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Copper-doped mesoporous activated carbons as electrode material for electrochemical capacitors

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Abstract

Cu-doped activated carbon composites were prepared from phenolic resins by a doping method. The structure and specific capacitance of Cu-doped activated carbon composites were investigated using nitrogen gas adsorption and constant current cycling (CCC) methods. The pore size distributions of activated carbon-Cu series indicated that the doped Cu had no drastic effect on the structure of ACs. The percentage of copper in the composite electrode was less than 1 wt. %. It was found that the AC-Cu series had higher capacitance than that of activated carbons; even though their BET surface area was not larger than that of the AC ones. The Cu-doped activated carbon composite prepared by activating at 800 °C for 2 h had high capacitance (120 F g^{-1}) which was more than 25% than that of the ACs. XRD and TEM showed that copper existed in the form of oxidation state and the diameter of particles was under 100 nm.

1. Introduction

Electrochemical capacitors have attracted considerable attention as an intermediate power source between conventional capacitors and rechargeable batteries, which can be used in many applications such as memory back-up devices or electric vehicles. Electrochemical capacitors can be classified into two different categories depending on the charge–discharge mechanism. These are electric double layer capacitors (EDLC) and supercapacitors. The more suitable material for EDLC must have high surface area, better pore size distribution and electrochemical stable surface. In recent years, activated carbon has been the most frequently used as electrode material for EDLCs. A previous study [1, 2] had shown that, mesoporous activated carbons possessed of the suitable pore size distributions for the electrolyte permeation to form the double layer to store energy. However, mesoporous activated carbons could only provide low surface area (<1500 m^2 g^{-1}) to form the electric double layer at the interface between the electrode and the electrolyte, which led to the very low energy and power density of EDLC. In contrast with EDLCs, supercapacitors include the faradaic redox reactions of conducting polymers [3–5] and metal oxides [6–9] that can be reversibly oxidized or reduced over a potential range. Metal oxides, such as RuO_2, IrO_2 exhibit oxidation/reduction properties but they are very expensive.

Since the energy density of electrochemical capacitors is only several Wh kg^{-1} and therefore much lower than that of rechargeable batteries, the capacitance of electrochemical capacitors has to be increased to make them competitive. So we intended to prepare an electrochemical capacitor of high specific capacitance from an electrode material, not only possessing large specific surface area, but also coupling with active species. Such an electrochemical capacitor would exhibit both double-layer capacitance and faradaic pseudocapacitance simultaneously in energy storage. Hence, a metal oxide-carbon composite with these properties could be suitably used as electrode material for secondary batteries and capacitors.

The objective of the present research work is to enhance the capacitance of an electrochemical capacitor through introduction of copper, which provides pseudocapacitance for the carbon electrodes. Deposition of copper on the activated carbons also provides an economical means of enhancing energy storage of the resulting electrodes via the redox transition of this metal. However, in order to avoid the conglomeration of the metals, the Cu-doped activated carbon composites were prepared from phenolic resins by a doping method.

The chemical composition and microstructure of the composite electrode was characterized by XRD and SEM. The electrochemical characteristics of electrodes were examined by using cyclic constant current charge–discharge, in the attempt to clarify the contribution of copper to the overall capacitance.

2. Experimental

2.1. *Preparation of activated carbons (AC)*

Phenolic resins were used as the starting materials for the preparation of porous carbons. The detailed procedure was as follows. Firstly, the phenolic resin, ferrocene and hexamethylenetetramine (weight ratio = 100:0.6:12.4), were mixed with or without $Cu(CH_3COO)_2 \cdot 2H_2O$ by blending them in methanol. The percentage of copper in the raw materials was 1~2 wt. %. The methanol was removed under reduced pressure to obtain a mixed resin. After curing copper–carbon composites were obtained. The AC without copper was also prepared in the same way as the above preparation process. After stabilization of the mixed resin it was heated to 800 °C in nitrogen atmosphere and continuously activated in steam at 800 °C for 1 and 2 h, respectively.

2.2. *Preparation of electrochemical capacitors*

Activated carbon (78 wt. %), graphite (20 wt. %) and polytetrafluoroethylene (PTFE) (2 wt. %) were mixed in order to obtain a powder and the powder was pressed on to the Nickel collector electrode. The electrode had a surface of 1 cm^2 and thickness of 0.4 mm. A polypropylene separator separated the two carbon electrodes. The electrolyte was a 30 wt. % KOH aqueous solution. The constant charge–discharge current was 1 mA.

2.3. *Electrochemical measurement of specific capacitance of composite electrodes*

Electrochemical measurements (CCC) were carried out at ambient temperature using KOH aqueous solution as electrolyte to examine the electrochemical performance of composite electrodes. The dc capacitances of activated carbons were measured using a self-designed reassemble test cell. The measurements were carried out at 25 °C using an Arbin Instruments BT4+ device (America).

The dc capacitance C in farad per gram was calculated from the following Equation (1) [10]:

$$C = 2(i \times \Delta t)/\Delta Vm, \tag{1}$$

where i is the constant discharge current A,
Δt is the time for discharge s,
ΔV is the potential change of the capacitor caused by discharge V,
and m is the single electrode mass g.

2.4. *XRD measurements*

X-ray diffraction (XRD) was performed on the samples to determine the degree of crystallinity of the activated carbon. The XRD data were collected on a D/max-rA powder X-ray diffractometer with CuKα radiation.

3. Results and discussions

3.1. *Characteristics of the activated carbons*

TG and DTG are useful techniques to evaluate the structure change of the resin under different temperatures. Figure 1 shows the relationship between the weight loss of AC and AC-Cu and the heat-treatment temperature. In Figure 1 all samples showed a decrease in weight as the temperature increased. Figure 2 also shows that the more drastic weight variation of the samples occurred at about 350 °C, with a maximum value at 500 °C. The carbon yields obtained after heat-treatment at 900 °C were 66.11% for AC-Cu and 64.50 wt. % for AC, respectively. The similar carbonization yield of AC-Cu meant that the addition of

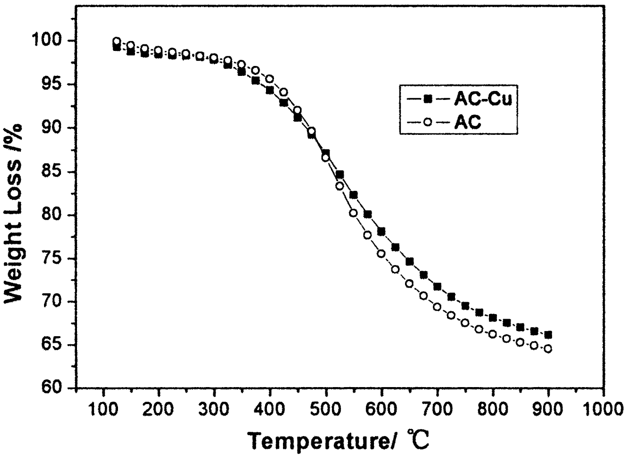

Fig. 1. TG curves of AC and AC-Cu.

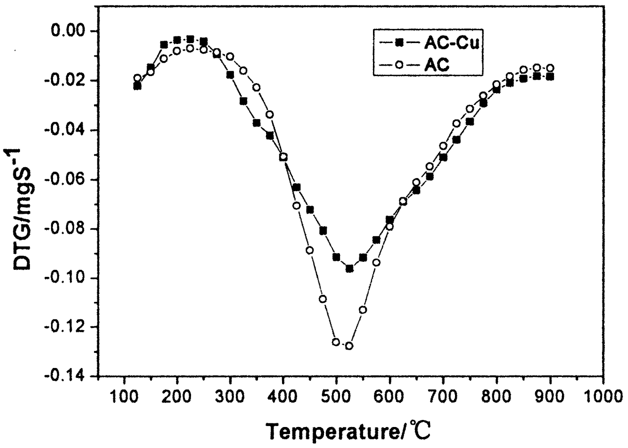

Fig. 2. DTG curves of AC and AC-Cu.

Table 1. Properties of activated carbons based on resins

Sample	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})		Ratio$_{meso}$ (%)	D (nm)	Cu Content (wt. %)	Capacitance (F g^{-1})
		V_{total}	V_{meso}				
AC-T	345	0.26	0.17	65.4	3.01	–	80
AC-A-1	797	0.62	0.46	74.2	3.11	–	87
AC-A-2	847	0.76	0.51	67.1	3.59	–	97
AC-Cu	299	0.25	0.17	68.0	3.33	0.39	102
AC-Cu-1	692	0.63	0.44	69.8	3.64	0.64	112
AC-Cu-2	781	0.74	0.47	63.5	3.43	0.86	120

AC-T, AC-Cu: carbonization at 800 °C for 1 h; AC-A-1, AC-Cu-1: activation at 800 °C for 1 h; AC-A-2, AC-Cu-2: activation at 800 °C for 2 h; Average pore diameter: $D = 4\ V_{total}/S_{BET}$.

copper had a very small influence on the structure of the activated carbon.

Specific surface area and pore size distribution are important parameters to control in order to optimize the specific capacitance of the electrode material. Composites with different porosities were prepared by varying the Cu/resin weight ratio and activation time. The surface characteristics of the activated carbons with and without copper are summarized in Table 1. Table 1 exhibited BET surface areas, pore volumes and pore diameter obtained from adsorption isotherms for the AC and AC-Cu series. It was shown that the values of total pore volume and BET specific surface areas increased with increasing activation time regardless of the AC and AC-Cu series. This meant that the pore structure in the AC-series was well developed with longer activation time. The maximum values of surface area and pore volume were approached to 847 m^2 g^{-1} and 0.76 cm^3 g^{-1} for AC-series, 781 m^2 g^{-1} and 0.74 cm^3 g^{-1} for AC-Cu series, respectively. The BET surface areas of AC-Cu series were lower than that of the AC series for the same preparation process, which indicated that the influence of copper on the BET surface area was negative. However, little difference was observed in the mesopore volume ratio and the average mesopore width between AC and AC-Cu series with the different BET surface area.

The pore size distribution values listed in Table 1 indicate that the pores developed by H_2O steam activation were mainly mesoporous; thus the dominant pores in these samples were mesopores. The pore size distributions of the mesopores for the four samples calculated by the adsorption isotherms using the Barret–Joyner–Halenda (BJH) method are shown in Figure 3. The mesopore size distribution curves of these carbons were similar, which meant that the doped Cu had no drastic effect on the structure of ACs. When the samples were activated by steam at 800 °C for 2 h, the increase in porosity mainly came from the development of the mesoporosity. Especially, AC-Cu-2 had a relatively large size mesopore in the range of 5–20 nm pores. In comparison with the characteristics of the AC series, the surface area and pore volume of the AC-Cu series were a little smaller, indicating that the Cu particles hindered the degree of H_2O activation.

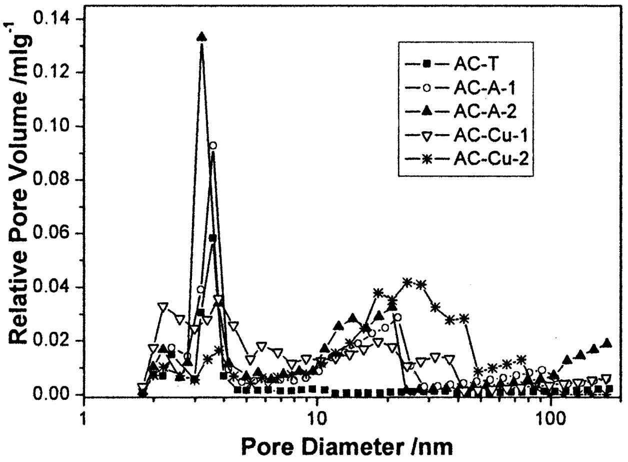

Fig. 3. Pore size distributions of activated carbons.

3.2. *Electrochemical characteristics of materials*

Since the activated carbons used in the present work were derived from the same precursor, the specific discharge capacitances of different carbon composite electrodes could be calculated according to Equation (1). The data in Table 1 show that the values of discharge capacitance of activated carbons increased with increase in BET surface area. The load amounts of copper in the AC-Cu series were 0.39, 0.64, 0.86%, respectively by atom emission spectra, which affected specific capacitance of the composite electrode. The AC-Cu series had greater capacitance than that of activated carbons, even though their BET surface area was not larger than that of the AC ones. In particular, the AC-Cu-2 showed the highest capacitance (120 F g^{-1}). This value was almost increased by one-fourth over that of the AC-A-1 (87 F g^{-1}) and AC-A-2 (97 F g^{-1}), which means that the energy stored in these electrodes comes from both the electric double layer capacitance of the materials with high specific surfaces areas and the faradaic pseudocapacitance of electroactive materials with several oxidation states of copper.

Figure 4 shows the typical cell voltage against time curves of AC and AC-Cu series discharged at a constant current of 1 mA. The straight line in the figure is a linear fit between 0.0 and 0.6 V, which indicates that the

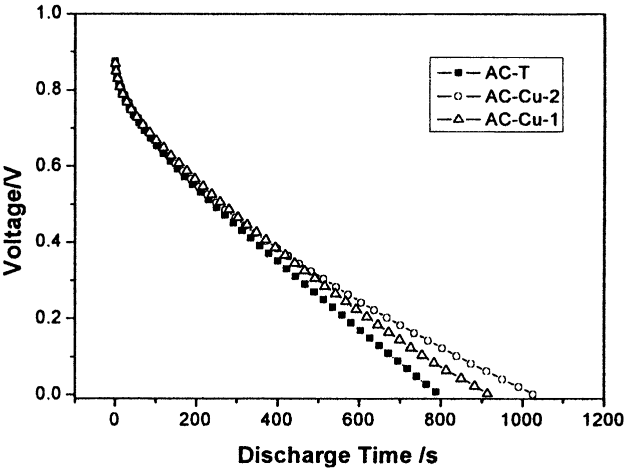

Fig. 4. Discharge curve of the AC-Cu-2 and AC-T electrodes.

electrodes have excellent electrochemical properties. More than 25% of capacitance can be achieved from the deposition of copper. Figure 5 shows that the charge–discharge capacitances of AC-Cu remained stable after about 50 cycles; moreover the efficiency was 99% at all times. These results suggest that the superior capacitances of the AC-Cu series may be attributed to the presence of copper, which assists energy storage through Faradaic reaction.

3.3. *Micro-structure of copper–carbon composite electrodes*

Figure 6 depicts XRD patterns of the samples AC-Cu and AC-Cu-2 produced by doping different contents of the copper. XRD measurements showed that activated carbons were not composed of highly crystalline graphites but of poorly crystalline micrographites. With increasing Cu addition the CuO peak around 34° became intense. Figure 7 shows the TEM micrographs of the AC-Cu sample. These micrographs show that the particle diameter was under 100 nm, which shows that highly dispersed nanometer scale copper–carbon composites can be prepared by the doping method.

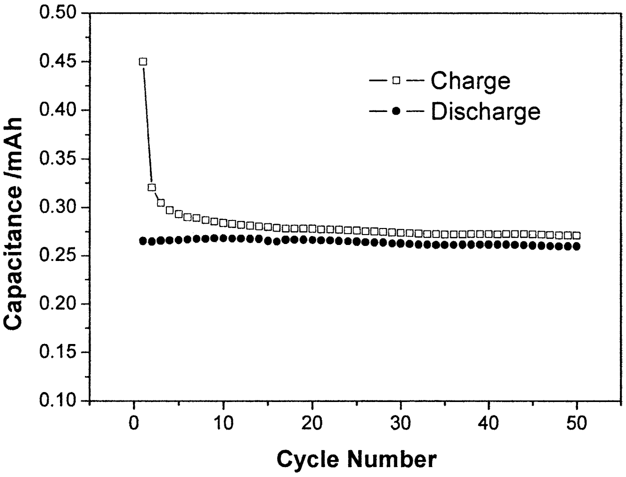

Fig. 5. Charge–discharge capacitances of the AC-Cu electrodes.

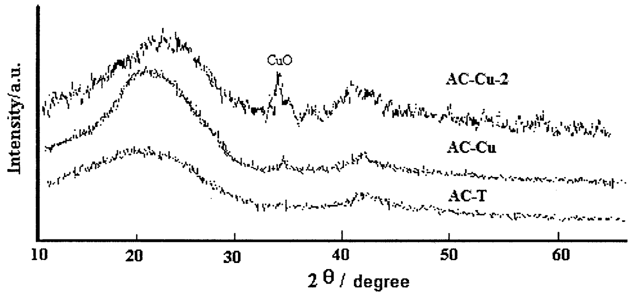

Fig. 6. XRD pattern of AC-Cu series.

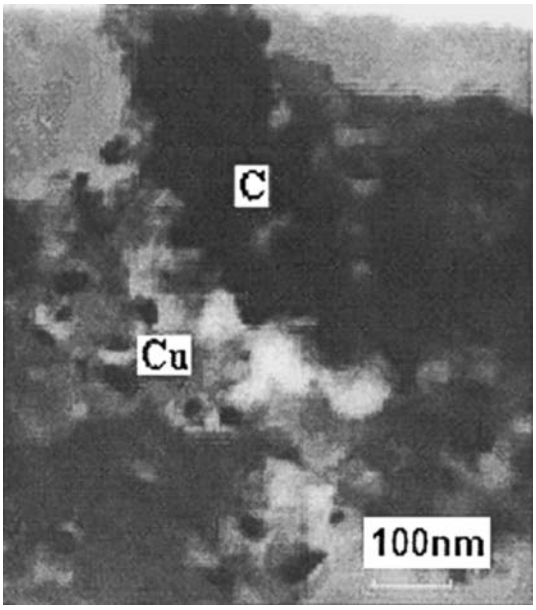

Fig. 7. TEM photos of AC-Cu composite.

4. Conclusions

The TG and pore size distribution of AC and AC-Cu indicate that the doped Cu did not have a significant effect on the structure of ACs. It was found that the AC-Cu series had greater capacitance than activated carbons, even though their BET surface area was not larger than that of the AC. The copper-porous carbon composite prepared by activating at 800 °C for 2 h had high capacitance (120 F g^{-1}). It is suggested that the presence of copper is an important factor for higher capacitance compared with the AC series. The charge–discharge efficiency of the composite electrode was 95% at all times. XRD and TEM showed that copper exists is in an oxidized state and the diameter of particles is under 100 nm, which shows that the doping method was effective in preparing nano-scale metallic carbon composites.

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