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Characterization of the porous carbon prepared by using halloysite as template and its application to EDLC

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Abstract

A porous carbon was prepared using halloysite as a template and sucrose as carbon source by means of template method. Nitrogen adsorption analysis showed that the obtained porous carbon material possess a wide pore size distribution and a large pore volume, especially in the range of mesopores. The application of the resultant carbon for electrodes of electric double layers capacitor (EDLC) in organic LiPF₆/PE + CE electrolyte indicated that the specific capacitance, as high as 232 F/g at a current density of 0.05 mA/cm², was larger than for commercially activated carbons. Cyclic voltammetry (CV) also showed that the performance of templated carbon in 1 mol/l aqueous solution of H₂SO₄ was better at a large scan rate than for the commercial activated carbons.

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1. Introduction

The template method to prepare carbons with wellcontrolled nanostructures has been regarded as a unique and versatile technique. Most of the nanostructures gained by the template method may be infeasible using other methods. Pioneering study on this method was done by Kyotani et al. [1] using clay minerals as templates to prepare layer-like carbons. And then, various novel structure carbons were obtained by this process such as ordered mesoporous carbon by using MCM-48 as a template [2], micropore carbon with high specific surface area by using Y zeolite as a template [3] and so on. However, the high cost of the template materials reported by far leads to a higher cost of the template carbon and limits its usage greatly. To solve this problem we tried to use a natural porous mineral halloysite as a template. Usually the framework of halloysite is made of number of rods with the length of dozens to hundreds nanometers and with the diameter of several nanometers. In each rod, there is a straight hole with a diameter of 0.7 or 1 nm. Low cost as well as stable structure gives us a potential to use holloysite as a template to prepare porous carbons.

On the other hand, for energy storage the use of porous carbons in EDLC has been widely documented. Different kinds of porous carbons used as the electrodes of EDLC [4] such as activated carbon fabric [5], carbon aerogel [6], carbon nanotube [7], templated carbon [8], and so on, displayed dissimilar performances. The present paper mainly describes the pore structure and electrochemical performance of the halloysite templated carbon in $\text{LiPF}_6/\text{PE} + \text{CE}$ and H_2SO_4 electrolytes. In order to close more tightly to the practical usage, the resultant carbon was compared with commercial activated carbon for electrodes performance of EDLC.

2. Experimental

2.1. Sample preparation

The process of preparation was described as follows: (i) the pretreatment of halloysite: baked in a beaker at 150 K for 3 h; (ii) impregnation of sucrose and sulfuric acid into the halloysite pores: stirred 4 h in the solution with the weight ratio of sucrose: $H_2O:H_2SO_4=5:10:1$; (iii) polymerization and carbonization of sucrose: dried in air at 100 K for 4 h and heated at 150 K for 2 h for polymerization and then at a heating rate of 5 K/min to 800 K under a nitrogen flow 4 h for carbonization; and (iv) removal of the halloysite template: treated with multiple cycles of concentrated HF/HCl, and distilled water.

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Fig. 1. N_2 adsorption isotherms and BJH pore size distribution of the carbon samples.

 Table 1

 Specific surface areas and pore volumes of porous carbons

Samples	$\frac{S_{\rm BET}}{(m^2/g)^a}$	$S_{\rm mic}$ $(m^2/g)^b$	V _{total} (cm ³ /g) ^c	V _{meso} (cm ³ /g) ^d	Mesoporosity (%) ^e
SHC	1142	179	1.715	1.287	75.1
AC1	1667	1152	0.825	0.106	12.9
AC2	2322	723	1.181	0.281	23.8

^a BET-specific surface area.

^b Microsurface area.

^c Total pore volume.

^d Mesopore volume.

^e Determined by V_{meso}/V_{total}.

2.2. Characterization

Nitrogen adsorption at 77 K gave the BET-specific surface area and pore structure. BET-specific surface area was obtained by BET method [8]; the mesopore distribution was gained from BJH method [9]; pore volume was determined by using the data of N_2 adsorbed [10]; and micropores surface area was obtained from *t*-plot method [11].

2.3. Electrochemical study

In an organic electrolyte system, the 2 cm^2 pressed plates of the mixture of the templated carbon, PTFE (polytetrafluor-oethylene) and carbon black with the weight ratio of 80:10:10

were used as the electrodes of coin-style EDLC in $\text{LiPF}_6/\text{PE} + \text{CE}$ electrolyte. The specific capacitance was calculated by the following Eq. (1) [12]

$$C_m = 2 \frac{I\Delta t}{\Delta V m} \tag{1}$$

where C_m is the specific capacitance; *I* is the discharge current; Δt is the space-time when the alteration of voltage was ΔV , and *m* is the mass of carbon.

In an inorganic system, cyclic voltammetry (CV) method with three electrodes would be used to evaluate the performance in $1 \text{ M H}_2\text{SO}_4$ aqueous solution electrolyte. From the CV the specific capacitance could be deduced from the definition of capacitance

$$C = \frac{\mathrm{d}Q}{\mathrm{d}U} = \frac{\mathrm{d}Q/\mathrm{d}t}{\mathrm{d}U/\mathrm{d}t} = \frac{I}{\nu} \Rightarrow C_m = \frac{I}{\nu m}$$
(2)

where C_m is the specific capacitance; *I* is the instant current; *v* is the scanning rate and *m* is the mass of carbon. For convenience, in this work, the specific capacitance was calculated from half of the difference between charge and discharge current at 650 mV on the CV curves observed.

3. Results and discussion

3.1. Porosity and pore structure

Fig. 1 shows the nitrogen adsorption isotherms of the templated carbon (SHC) and two commercial activated carbons (denoted as AC1, AC2, respectively).

The type-I isotherms (in terms of IUPAC) of AC1 and AC2 indicated that almost all the pores inside them were micropores; the type-II isotherm of SHC showed that SHC possessed micropores and mesopores [10]. BJH mesopore size distribution displayed that AC1 and AC2 had few mesopores, and SHC had very rich mesopores mainly at the diameter of 4 nm. Table 1 showed that the BET-specific surface area of SHC was much smaller than AC1's and AC2's, but its total pore volume and mesopore volume, especially the mesoporosity were larger than others'. Above results indicated that SHC was a mesopore carbon with large pore volume and high mesoporosity.



Fig. 2. Constant-current discharge curves of the carbons in EDLC with LiPF₆/PE+CE electrolyte (a, at 0.05 mA/cm²; b, at 0.5 mA/cm²).

 Table 2

 Specific capacitances of the carbon samples

Samples	Ash content (%)	Specific capacitance (F/g)				
		Organic system (mA/cm ²)		Inorganic system (mV/s)		
		0.05	0.5	5	100	
SHC AC1	10.7 0.2	232 173	180 154	261	210	
AC2	3.0	195	177	308	154	



Fig. 3. Charge/discharge curves of the carbons in EDLC with $LiPF_6/PE + CE$ electrolyte (at 1 mA/cm²).

3.2. Electrochemical performance

When the current density was 0.05 mA/cm^2 , the discharge curve of the three kind of carbons (Fig. 2a) indicated that the specific capacitance of SHC was the highest; when the current density increased to 0.5 mA/cm^2 (Fig. 2b) the trend was the same. According to Eq. (1), the specific capacitance of SHC was calculated to be 232 F/g (see Table 2) at the current density of 0.05 mA/cm^2 , much more than the AC1's 173 F/g its specific surface area was 1667 m²/g even comparing with the AC2 with specific surface area of 2332 m²/g its specific capacitance was 195 F/g. When the current density increased to 0.5 mA/cm^2 , the specific capacitance of SHC also kept the highest value.

It was much interesting that the specific surface area of templated carbon is not larger, but its specific capacitance is higher. In Lozano-Castelló et al.'s report [13] at the similar conditions, if the specific capacitance of activated carbons closed to SHC's its BET-specific surface area might be nearly $3000 \text{ m}^2/\text{g}$. Comparing the differences of the pore information between SHC and AC1, AC2, we reasoned that the larger pore size of SHC could easily form the electric double layer but AC1's and AC2's could not form it because of their small pore size and the large ion diameter of the electrolyte.

The charge/discharge curves (Fig. 3) showed that the charge/discharge efficiency of carbons was in the sequence: SHC < AC1 < AC2; it might be the effect of impurities (Table 2 showed the ash contents of the samples). The impurities might react with the electrolyte and caused dilution of the electrolyte. The nonlinear character indicated that SHC possessed pseudo capacitance and a large drop of the voltage, which was due to the IR contributions from charging to discharging which showed that SHC had larger resistance.

Cyclic voltammograms of SHC in 1 M H_2SO_4 at different scanning rate (Fig. 4a) showed almost rectangular curves. When the scanning rate increased from 20 to 200 mV/s the similar shape of the CV curves indicated that SHC possessed a good electrochemical stability. The specific capacitance of SHC was calculated to be 261 F/g at 5 mV/s, smaller than the AC2's 308 F/g. When the rate was at 100 mV/s, the specific capacitance of SHC decreased to 210 F/g, but AC2's decreased to 154 F/g, around half of the value at 5 mV/s (Table 2).

Fig. 4b indicated that the specific capacitances of all the carbon samples reduced when the scanning rate increased. As the scanning rate increases, the specific capacitance of SHC was higher than AC2's, but it was much lower than AC2's at the slow scanning rate. It indicated that the large-current performance of SHC was excellent in H_2SO_4 system.

The specific capacitance depended on the formation of electric double layer. The size of hydrogen ions was small enough for diffusing into micopores of carbons in 1 M H_2SO_4 , thus for AC2 due to its large specific surface area and nearly all the micopores, the specific capacitance was higher at the low scanning rate; as the scanning rate increases so many ions needed a large channel to transfer thus the decrement of the



Fig. 4. Cyclic voltammetry (CV) analysis in 1 M H₂SO₄ aqueous solution (a, cyclic voltammograms of SHC; b, specific capacitance at different scanning rates).

specific capacitance of SHC with big pore size and large pore volume was lower than AC2's.

4. Conclusions

Porous carbon SHC could be prepared using halloysite as a template. The application to EDLC found that in organic electrolyte, the specific capacitance of SHC was larger than the commercially activated carbons AC1s and AC2s; but in inorganic electrolyte, it was smaller at low scanning rate but larger at high scanning rate compared to AC2s. The templated carbon SHC was a mesoporous carbon with large specific capacitance in EDLC with organic electrolyte and with good performance in H_2SO_4 system at large current.

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