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Preparation and characterization of copper-activated carbon composite electrodes for supercapacitors

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Recently, supercapacitors have been developed as a new type of energy storage device. They are expected to be used in many applications such as the power source or electric vehicles because of their high power density. However, since the energy density of supercapacitors is only several Wh·kg^{-1} and therefore much lower than that of rechargeable batteries, the capacitance of supercapacitors has to be increased to make them competitive. Energy storage mechanisms of supercapacitors are explained in two ways, which are double layer capacitance and pseudocapacitance. High surface area carbon materials, such as activated carbon [1], activated carbon fiber [2], carbon aerogel [3], and so on, have been developed to improve the characteristics of the high energy density supercapacitors. Deposition of copper on the activated carbons may provide an economical means of enhancing energy storage of the resulting electrodes via the redox transition of this metal. Carbon composite materials in which the nanometer scale metallic compounds were highly dispersed could be prepared by a doping method [4]. In this study, copper–carbon composites were prepared by a simple doping method. They were characterized as the electrode for supercapacitors, and the effect of the copper on the BET surface area and pore size distribution of the activated carbons was analyzed.

Phenolic resins were used as the starting materials for the preparation of activated carbons (AC). The detailed procedure was as follows. At first, the phenolic resin and hexamethylenetetramine 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 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. The samples containing Cu species or without a Cu agent were referred to as AC-Cu-1 or AC-1, respectively, where 1 represented activation duration (hour).

Activated carbon (78 wt%), graphite (20 wt%), and polytetrafluoroethylene (PTFE) (2 wt%) were mixed in order to obtain a powder, and then the powder was pressed to the Nickel collector electrode. The electrode had a surface of 100 mm^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 dc capacitances of activated carbons were measured using a self-designed coin-like test cell. The measurements were carried out at 25 °C using Arbin Instruments BT-4+ (America). The dc capacitance C in Farad was calculated from the following equation [5].

$$C = (i \times t)/v, \qquad (1)$$

where i is the constant discharge current in ampere, t is the time for discharge in seconds, and V is the potential change of the capacitor caused by discharge in volts.

Fig. 1 shows N_2 adsorption isotherms of activated carbons derived from phenolic resin with and without copper. All four isotherms show a transition from type I to type II according to the IUPAC classification, which meant that the dominant pores in these samples were mesopores. It was considered that the increase of the adsorbed volume at the high relative pressure was due to the effect of pore saturation on the mesopores. The amount adsorbed nitrogen on the sample AC-2 was the greatest. From the isotherm, the doped Cu had no drastic effect on the structure of the ACs. The pore structure distributions of the mesopores for the four samples calculated by the adsorption isotherms using the Barret–Joyner–Halenda (BJH) method are shown in Fig. 2. It could be seen that the samples of AC-1 and AC-Cu-1 had the same pore size distribution. 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-2 and AC-Cu-2 had a relatively large size mesopore in the range of 5–20-nm pores.

Table I gives 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 were increased with increasing time of activation regardless which series of samples (AC, AC-Cu) were used. This meant that the pore structure in the AC series

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TABLE I Properties of samples

Sample	S_{BET} (m^2/g)	Pore volume (10^{-3}/m^3/kg) V_{total}	V_{micro}	V_{meso}	Ratio$_{\mathrm{meso}}$ (%)	D (nm)	Capacitance (F/g)
AC-1	797	0.62	0.16	0.46	74.2	3.11	87
AC-2	847	0.76	0.25	0.51	67.1	3.59	97
AC-Cu-1	692	0.63	0.19	0.44	69.8	3.64	112
AC-Cu-2	781	0.74	0.20	0.47	63.5	3.43	120

AC-1: Activation at 800 °C for 1 h, AC-2: Activation at 800 °C for 2 h.
Average pore diameter: $D = 4V_{\mathrm{total}}/S_{\mathrm{BET}}$.

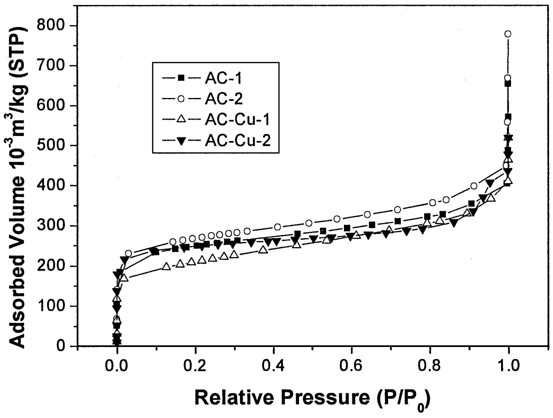

Figure 1 Nitrogen adsorption isotherms of activated carbons.

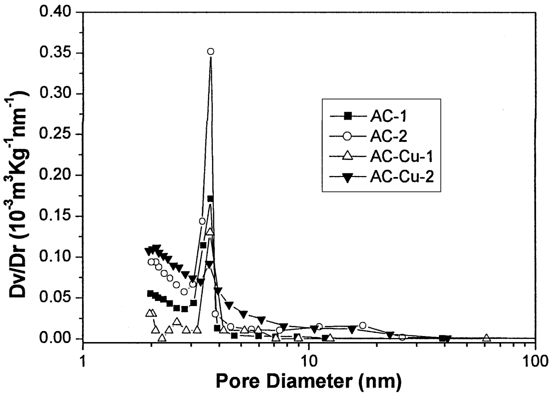

Figure 2 Pore size distribution of activated carbons.

was well developed with longer activation time. The BET surface areas of AC-Cu series were lower than those of the AC series, which indicated that the influence of copper on the BET surface area was negative. However, little difference was observed in the mesopore volume and the average mesopore width between AC and AC-Cu series with the different BET surface areas.

The specific discharge capacitances of different carbon electrodes were calculated according to Equation 1, the data in Table I showed that the values of discharge capacitance of activated carbons were increased with the increase in the BET surface area. The AC-Cu series had greater capacitance than that of activated carbons; even through their BET surface area was not larger than the AC ones. Especially, the AC-Cu-2 showed the highest capacitance (120 F/g). This value was increased almost one-fourth of that of the AC-1 (87 F/g) and AC-2 (97 F/g). Fig. 3 showed the typical cell voltage against time curves of EDLCs discharged at a constant current of 1 mA. The straight line in the figure was a linear fit between 0.0 and 0.7 V, which meant that the electrodes had excellent electrochemical characterizations. Fig. 4 shows Charge–discharge capacitances maintained stable after about 120 cycles, moreover the efficiency kept at 99% at all times. Those results suggested that the advantage of the capacitances of the AC-Cu series could be attributed to the presence of copper, which assisted the storage of the energy through Faradic reaction.

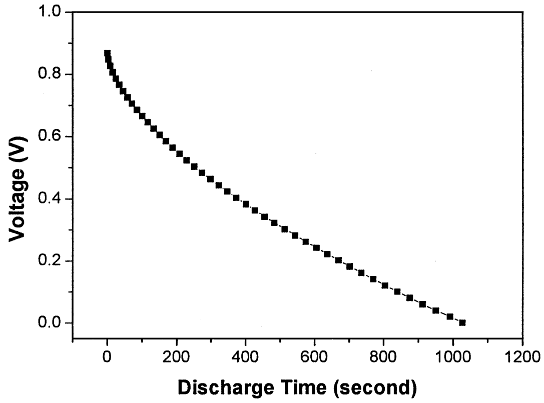

Figure 3 Discharge curve of the AC–Cu-2 electrodes.

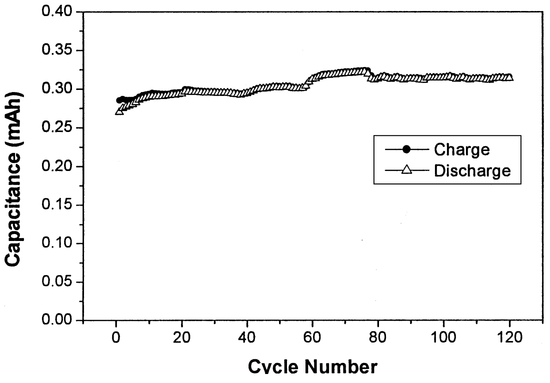

Figure 4 Charge–discharge capacitances of the AC–Cu-2 electrodes.

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