Preparation of Templated Mesoporous Soft Carbon from Synthesized Quinoline Pitch

Minato EGASHIRA,‡* Ryo IKENARI, Nobuko YOSHIMOTO,‡ and Masayuki MORITA‡

Graduate School of Science and Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755-8611, Japan

* Corresponding author: egashira.minato@nihon-u.ac.jp

ABSTRACT

A mesoporous soft carbon has been prepared using a novel method based on aggregation to metal nanoparticles, along with heat treatment of a nitrogen-rich precursor designated as quinolone pitch. From this newly prepared method using quinolone pitch and nickel acetate, mesoporous soft carbon has been prepared. This mesoporous soft carbon exhibits increased capacitance by anodic oxidation in non-aqueous lithium salt electrolyte, even though the activation effect was limited compared with previous reports.

Keywords : Mesoporous Soft Carbon, Quinolone Pitch, Supercapacitor

1. Introduction

Porous carbons are commonly used as electrode materials for supercapacitors because of their light weight, electronic conductivity, high surface area, and low cost. The properties of carbon materials, including porous carbon, are dependent on their graphitic structure, i.e., orientation of stacking of nano-sized to micro-sized graphitic planes. A carbon material is generally prepared by heat treatment of an organic precursor under inert atmosphere. The precursor and preparation process are parameters that are useful to ascertain the graphitic structure of the carbon material. Most porous carbons are prepared from non-graphitizable “hard” carbons because spaces created by random stacking and the microstructure at the precursor surface are the sources of pores in porous carbon products.1 By contrast, graphitizable “soft” carbons are minority sources of porous carbons. Although some attempts have been undertaken to prepare porous graphitizable “soft” carbon using hard template methods,2–4 the insufficient wettability of polyaromatic precursors of soft carbon to mesoporous ceramic templates makes it difficult to control the micro pore–mesopore structure. Polarization of an alkaline-activated soft carbon electrode in non-aqueous lithium salt electrolyte beyond its stable potential range has been investigated to improve its capacitance markedly, up to 150 F per gram of the electrode. This attractive process, known as “electrochemical activation,” has been observed only for soft carbon electrodes.5–8 Most soft carbons have low surface area, even after activation. Therefore, the surface nanostructure improvement remains as a challenge for soft carbon electrodes. Particularly, mesopores of 2–50 nm pore diameter are favorable for the transport of bulky ions of non-aqueous electrolytes. This study was conducted to produce soft carbon having high surface area and which is rich in mesopores for supercapacitor application. For the formation of mesopores on soft carbon, the reduction of metal ions in the precursor has been expected, with subsequent aggregation to metal nanoparticles during heat-treatment. To assure the dissolution of metal salt, a nitrogen-rich precursor obtained using the condensation of quinoline, denoted as “quinolone pitch” in a preparation report,10 has been selected. The graphitic, porous characteristics and the electrode properties of a new type of mesoporous soft carbon are preliminarily reported from results of the present study.

2. Experimental

The precursor, quinolone pitch, has been prepared fundamentally according to an earlier report,10 with modification of some conditions. Quinoline and four times larger mass of aluminum chloride were stirred for 30 min at 543 K in nitrogen flow. Polyaromatic resin of a dark brown color was obtained after the mixture was washed with 0.1 mol dm⁻³ hydrochloric acid (diluted from 1.0 mol dm⁻³ solution, Kanto Chemical Co., Inc., Japan). The resin-like material, quinolone pitch, softens at around 480 K. A typical gravimetric ratio C:H:N:O (in differential) for the obtained quinolone pitch was 73:5:9:13, indicating that this polyaromatic resin is rich in nitrogen.

The preparation of porous carbon from the quinolone pitch includes the steps of carbonization of a mixture of the quinolone pitch with 15 wt% nickel acetate and the removal of nickel from the obtained coke by washing with hydrochloric acid. The carbonization condition has been optimized, with the mixture first heated at 473 K 1 h and subsequently at 773 K 1 h under Ar flow. A coke containing reduced metal nanoparticles was expected to be obtained at this stage. The obtained coke was washed with 1.0 mol dm⁻³ hydrochloric acid (Kanto Chemical Co., Inc.) at 333 K, dried under open air overnight, and heated at 1273 K under Ar flow. The product in this stage is hereinafter denoted as NiTSC.

The crystal structure of NiTSC was evaluated using X-ray diffraction (Ultima IV Protec tus; Rigaku Corp., Japan) at the scanned 2-theta range of 10–90 degree. The microscopic structure of NiTSC was observed further using transmission electron microscopy (TEM, JEM-2100; JEOL Ltd., Japan). The surface and pore properties of NiTSC were monitored using nitrogen adsorption
(NOVA9000; Quantachrome Instruments) and Brunauer–Emmett–Teller (BET) analyses together with Barrett–Joyner–Halenda (BJH) modification. The electrode properties of NiTSC were monitored using cyclic voltammetry. For those measurements, a sealed three-electrode cell was assembled with molded NiTSC with 5 wt% of acetylene black (Denki Kagaku Kogyo K.K., Japan) and 10 wt% of PTFE (DuPont-Mitsui Fluorochemicals Co., Ltd., Japan), pressed on a stainless steel current collector as the working electrode, a platinum wire as a counter electrode, and Ag/Ag⁺ as a reference electrode. They were in 1.0 mol dm⁻³ LiPF₆ (Battery grade; Kishida Chemical Co., Ltd., Japan) in ethylene carbonate (EC)-dimethyl carbonate (DMC) electrolyte solution (volumetric ratio of EC:DMC = 1:1, Kishida Chemical Co., Ltd.) in a glove box filled with Ar. The cyclic voltammetry measurement was conducted with a potentiosstat (1286; Solartron Analytical) under a scan rate of 2.0 mV s⁻¹, with potential of −1.0 to 1.0 V. In some cases, the “electrochemical activation” process, anodic oxidation to 1.5 V potentiodynamically under a scan rate of 2.0 mV s⁻¹ was applied as a pretreatment using the same cell configuration.

3. Results and Discussion

The TEM image of the coke from the mixture of quinolone pitch and nickel acetate is shown in Fig. 1(a). Mainly amorphous features are observable. Inside the amorphous structure, black spots having ca. 10 nm diameter are dispersed. These spots are assigned to nanoparticles of nickel metal by energy dispersive X-ray spectroscopy (EDX). As expected, the coke has a mainly amorphous carbon structure with nickel nanoparticles dispersed in the coke. A typical TEM image of NiTSC after washing out of nickel and further heat treatment is shown in Fig. 1(b). Hollow figures with ca. 10 nm diameter surrounded by stacking of graphitic planes with moires are observable instead of black spots. The X-ray diffraction pattern of NiTSC is portrayed in Fig. 1(c). Rather sharp peaks are observable at 26.0° and 44.1°, assigned to (002) and (101) diffractions from graphite. The X-ray diffraction pattern indicates that NiTSC has developed a graphitic structure, which corresponds to the stacking structure in the TEM image. Furthermore, no peak of nickel metal is observable, indicating the absence of the nickel metal in NiTSC. These structural changes suggest that the nickel acetate dissolved in quinolone pitch is reduced to metallic nickel with aggregates to nanoparticles with 10 nm, as expected. These nickel particles are removed almost entirely by subsequent washing. The hollows after nickel removal remain after the second heating. The hollows might provide structural stress during carbonization and might cause the characteristic graphitic stacking surrounded with hollows.

Nitrogen adsorption and desorption isotherms, and the pore size distribution estimated from the isotherms for NiTSC are shown in Fig. 1(d) and 1(e), respectively. The isotherm with hysteresis corresponds to the type IV isotherm by IUPAC classification. Thus the material has a mesoporous structure. The steep rise of adsorbed nitrogen at the low pressure end and the subsequent gradual increase suggest the mesoporous nature of NiTSC. The specific surface area and pore volume are, respectively, 169 m² g⁻¹ and 0.23 cm³ g⁻¹. The modal pore diameter is 3.7 nm. The mesoporous feature of NiTSC is clearly displayed in the pore size distribution. The specific surface area of NiTSC is significantly larger compared with a soft carbon obtained from quinolone pitch without nickel acetate (6 m² g⁻¹) by the introduction of mesopores. Although the surface area and pore volume are lower than that of conventional activated carbon, NiTSC has a designed mesoporous structure.

The cyclic voltammograms of NiTSC in 1.0 mol dm⁻³ LiPF₆/EC-DMC electrolyte (a) before and (b) after “electrochemical activation” pretreatment are shown in Fig. 2. They show that NiTSC exhibits a rectangular voltammogram that is similar to that of a typical porous carbon electrode. At the potential range applied here, NiTSC clearly works stably. Small redox signs around −0.4 V and 0.2 V might reflect that the contribution from nickel species remained in a small amount even after washing processes. The specific capacitance of NiTSC calculated from this voltammogram is 11 F g⁻¹, a rather low value reflected from the lower surface

Figure 1. (a) TEM image of the heat-treated product of the mixture of quinolone pitch with nickel acetate at 773 K. (b) TEM image of the NiTSC after heat-treatment at 1273 K. (c) X-ray diffraction pattern of NiTSC. (d) Nitrogen adsorption–desorption isotherm of NiTSC. (e) Pore size distribution profile of NiTSC.

Figure 2. Cyclic voltammograms of NiTSC electrode before and after anodic oxidation. Electrolyte: 1 mol dm⁻³ LiPF₆/EC-DMC, scan rate: 2.0 mV s⁻¹.
area compared with that of conventional activated carbon. The capacitance value is reasonable for NiTSC having specific surface area that is one-tenth of that of activated carbons. Therefore, even if the redox reaction of nickel exists, the pseudo-capacitive contribution is minor. “Electrochemical activation” treatment clearly increases the charging current on the voltammogram. The specific capacitance also increases to 24 F g⁻¹. This capacitance improvement indicates that NiTSC has characteristics of soft carbon also in terms of electrode behavior. The extent of the capacitance increase is limited, probably because of the lack of a pre-treatment which has been conducted in previous cases. Although the authors expected that the acid treatment to remove nickel nanoparticles had also an effect to activate the surface of NiTSC sufficiently for accepting electrochemical activation, such an effect appears to be limited.

At the present stage, the specific capacitance is far smaller than those of conventional activated carbons even after the electrochemical activation, probably because of the graphitic edge structure of NiTSC may not be suitable for the insertion of ions as well as its limited pore space for ion accommodation. As indicated in previous papers, the effective electrochemical activation of a soft carbon electrode requires chemical pre-treatment. To achieve sufficient capacitance for practical application, the surface and pore structures of templated soft carbon must be further optimized. The main concern at the present, preliminary stage is to propose a potential strategy of the metal-particle template carbonization for the preparation of high-surface-area soft carbon materials.

References

1. H. Marsh and F. Rodriguez-Reinoso, *Activated Carbon*, Elsevier, London (2006).
2. C. H. Kim, D. K. Lee, and T. J. Pinnavaia, *Langmuir*, 20, 5157 (2004).
3. A. B. Fuertes and T. A. Centeno, *J. Mater. Chem.*, 15, 1079 (2005).
4. B. Cao, H. Liu, B. Xu, Y. Lei, X. Chen, and H. Song, *J. Mater. Chem. A.*, 4, 6472 (2016).
5. S. Mitani, S. I. Lee, K. Saito, S. H. Yoon, Y. Korai, and I. Mochida, *Carbon*, 43, 2960 (2005).
6. T. Aida, I. Murayama, K. Yamada, and M. Morita, *J. Power Sources*, 166, 462 (2007).
7. T. Ohta, I. T. Kim, M. Egashira, N. Yoshimoto, and M. Morita, *J. Power Sources*, 198, 408 (2012).
8. I. T. Kim, M. Egashira, N. Yoshimoto, and M. Morita, *Electrochemistry*, 80, 415 (2012).
9. M. Morita, R. Arizono, N. Yoshimoto, and M. Egashira, *J. Appl. Electrochem.*, 44, 447 (2014).
10. I. Mochida, K. H. Ahn, and Y. Korai, *Carbon*, 33, 1069 (1995).