Preparation and Properties of Supercapacitor with Composite Electrodes

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Abstract

In this study, composite activated carbon of NiO coated mesocarbon microbeads with a high-specific surface area (2685 m²/g) were formed by the chemical method. In this experiment, the composite activated carbon was prepared by filtering the composite solution and heat treatment. For finding the optimal processing parameters of composite electrode, the temperature of heat treatment, the amount of carbon black on the capacitive properties of supercapacitor were investigated. The structural characteristics of composite activated carbon and electrodes were observed by using XRD, SEM and EDS composition analysis. The capacitive performance of composite electrodes was evaluated by the cyclic voltammograms (CV) in 1 M LiClO₄ electrolytic solution. Experimental results reveal that the optimum composite electrode was prepared for the molarity 1 M NiO and temperature of heat treatment 250°C and adding 25 wt.% carbon black and the specific capacitances of composite electrodes is 210 F/g.

Keywords: Mesocarbon microbeads, Nickel oxide, Supercapacitor, Composite electrode, Specific capacitance.

1. Introduction

A supercapacitor is a new storage device positioned between traditional capacitors and batteries, which use electrochemical activated materials or porous materials for storage. The advantages of supercapacitors are high power density, high energy density, good cycle life, and fast charge/discharge times⁽¹⁻²⁾. Therefore, supercapacitors could improve the disadvantages of the traditional batteries and capacitors, and they have attracted considerable attention in recent years.

Helmholtz (1879) discovered that charge can be separated by coulomb electrostatic force and form double

layers across the surface of the electrode and the electrolyte⁽³⁾. The concept of an electrical double-layer capacitor (EDLC) is applying DC voltage to electrodes that are typically porous carbon. Becker *et al.* first introduced activated carbon (AC) as the electrode material of EDLC in 1957⁽⁴⁾. In 2000, Salitra *et al.* used different electrolytes including LiCl, NaCl, KCl, LiBF₄ and Et₄NBF₄ to investigate the capacitive performances of the activated carbon of different pore structures⁽⁵⁾. Experimental results reveal that the activated carbon of different pore structures need to use the appropriate electrolytes.

In recent years, to improve capacitive performance, many studies have used composite materials to fabricate composite electrodes for use in supercapacitor applications. In this study, activated carbon with a highly-specific surface area was combined with transition metal oxide to fabricate composite electrodes. The composite electrodes exhibited advantages of double-layer capacitance and pseudo-capacitance. Composite electrodes also increased the charge adsorption and electric conductivity by activated carbon and upgrading the specific capacitances of transition metal oxide through a redox reaction. Composite electrodes increase both the power and energy densities of composite materials. In literatures, Beliakov *et al.* first introduced composite materials as composite electrodes in 1997⁽⁶⁾. Li *et al.* synthesized composite electrodes by using RuO₂·H₂O and porous carbon, and investigated the characteristics of the capacitor regarding annealing temperature⁽⁷⁾.

In this study, composite activated carbon was formed by using a chemical method. The influence of heating temperature and the amount of carbon black on the properties of a supercapacitor were investigated to determine the optimal processing parameters of composite electrodes.

2. Experimental

2.1 Preparation of composite activated carbon

First, a solution of composite activated carbon was produced by uniformly mixing 1 M of NiO solution and mesocarbon microbeads. Subsequently, the composite solution was filtered by using filter paper with a 150-nm pore size and a composite slurry was obtained to execute the heat treatment in a Thermolyne-1400 Furnace at 200, 250, 300, and 400°C in air for 1 h. Finally, the core-shell structure composite activated carbon (MCMB@NiO) was obtained.

2.2 Fabrication of composite electrodes

The composite electrodes in this study were fabricated by treating composite activated carbon four different temperatures of heat treatment. Carbon black was added to improve electrode conductivity. The carbon black content was between 0 and 50 wt.%. After the composite carbon and carbon black powder were uniformly mixed, they were added to a solution of polyvinyl butyral (PVB) in dimethylacetamide (DMA), and the PVB content was 2 wt.%. The mixture was mixed at room temperature to form a composite carbon slurry. The composite electrodes were prepared by spin-coating the composite carbon slurry onto the ITO glass and then evaporating the DMA solvent in an oven at 150°C in air for 15 min.

In this study, a physical adsorption analyzer was used to explore the BET surface area and the pore structure of AC. The surface morphology of the carbon electrode was analyzed using a field emission scanning microscope (FE-SEM). Cyclic voltammetry measurements of the carbon electrodes were performed using an electrochemical analyzer (CH Instruments, 6273E) in two-electrode cells.

2.3 The analyses of MCMB@NiO and electrodes

In the physical analyses conducted for this study, we used a field emission scanning microscope (FE-SEM), X-ray diffraction (XRD) and an energy dispersive spectrometer (EDS) to examine the composite carbon and electrodes. In electrical analysis, we used cyclic voltammetry measurements (CH Instruments, 6273E) in two-electrode cells to investigate the effects of the temperature of the heat treatment and the amount of carbon black on the capacitance properties of the supercapacitor.

In the CV curve analysis, a scan rate of 25 mV/s was used to measure the voltage current change in 1 M of LiClO₄ electrolyte with a voltage range of -3 V to 3 V. The following equation was used to calculate specific

capacitance:

$$C_s = \frac{dQ}{dV} = \frac{1}{m\Delta V} \int_{V_1}^{V_2} I(V)dV \quad (1)$$

where $\int_{V_1}^{V_2} I(V)dV$ is the hysteresis loop area, v is scan rate, ΔV is the range of potential, m is the whole weight of the electrode material.

3. Results and discussion

Figure 1 shows the X-ray diffraction plot of the composite activated carbon which formed by using heat treatment at different temperatures. The intensities of the NiO peaks (111), (200), and (220) clearly increased as heating temperature was increased. The peaks of NiO were observed by using JCPDS card 47-1049⁽⁸⁾.

Figures 2 (a)~(e) presents SEM micrographs of the composite activated carbon surfaces heated at different temperatures. When the temperature increased, the NiO crystal structures became more obvious and the MCMB@NiO core-shell structure of NiO coated at mesocarbon microbeads became complete.

Fig 1. The XRD patterns of the composite activated carbon heated at (a) AC, (b) 200°C, (c) 250°C, (d) 300°C, (e) 400°C.

Fig 2. SEM micrographs of the composite activated carbon surfaces heated at (a) MCMB, (b) 200°C, (c) 250°C, (d) 300°C, (e) 400°C.

Based on the preparation of MCMB@NiO electrodes, composite powders with the heat treatment of different temperatures were used for finishing the electrodes. In this experiment, 30 wt.% CB was added to the MCMB@NiO carbon slurry to improve electrode conductivity. During a follow-up experiment, the effect of adding various CB contents on capacitance was examined and is discussed in detail. After the composite electrodes were finished, the capacitive characteristic was analysed by using CV in 1 M of LiClO_4 with a voltage range of -3 V to 3 V and a scan rate of 25 mV/s. Figures 3 shows the CV results from the composite activated carbon according to different heating temperatures.

Fig 3. Cyclic voltammograms of MCMB@NiO electrodes using composite activated carbon with different heating temperature.

Fig 4. Specific capacitances with different heating temperatures.

In the heating temperatures of 250°C, the hysteresis loop area is obviously the largest and its specific capacitance, which was calculated using Eq. (1), was 193 F/g. Figures 4 show all the specific capacitances which were calculated at different heating temperatures.

Adding conductive carbon black in the MCMB@NiO electrodes can promote the capacitive characteristic. Figures 5 (a)~(g) presents SEM micrographs of the MCMB@NiO electrode surfaces, showing that the surface of the composite powders were covered with tiny CB powder. When the CB content was greater than 25 wt.%, the surfaces of electrode were almost covered with CB and caused the mass of the electrode to increase.

Fig 5. SEM morphology of MCMB@NiO electrodes with different amount of carbon black: (a) 0 wt.%, (b) 10 wt.%, (c) 20 wt.%, (d) 25 wt.%, (e) 30 wt.%, (f) 40 wt.%, (g) 50 wt.%.

Figures 6 shows the CV results of adding various CB contents. The hysteresis area obviously increased when the CB content increased. However, the mass of electrodes increased rapidly when the content was greater than 25 wt.%. According to Eq. (1), the specific capacitance was 210 F/g.

Table 1 shows the EDS analysis of MCMB@NiO electrodes. The proportion of nickel was investigated by adding conductive CB powder. When 0 wt.%, 25 wt.% and 50 wt.%, CB was added, the nickel proportion decreased and the carbon proportion increased gradually. The results indicate that the nickel proportion is reduced when CB is added. According to the literature⁽⁸⁾, the characteristics of capacitance could be improved by adding conductive CB powder to electrodes. Therefore, the composite electrodes that had 25 wt.% conductive CB powders exhibited the maximum specific capacitance and energy density⁽¹⁰⁾.

Table 1. EDS analysis of composite electrodes.

	Carbon element proportion (%)	Nickel element proportion (%)	Specific Capacitance (F/g)	Energy density (Wh/kg)
0 wt.%	72.26	3.77	52	65
25 wt.%	76.40	2.19	210	262
50 wt.%	81.85	1.51	50	62

Fig 6. Cyclic voltammograms of MCMB@NiO electrodes with different content of carbon black.

4. Conclusions

This study focused on composite activated carbon and composite electrodes. Composite activated carbon was formed by using a chemical method. When the heating temperature increased, the NiO crystal structures became more obvious and the composite core-shell structure of NiO coated mesocarbon microbeads became complete. In the heating temperature of 250°C, the hysteresis loop area was obviously the largest and its specific capacitance was 193 F/g. Regarding composite electrodes, when carbon black was increased, the specific capacitance decreased. In conclusion, the optimal parameters of composite electrodes were obtained by using 1 M of NiO, a heat temperature of 250°C, the addition of 25 wt.% carbon black, and the specific capacitance is 210 F/g.

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