1 **HyperCoal-derived porous carbons with alkaline hydroxides and carbonate activation for**
2 **electric double-layer capacitors**

3 Xiao-Yan Zhao ^a, Shan-Shan Huang ^a, Jing-Pei Cao ^{a,b*}, Xian-Yong Wei ^a, Kazushi Magarisawa ^b,
4 Takayuki Takarada ^b

5 ^a *Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), China*
6 *University of Mining & Technology, Xuzhou 221116, Jiangsu, China*

7 ^b *Division of Environmental Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515,*
8 *Japan*

9 **Abstract.** Electrical double layer capacitors (EDLCs) with HyperCoal-derived activated carbons
10 (ACs) as electrodes are reported in this work. The ACs were prepared by the carbonization of
11 HyperCoal at 600 °C followed by the activation with KOH and NaOH for 2 h between 500 and 800
12 °C to achieve high total pore volume (TPV) and specific surface area (SSA). The porosity of the
13 ACs was characterized with N₂ adsorption at 77 K. The results show that the ACs prepared with
14 KOH and NaOH activations at 700 °C have a SSA of 2594 and 3010 m² g⁻¹ and a TPV of 1.36 and
15 1.77 cm³ g⁻¹, respectively, leading to the highest specific capacitance of 43.1 and 43.9 F g⁻¹,
16 respectively, in a two-electrode EDLC cell with 0.5 M tetraethylammonium
17 tetrafluoroborate/propylene carbonate (TEABF₄/PC) electrolyte. CaCO₃ and KOH/CaCO₃ mixture
18 activation were also investigated to understand the effect of CaCO₃ on the properties of the ACs.
19 CaCO₃ significantly inhibited the porosity development during KOH activation and gave an ACs
20 with quite low SAA and specific capacitance. The results demonstrated that the alkaline hydroxides
21 activation is an efficient approach to the preparation of ACs from HyperCoal with
22 high-performance for EDLCs.

* Corresponding author. Tel.fax: +86 516 83591059. E-mail address: beyondcao@hotmail.com (J. P. Cao)

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1. Introduction

Electric double-layer capacitor (EDLC) is an energy storage device that utilizes the electric double layer formed at the interface between the electrode and the electrolyte [1]. As an energy storage/conversion device, EDLC exhibits higher power density and longer cycling life than common batteries, and has much higher energy density compared with traditional dielectric capacitors [2,3]. At present, carbon materials, including activated carbons (ACs), carbon nanotubes, carbon nanofibers, and graphene sheets are widely used for EDLC electrode materials [3-6]. Especially, porous AC with a high specific surface area (SSA) has attracted significant interest due to their exceptional characteristics, such as moderate cost, good chemical stability, and high electrical conductivity.

The preparation conditions of the activation process can be changed largely, not only because there are many variables that affect the activation process, but also because of the variety of raw precursors and activating agents that can be used [7,8]. Chemical and physical activation are mostly used for AC preparation. Chemical activation is known as a single step method of preparation of AC in the presence of chemical agents. Among the chemical activation agents, KOH and NaOH are usually used because both the alkaline hydroxides can act as a dehydrating agent allowing more carbon to keep fixed for producing a well-developed porosity AC in high yield [9,10]. Alkaline hydroxide activation can provides AC with a SSA higher than $2000 \text{ m}^2 \text{ g}^{-1}$ [2, 11,12], and results in a quite high specific capacitance value when the AC was further used as EDLC electrode [13,14].

Generally, CO_2 and KOH activation can greatly promote the formation of micropores and small mesopores for providing high SSA of ACs [15]. It is well known that CaCO_3 can be decomposed to CO_2 at a high temperature [16]. Physical activation with CO_2 is a usual procedure for ACs

preparation [17]. Sato et al. [16] reported a simple fabrication route of ACs in high SSA from chicken droppings without any additional activation process and revealed that activation was achieved through the catalytic gasification with CO₂ evolved from decomposition of CaCO₃ in the droppings. However, the effect of CaCO₃ on the preparation of ACs is yet unclear at present. Furthermore, coal usually contains ash in carbonate form, such as CaCO₃, which should affect the performance of the obtained ACs simultaneously.

HyperCoal is an ashless coal obtained by a mild thermal extraction of coal (HyperCoal process), which eliminates the effects of ash and carbonates [18]. HyperCoal was reported to be an excellent and low-cost candidate for manufacturing ACs for high-performance electrodes of EDLC [19]. Nevertheless, it is yet necessary to [optimizing](#) the preparation process, choosing the best activation agents and conditions to obtain the best capacitance performance. Some researchers [15] used KOH etching and CO₂ gasification to prepare porous ACs and found [that](#) the pore size distribution of the ACs was widened and the total pore volume (TPV) was increased, [resulting](#) in a high specific capacitance of 197 F g⁻¹ in 0.5 M H₂SO₄ aqueous electrolyte. CaCO₃ is desired to play a role in physical activation when mixed with KOH. Addition of CaCO₃ during activation of HyperCoal is also important for understanding the effect of carbonates in coal on the performance of prepared ACs.

The aim of this work is to prepare high-performance ACs by two-step activation of HyperCoal in the presence of NaOH, KOH, CaCO₃, and KOH/CaCO₃ mixture for EDLC. The effects of activation temperature on the pore structure parameter and electrochemical performance of the resulting ACs for EDLC in 0.5 M [tetraethylammonium tetrafluoroborate/propylene carbonate \(TEABF₄/PC\)](#) electrolyte [were](#) addressed in detail.

2. Experimental

2.1. Material and reagents

The HyperCoal was provided by Kobe Steel, Ltd., in Japan. The production and main characteristics of the HyperCoal was described in detail previously [18,19]. The HyperCoal contains 0.03% of ash, 37.8% of volatile matter and 62.17% of fixed carbon (wt. %, dried basis). The elemental content (wt.%, dried and ash-free basis) of C, H, N, S, and O are 83.5%, 5.4%, 2.2%, 0.6%, and 8.3%, respectively.

2.2. Preparation and characterization of ACs

Two-step activation was adopted for preparation of porous carbons. The HyperCoal was heated to 600 °C at 10 °C min⁻¹ under Ar flow and carbonized at that temperature for 7 min. The carbonized residue was mixed with KOH, NaOH, CaCO₃, and KOH/CaCO₃ mixture at a certain weight ratio. The mixture was heated to a prescribed temperature between 500 and 800 °C and then held at that temperature for 2 h under Ar flow. After cooling down, the residue was washed with 2 M HCl and rinsed with distilled water until neutral and then dried in vacuum at 200 °C for 2 h. The preparation conditions and characterization of the resulting ACs are listed in Table1. The ACs were designated as AX-Y, where A, Y, and X represent activating agent, activation temperature, and mass ratio of activating agents/char, respectively.

The porous texture and the SSA of the ACs were characterized with nitrogen adsorption and desorption studies at 77 K in a BELSORP-max constant volume adsorption apparatus. A JEOL JEM-2010 transmission electron microscope (TEM) was employed for ACs characterization.

2.3. Determination of specific capacitance

The EDLC electrode was prepared by mixing of AC, acetylene black, and polytetrafluoroethylene (PTFE) at a weight ratio of 87:10:3 using an agate mortar and then pressed onto an aluminum mesh current collector at 10 kg cm⁻². The diameter of the electrode was 13 mm.

After dried in vacuum at 200 °C for 2 h, two of the electrode were assembled at room temperature in a clean and dry Ar atmosphere into a hermetic aluminum Hohsen HS Test Cell and filled with 0.5 M TEABF₄/PC as electrolyte. The galvanostatic charge/discharge test of the EDLC electrode was performed between 0 and 2.5 V using a Hokuto Denko HJ1001SM8A battery charge/discharge unit under constant current density of 10 mA g⁻¹. Capacitance was deduced from the formula $C = It/dV$, where I is the discharge current density (mA g⁻¹), dt is the discharge time variation, and dV is the voltage variation in discharge [20,21].

3. Results and Discussion

3.1. KOH and NaOH activation

3.1.1. Structural characterization of ACs

Figs. 1a and 1b show N₂ adsorption isotherms of ACs activated with KOH and NaOH, respectively. All the isotherms are type I according to the IUPAC classification [22]. The nitrogen adsorption major occurs at a relative pressure less than 0.3. A relatively horizontal adsorption plateau appears at the high P/P₀ value, indicating that the micropores are dominant in the resulting ACs. As can be deduced from Fig. 2, the pore diameters of the two series of ACs are about 0.6-1 nm. At the same time, it can be observed that the ACs activated with NaOH exhibit larger adsorption volume than that with KOH at both low and high relative pressures.

For comparison, the SSA, TPV, and average pore size of all the ACs are listed in Table 1. At 600 and 700 °C, the adsorption capacity and the TPV of the AC obtained from NaOH activation are more considerable than that from KOH activation, although KOH activation leads to a higher AC yield than NaOH activation. In addition, the porosity distributions of the ACs prepared by KOH activation show narrower microporous distributions than those prepared by NaOH activation. As can be deduced from Table 1, the SSA of ACs covers a very wide range from 1261 m² g⁻¹ up to

115 higher than $3000 \text{ m}^2 \text{ g}^{-1}$. It is worth emphasizing that Na4-700 reached a SSA of $3010 \text{ m}^2 \text{ g}^{-1}$ and a
116 TPV of $1.77 \text{ cm}^3 \text{ g}^{-1}$. Generally, NaOH and KOH are interestingly stable chemicals that melt
117 without decomposition at 318 and 360 °C, respectively [23]. At a high temperature, both the alkaline
118 hydroxides can react with most of the precursors, even with the quite inert carbon materials. The
119 redox reaction between precursors and alkaline hydroxides (both NaOH and KOH) causing the
120 conversion to hydrogen, alkaline metals and alkaline carbonates [24-26]. During this reaction, the
121 number of pores of the carbon precursor is increased considerably, as well as the size of the existing
122 ones. Hence, it can prepare ACs in high SSA containing an enormous amount of micropores and
123 small mesopores via this hydroxide-carbon reaction.

124 Fig. 3 shows the SSA and AC yield obtained from KOH and NaOH activations at different
125 temperatures. When raising the temperature from 500 to 700 °C, the SSA of the ACs obtained from
126 KOH and NaOH activations increased and reached the maximum value of 2594 and $3010 \text{ m}^2 \text{ g}^{-1}$,
127 respectively. KOH activation of biomass wastes [17,27] also gave a similar increase trend in SSA of
128 the ACs with raising activation temperature. Azargohar and Dalai [17] proposed that the increase in
129 porosity was due to the enhancement of creation of new pores from the reaction between char and
130 KOH or NaOH with the raising temperature. Further raising the temperature to 800 °C led to the
131 decrease in SSA, especially for Na4-800, which should be due to the severe activation at high
132 temperatures that has a detrimental impact on the development of porosity on ACs. At a temperature
133 range from 500 to 700 °C, the porosity development of ACs prepared from NaOH activation is
134 better than those from KOH activation. However, this trend changes when further raising activation
135 temperature to 800 °C, during when a significant decrease in SSA of the Na4-800 can be found.
136 Therefore, ACs prepared with NaOH activation should not exceed 700 °C.

137 As mentioned above, the representative AC of K4-700 possessed both high SSA and TPV.

TEM was used to further study the porous texture of the AC, detailed in Fig. 4. Apparently, K4-700 consists of small particles, as shown in Figs. 4a. The particles connect to each other and form an aggregate in irregular shapes. This structure appeared on the surface of the K4-700 when activation was carried out with a certain amount of KOH. This trend suggested that the pyrolysis and etching process occurred simultaneously during the activation. In addition, an obvious graphitic structure can also be observed after the KOH treatment. TEM image in a high-resolution is shown in Figs. 4b. It should be noticed that the amorphous carbon in a turbostratic structure can be observed in K4-700.

3.1.2. Electrochemical performances of the ACs

Galvanostatic charge-discharge measurements were carried out to examine the electrochemical performances of the obtained porous carbons. Figs. 5a and 5b display the charge-discharge curves of the ACs obtained from KOH and NaOH activations, respectively. It can be seen that the charge-discharge curves of the ACs are closely linear with a small deviation from ideal voltage-time curves, which may be associated with the internal resistance during the changing of polarity [28]. The gravimetric and volumetric specific capacitances of the ACs at a current density of 10 mA g⁻¹ are given in Table 1. The gravimetric specific capacitance of K4-700 and Na4-700 reached 43.1 and 43.9 F g⁻¹, respectively. Meanwhile both the ACs owed the highest SSA. It should be noted that the SSA of Na4-700 (3010 m² g⁻¹) is significantly greater than K4-700 (2594 m² g⁻¹). However, the capacitance of Na4-700 is only slightly higher than K4-700. This observation may be explained by restriction accessibility of electrolyte ions to the pores or the surface of ACs was not completely wetted, leading to the partly utilization of the SSA. The double layer capacitance is correlated with the morphological property of the porous electrode, such as the SSA and the pore size distribution of the ACs [29]. Pores that are too large or too small can reduce the density of the electrode and

keep the electrolyte out of the pores, respectively [30]. Thus, tailoring the porous structure of carbon material is a major goal for EDLC optimization. The gravimetric specific capacitances of the ACs prepared under different conditions are presented in Fig. 6. It can be observed that a similar tendency was achieved by NaOH and KOH activations, whereas NaOH shows higher specific capacitances than KOH at 600-800 °C.

It is interesting that the SSA of K4-600 and Na4-600 (2171 and 2922 m² g⁻¹) are smaller than K4-700 and Na4-700 (2594 and 3010 m² g⁻¹), whereas the volumetric specific capacitance of K4-600 and Na4-600 (22.5 and 21.8 F cm⁻³) are larger than that of K4-700 and Na4-700 (20.1 and 20.2 F cm⁻³). Such excellent electrochemical performance of K4-600 and Na4-600 illustrate that the ACs activated at 600 °C should have more accessible SSA for the formation of electric double layer. Some researchers proved that the higher capacitance per volume must be obtained with pores of right size which can adsorb the larger amount of electrolyte on their wall with lower amount of un-adsorbed electrolyte in the same pore [31]. The relatively high volumetric capacitance of K4-600 and Na4-600 should be due to the enhanced accessibility of the electrolyte ions to a suitable pore size. Similar trend were reported for black liquor- [27] and corncob-derived ACs [28].

Consequently, NaOH activation can achieve almost the same performance as KOH activation, such as total yield, SSA, and specific capacitance. Although KOH and NaOH can be used interchangeably in a large number of applications, NaOH was emphasized especially here in regard to its low cost and corrosive.

3.2. HyperCoal activated with CaCO₃ and KOH/CaCO₃ mixture

3.2.1. Structural characterization of ACs

HyperCoal was activated with CaCO₃ at 700-900 °C for 2 h under Ar flow in a CaCO₃/char ratio of 2. For comparison, activation of HyperCoal char with the same amount of KOH and

KOH/CaCO₃ mixture were also carried out in the same manner. The preparation conditions and characterization of resulting ACs are also summarized in Table 1. The isotherms of N₂ adsorption at 77K are presented in Fig. 7. It can be observed that the isotherms belong to type I for micropore materials activated with KOH and KOH/CaCO₃ mixture according to the IUPAC classification, as shown in Figs. 7a and 7c. In the case of ACs from CaCO₃ activation (Figs. 7b), the isotherms were similar to type I and IV according to the IUPAC classification [22]. The adsorption isotherms rapidly increased in the region of middle and high relative pressure and no platform appeared, indicating that the ACs might contain mesopores, which can be further proved by the pore size distribution as shown in Fig. 8. From Fig. 8b, it can be seen that there are three peaks with pore size of 0.5-1, 1-2, and 2-4 nm, which is well consistent with the adsorption isotherms.

As shown in Fig. 9, the ACs from CaCO₃ activation at 700-900 °C showed SSA value of 11-30 m² g⁻¹. CaCO₃ practically has an unfavorable effect on porosity development. In contrast, KOH with same mass ratio of 2:1 provided a large SSA of around 2400 m² g⁻¹ at 800 °C. Nevertheless, the SSA decreased to 988 m² g⁻¹ when CaCO₃ was added for KOH activation at the same temperature. The same phenomenon also occurs in the temperature below or above 800 °C. Therefore, it can be concluded that CaCO₃ activation does not play a role in physical activation to increase the amount of micropores for providing high SSA AC as expected. Furthermore, CaCO₃ has an inhibitory effect on the KOH activation to a certain extent. It should be noted that CaCO₃ activation could give a high yield of ACs around 50%, whereas the yields from KOH and KOH/CaCO₃ activations were around 40%. Activation with KOH/CaCO₃ mixture above 800 °C reduced the yield sharply.

3.2.2. Electrochemical performances of the ACs

As shown in Table 1, the gravimetric specific capacitances of ACs obtained from CaCO₃ activation are lower than 1 F g⁻¹. In contrast, KOH activation provided ACs with high specific

capacitance, reached an acceptable value of 40.8 F g^{-1} at 800°C . However, further raising activation temperature to 900°C reduced the capacitance of the ACs. As expected, adding CaCO_3 during KOH activation significantly decreased the specific capacitance (below 20 F g^{-1}). AC with a large SSA was considered to be a basic guiding principle for large capacitance electrode production [31,32].

Although the BET method plays important role in porous materials, it is a restriction to analyze the SSA with different pore size ranges. In general, the porous AC for EDLC electrode usually has relatively high SSA and unique porous structure [33-35]. The non-accessible pores have little contribution to the capacitance, and an excessively large pore size will also produces non-accessible pores [27]. Yet, CaCO_3 as activating agent gave an AC with relatively low SSA and TPV, as well as a low specific capacitance. In this study, the AC obtained from CaCO_3/KOH mixture activation presents a certain number of mesopores, which has little contribution to the capacitance, resulting in a relatively low specific capacitance. As listed in Table 1, the average pore size of ACs activated with KOH and KOH/ CaCO_3 mixture concentrated in 1-2 nm, while those from CaCO_3 activation are larger than 2 nm. The AC with a relatively narrow pores (1-2 nm) shows a higher specific capacitance than that with mesopores ($>2 \text{ nm}$). It is implied that the contribution of the pores in 1-2 nm to the performance of EDLC is higher than the pores above 2 nm. This trend is well consistent with the results reported [36]. Fig. 10 demonstrates the charge-discharge curves of the three typical ACs. As revealed in the charge-discharge curves, the discharge times of the K2-800 electrode is much longer than that of Ca2-800 and K2Ca2-800 electrodes, indicating that the specific capacitances of the ACs are remarkably enhanced by the KOH activation and CaCO_3 is not suitable for the preparation of high-performance ACs electrode. Simultaneously, their plots present good linearity and symmetrical triangle, indicating good EDLC behaviors.

As discussed above, the SSA and the specific capacitance of ACs from KOH activation are

higher than the other two series ACs. The sharply reduce in capacitance reflects that CaCO_3 does not play the same role as CO_2 activation for developing pores and is not benefit for the properties of the resulting ACs. Consequently, the CaCO_3 content should be significantly reduced when coal was used as a precursor for high-performance ACs preparation.

4. Conclusions

The ACs with SSA of 2594 and 3010 $\text{m}^2 \text{g}^{-1}$ and TPV of 1.36 and 1.77 $\text{cm}^3 \text{g}^{-1}$ were produced from carbonization and activation of HyperCoal with KOH and NaOH, respectively. The ACs obtained from KOH and NaOH activations at 700 °C exhibit the highest specific capacitances of 43.1 and 43.9 F g^{-1} , respectively, at a current density of 10 mA g^{-1} in 0.5 M TEABF₄/PC electrolyte. The AC electrodes exhibited good charge-discharge performance. Meanwhile, the ACs prepared by CaCO_3 and KOH/ CaCO_3 mixture activations, which have SSA of 30 and 988 $\text{m}^2 \text{g}^{-1}$ and TPV of 0.02 and 0.49 $\text{cm}^3 \text{g}^{-1}$, respectively, resulted in quite low capacitance. CaCO_3 significantly inhibits the pore development during KOH activation and is not benefit for high specific capacitance ACs preparation. The electrochemical performance of the ACs significantly depended on the SSA and the pore size distribution. Such an approach may lead to the development of high-performance EDLC electrodes from HyperCoal.

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Figure captions

Table 1 Characteristics of the ACs.

Figure 1 Nitrogen adsorption isotherms of the ACs from KOH (a) and NaOH (b) activations.

Figure 2 Pore distribution of ACs from KOH (a) and NaOH (b) activations.

Figure 3 SSA and yield of ACs at different temperatures.

Figure 4 TEM images of K4-700 at low- (a) and high-resolution (b).

Figure 6 Specific capacitances of the ACs from NaOH and KOH activations.

Figure 5 Charge-discharge curves of AC electrodes from KOH (a) and NaOH (b) activations.

Figure 7 Nitrogen adsorption isotherms of the ACs from KOH (a), CaCO_3 (b), and KOH/ CaCO_3 mixture (c) activations.

Figure 8 Pore distribution of ACs from KOH (a), CaCO_3 (b), and KOH/ CaCO_3 mixture (c) activations.

Figure 9 SSA and yields of ACs at different temperatures.

Figure 10 Charge-discharge curves of AC electrodes activated with KOH, CaCO_3 , and KOH/ CaCO_3 mixture.

Table 1

Characteristics of the ACs.

Sample	AT [°C]	Reagent	Ratio	Y _c [%]	Y _{total} [%]	S _{BET} [m ² g ⁻¹]	V _{total} [cm ³ g ⁻¹]	D _{ave} [nm]	C _g [F g ⁻¹]	C _v [F cm ⁻³]
K4-500	500	KOH	4	69.3	58.2	1186	0.55	1.77	29.2	20.0
K4-600	600	KOH	4	69.3	46.8	2171	1.10	1.79	39.5	22.5
K4-700	700	KOH	4	69.3	43.6	2594	1.36	1.84	43.1	20.1
K4-800	800	KOH	4	69.1	38.6	2447	1.46	1.92	42.5	17.9
Na4-500	500	NaOH	4	71.1	54.6	1261	0.55	1.99	26.9	19.0
Na4-600	600	NaOH	4	70.6	32.9	2922	1.62	1.91	42.5	21.8
Na4-700	700	NaOH	4	70.6	32.0	3010	1.77	1.99	43.9	20.2
Na4-800	800	NaOH	4	70.6	27.6	2007	1.27	2.03	42.8	18.6
K2-700	700	KOH	2	68.7	50.3	1834	0.79	1.88	34.6	20.6
K2-800	800	KOH	2	68.7	42.4	2378	1.12	1.77	40.8	21.2
K2-900	900	KOH	2	68.7	31.9	1545	0.85	2.08	34.5	18.7
Ca2-700	700	CaCO ₃	2	68.1	56.4	30	0.02	3.13	0.38	0.34
Ca2-800	800	CaCO ₃	2	68.1	53.6	11	0.01	2.83	0.35	0.33
Ca2-900	900	CaCO ₃	2	68.1	52.3	15	0.01	3.42	0.32	0.30
K2Ca2-700	700	KOH/CaCO ₃	2/2	69.9	50.4	643	0.31	1.93	12.7	9.6
K2Ca2-800	800	KOH/CaCO ₃	2/2	69.9	42.4	988	0.49	1.92	16.4	11.5
K2Ca2-900	900	KOH/CaCO ₃	2/2	69.9	21.8	566	0.30	1.98	13.4	10.1

AT: activation temperature; Y_c: char yield; Y_{total}: total yield; C_g: gravimetric specific capacitances; C_v: volumetric specific capacitances.

Fig. 1. Nitrogen adsorption isotherms of the ACs from KOH (a) and NaOH (b) activations.

Fig. 2. Pore distribution of ACs from KOH (a) and NaOH (b) activations.

Fig. 3. SSA and yield of ACs at different temperatures.

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