

# Influence of physical properties of activated carbons on characteristics of electric double-layer capacitors

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## Abstract

Electrochemical characterization has been carried out for several activated carbons used as polarizable electrodes of electric double-layer capacitors in an aqueous electrolytic solution. The rest potential of the activated carbon was proportional to the logarithm of the oxygen content or to the concentration of the acidic surface functional groups of the activated carbon. The result of triangular voltage-sweep cyclic voltammetry was the same as that of the residual current measurement. The oxygen content and concentration of the acidic surface groups of activated carbon influenced the electrochemical characteristics of the activated carbon. Under anodic polarization, gas evolution was observed at the electrode surface of activated carbon with high oxygen content at 0.8 V versus saturated calomel electrode (SCE). Gas evolution was not observed at the electrode surface of activated carbon with low oxygen content even to 1.0 V versus SCE. Under cathodic polarization of activated carbon with high oxygen content, the peak was observed at approximately  $-0.2$  V versus SCE, but there was no gas evolution at the electrode surface of the activated carbon. Bubbles were not observed at the electrode surface of activated carbon with low oxygen content at  $-0.5$  V versus SCE. Electric double-layer capacitors were made from activated carbons used for electrochemical measurements; load-life tests have been carried out. Thickness and internal resistance of the capacitor composed of activated carbon with high oxygen content increased. The changes in thickness and internal resistance of the capacitor composed of activated carbon with low oxygen content were small.

*Keywords:* Carbon; Double-layer capacitors; Oxygen content; Acidic surface functional groups

## 1. Introduction

Activated carbons are used as the materials for polarizable electrodes of electric double-layer capacitors. Because activated carbons have large specific surface area, many charges can be stored. Activated carbons are suitable materials for the polarizable electrodes of electric double-layer capacitors, because of its good electric conductivity and electrochemical stability. Several research papers report on the characteristics and manufacturing methods of electric double-layer capacitors [1–6], but only a few papers reveal data of the influence of surface functional groups of activated carbon on the characteristics of the electric double-layer capacitor. Tanahashi et al. [7] carried out electrochemical measurements with activated carbon fiber cloths in an organic electrolyte. They found that the temperature dependence of the capacitance was influenced by the pore-size distribution of the activated carbon fiber cloth. The rest potential of activated carbon was proportional to the oxygen content [8]. Tabuchi and co-workers [8,9] found that capacitance of the activated carbon with high oxygen content was greater than that with a low oxygen content. In this paper, the relationship between the

surface condition of activated carbons and electrochemical characteristics has been clarified, and the influence of the surface functional groups of activated carbon on the characteristics of the electric double-layer capacitor has been evaluated.

## 2. Experimental

### 2.1. Preparation of activated carbons

The raw materials, manufacturing methods and surface conditions of twelve activated carbons are given in Table 1. The activation time of activated carbon A is different from that of activated carbon C, that of the activated carbon G is different from that of activated carbon I. The activated carbons B and H were prepared by heating activated carbon A and G at 1300 °C in hydrogen gas. The activated carbons E and F were prepared by heating activated carbon D at 800 °C in nitrogen gas and at 350 °C in air, respectively. The activated carbons K and L were prepared by cutting off activated carbon fiber.

Table 1  
Origin, activation and treatment of activated carbons

Sample	Origin	Activation	Treatment	Specific surface area (m <sup>2</sup> /g)
A	Coconut shell	Steam		1860
B	Coconut shell	Steam	Heating A at 1300 °C in hydrogen gas	1350
C	Coconut shell	Steam		2070
D	Phenolic resin	Steam		2030
E	Phenolic resin	Steam	Heating D at 800 °C in nitrogen gas	1700
F	Phenolic resin	Steam	Heating D at 350 °C in air	2040
G	Mineral oil	KOH		2950
H	Mineral oil	KOH	Heating G at 1300 °C in hydrogen gas	2460
I	Mineral oil	KOH		2410
J	Coal	KOH		2510
K	Coal	Steam		1460
L	Coal	Steam		2120

## 2.2. Analysis of activated carbons

The specific surface areas of the activated carbons were obtained from nitrogen adsorption measurements. The concentration of the acidic surface functional groups were estimated by the method of Boehm [10]. Aqueous solutions of 0.1 N NaHCO<sub>3</sub>, 0.05 N Na<sub>2</sub>CO<sub>3</sub>, 0.1 N NaOH and 0.1 N C<sub>2</sub>H<sub>5</sub>ONa were prepared. A glass pot with 1 g of activated carbon and 50 ml of the aqueous solution was kept at 25 °C, and shaken several times a day. After five days, the activated carbon was removed by filtration, and 10 ml of the solution was back-titrated with 0.1 N aqueous NaOH solution. The decrease in the concentration of the solution gives an estimation of the acidic surface functional groups. The oxygen content of the activated carbon was measured with a CHNS/O analyzer (Perkin-Elmer, Model PE2400).

## 2.3. Preparation of electrodes

Activated carbon (98 wt.%) and polytetrafluoroethylene (PTFE) (2 wt.%) were mixed in order to obtain a powder with a grain size of 0.6 mm. From this powder a pellet was formed, diameter: 15 mm, thickness: about 1 mm, and weight: 50 mg. The pellet was pressed to the collector electrode. This

electrode was used as the working electrode. The collector electrode was composed of copper plate with an electric conductive film, and covered with Teflon adhesive tapes in order not to touch the aqueous electrolytic solution. The electric conductive film used in this measurement was made from the resin and graphite.

## 2.4. Electrochemical measurements

The schematic diagram of the cell for the electrochemical measurements is shown in Fig. 1. The measurements were carried out at room temperature (25 ± 2 °C) using a potentiostat (Hokuto Denko, Model HAB-151) and an x-y recorder (Graphtec, Model WX4000). A 30 wt.% sulfuric acid solution was used as the electrolyte. Prior to the analysis, bubbling of nitrogen gas through the electrolyte for 30 min was carried out in order to remove the dissolved oxygen. A saturated calomel electrode (SCE) and an activated carbon electrode (diameter: 20 mm and thickness: 1.2 mm) were used as the reference and counter electrode, respectively. The working and counter electrode in the electrolyte were decompressed in desiccator for 30 min so that the electrolyte might filtrate into the pores of the activated carbon. After decompressing, the desiccator was purged to atmospheric pressure by using nitrogen gas.

Cyclic voltammetric experiments started from the rest potential of each specimen to either side of the cathodic or anodic side. The sweep rate was 1 mV/s, and the sweep was two times at each potential.

The current was kept at a fixed potential for 1 h, then its residual value was measured, by using a potentiostat (Hokuto Denko, Model HA-151). The cell configuration was the same as that used in the triangular voltage-sweep cyclic voltammetry.

## 2.5. Preparation of electric double-layer capacitors

The setup of the electric double-layer capacitor is given in Fig. 2. The current collecting plate was made from nickel-plated stainless steel, the gasket of polyethylene resin, and

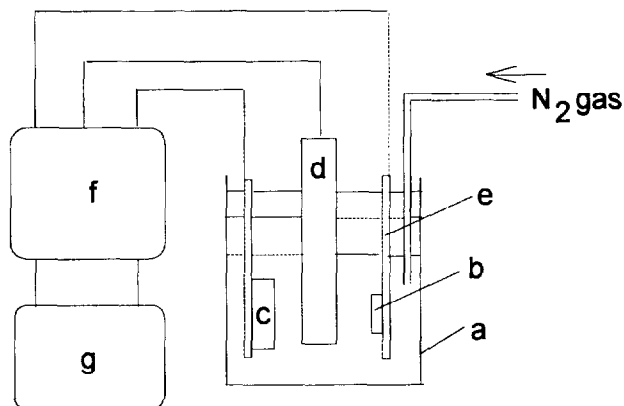


Fig. 1. Schematic diagram of cyclic voltammetry experiment: (a) beaker; (b) working electrode; (c) counter electrode; (d) reference electrode; (e) collector electrode; (f) potentiostat, and (g) x-y recorder.

Table 2  
Properties of activated carbons

Sample	Specific surface area (m <sup>2</sup> /g)	Base consumption (meq/g)				Surface group (meq/g)				Oxygen content (wt.%)	Rest potential at room temperature (V vs. SCE)
		NaHCO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	NaOH	C <sub>2</sub> H <sub>5</sub> ONa	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>c</sup>	4 <sup>d</sup>		
A	1860	0.03	0.08	0.22	0.30	0.03	0.05	0.14	0.08	2.0	0.170
B	1350	0.00	0.00	0.02	0.06	0.00	0.00	0.02	0.04	0.5	0.065
C	2070	0.00	0.05	0.14	0.14	0.00	0.05	0.09	0.00	0.8	0.094
D	2030	0.00	0.00	0.09	0.09	0.00	0.00	0.09	0.00	0.8	0.082
E	1700	0.00	0.00	0.05	0.05	0.00	0.00	0.05	0.00	0.8	0.096
F	2040	0.49	0.91	1.46	1.46	0.49	0.42	0.51	0.00	7.9	0.375
G	2950	0.66	1.20	1.75	1.84	0.66	0.54	0.55	0.09	8.8	0.351
H	2460	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.1	-0.036
I	2410	0.37	0.82	1.13	1.39	0.37	0.42	0.31	0.26	4.4	0.330
J	2510	0.09	0.41	0.72	0.82	0.09	0.32	0.31	0.10	2.3	0.269
K	1460	0.00	0.00	0.20	0.20	0.00	0.00	0.20	0.00	0.9	0.175
L	2120	0.00	0.00	0.17	0.17	0.00	0.00	0.17	0.00	0.8	0.080

<sup>a</sup> 1: Carboxyl group.

<sup>b</sup> 2: Carboxyl group that occurs as a lactone.

<sup>c</sup> 3: Phenolic hydroxyl group.

<sup>d</sup> 4: Carbonyl group that reacts with the carboxyl group 2 to form the lactone (or lactol).

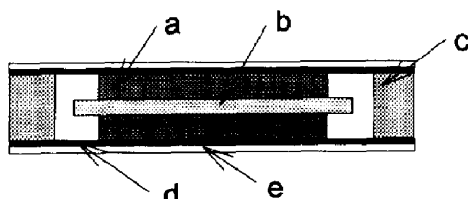


Fig. 2. Setup of electric double-layer capacitor: (a) activated carbon electrode; (b) separator; (c) gasket; (d) conductive film, and (e) current collecting plate.

the separator of non-woven cloth. The electrical conductive film used for this measurement was the same as that mentioned in Section 2.4. The polarizable electrode, composed of activated carbon, acetylene black as electrical conductive material and PTFE as binder, was pressed to the pellet (surface area: 6 cm<sup>2</sup>, thickness: about 1.2 mm). A 30 wt.% sulfuric acid solution was used as the electrolyte. The impedance of the resulting electric double-layer capacitor was measured by using an LCR meter (Kokuyo Electric, Model KC-535B). The capacitance of the electric double-layer capacitor was measured as follows. The capacitor was charged at 0.05 A/cm<sup>2</sup> constant-current density to 0.8 V, then discharged at 0.05 A/cm<sup>2</sup> constant-current density to 0.25 V. The capacitance was evaluated from the length of the discharge time to the final voltage. Under load-life testing, a 0.9 V constant voltage was applied to these capacitors at 60 °C. The changes in internal resistance, thickness and discharge capacity were measured for these capacitors.

### 3. Results and discussion

#### 3.1. Analysis of activated carbons

The physical properties of the activated carbons used are given in Table 2. The specific surface areas of the activated

carbon B and H, heat-treated at 1300 °C in hydrogen gas and the activated carbon E, heat-treated at 800 °C in nitrogen gas, became smaller than before treating, because the structure of the activated carbons shrunk and their pores closed during the heat treatment. Activated carbons with high oxygen content showed a high concentration of acidic surface functional groups. Activated carbons activated with KOH had a higher oxygen content than those activated with steam. Moreover, the acidic surface functional groups of the activated carbons B and H was almost removed by a heat treatment at 1300 °C in hydrogen gas and the oxygen content became 0.5 wt.% or less. The specific surface area of the activated carbon F, heat-treated at 350 °C in air, did not change, but its oxygen content increased.

#### 3.2. Measurement of rest potential

The relation between rest potential and oxygen content of the activated carbon is shown in Fig. 3. The rest potential of the activated carbon was proportional to the logarithm of the

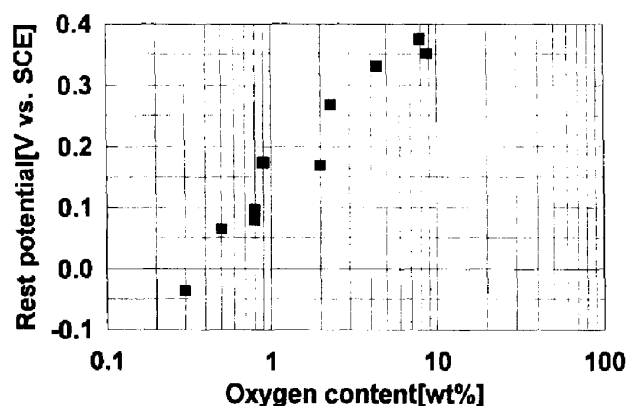


Fig. 3. Oxygen content vs. rest potential of activated carbon at room temperature.

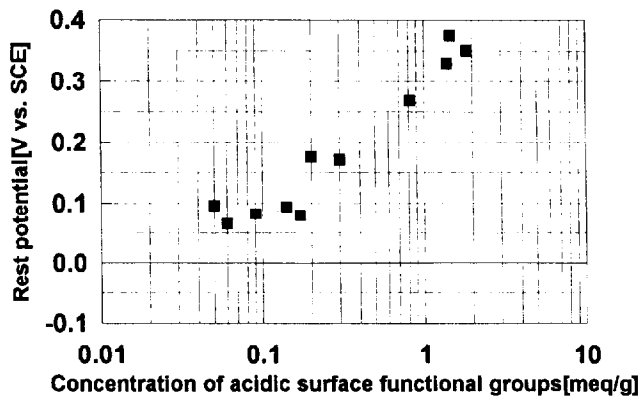


Fig. 4. Concentration of acidic surface functional groups vs. rest potential of activated carbon at room temperature.

oxygen content. It seemed that the oxygen content influences the rest potential of the activated carbons. The relation between the rest potential and the concentration of the acidic surface functional groups is shown in Fig. 4. The amount of the base of  $C_2H_5ONa$  adsorbed (see Boehm's method [10]) corresponds to the concentration of the acidic surface functional groups. Oxygen exists as a surface functional groups in activated carbons. The surface functional groups include acidic, neutral, and basic surface functional groups. The acidic surface functional groups influence the rest potential of activated carbons.

### 3.3. Electrochemical measurements

Although most of the electric double-layer capacitors with aqueous electrolyte solutions essentially operated in a 1.0 V d.c. range, the electrochemical experiments were carried out

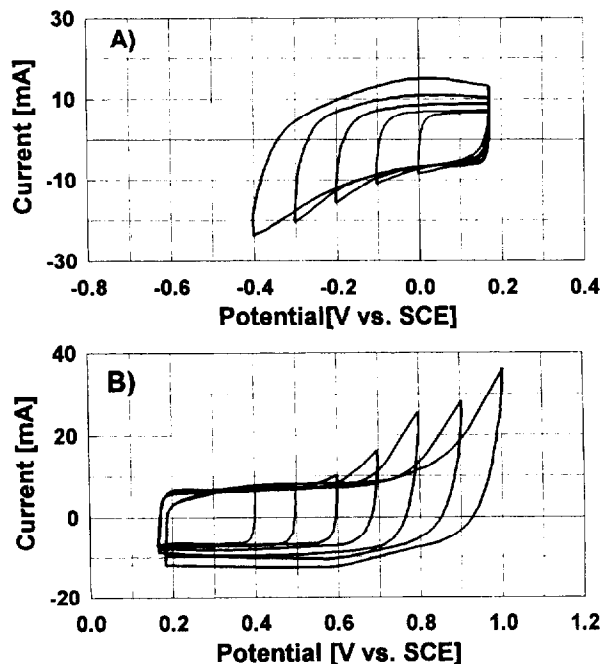


Fig. 5. Cyclic voltammogram of activated carbon A at room temperature, sweep rate = 1 mV/s; (a) cathodic polarization, and (b) anodic polarization.

from the rest potential to  $\pm 0.5$  V versus SCE for each electrode of the activated carbon. Triangular voltage-sweep cyclic voltammogram of the activated carbon A is given in Fig. 5. The faradaic current at each potential is shown in Figs. 6–9. The faradaic current is different from the peak current and the capacitive electric current. The residual current of each activated carbon is shown in Figs. 10–13. In the measurements of the residual current, the current value after 1 h at each potential was steady. In the range of this measurement, the conductive film used for the collecting electrode was electrochemically steady. The result of triangular volt-

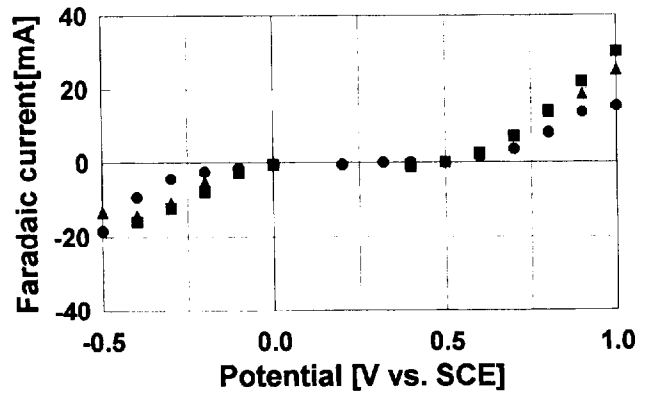


Fig. 6. Faradaic current vs. potential at room temperature: (■) activated carbon A; (●) activated carbon B, and (▲) activated carbon C.

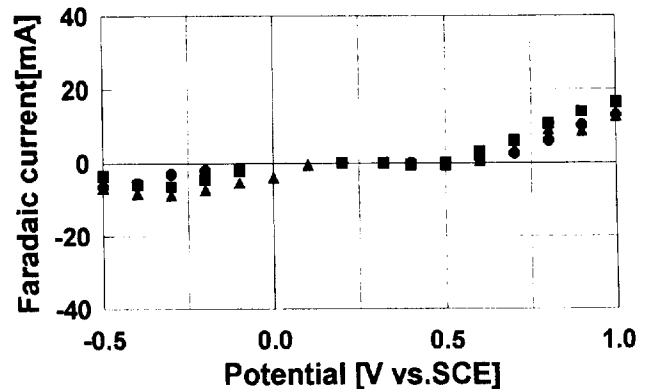


Fig. 7. Faradaic current vs. potential at room temperature: (■) activated carbon D; (●) activated carbon E, and (▲) activated carbon F.

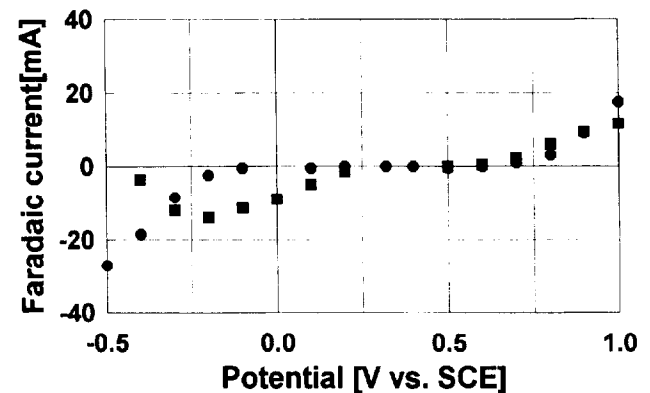


Fig. 8. Faradaic current vs. potential at room temperature: (■) activated carbon G, and (●) activated carbon H.

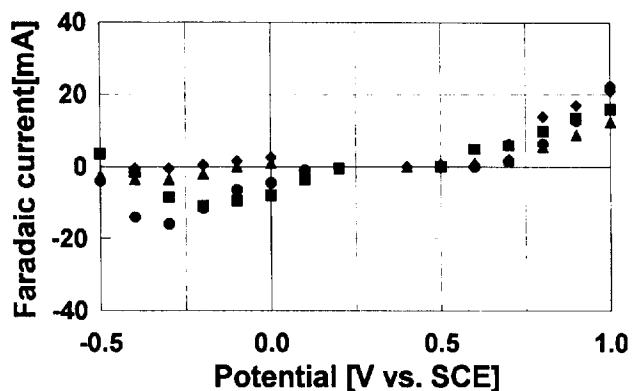


Fig. 9. Faradaic current vs. potential at room temperature: (■) activated carbon I; (▲) activated carbon J; (●) activated carbon K, and (◆) activated carbon L.

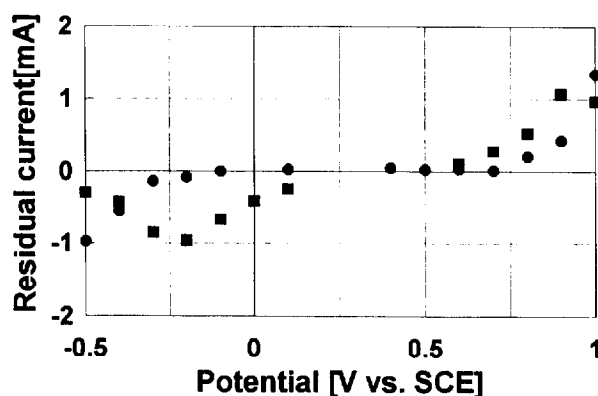


Fig. 12. Residual current of activated carbons at room temperature: (■) activated carbon G, and (●) activated carbon H.

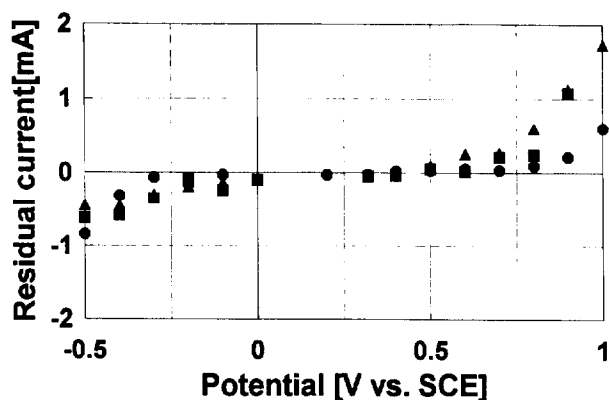


Fig. 10. Residual current of activated carbons at room temperature: (■) activated carbon A; (●) activated carbon B, and (▲) activated carbon C.

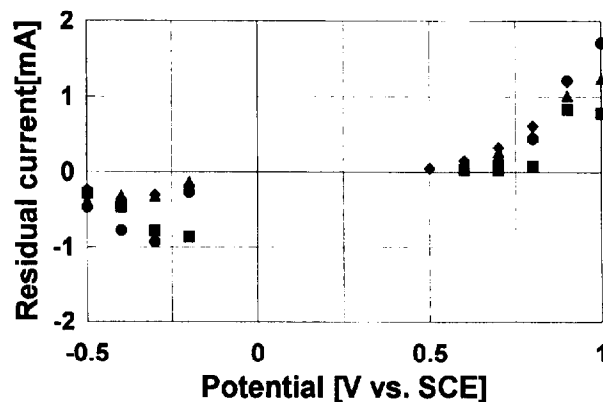


Fig. 13. Residual current of activated carbons at room temperature: (■) activated carbon I; (●) activated carbon J; (▲) activated carbon K, and (◆) activated carbon L.

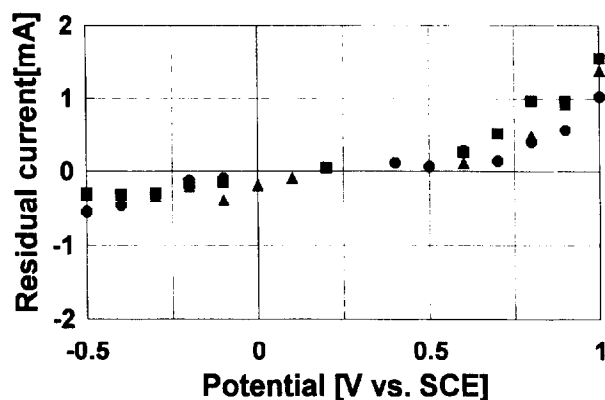


Fig. 11. Residual current of activated carbons at room temperature: (■) activated carbon D; (●) activated carbon E, and (▲) activated carbon F.

age-sweep cyclic voltammetry is the same as that of the residual current measurement. In the latter measurements gas evolution was observed at the electrode surface of the activated carbons, but was not observed in the triangular voltage-sweep cyclic voltammetry, because the period maintained at fixed potential is shorter.

Under anodic polarization, applied to the activated carbons with high oxygen content, gas evolution was observed at the electrode surface with the activated carbons F, G, I or J at 0.8 V versus SCE, and the activated carbons A, C, D, E, K or L

at 0.9 V versus SCE. It was not observed at the surface of the activated carbons B and H with a low oxygen content. The evolution gas was gathered and analyzed by gas chromatography. Carbon monoxide and carbon dioxide were detected as the main components. The reaction in the acidic surface functional groups might take place because more bubbles were observed at the electrode surface of the activated carbons with high concentration of acidic surface functional groups.

On the other hand, under cathodic polarization applied to the activated carbons F, G, I and J with high oxygen content, the peak was observed at about  $-0.2$  V versus SCE, shown in Figs. 7–9. However, in the residual current measurements bubbles were not observed at the electrode surface of these activated carbons. In the other activated carbons, this peak was not observed, but the increase in the residual current started at about  $-0.3$  V versus SCE, and the generation of gas started at  $-0.5$  V versus SCE at the electrode surface of the activated carbons. Mainly hydrogen was detected by means of gas chromatography. It is therefore thought that the electric decomposition of water occurs. In the activated carbons with low oxygen content, many bubbles were observed under cathodic polarization. A similar result was obtained concerning the concentration of the acidic surface functional groups of the activated carbon. The oxygen content and the

acidic surface functional groups of the activated carbon influenced not only the rest potential of the activated carbon but also its electrochemical characteristics. If the electric double-layer capacitor is made from activated carbon with high oxygen content, because the rest potential of the activated carbon is high, the potential of the positive electrode is likely to enter the region where the gas might be generated when the capacitor is charged. Therefore, the reliability of the electric double-layer capacitor might deteriorate.

### 3.4. Load-life test of electric double-layer capacitors

The electric double-layer capacitors were made from the activated carbons A or B. Load-life tests of these electric double-layer capacitors were carried out at 60 °C. The results are shown in Fig. 14. The changes in internal resistance and capacitance of the capacitor were shown as their ratio referenced to the initial capacitance prior to the load-life tests. The thickness of the capacitor was also related to the magnitude of this change. The thickness and internal resistance of the electric double-layer capacitor composed of the activated carbon A increased and its capacitance decreased immediately after starting the test. The change of thickness, internal resistance and capacity of the electric double-layer capacitor composed of the activated carbon B were small during the test.

Residual currents of the activated carbons A and B used for load-life test at 60 °C are given in Fig. 15. The residual current at 60 °C was larger than that at 25 °C. Under anodic

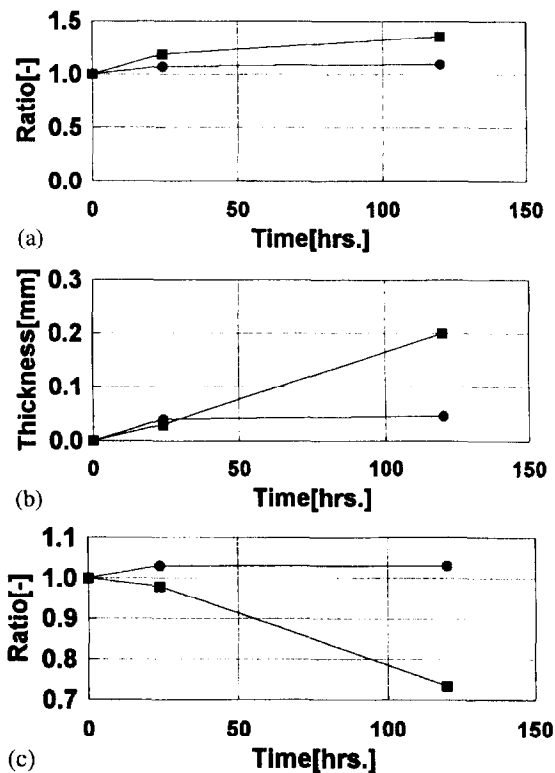


Fig. 14. Load-life tests at 60 °C: (a) ratio of initial resistance; (b) thickness change in mm; (c) ratio of initial capacitance. (■) activated carbon A, and (●) activated carbon B.

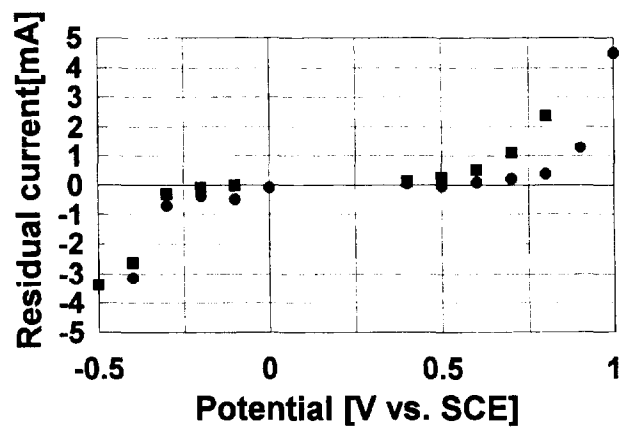


Fig. 15. Residual current of activated carbons A and B at 60 °C: (■) activated carbon A, and (●) activated carbon B.

polarization, the residual current of the activated carbon B with low oxygen content was smaller than that of the activated carbon A with high oxygen content. However, gas evolution was observed at the electrode surface of the activated carbon A at 0.6 V versus SCE and B at 0.8 V versus SCE. The potential at which bubbles were observed at 60 °C was lower than that at 25 °C.

Under cathodic polarization applied to the activated carbons A and B, the residual current began to increase at -0.3 V versus SCE and bubbles were observed at the electrode surface at -0.4 V versus SCE. Therefore, it is thought that activated carbon A is steady in the range from 0.6 to -0.4 V versus SCE and the activated carbon B is steady in the range from 0.8 to -0.4 V versus SCE.

Since the rest potential of the activated carbon A is 0.26 V versus SCE at 60 °C, the positive and negative electrodes of the electric double-layer capacitor composed of the activated carbon A operate from 0.26 to 0.71 V versus SCE, and from 0.26 to -0.19 V versus SCE, respectively, when the capacitor is operated from 0 to 0.9 V. As this range is included in the region where the gas might be generated, the characteristics of electric double-layer capacitor might be influenced. On the other hand, since the rest potential of the activated carbon B is 0.15 V versus SCE at 60 °C, the positive and negative electrodes of the electric double-layer capacitor composed of the activated carbon B operate from 0.15 to 0.60 V versus SCE, and from 0.15 to -0.30 V versus SCE, respectively, when the capacitor is operated from 0 to 0.9 V. Because the generation of gas does not occur, even if voltage is added to the electric double-layer capacitor, its characteristic will be steady. These results corresponded to those of load-life tests of electric double-layer capacitors.

## 4. Conclusions

The rest potential of activated carbons was proportional to the logarithm of the oxygen content or concentration of the acidic surface functional groups of the activated carbon. The rest potential was not influenced by raw materials or manu-

facturing methods. It was determined by the surface conditions of the activated carbon. The oxygen content and the concentration of acidic surface functional groups of activated carbons influenced the electrochemical characteristics of the activated carbon.

Under anodic polarization, the potential at which bubbles were observed at the electrode surface of the activated carbons was influenced by the oxygen content. The main components of the gas were carbon monoxide and carbon dioxide. The activated carbons with high concentration of acidic surface functional groups generated more gas, so that the reaction concerned in the acidic surface functional groups might take place. Under cathodic polarization for the activated carbons with high oxygen content, the peak was observed at approximately  $-0.2$  V versus SCE in cyclic voltammetry, but gas evolution was not observed at the electrode in the residual current measurements. In the other activated carbons, the increase in current started at approximately  $-0.3$  V versus SCE and the generation of gas at the electrode started at  $-0.5$  V versus SCE. The prime element of the gas is hydrogen and it is thought that electrolytic decomposition of water occurs. The results of load-life tests of the electric double-layer capacitors corresponded to those of the electrochemical

measurements. Because the rest potential of activated carbons with high oxygen content or high concentration of acidic surface functional groups is high, the potential of the electrodes reaches a region where the generation of the gas might occur when the voltage is added to the cell. Therefore, the load life of electric double-layer capacitor is diminished.

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