



Preparation and Li⁺ storage properties of hierarchical hollow porous carbon spheres



Xiaofeng Wu^a, Wenxiang Tang^{a,b}, Kejia Jiao^{a,b}, Yunfa Chen^{a,*}

^a State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Hollow ordered porous carbon spheres (HOPCS) with a hierarchical structure were prepared by templating with hollow ordered mesoporous silica spheres (HOMSS). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that HOPCS exhibited a spherical hollow morphology. High-resolution TEM, small angle X-ray diffraction (SAXRD) and N₂ sorption measurements confirmed that HOPCS inversely replicated the unconnected hexagonal-stacked pore structure of HOMSS, and possessed ordered porosity. HOPCS exhibited a higher storage capacity for Li⁺ ion battery (LIB) of 527.6 mA h/g, and good cycling performance. A large capacity loss during the first discharge–charge cycle was found attributed to the high content of micropores. The cycling performance was derived from the hierarchical structure.

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1. Introduction

Nanostructured carbon-based materials with desirable structures have attracted much interest, because of their adjustable chemical and physical properties, and potential in catalyst supports, gas hosts, and energy storage (Cheng, Tao, Liang & Chen, 2008; Joo et al., 2001; Largeot et al., 2008; Li, Yang, Shi, & Ruan, 2008; Long, Dunn, Rolison, & White, 2004; Ryoo, Joo, Kruk, & Jaroniec, 2001; Subramanian, Zhu, & Wei, 2006; Wang, Liu, Zhao, & Jiang, 2004; Xia & Mokaya, 2004, 2005; Zhou, Zhu, Hibino, Honma, & Ichihara, 2003). Because of these applications, many recent studies have reported the design and fabrication of nanostructured carbon materials with various dimensions, morphologies, and microstructures (Cheng et al., 2008; Long et al., 2004; Wang et al., 2004; Zhou et al., 2003). Nanostructured carbon materials with three-dimensional (3D) porous frameworks are good candidates for anodic Li storage materials, which require a high energy density and high-rate capacity (Wang et al., 2004; Zhou et al., 2003). Such materials possess more electrochemical active sites and shorter ion diffusion paths than their natural or conventional pyrolyzed counterparts (Cheng et al., 2008; Dahn, Zheng, Liu, & Xue, 1995; Long et al., 2004; Xu, 2004; Zhou et al., 2003). However, problems associated with 3D nanostructured carbon materials include a

large capacity loss and decreasing cycling capacity. These are due to the irreversible formation of a solid electrolyte interphase (SEI) and significant exposed hydrogen atoms on the carbon surface (Cheng et al., 2008; Zhou et al., 2003). The electrochemical behavior of porous nanostructured carbon materials strongly depends on the template used. The material's textural properties, including porosity, pore size, and tortuosity, can significantly influence electrolyte diffusion, electrode reactions, and current exchange (Cheng et al., 2008; Long et al., 2004). Despite abundant active sites from a large surface area, well-developed micropores hinder electrolyte penetration and ionic diffusion, thus deteriorating the electrochemical performance (Cheng et al., 2008). The design and tailoring of 3D porous architectures of nanostructured carbon materials remains challenging, and a topical focus for improving their Li⁺ storage properties.

Ordered mesoporous carbon (OMC) are a 3D nanostructured carbon material of interest because of their high specific storage capacity and good cycling ability in LIBs (Cheng et al., 2008; Long et al., 2004; Zhou et al., 2003). OMC synthesis involves the infiltration of carbon precursors into template pores, subsequent polymerization and carbonization of the precursors, and finally the removal of the template (Li et al., 2008; Ryoo et al., 2001; Wang et al., 2004; Zhang et al., 2002; Zhou et al., 2003). The microstructure of the carbon replica depends on that of the ordered mesoporous silica (OMS) or aluminosilicate (OMAS) template used (Li et al., 2008; Ryoo et al., 2001). A key factor in fabricating OMCs is interconnecting the stacked OMS or OMAS

* Corresponding author.

E-mail address: yfchen@mail.ipe.ac.cn (Y. Chen).

mesopores (Joo et al., 2001; Ryoo et al., 2001; Xia & Mokaya, 2005; Zhang et al., 2002). Achieving this produces bridges for supporting the 3D carbon framework after template removal. Various OMCs have been reported from this templating procedure, using different OMS/OMAS templates including MCM-48 (Ryoo et al., 2001), SBA-15 (Joo et al., 2001; Ryoo et al., 2001; Zhang et al., 2002; Zhou et al., 2003), SBA-1 (Ryoo et al., 2001), and FDU-5 (Wang et al., 2004). MCM-41 silica is generally considered unsatisfactory for constructing OMCs, because its unconnected hexagonal-packed mesopores result in collapse of the subsequent carbon structure (Joo et al., 2001; Ryoo et al., 2001; Xia & Mokaya, 2005; Zhang et al., 2002). To the best of our knowledge, only one study has reported fabricating OMCs using MCM-41 silica, in which microwave digestion pre-treatment before carbon precursor infiltration was required to produce micropores within the mesoporous walls (Tian et al., 2003). Directly preparing OMCs using silica with unconnected MCM-41 hexagonal porous structures has not been reported.

Herein, hollow ordered mesoporous silica spheres (HOMSS) containing a hierarchical structure of MCM-41 silica with a mesoporous shell were prepared as previously reported (Wu et al., 2007). Hollow ordered porous carbon spheres (HOPCS) containing a hierarchical structure were then fabricated by chemical vapor deposition (CVD) of methane. The Li^+ storage properties of HOPCS were investigated to gauge its potential in electrode materials and probe the relationship between electrode microstructure and storage.

2. Experimental

2.1. Synthesis of HOMSS and HOPCS

HOMSS was prepared as previously reported (Wu et al., 2007): In brief, 0.5 g of monodisperse polystyrene particles ($\sim 1 \mu\text{m}$ diameter, 5% size deviation) were dispersed in 68 mL of absolute ethanol by supersonic oscillation for 30 min. The obtained suspension was added to 50 mL of 0.14 mol/L aqueous cetyltrimethylammonium bromide (Beijing Chemical Reagents Co. Ltd), and the mixture stirred at room temperature for 1 h. The pH was adjusted to 13 with 25 wt% ammonia (Beijing Chemical Reagents Co. Ltd), and 3.14 mL of tetraethyl orthosilicate (Beijing Chemical Reagents Co. Ltd) was added. The mixture was stirred at room temperature for 10 h, hermetically aged at 80°C for 48 h, centrifuged, and the resulting white product was successively washed with distilled water and centrifuged three times. After drying, the powder was heated to 550°C in air at a rate of $1^\circ\text{C}/\text{min}$, and held there for 2 h to remove organic components. The powder was then used as a template for synthesizing HOPCS.

HOPCS was prepared in a CVD apparatus, comprising a horizontal tube furnace and quartz tube reaction chamber. Silica powder was transferred and uniformly dispersed in a clean alumina boat, in the center of the quartz tube. The carbon source and carrier gas were methane and hydrogen, respectively. The temperature was raised to 950°C under a 100 mL/min nitrogen flow rate, and methane was introduced into the reactor. Pyrolyzed carbon was deposited for 2 h at 950°C , under a 9:1 $\text{CH}_4:\text{H}_2$ atmosphere. The furnace was cooled to room temperature using a nitrogen flow. Resulting black powders were dispersed in 10% HF and stirred for 24 h. The mixture was centrifuged, washed with distilled water until the pH was near neutral, centrifuged again, and dried at 120°C for 24 h under vacuum. The sample was cooled to room temperature and used for measuring electrochemical performance. Elemental analysis and energy-dispersive X-ray analysis indicated negligible residual silica.

2.2. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a JEM 2010F instrument, operated at 200 kV. Scanning electron microscopy (SEM) images from a JSM-6700F (JEOL) instrument were used to characterize surface morphologies using field emission. Small angle X-ray diffraction (SAXRD) data from powder samples was collected on an X'Pert Pro diffractometer. N_2 sorption measurements were conducted on a Quantachrome Autosorb-1-MP automated gas adsorption system, with a degassing temperature of 300°C .

2.3. Electrochemical measurements

Electrochemical properties of HOPCS were investigated using a two-electrode Swagelok-type cell. The working electrode was prepared by mixing HOPCS and polytetrafluoroethylene (Aladdin® Shanghai Co. Ltd) in a 9:1 HOPCS:PTFE weight ratio. The counter electrode was Li foil (China Energy Lithium Co. Ltd), and the electrolyte was 1 mol/L lithium hexafluorophosphate in 1:1:1 volume ratio ethylene carbonate:diethyl carbonate:dimethyl carbonate (Shenzhen Capchem Technology Co. Ltd.). The LIB was assembled in an Ar-filled glove box. Discharge-charge measurements were performed on a cell measurement system (Land, CT 2001A). The voltage range was 0–2 V, at a constant current density of $0.1 \text{ mA}/\text{cm}^2$.

3. Results and discussion

3.1. Morphologies and structures

SEM and TEM images of the HOMSS morphology and microstructure are shown in Fig. 1. Fig. 1(a) shows that HOMSS is composed of free-standing spheres with uniform diameters of $\sim 1.2 \mu\text{m}$. The presence of crevasses suggests hollow interiors, consistent with the TEM image in Fig. 1(b). Contrast from electron beam transmission confirms hollow cores of $\sim 1 \mu\text{m}$ in diameter and 100 nm in thickness. The shell microstructure and ordering was investigated using HRTEM, as shown in Fig. 1(c) and (d). Along the direction of electron beam transmission, the selected area (rectangular box in Fig. 1(b)) exhibits clearly alternating contrast in electron beam density. Specifically, hexagonal-arranged white dot lattices (circle in Fig. 1(c)) indicate ordered stacking channels within shells. Ordered channels are $\sim 2.5 \text{ nm}$ wide and are likely arranged along the radial direction of a single HOMSS sphere. This is supported by the white dot lattices observed in Fig. 1(c), when the electron beam is transmitting through the shell microchannels (Blas et al., 2008; Djojoputro et al., 2006). The channels are not thought to coexist parallel or perpendicular to shells (Botterhuis, Sun, Magusin, van Santen, & Sommerdijk, 2006; Tan & Rankin, 2005). The structure's porosity is confirmed by the HRTEM image of the shell fringe in Fig. 1(d) (circle in Fig. 1(b)). A largely parallel porous structure is observed at the shell's external fringe. The SAXRD pattern in Fig. 2(a) shows a strong diffraction at $2\theta = 2.5^\circ$ and a broad weak peak at $4.5\text{--}5.0^\circ$, similar to that of MCM-41 ordered mesoporous silica (Kresge, Leonowicz, Roth, Vartuli, & Beck, 1992; Pauwels, Tendeloo, Thoelen, Rhijn, & Jacobs, 2001; Zeng, Qian, Yin, & Zhu, 2006). The high-angle shift of the (100) diffraction at $2\theta = 2.5^\circ$, and overlapping (110) and (200) diffractions at $2\theta = 4.5\text{--}5.0^\circ$, is attributed to compression of the hexagonal arrangement and subsequent geometrical deformation because of the curvature difference within the spherical shells. This is supported by the discrete domains of hexagonal-packed pores and nonuniform pore wall thicknesses observed in

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