

Performance of electric double layer capacitors using nanocarbons produced from nanoparticles of resorcinol-formaldehyde polymers

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Abstract

In this study, nanocarbons produced from nanoparticles of resorcinol-formaldehyde (RF) polymers were used instead of the conventional activated carbon for polarized electrodes in electric double layer capacitors (EDLCs) in order to improve their capacitance. The capacitances and internal resistances of the fabricated EDLCs were evaluated from their discharge characteristics. EDLCs with nanocarbon-based electrodes showed fairly high capacitance and had almost the same internal resistance as those using activated-carbon-based electrodes. In particular, capacitors using nanocarbons with a Brunauer–Emmett–Teller (BET) surface area of 2193 m²/g showed the highest capacitance among the fabricated samples. The specific capacitance of the best capacitor was evaluated to be 202 F/g. It was also found that the use of nanoparticles of resorcinol-formaldehyde polymers as nanocarbon precursors helps improve the energy density of the capacitors.

1. Introduction

Studies on the use of EDLCs [1] for use as energy storage devices in place of lead batteries are underway in Japan and in other countries. An EDLC is a type of physical battery, and hence has attracted significant attention from the viewpoint of prevention of global warming and satisfying the growing demand for energy. EDLCs, which contain activated carbon as the primary constituent, have a markedly longer life than normal batteries and have excellent discharge characteristics. EDLCs utilize the double layer formed at the interface

between the nanoporous carbonaceous electrode and the electrolyte solution. Activated carbons are used as the electrode materials for EDLCs because of their relatively low cost and very high specific surface area. In addition, since this electrode does not participate in redox reactions, it undergoes very less deterioration, has good cycle characteristics, and does not require maintenance. However, the main disadvantage of this electrode is its low energy density; hence, research on the development of a new electrolyte [2,3] and a new carbon electrode material [4–6] is underway. In our recent research on EDLCs, we attempted to increase the capacitance of EDLCs fabricated by mixing either Ketjen black or carbon nanotubes in the activated-carbon electrode material [7,8]. Also, we attempted to modify the surface of the carbon electrodes through plasma chemical reactions [9,10]. An EDLC consists of a collector electrode that collects electrons, a polarized electrode that stores charge, a highly insulating separator that only allows the passage of ions, and an electrolyte solution, which plays a critical role during charging and discharging. In recent years, there have been reports of the use of resorcinol (R)-formaldehyde (F) resin based mesoporous carbons with a uniform pore size as electrode materials for EDLCs. RF polymers can be easily substituted. RF polymers are known to maintain their morphology and can be easily prepared from the polymerization of R and F under slightly basic conditions. They have also been converted to mesoporous polymer gels via the aging and gelation processes. [11]. Moreover, it was found that even in the absence of any additional activation process, the specific surface area of the RF polymer reached 825 m²/g and the specific capacitance of the capacitor using this

electrode material exceeded 200 F/g when the molar ratio R/CA (curing agent: HTMA(hexamethylenetetramine)) reached 50 [12]. It has been reported that a modified activated carbon aerogel can be produced by the activation of a carbon aerogel under CO₂ flow, followed by surface modification with a surfactant such as sodium oleate. The capacitors using electrodes made from the modified activated carbon aerogel had a higher specific capacitance (130 F/g) than those using unmodified carbon electrodes [13]. However, the abovementioned carbonized polymers have a low BET surface area and low porosity. It has also been reported that RF polymers synthesized by the NaOH-catalyzed polymerization of R and F in the presence of cetyltrimethylammonium bromide (CTAB) and a cosurfactant could be topotactically converted into microporous carbon nanowires (diameter: 45–240 nm) and nanospheres (diameter: 260–650 nm) [14,15] for use as novel electrode materials in EDLCs.

In this study, nanocarbons produced from nanoparticles of RF polymers were used for the fabrication of the polarized electrodes in EDLCs. The effects of the surface characteristics of the electrodes such as pore size and specific surface area on the capacitance and internal resistance of EDLCs were studied.

2. Experimental

2.1. RF Carbon preparation

All the reagents used in the study, resorcinol (99%), formaldehyde solution (37% formaldehyde, 8% methanol), CTAB, NaOH (96%), tert-butanol (99%), hydrochloric acid (35–37%), and ethanol (99.5%), were purchased from Wako company and used as received.

In one polymerization process, an aqueous solution of F was added dropwise to a mixture of R, CTAB, NaOH, 1, 3, 5-trimethylbenzene (TMB), tert-butanol (tBuOH), and H₂O at 50 °C with vigorous stirring. R, F, CTAB, NaOH, TMB, tBuOH, and H₂O were mixed in the following molar ratios: 2.0:4.0:1.0:0.25:1.0:0:360, 2.0:4.0:1.0:0.25:1.0:1.0:360, 2.0:4.0:1.0:0.25:1.0:5.0:360, and 1.0:2.0:0.5:0.25:0.5:4.0:360. After stirring at 50 °C for 2 h, the reaction mixture was maintained at 90 °C for 24 h. The resulting products were washed with water. Acid treatment was carried out by adding 1 g of the RF/cetyltrimethylammonium (CTA) composites to a mixture of 1 ml of 36 wt% hydrochloric acid and 40 ml ethanol and stirring the resulting mixture vigorously at room temperature for 4 h.

In the polymerization process carried out without TMB and tBuOH, an aqueous solution of F was added dropwise to a mixture of R, CTAB, NaOH, and H₂O at 50 °C with slow stirring. The total molar ratio of R, F, CTAB, NaOH, and H₂O was 1.0:2.0:1.0:1.0:240. After stirring at 25 °C for 72 h, the reaction mixture was maintained at 90 °C for 24 h. The resulting products were washed with water and ethanol and then dried at 60 °C. Acid treatment was carried out by adding 1 g of the RF/CTA composites to a mixture containing 1 ml of 36 wt% hydrochloric acid and 40 ml ethanol and stirring the resulting suspension vigorously at room temperature for 6 h.

After filtration, the acid-treated samples were washed with ethanol, dried at 60 °C, heated to 1000 °C at a rate of 10 °C/min, and maintained at the same temperature for 4 h under a nitrogen atmosphere. Five types of RF carbons were obtained as a result of the aforementioned process.

2.2. Carbon characterization

The samples were analyzed using a scanning electron microscope (SEM), Hitachi S-4100. Various electrochemical characteristics of the EDLCs, including the BET specific surface area [16], pore volume, and pore size distribution were analyzed using the Barrett–Joyner–Halenda (BJH) method [17]. Nitrogen adsorption isotherms at 77 K (−196 °C) measured using a Tristar 3000 system manufactured by Shimadzu were used to obtain measurements for the analysis of the abovementioned electrochemical characteristics.

2.3. Preparation of EDLCs samples

The EDLC samples were fabricated by assembling two 100- μm -thick polarized electrodes made of RF carbon, polytetrafluoroethene (PTFE) (Aldrich, 60 wt% dispersion in H₂O) as a binder, and acetylene black (Stream Chemicals Co.). Acetylene black was added to decrease the ohmic resistance of the electroactive material. The polarized electrode was fabricated in the following manner: RF carbon, PTFE, and acetylene black were mixed in a mass ratio of 8.5:0.5:1.0. The mixture was dried for 1 h at 150 °C, and the polarized electrode was sealed in

a Pt container using a heat press at a pressure of 10 MPa. The Pt-covered polarized electrode was then dried under vacuum of 250 Pa for 30 min and then spot-welded to the required electrode size (diameter: 10 mm). A 20- μm -thick cellulose separator was inserted between the two polarized electrodes; the electrodes were set in a hermetic Pt container (thickness: 30 μm). The total thickness of the EDLC sample was 280 μm . Each component of the EDLC had a cross-sectional area of 78.5 mm². A schematic of an EDLC composed of five layers is shown in Figure 1. An aqueous electrolyte—9.5 mol/L H₂SO₄—was used.

2.4. Measurement of the charge–discharge performance of the EDLC samples

The performance of the EDLC samples was evaluated using a CDT510-4 (Power Systems Co.) measurement device. During charging, a constant charge current of 100 mA was supplied to the EDLC until a full-charge voltage of 1.0 V was built up. During discharging, the EDLC discharges through an electronic load at a constant discharge current of 10 mA. The energy conversion method [18] was used for calculating the capacitance during the discharge process. The internal resistance of the EDLC was calculated in the following manner: the best-fitted line representing the discharge characteristics corresponding to a stable voltage gradient after the transient period was found using the least squares method; then, the difference between the y-intercept of the abovementioned line and the voltage at the beginning of the discharge (1.0 V) was used to calculate the internal resistance.

3. Results and discussions

3.1. Characteristics of the nanocarbons used in electrodes

Figure 2 shows SEM images of the RF polymer/CTA composites recorded after carbonization at 1000 °C in N₂ and acid treatment. Table 1 shows the total molar ratio of R, F, CTAB, NaOH, TMB, tBuOH, and H₂O. The use of RF carbon in samples 1 and 2 resulted in nanowires with average diameters of ca. 50 nm and ca. 100 nm, respectively (Figures 2a and 2b). Furthermore, the use of RF carbon in samples 3 and 4 resulted in nanospheres with average diameters of ca. 500 nm and ca. 250 nm, respectively (Figures 2c and 2d). Microspheres and carbon particles obtained from polymerization without TMB and tBuOH are shown in Figure 2e (sample 5). The data obtained for the nitrogen adsorption–desorption isotherms revealed that the pore-size distribution curves shown in Figure 3 corresponded to essentially microporous materials with BET surface areas (S_{BET}) and pore volumes (V_{total}) of 701–2193 m²/g and 0.10–1.33 cm³/g, respectively. Further, it was clear that samples 1 and 2, which were nanowires, comprised mesopores of diameter 50 nm at a relative pressure of approximately 0.96. Samples 3 and 4, which were microspheres, had small micropores whose diameters were less than 0.8–2.0 nm at a relative pressure of approximately 0.2. Sample 5, in particular, contained a greater number of such micropores (diameters: 0.8–2.0 nm) than other samples. Sample 6, which was prepared from activated carbon powder to serve as a reference, retains the macropores. Table 1 shows the S_{BET} and V_{total} of the RF carbon obtained after calcination of the RF polymer as well as the S_{BET} and V_{total} of activated carbon powder as a

reference. The data in Table 1 indicate that calcination of the RF polymers under a N₂ atmosphere resulted in a loosely packed carbon framework with micropores because of their thermosetting properties.

3.2. Performance of EDLCs

The ratio of the surface area of the RF carbons in this experiment ranged from 701 m²/g (sample 1) to 2193 m²/g (sample 5). Figure 4 shows the discharge characteristics of sample 5, which was fabricated using RF carbon obtained from the RF polymer/CTA composites, and those of sample 6 as a reference. The discharge time of sample 5, which was made of RF carbon with a high specific surface area (2193 m²/g), was longer than that of sample 6, which was an activated-carbon-based EDLC. It is understood that the discharging time of RF carbon-based EDLCs is longer than that for activated-carbon-based EDLCs because the percentage of storage of electric charge is greater in the former than the latter. Therefore, the RF carbon-based EDLCs have a higher energy density than the activated-carbon-based EDLCs. This implies that to obtain EDLCs with high energy density, the electrode material must contain not only microspheres but also carbon particles so that the ratio of surface area of RF carbon is increased. Figure 5 shows the capacitance and internal resistance of EDLC samples obtained from charge-discharge measurements. The capacitance of the EDLC samples increased with the ratio of the surface area of RF carbon. The highest capacitance (202 F/g) was observed for the highest specific surface area of 2193 m²/g.

Nanocarbon-containing EDLCs showed a fairly high capacitance compared to the activated-carbon-based EDLCs. Further, a capacitance of approximately 140 F/g was observed for both the RF carbon-based EDLC with a BET surface area of 1140 m²/g and an activated-carbon-based EDLC with a BET surface area of 2132 m²/g. Commercially available carbon has the following four types of pore sizes (defined by diameter of the pores): submicropores (pore size: < 0.8 nm), micropores (pore size: 0.8–2 nm), mesopores (pore size: 2–50 nm), and macropores (pore size: > 50 nm). Electric double layers are formed on the micropores and mesopores in carbon. As shown in Figure 3, sample 5 of RF carbon does not contain many mesopores, and this contributes to charge accumulation on it. Micropores are distributed more uniformly in RF carbon than in activated carbon, which has micropores, mesopores, and macropores. Therefore, an electrolyte ion can easily penetrate the micropores of RF carbon. The aqueous electrolyte 9.5 mol/L H₂SO₄ decomposes into H⁺(cation) and SO₄²⁻(anion). Since the diameters of H⁺ and SO₄²⁻ are 0.08 nm and 0.398 nm, respectively, they easily penetrate pores with a diameter of approximately 0.5 nm; however, micropores with a diameter of 0.8–2 nm are necessary for storing these ions at the interface of the polarized electrode and the electrolyte. This is because the anions and cations can penetrate the polarized electrode easily through these pores on the electrode surface made of RF carbon. For this reason, the capacitance of our EDLCs based on RF carbon electrodes, whose pore size is in the abovementioned range, increased exponentially with the BET surface area (Figure 5). In addition, the internal resistance of our RF carbon-based EDLC samples

remained relatively constant when compared to that of the activated-carbon-based EDLCs. However, the internal resistance of RF polymer based EDLC samples was constant across all ratios of surface area. The specific volume resistance of RF carbon is supposed to be higher than that of activated carbon. Therefore, it is necessary to fabricate EDLCs from a mixture of several electroconductive materials in order to reduce their internal resistance.

4. Conclusions

In this research, nanocarbons produced from nanoparticles of resorcinol-formaldehyde polymers were used instead of conventionally used activated carbon to fabricate polarized electrodes for EDLCs in order to improve the capacitance of EDLCs. The specific surface area of RF carbon was found to be comparable to that of activated carbon; however, RF carbon had more micropores than activated carbon. It was also found that RF carbon-based EDLCs showed a higher capacitance than activated-carbon-based EDLCs. The maximum observed specific capacitance of RF carbon-based EDLCs was 202 F/g. Thus, the use of nanoparticles of resorcinol-formaldehyde polymers as carbon precursors was found to result in a marked increase in the energy density of EDLCs.

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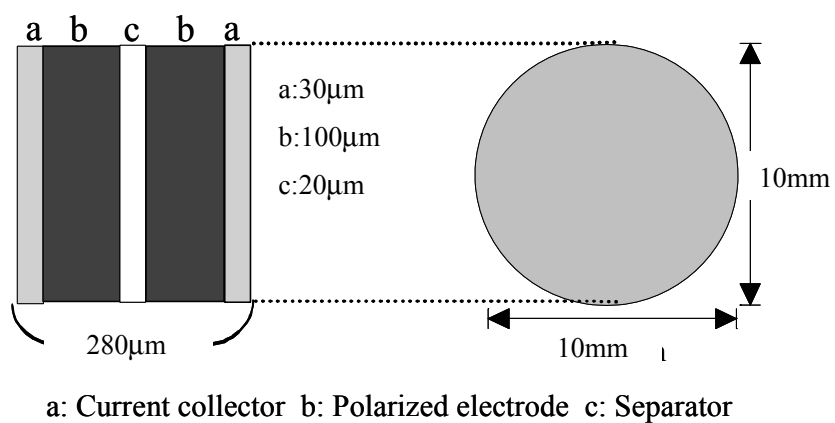
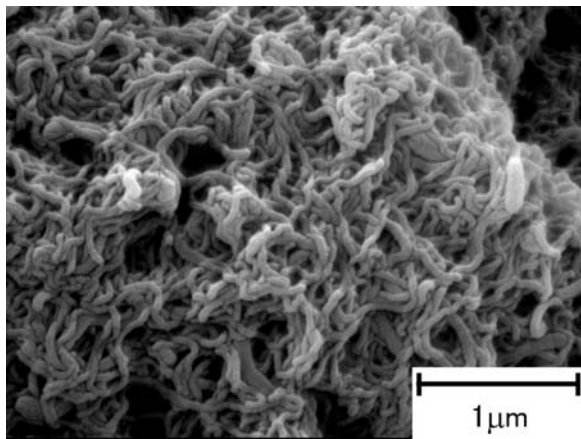
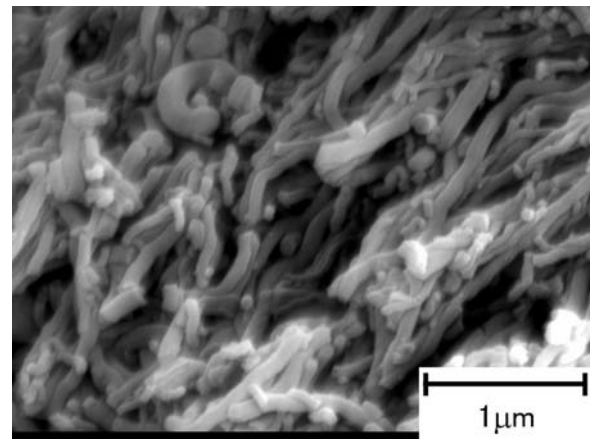


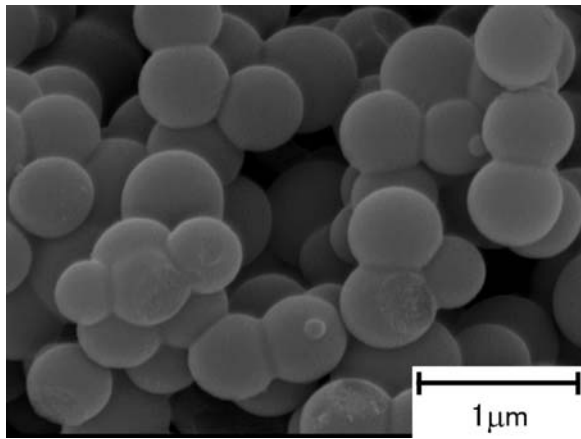
Fig. 1. Schematic of an EDLC sample fabricated by assembling two polarized electrodes made from a mixture of RF carbon, PTFE, and acetylene black.



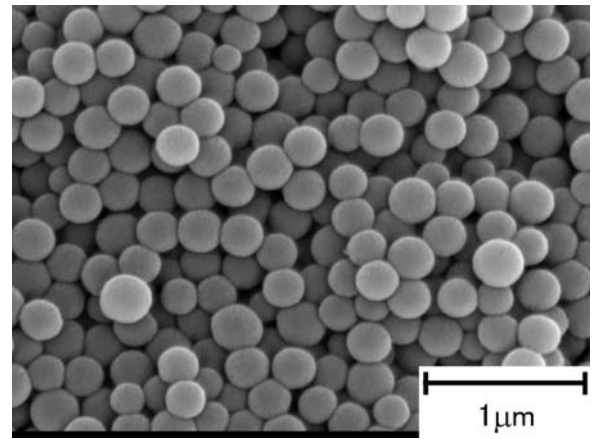
(a)



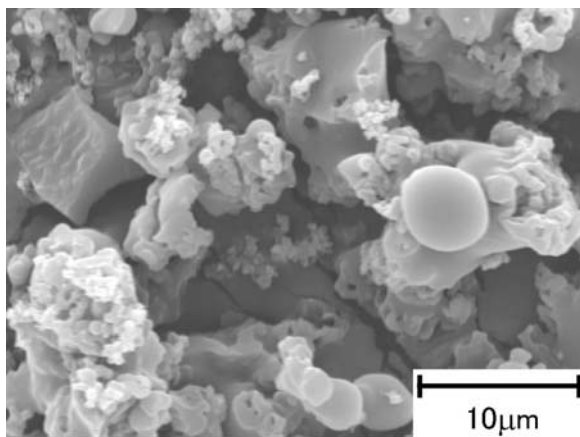
(b)



(c)



(d)



(e)

Fig. 2. SEM images of the RF polymer/CTA composites recorded after carbonization at 1000 °C in N₂ and acid treatment: (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 4; (e) Sample 5.

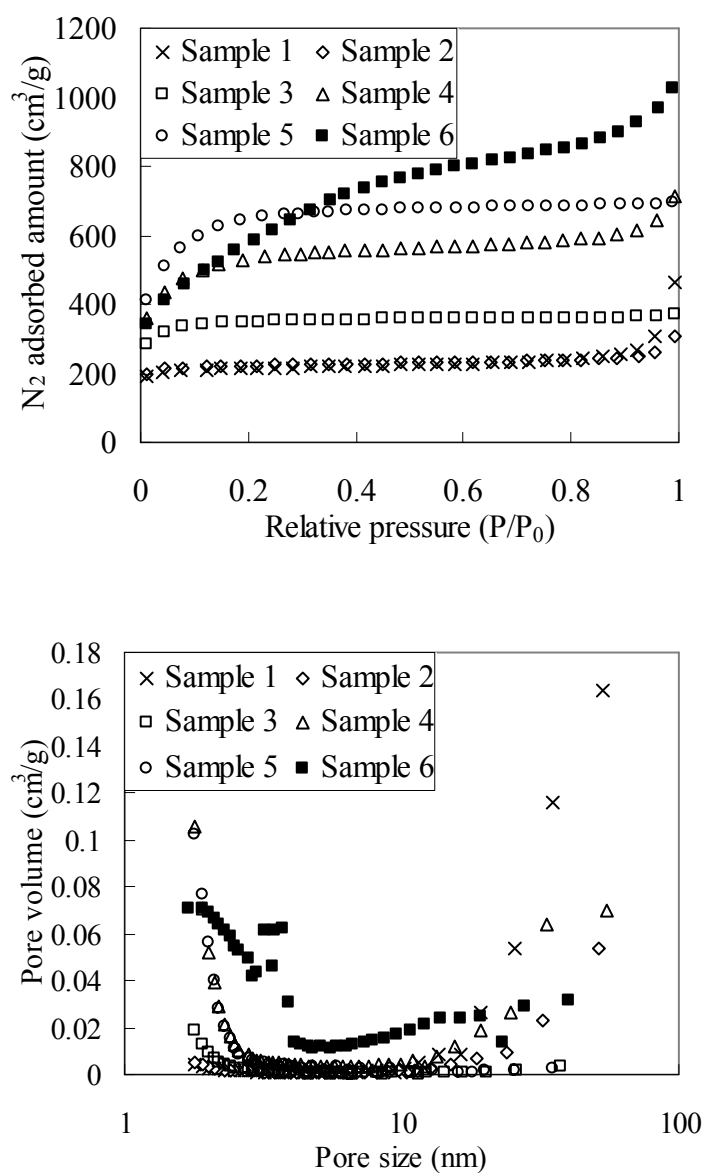


Fig. 3. N₂ adsorption–desorption isotherms and BJH pore-size distribution curves of the RF polymer/CTA composites carbonized at 1000 °C in N₂ after acid treatment (above); BET surface areas and pore volumes of each sample (below).

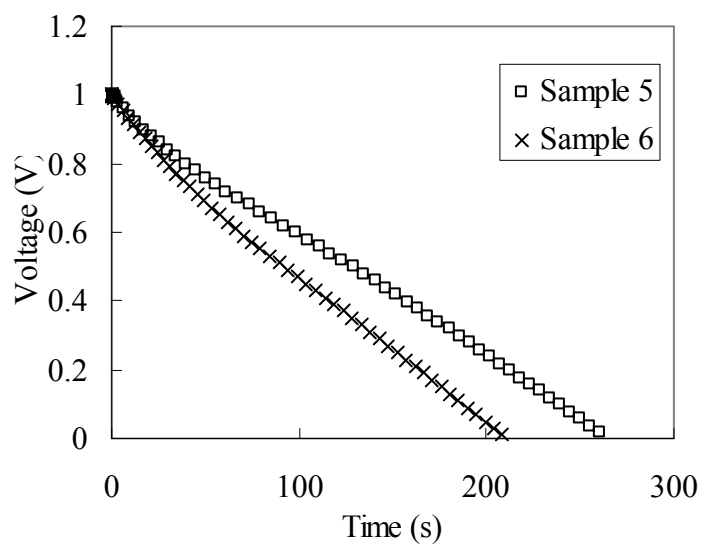


Fig. 4. Discharge characteristics of RF carbon-based EDLCs obtained from the RF polymer/CTA composites.

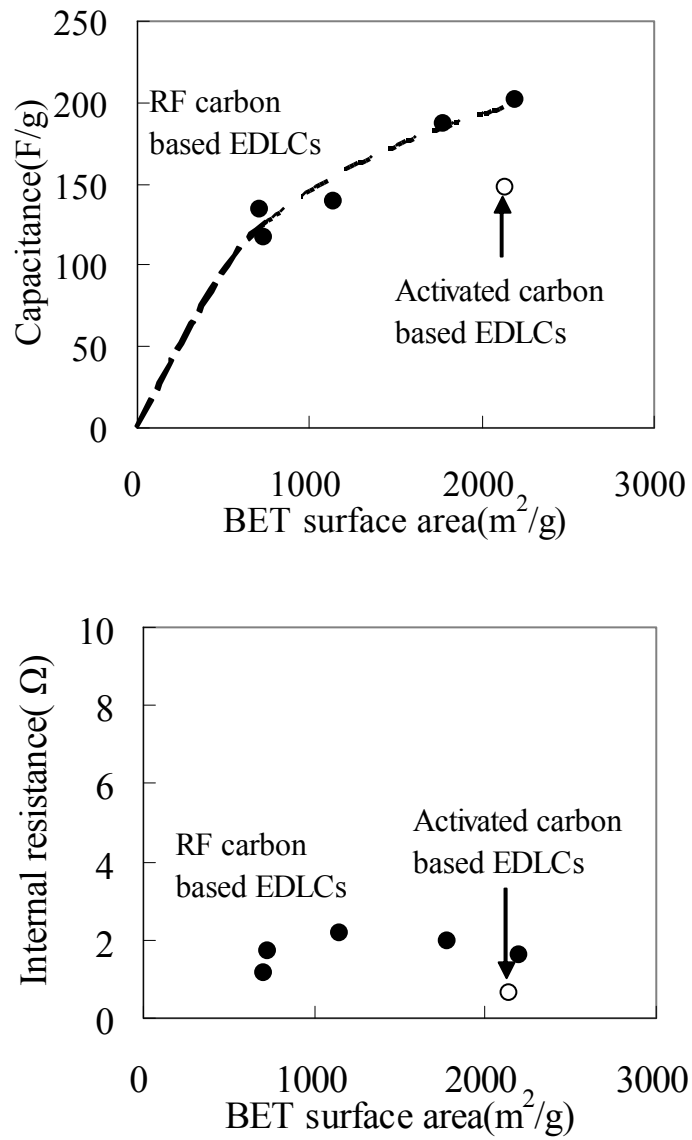


Fig. 5. Capacitance and internal resistance of EDLC samples obtained from charge-discharge measurements.

Table 1 Total molar ratio of R, F, CTAB, NaOH, TMB, tBuOH, H₂O, and BET surface area (S_{BET}) and total pore volume (V_{total}) of RF carbon obtained after the calcinations of the RF polymer; the S_{BET} and V_{total} of activated carbon powder are also provided for reference.

Samples	R	F	CTAB	NaOH	TMB	tBuOH	H ₂ O	S_{BET} (m ² /g)	V_{total} (cm ³ /g)
1	2.0	4.0	1.0	0.25	1.0	0.0	360.0	701	0.433
2	2.0	4.0	1.0	0.25	1.0	1.0	360.0	725	0.153
3	2.0	4.0	1.0	0.25	1.0	5.0	360.0	1140	0.669
4	1.0	2.0	0.5	0.25	0.5	4.0	360.0	1777	0.097
5	1.0	2.0	1.0	1.0	0.0	0.0	240.0	2193	0.440
6	Activated carbon powder							2132	1.326