Surface modification of soft-templated ordered mesoporous carbon for electrochemical supercapacitors

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ABSTRACT

The increasing demand for energy has triggered numerous research efforts for the development of electricity storage devices consisting of templated nanoporous carbons. In this study, ordered mesoporous carbon with a modest specific surface area (520 m^2/g) was prepared by a soft-templating method and surface-modified by a wet oxidation using nitric acid and ammonium peroxodisulfate. More oxygen-containing functional groups were introduced on the surface by oxidation using ammonium peroxodisulfate rather than nitric acid. Our study systematically investigates the effect of surface modification on electrochemical performance, based on comparisons with oxidized commercial activated microporous carbons. Oxygen functionalization leads to an increased capacitance for the ordered mesoporous carbon and a decreased capacitance for the activated microporous carbon at higher power densities. The ordered mesoporous carbon oxidized by nitric acid demonstrates excellent electrochemical performance with gravimetric capacitance of 290 F/g and volumetric capacitance of 300 F/cm^3 at 0.1 A/g and retains over 70% of the capacitance at high current density of 5 A/g even though its surface area remained moderate (430 m^2/g). The device demonstrates remarkable performance with an energy density of 17.4 Wh/kg, power density of 5.2 kW/kg, and excellent cycle life.

1. Introduction

Electrochemical double layer capacitors (EDLC) or supercapacitors represent a unique type of high power energy storage devices, where the capacitance arises from the charge separation at an electrode–electrolyte interface [1,2]. The energy storage in EDLC is based on the electro-adsorption of electrolyte ions on the large surface area of electrically conductive porous electrodes, most commonly porous carbons. EDLC has been widely used for several applications, such as an emergency or short-term secondary power source, copy machines, power booster for construction-equipments, since its commercialization in the 1970s. However, the main limitation of EDLC is their lower energy density than lithium-ion batteries. Thus, the improvement of their energy density is of significant for further expansion of their application fields.

The capacitance of electrically conductive porous electrodes should be in principle proportional to the surface area. However, many studies have shown an unfavorable divergence from this linear relation. The energy storage characteristics of EDLC are strongly affected by the capability of porous carbon to adsorb a large quantity of electrolyte ions under an applied potential and attract the ions closer to the pore walls. Therefore, aside from the surface area, the performance of EDLC strongly depends on the pore structure, pore size distribution, and surface functionality [3–9]. In addition, the capacitive rate performance is determined by how fast

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the electrolyte ions can travel within the pores. In order to achieve a higher energy density, it is important to appropriately design the pore structure. The templated nanoporous carbons are expected to draw a simple relationship between the structural characteristics of porous carbon and the EDLC performance [10,11].

Surface modification of carbon materials is effective not only for their dispersibility in various solvent [12] but also to improve the adsorptive performance as adsorbent [13]. A variety of functionalities can be introduced upon the surface of carbon materials by oxidative treatment involving dry or wet oxidation, plasma, and electrochemical treatments. In dry oxidation, oxygen, ozone, and carbon dioxide are usually used as gaseous oxidizing agents. Wet oxidation involves the use of nitric acid, sulfuric acid, phosphoric acid, ammonium peroxodisulfate, alone or in the combination with hydrogen peroxide, sodium hypochlorite, and so on [14–20].

In this study, the ordered mesoporous carbon (OMC) with channel pore structure was prepared through the soft-templating method. The soft-templated OMC contained a small quantity of functional groups on its surface. Pore wettability, surface hydrophobic/hydrophilic balance, in general, depends on the surface functional groups and determine penetration of guest species into the pore system. The pore surface of the OMC was therefore modified by the wet oxidation. The effects of the wet oxidation on the structural characteristics and electrochemical performances of the OMC electrodes were investigated by comparisons with oxidized commercial activated carbons. The structural properties were characterized by the combination of powder X-ray diffraction (PXRD) and nitrogen sorption measurements. The surface chemical properties were characterized by the combination of Fourier transform infrared (FTIR) measurement, thermogravimetric analysis, and the Boehm titration. The electrochemical properties were characterized by using cyclic voltammetry (CV) and galvanostatic charge–discharge techniques.

2. Experiment

2.1. Materials

Resorcinol, phloroglucinol, 37 wt% formaldehyde, hydrochloric acid, nitric acid, ammonium peroxodisulfate (APS), potassium hydroxide, sodium hydroxide, sodium carbonate, sodium bicarbonate, and ethanol were purchased from Wako Pure Chemical Industries and used as received. Pluronic F127 was purchased from Sigma-–Aldrich Chemical Co. and used as received. Polyflon polytetrafluoroethylene (F-104; PTFE) was received from Daikin Industries, Ltd. A commercial Maxsorb activated carbon was received from Kansai Coke & Chemical Co. Ltd. and used for the sake of comparison.

2.2. Synthesis of ordered mesoporous carbon

Resorcinol and phloroglucinol were completely dissolved in ethanol/water solution, hydrochloric acid was added, and the solution was stirred for 15 min. Pluronic F127 was then added, and after it was completely dissolved, formaldehyde was added. The final molar composition of the precursor solution was 3 resorcinol:1 phloroglucinol:9 formaldehyde:0.02 Pluronic F127:0.1 hydrochloric acid:40 water:100 ethanol. The solutions were left for 3 days at room temperature, during which they separated into two phases. The upper clear phase was discarded; the lower dark brown phases were thermopolymerized in air at 100 °C for 3 h. The resultant dark brown deposition was carbonized in a tubular furnace with nitrogen flow (100 mL/min). The furnace was heated at a ramping rate of 1 °C/min below 400 °C and 5 °C/min above 400 °C, then kept at 800 °C for 3 h.

2.3. Surface modification

Ordered mesoporous carbon was subsequently subjected to oxidation treatment with different oxidizing agents. For a typical run, 0.3 g of ordered mesoporous carbon was mixed with a 50 mL solution of 1 M nitric acid or 1 M APS, then heated at 90 °C for 6 h under stirring and refluxing conditions to obtain the surface-modified carbon samples, designated as OMC-x, where x denotes to the oxidizing agent, HNO_3 or APS. The resultant sample was extensively washed with deionized water until the pH of the filtrate water became neutral, then dried at 100 °C in air. The same oxidation treatment was also carried out for the commercial Maxsorb activated carbon.

2.4. Chemical activation

The post chemical activation treatment was also performed to compare the treatment effect of oxidation with that of activation. For a typical run, 0.3 g of ordered mesoporous carbon was impregnated with a 15 mL solution of 1 M potassium hydroxide followed by water evaporation at 120 °C. The activation process was performed with nitrogen flow (100 mL/min) at 800 °C, with a ramping rate of 10 °C/min, for 1 h. The resultant sample was washed with 0.1 M hydrochloric acid solution followed by deionized water until the pH of the filtrate water became neutral, then dried at 100 °C in air. The same post chemical activation treatment was also carried out for the commercial Maxsorb activated carbon.

2.5. Structural characterization

PXRD patterns were recorded on a RINT-TTR III diffractometer (Rigaku, Japan) using Cu Kα radiation; the copper anode was operated at 40 kV and 20 mA. Nitrogen adsorption/desorption isotherms of the samples were measured at 77 K using a BELSORP-max instrument (Bel Japan). The samples were degassed at 200 °C under vacuum. Brunauer–Emmett–Teller (BET) model surface areas, S_{BET}, were calculated from the nitrogen adsorption branches. A part of the nitrogen adsorption isotherm in the P/P_0 range 0.10–0.30 was fitted to the BET equation to estimate the S_{BET}. The pore size distributions were calculated from adsorption branch of isotherm using the Barrett–Joyner–Halenda (BJH) model. The total pore volumes, V_{total}, were calculated on the basis of the amount of nitrogen adsorbed at $P/P_0 = 0.99$. The micropore volumes, V_{micro}, were calculated from the α_s-plot method. The mesopore volumes were calculated by subtracting the value of V_{micro} from that of V_{total}. Transmission electron microscope (TEM) images of the samples were recorded on a JEM-2010 microscope (JEOL) at an acceleration voltage of 200 kV.

2.6. Surface chemical characterization

FTIR spectra were recorded on an IRAffinity-1 spectrometer (Shimadzu, Japan) using KBr pellet method. Thermogravimetric curves were recorded on a DTG-60H (Shimadzu, Japan) with nitrogen flow (100 mL/min) at a ramping rate of 5 °C/min. The surface functional groups were determined according to the Boehm titration method [21,22]. For a typical run, 0.1 g of dried active materials were added in the vials containing 100 mL of standard base solution as follows: 10 mmol/l sodium hydroxide, 0.5 mmol/l sodium carbonate, and 0.5 mmol/l sodium bicarbonate. The vials were sealed and shaken at room temperature for 48 h. Then, the solutions were filtered and 10 mL of each solution was taken for the subsequent titration. The filtration procedure was quite sensitive and done with extra care. The blank samples were analyzed as well. All experiments were run in triplicates. The number of acidic sites