



Improvement of cyclic behavior of a ball-milled SiO and carbon nanofiber composite anode for lithium-ion batteries

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ABSTRACT

The cyclic performance of a composite SiO and carbon nanofiber (CNF) anode was examined for lithium-ion batteries. SiO powder of several micrometers was pulverized using high energy mechanical milling. The SiO was ball-milled for 12 h with CNF to produce a composite electrode material that exhibited excellent cycling performance. A reversible capacity of approximately 700 mAh g^{-1} was observed after 200 cycles. The excellent cyclic performance was discussed with respect to the change of the valence state of Si by ball-milling. A large irreversible capacity at the first cycle for the SiO/CNF composite electrode was reduced to 2% by chemically pre-charging with a lithium film attached to the rim of the electrode.

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1. Introduction

Replacement of the Li metal anode in rechargeable Li batteries with Li-alloys has been under investigation since Dey demonstrated the possibility of the electrochemical formation of Li_xAl in liquid organic electrolytes in 1971 [1]. Numerous metals, such as Mg, Ca, Al, Si, Ge, Sn, Pb, Sb, and Bi, have been found to reversibly accommodate lithium under an electrochemical alloying process according to the reaction of $x\text{Li}^+ + xe^- + \text{M} = \text{Li}_x\text{M}$ [2]. Such a reaction can generate larger theoretical specific and volumetric capacities than the currently used lithiated graphite (LiC_6). However, there is a major problem that encumbers the application of Li-alloys, which is mainly caused by the comparatively large volume mismatch (typically in the scale of over ca. 200%) of the alloy hosts between Li insertion and extraction, and results in significant mechanical stress to the host matrix during charge and discharge. Such mechanical degradation results in cracks in the metal and pulverization of the host particles, which results in the loss of mechanical and electrical contact; eventually, capacity fading by cycling is inevitable. One of the methods to overcome the problem of pulverization of the Li-alloy is to employ composite or multiphase structures, in which the active material/phase is supported by a less-active or even non-active matrix to maintain the mechanical integrity [3].

In 1997, Idota et al. reported good cyclic performance for a lithium battery anode of a glass composite of tin oxide, where Li reacts electrochemically with tin oxide to form metallic Sn and an inert Li_2O matrix [4]. The special texture formed in the electrode alleviates the volume change during the subsequent reaction with Sn to form the Li alloy. We have investigated silicon monoxide powders with different oxygen content (SiO , $\text{SiO}_{0.8}$, $\text{SiO}_{1.1}$) as anode materials for lithium secondary batteries [5], in which the capacity retention was improved with decreased particle size; however, the capacity fade by cycling became marked with longer cycles. The problem of volume change in Li-alloy is difficult to completely eliminate. Although high specific reversible capacities

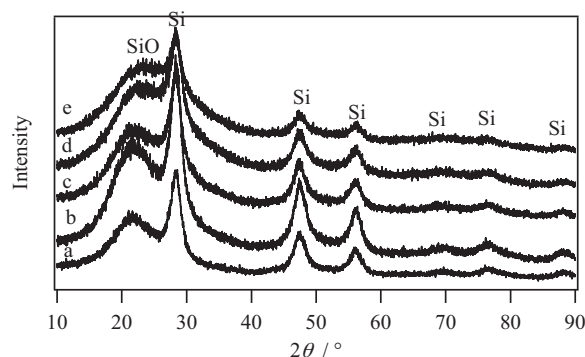


Fig. 1. XRD patterns of (a) as-received SiO and SiO ball-milled for (b) 6 h, (c) 12 h, (d) 24 h, and (e) 36 h.

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Table 1
Fraction of the various Si valence states estimated from Si 2p XPS spectra for the ball milled SiO.

Milling time (h)	Fraction of various Si valence states (%)					Average valence of Si
	Si ⁰	Si ⁺	Si ²⁺	Si ³⁺	Si ⁴⁺	
As received	12.1	7.6	61.6	5.8	12.9	2.01
6	12.2	21.7	29.3	24.1	12.7	2.03
12	12.6	20.0	27.2	22.1	18.1	2.13
24	8.9	13.1	20.1	25.9	32.1	2.59
36	0.1	6.9	21.6	26.1	45.3	3.08

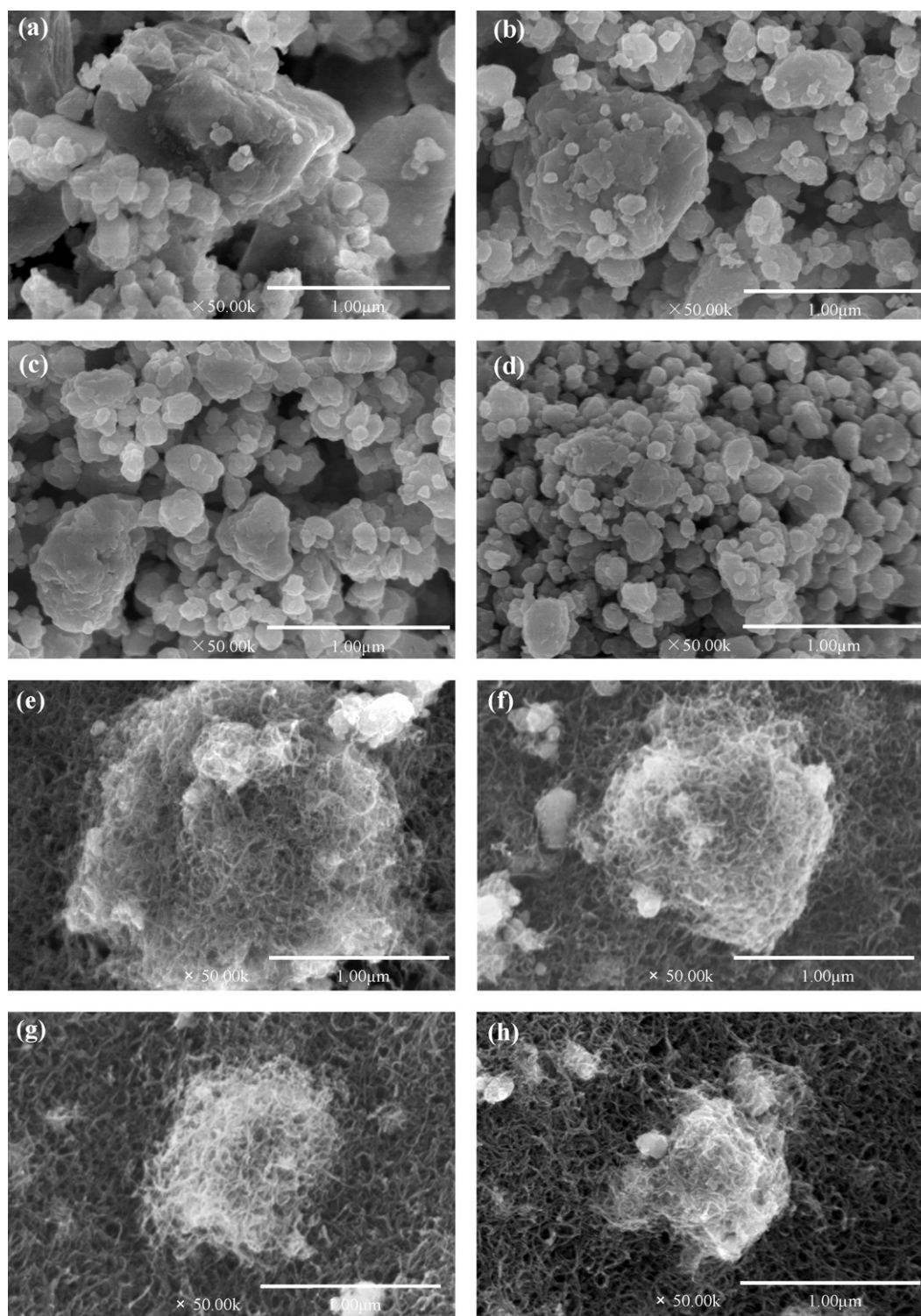


Fig. 2. SEM images of SiO ball-milled for (A) 6 h, (B) 12 h, (C) 24 h, (D) 36 h, and SiO/CNF composites ball-milled for (E) 6 h, (F) 12 h, (G) 24 h, and (H) 36 h.

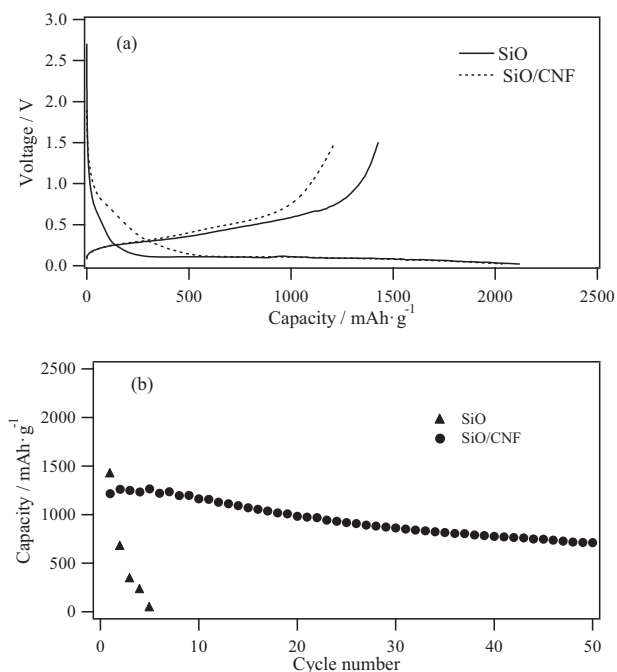


Fig. 3. (A) Charge–discharge curves (1/10 C rate) and (B) cycling performance of the SiO and SiO/CNF electrodes.

(above 800 mAh g⁻¹) and fairly good cycle life were obtained for nanosize SiO anodes, they had large irreversible capacities (almost 50%) from the formation of Li₂O. From an application standpoint, there is still considerable room for improvement of the first cycle efficiency and cycle life of such anode systems. In order to remove the large first irreversible capacity, the formation of composites with strong reducing agents such as Li metal powder [6] or lithium nitrides [7] have been effective at the laboratory scale.

Various methods have been reported for improvement of the cycle performance of SiO anodes, especially considering small SiO particles in a matrix. For example, Kim et al. [8] prepared a SiO-carbon composite by ball-milling and pyrolysis. The SiO-carbon composite demonstrated a first coulombic efficiency of 76% and reversible capacity of 710 mAh g⁻¹ over 100 cycles. This 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.

Recently, we reported [9] the excellent electrochemical performance of a silicon/carbon composite anode using carbon nanofiber (CNF). High reversible capacity and fairly good cyclability were achieved by utilizing the ductile CNF matrix to buffer the effect of Si volume expansion on the macro domain and maintain good contact with both the active materials and electrolyte after lithium insertion and extraction cycles.

In this study, inexpensive micron size SiO powder was pulverized using high energy mechanical milling (HEMM) and the pulverized SiO was then mixed with CNF. The electrode performance of the SiO/CNF composite anode was investigated as a function of the milling time and was discussed with respect to the change of the Si valence by the milling time. The high irreversible capacity at the first cycle was compensated by chemically precharging with a lithium thin film attached to the composite electrode.

2. Experimental

SiO powder with an average particle size of 8 μm was used as the starting material. The SiO powders were treated by HEMM

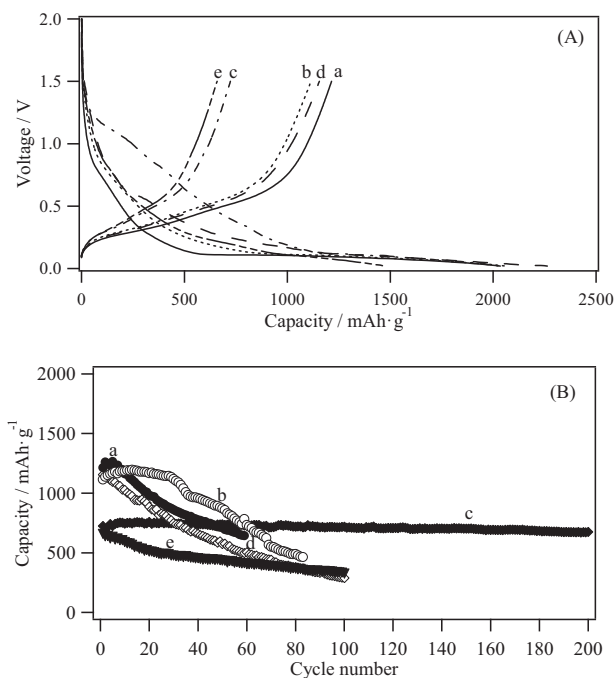


Fig. 4. (A) Charge–discharge curves (1/10 C rate) and (B) cycling performance for SiO/CNF electrode prepared from (a) as-received SiO, and SiO ball-milled for (b) 6 h, (c) 12 h, (d) 24 h, and (e) 36 h.

(Fritsch planetary micro mill) in a zirconia bowl with zirconia balls at a rotational speed of 500 rpm for 6, 12, 24 and 36 h. The SiO powders were placed and sealed in the milling bowl under an Ar atmosphere in a glove box. The weight ratio of zirconia balls (5 mm diameter) to the SiO powder was maintained at 5:1. The SiO electrodes were prepared as follows. The ball-milled SiO powder was mixed with CNF (Jemco, Japan, 10–20 nm diameter and 0.1–10 μm long) in a 1-methyl-2-pyrrolidone (NMP) solution using a mixer (Thinky, Japan). The weight ratio of SiO to CNF was 70:30. Acetylene black (AB; Denki Kagaku, Japan) and polyvinylidene fluoride (PVDF; Kynar, USA) were added into the solution. The weight ratio of SiO/CNF:AB:PVDF was 75:5:20. The slurry of electrode components was cast onto a copper foil and dried at 80 °C for 1 h in open air. The cast electrodes were cut to a size of 1 cm × 1 cm. The electrode thickness was in the range of 20–30 μm. The electrodes were further dried at 120 °C under vacuum for 2 h followed by pressing at 200 kgf cm⁻². The specific capacity was calculated according to the weight of SiO/CNF. Electrochemical tests of the composite electrodes were conducted using two-electrode coin-type cells (type 2025). The coin-cells were assembled in an Ar-filled glove box using 1 M LiClO₄ in an ethylene carbonate (EC) and diethylene carbonate (DEC) mixed solution (1:1, v/v) as the electrolyte and metallic lithium foil (20 μm thick) as the counter electrode. The electrochemical performance of the composite anode was evaluated using a constant current charge–discharge cycling test machine (Nagano BST 2004H, Japan) in the voltage range of 20–1500 mV with a charge–discharge rate of 1/10 C at room temperature. X-ray diffraction (XRD) patterns were obtained using a diffractometer (Rigaku, Rotaflex RU-200B) with Cu Kα radiation. The morphology of the ball-milled SiO powder was examined using scanning electron microscopy (SEM; Hitachi SEM S-4800). Surface area measurements were conducted using a gas absorption analyzer (Shimadzu Micromeritics Tri Star 3000). The change in the chemical structure of the SiO powder by ball-milling was examined by X-ray photoelectron spectroscopy (XPS) (Shimadzu ESCA 3400) analysis of the Si 2p values.

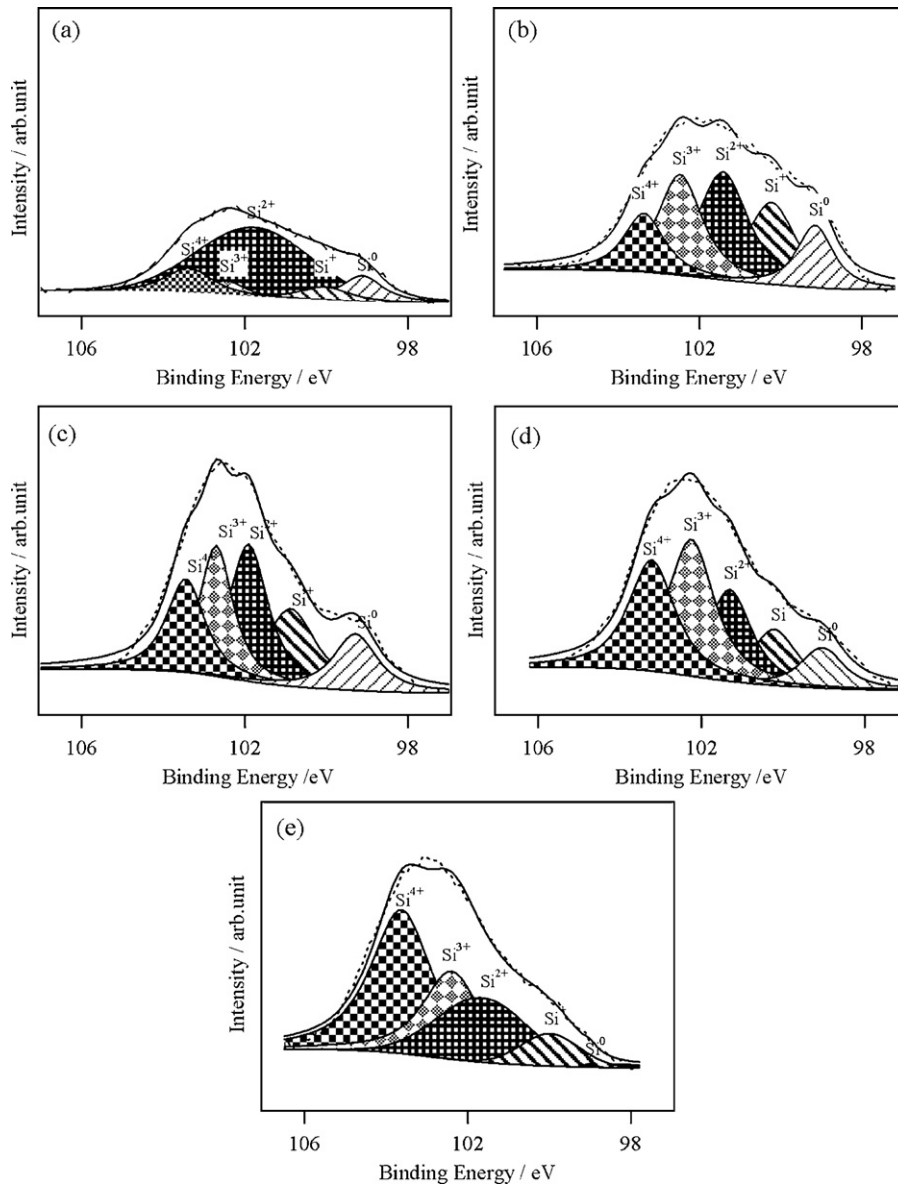


Fig. 5. Si 2p spectra of (A) as-received SiO, and SiO ball-milled for (B) 6 h, (C) 12 h, (D) 24 h, and (E) 36 h.

3. Results and discussion

Fig. 1 shows XRD patterns of the as-received and ball-milled SiO powder, which are similar to that for nanosize SiO_{1.1} (average particle size of 50 nm) reported by Yang et al. [5]. The diffraction peaks of Si and a broad SiO peak were detected in all samples. Ball-milling had no significant effect on the XRD peaks, although a slight decrease of the Si peak height and a slight increase of the SiO peak height were evident. Fig. 2(A–D) shows SEM images of the ball-milled SiO for various milling times and that of the SiO/CNF composite. The initial particle size of 8–10 μm was reduced to 0.1–0.4 μm by ball-milling and the BET surface area of the as-received SiO (4.8 m² g⁻¹) was increased to 19.5 m² g⁻¹ by ball-milling for 36 h. The particle size gradually decreases and equals with ball-milling treatment; the main particle size of SiO ball-milled for 12 h is between 0.1 and 1.0 μm and that for 36 h is between 0.1 and 0.4 μm. In the SiO/CNF composites, SiO particles homogeneously distributed in the CNF matrix, where CNFs cover the SiO particles like muskmelon's surface texture as shown in Fig. 2(E–H).

Fig. 3 compares the charge and discharge curves at the first cycle and the cycling stability of the as-received SiO and SiO/CNF composite electrodes at room temperature. The as-received SiO electrode exhibits a similar potential profile to that reported previously [5,10] in the first lithium insertion (charge) and extraction (discharge), and the observed charge and discharge capacities are 2117 and 1427 mAh g⁻¹, respectively. The high irreversible capacity could be explained by the formation of Li₂O and/or Li₄SiO₄ [10–12];



and



Miyachi et al. [11] estimated from XPS analysis that 60% of SiO is converted to Li₂O and lithium silicate. The fine Si particles produced by this conversion reaction react with Li to make an alloy;



The reversible and irreversible capacities calculated from reactions (1) and (3) are 2675 and 1216 mAh g⁻¹, respectively, and those

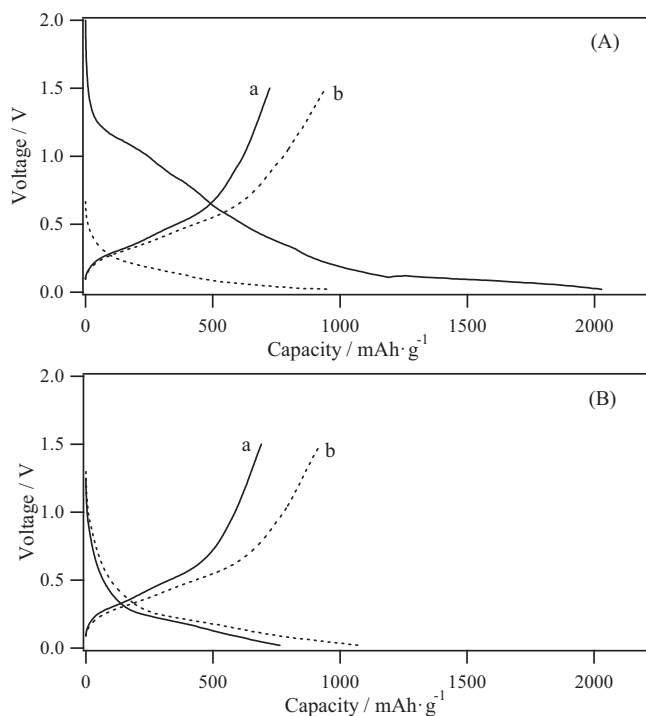


Fig. 6. Charge and discharge curves (1/10 C rate) for the (a) non-precharged and (b) precharged 12 h ball-milled SiO/CNF electrode at the first (A) and second cycles (B).

calculated from reactions (2) and (3) are 2006 and 1216 mAh g⁻¹, respectively. The irreversible capacity is calculated to be in a range of 30–38%. The observed irreversible capacity of the as-received SiO was estimated to be 33%. These results support the suggested reaction mechanism. The large size SiO particles exhibit a low irreversible capacity and a high reversible capacity at the first cycle; however, the capacity fade by cycling is significant, as shown in Fig. 3(B). We previously reported that the cyclic performance of the Si–C electrode was improved by addition of CNF [9]. The effect of CNF addition to SiO on the electrode performance was examined. The charge capacity of the SiO/CNF composite electrode at the first cycle is almost same as that of SiO. The charge capacity of CNF at the first cycle was reported to be approximately 660 mAh g⁻¹ [9]; therefore, the discharge capacity of SiO in the composite electrode is estimated to be 2760 mAh g⁻¹ from the weight of SiO in SiO/CNF (70 wt% SiO in SiO/CNF). The discharge capacity is in good agreement with that calculated from reactions (1) and (3). The charge capacity of 1215 mAh g⁻¹ for the SiO/CNF electrode corresponds to 1670 mAh g⁻¹ for SiO, where the discharge capacity of CNF was estimated to be 92 mAh g⁻¹ [9]. The charge capacity is slightly higher than 1460 mAh g⁻¹ calculated from reactions (1) and (3). The difference may be due to an uncertainty in the discharge capacity of CNF and the mass of SiO in the electrode. Fig. 3(B) shows that the SiO/CNF composite electrode has better cyclic performance than that observed for the Si–C/CNF electrode [9]. Several factors were considered for the contribution to improved cycling performance by addition of CNF. Firstly, flexible CNFs may function as a good electronic contact, and secondly, the dispersed network of CNFs shown in Fig. 2(E–H) acts as an effective buffer matrix for the volume change of Li_xSi by cycling [9]. However, the cyclic performance of the as-received SiO and CNF composite electrode is not as good as that of the nanosize SiO electrode reported by Yang et al. [5]. The capacity retention after 50 cycles was only 58%. On the other hand, the ball-milled SiO/CNF exhibits better charge–discharge cycling performance. The charge–discharge performance for the ball-milled SiO/CNF composite anode at the first cycle, and the

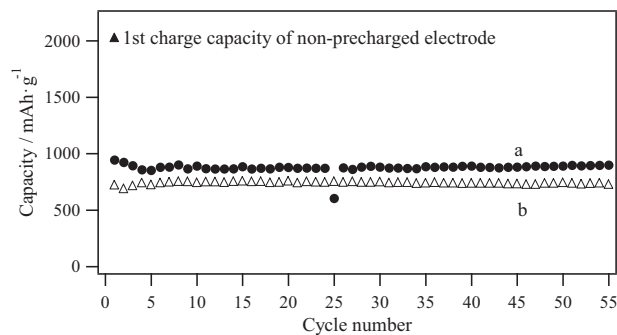


Fig. 7. Discharge capacity (1/10 C rate) vs. cycle number curves of the (a) precharged and (b) non-precharged 12 h ball-milled SiO/CNF electrode.

change in the discharge capacity by cycling are shown as a function of the ball-milling period in Fig. 4. The best cycling performance is found for the composite SiO/CNF anode with SiO ball-milled for 12 h, where the reversible capacity is more than 700 mAh g⁻¹ and the degradation rate is less than 1% per 100 cycles. The charge and discharge capacities at the first cycle are 2027 and 724 mAh g⁻¹, respectively. The irreversible capacity of the composite anode at the first cycle is as high as 64.3, which may be due to the irreversible reaction of (1) and/or (2) and the electrolyte decomposition observed in the lithium insertion curve in Fig. 4; similar electrolyte decomposition was observed in nanosize SiO [5].

Fig. 4 shows that ball-milling of the SiO powder has a significant influence on the lithium insertion and extraction performance. SiO is composed of Si and silicon sub-oxides with various valence states [11,12]. The valence state of Si on the surface for the ball-milled samples was examined using XPS. Typical Si 2p spectra are shown in Fig. 5, where the spectra were obtained after sputtering the SiO surface for 2 h. Each of the spectra was fit to five peaks that correspond to five different Si oxidation states, based on previously reported binding energy values [13]. The spectra in the range of 98–106 eV are attributed to Si⁰, Si⁺, Si²⁺, Si³⁺ and Si⁴⁺ from the low energy side, and the ratio of the valence state of SiO was estimated from the area ratio of these spectra. In Table 1, the valence states of ball-milled SiO are given as a function of the ball-milling period. The average valence state of Si on the as-received SiO surface is 2.01, which increases to 3.08 by ball-milling for 36 h. A significant change of the valence state of Si by ball-milling is observed in the decrease of the Si²⁺ state, which could explain the low first cycle capacity for the ball-milled SiO. The conversion reaction from SiO_x to Si may be easier for SiO. However, the excellent cyclic performance for the 12 h ball-milled SiO could not be explained by the change of the valence state of Si, but by the good contact between nanosize SiO and CNF. SiO ball-milled for 24 and 36 h exhibited a large Si⁴⁺ content; the high resistance of the SiO₂ phase may prevent the formation of conducting paths.

Although a high reversible capacity of 675 mAh g⁻¹ after 200 cycles was obtained in for the 12 h ball-milled SiO and CNF composite anode, the irreversible capacity was 64.3% at the first cycle, which is undesirable for practical application. Seong and Yoon proposed a new method to compensate the irreversible capacity of SiO using lithium powder [14] and we have reported that the attachment of a lithium thin film to the Si/CNF electrode is effective to reduce the irreversible capacity [15]. In this study, the large irreversible capacity at the first cycle was reduced by attaching a thin lithium sheet to the rim of the composite anode. The amount of lithium sheet calculated from the irreversible capacity was attached to the rim and the test cell was stored at room temperature overnight. The lithium metal reacted with SiO to produce fine Si particles in the CNF matrix (precharge). Fig. 6 shows the first and second cycle charge–discharge curves for the precharged and

non-precharged SiO/CNF electrode prepared from SiO ball-milled for 12 h. The irreversible capacity at the first cycle is significantly reduced to 1.9% by precharging and the reversible capacity is slightly increased to 944 mAh g^{-1} . The cycling performance of the precharged and non-precharged 12 h ball-milled SiO/CNF electrode is shown in Fig. 7. A reversible capacity of 890 mAh g^{-1} was observed after 56 cycles for the precharged 12 h ball-milled SiO/CNF composite electrode, and the capacity retention was as high as 94% for 56 cycles.

4. Conclusion

A composite electrode consisting of ball-milled SiO powder and CNF exhibited excellent cycling performance with a high reversible capacity. The best performance was observed for SiO ball-milled for 12 h, which was a mixture of particle sizes from 1 to $0.1 \mu\text{m}$. The average valence state of Si in the 12 h ball-milled SiO was 2.13 and the content of Si^{2+} and Si^{4+} were 27.2 and 18.1%, respectively. The excellent cycle performance could be explained by the presence of nanosized SiO and a low content of SiO_2 . However, the 12 h ball-milled SiO had high irreversible capacity at the first cycling. The irreversible capacity was reduced to 2% by attachment of a lithium thin film to the electrode, and excellent cycling performance with a high reversible capacity of approximately 900 mAh g^{-1} was observed.

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