High capacity supercapacitors based on modified activated carbon aerogel

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Abstract

Carbon aerogel derived from a modified resorcinol–formaldehyde (RF) method without supercritical drying step was activated under CO_2 flow and further modified with a surfactant sodium oleate solution. Carbon aerogel, activated carbon aerogel (ACA) and modified activated carbon aerogel (MACA) were characterized by Brunaver, Emmett and Teller(BET) surface measurement, constant-current charge–discharge and cyclic voltammetry(CV). It was found that the specific surface area of the ACA was twice that without activation. At relatively low discharge rates the specific capacitance and energy delivered from the capacitor were improved greatly by the activation of carbon aerogel. To apply the ACA at high discharge rate, a surface modification was introduced. After the surface modification the wettability of the organic electrolyte based on non-polar organic solvent (i.e. propylene carbonate) to the ACA was improved greatly and, as a result, the internal resistance of the capacitor decreased and the specific capacitance and energy delivered increased at all the test discharge rates. The effects from the modification become more marked at higher discharge rates, i.e. at 48 mA cm^{-2}, the energy delivered increased by ca. 70%, which indicates the MACA more suitable as electrode material in electric double-layer capacitors (EDLCs) for high current applications.

1. Introduction

Electric double-layer capacitors (EDLCs) are unique electrical storage devices, which can store much more energy than conventional capacitors, offer much higher power density than batteries and are capable of cycling millions of times. Carbon aerogels are promising and innovative materials because of their attractive properties such as a high electrical conductivity, controllable pore structure and relatively high useable surface area for double-layer formation, which make them very suitable for EDLCs use [1, 2]. However, the conventional method for carbon aerogel synthesis involves a supercritical drying step [3], which is usually the most time-consuming and costly step in aerogel synthesis. It would be desirable and possible to make aerogels without supercritical drying [4, 5]. In addition, carbon aerogels conventionally prepared provide predominantly meso-pores and some meso-pores are unnecessarily large. Without change in the skeletal carbon gel structure, introduction of micro-pores by activation of carbon aerogel, giving a unique carbon material with a bimodal pore structure would increase the useable surface area and increase the capacitance at relatively low discharge rate [6]. However, at high discharge rate the energy delivered becomes lower for the activated carbon aerogel(ACA), which is probably due to the narrowing of meso-pores, making motion of electrolyte ions difficult, and to poor wettability of the electrodes, causing a small usable surface area and a high internal resistance. To improve wettability and improve capacitance performance of carbon materials, chemical surface modification in nitric acid solutions have been reported by some authors [7–10]. It was reported that capacitance performance of carbon materials in aqueous solutions could be improved greatly 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 capacitance and energy storage performance 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 is expected.

2. Experimental

2.1. *Synthesis and activation of carbon aerogel*

Carbon aerogel was derived from pyrolysis of a resorcinol–formaldehyde (RF) gel according to a modified

RF method [4, 5] followed by activation under CO_2 flow at 1000 °C for 1 h. 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) $NaHCO_3$ was set at R/C=1500. RF gel was dried by microwave at 200 W for 10 min prior to carbonization.

2.2. Surface modification of ACA

Surface modification of ACA was performed as follows. Two grams of ACA was soaked by 20 mL surfactant (sodium oleate) aqueous solution and shaken for 24 h at 25 °C. After the filtration the carbon slurry was dried at 100 °C in 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.).

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.

2.3. Preparation of carbon electrodes

Carbon aerogel electrodes were prepared by a coating method as follows. Carbon aerogel (active material), graphite powder (conductivity enhancing material) and polytetrafluoroethylene (binder) were mixed in a mass ratio of 90:6:4 and dispersed in deionized 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 (16 mm in diameter) as electrodes. The apparent surface area of the electrode was ca. 2 cm^2 and the thickness was about 150 μm. The mass of active material in the carbon aerogel electrode was 4.89 mg.

2.4. Characterization of test capacitors

To remove air from carbon pores, ensure optimum volume fraction of electrolyte solution and ensure minimum resistance from retarded electrolyte transport, carbon electrode was immersed in and filled with the electrolyte solution (0.8 M Et_4NBF_4-PC) under gradually increasing vacuum in a glove box for some time. Upon construction of a capacitor, a separator (50% porosity, 20 mm in diameter) soaked with the electrolyte was sandwiched between two soaked electrodes.

Test capacitors were characterized by constant-current charge–discharge and cyclic voltammetry(CV). Constant-current charge-discharge tests 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. Capacitance (C) 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. The energy delivered to a load (E) by a capacitor was calculated according to the formula $E=1/2CV^2$, where V is the usable voltage. For CV measurements, one electrode of the capacitor was used as the working electrode and another electrode was used as the counter and reference electrodes.

3. Results and discussion

3.1. Surface area and pore structure of various carbon aerogels

Table 1 summarizes data obtained from BET measurements for carbon aerogel, ACA and modified activated carbon aerogel (MACA).

It is clear that the carbon aerogel produced in inert atmosphere (N_2) provided predominantly meso-pores, and its specific surface area was relatively small. After the activation by CO_2, lots of micro-pores (less than 2 nm in diameter) were produced and the specific surface area was ca. twice that without activation. After the surface modification with 0.25 wt % sodium oleate both the surface area and pore volume decreased for the ACA, which means that some sites of the carbon surface were occupied by the surfactant species. As a matter of fact, the results from TOC analysis show that carbon content in surfactant solution (0.25 wt %) before and after surface modification was ca. 1898 and 11 mg l^{-1}, respectively, which indicates that over 99% surfactant species ($CH_3(CH_2)_7CH=CH(CH_2)_7COO^-$, containing carbon) have been adsorbed (attached) to the carbon material during the period of surface modification. Surfactant loading was calculated as 0.018 mg m^{-2} based on a surface area of 1408 m^2 g^{-1} for the original ACA. The attached surfactant species were expected to improve wettability of the modified carbon electrodes and, improve capacitance and energy.

Table 1. Specific surface area and pores volume for the various carbon aerogel materials

Material	BET surface area /m^2 g^{-1}	Micropore volume/mL g^{-1}	Mesopore volume/mL g^{-1}
Carbon aerogel (CA)	661	0.02	0.99
Activated CA (ACA)	1408	0.61	0.57
Modified ACA (MACA)	1342	0.58	0.56

3.2. *Performance of the test capacitors based on various carbon aerogels*

Figure 1(a) and 1(b) shows specific capacitance (F g^{-1}) and energy delivered (Wh kg^{-1}) at various discharge rates, respectively, for the capacitors using carbon aerogel and ACA as electrode materials.

It is clear that both the specific capacitance and energy delivered for the capacitor using the ACA were greater than that without the activation especially at relatively low discharge rate, i.e., at 3 A cm^{-2}, about twice the specific capacitance and energy were available for the capacitor using the ACA electrodes. This is mainly attributable to the higher specific surface area of the ACA. However, the differences in the specific capacitance and, especially in the energy delivered, became smaller with increasing discharge rate and, finally, the energy delivered by the capacitor using the ACA electrodes was lower than that without activation. The reasons for this can be explained as follows. After activation the proportion of meso-pores in the carbon aerogel decreased and some meso-pores become narrowed, which results in retarded transport of the electrolyte ions into electrode pores, and a decrease in the useable surface area and an increase in the internal resistance occurs. This situation becomes especially conspicuous at high discharge rates. Due to a marked decrease in the useable surface area, the specific capacitance and the energy delivered decreased dramatically. In addition, the increase in internal resistance resulted in an increased energy loss during the charge–discharge cycle of the capacitor and resulted in a further decrease in energy.

To improve the properties of the ACA and improve the performance of the capacitor, surface modification of the ACA was performed with a 0.25 wt % sodium oleate aqueous solution.

Figure 2 shows the constant-current charge–discharge curves at $I=3$ mA cm^{-2} for capacitors using ACA or MACA as electrodes.

It is clear that the *IR* drop, which can be observed from the initial discharge, decreased after surface modification.

Figure 3 shows cyclic voltammograms at various scan rates for the capacitors using ACA and MACA as electrodes, in which the current responses (I) at various potentials have been converted to specific capacitance using the equation $C=I/(v \times m)$, where v and m stands for the scan rate and the mass of the active material (i.e., carbon aerogel), respectively. At a low scan rate (1 mV s^{-1}), the profiles of the two electrodes have rectangular-like shapes. As the scan rate increases, however, the profiles become gradually depressed. It is also noted that the depression is more pronounced in the ACA electrode. The degree of depression can be correlated with the rate capability of the electrode system which, in turn, is deeply related to the *RC* time constant. That is, if any capacitor system has a large *RC* time constant, the rate capability is poor. This feature is ascertained by the profiles shown in Figure 3, whereby the exponential transient appearing before the plateau becomes longer because more time is required to charge the capacitor [11]. Here R and C denote the equivalent series resistance (ESR) and capacitance, respectively. The ESR is the summation of electrode resistance, bulk
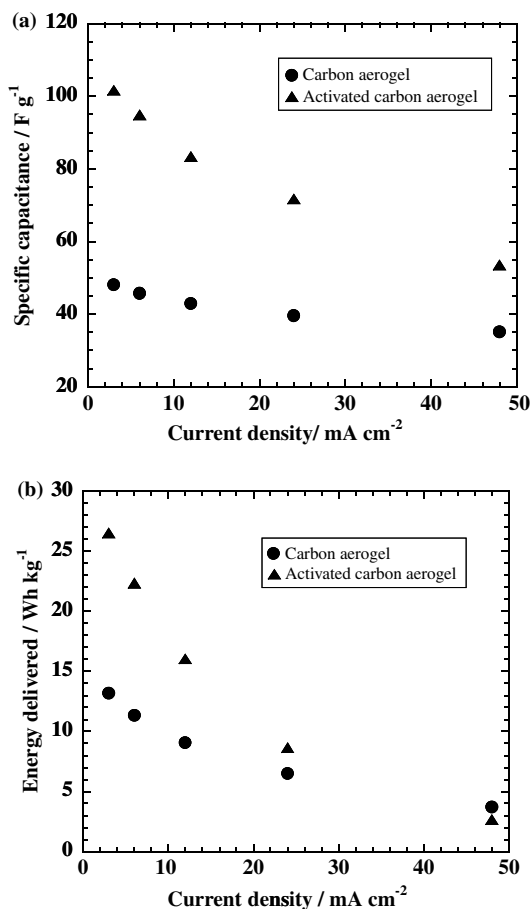

Fig. 1. Specific capacitance (Figure 1a) and energy delivered (Figure 1b) at various discharge rates for the capacitors using carbon aerogel and ACA as electrode materials.
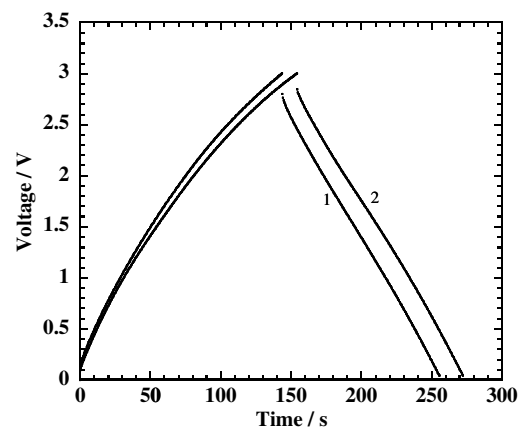

Fig. 2. Constant-current charge–discharge curves at $I=3$ mA cm^{-2} for the capacitors using the ACA or MACA as electrodes. 1=Activated carbon aerogel, and 2=Modified activated carbon aerogel.
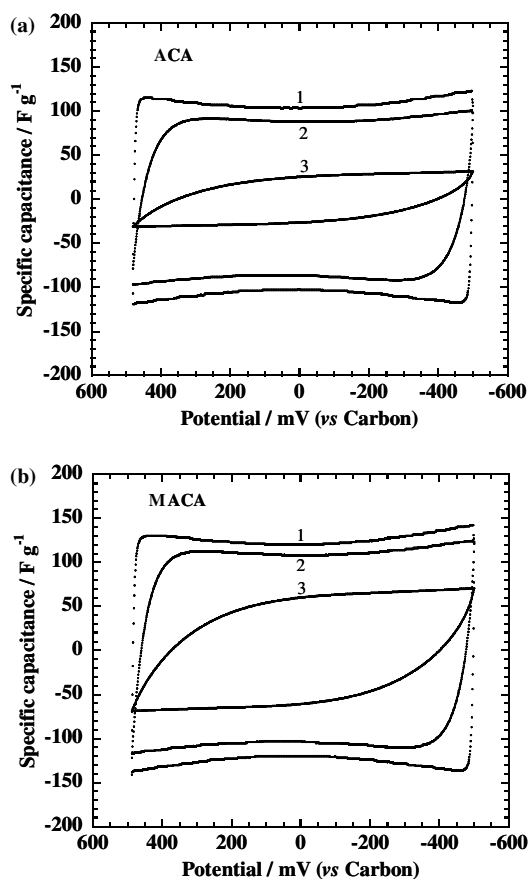
Fig. 3. Cyclic voltammograms at various scan rates for the capacitors using ACA and MACA as electrodes, Scan rates: (1) 1 V s^{-1}, (2) 10 mV s^{-1}, (3) 100 mV s^{-1}.
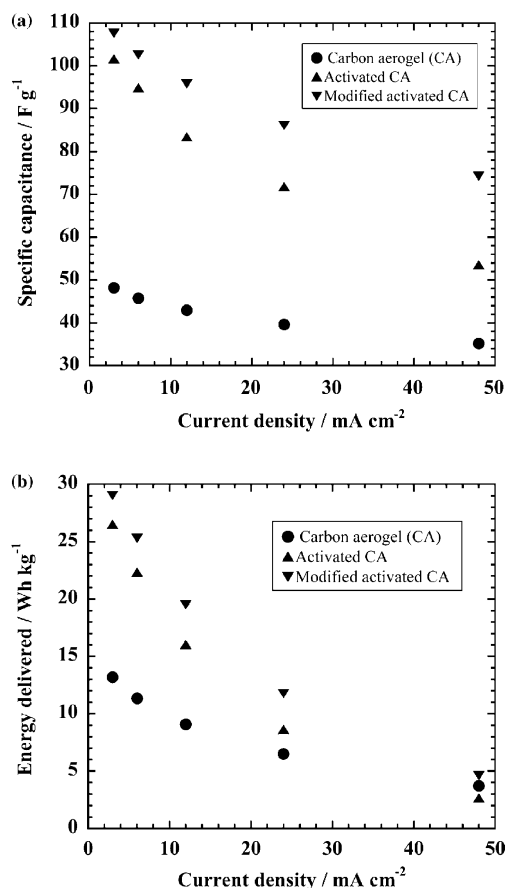

Fig. 4. Specific capacitance (Figure 4(a)) and energy delivered (Figure 4(b)) at various discharge rates for the capacitors using CA, ACA and MACA as electrode materials.

electrolyte resistance and electrolyte resistance within pores. The poorer rate capability observed with the ACA is caused by a larger value of ESR. A larger ESR for the ACA can be observed in the constant-current charge–discharge profiles shown in Figure 2, from which a larger ohmic voltage drop, which must be proportional to a large ESR, is observed.

A decrease in the internal resistance for the MACA is probably attributable to improvement in wettablilty of to the electrode material. The improvement in wettability makes it easier for the electrolyte ions to access the micro-pores of electrode material, which results in a decrease in internal resistance and an increase in useable surface area and consequently, a decrease in energy loss during the charge–discharge cycle and an increase in specific capacitance and energy available.

The improvement in wettability for the MACA is probably attributable to improvement in hydrophobization by the attachment of non-polar functional groups (CH$_3$(CH$_2$)$_7$CH =CH(CH$_2$)$_7$-) to the carbon surface.

The improvement in hydrophobization of the ACA improves affinity of the carbon surface to non-polar organic solvent, propylene carbonate (PC), and accordingly improves wettability of the electrodes.

Figure 4(a) and (b) shows the specific capacitance (F g^{-1}) and energy delivered (Wh kg^{-1}) at various discharge rates for capacitors using various carbon aerogels.

It was found that both the capacitance and energy delivered were higher for the MACA than for the ACA without modification at all the test discharge rates, especially at high discharge rate, i.e., an increase by ca. 38% and 72% for the capacitance and energy, respectively at a discharge rate of 48 Ma cm^{-2}. In addition, it is noteworthy that the MACA provided much higher specific capacitance and higher energy density than the carbon aerogel, even at a high discharge rate.

The results above indicate that the surface modification is effective and provides greater possibility for application of EDLCs based on carbonaceous materials in a broad range of frequency.

4. Conclusions

1. The activation of carbon aerogel by CO$_2$ introduces a bimodal pore structure. The specific surface area of the carbon aerogel increases greatly after activation.
2. Compared with the carbon aerogel without activation the specific capacitance and energy available increase considerably at relatively low discharge rate,

however, the energy delivered at high discharge rate is a little lower.

3. The wettability of carbon aerogel to organic electrolytes based on non-polar organic solvents can be improved by surface modification of the carbon aerogel with sodium oleate surfactant.

4. After surface modification, the internal resistance of the capacitors decreased and the specific capacitance and energy delivered increased. The effects become more marked at higher discharge rates, which indicate that the MACA is more suitable for EDLC applications at high current.

Acknowledgements

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