Activated carbon aerogel as electrode material for coin-type EDLC cell in organic electrolyte

Soon Hyung Kwon [a], Eunji Lee [a], Bum-Soo Kim [b], Sang-Gil Kim [b], Byung-Jun Lee [b], Myung-Soo Kim [a,*], Ji Chul Jung [a,**]

[a] Department of Chemical Engineering, Myongji University, Yongin 449-728, Republic of Korea
[b] R&D Center, Vitzrocell Co. Ltd., Chungnam 340-861, Republic of Korea

ABSTRACT

Carbon aerogel (CA) was prepared by a carbonization of resorcinol—formaldehyde (RF) polymer gels, and it was chemically activated with KOH to obtain activated carbon aerogel (ACA) for electrode material for EDLC in organic electrolyte. Coin-type EDLC cells with two symmetrical carbon electrode were assembled using the prepared carbon materials. Electrochemical performance of the carbon electrodes was measured by galvanostatic charge/discharge and cyclic voltammetry methods. Activated carbon aerogel (20.9 F/g) showed much higher specific capacitance than carbon aerogel (7.9 F/g) and commercial activated carbon (8.5 F/g) at a scan rate of 100 mV/s. This indicates that chemical activation with KOH served as an efficient method to improve electrochemical performance of carbon aerogel for EDLC electrode in organic electrolyte. The enhanced electrochemical performance of activated carbon aerogel was attributed to the high effective surface area and the well-developed pore structure with appropriate pore size obtained from activation with KOH.

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1. Introduction

Electric double layer capacitors (EDLCs) have attracted much attention as an electrochemical energy storage device due to their high power density and long durability [1—5]. They are widely used as alternative or complementary power sources in the portable electronic device, electric hybrid vehicles, and uninterruptible power supply (UPS). EDLC can store energy by accumulating the opposite charge on the double layer at the electrode/electrolyte interface through electrostatic force [2—4]. Therefore, it is generally accepted that electrode material for EDLC should have a high surface area for charge accumulation [5—7].

A number of carbon materials, such as activated carbons [8—10], carbon nanotubes [11—15], and carbon aerogels [16—20], have been widely used as electrode materials for EDLC. Among the various carbon materials, activated carbons are mainly employed as the electrode material for EDLC in the commercial industry due to their high surface area, chemical and thermal stability, and low cost [21,22]. However, it is well known that the activated carbons retain abundant micropores (<2 nm), which are not easily wetted by the organic electrolyte ions [22]. In addition, the ionic motion may be limited in such small pore during the charge/discharge at high current density [22]. Therefore, it is expected that carbon materials with a high surface area and well-developed mesopores (2—50 nm) will serve as efficient electrode materials for EDLC in organic electrolyte.

Carbon aerogel is a kind of mesoporous carbon material with a three-dimensional network structure of carbon particles [23]. It has been recognized as a promising electrode material for EDLC, due to an electrically conductive carbon network, a low density, and other interesting properties [6,16]. However, it was reported that surface area of carbon aerogel is much lower than that of activated carbon, leading to the limited energy and power densities of EDLC [16,23]. In other words, commercial application of carbon aerogel to EDLC electrode has been impeded by its relative low surface area.

In order to improve the electrochemical properties of carbon aerogel, various activation method such as physical and chemical activations have been attempted [24—30]. In the physical activation method, steam or CO_2 is employed as activation agent [24—27]. In the case of chemical activation, activation gases are penetrated into the matrix of carbon material to generate the new pore and expand the pore size. Various chemical agents, such as KOH, NaOH, H_2SO_4,

and H_3PO_4, are used as activation agents, which are soaked into the carbon material and have a reaction with a carbon material [28–30]. This chemical activation process increases surface area and pore volume of carbon material due to the formation of new pore structure. Therefore, it is expected that electrochemical properties of carbon aerogel for EDLC electrode can be improved using chemical activation method.

In this work, carbon aerogel was prepared by a polycondensation of resorcinol and formaldehyde in ambient conditions. There are four steps in the preparation of carbon aerogel, including sol–gel polymerization, solvent exchange, ambient drying, and pyrolysis. The prepared carbon aerogel was chemically activated with KOH to obtain activated carbon aerogel. Carbon materials were applied to the EDLC electrode in organic electrolyte. Coin-type EDLC cells with two symmetrical carbon electrodes were assembled using the prepared carbon materials, and their electrochemical performance was investigated.

2. Experimental

2.1. Preparation of carbon aerogel

Carbon aerogel was derived from carbonization of a resorcinol–formaldehyde (RF) gel, according to the similar method in the literature [16]. In order to obtain RF gel, resorcinol ($C_6H_6O_2$, Sigma–Aldrich) and formaldehyde (H_2CO, Sigma–Aldrich) were polymerized in the aqueous solution using sodium carbonate (Na_2CO_3, Sigma–Aldrich) as a base catalyst which help the two materials being a gel. Weight percent of reactants in the aqueous solution was about 40% and molar ratio of resorcinol:formaldehyde:sodium carbonate was fixed at 1:2:500. Solvent exchange of the synthesized RF gel was then done at 50 °C. Solvent in the synthesized RF gel was exchanged with fresh acetone every 3 h for 1 day. Then, it was dried at ambient condition for 1 day. Subsequently, the RF gel was carbonized at 800 °C for 2 h under a continuous nitrogen flow in a tube furnace to obtain the carbon aerogel (CA).

2.2. Activation of carbon aerogel with KOH

Activated carbon aerogel was prepared by the pyrolysis of carbon aerogel with KOH. The mass ratio of carbon aerogel with respect to KOH was fixed at 4:1. Known amounts of carbon aerogel and KOH were physically mixed, and then, it was loaded under nitrogen flow in a tube furnace. Furnace temperature was increased from room temperature to 800 °C at a heating rate of 5 °C/min under a flow of nitrogen. After activation of carbon aerogel at 800 °C for 2 h, the powder was thoroughly washed with distilled water to remove the remaining KOH. Finally, it was dried at 50 °C for 1 day to yield the activated carbon aerogel (ACA).

2.3. Characterization

Textural properties of carbon aerogel (CA) and activated carbon aerogel (ACA) were examined by N_2 adsorption/desorption measurements using an ASAP 2010 (Micromeritics) instrument. Surface areas of carbon aerogel and activated carbon aerogel were calculated by the Brunauer–Emmett–Teller (BET) plot. Pore size distribution was obtained by the Barret–Joyner–Hallender (BJH) method with the desorption branch of the N_2 adsorption/desorption isotherms. SEM analysis (Jeol, JSM-6700F) was carried out with an aim of investigating the surface morphology and porous structure of carbon aerogel and activated carbon aerogel. Graphitization of carbon aerogel and activated carbon aerogel was determined by

XRD measurements (Shimadzu, XRD-7000) using Cu-Kα radiation ($\lambda = 1.54056$ Å) operated at 40 kV and 30 mA.

2.4. Measurement of electrochemical performance

Electrode was prepared by mixing 80 wt% carbon material as a active material, 10 wt% Super-P as a conductive additive, and 10 wt% poly(vinylidene fluoride) (PVDF) as a binder in 1-methyl-2-pyrrolidone (NMP) to form slurry. Carbon aerogel (CA) and activated carbon aerogel (ACA) were employed as active carbon materials for electrode. The slurry was then coated onto etched aluminium foil as current collector. The coated foil was dried in an oven at 70 °C for 1 day. The dried foil had a thickness of about 80 μm and a loading of ∼10 mg/cm².

Coin-type EDLC cells were fabricated using two symmetrical carbon electrodes. The electrodes were punched into small disks with 18 mm diameter and placed into the coin cells. 19 mm diameter separator soaked with electrolyte solution was placed between the same electrodes. The coin cells were filled with 1 M tetracetylammonium tetrafluoroborate in acetonitrile (TEABF$_4$/ACN) electrolyte inside an argon filled glove box. Finally, the coin cell was sealed using a coin cell crimper.

Electrochemical performance of the coin cells was measured by galvanostatic charge/discharge and cyclic voltammetry methods. Charge/discharge measurements were carried out at constant current loads (1 A/g and 3 A/g) in the voltage range of 0–2.5 V. Cyclic voltammetry measurements were conducted at various scan rates from 10 to 100 mV/s in the same voltage range of charge/discharge measurements.

3. Results and discussion

3.1. Physical properties of carbon aerogel (CA) and activated carbon aerogel (ACA)

To investigate the textural properties of carbon aerogel (CA) and activated carbon aerogel (ACA), N_2 adsorption/desorption isotherm measurements were carried out, and the corresponding N_2 adsorption/desorption isotherm and pores size distributions are shown in Fig. 1. Both carbon materials showed type IV isotherms with H2 type hysteresis loop, indicating their well-developed pore structure characteristic. It is interesting to note that hysteresis loop of carbon aerogel was shifted to the lower relative pressure after activation with KOH. This result means that pore size of activated carbon aerogel was smaller than that of carbon aerogel, in good agreement with the pore size distribution (Fig. 1(b)). The average pore diameter of carbon aerogel and activated carbon aerogel was found to be 7.5 and 4.5 nm, respectively, calculated by BJH method. Activated carbon aerogel rather than carbon aerogel exhibited a sharper pore size distribution, indicative of highly developed pore structure. In addition, BET surface area of activated carbon aerogel (1645 m²/g) was much larger than that of carbon aerogel (647 m²/g). Therefore, it is believed that activation with KOH resulted in more well-developed pore structure of activated carbon aerogel with a smaller pore size, leading to an increment of surface area.

SEM images of carbon aerogel (CA) and activated carbon aerogel (ACA) are shown in Fig. 2. As expected, the morphology of carbon aerogel was obviously changed after activation with KOH. As shown in Fig. 2, carbon aerogel retained an interconnecting network structure of carbon particle with random pore size, while activated carbon aerogel exhibited a well-developed pore structure with regular pore size, in good agreement with the results of N_2 adsorption/desorption isotherm measurements. From the SEM
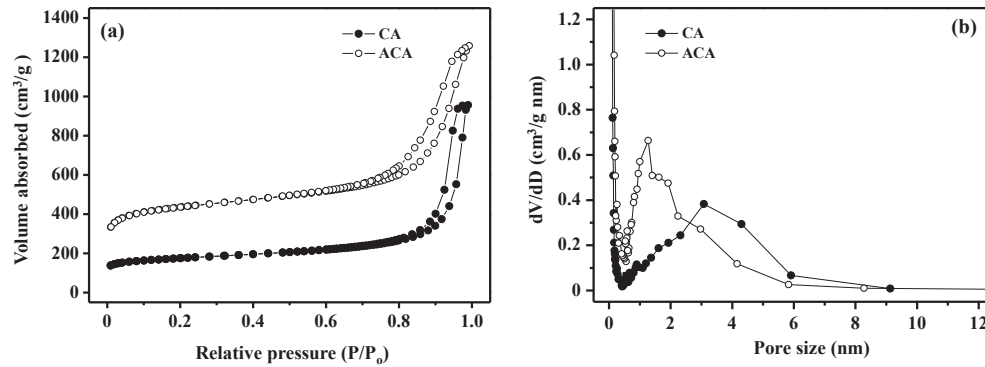
Fig. 1. (a) N$_2$ adsorption/desorption isotherms and (b) pore size distributions of carbon aerogel (CA) and activated carbon aerogel (ACA).
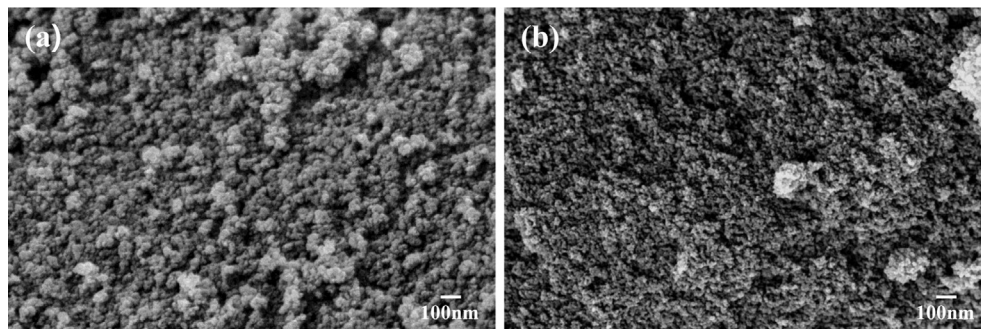

Fig. 2. SEM images of (a) carbon aerogel (CA) and (b) activated carbon aerogel (ACA).

analysis, it was also confirmed that pore size of activated carbon aerogel was smaller than that of carbon aerogel.

Fig. 3 shows the XRD patterns of carbon aerogel (CA) and activated carbon aerogel (ACA). Both carbon materials exhibited two broad XRD reflection peaks at $2\theta = 23.5°$ and $43.8°$, which were attributed to (002) and (101) reflections of graphite carbon, respectively. This result indicates that partly graphitic characteristic of carbon aerogel was maintained even after activation with KOH. It is well known that graphitic carbons retain a high electrical conductivity [2]. Therefore, it is expected that activated carbon aerogel
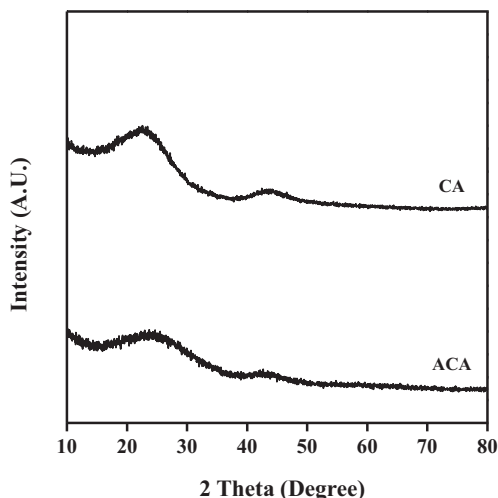
will show an excellent electrochemical performance at high current density.

3.2. Electrochemical performance of carbon aerogel (CA) and activated carbon aerogel (ACA)

To evaluate electrochemical performance of carbon materials for EDLC electrode, galvanostatic charge/discharge measurements were carried out. For comparison, a commercial activated carbon (AC), which is well known as MSP-20 (Kansai Coke & Chemicals Co., Japan), was also tested. As expected, N$_2$ adsorption/desorption isotherm analysis revealed that commercial activated carbon (AC) retains a high surface area (2447 m^2/g) with abundant micropores. Fig. 4 shows the discharge curves of carbon aerogel (CA), activated carbon aerogel (ACA), and commercial activated carbon (AC) electrodes at a constant current density (1 A/g and 3 A/g). The specific capacitance of each samples was calculated using the following equation, where I is the discharge current, Δt is the discharge time, m is the total weight of two electrode materials, and ΔV is the voltage change during discharging:

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V}.$$

The calculated specific capacitance of carbon aerogel, activated carbon aerogel, and commercial activated carbon are summarized in Table 1. It is noteworthy that the specific capacitance of activated carbon aerogel was about two times larger than that of carbon aerogel at a low current density (1 A/g). Furthermore, activated carbon aerogel retained a larger specific capacitance than commercial activated carbon. What is surprising is that activated carbon aerogel exhibited a good electrochemical performance with a
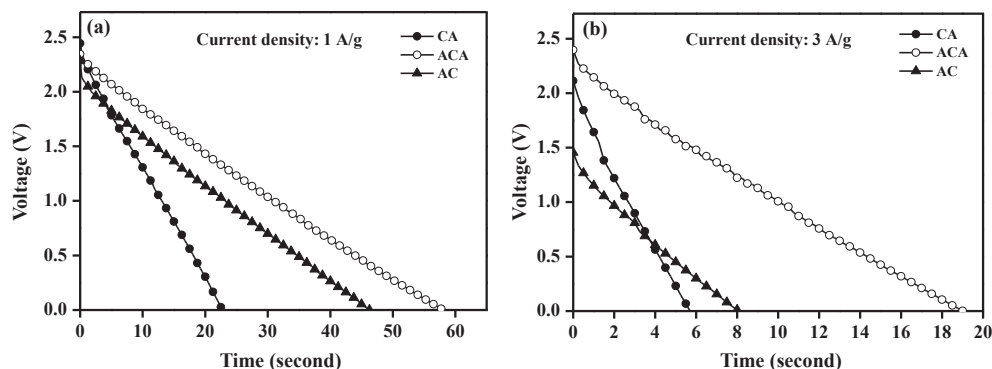

Fig. 3. XRD patterns of carbon aerogel (CA) and activated carbon aerogel (ACA).

Fig. 4. Charge/discharge profiles of carbon aerogel (CA), activated carbon aerogel (ACA), and commercial activated carbon (AC) electrodes measured at (a) 1 A/g and (b) 3 A/g.

Table 1
Specific capacitance of carbon aerogel (CA), activated carbon aerogel (ACA), and commercial activated carbon (AC) calculated from galvanostatic charge/discharge measurements.

	Specific capacitance (F/g)	
	1 A/g	3 A/g
CA	9.1	6.9
ACA	23.3	23.1
AC	18.6	9.9

slight IR (inner resistance) drop at a high current density (3 A/g). On the other hand, commercial activated carbon showed a severe IR drop at high current density, leading to a drastic decrease in specific capacitance with increasing current density. This indicates that activated carbon aerogel could serve as an excellent electrode material for EDLC with high energy and power densities. It is thought that the enhanced electrochemical performance of activated carbon aerogel was attributed to the high surface area and the well-developed pore structure with appropriate pore size obtained from activation with KOH. Therefore, it is believed that activation with KOH can be one of the efficient methods to improve electrochemical performance of carbon aerogel for EDLC electrode.

Cyclic voltammetry measurements were also conducted, with an aim of investigating electrochemical properties of carbon materials. Fig. 5 shows the cyclic voltammograms of carbon aerogel (CA), activated carbon aerogel (ACA), and commercial activated carbon (AC) electrodes. As shown in Fig. 5(a), CV curves of all carbon materials showed a rectangular, symmetric, and reversible shape in the voltage range of 0–2.5 V at a scan rate of 10 mV/s,

indicative of general electrochemical properties of carbon material. Even after scan rate was increased up to 100 mV/s, CV curves of carbon aerogel and activated carbon aerogel maintained the rectangular shape. The excellent capacitance behaviour of carbon aerogel and activated carbon aerogel at high scan rate implies that their equivalent series resistance (ESR) was very low. However, commercial activated carbon showed a narrow and rugby ball-shaped CV curve, indicating the decrement of specific capacitance. It is thought that the decrease in capacitance of activated carbon at a high scan rate is due to its low ion transfer rate in organic electrolyte. These results were well consistent with the results of galvanostatic charge/discharge measurements.

Fig. 6 shows the specific capacitance of carbon aerogel (CA), activated carbon aerogel (ACA), and activated carbon (AC) plotted as a function of scan rate. From the CV curve measured at different scan rates, the specific capacitance was calculated according to the following equation:

$$C = \frac{I_a + |I_c|}{2m \cdot (\mathrm{d}V/\mathrm{d}t)}.$$

Here, I_a and I_c are anodic current and cathodic current, respectively, m is the total weight of two electrode materials and $\mathrm{d}V/\mathrm{d}t$ is scan rate. As shown in Fig. 6, specific capacitance of carbon aerogel and activated carbon aerogel was slightly decreased with increasing scan rate due to its low ESR. On the other hand, commercial activated carbon exhibited a drastic decrease in specific capacitance with increasing scan rate. Finally, the specific capacitance was increased in the order of carbon aerogel (7.9 F/g) < activated carbon (8.5 F/g) < activated carbon aerogel (20.9 F/g) at a scan rate of 100 mV/s.
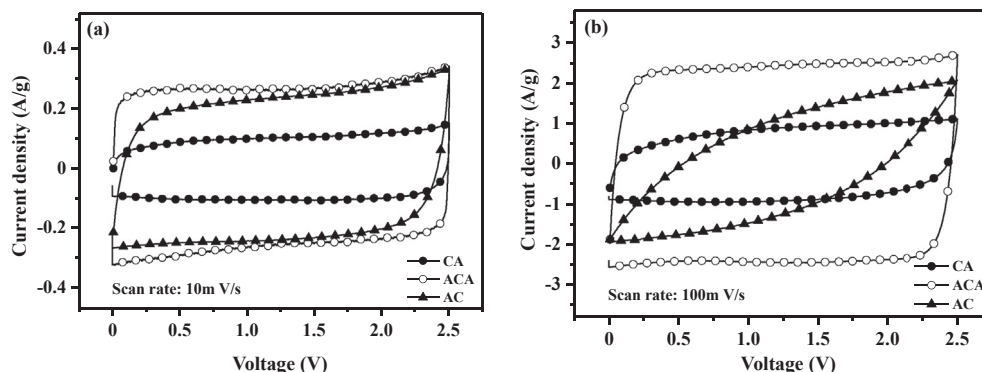

Fig. 5. Cyclic voltammograms of carbon aerogel (CA), activated carbon aerogel (ACA), and commercial activated carbon (AC) electrodes at a scan rate of (a) 10 mV/s and (b) 100 mV/s.
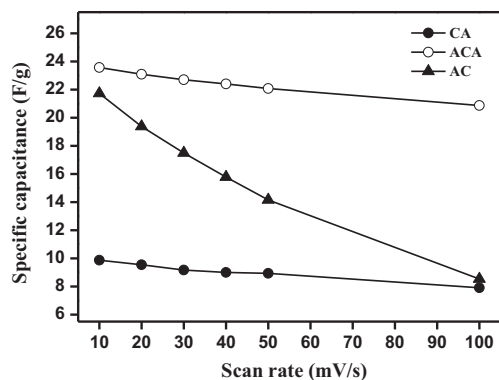
Fig. 6. Specific capacitance of carbon aerogel (CA), activated carbon aerogel (ACA), and commercial activated carbon (AC) plotted as a function of scan rate from 10 to 100 mV/s.

It is thought that activation of carbon aerogel with KOH played an important role not only in increasing surface area but also in developing pore structure with appropriate pore size for EDLC electrode in organic electrolyte, leading to the enhanced electrochemical performance of activated carbon aerogel. When considering the fact that activated carbon aerogel showed an excellent electrochemical performance at a high current density and a high scan rate, activation of carbon aerogel with KOH can serve as an efficient method for commercial application of carbon aerogel to the EDLC electrode in organic electrolyte.

4. Conclusion

Carbon aerogel was prepared by a polycondensation of resorcinol and formaldehyde in ambient conditions. In order to improve the electrochemical performance of carbon aerogel, it was chemically activated with KOH. The prepared carbon aerogel and activated carbon aerogel were applied to the EDLC electrode in organic electrolyte. It was found that activated carbon aerogel rather than carbon aerogel exhibited a higher surface area and a sharper pore size distribution with an appropriate pore size, leading to the enhanced electrochemical performance of activated carbon aerogel. Furthermore, activated carbon aerogel showed a better electrochemical performance for EDLC electrode in organic electrolyte than commercial activated carbon. This indicates that activated carbon aerogel could serve as an excellent electrode material for EDLC with high energy and power densities. Therefore, it is concluded that chemical activation of carbon aerogel with KOH can be one of the efficient methods for commercial application of carbon aerogel to the EDLC electrode in organic electrolyte.

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