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KOH activation of a HyperCoal to develop activated carbons for electric double-layer capacitors

Xiao-Yan Zhao [a], Shan-Shan Huang [a], Jing-Pei Cao [a,b,*], Shao-Chen Xi [a],
Xian-Yong Wei [a], Junpei Kamamoto [b], Takayuki Takarada [b]

[a] *Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), China University of Mining & Technology,*
Xuzhou 221008, Jiangsu, China
[b] *Division of Environmental Engineering Science, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515, Japan*

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ABSTRACT

A series of activated carbons (ACs) was prepared from HyperCoal by conventional and direct KOH activation methods, and was used as electrodes in electric double-layer capacitors (EDLCs) using 0.5 M $TEABF_4$/PC as the electrolytic solution. The effects of carbonization temperature (CT), activation temperature (AT) and KOH/sample ratio on BET surface area, average pore size and capacitance of ACs were investigated in this study. Nitrogen adsorption isotherms of all ACs indicated that the pores in ACs were mainly micropores. The BET surface area and capacitance decreased with raising CT from 500 to 900 °C, while the highest BET surface area of 2540 $m^2\,g^{-1}$ and maximum capacitance of 46.0 $F\,g^{-1}$ were achieved at CT of 500 °C and AT of 800 °C in conventional activation. On the contrary, in the direct activation, the BET surface area and the capacitance increased with the increase of AT and KOH/sample ratio, getting the maximum value of 2440 $m^2\,g^{-1}$ and 44.4 $F\,g^{-1}$, which is comparable with that of conventional method, at AT of 800 °C and KOH/sample ratio of 4.0. Such a procedure provides a cost-effective approach to preparation of high performance activated carbons from HyperCoal for EDLC.

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1. Introduction

Electric double-layer capacitor (EDLC), using activated carbons (ACs) as electrode materials, is recognized as an efficient storage device for electric power, due to its high power density, large capacity, low leakage current, simple charging and discharging process and long cycle life [1,2]. AC electrode is widely preferred [3] due to its excellent properties such as easy processability, high abundance, low cost, corrosion resistance and high endurance at high operating temperatures [4]. The ideal ACs for EDLC electrodes are required to have a high surface area and an optimal pore size distribution that are important to high specific capacitance of EDLC [5,6]. Particularly, raw materials and activation methods are two of the most important factors which may influence the final structure and cost of ACs.

Although the use of various biomass, resin and polymer materials to produce ACs becomes one of the hot topics [7–9], coal is still the main material for ACs at present. The coal with too much

ash has a great impact on the quality of ACs. For example, it not only affects the mechanical strength of products, but also reduces the adsorption capacity and chemical characteristics [10]. When the coal derived ACs are used as EDLC electrode materials, the impurities or ash will compromise the EDLC performance [11]. In these cases, since ash materials causes various problems, it is necessary to remove it before ACs preparation. HyperCoal is an ashless coal obtained by a mild thermal extraction of coal (HyperCoal process), has lower water content and softening point and higher liquidity than the raw coal, which shows significant advantages in energy saving, environmental protection and good prospects for development [12]. The utilization of HyperCoal at present is mainly concentrated on the gasification [13] and liquefaction [14], but as materials to produce ACs for EDLC electrode is rarely reported.

The main objective of the present work is to investigate the applicability of ACs derived from HyperCoal as supercapacitor electrodes. ACs were prepared from HyperCoal by conventional 2-step carbonization/KOH-activation and single step direct KOH-activation at argon atmosphere, which have the well developed textual properties on the ACs surface for application as a EDLC electrode material. The effects of carbonization temperature, activation temperature and KOH/sample ratio on the yield, BET surface area, pore structure, capacitance and their relationship of the prepared ACs were systematically investigated.

* Corresponding author at: Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), China University of Mining & Technology, Xuzhou 221008, Jiangsu, China. Tel.: +86 516 83591059; fax: +86 516 83591059.
E-mail addresses: beyondcao@hotmail.com, beyondcao_2000@163.com
(J.-P. Cao).

Table 1
Proximate and ultimate analyses of HyperCoal.

Proximate analysis (wt%, d)			Ultimate analysis (wt%, daf)				
Ash	VM	FC	C	H	N	S	O[a]
0.03	37.8	62.17	83.5	5.4	2.2	0.6	8.3

[a] By difference; d, dry basis; daf, dry and ash free basis.

2. Materials and methods

2.1. Materials

The HyperCoal used in this study is produced from Gregory coal by Kobe Steel, Ltd., Japan. Detailed information in regard to the HyperCoal production has been described in detail [12]. It was pulverized to pass through a 200-mesh sieve (<75 μm) followed by drying at 107 °C for 24 h and then stored in an airtight container before use. Table 1 shows the proximate and ultimate analyses of the HyperCoal sample.

2.2. Preparation and characterization of ACs

The conventional 2-step carbonization/KOH-activation method consists of the following sequential steps:

- The sample was carbonized in a muffle furnace under Ar flow at a heating rate of 10 °C min^{-1} and was held at the prescribed temperature between 500 °C and 900 °C for 2 h. The char was mixed with KOH in a KOH/sample ratio of 4 and then activated at 800 °C for 2 h under Ar flow. After completion of the heat treatment, the sample was allowed to cool to room temperature. The resultant material was washed with 2 M HCl solution, rinsed with distilled water until neutral and then dried at 200 °C in vacuum for 2 h. The ACs prepared by conventional activation were designated as AC-X, where X represents the final carbonization temperature.

The single step direct KOH-activation method implies:

- The HyperCoal was directly activated with KOH in the temperature range of 500–800 °C without carbonization in the same manner as above. Different KOH/sample ratios between 2 and 4 at activated temperature of 800 °C were investigated as well. The ACs prepared by direct activation were designated as AC-r-Y, where Y represents the final activation temperature or KOH/sample ratio. All subsequent data are expressed as the averages of values that were obtained from repeated experiments.

The porous texture and the BET surface area of all the ACs samples were characterized by nitrogen adsorption and desorption studies at 77 K (BELSORP-max, Japan).

2.3. Preparation of electrode and capacitance measurements

A mixture of 87 wt% AC, 10 wt% acetylene black, and 3 wt% PTFE binder was pressed into pellets (13 mm in diameter) as the electrodes. Then, the electrodes were dried under vacuum at 200 °C for 2 h. A button-type capacitor was assembled with two AC electrodes using 0.5 M TEABF$_4$/PC as the electrolyte. The capacitors were galvanostatically cycled between 0 and 2.5 V on a Land cell tester at a constant current discharge mode. The capacitance (C) of a single electrode was determined with the formula $C = IdT/2dV$ (1), where I is the discharge current, dT is the discharge time variation, and dV is the voltage variation in discharge.
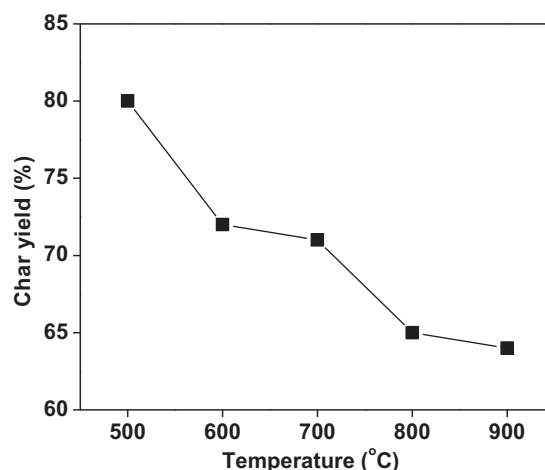

Fig. 1. The char yields of HyperCoal at different temperatures.

3. Results and discussion

3.1. Conventional activation method

As shown in Fig. 1, raising temperature from 500 to 900 °C decreased the char yield because of the progressive pyrolysis conversion. However, the rate of declination in the range of 800–900 °C is not as fast as that in the range of 500–800 °C. The results show that most of volatile matter from HyperCoal was evolved at about 800 °C.

The adsorption isotherms of N$_2$ on the prepared ACs at 77 K are shown in Fig. 2. In all cases, the obtained results correspond to typical type I isotherms microporous carbons according to the IUPAC classification [15]. When P/P_0 is 0.39 and 1.00, all of ACs represent different adsorption of micropores and total pores respectively, due to various pore structures. The ACs prepared at lower carbonization temperature show larger adsorption amounts.

As shown in Fig. 3, the ACs obtained at lower temperature show higher BET surface area value. The BET surface area almost keeps constant until 700 °C and then decreases sharply from 2440 to 1110 m^2 g^{-1}. This explains that the pores enlarge up to this temperature. Above 700 °C, the excess enlargement induces combination of pores, resulting in an increase in mesopores, and a decrease of
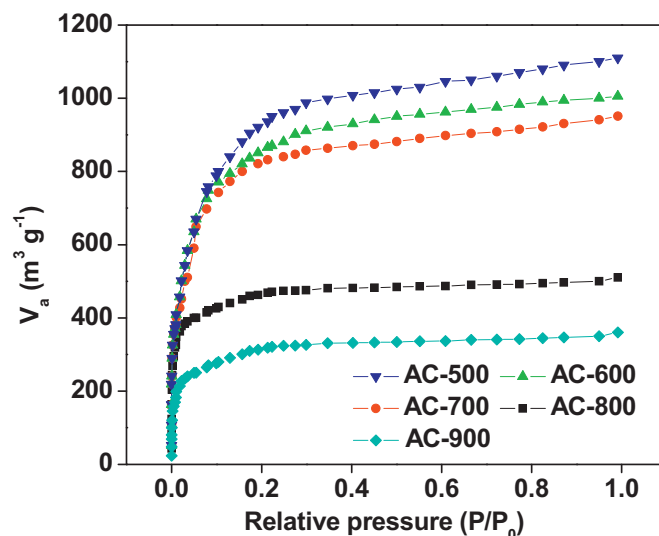

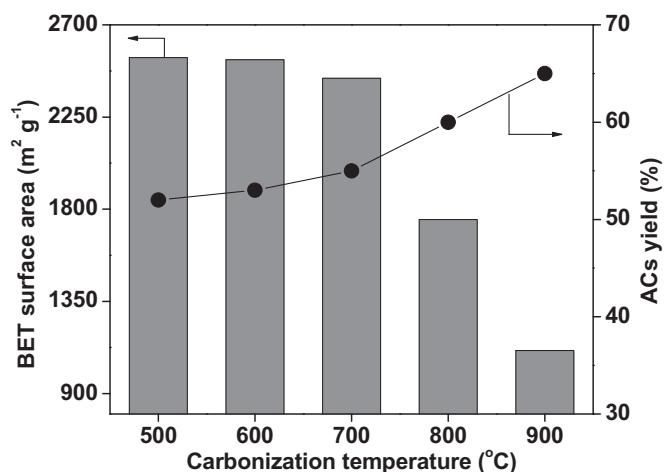**Fig. 2.** The nitrogen adsorption isotherms of the ACs at different temperatures.

Fig. 3. The BET surface area and yields of ACs at different temperatures.

micropore volume and surface area. The observation is consistent with the result reported in previous works [16,17]. In addition, the char-based yields of ACs increase continuously with raising carbonization temperature, which should be due to the residual volatile matter in chars obtained at low carbonization temperature of 500–700 °C were activated at 800 °C during activation process, so the residual volatile under 800 °C will evaporate, result in low ACs yields.

Several studies [4,15,18–21] have reported that the specific capacitance of EDLC is strongly affected not only by BET surface area of ACs, but also by other properties of carbon materials such as pore size distribution, surface chemistry and electrolyte. In this study, the electrolyte for all capacitors is the same. Simultaneously, the ACs obtained from the same precursor and by the same method should have similar surface chemistry. The relationship between the specific capacitance and BET surface area of the samples was given in Fig. 4. Similar to BET surface area, the specific capacitance also decreases with raising carbonization temperature. The AC samples with higher BET surface area offered higher capacitance, and at the same time a roughly linear relationship can be observed between BET surface area and specific capacitance. However, the capacitance of AC-500 is higher than that of AC-600 despite both of the ACs having the similar BET surface area indicating that besides
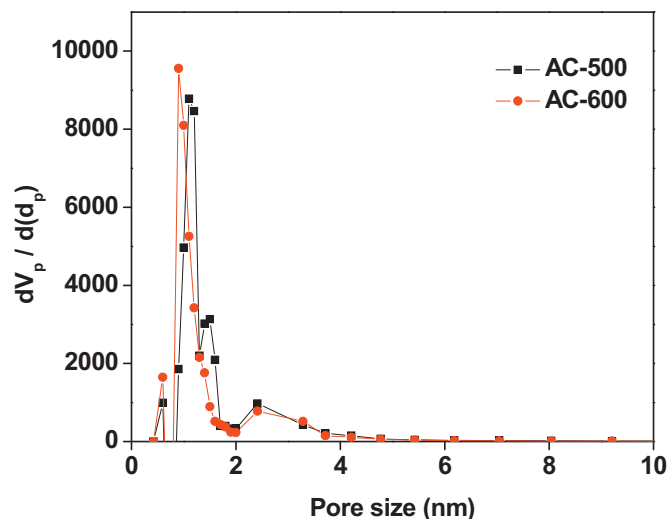

Fig. 5. Pore distribution of ACs.

the BET surface area, the pore size distribution also maybe affect the capacitance.

There are three types of pore structures such as micro (<2 nm), meso (2–50 nm) and macro (>50 nm) pores [22]. Fig. 5 exhibits the pore size distribution of two AC samples. It can be seen that both of them are microporous carbon. Wang et al. [23] has proved that the specific capacitance of carbon material is linked to the accessibility of the electrolyte for penetrating into the carbon pores. The ACs carbonized at the temperature of 500 °C, which has the maximum average pore size (2.60 nm) possessing the highest capacitance value of 46.0 F g⁻¹. As the carbonization temperature increases from 600 to 900 °C, the capacitance of ACs decreases continuously. This trend can be explained by the formation of the electric double layer [24–28]. Without doubts, high BET surface area is one of the most important features. The higher surface area of the ACs electrode, the more energy can be stored on its more developed electrode/electrolyte interface because the ACs surface provides the interface for the formation of the double layer. However, not all of the BET surface area is available. Only when the ACs with the appropriate pore size can make the electrolyte go through, a high capacitance can be obtained. That is why the AC-500 enables to achieve the highest capacitance.

3.2. Direct activation method

3.2.1. Effect of activation temperatures

The effects of activation temperatures on the porous properties of ACs are carried out under the condition that KOH/sample ratio was kept at 4. The estimated BET surface area values for corresponding ACs (AC-r-500 to AC-r-800) are observed to be 1020 m² g⁻¹, 1880 m² g⁻¹, 2310 m² g⁻¹ and 2440 m² g⁻¹, respectively, via N₂ adsorption isotherms at 77 K. Figs. 6 and 7 show N₂ adsorption isotherms and the BET surface area of prepared ACs, respectively. It can be easily observed that all of ACs belong Type I. In addition, the BET surface area increased with raising activation temperature, reaching 2440 m² g⁻¹ at 800 °C. On the other hand, the ACs yield decreased with raising activation temperature, which can be explained that more volatile matter of HyperCoal will be evaporated under higher temperature. As shown in Fig. 8, the AC-r-800 has the highest BET surface area and the largest pore size, also gives the highest gravimetric specific capacitance up to 44.4 F g⁻¹. Because of the activation reaction with KOH is an endothermic reaction, suitable activation temperature is important for the
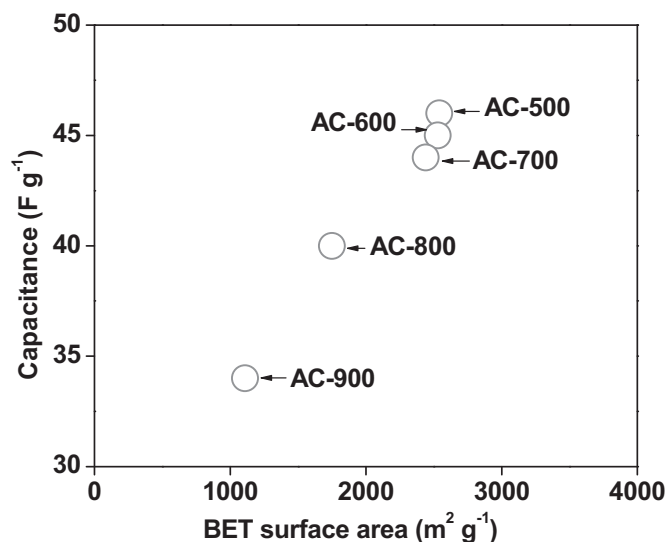

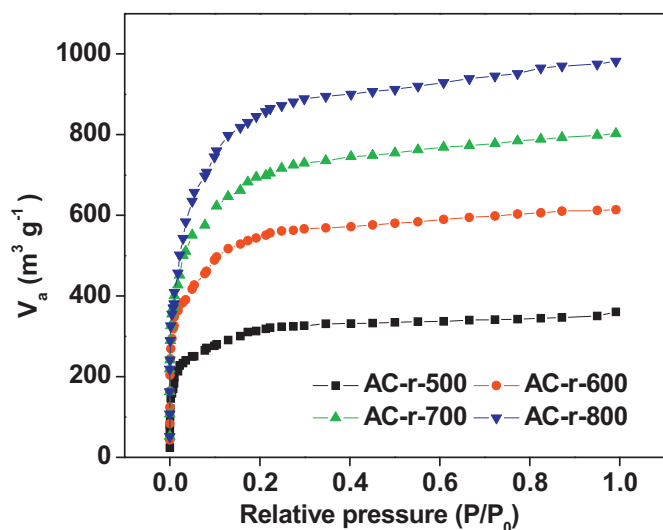**Fig. 4.** Effect of carbonization temperatures on capacitance of ACs.

Fig. 6. The nitrogen adsorption isotherms of the ACs at different activation temperatures.
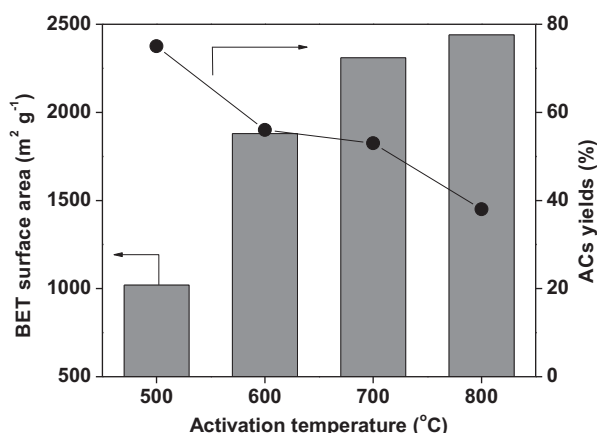

Fig. 7. The BET surface area and yields of ACs at different activation temperatures.

development of the porosity and BET surface area of ACs. This reaction may not complete at a low temperature (500 °C) due to the high energy requirement of C–KOH reaction, resulting in the small pore size and low BET surface area property. On the contrary, the vigorous reaction between KOH and C forced the reaction more
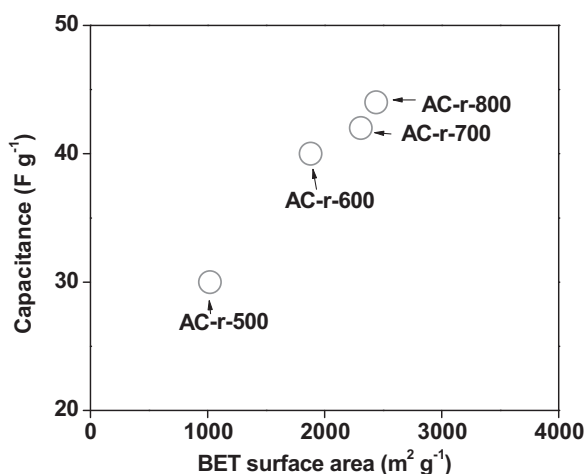

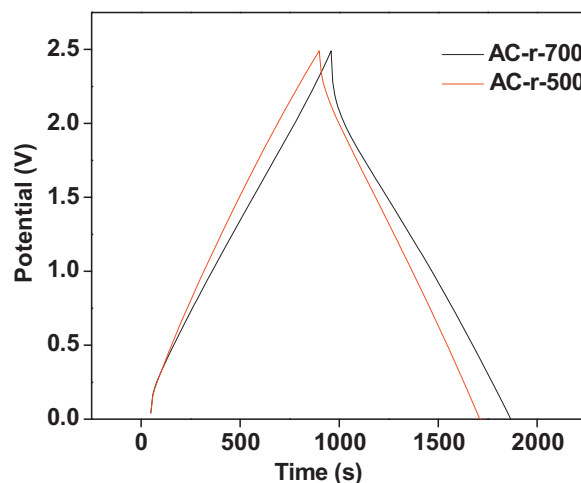Fig. 8. Effect of activation temperatures on capacitance of ACs.

Fig. 9. Charge–discharge curves of AC electrodes at different activation temperatures.

completely and could enhance the pore creation and enlargement under the relatively high temperature (700–800 °C). Therefore, it will produce an increasing BET surface area and capacitance with increasing activation temperature. However, in the conventional 2-step carbonization/KOH-activation method, some micropores have already been formed in the chars. Hence, under the same activation temperature of 800 °C, ACs (AC-500, AC-600 and AC-700) prepared by two-stage activation method show higher BET surface area value than AC (AC-r-800) prepared by direct activation method. Many studies [29–32] have suggested that the capacitance contributions by different pore sizes were different. So the AC-r-800 can get the highest specific capacitance in direct activation method.

Fig. 9 shows the charge/discharge curves of the two AC samples, both of which show regular triangular-shapes, indicating good electric double-layer capacitor behaviors. According to the formula (1), the specific capacitance values can be calculated from the slope of the discharge curve, which are listed in Table 2. As shown in the curves, the charge–discharge times of the AC-r-700 electrodes are longer than that of the AC-r-500 electrodes, suggesting that the electrochemical capacitances are enhanced at higher activation temperature. It is known that for the EDLCs, their specific capacitance is decided by the accessibility of aqueous solutions to the pores in ACs [23]. In principle, the pores larger than 0.5 nm are electrochemically accessible for electrolytic solutions [6]. In our study, the higher capacitance of AC-r-700 electrode is in proportion to its larger average pore size (2.22 nm) and higher BET surface area (2310 m^2 g^{-1}) compares to AC-r-500 electrode with average pore size is 2.06 nm and BET surface area is 1020 m^2 g^{-1}.

3.2.2. Effect of the KOH/sample ratios

To study the effects of KOH/sample on the porous properties of ACs, activations were carried out under the fixed activation temperature (800 °C). As exhibits in Table 2, it was difficult to obtain high value of BET surface area and capacitance with low KOH/sample ratio of 2.0. The BET surface area slightly increased with the increasing KOH/sample ratio according to Fig. 10, reaching 2440 m^2 g^{-1} when the ratio is 4.0. On the contrary, the yield decreased with the increasing ratio, which should be due to the HyperCoal was activated more completely at higher KOH/sample ratio. Fig. 11 shows the relationship between BET surface area and capacitance. In general, there are three stages in the pore development during activation: (1) opening of previously inaccessible pores; (2) creating of new pores; (3) widening of the existing pores [1,33,34]. When KOH/sample ratio is low, stages (1) and (2) contribute to

Table 2
The characterization of prepared ACs.

Sample	CT [°C]	AT [°C]	Ratio	Y_c [%]	Y_a [%]	Y_{total} [%]	S_{BET} [m² g⁻¹]	V_{micro} [cm³ g⁻¹]	V_{total} [cm³ g⁻¹]	D_{ave} [nm]	C_g [F g⁻¹]
AC-500	500	800	4.0	79.6	50.7	40.4	2540	1.03	1.65	2.60	46.0
AC-600	600	800	4.0	71.9	53.4	38.4	2530	1.03	1.57	2.48	45.3
AC-700	700	800	4.0	70.8	54.7	38.7	2440	1.03	1.49	2.44	43.6
AC-800	800	800	4.0	65.0	59.8	38.9	1750	0.69	1.02	2.33	39.7
AC-900	900	800	4.0	63.6	64.6	41.1	1110	0.44	0.58	2.10	33.8
AC-r-500	–	500	4.0	–	75.2	75.2	1020	0.41	0.52	2.06	30.4
AC-r-600	–	600	4.0	–	55.7	55.7	1880	0.75	0.98	2.08	40.0
AC-r-700	–	700	4.0	–	52.9	52.9	2310	0.92	1.28	2.22	42.3
AC-r-800	–	800	4.0	–	37.6	37.6	2440	1.01	1.48	2.43	44.4
AC-r-2.0	–	800	2.0	–	55.5	55.5	1880	0.73	0.87	1.86	36.1
AC-r-2.5	–	800	2.5	–	52.9	52.9	2270	0.92	1.18	2.07	39.7
AC-r-3.0	–	800	3.0	–	50.0	50.0	2310	0.93	1.35	2.33	42.8
AC-r-3.5	–	800	3.5	–	45.0	45.0	2360	0.95	1.37	2.30	41.5
AC-r-4.0	–	800	4.0	–	37.6	37.6	2440	1.01	1.48	2.43	44.4

CT, carbonization temperature; AT, activation temperature. Y_c, char yield; Y_a, activated carbon yield; Y_{total}, total yield. AC-r-800 = AC-r-4.0.

the micropore formation. With the increase of KOH/sample ratio, pore widening would take the domination in the reaction. Step (3) caused by reaction inside the opened pores, normally takes place after stages (1) and (2), especially under high KOH/sample ratio. Therefore, the average pore size of ACs increases continuously from 1.86 nm to 2.43 nm with the increase of KOH/sample ratio. Similar to that reported by Wang et al. [1], for AC-r-2.0, the lower KOH/sample weight ratio made the reaction stop at step (1) or (2),

resulting in microporous ACs (D_{ave} = 1.86 nm) with lower pore volume. When the ratio was raised up to 4 (AC-r-4.0), the reagent began to be enough for pore widening, and stage (3) should be take place under this circumstance, causing relatively large pore size (D_{ave} = 2.43 nm) property. As a result, KOH/sample ratio of 4.0 is the most favorable ratio for the preparation of EDLC from HyperCoal, which providing the highest capacitance of 44.4 F g⁻¹.

Based on the above results, ACs obtained by direct activation method can achieve almost the same performance, such as total yield, BET surface area and capacitance, as the ACs prepared by conventional activation method. So the relatively high performance ACs for EDLC can be prepared by cost-effective single step KOH-activation of low-cost HyperCoal.

4. Conclusions

The HyperCoal based ACs for EDLCs were prepared by conventional 2-step carbonization/KOH-activation and single step direct KOH-activation. The specific capacitance varies widely in the resultant ACs, from about 30.4 to 46.0 F g⁻¹, showing a maximum value with the largest BET surface area of 2540 m² g⁻¹ and pore size of 2.60 nm. There is a general trend of specific capacitance increase along with BET surface area. Additionally, the capacitance contribution by microporous and mesoporous are different. The ACs with the narrow pore size and a relatively low surface area appeared to be not suitable for the EDLC. The results indicated that capacitance not only depends on surface area, but also on pore size distribution. In addition, single step KOH-activation of HyperCoal can achieve almost the same performance as the ACs prepared by conventional 2-step carbonization/KOH-activation method. Accordingly, HyperCoal has been demonstrated to be an excellent and low-cost candidate for manufacturing ACs with favorable pore characteristics, aiming for high performance electrodes of EDLC.
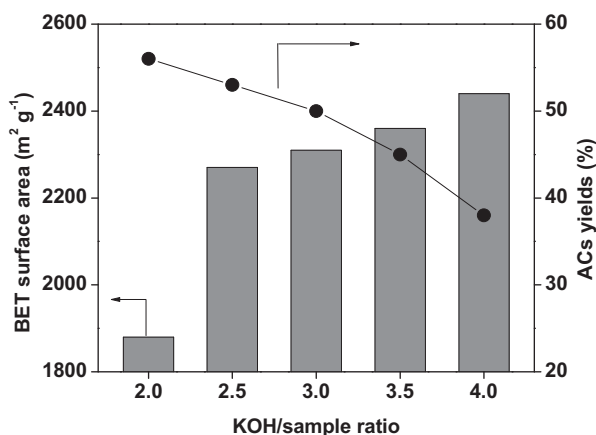

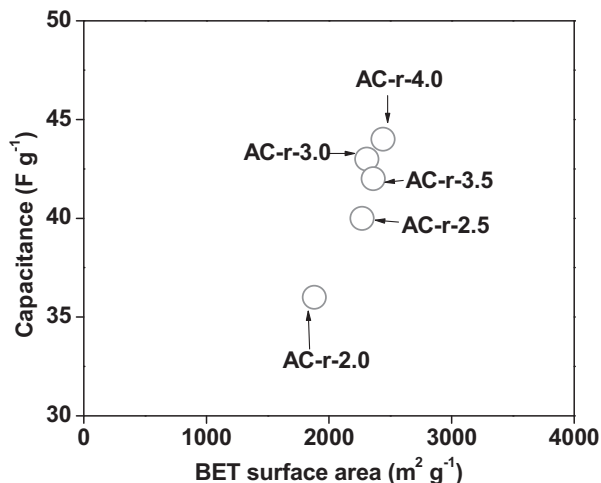**Fig. 10.** The BET surface area and yields of ACs at different KOH/sample ratios.

Fig. 11. Effect of KOH/samples ratio on capacitance of ACs.

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