

Amorphous nanosized silicon with hierarchically porous structure for high-performance lithium ion batteries

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ABSTRACT

Silicon is a promising alternative anode material for high-performance lithium ion batteries (LIBs) because of its high specific capacity. However, the practical application is still hampered by poor cycle and rate performance because of the tremendous volume expansions/contractions during the lithium ions insertions/extractions. Here we report a hierarchically porous silicon anode consisting of uniformly dispersed nanoparticles with amorphous structure that has been electrodeposited successfully on the copper foil and been utilized directly for LIBs. The typical size of silicon particle is ~100–200 nm, which is beneficial for the fast lithium ions diffusion in a short distance. The hierarchical pores with interconnect channels are easy for the electrolyte filling and ions transports, and can offer sufficient space for the volume expansions of silicon anode during lithium ions insertions. Furthermore, the amorphous feature of the silicon nanoparticles can effectively release the stress from the lithiation-induced large volume expansions and enhance the structure stability, which are beneficial for the long cycling lifetime. Combining the highly conductive copper substrate, the free-standing silicon anode shows high reversible capacity of 1200 mA/g, excellent cycling stability (~1000 mAh/g for 230 cycles) and outstanding rate performance (1000 and 600 mAh/g at 300 and 2000 mA/g, respectively). This study may pave a new way to develop silicon/copper composite materials as binder-free anodes for high-performance LIBs.

1. Introduction

The rechargeable lithium ion batteries (LIBs) have attracted extensive interest because of the high energy density and been widely applied in portable electronics, electric vehicles, and so on [1]. However, there are still increasing demands to develop LIBs with light weight, large capacity and long cycle life. Compared to the graphite-based anode (372 mAh/g), silicon (Si), with a much higher theoretical capacity (4200 mAh/g), has been considered as one of the most promising candidates to meet the demands of the high-performance LIBs [2–4]. A typical Si anode operates by the formation of Li_xSi phase through an alloying reaction in discharge and subsequently dealloying in charge, accompanied by the unavoidable particle pulverization, large volume expansion (~300%), loss of contact with the current collector, and the unstable solid-electrolyte-interface (SEI) film, which cause the capacity fading and short lifetime of the LIBs [4–7]. In the past decade, the nanostructured Si anodes, such as nanowires [8–11], nanotubes [12–14], nanoparticles [15–19], and porous architecture [20–27] have been demonstrated to overcome the above challenges and offer high capacity and cycling

stability by accommodating large volume changes and reducing stress during alloying/dealloying. However, most of the previous Si nanostructures were fabricated by the template-assisting or a complex method involving the expensive equipment, such as the chemical vapor deposition (CVD), which prevents the practical applications of the nanostructured Si anodes for LIBs. Alternatively, the Si anode with large capacity and long cycling lifetime that fabricated by the electrodeposition, has been greatly developed in the recent years [28–39]. Nevertheless, to our knowledge, there was little report about the porous Si anode consisting of nanoparticles by the direct deposition, excluding the involvement of the skeleton [34–38]. Aiming at it, in this study, a hierarchically porous Si anode composed of uniformly dispersed nanoparticles with amorphous structure has been successfully achieved by electrodeposition on the copper (Cu) foil. The obtained porous Si anode with high porosity can be utilized directly for LIBs, without any conductive additive and organic binder. With the unique porous architecture, the free-standing Si anode demonstrates high capacity, excellent cycling stability, and high rate performances.

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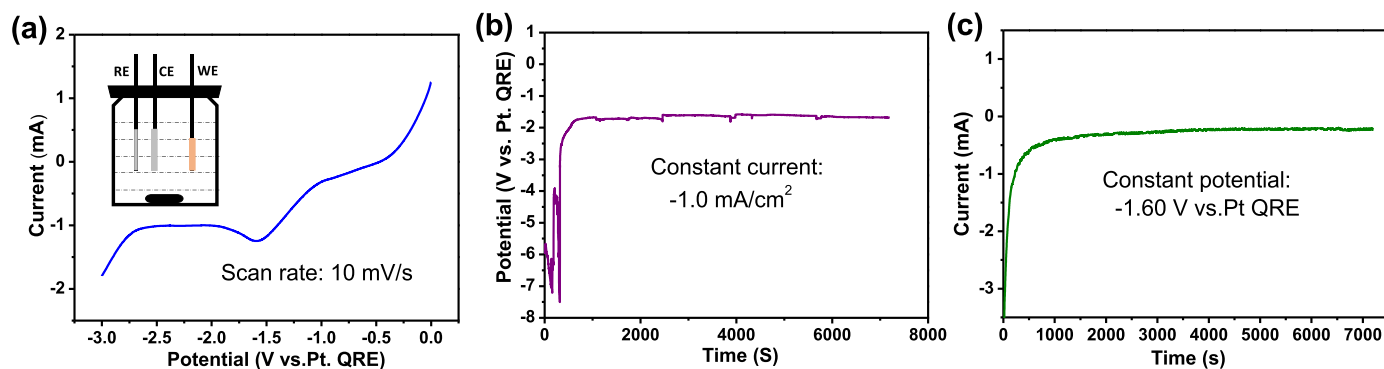


Fig. 1. (a) LSV of the Cu substrate in the SiCl_4 -TBACL-PC electrolyte at the scan rate of 10 mV/s. The insert is the diagram of the cell for electrodeposition. (b) Chronopotentiogram (current density: -1 mA/cm^2) and (c) Chronoamperogram (applied potential: -1.60 V) of Cu substrate in same electrolyte.

2. Experimental section

2.1. Fabrication of porous Si on Cu substrate

The porous Si anode was prepared by an electrodeposition method using silicon tetrachloride (SiCl_4 , 99.99%) as the precursor, propylene carbonate (PC, 99.9% anhydrous) as the solvent, and tetrabutylammonium chloride (TBACL, > 97%) as the additive for improving the ionic conductivity of electrolyte. Typically, the electrodeposition was carried out in a cylindrical three-electrode cell that made of glass and sealed with teflon cap in the glove box (inset in Fig. 1a). The electrolyte is 0.5 M SiCl_4 and 0.1 M TBACL dissolved in PC solvent. Cu foil was used as the working electrode, platinum (Pt) wire and Pt foil served as the reference and counter electrodes, respectively. The electrodes were cleaned carefully by water and ethanol before use. The electrodeposition potential was determined by the linear sweep voltammetry (LSV) of Cu electrode in the electrolyte, and the porous Si film was electrodeposited by chronoamperometric method with a reduction potential of $-1.60 \text{ V vs. Pt QRE}$ for 2 h using electrochemical workstation (Versa STAT 3 Princeton). After deposition, the Cu foils were thoroughly rinsed in PC to remove any residuals of electrolyte, and transferred to an argon (Ar) filled glove box for further test.

2.2. Microstructural characterization

The microstructure of electrodeposited Si was investigated using a field-emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer (FEI QUANTA 650) and a transmission electron microscope (TEM, JEM 2010 F). X-ray diffraction (XRD) was carried out using a Bruker D8 diffractometer with a rotating anode generator (Cu $\text{K}\alpha 1$ radiation; $\lambda=1.5406 \text{ \AA}$). To examine the Si anodes after test, the batteries were disassembled in the glove box, and the obtained electrodes were rinsed with dry dimethoxyethane (DMC) for several times and then dried under vacuum to remove the residual solvent. For SEM and TEM characterization, the obtained Si anodes in charged states after cycles were transferred to the SEM and TEM chambers. Impedance studies were performed using the same electrochemical workstation in the frequency range of 50 KHz to 100 mHz using 10 mV amplitude of an AC stimulus.

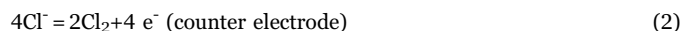
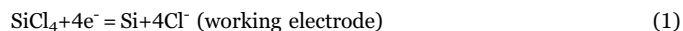
2.3. Electrochemical characterization

R2032-type coin cells (MTI Corporation) were used to investigate the electrochemical performance of Si anode in LIBs. The as-prepared composite electrodes were dried in vacuum and then transferred to an Ar filled glove box. The battery was assembled inside the glove box (water content < 1 ppm) using a free-standing Si/Cu composite electrode, a fresh Li metal plate, and a Celgard separator. 1.0 M LiPF_6 in EC/DMC was used as the electrolyte. Galvanostatic dis-

charge/charge tests were conducted at room temperature using a LAND battery testing system. The mass of the samples was measured by a micro balance. The current densities and specific capacities were calculated based on the mass of the deposited Si on Cu substrate.

3. Results and discussion

The porous Si anode was fabricated by an electrodeposition method in which Cu foil as the substrate and SiCl_4 as the precursor for Si growth by the following reactions [40–42]:



Firstly, the deposition potential of the Si film has been determined by a LSV of 0.5 M SiCl_4 and 0.1 M TBACL in PC electrolyte with a scan rate of 0.01 V/s (Fig. 1a). One cathodic peak is observed at $-1.58 \text{ V vs. Pt QRE}$ and can be attributed to the reduction of the precursor into elemental Si, which has been further confirmed by the chronoamperometry of the same cell. As shown in Fig. 1b, the chronopotentiogram at a constant current density of -1.0 mA/cm^2 shows a reduction potential plateau at $-1.60 \text{ V vs. Pt QRE}$ after stabilizing for 10 min, indicating the Si electrodeposition from SiCl_4 solution at around -1.60 V . Therefore, the electrodeposition potential of Si was applied at -1.60 V on the Cu substrate. The corresponding chronoamperometric deposition of Si at the reduction potential of $-1.60 \text{ V vs. Pt QRE}$ is shown in Fig. 1c, in which the current decreased with an increase of the plating time. The large initial current is caused by the charging of the double layer, followed by the reduction of the initially high concentration of Si precursor at the electrode/electrolyte interface, and the side reduction of the supporting electrolyte and solvent [43]. The shift of the reduction current density towards less negative currents in the chronoamperogram is caused by the increase of resistance due to the growth of the Si film [28,34,42]. As the electrodeposited Si film is sensitive and easy to be oxidized, it is not easy to calculate the amount of pure Si by the Faraday's law, even more, the efficiency of the electrodeposition from SiCl_4 to Si is always less than 100% [40,41]. Therefore, the active material was determined by measuring the weight of the Si/Cu composite electrode before and after the deposition [42], and the areal density of deposited Si can be estimated as $\sim 60\text{--}70 \mu\text{g/cm}^2$.

From the SEM image, the deposited Si anode has the hierarchically porous structure (Fig. 2a), which is composed of uniform nanoparticles with the average size of $\sim 100\text{--}200 \text{ nm}$ and nano-porosity (insert in Fig. 2a). It can be estimated that the high porosity can offer available space for accommodating the volume expansions during lithium ions (Li^+) insertion process and channels for electrolyte filling, while the small particles provide the short ions diffuse distance, which are beneficial for increasing the battery performances. EDX analysis

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