



Studies on electrochemical sodium storage into hard carbons with binder-free monolithic electrodes



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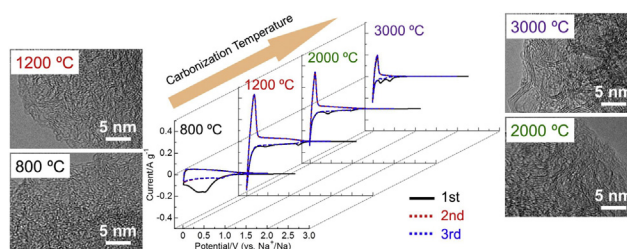
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HIGHLIGHTS

- Electrochemical Na⁺-storage in hard carbons is explored using monolithic electrodes.
- The Na⁺-insertion behaviors into hard carbons calcined at 800–3000 °C are compared.
- The difference between Li⁺ and Na⁺ ion-trapping in nanovoids is demonstrated.
- The effect of pore size on the initial irreversible capacity is discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 2 February 2016

Received in revised form

23 March 2016

Accepted 2 April 2016

Available online 8 April 2016

Keywords:

Carbon monoliths

Na-ion battery

Porous electrodes

Pore size effect

Irreversible capacity

Sol-gel

ABSTRACT

Hard carbons emerge as one of the most promising candidate for an anode of Na-ion batteries. This research focuses on the carbon monolith derived from resorcinol-formaldehyde (RF) gels as a model hard carbon electrode. A series of binder-free monolithic carbon electrodes heat-treated at varied temperatures allow the comparative investigation of the correlation between carbon nanotexture and electrochemical Na⁺-ion storage. The increase in carbonization temperature exerts a favorable influence on electrode performance, especially in the range between 1600 °C and 2500 °C. The comparison between Li⁺- and Na⁺-storage behaviors in the carbon electrodes discloses that the Na⁺-trapping in nanovoids is negligible when the carbonization temperature is higher than 1600 °C. On the other hand, the high-temperature sintering at 2500–3000 °C enlarges the resistance for Na⁺-insertion into interlayer spacing as well as Na⁺-filling into nanovoids. In addition, the study on the effect of pore size clearly demonstrates that not the BET surface area but the surface area related to meso- and macropores is a predominant factor for the initial irreversible capacity. The outcomes of this work are expected to become a benchmark for other hard carbon electrodes prepared from various precursors.

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1. Introduction

The increasing demand for electrical energy storage has aroused the development of carbon materials, which implement various requirements for electrodes, such as high surface area, low density, good electrical conductivity, and low cost. Except for the specific

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allotropes (fullerene, carbon nanotube, graphene, and their derivatives), the carbon materials for electrodes are classified into three types; graphite, graphitizable carbon (soft carbon), and non-graphitizable one (hard carbon). The recent upsurge of interest in Na-ion batteries (NIBs) as a possible alternative to Li-ion batteries (LIBs) has driven many researchers to explore carbon-based anodes as is the case with LIBs [1,2]. Since the early investigation on graphite intercalation compounds (GICs) has proven that graphite hardly accommodates Na^+ ions between the interlayer spacing [3–5] unless forming GICs with solvated Na^+ [6–8], the current research efforts mostly focus on disordered carbon materials, in particular, hard carbons [9–20].

As carbonization of diverse organic compounds (e.g. hydrocarbons, polymers, biomass, etc.) under various conditions provides different carbons in nature, hard carbons involve a huge family that cannot be completely identified in terms of chemical composition, pore property, and nanotexture. Among them, hard carbons derived from phenolic resins are favorable for the fundamental and comprehensive study on the electrochemical Na^+ -storage because the phenolic resins can be artificially synthesized with the deliberate and precise control of the physical and chemical properties, indicative of the better control of the carbon characteristics [21–24]. In addition, the phenolic resin-derived carbons are also promising in terms of the feasibility of commercial NIBs due to the low cost and large producibility.

To date, most of the electrochemical studies on active materials have been carried out with composite electrodes containing binders and conductive agents, which are however unsuitable for a fundamental investigation. The mechanical mixing process to prepare a slurry may change the original features of the active materials as well. In this context, monolithic electrodes [23–30] are useful because the electrode consisting of a single piece of the target active material without any additives can avoid the above-mentioned unfavorable factors. The main drawback of the monolithic electrodes is the necessity of designing porous structure to ensure the electrolyte penetration inside the monoliths for minimizing the ion diffusion length in solid. When it comes to the carbon electrodes, however, this is not a significant issue due to the well-developed research field of porous carbon monoliths [25–27,31–35].

In the previous communication [20], we demonstrated the potential of the hard carbon electrodes derived from phenolic resins as an anode for NIBs and put forward the designing strategy for a practical carbon anode. Here, we report the more detailed investigation of the electrochemical sodiation/desodiation in the hard carbons by employing a series of porous carbon monoliths treated at different carbonization temperatures and those with varied pore sizes. The correlation between the nanotextural change and the electrochemical Na^+ -storage behavior as a function of carbonization temperature is comprehensively discussed. We also compare the electrochemical Li^+ - and Na^+ -insertion behaviors into the hard carbon electrodes and give an insight into the ion-trapping in nanovoids.

2. Experimental procedure

2.1. Chemicals

Resorcinol and formaldehyde solution (37 wt% in H_2O containing 10–15% methanol) were purchased from Sigma-Aldrich Co. All other reagents were obtained from Kishida Chemical Co., Ltd. Distilled water was used in all experiments.

2.2. Preparation of activated carbon monoliths

Macroporous resorcinol-formaldehyde (RF) gels were prepared according to the sol–gel process reported previously [20]. In a typical preparation (M-RF), 2.20 g of resorcinol was dissolved in the mixture solvent of 4.0 mL of 10 mM HCl aq. and 0.80 mL of ethanol (EtOH). After obtaining a homogeneous solution, the solution was cooled at 0 °C in an ice-water bath, followed by adding formaldehyde solution with vigorous stirring. After mixing for 5 min, the solution was kept at 40 °C for 24 h for gelation. Afterwards, the obtained gels were aged at 80 °C for 24 h. Then, the gels were washed with ethanol at 60 °C for 4 h for 3 times and dried at 60 °C. The RF gels with larger (L-RF) and smaller (S-RF) macropore size were prepared with 0.60 mL and 1.00 mL of EtOH, respectively. The dried gels were subsequently carbonized at different temperatures for 2 h with under the stream of argon gas (1 L min^{-1}) at the heating rate of 4 °C min^{-1} . The high-temperature treatment (>2000 °C) was carried out in a graphite furnace. In this case, the samples were pre-treated under argon atmosphere at 1200 °C for 2 h. The furnace was rapidly ramped to 1300 °C followed by raising the temperature at 10 °C min^{-1} .

2.3. Characterization

The microstructures and nanotextures of the carbon electrodes were observed by scanning electron microscopy (SEM, JSM-6060S, JEOL) and transmission electron microscopy (TEM, JEM-2010, JEOL), respectively. A N_2 adsorption-desorption apparatus (BELSORP-Max, Bel Japan Inc.) was employed to characterize the micro- and mesopore properties, while helium pycnometry (Pentapyc 5200e, Quantachrome Instruments) was employed to determine the skeletal densities. Samples were degassed at 300 °C for more than 10 h under vacuum prior to the measurements. The elemental analysis was carried out by X-ray photoelectron spectroscopy (XPS, MT-5500, ULVAC-PHI, Inc.). The monochromatized Mg $K\alpha$ radiation (1253.6 eV) was used.

2.4. Electrochemical analysis

All the electrochemical tests were performed on a VMP3 potentiostat (Bio Logic Science Instruments) at room temperature (24–25 °C). The working electrodes were prepared by shaping the center of each carbon monolith into a 200 μm -thick plate. Thus obtained free-standing carbon monolithic electrodes were tested in a three-electrode cell configured with 0.8 M NaClO_4 electrolyte in 1:1 (v/v) ethylene carbonate/diethyl carbonate (EC/DEC) and Na metal as both counter and reference electrodes. Before the measurements, the counter Na metal was electrochemically dissolved and reprecipitated for several times to roughen the surface. Constant current charge-discharge tests were carried out with 0.005 and 2.0 V (vs. Na^+/Na) cutoff potentials. For cyclic voltammetry (CV) measurements, the potential was scanned between fixed potential values from 0 V to 2.0 V (vs. Na^+/Na) at 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were conducted with an AC amplitude of 20 mV in the 10 mHz–100 kHz frequency range. The charge-discharge measurements for Li-ion batteries were conducted in 1 M LiClO_4 (EC/DEC) with Li metal as counter and reference electrodes in the potential range from 0.005 to 2.0 V (vs. Li^+/Li).

3. Results and discussion

3.1. Structural characteristics of monolithic carbon electrodes

The porous carbon monoliths were prepared from the RF gels

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