Modification of the oxygen-containing functional group on activated carbon fiber in electrodes of an electric double-layer capacitor

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Abstract

In order to discuss quantitatively the effect of functional groups of activated carbon fibers (ACFs) on electric double-layer characteristics, ACFs with various amounts of functional groups were prepared from the same ACF by redox methods. The amount of functional groups of ACFs was compared between the method by back titration and by X-ray photoelectron spectroscopy (XPS). In the case of the aqueous electrolyte, the electric capacity depended more on oxygen functional groups than on BET surface area. At the greatest 30% of increase in electric capacity was obtained by using ACFs with different amount of oxygen functional groups between the positive electrode and the negative one. It was considered that a larger number of functional group promotes not only the wettability of electrodes but also the negative charge of electrodes leading to an increase in capacity. On the other hand, in the case of the organic electrolyte, pore structure seemed to be a more dominant factor than functional group. Also, the characteristics of the electrodes after 30,000-cycle charge–discharge were determined to confirm the reliability in an extended cycle operation. A significant increase in phenolic hydroxyl group was confirmed on the positive electrode.

1. Introduction

An electric double-layer capacitor (EDLC) is an energy-storing device that does not cause chemical reactions on the surface of an electrodes and that uses the physical ad-desorption of ions. It therefore has numerous desirable characteristics such as rapid charge/discharge and a long cycle life. EDLCs have recently been utilized as a power source for memory backup and supplementarily for hybrid cars. There has also been research regarding the use of EDLCs for power storage [1–3]. However, EDLCs have the drawback of low energy density compared to secondary batteries [1]. Consequently, there have been numerous studies of new materials such as carbon nano-tubes (CNT) [1–6], gel electrodes [7], and redox capacitors [8]. In recent years, many studies of electrodes have been reported.

EDLC electrodes generally use porous carbon materials. It is well known that the electric capacity of an electrode is affected by its physical and chemical properties [9–17], though it may also be related to differences in the nature of electrolytes divided into aqueous and organic solutions.

With regards to chemical properties, the effects of oxygen-containing functional groups (denoted as OCFG) on electric characteristics have been investigated qualitatively in terms of temperature-programmed desorption (TPD) [16–18]; however, there have been few quantitative investigations described in previous reports [9,10]. The authors [19] have researched the effects of OCFGs on capacitor performance using some aqueous electrolytes. In our investigation, a fractional determination was carried out because the surface of activated carbon has many types of OCFGs such as phenolic hydroxyl groups and carboxyl groups. The correlation between respective OCFGs and capacitance has been discussed [20]. However, we have not previously been able to determine the most effective OCFG for increasing capacitance. Consequently, in the present report, the effects of OCFGs on capacitance will be discussed quantitatively in

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terms of X-ray photoelectron spectroscopy (XPS) based on the use of activated carbon fibers (ACFs) whose OCFG content was controlled arbitrarily by methods of oxidation or reduction. We also attempt to identify the most effective OCFG for capacitance. The difference in the effects of OCFG on capacitance between aqueous and organic electrolytes will be discussed, and the experimental results for powdery activated carbon (PAC) are included for comparison.

With regard to physical properties, there have been numerous reports regarding the effects of pore structure on capacitor performance. Some investigations [15,16] have found that the appearance of capacitance is generally affected by mesopores with a pore diameter of more than 2 nm. There have therefore been numerous studies of the development of carbon electrodes, including the production followed by the defluorination of polytetrafluoro-ethylene (PTFE) with alkali metals [17], the activation to prepare mesoporous electrode materials by loading metals on a carbon precursor [21,22], and the production of porous carbon that has a uniform pore size, using porous silica templates [23,24]. The capacitance discussed in many reports is related to the hybrid adsorption characteristics of cations and anions. It is likely that the most effective pore size differs between cations and anions, as the cations (Li^+) in organic solvent (PC) are 1.5 times larger than the anions (ClO_4^-) [1,25]. Many researchers such as Shiraishi et al. [22] have reported the respective ion (cation and anion) capacitance separately for organic electrolytes. It is expected that in an aqueous system, which has low viscosity, one can obtain a high capacitance at a dense current and a low inner resistance due to the ease of ion transfer. Furthermore, aqueous systems are preferable with regard to safety and price because they are affected very little by moisture in the air. Consequently, in the present study, the relationship between the cation/anion capacitance and pore structure of electrodes was investigated, using a three-electrode cell for both aqueous and organic systems.

2. Experimental

2.1. Electrode material

A commercial activated carbon fiber (ACF, denoted as F) produced from phenol resin was used in this study. This ACF was oxidized by stirring in $0.1 \, mol \, l^{-1}$ of HNO_3 solution for 1 h (F-Ox) or by applying a dc voltage of 3 V in $0.1 \, mol \, l^{-1}$ of HNO_3 (denoted as F-EO) This method may prepare ACFs that have various contents of OCFGs with sustaining pore structures such as surface area and pore size distribution. On the other hand, the reduction of ACF was carried out in a hydrogen flow ($10 \, cm^3 \, min^{-1}$) at a temperature of 1173 K for 1 h (denoted as F-Re).

In this research, a powdery activated carbon prepared from petroleum cokes (PAC, denoted as P) was also used. This PAC was heat-treated in a nitrogen flow at 873 and 1173 K for 1 h (P-873HT and P-1173HT, respectively), and also treated in a hydrogen flow at 873 K for 1 h (P-873Re).

2.2. Characterization of ACF

For the respective ACF and PAC, the nitrogen adsorption isotherm at 77 K was measured using an automatic gas adsorption apparatus (ASAP 2010, Shimadzu—Micromeritics). The specific surface area, pore volume, and pore size distribution were analyzed by the BET, DR, and *t*-plot methods, respectively. The OCFG content was determined fractionally by back titration of neutralization and by using an X-ray photoelectron spectroscopic analyzer (JPS-9000MX, JEOL).

2.3. Measurement of capacitance

Electrical capacitance was measured using a charge–discharge apparatus (HJ-201B, Hokuto Denko) under the following conditions; the constant current density was $2.4 \, mA \, cm^{-2}$ on charge, and several densities in a range of 0.8–$24 \, mA \, cm^{-2}$ on discharge. The voltage was varied in a range of 0.2–0.8 V for aqueous electrolytes and of 1.2–2.4 V for organic electrolytes. The capacitance, represented in terms of the unit weight of ACF, was denoted as the average value of the 30-cycle measurement at a constant current. This research used a two-electrode cell consisting of a 1 cm × 1 cm ACF for both positive and negative electrodes with a weight of ca. 0.04 g. For the aqueous electrolyte, $1 \, mol \, l^{-1} \, H_2SO_4$ solution was applied, while $0.5 \, mol \, l^{-1} \, LiClO_4/PC$ solution was used for the organic electrolyte.

3. Results and discussion

3.1. Pore structures

Table 1 shows the characteristics of ACFs (F) prior to and after the modifications and also of powdery high-surface area AC (P). The OCFG content was determined by the back neutralization method. There are subtle differences in the specific surface areas of treated and untreated ACFs in a range of 1400–$1700 \, m^2 \, g^{-1}$. F-EO, oxidized under a severe condition, has a surface area and micropore volume approximately 20% less than the original ACF. This difference might be due to the pore closure caused by the OCFG formed. The ACF used in this research consisted primarily of micropores with a pore diameter of less than 2 nm. On the other hand, AC has micropore and mesopores volumes 1.6 and 10 times greater than ACF. AC also has a wide range of pore size distribution (diameters of 0.8–1.4 nm) as shown in Fig. 1.

3.2. Oxygen-containing functional groups

3.2.1. Titration results

The oxidation of ACF increased the number of OCFGs. F-Ox, liquid-oxidized ACF, has approximately five times as many OCFGs as the original, and F-EO, electrically oxidized ACF, approximately 10 times as many OCFGs. In the present study, OCFGs were determined by fractionating into phenolic and carboxyl groups. The original ACF and F-Ox have ca. 70% phenolic hydroxyl groups out of the total OCFGs, while F-EO have ca.

Table 1
Characteristics of the sample activated carbons used in this research

Samples	S_{BET} (m^2 g^{-1})	V_{micro} (ml g^{-1})	V_{meso} (ml g^{-1})	Total acidity[a] (mmol g^{-1})	Acidity (%)	
					COOH	OH
F	1670	0.64	0.037	0.19	31.6	68.4
F-Ox	1550	0.62	0.034	0.79	13.9	86.1
F-EO	1400	0.55	0.029	1.76	56.2	43.8
F-Re	1670	0.66	0.045	0.10	0.00	100
P	2280	1.05	0.38	1.30	35.4	64.6
P-873HT	2280	1.08	0.40	0.89	22.5	77.5
P-1173HT	2060	0.98	0.37	0.47	0.00	100
P-873Re	2400	1.16	0.43	0.53	0.00	100

[a] Back titration method.

60% carboxyl groups. This result might be consistent with the mechanism of OCFG formation that has been already proposed [26,27]. That is, a mild oxidation environment such as a F-Ox preparation might form phenolic hydroxyl groups. In contrast, a severe oxidation environment such as that of electrical oxidation might form carboxyl groups. Taking into account the report [27] that electrical oxidation primarily produces quinone groups, F-EO might include the quinone group among its carboxyl groups.

3.2.2. XPS analysis

The above titration method to determine the OCFG content is controlled by the wettability between the solution and the ACF surface. Another method, XPS, was used to compare the fractional OCFG content with the titration method. The C1 spectra obtained in terms of a narrow scan mode were separated [28–30] into the respective peaks of bonds attributed to OCFGs. Table 2 shows the fractions of the respective bonds, assuming the hydrophobic groups, C—C or C—H, to be 100. As in the case of the titration results, F-Ox has 65% more C—O bonds derived from the phenolic hydroxyl group; and F-EO has 80% more O—C=O bonds derived from the carboxyl group. Furthermore, Fig. 2 shows the ratio of the fraction of phenolic hydroxyl groups to that of total OCFG as determined by both methods in order to check the consistency. C-EO exhibited similar values between both analyses, probably because XPS primarily detects OCFGs on the external surface of ACF, mostly in the vicinity of the pore
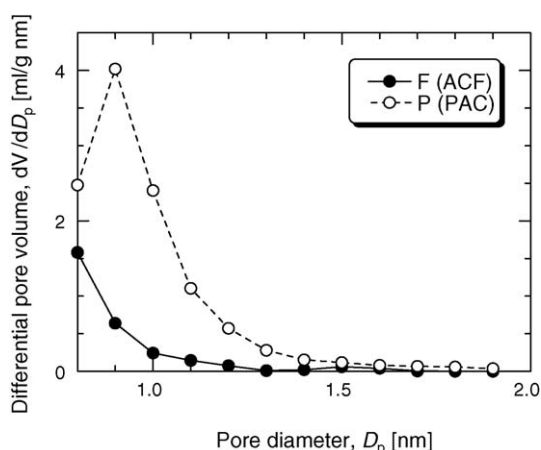
Table 2
XPS analysis of C 1s spectra of ACF (C)

ACF	C—C (284.7 eV)	C—O (286.3 eV)	C=O (287.5 eV)	O—C=O (289.0 eV)
F	100.0	15.2	10.1	5.6
F-Ox	100.0	25.2	11.7	6.2
F-EO	100.0	22.6	15.9	10.1
F-Re	100.0	11.5	7.6	4.9

X-ray source: Mg Kα.

entrances [29,31]. This result might suggest that ACF oxidation treatment produces new OCFGs on the external surface. The carboxyl group of F-Re was not detected by the titration method, while it was meagerly identified by XPS. It is possible that this analysis had a problem with drawing the base lines of the XPS, which should be rectified in the future.

3.3. Effects of OCFGs on capacitance

3.3.1. Aqueous solution

This research measured, in the aqueous electrolytes, the capacitance of ACF and PAC of which the OCFG content was controlled. Fig. 3 shows the relationship between capacitance and OCFG. The capacitances in this research were defined as the slope of the potential from the beginning to the end of discharge, except for the IR drop. Also, C_0 was assumed as the value at the current density of 0 mA cm^{-2} to which the capacitance–current density curve was extrapolated. This value was regarded as

Fig. 1. Pore size distribution of ACF (F) and PAC (P) analyzed by *t*-plot method.
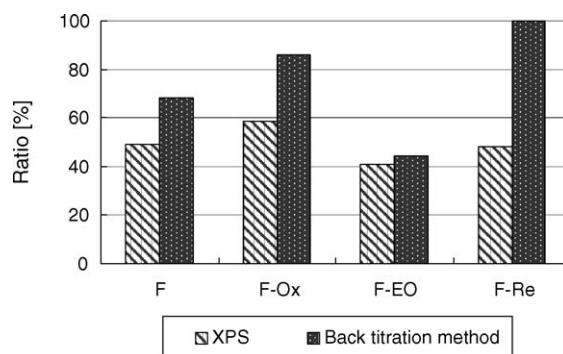

Fig. 2. Comparison of the ratio of phenolic hydroxyl functional groups between XPS and back titration method.
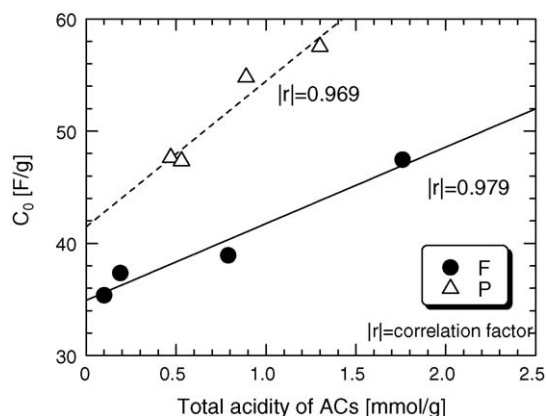
Fig. 3. Effect of the oxygen functional group on capacitance (electrolyte: $1.0 \, mol \, l^{-1} \, H_2SO_4$).

the maximum capacitance of the electrodes, since one could neglect the effects of pore structures, the chemical properties of the ACF electrodes, and the characteristics of electrolyte ions on the ion diffusion. The capacitances of both ACF and PAC increased with the OCFG concentrations, probably associated with the hydrophilicity of the electrode, as previously discussed [19]. Fig. 4 shows the relation between capacitance and OCFGs determined by the titration method, to investigate which OCFG affects capacitance more significantly. It seems that both phenolic hydroxyl and carboxyl groups correlate with the capacitances. Of these OCFGs, however, it appears that the phenolic hydroxyl group has a greater effect on the capacitance, as the increment ratio seems to be larger for the phenolic hydroxyl group (20% increase in capacitance with a six-fold increase in this functional group). To confirm this result, the F-EO carboxyl group, which produced the highest capacitance, was removed by heat treatment at a temperature of 673 K. The heat treatment decreased the number of carboxyl groups by approximately half without any removal of the phenolic hydroxyl groups. However, the treatment did not change the capacitance, as shown in Fig. 5; that is, it was confirmed that the carboxyl groups had no effect on the development of capacitance. To explain this result, Fig. 6 shows the cyclic voltamogram (CV) of F-Ox and F-EO. A clear peak
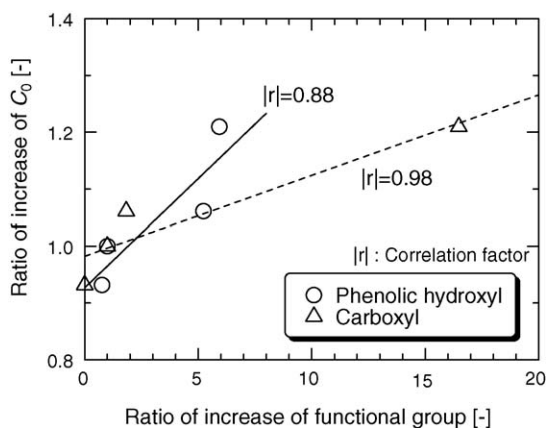
of the Faraday current can be seen for F-EO, which has many carboxyl groups. This result suggests that the carboxyl group has a strong polarity that causes a leak current due to a catalytic effect, as follows.

Catalysis of the carboxyl group
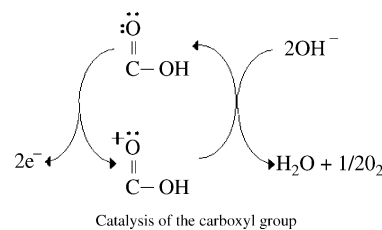
Other factors are probable; that is, a carboxyl group can cause steric hindrance due to its large molecular structure. The Faraday current, which causes a pseudo-capacitance, increases the apparent capacitance [10,16]. Thus, it might be concluded that the carboxyl group has a significant influence of steric hindrance on the development of capacitance. On the other hand, it is predicted that the phenolic hydroxyl group, which has a weaker polarity on OCFGs than the carboxyl group, might produce a charge bias, but no catalytic effect, thus enhancing the formation of an electric double-layer (EDL) according to the following equation:

$$C-OH^{\delta-} + H^+ \Leftrightarrow C-OH // H^+$$

Fig. 5. Comparison of the capacitance between F-EO and heat-treated F-EO (electrolyte: $1.0 \, mol \, l^{-1} \, H_2SO_4$).

Fig. 4. Relationship between the functional group and capacitance (electrolyte: $1.0 \, mol \, l^{-1} \, H_2SO_4$). Ratio of increase = measured value of treated ACF/measured value of original.

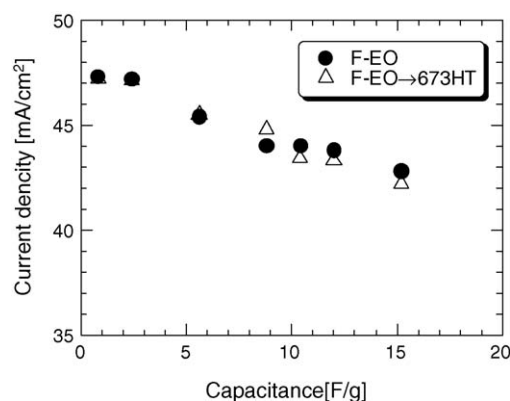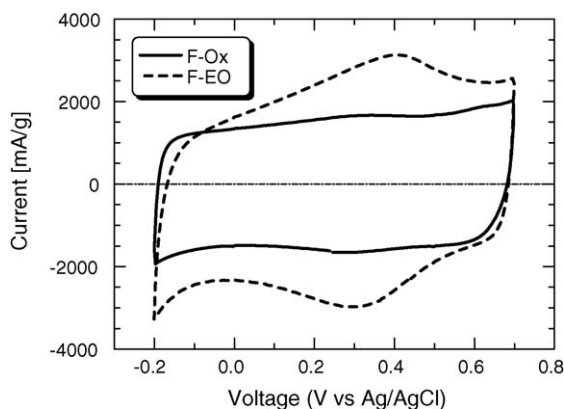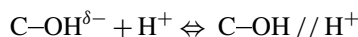Fig. 6. Comparison of the cyclic voltammograms of F-Ox and F-EO electrodes at $10 \, mV \, s^{-1}$.
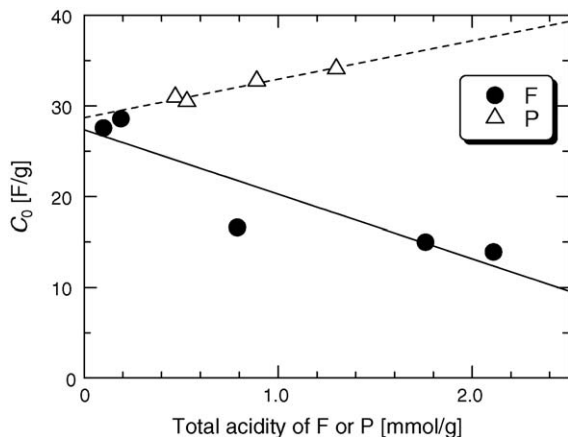
Fig. 7. Effect of the oxygen functional group on capacitance (electrolyte: $0.5\,mol\,l^{-1}$ LiClO$_4$/PC).

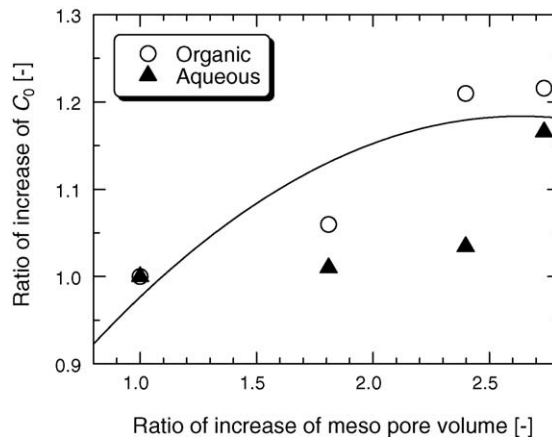
Fig. 8. Relationship between the mesopore volume and capacitance. Ratio of increase = measured value of treated ACs/measured value of original.

where H$^+$ indicates proton and the symbol "//" the adsorbed state by EDL.

3.3.2. Organic electrolyte

Fig. 7 shows the effects of OCFGs on capacitance for the organic electrolyte. It can be considered that the wettability of the electrode decreases, contrary to aqueous solution; therefore, as predicted, the capacitance of the ACFs decreases with the OCFG concentration. However, the PACs gave almost consistent (increased slightly) capacitance, irrespective of their OCFG concentrations. This result might be attributed to PACs having an approximately 10 times greater mesopore volume than ACFs, thus resulting in no significant steric hindrance of OCFGs. It is therefore suggested that mesopores are the major determinant of EDL capacitance for organic electrolytes. The capacitance of PAC, which tends to increase slightly with the OCFG concentration, is probably associated an enhancement of electrode charge due to the polarity of the OCFGs.

3.4. Effect of pore structure on capacitance

3.4.1. Two-electrode cell

In the previous section, it was shown that pore structure is more important than OCFGs to the development of capacitance. In this section, the effects of an electrode's pore structure on capacitance for an organic electrolyte are discussed. Palm shell-based activated carbon was burned at a temperature of 450 °C up to four different burn-off percentages. Fig. 8 shows the correlation between capacitance and mesopore volume. The capacitance was found to increase with the mesopore volume, by 20% at the maximum, demonstrating that mesopores seem to be the major determinant of capacitance for an organic electrolyte. However, greater than 2.5-fold increases in mesopore volume $(0.20\,ml\,g^{-1})$ did not further increase the capacitance, probably due to the excessive pore enlargement beyond the necessity to diffuse ions. The average pore diameter is 2.6 nm, while the size of solvated ions in PC is reported to be 0.52 nm for Li$^+$ and 0.82 nm for ClO$_4^-$, respectively [1,16]. Therefore, it might be suggested that the optimum pore size to diffuse ions is three to

five times larger than the ion size. On the other hand, the capacitance, which did not increase with mesopore volume, seems to be controlled by the micropores, possibly due to the significant difference in the solvated ion size between aqueous and organic electrolytes.

3.4.2. Three-electrode cell

The above data, which demonstrated that the capacitance of the organic electrolyte is strongly determined by the mesopores, while that of aqueous electrolyte is determined by the micropores, were, however, obtained for a two-electrode cell. Accordingly, the capacitance discussed above indicates the hybrid adsorption characteristics of cations and anions. It is likely that the most effective pore size differs between cations and anions since the cation (Li$^+$) in organic solvent (PC) is 1.5 times larger than the anion (ClO$_4^-$). We measured the respective capacitance in relation to the adsorption of cations or anions using a three-electrode cell. Fig. 9(a) plots the relationship between the respective capacitance and the increment ratio of mesopore volume with the use of an organic electrolyte. A smaller mesopore volume caused an ion-sieving effect on cations with larger pore size and produced a difference in capacitance of approximately $20\,F\,g^{-1}$. However, the increase in mesopore volume, probably related to an enlarged pore size, allowed a reduction in the difference in capacitance between cations and anions. A similar relationship for an aqueous system (H$_2$SO$_4$) is plotted in Fig. 9(b). Although the cation size is different from that of anions in H$_2$SO$_4$ solution, little difference in the respective ion capacitance occurred. This result might be attributed to the lack of an ion-sieving effect, as the solvated ion size in the aqueous system is half that in the organic system.

3.5. Extended charge–discharge cycle operation

EDLC, which stores the electricity only in terms of the physical transport phenomena of electrolyte ions onto electrodes, can suppress the degradation of the electrodes with charge–discharge. It is therefore believed that the charge–discharge operation can be repeated many more times

Table 3
Change in charactaristics of ACF in 30,000 cycles

	XPS				S_{BET} (m^2 g^{-1})	Pore volume (ml g)$^{-1}$	
	C—C	C—O	C=O	O—C=O		Micro	Meso
0 Cycle	100.0	22.6	15.9	10.1	1400	0.55	0.029
30,000 Cycles (+)	100.0	56.0	19.2	12.5	1270	0.49	0.016
30,000 Cycles (−)	100.0	35.5	16.7	16.7	1310	0.5	0.02

compared to a secondary cell [1]. With the use of an aqueous electrolyte, the modification of the electrode to F-EO could produce the maximum capacitance. Consequently, 30,000 cycles of operation were carried to investigate the reliability of the capacitance even at an extended charge–discharge. As shown in Fig. 10, the capacitance of this electrode decreased by 25% at 30,000 cycles of charge–discharge, which might be applicable to a practical operation. Table 3 represents the change in XPS analysis and the pore structure of the electrodes after 30,000 cycles of charge–discharge. It was demonstrated from XPS that the ratio of C 1s to O 1s increased by 1.4 times after the charge–discharge. An increase in the number of C—O bonds attributed to the phenolic hydroxyl groups on the electrodes after the operation was observed in terms of a narrow scan analysis of the C1 peak. The ratio of phenolic hydroxyl groups to C—C (C—H) bonds, compared to that prior to charge–discharge, increased by 1.6 times for the negative electrode and 2.5 times for the positive electrode. The micropore volume of the positive electrode decreased by 10%. These results might suggest that the extended charge–discharge cycle operation caused oxida-
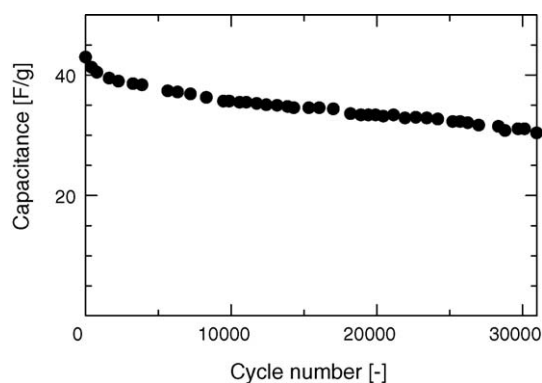

Fig. 10. Change in the capacitance according to the cycle number (elecyrolyte: 1 mol l^{-1} H$_2$SO$_4$).

tion on the positive electrode, and consequently, the capacitance decreased with the cycle number due to the increase in the number of OCFGs on the positive electrode.

4. Conclusion

(1) It was confirmed in terms of both titration and the XPS method that a mild oxidation of ACF increased the number of phenolic hydroxyl groups and caused a severe oxidation carboxyl group mainly.
(2) In the case of an aqueous electrolyte, the carboxyl group was found to be more effective for increasing capacitance. On the other hand, for organic solution, OCFGs on ACF with primarily micropores causes a degradation of capacitance, whereas OCFGs on electrodes with a broad pore size distribution such as a high-surface area activated carbon have few effects on capacitance.
(3) An extended charge–discharge cycle causes oxidation on the positive electrode to form phenolic groups, which decreases capacitance by ca. 25% after 30,000 cycles.

Acknowledgement

Fig. 9. Correlation between cation and anion adsorption capacitance. Elecyrolyte: (a) 0.5 mol l^{-1} LiClO$_4$/PC and (b) 1.0 mol l^{-1} H$_2$SO$_4$.

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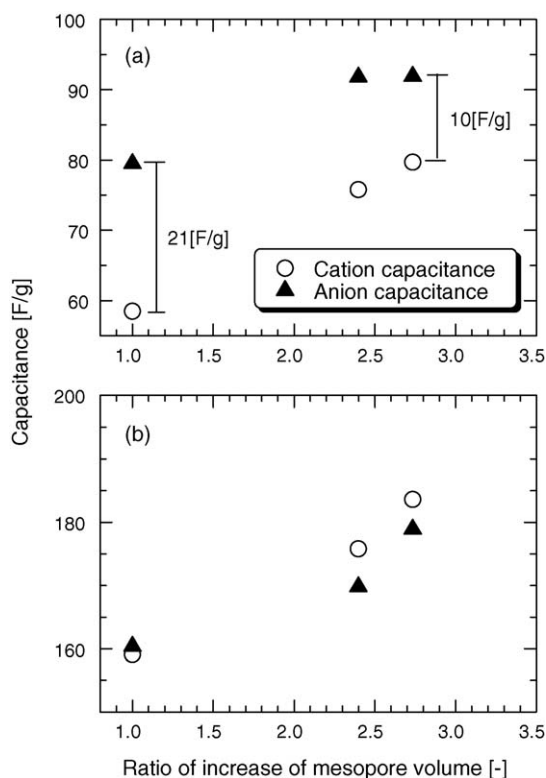[3] A. Yoshida, Denki Kagaku 66 (1998) 849–884 (in Japanese).

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