

Short communication

Enhanced cycle performance of SiO-C composite anode for lithium-ion batteries

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Abstract

A silicon monoxide (SiO)-carbon composite prepared by ball-milling and pyrolysis is evaluated as an anode material for lithium-ion batteries. Electrochemical tests demonstrated that the first charge and discharge capacities of the material are about 1050 and 800 mAh g⁻¹, respectively, with a first-cycle efficiency of 76%. The disproportionation reaction of pure SiO into Si and SiO₂ during pyrolysis is confirmed by means of XRD and ²⁹Si MAS NMR. The cycle performance of this material shows an excellent reversible capacity retention of 710 mAh g⁻¹ over 100 cycles without any potential or capacity restrictions. This improved cycle performance is attributed to the stable microstructure, enhanced electrical contact afforded by the pyrolyzed carbon, and the amorphous phase transformation of the active material during cycling.

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1. Introduction

The demand for rechargeable batteries with a higher energy density and specific energy has become more critical as applications emerge such as electric vehicles and various types of portable equipment. Carbonaceous materials are commonly used as a negative electrode (anode) material for commercial lithium-ion batteries because of their good cycle performance. They are, however, insufficient for the high-capacity batteries required in the coming years.

As an alternative anode material for lithium-ion batteries, silicon is one of the most attractive options in terms of its high theoretical specific capacity of about 3580 mAh g⁻¹ for Li₁₅Si₄ [1,2]. Nevertheless, silicon has not yet been applied to commercial lithium-ion batteries due to mechanical failure of the active materials caused by the large change in volume during charge–discharge processes. Recently, in order to solve these problems, the use of Si and SiO composite materials has been

examined [3–14]. The detrimental effect of the volume change during cycling and the resulting loss of electrical contact of the active materials may be compensated to some extent by using a properly designed electrode material.

In this work, a SiO-carbon composite material is prepared by simple ball-milling followed by pyrolyzing with polyvinyl alcohol (PVA). The electrochemical properties of this material as an anode material for lithium secondary batteries are investigated.

2. Experimental

SiO-C composite powders were synthesized as follows. Pure silicon monoxide powders (Aldrich, –325 mesh) were milled under an argon atmosphere using a vibratory mill for 12 h. Polyvinyl alcohol (PVA, >99%, Aldrich) was dissolved in distilled water, and then the produced powders were added and the mixture was evaporated under stirring to get a solid blend. The blended precursor was heated to 900 °C under an argon atmosphere at a heating rate of 3 °C min⁻¹. After pyrolysis at 900 °C for 2 h, the furnace was cooled to room temperature automatically. The final product, a SiO-C composite material, was

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ground and sieved. The resulting samples were characterized by means of X-ray diffraction (XRD, MacScience MXP18A-HF diffractometer). The morphology of the ball-milled powders was examined using a scanning electron microscope (SEM, JEOL JSM-6360) and the microstructure of the synthesized material was observed by means of a high resolution transmission electron microscope (HRTEM, JEOL 3000F) operating at 300 kV. Solid-state ^{29}Si nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DSX-400 NMR spectrometer operating at 79.54 MHz (tetramethylsilane, TMS, at 0 ppm) under magic angle spinning (MAS) conditions with a spinning rate of 7 kHz. A pulse length of 5 μs and a relaxation delay time of 10 s between pulses were used.

The electrodes were prepared by coating slurries containing the active material powders (70 wt.%), carbon black (15 wt.%) and polyvinylidene fluoride (PVDF) dissolved in *n*-methyl pyrrolidinone on copper foil substrates. After coating, the electrodes were pressed and dried for 4 h at 120 °C. The electrodes were cut into discs (10 mm in diameter and about 200 μm thick) and the mass of active material was approximately 3 mg. Coin-type test cells were assembled in an argon-filled glove-box using Celgard 2400 as a separator, 1 M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v, Cheil Industries) as an electrolyte, and Li foil as a counter electrode. Charge (Li insertion)–discharge (Li extraction) experiments were performed galvanostatically within a voltage window of 0.0–2.0 V (versus Li/Li^+).

3. Results and discussion

Scanning electron micrographs of the pure SiO and ball-milled SiO powders are presented in order to compare their morphologies (Fig. 1). After ball-milling for 12 h, the SiO powders have a spherical morphology with a reduced particle size in the range of 0.5–3 μm . The XRD patterns of pure SiO and the synthesized composite powders are shown in Fig. 2. There are no distinct diffraction peaks for pure SiO, which indicates the amorphous nature of the powders. After the pyrolysing process, diffraction peaks for Si appear due to a partial disproportionation reaction. In the case of the milled sample, a small amount of SiC is also formed and is inactive towards lithium. The mean crystalline size of Si estimated with the Debye–Scherrer formula is approximately 3.6 nm, which agrees well with the HRTEM image shown in Fig. 3. The size of the Si crystallite in pure SiO before heat treatment is approximately 1–2 nm [15] and growth of Si crystals by the disproportionation reaction of SiO occurs during heat treatment above 900 °C [16,17].

The disproportionation reaction of pure SiO into Si and SiO_2 in the presence of PVA is also confirmed in this study. The ^{29}Si MAS NMR spectra of the SiO-C composite and other reference samples are compared in Fig. 4. The ^{29}Si MAS NMR spectrum of pure SiO shows two peaks that can be assigned to elemental Si and SiO_2 . The spectrum of the SiO-C composite obtained by pyrolysing with PVA shows more definite peaks than those of pure SiO, which indicates that the disproportionation reaction of SiO into Si and SiO_2 has occurred.

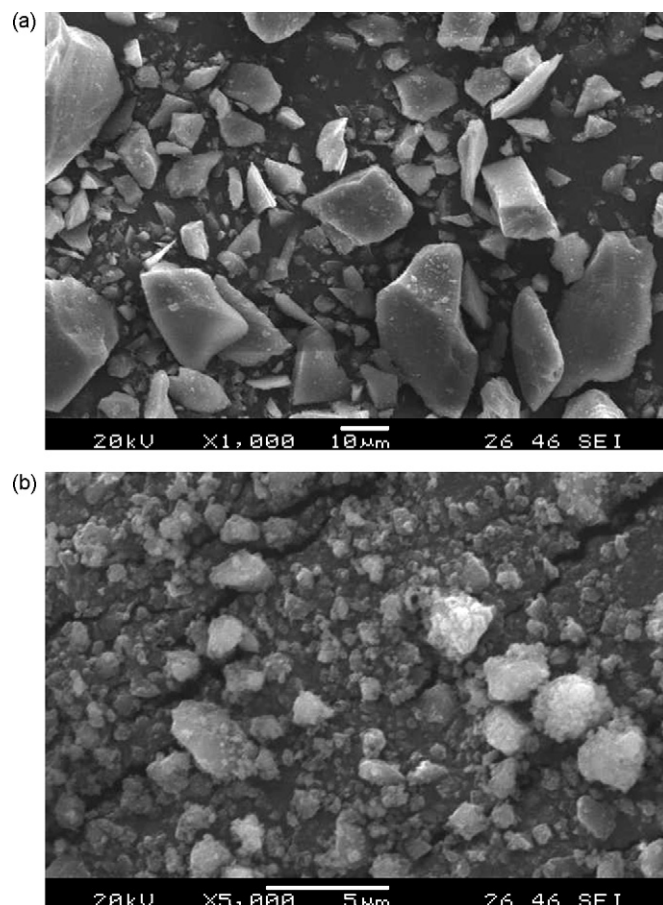


Fig. 1. Scanning electron micrographs of (a) pure SiO and (b) ball-milled SiO powders.

The first charge and discharge capacities of the SiO-C composite are approximately 1050 and 800 mAh g^{-1} , respectively, to give an initial efficiency of 76% which is higher than that of the pure SiO material (Fig. 5(a)). The increase of the initial efficiency is probably related to: (i) the disproportionation of SiO into Si nanocrystals and amorphous silicon oxide, which

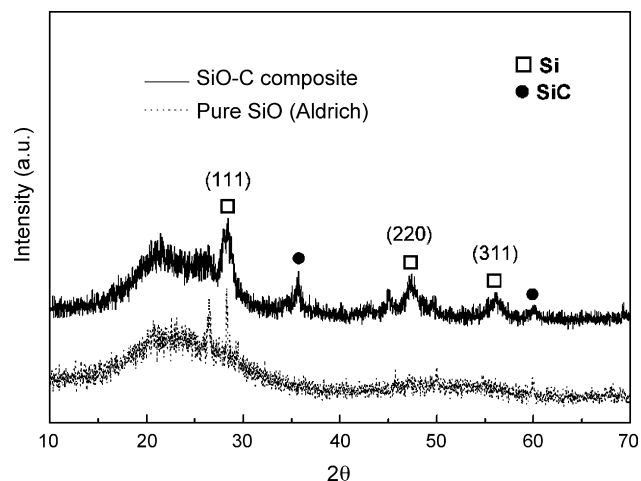


Fig. 2. X-ray diffraction patterns of pure SiO and synthesized SiO-C composite powders.

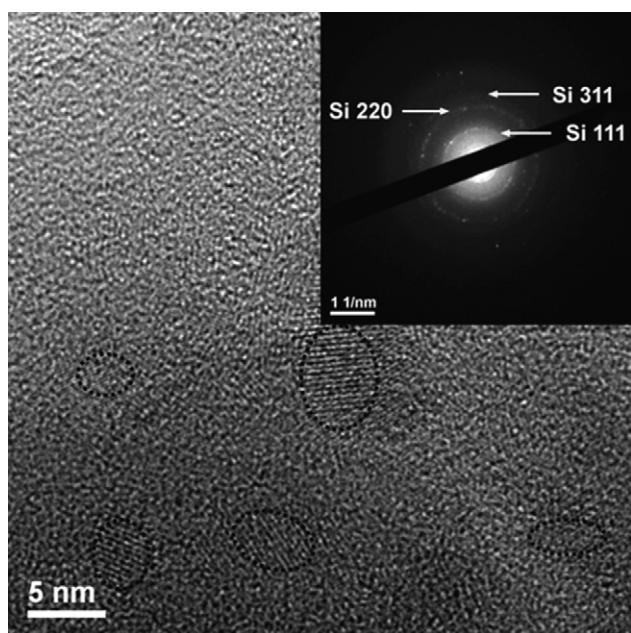


Fig. 3. HRTEM image and selected area diffraction pattern of SiO-C composite material.

reduces the role of oxygen in the first irreversible reaction; (ii) the pyrolyzed carbon effect, which is similar to that for pyrolyzed Si with carbon [4–6,11,12]. The voltage curves of this composite are different from those of the pure SiO. The formation of pyrolyzed carbon and the structural changes which SiO undergoes during the pyrolyzing process may result in the shift of the voltage plateau in a negative direction for the first lithium insertion. The shape of the differential capacity curves is similar to that of pure Si (Fig. 5(b)). During the first lithium removal, there is no clear peak. Lithium-insertion materials like this composite, with smooth voltage profiles and no characteristic peaks

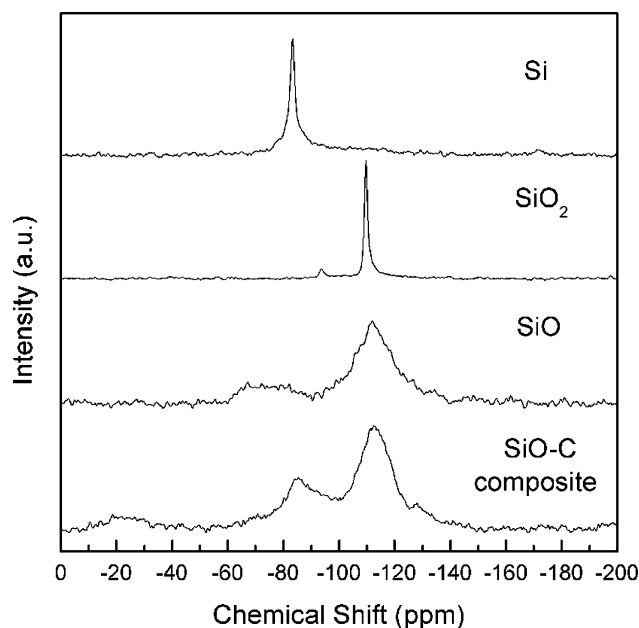


Fig. 4. ^{29}Si MAS NMR spectra for Si, SiO_2 , SiO and SiO-C composite powders.

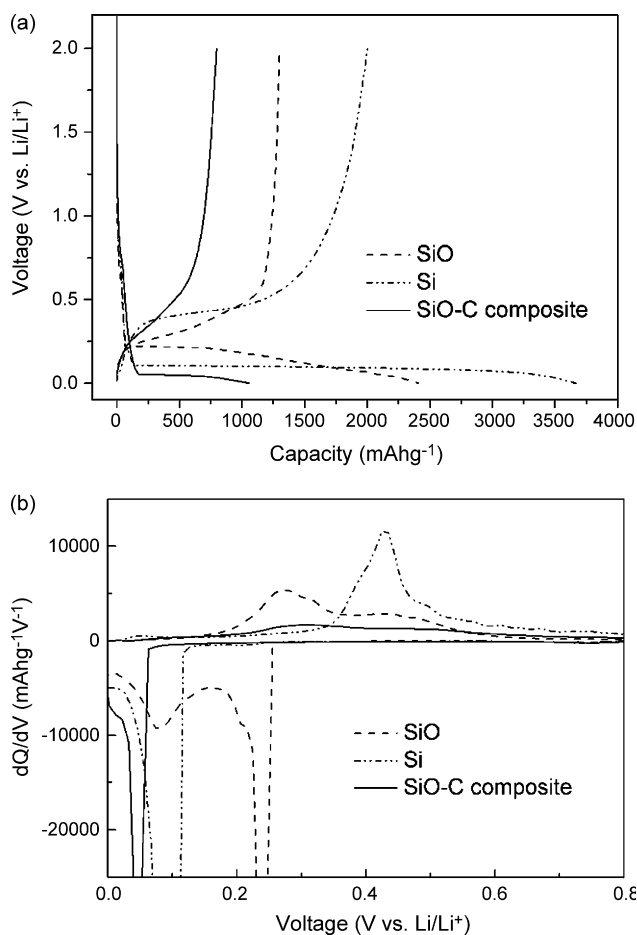


Fig. 5. (a) Voltage profiles of Si, SiO and SiO-C composite electrodes for first-cycle at constant current of 50 mA g^{-1} and (b) differential capacity curves of electrodes.

in the differential capacity curves, should generally cycle better than those with plateau-type voltage profiles. This is because the absence of any plateau indicates the occurrence of phase transformations during reaction with lithium [18].

The cycle performance of the SiO-C composite anode is presented in Fig. 6. All of the electrodes were tested within the

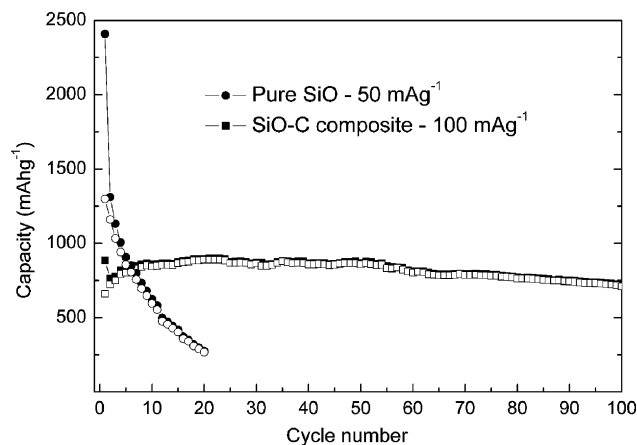


Fig. 6. Cycle performance of SiO and SiO-C composite electrodes cycled between 0.0 and 2.0 V (vs. Li/Li^+).

voltage range between 0.0 and 2.0 V. A comparison with pure SiO clearly reveals the enhanced cycle-life of the SiO-C composite with capacity retention. A reversible capacity of 710 mAh g^{-1} is maintained even after 100 cycles without voltage cut-off and control of the Li-insertion capacity. The improvement in cycleability is attributed mainly to three factors. First, the structure with Si nanocrystals in amorphous silicon oxide and the reduced particle size by ball-milling increases the mechanical stability of electrodes with cycling [6,14]. Second, the carbon resulting from PVA pyrolysis provides better electrical contact during cycling when volume expansion and contraction occur, as has recently been reported [4–6,11,12]. Finally, the electrode materials remain in an amorphous state during the lithiation/delithiation reactions according to the X-ray diffraction data, and this helps to maintain the integrity of the electrodes.

4. Conclusions

A SiO-C composite prepared by a ball-milling and pyrolyzing process displays improved initial cycling efficiency, higher reversible capacity than that of commercial graphite anodes, and excellent cycle performance. Based on these results, it is concluded that the composite has a considerable potential for use as an alternative anode material for lithium secondary batteries. Further studies are required to clarify the reaction mechanism of lithium with SiO and SiO-C composite.

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