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Synthesis and electrochemical properties of nanoporous carbon electrode materials for supercapacitors

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ABSTRACT

New microporous and mesoporous carbon electrode materials were synthesized via processes of carbonization of phenol-formaldehyde or resorcinol-formaldehyde resins followed by activation in which potassium hydroxide acted as both the catalyst of polymerization and the chemical activation reagent. Electrochemical properties of the carbon materials were investigated by cyclic voltammetry in basic and acidic media (6 M KOH or 1 M H_2SO_4) and non-aqueous electrolytes (1 M $LiClO_4$ in acetonitrile). The samples were shown to have high specific surface areas and show high capacitance. Surprisingly, materials prepared in this work have higher capacity in organic electrolytes rather than in water solutions that can be explained by a good wettability of carbon materials by organic solvents and with a suitable porous structure.

1. Introduction

Electric double-layer capacitors represent a unique type of high-power electrochemical energy storage devices, where the capacitance arises from the charge separation at an electrode/electrolyte interface. The energy storage in supercapacitors is based on the adsorption of electrolyte ions on the large specific surface area of electrically conductive porous electrodes, most commonly porous carbons. The advantages of capacitors over batteries are much higher power density, much lower internal resistance, broader temperature window of a stable operation, very rapid charging (in seconds or less), higher round-trip efficiencies and significantly longer cycle life (millions of cycles). The main limitation of supercapacitors is a relatively low energy density compared to batteries [1].

Activated carbons [2,3], templated carbons [4], carbon nanotubes and nanofibers [5] and mesoporous carbons [6–9] have been investigated as potential electrode materials for electrochemical double layer capacitors. Supercapacitors typically consist of two porous carbon electrodes separated by liquid electrolyte containing mobile ions [10]. Upon charging, electronic and ionic charges accumulate at the electrode/electrolyte interface to form an electrical double layer. The specific capacitance of electrochemical capacitors related to the mass unit [F/g] depends on specific surface area, S_{sp}, according to:

$$C = \frac{\varepsilon_r \varepsilon_0}{d} S_{sp} \quad (1)$$

where ε_r is the relative permittivity of the electrolyte, ε_0 is the permittivity of free space, d is the distance between charges in the electrical double layer, S_{sp} is the specific surface area of the electrode material, measured in units of [m^2/g], provided that all electrode surface is electrochemically active [11]. According to this equation carbon materials with high specific surface are the most suitable for use as electrodes for supercapacitors. Among the above mentioned carbon materials, activated carbons are the most attracting due to their high surface and relatively low cost. There are two main methods for preparing activated carbons: from natural materials (shells, wood, coal) and synthetic polymers by carbonization in inert atmosphere followed by activation via KOH or other agent. Activation of carbon materials may result in strong change in the morphology of the material. Thus, the aim of the present work was the synthesis of carbon materials with high surface area and optimal pore size distribution.

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2. Experimental

2.1. Synthesis of porous carbons

Phenol formaldehyde and resorcinol resins (resols) were used as precursors for preparation of porous carbon. The resols were prepared by polymerization of resol, dissolved in ethanol, and formaldehyde in the presence of KOH as catalyst with and without addition of surfactants (triblock copolymer Pluronic F127). The synthesis procedure started from dissolution of KOH in ethanol with stirring and cooling the solution to room temperature. Thereafter, a resol was added to the solution in the weight ratio of resol: KOH equal to 2: 3. After complete dissolution of the components alcohol solution of F127 with concentration of 40 g/l was added at a weight ratio of F127: resol equal to 1: 1. Then, formaldehyde solution (at a molar ratio of resol: formaldehyde equal to 1: 3) was added dropwise and the solution was boiled under reflux during 3 and 10 h, for resorcinol and phenol, respectively.

The obtained polymers were subjected to stepwise heating in an inert atmosphere:

- first, at a heating rate of 1°C/min up to temperature of 750° C followed by heating at this temperature for 2 h. On this stage the surfactant was removed;
- then, at a heating rate of 5°C/min up to temperature of 900° C followed by heating at this temperature for 2 h.

The resulting samples were washed with distilled water to pH = 7 and then dried at 120 °C for 2 h. Short abbreviations of the samples are given in Table 1.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded with X-ray diffractometer (Bruker D8 Diffractometer with Cu Kα radiation) at a scanning rate of 5° min^{-1} in the 2θ range of 10°–80° to evaluate the microstructure. Transmission electron microscopy (TEM) studies were carried out with JEM-2200FS-CS High Resolution Electron Microscope to characterize the morphology and structure of prepared samples. Nitrogen BET adsorption isotherms at 77 K were measured on a «Sorbtometer M» instrument. The electrochemical characteristics of electrode materials were investigated by cyclic voltammetry on a LAHNE CT2001 Electrochemical Station using two-electrode symmetrical cell. The electrodes was prepared by mixing of porous carbons with 10 wt% of carbon black in the ethanol, deposition of the suspension on the aluminum foil and subsequent heating in vacuum for complete evaporation of the liquid phase. The electrodes were cut, placed into a button cell and tested at room temperature in a voltage window of −1 to 1 V for the case of 6 M KOH or 1 M H_2SO_4 water solutions or at voltages of −2.7–2.7 V for the cells with a non-aqueous electrolyte 1 M $LiClO_4$ in acetonitrile.

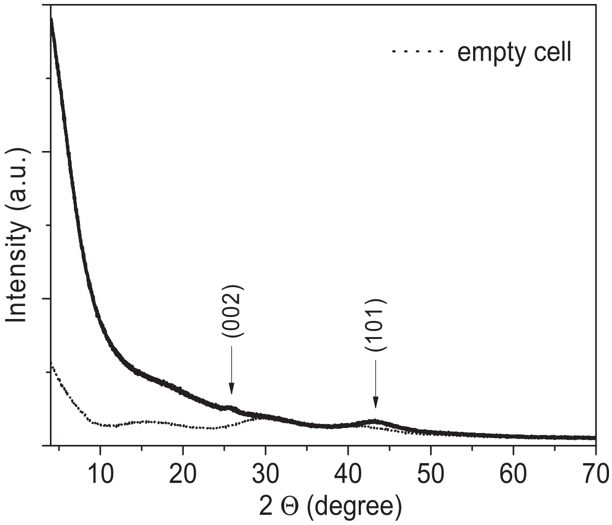

Fig. 1. XRD patterns of the sample FFR-F127 and empty cell. Peak positions of graphite phase are shown for comparison.

3. Results and discussion

3.1. Structure and morphology characterization

The analysis of BET adsorption isotherms of nitrogen was used to determine the specific surface area S_{sp} and pore volume of the samples. The results are given in Table 1. As seen, the carbon samples obtained from phenol-formaldehyde resins synthesized with and without addition of the F127 surfactant have the specific surface area values of 1700–2100 and 1000–1400 m^2/g, respectively. Samples obtained from resorcinol resins with and without addition of a surfactant have specific surface values of ~1000 and 1000–1200 m^2/g, respectively. From BET isotherms it was difficult to determine the pore size distribution, nevertheless, the average pore size and the pores volume in all the samples were in the range of 2.2–2.9 nm and 0.64–0.97 cm^3/g, i.e. the samples may be regarded as intermediate between micro- and mesoporous carbon materials. Specific surface area values of samples prepared without Pluronic F127 weakly depends on the nature of the polymer precursor. Addition of Pluronic F127 to phenol as a starting agent leads to an increase in the specific surface area of the carbon material.

A typical XRD pattern of samples is shown in Fig. 1. Two weak diffraction peaks are observed at around 2θ of 26° and 42–45° for all samples, which correspond to (002) and (101) lattice planes of graphite-like crystallites, respectively. The concentration of the solid phase seems to be very low. At small-angle an intensive background is observed attributed to the sample rather than to the empty cell (Fig. 1). Such background is likely to appear due to mesoporous structure of the carbons characterized by strong small-angle scattering.

Table 1
Textural characteristics of carbon materials obtained by different methods: specific surface area (S_{sp}), mean pore size (D), the pore volume (V_p) and the yield of the material.

Precursor	Surfactant	S_{sp} [m^2/g]	D [nm]	V_p [cm^3/g]	Yield [%]
Phenol formaldehyde resin (FFR)	No	1000–1400	2.4	0.73	3.7
Phenol formaldehyde resin (FFR-F127)	Pluronic F127	1700–2100	2.3	0.97	62
Resorcinol formaldehyde resin (RFR)	No	1000–1200	2.2	0.75	7.7
Resorcinol formaldehyde resin (RFR-F127)	Pluronic F127	~1000	2.9	0.64	70