



# Performance of electrochemical double layer capacitors using highly porous activated carbons prepared from beer lees

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## ABSTRACT

Beer lees precursor is chosen to prepare activated carbons having different physical and chemical properties. The beer lees-based activated carbons (BL-ACs) are characterized by N<sub>2</sub> adsorption/desorption isotherms, adsorption energy distributions (AEDs), and X-ray photoelectric spectroscopy (XPS). Furthermore the electrochemical properties of the BL-ACs are assessed using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and constant current charge/discharge method. The maximum specific capacitance (about 188 F/g at discharge current of 1 mA/cm<sup>2</sup>) is obtained in 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution, which is a relatively low electrolyte concentration. The overall results suggest that the BL-ACs are good candidates for EDLC electrode materials.

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## 1. Introduction

With growing concerns for alternative energy storage devices, the electrochemical capacitor has been actively investigated in recent years. The electric double layer capacitor (EDLC), which is one of the electrochemical storage devices, is considered as the promising one because of its specific advantages such as high power density and repetitive long cycle life [1,2]. In general, EDLCs reversibly operate in a cyclic way, the charge and discharge of electrical energy at electrode/electrolyte interface. Accordingly, its specific capacitance is greatly influenced by surface characteristics of electrodes such as specific surface area, pore size, pore size distribution, and oxygen functionality [3–8]. Therefore, it is very important to select electrode materials with specific characteristics in improving the specific capacitance of EDLCs.

Carbonaceous materials such as activated carbons (ACs), graphite oxides (GOs), and carbon nanotubes (CNTs) have been energetically investigated for application as the electrode of EDLCs owing to their positive properties such as large specific surface area, high pore volume, a wide range of pore size distribution, and electron mobility [9–12]. In recent years, there is the growing interest to prepare the ACs from biomass precursors because of relatively cheap and abundant resources compared to various precursors [13,14]. Especially, the residual waste (beer lees) after

beer extraction processes, which has been generally used in producing the feeds for domestic animals, was chosen to prepare the porous ACs [15]. This work is an attempt to assess the specific capacitance of the beer lees-based activated carbons (BL-ACs) as electrode materials for EDLCs.

In this work, the objective is to prepare the BL-ACs having the well developed textural properties as well as the formation of the proper oxygen functional groups on the AC surface for application as an electrode material for EDLCs. Besides, there is the characteristic assessment of the BL-ACs in 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution on the EDLC performance. In addition, the correlations between textural properties and energetic heterogeneities as well as oxygen functionalities are investigated in detail.

## 2. Experimental

### 2.1. Preparation of ACs from beer lees

Beer lees were obtained from Oriental Brewery Co., Ltd, Gwangju, Korea. The materials were dried at 60 °C for 48 h to remove the moisture content. The powdered samples after grinding were carbonized at 600 °C for 1 h under nitrogen atmosphere. Then, each of the samples physically mixed with varying mass ratio between the carbonized beer lees char and potassium hydroxide (KOH) was activated at 800 °C for 1 h. The activated samples were noted as BL-1/2, BL-1/3, and BL-1/4 according to the mass ratio. Finally, all the samples were washed with distilled hot water for pH neutralization and dried at 120 °C for 24 h in a vacuum drier.

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## 2.2. Properties of the BL-ACs

The textural properties were determined by N<sub>2</sub> adsorption/desorption isotherms at 77 K (Micrometrics ASAP 2020, USA). The specific surface area was calculated based on the Brunauer–Emmett–Teller (BET) equation in the relative pressure range of 0.01–0.05. The total pore volume ( $V_T$ ) was estimated from the nitrogen adsorption data at a relative pressure range of 0.99 and the average pore width was calculated using the equation,  $4 V_T / S_{BET}$ . Also the density functional theory (DFT) equation was used for the estimation of pore volume and pore size distribution. Besides, mesopore volumes were calculated by the Barrett, Joyner, Halenda (BJH) equation. The oxygen functionalities of the BL-ACs were analyzed by an X-ray photoelectric spectroscopy (Multilab 2000/Thermo electron corporation, England).

## 2.3. Capacitance measurements

The electrodes were prepared by the mixture of 80 wt% BL-ACs (BL-1/2, BL-1/3, and BL-1/4) and 20 wt% binder (Teflonized Acetylene Black, TAB). Then the prepared electrodes were dried at 60 °C for 24 h in a vacuum drier. All of the electrochemical measurements were conducted in 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution at room temperature. The cyclic voltammetry (CV) tests were carried out by three-electrode system consisted of voltammetry cell for VC-2 (BAS Inc.) and RE-2C reference electrode (Hg/Hg sulfate, BAS Inc.) in the potential range of 0–0.9 V at the sweep rate of 5 mV/s (Zahner Elektrik IM6e, Germany). The specific capacitances of the BL-ACs were measured using a WBCS-3000 battery cyclor system (Won A Tech. Co., Korea) as a function of discharge current density (1–10 mA/cm<sup>2</sup>). The discharge capacitance of each unit cell was calculated from the following equation.

$$C = \frac{2(I \times \Delta t)}{m \times \Delta V} \quad (1)$$

where  $C$  is the specific capacitance,  $I$  is the discharge current,  $m$  is the weight of an electrode,  $\Delta V$  is the voltage variation in the time range except the portion of IR drop, and  $\Delta t$  is the discharge time. The total specific capacitance obtained from the test cell was calculated from the sum of two equivalent single electrode capacitors.

The AC impedance measurements of all the samples were carried out in the range from 100 kHz to 10 mHz using the electrochemical impedance analyzer (Zahner Elektrik IM6e, Germany).

## 3. Results and discussion

### 3.1. Characterization of the BL-ACs

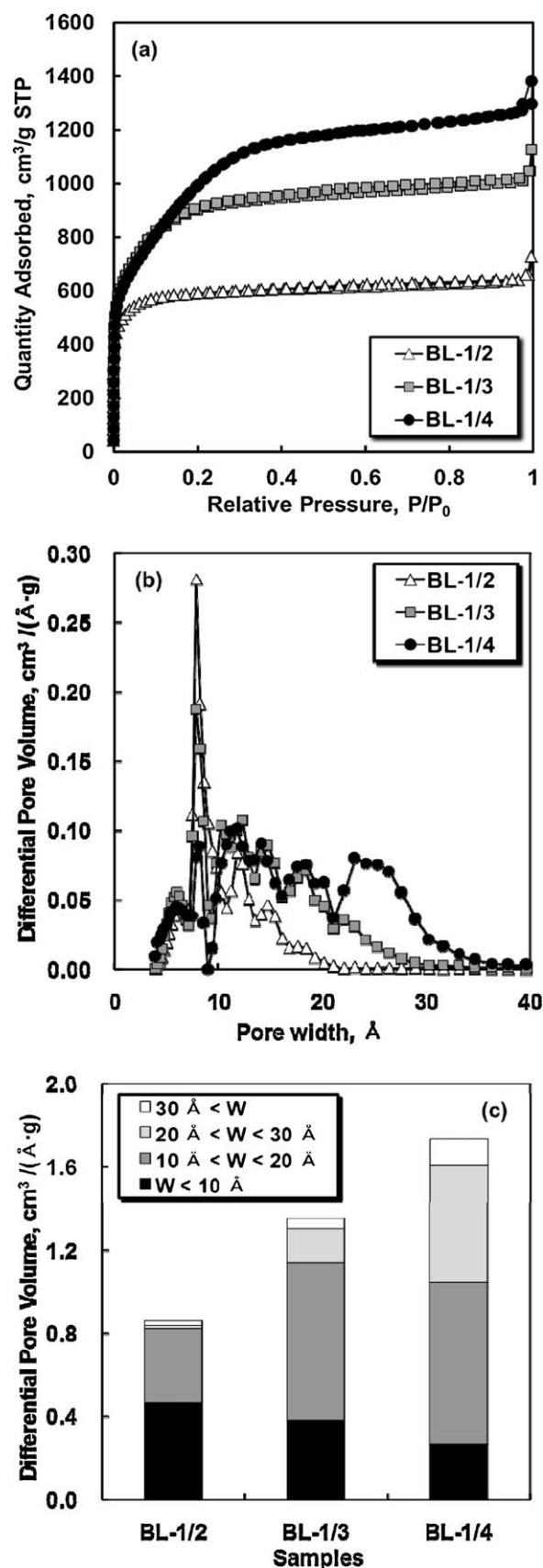
The textural properties of the BL-ACs were assessed by N<sub>2</sub> adsorption/desorption isotherms at 77 K. The results such as specific surface area, total pore volume, micro- and meso-pore volumes, and average pore width are listed in Table 1. Also N<sub>2</sub> adsorption/desorption isotherms and pore size distributions of all

**Table 1**  
Textual properties of BL-ACs.

Sample	$S_{BET}$ (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)			APW <sup>b</sup> (Å)
		$V_T^a$	$V_{DFT}$	$V_{BJH}$	
BL-1/2	2113	1.125	0.903	0.222	7.84
BL-1/3	3257	1.744	1.347	0.397	7.84
BL-1/4	3557	2.138	1.414	0.724	11.76

<sup>a</sup> Total pore volume.

<sup>b</sup> Average pore width.



**Fig. 1.** Textual properties of BL-ACs determined from N<sub>2</sub> adsorption/desorption isotherm data at 77 K; (a) N<sub>2</sub> adsorption/desorption isotherms of BL-ACs, (b) pore size distributions calculated by DFT equation and (c) pore volume distributions.

**Table 2**  
Oxygen functionalities of BL-ACs.

Sample	C1s				
	Graphitic (%)	C–O (%)	C=O (%)	O–C=O (%)	Carbonate (%)
BL-1/2	71.6	13.3	7.8	4.0	3.0
BL-1/3	66.8	17.8	6.9	5.1	3.1
BL-1/4	68.0	18.4	6.7	4.8	1.9

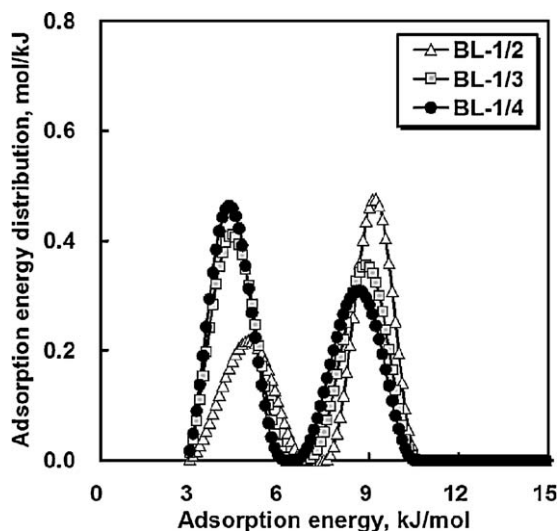
the samples are shown in Fig. 1(a) and (b). The textual properties of the BL-ACs such as specific surface area and pore volume are gradually developed with increasing the mass ratio between beer lees char and KOH. Especially, the BL-1/4 sample has highly large specific surface area ( $>3500 \text{ m}^2/\text{g}$ ) and high pore volume compared to the previous works [10–13]. In addition, the fractions of porosity in the ranges of  $W < 10 \text{ \AA}$ ,  $10 \text{ \AA} < W < 20 \text{ \AA}$ ,  $20 \text{ \AA} < W < 30 \text{ \AA}$ , and  $30 \text{ \AA} < W$  for each of the BL-ACs are shown in Fig. 1(c). The pore size distribution of the BL-1/2 is mostly located in the microporosity below  $10 \text{ \AA}$ . Also, the fractions of porosity over  $10 \text{ \AA}$  increase as the following order: BL-1/2 < BL-1/3 < BL-1/4. Especially, in the case of the BL-1/4 sample, the fraction of porosity in the range of  $20 \text{ \AA} < W < 30 \text{ \AA}$  is highly developed.

The oxygen functional groups on the BL-ACs were analyzed by XPS and listed in Table 2. The results show that the C–O type groups increase consistently with the mass ratio between the carbonized beer lees char and potassium hydroxide whereas the graphitic carbon and C=O groups slightly decrease.

### 3.2. Adsorption energy distributions (AEDs)

Adsorption energy distributions have been widely used for explanation of the energetic heterogeneity on AC surface. In general, the Fowler–Guggenheim (F–G) adsorption equation has been employed to evaluate the correlations between the low pressure nitrogen adsorption data and energy dependent localized monolayer adsorption [16,17]. In this work, the generalized nonlinear regularization method, which is one of the various approach methods such as the analytical, numerical, and local adsorption isotherm approximation methods, was adopted for solving the difficulties associated with numerically ill-posed problems [16,18–20].

The AEDs of all the BL-ACs are shown in Fig. 2. The values such as the peak location, the maximum peak height and the adsorption energy at the maximum peak height are listed in Table 3. All of the

**Fig. 2.** Adsorption energy distributions of BL-ACs derived from nitrogen adsorption isotherm data.**Table 3**  
Characterizations of AEDs for nitrogen on BL-ACs.

Sample	Peak location (kJ/mol)		MPH (mol/kJ)		Adsorption energy at peak height (kJ/mol)	
	LER <sup>a</sup>	HER <sup>b</sup>	LER <sup>a</sup>	HER <sup>b</sup>	LER <sup>a</sup>	HER <sup>b</sup>
BR-1/2	3.00–6.82	7.59–10.65	0.219	0.475	4.97	9.23
BR-1/3	3.00–6.27	6.93–10.53	0.411	0.355	4.42	8.90
BR-1/4	3.00–6.17	6.49–10.53	0.463	0.310	4.31	8.68

<sup>a</sup> LER, lower energy range.

<sup>b</sup> HER, higher energy range.

<sup>c</sup> MPH, maximum peak height.

BL-ACs have AEDs with two peaks in the range of 3.00–11.00, respectively. In general, it has been known that the AED in the range of low adsorption energy is considered as the effect of mesoporosity whereas the AED in the range of high adsorption energy is attributed to the microporosity [17]. The AEDs of the BL-ACs are noticeably altered with increasing the textual properties such as the specific surface area and the pore volume. Especially, the AED of the BL-1/4 shows the highest adsorption energy height in the low adsorption energy range and the broad energetic heterogeneity in the high adsorption energy range compared to those of BL-1/2 and BL-1/3.

### 3.3. Electrochemical capacitance

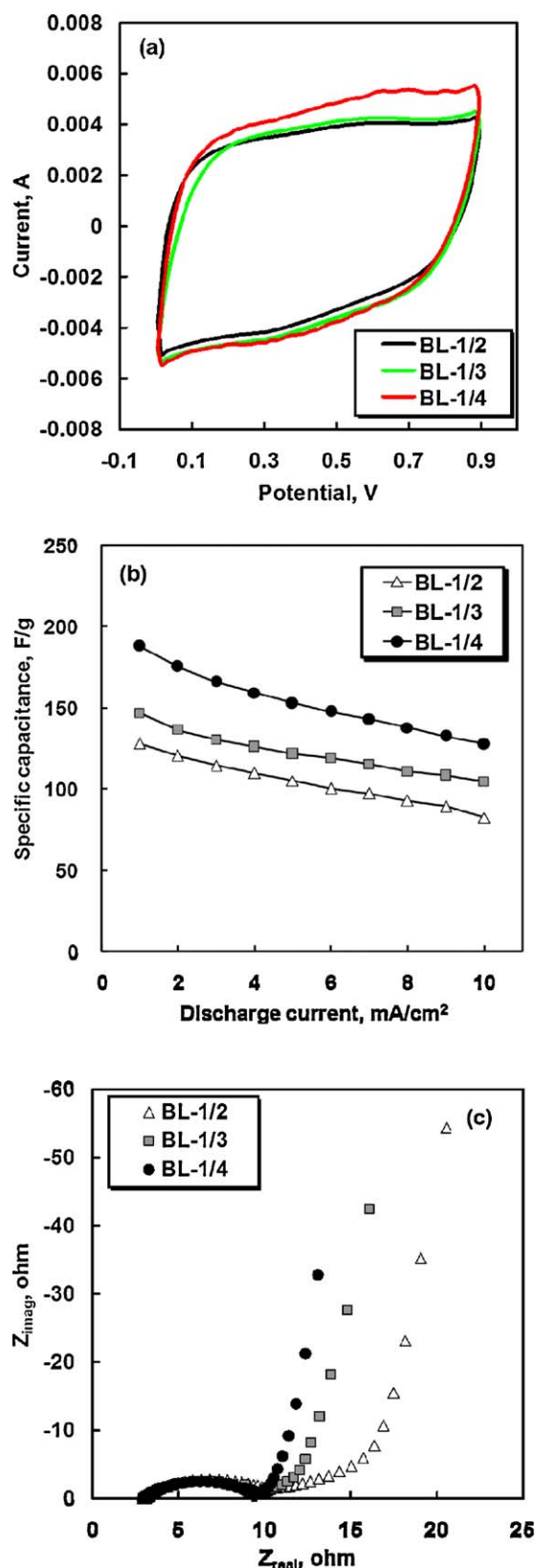
A cyclic voltammogram (CV) has been used for understanding the electrochemical surface reactions of electrode in EDLCs. The cyclic voltammograms of electrodes prepared from the BL-ACs are shown in Fig. 3(a). The voltammetry curves of all the samples are close to a rectangular shape without any current peak caused by a defect of redox reactions.

The specific capacitances of the BL-ACs were assessed in 0.1 M  $\text{H}_2\text{SO}_4$  solution as a function of discharge current density in the range of 1–10  $\text{mA}/\text{cm}^2$ . The results are shown in Fig. 3(b). The order of the maximum specific capacitance is as follows: BL-1/2 < BL-1/3 < BL-1/4. Moreover, it is observed that the specific capacitance of all the samples gradually decreases with increasing the discharge current density. It indicates that the deterioration of the specific capacitance is attributed to larger internal resistance in pores at higher discharge current density.

The electrochemical impedances of the BL-ACs such as the contact resistance, charge transfer resistance, and the diffusion resistance in pores of electrolyte ions are shown in Fig. 3(c). The values of impedances measured are also listed in Table 4. The BL-1/4, which has the highest specific capacitance, shows the lowest value of internal contact resistance and the diffusion resistance of electrolyte ions in pores compared to those of the BL-1/2 and BL-1/3.

### 3.4. Capacitance correlations

The correlations between the textual properties and the surface functionalities as well as the energetic heterogeneities of the BL-ACs on EDLC performance are reviewed. The BL-1/4, which possesses the largest specific surface area and the highest pore volume, has the highest specific capacitance compared to those of the BL-1/2 and BL-1/3. Interestingly, with increasing the pore fraction in the range of  $20 \text{ \AA} < W < 30 \text{ \AA}$ , the specific capacitance of the BL-ACs is remarkably enhanced. It indicates that the pore size in the range of  $20 \text{ \AA} < W < 30 \text{ \AA}$  helps a contact of sulfate ion with micropores on EDLCs. Based on the AED studies of the BL-ACs, the specific capacitance is enhanced with the maximum peak height of the AED in the range of low adsorption energy and the relatively broad energetic heterogeneity in the range of high adsorption



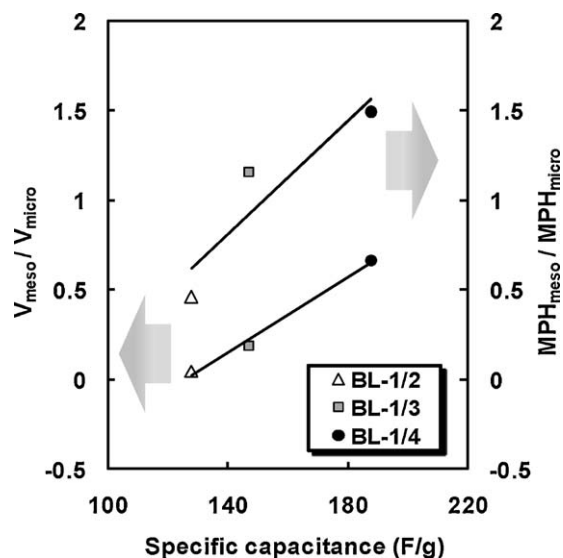
**Fig. 3.** Electrochemical properties of EDLC using the beer lees-based activated carbon electrodes in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution; (a) cyclic voltammetry characteristics of beer lees-based activated carbons at a potential sweep rate of 5 mV/s, (b) dependence of the specific capacitances on discharge current density (1–10 mA/cm<sup>2</sup>) and (c) impedance plots at amplitude of 5 mV.

**Table 4**

Resistance values for the EDLC cells.

Sample	Resistance			
	$R_t$ ( $\Omega$ )	$R_s$ ( $\Omega$ )	$R_c$ ( $\Omega$ )	$R_p$ ( $\Omega$ )
BL-1/2	20.57	2.94	7.56	10.06
BL-1/3	16.06	2.94	6.81	6.30
BL-1/4	13.09	2.94	6.41	3.73

$R_t$ , total resistance;  $R_s$ , resistance of ion migration in the bulk solution;  $R_c$ , internal contact resistance of the electrode;  $R_p$ , equivalent distributed pore resistance.



**Fig. 4.** Correlations among  $V_{\text{meso}} (W > 20 \text{ \AA})/V_{\text{micro}} (W < 20 \text{ \AA})$ ,  $\text{MPH}_{\text{meso}}/\text{MPH}_{\text{micro}}$ , and specific capacitances.

energy. Therefore, the results indicate that the AED of the BL-ACs on EDLC performance provides important information to obtain the high specific capacitance.

More especially, considering the overall effects influenced by textual properties on EDLC performance, the linear correlations among  $V_{\text{meso}} (20 \text{ \AA} < W)/V_{\text{micro}} (W < 20 \text{ \AA})$ ,  $\text{MPH}_{\text{meso}}/\text{MPH}_{\text{micro}}$ , and specific capacitances are once again assessed, as shown in Fig. 4. Here MPH is the maximum peak height. Interestingly, it is found that there are the close linear relationships with  $V_{\text{meso}}/V_{\text{micro}}$  versus specific capacitance and  $\text{MPH}_{\text{meso}}/\text{MPH}_{\text{micro}}$  versus specific capacitance. Consequently, it is confirmed from correlation studies that the specific capacitances of the BL-ACs are definitely influenced by the relative porosity fraction as well as the AED.

The effect of oxygen functional groups on EDLC performance is also investigated. In general, it has been known that the oxygen functional groups on the surface of ACs are the positive contribution to the capacitance of EDLCs owing to the enhanced wettability of ACs in an aqueous electrolyte solution [21–23]. In this work, the specific capacitances of the BL-ACs decrease with the contents of graphitic carbon and C=O functional groups whereas it is enhanced by C–O functional groups. The positive contribution of the C–O functional groups of the BL-ACs on the EDLC capacitance enhancement seems to be their high stability [22,23].

In overall, the results from correlation studies suggest that the fraction of the controlled pore size distribution, large specific surface area, AEDs, and tailored oxygen functionality on the BL-ACs surface may guarantee the high EDLC performance.

#### 4. Conclusion

High quality activated carbons were prepared from beer lees, the waste product after the beer extraction process. Among a series

of the BL-ACs, the BL-1/4 has the highest specific surface area ( $>3500 \text{ m}^2/\text{g}$ ), high pore volume ( $V_{\text{DFT}}: 1.414 \text{ cm}^3/\text{g}$ ,  $V_{\text{BJH}}: 0.724 \text{ cm}^3/\text{g}$ ), and wide pore size distribution. In assessment of the BL-ACs on EDLC performance in  $0.1 \text{ M H}_2\text{SO}_4$  electrolyte solution, which is a relatively low electrolyte concentration, the order of the maximum specific capacitance is as follows: BL-1/2 ( $128 \text{ F/g}$ )  $<$  BL-1/3 ( $147 \text{ F/g}$ )  $<$  BL-1/4 ( $188 \text{ F/g}$ ). Also from the correlation studies between specific capacitance and textural/chemical characteristics of the BL-ACs, it is found that there are linear relationships with  $V_{\text{meso}}/V_{\text{micro}}$  versus specific capacitance and  $\text{MPH}_{\text{meso}}/\text{MPH}_{\text{micro}}$  versus specific capacitance. Besides, the larger specific surface area, the broader AED in the high adsorption energy region, and the higher peak in the range of low adsorption energy as well as the C–O functional groups positively contribute to the specific capacitance and the performance of EDLCs. Based on the overall results, the BL-ACs are promising candidates as carbon materials for EDLC electrodes.

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