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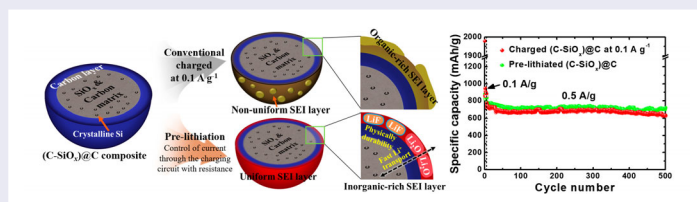
Formation of physically durable and performance sensitive solid-electrolyte interphase of SiO_x anode for lithium-ion battery

Hyeon-Woo Yang ^a, Dae In Lee ^a, Nayoung Kang ^a, Woo Seung Kang ^b and Sun-Jae Kim ^a

^aDepartment of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, Republic of Korea; ^bDepartment of Metallurgical and Materials Engineering, Inha Technical College, Incheon, Republic of Korea

ABSTRACT

Although SiO_x is a well-known promising anode material for Li-ion batteries because of its high energy density and cyclic stability, the inferior electron transport kinetics and morphologically unstable solid-electrolyte interphase (SEI) layer formed on the SiO_x anode result in inadequate electrochemical performance. Herein, to overcome the poor electron transport kinetics, a carbon-incorporated/carbon-coated SiO_x ($(\text{C-SiO}_x)_x/\text{C}$) composite is fabricated. In addition, the $(\text{C-SiO}_x)_x/\text{C}$ electrode is pre-lithiated using a charging circuit under an optimized resistance to form a structurally durable SEI layer with high Li^+ diffusivity during the charge–discharge processes. Thus, the $(\text{C-SiO}_x)_x/\text{C}$ composite exhibits highly improved cycle performance.



IMPACT STATEMENT

Elaborately designed SEI composed of LiF for physical sturdiness and Li_2O to achieve high Li^+ diffusivity resulted in highly improved cyclic performance as well as initial coulombic efficiency.

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KEYWORDS

Lithium ion battery; anode; solid-electrolyte interphase; SiO_x ; carbon

1. Introduction

With the widespread need for power sources for portable electronic devices and electric vehicles, silicon (Si) anodes have attracted interest for use in Li-ion batteries (LIBs) because of their large theoretical capacity and low reaction potential of approximately 0.4 V Li/Li^+ [1]. These Si anodes typically consist of the Si active material, conductive carbon, and a binder. Microstructural distortions or disintegrations caused by large volume changes (approximately 400%) during the intercalation/deintercalation of lithium ions, however, lead to a drastic capacity reduction for the Si active material [2]. To address these issues, silicon suboxide (SiO_x , $0 < x < 2$) has been proposed as a potential alternative to Si. SiO_x anodes generally exhibit cycling stability because of their amorphous structure as well as the formation of Li_2O and

Li silicates that serve as a buffer, effectively accommodating the volume variation of Si during the first lithiation process [3]. However, the irreversible formation of Li-O and Li-Si-O phases lead to consumption of lithium as part of the irreversible capacity, which significantly decreases the initial coulombic efficiency (ICE). Furthermore, the SiO_x active material exhibits inferior electron transport kinetics compared with that of Si because of the electrically insulating property of SiO_2 , and poor cyclic performance resulting from the unstable solid-electrolyte interphase (SEI) layer formed during lithiation [4,5].

Many researchers have attempted to perform additional carbon coating by complicated, multi-step, and high-temperature processes to improve the electrochemical performance of the SiO_x active material even though conductive carbon was already contained in the electrode

CONTACT Sun-Jae Kim ✉ sjkim1@sejong.ac.kr Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 05006, Republic of Korea; Woo Seung Kang ✉ wkang651@inhac.ac.kr Department of Metallurgical and Materials Engineering, Inha Technical College, Incheon 22212, Republic of Korea

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[6,7]. Therefore, the amount of SiO_x in the anode resulted in relatively low. For instance, Xu *et al.* [6] developed a SiO_x/C composite in which SiO_x particles were dispersed and anchored in the carbon materials by exploiting and restoring artificial graphite; the SiO_x content in the SiO_x/C composite measured by thermogravimetric analysis was 30 wt%. In addition, Liu *et al.* [7] fabricated monodisperse SiO_x/C composite microspheres with tunable size (300–1000 nm) and well-controlled carbon content (~ 20 –60 wt%) by a sol–gel method; the SiO_x/C with a carbon content of 39.75% showed optimal performance among ICE, reversible capacity and capacity retention. In these works, to achieve good cyclability and rate capability through improved electrical conductivity, a large amount of carbon was added to the SiO_x active material by carbon coating. A few industries have also attempted to commercialize SiO_x anodes containing 90 wt% or more graphite (with the balance being SiO_x). Hence, the primary advantage of SiO_x active material seemed to have not been fully utilized due to relatively small amount of SiO_x in the anode.

The ICE of SiO_x anodes is also generally low because of the formation of the SEI layer, which results in the continuous consumption of lithium ions supplied by the cathode material and limitation of the cycle life. To improve the ICE and cyclic performance, several pre-lithiation methods have been proposed to mitigate the loss of lithium ions during lithiation. Some pre-lithiation techniques are used to prestore lithium in anodes, including electrochemical pre-lithiation using lithium foil [8], stabilized lithium metal powder [9], or pre-lithiated Li_xSi nanoparticles [10]. Such pre-lithiation processes appear to compensate for the initial lithium consumption; however, the positive effect is limited to the early charge–discharge cycles. Beyond the early cycles, the capacity is continuously reduced, although the overall improved reversibility is maintained. Choi *et al.* [8] proposed that the ICE would increase from 73.6% to 94.9% using an external short circuit with a carbon-coated SiO_x electrode and lithium metal foil in the liquid environment of the electrolyte. Yom and co-workers [10] developed pre-lithiated SiO using a solid-state reaction with lithium powder; the initial charge–discharge reversibility of the solid-state-reacted SiO materials increased from 58.52% to 82.12% in a half cell. Most researchers have focused on improving the electrochemical performance, especially the initial charge–discharge reversibility. However, improvement of the reversibility using pre-lithiation techniques has some limitations, as the performance improvement is confined to the early cycles.

In the current study, in order to take full advantage of the SiO_x active material, we fabricated a carbon-incorporated/carbon-coated SiO_x ((C- SiO_x)@C)

composite containing a significant amount of SiO_x (~ 90 wt%) by a simple and cost-effective one-pot synthesis method. We also extended the reversibility and capacity improvements beyond the initial cycle by modifying the constitutional structure of the SEI in the (C- SiO_x)@C anode. In particular, among the components of the SEI, LiF is known to stabilize the SEI layer, especially during charging/discharging cycles [11]. Considering the severe volume changes of the Si anode electrode during lithiation/delithiation, kinetic stabilization of a component in the SEI is required to achieve high cyclic performance without significant capacity loss. In addition, the Li_2O phase can serve as a fast diffusion channel as the Li diffusivity in Li_2O has been shown to be at least two orders of magnitude faster than that in Li silicates [12]. Thus, the synthesized (C- SiO_x)@C electrode was pre-lithiated using an optimized charging system to form an SEI layer with LiF and Li_2O as the main components, enabling the formation of a durable layer with efficient lithiation/delithiation. The carefully designed pre-lithiation process produced a (C- SiO_x)@C electrode with greatly improved reversible capacity and capacity retention even after 500 cycles, with increases from 627 to 707 mAh g^{-1} and from 86.7% to 90.4%, respectively. In addition to the improved electrochemical performance after 500 cycles, the ICE also significantly increased from 43.3% to 93.6% with the pre-lithiation.

2. Experimental sections

2.1. Sample preparation

For the synthesis of (C- SiO_x)@C, 13 mL of ethylene glycol (EG, 99.9%, Samchun Co.) was dispersed in a solution containing 20 mL of SiCl_4 (99%, Wako Co.) and 50 mL of benzene (99.5%, Daejung Co.) with vigorous stirring. Benzene plays an important role in controlling the abrupt alcoholysis reaction between EG and SiCl_4 and forming the carbon matrix of SiO_x particles. The mixture was converted into a mineral-like solid through the alcoholysis reaction between SiCl_4 and EG with benzene. (C- SiO_x)@C was obtained after heat treatment of the mineral-like solid at 725°C for 1 h under vacuum. In addition, SiO powder was purchased from Sigma Aldrich.

2.2. Materials characterization

The structural information for the (C- SiO_x)@C was obtained using X-ray diffraction (XRD; Rigaku, D/MAX-2500), X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo Scientific Inc.), confocal Raman microscopy (FEX, Nost Co., Ltd.) with a 532 nm wavelength incident

laser light, field-emission scanning electron microscopy (FESEM; SU-8010, Hitachi Co.) with Energy-dispersive X-ray spectroscopy (EDS), focus ion beam preparation and SEM-analyses (FIB/SEM, Zeiss Crossbeam 540), and high-resolution transmission electron microscopy (HR-TEM; JEM 2100F, JEOL). The carbon content of the composite was measured using a carbon/sulfur analyzer (CS-2000, ELTRA GmbH).

2.3. Electrochemistry

The all samples were first mixed with Super P (TIM-CAL, Super P Li) and carboxymethyl cellulose (CMC, Sigma Aldrich Co.) in an active material/Super P/CMC weight ratio of 70/20/10; deionized water was added to form a homogeneous slurry. Electrochemical characterization of the electrode was performed using CR2032, with a Li foil as the counter electrode. The electrodes were dried in a vacuum oven at 80°C for 24 h before being transferred into an Ar-filled glove box for cell assembly. The electrolyte used was a solution of 1.2 M LiPF₆ in EC:DMC 3:7 by weight with 3% VC additives. The coin cells were charged and discharged between 0.01 and 1.5 V by applying various currents ranging from 0.1 to 5 A g⁻¹. EIS analysis (Bio-Logic Co., VMP3) performed in the frequency range of 1 MHz to 1 mHz with an AC amplitude of 10 mV. To perform the pre-lithiation, the charging circuit with a coin cell and resistor connected in series was used.

3. Results and discussion

The XRD pattern in Figure 1(a) reveals broad peaks over the range of 10°–30°, indicating that the (C-SiO_x)@C and SiO powder were composed of an amorphous phase. The elemental bonding properties of the (C-SiO_x)@C composites were investigated using XPS, as shown in Figures 1(b–d). The characteristic peaks of amorphous SiO₂ at 103.8 and 104.3 eV are observed in the Si (2p) spectra in Figure 1(b). Si-Si bonding was not detected, indicating that the Si particles were completely surrounded by SiO₂. The peaks for SiO₂ and C-O bonds were detected in the O (1s) spectra, as observed in Figure 1(c). The existence of carbon in the (C-SiO_x)@C composite was confirmed by the characteristic peaks of C (1s) for C-C bonds (285 eV), C-O bonds (286.7 eV), and C = O bonds (298.4 eV) (Figure 1(d)). The XPS analysis confirmed that the (C-SiO_x)@C composite was composed of Si⁴⁺ and C-C, C-O, and C = O bonds.

To identify the carbon framework derived from EG and benzene in further detail, SEM, TEM, and elemental mapping analyses were performed. The SEM and EDS results in Figure 2(a–e) indicate that the carbon element was uniformly distributed in the (C-SiO_x)@C composite. Furthermore, the presence of nano-sized silicon and the carbon layer in the SiO_x composite was investigated using HR-TEM. The TEM image in Figure 2(f–h) confirms the presence of Si and shows (111) planes with an interplanar spacing of 3.1 Å. Si nanoparticles were dispersed in

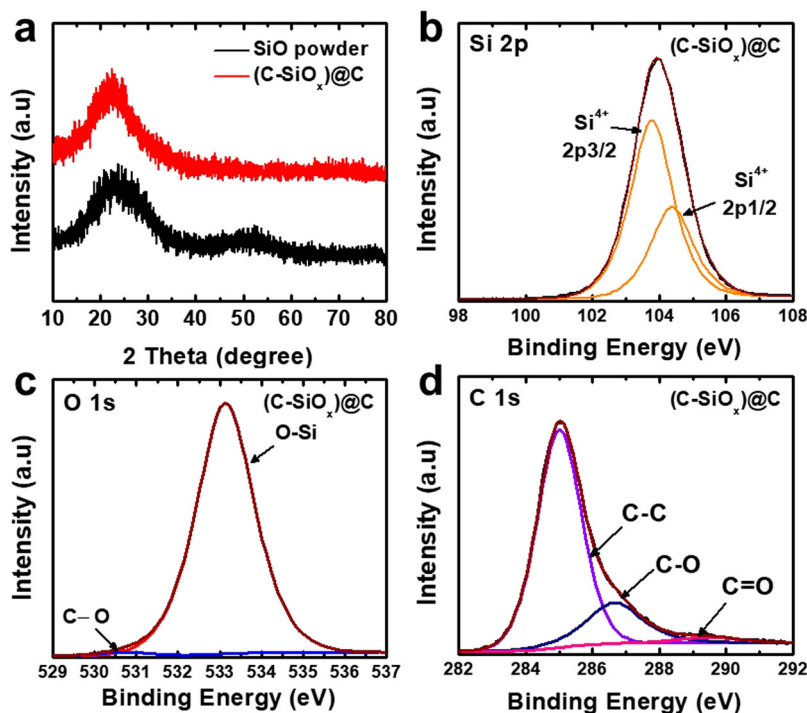


Figure 1. (a) XRD patterns of SiO powder and (C-SiO_x)@C composites. XPS spectra showing (b) Si 2p, (c) O 1s, and (d) C 1s peak of (C-SiO_x)@C composites.

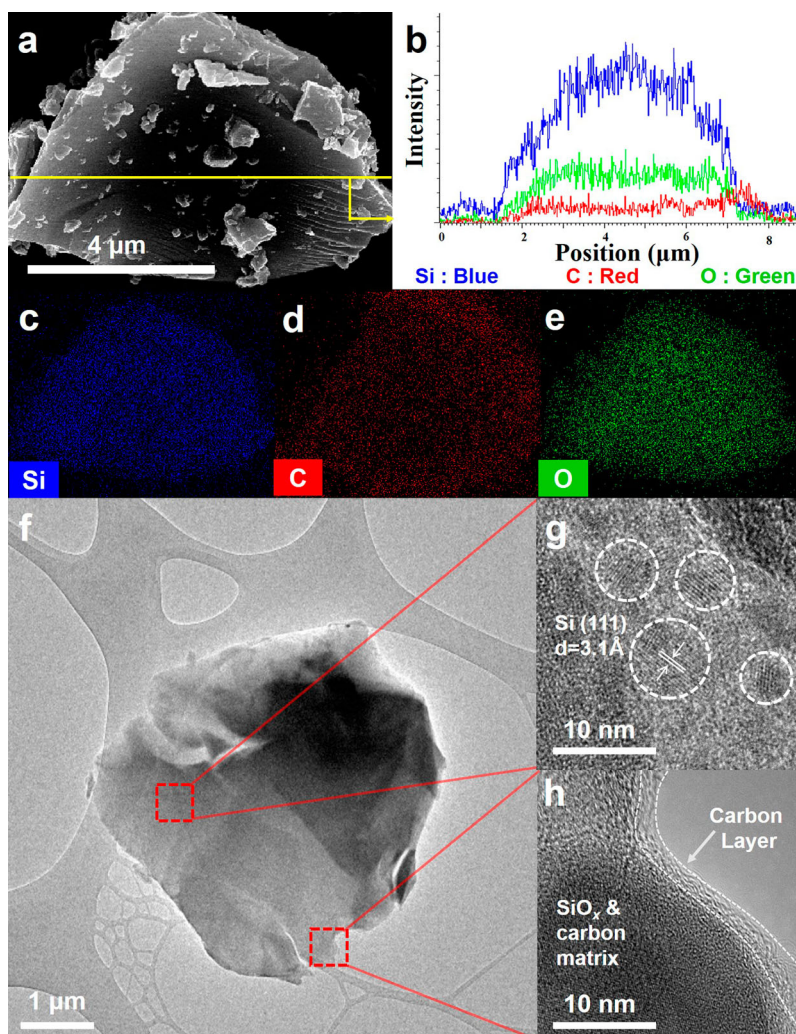


Figure 2. (a) SEM images, (b) EDS line profiles, and (c)–(e) EDS elemental mapping images of (C-SiO_x)@C composite. (f) TEM image, (g) TEM image showing the lattice fringes of the Si nanoparticles, and (h) TEM image of approximately 3-nm-thick carbon layer coated on amorphous carbon and SiO_x matrix of (C-SiO_x)@C composite.

the matrix of amorphous SiO₂ and carbon, contributing to the improved capacity of the (C-SiO_x)@C composite. Notably, the SiO_x particles were coated with an ~ 3 -nm-thick carbon layer. The carbon in the (C-SiO_x)@C composite is believed to play an important role in improving the cyclic stability and electronic conductivity in LIBs with SiO_x anodes. Additionally, the percentage of C in the (C-SiO_x)@C composite measured by a carbon/sulfur determinator was estimated to be 11 wt%.

The conductive C in the (C-SiO_x)@C composite was further characterized using Raman spectroscopy, as shown in Supporting Figure S1. After the carbonization was performed via the heat treatment, strong peaks centered at 1360 and 1580 cm⁻¹ appeared in the Raman spectra, corresponding to the disordered carbon band (D-band) and graphitic carbon band (G-band), respectively. This finding suggests the formation of interconnected carbon paths and carbon-coating layers in the

(C-SiO_x)@C composite. Additionally, Supporting Figure S2 shows the morphologies of the (C-SiO_x)@C and SiO powder with their micron-sized composites.

Figure 3(a) shows the cyclic performance of the (C-SiO_x)@C composite and SiO powder measured at 0.1 A g⁻¹ for the initial 5 cycles and at 0.5 A g⁻¹ for the following cycles in the voltage range of 0.01–1.5 V. The specific capacities of the (C-SiO_x)@C composite after the 1st and 5th cycles were 858 and 854 mAh g⁻¹, respectively, whereas those of the SiO powder were 1185 and 429 mAh g⁻¹, respectively. The capacity of the (C-SiO_x)@C composite at 0.5 A g⁻¹ was maintained up to 627 mAh g⁻¹ over 500 cycles with a coulombic efficiency (CE) of greater than 99.0%. Comparison of the capacity variation between the (C-SiO_x)@C composite and SiO powder confirmed the positive effect of the carbon component in the (C-SiO_x)@C composite, which resulted in significantly reduced capacity degradation.

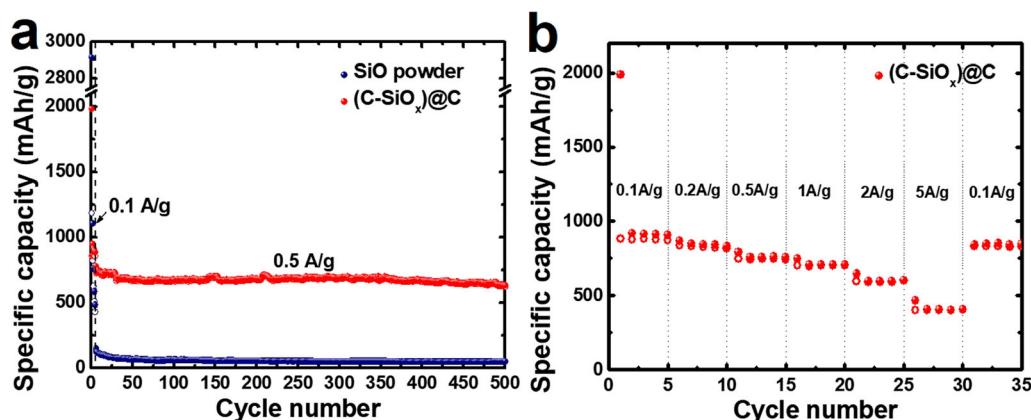


Figure 3. (a) Cycling performance of SiO powder and (C-SiO_x)@C composites over 600 cycles. (b) Power capability of (C-SiO_x)@C composite at various current densities.

The effect of the carbon in the (C-SiO_x)@C composite on the electrochemical performance was also investigated with capacity variations at different current densities (0.1, 0.2, 0.5, 1, 2, and 5 A g⁻¹), as shown in Figure 3(b). The specific capacity at the current density of 0.1 A g⁻¹ was 874 mAh g⁻¹. The capacity gradually decreased with increasing current density, decreasing to 702 mAh g⁻¹ at an increased current density of 1 A g⁻¹, which is approximately 80% of the capacity measured at 0.1 A g⁻¹. When the current density returned to 0.1 A g⁻¹, the capacity of the (C-SiO_x)@C composite was measured to be 830 mAh g⁻¹, which is similar to the previous capacity of 874 mAh g⁻¹ at the same current density. These results imply that the incorporation of carbon led to the formation of an overall homogeneous and interconnected electronic path in the (C-SiO_x)@C composite, resulting in excellent electrochemical performance.

The (C-SiO_x)@C composite exhibited a very low ICE of 43.3%. To improve the ICE, we investigated the mechanism for SEI formation in the Si anode. The SEI layer formed at high voltage (0.3–1.2 V) during the first lithiation is an organic SEI composed of a carbon-rich electrolyte decomposition product. The organic components of the SEI have been reported to be electrochemically stable compared with the inorganic phases; however, the organic phase significantly reduced the Li transport. This reduced Li transport increases site-specific Li deposition and induces the formation of an irregular SEI as well as low efficiency. However, the SEI formed at low voltage (< 0.3 V) is an inorganic SEI with components such as Li₂CO₃, Li₂O, and LiF. It is widely believed that these materials limit electron conductivity and that Li₂CO₃ and Li₂O permit fast Li transport [13]. LiF is also known to play an important role in the stabilization of the initially unstable SEI layer [11,13].

Considering these factors, we formed an inorganic SEI through a pre-lithiation process by supplying slow

current rate flows at a low potential; a resistor for current control was connected in series with the coin cell. The detailed experimental procedure is shown in Supporting Figure S3. The morphology evolution of the SEI layer formed on the electrode surface and inside was investigated by FIB/SEM. Figure 4(a,b) present SEM surface images of the (C-SiO_x)@C electrode after being charged at 0.1 A g⁻¹ and after pre-lithiation, respectively. The surface charged at 0.1 A g⁻¹ was covered with a highly irregular SEI layer, whereas that after pre-lithiation was composed of a very uniformly coated SEI. In addition, the cross-sectional FIB/SEM image of the pre-lithiated electrode showed that the SEI layer was relatively compact compared to the charged electrode at 0.1 A g⁻¹ (Figure 4(c,d)).

The high uniformity and compact feature of the SEI layer for the pre-lithiated (C-SiO_x)@C electrode was verified to favorably affect the electrochemical performance, as explained in Figure 5. According to the XPS analysis in Figure 4(e–h), the SEI layer derived from the pre-lithiation process contained more LiF and Li₂O than that of the electrode charged at 0.1 A g⁻¹, as intended. These distinct SEI characteristics affected not only the ICE but also the capacity retention after 500 cycles, as detailed in Figure 5.

The initial charge–discharge profiles of the (C-SiO_x)@C composite at 0.1 A g⁻¹ before and after pre-lithiation are presented in Figure 5(a,b), respectively. The ICE of the (C-SiO_x)@C composite before pre-lithiation was 43.3% and drastically increased to 93.6% after pre-lithiation. Figure 5(c) shows the capacity variations of the pristine and pre-lithiated (C-SiO_x)@C during cycling. After 500 cycles, excluding the 5 cycles at 0.1 A g⁻¹ followed by a higher current rate of 0.5 A g⁻¹, the fully charged electrode at 0.1 A g⁻¹ and the pre-lithiated electrode displayed capacities of 627 and 707 mAh g⁻¹, respectively. This result suggests that the positive effect of

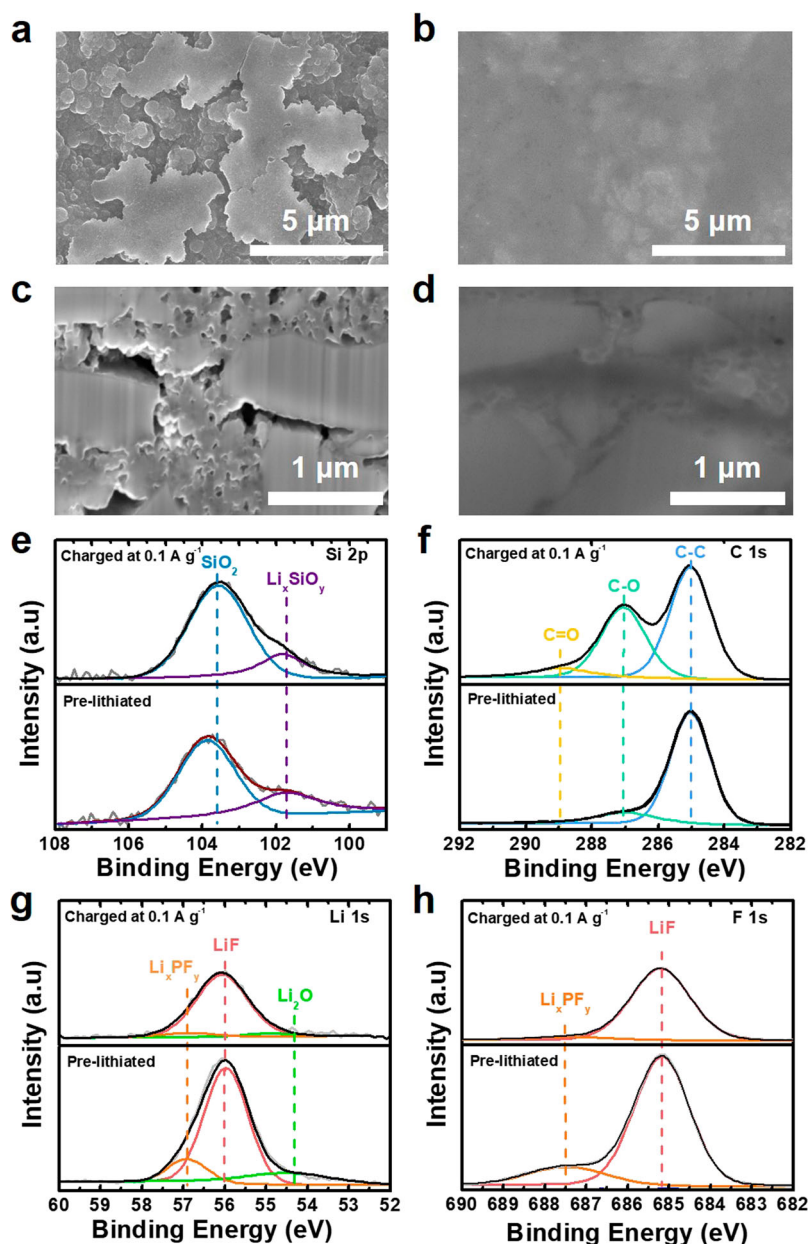


Figure 4. SEM images and cross-sectional SEM images of (a and c) charged electrode at 0.1 A g⁻¹ and (b and d) (C-SiO_x)@C electrode pre-lithiated for 12 h. XPS spectra of the surfaces of the charged electrode at 0.1 A g⁻¹ and (C-SiO_x)@C electrode pre-lithiated for 12 h for (e) Si 2p, (f) C 1s, (g) Li 1s, and (h) F 1s.

pre-lithiation of (C-SiO_x)@C anode was maintained for the entire 500 cycles.

The substantially improved ICE and capacity retention of the pre-lithiated (C-SiO_x)@C in this study suggest that sophisticated modification of the SEI is a promising approach to enhance the electrochemical performance of SiO_x anodes for practical commercial applications.

4. Conclusion

We proposed an approach to overcome the inferior electron transport kinetics and poor cyclic performance of

SiO_x active material for practical applications. Carbon-incorporated/carbon-coated SiO_x anode was fabricated to improve the electrical conductivity of the oxide-based electrode using a simple and cost-effective one-pot synthesis method. In addition, the cyclic performance was improved by forming a fatigue-resistant SEI layer, as this layer is exposed to repeated strains arising from the severe volume changes of the electrode during charge-discharge cycles. The physically durable SEI was also designed to contain a larger portion of Li₂O to improve the conductivity, as Li₂O is known to exhibit high Li⁺ diffusivity. As a result, the ICE increased

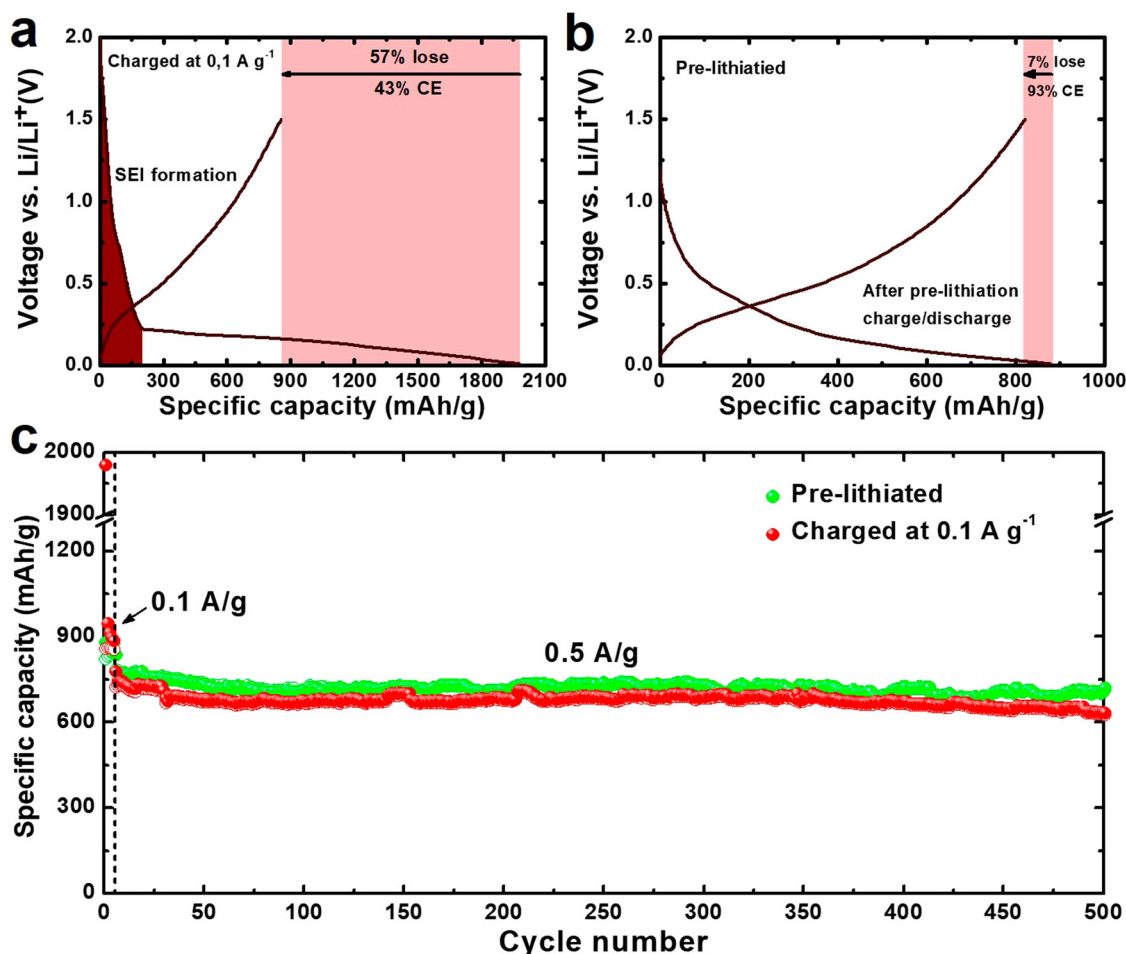


Figure 5. (a) First cycle charge/discharge voltage profiles for the charged (C-SiO_x)@C electrode at 0.1 A g⁻¹ and (b) pre-lithiated (C-SiO_x)@C. (c) Cycling performance for the charged (C-SiO_x)@C electrode and pre-lithiated (C-SiO_x)@C.

significantly from 43.3% to 93.6% and the capacity retention after 500 cycles was improved from 86.7% to 90.4%. Our results suggest that a SiO_x anode electrode that possesses cyclic stability and a reasonable capacity can be prepared through elaborate design of the SEI layer to achieve appropriate physical durability and high Li⁺ diffusivity.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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ORCID

Hyeon-Woo Yang <http://orcid.org/0000-0003-3863-9363>

Dae In Lee <http://orcid.org/0000-0001-8204-0572>

Nayoung Kang <http://orcid.org/0000-0001-9159-4665>

Sun-Jae Kim <http://orcid.org/0000-0002-7908-7086>

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