

Studies on Electrical Double Layer Capacitor Based on Mesoporous Activated Carbon

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(Received December 3, 2004; Accepted April 13, 2005)

Abstract

Mesoporous activated carbon (AC) was prepared from aged petroleum coke through chemical activation. The AC has a specific surface area of 1733 m²/g and a mean pore diameter of 2.37 nm. The volume fraction of 2 to 4nm pores is 56.74%. At a current density of 10 mA/cm², a specific capacitance of 240 F/g is achieved representing the use factor of the surface area of 69.2%. And the electrical double layer capacitor (EDLC) based on the AC shows an excellent power performance. This result suggests that the presence of high fraction of mesopores can effectively increase the adsorption efficiency of the specific surface area of the AC and enhance the power performance of EDLC based on the efficient surface area of the AC.

Keywords: Electric Double Layer Capacitor, Activated Carbon, Mesopore

1. Introduction

Activated carbon (AC) has been focused for an electrode material for electrical double layer capacitor (EDLC) on their porous structures and the unique electrochemical behaviors [1-6]. The EDLC is an electrochemical energy storage device with high power density. The mechanism of energy storage in EDLC is to create potential energy difference by the separations of charges on both electrodes of the AC electrode/electrolyte interfaces [7]. Therefore, it is understood that the higher surface area, the more ions can be adsorbed on the surface. However, in fact, some researchers have reported the non-linear relationship between the values of specific capacitance and the specific surface area, which would be caused by not enough size of the pores to fit in the ions and/or ion clusters. The pore size distribution (PSD) depends on the carbon precursor and the preparation method of the porous carbon. In this paper, mesoporous AC was prepared and the performance of EDLC prepared from the mesoporous AC was also discussed.

2. Experimental

2.1. Preparation and characterization of AC

Petroleum coke was ground to be powder with average particle diameter of about 16 μm. Then, 50 g of the petroleum coke powder was mixed with 250 g of KOH. The mixture was aged and then heat-treated at 300 °C for 1 hour,

and at 800 °C for 2 hours in nitrogen atmosphere. After cooling the samples, remained KOH was washed out with water, the powder was collected by filtration and followed by drying. The isotherms of the AC with N₂ were measured with a system (AUTOSORP ZXF-6) and the PSD of the AC was characterized by the BJH (Barrett-Joyner-Halenda) method.

2.2. Preparation of AC electrodes

AC electrodes (12 mm in diameter and 0.5 mm in thickness) for EDLCs were prepared by pressing a mixture of AC (75 wt.%) + graphite (20 wt.%) + polytetrafluoroethylene (PTFE) (5 wt.%) at 15 MPa for about 5 min. Unit cell was fabricated with two electrodes separated by a sheet of glass-fiber and the electrochemical measurements were conducted in 6 mol/L KOH aqueous solution. Before the measurements, all electrodes were vacuum-wetted.

2.3. Electrochemical measurements

Cyclic voltammetric measurement was performed with a potentiogalvanostat (TOHO PS-14, Japan). A platinum plate (40 × 30 mm) as a counter electrode and saturation calomel electrode (SCE) as a reference electrode were used. Charge/discharge tests were performed at various current densities. The specific capacitance of the active material was measured from the discharge curve by using equation $C = (2I\Delta t) / (m\Delta V)$, where I is the discharge current, t is the time, V is voltage and m is the amount of active material of one electrode.

3. Results and Discussion

3.1. Porous characterization of the AC

The BET specific surface area of the prepared AC is 1733 m²/g. According to the IUPAC classification, pores in a porous materials can be classified into three groups according to their size; micropores (pore width less than 2 nm), mesopores (between 2 and 50 nm) and macropores (larger than 50 nm). In addition, the total surface area is also conventionally divided into two kinds, the surface area from the micropores and that from external surface. The pore properties of the pores were summarized in Table 1 and the PSD of the AC is presented in Fig. 1 showing narrow PSD. The volume fractions of micropore, mesopore and macropore are 32.8%, 60.6% and 6.6%, respectively. The diameter is in the range less than 8nm and the volume fraction from pores with width less than 4nm is 89.57%. And the specific surface area from mesopore is 1073 m²/g from 56.74% volume fraction, which is 1.63 times larger than that of the micropore.

3.2. Electrochemical property

SEM image (Fig. 2) shows that the grains are well bound by the fibrous polytetrafluoroethylene expecting no hindrance of the access of the electrolyte to the electrode surface in achieving a high specific capacitance.

Cyclic voltammeteries of an AC electrode are presented in Fig. 3. It can be seen that no redox peak is observed in the whole potential range of investigation representing capacitance contributions from only the double layers.

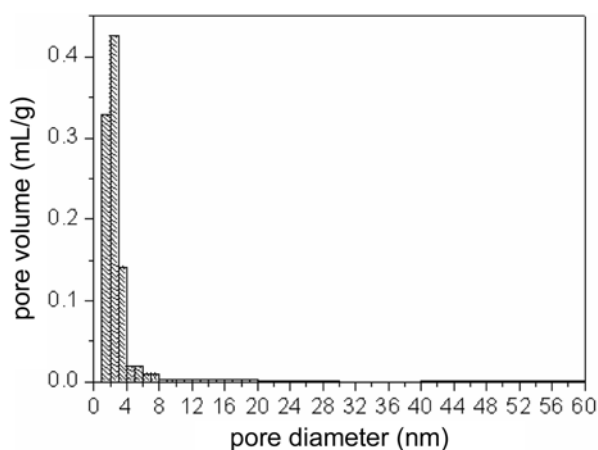


Fig. 1. Pore size distribution of the prepared AC.

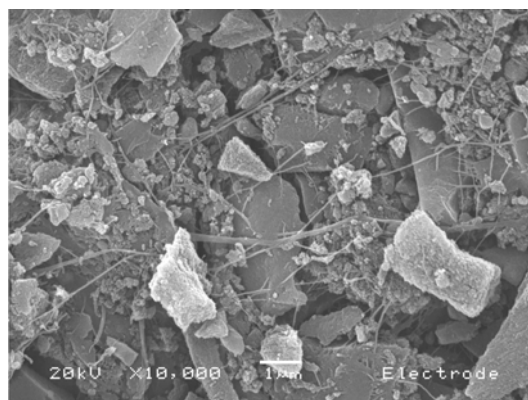


Fig. 2. SEM image of the AC electrode.

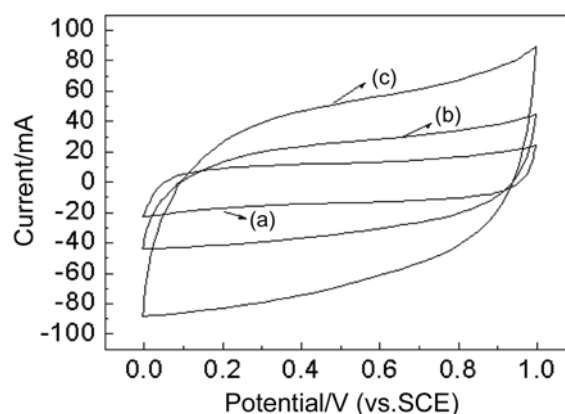


Fig. 3. Cyclic voltammograms of AC electrode in 6 mol/L KOH at various scan rates: (a) 10, (b) 20 and (c) 40 mV/s.

The apparent linearity of response current on the scan rate represents that the specific capacitance of the AC is not dependent much on the scan rate suggesting an excellent power performance.

Fig. 4 shows the galvanostatic charge-discharge of the EDLC cell at a current density of 10 mA/cm². The charge/discharge curves are very symmetric in the whole potential range. The measured specific discharge capacitance for the AC is calculated to be 240 F/g. In the consideration of specific surface area of 1733 m²/g, the specific capacitance of the AC electrode would be calculated to be 344.6 F/g on the basis of 20 µF/cm² of the double layer capacitance on a clean graphite surface [8]. The value represents that 69.2% of the total specific surface area has contributed to the specific capacitance. It has been reported that normal AC

Table 1. Pore characteristics of the AC

Micropore volume (cm ³ /g)	0.328	Surface area from micropores (m ² /g)	660
Mesopore volume (cm ³ /g)	0.606	Surface area from mesopores (m ² /g)	1073
Macropore volume (cm ³ /g)	0.066	Mean diameter (nm)	2.37

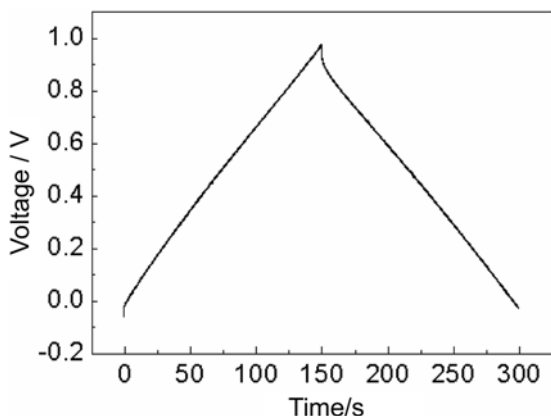


Fig. 4. Galvanostatic charge/discharge behaviors of the AC supercapacitor at current density of 10 mA/cm².

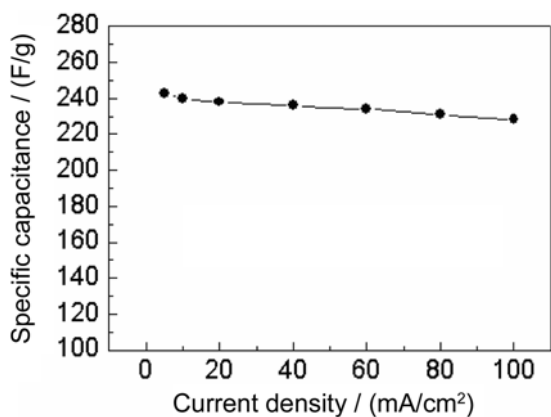


Fig. 5. Specific capacitance of the AC as a function of the current density.

shows capacitance of less than 50% of the theoretical value. And super activated carbon with a specific surface area of larger than 2200 m²/g often shows less than 30% [9-13].

The high efficiency of specific surface area would be attributed to its mesoporous characterization of the AC, because the normal AC has inevitably more fraction of micropores with pore width too narrow to be accessible for ion in electrolytes. Therefore, more and more attention is being paid to the researchs on preparations of mesoporous AC for EDLC application.

The EDLC from the prepared AC has an excellent power performance showing negligible dependence on the current density (Fig. 5). The behavior can be rationalized as the presence of many mesopores which would facilitate the motion of ions in the pore of the AC. So, the resistance (R) and the RC time constant of the capacitor will decrease resulting less capacitance dependence on the current density.

4. Conclusions

High specific surface area mesoporous AC with narrow PSD was prepared by activating the aged petroleum coke with KOH. The mesoporous AC shows a specific capacitance of 240F/g and the efficiency of specific surface area for the resulting capacitance of 69.2% on the basis of the theoretical value of graphite. EDLC base on the mesoporous AC has an excellent power performance. The presence of many mesopores can effectively increase not only the efficiency of specific surface area of AC but also enhance the power performance of the EDLC based on AC.

References

- [1] Deyang, Q.; Hang, S. *J. Power Sources* **2002**, *109*, 403.
- [2] J. Gamby, P. L.; Tabema, P. S. *J. Power Sources* **2001**, *101*, 109.
- [3] Mitsuhiro, N. *J. Power Sources* **1996**, *60*, 225.
- [4] Rychago, A. Yu.; Urisson, N. A.; Vol'fkovich Y. M. *Russian Journal of Electrochemistry* **2001**, *137*, 1172.
- [5] Celzard, A.; Collas, F.; Mareche, J. F. *J. Power Sources* **2002**, *108*, 153.
- [6] Endo, M.; Takeda, T.; Kim, Y. J. *Carbon Science* **2001**, *1*, 117.
- [7] Kotz, R.; Carlen, M. *Electrochimica Acta* **2000**, *45*, 2483.
- [8] Kinoshita, K. "Carbon: Electrochemical and Physicochemical Properties", New York, Kodansa Press, 1988, 326.
- [9] Deyang, Q. *J. Power Sources* **1998**, *74*, 99.
- [10] Hang, S. *Electrochimica Acta* **1996**, *41*, 1633.
- [11] Kierzek, K.; Frackowiak, E.; Lota, G. *Electrochimica Acta* **2004**, *49*, 515.
- [12] Frackowiak, E.; Beguin, F. *Carbon* **2001**, *39*, 937.
- [13] Hsieh, C.; Teng, H. *Carbon* **2000**, *38*, 863.