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DESIGN STABLE SOLID-ELECTROLYTE INTERPHASE FOR ANODES IN

RECHARGEABLE LITHIUM BATTERIES

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by

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ABSTRACT

Solid-electrolyte interphase (SEI) is a nanoscale composite layer of organic and inorganic lithium (Li) salts formed on the electrode surface by electrolyte decomposition. It is ionically conductive and electrically insulating, thus allowing facile Li-ion transport and preventing further electrolyte decomposition. Owing to these features, SEI stability is crucial to the performance of rechargeable Li batteries. Unfortunately, SEI layer are unstable for most advanced battery materials, including high-capacity anodes materials (e.g., silicon (Si) and Li) in liquid electrolyte and Li anodes in solid electrolytes (e.g., Li₁₀GeP₂S₁₂ (LGPS)). An unstable SEI layer may cause poor battery performance including consumption of active materials and electrolyte, capacity fading, resistance increase., etc. The structure and property of SEI have generally eluded rational control since its formation and growth processes involve a series of complex and competitive electrochemical reactions. The main efforts to addressing this issue have been made on the development of new electrolyte systems to form alternative SEI layers and preformed artificial SEI layers on the electrode surface to replace the electrolyte-derived SEI.

This dissertation focuses on intrinsically regulating the chemical composition and nanostructure of SEI for advanced battery materials in conventional electrolyte systems, which enables not only optimized chemical and physical properties of SEI but improved battery performance. This is realized by developing chemical and electrochemical reactive materials and allowing them to participate in the SEI formation. These materials can contribute functional components in the SEI layer and therefore alter the structure and property of the SEI deliberately. The design of functional material is based on the requirement of SEI layers for different anodes. In Chapters 2 and 3, I presented approaches to manipulating the formation process, chemical composition, and morphology of SEI for nano-sized and micro-sized Si anodes, respectively. The SEI layers were fabricated through a covalent anchoring of multiple functional components onto the Si surface, followed by electrochemical decomposition of the functional components and conventional electrolyte. We showed that to covalently bond organic oligomeric species at the surface of nano-sized Si anodes can effectively increase its SEI flexibility and realized an intimate contact between SEI and Si surface (Chapter 2). In the case of micro-sized Si anodes, we reported that to covalently bond a functional salt, *N*-methyl-*N*-propyl pyrrolidinium bis(fluorosulfonyl)imide (PYR₁₃FSI), at the surface of micro-sized Si anodes can effectively stabilize the interface and SEI (Chapter 3).

In Chapters 4 and 5, we designed chemically and electrochemically active organic polymer, namely poly((*N*-2,2-dimethyl-1,3-dioxolane-4-methyl)-5-norbornene-exo-2,3-dicarboximide), and polymeric composite containing poly(vinylsulfonyl fluoride-*ran*-2-vinyl-1,3-dioxolane) and graphene oxide (GO) nanosheets to alter SEI formation process and regulate the composition and nanostructure of SEI for Li metal anodes. The reactive organic polymer and polymeric composite can generate stable SEI layers *in situ* by reacting with Li to occupy surface sites and then electrochemically decomposing to form nanoscale SEI components. The formed SEI layers presented excellent surface passivation, homogeneity, and mechanical strength. Using the polymer, we can implant polymeric ether species in the electrolyte-derived SEI, enabling improved SEI flexibility and homogeneity. In the case of polymeric composite, the SEI is mainly generated by the composite instead of electrolyte. In this way, we realized an intrinsic control of SEI structure and property. The formed SEI presented excellent homogeneity, mechanical strength, ionic conductivity, and surface passivation.

In Chapter 6, we reported a novel approach based on the use of a nanocomposite consisting of organic elastomeric salts (LiO-(CH₂O)_n-Li) and inorganic nanoparticle salts (LiF, -NSO₂-Li, Li₂O), which serve as an interphase to protect Li₁₀GeP₂S₁₂ (LGPS), a highly conductive but reducible SSE. The nanocomposite is formed *in situ* on Li *via* the electrochemical decomposition of a liquid electrolyte, therefore possessing excellent chemical and electrochemical stability, affinity for Li and LGPS, and limited interfacial resistance. We concluded this dissertation work in Chapter 7 and briefly discussed the possible future work.

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organic groups (b) were designed to generate organic Li salts. The dioxolane (DOL)containing polymer provides the most enhanced CE among these organic building blocks.

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Chapter 1

Solid-Electrolyte Interphase in Rechargeable Lithium Batteries

Solid-electrolyte interphase (SEI) is one of the most crucial (but perhaps least understood) building blocks of rechargeable lithium (Li) batteries. It is a composite layer of organic and inorganic Li salts formed on the electrode surface by electrolyte decomposition. SEI is ionically conductive and electrically insulating, thus enabling Li-ion transport and protecting electrode materials and the electrolyte from interfacial reactions^{1–3}.

Owing to these features, SEI stability is crucial to the performance of rechargeable Li batteries including cycle life, safety, rate capability, etc. The presence of an SEI layer can effectively stabilize the interface between traditional intercalation material such as graphite and liquid electrolyte. However, high-capacity anode materials such as silicon (Si) and Li present a highly dynamic interface, which involves huge interfacial fluctuation and volume changes during the lithiation-delithiation process. Their SEI layers are accordingly heavily damaged under the external forces and are incapable of maintaining a stable interface, resulting in short cycle life and safety issues^{4,5}. Unfortunately, it is very challenging to regulate the structure and property of SEI, because SEI chemistry is ruled by the liquid electrolyte.

In this chapter, I will discuss the current understanding of the structure and property of SEI and state-of-art techniques to design stable SEI layers for Si and Li anodes.

1.1 Formation, Composition, and Structure of Solid-Electrolyte Interphase

Figure 1-1 illustrates the SEI formation process using graphite anodes as an example⁶. During the initial charging cycle of a battery cell, Li ions are transported to the electrode surface by liquid electrolyte and insert in the graphite via an intercalation process. Meanwhile, under low operating potentials (below 1.5 V vs. Li⁺/Li), electrolyte molecules including organic solvents and Li salts can accept electrons from the electrode and *in situ* decompose to form a nanoscale interphase layer on the electrode surface, which is the SEI layer (Figure 1-1c). For the SEI of Si and Li anodes, the reactions between electrolytes and active Si and Li materials are also involved in the SEI formation^{2,7}.



Figure 1-1: Schematic depiction of the SEI formation during initial charging cycles.⁶

The SEI is formed and grows in a series of complex competitive reactions of all electrolyte components. The Li salts, solvents, and impurities can decompose in a spontaneous and simultaneous manner when the potential at the electrode surface is sufficiently low. As a

result, SEI formation has generally eluded rational control, and this process is very difficult to be altered. Since the formation process of SEI is quite complicated and SEI layer is a nanoscale layer lying between a solid phase (electrode material) and liquid phase (electrolyte), it is very challenging to determine the precise composition and morphology of SEI using current techniques. Despite these difficulties, researchers have employed many techniques to study SEI and achieved a rough SEI composition. These include X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), Raman spectroscopy, mass spectroscopy, etc. For an SEI derived from a LiPF₆ salt-carbonate electrolyte, the SEI is composed of a large amount of inorganic Li salts such as Li₂O, Li₂CO₃, LiF, and Li_xPF_vO_z and a small amount of organic Li salts such as LiCO₂OR (R=hydrocarbons)^{2,5,8}. Based on these findings, several different SEI models have been put forward to help understand the SEI structure. In the mosaic model (Figure 1-2a), the decomposed species form lump-like nanoparticles. In the double layer model (Figure 1-2b), the SEI layer can immobilize positive charges and balance the negative charges at the graphite surface. In the multilayer model (Figure 1-2c), the inner part of SEI is dense and mainly consists of inorganic salts and the outer part of SEI is porous and mainly composed of organic Li salts.



Figure 1-2: Proposed models to understand SEI structure. (a) Mosaic model⁹, (b) Double layer model¹⁰, (c) Multilayer model¹¹.



Figure 1-3: Cryo-TEM images of SEI layers on Li anodes surface. (a) 1 M LiPF₆ in EC/DEC electrolyte was used to generate the SEI. (b) 1 M LiPF₆ in EC/DEC electrolyte with FEC as additives was used to produce the SEI.

Although the researchers have not been able to confirm the exact structure of SEI, the use of cryogenic electron microscopy (cryo-EM) techniques provides some very useful information on SEI structure^{12,13}. Figure 1-3a,b shows an SEI layer generated by 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte. Nanocrystals corresponding to Li₂O and Li₂CO₃ were found in the SEI, and the SEI morphology fits well with the proposed mosaic model (Figure 1-2a). Interestingly, the structure of the SEI layer formed by 1 M LiPF₆ in EC/DEC

electrolyte with fluoroethylene carbonate (FEC) as additives fits with the multilayer model (Figure 1-2c), in which a compact, amorphous phase at the inner part of SEI and a layered phase at the outer part of SEI were found (Figure 1-3c,d).

1.2 Unfavorable SEI Chemistry for Silicon and Lithium Anodes

The growing demand for portable electronics and electric vehicles has stimulated research on next-generation, high-energy-density batteries, which use Si and Li as anodes owing to their high theoretical capacities^{14,15}. These materials present a highly dynamic interface with electrolyte during battery operation. Si materials undergo huge volume expansions and contractions during the lithiation-delithiation process. This induces a highly dynamic interface, associated with repeated sacrifice and reformation of solid-electrolyte interphase (SEI)^{2,3,16,17}. The SEI layer is brittle and has a weak contact with Si^{18–20}. Therefore, it presents a strong tendency to break and peel off from the Si surface under volume changes (Figure 1-4)¹⁵. The exposed surface is immediately covered by newly formed SEI, accompanied by the consumption of active Si and electrolyte. Meanwhile, the peeled-off SEI components are accumulated in the cell as waste. This sacrifice and reformation process of SEI occurs in every cycle and results in rapidly faded capacity, reduced Coulombic efficiency (CE), and raised the interfacial resistance of Si anodes.



Figure 1-4: Schematic of a repeated break and repair process of Si anodes SEI.¹⁵

Li metal anode also suffers from an unstable solid-electrolyte interphase (SEI), which is incapable of maintaining a stable Li/electrolyte interface during Li electrodeposition cycles^{2,3,21–}²³. Li deposition induces huge interfacial fluctuations and surface morphology changes, resulting in a highly dynamic Li/electrolyte interface. The poor mechanical strength of the SEI results in a repeated breakdown-repair process, accompanied by continuous electrolyte consumption and SEI accumulation^{4,22}. The SEI progressively becomes structurally inhomogeneous²⁴, promoting uneven Li deposition (Figure 1-5)². Together, these problems lead to dendritic Li growth, low CE, short cycle life, and severe polarization of the Li metal anode.



Figure 1-5: Illustration of an unstable SEI layer and dendrite growth on a Li metal anode.²

A serious concern for current commercial batteries is the safety issue arising from the use of flammable liquid electrolytes²⁵. Solid-state batteries, powered by nonflammable solid-state electrolytes (SSEs), provide an ideal solution to this problem^{26,27}. In addition, solid-state batteries show great promise for achieving high energy density and long lifespans simultaneously by combining SSEs with high-capacity electrode materials such as Li metal^{28–30}. However, interfaces between SSEs and Li metal are unstable, presenting a major obstacle for the use of Li metal anode in solid-state batteries. Many SSEs in contact with Li can be reduced, and their reduction products form interfacial layers between the SSE and Li^{31–34}. In an ideal case, the formed layer presents high Li-ion conductivity and sufficiently low electronic conductivity, enabling facile Li-ion transport and avoiding continuous reduction of the SSE. A good example of such an

interfacial layer is a composite layer consisting of Li₂O, Li₃N, and Li₃P, which is formed by the lithium phosphorous oxide nitride (LiPON) electrolyte^{35,36}. Unfortunately, the Li-ion conductivity of LiPON is too low for practical batteries. For the most highly ionic conductive SSEs such as $Li_{10}GeP_2S_{12}$ (LGPS), $Li_{10}SnP_2S_{12}$, $Li_{0,33}La_{0.56}TiO_3$, and $Li_7P_3S_{11}$, the interfacial layers are both ionically and electronically conducting, thus allowing both Li-ion and electron transport at the interface^{37–39}. This result in continuous degradation of the SSE and growth of interfacial layers (Figure 1-6)^{33,38,40–42}, causing battery capacity fading, resistance increase, and short-circuiting.



Figure 1-6: Illustration of the interface between Li metal and $Li_{10}GeP_2S_{12}$ solid electrolyte, where the $Li_{10}GeP_2S_{12}$ is reduced by Li.³⁸

1.3 Approaches to Tuning SEI Chemistry for Silicon and Lithium Anodes

Many different approaches have been developed to address the SEI stability problem for Si and Li anodes. The developments of structured Si anodes (e.g., nanostructured Si^{18,43–47}, polymer-integrated Si^{48–53}, and Si-C composite^{54–58}, etc.) and structured Li anodes (e.g., three-dimensional Li hosts^{59–63}) can significantly alleviate the interfacial fluctuation and volume changes. The damage to the SEI are correspondingly reduced. Besides, another strategy is to replace the SEI derived from the conventional electrolyte by *ex-situ* fabricated artificial layers such as Li salts^{64–67}, Li-alloys⁶⁸, and polymers^{69–71}. While they inhibit the reaction of the electrolyte with Si or Li material, most artificial SEIs are composed of relatively simple chemical

components, thus lacking basic SEI properties such as adequate ionic conductivity and flexibility. Additionally, once damaged during cycling, layers fabricated *ex-situ* cannot be repaired, leading to poor interfacial stability. These two approaches do not change the intrinsic SEI chemistry and the interfacial issue between Si or Li and electrolyte.

This chapter will focus on the introduction to approaches those aims to intrinsically alter the formation, structure, and property of SEI for Si and Li anodes. A routinely adopted strategy is to optimize the electrolyte system to produce more stable SEI. This is a straightforward and convenient strategy since the SEI is directly formed by the electrochemical decomposition of electrolyte. The composition and structure are determined by electrolyte components including Li salt, organic solvents, and additives.

The addition of electrolyte additives can effectively modify the structure of electrolytederived SEI⁷². The additives generally have higher reduction potentials than that of electrolyte solvents and thus can preferentially decompose at the electrode surface to contribute SEI components. Figure 1-7 depicts a proposed working mechanism of FEC as electrolyte additives for Si and Li anodes⁷³. At a low potential, the FEC molecule can accept one electron to form a



Figure 1-7: A proposed working mechanism of FEC additives at the surface of Si and Li anodes.⁷³ free fluoride and the acetylene unit. The free fluoride combines with a Li ion to form lithium fluoride (LiF) and the acetylene units forms a polymer via a free-radical polymerization reaction. The produced polymer in the SEI can markedly improve the SEI flexibility, leading to an

enhanced tolerance to the volume changes and interfacial fluctuations of Si and Li anodes. The LiF salts can further passivate the SEI layer by increasing its density. Figure 1-8 describes the reduction mechanism of LiFSI proposed via a density functional theory (DFT) calculation method. The LiFSI additive is reduced in a gas-free manner and form inorganic Li salts including LiF, Li₂O, LiNSO, etc., which can improve the SEI passivation and density for Si and Li anodes. Many reductive species and polymerizeable agents have been used as additives, which include Li salts (e.g. lithium nitrate (LiNO₃)^{74,75}, lithium bis(oxalato)borate (LiBOB)⁷⁶, lithium bis(fluorosulfonyl)imide (LIFSI)⁷, etc.^{72,77}) and organic molecules (FEC)^{7,78}, vinylene carbonate (VC)^{79,80}, etc.^{72,81}). However, the improvements on the SEI stability is not sufficient. The main reason is that the SEI is still formed via an electrochemical deposition process, in which the all kinds of reactions occur simultaneously. Consequently, the chemical composition and nanostructure of SEI are incapable of being precisely controlled and further optimized.



Figure **1-8**: Suggested Chemistry for LiFSI salt based on the density functional theory calculation. In addition to the use of electrolyte additives, researchers have made great efforts on developing new electrolyte systems serving for Si and Li anodes. Several groups have reported that ionic liquids electrolyte can produce a more stable and resilient SEI layer than that of conventional carbonate electrolyte. For example, the SEI formed by 1.2 M LiFSI in *N*-Propyl-*N*-

methylpyrrolidinium bis(fluorosulfonyl)imide (PYR₁₃FSI) ionic liquid electrolyte presented a highly resilient SEI layer (Figure 1-9), which can help decrease the volume expansion of Si electrodes and reduce the SEI damage⁸². It has also been demonstrated that this electrolyte can reduce the SEI sacrifice and prevent Li dendrite growth for Li anodes⁸³.

Another favorable alternative electrolyte system is superconcentrated electrolyte, in which almost all of the solvent and anion molecules are coordinated to Li ion, forming a fluid polymeric network. Figure 1-10 presents a superconcentrated 4.2 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in acetylene nitrile electrolyte, in which no free ions



Figure 1-9: Composition of a Si anode SEI layer formed by a 1.2 M LiFSI in PYR₁₃FSI electrolyte. (a) EELS elemental mapping of Si from (b) TEM micrograph of cycled a Si electrode along with EELS elemental mapping and XPS analysis of (c,d) carbon, (e,f) sulfur, (g,h) fluorine, (i,j) lithium and (k,l) oxygen.

can be detected. Due to the formation of this network, the reductive stability of the electrolyte can be significantly improved^{84,85}. Using this concept, several concentrated electrolytes have been used for Li anodes^{86–88}, the formed SEI layers were thinner and less than the conventional SEI, owing to the reduced chemical and electrochemical reactivity of electrolyte. The coordinated network of electrolyte realized a fast Li ion transport, which eliminate the formation of Li dendrites. Despite these great achievements, some of these alternative electrolyte systems show compatibility issues with 4-V Li-ion battery cathodes and some of them have low ionic conductivity^{4,89}. So they still cannot replace the conventional carbonate electrolyte systems in practical use.



Figure 1-10: Raman spectra for (a) acetylene nitrile solvents (an asymmetric $C \equiv N(v2)$ stretching mode) and (b) TFSI anions in LiTFSI/acetylene nitrile solutions at various concentrations. c) Schematic diagrams of typical coordination structures of a dilute solution (~1 M) and a highly concentrated solution (~4.2 M).⁸⁴

1.4 Scope of the Dissertation

This dissertation focuses on intrinsically regulating the chemical composition and nanostructure of SEI for advanced battery materials in conventional electrolyte systems, which enables not only optimized chemical and physical properties of SEI but improved battery performance. This is realized by developing chemical and electrochemical reactive materials and allowing them to participate in the SEI formation. These materials can contribute functional components in the SEI layer and therefore regulate the structure and property of the SEI deliberately. We designed different functional materials used in different electrode-electrolyte systems. These include (1) organic and salt molecules and oligomers for Si anodes in liquid electrolyte systems, which will be discussed in Chapters 2 and 3; (2) polymeric organic and inorganic compounds for Li anodes in liquid electrolyte systems, which will be introduced in Chapters 4 and 5; and organic-inorganic composite materials for Li anodes in solid electrolyte systems, which will be shown in Chapter 6.

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Chapter 2

Manipulating Formation, Composition, and Morphology of Solid-Electrolyte Interphase for Nano-Sized Silicon Anodes

2.1 Introduction

As discussed in Chapter 1, Si materials are one of the most promising anode candidates for next-generation Li-ion batteries, with capacities several times greater than that of the conventional graphite anode^{1.5}. Si undergoes a huge volume change and pulverization and more importantly present poor stability of the solid-electrolyte interphase (SEI) during lithiationdelithiation^{6,7}. Despite considerable efforts on advanced material designs of nanostructures⁸⁻¹³, composites¹⁴⁻¹⁶, and functional polymer incorporation^{17,18} to address issues resulting from volume changes, the poor stability of the SEI is still a major obstacle to achieving desired electrochemical performance of Si anodes. For example, Si nanoparticle (SiNP) anode can effectively prevent the pulverization, loss of active material, delamination of electrodes but has severe interfacial issues associated with unstable SEI^{4,7}. The typical SEI, generated from electrolyte decomposition, presents not only insufficient integrity and a weak contact with active material surface, resulting in cracking and peeling-off issues during volume changes, but also a less efficient surface passivation, causing the electrolyte penetration (Figure 2-1a). These facts occurring in each cycle consumes additional electrolyte and material for the SEI repair and causes a poor electrochemical performance of the anode¹⁹⁻²⁷.

Two general strategies have been developed to address SEI stability issues. One is to insert a protective layer between Si anodes and the electrolyte, serving either as an artificial SEI^{28-³³ or forming a stable SEI on the protective layer surface³⁴⁻³⁸, circumventing the undesired SEI chemistry of Si anodes. During repeated volume changes upon cycling, it is still challenging to sufficiently protect Si anode materials from reactions with the electrolyte due to electrolyte} penetration from cracks and defects in the protective layers. The second strategy is to optimize SEI compositions of Si anode materials by tuning the electrolytes, including Li salts^{39,40}, aprotic solvents⁴¹ and additives^{39,42-45}. Despite improvements in the flexibility and surface passivation of the SEI, the SEI peeling-off issue remains unsolved. More importantly, the current technologies are not able to deliberately control the SEI composition and structure with desired properties. It is desirable to develop an approach, capable of designing and controlling SEI to understand composition-structure-property relationship of the SEI and direct the further SEI optimization.



Figure 2-1: Schematic illustration of CR-SEI. (a) Conventional SEI contains high-concentration inorganic Li salts and presents weak interactions with electrode material surface, showing poor tolerance to the volume change and insufficient surface passivation. During cycling, it breaks and loses contact with electrode material surface, resulting in severe consumption of electrode material and electrolyte and accumulation of "waste SEI". (b) CR-SEI, reinforced by diverse pre-anchored SEI components, with high-concentration organic oligomers and covalent bonding interactions (e.g. Si-C bonds) with electrode material surface presents good stability during cycling. Pristine SiNP was firstly anchored with multiple functional components (red and yellow lines) and used for electrode and cell fabrication. At the 1st lithiation, CR-SEI was *in-situ* formed, composed of the pre-anchored components after electrochemical activation and conventional SEI components (blue) from electrolyte decomposition.

We herein propose a general SEI reinforcement strategy for SiNP anodes (Figure 2-1b),

one manipulating the SEI formation process and chemical composition using a combination of

diverse functional components to reinforce its stability during cycling. The altered SEI formation process contains two steps. First, a variety of functional components were one-step covalently anchored onto the Si material surface with precisely controlled structure and amount via a click reaction. Second, these pre-anchored components were electrochemically activated along with the electrolyte decomposition, forming a chemically reinforced SEI (CR-SEI). The CR-SEI presents good tolerance to volume changes and surface passivation. Also, the covalent bonding between the pre-anchored components and SiNPs surface provides a durable contact between the SEI and the active material surface. A variety of single components and their combinations were covalently bonded onto the SiNPs to investigate their effects on SEI reinforcement. Among those components, an SEI reinforced by a combination of two organic oligomer components with a moderate anchoring amount presents the most optimized SEI stability. Unlike the conventional SEI, the CR-SEI is a thin layer intimately contacted to the SiNP surface that contains extensively increased concentrations of organic species, contributed by the pre-anchored functional components. Owing to these reinforced characteristics, it exhibits a durable chemical composition and morphology during cycling. Compared to SiNP electrodes with electrolyte additives, SiNPonly fabricated electrodes with CR-SEI in the absence of any electrolyte additives show significantly improved electrochemical performance, including increased 1st cycle Coulombic efficiency (CE), improved cycling CE and capacity retention, and limited increase in electrochemical impedance. This strategy was applied to the SEI reinforcement of Ge nanoparticles (GeNP) and significantly increased stability was also achieved, verifying its applicability to other Li-alloy materials.

2.2 Materials and Methods

Diverse pre-anchored components including four individual compounds and their combinations have been prepared for SEI reinforcement (Figure 2-2a). **2'** (*O*-(2-aizdoethyl)-*O*methyl undecaethylene glycol) and **3'** (*O*-(2-aizdoethyl)-*O*-methyl triethylene glycol), containing the repeating unit of ethylene oxide with different lengths, were designed as organic oligomers. **4'** (4-azidomethyl-5-methyl-1,3-dioxol-2-one) and **5'** (4-aizido-5-fluoro-1,3-dioxolan-2-one) were



Figure 2-2: Structural design and screening of chemically reinforced SEI. (a) Structural design and synthesis of SiNPs with various functional pre-anchored components. All these materials were prepared by the modular and high-efficiency click reaction. (b) Structural optimization of SiNP with pre-anchored components depicted in a through half-cell cycling performance measurement. The combination of 2'-4' (in the highlighted box) shows the better performance. (c) Anchoring amount optimization of SiNP with 2-4 through half-cell test. The SiNP with an optimized loading of 2' and 4' exhibits the best cycling stability (pink line in b and c).

designed as analogues of vinylene carbonate (VC) and fluoroethylene carbonate (FEC). Combinations of **2'-4'** and **3'-4'** were designed to functionalize the SEI synergistically.

All SiNPs with various pre-anchored components with different anchoring amounts were synthesized via Cu(I)-catalyzed click reaction (Figure 2-3). Briefly, pre-anchored components and SiNPs were first modified with azide and alkyne end groups respectively, and then covalently bonded together via a triazole linker. The detailed synthetic procedure is described as follow: The native oxide layer of SiNPs was removed by immersion in 5 % HF in ethanol-water for 3 min under nitrogen; The product, hydrogen-terminated SiNPs (9), were washed with an ethanol-water mixture 3 times and dried in a vacuum oven; Then, dried 9 were mixed with propargyl ether and Pt-dvs catalyst in a molar ratio of 100: 4 in anhydrous *N*, *N*-dimethylformamide (DMF) and heated at 170 °C with stirring for 4 h under nitrogen; The alkyne-terminated SiNPs (1) prepared in this way were rinsed with ethanol and toluene several times to remove unreacted residues and dried in a vacuum oven; To synthesize the SiNP with pre-modified SEI components, 1 was dispersed in aqueous solutions of azide-terminated components including 2', 3', 4', 5', combinations of 2' and 4', and combinations of 3' and 4' in designed molar ratios, and copper(II) sulfate pentahydrate and sodium ascorbate were added; This reaction was carried out at room



Figure 2-3: Synthetic route of SiNP with various pre-anchored components. Alkyne-terminated SiNP (compound 1) was prepared by the hydrosilylation reaction of hydrogen-terminated Si (compound 9) using propargyl ether. As-prepared azide-terminated functional components were bonded together via the Cu (I)-catalyzed Huisgen azide- alkyne 1,3-dipolar cycloaddition reaction in one step. R-N₃ represents 2', 3', 4', 5', 2'-4' and 3'-4', respectively.

temperature with stirring for 24 h under an air atmosphere⁴⁶; The product was washed with deionized water and analytical grade ethanol 3 times and was dried in a vacuum oven for material characterization and electrode fabrication.

This high-efficiency reaction has no selectivity to the structures of both material and preanchored components, presents nearly 100 % yield, and is conducted under mild conditions without by-product formation^{46,47}. These advantages enable the strategy serving as a facial and general approach for SEI construction and optimization of Si anodes.

The syntheses were verified by nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectra (FTIR) and thermal gravimetric analysis (TGA). Figure 2-4a displays the high-resolution C 1s and Si 2p XPS spectra. After the hydrosilylation of 9, the observed C-O (286.3 eV) and Si-C (99.8 eV) in the spectra of 1 demonstrate the formation of Si-C bond. Upon reaction of 2' and 4' on the surface of 1, the occur of the click reaction is also confirmed. The signal at 286.1 eV is attributed to C-O of the EO unit of **2** and C-N from the click reaction product. The appearance of O-C=O (289.0 eV) suggests the presence of 4. The triazole, characteristic product of click reaction, is confirmed by the peak at 399.8 eV in N 1s spectra of 3 (Figure 2-4d)⁴⁶. FTIR analyses of 9, 1 and SiNP with 2-4 show consistent result with XPS analysis (Figure 2-4b). The vSi-H_x signals are observed at 2081 and 2094 cm⁻¹ in the curve of **1**. After hydrosilylation, characteristic absorption bands at 1593, 2254, 2922 and 3321 cm⁻¹ corresponding to vSi-C=C, vC=C, vC-H_x and vC=CH, respectively, establish the formation of **2**. Once the click reaction is completed, $vC \equiv C$ and $vC \equiv CH$ absorptions disappear in the curve of **3**, while the strong absorptions at 1640 and 1223 cm⁻¹ are corresponding to vC=Oand vC-O bonds, respectively. This indicates the presence of 2 and 4. The triazole stretching vibration absorption is overlapped by this strong absorption⁴⁸. TGA comparison of pristine Si and **3** also evidences successful modification of additional SEI components (Figure 2-4c). TGA was



Figure 2-4: Synthetic characterizations of SiNP with 2-4. (a) High-resolution C 1s and Si 2p XPS spectra of 9 (hydrogen-terminated Si), 1 (alkyne-terminated Si), and SiNP with 2-4. (b) Transmission-mode FTIR spectra of 9 (black), 1 (blue) and SiNP with 2-4 (pink). (c) TGA curves of pristine Si (black) and SiNP with 2-4 (pink). All these techniques successfully confirm the formation of SiNP with 2-4. (d) High-resolution N 1s spectrum of SiNP with 2-4. The peak at 399.8 eV is corresponding to the 1,2,3-trazole functional group.

performed on a Q600 SDT using air flow with a balance sensitivity of 0.1 µg. 30 mg SiNPs

samples and 10 mg SiNP electrodes samples were used for TGA tests, respectively. The pristine

Si has no weight loss below 450 °C and the 1.2 % weight increase is from Si surface oxidation.

Contrastingly, there is a 7 % weight loss below 450 °C in the TGA curve of 3, implying the

presence of 2 and 4.

The synthesis of other SiNPs with SEI precursor candidates was confirmed by high-resolution XPS. Figure 2-5 displays the high-resolution C 1s and Si 2p XPS spectra of various SiNPs with pre-anchored components. In the C 1s and Si 2p XPS spectra of SiNP with 2 (Figure 2-5a,b), the high content of C-O (286.3 eV) and Si-C (99.8 eV) were observed. In the spectra of SiNP with 3, the C-O ratio was observed and lower than the one in the spectra of SiNP with 2 (Figure 2-5c,d). This result is consistent with the amounts of different EO ratios in 2' and 3'. In the spectra of SiNP with 4 (Figure 2-5c,f), the O-C=O (288.9 eV), C-O (286.3 eV) and Si-C (99.8 eV) were detected, indicating the presence of 4. In the spectra of SiNP with 5 (Figure 2-5g,h), The C-F (293.2 eV) was detected, implying the presence of pre-anchored components. In the spectra of SiNP with 3-4 (Figure 2-5i,j), the O-C=O (288.9 eV), C-O (286.3 eV) and Si-C (99.8 eV) were founded, suggesting the successful bonding of 3' and 4'.

The screening and optimization of these components were carried out based on their halfcell performances. First, the effects of different functional components were investigated (Figure 2-2b). The addition of **2**, **3**, **4**, **2**-**4** or **3**-**4** improves the cycling performance of SiNP anodes, implying the enhancement of SEI stability. Interestingly, the combination of **2**-**4** or **3**-**4** shows better cycling performance than any single component, indicating the benefits of multifunctionalizing the SEI. Second, we studied the effects of different anchoring amounts of the combination of **2**-**4**. As shown in Figure 2-2c, SiNPs with a molar ratio of SiNP: **2**': **4**' = 100: 1: 1.5 exhibit the most optimized cycling performance. SiNPs with a lower anchoring amount of **2**-**4** (SiNP: **2**': **4**' = 100: 0.5: 0.5) show faster capacity fading, indicating an insufficient functionalization of the SEI. The higher anchoring SiNPs (Si: **2**': **4**' = 100: 2.5: 2.5) present a decreased specific capacity but a good cyclability, since the high loading of pre-anchored components may have lowered the electrical conductivity of the entire SEI.



Figure 2-5: Synthetic characterizations of various SiNPs with pre-anchored components. High-resolution C 1s and Si 2p XPS spectra of SiNP with 2 (a,b), SiNP with 3 (c,d), SiNP with 4 (e,f), SiNP with 4 (g,h), and SiNP with 3-4 (i,j).

Finally, the CR-SEI reinforced by **2-4** with a moderate anchoring amount was used for further analysis. In this CR-SEI, **2** containing ethylene oxide chains possesses strong non-

covalent interactions with conventional SEI components such as lithium vinylene carbonate (ROCO₂Li), lithium carbonate (Li₂CO₃) and lithium oxide (Li₂O) and enhances the flexibility of the entire SEI.⁴⁹ **4** is electrochemically activated *in-situ* and forms oligomeric species with the electrolyte, and thus improves the surface passivation of the SEI. Meanwhile, the covalent bonding between both pre-anchored components and the SiNP surface allows the CR-SEI intimate contacted to SiNP electrode surface during cycling.

2.3 Results and Discussion

To investigate the reinforcing effects of the CR-SEI, we next evaluated the electrochemical performance of SiNP electrodes with the CR-SEI in the absence of any electrolyte additives and compared with the performance of SiNP electrodes containing conventional electrolyte-derived SEI (conventional SEI) and conventional electrolyte with a fluoroethylene carbonate additive-derived SEI (FEC-SEI). We followed the same procedure to prepare SiNP electrodes and ran cell tests. SiNP electrodes were prepared by mixing pristine SiNPs/SiNPs with pre-modified SEI components, Super P carbon and polyimide binder (7:2:1) in N-methyl pyrrolidine to make a slurry, casting this slurry on a Cu foil, and drying it at 200 °C in a vacuum oven overnight. The mass loading of the electrode was about 1 mg/cm². Baseline electrolyte, which is 1M LiPF₆ in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7, v/v), was used to generate conventional SEI and the conventional components in the CR-SEI. FEC-derived SEI was formed from the baseline electrolyte containing 10% FEC additive. The electrolyte amount was controlled to 25 μ l with a pipette. Electrochemical tests of cells were performed in CR 2016 coin cells under galvanostatic charging-discharging conditions at a C/3 rate (1C = 3000 mA/g Si) between 0.01 and 1.5 V. Full

cell fabrication followed a pre-conditioning method⁴¹. The SiNP anode was paired with a $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode with a ratio of the areal capacity of 1.6. The SiNP anode was pre-conditioned for 10 cycles in the half cell and terminated in the fully-lithiated state, while the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode was activated for 3 cycles in the half cell which ended at the fully-



Figure 2-6: Electrochemical performance of SiNP with the chemically reinforced SEI. (a) The voltage profile and SEI formation of SiNP electrodes with CR-SEI, FEC-SEI, and conventional SEI during initial cycles. SiNP electrode with CR-SEI shows a much lower capacity related to SEI formation, implying the decreased consumption of electrode and electrolyte materials. (b) Specific capacities and Coulombic efficiencies (CE) of SiNP electrodes with CR-SEI (pink), FEC-SEI (blue) and conventional SEI (gray) in half cells. Compared with SiNP electrode with FEC-SEI or conventional SEI, SiNP electrode with CR-SEI presents greatly improved cycling life and cycling CE, indicating its benefits to cycling performance. The significantly increased first cycle CE of SiNP electrode with CR-SEI also indicates the decreased consumption of electrolyte and material by SEI formation, consistent with the findings in a. (c) EIS measurements of SiNP electrodes with conventional SEI, FEC-SEI, and CR-SEI after different cycles. The resistance of SiNP electrode with CR-SEI increases quite slowly indicating limited SEI accumulation and good stability during cycling. (d) Full-cell capacity retention and CE of SiNP electrodes with CR-SEI (pink) and FEC-SEI (blue), paired with a LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode. SiNP electrode with CR-SEI delivers dramatically improved capacity retention and CE, compared with SiNP electrode with FEC-SEI, resulting from its enhanced SEI stability especially the decreased consumption of Li source during cycling.

delithiated state. Two pre-cycled electrodes were paired as a coin-cell type full cell. Cells were galvanostatically cycled at C/3 rate (1C = 3000 mA/g Si) from 3.0 to 4.2 V vs Li/Li⁺.

During the first lithiation, SiNP electrodes with the CR-SEI show a capacity of about 280 mAh/g in the voltage range of 1 V to 0.1 V (Figure 2-6a), which is mainly contributed to initial SEI formation. In contrast, the capacities for forming the conventional SEI and FEC-SEI in SiNP electrodes are 515 mAh/g and 523 mAh/g (Figure 2-6a), respectively. This result indicates much less consumption of electrolyte and electrode material for CR-SEI formation. This result is consistent with the increased first cycle efficiency to 91.3 % in SiNP with CR-SEI, compared to 73.2 % for a conventional SEI and 81.6 % for FEC-SEI (Figure 2-6b). In addition, the SiNP electrode with CR-SEI presents significantly improved cycling stability with a specific capacity of 2280 mAh/g for up to 200 cycles and a high cycling CE of 99.6 % in 200 cycles (Figure 2-6b). This is in dramatic contrast with the FEC-SEI and conventional SEI, which only delivers specific capacities of 1613 and 784 mAh/g after 100 cycles, and CE of 98.5 % and 97.3 %, respectively (Figure 2-6b). Meanwhile, the CE of the SiNP electrode with CR-SEI reaches 99 % in the 9th cycle and maintains this level afterward, indicating the accelerated formation of a stable SEI (Figure 2-6b). Furthermore, electrochemical impedance spectroscopy (EIS) measurements of a SiNP electrode after different cycles were also monitored. The overall charge-transfer resistances of SiNP electrodes with a CR-SEI are quite low and remain stable during cycling, in contrast to the continuously increasing resistances of electrodes with both SiNP with FEC-SEI and a conventional SEI (Figure 2-6c). Finally, we evaluated full-cell performances using the SiNP only as the anode paired with a commercial $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode to further verify the stability of the CR-SEI. As shown in Figure 2-6d, the full cell displays discharge capacity retentions of 90.2 %, 83.0 %, and 72.0 % after 20, 80 and 200 cycles, respectively, and a high average CE of 99.7 % during 240 cycles. This is much better than the performance of SiNP with an FEC-SEI,



Figure 2-7: Synthetic route and characterizations of GeNP with 2-4. (a) Synthetic route of GeNP pre-anchored with 2-4. The same click chemistry method has been employed for the preparation. (b) High-resolution C 1s and Si 2p XPS spectra of 10 (hydrogen-terminated GeNP), 11 (alkyne-terminated GeNP), and GeNP with 2-4.

which exhibits discharge capacity retentions of 50.5 %, 29.5 % and 13.8 % after 20, 80 and 200 cycles respectively and the low CE of 98.7 % in 50 cycles. As the Li source in the full-cell system is limited, the significantly improved cycling life and CE of the full cell using SiNP CR-SEI demonstrates a dramatic enhancement of the CR-SEI stability and the suppressed Li consumption during cycling. Overall, these improvements in electrochemical performance strongly verify the effective reinforcement of the pre-anchored components that leads to SEI stability. Since pure SiNP electrode with high areal capacity faces very extreme SEI issues, this is one of the best cycling performances, as far as we are aware. We also applied this optimized CR-SEI to germanium nanoparticles (GeNPs) anode, another promising Li-alloy anode. Following a similar

synthetic approach, GeNP with 2-4 was synthesized. Figure 2-7a displays the synthetic route of GeNP with pre-anchored 2-4. The same click reaction was used for the synthesis and the optimized pre-anchored components 2' and 4' were bonded on the material surface with the molar ratio of GeNP: 2': 4' = 100: 1: 1.5. In the C 1s and N 1s XPS spectra of GeNP with 2-4 (Figure 2-7b), the high content of C-O (286.3 eV) and the triazole (399.9 eV) from the click reaction product were detected, indicating the successful synthesis.

GeNP anode with the CR-SEI exhibits greatly enhanced cycling performance and CE compared with GeNPs with FEC-SEI and conventional SEI. (Figure 2-8). The GeNP with CR-SEI presents raised cycling stability with a specific capacity of 950 mAh/g for up to 200 cycles and a high cycling Coulombic efficiency (CE) of 99.7 % in 200 cycles. The discharge capacity retention is 98 % from the 2nd cycle to the 200th cycle. This is a great improvement compared with the ones of GeNP with FEC-SEI and GeNP with conventional SEI, which show the specific capacities of 400 and 200 mAh/g after 100 cycles. Also, the CE of GeNP with CR-SEI reaches 99% in 5 cycles, and this is in contrast with the low CEs of GeNP with FEC-SEI and conventional SEI.

To study the reinforcement mechanism of the pre-anchored components to the CR-SEI, we analyzed the chemical composition and compositional evolution of CR-SEI during cycling. High-resolution XPS measurements of both a cycled SiNP electrode with CR-SEI and a SiNP electrode with conventional SEI reveal clear differences in their chemical compositions because of the presence/absence of pre-anchored SEI components (Figure 2-9a). XPS analysis was carried



Figure **2-8**: Electrochemical performances of GeNP with CR-SEI. (a,b) Specific capacities and coulombic efficiencies of GeNP with CR-SEI (pink), FEC-SEI (blue) and conventional SEI (gray) in half cells. Compared to GeNP with FEC-SEI and GeNP with conventional SEI, GeNP with CR-SEI shows greatly improved cycling life and CE, indicating its benefits to cycling performance. (c) Voltage profiles of GeNP with CR-SEI at the 1st, 5th, 10th, 100th and 200th cycles.

out on a PHI VersaProbe II Scanning XPS Microprobe. Air- and moisture-sensitive samples were loaded in the glovebox and transferred into the instrument though a vacuum transfer vessel. The conventional SEI shows peaks at 289.2 and 282.3 eV attributed to C=O and R-Li respectively in the C 1s spectrum, peaks at 532.2 and 531.2 eV corresponding to C=O and Li₂CO₃ respectively in the O 1s spectrum, and peaks at 686.5 and 684.5 eV assigned to Li_xPO_yF_z and LiF respectively in the F 1s spectrum. This result is consistent with previous studies of SEI compositions using carbonate-based electrolytes^{21,50,51}. As to CR-SEI, new peaks appeared at 291.1 and 534.5 eV belonging to the oligomeric species of $4^{39,49}$. The concentrations of C-O in both C 1s and O 1s spectra are considerably increased, caused by the addition of both the ethylene oxide repeating unit from **2** and the C-O from **4**. This result clearly affirms the introduction of the covalently



Figure 2-9: Compositional analysis of CR-SEI. High-resolution XPS spectra (a) and FTIR analysis (b) of SiNP with CR-SEI (top) and SiNP with conventional SEI (bottom) after 30 cycles. Compared with conventional SEI, newly appeared peaks in the spectra of SiNP with CR-SEI are assigned to the increased concentrations of the organic and oligomeric species in the chemically reinforced SEI, demonstrating the presence of the pre-anchored components in the SEI. Elemental concentration analysis of conventional SEI (c) and CR-SEI (d) after different cycles. This trend analysis of the concentrations of C, O, Li, F, P and Si in the SEI reveals that CR-SEI contains significantly increased organic species and its composition retains stable during cycling. High-resolution XPS spectra (e) and TGA (f) of the Si with CR-SEI residue (pink) and Si with conventional SEI residue (black). After removing the SEI by the wash and ultrasonic treatment, the Si with CR-SEI presents the characteristic signals of pre-anchored components in the XPS spectrum and 8 % weight loss below 450 °C, both indicating the durable bonding of pre-anchored components on electrode material surface.

bonded components into the CR-SEI. Additionally, the concentration of Li-F is quite low and the $Li_xPO_yF_z$ signal is negligible, implying that LiPF₆ decomposition is limited due to the effective surface passivation of the CR-SEI⁴⁹. FTIR results are consistent with the findings from High-resolution XPS measurements. (Figure 2-9b). FTIR spectra were obtained on a Bruker Vertex V70 spectrometer. The electrode samples were tested in diffuse reflectance mode with a Spectra Tech Collector II cell filled with nitrogen. Spectra of SiNP electrode with CR-SEI and SiNP electrode with conventional SEI electrodes both display peaks from electrolyte-decomposed products, including ROCO₂Li with peaks at 2959 and 2865 cm⁻¹ (vC-H), 1624 cm⁻¹ (vC=O), 1462 cm⁻¹ (δ C-H), 1332 cm⁻¹ (vC=O) and 1108 cm⁻¹ (vC-O), and Li₂CO₃ with peaks at 1509 and 941 cm⁻¹. Notably, the peaks at 1775, 1249, 1050 and 831 cm⁻¹ in the spectra of the SiNP electrode with conventional SEI, suggesting the presence of pre-anchored components in the CR-SEI.

Apart from compositional analysis, the compositional evolution during cycling provides useful information on SEI stability. XPS elemental analysis of the SiNP electrodes cycled after 0, 1, 5, 50, and 100 cycles was carried out. In the LiPF₆/carbonate electrolyte system, Li and F concentrations in the SEI are related to the amount of decomposed LiPF₆ species. Particularly, the F concentration directly represents the LiPF₆ decomposition since LiPF₆ is the only F source. As shown in Figure 2-9c, conventional SEI presents high Li and F concentrations, both of about 15 % after 1 cycle, suggesting a severe decomposition of LiPF₆ and the formation of a large amount of Li salt species in the SEI. Their concentrations keep increasing to 25 % after 100 cycles, while the C and O concentrations are 5.6 % and 6.4 % after 1 cycle and increase to 10.5 % and 13.9 % after 100 cycles, respectively, remaining at a low level. Meanwhile, the C and O concentrations are relatively high (~ 40 %) and remain consistent during cycling (Figure 2-9d). The high concentration of organic oligomeric species in the CR-SEI represents the effective suppression of Li salt consumption, demonstrating a good stability of the CR-SEI. Additionally, the intensity of Si signal reflects the SEI thickness during cycling. The more strongly the Si signal is detected, the thinner the SEI is on the Si surface⁴³. The pristine SiNP electrode surface before cycling contains 34.3 % of Si (Figure 2-9c) and the value for the uncycled SiNP electrode with 2-4 is 17.9 % because of the presence of pre-anchored components and surface oxidation through the preparation process (Figure 2-9d). After 1 cycle, the apparent Si concentrations of the SiNP electrode with conventional SEI and with CR-SEI decrease to 3.3 % and 7.0 % respectively, indicating that the electrode surfaces are both covered by the SEI. The Si concentration of the SiNP electrode with conventional SEI further drops to 0.7 % after 5 cycles and the Si signal cannot be observed after 50 cycles, reflecting the formation of large amount of "waste SEI". In contrast, the apparent Si surface concentrations of the SiNP electrode with CR-SEI are 5.4 %, 2.1 % and 1.1 % after the 5, 50 and 100 cycles, respectively. The long-lasting presence of the Si signal on the surface proves that CR-SEI remains thin and has very limited accumulation during cycling. To further verify the long-lasting anchoring of pre-anchored components within the SEI on the Si surface during cycling, we studied the cycled SiNP electrodes with conventional SEI and CR-SEI after 100 cycles by XPS and TGA techniques after a thorough wash and ultrasonic treatment. No obvious carbonate-based species at 289.2 eV was detected by XPS measurements of the SiNP electrode with conventional SEI, indicating that the conventional SEI components are removed (Figure 2-9e). In contrast, the characteristic peaks of 2 and 4 such as C-O (286.2 eV), oligomeric O-C=O (291.3 eV) and triazole (399.5 eV) were still observed on the Si with CR-SEI surface, confirming the covalent bonding of pre-anchored SEI components to the SiNP surface after many cycles (Figure 2-9e). Meanwhile, TGA of SiNP electrode with CR-SEI after a wash

and ultrasonic treatment shows an 8 % weight loss below 450 °C, compared with SiNP electrode with conventional SEI. This finding also verifies the presence of the pre-anchored SEI components (Figure 2-9f).

To further demonstrate the stability of the CR-SEI, we next carried out morphological observations of the SEI during cycling. The thickness and elemental distribution of the CR-SEI were studied by energy-filtered transmission electron microscopy (EF-TEM). TEM samples were prepared by dispersing cycled SiNP electrodes in DEC and dripping them onto the TEM grid. EF-



Figure **2-10**: Morphological observation on CR-SEI. (a-e) EF-TEM images of SiNP with CR-SEI displays its thickness of about 10 nm and the uniform distribution of lithium (c), oxygen (d), and carbon (e) after 30 cycles. (f-j) TEM images of SiNP with conventional SEI: fresh Si (f), cycled Si after 1 cycle (g), 5 cycles (h), 50 cycles (i), and 100 cycles (j). The accumulation of "waste SEI" and the diminished SiNP imply the huge consumption of electrolyte and SiNP and the unstable conventional SEI. (k-o) TEM images of SiNP with CR-SEI: **3** (k), cycled Si after 1 cycle (l), 5 cycles (m), 50 cycles (n), and 100 cycles (o). Clear-edge SiNPs with retained size and limited electrolyte-decomposed products were captured after 50 and 100 cycles, evidencing the good stability of CR-SEI. All samples were prepared at the delithiated status.

TEM and TEM images were acquired from a Tecnai G2 20 XTWIN with a LaB6 source. The CR-SEI after 30 cycles is less than 10 nm thick and uniformly coated on the SiNP surface (Figure 2-10a-e), consistent with its good surface passivation and close contact with the Si surface. Furthermore, morphological changes in the CR-SEI during cycling were compared by TEM with those of the conventional SEI. Before cycling, fresh SiNPs with/without pre-anchored SEI components both show a perfectly round shape with a sharp edge (Figure 2-10k, f). The preanchored SEI components are veiled under this length scale. After 1 cycle, the conventional SEI is rough and thick once formed. After 5 cycles, a large amount of "waste SEI" accumulation and a dramatic decrease in SiNP particle size were observed indicating the severe consumption of electrolyte and SiNP material. No clear-edge SiNP particle can be recognized after 50 cycles (Figure 2-10g-h). This result is in accord with the poor electrochemical performance and the high concentrations of Li and F of SiNP electrodes with conventional SEI. In contrast, the thin SEI and clear-edge SiNPs of SiNP electrodes with CR-SEI were observed after 1, 5 and 50 cycles. Only a small amount of "waste SEI" was found after 100 cycles and the SiNP kept its round shape and size (Figure 2-101-0). In addition, thickness increases of the whole electrode can also imply the SEI accumulation. Electrode thickness measurement was conducted on a Nova NanoSEM 630. To make sure the consistency of electrode thickness, the same piece of the electrode was used for SEM experiments. Based on the measurements of electrode thicknesses from scanning electron microscopy (SEM) images, the SiNP electrode with CR-SEI presents a limited increase in electrode thickness compared SiNP electrode with the FEC-SEI during cycling, indicating the limited "waste SEI" accumulation (Figure 2-11). These observations confirm the significantly improved stability of the CR-SEI and are also consistent with results of the electrochemical and compositional analyses.



Figure 2-11: SEM images of Si electrodes with CR-SEI. (a) Electrode thickness increases of Si electrodes with CR-SEI and Si electrodes with FEC-SEI. The fresh electrode thicknesses were normalized as 100%. Compared with Si electrodes with FEC-SEI, the Si electrodes with CR-SEI shows limited increases in electrode thickness during cycling. (b-d) SEM images of Si electrodes with FEC-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e-g) SEM images of Si electrodes with CR-SEI after 0, 50 and 100 cycles. (e

2.4 Conclusions

In summary, we present a new general strategy for deliberately controlling formation,

composition, and morphology of the nano-sized Si anodes SEI via covalently anchoring a

combination of diverse functional components with precisely controlled structure and amount into the SEI using a one-step click chemistry. The CR-SEI presents improved tolerance to volume change, good surface passivation, and durable contact with the active materials surface during cycling.

This concept has been demonstrated by the significantly improved stability of the SiNP anode SEI. By optimizing chemical structures, combinations, and surface anchoring amounts of the pre-anchored SEI components, we construct a CR-SEI, which exhibits a different chemical structure containing a high-concentration organic species, stable composition, and durable morphology during cycling. The CR-SEI enables greatly enhanced electrochemical performance of SiNP anodes, including long cycle life and high CE in both half and full cells, elevated 1st cycle efficiency, and limited impedance increases during cycling. Moreover, this strategy has also been applied to GeNP SEI reinforcement with dramatic enhancement of the SEI stability, suggesting its viability for other Li-alloy materials.

Owing to the facility and modularity of click chemistry, this SEI reinforcement approach can be applied to other Li-alloy materials and more potential SEI components can be employed. This approach focuses on the interfacial construction of functional groups to construct a durable SEI. However, it is still unable to address the negative effects of pulverization on SEI stability of Li-alloy materials. Combining multiple approaches with this strategy shows promise in further improving SEI stability and enabling stable Li-alloy materials in lithium-ion batteries.

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Chapter 3

Semi-Immobilized Solid-Electrolyte Interphase Stabilizes the Interface of Micro-Sized Silicon Anodes

3.1 Introduction

As discussed in Chapter 1, silicon (Si) has been considered as a highly attractive anode material for lithium (Li)-ion batteries to meet the demand for electric vehicle and stationary energy storage applications, due to its high theoretical specific capacity, low discharge potential, and low cost¹⁻³. The solid-electrolyte interphase (SEI) of Si materials is highly unstable, associated with repeated sacrifice and reformation⁴⁻⁷. In Chapter 2, we introduced an approach to designing stable SEI for nano-sized Si anodes. However, it shows very limited effect on the SEI of micro-sized Si anodes since the volume expansions and contractions of micro-sized Si materials are too huge^{8,9}. In this case, SEI cracking still occurs. Meanwhile, Si SEI presents a strong tendency to break and peel off from the Si surface under volume changes (Figure 3-1a). The exposed surface is immediately covered by newly formed SEI, accompanied by the consumption of active Si and electrolyte. The peeled-off SEI cocurs in every cycle and results in rapidly faded capacity, reduced Coulombic efficiency (CE), and raised the interfacial resistance of Si anodes.

Researchers have been approached this problem in two ways. One is to develop artificial SEIs¹⁰⁻¹⁴ to replace the electrolyte-derived SEI. The other is to optimize electrolyte compositions¹⁵⁻²⁰ to produce more flexible SEI with enhanced tolerance to the volume changes of Si. Unfortunately, these approaches can effectively stabilize the SEI of nano-sized Si materials but show limited positive effects on micro-sized Si materials. The reason is that it is extremely difficult to enable durable integrity of SEI for micro-sized Si with an extremely dynamic interface



Figure 3-1: Illustration of the construction of a semi-immobilized SEI at the interface of microsized Si anodes. (a) Electrolyte-derived SEI undergoes repeated sacrifice and reformation, which is caused by the highly dynamic interface of micro-sized Si materials. This results in severe consumption of active Si and electrolyte. (b) Design of a semi-immobilized SEI for micro-sized Si anodes. A salt compound, namely *N*-methyl-*N*-propyl pyrrolidinium bis(fluorosulfonyl)imide, is covalently bonded at the Si surface. During SEI formation, this compound can provide not only pyrrolidinium-based species, which act as immobilized and stable SEI components to reduce SEI sacrifice but also LiF and -NSO_xF salts to passivate the Si surface and protect active Si from the formation of Li_xSiO_y .

and large volume changes^{8,21}. To this end, a novel approach to enhancing the SEI stability for micro-sized Si materials is urgently needed.

In this chapter, we showed that to covalently bond a functional salt, *N*-methyl-*N*-propyl pyrrolidinium bis(fluorosulfonyl)imide (PYR₁₃FSI), at the surface of micro-sized Si materials can effectively stabilize the interface and SEI (Figure 3-1b). Unlike conventional methods for improving the volume-change tolerance of SEI, this approach aims at building a semi-immobilized SEI with two unique features. Firstly, the pyrrolidinium-based species, cations of PYR₁₃FSI, are electrochemically inert and covalently bonded at the Si surface. These species occupy a part of Si surface and serve as non-consumable components to reduce SEI sacrifice

during cycling. Secondly, the FSI anions are electrochemically active and can generate LiF and -NSO_xF salts *in situ* to passivate Si surface, which prevent the formation of Li_xSiO_y and reduces the loss of active Si. We used Si microparticles (SiMPs) (1~5 µm) anodes to verify this design. X-ray photoelectron spectroscopy (XPS) depth profiling and transmission electron microscopy (TEM) studies indicated that the semi-immobilized SEI has a stable chemical composition and durable morphology during cycling. The use of semi-immobilized SEI enabled significantly enhanced cycling performance of a SiMP| $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM 523) cell, which displayed a capacity retention (CR) of 83.4% in 200 cycles in a carbonate electrolyte. Cells incorporating micro-sized porous Si and Si nanoparticles anodes also showed markedly extended lifespans, indicating a universal application of this approach for different Si materials.

3.2 Materials and Methods

The synthesis of SiMPs with covalently bonded PYR₁₃FSI was described in Figure 3-2a. Briefly, freshly synthesized *N*-methyl-*N*-(trimethoxysilyl)propyl pyrrolidinium chloride was bonded at SiMP surface via a silanization reaction²², and then the chloride anions in the product were replaced by FSI anions via an ion exchange reaction²³. The detailed synthetic procedures are as follow: SiMPs (Alfa Aesar, 1-5 μ m) were dispersed in ethanol under ultrasonication for 20 min to remove surface contaminants, washed with deionized water three times, and dried under vacuum; The samples were next immersed in a Piranha solution (H₂SO₄:H₂O₂, 7:3 v/v) for 30 min at room temperature to produce hydroxyl groups-terminated surface and then washed with deionized water three times; After drying, the SiMPs (0.1 mol) were dispersed in an anhydrous toluene solution of *N*-methyl-*N*-(trimethoxysilyl)propyl pyrrolidinium chloride (0.006 mol); The reaction was carried out at 60 °C for 12 h under a nitrogen atmosphere; The products were then washed with toluene and deionized water three times, respectively, and dried under vacuum;



Figure 3-2: Synthetic scheme of SiMP with covalently bonded SEI precursor.

Subsequently, the modified SiMP samples (0.01 mol) were dispersed in deionized water (50 ml), and lithium bis(fluorosulfonyl)imide (0.2 mol) were added into the mixture to replace the chloride anions with FSI inions. The reaction was performed at room temperature for 24 h. The products, SiMPs with covalently bonded PYR₁₃FSI, were washed with deionized water six times and dried under vacuum.

To synthesize the compound **1** (Figure 3-2b), namely *N*-methyl-*N*-

(trimethoxysilyl)propyl pyrrolidinium chloride, (3-chloropropyl)trimethoxysilane (1.99 g, 10 mmol) (Sigma Aldrich) and anhydrous *N*-methylpyrrolidine (1.02 g, 12 mmol) (Sigma Aldrich) were mixed in an anhydrous dimethylformamide (DMF) solution (100 mL). The mixture was heated at 60 °C for 12 h under a nitrogen atmosphere. After the reaction, the solution was added to anhydrous diethyl ether and centrifuged. The mixture solution was separated, and the brown liquid was washed with anhydrous diethyl ether six times to remove the unreacted *N*-methylpyrrolidine. The products were dried at 60 °C under vacuum 12 h before use.

The synthesis was confirmed by XPS and Fourier-transform infrared spectra (FTIR). The full-scan and high-resolution O 1s, Si 2p, and C 1s XPS spectra of pristine SiMPs were displayed in Figure 3-3. SiMPs were washed with ethanol and deionized water, respectively, three times



Figure **3-3**: High-resolution XPS spectra of the pristine SiMP.



Figure **3-4**: High-resolution XPS spectra of the compound **2**.

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before use. The SiMP surface was relatively clean, which was covered by SiO₂ (peaks at 103.5 eV in the Si 2p spectrum and 523.7 eV in the O 1s spectrum) and a small amount of hydrocarbons (peaks at 284.6 and 286.2 eV in the C 1s spectrum). The high-resolution C 1s, N 1s, Si 2p, F 1s, S 2p, and Cl 2p XPS spectra of the compound **2** were displayed in Figure 3-4. -C-Si-O- (peaks at 102.4 eV in the Si 2p spectrum and 283.2 eV in the C 1s spectrum), C-N (peaks at 402.8 eV in the N 1s spectrum and 286.0 eV in the C 1s spectrum), C-C (the peak at 284.6 eV in the C 1s spectrum), and Cl⁻ (the splitting peaks at 198.0 and 196.5 eV) were observed, indicating the presence of pyrrolidinium chloride species at the surface of SiMP. The high-resolution C 1s, N 1s, Si 2p, F 1s, S 2p, and Cl 2p XPS spectra of the compound **3** were displayed in Figure 3-5. -C-



Figure 3-5: High-resolution XPS spectra of the compound 3.

Si-O- (peaks at 102.4 eV in the Si 2p spectrum and 283.2 eV in the C 1s spectrum), C-N (peaks at 402.8 eV in the N 1s spectrum and 286.0 eV in the C 1s spectrum) and C-C (the peak at 284.6 eV in the C 1s spectrum) were found, implying the presence of pyrrolidinium-based compounds. In addition, bis(fluorosulfonyl)imide anion (peaks at 399.8 eV in the N 1s spectrum, 169.7 and 170.8 eV in the S 2p spectrum, and 687.6 eV in the F 1s spectrum) were observed. Meanwhile, the Cl⁻ signals were disappeared, indicating a complete ion exchange. The FT-IR spectra of pristine SiMP (black line), compound **2** (blue line), and compound **3** (red line) were shown in Figure 3-6. ν SiO_xH and ν Si-O-Si signals were recorded at 2257 and 1140 cm⁻¹, respectively, in the curve of pristine SiMP. After the silanization reaction, ν C-H, ∂ CH₂, and ν C-N were observed at 2919, 1470, and 952 cm⁻¹, respectively, in the curve of compound **2**. Once the ion exchange reaction is finished, the ν S=O, ∂ SO₂-F, and ∂ S=O appeared at 1345, 733, and 602 cm⁻¹ in the curve of compound **3**. These results are consistent with the XPS analysis.



Figure 3-6: Transmission-mode FTIR spectra of pristine SiMP, compound 2, and 3.

The as-synthesized SiMPs with covalently bonded PYR₁₃FSI were used for slurry and electrode fabrications. The SEI formation process was illustrated in Figure 3-1b. During the initial lithiation process of a SiMP anode, the semi-immobilized SEI is formed *in situ* at SiMP

surface, which consists of immobilized pyrrolidinium-based species (blue symbols), passive salts such as LiF and $-NSO_xF$. (orange lines), and electrolyte-derived SEI components such as Li₂CO₃, Li₂O, and LiCO₂R (green lines).

3.3 Results and Discussion

To verify this design, we investigated the electrochemical performance of SiMP anodes with semi-immobilized SEI and used SiMP anodes with electrolyte-derived SEI as a control study. The SiMP electrodes were fabricated as follow: As-synthesized SiMPs with SEI precursor/raw SiMPs, conductive carbon additives, and polyimide binder (6:2:2) were mixed in anhydrous N-methylpyrrolidine to prepare an electrode slurry; the slurry was then cast on a copper foil and dried at 230 °C under vacuum overnight. Si mass loading was 0.3-0.5 mg. The micro-sized porous Si and SiNP electrodes were fabricated following the same procedure. To prepare NCM 523 cathodes, NCM 523 powders (Umicore), conductive carbon additives, and polyvinylidene fluoride (90:4:6) were mixed in anhydrous dimethylformamide to make a slurry. The slurry was then cast on a carbon-coated aluminum foil and dried at 120 °C under vacuum overnight. Cell tests were conducted in coin cells under galvanostatic charge-discharge conditions at a rate of C/3 (1C = 2500 mA g⁻¹). A 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC), ethyl methyl carbonate (EMC), and VC (3:7:1, v/v/v) electrolyte (battery grade, BASF) was used for Li|Si half cells, and a 1 M LiPF₆ in EC/EMC/VC with 2% lithium bis(oxalate)borate (LiBOB) electrolyte (battery grade, BASF) was used for the Si|NCM 523 full cell test. The electrolyte amount was ~25 µL. The prelithiation of Si anodes and predelithiation of NCM 523 cathodes were conducted in half cells at a rate of C/30 for 1 cycle.



Figure 3-7: Electrochemical performances of silicon microparticles (SiMPs) anodes incorporating semi-immobilized SEI. (a and b) Cycling lives (a) and initial charge-discharge profiles (b) of SiMP electrodes with and without semi-immobilized SEI in half cells. (c) Impedance evolution of a SiMP electrode with semi-immobilized SEI. (d and e) Cycling life (d) and charge-discharge profiles (e) of a SiMP|LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM 523) cell with semi-immobilized SEI. (f) Rate performances of SiMP electrodes with and without semi-immobilized SEI. The use of semi-immobilized SEI enabled remarkably increased electrochemical performance of SiMP electrodes.

Figure 3-7a displays the cycling stability of SiMP anodes in Li|SiMP half cells. The cell

incorporating semi-immobilized SEI presented a CR of 81.0% in 100 cycles, which is a contrast

to the short cycle life of the control cell. We tuned the amount of covalently bonded PYR₁₃FSI

compound at the SiMP surface by tuning the molar ratio between SiMPs and compound **1** in the silanization reaction. The loading amount of covalently bonded PYR₁₃FSI was optimized by the half-cell performances of SiMP anodes (Figure 3-8). The molar ratio between SiMP and compound **1** for protected SiMP (red curve), SiMP with over bonded PYR₁₃FSI, and SiMP with insufficiently bonded PYR₁₃FSI was 100:6, 100:10, and 100:2, respectively. Overall, the uses of covalently bonded PYR₁₃FSI showed increased cycling stability of SiMP anodes. The insufficient bonding amount led to less enhanced lifespan, while the excessive bonding amount caused the lowered utilization of active Si materials.



Figure **3-8**: Optimization of the amount of the bonded PYR₁₃FSI at SiMP surface.

In the initial lithiation/delithiation voltage profiles (Figure 3-7b), we found that SiMP with semi-immobilized SEI has a higher initial delithiation capacity (2943 mAh g⁻¹) than that (2737 mAh g⁻¹) of the control cell, implying that the use of semi-immobilized SEI can markedly reduce the active Si consumption by the SEI formation. Meanwhile, the overall charge-transfer resistance of the cell incorporating semi-immobilized SEI increased slowly from 38 to 60 Ω in 100 cycles (Figure 3-7c and Figure 3-9), while the control cell showed rapid increasing resistances (Figure 3-10). This indicates the limited SEI accumulation in the cell.



Figure **3-9**: Impedance spectrum of a Li|protected SiMP cell after 100 cycles. An equivalent circuit is used as a fit model.



Figure **3-10**: Impedance evolution of a Li|unprotected SiMP cell along cycling. Rapidly increased interfacial resistances with cycle number were recorded.

We next examined the performance of full cells paired with NCM 523 cathodes in a conventional carbonate electrolyte. The cell incorporating a prelithiated SiMP anode and a predelithiated NCM 523 cathode had a capacity retention of 83.4% in 200 cycles (Figure 3-7d), which is in stark contrast to the severe capacity fading of the control cell. A full cell without any pretreatment presented a capacity retention of 77.0% in 160 cycles (Figure 3-11). Moreover, at an elevated temperature (45 °C), where SEI turns more compositional unstable²⁴, the use of semi-immobilized SEI also enabled markedly extended lifespan of the SiMP|NCM 523 cell (Figure 3-12). This is attributed to the high thermodynamic stability of the pyrrolidinium-based components in the semi-immobilized SEI. A major concern of this approach is the potentially lowered ionic conductivity of semi-immobilized SEI. Encouragingly, we found no noticeable electrode



Figure **3-11**: Cycling performance of a SiMP|NCM 523 cell without any pretreatment. The cell was assembled using a protected SiMP anode (fresh) and an NCM 523 cathode (fresh).



Figure **3-12**: Cycling performance of SiMP|NCM 523 cells cycled at an elevated temperature of 45 °C.

polarization based on the voltage profiles of the SiMP|NCM 523 cell with the use of the semiimmobilized SEI (Figure 3-7e). Meanwhile, SiMP anodes with semi-immobilized and electrolytederived SEIs had comparable rate performances (Figure 3-7f). It is also noted that to use PYR₁₃FSI as additives shows very limited improvements on the cell performance of SiMP anodes (Figure 3-13). Together, these experimental results verify that the use of semi-immobilized SEI can effectively improve the electrochemical performance of SiMP anodes.


Figure 3-13: Cycling performance of SiMP anodes with $PYR_{13}FSI$ as additives in Li|SiMP (a) and SiMP|NCM 523 (b) cells.

We verified the participation of covalently bonded PYR₁₃FSI in the SEI formation by cyclic voltammetry (CV) and ¹⁹F nuclear magnetic resonance (NMR) experiments. In the CV curves, decomposition peaks of both electrolyte and FSI anions were recorded, respectively. As shown in Figure 3-14a, the peak corresponding to the decomposition of the electrolyte was recorded at 1.0 to 0.6 V. In contrast, for the SiMP with SEI precursor, a peak at 1.3 to 1.1 V was found, which was assigned to the decomposition of FSI anion at the Si surface (Figure 3-14b). These results indicate that a different electrochemistry occurred during the formation of semi-immobilized SEI. In the ¹⁹F NMR spectra of the electrolytes before and after cycling, Signals belong to PF₆ anions were found at -71.8 and -73.3 ppm in the spectra of the electrolyte before cycling (Figure 3-15a). After battery cycling (Figure 3-15b), a small amount of PF₆-derived species was observed at -70.3 and -81.0 ppm. No FSI anion (~52 ppm) or its decomposed species

(soluble) can be founded in the electrolytes, which indicates the participation in the semiimmobilized SEI formation of the FSI anions²⁵.



Figure **3-14**: CV curves of Li|SiMP cells with (a) and without (b) semi-immobilized SEI. Different SEI formation processes were observed from the curves of raw SiMP anode and protected SiMP anode. The scan rate was 2 mV s⁻¹.



Figure 3-15: ¹⁹F NMR spectra of the 1 M LiPF₆ in EC/EMC/VC (3:7:1) electrolyte after 50 cycles. A protected SiMP anode was used for cycling. No FSI anion or its decomposed species can be founded in the electrolyte.

To investigate the chemical composition of SEI, we conducted depth-profiling and highresolution XPS studies on the surface of delithiated SiMP electrodes with semi-immobilized and electrolyte-derived SEIs, respectively. XPS depth profiling was used to examine the chemical evolution of active Si and covalent bonding of immobilized pyrrolidinium-based SEI components. XPS experiments were conducted on a PHI VersaProbe II scanning XPS microprobe. An atmosphere-controlled transfer vessel was employed to load the samples into the



Figure 3-16: Chemical composition of the semi-immobilized SEI of delithiated SiMP electrodes. (a and b) XPS depth profiling of Si 2p and N 1s of SiMP electrodes with semi-immobilized SEI (a) and electrolyte-derived SEI (b). Curves from top to bottom in (a) and (b) represent the spectra acquired after sputtering for 0, 50, 100, 150, 200, 250, and 300 s and for 600, 650, 700, 750, 800, 850, and 900 s, respectively. The sputtering rate is ~10 nm min⁻¹. (c and d) High-resolution XPS C 1s, Li 1s, F 1s, and N 1s spectra of SiMP electrodes with semi-immobilized SEI (c) and electrolyte-derived SEI (d). The spectra were acquired after sputtering after 200 s, corresponding to the asterisked curves in (a) and (b), respectively. The electrodes were cycled after 30 cycles.

XPS instrument chambers without any exposure to the ambient air. A 20 eV Argon ion beam and a scan area of $10x10 \ \mu\text{m}^2$ were used for XPS depth profiling tests. The spectra were collected with a time interval of 30 s. The sputtering rate of ~10 nm min⁻¹ was calculated based on SiO₂. Figure 3-16a depicts the depth-profiling spectra of a SiMP electrode with semi-immobilized SEI. No Si signals were found in the top two Si 2p spectra since XPS detecting depth is ~10 nm, and the inner part of SEI closed to the Si surface had not been reached. Meanwhile, N signals were also absent in the N 1s spectra, implying that the decomposed products of PYR₁₃FSI are not in the outer part of semi-immobilized SEI. Upon sputtering, Si-Si (peaks at ~99 eV in the Si 2p spectra), Li_xSiO_y (peaks at~102 eV in the Si 2p spectra)¹⁶, and SiO₂/lithiated SiO₂ (peaks at ~104 eV in the Si 2p spectra) started to be seen in the third to seventh curves. Correspondingly, C-N (peaks at ~403 eV in the N 1s spectra), belonging to pyrrolidinium-based species, and -NSO_xF (peaks at ~400 eV in the N 1s spectra) from FSI anion decomposition were detected in the meantime. We also conducted the same experiment on a cycled raw SiMP electrode with PYR₁₃FSI additives as a control. The N signals were found throughout the depth-profiling N 1s spectra (Figure 3-17). FSI anions were detected in the electrolyte by ¹⁹F NMR as well (Figure 3-18). The result of this control experiment indicates that the covalent bonding allows the pyrrolidinium-based species to partially occupy the SiMP surface during cycling, which confirms our proposed hypothesis of the immobilized and non-consumable SEI components. In addition, when performing depth profiling on a SiMP electrode with electrolyte-derived SEI (Figure 3-16b), it took 700 s to see Si signals, while it only took 20 s for that with semi-immobilized SEI. This implies the formation of a



Figure 3-17: XPS depth profiling of Si 2p and N 1s of a SiMP anode cycled in a carbonate electrolyte containing $PYR_{13}FSI$ as additives after 50 cycles. Curves from top to bottom represent the spectra acquired after sputtering for 0, 100, 200, and 300 s. The sputtering rate is 10 nm min⁻¹.



Figure **3-18**: ¹⁹F NMR spectra of the 1 M LiPF₆ in EC/EMC/VC (3:7:1) electrolyte with 5% PYR₁₃FSI as additives after 50 cycles. An unprotected SiMP anode was used for cycling.

thicker SEI and accumulation of sacrificed SEI in the control cell. Moreover, the ratio of Li_xSiO_y in the entire Si bonds in the Si 2p spectra of semi-immobilized SEI is lower than that of electrolyte-derived SEI, implying an effective suppression of active Si loss by semi-immobilized SEI.

To probe the chemical composition of semi-immobilized SEI, we conducted highresolution XPS analysis on the sputtered SiMP electrode. In the semi-immobilized SEI (Figure 3-16c), both electrolyte-derived and PYR₁₃FSI-derived SEI components were detected. Detailed peak assignments are as follows. C=O from vinylene carbonate (the peak at 290.6 eV in the C 1s spectrum), Li-CO₂- (peaks at 288.5 eV in the C 1s spectrum and 54.2 eV in the Li 1s spectrum), C-O (overlapped with C-N) (the peak at 286.2 eV in the C 1s spectrum), C-C (the peak at 284.6 eV in the C 1s spectrum) are assigned to electrolyte-derived SEI components. C-N from pyrrolidinium-based species (peaks at 286.2 eV in the C 1s spectrum and 402.8 eV in the N 1s spectrum), -NSO_xF (peaks at 399.8 eV in the N 1s spectrum, 169.9 and 168.7 eV in the S 2p spectrum, and 687.6 eV in the F 1s spectrum), and C-Si (peaks at 283.2 eV in the C 1s spectrum and 100.3 eV in the Si 2p spectrum) are attributed to the decomposition products of the covalently bonded PYR₁₃FSI. Both electrolyte and PYR₁₃FSI produced LiF (peaks at 55.7 eV in the Li 1s spectrum and 684.6 eV in the F spectrum) in the SEI. Interestingly, the concentrations of $Li_xPO_yF_z$ (peaks at 52.8 eV in the Li spectrum, 170.0 and 134.2 eV in the P 2p spectrum, and 687.0 eV in the F spectrum)²⁶ and Li-CO₂- are higher than that of LiF in the electrolyte-derived SEI (Figure 3-16d), while LiF and -NSO_xF are dominant in the semi-immobilized SEI. This could be a key reason for the insufficient passivation of electrolyte-derived SEI. Collectively, the semi-immobilized SEI mainly consists of pyrrolidinium-based species, LiF, -NSO_xF, Li carbonates, and polycarbonates. To further demonstrate the immobilization of the covalently bonded SEI components, we monitored the SEI composition of a lithiated SiMP electrode (Figure 3-19). The pyrrolidinium-based species, LiF, and -NSO_xF were found as well, indicating the good stability of the immobilized SEI components.



Figure **3-19**: High-resolution C 1s, S 2p, N 1s, and Si 2p XPS spectra of semi-immobilized SEI of a sputtered SiMP anode at the lithiated status after 50 cycles.

We next probed the morphology of SiMP electrodes with semi-immobilized SEI after 30 cycles using TEM and SEM techniques. TEM and energy-filtered TEM images were recorded on a Tecnai G2 20 XTWIN with a LaB6 source. TEM samples of SiMP were prepared on an FEI Helios Nanolab 660 Dual Beam focused ion beam (FIB) using an "*in situ* lift-out" technique. A thin slice of SiMP was prepared using an ion beam voltage of 30 kV, lifted out from the electrode, and loaded to a TEM grid. The sample was further thinned using at gradually lowered ion beams until 2 kV. The final thickness was ~200 nm without any noticeable damage on the



Figure **3-20**: Morphological observation on SiMP electrodes with semi-immobilized SEI. (a-d) A TEM image (a) and corresponding energy filtered-TEM images (b-d) of a SiMP after 30 cycles. N was used to probe the presence of immobilized SEI components at the interface. (e-g) SEM images of SiMP electrodes after 0, 50, and 100 cycles. The SiMPs sizes were retained, indicating an effective surface passivation and protection of active Si by semi-immobilized SEI.

particle. SEM samples after different cycles were taken from the same piece of SiMP electrode.

Figure 3-20a-d displays the TEM and corresponding energy-filtered TEM images of a SiMP with

semi-immobilized SEI. The SiMP surface is covered with a layer containing uniformly

distributed Li elements, which was assigned to the semi-immobilized SEI layer. This layer is

closely contacted with SiMP and has a thickness of merely ~80 nm, implying its good surface

passivation and durability. N element, which is a signature feature of the components derived

from PYR₁₃FSI, was mainly found in the inner part of the SEI layer, indicating the presence of

immobilized pyrrolidinium-based components. These findings are consistent with the experiment

results from XPS depth profiling. Furthermore, we captured SEM images of SiMP electrodes after 0, 50, and 100 cycles to investigate the size changes of the SiMPs. The cycled SiMPs with semi-immobilized SEI exhibited retained particle sizes of 1-5 μ m, compared to the fresh SiMPs (Figure 3-20e-g). Contrastingly, the size of most SiMPs with electrolyte-derived SEI was rapidly decreased below 1 μ m (Figure 3-21), indicating serious consumption of active Si. Besides, at the electrode level, cracks on the cycled SiMP electrodes with semi-immobilized SEI were also



Figure **3-21**: SEM images of the raw SiMP electrode after 0, 20, and 50 cycles. The size of the SiMPs was remarkably reduced due to the loss of active Si.



Figure **3-22**: Top-view SEM images of the raw (a and b) and protected (c and d) SiMP electrodes after 20 cycles.

markedly reduced (Figure 3-22). All these results demonstrate that the use of semi-immobilized SEI can stabilize the interface, leading to the improved integrity of SiMP electrodes.

To testify the potential application of semi-immobilized SEI in different Si anode systems, we prepared micro-sized porous Si (porous Si)²⁷ and Si nanoparticle (SiNP) anodes with the semi-immobilized SEI. The same procedure was followed to prepare the materials and electrodes. These anodes incorporating semi-immobilized SEI showed remarkably enhanced cycling lives in Li|Si half cells, compared to those of control cells with electrolyte-derived SEI (Figure 3-23a,b). Moreover, the porous Si|NCM 523 cell presented a CR of 77.5% in 300 cycles (Figure 3-23c), and the SiNP|NCM 523 cell had a CR of 72.6% in 200 cycles (Figure 3-23d). These results imply a universal application of semi-immobilized SEI for different Si materials.



Figure **3-23**: The application of semi-immobilized SEI in other Si anodes. (a and b) The cycling performances of Li|Si half cells incorporating micro-sized porous Si (porous Si) (a) and Si nanoparticle (SiNP) anodes (b), respectively. (c and d) The cycling performances of Si|NCM 523 full cells incorporating porous Si (c) and SiNP anodes (d), respectively. The use of semi-immobilized SEI effectively improved the interfacial stability and cycling performance of porous Si and SiNP anodes.

3.4 Conclusions

The design of semi-immobilized SEI is proposed as a novel concept to stabilize the highly dynamic interface of micro-sized Si anode materials. This design aims to not only reduce SEI sacrifice by bonding electrochemically stable pyrrolidinium-based compounds at the Si surface but also enhance SEI passivation by introducing LiF and -NSO_xF as SEI components. These features are distinguished from conventional methods, which mainly focus on improving the volume-change tolerance of SEI. Compositional and morphological characterizations verified the good stability of immobilized SEI components and effective prevention of active Si loss. Dramatically increased cycling performances of SiMP anodes were achieved.

It is noteworthy that this interfacial approach is not able to solve all the issues of Si anode technology since it focuses on the interface. Specifically, when the loading of Si is high (above 1 mg), the electrode has huge volume changes at the electrode level, causing serious pulverization and crack issues. Besides, the consumption of Si and Li ions in the initial SEI formation leads to a low first cycle CE (below 92%), which decreases the energy density of full cells in practical application²⁸. So we believe that to combine approaches to addressing interfacial stability (e.g. semi-immobilized SEI), poor electrode integrity (e.g., elastic binder and structured Si), and low first cycle CE (e.g., prelithiation of Si anode) problems could be an ultimate solution to Si anode technology.

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Chapter 4

Interfacial Chemistry Regulation via a Skin-Grafting Strategy Enables High-Performance Lithium-Metal Anodes

4.1 Introduction

Lithium (Li) metal is considered to be the ultimate anode material, owing to its high theoretical capacity (3860 mAh g⁻¹), low electrochemical potential (-3.04 V vs. the standard hydrogen electrode), low density (0.59 g cm⁻³), and irreplaceable role in Li-sulfur and Li-air battery systems.¹⁻³ Unfortunately, metallic Li is very reactive with most liquid organic electrolytes, especially the carbonate-based electrolytes that are compatible with current 4-V Liion cathodes technology.^{4,5} The solid-electrolyte interphase (SEI) of Li metal anodes with carbonate-based electrolytes is unstable and creates an unfavorable environment for Li deposition/dissolution.^{6,7} As a result, Li metal anodes suffer from dendritic/mossy Li growth, huge interfacial fluctuations,^{8,9} and severe electrolyte consumption by SEI formation¹⁰ during cycling (Figure 4-1a). These interfacial issues are mainly responsible for the poor electrochemical performance of Li-metal batteries including their low Coulombic efficiency (CE), short cycle life, and severe polarization of charging/discharging potentials. Despite much progress in addressing the problem of anode morphology changes by designing structured Li metal anodes¹¹⁻¹⁷ and using mechanically robust coating layers on the Li metal surface,¹⁸⁻²⁵ the control of Li interfacial chemistry is still pivotal for enabling higher performance Li-metal anodes. Currently, most efforts to enhance the interfacial stability have focused on engineering the liquid electrolyte, including ether-based electrolytes,¹⁰ ionic liquid electrolytes,^{26,27} superconcentrated electrolytes,²⁸⁻³⁰ and additives.³¹⁻³⁷ However, carbonate-based electrolytes, which exhibit excellent compatibility with current 4-V cathodes, are still plagued by interfacial reactions at the Li metal anode.

We report here a grafted-skin strategy that involves coating a chemically and electrochemically active polymer onto the Li metal surface in order to regulate the SEI structure and the Li deposition/dissolution behavior. We reasoned that a stiff polymer with a high volume fraction of cyclic ether groups, which have a strong affinity for Li, would compete effectively with monomeric cyclic carbonates from liquid electrolyte for Li metal surface sites. Li metal deposits/dissolves in a dendrite-free manner under this polymeric skin, protecting the electrode from over-reaction with the liquid electrolyte (Figure 4-1b). Li metal anodes with the grafted skin show significantly improved CE and stability over many Li deposition/dissolution cycles. Limetal batteries employing LiFePO₄ (LFP) and LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM 523) cathodes both show dramatically enhanced cycling performance in a carbonate electrolyte compared to batteries without the polymeric grafted skin.





Figure 4-1c illustrates the structure of the polymer, poly((N-2,2-dimethyl-1,3-dioxolane-

4-methyl)-5-norbornene-exo-2,3-dicarboximide). The cyclic ether group (pink), has high affinity

for the Li metal surface, reductively adsorbing and competing for surface sites with the carbonate-based electrolyte components in the SEI. This results in a more uniform SEI with improved density and flexibility. The polycyclic main chain imparts stiffness modulating the morphology of Li deposition^{38,39} and enabling lasting protection of the Li metal surface against over-reaction with the carbonate electrolyte.

4.2 Materials and Methods

The skin polymer was synthesized via ring-opening metathesis polymerization (Figure 4-2). *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (1.64 g, 10 mmol), 2,2-dimethyl-1,3dioxolane-4-methanamine (1.26 g, 12 mmol), and trimethylamine (0.1 g, 1 mmol) were dissolved in the toluene and then refluxed for 12 h. The reaction-generated H₂O was continuously removed during heating. The product was purified by the column chromatography. The ring open metathesis polymerization (ROMP) reaction was conducted in a nitrogen filled glovebox. Compound 1 (2.77 g, 10 mmol) and Grubbs' catalyst (II) (0.034 g, 0.04 mmol) were dissolved in the anhydrous dimethylformamide (DMF) and the flask was heated at 55 °C for 12 h. After that, the solution was added into the diethyl ether and the precipitate was washed by the diethyl ether 6 times and dried at 60 °C in a vacuum oven for 12 h.

The synthesis was confirmed by proton nuclear magnetic resonance spectroscopy (¹H NMR), high-resolution X-ray photoelectron spectroscopy (XPS), and gel permeation chromatography (GPC). Figures 4-3 shows the NMR spectra of compound 1 and 2. The bottom spectra of (*N*-2,2-dimethyl-1,3-dioxolane-4-methyl)-5-norbornene-*exo*-2,3-dicarboximide (compound 1) presents peaks at 6.28 ppm, attributed to the -CH=CH- in compound 1, was



Figure 4-2: Synthetic route of the grafted skin (compound 2) via a ring open metathesis polymerization method.



Figure 4-3: ¹H NMR spectra of compound 1 and 2.

observed. After polymerization, new peaks appeared at 5.36-5.80 ppm of the spectra of compound **2**, corresponding to the -CH=CH- in compound **2**, verified the successful polymerization. The molecular weight (Mw) of the skin polymer based on GPC calculation is around 10,000 g/mol with a polydispersity index (PDI) of 2.1. Figure 4-4 presents the high-resolution XPS spectra of compound **2**. The peaks at 532.4 and 532.0 eV are attributed to C=O



Figure 4-4: High-resolution O 2p, N 1s, and C 1s XPS spectra of compound 2.

and C-O respectively in the O 2p spectrum, peaks at 400.0 eV is corresponding to C-N in the N 1s spectra, and peaks at 288.2, 286.0, and 284.6 eV are assigned to C=O, C-O/C-N, and C-C/C-H respectively in the C 1s spectra. Also, the ratios of C=O: C-O and C-N to C-O/C=O are 1:1 and 1:4 respectively according to the areas of peaks, confirming the structure of the compound **2**.

In addition, the skin polymer, which has good compatibility with carbonate electrolytes, is not soluble in or reactive with the electrolyte. We used ¹H, ¹³C, ¹⁹F, and ⁷Li NMR to examine



Figure 4-5: ¹H NMR spectra of the skin polymer of before (a) and after (b) treatment with 1M LiPF₆ in the EC/EMC/FEC electrolyte.



Figure 4-6: ¹H NMR spectra (a, b), ¹³C NMR spectra (c, d), ¹⁹F NMR spectra (e, f), and ⁷Li NMR spectra (g, h) of 1M LiPF₆ in EC/EMC/FEC electrolyte before and after treatment with the skin polymer.

the solubility and chemical stability of the skin polymer in the electrolyte (1M LiPF₆ in EC/EMC/FEC). A polymer film was immersed in the electrolyte for 72 h in an argon-filled

glovebox. The insoluble polymer film was then washed with EMC solvent multiple times and was dried in a vacuum chamber. Proton nuclear magnetic resonance (¹H NMR) testing was conducted on a Bruker DRX-400 instrument and calibrated by using residual solvent peaks as the internal reference. ⁷Li NMR spectra were obtained on a Bruker AV-3-HD-500 instrument without an internal reference. We studied the H¹NMR spectra of the polymer, and obtained exactly the same spectra as the control sample that was not treated with the electrolyte (Figures 4-5). This result demonstrates that the polymer is chemically stable in the electrolyte. In addition, the electrolyte solution residue was analyzed by ¹H, ¹³C, ¹⁹F, and ⁷Li NMR (Figures 4-6). Compared to the spectra of fresh electrolyte, no new peaks appeared in the ¹H NMR and ¹³C NMR spectra of the electrolyte after treatment with the skin polymer, indicating that organic solvents including EC, EMC, and FEC are stable in contact with the skin polymer. Spectra of the electrolyte after treatment with the skin polymer gave the same peaks in the ¹⁹F and ⁷Li spectra, demonstrating the chemical stability of the skin polymer with $LiPF_6$ and FEC. In addition, the typical peaks of the skin polymer at 5.36-5.80 ppm in the ¹H spectrum were absent in the spectrum of the electrolyte after treatment with the skin polymer, confirming that there was no detectable polymer dissolution in the electrolyte.

4.3 Results and Discussion

The cyclic ether group is designed to be chemically reactive with Li metal, enabling the polymer to be grafted to Li and to act as a component of the SEI after electrochemical activation. After reacting the polymer with metallic Li, the broad peak from -0.3 to -0.9 ppm in the ⁷Li NMR spectrum (Figure 4-7a) and the peak at 53.6 eV in the high-resolution XPS spectrum (Figure 4-8) can be assigned to the R-O-Li bond, indicating ring opening of cyclic ether groups. Figure 4-7b displays the cyclic voltammogram of the polymer on a Cu electrode in the carbonate electrolyte.

To perform this experiment, Cu foil was coated with the skin polymer at a thickness of 0.2 μ m and employed as the working electrode using the carbonate electrolyte. For cyclic voltammetry of the cyclic ether group, DMDOL, bare Cu was used as the working electrode and 1 M LiPF₆ in



Figure 4-7: (a) ⁷Li NMR spectra of the polymer before/after metallic Li treatment. (b) Cyclic voltammetry of the polymer on a Cu electrode in the carbonate electrolyte.



Figure 4-8: High-resolution Li 1s XPS spectra of the skin before (bottom) and after (top) the metallic Li treatment.

DMDOL was used as the electrolyte. The current was 10 mV/s and the electrolyte area was about 1 cm². When no polymer was applied to the working electrode, an SEI formation peak was observe

d from 0.2 to -0.05 V vs. Li⁺/Li. When the polymer was added, SEI formation shifted by ~0.14 V in the positive direction, indicating that a chemically different SEI layer forms prior to deposition of the carbonate-based electrolyte derived SEI. This is consistent with our hypothesis that the polymer was deposited in the new SEI layer. The affinity of the cyclic ether group (2,2-dimethyl-1,3-dioxolane, DMDOL) for metallic Li was also investigated, and similar results were obtained. Figure 4-9a presents the ⁷Li NMR spectra of fresh DMDOL and DMDOL after Li treatment. A peak appeared at -0.7 ppm was assigned to R-O-Li bond. The peak of skin polymer after Li treatment is broaden and shifted, since the -O-Li was bonded on a polymer chain. Figure 4-9b shows the high-resolution Li 1s XPS spectra of the Li metal surface after being immersed in



Figure 4-9: (a) ⁷Li NMR spectra of the cyclic ether group (DMDOL) before (grey line) and after (blue line) the metallic Li treatment. The spectra of skin after the metallic Li treatment (pink line) is displayed as well for comparison. (b) High-resolution Li 1s XPS spectra of Li metal surface after treating with DMDOL.



Figure **4-10**: Cyclic voltammetry analysis of the DMDOL in the carbonate electrolyte using a Cu electrode as working electrode. The DMDOL electrochemically decomposes at a low potential.

the DMDOL. The peak at 53.6 eV is corresponding to the Li-O- bond, confirming the reaction between the cyclic ether group and metallic Li. Figure 4-10 displays the cyclic voltammetry curve of 1 M LiPF₆ in DMDOL electrolyte, which having the anodic decomposition from 0.5 to 0.2 V.

The Li deposition/dissolution behaviors of the Li metal anode with and without the grafted skin were compared in scanning electron microscope (SEM) images. The grafted skin forms a uniform coating on the Li metal anode surface, owing to its strong affinity for metallic Li (Figure 4-11). The coating thickness was optimized by measurement of the Li deposition overpotential (Figure 4-12) and was found to be 2.2 µm from SEM images (Figure 4-13).



Figure 4-11: Top- and side-view SEM images of Li metal coated with the grafted skin before cycling. The grafted skin uniformly covers the Li metal surface and closely contacts with the Li metal surface, indicating a good affinity.



Figure 4-12: Thickness optimization of the grafted skin on Li metal anode by measurement of the Li deposition overpotential.



Figure 4-13: Cross-sectional SEM images of the grafted skin polymer coated on a silicon (100) wafer.

The bare Li metal electrode displays a typical dendritic and loose morphology after 30 cycles (Figure 4-14a,b) in the carbonate electrolyte. In contrast, the Li metal anode with the grafted skin presents a flat surface, which is a typical polymer coated morphology,^{40,41} and no dendritic or mossy Li can be observed after 30 cycles (Figure 4-14c,d), suggesting that Li deposition occurs underneath the skin. We note that the polymer skin is not very dense from a top-view of the surface, thus allowing an electrolyte permeation and participation in the SEI formation.



Figure 4-14: SEM images of (a) fresh bare Li metal, (d) fresh Li metal with the grafted skin, (b, c) bare Li metal, and (e, f) Li metal with grafted skin after 30 cycles.

To investigate the SEI structure of Li metal with and without the grafted skin, we conducted XPS analyses on Li metal anode surfaces after 30 cycles in the carbonate electrolyte. Figure 4-15a-d shows high-resolution F 1s, N 1s, C 1s and Li 1s XPS spectra of the SEI of the bare Li metal anode, which represents typical components derived from a carbonate-based electrolyte.⁴² The characteristic peaks of Li carbonate salts appear at 289.0 eV in the C1s spectra, 55.1 eV in the Li 1s spectrum and 686.2 eV in the F 1s spectrum, corresponding to RO-CO₂-, LiCO₂OR, and Li_xPO_yF_z respectively. The peaks at 686.4 and 56.1 eV in the F 1s and Li 1s spectrum respectively are attributed to LiF, the peak at 688.6 eV in the F 1s spectrum corresponds to C-F, peaks at 286.3 and 284.6 eV in the C 1s spectrum are related to C-O and C-C/C-H respectively, and the peak at 53.2 eV in the Li 1s spectrum corresponds to Li-O. The N 1s signal is absent in this system. Interestingly, new peaks appeared in the spectra of the SEI of a Li metal anode with the polymeric grafted skin. As shown in Figure 4-15e-h, the peaks at 400.0 and 288.2 eV in the N 1s and C 1s spectra correspond to C-N and C=O, respectively, which are the



Figure 4-15: High-resolution XPS spectra of F 1s, N 1s, C 1s and Li 1s of (a-d) bare Li anode surface and (e-h) Li metal with grafted skin.

characteristic peaks of the polymer. This result verifies the presence of the polymeric grafted skin-derived components in the SEI. Meanwhile, the concentrations of C-O and C-N groups in the C 1s spectra and Li-O in the Li 1s spectra are much higher than those of the bare Li SEI, and very little $Li_xPO_yF_z$ or C-F was detected in the F 1s spectrum, indicating that the SEI is composed of a high concentration of ether-based species.^{6,7,43} There is relatively little of the components derived from the carbonate electrolyte in the new SEI layer.

XPS depth profiling was employed to investigate the different Li chemical environments from the top surface of the grafted skin to the Li surface underneath. As shown in Figure 4-16, the curves from top (light blue) to bottom (green) represent the spectra acquired after sputtering for 0, 30, 60, 90, 120, 150, 155, 160, 180, and 200 min. The top six curves show the same spectra as that of bulk skin polymer, indicating that the Li metal surface is well protected by a thick skin polymer, which acts as a buffer layer. Upon sputtering, the 7th and 8th curves (blue and pink) start to show the spectra of the SEI, in which the peaks of LiF (~ 56 eV), and Li carbonate salts (~ 289 eV) can be recognized. Meanwhile, the C-N peak at ~ 400 eV in the N 1s spectra demonstrates the presence of polymer components in the SEI. In the two curves at the bottom (yellow and green), C 1s and N 1s signals disappear and a metallic Li peak at ~ 53 eV appears, implying that the SEI layer has been removed and the deposited metallic Li underneath the SEI has been detected.

We next investigated the electrochemical performance of Li metal anodes with the polymeric grafted skin in the carbonate electrolyte. Figure 4-17a displays the cycling stability of symmetric Li metal cells with a capacity of 1.0 mAh/cm² at a current density of 0.5 mA/cm². The Li metal anode with the grafted skin has a stable deposition potential (~30 mV) for over 300 h, in dramatic contrast to bare Li metal with increasing overpotentials for Li deposition and dissolution beyond 100 cycles. Li deposition/dissolution on Cu foil with the polymer skin coating shows



Figure 4-17: (a) Voltage profiles of a symmetric Li cell over 300 h. (b) CEs of Li deposition/dissolution on a Cu electrode. (c, d) Cycling performance of Li-metal batteries using (c) LiFePO₄ and (e) NCM 523 cathodes.

excellent cycling stability and a high average CE of 98.3 % over 200 cycles at a capacity of 1.0 mAh/cm² and a current density of 0.5 mA/cm²; in contrast, a bare Cu exhibits a very poor CE and a short cycle life (Figure 4-17b). These improvements imply that both Li metal and the electrolyte are well protected by the grafted skin from excess consumption by the SEI "break and repair" process. Furthermore, a Li|LFP battery with a capacity of 2.0 mAh/cm² and a current density of 0.5 mA/cm² in the carbonate electrolyte delivers a capacity retention of 90.4 % after 400 cycles



Figure 4-18: Voltage profile of the Li|LFP cell after 1, 10, 50 and 100 cycles. This cell presents stable voltage plateaus along cycling, indicating a relative low resistance and stable SEI during cycling.



Figure 4-19: Voltage profile of the Li|NCM 523 cell after 1, 10, 50 and 100 cycles. This cell presents stable voltage plateaus along cycling, indicating a relative low resistance and stable SEI during cycling.

and stable charging/discharging voltage plateaus (Figures 4-17c, 4-18). Similar enhancement was achieved in a Li|NCM 523 cell with a capacity of 1.0 mAh/cm² and a current density of 0.3 mA/cm², with 90.0% capacity retention after 400 cycles and steady voltage plateaus (Figures 4-17d, 4-19). These results are in dramatic contrast to control batteries employing bare Li metal with LFP and NCM 523 cathodes, which give capacity retention of only 76.2% and 72.1% after 100 cycles, respectively (Figure 4-17c,d).

4.4 Conclusions

In conclusion, we report a new skin-grafting strategy, incorporating a chemically and electrochemically active polymer on the Li metal surface to regulate the SEI structure and Li deposition/dissolution behavior. An SEI containing a high concentration of cyclic ether groups and a durable and dendrite-free Li deposition/dissolution morphology were achieved. This strategy enables dramatically increased CE of the Li metal anode and long cycling lives of Li-metal batteries with 4-V Li-ion cathodes in a carbonate electrolyte. Moreover, this proof-of-concept study illustrates a new strategy for designing and optimizing the SEI structure of the Li

metal anode. Additional polymer skin candidates can be investigated to further stabilize the Li metal anode in liquid electrolytes.

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Chapter 5

Design and Architecture of a Stable Solid-Electrolyte Interphase for the Lithium Metal Battery Anode Using a Reactive Polymeric Composite

5.1 Introduction

As discussed in Chapter 4, Li metal has been viewed as the ultimate anode material. However, the Li metal anode suffers from an unstable solid-electrolyte interphase (SEI), which is incapable of maintaining a stable Li/electrolyte interface during Li electrodeposition cycles¹⁻⁵. The SEI provides ionic conductivity and electrical insulation, enabling Li-ion transport and protecting Li and the electrolyte from interfacial reactions. However, Li deposition induces huge interfacial fluctuations and surface morphology changes, resulting in a highly dynamic Li/electrolyte interface. The poor mechanical strength of the SEI results in a repeated breakdownrepair process, accompanied by continuous electrolyte consumption and SEI accumulation^{4,6}. The SEI progressively becomes structurally inhomogeneous⁷, promoting uneven Li deposition (Figure 5-1a). Together, these problems lead to low Coulombic efficiency (CE), short cycle life, and severe polarization of the Li metal anode. Although the development of three-dimensional Li hosts⁸⁻¹² and mechanically robust films^{13,14} can effectively prevent Li dendrite growth, the stability of Li deposition remains plagued by the unstable interface, and this limitation has become the key obstacle of the technology.

Researchers have for decades approached this problem in three ways. A routinely adopted strategy is to replace the SEI derived from the conventional electrolyte by *ex-situ* fabricated artificial layers such as Li salts¹⁵⁻¹⁸, Li-alloys¹⁹, and polymers²⁰⁻²². While they inhibit the reaction of the electrolyte with Li, most artificial SEIs are composed of relatively simple chemical components, thus lacking basic SEI properties such as adequate ionic conductivity and flexibility. Additionally, once damaged during cycling, layers fabricated *ex-situ* cannot be

repaired, leading to poor interfacial stability. Another solution is to develop new electrolytes that can generate chemically different SEIs with improved stability. For example, concentrated electrolytes^{23,24} and ionic liquids^{25,26} form highly inorganic SEIs with good surface passivation. However, these alternative electrolytes show poor compatibility with 4-V Li-ion battery cathodes and have low ionic conductivity^{6,27}. A compromise method is to use sacrificial additives²⁷⁻³⁴ with conventional electrolytes, which can retain the excellent compatibility and ionic conductivity of the electrolyte and partially alter SEI structure to enhance flexibility and passivation. The enhancement is unfortunately insufficient because of the electrolyte-ruled formation mechanism of the SEI. This mechanism is associated with the many competitive reactions of different electrolyte components. All the products of these reactions deposit on the Li surface in a spontaneous and inhomogeneous manner^{1,35}, leading to poorly controlled composition and distribution of SEI components derived from the additive-containing electrolyte.

Despite efforts made so far, the SEI of Li metal anodes lacks adequate stability for stable Li deposition. It is clear that the ideal SEI should possess several properties simultaneously, including excellent passivation, homogeneity, ionic conductivity, electrical insulation, and mechanical strength. This calls for an approach that can regulate the properties of the SEI by controlling its chemical composition and nanostructure on the nanometer length scale. To this end, we report here the bottom-up design and architecture of a polymeric nanocomposite SEI This involves the use of a reactive polymeric composite (RPC) as an SEI precursor, which is a composite containing poly(vinyl sulfonyl fluoride-*ran*-2-vinyl-1,3-dioxolane) and graphene oxide (GO) nanosheets (Figure 5-1b). The polymer in the RPC can enable the formation of the SEI layer in two steps: (1) the polymer layer, attached to the Li surface, occupies surface sites by chemically reacting with Li; and (2) the attached polymer then electrochemically decomposes at the interface to form nanoscale SEI components. Two-dimensional GO nanosheets complete the



Figure 5-1: Illustration of the bottom-up design and architecture of a polymeric nanocomposite SEI layer using a reactive polymeric composite (RPC). (a) Conventional SEI formation via the electrochemical decomposition of liquid electrolyte. The formed SEI (purple layer) cannot stabilize the Li/electrolyte interface and results in dendritic/mossy Li growth. (b) Two-step formation of a polymeric nanocomposite SEI derived from an RPC (SEI precursor), which is a composite containing poly(vinyl sulfonyl fluoride-*ran*-2-vinyl-1,3-dioxolane) and graphene oxide (GO) nanosheets. In step I, the RPC layer passivates the Li surface by chemically reacting with Li. The products form a dense layer (red layer) that blocks electrolyte access to the surface. In step II, the attached polymer in the RPC generates *in situ* a polymer with side groups of -SO₂-Li and -C-O-Li and nanoparticles of Li salts (LiF and LiOR (R=hydrocarbons)). Two-dimensional GO nanosheets complete the nanocomposite SEI (green layer). The excess RPC reservoir can accommodate surface morphology changes of Li by generating SEI on the newly exposed Li surface.

polymeric nanocomposite SEI. In this process, the electrolyte decomposition is very limited since the surface sites are primarily occupied by the attached RPC. The SEI derived from the RPC consists primarily of organic polymeric Li salts (-SO₂-Li, and -C-O-Li bonded to the polymer backbone), nanoparticles of inorganic Li salts (LiF and LiOR (R=hydrocarbons)), and GO nanosheets. The organic-inorganic composite structure provides good density and passivation; the polymer structure and *in situ* SEI formation process ensures excellent homogeneity; various Li salts offer adequate ionic conductivity and electrical insulation; and the two-dimensional GO nanosheets confer mechanical strength. In addition, a surface layer of the unreacted polymer is preserved as a reservoir to continuously generate the SEI on newly exposed surfaces of Li. We characterized the chemical composition, nanostructure, and mechanical properties of the RPC- derived SEI by cryogenic transmission electron microscopy (cryo-TEM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM). RPC-stabilized Li electrodes exhibit dendrite-free Li deposition, enhanced CE, and low interfacial resistance. A 950-cycle life is realized for a 4-V Li-metal battery cell paired with a LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM 523) cathode. Furthermore, under lean electrolyte conditions, the use of the RPC-stabilized Li anodes also enables dramatically extended cycle lives of the full cells, compared to those of cells containing bare Li anodes.

5.2 Materials and Methods

We identified several guidelines for the design of the RPC and accordingly tested a series functional compounds as building blocks to systemically optimize the RPC structure. We used a polymer containing sulfonyl fluoride (SF) groups to chemically fluorinate the Li surface and produce LiF and -SO₂-Li at the interface (confirmed by XPS and NMR spectra, as described below). It is worth noting that a highly reactive group is crucial in the surface passivation step since insufficient reactivity will lead to a partial surface coverage³⁶. To produce organic Li salts as SEI components, we used electrochemically decomposable organic groups, including ethylene oxide (EO), dioxolane (DOL), cyclic ethylene carbonate (CEC), and vinyl carbonate (VC). These groups were connected to the polymer backbone by random copolymerization. After the *in situ* decomposition step, the products preserve the original homogeneity of the polymer. The polymer and GO nanosheets form an integrated composite structure owing to non-covalent interactions between them.

Figure 5-2 presents the synthesis of poly(vinyl sulfonyl fluoride-*ran*-2-vinyl-1,3dioxolane) (P(SF-DOL)) via a free radical copolymerization. Specifically, vinyl sulfonyl fluoride (1.1 g, 10 mmol), 2-vinyl-1,3-dioxolane (2.0 g, 20 mmol), and AIBN (31 mg, 0.19 mmol) were added into a glass vial, the mixture without any solvent was heated at 67 °C for 48 h. All the



Figure 5-2: Synthetic route of the P(SF-DOL) polymer. Sulfonyl fluoride and dioxolane building blocks were bulk-polymerized via a free radical polymerization method catalyzed by a 2,2'- azobis(2-methylpropionitrile) (AIBN) initiator.

procedures were performed in an argon-filled glovebox. The reaction mixture was dissolved in anhydrous dichloromethane (DCM), and the resulting solution was added into anhydrous hexane dropwise. The precipitate was washed with anhydrous hexane 6 times and dried in the vacuum chamber for use. Other functional group-containing polymers were prepared following the same procedure. The structure of P(SF-DOL) was identified by ¹H NMR (Figure 5-3) and Gel permeation chromatography (GPC) measurements. The bottom spectrum (blue) of 2-vinyl-1,3-dioxolane shows peaks at 5.85-5.68, 5.36-5.25, and 5.19-5.08 ppm, corresponding to the -CH=CH₂ bond. The middle spectrum (green) of vinylene sulfonyl fluoride presents peaks at 7.50-7.38 and 6.80-6.62 ppm, attributed to the C=C bond. After the reaction (pink), the peaks belong to C=C bonds weredisappeared, indicating the successful polymerization. The molecular weight (Mw) of P(SF-DOL) based on the GPC calculation is $12,000 \text{ g mol}^{-1}$ with a polydispersity index (PDI) of 1.12. PVSF polymer was synthesized using a vinylene sulforyl fluoride monomer. In the spectra of the PVSF polymer (Figure 5-4a), C-S (285.5 eV in the C 1s spectrum), C-C (284.6 eV in the C 1s spectrum), and -SO₂-F (531.9 eV in the O 2p spectrum, 169.4 and 170.6 eV in the S 2p spectrum, and 688.3 eV in the F 1s spectrum) bonds were identified. PEO polymer was synthesized using a tetraethylene glycol methyl vinyl ether monomer. In the high-resolution XPS spectra (Figure 5-4b), C-C (284.6 eV in the C 1s spectrum), C-O (286.2 eV in the C 1s spectrum and 532.3 eV in the O



Figure **5-3**: ¹H NMR spectra of the P(SF-DOL) polymer.

2p spectrum) were found. PVEC polymer was synthesized using a 4-vinyl-1,3-dioxolan-2-one monomer. In the high-resolution XPS spectra (Figure 5-4c), C-C (284.6 eV in the C 1s spectrum), C-O (286.4 eV in the C 1s spectrum and 533.4 eV in the O 2p spectrum) were detected. PVC polymer was synthesized using a vinylene carbonate monomer. In the high-resolution XPS spectra (Figure 5-4d), C-C (284.6 eV in the C 1s spectrum), C-O (287.6 eV in the C 1s spectrum and 534.3 eV in the O 2p spectrum) were observed. This result is consistent with the previous report. PVDOL polymer was synthesized using a 2-vinyl-1,3-dioxolane monomer. In the high-resolution XPS spectra (Figure 5-4e), C-C (284.6 eV in the C 1s spectrum), C-O (286.3 eV in the C 1s spectrum and 532.3 eV in the O 2p spectrum) were observed. P(SF-DOL)' polymer was synthesized using vinylene sulfonyl fluoride and 2-vinyl-1,3-dioxolane monomers with a molar ratio of 1:4. In the spectra of the P(SF-DOL)' polymer (Figure 5-5a), C-S/C-O (286.3 eV in the C 1s spectrum), C-C (284.6 eV in the C 1s spectrum), C-C


Figure **5-4**: High-resolution XPS spectra of single building block-containing polymers for the RPC design.

eV in the S 2p spectrum) bonds were identified. P(SF-DOL) polymer was synthesized using vinylene sulfonyl fluoride and 2-vinyl-1,3-dioxolane monomers with a molar ratio of 1:2. In the spectra of the P(SF-DOL) polymer (Figure 5-5b), C-S/C-O (286.3 eV in the C 1s spectrum), C-C

(284.6 eV in the C 1s spectrum), and -SO₂-F (688.3 eV in the F 1s spectrum and 169.4 and 170.6 eV in the S 2p spectrum) bonds were identified. P(SF-DOL)" polymer was synthesized using



Figure 5-5: High-resolution XPS spectra of multiple building blocks-containing polymers and polymeric composites for the RPC design.

vinylene sulfonyl fluoride and 2-vinyl-1,3-dioxolane monomers with a molar ratio of 4:1. In the spectra of the P(SF-DOL)" polymer (Figure 5-5c), C-S/C-O (286.3 eV in the C 1s spectrum), C-C (284.6 eV in the C 1s spectrum), and -SO₂-F (688.3 eV in the F 1s spectrum and 169.4 and 170.6 eV in the S 2p spectrum) bonds were identified. 289.6 286.3. P(SF-DOL)-GO composite

was prepared by adding 20% single-sheet GO into the P(SF-DOL) polymer solution. In the highresolution XPS spectra (Figure 5-5d), C-C (284.6 eV in the C 1s spectrum), C-O/C-S (286.3 eV in the C 1s spectrum), -CO₂- (289.6 eV in the C 1s spectrum), -SO₂-F (688.3 eV in the F 1s spectrum and 169.4 and 170.6 eV in the S 2p spectrum) were observed. P(SF-DOL)-GO' composite was prepared by adding 50% single-sheet GO into the P(SF-DOL) polymer solution. In the high-resolution XPS spectra (Figure 5-5e), C-C (284.6 eV in the C 1s spectrum), C-O/C-S (286.3 eV in the C 1s spectrum), -CO₂- (289.7 eV in the C 1s spectrum), -SO₂-F (688.3 eV in the F 1s spectrum and 169.4 and 170.6 eV in the S 2p spectrum) were observed.

Single-sheet GO (Figure 5-6) solution was prepared following a modified Hummer's method. Preoxidation was conducted to ensure complete exfoliation of graphite powder. The graphite power (3 g) was added to a mixture of concentrated H_2SO_4 (25 mL), $K_2S_2O_8$ (2.5 g) and P_2O_5 (2.5 g) at 80 °C. The mixture was kept at the same temperature for 6 hours. The resulting mixture was then carefully diluted with 100 mL distilled water, filtered and washed, followed by dried at 60 °C overnight. The pre-oxidized graphite powder was slowly added to cold (0 °C) concentrated H₂SO₄ (120 mL). KMnO₄ (12 g) was added afterward while the mixture temperature was maintained below 10 °C with an ice bath. The mixture was stirred at 35 °C for 4 hours. Distilled water (100 mL) was added and the mixture was stirred at 45 °C for 2 more hours. To terminate the reaction, distilled water (300 mL) and H₂O₂ (6 mL) were added within 15 minutes, resulting in a bright yellow solution. The mixture was filtered and washed with 1:10 HCl solution to remove additional ions. The GO solution was diluted and subjected to dialysis for a week. Exfoliated GO was achieved by diluting the GO solution to 1 mg mL⁻¹ and sonication for 15 minutes. The aqueous solvent of GO solution was replaced by dimethylformamide (DMF) by the following method: 90 mL DMF was added into 10 mL as prepared GO solution (1 mg mL⁻¹). The solution was sonicated and afterward concentrated to ~10 mL on a rotary evaporator. This process was repeated 6 times to remove the water solvent. Anhydrous sodium sulfate was added to the solution and filtered after

being immersed over 15 min. 90 mL anhydrous toluene was added afterward to the solution, and the solution was concentrated on a rotary evaporator. After repeating this process 6 times, the solution was concentrated to $\sim 2 \text{ mg mL}^{-1}$ on a rotary evaporator. Freshly synthesized P(SF-DOL) was added to GO sheets dispersed in anhydrous tetrahydrofuran (THF). The solution was sonicated at 60 °C for 4 h under an argon atmosphere. Li chips were washed with anhydrous hexane three times and dried in a vacuum chamber before use. The P(SF-DOL)-GO solution was coated onto the surface of Li, and the sample was dried in a vacuum chamber for 6 hours. This coating procedure was conducted in an argon-filled glovebox.



Figure 5-6: TEM image of as-prepared single-sheet graphene oxide.

5.3 Results and Discussion

We evaluated these building block-containing polymers by studying the average CE of Li plating and stripping underneath the polymer film in a Li|Cu cell. All the building block-containing polymers were coated onto Cu foils with a thickness of $\sim 2 \mu m$. We pre-plated 1.0 mAh cm⁻² Li on the Cu electrode with an areal capacity of 0.5 mAh cm⁻² and calculated the CE by measuring the capacity of stripped Li. Meanwhile, the Li deposition morphologies of polymer-coated Li electrodes in a symmetric Li cell were captured by SEM. A carbonate electrolyte (1 M



Figure 5-7: Bottom-up design of the reactive polymeric composite. (a-d) Evaluation of various building blocks for constructing the RPC. These building blocks were modified onto a polymer chain and evaluated via the average CE of Li plating and stripping underneath the polymer. Sulfonyl fluoride (SF) groups (a) were designed to react chemically with Li and generate nanoparticles of LiF. Electrochemically decomposable organic groups (b) were designed to generate organic Li salts. The dioxolane (DOL)-containing polymer provides the most enhanced CE among these organic building blocks. Combinations of SF and DOL groups in a polymer (c) at different molar ratios. The P(SF-DOL) (purple) exhibits the most improved CE. Combinations of P(SF-DOL) and GO nanosheets (d) at different weight ratios. The P(SF-DOL)-GO (8:2) composite (red) delivers the optimal Li deposition behavior and an average CE of 98.5% in 300 cycles and was used as the RPC for further studies. (e and f) Side- and top-view SEM images of the uncycled RPC-stabilized Li. The RPC layer is uniformly distributed on the Li surface.

lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC): ethyl methyl carbonate (EMC): fluoroethylene carbonate (FEC) (3:7:1, v/v/v)) was used. The SF-containing polymer (PVSF) enables extended cycling life (Figure 5-7a) and dendrite-free Li deposition morphology (Figure 5-8e). However, the CE is not stable, and some cracks were observed on the polymer-coated surface. Among the polymers tested, the EO-containing polymer (PEO) shows low CE and Li dendrite growth, whereas DOL, EC, and VC-containing polymers (PVDOL, PVEC, and PVC, respectively) led to increased CEs (Figure 5-7b) and flat surface morphologies with minor defects (Figure 5-8a-d). PVDOL provided the most enhanced performance. Thus, we combined SF and DOL groups into a random polymer, poly(vinyl sulfonyl fluoride-*ran*-2-vinyl-1,3-dioxolane).



Figure 5-8: Surface morphologies of the cycled Li with building block-containing polymers. All Li electrodes were cycled in 1 M LiPF₆ in EC: EMC: FEC (3:7:1, v/v/v) electrolyte for 10 cycles with the areal capacity of 1.0 mAh cm⁻².



Figure **5-9**: Characterization of the integrity of the RPC. (a) XRD patterns of the RPC, P(SF-DOL), and GO sheets. (b and c) TGA curves of the RPC and P(SF-DOL). (d and e) AFM indentation curves of the RPC and P(SF-DOL).

These polymers gave improved CEs (Figure 5-7c) and Li deposition morphologies (Figure 5-8fh), compared to those of single building block-containing polymers. The ratio of SF and DOL affects the properties of the polymer. With a 1:2 molar ratio of SF and DOL, the polymer, named P(SF-DOL), shows optimal CE and Li deposition morphology. By then adding 20 % GO nanosheets into P(SF-DOL), a uniform and integrated composite was formed, stabilized by the strong non-covalent interactions between P(SF-DOL) and GO (Figure 5-9). This composite displayed a layered morphology on the Li surface, captured by SEM images (Figure 5-7e,f). The average CE reached 98.5% in 300 cycles (Figure 5-7d), and a flat surface morphology was observed (Figure 5-8i). In contrast, excessive GO in the composites resulted in poor CE (Figure 5-7d) and surface morphology (Figure 5-8j). Based on these testing results, the P(SF-DOL)-GO composite is the optimal RPC structure and was used for further studies.

We investigated the chemical and electrochemical processes associated with the Li



Figure 5-10: Structure of the surface passivating layer formed in the two-step SEI formation. (a) Illustration of the surface passivating layer (red layer) at the interface, which is formed by the chemical reaction between P(SF-DOL) (yellow layer) and Li (grey layer). (b-d) High-resolution XPS spectra of the unreacted P(SF-DOL) reservoir (b) and delaminated interface (both the P(SF-DOL) (c) and Li (d) sides) after the reaction. LiF and a polymer with side groups of $-SO_2$ -Li and $-CHO_2(CH_2)_2$ -) were observed at the Li/P(SF-DOL) interface.



Figure 5-11: ⁷Li NMR spectrum of the products of the chemical reaction between P(SF-DOL) and Li.



Figure 5-12: High-resolution F 1s and Li 1s XPS spectra of the Li surface before and after the electrolyte dropping.

surface passivation and RPC decomposition steps. To study the chemical reaction occurring at the Li surface, we physically pressed a P(SF-DOL) film into a clean Li chip and ran high-resolution XPS on the delaminated interface (both the P(SF-DOL) and Li chip sides) after the reaction (Figure 5-10a). A clear change in the chemical structure at the interface was observed. On the P(SF-DOL) side (Figure 5-10c), -SO₂-Li (peaks at 168.3 and 169.5 in the S 2p spectrum and 55.6 eV in the Li 1s spectrum) was converted into -SO₂-F (169.4 and 170.6 eV in the S 2p spectrum and 688.3 in the F 1s spectrum). Compared with the spectra of pristine P(SF-DOL) (Figure 5-5b), no noticeable change in the C 1s spectrum was found, indicating retention of the polymer backbone. Meanwhile, LiF appeared on the Li side (Figure 5-10d), as evidenced by peaks at 684.8 in the F 1s spectrum and 57.6 eV in the Li 1s spectrum. The excess P(SF-DOL) reservoir

(Figure 5-10a) remains intact, as verified by the presence of the same peaks as in the spectra of pristine P(SF-DOL). We also conducted ⁷Li NMR experiments to monitor the bulk reaction between P(SF-DOL) and Li. A single peak with a chemical shift of -0.92 ppm was observed in the ⁷Li NMR spectrum of the reaction solution (Figure 5-11), which can be assigned to -SO₂-Li. Based on these results, we identified the formation of a surface passivating layer at the Li/RPC interface, composed of a polymer with -CHO₂(CH₂)₂-) and -SO₂-Li side groups, GO nanosheets, and LiF. To check the surface passivating property of this layer, we dropped carbonate electrolyte onto the coated Li surface for 24 h and compared changes in Li 1s and F 1s XPS spectra of the Li surface before and after the contact with the electrolyte. Encouragingly, no change in the peaks was observed, indicating effective Li coverage by the RPC layer (Figure 5-12).

The second step in SEI formation is the electrochemical decomposition of the RPC layer. Initial investigation of this process was carried out by cyclic voltammetry (CV) of Cu electrodes with and without a thin RPC coating in a carbonate electrolyte. The anodic peak related to the formation of the RPC-derived SEI was shifted by ~ 0.18 V in the positive direction relative to that found in the formation of the electrolyte-derived SEI. This indicates a different electrochemical



Figure **5-13**: Cyclic voltammetry test of Cu electrodes with and without the RPC coating. The RPC reductively decomposes irreversibly at low potentials. The decomposition peak shift between bare Cu (left curve in blue) and RPC-coated Cu (right curve in pink) in a carbonate electrolyte samples implies the formation of a chemically different SEI from the electrolyte-derived one.



Figure 5-14: Chemical composition of the SEI derived from the reactive polymeric composite. (a) Illustration of the cycled RPC-stabilized Li. The electrode surface is covered by an RPC reservoir layer (yellow layer), and the RPC-derived SEI (green layer) lies in between the reservoir and Li. Black lines represent the GO nanosheets. (b) Comparison of the elemental concentrations of the RPC-derived SEI and carbonate electrolyte-derived SEI. The RPC-derived SEI containing high concentrations of C and O is highly organic, compared to the electrolyte-derived SEI containing high concentrations of Li and F. (c and d) High-resolution XPS spectra of the RPC reservoir (c) and RPC-derived SEI (d) layers. The reservoir retains its chemical structure, and the SEI is composed primarily of a polymer integrating side groups of -SO₂-Li, -C-O-Li, and -SO₂-F, inorganic Li salts (LiF and LiOR), and GO nanosheets.

process occurs in on the Li surface in the presence of the RPC layer (Figure 5-13). To identify the chemical composition of the RPC-derived SEI, we performed high-resolution XPS, elemental concentration, and Fourier transform infrared (FT-IR) spectroscopy analyses on the cycled Li after 30 cycles. The top surface of the electrode is covered by the RPC reservoir, and the SEI resides in between this reservoir and Li, as schematically illustrated in Figure 5-14a. Figure 5-14c shows high-resolution XPS spectra of the reservoir. -SO₂-F groups (688.3, 169.4, and 170.6 eV in the F 1s and S 2p spectra, respectively), C-O-C/C-S bonds (286.2 eV in the C 1s spectrum), and - CO₂- groups from GO (289.8 eV in the C 1s spectrum) were observed. These peaks are consistent with those of the pristine RPC (Figure 5-5d), indicating the chemical structure of the reservoir is unaltered. As depicted in Figure 5-14a, to access the RPC-derived SEI, we electrochemically stripped off the Li underneath the SEI layer and probed the exposed bottom surface. A highly

polymeric and organic SEI was detected, the structure of which is distinct from the electrolytederived SEI (Figure 5-14d). The detailed peak interpretation is as follows: peaks at 688.5 and 684.5 eV in the F 1s spectrum are attributed to -SO₂-F and LiF, respectively; peaks at 289.9, 288.4, 285.9, and 284.6 eV in the C 1s spectrum belong to -CO₂- from GO, -CO₂-Li from reduced GO and the carbonate electrolyte, C-O and C-S bonds (overlapped) from reduced DOL and -SO₂groups, and C-C bonds from the polymer backbone, respectively; split peaks at 170.2 and 169.0 eV in the S 2p spectrum are assigned to overlapped -SO₂-F and -SO₂-Li groups; peaks at 57.8 eV in the Li 1s spectrum are assigned to Li-F/-O-Li bonds from reduced SF and DOL. Collectively, the RPC-derived SEI is composed of a polymer integrating several side groups of -SO₂-Li, -C-O-Li, and -SO₂-F, inorganic Li salts (LiF and LiOR), and GO nanosheets. We emphasize that the electrolyte produces only trace amounts of SEI components. Therefore, its influence on the chemical and physical properties of the SEI is negligible. Meanwhile, XPS elemental concentration analysis reveals that this SEI contains high concentrations of C (37.8%) and O (26.3%) (Figures 5-14b and 5-15). This is in dramatic contrast with the electrolyte-derived SEI, which consists mainly of Li carbonate salts, LiF, and Li_xPO_yF_z (Figure 5-16) and presents high concentrations of Li (37.3%) and F (33.6%) (Figures 5-14b and 5-15). A similar conclusion can



Figure 5-15: Elemental concentrations of S, F, O, Li, P, and C in the electrolyte-derived SEI and RPC-derived SEI.



Figure 5-16: High-resolution XPS spectra of the SEI derived from a carbonate electrolyte (1 M $LiPF_6$ in EC: EMC:FEC (3:7:1)).



Figure 5-17: FT-IR spectra of the cycled bare Li (black) and RPC-stabilized Li (red) anodes.

be reached from the FT-IR experimental results (Figure 5-17).

After identifying the unique highly polymeric composition of the RPC-derived SEI, we studied its morphology using SEM, cryo-TEM, and optical profilometry techniques. The cycled RPCstabilized Li has a flat surface morphology, as observed in the top- and side-view SEM images (Figure 5-18a,b). By mapping the elements based on the side-view SEM image, we identified a layer covering the top surface of Li, which contains C, F, and S, corresponding to the reservoir and SEI layers (Figure 5-19). The optical profilometry image of the RPC-stabilized Li depicts a defect-free surface with small height differences up to 0.8 μ m (Figure 5-18c). In contrast, the surface of cycled bare Li is very rough (Figure 5-18d,e) with height differences up to 7.2 µm (Figure 5-18f), correlating with dendritic Li. These characterization studies demonstrate improved interfacial stability at the electrode level. We next probed the nanostructure and chemical composition of the cycled RPC-stabilized Li using cryo-TEM. Figure 5-18g shows a cryo-TEM image of the interface. We observed a three-layer structure, and these three layers, displaying different contrast, can be recognized as the RPC reservoir, RPC-derived SEI, and Li (from the top to the bottom in Figure 5-18g), respectively. The SEI has a thickness of 50-80 nm and lies in between the reservoir and Li. To study the specific nanostructure of these three layers, we captured high-resolution images in the squared regions. In the Li layer (Figure 5-18h, the squared region in purple), we observed the $\{110\}$ Li plane with a lattice spacing of 0.25 nm, consistent with the electrochemical deposited Li^{37,38}. The lattice spacing was confirmed in the corresponding fast Fourier transform (FFT) image (Figure 5-20). In the RPC-derived SEI (Figure 5-18i, the squared region in orange), we saw an amorphous layer containing embedded nanocrystals. The lattice spacings of these nanocrystals are 0.20 and 0.23 nm, corresponding to the {200} and {111} LiF planes, respectively. The majority of the SEI is the amorphous species, which can be assigned to polymeric Li salts. Another RPC component, the GO nanosheets, show wavy morphologies in both the reservoir (Figure 5-21) and the SEI (Figure 5-22). It is worth noting that



Figure 5-18: Morphological and mechanical characterization of the cycled reactive polymeric composite-stabilized Li. (a and b) Top- and side-view SEM images of the cycled RPC-stabilized Li. (d and e) Top- and side-view SEM images of the cycled bare Li. (f) Optical profilometry image of the surface of the cycled RPC-stabilized Li. (d and e) Top- and side-view SEM images of the cycled bare Li. (f) Optical profilometry image of the surface of the cycled bare Li. The Li electrodes were cycled for 50 cycles with a Li plating/stripping amount of 1.0 mAh cm⁻². (g-i) TEM images of the interface of the RPC-stabilized Li. Three layers were found at the interface (g), which can be recognized as the RPC reservoir, RPC-derived SEI, and Li, respectively. In the Li region (h), the metallic Li lattice was observed and indicated by the red circles. In the RPC-derived SEI layer (i), we saw an amorphous layer containing embedded LiF nanocrystals (indicated by the orange circles). (j) STEM image of the interface of the RPC-stabilized Li. (k) Li K-edge spectra of the boxed regions in j. (l) EDS image based on j. The three-layer structure at the Li/RPC interface was confirmed. (m and n) Force-displacement plots of the SEIs derived from the electrolyte (m) and the RPC (n). The RPC-derived SEI is more viscoelastic, enabling good flexibility and stiffness against the surface morphology changes of Li during cycling.



Figure **5-19**: Elemental mapping of the RPC-derived SEI. (a-d) Elemental mapping images of C, F, and S based on a (top view). (e-h) Elemental mapping images of C, F, and S based on e (side view).

no components derived from electrolyte reduction, such as Li₂CO₃, were detected in the RPC-

derived SEI.

We further elucidated the chemical composition at the interface using electron energy

loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS). Figure 5-18j shows a



Figure 5-20: FFT images of the RPC-derived SEI (left) and Li (right) regions taken from the interface of the RPC-stabilized Li.



Figure **5-21**: The high-resolution TEM image of the RPC reservoir region taken from the interface of the RPC-stabilized Li.



Figure **5-22**: TEM and STEM images of the RPC-derived SEI regions taken from the interface of the RPC-stabilized Li.

scanning transmission electron microscopy (STEM) image of the cycled RPC-stabilized Li. We boxed a region containing the reservoir, SEI, and Li and analyzed the chemical composition pixel-by-pixel (Figure 5-18k). The Li K-edge spectrum taken from the bottom purple area shows a broad peak centered at 63 eV, corresponding to metallic Li. The peak shape in the orange area spectrum corresponds to LiF, indicating that this area belongs to the SEI. We observed a very low Li intensity in the green top region and thus identified it as the reservoir. The presence of the weak Li signal is probably caused by beam-induced diffusion of Li. In the EDS image based on



Figure 5-23: XPS depth profiling of the cycled RPC-stabilized Li.

STEM image (Figure 5-18j), we mapped C, F, and S (Figure 5-18l) and observed three different layers. The top layer containing S, F, and concentrated C is assigned to the reservoir. The middle layer showing S and concentrated F is identified as the SEI. The bottom layer shows very weak C, F, and S signals, which can be attributed to Li. XPS depth profiling further confirms the three-layer structure. As shown in Figure 5-23, the top three curves (purple, green, and blue lines) present the -SO₂-F signal (peaks at 688.3 eV in the F 1s spectrum) and show no Li signal, and thus can be assigned to the RPC reservoir. The middle two curves (pink and orange lines) present Li salt signals (peaks at 684.8 eV in the F 1s spectrum and 57.8 eV in the Li 1s spectrum), which correspond to the RPC-derived SEI. The bottom curve in grey contains the metallic Li signal (peaks at 53.2 eV in the Li 1s spectrum) and has no F signal, which can be attributed to metallic Li. Taken together, these data clearly show that the RPC-derived SEI is primarily composed of polymeric Li salts, GO nanosheets, and embedded nanoparticles of LiF and LiOR. As mentioned above, an ideal SEI should have the necessary mechanical properties to tolerate the Li surface morphology changes that occur in battery cycling. AFM indentation was used to compare the mechanical properties of the RPC-derived SEI with the electrolyte-derived SEI^{15,33}. The

electrolyte-derived SEI shows loading and unloading curves almost perfectly overlapping with little hysteresis (Figure 5-18m), and the calculated modulus is 820 MPa (Figure 5-24). This result implies that the electrolyte-derived SEI is both brittle and rigid. In contrast, a clear hysteresis between the loading and unloading curves and meniscus dragging during the tip snap-off were observed for RPC-stabilized Li (Figure 5-18n), and the calculated modulus was 714 MPa, implying good flexibility and stiffness. The elastic modulus of the RPC-derived SEI was



Figure 5-24: Fitting based on Oliver-Pharr and DMT contact models.

investigated from AFM indentation tests. The Oliver-Pharr model can be used when the surface energy is neglected; here, the stiffness is calculated from the unloading curve. The Poisson ratio of the surfaces was roughly estimated as 0.4, which can be found in some studies^{39,40}. Alternatively, the Derjaguin-Muller-Toporov (DMT) contact mechanical model can also be employed to determine the elastic modulus of surfaces taking into account surface energy. The DMT equation is derived as given below:

To simplify the fitting equation, the contact radius a and normal load F are expressed as the following non-dimensional relationship^{41,42}:

$$\frac{a}{a_0} = \left(1 - \frac{F}{F_{adh}}\right)^{\frac{1}{3}} \tag{1}$$

where a_0 is the contact radius at zero load, and F_{adh} is the "pull-off force" in the AFM forcedistance curve. The pull-off force is given by the DMT theory as:

$$F_{adh} = 2\pi\gamma R \tag{2}$$

where γ is the interfacial energy and R is the curvature radius of the contact asperity (AFM tip). The relationship between sample deformation *d* and normal load *F* (which is obtained from the force-distance curve) can be obtained by substituting equation (1) into:

$$d = \frac{a^2}{R} \tag{3}$$

yielding the following equation for fitting:

$$d - d_{contact} = \frac{a_0^2}{R} \left(1 - \frac{F}{F_{adh}}\right)^{\frac{2}{3}}$$
(4)

where $d_{contact}$ represents the apparent displacement at which the tip first contacts the surface⁴³. From the fitting parameters, the reduced elastic modulus can be calculated by:

$$E_r = \frac{3RF_{adh}}{4a_0^3} \tag{5}$$

In our design, GO nanosheets serve to strengthen the SEI layer mechanically. To verify this, we used the P(SF-DOL) as a control sample and analyzed the Li deposition and indentation behaviors. The cycled Li with P(SF-DOL) displays a dendrite-free surface morphology within 50 cycles. However, Li dendrites were found after 100 cycles (Figure 5-25). In addition, the P(SF-DOL) shows a reduced stiffness, indicated by the prolonged hysteresis and meniscus and lower



Figure 5-25: SEM images of the cycled Li with P(SF-DOL) after 50 cycles in a carbonate electrolyte.



Figure 5-26: AFM indentation curve of the P(SF-DOL)-derived SEI.

modulus (Figures 5-24 and 5-26). This comparison reveals that the addition of GO nanosheets into RPC gave good flexibility and high stiffness, which are normally mutually exclusive.

To evaluate the interfacial stability of the Li anode, we studied the Li deposition behavior in a symmetric Li|Li cell using a carbonate electrolyte. Practical capacity of 2.0 mAh cm⁻² and current density of 1.0 mA cm⁻² were applied. The RPC-stabilized Li shows stable voltage profiles over 800 h, whereas the deposition overpotential of bare Li increases upon cycling (Figure 5-27a). The charge-transfer resistance of the symmetric cell was measured by electrochemical impedance spectroscopy (EIS). RPC-stabilized Li displays stable resistance during cycling (Figure 5-27b), while that of the bare Li increases severely (Figure 5-27c). These performances were achieved by using an RPC layer with an optimal thickness of 3 μ m. A thicker layer (5 μ m) induces a high Li deposition overpotential, and a thinner one (1 μ m) leads to shorter cycle life (Figure 5-28). We next monitored the full-cell performance of Li-metal batteries paired with NCM 523 cathodes in a carbonate electrolyte (1 M LiPF₆ in EC: EMC: FEC (3:7:1) with 2% lithium bis(oxolato)borate (LiBOB)). The use of the RPC-stabilized Li anode enables significantly enhanced cycling stability of a Li-metal battery cell, which delivers a capacity retention of 74.6% over 950 cycles with an areal capacity of 0.5 mAh cm⁻² at a current density of 0.5 mA cm⁻² (Figure 5-27d). In contrast, the control cell, using a bare Li anode, presents a capacity retention of only 50% over 205 cycles. In addition, cells with higher areal capacities of 1.0 and 1.5 mAh cm⁻² also achieved markedly extended cycle lives (Figure 5-29).

We further examined the SEI stability by operating the Li|NCM 523 cells under lean electrolyte conditions (1 M LiPF₆ with a low electrolyte-to-capacity ratio of 12 μ L mAh⁻¹). As shown in Figure 5-27e, the capacity of the cell using bare Li anodes fades very fast under this harsh condition. This can be explained by the fact that the electrolyte (Li ion and solvent) is continuously consumed in repeated breakdown and repair cycles of the SEI, and the remaining amount of electrolyte is insufficient for battery operation. Encouragingly, the cell using the RPC-stabilized Li anode presented a capacity retention of 77.3% in 600 cycles. The voltage profile is also much more stable than that of the cell using the bare Li (Figure 5-30). This increase in the full-cell performance can be attributed to the excellent stability of the RPC-derived SEI, which protects the electrolyte from the consumption by SEI formation. Besides, we used a thicker Li (400 μ m) as the anode, and cell performance is very similar to that of the use of a thin Li (120 μ m) (Figure 5-31). This result demonstrates that the bottom neck of the Li metal batteries cells under lean electrolyte conditions is the SEI stability and electrolyte consumption.



Figure 5-27: Electrochemical performance of the RPC-stabilized Li. (a) Voltage profiles of symmetric Li|Li cells. The RPC-stabilized Li exhibits stable profiles over 800 h. (b and c) EIS measurement of the symmetric cells using the RPC-stabilized Li (b) and bare Li (c) electrodes. The charge-transfer resistance of the RPC-stabilized Li maintains low during cycling. (d) Cycling performance of Li|NCM 523 cells in a flooded electrolyte (1 M LiPF₆ in EC/EMC/FEC (3:7:1) with 2% LiBOB). The electrolyte-to-capacity ratio is 50 μ L mAh⁻¹. (e) Cycling performance of a Li|NCM 523 cell in the lean electrolytes (1 M LiPF₆ in EC/EMC/FEC with 2% LiBOB). The electrolyte-to-capacity ratio is 12 μ L mAh⁻¹. The Li thickness is 120 μ m. The use of the RPC-stabilized Li anodes result in significantly extended batteries lives, owing to the stabilized interface.



Figure 5-28: Thickness optimization of the RPC layer. (a) The Li deposition overpotential of the Li electrodes coated with RPC with different thicknesses. (b) Cycling performance of Li|NCM 523 cell using an RPC-stabilized Li anode. The RPC thickness is 1 μ m.



Figure 5-29: Cycling performance of the Li|NCM 523 cells using the RPC-stabilized Li anodes with areal capacities of 1.0 and 1.5 mAh cm⁻², respectively.



Figure 5-30: Voltage profiles of the Li|NCM 523 cell under lean electrolyte conditions. (a) A cell using the RPC-stabilized Li anode in a 1 M LiPF₆ lean electrolyte. (b) A cell using the bare Li anode in a 1 M LiPF₆ lean electrolyte.



Figure 5-31: Voltage profiles of the Li|NCM 523 cell under lean electrolyte conditions. (a) A cell using the RPC-stabilized Li anode in a 1 M LiPF₆ lean electrolyte. (b) A cell using the bare Li anode in a 1 M LiPF₆ lean electrolyte.

5.4 Conclusions

In summary, we have demonstrated a new, effective approach to the design and architecture of a stable polymeric nanocomposite SEI with tunable chemical composition, structure, and physical properties. This was realized by the use of a reactive polymeric composite containing poly(vinyl sulfonyl fluoride-*ran*-2-vinyl-1,3-dioxolane) and graphene oxide nanosheets. The polymer can preferentially occupy Li surface sites and decomposes at the interface to form the nanocomposite SEI. The SEI is composed of organic polymeric Li salts,

nanoparticles of inorganic Li salts, and GO nanosheets. This multi-component SEI provides excellent passivation, homogeneity, ionic conductivity, and mechanical strength. Li electrodes with a reactive polymeric composite layer show dendrite-free Li electrodeposition in a carbonate electrolyte. Li-metal battery cells display significantly extended cycle lives using NCM 523 cathodes under lean carbonate electrolyte conditions. The unique advantages of this approach lie in the capability of bottom-up design of the structure of the nanocomposite and *in situ* generation of the SEI via chemical and electrochemical reactions. These findings open up a new avenue for designing stable SEI layers with tunable chemical composition, nanostructure and properties for Li metal anode.

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Chapter 6

Salt-Based Organic-Inorganic Nanocomposites: towards a Stable Lithium Metal/Li₁₀GeP₂S₁₂ Solid Electrolyte Interface

6.1 Introduction

As discussed in Chapter 4, rechargeable lithium (Li) batteries have nowadays enabled the rise of portable electronics and electric vehicles. However, a serious concern is the safety issue arising from the use of flammable liquid electrolytes¹. Solid-state batteries, powered by solidstate electrolytes (SSEs), provide an ideal solution to this problem^{2,3}. In addition, solid-state batteries show great promise for achieving high energy density and long lifespans simultaneously⁴⁻⁸. Owing to these attractive features, intense efforts have been dedicated to the development of solid-state Li batteries. The primary target of this research has been to design SSE materials with high Li-ion conductivity. Various types of SSEs have been reported, and some materials exhibit conductivities, comparable to that of liquid electrolytes⁹⁻¹³. These breakthroughs allow researchers to move forward to study the construction of solid-state batteries. Li metal is an ideal anode for solid-state batteries, due to its highest theoretical capacity¹⁴⁻¹⁶. However, interfaces between SSEs and Li metal are unstable, presenting a major obstacle for the battery performance. Many SSEs in contact with Li can be reduced, and their reduction products form interfacial layers between the SSE and Li¹⁷⁻²⁰. In an ideal case, the formed layer presents high Li-ion conductivity and sufficiently low electronic conductivity, enabling facile Li-ion transport and avoiding continuous reduction of the SSE. A good example of such interfacial layers is a composite layer consisting of Li₂O, Li₃N, and Li₃P, which is formed by the reduction of lithium phosphorous oxide nitride (LiPON) electrolyte^{21,22}. Unfortunately, the Li-ion conductivity of LiPON is too low for practical batteries. For the most highly ionic conductive SSEs such as $Li_{10}GeP_2S_{12}$ (LGPS), $Li_{10}SnP_2S_{12}$, $Li_{0.33}La_{0.56}TiO_3$, and $Li_7P_3S_{11}$, the

interfacial layers are electronically conductive, allowing electron transport at the interface²³⁻²⁵. This result in continuous degradation of these SSEs and growth of interfacial layers (Figure 6-1a)^{19,26-28}, causing battery capacity fading, resistance increase, and short-circuiting.

The interfacial stability issue has been tentatively approached in several ways. One is to employ a bilayer SSE containing a highly conductive SSE layer (e.g., LGPS) and a Li-compatible SSE layer (e.g., 75% Li₂S-24% P₂S₅-1% P₂O₅) in contact with Li²⁹⁻³². Although interfacial stability is improved, the overall Li-ion conductivity is markedly lowered. Another strategy is to use Li-alloys (e.g., Li-In alloys) as anodes, which lower the reducing power of the anode but sacrifice the battery energy density¹³. Several studies have used simple elements/compounds such as Si, Ge, and LiH₂PO₄ as protective layers to stabilize the Li/SSE interface³³⁻³⁵. Despite improvements, they still lack essential properties such as low resistance and adequate stability against Li³⁶. All told, there is still a lack of stable interface chemistries that could enable Li anode technology in solid-state batteries.



Organic elastomeric salts (LiO-(CH2O)n-Li) & inorganic nanoparticle salts (LiF, -NSO2-Li, Li2O, etc.)

Figure 6-1: Illustration of the Li salt-based organic-inorganic nanocomposite as an interfacial protective layer for stabilizing the Li/LGPS interface. (a) Poor interfacial stability between Li and LGPS. LGPS is reduced by metallic Li, and some poorly ionic conductive products (Li₃P, Li₂S, Ge, etc.) are formed at the interface. (b) A stable Li/LGPS interface enabled by a nanocomposite interphase consisting of organic elastomeric Li salts (LiO-(CH₂O)_n-Li) and inorganic nanoparticle salts (LiF, -NSO₂-Li, Li₂O). This nanocomposite layer not only has good stability and affinity for both the Li and LGPS but also provides fast ion conduction at the interface.

We report here the use of a nanocomposite of organic and inorganic Li salts as an interphase to stabilize the Li/SSE interface (Figure 6-1b). This nanocomposite interphase was formed *in situ* by electrochemically reducing a liquid electrolyte on the Li electrode. There are several advantages of such nanocomposites as an ideal protective interphase. First, the electrochemistry-controlled formation process of the nanocomposite enables its excellent chemical and electrochemical stability against Li reduction and limited interfacial resistance. Second, we can design the chemical structure of the nanocomposite by using an appropriate liquid electrolyte to maximize its affinity to a given SSE. In this work, LGPS, which has a high Li-ion conductivity¹³ of 12 mS cm⁻¹ and strong tendency to be reduced by Li^{24,37}, was employed as a platform to investigate our design. We screened interphases formed by different electrolytes and achieved an optimal one, composed of organic elastomeric Li salts (LiO-(CH_2O)_n-Li) and inorganic nanoparticle salts (LiF, -NSO₂-Li, Li₂O). Spectroscopic and microscopic studies indicated that this nanocomposite acts as a stable protective layer between LGPS and Li, which prevents LGPS reduction during cycling. The use of the nanocomposite interphase enabled electrodeposition over 3000 h of repeated Li plating/stripping. A 200-cycle life with a capacity retention of 91.7% was achieved for a solid-state Li|LGPS|TiS₂ cell.

6.2 Materials and Methods

The *in situ* preparation of the nanocomposite interphase on Li is depicted in Figure 6-2a. Liquid electrolytes can electrochemically deposit on Li by applying a constant current. Specifically, Li chips ($\sim 2 \text{ cm}^2$) were thoroughly washed with anhydrous hexane before being used to assemble Li|Cu cells operated in liquid electrolytes. A constant current of 0.05 mA for Li stripping was applied for 6 s, followed by a 12-second rest. The process was repeated 200 times to achieve flat Li electrodes attached to the nanocomposite interphase. The Li electrodes were



Figure 6-2: Design of the nanocomposite interphase. (a) Illustration of the formation of the nanocomposite on Li *via* the electrochemical decomposition of a liquid electrolyte. (b) Comparison of the voltage profiles of Li deposition in Li|LGPS|Li cells. Interphase **3** enabled the optimal interfacial stability. (c) High-resolution XPS spectra of interphase **3**, composed of organic and inorganic salts.

then washed gently with DOL or EMC solvent 2 times and dried before use. We prepared

nanocomposite interphases with different chemical compositions by using several different liquid

electrolytes. Interphase candidates **1-4** shown in Figure 6-2b were formed by 7, 4, and 1 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in dioxolane (DOL)/1,2-dimethoxyethane (DME) (1:1, v/v) and 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7, v/v), respectively. We compared the interphase candidates by studying Li deposition stability in symmetric Li|LGPS|Li cells (Figure 6-2b and Figures 6-3 to 6-7). All these candidates showed stabilized Li deposition, and the optimal performance was obtained by the use of interphase **3**, which enabled Li deposition over 3000 h with an



Figure 6-3: Enlarged voltage profiles of the Li|LGPS|Li cell with nanocomposite interphase 3 at the Li/LGPS interface. The overpotentials of Li deposition were 22, 32, 39, and 45 mV after 20 (a), 120 (b), 520 (c), and 1020 h (d), respectively. The stable profiles over 3000 h indicate the excellent stability of the Li/LGPS interface.



Figure 6-4: Enlarged voltage profiles of the Li|LGPS|Li cell with nanocomposite interphase 1 at the Li/LGPS interface. The overpotentials of Li deposition were 66, 71, 79, and 83 mV after 20 (a), 120 (b), 620 (c), and 1020 h (d), respectively. The use of interphase 1 markedly improved the stability of the Li/LGPS interface.



Figure 6-5: Enlarged voltage profiles of the Li|LGPS|Li cell with nanocomposite interphase 2 at the Li/LGPS interface. The overpotentials of Li deposition were 71, 74, 74, and 77 mV after 20 (a), 120 (b), 520 (c), and 920 h (d), respectively.



Figure 6-6: Enlarged voltage profiles of the Li|LGPS|Li cell with nanocomposite interphase 4 at the Li/LGPS interface. The overpotentials of Li deposition were 125, 82, 81, and 50 (short-circuited) mV after 20 (a), 120 (b), 320 (c), and 620 h (d), respectively.



Figure 6-7: Enlarged voltage profiles of the Li|LGPS|Li cell using unprotected Li electrodes. The overpotentials of Li deposition were 24, 103, 167, and 220 mV after 20 (a), 120 (b), 220 (c), and 320 h (d), respectively. This fast growth of overpotentials implies an unstable interface between Li metal and LGPS.

overpotential of ~57 mV. This was in stark contrast with that of the cell containing an

unprotected Li/LGPS interface, which had a short lifespan and high overpotentials.

X-ray photoelectron spectroscopy (XPS) analysis was conducted to study the

compositional differences among these candidates. The experiments were performed on a PHI

VersaProbe II Scanning XPS Microprobe. A vacuum transfer vessel was used to load samples in a glove box and transfer samples into the XPS instrument. In the spectra of interphase **3** (Figure 6-2c and 6-8), we observed organic elastomeric LiO-(CH₂O)_n-Li species (peaks at 238.7, 284.6, 287.4 eV in the C 1s spectrum and 53.5 eV in the Li 1s spectrum)³⁸ and inorganic salts including -N-SO- bond (peaks at 400.1 eV in the N 1s spectrum and 169.3 and 170.5 eV in the S 2p spectrum), C-F bonds (peaks at 291.4 eV in the C 1s spectrum and 688.6 eV in the F 1s spectrum), and LiF (peaks at 55.4 eV in the Li 1s spectrum and 684.7 in the F 1s spectrum). The thickness of the interphase **3** was ~90 nm, calculated by XPS depth profiling (Figure 6-9). XPS analyses were performed on a PHI VersaProbe II Scanning XPS Microprobe. A vacuum transfer



Figure 6-8: Elemental concentration analysis of nanocomposite interphase 3.



Figure 6-9: XPS depth profiling of Li 1s, F 1s, and N 1s of nanocomposite interphase 3 attached to Li. Curves from top to the bottom represent spectra acquired after sputtering for 0 (red), 3 (blue),
6 (yellow), 9 (green), and 12 min (purple). The sputtering rate was ~10 nm min⁻¹ based on SiO₂. The top three curves show similar spectra to that of the pristine nanocomposite interphase **3**, indicating that the thickness of the interfacial layer is ~90 nm. The bottom two curves contain the spectral features of metallic Li (peak at ~53 eV), which can be assigned to be the metallic Li layer.

vessel was used to load samples in a glove box and transfer samples into the XPS instrument. A 20 eV Argon ion beam and a scan area of $20x20 \ \mu\text{m}^2$ were employed for XPS depth profiling experiments. In contrast, interphases **1**, **2**, and **4** mainly consist of inorganic salts. Figure 6-10a shows high-resolution XPS spectra of interphase **1**, formed by the electrochemical decomposition of a 7 M LiTFSI in DOL/DME electrolyte, containing mainly inorganic Li salts. These include C- F_x (292.3 and 289.6 eV in the C 1s spectrum and 688.2 eV in the F 1s spectrum), -N-SO- (399.9



Figure 6-10: Chemical composition of nanocomposite interphase 1. (a) High-resolution C 1s, F 1s, Li 1s, N 1s, and S 2p XPS spectra of the nanocomposite interphase 1 attached to Li. (b) Elemental concentration analysis of nanocomposite interphase 1.

eV in the N 1s spectrum and 168.7 eV in the S 2p spectrum), LiF (684.6 eV in the F 1s spectrum and 55.9 eV in the Li 1s spectrum), Li₃N (397.9 eV in the N 1s spectrum and 55.9 eV in the Li 1s spectrum). Interphase **1** contains high elemental concentrations of Li (34.9%), F (9.7%), S (7.0%), and N (4.7%), which are attributed mainly to the inorganic components, and has a low concentration of C (12.0%), which is mainly derived from the organic components (Figure 6-

10b). Figure 6-11a shows high-resolution XPS spectra of interphase **2**, formed by the electrochemical decomposition of a 4 M LiTFSI in DOL/DME electrolyte, which contains a high concentration of inorganic Li salts and a low concentration of organic Li salts. These include C-F_x (292.3 and 289.7 eV in the C 1s spectrum and 688.3 eV in the F 1s spectrum), -N-SO- (399.9 eV in the N 1s spectrum and 168.7 eV in the S 2p spectrum), LiF (684.6 eV in the F 1s spectrum and 55.6 eV in the Li 1s spectrum), Li₃N (397.8 eV in the N 1s spectrum and 54.2 eV in the Li 1s spectrum). In addition, interphase **2** shows high elemental concentrations of Li (31.7%), F (7.6%), S (4.7%), and N (3.0%), which are attributed mainly to the inorganic components, and a low concentration of C (20.8%), which is mainly attributed from the organic components (Figure 6-



Figure 6-11: Chemical composition of nanocomposite interphase 2. (a) High-resolution C 1s, F 1s, Li 1s, N 1s, and S 2p XPS spectra of nanocomposite interphase 2 attached to Li. (b) Elemental concentration analysis of nanocomposite interphase 2.



Figure 6-12: Chemical composition of nanocomposite interphase 4. (a) High-resolution C 1s, F 1s, Li 1s, O 1s, and P 2p XPS spectra of nanocomposite interphase 4 attached to Li. (b) Elemental concentration analysis of nanocomposite interphase 4.

11b). Compared to interphase **1**, the fraction of organic components is higher. Figure 6-12a shows high-resolution XPS spectra of interphase **4**, formed by the electrochemical decomposition of a 1 M LiPF₆ in EC/EMC electrolyte. Li-CO₂- (289.5 eV in the C 1s spectrum, 55.3 eV in the Li 1s spectrum, and 531.7 eV in the O 1s spectrum), LiP_xF_y (137.0 eV in the P 2p spectrum, 686.8 eV in the F 1s spectrum, and 53.7 eV in the Li 1s spectrum), $\text{LiP}_x\text{O}_y\text{F}_z$ (133.7 eV in the P 2p spectrum, 686.8 eV in the F 1s spectrum, 533.5 eV in the O 1s spectrum, and 53.7 eV in the Li 1s spectrum), $\text{LiP}_x\text{O}_y\text{F}_z$ (133.7 eV in the Li 1s spectrum), LiF (684.8 eV in the F 1s spectrum and 56.3 eV in the Li 1s spectrum), and Li-O-C (286.4 eV in the C 1s spectrum and 530.4 in the O 1s spectrum) were observed. The concentrations of Li, F, C, O, and P are 34.0%, 18.6%, 19.3%, 26.6%, and 1.5%, respectively (Figure 6-12b).

6.3 Results and Discussion

To investigate the stability of Li/LGPS interface, we employed XPS depth profiling to analyze chemical environments at the Li/LGPS interfaces. Figure 6-13a shows XPS spectra

acquired from an unprotected Li/LGPS interface after 1000 h of operation. Peaks in the top three spectra were attributed to a mixture of pristine and reduced LGPS. The presence of reduced LGPS is evidenced by the spectral features of Li₂S (peaks at 160.0 eV in the S 2p spectra and 55.3 eV in the Li 1s spectra), elemental Ge (peaks at 28.6 and 27.0 eV in the Ge 3d spectra), reduced P (peaks at 130.4 eV in the P 2p spectra and 55.3 eV in the Li 1s spectra), and pristine LGPS is evidenced by Ge/P-S-Li (peaks at 161.5 eV in the S 2p spectra), Ge⁴⁺ (peaks at 30.9 eV in the Ge 3d spectra and 127.1 and 123.0 eV in the Ge 3p spectra (incorporated in the P 2p spectra)), and PS_4^{3+} (peaks at 132.1eV in the P 2p spectra). After sputtering, pristine LGPS signals disappeared in curves 4 to 11, accompanied by the appearance of elemental Li signals (peaks at 53.1 eV in the Li 1s spectra). Meanwhile, reduced LGPS spectral features were seen throughout the interface, and peaks attributed to Li and reduced LGPS appeared together without separation. These results imply that LGPS was reduced by Li at the interface during cycling, and Li and reduced LGPS are overlapping in the interface. In contrast, no reduced LGPS were seen at the Li/LGPS interface stabilized by a nanocomposite interphase layer (Figure 6-13b). Specifically, the top three spectra have pristine LGPS without any signals that can be attributed to reduced LGPS species or Li. In the 4th to 9th curves, signature features of the nanocomposite interphase, including -N-SO- (peaks at 170.2 eV in the S 2p spectra) and LiF/Li-O- (peaks at 55.3 eV in the Li 1s spectra and 684.6 eV in the F 1s spectra) began to appear, and the intensities grew with increasing sputtering depth. Peaks attributed to LGPS decreased correspondingly and finally disappeared. Only Li metal features (peaks at 53.6 eV in the Li 1s spectra) were found in the bottom two curves, indicating that the nanocomposite layer had been removed and the deposited Li underneath was detected. The retention of unreduced LGPS and the clear separation of Li, nanocomposite, and LGPS layers demonstrate the effective stabilization of the Li/LGPS interface.



Figure 6-13: Chemical environment of the nanocomposite-stabilized Li/LGPS interface studied by XPS depth profiling analysis. (a) XPS spectra of S 2p, Ge 3d, P 2p, Li 1s, and F 1s of the bare Li/LGPS interface. Reduced LGPS species including Li₂S, Ge, Li₃P were observed throughout the interface. (b) XPS spectra of S 2p, Ge 3d, P 2p, Li 1s, and F 1s of the nanocomposite-stabilized Li/LGPS interface. The LGPS (top three curves) and metallic Li (bottom two curves) were identified in different sputtering depths, and the Li, nanocomposite interphase, and LGPS layers had clear separation. No reduced LGPS species were found.

After identifying the stable composition at the Li/LGPS interface, we studied the interfacial morphology using scanning electron microscopy (SEM). The nanocomposite-stabilized Li electrode shows a flat surface, which is uniformly covered by the *in situ* formed nanocomposite (Figure 6-14). After operating Li|LGPS|Li cells for 500 h, the unprotected LGPS pellet had been pulverized (Figure 6-15a,b). Because only a small amount of Li (0.1 mAh cm⁻²) was deposited, we attributed the pulverization to the LGPS reduction. Specifically, the LGPS pellet is lithiated continuously, accompanied by a large volume expansion, which finally results in its mechanical breakdown. Encouragingly, after cycling for 2000 h, the nanocomposite-



Figure 6-14: Morphological characterization of the nanocomposite-stabilized Li/LGPS interface. (a) Top-view SEM image of an as-prepared Li electrode with the nanocomposite interphase. (b-e) EDS mapping of C, F, N, and S elements based on a. A flat Li surface covered with a nanocomposite interphase layer was prepared. (f) EDS spectrum of nanocomposite interphase **3** attached to Li. C, F, N, S in the nanocomposite interphase **3** were observed.

stabilized LGPS pellet retained its intact form without noticeable structural damage (Figure 6-15c,d), compared to as-prepared and uncycled pellets (Figure 6-16). In addition, we probed the morphology at the contact interface by delaminating the LGPS and Li layers of cycled Li|LGPS|Li cells after 200 h. A LGPS pellet taken from the unprotected Li|LGPS|Li cell broke heavily, and many LGPS particles were attached to the Li electrode. As shown in Figure 6-17, after delaminating the Li and LGPS layers from the cycled Li|LGPS|Li cell without the nanocomposite interphase, the Li surface was covered by particles containing Ge, S, P, C, and O. Combined with the results of the XPS analysis (Figure 6-13a), we can identify this particle layer



Figure 6-15: Side-view SEM images of the cycled Li|LGPS|Li cells using bare Li (a and b) and nanocomposite-stabilized Li (c and d) electrodes, respectively.



Figure 6-16: SEM images of the uncycled Li|LGPS|Li cell with nanocomposite interphase 3.

as reduced LGPS. Contrastingly, the nanocomposite-stabilized Li and LGPS layers can be separated easily, and no noticeable Li dendrites can be found at the Li surface (Figure 6-18)³⁹. After delaminating the Li and LGPS layers from the cycled Li|LGPS|Li cell with the nanocomposite interphase, the Li surface showed a flat morphology and was attached to a small amount of particles on the surface (Figure 6-18a-c). EDS mapping confirmed that the particles consist of Ge, P, and S and the surface layer of Li contains C, N, F, and O (Figure 6-18d-j).

Combined with the XPS analysis results (Figure 6-13b), the data show the surface layer to be the nanocomposite interphase and the isolated particles to be LGPS.



Figure 6-17: Morphology of the cycled Li|LGPS|Li cell without the nanocomposite interphase. (ac) SEM images of the delaminated Li surface taken from the cycled Li|LGPS|Li cell. (d-g) EDS mapping of Ge, S, P, and C based on B. (h) The corresponding EDS spectrum.



Figure 6-18: Morphology of the cycled Li|LGPS|Li cell with the nanocomposite interphase. (a-c) SEM images of the delaminated Li surface. (d-i) EDS mapping of Ge, P, S, C, N, and F based on b. (h) The corresponding EDS spectrum. The delaminated Li surface was covered by unreduced LGPS.

We next investigated the electrochemical performance of Li anodes using LGPS electrolytes. The electrochemical stability of the nanocomposite interphase against LGPS was examined by cyclic voltammetry (CV) of a Li|LGPS|Ni cell (Figure 6-19a). Cathodic and anodic peaks were detected, which correspond to Li plating and stripping, respectively. No significant peaks representing the nanocomposite decomposition were found within a scan range of -0.5 to 3.0 V, consistent with stability of pristine LGPS¹³. Because LGPS reduction will cause a rapid impedance increase with time²⁴, we tested impedance evolution of a nanocomposite-stabilized Li|LGPS|Li cell 1, 24, and 48 h after cell assembly (Figure 6-19b and 6-20). The overall impedances recorded show very little increase with time.



Figure 6-19: Electrochemical stability of the nanocomposite-stabilized Li/LGPS interface. (a) CV curve of a nanocomposite-stabilized Li/LGPS|Ni cell at a scan rate of 1 mV s⁻¹. (b) Time-dependent Nyquist plots showing impedance evolution of a nanocomposite-stabilized Li/LGPS|Li cell. (c and d) Cycling performance of Li/LGPS|TiS₂ cells. The cell incorporating a nanocomposite-stabilized Li anode had markedly extended cycle life (c) and stable voltage profiles (d).



Figure 6-20: Impedance spectrum of a Li|LGPS|Li cell after 24 h. The equivalent circuit is used as a fit model.

Furthermore, the use of the nanocomposite-stabilized Li anode enabled markedly extended lifespan of a solid-state Li|LGPS|TiS₂ cell, which had a capacity retention of 91.7% in 200 cycles with an areal capacity of 0.18 mAh cm⁻² at a current density of 0.1 mA cm⁻² (Figure 6-19c). No clear polarization was observed in the voltage profile curves during cycling (Figure 6-19d). In contrast, the cell with an unprotected Li anode displayed a capacity retention of 76.1% in 70 cycles (Figure 6-19c) and severe polarization (Figure 6-21). To test the rate capability, we



Figure 6-21: Voltage profile of the control Li $|LGPS|TiS_2$ cell with an areal capacity of 0.18 mAh cm⁻².

cycled the cells at current densities of 0.05, 0.1, 0.25, 0.5 mA cm⁻² during the initial 20 cycles, obtaining specific capacities of ~190, 179, 167, and 161 mAh g⁻¹, respectively (Figure 6-19c). Moreover, the Li|LGPS|TiS₂ cells showed improved cycling stability at elevated areal capacities. A Li|LGPS|TiS₂ cell with an areal capacity of 0.72 mAh cm⁻² had a capacity retention of 81.7% in 100 cycles (Figure 6-22a) and stable voltage profiles without remarkably increased polarization (Figure 6-22b). This result further supports the effective stabilization of Li/LGPS interface.



Figure 6-22: Cycling performance of the Li|LGPS|TiS₂ cells with and without the nanocomposite interphase. (a) Cycle lives of the Li|LGPS|TiS₂ cells with and without the nanocomposite interphase. The areal capacities are 0.72 mAh cm⁻². (b and c) Voltage profiles of the cells with (b) and without (c) the nanocomposite interphase.

6.4 Conclusions

In summary, we have demonstrated a novel, efficient approach to stabilizing the Li/LGPS interface, which involves the use of a nanocomposite interphase consists of organic elastomeric Li salts (LiO-(CH₂O)_n-Li) and inorganic nanoparticle salts (LiF, -NSO₂-Li, Li₂O). The nanocomposite is formed *in situ* on Li *via* the electrochemical decomposition of a liquid electrolyte, therefore possessing excellent chemical and electrochemical stability, affinity for Li and LGPS, and limited interfacial resistance. XPS depth profiling and SEM results show that the nanocomposite effectively restrained the reduction of LGPS. Stable Li electrodeposition over 3000 h and a 200-cycle life for a full cell were achieved. These findings may provide a new direction in stabilizing the interface between Li and different reducible SSEs.

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Chapter 7

Concluding Remarks and Future Outlook

6.1 Summary

This dissertation focuses on the design of chemically and electrochemically active materials to regulate the formation, composition, and structure of SEI for Si and Li anodes. Based on the different requirements on the SEI structure, we developed organic and inorganic small molecules chemically bonded on the surface of Si to strengthen its SEI flexibility, density, and adhesion to the Si surface. In Chapter 2, for nano-sized Si anodes, we demonstrated that to improve the flexibility of the SEI layer and adhesion between SEI and Si surface can dramatically improve the SEI stability. We developed organic oligometric compounds and covalently bonded them at the surface of Si nanoparticles. Owing to the presence of these compounds in the SEI layer, the flexibility and adhesion were significantly improved. This approach focuses on the interfacial construction of functional groups to construct a durable SEI. Following this concept, we regulated the SEI chemistry for micro-sized Si anodes using a similar approach. In Chapter 3, we reported that to covalently bond a functional salt, N-methyl-N-propyl pyrrolidinium bis(fluorosulfonyl)imide, at the surface of micro-sized Si materials can effectively stabilize the interface and SEI. In the case of micro-sized Si materials, we considered that the surface changes are extremely huge and to maintain the SEI stability by improving the flexibility is too difficult. So we aimed to reduce the SEI sacrifice during the SEI break and repair process. Specifically, pyrrolidinium-based species, the cations of $PYR_{13}FSI$, are electrochemically inert and covalently bonded at the Si surface. These species occupy a part of Si surface and serve as non-consumable components to reduce SEI sacrifice during cycling. Meanwhile, the FSI anions are

electrochemically active and can generate LiF and -NSO_xF salts *in situ* to passivate Si surface, which prevent the formation of Li_xSiO_y and reduces the loss of active Si.

We also tuned the structure and composition of the SEI layer for Li anodes. The approach involves the use of chemically and electrochemically reactive polymer-based materials, which is coated on the surface of Li. The reactive materials can chemically react with Li to occupy the Li surface and subsequently electrochemically decompose to generate SEI components. In Chapter 4, we discussed the use of a reactive polymer, poly((N-2,2-dimethyl-1,3-dioxolane-4-methyl)-5norbornene-*exo*-2,3-dicarboximide), which not only to incorporate ether-based polymeric components into the SEI but also to accommodate Li deposition and dissolution under the skin in a dendrite/moss-free manner. In Chapter 5, we introduced an further optimized reactive polymeric material, namely RPC, which is a composite containing poly(vinyl sulforyl fluoride-ran-2-vinyl-1,3-dioxolane) and graphene oxide nanosheets. The SEI derived from the RPC consists primarily of organic polymeric Li salts (-SO₂-Li, and -C-O-Li bonded to the polymer backbone), nanoparticles of inorganic Li salts (LiF and LiOR (R=hydrocarbons)), and GO nanosheets. The organic-inorganic composite structure provides good density and passivation; the polymer structure and *in situ* SEI formation process ensures excellent homogeneity; various Li salts offer adequate ionic conductivity and electrical insulation; and the two-dimensional GO nanosheets confer mechanical strength. In addition, a surface layer of the unreacted polymer is preserved as a reservoir to continuously generate the SEI on newly exposed surfaces of Li. In this process, the electrolyte decomposition is very limited since the surface sites are primarily occupied by the attached RPC. This conformal nanocomposite SEI can stabilize the interface for dendrite-free Li deposition in a conventional carbonate electrolyte. We also designed functional materials to stabilize the interface between Li anodes and LGPS solid electrolyte. In Chapter 6, we reported a novel approach based on the use of a nanocomposite consisting of organic elastomeric salts (LiO-(CH₂O)_n-Li) and inorganic nanoparticle salts (LiF, -NSO₂-Li, Li₂O), which serve as an interphase

to protect $Li_{10}GeP_2S_{12}$ (LGPS), a highly conductive but reducible SSE. The nanocomposite is formed *in situ* on Li *via* the electrochemical decomposition of a liquid electrolyte, and is therefore capable of self-optimizing its chemical composition and nanostructure to provide good chemical stability, affinity for Li and LGPS, and limited interfacial resistance.

To understand the chemical process occurring at the interface, I performed a variety of spectroscopic and microscopic techniques to characterize the chemical composition, nanostructure, and physical/chemical properties of the SEI layer. These include high-resolution XPS, depth-profiling XPS, NMR, FTIR, TGA, and XRD which are used for compositional analysis of SEI; SEM, TEM, Cryo-TEM, and 3D optical profilometry which are employed to probe the structural information of SEI, and AFM indentation that is to monitor the mechanical property of SEI. To investigate the effects of the stabilized SEI on the battery performance, I ran various electrochemical characterizations including coin cell tests, impedance test, CV, etc.

6.2 Future Outlook

Based on the findings and understandings of the works discussed in this dissertation, we delightedly realized that to chemically regulate the SEI chemistry is an effective way to improve the SEI stability for many advanced battery materials. However, there are still a lot of efforts those can be made to the further understanding and regulation of SEI.

Current technologies cannot make an ideal SEI yet that is completely stable without a damage and reformation process. This may need further material design and understanding on the SEI chemistry. Besides, rechargeable lithium batteries still have safety issues when exposed in air. A stable interphase with high thermodynamic stability may be very helpful to address this problem. The main obstacle to operating lithium batteries under extreme temperatures (extremely elevated and low temperatures) also reside in the unstable interface, which leads to accelerated

interfacial reactions at elevated temperatures and reduced lithium ions conduction at low temperature. In addition, this concept can be further explored and applied to not only other interfaces in rechargeable lithium batteries such as the cathode-electrolyte interface but other metal batteries systems such as zinc and magnesium, in which the interfacial stability is one of the major obstacles hindering their developments.

Enlightened by a discussion with my committee member, Prof. Ralph Colby, I realized that it is also possible to design SEI-free interface for advanced battery materials. Such a material can be viewed as an ultimate SEI layer, which does not have problems associated with electrochemical decomposition and reactions with electrode materials. The elimination of SEI layer can exclude the decrease of rate capability, the growth of metallic dendrite, inhomogeneity of ions and electrons at the electrode surface.

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