

High double layer capacitance per volume of spherical carbon activated with NaOH

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1. INTRODUCTION

The electric double-layer capacitor (EDLC) using activated carbon as an electrode has been recognized as a efficient high power energy device in the electric power storage because of its better rate capability and longer cycle life as compared to secondary batteries [1,2]. Recently new applications utilizing such a performance have been attempted as an energy storage device for electric vehicle or pulse-current supply. In order to meet the need of new application, it is necessary for particular activated carbon to have higher energy density per weight or volume than conventional one.

Activated carbons with a very large surface area beyond $2000\text{m}^2/\text{g}$ have been prepared from the anisotropic carbon by chemical activation, resulting in high capacity per weight [3-5]. Nevertheless, they still suffer from low electrode density and capacitance per volume which is not helpful to the compactness of EDLC. To overcome those drawbacks, it is desirable to select dense precursor and to prepare the activated carbon of relatively low surface area with high capacitance per weight. Fujino et al reported briefly high capacitance per volume near $35\text{F}/\text{ml}$ on activated carbon basis by activating the mesophase pitch with KOH [6]. Their preparation procedure looks to stand on a similar concept, although experimental details are not disclosed.

In the present study, optically anisotropic spherical carbon (average particle size; 25

micron, quinoline soluble; 5%) prepared from coal based isotropic pitch was selected as a precursor because of its high packing density, and pre-calcined to control its graphitization extent, density and gasification reactivity with activating chemical [7]. NaOH and KOH were used as activating chemicals, and NaOH was emphasized especially here because it is low in reactivity and less corrosive.

2. EXPERIMENTAL

Spherical carbon with or without pre-calcination was mixed with 4 times of NaOH or KOH in weight. The mixture was activated in a nickel-made crucible at respective temperature for 1h under Ar flow, washed with 5% hydrochloric acid thoroughly 3 times, and then dried under vacuum at 150°C. Activated carbon was post-calcined at the temperature shown in Table 1.

Capacitance was measured at 25°C in a two-electrode system (galvanostatic mode) using 1M Et₄NBF₄ in propylene carbonate as an electrolyte [8]. Three-electrode system will give a capacitance around 4 times higher than that of two-electrode system [9]. The electrode was composed of activated spherical carbon (80wt%), PTFE as a binder (10%), and carbon black as a conductive (10%). The test cell was charged to 2.7V at a current density of 200mA/g, and then discharged to 0V at the same current density. In the present study, all specific capacitances were calculated from the time period of voltage change which was divided by the weight sum of each electrode including the binder and conductive.

3. RESULTS AND DISCUSSION

Table 1 summarizes the yield and surface characteristics of spherical carbons activated with NaOH or KOH under a series of conditions such as pre-calcination

temperatures (from as-prepared to 900°C), activation temperatures (from 600 to 900°C), and post-calcination temperatures (from 800 to 1000°C).

Table 1. Preparation conditions, yields, surface characteristics, and capacitances of spherical carbons activated by NaOH or KOH (sample K). Pre, A, and Post imply pre-calcination, activation, and post-calcination, respectively.

Sample	Pre (°C)	A (°C)	Post (°C)	Yield (%)	S _{N2} (m ² /g)	PV (ml/g)	Capacitance	
							F/g	F/ml
A1	-	700	-	55	1210	0.78	39	23
A2	-	700	800	51	1120	0.67	33	19
A3	-	700	1000	51	650	0.37	20	13
B	800	600	-	75	380	0.24	32	33
C1	800	700	-	56	470	0.29	36	35
C2	800	700	800	53	130	0.09	11	11
D	800	800	-	52	180	0.13	30	29
E	800	900	-	51	150	0.18	24	23
K	800	800	-	54	890	0.55	29	27

The as-prepared spherical carbon (A1) showed a fairly large surface area of 1210m²/g at a yield of 55% by activation at 700°C. The post-calcination (A2 and A3) decreased the surface area according to the calcination temperature of 800 and 1000°C to 1120 and 650m²/g, respectively.

The pre-calcination at 800°C (C1) reduced the surface area after NaOH activation at 700°C, although the yield was similar. It is noticeable that the activation at 600°C provided the moderate surface area (B), while the activation at 800°C and 900°C failed to give high surface area to spherical carbon pre-calcined at 800°C (D and E). Activation at both lower and higher temperatures than 700°C reduced the surface area. The post-calcination (C2) at 800°C of sample C1 pre-calcined at 800°C reduced sharply

the surface area to 130m²/g. Thus, the activation, pre- and post-calcination temperatures were found to influence profoundly the properties of spherical carbons activated with NaOH. Specific pore volume of activated carbons by NaOH was linearly correlated with specific surface area. Spherical carbon (K) activated by KOH after pre-calcination at 800°C showed higher specific surface area and pore volume than those of the counterpart (C1).

Table 1 shows the capacitance per both weight and volume of a series of activated spherical carbons. Capacitance per weight and volume was significantly influenced by preparation method of activated spherical carbon. The larger surface area obtained with as-prepared spherical carbon tended to provide larger capacitance per weight, however their capacitance per volume was rather low. The capacitance per volume was strongly improved by the pre-calcination. Very high capacitance per both weight and volume was obtained with the pre-calcination at 800°C and activation at 600 or 700°C of spherical carbon (33 to 35 F/ml). Also, activated carbon C1 lost 2% of first cycle capacitance after 40 cycles, although the number was not so large. The higher activation temperature reduced capacitance per both weight and volume. The smaller difference between capacitance per weight and capacitance per volume was characteristic in the pre-calcined spherical carbon. Post-calcination (C2) at 800°C after the activation at 700°C decreased the capacitance markedly. Capacitance of sample K activated by KOH was lower than that of the counterpart (C1) activated by NaOH, in spite of its larger surface area.

Fig. 1 illustrates XRD profiles of precursors and activated spherical carbons. According to the activation, 002 peak was broadened and shifted to downfield, as

shown with samples B and C1. However, 002 peak of samples B and C1 showed higher intensity than those of activated carbons without pre-calcination as shown in Fig. 2. High extent of graphene stacking results in high electrode density to give high capacitance per volume. Activation at higher temperature above 700°C intensified the broadening and downward shift of 002 peak, emphasizing non-graphitic nature. Post-calcination (C2) at 800°C recovered 002 peak slightly. Activation (samples D and E) of pre-calcined spherical carbons above 800°C showed a sharp peak at 26.5° overlapped with a broad 002 peak. The catalytic graphitization by metal contaminants from the nickel-made crucible is suspected.

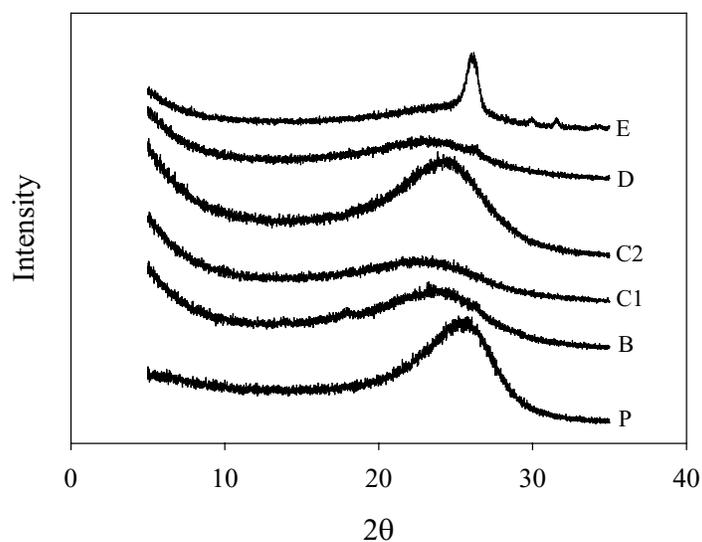


Fig. 1. X-ray diffraction patterns of spherical carbon and its s activated ones prepared by NaOH activation. P; spherical carbon pre-calcined at 800°C before activation.

Fig. 2 shows XRD profiles of the spherical carbon activated at 700°C without pre-calcination (A1) and its post-calcined ones (A2 and A3). The post-calcination sharpened slightly and shifted upward the 002 peak of the activated spherical carbon

without pre-calcination in contrast to that of the activated carbon after the pre-calcination. The peak in the low angle region around 5° still remained high after the post-calcination.

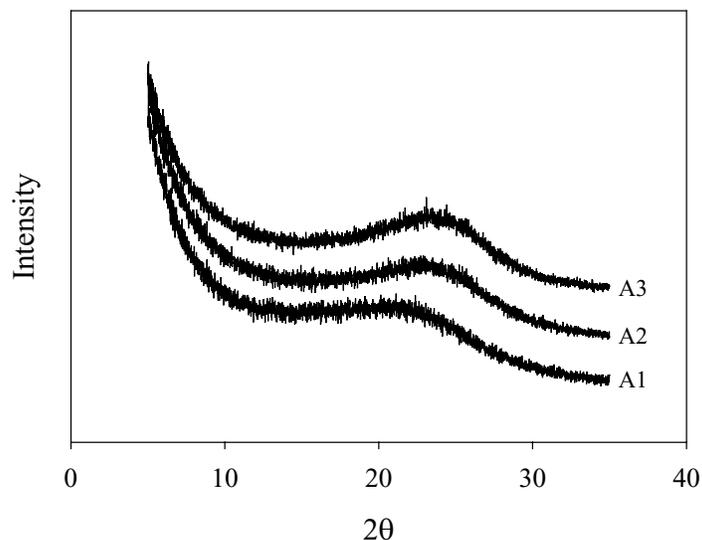


Fig. 2. X-ray diffraction patterns of spherical carbon activated by NaOH without pre-calcination and its post-calcined ones.

Fig. 3a and 3b compare capacitance as the function of surface area between spherical carbons activated by NaOH and the activated carbons from anisotropic precursors including spherical carbon, mesophase pitch derived carbon fiber and needle cokes. Capacitance per weight of spherical carbon with NaOH became saturated at surface area of $500\text{m}^2/\text{g}$, where the particular spherical carbon activated with NaOH showed the maximum capacitance per volume. Although anisotropic carbons activated with 4 times KOH in weight of precursor gave a high surface area and capacitance per weight near $40\text{F}/\text{g}$, they failed to give capacitance per volume over $20\text{F}/\text{ml}$. Therefore, the effective pore must be introduced into the spherical carbon by NaOH activation.

The high density and moderate reactivity of anisotropic spherical carbon balanced by the pre-calcination and moderate activation with NaOH resulted in the capacitance per

volume. When carbon materials and alkaline hydroxide are heated together in an inert atmosphere at a temperature higher than 700 °C, the alkaline hydroxide gasifies the carbon to be reduced into alkali metal which intercalates and deintercalates repeatedly to expand the layers with the increase of surface area [10].

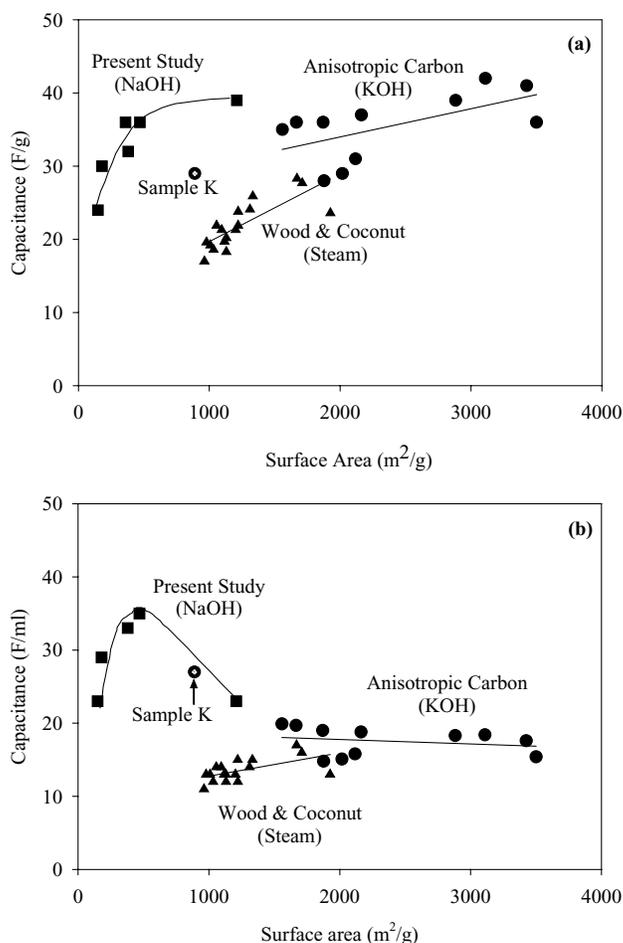


Fig. 3. Comparison of capacitance as the function of surface area between spherical carbons activated by NaOH and other activated carbons from their anisotropic precursors (spherical carbon, mesophase pitch derived carbon fiber, needle cokes). (a) Capacitance per weight (F/g) vs. surface area (m²/g). (b) Capacitance per volume (F/ml) vs. surface area (m²/g).

KOH is more powerful in both gasification and intercalation, providing too much

porosity useless for double layer capacitance than NaOH [11]. More moderate activation with KOH must be designed for higher capacitance per volume. Too larger pore must be recognized to reduce the effective surface area through introducing useless void in the carbon and decreasing the effective polarization of the adsorbed electrolyte on the wall. The pre-calcination at proper temperature increased the density and stacking of the carbon to be activated. The latter moderates the gasification and controls the expansion through intercalation and deintercalation as indicated by XRD results. Thus the pre-calcination is very important to adjust the structure and property of precursor carbon.

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