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Amorphous-silicon@silicon oxide/chromium/carbon as an anode for lithium-ion batteries with excellent cyclic stability

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ABSTRACT

A new amorphous-Si@SiO$_x$/Cr/carbon (a-Si@SiO$_x$/Cr/C) anode composite for lithium-ion batteries is synthesized, using SiO, chromium powder and graphite as starting materials. X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), scanning electron microscope (SEM) and high resolution transmission electron microscope (HRTEM) are employed to characterize the composition, morphology and microstructure of the composite. Coin-type cells are assembled to investigate the electrochemical behaviors of the as-prepared composites by constant current charge–discharge technique, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results show that chromium facilitates the crush of Si@SiO$_x$ and graphite during milling, and thus improves their mutual dispersion in the composite. When cycled at 100 mA g^{-1}, the a-Si@SiO$_x$/Cr/C exhibits a stable discharge capacity of about 810 mAh g^{-1} (calculated on the mass of a-Si@SiO$_x$/Cr/C) with good capacity retention up to 200 cycles. The improved electrochemical

performance is attributed to the reduced particle size of a-Si@SiO$_x$ and the synergistic effect of carbon and chromium.

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1. Introduction

Silicon has been regarded as the most suitable anode material for high-energy lithium-ion batteries because of high theoretical capacity, satisfying lithium insertion/extraction potentials and rich resources [1,2]. However, since the large volume change of silicon inflicts a heavy damage on the electrode structure during cycling, the silicon electrodes often show poor cyclic performance [3]. Although the use of nano-sized silicons, such as nanowires [4], nanotubes [5] and nanoparticles [6], or their composites [7–10], significantly improve the structural stability of electrodes, the synthesis of nano-sized silicons either needs strict production conditions or experiences complicate preparation procedure with a low yield, which largely increases cost [1,11]. Moreover, pure nano-scaled silicon is not suitable for anodes in a practical battery due to some intrinsic drawbacks like physical aggregation, electrochemical fuse and other side reactions [11]. Additionally, the dispersion of nanometer silicon is also a large challenge in the case of scale-up production.

As an alternative to nanosilicon, SiO has attracted many researchers' interest [12–19]. At a high temperature, SiO can be disproportionated and the formed nanosilicon particles are surrounded by amorphous SiO$_x$ ($0 < x \leq 2$) [20–23]. Moreover, the formed oxygen-containing compounds during the initial Li insertion, such as Li$_2$O and lithium silicate, can act as buffer matrixes for the volume change effect of silicon in the subsequent cycles [24,25]. However, when SiO is used as an anode in lithium-ion batteries, there are three main drawbacks: poor electronic conductivity, instable electrode structure and low initial charge–discharge efficiency. Because of poor electronic conductivity, SiO often shows a low capacity or bad rate capability. Next, compared with pure silicon with the same particle size, although SiO has a relatively smaller volume change upon cycling, its cyclic stability is still far away from the requirements of practical application [19,23,24]. In the recent decade, many efforts have been done to overcome the above problems. For example, Takami et al. synthesized nano-Si-SiO$_x$-C composites by the in-situ polymerization of furfuryl alcohol on the surface of SiO, and a subsequent high-temperature treatment. The composite delivered a reversible capacity of about 700 mAh g^{-1} and the capacity could be kept up to 200 cycles [22]. Liu et al. synthesized Si–SiO$_2$–C composites by ball milling the mixture of SiO, graphite and coal pitch, followed by a heat treatment. The composite exhibited a reversible capacity of

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about 700 mAh g^{-1} and good cyclic stability at the 90th cycle [26]. Recently, the SiO etched by HF or NaOH was investigated. The SiO etched by NaOH showed a reversible capacity of 1260 mAh g^{-1} over 50 cycles [27]. Park et al. synthesized carbon-coated Si–SiO–SiO$_2$ composite using SiO as precursor via a high-temperature annealing process in the presence of sodium hydroxide, followed by a chemical vapor deposition of carbon. The composite exhibited a reversible capacity of 1280 mAh g^{-1} with excellent capacity retention [19]. These studies indicate that the electrochemical performance of the SiO-based electrodes is closely related with the preparation method, composition and microstructure of materials. Herein, we report a new SiO-based composite synthesized by a high-temperature treatment and two-step simple mechanical milling, using commercially available SiO, chromium and graphite as starting materials. The previous study has demonstrated that the pre-heat treatment of SiO is important for achieving good cyclic performance because the annealed SiO possesses more desirable microstructure than the raw SiO after cycling [19]. That chromium is selected as a component of the resultant composite is because it has good electronic conductivity and superior mechanical properties like high hardness and excellent wear and corrosion resistance [28]. But improving the conductivity of the composite, chromium contributes to facilitating the crush of Si@SiO$_x$ particles during milling and suppressing the volume change of silicon during cycling because of its high hardness. The results show that the combination of chromium and carbon significantly reinforces the structural stability of the electrode and enhances the utilization of silicon oxide.

2. Experimental

Synthesis of the a-Si@SiO$_x$/Cr/C: Commercially available SiO powder (Sigma, 300 mesh) was annealed at 1000 °C for 3 h in argon flow. Subsequently, the annealed SiO and chromium powder (Alfa, 200 mesh) as a mass ratio of 2:1 were batched into a zirconia vial with a ball to powder ratio of 10:1 by weight, and then was ground at 400 rpm for 16 h. Finally, graphite powder (Sigma) was added to the above mixture at a mass ratio of 1:3, followed by a further milling at 500 rpm for 2 h. For comparison, the m-c-Si@SiO$_x$/graphite and a-Si@SiO$_x$/Cr with the same mass fraction of Si@SiO$_x$ were also prepared by similar method. Specifically, to synthesize the m-c-Si@SiO$_x$/graphite, the annealed-SiO was milled at 400 rpm for 16 h and then mixed with graphite at 500 rpm for 2 h. The a-Si@SiO$_x$/Cr is prepared by milling the mixture of the annealed-SiO and chromium at 400 rpm for 16 h. All mechanical milling was conducted in a planetary milling machine (QM-3SP2, Nanjing, China) under the protection of argon.

The crystal structures of samples were measured on an X-ray diffractometer (X'Pert MPD X) at 2500 V using Cu Ka radiation. XPS analysis was performed by a multi-technique ultra-high vacuum Imaging XPS Microprobe system (Thermo VG Scientific ESCALab 250). The morphology and microstructure of samples were characterized by a scanning electron microscope (SEM, JEOL 5900LV) and high resolution transmission electron microscope (HRTEM, JEM 2100F). Coin-type cells 2032 were employed and assembled in a glove box filled with high-purity argon. The tested electrodes consisted of 75% the prepared materials above, 10% Super P as a conductive agent, and 15% sodium alginate as a binder. Sodium alginate was chosen as the binder because it has a better binding effect in Si-based electrodes [29]. Copper foil was used as current collector. The counter electrode and reference electrode were lithium foil. The electrolyte was 1 M LiPF$_6$ with 5 wt% fluorinated ethylene carbonate (FEC) and 2 wt% vinylene carbonate (VC) as the electrolyte additives, which were dissolved in ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate with a volume ratio of 1:1:1. Herein, the use of FEC and VC as additives is

to form a compact and stable solid–liquid interface (SEI) film on the surface of the electrode materials [30,31]. The charge–discharge measurements of the cells were performed at different current densities over a potential window of 0.0–1.5 V using Neware instruments. Unless otherwise stated, the mentioned specific capacity in this paper is calculated on the mass of the whole composite. After the desired cycles were over, the electrode was taken out of the cell in a glove box filled with high-purity argon and washed with DMC. The cleaned sample was evacuated in the chamber of the glove box for 12 h to remove DMC. Subsequently, SEM was used to examine the microstructure change in the electrode. Electrochemical impedance spectroscopy (EIS) was performed using an M283 electrochemical workstation (EG&G Corporation) with a frequency range from 0.01 Hz to 100 kHz over a signal amplitude of 10 mV. The EIS measurements were conducted after the cycled cells (charged to 1.5 V) were left at an open-circuit state for 1 h.

3. Results and discussion

Commercially available SiO is firstly annealed in an inert atmosphere at 1000 °C for 3 h, which is an optimal condition for the disproportionation reaction of SiO [20]. From Fig. 1, only two broad and weak peaks are observed in the XRD pattern of the raw SiO, indicating the raw SiO is amorphous. After annealing, three pronounced peaks corresponding to (1 1 1), (2 2 0) and (3 1 1) lattice planes of crystalline silicon, appear in the XRD pattern of the annealed SiO. According to the Scherrer equation, the average size of Si crystallite in the annealed sample is approximately 10.4 nm.
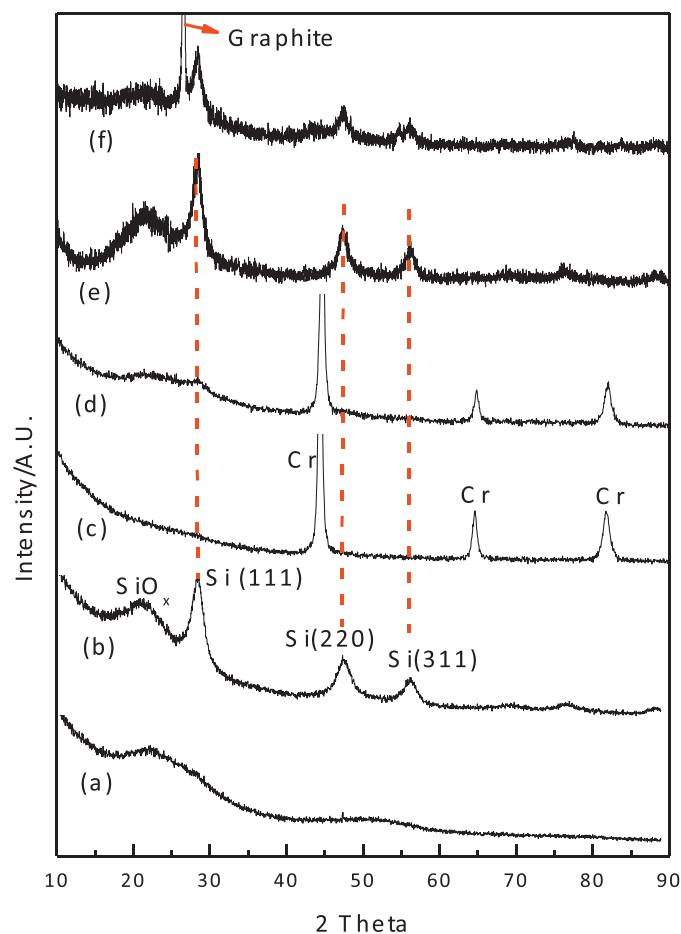

Fig. 1. XRD patterns of the raw SiO (a), c-Si@SiO$_x$ (b), a-Si@SiO$_x$/Cr (c), a-Si@SiO$_x$/C (d), m-c-Si@SiO$_x$ (e) and m-c-Si@SiO$_x$/graphite (f).