CONTROL OF PORE STRUCTURE OF ACTIVATED CARBONS FOR EDLC THROUGH TWO-STEP ACTIVATION

Masanori Saito[1], *Jin Miyawaki*[2], *Seong-Ho Yoon*[2], *Isao Mochida*[2]

[1]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Japan; [2]Institute for Materials Chemistry and Engineering, Kyushu University, Japan

Introduction

In this study, the present authors investigated two step activation method for the controls of pore size and oxygen containing amounts in the alkaline and stream activation processes.

Experimental

1. Material

Spherical type of phenol resin (s-beap, Ashahi Organic Co. Ltd., Japan) was used as a starting material for this study. S-beaps were pretreated for 1h at 600 oC under nitrogen atmosphere.

2. 1st activation

1st activation of preheat treated s-beaps were carried out by KOH activation method using self-designed apparatus (Fig.1 (a)). The ratio of KOH/s-beaps was adjusted by 6. The activation was carried out at 700 oC for 1h under nitrogen atmosphere.

3. 2nd activation

2nd activation was carried out using KOH and steam activation methods using self-designed apparatuses (Fig. 1). In the KOH activation method, the ratios of KOH/s-beaps were adjusted by 1~4. In the steam activation, the activation temperature was changed from 400 oC to 600 oC.

4. Nomenclature of prepared samples

Table 1 showed sample code and preparation conditions.

5. Analyses of prepared samples

The prepared samples were characterized by SEM, XRD and N2-BET method.

6. Capacitance evaluation of samples

As for the preparation of electrode, ativated carbon, Ketjen Black and plytetorafluoroethylene were mixed at the rate of 1:1:1 (wt%). Et_4NBF_4(1M)/PC was used as an ectrolyte in EDLC. The capacitance was measured by charge up to 2.7 V and discharge at constant voltage and current.

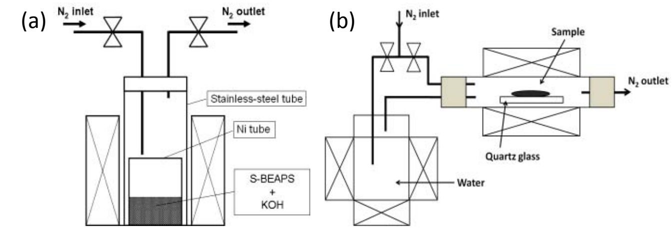

Fig.1 schematic diagrams of KOH and Steam activation; (a) KOH activation (b) Steam activation.

Table 1. Sample names of activated carbons.

Code	Pretreatment (600℃, 1h)	1st activation (700℃, KOH×6, 1h)	2nd Activation	
			KOH activation	Steam activation
SB	-	-	-	-
SBH	O	-	-	-
AK	O	O	-	-
AAK1400	O	O	400℃, KOH×1, 1h	-
AAK2400	O	O	400℃, KOH×2, 1h	-
AAK4400	O	O	400℃, KOH×4, 1h	-
AAK6400	O	O	400℃, KOH×6, 1h	-
AAK1500	O	O	500℃, KOH×1, 1h	-
AAK2500	O	O	500℃, KOH×2, 1h	-
AAK4500	O	O	500℃, KOH×4, 1h	-
AAK6500	O	O	500℃, KOH×6, 1h	-
AAK1600	O	O	600℃, KOH×1, 1h	-
AAK2600	O	O	600℃, KOH×2, 1h	-
AAK4600	O	O	600℃, KOH×4, 1h	-
AAK6600	O	O	600℃, KOH×6, 1h	-
AAS400	O	O	-	400℃, 1h
AAS500	O	O	-	500℃, 1h
AAS600	O	O	-	600℃, 1h

Results and Discussion

1. Characterization of prepared samples

Table 2 shows the yield and atomic ratios of raw material, pretreated and 1st activated samples (SB, SBH and AK). Atomic ratios of SB showed the similar values with raw PF resin. Preheat treated sample (SBH) had higher C ratios by elution out of volatile matters.

Table 3 shows the results of BET and capacitance evaluation of raw material, pretreated and 1st activated samples (SB, SBH and AK). SB did not have a surface area and capacitance. SBH showed the surface area of 454 m2/g but did show little capacitance, which meant the pore size was too small to adsorb the solvated ions of electrolyte. KOH activated AK showed very large surface area of 3360 m2/g and capacitance value of 42.5 F/g.

2. Effect of 2nd activation

Figure 2 showed the Langmuir isotherms of 1st and 2nd activated carbons at various 2nd activation conditions.

Table 2. Analyses of raw material, pretreated and 1st activated carbons

Sample Name	Yield [%]	Final yield [%]	elemental analysis [wt%]				
			H	C	N	O	Ash
SB	-	100	5.79	75.27	0.01	18.93	0
SBH	60	60	3.36	91.66	0.02	4.92	0.04
AK	40	24	1.33	90.35	0.13	7.19	1.00

Table 3. Surface areas and capacitances of raw material, pretreated and 1st activated carbons

Sample Name	BET surface area	Density of electrode	Capacitance		
	[m2/g]	[g/ml]	[F/g]	[F/ml]	[F/m2]
SB	3	-	-	-	-
SBH	454	0.86	1.54	1.06	0.003
AK	3360	0.42	42.5	14.4	0.013

Through the 2nd KOH activation, the most distinguished change was the preferential removal of relatively larger micropores and mesopores with almost no change of smaller micropores as shown in Fig. 2 (a), (b) and (c). In contrast, after 2nd steam activation at different activation temperatures, the difference of pore size distribution was hard to find.

Figure 3 showed the changes of BET surface area and capacitance after 2nd activations by both of KOH and steam activations. In the 2nd activation of KOH method, the decrease amount of BET surface area is always larger than that of capacitance value. From this result, we can conjecture that the 2nd KOH activation preferentially removes the relatively larger pores which can't contribute on the capacitance revelation, that is, the 2nd KOH activation is very effective to increase the volumetric capacitance by the removal of inefficient pores of the 1st activated carbons. In contrast to the 2nd KOH activation, the 2nd steam activation resulted in a little increasing of surface area and capacitance.

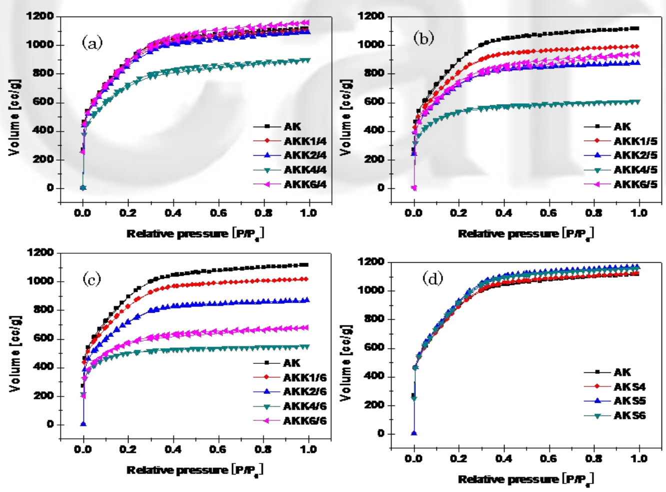

Fig. 2 Nitrogen adsorption and desorption isotherms at 77K for After-activated carbons; (a) KOH activation at 400 deg C, (b) KOH activation at 500 deg C, (c) KOH activation at 600 deg C, (d) Steam activation.

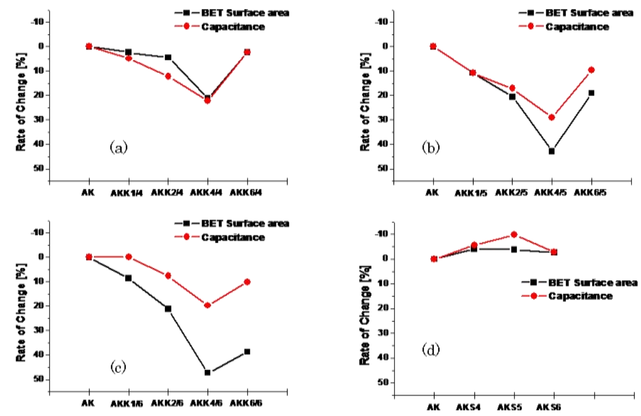

Fig. 4 Raito of changes of BET surface area and capacitance; (a) KOH activation at 400 deg C, (b) KOH activation at 500 deg C, (c) KOH activation at 600 deg C, (d) Steam activation.

The elemental analyses of the 2nd activated carbons. In the KOH 2nd activated carbons showed the increase of oxygen ratios compared to the 1st activated carbons, whereas the steam 2nd activated carbons did the decrease of oxygen rations.

Conclusion

We found that two step activation which is composed of 1st KOH activation at 700 oC and continuous 2nd KOH activation at 400~600 oC is very effective to remove the relatively large pores that are unnecessary to reveal the capacitance.

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