High-capacitance carbon electrode prepared by PVDC carbonization for aqueous EDLCs

Bin Xu [a,b], Feng Wu [a,*], Shi Chen [a], Zhiming Zhou [a], Gaoping Cao [b], Yusheng Yang [b]

[a] Beijing Key Laboratory of Environmental Science and Engineering, School of Chemical Engineering & the Environment, Beijing Institute of Technology, Beijing 100081, China
[b] Research Institute of Chemical Defense, Beijing 100083, China

ARTICLE INFO

ABSTRACT

Porous carbons with high-volumetric capacitance in aqueous electric double layer capacitors (EDLCs) were simply prepared by poly(vinylidene chloride) (PVDC) carbonization at high temperature without activation or any other additional processes. The PVDC-derived carbon is microporous with Brunauer–Emmett–Teller (BET) surface area about $1200\,m^2\,g^{-1}$. As it possesses not only high-gravimetric capacitance ($262\,F\,g^{-1}$) but also high-electrode density ($0.815\,g\,cm^{-3}$), the PVDC-derived carbon present an outstanding high-volumetric capacitance of $214\,F\,cm^{-3}$, twice over of the commercial carbon Maxsorb-3 with a high-surface area of $3200\,m^2\,g^{-1}$. The PVDC-derived carbon also exhibit good rate performance, indicating that it is a promising electrode material for EDLCs.

1. Introduction

Electric double layer capacitor (EDLC) is an energy storage device characterized as high-power density, long cycle life, quick charge/discharge capability, environmental friendliness and good perdurability at low temperature. It is of great interest in recent years because of their wide potential applications in electric vehicles, uninterruptible power sources (UPS), digital telecommunication system and other high-power apparatuses [1]. The carbon electrode plays a crucial role in EDLCs. Porous carbons with high-surface area such as activated carbon, activated carbon fiber, carbon aerogel, templated carbon and carbon nanotubes have been used as electrode materials for EDLCs [2–9]. Among the various carbons, activated carbon is the most widely used electrode materials for commercial EDLCs due to their high-specific surface area and low cost.

At present, the energy density of the commercial EDLC is generally $3–5\,Wh\,kg^{-1}$, much lower than that of the second batteries. Therefore, it is desirable to prepare porous carbon electrode materials with high capacitance for EDLCs. Most of literatures express capacitance as $F\,g^{-1}$. However, for practical application, the volumetric value which is the combination of the gravimetric capacitance and the apparent density of the electrode is of

great importance [2]. Generally, values of capacitance of the order of $60\,F\,cm^{-3}$ are demanded for practical applications [10]. As it is known, a high density is often in contradiction with a very developed porous structure. So, the preparation conditions of the carbon should be optimized to balance the porosity and density to maximum the volumetric capacitance. Activated carbon with extremely high-surface area over $3000\,m^2\,g^{-1}$ prepared by KOH or NaOH activation has attracted great attention as electrode materials for EDLCs [11–13]. Although the gravimetric capacitance of these carbons can reach over $300\,F\,g^{-1}$, their volumetric capacitance is not satisfactory because of their poor density.

Recent studies on carbon materials prepared without activation are of special interest because they provide materials of high density. 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. Endo et al. [14] have obtained carbon with surface area $772\,m^2\,g^{-1}$ by PVDC carbonization, which shows a capacitance as high as $64\,F\,g^{-1}$ (equivalent to $256\,F\,g^{-1}$ for a three-compartment cell) in 30% H_2SO_4 aqueous solution. In our previous report [15], porous carbon with surface area as high as $1230\,m^2\,g^{-1}$ have been simply obtained by carbonized the homogeneous PVDC. In this paper, we will investigate the electrochemical performances of the PVDC-derived carbon in aqueous EDLCs in detail. It will be seen that the carbon presents both high-apparent electrode density and high-gravimetric capacitance in $6\,mol\,L^{-1}$ KOH aqueous electrolytes, resulting in an outstanding high-volumetric capacitance of

* Corresponding author. Tel.: +86 10 68912508; fax: +86 10 68451429.
E-mail addresses: xubin@bit.edu.cn (B. Xu), wufeng863@vip.sina.com (F. Wu).

214 F cm^{-3} with good rate performance, which makes it a promising electrode material for aqueous EDLCs.

2. Experimental

2.1. Preparation and characterization

The detailed preparation of the PVDC-derived carbon has been described in our previous report [15]. In short, homogeneous poly(vinylidene chloride) (PVDC) was heated to the carbonization temperature (400–900 °C) at 10 °C min^{-1} under the protection of nitrogen and kept there for 1 h to accomplish pyrolysis. After cooled to room temperature, the PVDC-derived porous carbons were obtained. The sample prepared at temperature T °C was denoted as PVTT.

The specific surface area and pore structure of the PVDC-derived carbons were determined by nitrogen adsorption/desorption isotherms at 77 K (Quantachrome NOVA 1200). The specific surface area was calculated by the conventional Brunauer–Emmett–Teller (BET) method, and the total pore volume was estimated by the amount of N$_2$ adsorption at a relative pressure of 0.95. The pore size distribution was obtained by density function theory (DFT) method.

2.2. Electrochemical measurements

In order to evaluate the electrochemical performances of the as-prepared PVDC-derived carbon in EDLCs, a mixture of 87 wt% of PVDC-derived carbon, 10 wt% of acetylene black and 3 wt% of PTFE binder was pressed into pellets (19 mm in diameter) as electrodes. A button-type capacitor was assembled with two carbon electrodes separated by polypropylene membrane using 6 mol L^{-1} KOH aqueous solutions as electrolyte.

The cyclic voltammetry (CV) and ac impedance spectroscopy were recorded on an electrochemical workstation Solartron 1280B. Equivalent series resistance (ESR) was measured at 1 kHz. The galvanostatic charge/discharge test was carried out on a Land cell tester between 0 and 1 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, ΔV is the potential change in discharge and m is the mass of the active electrode material.

3. Results and discussion

3.1. Characterization of PVDC-derived carbon

The PVDC-derived carbons were simply prepared by PVDC pyrolysis at 400–900 °C for 1 h. Their microstructure parameters are listed in Table 1. Except for PVT400, all of the other samples have a large surface area about 1200 m^2 g^{-1}. The pore volume can reach 0.480 cm^3 g^{-1}. It indicates that PVDC carbonization is a simple and effective method to prepare porous carbon with high-surface area. The highly porous structure of the PVDC-derived carbon is attributed to the complete release of HCl from the carbon chain in PVDC. As shown in our previous report [15], the carbon samples prepared at different carbonization temperatures exhibit similar pore size distribution curves. The pore size of all samples is distributed in 1–2 nm, mainly in 1.0–1.5 nm, indicating they are highly microporous materials.

Fig. 1 shows the XRD profiles of the PVDC-derived carbons prepared at different carbonization temperature. All samples show only one obvious broad diffraction peak at $2\theta \approx 44°$ corresponding to the (0 1 0) diffraction peak, indicating that they are amorphous carbon. As the carbonization temperature increases, the peak rep-
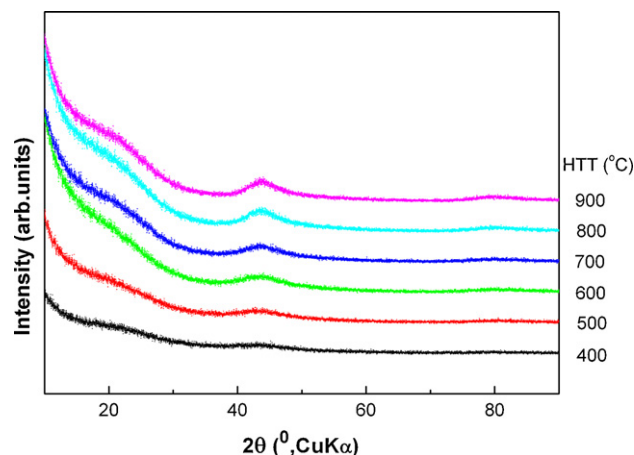

Fig. 1. XRD profiles of PVDC-derived carbons.

resenting (0 1 0) diffraction slightly sharpens and upshifts, and the peaks at 24° representing (0 0 2) and at 83° representing (1 1 2) diffraction become more recognizable, which indicates a more ordered structure, though the structure of all the PVDC-derived carbons are far from graphitized structure. This suggestion is supported with the following Raman spectroscopic analysis.

The Raman spectrum of perfect graphite has only a single peak at 1580 cm^{-1} (the G band) in the range studied, corresponding to its in-plane stretching mode. Disordered carbons usually exhibit a second disorder-induced peak at ∼1350 cm^{-1} (the D band), generally associated with a double-resonance effect [16]. The Raman analysis of the PVDC-derived carbon shows two strong peaks corresponding to the D- and G-bands of graphitic carbon (Fig. 2), suggesting the disordered nature of the carbon. Fig. 2 indicates that the full-width at half-maximum (FWHM) of both the D- and the G-bands decrease with increasing carbonization temperature, implying that the carbon ordering in the material becomes higher. That is, the graphitization becomes higher with increasing temperature. In addition, the up-shifting G-band in the PVDC-derived carbon might be due to the smaller effective mass of C–C than C–Cl when more of the Cl atoms in PVDC are removed at higher pyrolysis temperature ($f \propto (\kappa/\mu)^{1/2}$, f for vibrational frequency, κ for the bonding strength of the atoms and μ for the effective mass of the bonded atoms).
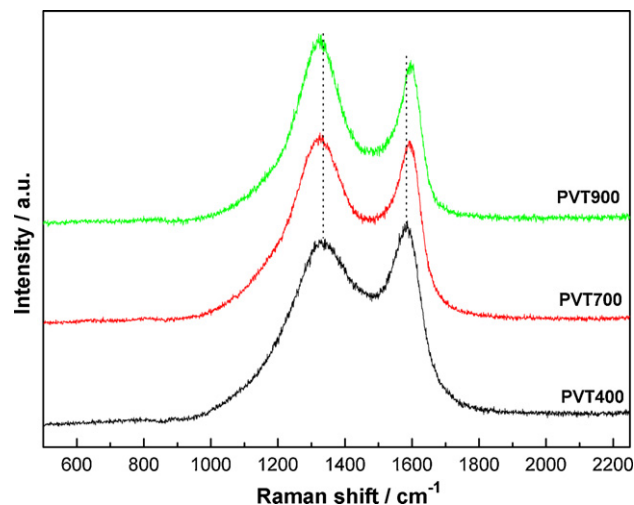

Fig. 2. Raman spectra of PVDC-derived carbons.

Table 1
Properties of PVDC-derived carbons.

Samples	HTT (°C)	S_{BET} (m^2 g^{-1})	V_t (cm^3 g^{-1})	Apparent density (g cm^{-3})	Pore diameter (nm)	Cl content (%)	Capacitance	
							F g^{-1}	F cm^{-3}
PVT400	400	1062	0.424	0.832	1.597	9.50	221	184
PVT500	500	1193	0.465	0.815	1.559	5.68	262	214
PVT600	600	1226	0.480	0.802	1.566	2.75	255	204
PVT700	700	1228	0.479	0.805	1.562	1.46	224	180
PVT800	800	1214	0.476	0.798	1.569	0.44	184	147
PVT900	900	1198	0.471	0.794	1.574	<0.3	155	123

Both the XRD and Raman spectra show that the PVDC-derived carbon is disordered. However, the graphitization of all these samples increases with increasing pyrolysis temperature. With this, the conductivity of the PVDC-derived carbons is expected to increase with the increasing carbonization temperature. Higher conductivity will be helpful for improving the power density of EDLCs.

3.2. Electrochemical performances in aqueous EDLC

Fig. 3 shows cyclic voltammograms of the PVDC-derived carbon prepared at 400, 600, and 800 °C between 0 and 1 V at the scan rate of 5 mV s^{-1}. The CV curves of PVT800 sample (Fig. 3c) shows a typical rectangular shape, implying pure electric double layer capacitance. As for the sample PVT400 (Fig. 3a) and PVT600 (Fig. 3b), especially for PVT400, the CV curves show a box-like shape with a well significant deviation at lower potentials, indicating the presence of pseudo-capacitance. Fig. 4 shows the galvanostatic charge/discharge curves of the carbons under a current density of 50 mA g^{-1}. The voltage–time curves of the sample PVT800 shows ideal linear shape, while a little deviation from the line at lower potentials can be observed for the sample PVT400 and PVT600, especially for PVT400, consisting with the results of CV curves. The deviations of the V–t and CV curves at lower potentials are usually related to the quick Faradaic reactions, due to the presence of heteroatoms [17–19]. The presence of heteroatoms can be advantageous, as they can considerably contribute to an additional pseudo-capacitance as well as improve the wettability on the carbon surface. In these PVDC-derived carbons, the heteroatoms are only hydrogen and chlorine. The pseudo-capacitance may be from the residual chlorine atoms. The element analysis of the residual chlorine in the char was measured by hydrargyrum titration method. As listed in Table 1, the lower the carbonization temperature used, the more the residual chlorine will be present, resulting in a more remarkable deviation for V–t and CV curves.

The specific capacitance of the PVDC-derived carbons calculated from discharge curves under the current density of 50 mA g^{-1} is also listed in Table 1. Although the BET surface area of the carbon prepared at different carbonization temperature is very similar, their specific capacitance is much different from each other. With increasing carbonization temperature, the specific capacitance increases from 221 F g^{-1} at 400 °C to 262 F g^{-1} at 500 °C, then it decreases continually to 155 F g^{-1} at 900 °C. The BET surface area of the sample PVT500 is only 1193 m^2 g^{-1}, while its capacitance reaches as high as 262 F g^{-1}. This outstanding high capacitance is the co-contribution of electric double layer capacitance and pseudo-capacitance by the residual chlorine atoms. As the carbonization temperature increases from 500 to 900 °C, the BET surface area of the carbon has no obvious change, but the capacitance decreases remarkably. It may be because of the decrease of the residual chlorine atoms, which negatively impacts psuedo-capacitance and the wettability of the carbon.

Apart from the gravimetric capacitance, the volumetric value of the carbon is of great importance for practical application in EDLCs [2]. As shown in Table 1, the PVDC-derived carbon electrode presents a very high-apparent density varying in the range of 0.794–0.832 g cm^{-3}. The lack of an additional activation
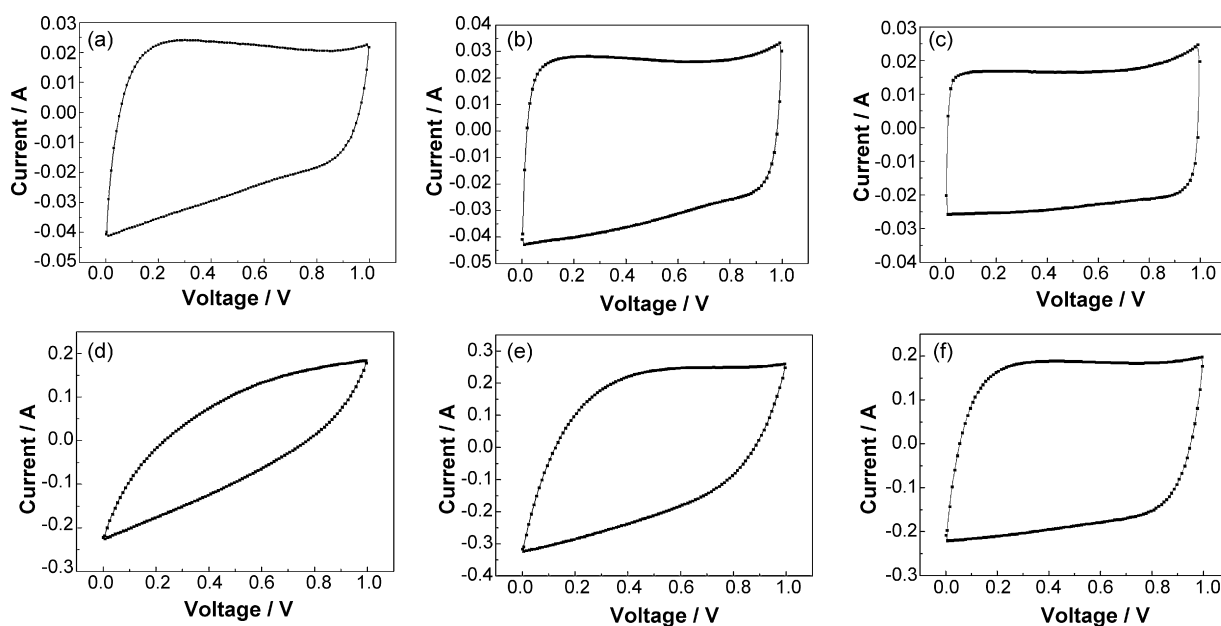
Fig. 3. Cyclic voltammogram for EDLCs based on PVDC-derived carbons: (a) PVT400-5 mV s^{-1}, (b) PVT600-5 mV s^{-1}, (c) PVT800-5 mV s^{-1}, (d) PVT400-50 mV s^{-1}, (e) PVT600-50 mV s^{-1}, (f) PVT800-50 mV s^{-1}.
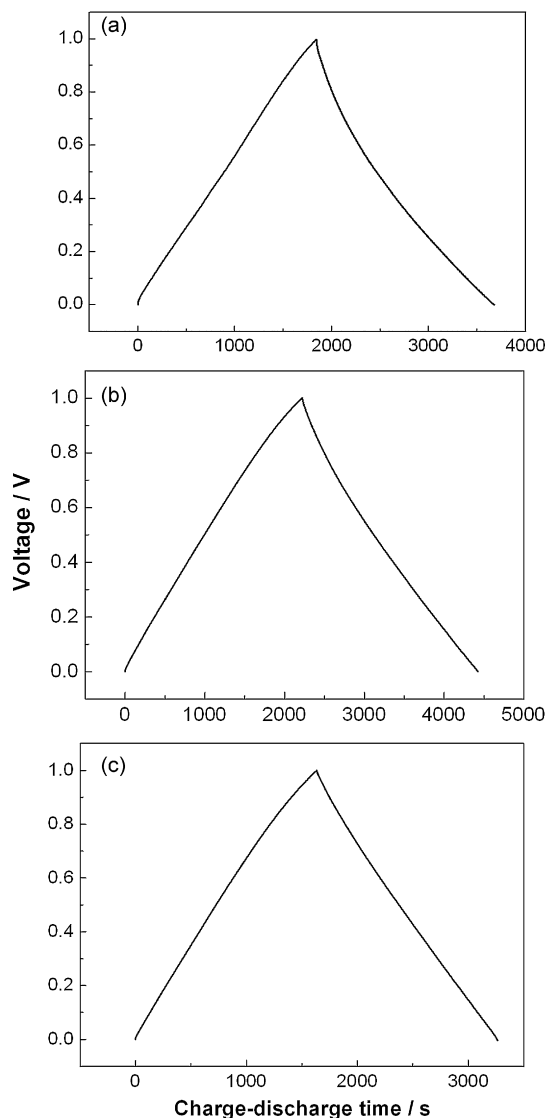
Fig. 4. Charge–discharge curves of PVDC-derived carbon-based EDLCs: (a) PVT400, (b) PVT600, (c) PVT800.

process is the reason for their remarkable high density. As it has not only high-gravimetric capacitance but also high-electrode density, a volumetric capacitance as high as 214 F cm^{-3} has been obtained at 500 °C. For comparison, the capacitive performance of the commercial carbon Maxsorb-3 with a super high-surface area of 3200 m^2 g^{-1} is also measured. The gravimetric capacitance of the Maxsorb-3 reaches 320 F g^{-1}, higher than PVT500. However, its apparent density is only 0.306 g cm^{-3}, much lower than PVDC-derived carbons. As a result, the volumetric capacitance of Maxsorb-3 is only 98 F cm^{-3}, less than half of the PVT500. It indicates that the PVDC-derived carbon is a very attractive electrode material for practical EDLCs as it has outstanding high-volumetric capacitance.

As an energy storage device characterized with high-power density, the rate performance is very important for carbon electrode in EDLC. From the CV curves at elevated scan rates (Fig. 3), it can be seen that the carbon prepared at higher carbonization temperature has better rate performance. As the scan rate increases to 50 mV s^{-1}, the sample PVT400 shows a shuttle-like CV curves (Fig. 3d), indicating serious polarization. The CV curves of PVT600 (Fig. 3e) basically retain a box-like shape. The CV curves of PVT800 (Fig. 3f) show
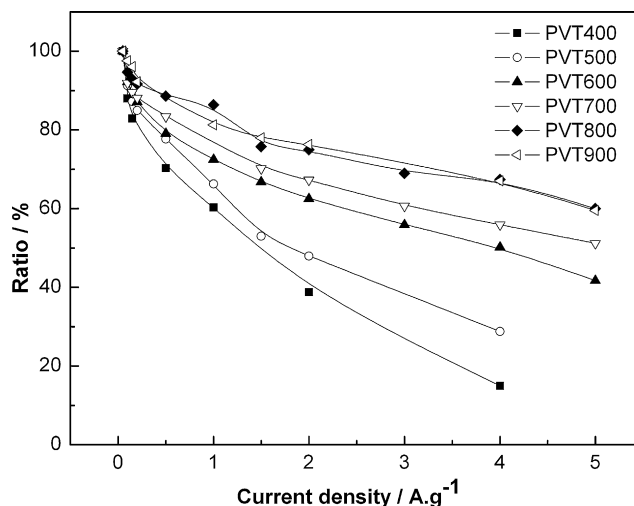

Fig. 5. Capacitance retention of PVDC-derived carbons.

a rectangle shape, exhibiting a quick charge propagation capability.

The rate performance of the PVDC-derived carbon is also evaluated by galvanostatic charge/discharge under enhanced current density. Fig. 5 shows the capacitance retention ratio of the carbon, which is defined as ratio of capacitance at the elevated current density to that at 50 mA g^{-1}. For all the samples, the capacitance retention ratio decreases continually with an increase in current density. Comparing the curves of the different carbon samples, it is found that the higher the carbonization temperature used, the higher the capacitance retention ratio at same current density will be. The carbon with higher carbonization temperature has better rate capability than that with lower carbonization temperature, in accordance with the results of CV curves at elevated scan rate.

The power characterization of the EDLCs is determined mainly by their equivalent series resistance (ESR). Fig. 6 shows the electrochemical impedance spectroscopy of the PVDC-derived carbon. The Nyquest plot shape of all the samples are very similar, composed of a semicircle at high frequency, a sloping (*ca.* 45°) linear region at high-to-medium frequency and an nearly vertical line at low frequency, where the behavior becomes mainly capacitive. However, the ESR value (Fig. 7) depends strongly on the carbonization temperature. It decreases dramatically from 0.648 Ω at 400 °C to 0.229 Ω at 700 °C, and then to 0.164 Ω at 900 °C. The ESR of the capacitor is the ionic conductivity which relates to the mobility of ions inside the pores and the electric conductivity of carbon materials. Since carbon prepared at different carbonization temperatures has similar pore size distribution, the ESR differ-
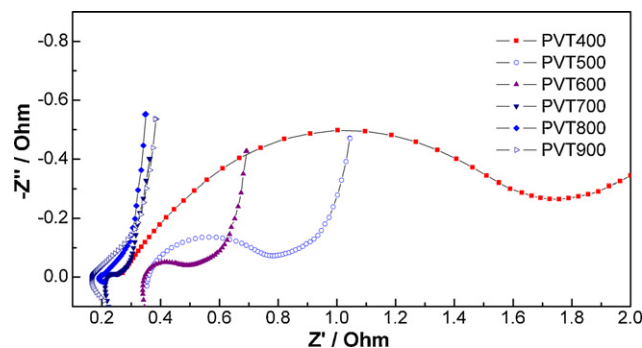

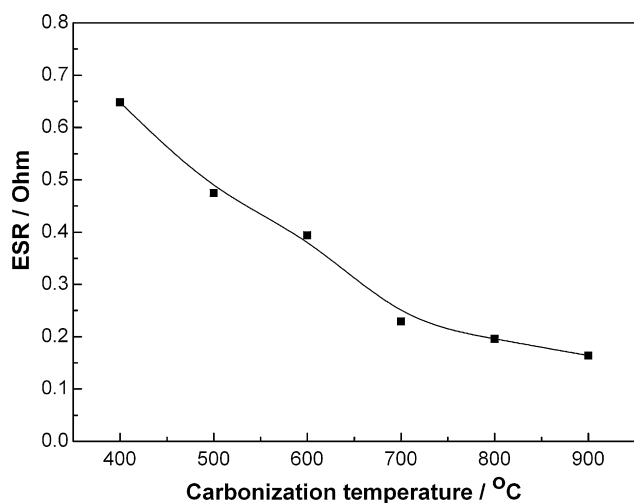**Fig. 6.** Nyquist plots for EDLCs based on PVDC-derived carbons.

Fig. 7. Effect of carbonization temperature on the ESR of EDLCs based on PVDC-derived carbons.
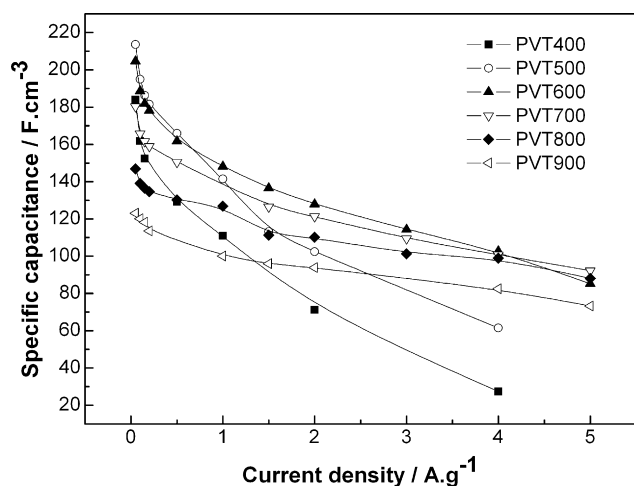

Fig. 8. Specific capacitance of PVDC-derived carbons as a function of current density.

ence can be attributed to the different conductivity of the carbon. Previous discussion including XRD and Raman analysis showed that a higher carbonization resulted in more ordered microcrystalline structure leading to higher conductivity. Additionally, for this PVDC-derived carbon, the decreased rate performance of the carbon prepared at lower temperature may also related to the presence of pseudo-capacitance, which has decreased endurance at large current density than double layer capacitance because of electrochemical polarization.

Carbonization temperature has complex effects on the electrochemical performance of the PVDC-derived carbon. With lower carbonization temperature, the resultant carbon has higher specific capacitance due to the contribution of pseudo-capacitance by the residual chlorine atoms. However, the carbon prepared at higher carbonization temperature has better rate performance, because of its lower resistance and the better endurance of the pure electric double layer capacitance than the pseudo-capacitance. As a result, the volumetric capacitance of the PVDC-derived carbon as a function of current density shows variation tendency as plotted in Fig. 8. It can be seen that the sample prepared with a moderate carbonization temperature shows better rate capability. As

the current density increases from 50 to 5000 mA g^{-1}, the volumetric capacitance of PVT700 can remain 92 F cm^{-3}. As far as gravimetric capacitance, volumetric capacitance and rate capacity are concerned, the PVT600 has the optimized performances. Its gravimetric capacitance is 255 F g^{-1}. Its volumetric capacitance reaches 204 F cm^{-3}, remaining 85 F cm^{-3} as the current density increases to 5000 mA g^{-1}.

4. Conclusion

Porous carbon with surface area as high as 1200 m^2 g^{-1} for aqueous EDLCs has been simply prepared by PVDC carbonization at high temperature without activation or any other additional processes. The carbonization temperature has a slight effect on the BET surface area and pore volume of the resultant carbons but very strong effect on their electrochemical performances. The sample prepared at lower carbonization temperature presents a high capacitance, which is the co-contribution of double layer capacitance and pseudo-capacitance from the residual chloride. Due to the lack of an additional activation process, the PVDC-derived carbon also shows a very high-apparent density varying in the range of 0.794–0.832 g cm^{-3}. As it has not only high-gravimetric capacitance (262 F g^{-1}), but also high-electrode density (0.815 g cm^{-3}), the volumetric capacitance of the sample PVT500 reaches as high as 214 F cm^{-3}, twice over of the commercial carbon Maxsorb-3 with a high-surface area 3200 m^2 g^{-1}. The PVDC-derived carbon also exhibit good rate performance, indicating that it is a promising electrode material for EDLCs.

Acknowledgements

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