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Effect of treatment of activated carbon fiber cloth electrodes with cold plasma upon performance of electric double-layer capacitors

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Abstract

Charge/discharge behavior of electric double-layer capacitors composed of activated carbon fiber cloth (ACFC) electrodes and an organic electrolyte was investigated. The modification of the ACFC electrodes was performed using cold plasma generated in argon–oxygen atmosphere. The effect of the cold plasma treatment of the ACFC electrodes on the capacitor performance was discussed on the basis of the physical and chemical properties of the ACFC surface such as pore radius distribution and surface atom concentration.

Keywords: Electric double-layer capacitors; Cold plasma; Activated carbon fibers; Organic electrolytes

1. Introduction

The electric double-layer capacitor has been considered as one of the most attractive rechargeable power devices, because of its excellent high-rate charge/discharge ability with high energy density comparable with the energy density of the common rechargeable batteries [1]. This type of capacitor is typically composed of an electrolyte and activated carbon (fiber) or activated carbon fiber cloth (ACFC) electrodes which have large specific surface areas [2–13]. Electric charges are stored in an electric double layer at the interface between electrode and electrolyte. It has been widely known that the capacitor performance, such as capacitance, depends on the physical properties of the carbon electrodes [2–8,13]. The specific surface area of the electrodes and the pore-size distribution in the electrodes affect the charge/discharge properties of the capacitors [3–8,13]. Moreover, chemical properties, such as atomic and functional group distribution on the surface of the carbon electrodes, influence the capacitor performance [7]. Recently, the treatment with 'cold plasma', plasma generated at low temperature, has been used as a novel method for the modification of the physical and chemical properties of carbon materials [14–17]. This treatment can modify the surface properties of carbon materials without changing the chemical and physical properties of the bulk of the materials.

We report herein the effect of the surface treatment of ACFC electrodes with cold plasma upon the charge/discharge performance of electric double-layer capacitors. The effect of the cold plasma treatment of the ACFC electrodes upon the capacitor performance is discussed on the basis of the physical and chemical properties of the carbon surface, such as pore radius distribution and surface atom concentration.

2. Experimental

The ACFC (Toyobo, BW552) was used as the polarizable electrode in the capacitors. This carbon cloth (180 g m^{-2}, thickness: 0.62 mm) was made from a phenolic resin and has a high surface area; specific surface area is about 1.3×10^3 m^2 g^{-1}. The ACFC was used as the capacitor electrode with and without cold plasma treatment. The cold plasma treatment was performed in a plasma chemical vapor deposition apparatus (Sinko Seiki, APP-330). This apparatus has two types of high-frequency power supply (13.65 MHz); one generates pulsed electric power (maximum power: 50 kW), and the other gives continuous electric power (maximum power: 500 W). Argon–oxygen ($Ar–O_2$) mixed gas was introduced to a chamber of the apparatus for plasma treat-

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ment. The procedure for the ACFC plasma treatment was classified into two types: (i) treatment with the plasma generated by pulsed electric power, and (ii) treatment by continuous electric power.

In the former case, the reaction chamber was degassed until 0.1 Torr after introducing the ACFC into the chamber. Next, the pre-treatment of the ACFC was performed in the plasma gas generated by continuous power supply (100 W) with flowing argon gas (the flow rate was 500 cm^3 min^{-1}); the pre-treatment period was 10 s. Finally, the resulting cloth was exposed to the plasma gas generated by pulsed power supply (10 kW) for 30 min; pulse on-time and off-time was 0.15 and 34.85 ms, respectively. Throughout this treatment the Ar–O_2 mixed gas was intermittently supplied into the chamber; the flow rate was 500 cm^3 min^{-1}, the on-time and the off-time of the gas supply were 7 ms. The composition of the supplying gas was Ar–O_2 (2 vol.%), Ar–O_2 (6 vol.%), or Ar–O_2 (10 vol.%); vol.% represents the vol.% of O_2 in the supplying Ar–O_2 mixed gas.

On the other hand, in the latter case, after the reaction chamber was degassed until 0.1 Torr, the ACFC was treated with plasma gas generated by continuous electric power (50 W) for 30 min with supplying the Ar–O_2 gas; the flow rate was 500 cm^3 min^{-1}. The composition of the supplying gas was Ar–O_2 (6 vol.%) or Ar–O_2 (10 vol.%).

X-ray photoelectron spectroscopy (XPS) was performed to analyze the distribution of the atoms and functional groups on the surface of the treated and untreated ACFC. BET method was applied to determine the specific surface area and the pore-size distribution on the ACFC surface.

The solvent, high-purity propylene carbonate (PC) (Mitsubishi Chemical, battery grade) was used as received. The electrolytic salt, tetraethylammonium tetrafluoroborate ($TEABF_4$), was used after vacuum drying at 80°C for 24 h. The electrolyte solution was prepared in a glove box filled with dry argon. A model capacitor was fabricated with a

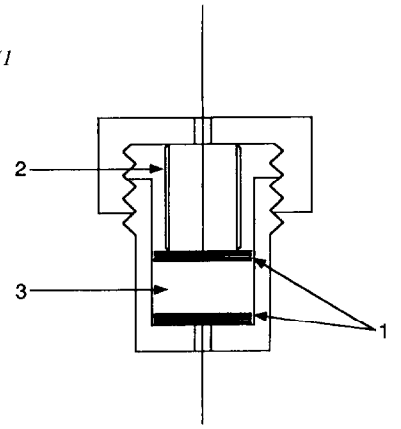

Fig. 1. Schematic diagram for the model capacitor: (1) activated carbon fiber cloth electrodes; (2) Teflon spacer, and (3) electrolyte + separators.

Teflon cell case (inner diameter: 13 mm, 15 mm height). The capacitor setup is given in Fig. 1. The untreated and plasma-treated ACFC was used as the polarizable electrode. The current collector of the electrode was a nickel mesh. A polypropylene non-woven cloth was used as the separator, which was impregnated with the electrolyte solution. The charge/discharge characteristics of the model capacitor were measured under a constant current cycling [9–13]. The cutoff voltages of the cell were 2 V for charging and 1 V for discharging. The cell assembly and all capacitor tests were carried out in a dry argon atmosphere at room temperature (20–25 °C).

3. Results and discussion

The activated carbon fiber clothes (ACFCs) were treated with cold plasma generated by two types of the power supply; pulsed or continuous electric power, see Experimental. Fig. 2 shows the distribution of the pore radius on the ACFC surface treated with cold plasma generated by pulsed electric power in the various gas-supplying conditions. In each of the treatment conditions, i.e., Ar–O_2 (2 vol.%), Ar–O_2 (6 vol.%),

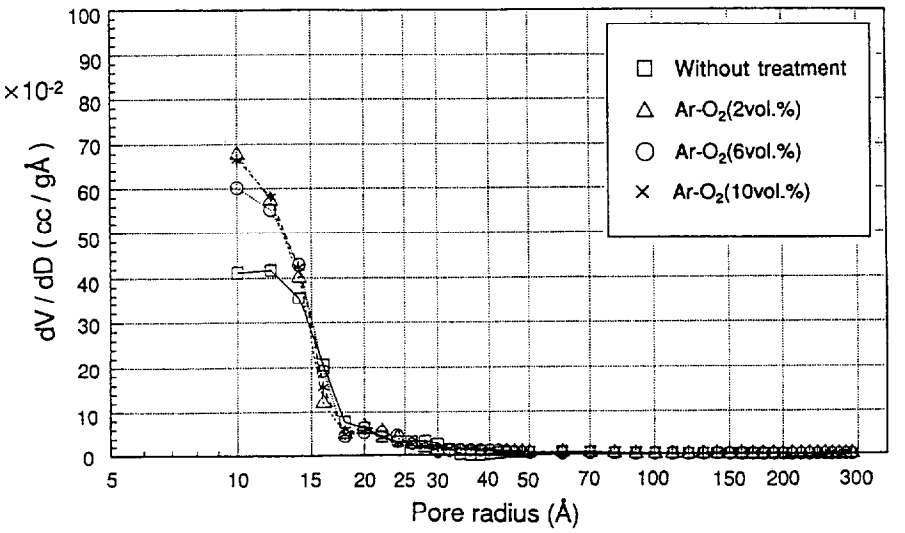

Fig. 2. Pore radius (D) vs. dV/dD in case of pulsed electric power.

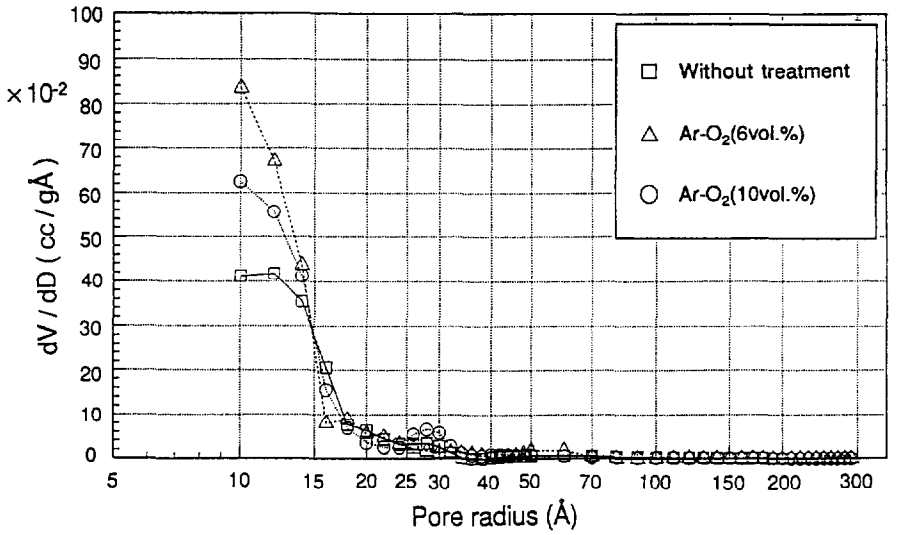

Fig. 3. Pore radius (D) vs. dV/dD in case of continuous electric power.

and Ar–O_2 (10 vol.%), the relative amount of pores in the 10–15 Å range increased in comparison with that without treatment. Furthermore, a similar change in the pore-size distribution was observed on the surface of ACFCs treated with the plasma generated by continuous electric power; in the case of Ar–O_2 (6 vol.%) and Ar–O_2 (10 vol.%) the relative amount of pores in the 10–15 Å range increased in comparison with that without treatment as shown in Fig. 3. The specific surface area of the ACFCs with and without treatment was between 12.7×10^2 and 13.1×10^2 m^2 g^{-1}, and the magnitude of the area was found to be independent of the plasma-treatment condition. Thus, it is concluded that the cold plasma treatment in the above-mentioned conditions did not affect the specific surface area but affected the pore-size distribution on the ACFCs.

In order to examine the effect of plasma treatment on the performance of the capacitors with ACFC electrodes, model capacitors were fabricated using the ACFC electrodes (see Experimental) and the charge/discharge tests of the capacitors were carried out. The electrolyte was PC containing 0.8 M $TEABF_4$ in each test, and the charge/discharge current and operating voltage were 1.0 mA and between 1 and 2 V, respectively. Fig. 4 shows the discharge capacitance of the model capacitors with ACFC electrodes treated with plasma generated by pulsed electric power. The discharge capacitance is indicated as the total cell capacitance per ACFC weight (F g^{-1}). The discharge capacitance increased by the plasma treatment. On the other hand, in the case of treatment with plasma generated by continuous electric power, the initial capacitance of the capacitor with the treated ACFC electrodes was lower than that of the capacitor with the ACFC electrodes without treatment as shown in Fig. 5. However, the subsequent charge/discharge cycling increased the capacitance of the capacitors with the treated electrodes, and after the 15th cycle the order of the capacitance changed; Ar–O_2 (6 vol.%) > without the treatment > Ar–O_2 (10 vol.%). With a lower charge/discharge current, 0.5 mA, the cycle dependence on the discharge capacitance of the model capacitors was similar to that with 1.0 mA of charge/discharge current as shown in Figs. 6 and 7. Each capacitance indicated in these

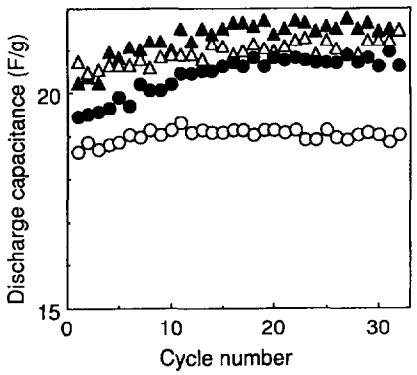

Fig. 4. Discharge capacitance of the model capacitor with activated carbon fiber cloth electrodes treated with plasma generated by pulsed electric power. Electrolyte: PC/0.8 M $TEABF_4$; charge/discharge current: 1.0 mA, and operation voltage: 1–2 V, (○) without treatment; (●) Ar–O_2 (2 vol.%) treatment; (△) Ar–O_2 (6 vol.%) treatment, and (▲) Ar–O_2 (10 vol.%) treatment.

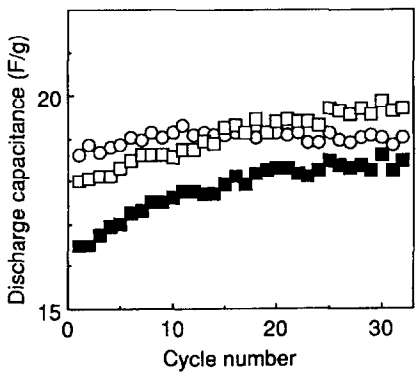

Fig. 5. Discharge capacitance of the model capacitor with activated carbon fiber cloth electrodes treated with plasma generated by continuous electric power. Electrolyte: PC/0.8 M $TEABF_4$; charge/discharge current: 1.0 mA, and operation voltage: 1–2 V. (○) without treatment; (□) Ar–O_2 (6 vol.%) treatment, and (■) Ar–O_2 (10 vol.%) treatment.

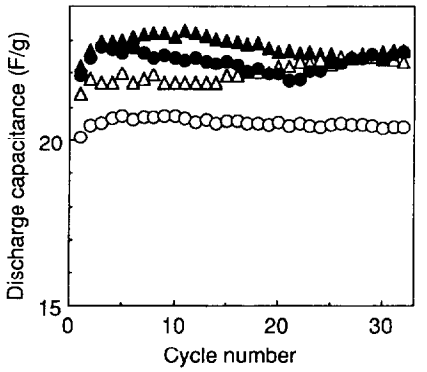

Fig. 6. Discharge capacitance of the model capacitor with activated carbon fiber cloth electrodes treated with plasma generated by pulsed electric power. Electrolyte: PC/0.8 M $TEABF_4$; charge/discharge current: 0.5 mA, and operation voltage: 1–2 V. (○) without treatment; (●) Ar–O_2 (2 vol.%) treatment, and (△) Ar–O_2 (6 vol.%) treatment, and (▲) Ar–O_2 (10 vol.%) treatment.

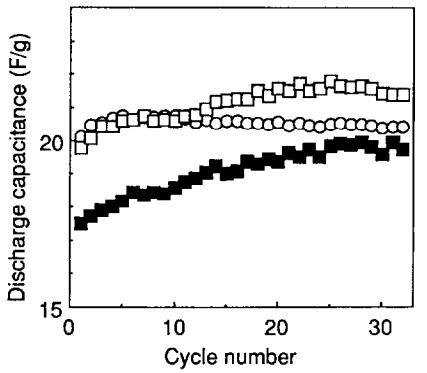

Fig. 7. Discharge capacitance of the model capacitor with activated carbon fiber cloth electrodes treated with plasma generated by continuous electric power. Electrolyte: PC/0.8 M $TEABF_4$; charge/discharge current: 0.5 mA, and operation voltage: 1–2 V. (○) without treatment; (□) Ar–O_2 (6 vol.%) treatment, and (■) Ar–O_2 (10 vol.%) treatment.

figures was somewhat higher than the respective cell capacitance at 1.0 mA of the charge/discharge current displayed in Figs. 4 and 5. Low charge/discharge current increases the utility of the carbon electrodes, resulting in an increase in the discharge capacitance; the relationship between the cycling current and the discharge capacitance was discussed in our previous papers [9–11]. The increase in the discharge capacitance of the capacitors with the plasma-treated electrodes may be ascribed to an increase in the amount of the pore-size distribution in the 10–15 Å radius range that increased in comparison with that without treatment. In the case of capacitors with ACFC electrodes treated with plasma generated by continuous electric power, however, the discharge capacitance for the initial few cycles was lower than that without the plasma treatment as described above. This suggests that some factors other than the pore distribution might play an important role in influencing the discharge capacitance.

In this context we focused on the chemical properties on the surface of the ACFC electrodes, i.e., the surface atomic concentration and the functional group on the carbon fiber surface. The surface atomic concentration of ACFCs treated with plasma is listed in Table 1 where the values were determined by XPS measurements. Major atoms existing on the surface of ACFC were carbon and oxygen. The amount of the other atoms (P, N, Si, Fe, Na) was negligible; these atoms may be mainly derived from contamination in the plasma chamber. Obviously, the ratio of oxygen on the ACFC surface increased with plasma treatment especially with the plasma generated by continuous electric power. Furthermore, the distribution of functional groups on the surface of ACFCs was determined on the basis of the XPS analysis as listed in Table 2. The main functional groups were composed of carbon–carbon (C–C) and carbon–hydrogen (C–H) bonds both with and without treatment. Other major functional groups on the surface contained carbon–oxygen single and double bond (C–O, C=O), and carboxyl moiety (–COO). The ratio of these functional groups containing oxygen increased with plasma treatment. As shown in Table 1, therefore, the ratio of oxygen on the ACFCs increased remarkably with the plasma treatment. Fig. 8 shows oxygen:carbon (O:C) concentration ratio on the surface of the ACFCs. The series of the treatment with plasma generated by pulsed electric power gave about 0.3 of the O:C ratio, while the series of the treatment with plasma generated by continuous electric power resulted in about 0.5 of the O:C ratio. The surface oxygen concentration in the case of plasma treatment with continuous electric power was higher than that in the case of plasma treatment with pulsed electric power.

As described above, plasma treatment affects the discharge capacitance; the capacitance of the cell with the electrodes treated by pulsed electric power plasma increased in comparison with the cell with untreated electrodes, although the treatment with plasma generated by continuous electric power did not always enhance the capacitance. There were

Table 1
Surface atomic concentration of activated carbon fiber cloth treated with plasma

Plasma condition	Electric power	C (%)	O (%)	P (%)	N (%)	Si (%)	Fe (%)	Na (%)
Without treatment		94.1	4.02	0.25		0.59		
Ar–O_2 (2 vol.%) treatment	pulse	73.9	23.1	0.44	0.56	0.71	0.15	0.28
Ar–O_2 (6 vol.%) treatment	pulse	72.1	24.8	0.61	0.37	0.82	0.22	0.23
Ar–O_2 (10 vol.%) treatment	pulse	71.8	25.2	0.59	0.30	0.76	0.19	0.29
Ar–O_2 (6 vol.%) treatment	continuous	65.5	31.1	1.02	0.29	0.93	0.46	0.21
Ar–O_2 (10 vol.%) treatment	continuous	65.0	31.6	1.13	0.30	0.77	0.52	0.20

Table 2
Ratio of functional groups on the surface of activated carbon fiber cloth treated with plasma

Plasma condition	Electric power	C–C, C–H (%)	C–O, C=O (%)	–COO (%)	$-CO_3$, C–F (%)
Without treatment		72.4	14.3	6.1	7.1
Ar–O_2 (2 vol.%) treatment	pulse	66.0	19.6	10.3	4.1
Ar–O_2 (6 vol.%) treatment	pulse	62.9	21.6	11.3	4.1
Ar–O_2 (10 vol.%) treatment	pulse	61.2	22.4	12.2	4.1
Ar–O_2 (6 vol.%) treatment	continuous	56.7	25.8	14.4	3.1
Ar–O_2 (10 vol.%) treatment	continuous	55.7	25.8	15.5	3.1

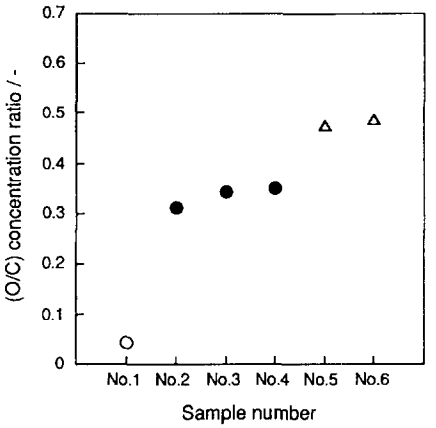

Fig. 8. Oxygen:carbon (O:C) concentration ratio on the surface of the activated carbon fiber cloth, (No. 1) without treatment; (No. 2) Ar–O_2 (2 vol.%) treatment (pulsed power); (No. 3) Ar–O_2 (6 vol.%) treatment (pulsed power); (No. 4) Ar–O_2 (10 vol.%) treatment (pulsed power); (No. 5) Ar–O_2 (6 vol.%) treatment (continuous power), and (No. 6) Ar–O_2 (10 vol.%) treatment (continuous power).

cases where plasma treatment by continuous electric power had a negative effect on the discharge capacitance. The increased quantities of 'micropores' on the ACFC surface contributed obviously to an increase in the discharge capacitance [13,18]. However, the effect of the surface oxygen concentration on the discharge capacitance is not fully understood. Hiratsuka et al. [7] reported that the oxygen excess on the electrode surface induces the self-discharge of the electric double-layer capacitors. They suggested that the electrodes with the oxygen excess accelerate the degradation of electrolytes [7]. Moreover, it is supposed that the functional groups containing oxygen (C–O, C=O, –COO, etc.) on the ACFC surface may stabilize the negative charge and thus enhance the cation absorption but not stabilize the positive charge, resulting in the retardation of the anion absorption. Therefore, the discharge capacitance may be limited by the electrode positively polarized, and the overall discharge capacitance may therefore decrease. Thus, the negative effect induced by the oxygen excess and the positive effect derived from the increase in the micropore distribution may be competitive in the case of capacitors with electrodes treated with plasma generated by continuous electric power. The study on the difference in affinity of the treated electrodes to the cation and the anion is in progress.

4. Conclusions

The modification of ACFC electrodes for the electric double-layer capacitors has been performed using 'cold plasma' generated in the Ar–O_2 atmosphere. Both the relative amount of micropores in the 10–15 Å radius range and the oxygen concentration on the surface of the ACFC increased with the cold plasma treatment. The discharge capacitance of the capacitors with ACFC electrodes treated with cold plasma generated by pulsed electric power was higher than that of the capacitors with untreated ACFC electrodes, although the treatment of ACFC electrodes with cold plasma generated by continuous electric power did not necessarily enhance the discharge capacitance. With respect to the treatment with plasma generated by pulsed electric power, the increase in the micropores on the ACFC surface obviously contributed to an increase in the discharge capacitance. On the other hand, the negative effect induced by the oxygen excess and the positive effect derived from the increase in the micropores distribution may be competitive in the case of the ACFC electrodes treated with plasma generated by continuous electric power.

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