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Full paper

Rational design of Si@carbon with robust hierarchically porous custard-apple-like structure to boost lithium storage

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ABSTRACT

In this work, we have developed a simple approach to rationally design and controllably synthesize custard-apple-like Si@N, O-dual-doped carbon with hierarchical porosity. This material delivers outstanding reversible capacity at high current density with good rate capability and a long cycling life of over 4000 cycles as an anode for Li-ion batteries. A detailed eletrochemical kinetic analysis reveals that the lithium ion charge storage partly depends on the capacitance-controlled behavior, with a high capacitive contribution up to 30.3% for the total capacity at 1 mV s^{-1}. The impressive eletrochemical performance demonstrates that the Si@mNOC anode has great potential to meet the challenges arising from the use of Si nanoparticles as anode for next-generation large-scale energy storage.

1. Introduction

For further development of high-performance lithium ion batteries (LIBs) to make them suitable for large-scale applications in electric vehicles and grid-scale energy storage systems that require high energy and power density, excellent rate capability, and long cycling life, many efforts have been devoted to studying battery systems, and especially, anode and cathode materials [1–4]. The anode plays a crucial role by acting as a reversible storage depot for lithium ions [3,5–7]. Different anode materials prepared by various strategies have been proposed to replace the current commercial graphite anode [3,5]. Si has been believed to be one of the most promising candidates due to its low discharge potential (~ 0.5 V vs. Li/Li^+) and because it has the highest theoretical capacity per unit mass, providing a greater capacity compared with graphite anode [8–11]. Additionally, its other appealing characteristics, including environmental benignity and abundance, make it one of the most attractive anode materials for LIBs. Nevertheless, commercial applications of Si-based anode have been impeded by its poor kinetics, including low ionic diffusion and electrical conductivity, and the huge volume changes (about 400%) that occur in the charging/discharging processes [12,13]. Also, the volume changes will inevitably cause the cracking and reformation of unstable solid electrolyte interphase layers (SEI), and harmful pulverization, resulting in fast capacity fading and poor rate capability [14–16].

To meet these challenges, a wide range of material design concepts has been proposed and developed, mainly including two strategies: utilizing conducting materials to improve conductivity and nanotechnology to reduce mechanical fracturing [5,14,17–22]. In particular, nanoscale Si materials with nanotubular and porous structures were developed to avoid mechanical fracturing and increase electrochemical activity [5,17,23]. Among them, a perfect design, the Si-C yolk-shell structure, was initially proposed with interior void space, which can accommodate the volume changes [3]. Also, the carbon shell will prevent the continual rupturing of the SEI. Similar concepts were further proposed and confirmed, including pomegranate-like structures [24] and graphene cages on particles [1]. In another strategy, conducting materials such as carbon, graphene, or polymer were combined with silicon to facilitate electronic and ionic transportation, as well as good cycling performance [12,25,26]. In addition, a variety of new binders such as alginate, gum arabic, and self-healing polymers have been explored to enhance the electrochemistry of Si anode [27–29].

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Despite these impressive advances in silicon anodes, several critical challenges must still be overcome, including poor rate capability and cycling stability at high current density, which is due to the low ionic and electrical conductivity of silicon. With regards to improving their electrical conductivity, recently, heteroatom doping of carbon has emerged as one of the most effective and significant strategies. N, S, and O have already been used as dopants to modify the electronic and crystalline structures of carbon, facilitating a great increase in its electrochemical performance [30–33]. In particular, O, N-dual-doping has been demonstrated as the most effective method due to the natural characteristics of these elements, such as small atomic diameter, high electronegativity, and additional free electrons contributing to the conduction band of carbon [30,31]. Additionally, the doping could increase the surface hydrophilicity of carbon-based electrodes, leading to additional improvement to the lithium storage [30,31,34]. Another focus, improving the kinetics of ion diffusion, could be resolved by utilizing hierarchical porous structure with interconnected micropores, macropores, and mesopores [34–36]. By adopting hierarchical porosity, the ionic diffusion distance could be remarkably reduced to a thin dimension. The Si materials with the above characteristics would demonstrate synergistic effects towards improving lithium storage.

Compared with diffusion-controlled processes (insertion, conversion, and alloying), capacitive charge storage allows faster charging rates and higher power density. The highly porous carbon has high accessible surface area, so that it can form electrical double-layers, suitable pore channels to favour the diffusion of electrolyte ions, and good conductivity for the rapid transport of electrons [37]. Application of N, O doped carbon can induce a favorable pseudocapacitance effect [34,38].

Herein, we demonstrate a facile method to prepare a custard-apple-like silicon@N, O-doped carbon hierarchical porous structure (denoted as Si@mNOC, with m = mesoporous). The custard-apple-like Si-mNOC composite can be expected to deliver good electrochemical performance in terms of stable cycling at high current density and outstanding rate capability. The use of electrochemical kinetic analysis enabled us to explore the nature of the charge storage process. The diffusion-controlled process and the capacitance-type reaction can work together to endow the anode material with outstanding electrochemical characteristics, especially at high current density.

2. Experimental section

2.1. Synthesis of Si@SiO_2 nanoparticles

For the SiO_2 coating layer with thickness of about 10–20 nm, 0.1 g commercial silicon nanoparticles (Hongwu Nano, Inc.) were dispersed in a beaker with 70 mL deionized water and 280 mL ethanol under constant ultrasonication for 50 min at room temperature and then stirred for 20 min. Then, a suitable amount of ammonia (25–28%) was added to the above solution. The coating layer was formed after 0.2 mL tetraethyl orthosilicate (TEOS, 28.4%) was added dropwise and allowed to react for 2 h under vigorous stirring. The resultant Si@SiO_2 sample was collected by centrifugation and washed four times with ethanol.

2.2. Synthesis of Si@mNOC custard-apple-like composite

Typically, the Si@SiO_2 sample was dispersed in 15 mL deionized water under ultrasonication for 40 min. After sonication, 2.5 mL HCl (1 M) was added slowly under stirring. Then, 0.2 mL aniline was dispersed into the above dispersion by stirring for 30 min. Subsequently, 0.5 g ammonium persulfate (APS) dissolved in 1 mL HCl (1 M) was added dropwise under vigorous stirring for 24 h to the above dispersion in an ice bath. The Si@SiO_2@PANI sample was obtained after centrifugation and washing three times with deionized water, followed by drying at 60 °C overnight. The final Si@mNOC sample was obtained after heat-treatment at 800 °C for 4 h under flowing N_2 gas, with a heating rate of 2 °C/min, and HF etching.

2.3. Synthesis of Si@C nanoparticles

For comparison purposes, Si@C nanoparticles were also prepared by carbonization of Si@resorcinol-formaldehyde resin (RF) at 800 °C in flowing N_2 gas. To prepare Si@RF, 20 mg Si and 61 mg hexadecyltrimethylammonium bromide (CTAB) were dispersed in 28 mL deionized water under ultrasonication for 30 min. Afterwards, 11.28 mL ethanol, 0.28 g resorcinol, 0.1 mL ammonia, and then 0.4 mL of formaldehyde were added under stirring. Then the Si@RF precursor was obtained after stirring for 6 h at 35 °C.

2.4. Materials characterizations

The crystal structure of the as-prepared samples was characterized by X-ray diffraction (XRD) (D/max 2500V, Rigaku, Cu Kα radiation, $\lambda = 1.5406$ Å). The structures and morphologies were observed with a field-emission scanning electron microscope (FESEM; JEOL JSM-7500FA) and a transmission electron microscope (TEM; JEM-2011F). Elemental mapping was conducted on the X-ray spectrometer attached to the TEM. Thermogravimetric analysis (TGA) was performed on a thermal analyser (TAI/DSC Q2000) at a heating rate of 10 °C from room temperature to 800 °C under flowing air. The Raman spectrum of the dried Si@mNOC was collected using a Renishaw System 1000 micro-Raman spectrometer. The N_2 adsorption-desorption isotherms were collected using a Quantachrome Instruments Autosorb AS-6B. The specific surface area and pore size distribution of the as-prepared material were analysed based on the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. X-ray photoemission spectroscopy experiments were performed at the Catalysis and Surface Science End station at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.

2.5. Electrochemical characterizations

The working electrode was prepared by mixing the active materials, carbon black, and poly(vinylidene difluoride) (PVDF) binder in N-methyl pyrrolidone (NMP) in a weight ratio of 7:2:1 to form a homogeneous slurry. Afterwards, the slurry was pasted onto copper foil. After drying at 80 °C in vacuum overnight, the electrode was ready for use. The 2032-type half cells, consisting of the active materials as the working electrode, Li foil as the counter and reference electrode, a Celgard 2300 membrane as the separator, and 1 M $LiPF_6$ in a 3:4:3 (v/v/v) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) as the electrolyte, were assembled in an Ar-filled glove box (H_2O, O_2 $<$ 0.1 ppm, Mbraun, Unilab, USA). Galvanostatic measurements were performed on a Land Battery Measurement System (Land, China) in the voltage range of 0.01–3 V. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were conducted on an electrochemical workstation (CHI 760D).

3. Results and discussion

The synthesis strategy is schematically depicted in Fig. 1a. In the first step, silica layers are uniformly deposited on the silicon nanoparticles using the sol-gel method. Considering the diameter of Si used here (about 30–50 nm) and the volume change of Si in the discharging process, the thickness of about 20 nm is enough for volume expansion. Afterwards, the as-prepared Si@SiO_2 core-shell spheres are mixed with aniline in HCl solution to start the polymerization and self-assembly processes, and are finally subjected to calcination and HF etching. During the self-assembly, significantly, the silica layer not only functions as a sacrificial pore-forming agent to produce a tunable interior