



Highly porous electrodes from novel corn grains-based activated carbons for electrical double layer capacitors

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ABSTRACT

In this study, novel corn grains-based activated carbons (CG-ACs) were prepared and their use as electrodes in the electrical double layer capacitor (EDLC) performed successfully. The structural properties, energetic heterogeneities and surface functional groups of CG-ACs were characterized using different techniques like nitrogen sorption data, adsorption energy distribution (AED) and X-ray photoelectric spectroscopy (XPS). The electrochemical properties of various CG-ACs were evaluated by using cyclic voltammetry. The maximum specific capacitance value as 257 F g^{-1} was obtained in 6 M KOH electrolyte solution. The effects of various properties of the porous carbon materials on the EDLC performance were discussed.

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1. Introduction

Electrochemical capacitor is a promising energy storage device, which usually provides high power density and longer cycle life with lower energy density [1]. The electrical double layer capacitor (EDLC) is an electrochemical storage device, in which the electrical energy is stored in an electrochemical double layer based on the separation and the pure electrostatic attraction of charge at the interface between the charged surface on an electrode and ionically conductive electrolyte [2]. Activated carbon is a feasible material for the storage of energy, particularly for electrochemical purposes because of its unique surface characteristics [3]. Especially, activated carbons with specific capacitance values of $>200 \text{ F g}^{-1}$ in aqueous electrolytes and $>120 \text{ F g}^{-1}$ in organic electrolytes have been recommended [1]. The activated carbon sample with high surface area generally offers high capacitance and at the same time, a non-linear relationship has been observed between the surface area and specific capacitance, where the surface area of the activated carbon is over $1000 \text{ m}^2 \text{ g}^{-1}$ [4–7]. It has been suggested that apart from the surface area, some other parameters such as pore geometry, pore size, pore size distribution surface functional groups, and size of the electrolyte ions are also greatly influencing the EDLC performance [4–9].

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In a successful attempt, CG-ACs were prepared and the electrodes from these activated carbons were made for the EDLC to examine the commercial applicability of these materials. Here we explored some information on the various influencing parameters, which affect the EDLC performance by analyzing the structural properties, energetic heterogeneities as well as surface functional groups.

2. Experimental

The activated carbon samples were produced from corn grains by varying the activation time from 30 min to 240 min and the prepared samples were named as K-30, K-60, K-180, and K-240 (K-series). The recipe for the preparation of CG-ACs has been given in elsewhere [10]. The porous texture of all the activated carbon samples was characterized by nitrogen adsorption and desorption studies at 77 K (Micrometrics ASAP 2020, USA). Prior to the adsorption analysis, the sample was outgassed at 423 K for 12 h under vacuum condition for the removal of moisture and other impurities. The specific surface area was determined on the basis of the Brunauer–Emmett–Teller (BET) equation using the nitrogen relative pressure (P/P_0) range of 0.01–0.05, as suggested by Kaneko et al. [11] for analyzing porous carbons with very high surface area. The pore size distribution, pore volume, and average pore width were obtained by employing the density functional theory (DFT). The Barrett, Joyner, and Halenda (BJH) method was used for the evaluation of mesopore volume [12]. The X-ray photoelectric spectroscopy

(XPS, Multilab 2000/Thermo electron corporation, England) equipped with an electron energy analyzer (Alpha 110 analyzer) was used to determine the quantitative atomic compositions.

The electrodes were prepared from K-series activated carbons. Four different electrodes with a dimension of 1.5 cm² were made by compressing a mixture of activated carbon (90 wt%) and a binder (PTFE, 10 wt%). The capacitor cells were built by assembling two electrodes separated by glassy fiber. Then, a pair of nickel plates (thickness 50 μm) was attached on both sides to collect currents on the surface of the electrodes. The prepared capacitor cells were dried in a vacuum drier at 120 °C for 24 h. The cyclic voltammetry (CV) tests were performed in the potential range of 0–0.9 V by varying the scan rate from 10 to 500 mV s^{−1} (Jahner Elektrik IM6, Germany). The discharge capacitance of each unit cell was obtained by conducting CV experiments in an aqueous 6.0 M KOH solution at room temperature. The capacitance, *C*, is calculated from the CV for a two-electrode system on the basis of the following equation

$$C = \int i dt / dv \quad (1)$$

where *i* is the current, *t* is the time, and *v* is the voltage.

3. Results and discussion

3.1. Porous texture characterization

The adsorption and desorption isotherms of nitrogen on the prepared K-series activated carbons at 77 K are shown in Fig. 1a. In all cases, the obtained results correspond to Type I isotherms (characteristic of microporous materials) according to the IUPAC classification [13]. The physical properties of the prepared activated carbons are listed in Table 1.

3.2. Adsorption energy distribution

Usually, the energetic heterogeneity properties of the all activated carbons are characterized in terms of the adsorption energy distribution. The low pressure nitrogen adsorption data and the energy dependent local adsorption have been used for the prediction of adsorption energy distribution (AED), using the Fowler–Guggenheim equation [14]. The distribution function *F*(*U*) is given as follows:

$$\theta(P) = \int_{\Delta} \theta_1(P, U) F(U) dU \quad (2)$$

where $\theta(P)$ is the submonolayer surface coverage, $\theta_1(P, U)$ is the energy dependent local adsorption isotherm and $F(U)dU$ denotes the fraction of the surface with adsorption energies between *U* and *U* + *dU*.

The AED functions for nitrogen on K-series activated carbons are shown in Fig. 1b. The AEDs with two peaks indicate that the prepared activated carbons have two distinct bimicroporous structures with high surface areas. The characteristics of the AEDs such as the peak location, the maximum peak height and the adsorption energy at the maximum peak height are given in Table 2. Usually, the narrow AED represents the smaller energetic heterogeneity, whereas the broader AED indicates the larger energetic heterogeneity [14]. Based on the energy distribution and the maximum peak height, the order of the energetic heterogeneity was found as follows, K-30 > K-240 > K-180 > K-60.

3.3. Surface chemistry characterization

The surface functional groups especially, oxygen functional groups highly dominate the working capacity of the capacitor.

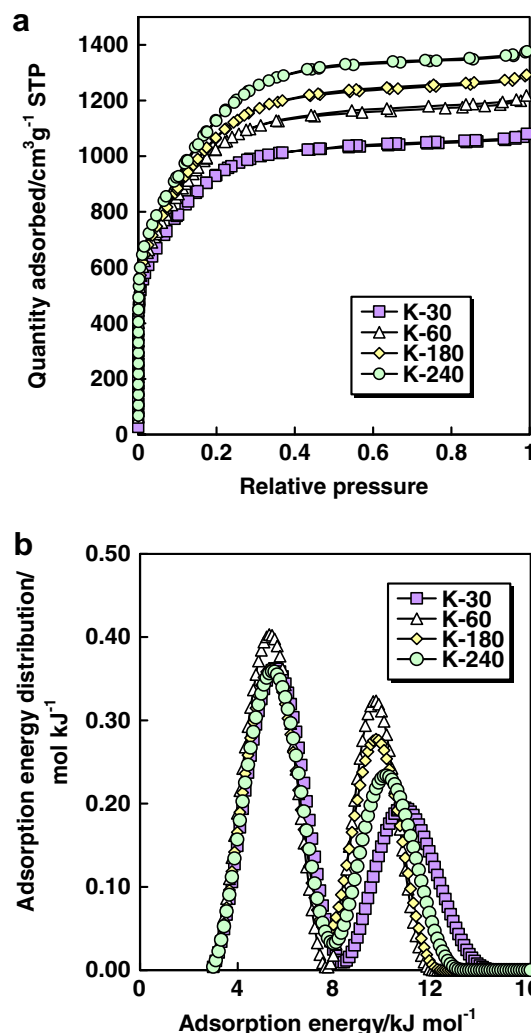


Fig. 1. Characterizations of K-series activated carbons, (a) the adsorption and desorption of nitrogen at 77 K, and (b) adsorption energy distributions based on the nitrogen adsorption.

Table 1
Physical properties of K-series activated carbons

Sample I.D	BET S.S.A ^a (m ² g ^{−1})	Pore volume ^b (cm ³ g ^{−1})	Pore volume fraction (%)		Average pore width ^b (nm)
			Micro	Meso ^c	
K-30	2936	1.479	65.5	34.5	1.18
K-60	3199	1.645	61.7	38.3	1.08
K-180	3270	1.760	57.8	42.2	1.08
K-240	3420	1.895	54.7	45.3	1.03

^a BET specific surface area.

^b Based on the DFT theory.

^c Based on the BJH equation.

The wettability of the microporous activated carbon in an aqueous electrolyte solution [15] is low due to its hydrophobic nature and it can be increased in the presence of oxygen functional groups (CO groups (hydroxyl, carbonyl or quinone)) [9,15,16]. However, the detailed discussion of the influence of specific CO group on the capacitor performance is limited [17–19]. In this study, the surface functional groups of CG-ACs were evaluated by an XPS to obtain exact informations of each oxygen functional groups, as given in Table 3.

Table 2Characterization of AEDs for N₂ on K-series activated carbons

Sample I.D.	Peak location (kJ mol ⁻¹)		Maximum peak height (mol kJ ⁻¹)		Adsorption energy at the maximum peak height (kJ mol ⁻¹)	
	L.E.P ^a	H.E.P ^b	L.E.P ^a	H.E.P ^b	L.E.P ^a	H.E.P ^b
K-30	3.00–8.24	8.24–13.38	0.362	0.195	5.51	11.90
K-60	3.00–7.70	7.70–11.20	0.403	0.323	5.29	9.66
K-180	3.00–7.70	7.70–12.40	0.363	0.277	5.40	9.66
K-240	3.00–7.92	7.92–13.20	0.359	0.234	5.40	10.10

^a L.E.P = lower energy part.^b H.E.P = higher energy part.**Table 3**

XPS results (high resolution C1s spectra analyzes results) of K-series activated carbons

Sample	C1s				
	Graphitic	Phenol–ether	Carbonyl–quinone	Carboxyl–ester	Carbonate
Peak (eV)	284.59–285.01	286.06–286.79	287.14–288.05	288.80–289.37	290.39–290.95
K-30	65.31%	16.23%	7.64%	5.27%	5.55%
K-60	68.15%	8.02%	10.28%	7.22%	6.33%
K-180	70.26%	10.43%	8.50%	5.97%	4.84%
K-240	64.94%	13.94%	9.35%	5.39%	6.38%

3.4. Electrochemical measurements

The electrode pairs from various K-series activated carbons were tested in 6 M KOH aqueous solution at room temperature. A linear relationship between the specific capacitance and discharge density was studied for K-series activated carbons as shown in Fig. 2a. The sample K-60 showed the maximum specific capacitance value as 257 F g⁻¹, which is higher than the recently reported results (<200 F g⁻¹) [1]. The specific capacitance of K-30 is low compared to other samples that may be due to the large internal resistance [20]. The decreasing capacitance with increasing discharge current density implies the potential difference in micropores because of the ohmic resistance of the electrolyte [20].

Cyclic voltammograms (CVs) of K-series electrodes in 6 M KOH electrolyte at the 50 mV s⁻¹ sweep rate are shown in Fig. 2b. The figure indicates that the electrodes are stable in alkaline solution within the potential range (0–0.9 V) employed. It is well known that the CV for the ideal double-layer capacitor is characterized by the perfectly rectangular-shaped profile. In our samples, the CV profiles are deviated from the ideal shape, but the shape of the curve is still satisfactory, even at the 50 mV s⁻¹ scan rate. The observed satisfactory shape may be due to a quick kinetic process for the diffusion of ions in the large pores of CG-ACs [4].

3.5. Capacitance correlation

The correlation between the energetic heterogeneity, surface functional groups with relative capacitance of CG-ACs can be critically analyzed with observed results. A non-linear relationship was found between the surface area of various K-series activated carbons and their capacitance values. At that same time, the capacitance results sequence of K-series activated carbons were matched well with the results of energetic heterogeneity. This correlation indicated the benefit of the relatively smaller energetic heterogeneity surface for the achievement of high capacitance. For example, the sample K-60 showed the highest capacitance, also because of its relatively smaller energetic heterogeneity contrast to other K-series activated carbons. Hence, the effect of the energetic heterogeneity also should be considered for the design of the EDLC. Also the relationship between the capacitor performance and the surface functional group was observed from XPS results (see Table 3). Here we report our experimental results on the domination of quinone group. Quinone is basically an electron capacitor and it in-

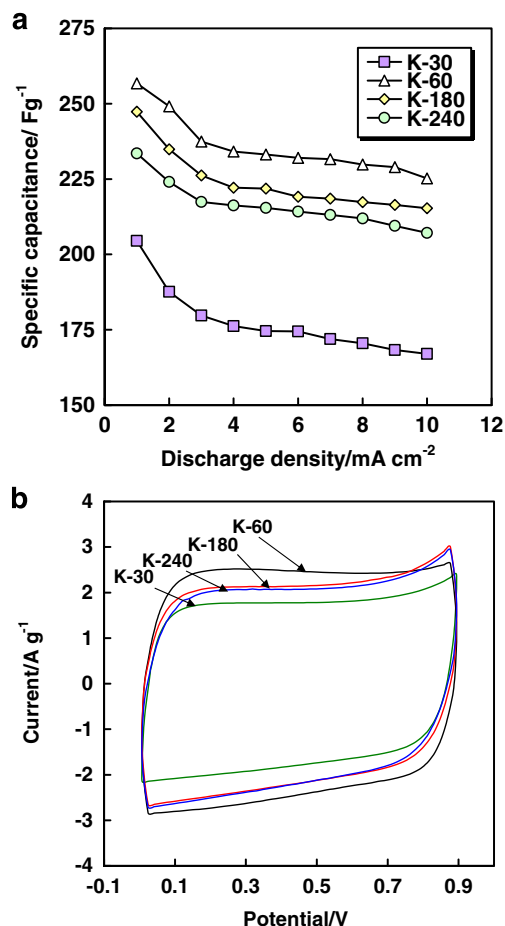


Fig. 2. Electrochemical properties of EDLC using the K-series electrodes in an aqueous 6 M KOH solution. (a) Dependence of specific capacitance on the current density. (b) Cyclic voltammograms at a potential sweep rate of 50 mV s⁻¹.

creases the capacitance through the pseudocapacitance via redox mechanism [17]. For each activated carbon, the correlation between the available quinone group in the surface and its capacitance value was studied. It was observed that the highest quinone fraction value in sample K-60 shows the better EDLC performance

compared to other samples; although it has a higher amount of carboxyl group [17,18]. In overall, the EDLC results and the amount of available quinone group of different activated carbons have more or less good correlation with one deviation (K-240). Although the sample K-240 has higher fraction of quinone group compared to the sample K-180, its capacitance value is lower than the sample K-180 because of its energetically heterogeneous surface and the higher amount of mesoporosity compare to the sample K-180. In addition, the sample K-30 has the lowest fraction of quinone and relatively higher energetic heterogeneity contrasts to other samples, thereby resulting in lowest capacitance among all the K-series activated carbon.

4. Conclusions

The potential applications of corn-grains based activated carbons in EDLCs performance have been confirmed successfully from the results of K-series activated carbons. Among all the K-series activated carbons, the sample K-60 shows the highest specific capacitance value of 257 F g^{-1} in an aqueous 6 M KOH electrolyte solution. The results of the cyclic voltammogram also emphasize the high specific capacitance of the sample K-60 compared to other activated carbons. A non-linear relationship between the surface area and the specific capacitance represents the influence of numerous structural properties and surface functional groups. The possibility of correlating the results of the energetic heterogeneity property from the adsorption energy distribution and the specific capacitance was effectively analyzed. The results of adsorption energy distributions well match with the EDLC results and evidently indicate the effect of energetic heterogeneity. In addition, the domination of quinone surface functional group on the EDLC performance was also detected.

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