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Novel design of silicon-based lithium-ion battery anode for highly stable cycling at elevated temperature

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Despite Si being one of the most promising anode materials in lithium-ion batteries, significant challenges remain, including a large volume change, low electrical conductivity and high temperature operation for practical use. Herein, we demonstrate a facile synthesis of Si particles with double-shell coating layers, in which aluminum trifluoride (AlF₃) acts as an artificial defensive matrix, and carbon layers enhance electrical conductivity and compatibility with carbon black. Our study reveals that Si anodes with double shell layers composed of AlF₃ exhibit excellent electrochemical properties at 25 °C and 60 °C, owing to a formation of stable solid-electrolyte-interface layer on the Si surface, and good mechanical strength and chemical nature of AlF₃ layers. The Si@AlF₃@C anode shows a significantly improved cycling performance (capacity retention of 75.8% after 125 cycles at 25 °C and 73.7% at 60 °C after 150 cycles, compared to the specific capacity in the first cycle) and excellent rate capability of >1600mAh/g, even at a 5C rate (at 25 °C). Furthermore, the AlF₃ assisted Si electrode exhibits remarkably reduced volume expansion (thickness change of 71% after 125 cycle at 25 °C and 128% after 150 cycles at 60 °C).

Introduction

Since lithium-ion batteries (LIBs) have been commercialized in 1991, human life has changed a lot using electrical equipment operating from LIBs, like mobile phones, laptop computers, plug-in hybrid electric vehicles, hybrid electric vehicles, and full electric vehicles, due to the batteries’ high energy storage and portable properties.¹ However, demand for energy is rapidly increased owing to a fast developing speed of advanced electronic devices. To meet the requirement of energy demand, it is essential to increase the energy, power density, and operation time of LIBs. Furthermore, LIBs should satisfy a stable operation at high temperature, to be used in vehicles, military equipment, and countries near the equator.²

Silicon (Si) is one of the most promising next generation anode materials in LIBs due to its high theoretical capacity (3579 mAh g⁻¹ for Li₂Si₄ at room temperature), low cost among Li hosting materials (e.g., Sn, Ge, CuO, SnO₂, etc.), and a low reaction potential of <0.4 V (versus Li/Li⁺).³ However, the large volume change during lithiation/delithiation processes leads to a pulverization of Si and a formation of thick insulating solid-electrolyte-interface (SEI) layers by the cracking of Si, resulting in significant capacity fading.⁴⁻⁷ That is why Si has not been used in commercialized LIBs. These main challenges remain for practical usage of Si electrodes in LIBs. To overcome these problems, many types of Si structures have been suggested, such as Si thin film,⁸⁻¹¹ Si nanoparticles,¹²⁻¹⁵ Si nanotubes,¹⁶⁻¹⁸ Si nanowires,¹⁹⁻²² bulk porous Si²³⁻²⁵ and yolk-shell Si²⁶⁻³⁰, to enhance electrochemical performances at room temperature, including a high specific capacity and a stable cycling performance.

In addition, LIBs are increasingly required to stably operate at elevated temperatures of >60 °C, especially in a full electric vehicle application. Recent research of high temperature LIBs has focused on controlling non-liquid type electrolytes, such as gel polymers and solid state electrolytes. For example, poly(vinylidenefluoride-co-hexafluoropropylene), thirty, polyacrylonitrile,³³⁻³⁶ poly(vinyl chloride)/poly(methyl methacrylate) blend,³⁷⁻³⁹ poly(ethylene oxide),⁴⁰⁻⁴¹ and poly(styrene-b-ethylene oxide)⁴² were investigated as polymer based electrolytes. Also, full solid state electrolytes were studied with Li₂S–P₂S₅,⁴³ Li₂La₂Zr₂O₁₂,⁴⁷⁻⁴⁹ Li₂O–V₂O₅–SiO₂,⁵⁰ and Li₂S–GeS₂–P₂S₅(thio-LISICON)⁵¹ for LIB operation at elevated temperatures, by reducing a serious side reaction at the interface between electrolyte and electrode. However, these electrolytes are still hindered for practical use due to several problems, including limited power by a low ionic...
conductivity, difficulty of high temperature synthesis in the case of solid state electrolyte, and high cost. Meanwhile, conventional carbonate-based liquids and aqueous electrolytes showed unstable characteristics at elevated temperatures, including the formation of thick SEI layers and gas evolution (e.g., CO₂ and PF₃), due to a serious side reaction and the decomposition of electrolyte and lithium salt at the interface between Si electrode and electrolyte. In addition, volume expansion of Si electrodes could be maximized at elevated temperature. In cases of solid state electrolyte, numerous studies have been explored with coating, structure alteration, controlling electrolytes, and additives to resolve poor cycling properties due to Jahn-Teller distortion at elevated temperatures. Compared to electrolytes and cathode materials, the electrochemical properties of Si-based anode materials at elevated temperatures are rarely reported. Recently, Etacheri et al. reported that the distinctive surface chemistry of a Si nanowire electrode in 1,3-dioxolane-based electrolytes could remarkably improve the electrochemical properties of the Si electrode, including reduced irreversible capacity loss, stable reversible capacities over prolonged cycling at 60 °C, and lower impedance, compared to alkyl carbonate electrolytes. Other strategies include the introduction of artificial coating layers such as Cu, Ag, Au, NiO, Ti₃SiO₅, Al₂O₃, conducting polymers, TiN, and carbon on the Si surfaces. These results showed reduced polarization and stabilized SEI layers formed on the surface of Si electrodes in conventional liquid electrolytes. Among them, Ti₃SiO₅-coated Si electrodes showed excellent electrochemical performances in terms of cycling stability, rate capability, and remarkably reduced exothermic heat. Carbon-coated porous Si electrodes displayed considerable performance, assisted with a fluoroethylene carbonate (FEC) based electrolyte at elevated temperatures, due to a suppression of electrolyte decomposition.

Herein, we demonstrate a novel design of Si-based anode material exhibiting excellent electrochemical performances at 25 °C and 60 °C, in which double coating layers consisting of AlF₃ and amorphous carbon are introduced on a Si surface. The AlF₃ acts as an artificial defensive matrix for enhancing the mechanical strength and electrochemical stability of Si electrodes at 60 °C, while the outermost carbon layers play an important role in increasing the electrical conductivity of AlF₃-coated Si particles. Our investigations verify that AlF₃ layers provide strong enough mechanical strength to endure the volume expansion of Si electrodes during repeated long-term cycling at 25 °C and 60 °C. Compared to carbon-coated Si electrodes, Si electrodes coated with double layers exhibit a significantly improved cycling performance and reduced electrode thickness at 25 °C and 60 °C.

**Synthesis of AlF₃-coated Si nanoparticles:** 1 g of Si nanoparticles (Alfa Aesar, an average diameter of 100 nm) were dispersed into 10 mL of 1 wt% hydrofluoric acid (HF, J.T. Baker) aqueous solution at room temperature in order to remove the native oxide layer, followed by rinsing with deionized (DI) water several times. Then, the obtained powder was completely dried in a vacuum oven at 80 °C for 24 h. HF-treated Si nanoparticles were dispersed in 25 mL of ethanol (J.T. Baker). A mixture of 0.1 mL [3-(2-Aminoethylamino)propyl] trimethoxysilane (AEAPTMS, Sigma Aldrich) and 25 mL DI water was added to the Si dispersed solution and stirred for 10 min at room temperature. After the reaction, the solution was filtered and dried in a vacuum oven at 80 °C for 12 h. To prepare AlF₃-coated Si nanoparticles, 0.1 M of aluminum nitrate nonahydrate (Sigma Aldrich) aqueous solution (10 mL for 7 wt% AlF₃ relative to Si and 2.17 mL for 1.5 wt%) was mixed together with 1 g of AEAPTMS coated Si nanoparticles. Subsequently, 0.6 M of ammonium fluoride (NH₄F, Sigma Aldrich) aqueous solution (5 mL for 7 wt% and 1.08 mL for 1.5 wt%) was added to the as-prepared solution. All mixtures were continuously stirred at 80 °C for 3 h and dried in a vacuum oven at 80 °C for 12 h to make AlF₃-coated Si particles.

**Synthesis of Si@C and Si@AlF₃@C nanoparticles:** To introduce carbon layers (carbon contents of ~10 wt%) onto the surface of Si and Si@AlF₃ nanoparticles, a chemical vapor deposition process of toluene (Sigma Aldrich) was performed in a quartz furnace (MTI, GSL-1100X) at 900 °C for 7 min.

**Characterization of Si@C and Si@AlF₃@C particles:** Transmission electron microscopy (TEM, JEM-14000) was used to investigate the morphologies of the Si@C and Si@AlF₃@C particles before and after cycles. Also, scanning electron microscopy (Nano SEM 230, FEI) was used to characterize the thickness change of Si electrodes before and after cycles at an accelerating voltage of 10 kV. X-ray diffractometer (D8 ADVANCE, Bruker) was employed to investigate the microstructures of Si, AlF₃ and carbon. A carbon coating layer on the Si surface was characterized by Raman spectrometer (Alpha 300s, WITec GmbH) operating with a laser excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (K-alpha, Thermo Fisher) measurement was used to characterize the SEI layer formed on the surface of the Si@C and Si@AlF₃@C. An electrochemical impedance analysis was performed on the IVIUM frequency response analyzer ranging from 0.01 Hz to 100 KHz.

**Electrochemical tests:** The coin type half-cell (CR2016) was assembled to test the electrochemical properties of the Si@C and the Si@AlF₃@C electrodes. The Si electrodes were prepared by spraying a slurry mixture of surface modified Si powder as an active material, super P carbon black as conductive materials, and poly (acrylic acid) (PAA, weight average molecular weight = 100 kg/mol, Sigma Aldrich)/sodium carboxymethyl cellulose (CMC, 4wt% in H₂O, Sigma Aldrich) (PAA/CMC = 50/50, wt/wt) as polymeric binder with a weight ratio of 80:10:10 on a Cu foil. The electrochemical test was performed in the potential window from 0.005 to 2.0 V.
Polyethylene film (Celgard 2400) was used as a separator. Battery cell assembly and disassembly were carried out in an argon-filled glove box with less than 1 ppm of both oxygen and moisture. After cycling, the cells were opened, rinsed with DMC for 1 h to remove residual Li salts and carbonate based electrolytes, and dried at room temperature in a glove box.

**Results and discussion**

**Synthesis of AlF$_3$-coated Si particles**

The surface modification process of Si particles with AlF$_3$ and amorphous carbon (Si@AlF$_3$@C) is schematically illustrated, as shown in Figure 1a. Before applying the AlF$_3$ coating to a Si surface, the native oxide layer on the surface of Si particles was removed by hydrofluoric acid (HF). TEM image shows that the silicon oxide layers were mostly removed from the Si particle (Fig. 1b). Subsequently, the AlF$_3$ coating layers were introduced on the surface of HF-treated Si nanoparticles. Firstly, 0.1 mL of [3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPTMS) was dissolved in 25 mL of deionized water and 1 g of Si nanoparticles was added with vigorous stirring for 10 min at room temperature to make AEAPTMS-modified Si particles. Secondly, 0.1 M of aqueous aluminum nitrate solution, 1 g of dried AEAPTMS modified Si, and 0.6 M of aqueous ammonium fluoride solution were mixed together and stirred at 80 °C for 3 hr to synthesize AlF$_3$-coated Si (Si@AlF$_3$) nanoparticles. When 2 mL of 0.1 M aluminum precursors were used, AlF$_3$ layers of 5-6 nm were uniformly coated on the surface of the Si particles (Fig. 1c). With an increasing concentration of 0.1 M aluminum precursor (10 mL), thick AlF$_3$ layers of 15-20 nm could be introduced onto the Si surface (Fig. 1d). To confirm the existence of the AlF$_3$ layers, X-ray diffraction (XRD) patterns were obtained from the Si particles with 5-6 nm thick AlF$_3$ layers (Fig. 1e). All XRD peaks correspond to pure crystalline Si. Also, AlF$_3$ is not detected, even though 1.5 wt% of AlF$_3$ was confirmed by an energy dispersive X-ray spectroscopy (EDS) analysis (see ESI, Fig. S1). Presumably, the amount of AlF$_3$ was not enough to detect with XRD, due to the detection limit or the amorphous AlF$_3$ layers were coated on the Si surface. In contrast, when 7 wt% of AlF$_3$ was coated on the Si particles, XRD patterns corresponding to crystalline AlF$_3$ were clearly seen (Fig. 1f). It suggested that a thin AlF$_3$ layer (5-6 nm thick) was successfully coated on the Si surface (Fig. 1c), but the XRD peaks of the AlF$_3$ were not detected owing to the detection limit. In addition, we confirmed the uniform coating of the AlF$_3$ by using selective etching of Si nanoparticles. When the AlF$_3$-coated Si particles (seen in Fig. 1d) were immersed in 5% of sodium hydroxide (NaOH), the inner crystalline Si was completely dissolved and AlF$_3$ hollow structures were observed without changing the AlF$_3$ thickness, compared to pristine AlF$_3$-coated Si (Fig. 1g). Furthermore, the EDS measurement of AlF$_3$-coated Si particles showed the uniform coating of the AlF$_3$ on the surface of Si nanoparticles (ESI, Fig. S1).

As seen in Figure 1, AlF$_3$ was successfully introduced on the Si surface, and a high mechanical property of the AlF$_3$ would be helpful in Si-based anode material for LIBs. However, the poor electrical conductivity of the AlF$_3$-coated Si can be a serious problem for high-power Si-based batteries. To increase the electrical conductivity of the AlF$_3$-coated Si, amorphous carbon layers were introduced using a chemical vapor deposition (CVD) process of toluene at 900 °C for 7 min. The carbon contents of 10 wt% were confirmed by elemental analysis. The TEM image of the carbon-coated Si (Si@C) nanoparticle shows that 5-7 nm thick carbon layers were uniformly coated on the Si surface (Fig. 2a).

When the same carbon coating process was applied to AlF$_3$-coated Si particles, 5-8 nm thick carbon layers were coated on the surface of the AlF$_3$ layers (Fig. 2b). Carbon prepared from the CVD process of toluene vapor was characterized by Raman spectroscopy. The Raman spectrum obtained from carbon-coated Si particles shows that the ratio of the disordered (D) band and graphene (G) band (D/G ratio) is 1.84, indicating the characteristics of amorphous carbon (Fig. 2c). After carbon coating, the XRD patterns of AlF$_3$-coated Si particles are quite similar to those of the pristine AlF$_3$-coated Si sample,
suggested that carbon coating does not affect the microstructure of the AlF$_3$ and Si (Fig. 2d).

**Electrochemical performances of AlF$_3$-coated Si anode**

We investigated the electrochemical properties of two Si-based anode materials (Si@C and Si@AlF$_3$@C) assembled with a coin type half-cell in a range of 0.005-2.0 V (versus Li/Li$^+$). Figure 3a shows the first cycle voltage profiles of Si@C and Si@AlF$_3$@C electrodes obtained at a rate of C/20. The Si@C electrode shows a high initial coulombic efficiency (ICE) of 86.9% with a discharging (lithiation) capacity of 2808 mAh g$^{-1}$ and a charging (delithiation) capacity of 2441 mAh g$^{-1}$. In contrast, the Si@AlF$_3$@C electrode exhibits an initial coulombic efficiency of 81.8% with a discharging capacity of 2457 mAh g$^{-1}$ at the same rate. It may be attributed to the reduced electrical conductivity by the insulting AlF$_3$ layers at the interface between Si and carbon, compared to Si@C system. However, the Si@AlF$_3$@C electrode shows much more stable cycling performance at a rate of C/2 with a specific charge capacity of 1001 mAh g$^{-1}$ after 125 cycles at 25 °C, corresponding to the capacity retention of 75.8%. In contrast, the Si@C electrode exhibits a poor cycling retention of 501 mAh g$^{-1}$ after 125 cycles at a same rate. It may be attributed to a formation of a thick SEI layer in the Si@C electrodes, as will be discussed later. This result suggests that only carbon coating is not enough to achieve a highly stable cycling property of Si-based anode materials. In the case of the Si@AlF$_3$@C electrode, since the AlF$_3$ layers act as an artificial defensive matrix which may form a stable SEI layer and accommodate a large volume change of a Si electrode due to its good mechanical property, highly stable cycling performance was obtained.

![Fig. 2 TEM images of (a) Si@C nanoparticles and (b) Si@AlF$_3$@C nanoparticles. (c) Raman spectrum of Si@C nanoparticles and (d) XRD pattern of Si@AlF$_3$@C nanoparticles show that amorphous carbon layers are coated on the surface of Si and Si@AlF$_3$ particles.](Image)

![Fig. 3 Electrochemical performances of Si@C and Si@AlF$_3$@C electrodes. (a) First cycle discharge and charge curves of Si@C and Si@AlF$_3$@C electrodes obtained in the range of 0.005-2.0 V at a rate of C/20. (b) Cycling performances and (c) rate capabilities of Si@C and Si@AlF$_3$@C electrodes obtained with a rate of C/2 at 25 °C. (d) Cycling performances of Si@C and Si@AlF$_3$@C electrodes obtained with a rate of C/2 at 60 °C. Impedance spectra of Si@C and Si@AlF$_3$@C electrodes obtained at (e) 25 °C and (f) 60 °C.](Image)
On the contrary, the Si@AlF$_3$@C electrode exhibited highly stable cycle performance with a specific capacity of 1977 mAh g$^{-1}$ in the first cycle and 1457 mAh g$^{-1}$ after 150 cycles at a rate of C/2, corresponding to the capacity retention of 73.7%. To further understand the superior electrochemical properties of the Si@AlF$_3$@C electrode, an electrochemical impedance spectroscopy (EIS) measurement was employed. Si@AlF$_3$@C electrode showed slightly larger impedance value that of Si@C electrode due to AlF$_3$ insulating property (see ESI, Fig. S2). However, both the Si@C and Si@AlF$_3$@C electrodes exhibited similar ohmic and charge transfer resistance until 50 cycles at 25 °C (Fig. 3e). After 125 cycles, the Si@C electrode showed a tremendously increased charge transfer resistance (3 times larger than that of the electrode after 50 cycles). In contrast, the Si@AlF$_3$@C electrode displayed much less increased resistance after 125 cycles. The difference of resistance between the Si@C and the Si@AlF$_3$@C electrodes was significantly increased at the elevated temperature of 60 °C. In the case of the Si@AlF$_3$@C electrode, the 150-cycled electrode exhibited a slightly increased resistance value at 60 °C, compared to the 125-cycled electrode at 25 °C. However, the Si@C electrode showed tremendously increased resistance, owing to the formation of thick SEI layers by a serious decomposition of the electrolyte at 60 °C.

In addition to stable cycling retention, swelling of electrodes after cycling is also a critical issue in battery anodes. We obtained cross-sectional SEM images from pristine and cycled electrodes (125 cycle at 25 °C and 150 cycles at 60 °C), as shown in Figure 4. The 30 µm thick pristine Si@C electrode showed a tremendous thickness alternation (94-103 µm corresponding to 213-243% expansion) after 125 cycle at 25 °C (Fig. 4b). At an elevated temperature of 60 °C, the thickness of the electrodes was further increased to expansion of 280-306% (Fig. 4c). In particular, when the 150-cycled Si@C electrode was disassembled in an argon-filled glove box, most electrolytes were dried, indicating that a serious decomposition of the electrolytes had occurred. Compared to the Si@C electrodes, the Si@AlF$_3$@C electrode showed a much lower volume expansion of 71% and 128% at 25 °C and at 60 °C, respectively (Fig. 4d-4f). These results suggest that the AlF$_3$ layer between the Si and carbon can restrict a large volume change of the Si electrodes and form a stable SEI layer, compared to the Si@C electrode.

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As further evidence for stable cycling of the Si@AlF$_3$@C electrode, we obtained TEM images of Si particles after 125 cycles at 25 °C and after 150 cycles at 60 °C. Figure 5a shows a low-magnified TEM image of expanded Si@C particles after 125 cycles. In the magnified image, sponge-like Si@C structures were observed as being similar to those Iwamura et al. reported previously (Fig. 5b)\[80\]. In contrast, the Si@AlF$_3$@C particles maintained the original dimensions, except for the trapping of amorphous Si particles within the AlF$_3$@C hollow structure at 25 °C (Fig. 5c). In the magnified TEM image of Figure 5d, the shell thickness of a hollow structure consisting of AlF$_3$, carbon and SEI layers are 13-18 nm, which is slightly increased compared to the thickness of AlF$_3$@C in the original Si@AlF$_3$@C particles. It may be attributed to the sufficient mechanical strength of the AlF$_3$ protective layers. To prove the elements of Si, Al and F, the high-angle annular dark field (HAADF) TEM image of the sample seen in Figure 5c was obtained (Fig. 5e), and the EDS analysis (from the rectangular area seen in Fig. 1e) was...
performed (Fig. 5f). From these results, the AlF$_3$ and carbon layers in the Si@AlF$_3$@C particles were still strongly adhered to the amorphous Si after 125 cycles at 25 °C. At the elevated temperature of 60 °C, the morphology of Si@C particles after 150 cycles seems to be a significantly expanded sponge-like structure, due to a serious side reaction at the higher temperature (Fig. 5g and 5h). The TEM image of Si@AlF$_3$@C particles also showed a volume expansion of particles, but a hollow shell consisting of AlF$_3$, carbon, and SEI layers still remained after cycling (Fig. 5i and 5j). The HAADF TEM image and EDS analyses of the sample seen in Figure 5i indicated that cycled Si particles are composed of Si, AlF$_3$ and carbon. Even after long-term cycling at 60 °C, the double coating layers of AlF$_3$ and carbon play an important role in keeping the mechanical integrity of the Si-based particles.

Importantly, a mechanically stable AlF$_3$ layer uniformly covering the Si surface could effectively endure a large volume change of Si particles during cycling, while the outer amorphous carbon shell is partially disconnected, as depicted in Fig. 6a. In this regard, the AlF$_3$ layer coated on the Si particle is expected to avoid the direct contact of the electrolyte with the Si active materials and alleviate the undesirable electrolyte decomposition. Also, the chemical nature of AlF$_3$ can promote formation of stable SEI layers due to its unreactive characteristics with electrolyte and HF species. The effect of AlF$_3$ coating layer on the interaction between Si electrode surface and electrolyte was characterized by XPS analyses. To investigate the surface chemistry of both Si@C and Si@AlF$_3$@C electrodes after 150 cycles at 60 °C, XPS measurements of cycled Si anodes were performed, as shown in Fig. 6b. In C 1s spectra, the pronounced peak corresponding to carbon bonded to hydrogen (C-H) was observed at 285.0 eV for both electrodes with similar levels of intensity. A noticeable feature in the C 1s XPS spectra of Fig. 6b is that the Si@AlF$_3$@C electrode exhibits a significantly reduced peak intensity attributed to Li$_2$CO$_3$, which is generated by the EC decomposition, compared to the Si@C electrode. This result suggests that interfacial architecture based on the AlF$_3$ coating layer inhibits the reductive decomposition of the EC solvent at the Si anode. The LiF peak at 684.9 eV appeared for both electrodes. This is because using FEC as a reducible additive produces an SEI layer mainly composed of LiF. The C1s XPS spectrum obtained from the Si@C electrode showed a relatively strong peak ascribed to Li$_2$PO$_3$F$_2$ and Li$_2$PF$_5$ at 687 eV, compared with the Si@AlF$_3$@C electrode. This is persuasive evidence that the AlF$_3$ coating layer effectively suppresses LiPF$_6$ salt decomposition.

Proposed mechanism of SEI layer formation

Figure 6a displays possible mechanisms for the cracking of Si anode materials with and without AlF$_3$. The interfacial layers with only amorphous carbon can readily break due to a weak mechanical strength of carbon anchored on the Si particles, and thus thick SEI layers are produced via continuous unwanted electrolyte decomposition on the exposed active Si surface. The open circuit voltage (OCV) variation of fully lithiated Si@C and Si@AlF$_3$@C electrodes stored at 60 °C was monitored, as shown in Fig. 7a. The OCV of the fully lithiated Si@C electrode continuously increased for 15 days, whereas the fully lithiated Si@AlF$_3$@C electrode showed a lower OCV increase. This indicates that the AlF$_3$ coating layer effectively restrains the self-discharging behavior by preventing some side reactions between the Si electrode and the electrolyte. Figure 7b presents the voltage profiles of lithiated Si@C and Si@AlF$_3$@C electrodes during the Li extraction after they were
stored at 60 °C for 15 days (seen in Fig. 7a). The charge capacity of the Si@C electrode significantly declined to 1520 mAh g⁻¹ (a value of approximately 63 % relative to the Si@C electrode before storing) after storage. On the other hand, the Si@AlF₃@C electrode maintained a superior specific capacity of 1865 mAh g⁻¹ (a value of approximately 92.7% relative to the Si@AlF₃@C electrode before storing) under the same condition. This implies that the AlF₃ coating layer is very effective to prevent the Li extraction from the Si electrode indicating the self-discharge.

Conclusion

We demonstrated a facile synthesis of Si nanoparticles with double shell layers, in which AlF₃ layers enhance the mechanical and electrochemical stability while amorphous carbon increases the electrical conductivity of Si particles. Synergistic coupling of AlF₃ and amorphous carbon layers enabled the Si anode to exhibit significantly improved long-term cycling stability at 25 °C, and even at a high temperature of 60 °C. Moreover, the AlF₃ assisted Si electrode showed remarkably reduced volume expansion (a thickness change of 71% after 125cycle at 25 °C and 128% after 150 cycles at 60 °C). This novel design of a Si anode with double shell layers can be extended to other lithium alloying materials (e.g., germanium and tin) which have a large volume change during the lithiation and delithiation process.

Acknowledgements

This work was supported by the IT R&D program of MOTIE/KEIT (10046309).

Notes and references

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† Electronic Supplementary Information (ESI) available: EDS measurement of Si@AlF₃@C particles and EIS measurement of both Si@C and Si@AlF₃@C electrodes. See DOI:10.1002/jmca
We demonstrate a facile method for synthesizing silicon particles with double coating layer consisting of aluminum trifluoride and amorphous carbon to use as anode material for high-performance lithium-ion battery at elevated temperature.