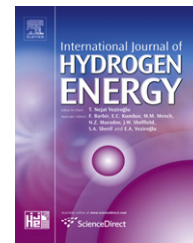


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# Activated carbon prepared from PVDC by NaOH activation as electrode materials for high performance EDLCs with non-aqueous electrolyte

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## ABSTRACT

Mesoporous activated carbons with high surface area have been prepared from PVDC by NaOH activation for non-aqueous electric double layer capacitors (EDLCs). The BET surface area and pore volume of the carbon reach as high as  $2675 \text{ m}^2 \text{ g}^{-1}$  and  $1.683 \text{ cm}^3 \text{ g}^{-1}$ , respectively. The pore size of the carbon distributes mainly in small mesopore of  $2\sim 4 \text{ nm}$ , which is ideal for non-aqueous electrolyte EDLCs. The unique microstructure features, i.e. very high surface area and optimized pore size make the carbon present both a high capacitance of  $155 \text{ F/g}$  and outstanding rate capability in non-aqueous electrolytes. As the current density increases to  $18000 \text{ mA/g}$ , it remains  $109 \text{ F/g}$ , an attractive value for EDLCs.

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## 1. Introduction

Electric double layer capacitors (EDLCs) are promising energy storage devices with high power density and long cycle life, and found applications in electric vehicles and other high power apparatuses [1–4]. The carbon electrode plays a crucial role in EDLCs. Much effort has been done to develop advanced carbons for meeting the demand of high performance EDLCs [5–9]. Generally, the larger the specific surface area of carbons, the higher the capacitance value will be. However, for a wide variety of activated carbons, this trend is not perfectly followed. In fact, the narrow micropores may not contribute to the double layer capacitance due to a sieving effect whose extent depends on the size of the electrolyte ions. The pore size of the carbons should much larger than the size of the

ions. Moreover, the large pores of the carbon facilitates to enhance the good dynamic charge propagation and hence the power properties. Therefore, mesopores are more useful than micropores for EDLCs, especially for non-aqueous EDLCs with larger ions [5]. Although carbon aerogels [10,11], carbon nanotubes [12–14], and template carbons [15–17] have highly mesoporous structure, their capacitance is not satisfactory due to their low specific surface area. Consequently, the carbon electrode for high performance EDLCs should have both high surface area and large pore size. However, it is well-known that these two factors are usually conflicting between each other. Therefore, it is important to design carbon electrode materials with pores that are large enough for the electrolyte to access completely, but small enough to ensure a large surface area [18,19].

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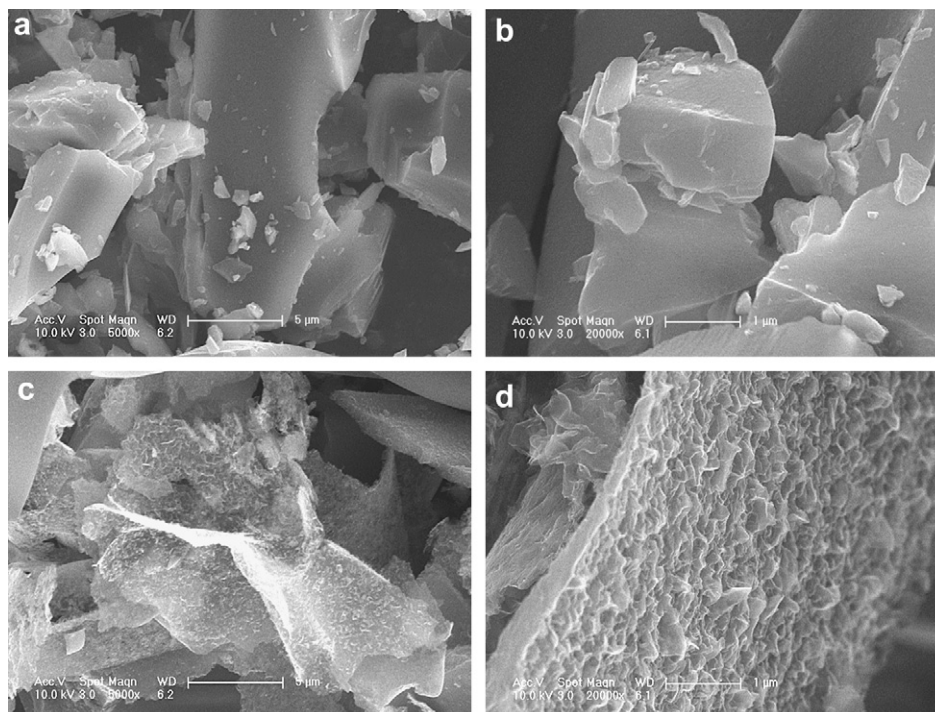


Fig. 1 – SEM images of the PVDC-derived char (a, b) and the activated carbon NPV3 (c, d).

Poly(vinylidene chloride) (PVDC) is an attractive precursor which can create a porous structure only by carbonized at high temperature without activation or any other additional processes. In our previous report [20,21], microporous carbon with surface area as high as  $1230 \text{ m}^2 \text{ g}^{-1}$  has been simply obtained by carbonized the homogeneous PVDC, and it presents high capacitance with good rate performances in aqueous electrolyte. However, the capacitance of this carbon in non-aqueous electrolyte is very poor as most of their pores are too small to be accessible. In this paper, we activated the PVDC-derived char with NaOH to prepare high performance carbon for non-aqueous EDLCs. After activation, the surface area of the carbon is well-enhanced and the pore size is widened to small mesopores ( $2 \sim 4 \text{ nm}$ ). Their unique microstructure features enable the activated carbon to present both high capacitance and outstanding rate capability in non-aqueous EDLCs.

## 2. Experimental

### 2.1. Preparation and characterization

Homogeneous poly(vinylidene chloride) (PVDC) was used as the precursor. PVDC was put into a horizontal furnace, pyrolyzed at  $400^\circ\text{C}$  for 1 h under the protection of nitrogen (99.999%). Then the char was mixed with the sodium hydroxide in the desired proportions. The mixture was ground in an agate mortar and then heated in a horizontal furnace to the activation temperature  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  and maintained under these conditions for 1 h. After activation, the samples were washed with  $0.5 \text{ mol L}^{-1}$

HCl, hot water and distilled water in sequence to remove the residual alkali completely, followed by drying at  $120^\circ\text{C}$  for 12 h, then the final activated carbon was obtained. The weight ratio of NaOH to the char varies in the range of  $1 \sim 4:1$ . The activated carbon prepared with a weight ratio of NaOH/char R labeled as NPVR. PVDC-derived char without activation was also prepared by pyrolyzing the PVDC at  $600^\circ\text{C}$  for 1 h, which is denoted as PVT.

The specific surface area and pore structure of the activated carbons were determined by nitrogen adsorption/desorption isotherms at 77 K (Quantachrome NOVA 1200). The specific surface area and pore size distribution were

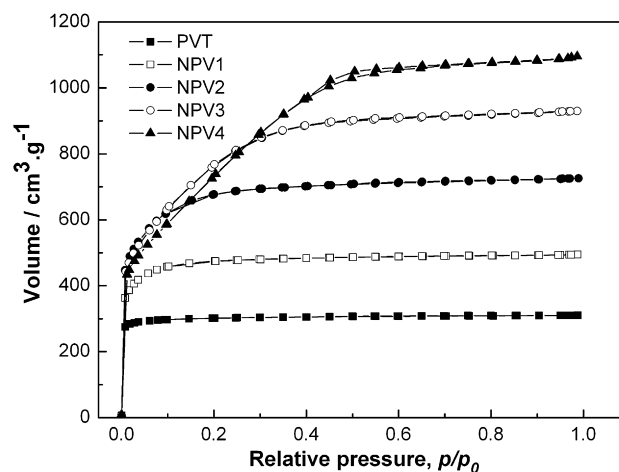
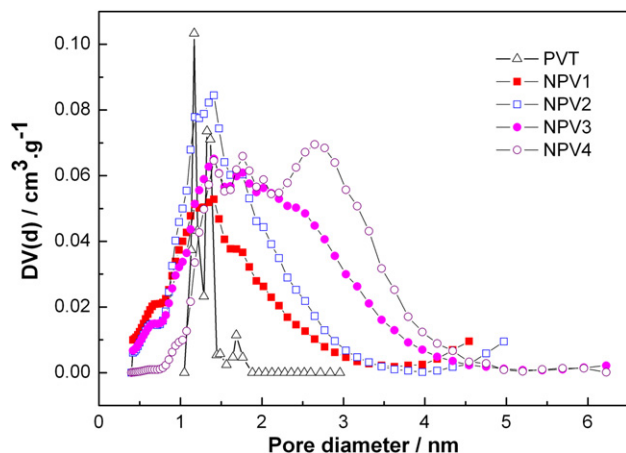


Fig. 2 – Nitrogen (77 K) adsorption/desorption isotherms of the PVDC-derived char and the activated carbons prepared with different R values.



**Fig. 3 – Pore size distribution of the PVDC-derived char and the activated carbons prepared with different R values.**

calculated by the conventional BET (Brunauer–Emmett–Teller) method and density function theory (DFT) method, respectively. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-5600LV scanning electron microscope operated at an acceleration voltage of 10 kV.

## 2.2. Electrochemical measurements

Slurries containing 85 wt% activated carbon, 10 wt% acetylene black, and 5 wt% polyvinylidene fluoride (PVDF) dissolved in *n*-methyl-2-pyrrolidinone were spread evenly on a piece of Al foil. The thickness of the carbon sheet was around 30  $\mu\text{m}$ . The sheet was subsequently cut into  $8 \times 8$  mm pieces and then dried at 120  $^{\circ}\text{C}$  for 10 h to be used as electrode. Button-type capacitor was assembled with two carbon electrodes separated by polypropylene membrane using 1 mol  $\text{L}^{-1}$   $\text{Et}_4\text{NBF}_4/\text{PC}$  as electrolyte in an Ar-filled glovebox (LabMaster 130, M. Braun Co.).

The cyclic voltammetry (CV) was recorded on an electrochemical workstation Solartron 1280B. The galvanostatic charge/discharge test was carried out on an Arbin cell tester between 0 and 2.5 V. The specific capacitance ( $C$ ) of a single carbon electrode was determined with the formula:

$$C = 2It/\Delta Vm,$$

where  $I$  is the discharge current,  $t$  is the discharge time,  $\Delta V$  is the potential change in discharge and  $m$  is the mass of the active material in a single electrode.

## 3. Results and discussion

### 3.1. Structure characterization of the carbon

The SEM images of the PVDC-derived char (PVT) and the activated carbon prepared by NaOH activation are shown in Fig. 1. The carbons all have an irregular granular morphology. However, compared with the PVT, the activated carbon has a smaller particle size and its surface becomes very scraggly due to NaOH etching at high temperature, indicating a more porous structure.

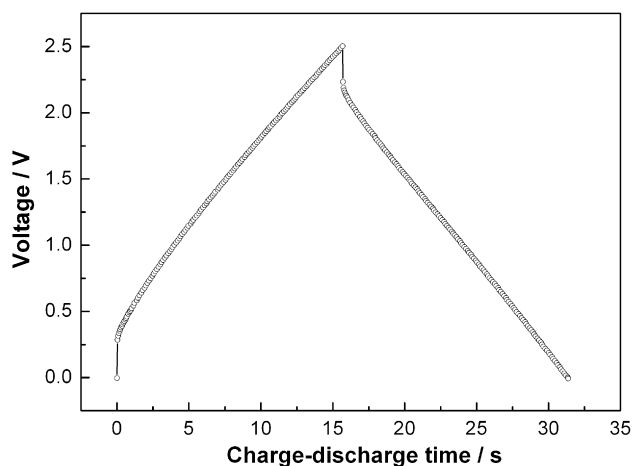
Fig. 2 shows the  $\text{N}_2$  (77 K) adsorption/desorption isotherms of the PVT and the activated carbons prepared with different ratios of NaOH/char ( $R$  value). The PVT exhibits a type I isotherms according to the IUPAC classification, i.e., very high uptakes at the lowest relative pressures followed by a horizontal plateau, characterizing microporous material. After activation, the isotherm morphology of the carbon varies remarkably with the increase of  $R$  value. Although NPV1 and NPV2 also show type I isotherms, a wider knee indicates the development of a wider micropores. Different from NPV1 and NPV2, the isotherm of NPV3 has a glasis knee and the slope of the plateau increases due to multi-layer adsorption, suggesting the coexistence of larger micropores and mesopores in the carbon. When  $R$  increases to 4, the adsorption volume of the carbons proportionally increases with the relative pressure until  $p/p_0 \approx 0.5$ . The widely opened knees indicate the presence of a considerable amount of mesopores in NPV4.

Fig. 3 presents the pore size distribution of the carbons calculated by DFT method, which are in good accordance with the results of the adsorption/desorption isotherms in Fig. 2. The pore size of the PVT distribute in 1–2 nm, mainly in 1.0–1.5 nm. After activation, the carbon shows a wider pore size distribution, increases to 1–3 nm for NPV1 and 1–5 nm for NPV4. The higher the  $R$  value, the larger the pore size is obtained.

The pore characteristics of the carbons are listed in Table 1. The BET surface area and pore volume of the PVT are only  $1226 \text{ m}^2 \text{ g}^{-1}$  and  $0.480 \text{ cm}^3 \text{ g}^{-1}$ , respectively. After activation, the BET surface area and the pore volume of the carbon all increase with  $R$  value and obtain the maximum value of  $2675 \text{ m}^2 \text{ g}^{-1}$  and  $1.683 \text{ cm}^3 \text{ g}^{-1}$  at  $R = 4$  respectively, indicating a highly developed porous structure. As the  $R$  value increases over 2, the microporous volume begins to decrease while the mesopore volume increases markedly, implying the pore widening mechanism becomes dominate than the pore creating mechanism in NaOH activation. The mesopore percentage (the ratio of the mesopore volume to the total

**Table 1 – Porosity characterization and capacitance of the PVDC-derived char and the activated carbons.**

Sample	Activation condition			$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	Pore volume ( $\text{cm}^3 \text{ g}^{-1}$ )			$V_{\text{mes}}/V_{\text{t}}$ (%)	Capacitance ( $\text{F g}^{-1}$ )
	NaOH/C	Temp. ( $^{\circ}\text{C}$ )	Time (h)		$V_{\text{t}}$	$V_{\text{mic}}$	$V_{\text{mes}}$		
PVT				1226	0.480	0.480	0	0	14
NPV1	1	600	1	1829	0.763	0.713	0.050	6.55	108
NPV2	2	600	1	2527	1.123	0.998	0.125	11.1	142
NPV3	3	600	1	2630	1.436	0.982	0.454	31.6	147
NPV4	4	600	1	2675	1.683	0.663	1.020	60.6	155



**Fig. 4 – Charge-discharge curve of NPV4 in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC electrolyte at a current density of 5000 mA/g.**

pore volume) increases dramatically, and it reaches 60.6% at  $R = 4$ , indicating highly mesoporous structure.

Poly(vinylidene chloride) is an unique precursor which can create a porous structure only by carbonized at high temperature without any additional activation process. The PVDC-based char carbonized at 400 °C has a well-developed microporous structure with a surface area of 1062 m<sup>2</sup> g<sup>-1</sup> [21]. Two processes are involved in chemical activation, the pore formation and pore widening [22]. As abundant micropores have already existed in PVDC-derived char, pore widening is very significant in NaOH activation especially at high  $R$  value. The size of some micropores is widened to larger than 2 nm, i.e. they became mesopores, so the mesopore volume increases while the micropore volume decreases. Therefore, activated carbon with high surface area and well-developed small mesopores is obtained at high  $R$  value, which is a very attractive structure for EDLCs.

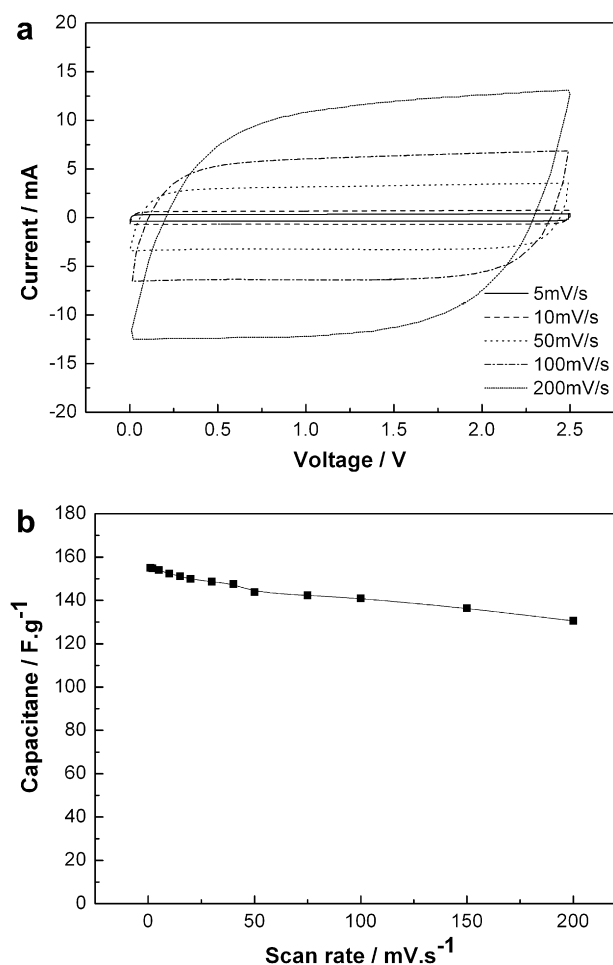
### 3.2. Electrochemical performances

Galvanostatic charge/discharge test between 0.0 and 2.5 V was performed to determine the capacitance of the activated carbons in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC electrolyte. The specific capacitance of the carbons at the current density of 50 mA g<sup>-1</sup> is also listed in Table 1. Although the PVDC-derived char has a surface area of 1226 m<sup>2</sup> g<sup>-1</sup> and its capacitance in 6 mol L<sup>-1</sup> KOH aqueous electrolyte reaches as high as 255 F g<sup>-1</sup> [21], its capacitance in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC electrolyte is only 14 F g<sup>-1</sup>, implying that almost all of its pores are too small to be accessed for the larger ions in the non-aqueous electrolyte. After activation, the capacitance increases remarkably and it reaches 108 F/g at  $R = 1$  and obtains the maximum value 155 F g<sup>-1</sup> at  $R = 4$ , which is much greater than the reported values of 80–120 F g<sup>-1</sup> for the carbon in organic electrolytes [7]. The enhancement of the capacitance in non-aqueous electrolyte may be attributed to the enhanced BET surface area and the widened pore size that is large enough to be accessed for the large ions.

Rate capability is an important feature of the EDLCs. Even when the current density increases to 5000 mA g<sup>-1</sup>, the

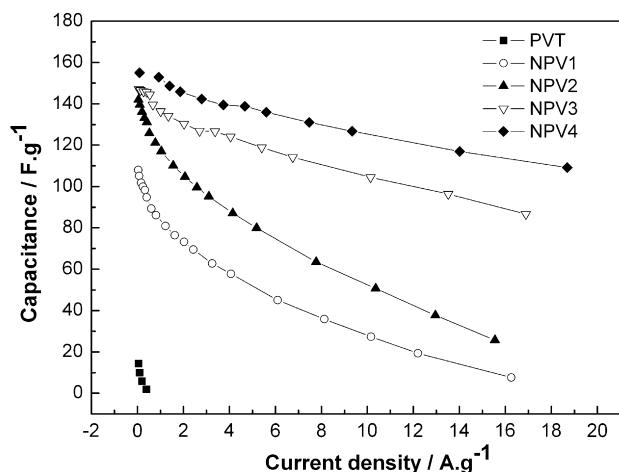
charge/discharge voltage profile of the capacitor remains its linear shape (Fig. 4) with a small IR drop at the beginning of the discharge, indicating the good rapid discharge capability and low equivalent series resistance of the test capacitor. At higher scan rates, the cyclic voltammograms will usually deviate from the ideal rectangular shape due to polarization, especially for non-aqueous EDLCs. As shown in Fig. 5a, until the scan rate increases to 200 mV s<sup>-1</sup>, the CV curve of the NPV4-based capacitor still remains its symmetrical rectangular shape, almost perfect for EDLCs. The specific capacitance calculated from CV curves is plotted in Fig. 5b. As the scan rate rises to 200 mV s<sup>-1</sup>, its capacitance remains 131 F g<sup>-1</sup>, 84.5% of that measured at 1 mV s<sup>-1</sup>, which is an attractive value for non-aqueous EDLCs. The slight capacitance decay at so high potential scan rate demonstrates the good rate performance of the activated carbon, which is related to its mesoporous structure.

The dependence of the capacitance on the charge/discharge current density is plotted in Fig. 6. The rate performance of the PVDC-derived char is very poor due to its small pore size. After activation, the rate performance of the PVDC-based activated carbons is improved dramatically, as their pores are widened to facilitate to enhance the good dynamic



**Fig. 5 – (a) Cyclic voltammogram of the activated carbon NPV4 in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC electrolyte; (b) capacitance of NPV4 as a function of scan rate.**





**Fig. 6 – The dependence of the capacitance of the carbons on the current density.**

charge propagation. Activated carbon with higher  $R$  value shows better rate capability, correlated to the larger pore size. NPV4 with largest pore size exhibits best rate capability. As the current density increases from 50 to 18 000 mA/g, its capacitance can remain 109 F/g, confirming the good rate capability of the activated carbon. The NPV4 exhibits high capacitance and good rate capability, which is associated with its characteristics. The pore size of the NPV4 distributes in 1 ~ 5 nm, mainly in small mesopore of 2 ~ 4 nm, which is ideal for non-aqueous electrolyte EDLCs. The well-developed small mesopore is large enough for the ions in non-aqueous electrolyte to be accessed and transferred freely but small enough to ensure a large surface area of 2675 m<sup>2</sup> g<sup>-1</sup>. The unique microstructure, i.e. very high surface area and optimized pore size makes the carbon present both high capacitance and superior rate performance, which is attractive for EDLCs.

#### 4. Conclusion

Activated carbons with high surface area and large small mesopores have been prepared by NaOH activating PVDC-derived char for non-aqueous EDLCs. The BET surface area of the carbon reaches 2675 m<sup>2</sup> g<sup>-1</sup> with a pore volume of 1.683 cm<sup>3</sup> g<sup>-1</sup>, among which the mesopore distributed in 2 ~ 4 nm attributes almost 60%. The unique microstructure features, i.e. very high surface area and optimized pore size make the carbon present both high capacitance and outstanding rate capability in 1 mol L<sup>-1</sup> Et<sub>4</sub>NBF<sub>4</sub>/PC electrolytes. The capacitance of the carbon is 155 F/g. As the current density increases from 50 to 18 000 mA/g, it maintains 109 F/g, an attractive value for EDLCs.

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