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Article

Interplay between solid-electrolyte interphase and (in)active Li_xSi in silicon anode



Zhang et al. apply a set of techniques to qualitatively and quantitatively study the SEI and its dynamic interplay with the silicon anode, focusing on charge transfer, content, composition, nanostructure, element distribution, and mechanical and electrochemical properties. The correlation between SEI stability and battery performance is analyzed.

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Highlights

A modified TGC method quantifies the evolution of SEI and Li_xSi amount

Some SEI components are electrochemically active during delithiation

The nonequilibrium interplay between SEI and Si deteriorates the cycling life

The LiF-rich SEI enables a lasting equilibrium interplay between SEI and Si

Zhang et al., Cell Reports Physical Science 2, 100668 December 22, 2021 © 2021 The Author(s). https://doi.org/10.1016/j.xcrp.2021.100668

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Article Interplay between solid-electrolyte interphase and (in)active Li_xSi in silicon anode

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SUMMARY

Solid-electrolyte interphase (SEI) is regarded as the most important but the least understood part of lithium (Li)-ion batteries. A comprehensive understanding of the nature of the SEI and especially its interplay with active materials during cycling is crucial since it governs the charge transfer and Li⁺ transport. Herein, the dynamic interplay between SEI and silicon (Si) anode during cycling is revealed quantitatively and qualitatively by titration gas chromatography (TGC), cryogenic transmission electron microscopy (cryo-TEM), and other techniques to probe charge transfer, nanostructure, and equilibrium. The results show that it is difficult to construct an equilibrium interplay between the SEI and Li_xSi due to the intrinsic instability of some SEI components (e.g., Li₂O and carbonates) and the pulverization of Si anode, resulting in the continuous formation of the SEI and inactive Li_xSi. The addition of fluoroethylene carbonate helps construct such equilibrium interplay through formation of a LiF-rich SEI, thus improving cyclability.

INTRODUCTION

The charge-transfer reactions are the foundation of rechargeable batteries. Ideally, all of the charges are going through the active materials, generating/storing the energy and power for use. In fact, part of the charges is consumed by the side reactions and causes capacity loss, including the inevitable formation of the well-known solidelectrolyte interphase (SEI) on the electrode surface.^{1–5} SEI is regarded as the most important but the least understood part inside rechargeable batteries.⁶ Its intrinsic properties govern the lithium (Li)⁺ transport, charge transfer, and thermal stability and thus determine the capacity loss, self-discharge, fast charging capabilities, low/high-temperature performance, and even safety of the batteries.^{7–13} Undoubtedly, a comprehensive understanding of the SEI nature and especially its interplay with the active materials during cycling is crucial for both fundamental and applied research of rechargeable batteries.

The interplay between SEI and active materials will be significantly magnified due to the high reactivity and large volume variation of the high-capacity anodes, such as Li metal and silicon (Si). An anisotropic volume expansion/shrinkage of up to 400% will result in particle cracking or pulverization in bulk and on the surface, triggering continuous SEI formation at the expense of more charge/Li⁺ consumption in the SEI and electrolyte dry-out.^{14–19} Alternatively, the accumulation of SEI will increase cell resistance and lead to an incomplete reaction, reducing the utilization of active materials and forming the electronically isolated species (inactive Li or Li_xSi), temporarily or permanently.^{20–22} However, the dynamic picture of the interplay between

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(A) Initial voltage profiles of the Si electrodes cycled at a specific current density of 100 mA/g.(B) Cycling stability of the Si anodes at a specific current density of 100 mA/g for the first two cycles and 1.5 A/g for the subsequent cycles.

SEI and active materials during cycling is still lacking, especially combining the qualitative and quantitative analyses. It is critical to differentiate and quantify the individual contributions of SEI and electrode active materials to the charge transfer, and uncover their interplay with the battery performance.

In this work, the Si anode is used as a model material for high-energy anodes since its SEI has never been quantitatively explored. Titration gas chromatography (TGC) was recently proved to be a powerful tool to quantitatively distinguish the metallic Li and Li⁺-containing species in SEI of the electrochemical Li deposits and graphite.^{23,24} It also works for Si anodes. TGC, cryogenic transmission electron microscopy (cryo-TEM), X-ray photoelectron spectroscopy (XPS), and other techniques are combined to quantitatively and qualitatively reveal the SEI evolution and its interplay with the active/inactive Si during initial lithiation/delithiation and long-term cycling. The results demonstrate that the SEI electrochemically forms before and during Si lithiation, and it decomposes during delithiation processes. It consumes more than 10% of charges and triggers the formation of inactive Li_xSi by isolating it from the electrical network. Fluoroethylene carbonate (FEC) as an electrolyte additive is found to be beneficial for forming a relatively stable SEI and, therefore, enhancing the cycling life of Si anodes. Our findings depict a comprehensive picture of the SEI evolution and its interplay with the active/inactive Si anode during cycling and unravel the correlation between SEI stability and battery performance.

RESULTS

Electrochemical behavior of Si anodes

As shown in Figure 1, commercial Si nanoparticles (100–500 nm, Figure S1) exhibit an initial discharge capacity of 3,580 mAh/g and charge capacity of 3,147 mAh/g (Figure 1A) in 1 mol/L LiPF₆ in 1:1 (v/v) ethylene carbonate/dimethyl carbonate (EC/DMC) with a low initial Coulombic efficiency (CE, 83% in Figure 1A). Questions are raised associated with the Li-Si alloy/de-alloy reaction and SEI formation/decomposition. (1) When do they start? (2) How many reversible/irreversible charges/capacities are from them individually? (3) What are their nanostructures? (4) How do they interplay during cycling? In order to answer these questions, a combination of TGC, cryo-TEM, XPS, and electrochemical impedance spectroscopy (EIS) was applied on Si anodes at different stages. The goal is to distinguish the active/inactive Li_xSi alloy and SEI, probe their evolution and interplay quantitatively and qualitatively, and ultimately correlate them with the battery performance.

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Figure 2. TGC results of the Si anode at various lithiation/delithiation states in the first cycle

(A) Evolution of Li content in Li_xSi.

(B) Content of ${\rm Li}^+$ consumed for SEI formation.

(C) Selected states for TGC tests on the potential curve for the lithiation/delithiation of the Si anode.

(D) Capacity contribution from $\mathrm{Li}_{\mathrm{x}}\mathrm{Si}$ and SEI in the first cycle.

Error bars indicate the standard deviation.

The charge-transfer interplay between ${\rm Li}_{\rm x}{\rm Si}$ alloy and SEI during the first cycle

In order to differentiate the capacity of the Li_xSi alloying reaction from that for the SEI formation, a modified TGC was developed (Figures S2–S4; Table S1), where NaOH solution was added to react with the Li_xSi (as discussed in Supplemental experimental procedures). As far as we know, none of the SEI components will react with NaOH and produce H₂ (Table S2). Therefore, the corresponding Li_xSi alloy content was determined based on the following reaction:

$$Li_{x}Si + (1 + x)H_{2}O + (2 - x)OH^{-} = xLi^{+} + SiO_{3}^{2-} + (\frac{x}{2} + 2)H_{2}\uparrow.$$
 (1)

Once the Li concentration in the Li_xSi is determined, the Li^+ content in the electrochemically formed SEI can be calculated based on the charge balance:

$$Q_{SEI} = Q_{total} - Q_{Li_xSi}.$$
 (2)

As displayed in Figure 2, SEI forms before the Li-Si alloying reaction, and the detected content of Li in Li_xSi alloy starts at the end of the voltage slope (~130 mAh/g, 0.13 V). Both Li-Si alloying reaction and SEI formation proceed fast during lithiation, reaching ~3,000 mAh/g (0.8 mg_(Li)/mg_(Si), Figure 2A) and 400 mAh/g_(Si) (Figure 2B), respectively, at the end of lithiation. When the cell was charged to 1.5 V, plenty of inactive Li_xSi remained in the electrodes (Figure 2A), responsible for ~500 mAh/g of capacity loss in the first cycle. Meanwhile, the SEI amount is decreased by 48.2% when the cell is charged to 1.5 V, indicating that some of the SEI components are electrochemically decomposed. This behavior demonstrates the intrinsic instability of the SEI on Si anodes.^{25–27}

Figure 2D summarizes the capacity contribution in the first cycle. At the first discharge, 12.1% capacity is ascribed to the SEI formation, and the CE is estimated to be 87.9% if all of the Li_xSi alloys are electrochemically reversible while the SEI is not, as commonly assumed. However, the actual situation is much more complex than the above assumption. Some of the active Li_xSi alloys become "inactive" and part of the SEI is electrochemically decomposed during recharge. It is difficult to

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Figure 3. XPS spectra of Si electrodes at various lithiation/delithiation states (A–C) C 1 s (A), Si 2p (B), and F 1 s (C) spectra of Si anodes cycled in the FEC-free electrolyte. (D–F) C 1 s (D), Si 2p (E), and F 1 s (F) spectra of Si anodes cycled in the FEC-containing electrolyte.

directly predict the accurate CE after the first cycle, which was measured to be 83.6% by the Coulombic titration (Figure 1A). Quantitative analysis of the TGC results indicates that the inactive Li_xSi alloy is responsible for 70.8% of the capacity loss (16.4% of the discharge capacity) during the first cycle. Li is trapped in the Li_xSi alloy electrically isolated by SEI.

The nanostructure interplay between Li_xSi alloy and SEI during the first cycle

Since the TGC method cannot provide information on the chemical composition and nanostructure of SEI, we performed XPS and cryo-TEM measurements to elucidate the structural interplay between SEI and Li_xSi in the first cycle.

Figure 3 exhibits the XPS spectra of Si 2p, C 1s, and F 1s at various lithiation/delithiation states. Organic species such as C-C (284.8 eV), C-O (286.7 eV), O-C=O (288.3 eV), and -ROCOOLi (289.7 eV)²⁸ (Figure 3A) and inorganic species such as LiF (684.5 eV) and Li_xPF_yO_z (686.9 eV)²⁹ (Figure 3C) are detected as the Si anode is discharged to 130 mAh/g (~0.13 V). The SEI at this stage is rather thin, as the Si signals were detectable in the Si 2p spectra (Figure 3B). When the Si anode was discharged to 1,500 mAh/g, the Li_xSi is fully covered by thick SEI since no Si element (in forms of SiO₂, Si, or Li_xSi) can be detected even after the electrode was Ar⁺ etched for 300 s (Figure 3B). The enhanced signals for the carbonate (289.7 eV) suggest the massive solvent decomposition. As the Si anode is discharged to 0.0 V, the signals from the carbonate species (289.7 eV) are slightly reduced (Figure 3A). The SEI becomes thinner and the signal for Li_xSiO_y becomes more obvious at 0.0 V than at 1,500 mAh/g after etching for 300 s (Figure 3B). This suggests that some organic species in the outer SEI were partially dissolved or peeled off from the Si particle owing to their loose structure.^{30,31} When the Si anode is charged to 1.5 V, the signals for

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Figure 4. Cryo-TEM and EDS mapping of Si anodes during the first cycle

(A–D) High-resolution (HR)TEM of Si anodes after first lithiation (A) and first delithiation (B) in the FEC-free electrolyte, after first discharge (C), and first charge (D) in the FEC-containing electrolyte.

(E–H) EDS mapping of Si anodes after first discharge (E) and first charge (F) in the FEC-free electrolyte, after first discharge (G), and first charge (H) in FEC-containing electrolyte.

The red points and green points in EDS mapping represent the signal from Si and O, respectively. More images can be found in Figures S5–S8.

 Li_xSi and Li_xSiO_y re-appear even without any etching (Figure 3B), suggesting the thinning of the SEI, which agrees well with the SEI content reduction probed by the TGC.

The nanostructure of the SEI on the Si anode was visualized through cryo-TEM and energy dispersive spectroscopy (EDS) mapping. Discharging to 0 V leads to the formation of the crystalline $Li_{15}Si_4$ with a characteristic spacing distance of 3.76 Å (Figure 4A). The SEI is present on the surface of Li_xSi alloy and exhibits a mosaic configuration where inorganic nanocrystals, such as Li_2O and LiF, are embedded in the amorphous organic species (Figure 4A). Upon delithiation, crystalline Si was found at the end of the first charge (1.5 V), which is isolated by the SEI and thus becomes inactive³² (Figure 4B). Meanwhile, it is difficult to find any Li_2O particles on the electrode surface (Figure 4B), probably due to the electrochemical reaction between Li_2O and Si for Li_xSiO_y during charging as follows:^{25,33,34}

$$Li_2O + Si \xrightarrow{e} Li_xSiO_y + Li^+$$
. (3)

EDS mapping was performed to distinguish the interface between amorphous Li_xSi and SEI, and thus determine the SEI thickness. The O and C signals (Figures S5–S8) mainly originate from the SEI and enrich at the outer shell of Si particles at the lithiation state (Figure 4E). The thickness of SEI was measured to be ~41 nm. After delithiation, both O and C signals were significantly reduced (Figure 4F), suggesting the decomposition of some SEI species during charging. The increase (during lithiation) and reduction (during de-lithiation) of the SEI thickness agrees with the "breathing" behavior of SEI, as revealed by the above TGC and XPS results (Figures 2B and 3B).





1600 (B/HAm) 1200

₫

ł

without FEC

50

with FEC

0

30

Cycle number

10 20

capacity





С

Figure 5. TGC results for long-term cycling

(A) Content evolution of the SEI Li⁺ in the first two cycles.
(B) Content evolution of the SEI Li⁺ amount in the extended cycling.
(C) Content evolution of the Li in the inactive Li_xSi in the extended cycling. Error bars indicate the standard deviation.

Nonequilibrium interplay between LixSi alloy and SEI during long-term cycles

A proper SEI should act as a passivation layer protecting the electrodes from continuous electrolyte corrosion, and its interplay with LixSi alloy should maintain equilibrium. The SEI with reduced thickness after the first charge will break the above equilibrium, weaken its passivation function, and even expose the fresh surface of the newly pulverized particles to the electrolyte in the subsequent cycling. As a result, the content of the Li⁺ consumed for the SEI dramatically increases in the subsequent lithiation processes, triple that at the first lithiation due to the accelerated deterioration by the particle pulverization of Si (Figure 5A). It was much reduced (0.12 mg_(Li)/mg_(Si)) again after the second delithiation, indicative of the repeated "breathing" behavior of the SEI (Figures S9 and S10 for the XPS and TEM results during the second cycle). These results suggest that the SEI formed in the conventional electrolyte is unstable and fragile with low Young's modulus (Figure S11), which cannot tolerate the significant volume change of Si (Figure S12), leading to a repeated building-breaking-repairing nonequilibrium interplay between SEI and the Si anode. Consequently, the SEI keeps accumulating during cycling that results in a total irreversible capacity of up to 1,500 mAh/g in 53 cycles, representing what we think to be the primary source of capacity loss (Figure 5B). Meanwhile, the thick SEI will further hinder the charge transfer, leading to more inactive Li_xSi residue, ^{35,36} contributing up to another ~900 mAh/g capacity loss in 53 cycles (Figure 5C). Therefore, it is essential to maintain an equilibrium interplay between SEI and the Si anode during cycling.

Building equilibrium interplay between $\mathrm{Li}_{\mathrm{x}}\mathrm{Si}$ alloy and SEI for improved performance

The above nonequilibrium interplay between Li_xSi alloy and SEI mainly originates from the intrinsic instability of the SEI and pulverization of the Si particles. Electrochemical SEI decomposition during charging makes SEI unstable and too fragile to prevent the pulverization of the Si particles. Therefore, constructing stable SEI and Si particles is the key to maintaining a long-lasting equilibrium interplay between Li_xSi alloy and SEI and thus achieving a high-performance Si anode.

As a proof of concept, FEC was added into the electrolyte and was expected to strengthen the SEI by forming more "inert" LiF inside. TGC results demonstrate that FEC facilitates the generation of more SEI in the first lithiation process (corresponding to \sim 700 mAh/g_(Si) versus 400 mAh/g_(Si) in the FEC-free electrolyte, Figure 2B) but reduces the inactive Li_xSi alloy (60.2% irreversible capacity versus

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70.8% in the FEC-free electrolyte, Figure 2D). In-depth analysis by XPS and cryo-TEM indicates that this SEI is thinner, more compact, and contains more LiF inside (Figure 4C) as evidenced by its detectable Si signal after 120s-etching (Figure 3E) and stronger F signals (Figure 3F) during lithiation. Its thickness was determined to be ~26 nm after the first lithiation (Figure 4G). Such an SEI results in lower interfacial resistances (Figure S13) and higher Young's modulus (Figure S11), which are beneficial for charge transfer and maintaining the particle integrity of the Si anode.

The "active" Li₂O is still present in the SEI but has less concentration as shown in Figure 4D, which leads to less Li_xSiO_v formed during charging (Figure 3E). The "breathing" behavior of the SEI also occurs in the FEC-containing electrolyte in the first cycle (Figures 2B and 5A). However, LiF, as an inert component, was gradually enriched in the SEI during cycling (Figures 4C, 4D, and S11), albeit part of it may be detached in the mosaic SEI, especially when organic species were decomposed or dissolved during charge, as indicated by the slightly reduced F signal after the charge (Figure 3F). Such LiF-rich SEI is very helpful in alleviating the breathing behavior of the SEI and constructing an equilibrium interplay between LixSi alloy and SEI in the subsequent cycles. (Potential mechanisms are discussed in Note S1 in Supplemental experimental procedures.) The amount of SEI was increased first but slightly decreased during the second cycle in the FEC-containing electrolyte (Figure 5A), suggesting the tendency of forming a gradually stabilized interphase and equilibrium interplay between SEI and Li_xSi (Figure 5B). As a consequence, the capacity retention of Si anodes was much improved (49.2% versus 7.3%, Figure 1B) in 150 cycles.

DISCUSSION

A combination of the above TGC, XPS, Cryo-TEM, EDS, EIS, and atomic force microscopy (AFM) techniques reveals a vivid landscape for the interplay between the SEI and Li_xSi alloy on Si anodes during cycling in terms of charge transfer, nanostructure, and equilibrium (Figure 6). SEI forms before and through the Li-Si alloy reaction and contributes to more than 10% of the initial discharge capacity. It has a loose structure with a low mechanical strength, which is hard to prevent the pulverization of Si particles. As a result, the fresh surface of Si was exposed and triggers the formation of more SEI at the expense of more charges/Li⁺ consumption in the SEI. Alternatively, SEI will trap the active Li_xSi, hinder the charge transfer, and form the inactive Li_xSi temporarily or permanently. The above processes are repeated over cycles and result in the continuous accumulation of SEI and inactive Li_xSi, both of which cause capacity loss and ultimately failure in the battery.

The equilibrium interplay between the SEI and Li_xSi alloy is further broken by the intrinsic instability of the SEI on Si anodes, some of which components are unstable and involve electrochemical decomposition/reaction during charging, such as Li₂O. Especially, Li₂O nanoparticles in the SEI could react with Si to form Li_xSiO_y and thus were consumed. Therefore, active Li₂O is incompatible with the Si anode, while inert LiF is helpful to construct a thin, dense, robust, and stable SEI. Such LiF-rich SEI on the Si anode helps to form and maintain an equilibrium interplay between Li_xSi alloy and SEI, which improves the cycling performance of the Si anode. These findings not only enrich the fundamental understanding of the SEI nature and evolution but also highlight the interplay between the SEI and Li_xSi during cycling, which points out the right way to achieve a high-performance Si anode for practical use by constructing and maintaining an equilibrium interplay between SEI and Li_xSi, such as through an LiF-rich interphase.



Figure 6. Schematic illustration of the SEI evolution and its impact on Si anodes

SEI continues to form during lithiation but reduces during delithiation. This "breathing" behavior is harmful, as it leads to more electrolyte decomposition, SEI accumulation, and SEI-isolated Li_xSi. The beneficial role of electrolyte additive FEC is to form a LiF-rich, gradually stabilized SEI on the Si surface, thus maintaining an equilibrium interplay between SEI and Li_xSi and enhancing the integrity of the Si anodes.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Xuefeng Wang (wxf@iphy.ac.cn).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All data related to this study included in the article and Supplemental information will be provided by the lead contact upon reasonable request.

Electrochemical testing

The Si electrodes were prepared using a conventional slurry method. Nano Si particles, carbon nanotube, and polyacrylic acid (PAA) binder with a mass ratio of 7:1:2 were mixed in N-methyl pyrrolidone (NMP) and cast on the Cu foil. After being dried at 80°C in a vacuum oven, the Si electrodes were cut into disks with a diameter of 1 cm. Celgard 2300 and glass fiber separators were sandwiched between the Si electrode and Li metal foil, with the Celgard 2300 facing the Si electrode. 150 μ L of electrolyte was added, consisting of 1 M LiPF₆ in 1:1 (v/v) EC/DMC with or without the addition of 10 vol% FEC. The coin cells were tested using a Neware battery cycler (CT-4008T-5V10mA-164). The first two cycles were cycled between 0 and 1.5 V at a specific current density of 100 mA/g to fully activate the Si electrodes, and the following cycles were cycled between 0.01 and 1.5 V at a specific current density of 1.5 A/g. For EIS, the SP-200 system (Biologic) was used. The amplitude was 5 mV, and the frequency range was 100 kHz to 10 mHz. The cell was rested at an

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open circuit for 2 h at the different states of charge/discharge before conducting the measurement.

TGC

After cycling, the Si electrodes together with Celgard separators were carefully separated from the other components of batteries and sealed in a container with an open-top cap without washing. The assembling and disassembling of coin cells were conducted in an argon-filled glovebox with O_2 and H_2O contents <0.5 ppm.

To determine the amount of Li in Li_xSi, 0.5 mL of 1 M NaOH was injected into the container to react with Li_xSi (Figure S2). The reaction will take about 1 h to complete (Figure S3). Just to be safe, we performed the following tests after reacting for 3 h with no bubble visible. The H₂ concentration was measured by a Shimadzu Nexis GC-2030 gas chromatography (GC) system equipped with a barrier ionization discharge (BID) detector. Helium (99.9999%) was used as the carrier gas. The split temperature was kept at 250°C with a split ratio of 5. The micropacked ST column was maintained at 35°C, and the BID detector was held at 280°C with a gas flow of 8.07 mL/min. A gas-tight syringe was used to transfer 50 µL of the resultant gas from the container into the GC system. Three cells were tested in parallel at each state of lithiation/delithiation to obtain average results. The calibration curve of H₂ was plotted by testing H₂ standard gas with varying concentrations at room temperature and pressure. Commercial Li metal and Si electrodes with known mass were used to verify the accuracy of this method as described in Table S1.

Physical characterization

After cycling, cells were disassembled in an Ar-filled glove box. Si electrodes were rinsed by DMC to remove residual Li salts and then dried in the vacuum chamber. The XPS characterization was implemented on a Thermo Fisher Scientific ESCALAB 250 Xi with monochromatic 150 W Al K α radiation. All the samples were transferred from the glove box to the XPS chamber using a sealed vessel to avoid exposure to air. The TEM characterizations were conducted on the JEOL ARM200F. To minimize the damage of the SEI from the electron beam, a liquid nitrogen cryo-EM holder (Fischione 2550) was employed. The morphology of pristine Si was characterized on a Hitachi S-4800 scanning electron microscope (SEM). The Young's modulus of SEI film was obtained by PeakForce QNM mode (Bruker Multimode8) with the RTESPA-525 tip.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.xcrp. 2021.100668.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC no. 22005334 and 21773301) and the Natural Science Foundation of Beijing (Grant no. Z200013).

AUTHOR CONTRIBUTIONS

X.Z., X.W., Y.L., and Z.W. conceived the idea and designed the project. S.W. conducted cryo-TEM. G.Y. performed XPS measurements. X.Z. performed all other data collection and analysis. H.L., D.S., L.G., Y.L, and L.C. contributed to discussions and interpretation of results. X.Z, Y.L., X.W., and Z.W. co-wrote the manuscript, with input from all authors.



DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: September 20, 2021 Revised: October 18, 2021 Accepted: November 5, 2021 Published: November 22, 2021

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Supplemental information

Interplay between solid-electrolyte interphase

and (in)active Li_xSi in silicon anode

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Supplemental Experimental Procedures

The choose of NaOH solution as titration solution for modified TGC method

To develop the TGC method for Si anodes, we fist screened the suitable titration solution. Although water was used as titration solution for lithium metal and graphite anodes, it is not suitable for Si anodes. The initial chemical reaction formula between water and Li_xSi is

 $2Li_xSi(s) + 2xH_2O(aq.) = 2xLiOH(aq.) + 2Si(s) + xH_2(g)$ (Equation 1) Li_xSi along with some SEI components, such as Li₂O. CH₃Li and ROLi will react with water and produce LiOH. The alkaline solution will further oxidize Si particles and produce excess H₂, which is an obstacle for determining the accurate amount of H₂ related to equation 1. Apart from water, acid solution is not suitable either since LiF or the remaining LiPF₆ salt will react with it and produce HF, which will further react with Si and yield excess H₂. In view of the excess H₂ produced by side reactions in water or acid solution, we used NaOH solution to fully consume the Li_xSi and the accurate H₂ amount involved in the reaction can be obtained.

As far as we know, none of the SEI components will react with NaOH and produce H_2 . Table S2 lists the reactivity of known SEI components with H_2O and NaOH solution. In addition, we tested the SEI on the Cu electrodes with the TGC method, which were obtained by discharging to 0V both in EC/DMC and EC/DMC/FEC electrolytes, and no H_2 gas was detected as shown in Figure S4.

Determining the reaction rate between NaOH solution and LixSi

Figure S2 shows the titration process. It is vital to make sure that the reaction is completed. We tested the reaction between a thick pristine Si electrode and the NaOH solution. As shown in Figure S3, the amount of H_2 stays nearly constant after 1h-reaction. If the lithiated electrode is used, the reaction will be faster because of the increased reactivity of LixSi by the increased solution basicity with the production of LiOH. Just to be safe, we performed the GC tests after reacting for 3h with no bubble visible.

Calculation method in TGC measurements

The total capacity is the difference between discharge and charge in every cycle:

$$Q_{total} = Q_{dis} - Q_{char}$$
 (Equation 2)

After titrating with NaOH solution, the following reaction will occur:

$$\text{Li}_{x}\text{Si} + (1+x)\text{H}_{2}0 + (2-x)0\text{H}^{-} = x\text{Li}^{+} + \text{Si}0_{3}^{2-} + (\frac{x}{2}+2)\text{H}_{2} \uparrow \text{(Equation 3)}$$

The amount of H₂ will be determined by GC. Thus, the mass of Li inside Li_xSi can be obtained after subtracting the Si contribution. The mass can be converted into capacity (Q_{Li_xSi}) for 1 mAh of capacity corresponding to 0.2594 mg lithium involved in the charge-transfer reactions. The amount of Li⁺ in SEI can be calculated based on charge balance:

$$Q_{SEI} = Q_{totall} - Q_{Li_xSi}$$
 (Equation 4)

Note S1 The mechanism of the gradually stabilized SEI in the FEC-containing electrolyte To figure out the underlying mechanism of the gradually stabilized SEI in the FEC-containing electrolyte, XPS, TEM, and EDS tests were performed during the 2nd cycle. As shown in the XPS results (Figure S9), after the 2nd discharge, the signals of carbonate species were enhanced significantly in both electrolytes, indicating the repairing of SEI. It is worth noting that the LiF signal on the electrode surface in the FEC-containing electrolyte is weak after the 2nd discharge, while it becomes evident after etching for 150s. It means a thick organic-rich layer grows on the top of the previous SEI in the repairing process. Combined with the results discussed above, a detailed picture of the SEI "breathing" behavior is uncovered: in the delithiation process, some species in the inner interface will participate in electrochemical reaction; in the following lithiation process, lots of organic species deposit on the top of SEI for repairing. These behaviors will repeat over cycling. In the meantime, the structure change of SEI will make the inert species such as LiF gradually move forward into the inner interface of SEI and thus inhibit the SEI decomposition/reaction. As verified with TEM and EDS, SEI was repaired after the 2nd discharge (Figure S10 A, C, E, and G). But it reduced significantly in the FEC-free electrolyte after the 2nd charge (Figure S10F), and Li₂O is not detectable (Figure S10B). In contrast, a considerable content of SEI (~21.9 nm) remains in the FEC-containing electrolyte (Figure S10H), with a few Li₂O particles still visible after the 2^{nd} charge (Figure S10D). With the help of the LiF-rich SEI derived by FEC, the SEI will eventually become a stable passivating layer, which is vital for enhancing the reversibility of Li_xSi and extending the cycle life of Si anodes.



Figure S1. SEM image of silicon nanoparticles.



Figure S2. The titration process of silicon electrodes. The silicon electrodes were sealed in the vessel. 0.5ml of 1M NaOH solution was injected into the vessel through a syringe, and bubbles emerged immediately containing H_2 . After resting for 3 hours, the reactions finished, and no more bubbles appeared.



Figure S3. GC chromatogram of H_2 after NaOH titration on a thick pristine Si electrode. The amount of H_2 stays nearly constant after 1h-reaction.

Table S1. The accuracy of the modified-TGC method.			
Li	1	2	3
Balance/mg	1.54	0.37	0.72
GC/mg	1.55443	0.38971	0.72729
Si	1	2	3
Balance/mg	0.36	0.62	1.22
GC/mg	0.3646	0.6195	1.2408

Three pieces of Li metal and silicon electrodes with known mass were tested using the modified-TGC method with 0.5ml of 1M NaOH as titrating solution. The little deviation between balance-measured and TGC-measured results exhibits the accuracy of the TGC method.



Figure S4. Reaction between SEI and NaOH solution. (A) The voltage profiles for SEI formation on Cu electrodes in EC/DMC and EC/DMC/FEC electrolyte; (B) GC chromatogram after NaOH titration on the above Cu electrodes and no H₂ was detected.

SEI components	Stability in H ₂ O	Stability in NaOH solution
LiF	stable	stable
Li ₂ CO ₃	stable	stable
LiOH	stable	stable
Li _x SiO _y	stable	stable
Li ₂ O	$Li_2O + H_2O = 2LiOH$	$Li_2O + H_2O = 2LiOH$
SiO ₂	H_2O + SiO ₂ = H_2SiO_3	$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$
CH ₃ Li	$CH_3Li + H_2O = LiOH + CH_4$	$CH_3Li + H_2O = LiOH + CH_4$
ROLi	ROLi + H ₂ O = LiOH + ROH	ROLi + NaOH= LiOH + RONa
LiOCO ₂ R	$2 \text{ LiOCO}_2 \text{R} + \text{H}_2 \text{O} = \text{Li}_2 \text{CO}_3 + \text{LiOCO}_3 + $	$2 \operatorname{LiOCO}_2 R + 2 \operatorname{NaOH} = \operatorname{Li}_2 \operatorname{CO}_3 +$
	2ROH + CO ₂	2ROH + Na ₂ CO ₃

Table S2. The reactivity of some SEI components with H_2O and NaOH solution^{1,2}



Figure S5. EDS mapping of silicon anode in FEC-free electrolyte after the 1st discharge.



Figure S6. EDS mapping of silicon anode in FEC-free electrolyte after the 1st charge.



Figure S7. EDS mapping of silicon anode in FEC-containing electrolyte after the 1st discharge.



Figure S8. EDS mapping of silicon anode in FEC-containing electrolyte after the 1st charge.



Figure S9. XPS spectra of Si electrodes during the 2nd cycle.



Figure S10. cryo-TEM and EDS mapping of Si anodes during the 2nd cycle.

(A-D) HRTEM of Si anodes after 2^{nd} discharge (A) and 2^{nd} charge (B) in the FEC-free electrolyte, after 2^{nd} discharge (C), and 2^{nd} charge (D) in the FEC-containing electrolyte.

(E-H) EDS mapping of Si anodes after 2nd discharge (E) and 2nd charge (F) in the FEC-free electrolyte, after 2nd discharge (G), and 2nd charge (H) in FEC-containing electrolyte.

The red points and green points in EDS mapping represent the signal from Si and O, respectively.



Figure S11. Young's modulus of FEC-free and FEC-containing electrolytes. The overall modulus of SEI in the FEC-containing electrolyte is larger than that in the FEC-free electrolyte. The reduction of modulus after the 1st charge may ascribe to the vanish of Li₂O particles.



Figure S12. Volume change of Si particles during the 1st lithiation. The particle size distributions (A and B) and the corresponding TEM images (C and D) of the pristine Si (A and C) and the fully lithiated Si (B and D). We analyzed the volume change of Si particles before and after lithiation via TEM. We measured the particle size for more than 30 particles and the results are shown below. The mean particle diameter of Si is 132.1nm and 545.8nm before and after lithiation. It expands by 413%, consistent with previous reports.^{3,4}



Figure S13. EIS profiles and fitting results of the FEC-free electrolyte (A) and the FECcontaining electrolyte (B) during the 1st cycle; (C) the equivalent circuit diagram adopted in the fitting process.

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