

PVDC-BASED CARBON FOR HIGH CAPACITANCE ELECTRIC DOUBLE LAYER CAPACITORS

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Abstract

Porous carbon with high electric double layer capacitance has been simply prepared by carbonization of poly(vinylidene chloride) (PVDC) without any additional activation process. The effect of carbonization temperature on the microstructure and electrochemical performances of the PVDC-based carbon were investigated in detail. The surface area and pore volume of the PVDC-based carbon reaches about $1200 \text{ m}^2 \cdot \text{g}^{-1}$ and $0.47 \text{ cm}^3 \cdot \text{g}^{-1}$ respectively, while the specific capacitance can reach $262 \text{ F} \cdot \text{g}^{-1}$ in $7 \text{ mol} \cdot \text{L}^{-1}$ KOH aqueous electrolyte. The PVDC-based carbons also show good rate capability. PVDC carbonization is a promising method for the preparation of carbon electrode materials for aqueous supercapacitors.

Introduction

Electric double layer capacitors (EDLCs) have attracted great attention in recent years because of their wide potential applications in electric vehicles and other high-power apparatuses due to their high power density and long cycling life. Various porous carbons, such as activated carbon, activated carbon fiber, carbon nanotube and glassy carbon have been used as electrode materials for EDLCs. Due to their high specific surface area and low cost, activated carbon is the preferred electrode materials for commercial EDLCs.

The manufacture of porous carbon usually involves two steps: the carbonization of the precursor under an inert atmosphere and the activation of carbonized product with activation agent such as H_2O , CO_2 , KOH, H_3PO_4 . The carbonization process consists of a thermal decomposition of the organic precursors, eliminating non-carbon atoms and producing a char with rudimentary pore structure. Activation is to selectively erode some active sites of the char by the oxidative activation agents to create porous structure. The highly developed porosity in the carbon is formed predominately in activation period, which is also the most complex and expensive stage in the overall manufacture process.

Poly(vinylidene chloride) (PVDC) is an attractive precursor which can create a porous structure only by carbonized at high temperature without any additional activation process. In this paper, we prepared porous carbon with surface area and investigate their electrochemical performance as electrode materials for EDLCs.

Experimental

The homogeneous poly(vinylidene chloride) (PVDC) was used as starting materials. The PVDC powder were put into a tubular furnace, heated to the carbonization temperature at $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under the protection of nitrogen (99.999 %) and kept there for 1 hour to accomplish pyrolysis. After cooled to room temperature, the PVDC-based porous carbons were obtained. The carbonization temperature varied in the range of 400-900 $^\circ\text{C}$.

The thermal gravity analysis (TGA) (Dupont 1090B) were employed to investigate the thermal decomposition behavior of the pristine PVDC powder under the protection of nitrogen. The specific surface area and pore structure of the PVDC-based carbons were determined by nitrogen adsorption/desorption isotherms at 77 K (Quantachrome Co., NOVA 1200). The specific surface area was calculated by the conventional BET (Brunauer-Emmett-Teller) method, and the total pore volume was estimated by the amount of N_2 adsorption at a relative pressure of 0.95.

A mixture of 87 wt% of PVDC-based carbon, 10 wt% of acetylene black and 3 wt% of PTFE binder was pressed into pellets (19 mm in diameter) as electrodes. Then the electrodes were dried under vacuum at 120 $^\circ\text{C}$ for 12 h. Button-type capacitor was assembled with two carbon electrodes using aqueous KOH ($7 \text{ mol} \cdot \text{L}^{-1}$) as electrolyte. The galvanostatic charge/discharge was carried out on a Land cell tester to evaluate the specific capacitance. The capacitors were cycled between 0 and 1.0 V unless specified. 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 the discharge time, ΔV the potential change in discharge and m the mass of the active electrode material.

Results and discussion

TGA

Figure 1 shows the results of thermogravimetric analysis (TGA). The dramatic weight loss of PVDC occurred at 200–600 °C with the sharp peak at 246 °C, resulted in a carbon yield of 21% at 600 °C. The weight variation at temperature higher than 600 °C is very small. The weight loss is related to the evolution of HCl from the PVDC. The thermal decomposition reaction is as follow:

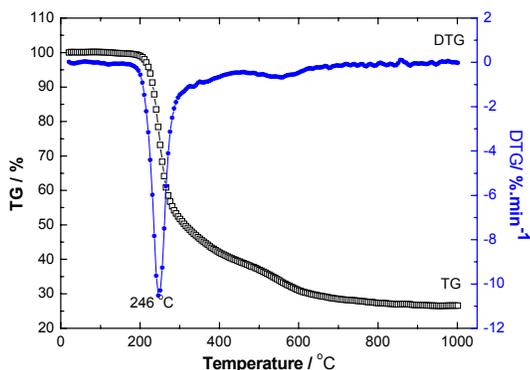
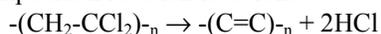


Figure 1. Thermogravimetric Curve for PVDC in Flow of Nitrogen Gas.

Characterization of porous structure

Figure 2 shows the nitrogen adsorption isotherms of the PVDC-based porous carbons prepared at different carbonization temperature. According to the classification of IUPAC, all of the samples exhibit a typical type I isotherms. After a sharp increase to $p/p_0 = 0.05$, adsorption level off with further increase of relative pressure. The plateau is fairly flat. Nearly all of the pore volumes of the samples are filled below $p/p_0 = 0.05$, which is a very low relative pressure, indicating all these samples are highly microporous.

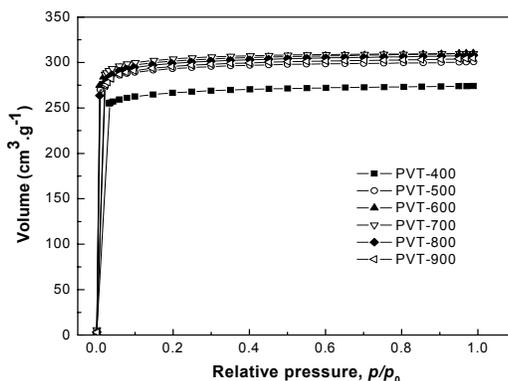


Figure 2. Nitrogen Adsorption Isotherms of PVDC-Based Carbons.

Figure 3 presents the specific surface area (S_{BET}) and pore volume of the PVDC-based carbons as a function of carbonization temperature. The S_{BET} of PVT-400 sample which carbonized at 400 °C reaches $1062 \text{ m}^2\cdot\text{g}^{-1}$. The S_{BET} increases with the increase of carbonization temperature, and reaches nearly $1230 \text{ m}^2\cdot\text{g}^{-1}$ at 600–700 °C. Then it decreases slightly with further increasing of carbonization temperature. Besides of PVT-400, all of the PVDC-based carbons have a large surface area higher than $1200 \text{ m}^2\cdot\text{g}^{-1}$. The pore volume of the PVDC-based carbons varies in a similar trend to the specific surface area with the increasing of carbonization temperature. The carbon prepared at 600 °C has the highest pore volume of $0.480 \text{ cm}^3\cdot\text{g}^{-1}$. As we know, the specific surface area of the commercial activated carbons prepared by conventional physical activation with H_2O or carbon dioxide as activation agent is usually about $1000 \text{ m}^2\cdot\text{g}^{-1}$, while the specific surface area of the PVDC-based carbons without any additional activation process can reach $1230 \text{ m}^2\cdot\text{g}^{-1}$. It indicates that PVDC carbonization is a simple and effective method to prepare porous carbon with high surface area.

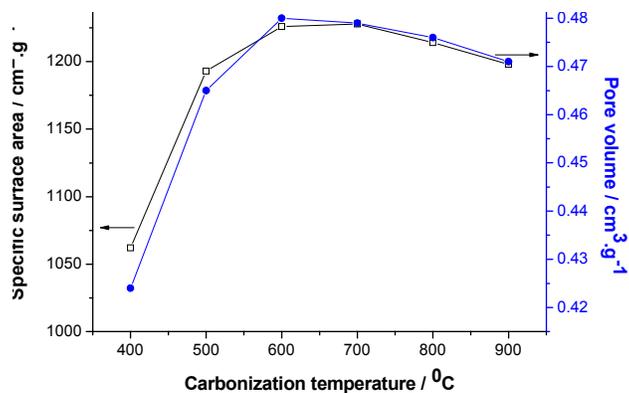


Figure 3. Effect of Carbonization Temperature on Specific Surface Area and Pore Volume of PVDC-Based Carbons.

Electrochemical performances

Galvanostatic charge/discharge was performed to determine the capacitance of the PVDC-based carbons. The voltage range of charge/discharge is limited between 1.0 and 0 V. The capacitance of the PVDC-based carbon as a function of carbonization temperature is presented in Figure 4. It increases with the increasing of the carbonization temperature and reaches the maximum value of 262 F·g⁻¹ at 500 °C, then decreases with the further increase of carbonization temperature. As we know, the capacitance of the commercial activated carbon is less than 150 F·g⁻¹. That is to say, PVDC-based carbon is an attractive material for high capacitance EDLCs.

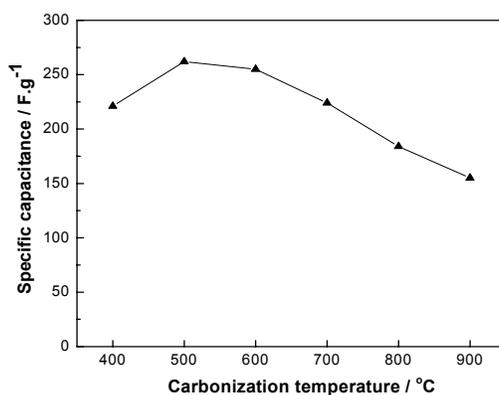


Figure 4. Effect of Carbonization Temperature on the Specific Capacitance of PVDC-Derived Carbons.

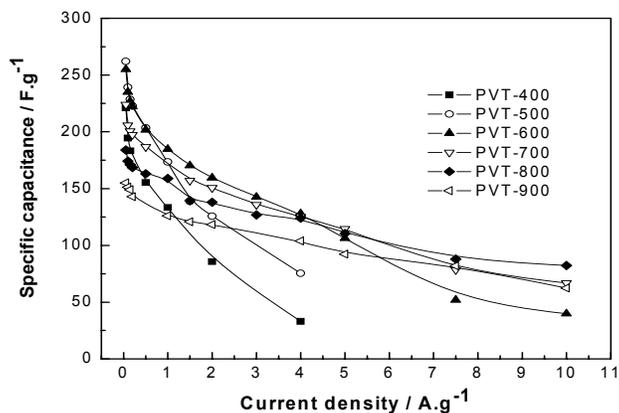


Figure 5. Specific Capacitance of PVDC-Based Carbons as a Function of Current Density.

The EDLCs are superior over batteries in high power density. Therefore, the rate performance is an important feature for EDLCs. Figure 5 shows that the specific capacitance decreases slightly with increasing current density, indicating that these PVDC-based carbons allow rapid ion diffusion. The PVT-800 has a better rate capability. As the current density increases from 50 mA g⁻¹ to 10 000 mA g⁻¹, its specific capacitance can remain 82 F g⁻¹, an attractive value for EDLCs.

Conclusion

PVDC carbonization is a simple and attractive method to prepare porous carbon for high capacitance electric double layer capacitors. The surface area and pore volume of the PVDC-based carbon reaches about 1200 m²·g⁻¹, while the specific capacitance can reach 262 F·g⁻¹. The PVDC-based carbon also show good rate capability. As the current density increases from 50 mA·g⁻¹ to 10 000 mA·g⁻¹, the specific capacitance of PVT-800 can remain 82 F·g⁻¹, an attractive value for EDLCs.

References

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