Modified carbon materials for high-rate EDLCs application

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Abstract

Porous carbon materials, such as activated carbon and activated carbon aerogel, were modified chemically by using a surfactant sodium oleate to improve their specific capacity for high-rate electrochemical double layer capacitors (EDLCs) application. Main impacting factors have been examined for surface modification of activated carbon. Specific capacity can be improved significantly by the surface modification. The enhancement in specific capacity is mainly attributable to improvement in wettability of carbon materials, resulting in a higher usable surface area and a smaller internal resistance. The effects from surface modification become more marked at higher discharge rates, and a much higher energy density can be achieved for the modified carbon materials. In addition, the modified carbon materials possess comparable cycle stability to the original carbon.
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1. Introduction

Activated carbons and carbon aerogels are promising electrode materials for EDLCs because of their relatively low cost and high specific surface area [1–6]. However, specific capacitance obtained from carbon materials especially activated carbon is much lower than that expected. The lower capacitance is mainly attributed to lower useable surface area partially resulting from poor wettability of electrode material. To improve wettability and capacitance performance of carbon materials, chemical surface modification in nitric acid solutions have been conducted by some authors [7–10]. It was reported that capacitance performance of carbon materials in aqueous solutions could be improved markedly due to introduction of hydrophilic functional groups onto the carbon material by surface treatment. However, no any positive effect has been observed in an organic electrolyte solution

from surface modification of carbons with nitric acid. To improve specific capacity of carbon materials in organic electrolyte solutions a novel surface modification approach using sodium oleate surfactant was investigated in this study. By attachment of hydrophobic functional groups to carbon surface, an improvement in wettability of the carbon materials to organic electrolyte solution and, accordingly an improvement in capacity of EDLC, are expected.

2. Experimental

2.1. Preparation of carbon electrodes

Activated carbon (Norit, "SX plus") was commercially available with a specific surface area of ca. 826 $m^2 g^{-1}$.

Carbon aerogel was derived from pyrolysis of a resorcinol-formaldehyde (RF) gel according to a method proposed by Pekala [11]. Upon preparation of a RF gel, the mass percentage of the reactants in solution was set at RF = 20% and the molar ratio of resorcinol (R) to catalyst (C) was set at $R/C = 1500$. NaHCO$_3$ was used as the catalyst for a fine pore structure and a high specific surface area [12]. The

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molar ratio of formaldehyde to resorcinol was held constant at 2.

After weighing out the required amounts of each component, the components were combined in a glass tube and the resulting solution briefly stirred. To avoid sedimentation of RF polymers in the solution, the initial pH of RF solution was adjusted to ca. 7 by addition of a few drops of 1 M NaOH solution. The RF solution was treated with a standard gelation/aging cycle $t_1/t_2/t_3$ of 1/1/1 (where t_{1-3} denote the days at 25, 50 and 90 °C, respectively). The resulting RF gel was then removed from the glass tube, wrapped with a piece of cheesecloth and tightened with nylon twine against cracking during the solvent exchange steps. The wrapped gel was suspended in an agitated bath of 0.125 wt.% trifluoroacetic acid at 45 °C for 3 days to stop the poly-condensation process and to extend the cross-linking between the resorcinol and formaldehyde in the gel. After that, the RF gel was treated with pure acetone in an agitated bath for 4 days at the same temperature to replace the trifluoroacetic acid solution with acetone as the pore liquid. The acetone bath was exchanged daily to remove the residual trifluoroacetic acid and water. The acetone-filled RF gel was then dried at 80 °C for an hour. Carbonization was carried out in a N_2 flow in a tube furnace. The heating profile was as follows: temperature was raised to 250 °C at a heating rate of 2 °C min^{-1}, and then held for 4 h. After that, the temperature was raised to 1000 °C and held for 4 h.

Activated carbon aerogel was obtained by carbonization of the dried RF gel under a CO_2 flow at 1000 °C for 4 h. The heating profile was the same as that for preparation of carbon aerogel.

Surface modification of carbonaceous materials was carried out as follows. An amount of 1 g of carbon were soaked by 10 ml of sodium oleate aqueous solution and shaken for some time at 25 °C. Filtration was conducted under a suction condition. The resulting carbon slurry was dried at 100 °C in an inert atmosphere for 24 h. Concentration of the surfactant before and after the treatment was characterized by total organic carbon (TOC) analysis (TOC-V$_{CPN}$, Shimadzu Corp.). The modified carbon was characterized by Fourier transform infrared (FT-IR) spectrum to ascertain the attachment of surfactant species, which was recorded on a FT-IR spectrometer (FT-IR-6200, PS-4000, JASCO). Each of the IR spectra was the average of 32 scans at a speed of 2 s per scan. The resolution of the spectrometer was set to 4 cm^{-1}.

Surface area and pore-size distribution of various carbonaceous materials were calculated from nitrogen adsorption isotherms at 77 K (Micrometrics ASAP2010) using the Brunauer, Emmett and Teller (BET), and Barrett, Joyner and Halenda (BJH) methods, respectively.

The preparation of carbon electrodes was as follows. Carbon (active material), graphite powder (conductivity enhancing material) and polytetrafluoroethylene (binder) were mixed in a mass ratio of 90:6:4 and dispersed in deionised water. The slurry was cast onto an Al foil (as a current collector, 50 μm in thickness) with an applicator.

The carbon coated Al foil was then dried under vacuum at 120 °C for ca. 12 h, and punched in required size as electrodes. Apparent surface area of the electrode was ca. 2 cm^2 and thickness was about 150 μm. Mass of active material in the activated carbon and carbon aerogel electrode was 6.09 and 4.89 mg, respectively.

Wettability of carbonaceous materials was examined by a method as follows. Carbon electrodes with the same specification were immersed in 0.8 M Et$_4$NBF$_4$–PC solution for 30 min in a glove box filled with nitrogen. After that, uptake capacity of the electrolyte on the electrodes was calculated according to the mass change of the electrodes.

2.2. Characterization of EDLCs

Electrochemical measurements were carried out in a two-electrode disc-type cell (capacitor), in which a separator soaked with 200 μl organic electrolyte solution (0.8 M Et$_4$NBF$_4$–PC) was sandwiched between two carbon electrodes.

Capacity of a capacitor was examined by constant-current charge–discharge tests, which were carried out in a voltage range of 0.05–3.0 V with a battery test system HJ1010SM8 (Hokuto Denko Corp.). Current density for charging was set at 3 mA cm^{-2} in all cases except that stated otherwise. Discharging capacitance (C) of a capacitor was obtained by integration of the constant-current discharge curve. Specific capacitance of electrode material was defined as the electrode capacitance per unit mass active material in the electrode. Energy delivered to a load (E_{load}) by a capacitor was calculated according to the formula $E_{load} = \frac{1}{2}C[(V_{initial} - IR)^2 - V_{final}^2]$, where $V_{initial}$, V_{final}, I and R stands for the initial voltage, final voltage, discharging current and the direct current internal resistance of a discharge process, respectively. Voltage drop (IR drop) was collected at the beginning of a discharge process. Specific energy of a capacitor was defined as the energy delivered to a load divided by total mass of active material in two electrodes. Cycling stability of the modified carbon materials was examined by constant-current charge–discharge tests in a voltage range of 1.5–3.0 V at 3 mA cm^{-2}.

3. Results and discussion

3.1. Surface characterization of various carbon materials

Table 1 summarizes data obtained from BET measurements for the original carbons and modified carbons treated with 0.25 wt.% surfactant for 24 h at 25 °C.

It is clear that all the test samples contained micro- and meso-pores. After surface modification, the surface area and pore volume decreased, which imply that some sites of the carbon surface were occupied by the surfactant species. As a matter of fact, FT-IR spectrum in Fig. 1 clearly shows that

Material	BET surface area (m² g⁻¹)	Micropore volume (ml g⁻¹)	Mesopore volume (ml g⁻¹)
Activated carbon (AC)	826	0.30	0.55
Modified AC	785	0.27	0.54
Activated carbon aerogel (ACA)	1886	0.61	0.57
Modified ACA	1791	0.57	0.56

the existence of sodium oleate species on the modified carbon material.

The results from total organic carbon (TOC) analysis show that carbon content in surfactant solution (0.25 wt.%) before and after surface modification was ca. 1897.6 and 11.3 mg l⁻¹, respectively, which indicates that over 99% surfactant species have been adsorbed (attached) to the carbon material during the period of surface modification. The attached surfactant species were expected to improve wettability of the modified carbon electrodes and, accordingly improve capacitance and energy performance of a capacitor.

3.2. Capacity feature of the original and modified carbon

Fig. 2a and b show specific capacitance (F g⁻¹) and specific energy (Wh kg⁻¹) at various discharge rates, respectively, for the activated carbon modified by surfactant solutions with various concentrations for 24 h at 25 °C.

At all the discharged rates, both the specific capacitance and specific energy increased with increasing concentration of the surfactant up to 0.25 wt.%. The enhancement in capacitance and energy density is partially attributed to the improvement in wettability of the electrode material, resulting in a higher usable surface area and a lower internal resistance. The results from wettability tests of the electrode materials
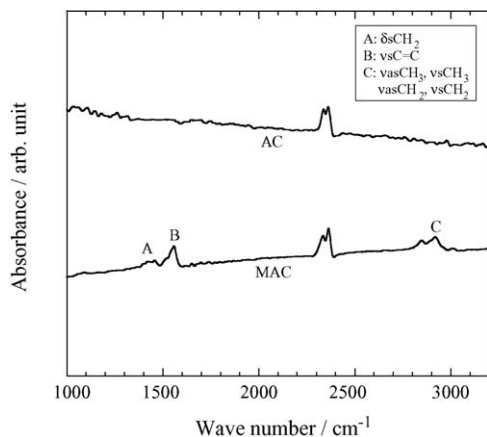

Fig. 1. FT-IR spectra for the original activated carbon (AC) and modified activated carbon (MAC).
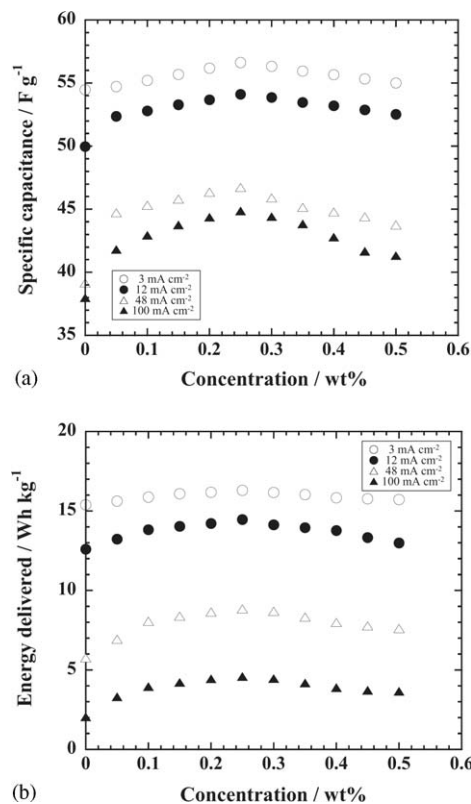

Fig. 2. Specific capacitance (Fig. 1a) and specific energy (Fig. 1b) obtained at various discharge rates for the capacitors using the activated carbons modified by the surfactant with various concentrations.

show that uptake capacity of the electrolyte on the electrodes was 0.43 and 0.68 g g⁻¹ for the original carbon and carbon modified by 0.25 wt.% surfactant, respectively, which mean that after surface modification the wettability of the electrode material to the electrolyte has been improved.

In addition to the contribution from the improved wettability, the surfactant species attached on the carbon surface probably affect the structure of electric double layer (EDL) and also contributes a lot to the capacitance. The decaying capacitance observed at a concentration greater than 0.25 wt.% is probably attributed to the decrease in the usable electrode surface area due to the excessive occupation of carbon surface by the surfactant species, and attributed to the increase in particle size of the surfactant species due to the aggregation, resulting in retarded transport of electrolyte ions in pores of the activated carbon.

Fig. 3a and b shows specific capacitance and energy density at various discharge rates, respectively, for the activated carbon modified by 0.25 wt.% of surfactant solution at 25 °C for various time.

At all the test discharge rates, both the specific capacitance and specific energy increased with the increasing treatment time up to 24 h, and after that, they almost stayed constant, which probably indicates that an equilibrium has been reached between the adsorption and desorption of the surfactant species after 24 h.

Table 2
The IR drop (IR), specific capacitance (C) and specific energy (E) at various discharge rates for the capacitors using the original activated carbon (AC) or modified activated carbon (MAC) as electrodes material

Current density (mA cm^{-2})	IR (V)		$\Delta(IR)/(IR)$ (%)		C (F g^{-1})	$\Delta C/C$ (%)		E (Wh kg^{-1})	$\Delta E/E$ (%)
	AC	MAC	AC	MAC		AC	MAC		
3	0.147	0.116	−21.10	54.47	56.63	3.97	15.39	16.35	6.24
12	0.306	0.225	−35.94	49.97	54.11	8.28	12.60	14.46	14.76
100	1.708	1.234	−27.75	37.98	44.87	18.14	2.05	4.60	124.39

According to the above results, the optimal conditions for surface modification of the activated carbon was chosen as a concentration of 0.25 wt.% of surfactant with a surface treatment time of 24 h at room temperature (25 °C).

For a better understanding of the mechanisms for surface modification more detailed information derived from the constant-current discharge profiles is shown in Table 2 for the original activated carbon (AC) and modified activated carbon (MAC), where $\Delta(IR)/(IR)$, $\Delta C/C$, $\Delta E/E$ stands for variation percentage of IR (voltage drop caused by internal resistance), C (specific capacitance), and E (specific energy) after surface modification, respectively.

At all the discharge rates, IR drop decreased after surface modification while specific capacitance and energy increased. The decrease in IR drop is mainly attributable to improvement of wettability of the elec-

trode material due to the improvement in hydrophobisation by the attachment of non-polar organic functional groups ($CH_3(CH_2)_7CH=CH(CH_2)_7-$). The improvement in hydrophobisation of the electrode material improves the affinity of the carbon surface to non-polar organic solvent, propylene carbonate (PC), and makes it easy for the electrolyte ions to access micro-pores of the electrode material.

The enhancement in capacitance is probably attributed to the two improvements, in the wettability and in the EDL structure, as mentioned previously.

The improvement in energy density is attributed to the increase in capacitance and attributed to the decrease in IR drop. From the expression for energy to a load (E_{load}), $E_{load} = \frac{1}{2}C[(V_{initial} - IR)^2 - V_{final}^2]$, it is clear that E_{load} is approximately proportional to $(V_{initial} - IR)^2$, which means that internal resistance (R) plays a very important role in energy delivery, especially at a high discharge rate, at which a large energy loss is inevitable if internal resistance is high. For instance, at a discharge rate of 100 mA cm^{-2}, the variation in IR drop and specific capacitance is ca. 28 and 18%, respectively, but the improvement in the energy density is ca. 124%, which indicates that the improvement in energy density is mainly due to the decrease in internal resistance, resulting in a much higher $(V_{initial} - IR)^2$.

Therefore, the improvement in wettability not only enhances the capacitance by increasing the useable surface area, but also lowers energy loss (i.e. the energy dissipated by a capacitor itself) by lowering the internal resistance. Both improvements in capacitance and energy loss contribute to the enhancement in the energy delivery.

To further confirm that surface modification with sodium oleate is also effective for the improvement in capacitance of other carbon materials, carbon aerogel was synthesized and employed for this goal. The optimal conditions derived from the activated carbon was used for surface modification of activated carbon aerogels.

Table 3 shows data obtained from the constant-current charge/discharge measurements for various carbon aerogels, i.e. activated carbon aerogel (ACA) and modified activated carbon aerogel (MACA).

It is clear that at all the discharge rates, internal resistance decreased after surface modification while specific capacitance and energy density increased. Significant improvements in capacitance and energy were also observed for the modified activated carbon aerogel at high discharge rates, which means that the modified carbon is more
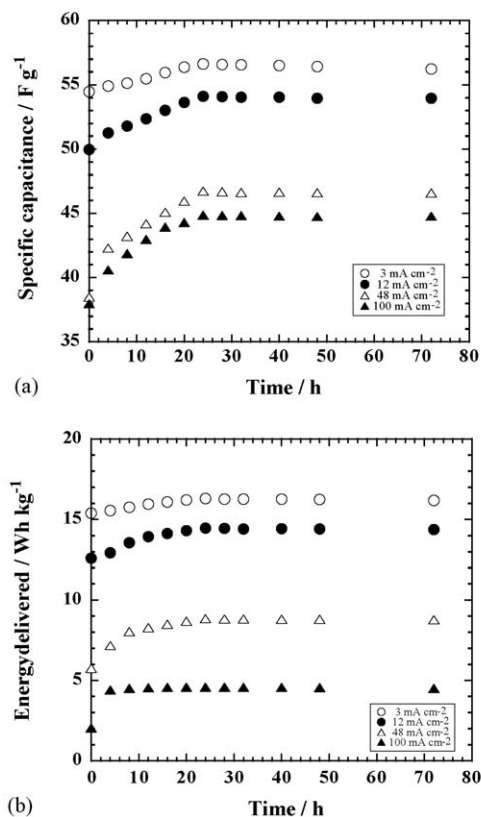

Fig. 3. Specific capacitance (Fig. 2a) and specific energy (Fig. 2b) obtained at various discharge rates for the capacitors using the activated carbons modified for various times.

Table 3
IR drop (*IR*), specific capacitance (*C*) and specific energy (*E*) at various discharge rates for the test capacitors using carbon aerogel (CA) or modified carbon aerogel (MCA) as electrodes material

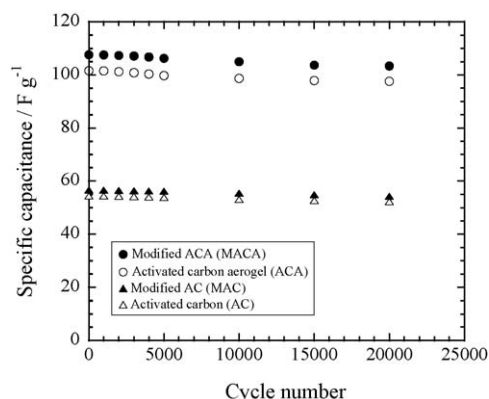| Current density (mA cm^{-2})	*IR* (V)		$\Delta(IR)/(IR)$ (%)		*C* (F g^{-1})	$\Delta C/C$ (%)		*E* (Wh kg^{-1})	$\Delta E/E$ (%)
	CA	MCA	CA	MCA		CA	MCA		
3	0.259	0.213	−17.63	101.62	107.60	5.88	26.51	29.02	9.47
12	0.647	0.560	−13.39	83.40	94.44	12.04	16.03	19.51	21.71
48	1.802	1.664	−7.67	53.53	74.20	38.61	2.66	4.59	72.56

Fig. 4. Specific capacitances obtained at 3 mA cm^{-2} for various carbon materials shown against charge–discharge cycle number.

suitable as electrode material in EDLCs for high rate applications.

One of the merits of electrochemical capacitors is cycle durability. Cycling stability of the capacitors using the original or modified carbon materials were examined in a voltage range of 1.5–3.0 V at 3 mA cm^{-2}. After some cycles of charge–discharge, discharge capacitances were collected and shown in Fig. 4.

It was found that the capacity decay was only 4% after 20,000 cycles for the modified carbons, which indicates that the modified carbons possess excellent cycle stability. In addition, it is also found that the difference in capacity decay between the original carbon and modified carbon is very small, which indicates that surface modification with sodium oleate surfactant does not degrade the cycle performance of the original carbons.

4. Conclusions

(I) Wettability of carbon materials to organic electrolyte with non-polar organic solvent can be improved by surface modification with sodium oleate surfactant.

(II) After surface modification, internal resistance of the capacitors decreases and, specific capacitance and energy density increase. Effects from surface modification become more marked at higher discharge rates, suggesting that the modified carbon materials are more suitable for high-rate EDLCs applications.

(III) Surface modification does not degrade the cyclability of a capacitor. The modified carbon materials possess excellent cycle stability comparable to the original carbon.

Acknowledgment

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