



Hollow silica spheres with facile carbon modification as an anode material for lithium-ion batteries

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ABSTRACT

Hollow silica (H-SiO₂) spheres are prepared via a self-assembly approach without sacrificial templates. To address the poor electrical conductivity and mechanical stability problems of H-SiO₂, carbon coating is adopted to modify the H-SiO₂ spheres through a facile solution-mixing method. In the obtained micron-level H-SiO₂/C composite, the carbon coating layer can act as a mechanical support layer to maintain the structure stability of the H-SiO₂ spheres, while the inner hollow space can accommodate the volume expansion during cycling. Moreover, the N-doped carbon can provide a fast electron transfer channel for the H-SiO₂/C electrode during lithiation/delithiation process, helping the electrode exhibiting significantly improved cycling and rate performance. The reversible capacity of the H-SiO₂/C electrode after 400 cycles is 564.0 mA h g⁻¹ at a current density of 200 mA g⁻¹, with a capacity retention of 88.3% as against the first cycle. The electrode delivers a reversible capacity of 423.1 mA h g⁻¹, 280.8 mA h g⁻¹ and 190.3 mA h g⁻¹ at the current density of 1 A g⁻¹, 3 A g⁻¹ and 5 A g⁻¹, respectively. This work provides a facile strategy for the large-scale production of H-SiO₂/C anode materials for LIBs.

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1. Introduction

In recent years, lithium-ion batteries (LIBs) and supercapacitors are two types of widely developed energy conversion and storage devices [1–4]. LIBs are characteristic of high energy density, while supercapacitors are famous for high-power density. LIBs are widely used in electric vehicles and portable electronics. With the development of science and technology, the demand for high energy lithium-ion batteries (LIBs) is increasing. As the commercial anode, graphite with a theoretical capacity of 372 mA h g⁻¹ cannot meet the increasing demand for LIBs. For replacing graphite, Silicon has drawn great attention for its large theoretical capacity [5–8]. However, the large volume changes of silicon (~400%) during cycling is a serious problem in application as an anode material, which results in particle pulverization, fast capacity decay and even electrode failure [9–12].

The dioxide of silicon (SiO₂), which has a high theoretical

capacity of 1965 mA h g⁻¹ [13–15] and less volume changes during cycling [16,17], has attracted lots of attention. Moreover, as the major component of sand, SiO₂ is naturally abundant with low price. But, the volume changes during cycling can still effect the long period cycling [14,18]. To address this issue, the idea of hollow structure for SiO₂ is promoted [19–21]. In the hollow structure, the inner hollow space can provide spaces for the volume expansion. However, there are still two problems need to be solved before H-SiO₂ is used as an anode material for LIBs. One is that the hollow structure without an external support material can easily collapse due to the volume changes during lithiation/delithiation process, resulting in capacity fading and battery failure. The other one is the poor electrical conductivity of SiO₂ which leads to low specific capacity and poor rate performance [22,23]. To address the particle collapse and poor electrical conductivity problems, carbon coating is a good choice due to its excellent electrical conductivity, mechanical stability, safety and easy preparation [24–27].

Herein, we use a facile solution-mixing carbon coating approach to prepare the H-SiO₂/C electrode materials, which has an excellent cycling stability and well rate performance. A similar fabrication approach of H-SiO₂ invented by Teng et al. [28] is adopted in this

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paper. Different from the approaches using sacrificial templates in which the preparation and removal of the templates are usually complicated and uneconomic [29–31], there is no need of sacrificial templates in Teng's approach. Polyacrylonitrile (PAN) is chosen as the carbon source. The carbon coating layer can act as a mechanical support layer to maintain the structure stability of the H-SiO₂ spheres during lithiation/delithiation process, allowing for forming a stable solid electrolyte interface (SEI) layer on the H-SiO₂/C electrode, which is beneficial to gaining a higher coulombic efficiency and better cycling stability. The nitrogen element in PAN turns into N-doped carbon, which provides a fast electron transfer channel for the H-SiO₂/C electrode, helping to enhance the electronic conductivity [32] and improve the rate performance of the H-SiO₂/C electrode.

2. Material and methods

2.1. H-SiO₂ hollow spheres

The preparation process is similar to reference [28]. Firstly, 0.6 g cetyltrimethylammonium bromide (CTAB, Beijing Tong Guang Fine Chemical Company) was dissolved in the mixed solution of 120 ml ethanol, 200 ml distilled water and 4 ml concentrated ammonia aqueous solution. Then, 4 ml tetraethoxysilane (TEOS, Beijing Tong Guang Fine Chemical Company) was quickly added in under stirring at 35 °C. After keeping stirring for 24 h, the solution was centrifuged and washed three times with ethanol, gaining the precursor particles.

The precursor particles were dispersed in distilled water and kept stirring at 80 °C for 10 h to remove the CTAB-silicane in the core of the precursor particles. After centrifuging and drying, hollow SiO₂ spheres were obtained and named as H-SiO₂.

2.2. H-SiO₂/C composites

Solution-mixing carbon coating process: Firstly, 200 mg PAN (molecular weight~150,000, J&K Scientific Ltd.) was dissolved in 6 ml *N,N*-dimethyl formamide (DMF, Beijing Tong Guang Fine Chemical Company) solution. Secondly, 120 mg H-SiO₂ spheres were dispersed in the PAN-DMF solution. After uniform mixing and drying, the mixture was thermal-treated under 1000 °C for 2 h under Ar atmosphere at a rate of 10 °C min⁻¹, gaining the H-SiO₂/C composite. Pure carbon sample carbonized from PAN was prepared under the same condition.

2.3. Coin-type cells preparation

The electrode was made up of active material, Super P and Carboxymethyl cellulose (CMC-Na) with a weight ratio of 7: 2: 1 on a Cu foil. The coin-type cells were assembled in an Ar-filled glovebox with a lithium sheet as counter electrode, a Celgard 2300 membrane as separator, and 1 mol L⁻¹ LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) as electrolyte.

2.4. Material characterization

The morphology was observed by field-emission scanning electron microscope (FE-SEM, QUANTA 6000) and transmission electron microscopy (TEM, JEM-2010 instrument). Fourier transform infrared spectroscopy (FTIR) was carried out on IRTTracer-100 spectrometer. X-ray diffraction (XRD, Rigaku Ultima IV-185 with a Cu K α source) technique at a scan rate of 8° min⁻¹ was used to characterize the samples. The elemental states were determined by X-ray photoelectron spectrometer (XPS, PHI QUANTERA-II SXM system with a monochromatized Mg K α radiation source). The N₂

adsorption-desorption isotherm and pore size distribution were measured by an automatic surface area analyzer (3H-2000PA2, BeiShiDe Instrument). Thermogravimetric (TG, Mettler Toledo TGA 851) analysis was tested under air with a heating rate of 10 °C min⁻¹ to 800 °C.

The charge/discharge performance was performed with coin-type cells and measured on a LAND CT2001A battery testing system in the voltage range of 0.01 V–3.0 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed on a CHI 608 1D electrochemical workstation. The CV test was measured with a scan rate of 0.2 mV s⁻¹ between 0.01 V and 3 V.

3. Results and discussion

The schematic illustration of the preparation process for H-SiO₂ spheres is shown in Fig. 1a. In ethanol aqueous solution, CTAB undergoes a self-assembly process. Thus, the SiO₂ nanoparticles generated by the hydrolysis of TEOS [33] can aggregate along with the self-assembled CTAB, gaining the precursor spheres for hollow SiO₂. When the precursor spheres are immersed in warm water, the inner part of the precursor spheres made up of CTAB-silicane can be dissolved [28]. This is because the precursor sphere is formed from the outside towards the middle. The inner part composed of freshly formed SiO₂ nanoparticles dissolves more easily than the shell part. Thus, hollow SiO₂ spheres can be obtained.

The SEM and TEM images of the precursor and H-SiO₂ samples are provided. As seen from Fig. 1b and c, the precursor sample is spherical and solid with a diameter of about 670 nm. For the H-SiO₂ sample in Fig. 1d and e, its diameter is the same as that of the precursor spheres, and it is hollow spheres with a shell thickness of about 135 nm. Fig. 1e shows the selected area electron diffraction (SAED) pattern of H-SiO₂ sample, the characteristic ring certifies the amorphous structure of the H-SiO₂ spheres. The FTIR spectra of the precursor, H-SiO₂ spheres and commercial SiO₂ particles are provided in Fig. 1f. The FTIR spectra of H-SiO₂ contains the characteristic peaks of SiO₂ and CTAB, confirming the existence of CTAB in the shell of H-SiO₂ spheres, which is consistent with the schematic illustration of the H-SiO₂ sphere. It should be noted that no other steps are adopted to remove the CTAB in H-SiO₂ spheres, because the CTAB can be carbonized during the following carbon coating process.

The poor electrical conductivity and particle collapse problems are the major limits for H-SiO₂ spheres being used as an anode material for LIBs. Thus, carbon coating is adopted to enhance the electrical conductivity and the mechanical stability. In the following, the structure and constituents of the carbon modified H-SiO₂ spheres (H-SiO₂/C sample) are firstly studied. As seen from the SEM image in Fig. 2a, the size of the H-SiO₂/C particles are micron-level. In Fig. 2b and c, the TEM image and elemental mapping of H-SiO₂/C particles demonstrate the H-SiO₂ spheres are covered by non-uniform carbon, which is due to the facile solution-mixing carbon coating process. The characteristic ring of SAED pattern of H-SiO₂/C in Fig. 2d demonstrates the amorphous feature of the H-SiO₂/C sample, which states the amorphous feature of the carbon in H-SiO₂/C sample.

The XRD patterns of H-SiO₂ and H-SiO₂/C samples are given in Fig. 2e. For H-SiO₂ and H-SiO₂/C samples, the broad peak at 23° corresponds to the characteristic peak of amorphous SiO₂. For H-SiO₂/C sample, the peak at around 44° owes to the (100) plane of amorphous carbon. Thus, it can be concluded from the XRD results that the carbon in H-SiO₂/C sample is amorphous, which agrees well with the SAED pattern of H-SiO₂/C. In addition, no characteristic peak of silicon is observed in the XRD pattern of H-SiO₂/C, indicating that no carbothermal reduction of silica to silicon occurs

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