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The effect of heat-treatment on the properties of activated carbon fibre cloth polarizable electrodes

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The effect of heat-treatment on the properties of activated carbon fibre cloths (ACFC) as polarizable electrodes has been investigated. The heat-treated ACFC was prepared by heating phenolic resin-based activated carbon fibre cloths at temperatures higher than 1000° C in an inert gas atmosphere. The electrical resistance of ACFC and the specific surface area began to decrease at 1000° C and 1500° C, respectively. The ACFC maintained amorphous structure even when it was treated at 2000° C. The cyclic voltammogram of ACFC heat-treated at 1000° C showed a stable electric double layer in organic electrolytes in the range between − 1.5 and 1.5V with respect to SCE. In accordance with the lower resistance of heat-treated ACFC, electric double layer capacitors with ACFC heat-treated at 1000° C showed lower d.c. resistance in comparison with capacitors without heat-treated ACFC.

1. Introduction

Electric double layer capacitors have been widely used as a memory back-up device. Activated carbons, which have a large specific surface area and a high electrical conductivity, have been used as the polarizable electrodes of the capacitors [1, 2]. We have developed capacitors with phenolic resin-based activated carbon fibre cloths (ACFC) which have the advantages of high capacitance, high working voltage and high reliability [3–6]. Usually, the capacitors are used at the microampere order of discharge. In devices requiring larger discharge currents, such as in the order of milliamperes, the lower d.c. resistance of the capacitors becomes an important factor in achieving high performance. The electrical and electrochemical properties of phenolic resin-based ACFC have been examined in order to decrease the d.c. resistance of the capacitors. This resistance was found to be influenced by the electrical resistance and the pore size distribution of ACFC.

In this paper, we report on the measurements of the specific surface area, the pore size distribution, the electrical resistance of ACFC with and without heat-treatment, and the characteristics of electric double layer capacitors with ACFC.

2. Experimental details

2.1. *Preparation of ACFC*

Phenolic resin-based fibres [8, 9] (Nippon Kynol Inc.) were carbonized and activated directly in a nitrogen atmosphere at 1000° C with water vapour as activation gas. The ACFC showed a specific surface area of 1590 $m^2 g^{-1}$, an areal density of 160 $g m^{-2}$, and a fibre diameter of 10–15 μm. The ACFC was heated from room temperature up to 1000, 1500, and 2000° C at a rate of 10° C min^{-1}, held at these temperatures for 60 min and then cooled under an argon atmosphere in a furnace (Tokyo Vacuum Co. Ltd, SUN-VAC-13). The specific surface area and the pore size distribution of ACFC were obtained from the methanol vapour adsorption isotherm at 50° C. The details of the measurements were described previously [6].

The crystallinity of ACFC was examined by X-ray diffraction.

An aluminium layer (100–150 μm) was formed on one side of the ACFC as a collector electrode by a plasma spraying method.

A propylene carbonate solution (PC), containing 0.51 mol dm^{-3} of tetraethylammonium fluoroborate (Et_4NBF_4), was used as the electrolyte.

2.2. *Electrical measurement*

The electrical resistance of ACFC (size: 1 cm wide × 5 cm long) was measured using a digital multimeter (Takeda Riken, TR 6843).

Triangular voltage sweep cyclic voltammetric experiments were carried out using a potentiostat (Hokuto Denko, Model HA-303) and a function generator (Hokuto Denko, Model HB-104) at 25° C in a dry box. The ACFC (6 mm diam.) with a plasma sprayed aluminium layer was prepared as a working electrode. The measurement was carried out between − 1.5 and 1.5 V with respect to SCE at 25° C and the sweep rate was 5 mV s^{-1}. Experimental details for this have been described previously [7].

The capacitance of coin type electric double layer capacitors was measured at 25 and − 25° C. Constructional details and capacitance measurements for these

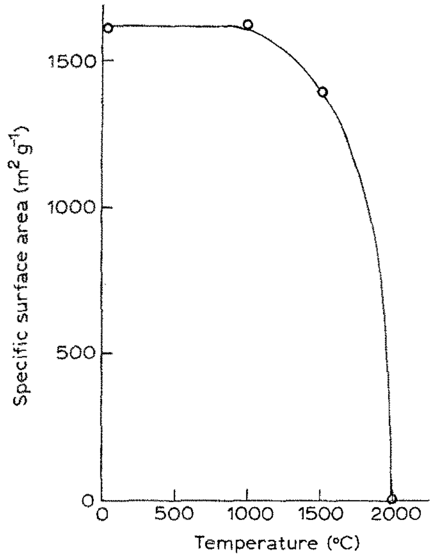

Fig. 1. Specific surface area of ACFC against heat-treatment temperature.

capacitors were described previously [6]. The capacitors were charged at 2 V d.c., and the capacitance, C, was calculated from the usual equation, $C = it/V$, where i is the constant discharge current (0.5–3.0 mA), t the time for discharge, and V the potential change of the capacitor (from 1.5 to 0.5 V) caused by discharge.

The d.c. resistance of the capacitor was calculated from an initial voltage drop when the capacitor was discharged. The details of the measurement have been described previously [5].

3. Results and discussion

3.1. *Properties of ACFC*

Figure 1 shows the relation between the specific surface area of ACFC and the heat-treatment temperature. The specific surface area begins to decrease at 1500° C and decreases drastically at 2000° C. The pore size distribution was evaluated from the ratio of the pore volume of the large pores with diameters larger than 2 nm to the total pore volume of ACFC. The ratio was 37% (treatment at 1000° C), 26% (treatment

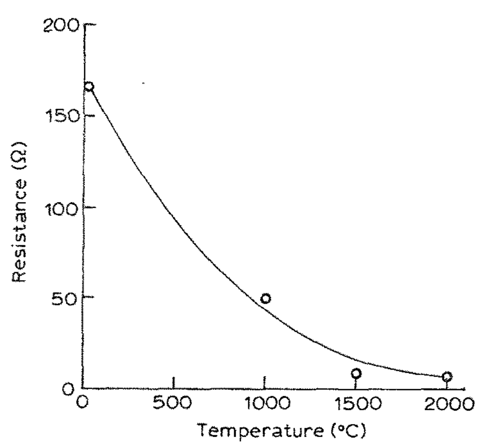

Fig. 2. Electrical resistance of ACFC against heat-treatment temperature.

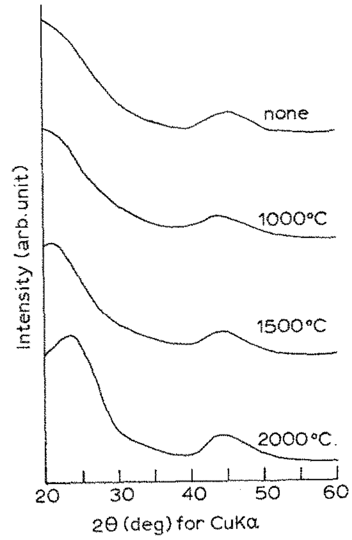

Fig. 3. X-ray diffraction profiles of heat-treated ACFC.

at 1500° C), and 38% (without heat-treatment). The pore size of ACFC began to decrease at 1500° C with decreasing specific surface area. For heat treatment at 2000° C the pore size distribution was difficult to measure, since the specific surface area was smaller than $10\,m^2\,g^{-1}$.

Figure 2 shows the relation between the electrical resistance of ACFC and the heat-treatment temperature. The electrical resistance decreases with increasing temperature. For heat treatment at 1000° C the electrical resistance of ACFC is about one third that without heat-treatment. Above 1500° C, the electrical resistance decreases very slowly.

Figure 3 shows X-ray diffraction patterns of ACFC. With increasing heat-treatment temperature, the broad peak around 25° becomes intense. The peak of the graphite structure (26.5°), however, is not observed even for heat-treatment at 2000° C thus indicating that the ACFC maintained amorphous structure. Hence the ACFC appears to be a non-graphitizable carbon.

Figure 4 shows scanning electron micrographs for the ACFC. Many pores are observed on the surface for heat-treatment at 1000° C. At 1500° C the surface is rather smooth in comparison with that heat-treated at 1000° C. Some substances which were not identified are observed on the ACFC surface heat-treated at 2000° C. The pores on the surface decrease with increasing heat-treatment temperature.

Cyclic voltammetry is a useful technique to evaluate activated carbons as electrodes [10, 11]. Figure 5 shows the cyclic voltammograms of ACFC heat-treated at 1000° C, 1500° C, and without heat-treatment. The voltammograms for heat-treatment at 1000° C and without heat-treatment show a similar pattern and their capacitive currents are almost constant in this sweep region. On the other hand, the voltammogram for heat-treatment at 1500° C shows a smaller current under cathodic polarization. This is because the cations enter the narrow micro-pores with difficulty in comparison with those for heat-treatment at 1000° C and those without heat-treatment. The result is supported by the difference in the specific surface area and

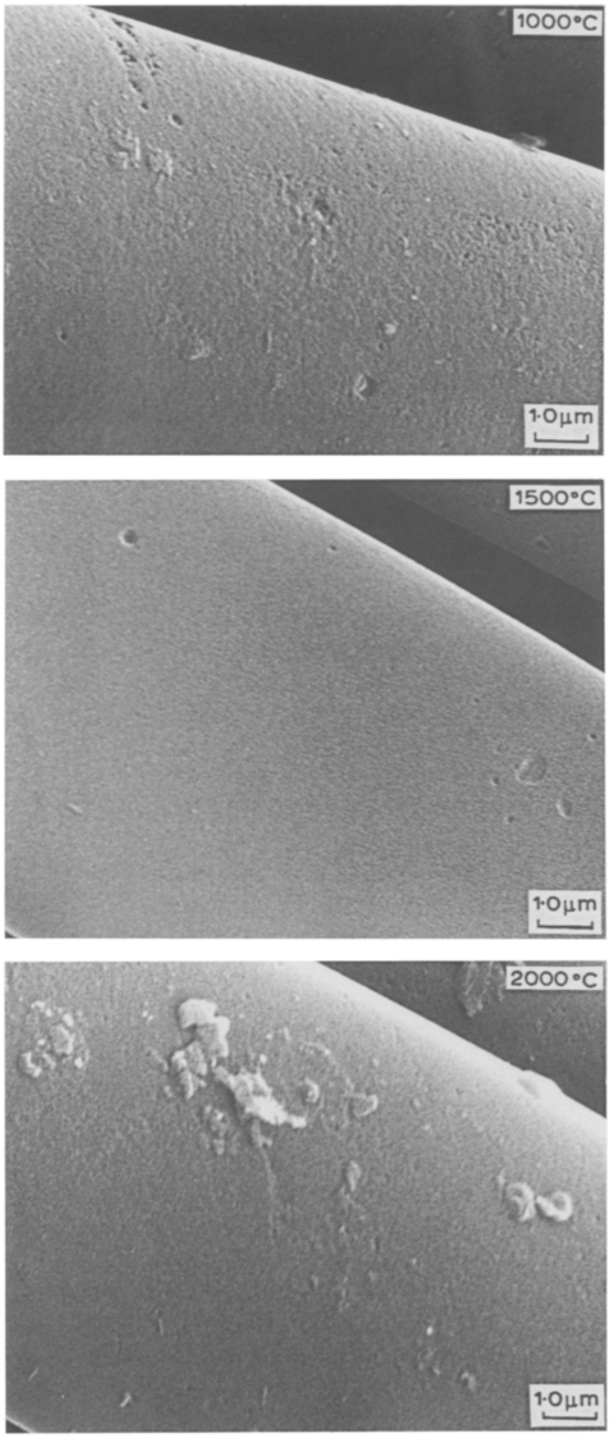

Fig. 4. SEM micrographs of heat-treated ACFC.

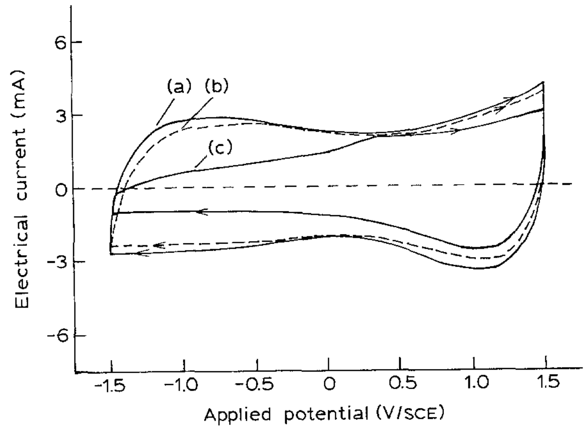

Fig. 5. Cyclic voltammograms of heat-treated ACFC (a) without heat-treatment, (b) at 1000° C, and (c) at 1500° C.

the pore size distributions for heat-treatment at 1000° C and at 1500° C. The kinds and concentrations of functional groups on the surface of the ACFC were probably changed by heat-treatment although further investigation is necessary to clarify this.

Figure 6 shows the cyclic voltammogram of ACFC heat-treated at 2000° C and a carbon fibre cloth which was prepared by carbonization of a phenolic resin fibre cloth in a nitrogen atmosphere at 1000° C. The voltammogram for the ACFC and the carbon fibre cloth shows a similar pattern. The capacitive current of ACFC for this heat-treatment at 2000° C and of the carbon fibre cloth is very small in comparison with that for treatments at 1000° C, at 1500° C, and without heat-treatment. The broad peaks at 0.7 and −0.7 V with respect to SCE are probably attributable to the oxidation and reduction of the surface functional groups of ACFC and the carbon fibre cloth.

3.2. *Characteristics of capacitors*

Figure 7 shows the capacitance and d.c. resistance of the capacitors with ACFC. The temperature dependence of the capacitors with ACFC heat-treated at 1000° C and ACFC without heat-treatment is small. The d.c. resistance of ACFC heat-treated at 1000° C shows a lower value by 10 Ω compared with that of ACFC without heat-treatment. The temperature dependence of the capacitors with ACFC heat-treated at 1500° C is large, because the pore size was small in comparison with that of ACFC heat-treated at 1000° C and ACFC without heat-treatment. At a lower temperature (−25° C), the mobility of ions becomes small, especially in the micropores for treatments at 1500° C. For heat treatments at 1000° C the capacitors showed good performance with low d.c. resistance and small temperature dependence among the investigated capacitors with ACFC.

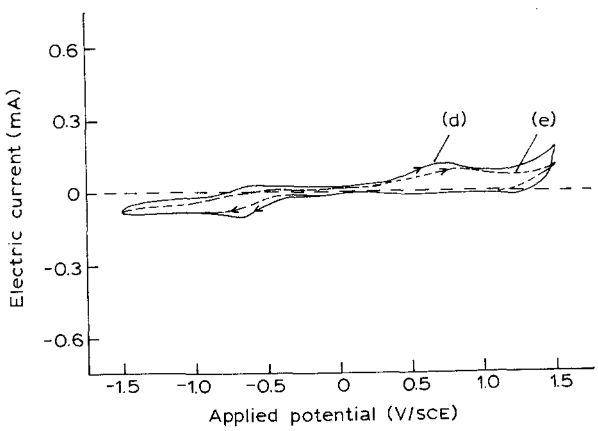

Fig. 6. Cyclic voltammograms of ACFC heat-treated at 2000° C (d) and carbon fibre cloth (e).

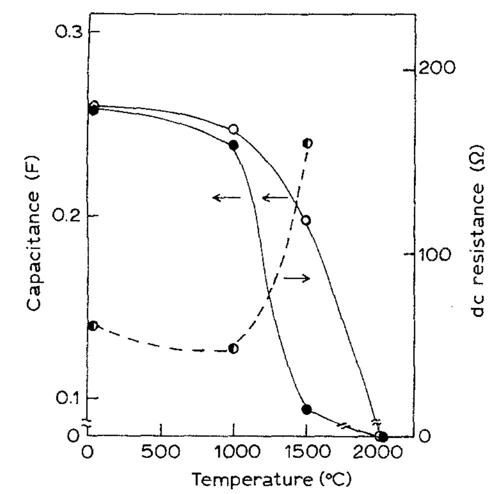

Fig. 7. Capacitance and d.c. resistance of the capacitors with ACFC against heat-treatment temperature. (○) capacitance at room temperature, (●) capacitance at −25° C, (◐) d.c. resistance.

4. Conclusion

1. The electrical resistance of ACFC heat-treated at 1000° C was smaller by comparison to that without heat-treatment. The specific surface area of ACFC decreased by heat-treatment at 1000° C and the pore size began to decrease at 1500° C.
2. In the organic electrolyte, ACFC heat-treated at 1000° C and ACFC without heat-treatment showed a stable electric double layer in the range between −1.5 and 1.5 V with respect to SCE. The cyclic voltammogram of ACFC heat-treatment at 2000° C was similar to that of the phenolic resin-based carbon fibre cloths.
3. The d.c. resistance of the electric double layer capacitors with ACFC heat-treated at 1000° C decreased by 10 Ω in comparison with that of the capacitors with ACFC which was not heat-treated.

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