

PREPARATION OF HIGH PERFORMANCE ACTIVATED CARBON ELECTRODE FROM WASTE FIBREBOARD FOR ELECTRIC DOUBLE LAYER CAPACITOR BY KOH ACTIVATION

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ABSTRACT

Waste medium density fibreboard (MDF) containing 12 % urea-formaldehyde resin adhesive prepared for nitrogen-enriched activated carbon electrodes were carbonized with different carbonized temperatures of 300, 400, 500 and 600°C primarily. And then activated carbons (AC_s) were obtained by 16 h impregnation and 1 h activation agent of KOH at 800°C with KOH/coke mass ratio of 3. The AC_s was investigated by porosity and elemental analysis. The results obtained by Brunauer-Emmett-Teller (BET) analysis showed specific surface area of AC_s varied from 455 to 1793 m².g⁻¹, and the total pore volume of AC_s varied from 0.233 to 0.932 cm³.g⁻¹, which was affected by different carbonization temperatures. Furthermore, electrochemical properties of electric double layer capacitors were studied. The results indicated that specific capacitances of activated carbon electrode ranged from 148 to 213 F.g⁻¹. The good electrochemical capacities suggested that waste MDF could be used as a candidate material for electric double layer capacitor electrode.

KEYWORDS: Waste medium density fibreboard, KOH activation, nitrogen-enriched activated carbon electrode, electric double layer capacitor.

INTRODUCTION

With development of technology, sustainable energy utilization of energy has become a popular strategy all over the world. Electric energy, as a final form of energy, is an indispensable necessity in our daily life, but we are threatened with more and more increase of power needs and shortage of resource (Du-Pasquier et al. 2003).

Electric double layer capacitor (EDLC) has recently become a promising energy storage technology at a number of research centres in the world. The main reason for this interest is the possibility of their use for keeping a balance on power needs and scarce resources. As all we know, the critical factors for obtaining a capacitor of high power are not only using of a stable electrode materials characterizing high capacity, but also having high charge-exchange performance (Li et al. 2011; Pietrzak et al. 2010). And in the past several years, various carbonaceous materials, including activated carbons (AC_s) (Tian et al. 2008), activated carbon fiber (Nian and Teng 2003), carbon nanotube (An et al. 2001), carbon aerogel (Baumann et al. 2008), carbon black (Zhang et al. 2004), have been investigated as electrode materials of EDLC. Comparatively, activated carbon is the best electrode material to prepare for EDLC (Du-Pasquier et al. 2003).

Recently, much attention has been devoted to prepare nitrogen enriched activated carbons (AC_s) for EDLC with good electrochemical performance. Li et al. (2007) use melamine-formaldehyde resin as the carbon precursor, and commercial fumed silica (Aerosil-200) as a hard template by carbonization at 1000°C and HF treatment to prepare mesoporous carbon spheres (MCS) with diameter size of ~ 1.2 µm, high specific surface area. The MCS product presents a high specific capacitance as 159 F.g⁻¹ at 0.5 A.g⁻¹. And 130 F.g⁻¹ can be remained even at high current density of 20 A.g⁻¹. Seo et al. (2010) use sunflower seed shell by two different strategies to prepare nanoporous carbons as electrode materials for supercapacitors. The results demonstrate that the enriched nitrogen content and the large pore size of the MCS affect the surface wettability, resistance, and ion diffusion process in the pores, and the MCS show a high specific capacitance of 196 F.g⁻¹ in 5 mol.L⁻¹ H₂SO₄ electrolytes at a discharge current density of 1 A.g⁻¹. Jurewicz et al. (2008) prepare AC_s with different contents of nitrogen obtained from brown coal by nitrogenation and activation processes. Due to nitrogen heteroatoms in carbonaceous materials, their capacitance increased when they work as capacitor electrodes in alkaline capacitor, especially as the negative electrode, specific capacitance has been as high as 368 F.g⁻¹. Therefore, good electrochemical performance of the carbon attributes to large specific surface area. On the other hand, nitrogen-containing functional groups can also make pseudocapacitance contribution to the overall capacitance (Senthilkumar et al. 2011).

In China, a lot of old furniture made from fibreboard is disposed every year, and most of them are always to be burned to heating. However, in order to promote recycling, a better use of fibreboard waste is an effective way to decrease production costs (Hu et al. 2006; Wu et al. 2012). More importantly, waste medium density fibreboard (MDF), containing aldehyde resin adhesive, can be a good raw material to prepare N-enriched activated carbon electrode for EDLC. It has come to our knowledge that no one has prepared for electrode material by using waste MDF boards.

In this study, waste MDF boards, containing 12 % urea-formaldehyde resin adhesive which was enriched by nitrogen, were used as raw material to prepare nitrogen-enriched activated carbon electrode for EDLC. Different carbonization temperature was applied to prepare a series of AC_s. The relationship between pore-structure of AC_s and their electrochemistry performances as EDLC electrode had also been elucidated.

MATERIAL AND METHODS

Preparation of AC_s from waste MDF

Carbonization

The waste MDF was collected from a furniture factory in Beijing, China. The elemental

analysis of raw material named C0 was shown in Tab. 1. The waste MDF sample was heated up at different carbonization temperatures (300, 400, 500, and 600°C) with the heating rate of 100°C . h⁻¹. Then the carbonization system was cooled to room temperature. Nitrogen was flushed through the carbonization system in order to maintain an inert atmosphere during the process. Furthermore, the obtained carbides at different carbonization temperatures were grinded by a high-speed disintegrator and sifted out the particle diameter ranged from in the range of 40-60 grit numbers by standard sieve to get four samples for activation and samples above 100 grit numbers designated as C300, C400, C500 and C600 for testing.

Tab. 1: Nitrogen, carbon, hydrogen (%) in raw material, carbides and activated carbons from elemental.

Samples	N (%)	C (%)	H (%)
C0	8.388	45.16	5.764
C300	7.058	70.35	3.623
C400	6.835	74.85	2.682
C500	6.307	77.5	2.085
C600	5.772	79.38	1.498
AC300	3.194	85.45	2.074
AC400	2.171	88.31	3.261
AC500	1.785	92.09	2.039
AC600	0.935	94.60	1.052

Impregnation-activation process

In this work, dried carbide scrap samples were mixed with 50 % KOH solution with mass ratio of 3 based on KOH, stirred and then settled in room for 16 h. Then the mixtures were dried in an electric stove. The AC_s finally obtained were designated as ACX, where X represents the final carbonization temperature, namely, AC300, AC400, AC500, AC600. Dried products were to preserve activation temperature at 800°C for 1 h in an electrical resistance furnace under a flow of N₂ gas. After cooling under nitrogen flow, the activated resultant was boiled with 0.5 mol.L⁻¹ HCl and thoroughly washed with distilled water until the pH value of the filtrate became neutral. Finally, the samples were dried in a 105°C oven for 4 h.

Material characterization of AC_s

Pore analysis

Porous structures of AC_s were characterized by N₂ adsorption/desorption at 77 K on surface area and porosity measurements (Tristar II 3020, Micrometrics, USA). Samples were degassed under high vacuum at 300°C for 4 h before the measurements.

Elemental analysis

The elemental compositions were determined by an elemental analyzer (vario EL, III ELEMENTAR, Germany) at CHN mode under a N₂ flow rate of 201 ml.min⁻¹. Flame gas is oxygen and standard sample is the acetanilide.

Electrode preparation and electrochemical measurements

Electrode preparation

The dried activated carbon samples including AC300, AC400, AC500 and AC600 were grinded in an agate mortar. And then electrodes for the electrochemical measurements were fabricated by mixing the sample with acetylene black, 60 % polytetrafluoroethylene in a mass ratio of 87:10:3. The mixtures were sandwiched by nickel foam (square, about 1 cm²) and pressed under a pressure of 20 MPa with a nickel tape for connection to one disk (Jiang et al. 2009).

Electrochemical analysis

Electrochemical characters were tested in 7 M KOH solution. Constant current density charge-discharge and rate performance were tested using the BT2000 battery testing system (Arbin Instruments, USA) at room temperature. Cyclic voltammetry (CV) and alternating current impedance were employed in each sample for the electrochemical measurements using the 1260 electrochemical workstation (Solartron Metrology, UK) at room temperature. The gravimetric capacitance (Cp) analyzed, which mean the specific capacitance per mass weight activated carbon in the electrode, is expressed in F.g⁻¹ and calculated by the following formulas of (1) and (2):

$$C = \frac{Q}{U} = \frac{Q}{t} \times \frac{t}{U} = I \times \frac{t}{U} = \frac{I}{U/t} \quad (1)$$

$$C_p = \frac{C}{m} = \frac{I/m}{U/t} = \frac{I/m}{v} \quad (2)$$

where: I - observed value (A),
 m - average weight of each activated carbon disk (g),
 v - the voltage scan rate (mV.s⁻¹).

RESULTS AND DISCUSSION

Characterization of AC_s

Porosity characterization of AC_s

Pore structure parameters of AC_s were tested by N₂ adsorption/desorption. The isotherms of N₂ adsorption/desorption were presented in Fig. 1.

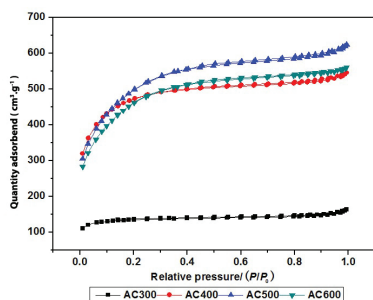


Fig. 1: N₂ adsorption isotherms of AC_s with different carbonization temperatures.

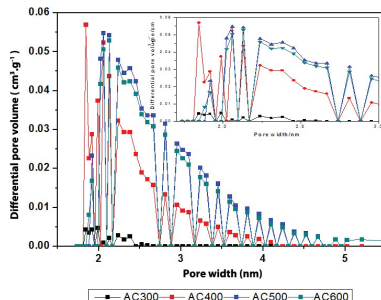


Fig. 2: Pore size distributions of AC_s with different carbonization temperatures.

The nitrogen adsorption capacity increased significantly with the carbonization temperatures. As for the adsorption-desorption curves from each activated carbon sample, the above shorter curve was desorption isotherm while another was the adsorption isotherm. Four activated carbon samples were similar and showed obvious microporous characteristics of Type I isotherm according to IUPAC classification. But the small hysteresis loops seen on the adsorption-desorption isotherms were due to the existence of mesopores (Feng et al. 2010). In the isotherms, the adsorption at the lower pressure was an indicator of micropores, while the desorption hysteresis in the plateau area in the higher pressure range indicated mesopores, which could be further proved by the pore size distribution as shown in Fig. 2 and Tab. 2.

Tab. 2: Porosity parameters of AC_s .

Temperature (°C)	S_{BET}	S_{mi}	V_{tot}	V_{mi}	S_{me}	V_{me}
	(m ² .g ⁻¹)		(cm ³ .g ⁻¹)		(%)	
AC300	455	257	0.233	0.085	43.55	63.46
AC400	1644	794	0.817	0.356	51.73	56.46
AC500	1793	330	0.932	0.127	81.59	86.36

For comparison, Brunauer-Emmett-Teller specific surface area (BET SSA), total pore volume and mesopore fraction of all the samples were listed in Tab. 2. The results indicated that the BET SSA above 1000 m².g⁻¹ of our samples covered a narrow range from 1644 to 1793 m².g⁻¹. And AC500 could achieve a high BET SSA of 1793 m².g⁻¹. The total pore volume had a same changing trend that total pore volume of 0.233, 0.817, 0.932 and 0.849 cm³.g⁻¹ were achieved. Fig. 2 showed the pore size distributions obtained by applying the non-local density functional theory based on the nitrogen adsorption isotherms. There were three peak zones of pore diameters of 1.8-2, 2-3 and 3-5 nm. The pore size distribution showed the same trend as BET SSA with the final carbonization temperatures, which was in accord with the nitrogen adsorption capacity and can explain the large loop sizes of AC400, AC500 and AC600 in Fig. 1.

Elemental analysis of AC_s

The elemental data presented in Tab. 1 showed that a list of the obtained carbides (C300, C400, C500, and C600), which resulted in an increase of carbon content, and a similar observation was made by Pietrzak et al. (2006). However, N element content in carbides did a down trend with increasing carbonization temperature, which was an indication of the thermal degradation of the nitrogen-containing functional groups present in the structure of MDF waste.

The elemental compositions of activated carbon samples obtained AC300, AC400, AC500 and AC600 were given in Tab. 1. In accordance with the results, the activation with KOH gave samples with higher content of C, but lower contents of H and N than in the raw material and carbides. The same results could be found in Nowicki et al. (2008), they used Polish brown coal from the "Konin" colliery to prepare nitrogen-enriched active carbon, then discussed to the elemental changes after carbonization and activation with KOH, which resulted in that upon activation with KOH the coal undergoes significant oxidation, and KOH could cause a greater extent of oxidation of carbon. Therefore, these results from elemental analysis of AC_s suggested that the nitrogen-enriched activated carbon could be obtained from activation with KOH.

Electrochemical performances of activated carbon electrodes

Charge-discharge behaviour of activated carbon electrodes

Fig. 3 exhibited constant current charge-discharge curves of AC300-AC600 electrodes in 7 M KOH solution at 50 mA.g⁻¹ current density (9th cycle) as an example. The specific capacitance of activated carbon electrode in EDLC was usually calculated from the slope of the discharge curve (Portet et al. 2008). The linear curves were evidences for the ideal EDLC behaviours of all the samples. Obviously, electrode materials with higher S_{BET} showed longer charging/discharging time, expressing their larger specific capacitance, according to Tab. 1 and Fig. 3.

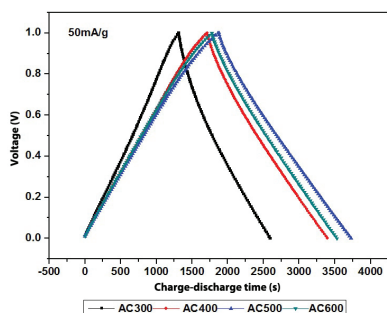


Fig. 3: Constant current density charge-discharge curves of AC300-AC600 capacitors.

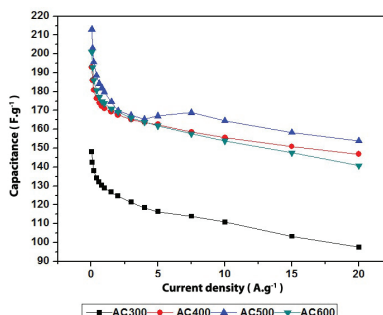


Fig. 4: Rate performances of AC300-AC600 capacitor.

In addition, the specific capacitance of different activated carbon electrodes at different current density (1st cycle) were illustrated in Fig. 4, which showed that the specific capacitance of activated carbon electrodes ranged from 148 to 213 F.g⁻¹ in a 0.5 A.g⁻¹, and the specific capacitance did a down trend in a quite wide range from 0.5 to 20 A.g⁻¹ because part micropores on AC_s were not used at higher discharge current density due to the diffusion delay of ions in the electrolyte (He et al. 2010). It was interesting to note that the specific capacitance of AC500 of 213 F.g⁻¹ was bigger than that of AC300, AC400 and AC600 because the S_{BET} or V_{tot} of the former was obviously bigger than the latter, which reached the results reported in the literature (He et al. 2010, Wang et al. 2011).

It had been known that for carbon materials for electrodes of EDLC, moderate content of nitrogen in carbon matrix clearly led to improve the wettability of carbon surface, and benefited on its capacitance behaviour (Li et al. 2007, Seo et al. 2010, Jurewicz et al. 2008). In view of the fact that urea-formaldehyde resin contains nitrogen, it was conceivable that resulting mesoporous carbon materials could be enriched in nitrogen. The chemical composition of the activated carbon products obtained after carbonization at 600°C still reserve 0.935 % of nitrogen content. According to research by Li et al. (2007), the most popularly applied activated carbon, YA-1 without nitrogen from Calgon Mitsubishi Chemical Corporation, was used as a reference. Despite its BET SSA was 2200 m².g⁻¹, which was larger than AC500 of 1793 m².g⁻¹. However, the specific capacitance of YA-1 (The commercial carbon used in reference as an EDLC electrode material under the same experimental condition) decreased from 105 to 38 F.g⁻¹ in a quite wide range from 0.5 to 20 A.g⁻¹, which was smaller than activated carbon electrode of AC500. And best specific capacitance of AC 500, which BET SSA only 1793 m².g⁻¹, could reach up to 213 F.g⁻¹ because of 1.785 % nitrogen obtained in activated carbon. The results clearly indicated that the activated carbon enriched nitrogen electrode materials possess larger specific capacitance

and better rate capability than the activated carbon YA-1 without nitrogen when constantly charged/discharged was over a wide loading current range (0.5-20 A.g⁻¹).

CV behaviour of activated carbon electrodes

Fig. 5 presented voltammetry characteristics for AC300-AC600 electrodes at voltage scan rate of 5 mV.s⁻¹ to test CV behaviour. The curves presented nearly regular, especially for samples with high mesopore proportion (AC500 and AC600). As expected, samples with higher specific capacitance showed larger area of CV curves. So AC500 electrode was a highly capacitive and electrochemical reversible, with good stability in the alkaline KOH electrolyte.

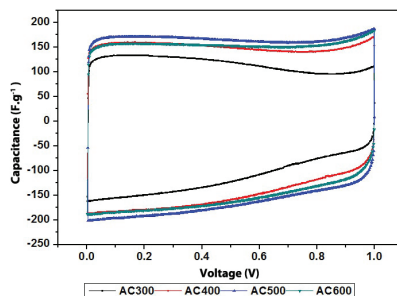


Fig. 5: CV curves of AC_s electrodes obtained at voltage scan rate of 5 mV.s⁻¹.

And Fig. 6 showed CV curves of AC500 electrodes between 0 and 1 V at different scan rates. Compared with CV curves at different scan rates in Fig. 6, the CV curves at lower scan rates were similar to rectangle due to the adequate soakage of electrolyte into the micropores on AC_s (Portet et al. 2008). As same as the literature (Hulicova et al. 2006), samples with higher specific capacitance showed larger area of CV curves.

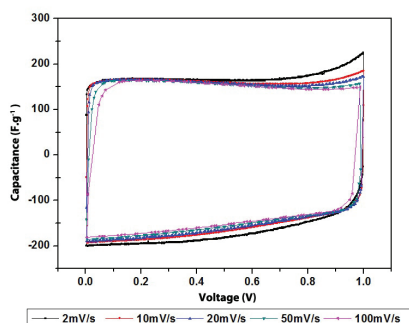


Fig. 6: Cyclic voltammograms of AC500 capacitor at different sweep rate.

Alternating current impedance behaviour of activated carbon electrodes

The typical Nyquist diagram was given in Fig. 7, where the semicircle in the high frequency region was correlated with the resistance of the electrode itself and the contact resistance between electrode and current collector.

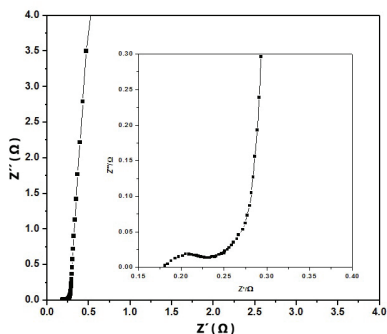


Fig. 7: Impedance spectrum of AC500 capacitor at sweep frequency of 0.01 Hz and control voltage of 1 V.

For AC500 electrode, medium particle size brought in a well electrical contact between particles throughout the electrode. Hence, the resistance in this region was less than 0.05 Ω . At low frequency, the imaginary part sharply increases and a nearly vertical line was observed, suggesting the pure capacitive behaviour of the electrode (Hulicova et al. 2006).

So we could get a conclusion that the high specific capacitance of the activated carbon product was believed to be associated with its suitable nitrogen content that could afford pseudocapacitance as well as the high specific surface area. And it could be used as a candidate for EDLC electrode materials.

CONCLUSIONS

The study results indicated that the BET SSA of AC_s varied from 455 to 1793 $\text{m}^2\cdot\text{g}^{-1}$, and the total pore volume of AC_s varied from 0.233 to 0.932 $\text{cm}^3\cdot\text{g}^{-1}$. Moreover, the specific capacitance of different activated carbon electrodes ranged from 148 to 213 $\text{F}\cdot\text{g}^{-1}$. These data suggested that the nitrogen-enriched activated carbon electrode made from waste MDF had a significantly higher electrochemical capacity in comparison to other non-nitrogen containing activated carbon electrode, and waste MDF could be used as a candidate for EDLC electrode materials.

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