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Perspective—Structure and Stability of the Solid Electrolyte Interphase on Silicon Anodes of Lithium-ion Batteries

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The solid electrolyte interphase (SEI) acts as a protection layer on the surface the anodes of lithium ion batteries to prevent further electrolyte decomposition. Understanding the fundamental properties of the SEI is essential to the development of high capacity silicon anodes. However, the detailed mechanism of the generation of the evolution of the SEI on the silicon anodes is not fully understood. This manuscript reviews our recent investigations of the SEI on silicon anodes. We have studied the fundamental formation mechanism of the SEI on silicon anodes, along with the evolution which occurs to the SEI upon cycling.

Demand for increased energy density in lithium-ion batteries (LIBs) for electric vehicles (EV) necessitates a move away from the industry standard graphite anode. With a theoretical specific capacity of 3580 mAh g^{-1}, silicon can offer an increase of almost an order of magnitude over graphite (372 mAh g^{-1}).[1,2] Silicon also has a low working potential, below 0.5 V vs Li/Li^+, enabling silicon to have very high energy density. The advantages of silicon have resulted in the incorporation of silicon into silicon/graphite composite electrodes for many commercial lithium ion batteries.[3,4] However, due to the instability of conventional lithium hexafluorophosphate ($LiPF_6$)/carbonate-based electrolytes under highly reductive conditions, the electrochemical decomposition of electrolytes occurs during the first charging cycle, followed by the deposition of the electrolyte decomposition products to generate a passivating solid electrolyte interphase (SEI) on the surface of the silicon anodes.[5,6] The SEI must have good lithium-ion conductivity and be electrically insulating to prevent further reduction of the electrolyte by the surface of the lithiated silicon, which enables lithium-ion batteries to reversibly charge and discharge for hundreds of cycles. However, the generation and evolution mechanism of the SEI is not particularly well understood, especially related to the silicon anode where large volumetric changes (∼280%) occur during lithiation and delithiation resulting in significant changes to the surface area of silicon.[7]

The SEI on silicon anodes has been reported to be composed of a combination of lithium silicate (Li_xSiO_y), lithium carbonate (Li_2CO_3), lithium fluoride (LiF), lithium alkyl carbonates and related decomposition products of the electrolyte.[8,9] While there is a general understanding of the composition of the SEI, the composition of the initial SEI formed on silicon anodes and the subsequent changes to the composition of the SEI upon cycling are poorly understood.[9,10] In particular, a general understanding of which species are important for both function and stability of the SEI are relatively poorly understood. However, it has been reported that the stability of the SEI on silicon anode is very problematic, due to the large changes in surface area during cycling.[11] The changes in the surface area upon lithiation and de-lithiation result in repeated formation and destruction of the SEI leading to thickening of the SEI layers.[11,12] However, the detailed mechanism of evolution and thickening of the SEI is not well understood. While the instability of the SEI on silicon anodes is well documented, one method to inhibit this instability problem is the use of SEI forming electrolyte additives additives.[13,14] While many electrolyte additives have been investigated for silicon anodes, the most promising are fluorinated additives,[15,16] especially fluoroethylene carbonate (FEC).[13,17–25] However, while there have been many investigations of the mechanism of function of FEC, the role of

FEC in generating a "better" SEI remains unclear. However, previous researchers have reported that incorporation of FEC results in "the formation of highly effective compact surface films" containing polymeric species and high concentrations of LiF.[21,26] Alternatively, researchers have developed methods to modify the surface of silicon particles to inhibit electrolyte reduction and improve SEI stability.[27–29] Modifying electrolyte formulations is another method to improve the cycle performance of Silicon based cells. It was reported that dioxolane based electrolyte solutions increase the cycle performance of silicon-based cells,[30,31] and ionic liquid based electrolyte solution could stabilize the interphase of silicon particles leading to improved cycle performance.[32–34]

This manuscript is a Perspective article providing an overview of our recent systematic investigations of the role of salt, solvent, additive, and binder in SEI formation and evolution mechanisms on silicon anodes. Each component of the electrolytes (salt, solvent, additive) has been systematically isolated to study the individual role in SEI formation and evolution. In addition, the effect of binders modifying the surface of the silicon particles and the generation and evolution of the SEI will also be discussed.
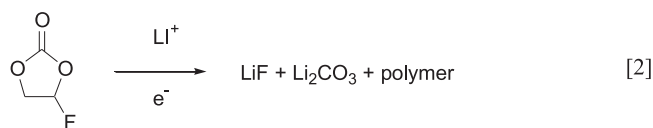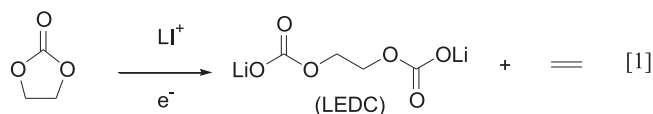
Current Status

Initial components of the SEI layers.—The reduction product of ethylene carbonate (EC) is one of the primary components of the SEI in commercial lithium ion batteries.[35] It has also been reported that lithium hexafluorophosphate ($LiPF_6$) which is the conventional salt utilized in commercial lithium-ion batteries plays a role in the generation of the SEI. The investigation of silicon anodes in EC electrolytes (1.2 M $LiPF_6$ in EC) suggests that the initial SEI is primarily composed of lithium ethylene dicarbonate (LEDC) and lithium fluoride,[36,37] which result from the reduction of electrolyte components (EC and $LiPF_6$) and is similar in composition to that observed on graphite electrodes.[38] However, the surface of the fresh silicon electrode contains SiO_2 which is also converted to lithium silicate, making the initial SEI on silicon more complicated than that observed on graphite. Upon cycling the composition of the SEI evolves and electrolyte decomposition products become integrated with the silicon particles. The outer SEI is still primarily composed of LEDC and LiF, while the inner SEI is composed of Li_2CO_3, LiF and Li_xSiO_y.[39] Discussion of the mechanism for these changes is provided below.

Electrolyte additives have been reported to be critical for the formation of the SEI on silicon anodes and understanding the role of the additives in the SEI structure and stability on silicon anodes is critical for the further development of silicon anodes for advanced lithium batteries. Fluoroethylene carbonate (FEC) is one of the best known electrolyte additives for silicon anodes.[40,41] Groundbreaking research on FEC provided significant insight into changes in the

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composition of the SEI resulting from the generation of an SEI dominated by LiF and polymeric species.[26] These results were further supported by additional characterization of the species generated by the independent reduction of FEC.[42] In an effort to better understand the role of FEC in SEI formation, an investigation of silicon anode with an FEC electrolyte (1.2 M $LiPF_6$ in FEC) was conducted which revealed that the SEI derived from an FEC electrolyte has different electrolyte decomposition products than that observed for the EC electrolyte. The SEI generated from the FEC electrolyte is primarily composed of Li_2CO_3, LiF, and polycarbonate.[9] Interestingly, nano-structured lithium fluoride is also observed on the surface of silicon particles cycled with FEC based electrolytes.[9] While it is unclear how the LiF nanoparticles relate to the cycling improvement of silicon anodes in the presence of FEC, similar LiF nanoparticles have been observed on lithium metal anodes and correlate well with the improvement of capacity retention of lithium metal anodes.[43] Thus, in addition to trying to understand the role of Li_2CO_3 and polycarbonate in the stability of the SEI on silicon anodes, it is also important to understand the role of LiF nanoparticles in the overall improved capacity retention of the silicon electrodes. The primary initial reduction products of EC and FEC are summarized in Eqs. 1 and 2.

While it is unclear why LEDC decomposition is enhanced upon cycling silicon electrodes, it is likely attributable to either mechanical damage to the SEI from the large volumetric changes of the silicon particles[11] or a catalyzed decomposition by the silica or lithium silicate surface. In the first case an LEDC based SEI is a mechanically rigid solid. Upon changes to the surface area of the silicon particles during the volumetric expansion and contraction, the SEI will crack increasing the surface area of the LEDC particles and thus increasing the interaction with the electrolyte. The increased contact of the SEI with the electrolyte increases the reactivity of the acidic decomposition products of $LiPF_6$ (PF_5, POF_3, and HF) with the LEDC resulting in more rapid conversion of the

Evolution and aging of the SEI on silicon anode.—The evolution of the SEI on the silicon anodes upon cycling for EC based electrolytes was investigated through Hard X-ray photoelectron spectroscopy (HAXPES) which allows analyzing depth profiling of the SEI layers.[39,44] The investigations revealed a significant evolution of the inner SEI for EC based electrolytes which were attributed to the instability of the SEI components. The initial reduction reaction of EC in $LiPF_6$ electrolyte is very similar to that reported for graphite anodes, as described above, and is dominated by LEDC. However, upon cycling the SEI on the silicon anode evolves much more rapidly than the SEI on graphite anodes. The LEDC decomposes to generate Li_2CO_3 and other species similar to that observed for the SEI on graphite anodes, but the decomposition reactions are much more facile on the silicon anodes.[38] As the LEDC decomposes to generate Li_2CO_3 along with gaseous and electrolyte soluble products,[35] the surface of the silicon particles is exposed to the electrolyte resulting in further electrolyte reduction. This results in the generation of a layered SEI on the silicon particles. A high concentration of lithium silicate and silica are observed near the surface of the silicon followed by an intermediate Li_2CO_3 and LiF rich layer with an outer surface layer predominantly composed of LEDC.

LEDC and $LiPF_6$ to LiF, CO_2, fluorophosphates, lithium alkoxides, and poly(ethers).[45] Alternatively, the silica or lithium silicate could catalyze related thermal decomposition reactions of LEDC resulting in the generation of Li_2CO_3, Li_2O, CO_2, ethylene, and lithium carboxylates.[46] In addition, a combination of these two reactions may be contributing to the increased rate of LEDC decomposition on silicon anodes compared to graphite anodes. Regardless, LEDC clearly has much lower stability on the surface of silicon particles than on graphite during electrochemical cycling.

The decomposition reactions of initial components of the SEI result in increasing complexity of the SEI which can also be used to explain the differences in the SEI components reported from one research group to another since that conditions of the experiments may differ. For example, many in situ experiments are conducted with a much higher ratio of electrolyte to silicon electrode than is observed in commercial cells. A higher concentration of electrolyte would result in a higher relative concentration of impurities to the surface area of the silicon particles and thus the quantity of the SEI. The higher relative concentration of impurities will result in a faster evolution of the SEI and a more complex mixture of compounds. In addition, experiments utilizing electrolytes with higher concentrations of impurities would also result in faster rates of SEI evolution on the silicon electrode.

In summary, we have proposed the mechanism for the evolution of the SEI generated from EC based electrolytes on silicon anodes. The initial SEI is primarily composed of the reduction products of the electrolyte, LEDC and LiF. The volumetric changes upon lithiation and de-lithiation of the silicon anode result in significant mechanical damage to the SEI components. As the SEI components fracture the surface area of the SEI particles is increased. The increased surface area of the particles increases the reactivity of the unstable SEI component LEDC with the acidic species in the electrolyte which results in an increased rate of SEI decomposition. The initial SEI, primarily composed of LEDC and LiF, degrades to generate Li_2CO_3, lithium alkoxides, CO_2, and oligoethylene oxide (Fig. 1). A critical aspect of these decomposition reactions is that many of these components are either soluble in the electrolyte or gaseous which results in an increase in the porosity of the SEI allowing more electrolyte to interact with the surface of the SEI leading to further electrolyte reduction and a thicker SEI. The model is also consistent with previous reports on the structure of the SEI where the inner SEI is more inorganic-rich while outer SEI which is more organic-rich.[47,48]
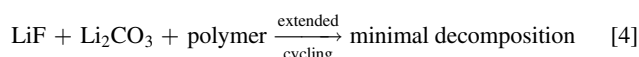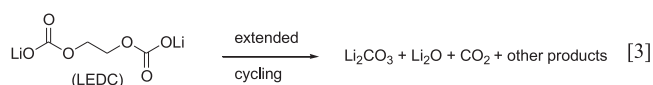
The stability of the SEI on the silicon anode plays an important role in the performance of the cells. It has been reported that the instability of the SEI on silicon anodes upon extended cycling or aging is a primary contributor to the poor cycling performance of lithium batteries with silicon-based anodes.[11,49,50] Continuous SEI decomposition/reformation on the surface of silicon particles leads to the generation of an insulating film on silicon particles which weakens the electrical conductivity of the electrode. As a result, lithium ions are trapped within the silicon matrix which is responsible for the severe capacity fading.[51,52] Aging of the SEI at high temperature storage is another critical issue for silicon-based anodes.[48] Due to the vigorous decomposition/reformation of the SEI caused by the acidic and thermal decomposition, the SEI on silicon anodes thickens leading to severe cell polarization and failure.

The incorporation of FEC electrolytes results in a significant change in the composition and stability of the SEI. The SEI generated from EC based electrolytes is initially primarily composed of LEDC and LiF while the initial SEI generated from FEC electrolytes is primarily composed of Li_2CO_3, polycarbonate, and LiF. An investigation utilizing HAXPES revealed that upon cycling an inner layer of lithium silicate and silica is still observed with FEC based electrolytes, but the composition of the outer layer of the SEI does not change significantly.[38] The composition of the outer layer is still composed of a mixture of LiF, Li_2CO_3, and polycarbonate. This suggests that the SEI components generated from the reduction of FEC are more stable and do not decompose which would accelerate
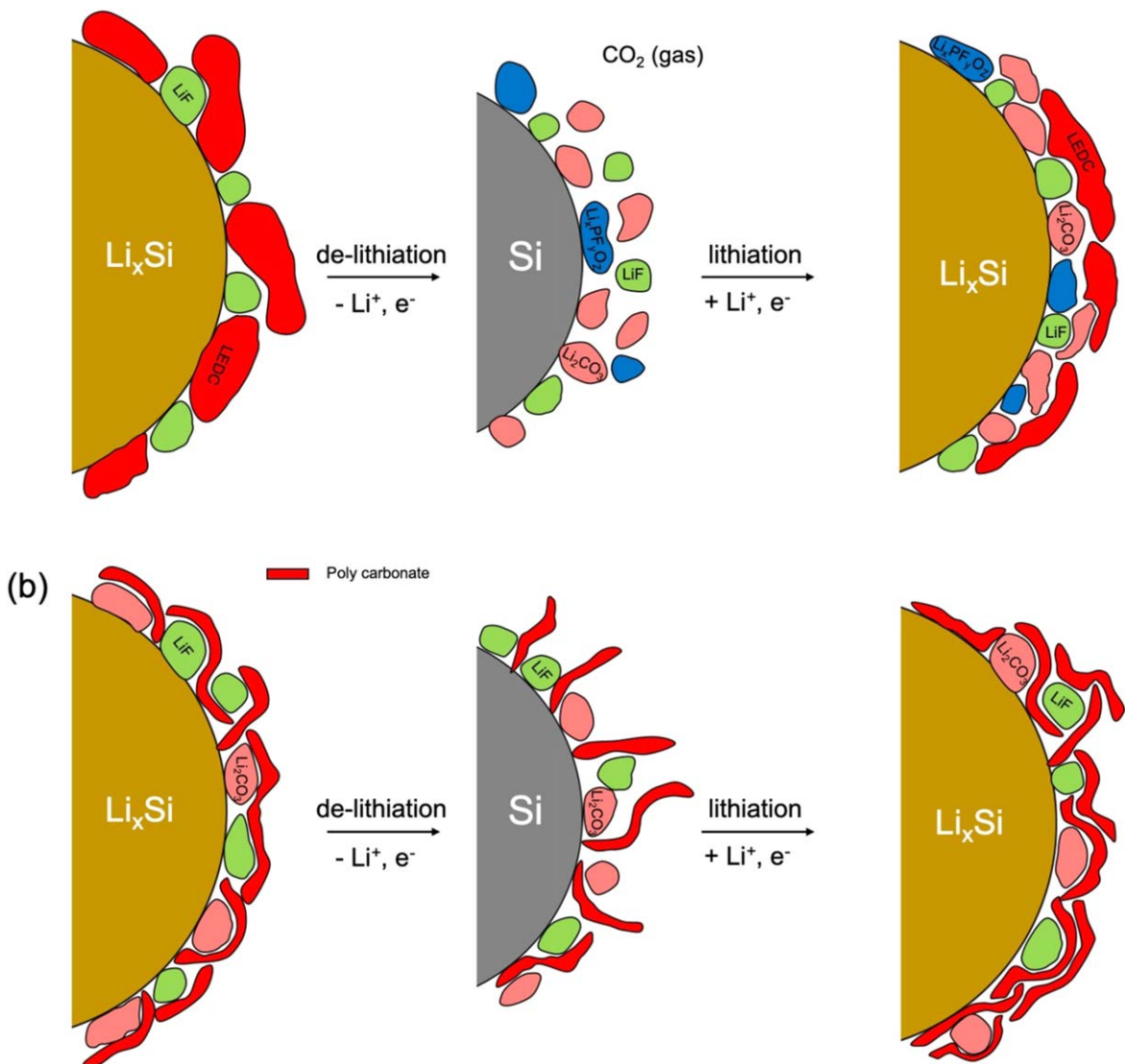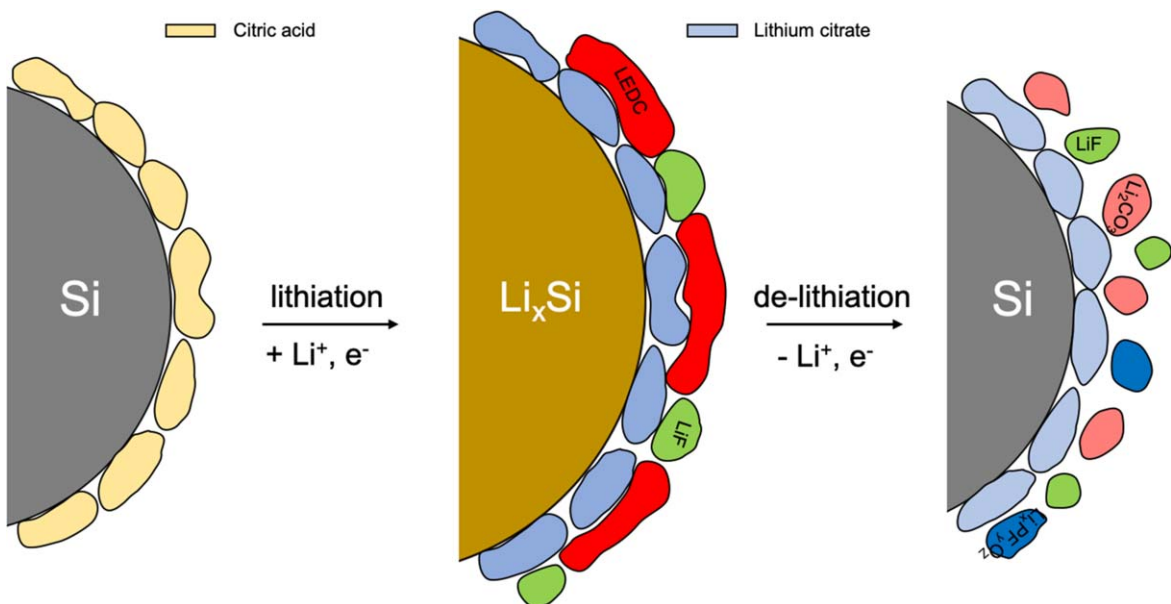
Figure 1. Schematic diagram for the initial generation and evolution of the SEI layers on silicon electrodes derived by (a) EC based electrolytes and (b) FEC based electrolytes. The composition and structure of the SEI layers become complicated upon cycling due to the instability of the initially formed SEI components.

the growth of the SEI. While it is not clear which components are the most important for the improved stability, Li_2CO_3 is more stable than LEDC.[53] When the SEI is composed of more stable components such as Li_2CO_3 similar mechanical fracturing will occur, but the lower reactivity of Li_2CO_3 with the electrolyte slows the rate of SEI evolution. The presence of polycarbonate also likely improves the elasticity of the SEI improving the mechanical strength of the SEI. In addition, there is a higher concentration of LiF and the LiF is present in the form of nanostructured LiF particles. While the importance of the nanostructure LiF remains unclear, similar nanostructured LiF particles have been reported to correlate with improved stability of the SEI on lithium metal anodes.[43] The primary decomposition reactions of the SEI components derived from EC and FEC are summarized in Eqs. 3 and 4, respectively.

$$LEDC \xrightarrow[\text{cycling}]{\text{extended}} Li_2CO_3 + Li_2O + CO_2 + \text{other products} \quad [3]$$

$$LiF + Li_2CO_3 + polymer \xrightarrow[\text{cycling}]{\text{extended}} \text{minimal decomposition} \quad [4]$$

Surface modification by binder.—Another method to improve the performance of silicon anodes involves the use of different polymer binders in the electrode laminate. Previous studies revealed a significant difference in the performance of silicon anodes in the presence of different polymer binders, which is not typically observed for graphite anodes.[54] While initial investigations suggested that the performance improvements were the result of changes in the mechanical properties of the binders, further investigations suggested that the binders may be chemically interacting with the silicon particles to modify the surface. In particular, binders that contain either alcohol functional groups or carboxylic acid functional groups such as poly(acrylic acid) (PAA) or carboxymethyl cellulose (CMC) show significantly better performance than the traditional binders such as poly(vinylidene fluoride) (PVDF).[55,56] To understand why the PAA or CMC binders provide significant improvements in capacity retention of silicon anodes, the interaction of binders with the surface of the silicon particles has been investigated. These investigations revealed that the surface of silicon reacts with PAA via carboxylic acid groups on the surface of silicon before cycling.[57] The PAA is then converted into lithium poly(acrylic acid) (LiPAA) during the first lithiation by electrochemical reaction with lithium, resulting in the

Figure 2. Schematic diagram for the initial generation and evolution of the SEI layers on silicon electrodes with citric acid as a surface modifying agent. The citric acid modification results in the generation of a pre-SEI which stabilizes the surface of silicon electrodes.

generation of a more stable SEI layer on silicon anode, which leads to less electrolyte decomposition upon cycling.

Modification of the silicon surface via reaction with PAA binders led to the use of citric acid (CA) as a surface-modifying agent for silicon particles.[28,29] The carboxylic acid and alcohol functional groups in CA react with the surface of the silicon nanoparticles before cycling, generating silyl esters (–Si–O–C(O)–C–) on the surface of silicon nanoparticles which was confirmed via a combination of IR-ATR and TGA. Furthermore, the surface layer of CA is electrochemically reduced to lithium citrate during the first lithiation forming a stable SEI layer which reduces the generation of electrolyte decomposition products such as LEDC and Li_2CO_3 after the initial formation cycling and upon extended cycling. Surprisingly, the cycling performance of silicon anodes with CA have comparable improvements to that observed for silicon anodes with PAA binder. The CA derived surface layer acts as a pre-SEI stabilizing the surface of the silicon particles and improving the electrochemical cycling performance (Fig. 2). The reaction of citric acid with the surface of silicon particles can be used as a pre-treatment of the particles which can then be added to graphite to make graphite/silicon composite anodes.[29] The modified silicon graphite composite anodes significantly improve the capacity retention of the composite electrodes due to the generation of a pre-SEI on the silicon particles (Fig. 3).

Future Needs and Prospects

Developing a strong understanding of the composition and mechanism of function of the SEI is critical for the performance improvements needed for silicon anodes in lithium ion batteries. While there is a general understanding of the composition of the SEI, the composition of the initial SEI formed on silicon anodes and the subsequent changes to the composition of the SEI upon cycling are poorly understood. We have reviewed the generation and evolution mechanisms of the SEI on silicon anodes and the effect of SEI modification by utilizing electrolyte additives or novel surface modifiers which have been reported over the last decade.

1) The reduction products of electrolyte, in particular EC and $LiPF_6$, are the fundamental components of the SEI. EC is reduced to generate LEDC and ethylene, and $LiPF_6$ is reduced to generate LiF and lithium fluorophosphates. The initial SEI
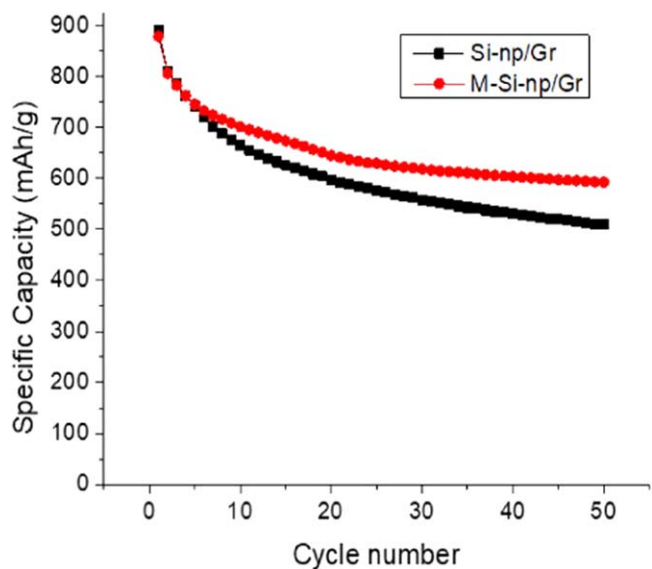
Figure 3. Specific capacity retention of silicon graphite composite electrodes with silicon nanoparticles (Si-np/Gr) and silicon nanoparticles surface modified with citric acid (M-Si-np/Gr)[29] figure reproduced with permission of J. Electrochem. Soc.

layers on both silicon and graphite are composed of primarily LEDC and LiF and are not a complicated mixture of components. However, the instability of components of the SEI, such as LEDC, to hydrolytic, acidic, and thermally induced decomposition results in an evolution of the SEI generating a complex mixture of species including Li_2CO_3, lithium alkoxides, fluorophosphates, oligo ethylene oxides, LiF, and related species. The evolution of the SEI also results in a thickening of the SEI, electrical isolation of silicon particles, and significant capacity loss.

2) The incorporation of electrolyte additives, such as FEC, into the electrolyte results in a significant change in the composition of the initially generated SEI. The SEI derived from FEC is primarily composed of Li_2CO_3 and polycarbonate. In addition,

nano-structured LiF is observed in the SEI for FEC containing electrolytes, which may contribute to improvements in the stability of the SEI. We have proposed that the thermal stability Li_2CO_3 improves the stability of the SEI upon cycling.[58] Furthermore, the elasticity of polycarbonate helps to retain the integrity of the SEI against the mechanical damage which occurs during the volume expansion/contraction of silicon particles during electrochemical cycling.

3) The surface of silicon can also be modified by polymers or small molecules containing alcohol or carboxylic acid functional groups prior to cell construction or cycling. Citric acid (CA) can be utilized as a surface modifying agent to generate surface silyl esters (-Si-O-C(O)-C-) which function as a pre-SEI on the surface of the silicon particles. In addition, the surface layers derived by CA are reduced during formation cycling to generate a stable SEI resulting in less electrolyte reduction and a thinner more stable SEI. The surface modification results in significant improvements in capacity retention of silicon anodes. The surface modified silicon particles can be incorporated into graphite/silicon composite electrodes to enhance the performance of current lithium-ion batteries.

4) These investigations have led to some recommendations for future researchers attempting to design better silicon anodes for lithium ion batteries. The electrolyte formulation should be chosen such that the initial reduction products are stable lithium salts such as Li_2CO_3, LiF, or lithium carboxylates. However, these species should be deposited with the optimal morphology which allows fast lithium ion conduction along the grain boundaries of the primary nanoparticles. The optimal electrolyte formulation will likely also include an electrolyte additive which can generate an elastic polymeric species with good mechanical stability and high lithium ion conductivity. Finally, the silicon particles should be pretreated with a surface modifying agent, which can be reduced at the surface to generate a mechanically stable and highly lithium ion conducting pre-SEI. The generation of superior interphases for silicon particles is critical for the development of silicon anodes for advanced high energy density lithium ion batteries. Optimized interphase generation will likely be afforded via a combination of surface modification and electrolyte additives.

5) The improvements in the stability of the stability of the SEI on silicon particles will enable the incorporation of higher concentrations of silicon particles in graphite/silicon composite anodes. These concentrations may exceed 25%. However, it is unlikely that these improvements will enable the used of pure silicon anodes for lithium ion batteries.

Summary

The generation and evolution of the solid electrolyte interphase (SEI) on silicon anodes has been reviewed. The stability of the SEI components is a significant contributor to the performance degradation of silicon anodes in lithium ion batteries. Both electrolyte additives and surface modification of the silicon particles results in the generation of a more stable SEI which leads to improved performance. The combination of improved electrolyte additives and surface modified silicon particles will lead to significant improvements in the cycling stability of silicon particles affording the development of silicon/graphite composite anodes with higher capacity.

Acknowledgments

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