 77 Fg⁻¹, at 0.1, 0.5, and 1 Ag⁻¹, respectively. Also, the RCT values are found to be 33 ohm. Analysis of CV, galvanostatic charge/discharge, and EIS confirm that the electrochemical properties of MnO₂ were improved by MC.

Acknowledgements

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References

1. B.E. Conway, "Electrochemical Supercapacitors, Scientific Fundamental and Technological Applications" (Kluwer Academic/Plenum, New York, 1999).
2. B.E. Conway, J. Electrochem. Soc. 138 (1991) 1539-1548.
3. J.P. Zheng, P.J. Cygan, T.R. Jow, J. Electrochem. Soc. 142 (2001) 2699.
4. C.H. Doh, S.J. Choi, S.I. Moon, M.S. Yun, G.C. Yung, S.G. Kim, J.W. Lee, J. Koera Electrochemical. Soc. 6 (2003) 93-97.
5. Y.S. Yoon, W.I. Cho, J.H. Lim, D.J. Choi, J. Power Sources. 101 (2001) 126.
6. B.E. Conway, V. Briss, J. Wojtowicz, J. Power Sources. 66 (1997) 1.
7. C. Lin, J. Ritter, B.N. Popov, J. Electrochem. Soc. 145 (1998) 4097.
8. Y.U. Jeong, A. Manthiram, J. Electrochem. Soc. 149 (2002) 1419-1422.
9. M. Toupin, T. Brousse, D. Belanger, Chem. Mater. 14 (2002) 3946-3952.
10. Y. Chen, Y. Zhang, D. Geng, R. Li, H. Hong, J. Chen, X. Sun, Carbon 49 (2011) 4434-4442.
11. Y.T. Wu, C.C. Hu, J. Electrochem. Soc. 151 (2004) A2060-A2066.
12. W. Li, D. Chen, Z. Li, Y. Shi, Y. Wan, J. Huang, J. Yang, D. Zhao, Z. Jiang, Electrochem. Commun. 9 (2007) 569-573.
13. M. Toupin, T. Brousee, D. Bélanger, Chem. Mater. 16 (2004) 3184.
14. Y. Chen, M.L. Zhang, Z.H. Shi, J. Electrochem. Soc. 152 (2005) A1272.
15. S. Devaraj, N. Munichandraiah, J. Phys. Chem. C 112 (2008) 4406.
16. J.Y. Luo, Y.Y. Xia, J. Electrochem. Soc. 154 (2007) A987.
17. M. Seredych, D.H. Jurcakova, G.Q. Lu, T.J. Bandoz, Carbon. 46 (2008) 1475.
18. W. Xiao, H. Xia, J.Y.H. Fuh, L. Lu, J. Power Sources 193 (2009) 935.
19. P.K. Nayak, N. Munichandraiah, Microporous Mesoporous Mater. 143 (2011) 206.
20. F. Ataherian, N.L. Wu, Electrochem. Commun. 13 (2011) 1264.