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Hollow-in-Hollow Carbon Spheres for Lithium-ion Batteries with Superior Capacity and Cyclic Performance

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ABSTRACT

Hollow spheres structured materials have been intensively pursued due to their unique properties for energy storage. In this paper, hollow-in-hollow carbon spheres (HIHCS) with a multi-shelled structure were successfully synthesized using a facile hard-templating procedure. When evaluated as anode material for lithium-ion batteries, the resultant HIHCS anode exhibited superior capacity and cycling stability than HCS. It could deliver reversible capacities of 937, 481, 401, 304 and 236 mAh g^{-1} at current densities of 0.1 A g^{-1}, 1 A g^{-1}, 2 A g^{-1}, 5 A g^{-1} and 10 A g^{-1}, respectively. And capacity fading is not apparent in 500 cycles at 5 A g^{-1}. The excellent performance of the HIHCS anode is ascribed to its unique hollow-in-hollow structure and high specific surface area.

1. Introduction

Currently, rechargeable lithium ion batteries (LIBs) have been widely used as the power source in portable electronic devices and electric vehicles [1,2]. Electrode materials are the determining factor for the battery performance. Although graphite performs well as the anode material for commercial LIBs, its theoretical capacity (372 mAh g^{-1} for the nominal composition LiC_6) and relatively low lithium diffusion coefficient (10^{-7}~10^{-10} cm^2 s^{-1}) are insufficient to satisfy the increasing demand for batteries with higher capacity and rate capability [3–5]. Therefore, continued efforts have been devoted to exploring new anode materials during the past decade.

Based on the improved electrochemical performance and structure stability during discharge/charge processes, carbonaceous nanomaterials are still the preferred choices. It is believed that morphology and structure are important factors for the electrochemical performance of the carbonaceous nanomaterials. Many carbon nanoarchitectures, such as nanotubes, nanosheets, and nanospheres, have been used to fabricate high-preformance anodes [6–9]. Among these materials, hollow carbon spheres (HCS) are thought to be profitable for achieving improved performance owing to their high surface area and short path length for Li transport [10–12]. It is well-known that high surface area can accommodate extra lithium ions at the electrode surface and in the inner cavities and a reduced lithium transport path length can allow better reaction kinetics, resulting in improved capacity and rate performance [13,14]. For instance, Tang et al. synthesized the monodisperse hollow carbon nanospheres via a combined polystyrene latex/hydrothermal carbonization templating approach. A high rate performance of ca. 100 mAh g^{-1} at 50 C (18.6 A g^{-1}) was achieved [12]. However, compared with solid structures, the low packing density of HCS originated from its large empty space usually leads to the low volumetric energy density, which is undesirable for practical applications. As a special class of hollow structures, multi-shelled hollow structures have recently attracted increasing attention since they can significantly reduce lithium ions and electrons diffusion paths, meanwhile increase the volumetric capacity [15]. When used as the anode materials for Li-ion batteries, hollow metal oxide spheres with a multi-shelled structure exhibited excellent rate capability, good cycling performance, and ultrahigh specific capacity [16–20]. From the viewpoint of fundamental research and practical application, the multi-shelled hollow structures provide new opportunities to upgrade the electrochemical performance of LIB anodes.

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Herein, we utilized a facile hard-templating route to synthesize a hollow-in-hollow structured carbon spheres (HIHCS). The as-sythesized HIHCS has a uniform multi-shelled structure and high specific surface area. These characteristics make HIHCS a potential anode material for lithium ion batteries. Compared with HCS, the multi-shelled structure endowed HIHCS with much higher capacity and rate capability

2. Experimental

2.1. Synthesis of HCS and HIHCS

HCS and HIHCS were prepared by a facile hard-templating method [21]. The starting material SiO_2 spheres were obtained by the hydrolysis of tetraethyl orthosilicate (TEOS) in a mixture containing ethanol and ammonium aqueous solution. After treated with the resorcinol formaldehyde resin (RF) coating process and silica coating process in sequence, the SiO_2 spheres were converted into SiO_2@RF@SiO_2 spheres or SiO_2@RF@SiO_2@RF@SiO_2 spheres. The procedures for RF coating and silica coating were carried out according to Ref. [22] and [23].

Subsequently, the as-synthesized SiO_2@RF@SiO_2 spheres and SiO_2@RF@SiO_2@RF@SiO_2 spheres were further sintered to achieve the intermediates SiO_2@C@SiO_2 spheres and SiO_2@C@SiO_2@C@SiO_2 spheres under nitrogen atmosphere at 800 °C for 2 h with a heating rate of 1.5 °C/min. After washing with a 10% HF aqueous solution for one day, the intermediates were converted into HCS and HIHCS, respectively.

2.2. Characterization

Product morphologies were observed on a Hitachi S-4800 scanning electron microscopy (SEM) with a field-emission electron gun. Transmission electron microscopy (TEM) images were taken on a TECNAI F-30 high-resolution transmission electron microscope operated at 300 kV. The structure was characterized by X-ray powder diffraction (XRD, Philips Panalytical X-pert) using Cu Kα1 radiation $\lambda = 1.5405$ Å. Nitrogen adsorption and desorption isotherms were measured at 77 K with a Micrometrics ASAP 3020 system. The specific surface area and pore size distributions of HCS and HIHCS were obtained by the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method, respectively.

2.3. Electrochemical Measurements

Two-electrode CR2016 type coin cells were used to evaluate the electrochemical performance of the products. The working electrode was made up by 80wt% active materials, 10wt% Super P Li and 10wt% poly(vinylidenedifluoride) (PVDF). The current collector was copper foil and the counter electrode was Li foil. Celgard 2400 polypropylene membrane was utilized as the separator. The electrolyte was 1 M $LiPF_6$ in a 1:1:1 v/v/v mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (Zhuhai, China). The cells was assembled in an Ar-filled glovebox with the concentrations of moisture and oxygen below 1.0 ppm. The cells were galvanostatically charged and discharged between 0.01 V and 3.0 V vs. Li/Li^+ using a BTS Battery test system (Neware, Shenzhen, China) under various current densities (100 mA g^{-1}, 500 mA g^{-1}, 1 A g^{-1}, 2 A g^{-1}, 5 A g^{-1}, and 10 A g^{-1}). Electrochemical impedance spectrometry (EIS) tests were performed on IM6 (Zahner elektrik) in the frequency range from 100 kHz to 100 mHz.

3. Results and discussion

Fig. 1 presents the typical hard-templating procedure for the synthesis of HCS and HIHCS. Firstly, the SiO_2 spheres were coated with RF resin and silica to form a sandwich-like SiO_2@RF@SiO_2 spheres [22]. Secondly, according to the same procedure, SiO_2@RF@SiO_2@RF@SiO_2 spheres were obtained by using the SiO_2@RF@SiO_2 spheres as the templates. The weight ratio of inner layer RF precursors and outer layer RF precursors in SiO_2@RF@SiO_2@RF@SiO_2 spheres was 1:1. Finally, after the carbonization under N_2 atmosphere and the subsequent removal of SiO_2, the-synthesized SiO_2@RF@SiO_2 spheres and SiO_2@RF@SiO_2@RF@SiO_2 spheres were converted into HCS and hollow-in-hollow structured HIHCS, respectively.

Generally, SEM and TEM were used to characterize the morphology and structure of HCS and HIHCS. As shown in Fig. 2a, uniform HCS has a well-defined spherical morphology with an average diameter of ~300 nm. The TEM image of HCS (Fig. 2b) further indicates that the HCS possesses a uniform hollow structure. The void volume of HCS conforms with the original SiO_2 template size (see Supplementary Materials, Fig. S1). Whilst the average thickness of the porous carbon shell in HCS is ca. 30 nm. Additionally, the external surface of HCS is clean and smooth, indicating no impurities left over the carbonization process. High-

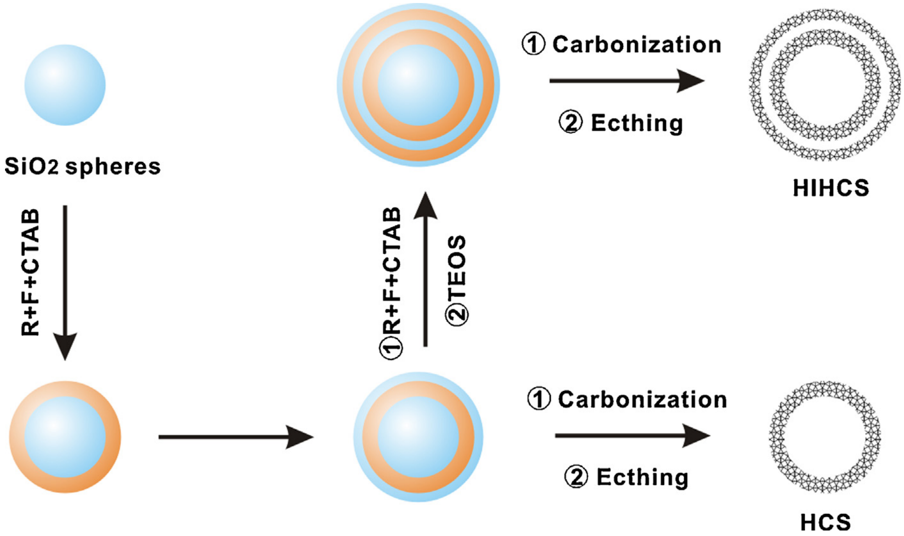

Fig. 1. Schematic illustration: the hard-templating procedures for the synthesis of HCS and HIHCS.