

Activation of raw pitch coke with alkali hydroxide to prepare high performance carbon for electric double layer capacitor

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Abstract

Powder of raw pitch coke was activated with alkali hydroxides at 500–900 °C to prepare carbon electrode of high capacitance for electric double layer capacitor (EDLC). KOH provided very high surface area of 2320 m²/g at 800 °C, while NaOH did moderate surface area of 1000 m²/g at 650–750 °C. High surface area provided by KOH led to a high capacitance per weight of 39 F/g. However, its capacitance per volume was as low as 16 F/ml. Although the coke of moderate surface area activated with NaOH showed a similar capacitance per weight, its capacity per volume was as high as 28 F/ml because of its high density. Adequate porosity must be selectively introduced by NaOH activation to the coke to obtain moderate surface area. Much smaller expansion of layers in the present needle type coke activated by NaOH than that by KOH is indicative for the higher density of the former activated coke.

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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 [1,2]. Its task to be solved is believed to be larger energy density comparable to that of nickel metal hydride or lithium ion batteries [3]. As EDLC stores the electric power by adsorbing electrolyte on the surface of polarizable carbon electrodes, the capacitance is subjective to be its effective surface area. 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 3000 m²/g, was applied to a variety of carbons [4–8]. 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 [9].

Potassium hydroxide has been applied uniquely for the activation of anisotropic carbons to obtain very large surface area. Safety as for hydrogen and very reactive alkali metal produced at the oxidative activation, and corrosion by melting hydroxide are concerned for the mass production.

In the present study, activation by potassium and sodium hydroxides were applied to the raw needle coke derived from coal tar pitch to prepare carbon grain of moderate surface area and high density, targeting reasonable capacitance per volume around 30 F/ml, which is roughly double of the current capacitance per volume obtained with isotopic carbon. Moderate reactivity of sodium hydroxide is expected to introduce moderate surface area [10], and additionally may reduce the amount of hydrogen and metal produced as well as corrosion during the activation process.

2. Experimental

2.1. Activation

Anisotropic needle coke produced in a commercial delayed coker was provided from Nippon Steel Chemical Co. Ltd. The anisotropic coke had a fully developed needle type texture of optical anisotropy. Volatile matter of the raw coke was estimated to be around 5 wt.%. Activation was carried

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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 °C for 1–3 h under Ar flow, and coke/NaOH ratio was fixed at 1/4 weight. KOH activation was carried out at 800 °C for 1–2 h 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 two-electrode system in a galvanostatic mode using 1 M Et₄NBF₄ in PC as an electrolyte. The test cell was charged to 2.7 V at constant current and voltage, and then discharged at a constant current to 0 V. The specific capacitance was calculated by the following equation [11],

$$C = \frac{I \times (T_2 - T_1)}{(V_1 - V_2)(W_1 + W_2)}$$

where V_1 and V_2 are 2.16 and 1.08 V, respectively. $W_1 + W_2$ is weight sum of each electrodes.

Cyclic voltammetry was conducted at a potential sweep rate of 3 mV/s in 1 M Et₄NBF₄ in PC using conventional three-electrode cell. Ag/Ag⁺ (acetonitrile) electrode was used as a reference electrode. Open voltage between carbon and reference electrodes was confirmed to be 0.49 V. Stability of the system was confirmed by the blank test without carbon electrode. Activated carbon twice in weight over working electrode was used as a counter electrode.

2.3. Analyses of activated carbon

The activated carbon morphology was observed with a scanning electron microscopy (SEM; Jeol). The degree of graphitization of the activated carbon was measured by X-ray powder diffraction (XRD) using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Surface area and pore size distribution of activated coke were obtained from N₂ gas adsorption isotherm

measured at 77 K using an automatic adsorption system (Fisons Instruments Sorptomatic 1990) according to BET and BJH methods, respectively.

3. Results

3.1. Activation by NaOH and KOH

Table 1 summarizes the yield and surface area of the cokes activated with four times NaOH and KOH by weight. NaOH activated the coke efficiently above 550 °C, providing the largest surface of 990 m²/g at 750 °C. The sharp increase and decrease of surface area were found at 500–550 and 850–900 °C, respectively, the change being moderate at 550–880 °C (600–900 m²/g), particularly at 600–750 °C (880–900 m²/g). The moderate yields of activated cokes were obtained, ranging between 53 and 77%. The same amount of KOH was certainly more effective to provide larger surface area, and the highest area of 2320 m²/g was obtained at 800 °C. Smaller amount of KOH reduced sharply the surface area according to its amount, such as 1280 m²/g with two times and 480 m²/g with the equivalent amount of KOH.

3.2. Capacitance

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

Activation with smaller amount of KOH provided smaller capacitance per weight and surface area, whereas the capacitance per volume stayed at 13–18 F/ml which was comparable to that of the coke with very large surface area. Such results imply that the surface area is not a unique parameter,

Table 1
Activation conditions and some properties of activated coke chemically

Sample	Activation chemical	Reaction condition		Reagent/coke	Yield (%)	Surface area (m ² /g)	E.A.		Capacitance	
		Temperature (°C)	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

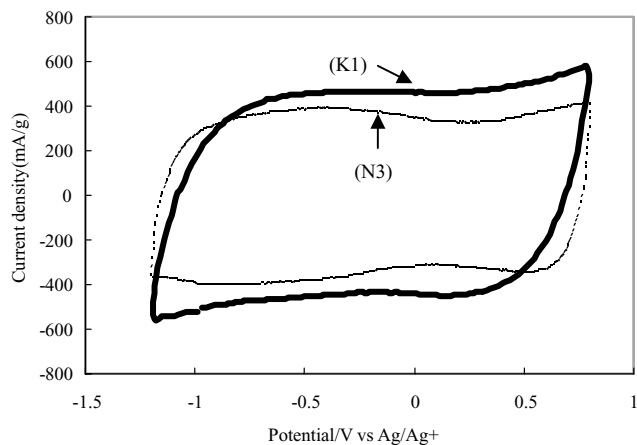


Fig. 1. Cyclic voltammograms of KOH-activated coke (K1) and NaOH-activated coke (N3) at the scan rate of 3 mV/s.

and adequate pores must be introduced into the raw coke through the adequate activation.

Fig. 1 illustrates cyclic voltammograms of cokes activated with KOH (K1) at 800 °C and NaOH (N3) at 600 °C, respectively. Very similar profiles of voltammograms were obtained with both cokes, a similar charge/discharge mechanism being suggested to operate.

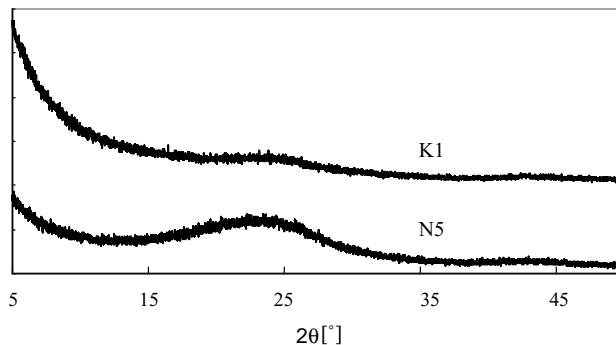


Fig. 2. X-ray diffraction patterns of the needle coke and activated needle cokes by KOH (K1) or NaOH (N5).

3.3. Feature of activated coke

Fig. 2 illustrates XRD profiles of cokes activated with KOH and NaOH. NaOH-activated coke showed certainly a more definite peak at 26° and smaller diffraction below 10° than those of KOH-activated coke. More graphitic structure is suggested to be present even after the activation with NaOH, resulting in the high density.

Fig. 3 illustrates SEM photographs of cokes activated with KOH and NaOH. Although both activations expanded the

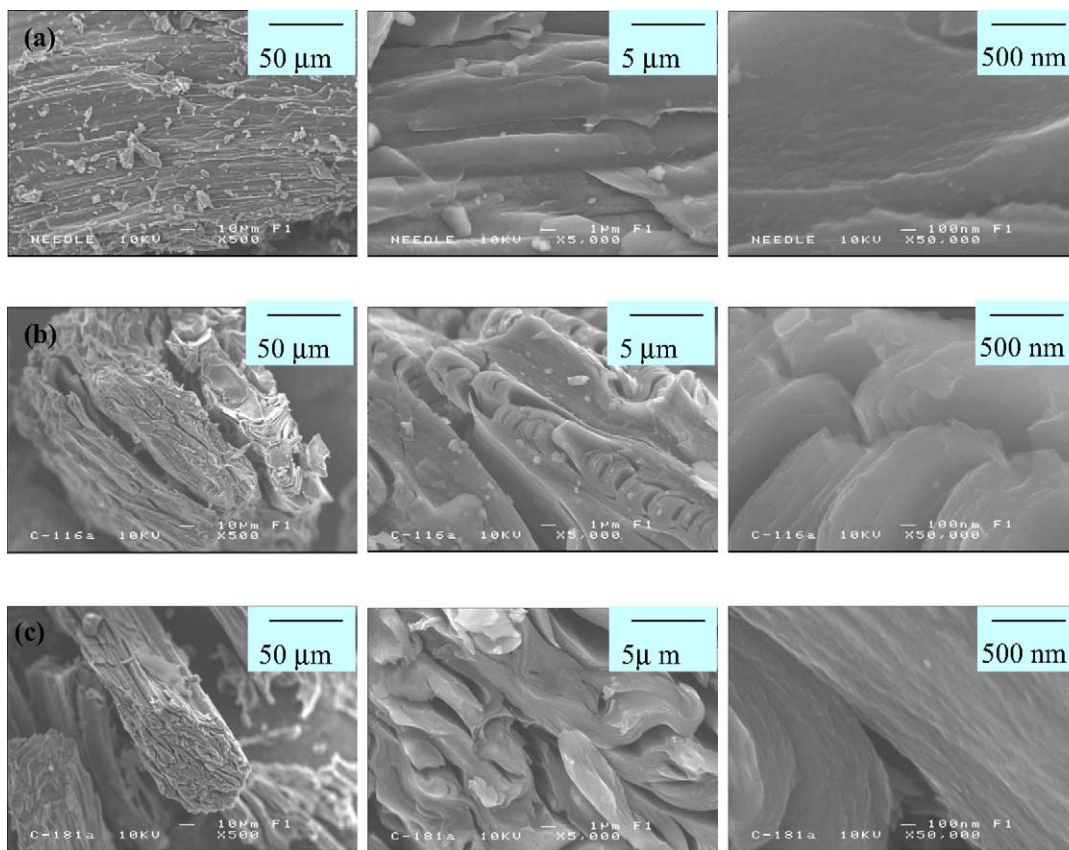


Fig. 3. SEM photographs of needle cokes activated by KOH (K1) or NaOH (N3): (a) as-received (b) the activated by KOH (K1) (c) the activated by NaOH (N3).

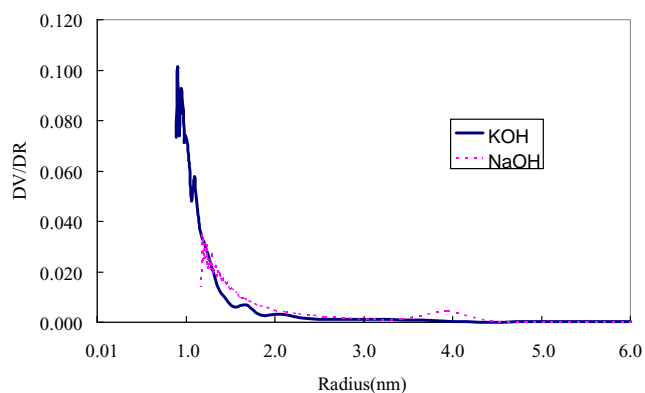


Fig. 4. Pore size distribution of KOH (K1) and NaOH (N2) activated coke.

spaces among grains, blocks and layers, and KOH activation appears to induce larger spaces at all scales. Such spaces must be induced through the expansion caused by intercalation and deintercalation of alkali metals. Smaller packing density of the coke activated with KOH may result from the expanded spaces as shown under SEM.

Fig. 4 shows pore size distribution of cokes activated with KOH and NaOH, respectively. NaOH-activated coke carried major pore around 2.5 nm in diameter with minor pores of 8 nm in diameter, while KOH-activated coke carried a larger number of pores below 2.5 nm diameter. Very minor but distinct pore was observed to have 3 nm diameter. Much larger pore volume of KOH activated coke must be noted.

4. Discussion

The present study reported that a marked increase of capacitance per volume was obtained by activating raw needle coke from coal tar pitch with NaOH at a temperature range of 550–650 °C. The obtained capacitance was as high as 26–28 F/ml which was much higher than those of cokes of similar and much larger surface areas activated by KOH. It must be noted that the activated coke of the largest capacitance per volume prepared in the present study had surface area of 700–900 m²/g.

The higher capacity per volume must be obtained with pores of right size which can hold or adsorb the largest amount of electrolyte on their wall with minimum amount of unadsorbed electrolyte in the same pore. Thus, too small or too large pores are both ineffective to obtain the largest capacity per volume. The largest surface area of the right pore wall must be introduced by the selection of carbon precursor, activating agent and conditions.

The present study claims that NaOH is a better agent for activation than KOH to obtain the right pores in the raw needle coke from coal tar pitch. NaOH reacts moderately with the coke in the present study to produce less metal, which may result in less expansion and higher density. Of course,

activation conditions in terms of its quantity, activation temperature and time are also carefully selected. According to SEM observation, KOH tends to induce large cracks among grains, domains, and plate layers, which are not counted by gas adsorption. Although the right pores to count the surface area for the capacitance was not observed under SEM of the present magnification, useless cracks which reduce the density are clearly observed. Well-developed needle coke may not be an ideal precursor for the electrode because larger expansion with needle-like feature may be inevitable at the intercalation/deintercalation activation.

Pore size distributions measured by gas adsorptions indicated that the KOH-activated carbon carried basically micro pores less than the 2.5 nm in diameter, while NaOH-activated carbon carried selective pores of 2.5 nm in diameter, which appears just adequate size. Very large pore volume of KOH-activated coke is not favorable for higher capacitance per volume.

It is noted that reduction of NaOH appears much less than that of KOH under the optimum activation conditions to give the respective largest surface area. Hence, higher yield of activated coke was obtained with NaOH. Less amount of activating agent is also desirable by the safety reasons. Lower temperature for optimum activation with NaOH can be another advantage for less corrosion of the metal reactor. Smaller consumption of NaOH is a suggestive possibility to reduce the amount of NaOH to be charged for optimum activation, when the uniform contact of the hydrokinetics with the coke is established.

The mechanism to obtain capacitance in the electric double layer appears similar with both cokes activated with NaOH and KOH as indicated by cyclic voltammetry. Pseudo-capacitance due to the Faradic reactions can be ruled out with cokes activated with both agents. Stable operation of this electrode is also confirmed by cyclic voltammetry.

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