Performance of KOH of NaOH activation to Prepare EDLC electrode carbon

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1. Introduction

Electric double layer capacitor (EDLC) has been expected as a secondary electric power supplier for the automobiles with hybrid engine or fuel cell motor because of its rapid charge and discharge. Larger surface area has been considered to be a basic guiding principle for the larger capacity. KOH activation, which has been recognized to be the most effective procedure to introduce the large surface area reaching $3000m^2/g$, was applied to a variety of carbons. However, as the consequence of too large surface area, the activated carbon tends often to be low in density, which decreases sharply the capacitance per volume even if the capacitance per weight is fairly high. Hence, the effective pore must be exclusively introduced into the carbon of high density. Anisotropic carbons of high density with moderate surface area are promising candidates for the electrode with high capacitance per volume. In the present study, KOH and NaOH were compared as activating agents against needle coke whether they can provide optimum surface.

2. Experiment

2.1 Activation

Anisotropic needle coke produced in a commercial delayed coker was provided from Nippon Steel Chemical Co., Ltd. The anisotropic coke showed a fully developed needle type texture of optical anisotropy. Volatile matter of the raw coke was estimated to be around 5wt%. Activation was carried out using reagent grade alkali hydroxides. The reaction apparatus consisted of stainless tube and nickel sample holder. NaOH activation was carried out at 500-900^{o}C for 1-3h under Ar flow, and coke / NaOH ratio was fixed at 1/4 weight. KOH activation was carried out at 800^{o}C for 1-2h under Ar flow, and coke/KOH ratio was varied at 1/1-1/4.

2.2 Determination of specific capacitance

The electrode for EDLC was composed of coke, carbon black (Ketjen black-E) and PTFE (polytetrafluoroethylene); Coke/KB/PTFE=8/1/1 by weight. The specific capacitance was measured by 2-electrde system in a galvanostatic mode using 1M Et_4NBF_4 in PC as an electrolyte. The test cell was charged to 2.7V at constant current and voltage, and then discharged at a constant current to 0V.

3. Results and discussion

Table 1 summarizes capacitance per weight and volume of a series of the cokes activated with KOH and NaOH. NaOH and KOH activations provided capacitance per weight above 39F/g, as far as the large surface area was introduced. The capacitance per volume as high as 28F/ml was obtained exclusively with NaOH,whereas KOH-activated coke gave only 17F/ml because of much smaller bulk density.

Figure 1 illustrates SEM photographs of cokes activated with KOH and NaOH. More numbers of small and large cracks were observed along with optical anisotropy in the coke after the activation with KOH, while the claws among particles were exclusively observed, no crack being found in the particle. Such spaces must be introduced through the expansion caused by intercalation and deintercalation of alkali metals. Definitely smaller packing density of the coke activated with KOH as shown under SEM may reduce the capacitance especially per volume. In addition, the optimum pore must be developed in the coke activated with NaOH.

Table 1 Activation conditions and some properties of coke activated chemically.

Sample	Activation chemical	Reaction condition		Reagent /Coke	Yield (%)	Surface area (m^2/g)	E.A.		Capacitance	
		Temp(℃)	Time(h)				H/C	O/C	F/g	F/ml
N1	NaOH	500	2	4/1	88	40	0.308	1.171	4.3	3.7
N2	NaOH	550	2	4/1	77	660	0.121	0.863	33.3	28.3
N3	NaOH	600	2	4/1	65	880	0.101	1.085	39.3	26.2
N4	NaOH	650	2	4/1	54	960	0.055	0.883	38.7	27.2
N5	NaOH	700	2	4/1	53	910	0.061	0.589	38.7	22.5
N6	NaOH	750	2	4/1	57	990	0.041	0.813	34.7	25.0
N7	NaOH	800	2	4/1	56	730	0.068	1.092	32.3	20.3
N8	NaOH	850	2	4/1	54	740	0.039	0.444	28.6	21.9
N9	NaOH	900	2	4/1	53	430	0.026	0.278	24.5	11.9
K1	KOH	800	2	4/1	61	2320	0.028	0.141	39.4	16.2
K2	KOH	800	1	2/1	83	1280	0.084	1.070	22.6	17.8
K3	KOH	800	1	1/1	88	480	0.093	1.216	12.6	12.6

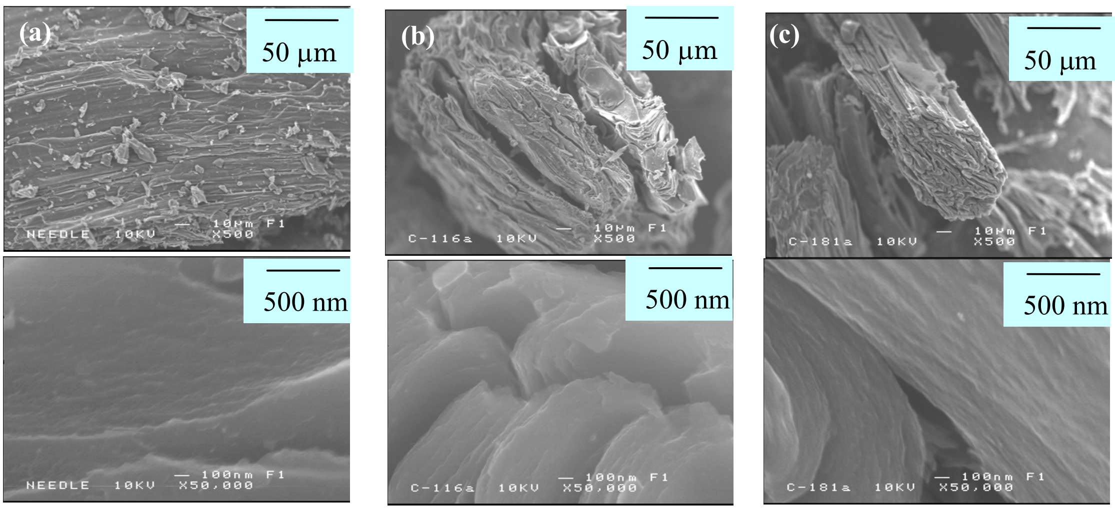

Fig. 1. SEM photographs of needle cokes activated by KOH(K1) or NaOH(N3).
(a) as-received (b) the activated by KOH (K1) (c) the activated by NaOH (N3).