Fabrication of high-power electric double-layer capacitors

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Abstract

The electrochemical behavior of activated carbon/carbon (AC/C) composite electrodes was investigated for high-power electric double-layer capacitors (EDLCs). It was found that high-rate charge/discharge characteristics are affected by the resistance of the electrolyte phase in the pores of the electrode. The charge/discharge characteristics were improved by optimizing the pore-size distribution of the electrodes. The size and total volume of the macro-pores in the electrodes were controlled by mixing and burning out polymer spheres. A high-power EDLC (15 V, 470 F), which can discharge as much as 500 A, was fabricated by using improved AC/C composite electrodes.

1. Introduction

Electric double-layer capacitors (EDLCs) have been widely used because of their advantages such as large capacitance, free of maintenance, and free from toxic materials. NEC Corporation has been commercializing EDLCs called 'SuperCapacitor' since 1980. They are composed of activated carbon powders as the polarizable electrodes and an aqueous solution of sulfuric acid as the electrolyte. However, their application has been limited to backing-up products such as microcomputers and memories because of their large equivalent series resistance (ESR).

Recently, the authors have developed a block-form polarizable electrode for EDLCs, which is called activated carbon/carbon (AC/C) composite [1,2]. Using this new polarizable electrode, EDLCs with a capacitance of several thousands farads and low ESR have been obtained [2]. These EDLCs are expected to be applied to pulse-power accumulators for electric vehicles, motors, actuators, etc. EDLCs are, therefore, required to supply a large current in one instance. The electrochemical behavior of the AC/C composite electrodes suggests that the resistance of electrolyte phase in the pores of the electrode affects high-rate charge/discharge characteristics [3,4].

This paper reports on the improvement of the high-rate charge/discharge characteristics by optimizing the pore-size distribution of the electrodes. A fabrication process and the performance of a high-power EDLC (15 V, 470 F), that utilizes the improved electrodes and can discharge 500 A, are also described.

2. Experimental

2.1. Preparation of AC/C composite electrodes

A synthesis process flow-chart for the AC/C composite electrodes is shown in Fig. 1. The AC/C composite is a block-form porous material obtained by carbonization of a cured mixture of activated carbon (AC) powder and phenol–formaldehyde (PF) powder. The AC/C composite has pores of two different sizes. The first composite has micro-pores with a diameter less than 3 nm which is mainly derived from activated carbon, and the second has macro-pores with a sub-micron diameter and is formed through the decomposition of the resin during the carbonization process. The capacitance of the electrode is mainly due to the surface area of the micro-pores, and the role of the macro-pores is to pass the electrolyte
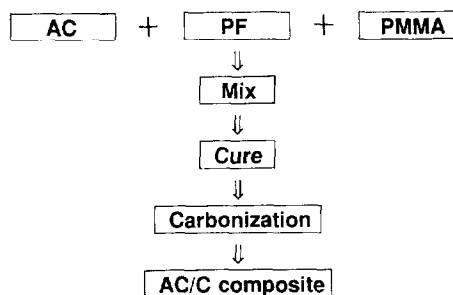

Fig. 1. Process flow-chart for the synthesis of AC/C composite electrodes: AC, activated carbon; PF, phenol formaldehyde; and PMMA, poly(methyl methacrylate). The starting material composition was AC/PF/PMMA = 70/30/0 and 70/30/20 in weight ratio, respectively. The carbonization was carried out at 900 °C under nitrogen flow.
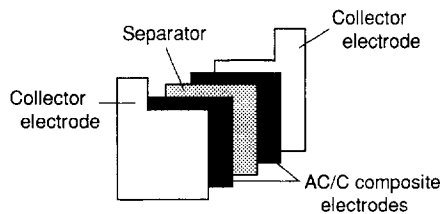
Fig. 2. Test cell for a.c. impedance and d.c. capacitance measurements: AC/ C, composite electrode, a pair of AC/C composite electrodes, whose size was 2 cm × 2cm × 0.1 cm; separator, composed of glass fibers; collector electrode, a pair of current collectors composed of gold foil, and electrolyte, 30 wt.% solution of sulfuric acid.
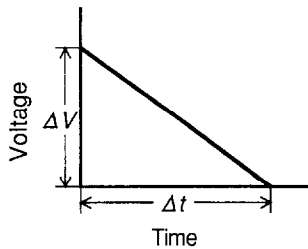

Fig. 3. Typical discharge curve of the AC/C composite electrodes with a constant discharge current: ΔV, voltage change, and Δt, discharge time.

solution into the micro-pores. Poly(methyl methacrylate) (PMMA) resin was added to the raw material. It was subsequently burned out to control the size and total volume of macro-pores in the electrodes. The tested AC/C composites, in which the starting material composition was AC/PF/ PMMA = 70/30/0 and 70/30/20 in weight ratio, were carbonized at 900 °C under nitrogen flow. The size and total volume of the open pores were measured using a mercury porosimeter.

2.2. Capacitor characteristics

A.c. impedance and d.c. capacitance measurements were carried out in a test cell, see Fig. 2. The test cell has a pair of AC/C composite electrodes, whose size was 2 cm × 2 cm × 0.1 cm. First, each of the AC/C composite electrodes was immersed in a 30 wt.% solution of sulfuric acid. A glass-fiber separator was sandwiched between the pair of electrodes so that the electrodes were faced to each other. As the current collector, a pair of gold foil collectors was attached to the AC/C composite electrodes.

The a.c. impedance was measured by applying an alternating current in the frequency range from 1 mHz to 1 kHz at 10 mV$_{rms}$ amplitude.
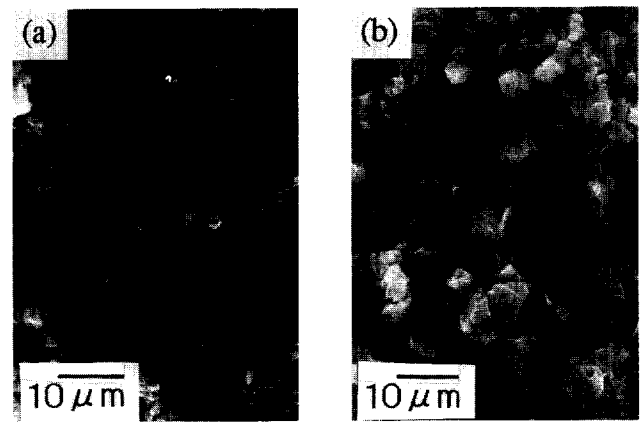

Fig. 4. Scanning electron graphs of a fractional surface of the AC/C composite: (a) AC/PF/PMMA = 70/30/0, and (b) AC/PF/PMMA = 70/30/ 20.

For measuring d.c. capacitance, the test cells were charged at a constant voltage of 0.9 V for 30 min. Then, each of the cells was discharged at a constant current from 0.001 to 0.5 A/cm^2 until the 0.9 V decreased to 0 V. Fig. 3 shows a typical discharge curve of the AC/C composite electrodes with a constant discharge current. The d.c. capacitance was calculated from the time period, Δt, voltage change, ΔV, and a constant discharge current, i, using the following equation:

$$C = \frac{i\Delta t}{\Delta V} \qquad (1)$$

3. Results and discussion

3.1. Properties of AC/C composite electrodes

The scanning electron microscope (SEM) pictures of a fracture surface of the AC/C composites are shown in Fig. 4. The electrode made using PMMA spheres (Fig. 4 (b)) is more porous than that not using PMMA spheres (Fig. 4(a)). Table 1 lists the density and resistivity values of the AC/C composite electrodes. Using PMMA spheres, the density decreased and the resistivity slightly increased. Fig. 5 shows the pore-size distribution of the AC/C composites measured using a mercury porosimeter. Fig. 5 indicates that both the maximum radius and the total volume of open pores increased by using PMMA spheres. The values of the maximum radius and the total volume are also listed in Table 1.

Table 1
Properties of AC/C composite electrodes

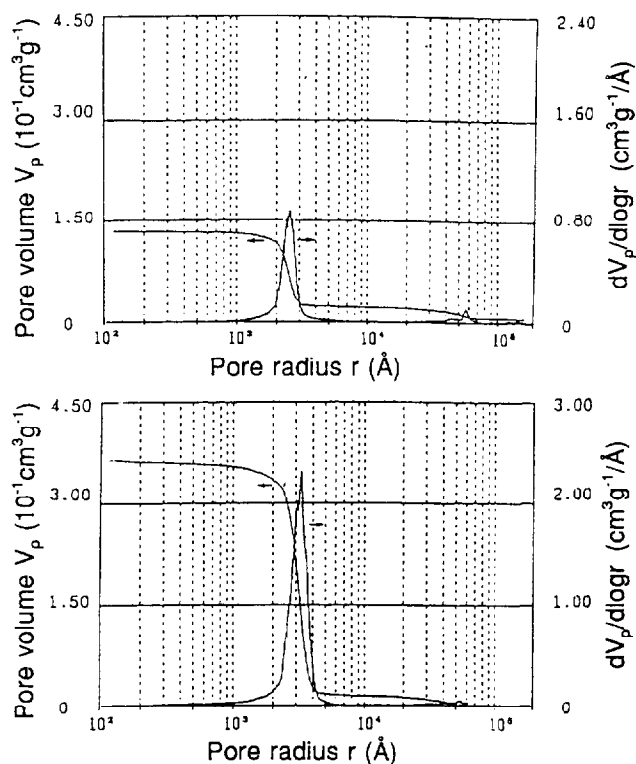| AC/PF/PMMA (weight ratio)	Density (g/cm^3)	Resistivity (Ω cm)	Pore-size distribution	
			Maximum radius (Å)	Volume (mm^3/g)
70/30/0	0.97	0.039	5200	135
70/30/20	0.78	0.048	6400	370

Fig. 5. Pore-size distribution of the AC/C composites measured by a mercury porosimeter: (a) AC/PF/PMMA = 70/30/0, and (b) AC/PF/PMMA = 70/30/20.
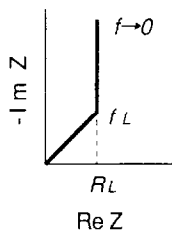

Fig. 6. Typical Cole–Cole plots of the AC/C composite electrodes: R_L, resistance obtained by extrapolating the low frequency data, and f_L, highest frequency in the vertical lines.

3.2. Capacitor characteristics

3.2.1. A.c. impedance

Fig. 6 shows the typical Cole–Cole plots of the AC/C composite electrodes. At higher frequencies, straight lines with a 45° slope were obtained. At these frequencies, the impedance behavior is similar to that of electrodes with cylindrical pores [5]. At lower frequencies, vertical lines were obtained where charge saturation dominates. As shown in Fig. 6, R_L is the limiting resistance obtained by extrapolating the low frequency impedance line to the x-axis. The value of R_L is considered to be proportional to the resistance of the electrolyte phase in the pores. In Fig. 6, f_L is defined as the highest frequency in the charge saturation region. The larger the value of f_L of the electrode, the higher the frequency that electrodes can follow. The electrode with the higher value of f_L can more rapidly charge and discharge.
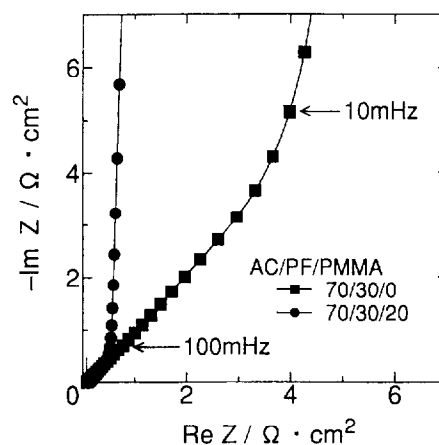

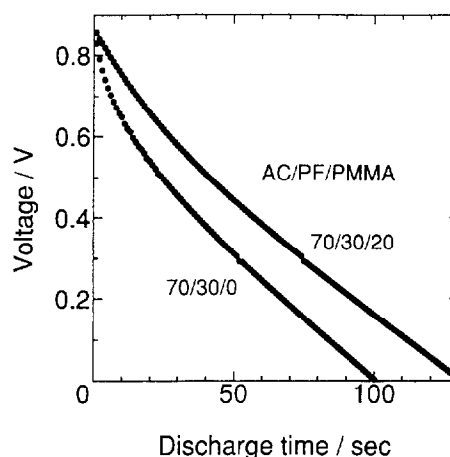Fig. 7. Cole–Cole plots of AC/C composite electrodes.

Fig. 8. Discharge curves of the AC/C composite electrodes; discharge current density: 0.05 A/cm².

Fig. 7 shows Cole–Cole plots of the AC/C composite electrodes of which the starting material was AC/PF/PMMA = 70/30/0 and 70/30/20, respectively. As shown in Fig. 7, the value of R_L decreased and the value of f_L increased by using PMMA spheres. These plots indicate that the highly porous electrode made by using PMMA spheres can follow a higher frequency and a rapid charge and discharge.

3.2.2. D.c. capacitance

Fig. 8 shows the discharge curves of the AC/C composite electrodes of which the starting material was AC/PF/PMMA = 70/30/0 and 70/30/20, respectively. The volume of both electrodes was 0.4 cm³ and the discharge current density was 0.05 A/cm². If the specific surface areas are the same, the capacitance should be proportional to the density of the electrode. The density of the electrodes composed of PMMA spheres was smaller than that not using PMMA spheres as shown in Table 1. However, Fig. 8 shows that the voltage of the relatively dense electrode not using PMMA spheres decreased more rapidly, and the capacitance was smaller than that of the porous electrodes using PMMA spheres. The decrease in capacitance of the relatively dense
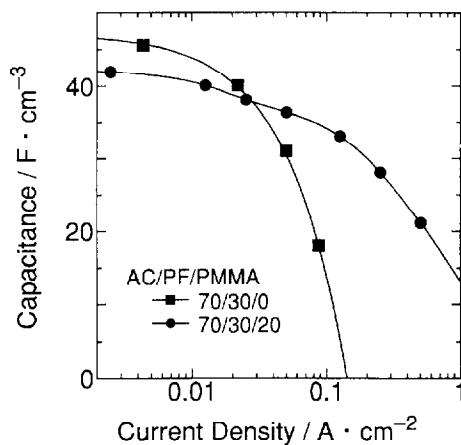
Fig. 9. Capacitance vs. discharge current of AC/C composite electrodes.

Fig. 11. Schematic setup of high-power EDLC; 15 V, 470 F: (a) AC/C composite electrode; (b) separator; (c) collector electrode; (d) gasket; (e)terminal, and (f) pressurize plate.

discharge current increases. Thus, the high-rate discharge characteristics can be improved by controlling the pore-size distribution of the electrodes.

4. High-power EDLC

4.1. Fabrication

A high-power EDLC (15 V, 470 F) was fabricated by using the improved AC/C composite electrodes. Fig. 10 shows the external view and Fig. 11 the schematic setup of the EDLC. The EDLC consists of stacked 18 unit cells because 0.9 V per unit cell was adopted as the working voltage [7]. A bipolar-type arrangement was used, where the collector electrode was co-used for adjacent unit cells. The polarizable electrodes were the improved AC/C composite electrodes (AC/PF/PMMA = 70/30/20) with a thickness of 1 mm. The collector electrodes were composed of conductive rubber. The separators were made of glass fibers, which maintain the electrolyte solution and has a high ion permeability. The gaskets were made of a thermoplastic resin and formed the framework of the unit cell. A solution of sulfuric acid (30 wt.%) was used as the electrolyte.

4.2. Characteristics of high-power EDLC

Table 2 lists the properties of the EDLC. The working voltage was 15 V. The capacitance was 476.1 F measured at a discharge of 5 A. The ESR at 1 kHz was 4.2 mΩ.

4.2.1. Charge characteristics

Fig. 12 shows the charge curves of EDLC when a 15 V constant voltage was applied.

The charge current was limited for the first 50 s, because the maximum current of the power source used was 100 A.
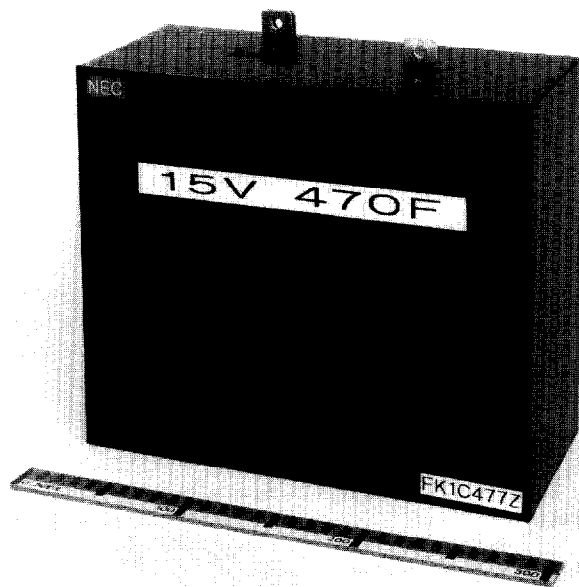

Fig. 10. External view of high-power EDLC: 15 V, 470 F.

electrodes was considered as follows. The voltage change of these electrodes was not linear as shown in Fig. 8. This phenomenon can be explained by the model of a cylindrical porous electrode reported by Posey and Morozumi [6]. Within the initial period after the start of the discharge, the voltage suddenly drops. This voltage drop is caused by a gradient of potential throughout the pores in the electrodes. Then, the voltage decrease is linear, because the pore effect is finite. The voltage drop is proportional to the electrolyte resistance in the pores.

The capacitance at various discharge currents is shown in Fig. 9. The figure shows that electrolyte resistance in the pores remarkably affects the discharge characteristics as the
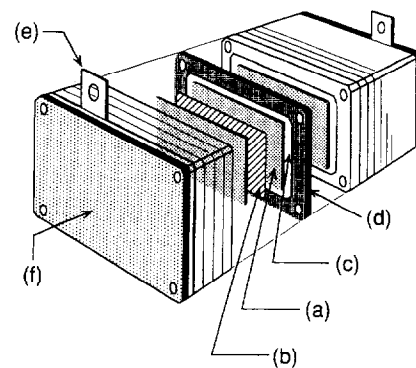
Table 2
Properties of high-power EDLC

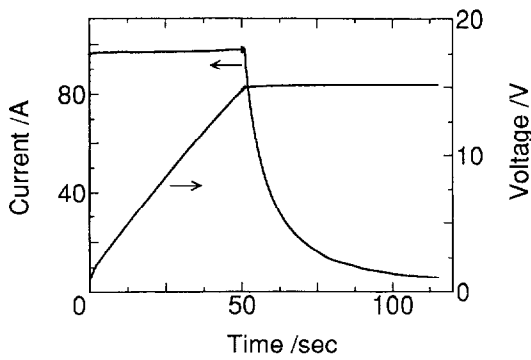| Working voltage (V)	Capacitance (F)	ESR (mΩ)	Weight (kg)	Size (mm)
15	476.1	4.2	11.2	226×114×225

Fig. 12. Charge curves of the high-power EDLC when 15 V constant voltage is applied.

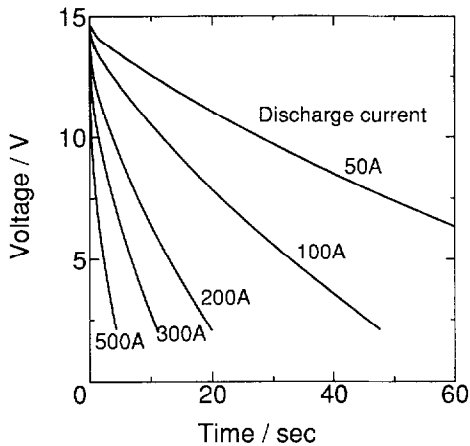Fig. 13. Discharge curves of the high-power EDLC after being charged with a constant voltage of 15 V for 30 min.

Fig. 14. Voltage drop in the first 10 ms by internal d.c. resistance.
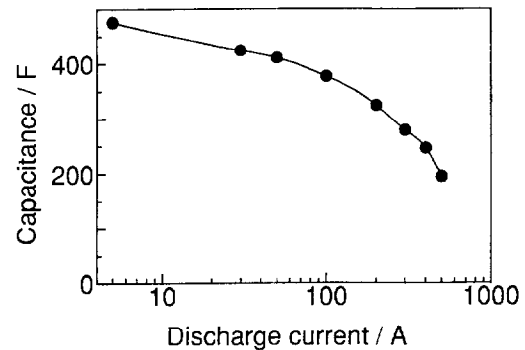
Fig. 15. Capacitance vs. discharge current of high-power EDLC.

The charge current, 100 A, is equal to a charge-current density of 0.113 A/cm^2 for the AC/C composite electrode. The stored charge in the first 50 s, which was calculated by integrating the current with respect to time, was 70% of the full charge; this was defined from the capacitance at 100 A of discharge.

4.2.2. Discharge characteristics

Fig. 13 shows the discharge curves of the EDLC after being charged at 15 V constant voltage for 30 min. The discharge current was 50, 100, 200, 300 and 500 A, respectively. The discharge time at 500 A was about 6 s.

The value of the voltage drop in the first 10 ms, ΔV_{init}, due to internal d.c. resistance is shown in Fig. 14. It was found that the d.c. resistance was 5.2 mΩ, which was almost equal to the ESR value measured at 1 kHz.

Fig. 15 shows the capacitance–discharge current relationship. When discharged at 100 A or more, the capacitance decreased clearly along with the discharge current. Even at a discharge of 500 A, the EDLC operates.

4.2.3. Energy and power density

The EDLC discharges 75% of its total energy when the limiting voltage is 50% of the charging voltage. The energy density of the EDLC is 1.0 Wh/kg or 1.6 Wh/l when the
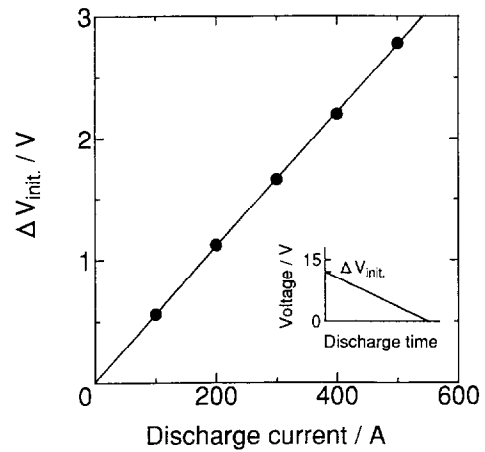
EDLC discharged until the voltage decreased form 15 to 7.5 V. The energy density of the EDLC is less than that of a lead/acid battery by about 100 times. However, the power density of the EDLC is 670 W/kg or 1.1 kW/l, which is almost equivalent to that of a lead/acid battery. Therefore, EDLCs will fit the applications requiring a high power to energy ratio.

5. Conclusions

The high-rate charge/discharge characteristics of the AC/C composite electrodes was improved by controlling the macro-pores of the electrodes. The size and total volume of macro-pores in the AC/C composites could be controlled by mixing and burning out PMMA spheres. A high-power EDLC with these improved AC/C composite electrodes was fabricated. The EDLC is able to discharge more than 500 A and is promising for the use in pulse-power accumulators.

References

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