

# A novel electrode material for electric double-layer capacitors

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Received 5 July 2004; received in revised form 6 September 2004; accepted 1 October 2004

Available online 26 November 2004

## Abstract

In this study, a novel electrode material, modified activated carbon aerogel, has been developed for electric double-layer capacitors (EDLCs). This novel material was produced by the activation of carbon aerogel under CO<sub>2</sub> flow, followed by surface modification with a surfactant, sodium oleate. It has been characterized by BET measurement and BJH method for its surface area and pore-size distribution, and by constant-current charge–discharge technique, cyclic voltammetry and electrochemical impedance spectrum (EIS) for its specific capacitance, equivalent series resistance and power capability. It was found that, after the surface modification, the wettability of the organic electrolyte based on non-polar organic solvent (i.e., propylene carbonate) to the activated carbon aerogel was improved greatly, which resulted in a lower internal resistance and a higher usable surface area. As results, a higher specific capacitance, energy density and power capability were achieved for the capacitor using the modified activated carbon aerogel electrodes than those without the surface modification. The effects from the surface modification became more significant at higher charge–discharge rates, at which the wettability of the electrolyte to the electrode material usually becomes more important and critical.

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**Keywords:** Electric double-layer capacitor; Carbon aerogel; Activation; Surface modification; Surfactant/sodium oleate; Propylene carbonate

## 1. Introduction

Electric double-layer capacitor (EDLC) is a unique electrical storage device, which can store much more energy than conventional capacitors and offer much higher power density than batteries. EDLCs fill up the gap between the batteries and the conventional capacitors, allowing applications for various power and energy requirements, i.e., back up power sources for electronic devices, load-leveling, engine start or acceleration for hybrid electric vehicles and electricity storage generated from solar or wind energy. EDLCs based on carbon materials have been attracting much attention because of their high performance and low cost. Activated carbons have been commonly used as electrodes material in EDLCs for its high specific surface area and relatively low cost; however, the electronic conductivity of activated carbons is low, usually 0.1–1 S cm<sup>-1</sup>, which results

in a high internal resistance for the capacitors. In addition, a large fraction of pores of activated carbon are micropores (less than 1 nm), which are too small to be accessed by the electrolyte especially organic electrolyte with large ions size and do not contribute to the double layer capacitance [1,2]. In contrast, carbon aerogels, which are highly porous materials consisting of a continuous rigid solid framework and an open, continuous network of pores, represent a promising and innovative materials because of their attractive properties such as a high electrical conductivity (25–100 S cm<sup>-1</sup>), controllable pore structure and highly useable surface area (up to 1100 m<sup>2</sup> g<sup>-1</sup>) for double-layer formation, which make carbon aerogels very suitable for EDLCs use [3–9]. However, carbon aerogels conventionally prepared provide predominantly mesopores and some mesopores are unnecessarily large (i.e., greater than 20 nm). Without change of the skeletal carbon gel structure, introduction of micropores by activation of carbon aerogel, giving a unique carbon material with a bimodal pore structure could increase the useable surface area and accordingly the capacitance considerably at

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relatively low charge–discharge rates [6]. However, at a high discharge rate, the energy delivered by the capacitor using the activated carbon aerogel electrodes became lower than that without the activation, which was probably attributed to the narrowing of mesopores, making motion of electrolyte ions difficult, and attributed to poor wettability of the electrolyte to the electrodes, causing a small usable surface area and a high internal resistance. To improve the wettability of the organic electrolyte to the activated carbon aerogel, and accordingly to improve the performance of the capacitor especially at high charge–discharge rates, a novel approach, surface modification with the surfactant sodium oleate has been developed in our study. By attaching non-polar organic functional group (i.e.,  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7^-$ ) to carbon surface, hydrophobisation of the carbonaceous material was expected to be improved, which would improve the affinity of the carbon surface to non-polar organic solvent (i.e., propylene carbonate), and accordingly improve the wettability of the organic electrolyte to the carbon electrodes. Effective activation and modification of carbon aerogel is expected to greatly improve the performance of the EDLCs, which enables EDLCs to provide both high energy and high power capability for various applications.

## 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 method proposed by Pekala [9]. Upon preparation of a RF gel, the mass percentage of the reactants in solution was set at  $\text{RF} = 20\%$  and the molar ratio of resorcinol (R) to catalyst (C) was set at  $\text{R/C} = 1500$ .  $\text{NaHCO}_3$  was used as the catalyst for a fine pore structure and a high specific surface area [10]. The molar ratio of formaldehyde to resorcinol was held at a constant value of 2.

After weighing out the required amounts of each component, the components were combined in a glass tube (40 ml in capacity) and the resulting solution briefly stirred. To avoid sedimentation of RF polymers in the solution, the initial pH of RF solution was adjusted to 6.5–7.4 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 °C, 50 °C and 90 °C, respectively). The gelation/aging cycle was accomplished by placing the glass tube containing the reactants into an oven for which the temperature was adjusted over several days. To accomplish this, the tube was placed into a sealed glass jar containing a few milliliters of distilled water to provide a saturated humidity environment, which prevented water evaporation during the gelation/aging cycle. At the end of this process, the monomers had been converted into the RF gel, which existed as a dark red, soft and porous solid. After the gelation/aging cycle was completed, the resulting gel cylinder was

removed from the glass tube and then wrapped with a piece of cheesecloth and tightened with nylon twine for protection from cracking during the solvent exchange steps. Next, the wrapped gel cylinder was suspended in an agitated bath of 0.125% trifluoroacetic acid in water at 45 °C for three days to stop the poly-condensation process and to extend the cross-linking between the resorcinol and formaldehyde in the gel. Then, the trifluoroacetic acid solution-filled gel was treated with pure acetone in an agitated bath for four days at 45 °C 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 that entered the bath during the solvent exchange process. The acetone-filled RF gel was then dried with microwave at 500 W for 10 min prior to carbonization. Pyrolysis was carried out under a flow of pure  $\text{N}_2$  gas in a quartz tube (2 in. in diameter) containing the dried RF gel set in a tube furnace. The heating profile was as follows: heating from room temperature to 250 °C within 2 h at a heating rate of 2 °C  $\text{min}^{-1}$ , holding this temperature for 4 h, and then raising temperature to 1000 °C at the same heating rate, holding this temperature for 4 h and then cooling down to room temperature by turning off the furnace.

Activated carbon aerogel was obtained by carbonization of the dried RF gel under a  $\text{CO}_2$  flow of 50  $\text{ml min}^{-1}$  at 1000 °C for 4 h. The heating profile was the same as that for preparation of carbon aerogel.

### 2.2. Surface modification of activated carbon aerogel

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

The solution after filtration was characterized by TOC (total organic carbon) analysis for the carbon content. The instrument for TOC analysis: TOC-V<sub>CPN</sub>, Total Organic Carbon Analyzer (Shimadzu Corp., Japan).

### 2.3. Preparation of carbon electrodes and construction of a test capacitor

Procedures for electrode preparation are as follows: carbon aerogel powder, graphite powder (as a conductivity enhancing material) and polytetrafluoroethylene (as a binder) were mixed in a mass ratio of 90:6:4 and dissolved in deionized water. The slurry was cast onto an Al foil (as a current collector, 75  $\mu\text{m}$  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 thickness of the electrode was about 150  $\mu\text{m}$ .

All the test capacitors were constructed in a glove box, which had been evacuated and then filled with inert gas ( $\text{N}_2$ ). 1.5 M  $\text{Et}_3\text{MeNBF}_4\text{-PC}$  was used as electrolyte.

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

Material	BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	Micropore volume ( $\text{ml g}^{-1}$ )	Mesopore volume ( $\text{ml g}^{-1}$ )
Carbon aerogel (CA)	835	0.03	0.97
Activated CA (ACA)	1655	0.71	0.83

#### 2.4. Characterization of carbon aerogels and test capacitors

The surface area and pore-size distribution of various carbon aerogels 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.

Test capacitors were characterized by constant-current charge–discharge, cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) measurement. Constant-current charge–discharge tests were performed with a battery test system HJ1010SM8 (Hokuto Denko Corp.) in a voltage range of 0.05–3.0 V. Current density for charging was set at  $3 \text{ mA cm}^{-2}$  in all cases. Capacitance ( $C$ , in Farads) was calculated according to  $C = I \Delta t / \Delta V$ , where  $I$  is the discharge current (in amperes) and  $\Delta t$  is the time period (in seconds) for the voltage change ( $\Delta V$ , in volts). Energy ( $E$ ) delivered during the discharge was calculated according to  $E = (1/2) CV^2$ , where  $V$  stands for the usable voltage. Electrochemical impedance spectrum measurements were made over the frequency range  $10^6$  to  $1 \times 10^{-3}$  Hz, and the instruments for EIS measurements were: model S-5720C frequency response analyzer (NF Electronics Instruments), model PS 2000 potentiostat/galvanostat and model FG-02 function generator (TOHO technical research).

### 3. Results and discussion

#### 3.1. Surface area and pore-size distribution of various carbon aerogels

Table 1 summarizes some data obtained from BET measurements for various carbon aerogels, i.e., the carbon aerogel produced in inert atmosphere ( $\text{N}_2$ ) and the carbon aerogel activated in  $\text{CO}_2$  flow. Fig. 1 shows their pore-size distribution.

It is clear that the carbon aerogel produced in inert atmosphere ( $\text{N}_2$ ) without further activation provides predominantly mesopores, which has a relatively narrow pore-size distribution with a peak value of 4.2 nm. The specific surface area for the carbon aerogel without the activation is relatively small (ca.  $835 \text{ m}^2 \text{g}^{-1}$ ). After the activation in  $\text{CO}_2$  flow, the peak at 4.2 nm shifts to the left to 3.7 nm, which indicates that lots of mesopores became narrow after the activation. In addition, lots of micropores ( $<2 \text{ nm}$  in diameter) were introduced to the carbon aerogel, which can be evidently observed in Fig. 1. The specific surface area for the activated carbon aerogel is about twice that without the activation.

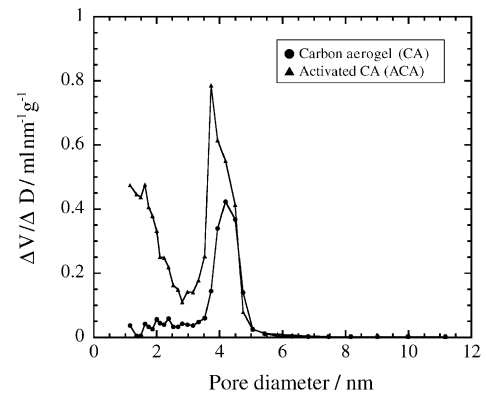


Fig. 1. Pore-size distribution for the carbon aerogel (CA) produced in inert atmosphere ( $\text{N}_2$ ) and for the activated carbon aerogel (ACA) in  $\text{CO}_2$  flow.

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

Fig. 2 shows the ratios of specific capacitance ( $\text{F g}^{-1}$ ) or energy delivered ( $\text{Wh kg}^{-1}$ ) of the capacitor using the activated carbon aerogel electrodes to that of the capacitor using the carbon aerogel electrodes at various discharge rates.

It is clear that both the specific capacitance and energy delivered for the capacitor using the activated carbon aerogel electrodes are greater than that without the activation especially at relatively low discharge rate, i.e., at  $3 \text{ mA cm}^{-2}$ , about two times of specific capacitance and energy are available for the capacitor using the activated carbon aerogel electrodes, which are mainly attributed to higher specific surface area of the activated carbon aerogel. However, the ratio of spe-

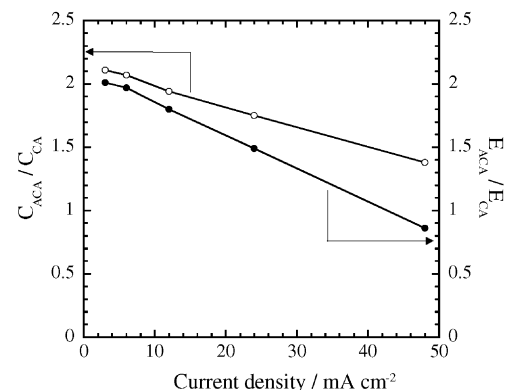


Fig. 2. The ratios of specific capacitance ( $\text{F g}^{-1}$ ) or energy delivered ( $\text{Wh kg}^{-1}$ ) of the capacitor using the activated carbon aerogel (ACA) electrodes to that of the capacitor using the carbon aerogel (CA) electrodes at various discharge rates.

cific capacitance and especially the ratio of energy delivered decreases markedly with the increasing discharge rates and finally at a relatively high discharge rate, i.e.,  $48 \text{ mA cm}^{-2}$ , the energy delivered by the capacitor using the activated carbon aerogel electrodes is lower than that without the activation. The reasons can be explained as follows. After the activation lots of micropores were introduced into the carbon aerogel. The proportion of mesopores in the carbon aerogel decreased and some mesopores narrowed, which resulted in a difficulty in the motion of the electrolyte ions in such small pores of electrodes material, and accordingly a decrease in the useable surface area and an increase in the internal resistance. This situation became especially conspicuous at high discharge rates, at which the electrolyte within pores contributes a lot to the internal resistance. Due to a marked decrease in the useable surface area, the specific capacitance, and accordingly the energy delivered decreased dramatically. In addition, the increase in the internal resistance resulted in an increasing energy loss during the charge–discharge cycle of the capacitor and resulted in a further decrease in the energy.

To improve the property of the activated carbon aerogel and improve the performance of the capacitor, especially at high frequency, surface modification of the activated carbon aerogel was performed with a 0.25 wt.% sodium oleate aqueous solution to improve the wettability of the electrolyte to the electrode material.

Fig. 3 shows the cyclic voltammograms for the capacitors using the activated carbon aerogel or the modified activated carbon aerogel as electrodes.

The inner integrated area, the current times voltage, is the power. This power will be larger if the internal resistance of the capacitor, the slope of  $V/I$  is smaller. From Fig. 3 it is clear that after the surface modification, the internal resistance of the capacitor decreased and power capability has been improved.

For an ideal supercapacitor, its capacitance is independent of frequency, so the charge stored by a capacitor is propor-

tional to the voltage imposed. Therefore, in the case of the CV measurements, for a constant sweep rate ( $\text{mV s}^{-1}$ ), current response will keep constant. From Fig. 3 it is also clear that the capacitor using the modified activated carbon aerogel behaved like an ideal supercapacitor more.

The results from the constant-current charge–discharge tests also show that the internal resistance of the capacitors decreased after the surface modification of the activated carbon aerogel.

A decrease in the internal resistance for the modified activated carbon aerogel was probably attributed to the improvement in the wettability of the electrodes material. The improvement in the wettability made it easier for the electrolyte ions to access the micropores of electrodes material, which resulted in a decrease in the internal resistance and an increase in the useable surface area and accordingly a decrease in the energy loss during the charge–discharge cycle and an increase in the specific capacitance and energy available.

The improvement in the wettability for the modified activated carbon aerogel was probably attributed to the improvement in hydrophobisation by attaching non-polar organic functional group ( $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7^-$ ) to carbon surface. The result from TOC analysis for the modified activated carbon aerogel shows that almost all the surfactant anions ( $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}^-$ ) have attached to the carbon surface during the modification.

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

For further investigation on performance of the capacitors based on various carbon aerogels electrodes, EIS measurements were made to determine  $RC$  time constant ( $R$  and  $C$  denote the equivalent series resistance (ESR) and capacitance, respectively). To our knowledge, if any capacitor has a large  $RC$  time constant, the rate capability is poor. In order to compare the  $RC$  time constant for the capacitors using various carbon aerogels electrodes, the frequency-dependent capacitance was obtained by taking the imaginary part of complex impedance,  $C(f) = 1/(i2\pi fZ(f))$ , where  $i$ ,  $f$  and  $Z(f)$  are the imaginary unit, ac frequency and complex impedance at a frequency, respectively. A typical Nyquist plot for the capacitor using the modified activated carbon aerogel electrodes is shown in Fig. 4. It is clear that when the frequency is lower than 100 mHz, the capacitive characteristic is observed as a vertical line. At relatively high frequencies, a depressed semi-circle is observed, which represents a parallel combination of resistive and capacitive components.

The frequency-dependent capacitances of the capacitors using the activated carbon aerogel electrodes or modified activated carbon aerogel electrodes, normalized to the lowest frequency (1 mHz) values are shown in Fig. 5.

The frequency-dependent capacitance of porous electrodes can be analyzed using the transmission line model, which was proposed by Levie [11] with an assumption that pores are uniform and cylindrical. The parameter ‘pene-

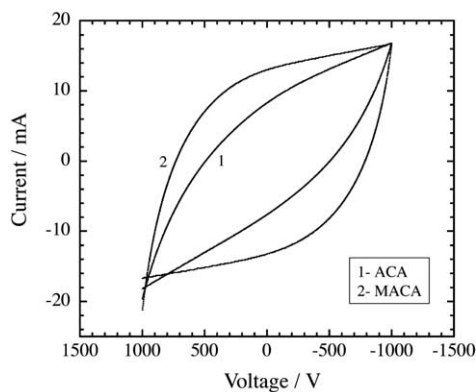


Fig. 3. The cyclic voltammograms for the capacitors using the activated carbon aerogel (ACA) or the modified activated carbon aerogel (MACA) as electrodes; scan rate:  $100 \text{ mV s}^{-1}$ .

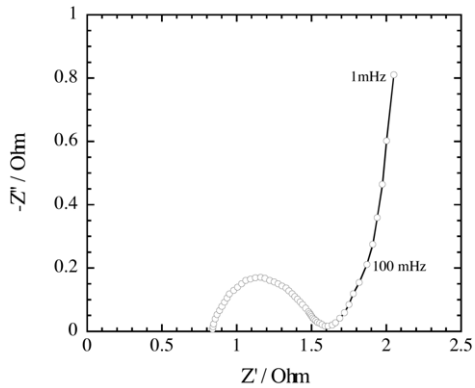


Fig. 4. A typical Nyquist plot for the capacitor using the modified activated carbon aerogel electrodes.

tration depth',  $l = 1/(\pi f R' C')^{1/2}$ , is useful to understand the impedance behavior of porous electrodes, where  $R'$  and  $C'$  represent the pore resistance and pore capacitance per unit pore length, respectively. It is clear that when the ac frequency is sufficiently high for the penetration depth ( $l$ ) to be smaller than the pore length ( $l_p$ ) of porous electrodes, only the outer surface (near pore opening) is influenced by the ac voltage signal, and as a result, a small capacitance is observed because only a limited part of electrode surface is utilized for the formation of electric double layer. In the low-frequency extreme, where the condition  $l > l_p$  holds, most of the pore surface is utilized and results in a maximum capacitance. In the intermediate frequency region, a monotonous capacitance change is observed.

The  $RC$  time constant can be compared for the capacitors using various carbon aerogels electrodes by analyzing the capacitance profiles in the intermediate-frequency region, where the cutoff frequency is taken as the frequency at which the capacitance is 50% the value at the lowest frequency (1 mHz). The relative  $R'C'$  values are extracted at the cut-off frequency using the above equation with the penetration depth ( $l$ ) being assumed to be the same for the two carbon

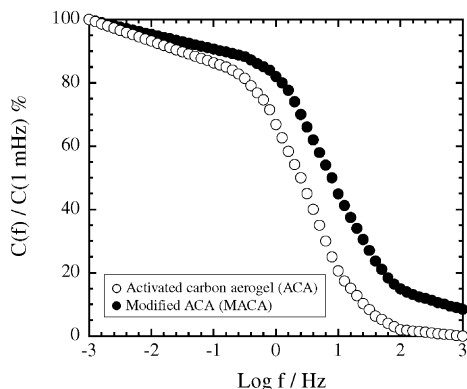


Fig. 5. The frequency-dependent capacitances of the capacitors using the activated carbon aerogel electrodes (ACA) or modified activated carbon aerogel (MACA) electrodes, normalized to the lowest frequency (1 mHz) values.

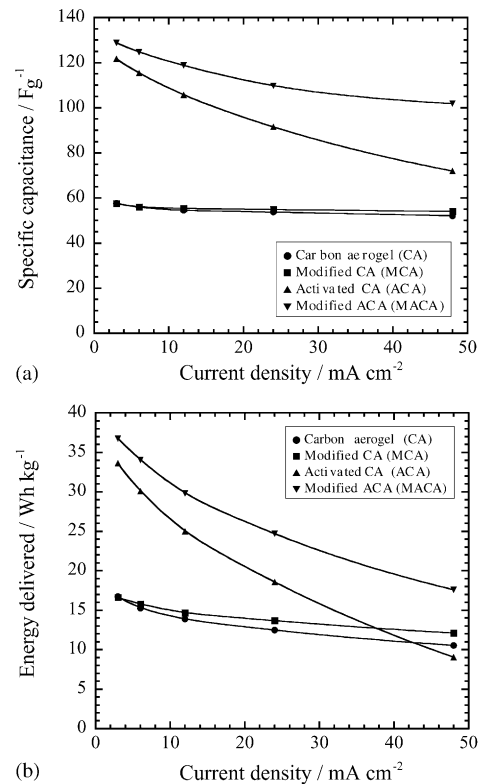


Fig. 6. (a) Specific capacitance and (b) energy delivered at various discharge rates for the capacitors using various carbon aerogels as electrodes material.

aerogel materials, i.e., the activated carbon aerogel and the modified activated carbon aerogel. The cutoff frequencies are 2.51 and 7.94 Hz for the activated carbon aerogel and the modified activated carbon aerogel, respectively, and the  $RC$  time constants of the activated carbon aerogel electrodes are calculated as 3.16 times that of the modified activated carbon aerogel electrodes, which indicates that after the surface modification the power capability of the activated carbon aerogel electrodes has been improved greatly. This conclusion is consistent with that drawn from the CV tests.

Fig. 6a and b shows the specific capacitance ( $F g^{-1}$ ) and energy delivered ( $Wh kg^{-1}$ ) at various discharge rates, respectively, for the capacitors using various carbon aerogels electrodes.

It is clear that both the capacitance and energy density have been improved significantly after the surface modification. A specific capacitance of ca.  $130 F g^{-1}$  was achieved at  $3 mA cm^{-2}$  for the modified activated carbon aerogel, and the specific capacitance still stays high (over  $100 F g^{-1}$ ) even if at a high discharge rate, i.e.,  $48 mA cm^{-2}$ . The improvement in the energy density is also considerable after the surface modification especially at high discharge rates, i.e., an increase by ca. 100% was observed at a discharge rate of  $48 mA cm^{-2}$ . In addition, it is noteworthy that the modified activated carbon aerogel could provide much higher specific capacitance and higher energy density than the carbon aerogel even though at a high discharge rate. The modified carbon aerogel could



provide higher specific capacitance and energy density than the carbon aerogel.

The results above indicate that the surface modification is effective for the carbon materials, which enables EDLCs to provide both high energy and power capability.

#### 4. Conclusions

- I) The activation of carbon aerogel under CO<sub>2</sub> flow could introduce a bimodal pore structure into the carbon aerogel. The specific surface area of carbon aerogel increased greatly after the activation.
- II) Comparing with the carbon aerogel without the activation the specific capacitance and energy available from the activated carbon aerogel increased considerably at relatively low discharge rate, however, the energy delivered at high discharge rate was a little lower.
- III) The wettability of organic electrolyte based on non-polar organic solvent to carbon aerogel could be improved by the surface modification of carbon aerogel with the surfactant sodium oleate.
- IV) After the surface modification, the internal resistance of the capacitor decreased and the specific capacitance and energy density increased. In addition, the power capability could be also improved. The impacts from the modification became more significant at higher discharge rates.

#### Acknowledgment

This work was financed by NEDO, the New Energy and Industrial Technology Development Organization, Japan.

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