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Electrochemical and mechanical processes at surfaces and interfaces of advanced materials for energy storage

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Author
Shi, Feifei

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Electrochemical and mechanical processes at surfaces and interfaces of advanced materials for energy storage

By
Feifei Shi
A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Engineering - Mechanical Engineering in the Graduate Division of the University of California, Berkeley

Committee in charge:
Professor Kyriakos Komvopoulos, Chair
Professor Gabor A. Somorjai
Professor Robert O. Ritchie

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Electrochemical and mechanical processes at surfaces and interfaces of advanced materials for energy storage

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by

Feifei Shi
Abstract

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Feifei Shi

Doctor of Philosophy in Engineering - Mechanical Engineering

University of California, Berkeley

Professor Kyriakos Komvopoulos, Chair

Energy storage is a rapidly emerging field. In almost all energy storage applications, surfaces and interfaces are playing dominant roles. Examples are fuel cell electrodes, where electro-catalytic reactions occur, Li-ion battery (LIB) electrodes, where electrolyte decomposition and passivation commence simultaneously, and failure (fracture) of battery electrodes, where surface crack initiation greatly affects battery endurance. The most fundamental chemical, electrochemical, and mechanical problems in energy storage applications originate from surfaces and interfaces. This thesis investigates the electrochemical and mechanical processes at surfaces and interfaces of advanced materials for energy applications. The thesis includes the following five main research topics.

The fuel cell electrodes’ electronic structure was tuned by modifying the metal oxide substrate with oxygen vacancies and/or fluorine doping. The electro-catalyst performance of metal oxide supported platinum nanoparticles was systematically investigated. Compared to Pt nanoparticles on pristine TiO₂ support, a two-fold higher activity and three-fold higher stability in methanol oxidation reaction, a 0.12 V negative shift of the CO oxidation peak potential, and a 0.07 V positive shift of the oxygen reaction potential were achieved. Experimental trends were interpreted in the context of an electronic structure model, showing an improvement in electrochemical activity, when the Fermi level of the support material in Pt/TiOₓ systems was close to the Pt Fermi level and the redox potential of the reaction. The findings of this work provide a better understanding of the substrate effect on electro-catalysis and valuable guidance for selecting the support material of Pt/TiOₓ systems.

The reference compounds, diethyl 2,5-dioxahexane dicarboxylate (DEDOHC) and polyethylene carbonate (poly-EC), were synthesized and their chemical structures were characterized by FTIR spectroscopy and nuclear magnetic resonance (NMR). The effect of Li-ion solvation on the FTIR spectra was studied by introducing the synthesized reference compounds into the electrolyte. EC decomposition products formed on Sn and Ni
electrodes were identified as DEDOHC and poly-EC by matching the features of the surface species forming on electrode surfaces with reference spectra. The results demonstrate the importance of accounting for the solvation effect in FTIR analysis of the decomposition products forming on LIB electrodes.

The composition, structure, and formation mechanisms of the solid electrolyte interface (SEI) on the surfaces of LIB anode electrodes during charge/discharge cycles were investigated with advanced in-situ vibrational spectroscopy. This technique allows us to determine how the SEI properties contribute to the failure of anodes in LIBs used in vehicular applications. Two model surfaces (Au and Sn) were investigated by in-situ attenuated total reflection-infrared (ATR-IR) spectroscopy. The variation of the SEI components on the Au and Sn model surfaces is attributed to surface functional group differences and associated reduction mechanisms. For the first time, we have detected the formation of DEDOHC and Li propionate reductive products by in-situ IR spectroscopy. The results from the model system investigation can be applied to other anode materials of LIBs to improve future battery performance.

The SEI components at the interface of single-crystal Si(100) electrode and electrolyte were studied by ATR-FTIR spectroscopy. High-energy-density Si anodes have large irreversible capacity and poor reliability/durability. These failures are due in part to loss of electrolyte by reduction and the formation of unstable SEI during cycling. To elucidate the mechanism of Si electrode failure during battery cycling, a novel in-situ ATR-FTIR electrochemical cell was constructed, which allows the tuning of the depth of probing in vibrational spectra of molecules at the electrode surface.

Electrochemical experiments, microstructure characterization, and finite element analysis were combined to explore the failure mechanism of single-crystal Si electrodes over cycles. It was found that surface cracks initiating perpendicular to the electrode surface propagate in the depth direction and eventually are deflected along the lithiation boundary, causing electrode material to delaminate. Although crack initiation and growth occur during delithiation, they are essentially driven by irreversible plastic deformation accumulating during the lithiation phase. When the tip of the cracks approaches the lithiation boundary, the low fracture toughness of the crystalline Si (c-Si)/amorphous Si (a-Si) interface, i.e., the “weakest” microstructural path, causes crack deflection along the c-Si/a-Si interface. The findings of this study provide a comprehensive understanding of the failure mechanism of silicon electrodes and guidance for electrode material selection and design optimization.

This ultimate objective of this thesis is the examination of surface and interface material problems in energy applications. The findings of this work reveal a generic behavior comprising interactive chemical/electrochemical reactions and mechanical effects.
Dedicated to my parents and my husband
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Feifei
Berkeley, CA
2015.12
Chapter 1 – Introduction

“God made the bulk; surfaces were invented by the devil” — W. Pauli

This chapter provides a general overview of surface science, with special emphasis on the physical explanation of why surfaces behave differently than bulk materials and the role of surfaces and interfaces in material science at the nanoscale. In addition, several specific challenges in surface science of energy materials, such as the improvement of the activity and lowering of the cost of electro-catalysts in fuel cells, accurate characterization of the chemical composition and probing of the electro-chemical processes commencing at the solid electrolyte interface (SEI) of LIBs, and understanding of crack initiation and growth at electrode surfaces leading to electrode fracture and possible ways to mitigate, are discussed. With the main objective to explore and resolve the above challenges, this chapter is concluded with the organization of this dissertation.

1.1 Overview of surface science

A surface is the physical boundary of a phase (e.g., solid or liquid phase), which generally is not atomically clean. Based on the kinetic theory of gases, molecules strike a material surface at a given ambient pressure and, typically, ultrahigh vacuum (UHV) conditions (<10\(^{-9}\) Torr) are required to maintain an atomically clean surface for ~1 h. An interface is the physical boundary between two adjacent bulk phases. In practice, we are mostly concerned with the properties of different solid-liquid, solid-gas, liquid-gas interfaces, rather than a single surface in absolute vacuum. In many cases, the terms surface and interface are used interchangeably when the emphasis is on the solid or liquid phase.\(^1\) Surface science is the study of physical and chemical phenomena occurring at solid-vacuum or two-phase interfaces. The surface science encompasses multidisciplinary fields, such as heterogeneous catalysis, semiconductor device fabrication, fuel cells, and adhesives.

Due to their “broken symmetry”, molecules at phase boundaries exhibit different behaviors than those in the bulk phase. For example, molecules at or near a fluid surface will be orientated differently with respect to each other than those in the bulk fluid. Any molecule at the fluid surface would be under an asymmetrical force field, resulting in the development of surface or interface tension. The closer a molecule to an interface, the higher the force due to asymmetry. With increasing distance from the interface, the effect of the asymmetric force field decreases and vanishes beyond a critical distance. Therefore, the location of the so-called mathematically dividing surface is only a theoretical concept, which enables us to apply thermodynamics and statistical mechanics. Instead of an infinitely sharp interfacial boundary separating two phases, changes in both density and orientation of interface molecules results in a finite molecular gradient and a surface or an interface may be defined as either one atomic layer or several atomic layers in the near-
surface region of the material. Surface crystallography shows that on the atomic scale, most clean metals tend to minimize their surface energy by two kinds of surface atomic arrangements: relaxation and reconstruction. Typically, in the near-surface region, the top layer of atoms relaxes inwards (i.e., toward the bulk), whereas one or more of the underlying layers of atoms exhibit slightly outward relaxation. The low coordination number of surface atoms is the main driving force for the relaxation of clean metal surfaces. In some metals, surface relaxation may change the equilibrium position and bonding of surface atoms (displacements both perpendicular to and parallel to the surface plane), resulting in the reconstruction of the outermost layers.

The last decade has witnessed a blooming of nanomaterials. As the physical dimensions of materials are reduced to the nanometer scale, the material behavior is controlled only by a few atomic layers. As the surface-to-volume ratio increases and core dimensions decrease, materials exhibit new and unexpected properties that are quantum-mechanical in origin. To design new nanomaterials, it is necessary to understand the physics and laws that govern nanomaterial behavior. Of particular importance is to understand the origins of electronic, magnetic, catalytic, mechanical, and biological properties at the nanoscale. This is essential for tailoring material properties by manipulating surface and interface characteristics. Surface science strives to provide solutions to these challenges by shedding light into fundamental physical and chemical processes occurring at surfaces and interfaces.

1.2 Importance of surfaces and interfaces in energy storage devices

1.2.1 Electro-chemical processes at interfaces in fuel cells: electro-catalysis

The electrode/electrolyte interface is at the heart of electrochemistry because it is where electronic charge transfer, reactant molecular adsorption, and product molecular desorption occur. The classical model of the metal/solution interface is that of a plate condenser of molecular dimensions (Figure 1.1 – double layer structure). One plate is the metal with its surface excess charge, the other plate comprises solvated ions at close proximity, and is held in place by purely electrostatic forces (such ions are referred to as ‘‘non-specifically adsorbed’’). This plane is called the outer Helmholtz plane (OHP). Its distance from the metal surface is estimated to be sub-nanometer – the radius of a solvated ion. Ions with weakly bound solvation shells (e.g., anions, particularly halide ions like Cl\(^-\), Br\(^-\), and I\(^-\)) may give away part of those solvation shells to form a chemical bond with the electrode surface. These ions are called ‘‘specifically adsorbed’’ and their centers define the inner Helmholtz plane (IHP).
Nowadays, the demand for clean and sustainable energy sources has become a strong driving force for continuing economic development. Fuel cells are electrochemical devices which continuously and directly convert the chemical energy of externally supplied fuel and oxidant to electrical energy. As clean energy-converting devices, fuel cells have drawn a great deal of attention in recent years due to their high efficiency, high energy density, and low or zero emissions. It is also one of the most promising candidates for transportation power applications. Nonetheless, two major issues prevent the successful implementation of fuel cells – high cost and low reliability/durability. Fuel cell catalyst layers, mainly platinum (Pt)-based catalysts, is the main factor in these challenges. Tremendous efforts have been made to overcome these obstacles. For example, alloying and surface modification with other metals result in improved electro-catalysis with lower loading owing to the synergy effect of alloys, or adjustment of surface electronic structure and substrate effect. However, more systematic work must be devoted to non-noble catalyst materials design, synthesis, and in-depth understanding of fundamental mechanisms for fuel cell technology to find widespread application.

1.2.2 Electro-chemical and chemical processes at interfaces in Li-ion batteries: The solid electrolyte interphase (SEI)

Access to energy and rechargeable batteries are becoming immensely important as a mobile energy resource. Despite of the extraordinary theoretical limit and excellent initial
performance, batteries usually experience severe functional degradation over prolonged cycling (repeated charge and discharge) or long-term storage, which typically includes capacity loss, poor cyclability, power fade, and self-discharge. In an electrochemical device, interfaces between electrolyte and electrodes are the only “legitimate” sites for electron exchange; therefore, aforementioned issues have to be related to the interface reversibility at the anodes and cathodes.7

Because of the large potential range of the anodes and cathodes of LIBs, the electrolyte is not thermodynamically stable, resulting in the decomposition of sacrificial electrolyte components (Figure 1.2(a)). The interfaces are termed solid electrolyte interphase (SEI) because they act as an interphase between the metal and the solution, with the properties of a solid electrolyte of high electronic resistivity (Figure 1.2(b)). These passivation layers make the electrode surface kinetically stable and guarantee reversible cycling of the battery; therefore, they are “the most important but least understood component of LIBs.”8,9 This is because they are essentially responsible for the reversibility of Li+-intercalation chemistries and for dictating the kinetics of overall cell reactions. SEI characterization is difficult because of its small (~50 nm) thickness, chemical sensitivity, and elusive manner of formation. Moreover, the selective sensitivity to certain chemical species and simultaneous blindness to others often prevent most spectroscopy methods to provide a comprehensive understanding about the interphase. Although significant advances have been made during the past decade with the development of various new models and tools, many SEI issues remain controversial. Clearly, there is a demanding need for an in-situ nondestructive technique, which will enable the precise characterization of the complicated processes at electrolyte/electrode interphases.

Figure 1.2 Passivation of electrode surface – Solid Electrolyte Interphase (SEI). (a) Schematic of open-circuit energy diagram of an aqueous electrolyte. $\Phi_A$ and $\Phi_C$ are the anode and cathode work functions, $E_g$ is the window of the electrolyte for thermodynamic stability. A $\mu_A > \text{LUMO}$ and/or a $\mu_C < \text{HOMO}$ requires a kinetic stability by the formation
of an SEI layer;\(^1\) (b) Solid electrolyte interphase – the layer acts as an interphase between the metal and the solution and behaves as a solid electrolyte of high electronic resistivity.\(^1\)

1.2.3 Mechanical processes at Li-ion battery interfaces: An electrode fracture mechanics approach

LIBs have been widely used in portable electronic devices because of their high energy density. However, due to the poor long-term durability and performance degradation, the commercialization of LIBs in heavy duty, long lifetime systems is quite limited. Electrode fracture is one of the most important failure modes accounting for the functional degradation of LIBs, and is driven by coupled electrochemical and mechanical mechanisms. As with all other traditional rechargeable batteries, LIBs have two electrodes, which host the Li\(^+\) ion insertion/extraction reversibly. To increase the capacity density, the electrode material has to host more Li\(^+\) ions. This implies larger volume expansion and, in turn, a higher risk for irreversible electrode deformation and fracture during cycling, as shown in Figure 1.3.

![Figure 1.3](image)

Figure 1.3 Electrode fracture in LIBs. (a) Thin (500 nm) film of amorphous silicon cracked after the 10 charge/discharge cycles,\(^1\) (b) nanoscale fracture in a 540-nm crystalline silicon particle after 138 s of lithiation,\(^1\) and (c) cracking of 20-µm SnO\(_x\) particles after 196-269 min of lithiation.\(^1\)

Silicon is a promising electrode material for next-generation high-energy-density LIBs because of its capability to reversibly incorporate a high concentration of Li\(^+\) ions. However, the brittle nature of Si and excessive volume expansion (~300%) induced by Li alloying makes Si electrodes extremely vulnerable to surface cracking, fracture, and delamination. To obtain a fundamental understanding of the Si anode failure and facilitate further rational development of tailor-made battery electrodes, it is essential to elucidate the evolution of stresses in the electrode material over cycles and identify the propagation path of cracks. This requires modeling of electrode system. A representative model system can further serve as theoretical foundation for design improvement and material selection, toward the development of high-energy-density and mechanically strong electrodes.
1.3 Objectives

The main objective of this dissertation is twofold. First, is to study the fundamental chemical, electrochemical, and mechanical processes commencing at electrode surfaces affecting the performance of fuel cells and rechargeable batteries, such as electrochemical fuel cell catalysis, LIBs electrode passivation reaction, and mechanical degradation (e.g., fracture). Second, is to provide guidance for material selection, electrode design, and process optimization by tuning the surface behavior and, in turn, improving fuel cell and battery efficiency, capacity, and durability.

1.4 Thesis organization

This dissertation consists of eight chapters. As stated in Chapter 1, the principal motivation was to investigate surface and interface problems for energy material applications. Chapter 2 provides details of the experimental and characterization techniques used in this dissertation. Chapter 3 deals with the substrate effect in electro-catalysis, and provides guidance for tuning the electro-catalytic performance of Pt/TiO\textsubscript{x} systems by engineering the composition of the support material. Chapters 4, 5, and 6 focus on SEI components and the formation mechanisms of SEI on different electrode surfaces (e.g., Au, Ni, Sn, and Si). The substrate dependence of SEI formation has been validated, and a catalytic reaction has been observed on Sn and Si electrodes. Diethyl 2,5-dioxahexane dicarboxylate, poly-ethylene carbonate, lithium ethyl dicarbonate, and lithium propionate have been identified as SEI components from infrared spectra peak assignment. Chapter 7 reveals how cracks initiate at Si electrode surfaces and then propagate through the electrode thickness, eventually causing catastrophic failure (delamination) over extended charge/discharge cycles. Based on the understanding of the failure mechanism, several strategies are proposed to improve the current electrode design. Finally, Chapter 8 summarizes the main findings and innovative contributions of this dissertation and gives a brief outlook of future directions.

1.5 References

(12) Juchuan Li; Alan K. Dozier; Yunchao Li; Fuqian Yang; Chenga, Y.-T. J. Electrochem. Soc. 2011, 158, A689.
(14) Martin Ebner; Federica Marone; Marco Stampanoni, V. W. Science. 2013, 342, 716.
Chapter 2 – Experimental methods

This chapter provides an introduction to the two surface characterization techniques mainly used in this dissertation: X-ray photoelectron Spectroscopy (XPS) and attenuated total reflection-Fourier transfer infrared (ATR-FTIR) spectroscopy. The working principles, main applications, and advantages of these techniques are discussed. Electrochemical characterization systems are also introduced, including two-electrode and three-electrode systems. Two types of in-situ electrochemical-spectroscopy cell designs, which are used for surface characterization in the following chapters are also presented.

2.1 Surfaces and interfaces

Surface or interface properties of different phases typically exhibit drastically different properties than those of their bulk. These properties control how a phase interacts with its neighbors, and affect various physical and chemical processes at surfaces and interfaces, such as corrosion, catalysis, adhesion, friction, heat transfer to name a few. These properties are determined by a very small population of atoms/molecules near the surface/interface. Surface and interface characterization is instrumental to understanding surface/interface behavior. The major difficulty in surface/interface characterization is the reliable detection of elemental composition, electronic state, and chemical bonding, and to efficiently filtering out the signals from the vast majority of the atoms in the bulk.

Most surface sensitive techniques detect photons, electrons, or ions excited, diffracted, or scattered at surfaces and interfaces. Examples include X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS). However, these techniques normally operate at high vacuum (~10⁻⁸ mbar) or ultra-high vacuum (UHV) (<10⁻⁹ mbar) conditions¹ because they require a long mean-free path. In view of the required low vacuum conditions, differential pumping systems have been invented, in which different pressure stages in the way of photoelectrons to the analyzer are achieved with the pressure difference maintained by a small aperture and extra pumps. This has signaled the birth of ambient-pressure XPS (AP-XPS).² Photoelectron spectroscopy provides the elemental composition of the surface and electronic state of each element at the surface (~10 nm) at high sensitivity (measured in parts per thousand).

Vibrational spectroscopy is more applicable to solid/liquid or solid/gas interfaces. Sum frequency generation (SFG) vibrational spectroscopy is exclusively surface sensitive because it requires the breaking of central symmetry that occurs only at the interface.³ Due to the exponential decay of the evanescent wave signal in ATR-FTIR, the IR beam’s penetration depth is very small (e.g., for a 45° angle with respect to the Ge prism, the penetration depth is ~500 nm), which makes it a good candidate for detecting chemical bonding and functional groups at surfaces and interfaces. The following sections are
devoted to the general features and working principles of the ATR-FTIR and XPS techniques.

2.1.1 ATR-FTIR

Infrared (IR) spectroscopy is an incisive and nondestructive technique for surface or interface characterization, which provides valuable information about chemical forces among atoms, vibrational frequencies of molecules, and motion of electrons. Chemical species at surfaces or interfaces can be identified with this tool, often including molecular functional groups. Because the absorption of IR radiation is only possible by the bonds of molecules, IR radiation can change the dipole moment. Such types of vibrational transitions involving the change of dipole moment are known as infrared transitions (Figure 2.1(a)). The Fourier transform (FT) process is a less intuitive method to obtain the same information. Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many frequencies of light, and measures the beam absorption by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. Fourier transform infrared (FTIR) spectrometers have revolutionized the measurement of IR spectra and allowed IR spectra to be used beyond structural elucidation. As a result, transmission, reflection, and even emission spectra can be measured much faster and with higher sensitivity than before.

At an interface between materials of different refractive index values, total internal reflection occurs in the high refractive index material when the incidence angle $\theta_i$ (measured from the surface normal) is greater than a critical angle $\theta_c$ (Figure 2.1(b)). In total internal reflection, the reflected light penetrates into the medium of lower refractive index by a distance equal to the light wavelength and the actual value depends on the ratio of the two refractive indices (Equation 2.1). Attenuated total reflection (ATR) is a spectroscopic technique which uses the interaction of photons at the internal surface of the crystal, known as the evanescent wave. Energy absorption by molecules at the external crystal surface can be determined by monitoring the loss of internal transmission and is wavelength dependent.

![Figure 2.1](image)

Figure 2.1 (a) Typical effective potential energy versus inter-nuclear separation, and (b) schematic of single-bounce ATR.
The ATR spectrum is similar to a transmission spectrum with a very short path length, because of the small penetration depth of the evanescent field into the rarefied medium.

\[ d_p = \frac{\lambda}{2\pi n_1 (\sin^2 \phi - n_{21}^2)^{1/2}} \]  

Eq. (2.1)

In Equation 2.1, \(d_p\) is the penetration depth, \(\lambda\) is the light’s wavelength, \(n_1\) is the refractive index of the crystal, \(\phi\) is the internal angle of incidence, and \(n_{21}\) is the refractive index ratio of the sample at the surface and the crystal. By varying the internal reflection crystal and the angle of incidence, chemical species along the depth direction, in the range from 0.1 μm to a few micrometers, can be detected.

2.1.2 XPS

The XPS relies on the photoelectric effect in which electrons are emitted from materials adsorbing photons of sufficiently high energy. X-rays from either metal anodes or synchrotron radiation are used as the excitation source for photoemission in XPS measurements. The kinetic energy of the ejected photoelectrons is measured. The corresponding binding energy of electrons in core levels or valence levels is given by

\[ E_B = h\nu - E_k - \Phi_a \]  

Eq. (2.2)

where \(\nu\) is the photon frequency, \(E_k\) is the electron kinetic energy, and \(\Phi_a\) is the analyzer work function. The binding energy of electrons at the Fermi level is set equal to zero. An XPS spectrum is constructed by plotting the number of photoelectrons detected per second as a function of binding energy.

![Figure 2.2 Schematic of the X-ray photoemission process and measurement of the kinetic](image)
energy of emitted photoelectrons.

The peaks in the XPS spectrum are used for elemental composition analysis (Figure 2.2). Core-electron binding energies are unique for each element; therefore, they can be used as a fingerprint in the analysis. Tiny changes in the chemical environment and oxidation state of a certain atom induce shifting of the core-binding energies (chemical shifts), even if the core orbitals are not involved in any bonding. The chemical shifts can be viewed as the influence of electron density change of the valence orbitals on the emitted photoelectron.\(^7\) XPS is a highly surface sensitive technique, where the analysis depth is limited by the shallow escape depth of the ejected photoelectrons. The escape depth of the photoelectrons can be estimated from the quantity \(\lambda_M \cos \theta\), where \(\lambda_M\) is the inelastic mean-free-path of an electron with kinetic energy \(E_k\), and \(\theta\) is the angle of emission of the electron from the surface normal. Thus, the detection depth can be decreased by reducing the kinetic energy and increasing the incidence angle.

2.2 Electrochemical measurements

2.2.1 Two- and three-electrode systems

Electrochemical characterization is crucial for all energy storage devices, since all of them involve transformation between chemical energy and electric energy. Often the interest is on the reactions occurring at the anode or the cathode. Electrochemical reactions can be studied with a simplified cell consisting of the electrode of interest, called the working electrode, and an electrode of known potential approaching ideal nonpolarizability, called the reference electrode. A potentiostat is used to adjust the voltage/current applied to the working-reference electrode pair. The two-electrode cell (Figure 2.3(a)) is used to measure the complete voltage dropped by the current across the whole electrochemical cell. It is applicable when measurement of the whole cell voltage is significant or the counter electrode potential is expected not to drift over the course of the experiment.

When the above conditions cannot be satisfied (e.g., large-scale electrolytic or galvanic cells and experiments involving non-aqueous solutions with low conductivities), it is preferred to use a three-electrode cell (Figure 2.3(b)). In this cell, the current is passed only between the working electrode and the counter electrode, while the potential changes of the working electrode are measured against the reference electrode alone. The device used to measure the potential difference between the working electrode and the reference electrode has high input impedance, so that the current drawn through the reference electrode is negligible. Consequently, its potential remains constant and is equal to the open-circuit value.
2.2.2 In-situ ATR-FTIR apparatus

With the in-situ ATR-FTIR apparatus, species are probed at the electrode surface and in a thin layer of solution near the surface. The most commonly used configurations of ATR-FTIR are schematically shown in Figure 2.4. In the external reflection mode, IR radiation passes through a window and a thin layer of solution, reflects on the electrode surface, and is detected (Figure 2.4(a)). The solution layer between the window and electrode must be thin, because most solvents are good absorbers of IR radiation. Even though the solution layer is thin, the absorbance of the species of interest is usually much smaller than that of the bulk solution; therefore, modulation or different techniques are often used to extract useful signals. Either the potential or the polarization of the incidence radiation can be modulated. The electronic field distortion and resistance increase caused by thin layer diffusion are major drawbacks of the internal reflection model (Figure 2.4(b)).
Figure 2.4 Schematics electro-chemical spectroscopy cells for (a) external reflection and (b) internal reflection.

When the IR beam is coupled to the film through the prism in internal reflection mode, the intensity of the optical field decays exponentially with distance into the solution away from the electrode surface; thus, this field is sensitive to thin layers at the interface. Stable adhesion between the working electrode and the prism is one of the biggest challenges in designing internal reflection mode systems, and the rigorous reaction of the working electrode may damage the expensive underlying prism. While the schematics shown in Figure 2.4 provide a general framework for the design of an in-situ ATR-FTIR apparatus, specific design modifications are needed for different experiments.

2.3 References

Chapter 3 – Effect of strong metal support interaction on electrochemical catalyst

This chapter focuses on tuning the electronic structure of the titanium oxide TiO$_2$ support of Pt nanoparticle catalysts (by adding oxygen vacancies or doping with fluorine). About two times higher activity and three times higher stability in methanol oxidation reaction, 0.12 V negative shift of the CO oxidation peak potential, and 0.07V positive shift of the oxygen reaction potential compared to Pt nanoparticles on pristine TiO$_2$ support were achieved. Experimental trends are interpreted in the context of an electronic structure model, showing an improvement in electrochemical activity when the Fermi level of the support material in Pt/TiO$_x$ systems is close to the Pt Fermi level and the redox potential of the reaction. The approach presented in this chapter provides guidance for the selection of the support material of Pt/TiO$_x$ systems and may be applied to other metal-oxide support materials, thus having direct implications in the design and optimization of fuel cell catalyst supports.

3.1 Introduction

Noble metal nanoparticles are widely used in heterogeneous catalysis. To satisfy different reaction requirements, the most commonly used technique is to fabricate bimetallic particles. An optimum electronic state can be achieved for certain reactions by adjusting the d-band energy of the bimetallic catalyst, e.g., Pt Ru for methanol (CH$_3$OH) oxidation reaction (MOR) and Pt Co for oxygen reduction reaction (ORR). Recent research has shown that the catalytic behavior of metallic nanoparticles dispersed on a metal oxide support, which is usually inert by itself, can be significantly enhanced by the oxide support, a widely known phenomenon which is loosely referred to here as the strong metal support interaction (SMSI) effect.

Metal oxides, TiO$_2$ in particular, have been used as supports of metal nanoparticles, such as Pt, Au, and Pd, because of their superior chemical stability under reducing and oxidizing conditions. However, the use of these metal oxides as electrocatalysts is limited by their intrinsic low electrical conductivity. It is therefore essential to design the structure of the catalyst so that to reduce undesirable side effects due to the low electrical conductivity and poor interaction between the active Pt nanoparticles and the TiO$_x$ support. Metallic or semiconducting behavior has been observed by reducing the metal oxide or doping it with other metal cations. While all of these approaches have shown that metal oxides are promising candidates for electrocatalyst supports, a systematic screening of potential semiconductor materials for electrochemical catalysis is still lacking.
Significantly enhanced electrocatalytic performance in important fuel cell reactions was achieved in this study via oxide support modification by either adding oxygen vacancies or doping with fluorine. Both of these methods adjust the electronic structure of the titanium oxide support, producing high electronic conductivity. As a result, the MOR activity and stability increase by a factor of 1.75 and 2.7, respectively, relative to Pt nanoparticles on pristine TiO$_2$ support, the peak potential of CO oxidation is negatively shifted by 0.12 V, while the ORR potential is positively shifted by 0.07 V. An electronic structure model is developed by considering the combined effects of the support material Fermi level, the Pt Fermi level, and the redox potential of the reaction.

3.2 Experimental

3.2.1 Catalyst sample preparation

Two different stoichiometric titanium oxide (i.e., TiO$_{1.9}$ and TiO$_2$) substrates were synthesized as previously described.$^{21-23}$ However, polished Ti plates were used in this study as support material instead of a Si wafer. Thin films consisting of TiO$_x$ were deposited by dc magnetron sputtering. The oxygen vacancy concentration of the highly oxygen deficient sputtered films was tuned by rapid thermal annealing in O$_2$ at various temperatures. All of the samples were first annealed in N$_2$ to minimize variation in grain size. TiO$_x$ films of two different stoichiometries (TiO$_2$ and TiO$_{1.9}$) were prepared for this study. Fluorine doping was accomplished by plasma treatment in N$_2$ gas and trace amounts of sulfur hexafluoride (SF$_6$). This treatment yielded two fluorine-doped TiO$_x$ surfaces (designated as TiO$_{1.9}$+F and TiO$_2$+F) with different amounts of O vacancies.

Platinum films were electroplated using 0.5M chloroplatinic acid (H$_2$PtCl$_6$) as the precursor and 0.1M KCl as the support electrolyte. Electroplating was accomplished by performing 10 cycles of potentials can between –0.1 and –0.9V (vs. SCE) at a rate of 50 mV/s using differently treated TiO$_x$ substrates. Loading of Pt was controlled by the number of scan cycles. The lower and upper bound of the cyclic voltammetry affected the size and dispersion of the Pt nanoparticles.$^{24}$ The same electroplating conditions were used for all substrate materials.

3.2.2 Surface Characterization and Electrochemical Measurement

The surface morphology of the Pt nanoparticles on different substrates was examined with a scanning electron microscope (SEM, JEOL, JSM-6700F). The structure and size distribution of the nanoparticles were measured with a transmission electron microscope (TEM, JEOL, JEM-3000F). TEM samples were prepared by removing the Pt film from the Ti substrate with a pair of dissecting forceps in the presence of a small amount of ethanol and then placing the Pt film onto a copper grid and drying in air at room temperature.

Stoichiometries of the TiO$_x$ films were determined from X-ray photoelectron spectroscopy (XPS) spectra obtained with a PHI 5400 ESCA/XPS system (Physical Electronics) equipped with an Al-Ka X-ray source of energy 1486.6 eV. The energy resolution for each point is 0.1 eV. All of the binding energies were calibrated to the C1s
core-level peak. Ti 2p and F 1s core-level XPS spectra of undoped and F-doped TiO$_x$ films used as supports in the present study.

Electrochemical measurements were obtained with a CHI 660D electrochemistry work station connected to a three-electrode cell system (see Figure 3.1). The working electrode consisted of a thin Pt film deposited on a TiO$_x$ substrate and was vertically placed in the cell, while the counter and reference electrodes consisted of Au foil and Ag/AgCl, respectively. However, all reported potentials are referred to a saturated calomel electrode (SCE) or a normal hydrogen electrode NHE (only for ORR and hydrogen evolution reaction (HER)). To avoid different surface resistance effects, iR-compensation correction was used in all electrochemical experiments. The electrolyte consisted of de-aerated (by purging high-purity N$_2$ gas) 0.5M H$_2$SO$_4$ with or without 0.5 M CH$_3$OH, 0.5M H$_2$SO$_4$ saturated with CO, or 0.5M H$_2$SO$_4$ saturated with O$_2$. High-purity chemicals, gases, and H$_2$O (~18M) were used in all the electrochemical experiments, which were performed at room temperature (25 ± 1 °C).

![Figure 3.1 Photograph of the three-electrode electrochemical cell.](image)

### 3.3 Results and Discussion

#### 3.3.1 Material characterization

Figure 3.2(a) shows a plane-view SEM image of as-prepared Pt nanoparticles deposited on a TiO$_{1.9}$ substrate. The nanoparticles demonstrate cluster-like morphology of relatively uniform size distribution (15–20 nm) and good dispersion on the substrate surface. Figure 3.2(b) shows a bright-field TEM image of the Pt nanoparticles (dark) deposited onto the TiO$_{1.9}$ substrate. The lattice fringe of the Pt (111) plane (2.3 Å) measured from the high-resolution TEM (HRTEM) image shown in Figure 3.2(c) and the TiO$_2$ anatase (101) plane (3.5 Å) indexed in Figure 3.2(b) indicate the formation of
polycrystalline Pt nanoparticle clusters on the TiO$_{1.9}$ substrate. These TEM images reveal that Pt nanoparticles of ~5 nm average size clustered and adhered to the TiO$_{1.9}$ substrate, producing a polycrystalline Pt structure. The stoichiometric ratios of substrates were confirmed from the Ti$^{3+}$-to-Ti$^{4+}$ ratio obtained from the Ti 2p X-ray photoelectron spectroscopy (XPS) spectra in Figure 3.3(a). The Fluorine 1s XPS spectra of Fluorine doped TiO$_{1.9}$ and TiO$_2$ substrates are shown in Figure 3.3(b). Since differences in the morphology and polycrystalline structure of the Pt nanoparticles were not observed with other samples, SEM and TEM images of these nanoparticles are not shown here.

In view of the similar morphology and polycrystalline structure of the Pt nanoparticles synthesized on different TiO$_x$ substrates under the same conditions, differences in electrochemical performance among different samples (discussed in the following sections) are attributed to the SMSI effect.

The electrochemically active Pt surface area was characterized by cyclic voltammetry (CV) experiments performed at room temperature with different Pt/TiO$_x$ and Pt/TiO$_x$+F electrodes in sulfuric acid (H$_2$SO$_4$) solution, as shown in Figure 3.4(a). The electrodes were cycled between −0.2 and 1.2 V at a scan rate of 50 mV/s, while the electrolyte was continuously purged with Ar. A typical CV curve of polycrystalline Pt in the H-adsorption/desorption region and a similar double-layer capacitance were obtained with all Pt/TiO$_x$ samples. To normalize the activity in other reactions, the Pt surface area of different substrates was determined by integrating the H-adsorption/desorption interval, subtracting the double-layer charging current, and dividing the resulting Coulomb charge by 2 and 210 C/cm$^2$ (the charge to remove a monolayer of hydrogen from a platinum surface$^{25}$).
Figure 3.3 (a) Ti 2p and (b) F 1s XPS spectra of undoped and F-doped TiO$_{1.9}$, and TiO$_2$. Open circles are raw data, while curves present the results of a Gaussian deconvolution.

The roughness factor of different Pt/TiO$_x$ catalysts, defined as the ratio of the electrochemically active area (ECA) to the nominal electrode area, is given in Table 1. The similar roughness factor of the Pt catalyst on different TiO$_x$ substrates is due to the similar loading and structure of the Pt nanoparticles, as shown in SEM and TEM results (see Figure 3.2). The significantly higher ECA of the Pt/TiO$_x$ and Pt/TiO$_x$ +F catalysts than the typical two-dimensional Pt catalyst (Pt foil) may be attributed to the small size and good dispersion of the Pt nanoparticles. The absence of any other oxidation or reduction peak in the CV curves showed in Figure 1(a) indicates that the TiO$_x$ and TiO$_x$ +F substrates are electrochemically stable in acidic solutions and oxidative environments.

3.3.2 Electrochemical oxidation of methanol and CO

MOR CV curves obtained at room temperature with Pt/TiO$_x$ and Pt/TiO$_x$ +F electrodes in an aqueous solution of 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ revealed a much higher current density for the Pt/TiO$_{1.9}$ electrode than any other electrode Figure 3.4(b). The CH$_3$OH electro-oxidation positive-scan peak of the Pt/TiO$_{1.9}$ electrode was at ~0.64 V with a 0.28 V onset potential (defined as the potential corresponding to a 0.1 mA/cm$^2$ current density). In the case of the Pt/TiO$_{1.9}$ + F, Pt/TiO$_2$, and Pt/TiO$_2$ + F electrodes, the anodic peak potential was observed at 0.64, 0.66, and 0.65 V and the corresponding onset potential was equal to 0.35, 0.48, and 0.41 V, respectively. Considering the significance of lower onset potential and higher peak current density in MOR, the TiO$_{1.9}$ substrate with oxygen vacancies shows the best electrochemical performance, while the TiO$_2$+F substrate is ranked third among all samples. However, both treatments enhance the catalytic performance compared to the Pt/TiO$_2$ electrode.
Chronoamperograms of the electroactivity of the four electrodes in a 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ aqueous solution were obtained at room temperature. At an oxidation potential of 0.5 V (vs. SCE), a gradual decrease in MOR electroactivity with increasing time and a strong dependence of the rate of current density decrease on the type of TiO$_x$ substrate can be observed in Figure 3.4(c). The Pt/TiO$_{1.9}$ electrode shows the smallest decrease in current density, while the electron density corresponding to the Pt/TiO$_2$ electrode shows a decrease by 50% within 1000 s. The higher current density of the Pt/TiO$_{1.9}$ electrode may be attributed to the increased CO tolerance, i.e., CO can be effectively oxidized and removed from the surface of the Pt nanoparticles.

Voltammetry experiments of pre-adsorbed CO were performed with a 0.5 M H$_2$SO$_4$ electrolyte (purged with N$_2$ for 30 min at 0 V after CO adsorption) using a scan rate of 10 mV/s. The CO stripping voltammograms indicate that the Pt/TiO$_{1.9}$ electrode exhibits the highest CO tolerance. The Pt/TiO$_{1.9}$ peak potential (0.43 V vs. SCE) shows a negative shift of 0.12 V relative to Pt/TiO$_2$ (0.55 V vs. SCE).

Since the same electro-deposition method was used to prepare all Pt nanoparticle catalysts and differences between the catalysts were not visible in the SEM and TEM results, implying no influence of other factors (e.g., Pt nanoparticle size or treatment conditions) on the CO oxidation peak, the peak shifting is attributed to the SMSI effect. Since CO is an important intermediate product, its oxidation capability significantly influences the activity of the MOR. With CO more effectively oxidized and removed from the Pt surface, better electro-catalysis performance will be achieved, which is in good agreement with the present result that both the peak current density, and the long-term test current density increase as CO oxidation peak potential decreases. Detailed information about the roughness factor, peak current density $i_p$, current density after 3000 s of testing $i_{3000}$, MOR peak potential $U_{MOR}$, and peak potential of CO stripping $U_{CO}$ for the four electrodes and pure Pt foil are given in Table 3.1. The results shown in Figure 3.4 and Table 3.1 indicate an enhancement of the catalytic performance (i.e., activity, stability, and toxic tolerance) in the following electrode order: Pt < Pt/TiO$_2$ < Pt/TiO$_2$+F < Pt/TiO$_{1.9}$+F < Pt/TiO$_{1.9}$.

Table 3.1 Electrochemical characterization of Pt nanoparticles on different TiO$_x$ supports.

<table>
<thead>
<tr>
<th>System</th>
<th>Roughness factor$^{(a)}$ (cm$^2$/cm$^2$)</th>
<th>Current density (mA/cm$^2$)</th>
<th>Potential (V vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$i_p^{(b)}$</td>
<td>$i_{3000}^{(c)}$</td>
</tr>
<tr>
<td>Pt/TiO$_{1.9}$</td>
<td>13.3</td>
<td>1.40</td>
<td>0.38</td>
</tr>
<tr>
<td>Pt/TiO$_{1.9}$+F</td>
<td>14.1</td>
<td>1.10</td>
<td>0.24</td>
</tr>
<tr>
<td>Pt/TiO$_2$+F</td>
<td>12.9</td>
<td>0.97</td>
<td>0.23</td>
</tr>
<tr>
<td>Pt/TiO$_2$</td>
<td>12.1</td>
<td>0.80</td>
<td>0.14</td>
</tr>
<tr>
<td>Pt foil</td>
<td>3.1</td>
<td>0.48</td>
<td>0.05</td>
</tr>
</tbody>
</table>

$^{(a)}$ Specific mass area measured from the evolution of the hydrogen area.
(b) Normalized peak current density of the positive scan measured in 0.5 M methanol and 0.5 M H$_2$SO$_4$ (scan rate = 20 mV/s).
(c) Normalized current density measured by chronoamperometry after 3000 s at 0.5 V (vs. SCE).
(d) Peak position of methanol oxidation reaction in positive scan measured in 0.5 M methanol and 0.5 M H$_2$SO$_4$ (scan rate = 20 mV/s).
(e) Peak position of CO stripping (scan rate = 10 mV/s).

Figure 3.4 Cyclic voltammograms of (a) 0.5 M H$_2$SO$_4$ solution (scan rate= 50 mV/s) and (b) 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ solution (scan rate =20 mV/s), (c) current versus time measured at 0.5 V vs. SCE for 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ solution, (d) CO stripping voltammograms for 0.5 M H$_2$SO$_4$ solution (scan rate = 10 mV/s). (Arrows indicating upward and downward scanning are only shown for the Pt/TiO$_{1.9}$ electrode for clarity.)

3.3.3 Polarization curves

The substrate effect in small-molecule oxidation reactions of Pt catalysts and trend in catalyst performance demonstrated by the results shown in Figure 3.4 and Table 3.1 raise a question about whether a similar substrate effect and trends exist in reduction reactions, such as HER and ORR. To examine this prospect, HER and ORR polarization curves were obtained with different Pt/TiO$_x$ electrodes in N$_2$- or O$_2$- saturated aqueous solution of 0.5 M H$_2$SO$_4$ using a scan rate of 10 mV/s and stationary electrodes oriented vertically. The HER current-potential response shows weak correlation with substrate material seen in Figure 3.5(a). The absence of a substrate effect is attributed to the fast kinetics under room-
temperatures. However, the ORR polarization curves indicate a higher onset potential for Pt/TiO$_{1.9}$ and Pt/TiO$_{1.9}$+F electrodes compared to Pt/TiO$_2$+F and Pt/TiO$_2$ electrodes (Figure 3.5(b)). Based on the onset potential, the electrode performance under ORR conditions is ranked as Pt/TiO$_2$<Pt/TiO$_2$+F< Pt/TiO$_{1.9}$+F< Pt/TiO$_{1.9}$, which is the same with the ranking of small molecule oxidation reactions, i.e., MOR and CO oxidation.

![Figure 3.5](image.png)

Figure 3.5 Polarization curves of (a) hydrogen current in N$_2$-saturated electrolyte, and (b) ORR current in O$_2$-saturated electrolyte for different catalyst systems. The current was normalized by the apparent area (0.1964 cm$^2$) of the electrode. (scan rate = 10 mV/s, electrolyte = 0.5 M H$_2$SO$_4$).

### 3.3.4 Charge transfer mechanism

A model of the charge transfer mechanism in nonstoichiometric and F-doped stoichiometric TiO$_2$ can explain the SMSI effect observed in this study (Figure 3.6). TiO$_2$ has a band gap of 3.2 eV, while the work function of poly crystalline Pt is about 5.6–5.8 eV. Oxygen vacancies introduced in the lattice of TiO$_2$ produce energy levels in the band gap (mid-gap states) between 0.5 and 1.0 eV below the conduction band $E_c$. Because mid-gap states do not exist in stoichiometric TiO$_2$, fluorine acts as n-type dopant, producing donor states just below the conduction band (by $\sim k_BT$). The electronic structures of various substrates used in the present paper have been characterized previously. Both oxygen vacancies and fluorine doping generate a population of surface electrons available for conduction. In the case of F-doped titanium sub-oxide (TiO$_x$, $x < 2$), the primary effect of F is to passivate oxygen-vacancy defect states. However, because F doping can never fully passivate this sub-band, the remaining O vacancy states pin the Fermi level $E_F$. As a result, F doping produces an opposite effect in stoichiometric TiO$_2$ than reduced TiO$_x$. This contrasting effect of F-doping is reflected in the electrode performance trend, i.e., Pt/TiO$_2$ < Pt/TiO$_2$+F < Pt/TiO$_{1.9}$+F < Pt/TiO$_{1.9}$.

The charge transfer capability of a semiconductor electrode depends on the existence of an energy barrier. In the absence of an energy barrier, the behavior of a semiconductor electrode is similar to that of a metallic electrode because most of the charge carriers are available for charge transfer. However, in the presence of an energy barrier, only a few charge carriers are available for charge transfer, and reactions induced by electron transfer
are relatively slow.\textsuperscript{34-36} For non stoichiometric TiO\textsubscript{x}, the mid-gap states yield a relatively low Fermi level (5.0–5.5 eV), assisting in electron transfer among the electrode, the Pt catalyst (5.6–5.8 eV), and the electrolyte (4.44–5.67 eV) (Figure 3.6(a)). In contrast, because F-doped TiO\textsubscript{2} has a higher Fermi level (~4.5 eV) than TiO\textsubscript{x} (x < 2), an energy barrier (i.e. band bending) is produced to maintain equilibrium, which inhibits electron transfer and, in turn, reaction (Figure 3.6(b)). This explains the higher reactivity of TiO\textsubscript{1.9} than TiO\textsubscript{2}+Fin the lower redox potential reactions, i.e., MOR, ORR, and CO oxidation. However, for reactions with a high redox potential, such as HER (~4.44 eV, pH=1),\textsuperscript{15} all substrate surfaces exhibit a similar effect.

3.4 Conclusions

Two different methods, i.e., addition of oxygen vacancies and fluorine doping, were used in this study to modify the electronic structure of the titanium oxide TiO\textsubscript{2} support of Pt nanoparticle catalysts and systematically evaluate the resulting electrochemical activity. Among the reactions studied, only HER is support insensitive, while MOR shows an increase in activity and stability by a factor of 1.75 and 2.7, respectively, the CO oxidation peak shows a negative shift by 0.12 V, implying better anti-poisoning capability, and the ORR potential shows a positive shift by 0.07 V compared to Pt nanoparticles on pristine TiO\textsubscript{2} support.

To explain the observed trends, an electronic structure model of Pt/TiO\textsubscript{x} electrocatalyst systems was introduced. It shows that the electrochemical activity of the Pt nanoparticles is enhanced when the Fermi level of the support material is close to the Pt Fermi level and the redox potential of the reaction to facilitate electron transfer among the electrode, the Pt nanoparticles, and the electrolyte. The present approach provides guidance for selecting the support material of Pt/TiO\textsubscript{x} systems and can be applied to other metal-oxide support materials, affecting the design and optimization of new support materials of fuel cell catalysts.
Figure 3.5 Schematic of charge transfer mechanism in (a) non stoichiometric TiO\textsubscript{1.9} and (b) F-doped stoichiometric TiO\textsubscript{2}. Mid-gap states in TiO\textsubscript{1.9} produce a relatively low Fermi level, assisting electron transfer from the oxide to adsorbed species. However, in the case of F-doped TiO\textsubscript{2}, an energy barrier (band bending) is produced to maintain equilibrium, which inhibits electron transfer and, in turn, chemical reaction. (\(E_C\), \(E_F\), and \(E_V\) denote conduction, Fermi, and valence energy levels, respectively.)

3.5 References


Chapter 4 – Identification of diethyl 2,5-dioxahexane dicarboxylate (DEDOHC) and poly-ethylene carbonate (poly-EC) as decomposition products of ethylene carbonate-based electrolytes by Fourier transform infrared spectroscopy

The formation of passive films on electrodes due to electrolyte decomposition significantly affects the reversibility of Li-ion batteries (LIBs); however, understanding of the electrolyte decomposition process is still lacking. This chapter investigates the decomposition products of ethylene carbonate (EC)-based electrolytes on Sn and Ni electrodes by Fourier transform infrared (FTIR) spectroscopy. The reference compounds, diethyl 2,5-dioxahexane dicarboxylate (DEDOHC) and polyethylene carbonate (poly-EC), were synthesized and their chemical structures were characterized by FTIR spectroscopy and nuclear magnetic resonance (NMR). Assignment of the vibration frequencies of these compounds was assisted by quantum chemical (Hartree-Fock) calculations. The effect of Li-ion solvation on the FTIR spectra was studied by introducing the synthesized reference compounds into the electrolyte. EC decomposition products formed on Sn and Ni electrodes were identified as DEDOHC and poly-EC by matching the features of surface species formed on the electrodes with reference spectra. The results of this study demonstrate the importance of accounting for the solvation effect in FTIR analysis of the decomposition products forming on LIB electrodes.

4.1 Introduction

Li-ion batteries (LIBs) have been widely used for long-term energy storage in various applications ranging from portable electronics to hybrid vehicles. However, the chemical instability of the electrolyte during operation negatively affects the reliability and durability of LIBs. Ethylene carbonate (EC)-based electrolytes are most commonly used in LIBs due to their superior bulk ion conductivity and interfacial properties. Because of the higher dielectric constant of EC than that of linear carbonate co-solvents, EC is the primary molecule in the inner solvation shell of Li ions in EC-based electrolytes. Therefore, as an indispensable electrolyte component of state-of-art LIBs, EC plays an important role in the electrolyte decomposition process. Decomposition products are widely known to contain both organic and inorganic compounds, such as lithium alkyl carbonates (e.g., (CH2OCO2Li)2 and ROCO2Li), oxalate, alkoxides (e.g., ROLi and HCOLi), and other lithium salts (e.g., LiF, Li2CO3, and Li2O).

The present study is focused on two less known compounds, namely diethyl 2,5-dioxahexane dicarboxylate (DEDOHC) and a polymerized form of ethylene carbonate (poly-EC), both considered as decomposition products of EC-based electrolytes in LIBs. Yoshida et al. first reported the formation of DEDOHC in LIBs with 1 M of EC/DEC/LiPF6 (EC:DEC = 1:1 v/v) electrolyte. Other groups have detected the formation of DEDOHC using gas chromatography/mass spectroscopy, and storage tests have indicated DEDOHC catalysis by lithium alkoxide. Poly-EC has also been identified as a product of EC electrolyte degradation initiated by a Lewis acid, such as PF5.
4.1 shows proposed reduction pathways of DEDOHC and poly-EC, respectively. However, neither DEDOHC nor poly-EC has been detected either in situ or ex situ by Fourier transform infrared (FTIR) spectroscopy. This can be attributed to the lack of reference spectra for these compounds and the similar chemical structure of these compounds to that of solvent molecules. Therefore, reference spectra for chemical identification of electrolyte decomposition products in LIBs by FTIR spectroscopy are of paramount importance.

Electrochemical reduction of the electrolyte plays a critical role in electrolyte decomposition at the anode of LIBs, and individual ion solvation and ion pairing are important processes in reduction chemistry. Several theoretical and experimental studies have been carried out to determine the effect of Li-ion solvation on the FTIR spectra of electrolyte solvents and the electrolyte decomposition process. Although DEDOHC and poly-EC are not lithium compounds, lithium salt can be dissolved in these compounds. Therefore, it is essential that FTIR reference spectra include this solvation contribution. In this study, two important electrolyte decomposition products, DEDOHC and poly-EC, were synthesized and characterized by FTIR spectroscopy and nuclear magnetic resonance (NMR). The assignment of the vibration frequencies of these compounds was based on theoretical calculations and experimental findings. Reference spectra were acquired by introducing the synthesized pure compounds into different battery electrolyte environments, such as LiPF₆, EC/LiPF₆, and DEC/EC/LiPF₆. DEDOHC and poly-EC were identified as electrolyte decomposition products by matching the FTIR spectra of Sn and Ni electrode surfaces acquired after electrolysis to those of reference compounds, while accounting for the solvation effect.

4.2 Experimental

4.2.1 Reference compound synthesis

The synthesis of DEDOHC is shown in Scheme 4.2.
Scheme 4.2 Synthesis procedure of DEDOHC.

Anionic polymerization of EC follows a procedure that uses phosphazene base \( t-BuP_4 \) as shown in Scheme 4.3. The product is precipitated in diethyl ether to remove any unreacted monomer, dissolved in dichloromethane, and, finally, precipitated in diethyl ether. To obtain a pure product, this dissolution-precipitation process was repeated three times. All reagents and battery-grade EC (purchased from Sigma-Aldrich and BASF, respectively) were used without further purification.

Scheme 4.3 Synthesis procedure of poly-EC.

4.2.2 Reference compound Characterization and solvation effect Measurement

Proton and carbon NMR spectra of the synthesized products were collected with a 500-MHz NMR spectrometer (Biospin Advance II, Bruker). FTIR spectra were acquired in attenuated total reflection (ATR) mode with a spectrometer (Nicolet Nexus 670 Fourier) equipped with a broad band mercury-cadmium-telluride detector. Spectra were acquired with a 4 cm\(^{-1}\) resolution and summed over 512 scans. Details about ATR-FTIR spectrum analysis can be found elsewhere.\(^{21,22}\) The electrolytes used in this study are 1 M EC/DEC/LiPF\(_6\) (diethyl carbonate) (Novolyte Technologies, BASF) with EC: DEC = 1:2 v/v, in which either DEDOHC or poly-EC were dissolved (1:5 v/v), hereafter referred to as DEDOHC/EC/DEC/LiPF\(_6\) and poly-EC/EC/DEC/LiPF\(_6\), respectively. These electrolyte samples were then dried in a glove box to remove DEC from the mixtures. Hereafter, these samples will be referred to as DEDOHC/EC/LiPF\(_6\) and poly-EC/EC/LiPF\(_6\), correspondingly. LiPF\(_6\) salt was added to the synthesized compounds (~1 M), referred to as DEDOHC/LiPF\(_6\) and poly-EC/LiPF\(_6\). Electrolyte decomposition product-to-electrolyte ratios were chosen to be sufficiently high (~20% v/v) to facilitate the identification of new
features in the electrolyte background spectrum. EC/LiPF₆ and EC were used as control samples. The samples were handled under an inert atmosphere without any exposure to the ambient air.

4.2.3 Ex-situ FTIR measurements

A single compartment Teflon cell with two electrodes was used to perform Sn foil electrochemical experiments. Li metal electrodes were used as both counter and reference electrodes, whereas Sn foil (99.99%, Sigma-Aldrich) was used as working electrode. All potentials reported herein are referred to the Li/Li⁺ redox couple. All electrochemical cells were assembled in an Ar filled glove box (water and oxygen contents were <10 ppm). In the ex-situ FTIR experiments, the Sn electrode was twice cycled between 0 and 2 V at a rate of 1 mV/s. In all the experiments, the emersion potential was set at 2 V. FTIR spectra were acquired in ATR mode directly from the electrode surfaces after DMC rinsing to remove any residual bulk electrolyte. After the evaporation of the volatile electrolyte component DEC in the glove box and rinsing with DMC, the anodes were directly transferred to the N₂-purged sample cavity of the FTIR spectrometer. Details about ex-situ ATR-FTIR analysis can be found in previous publications.²¹-²³ Experiments involving the Ni foil and associated FTIR spectra are quoted from a previous study.⁴

4.2.4 Computational methods

Ab initio quantum chemical calculations were performed with Gaussian 09²⁴ at the Hartree-Fock (HF) theory level with a 6-31+G(d, p) basis set. Before performing frequency calculations, the molecular structure was optimized at the same theory level and with the basis set. Systematic error in the calculated vibrational frequencies at the HF-level was corrected by an empirical scaling factor of 0.8929.²⁵

4.3 Results and discussion

4.3.1 Structure identification of synthesized DEDOHC and poly-EC

Figures 4.1(a) and (b) respectively show ¹H and ¹³C NMR spectra of the synthesized DEDOHC collected from a suspension in CDCl₃-d. (Hereafter, atoms associated with a particular peak will be designated as underlined.) The high molecular symmetry of DEDOHC produces fairly simple ¹H and ¹³C spectra. The triplet at 1.31 ppm indicates a –CH₂–CH₃ substructure, the quartet at 4.19 ppm represents a characteristic split pattern and proton position of the –O–CH₂–CH₃ substructure, and the triplet at 4.38 ppm indicates a –O–CH₂–O– substructure (Figures 4.1(a)). Peak area integration further confirmed the former substructures with a proton ratio of 3:2:2. ¹³C NMR detected four nonisotropic ¹³C nuclei located at 14.22 ppm (–CH₃), 64.81 ppm (–O–CH₂–CH₃), 65.13 ppm (–O–CH₂–CH₂–O–), and 155.03 ppm (–C(O)–) (Figures 4.1(b)). The –C(O)– carbon at 155.03 ppm shows relatively lower abundance than the other carbons because it is an sp²-hybridized carbon peak.
Figure 4.1 (a) $^1$H and (b) $^{13}$C NMR spectra of DEDOHC, and (c) $^1$H and (d) $^{13}$CNMR spectra of poly-EC collected in CDCl$_3$-$d$. Solvent signals arising from proton residuals due to incomplete deuteration are denoted by an asterisk (*).

Figures 4.1(c) and (d) respectively show $^1$H and $^{13}$C NMR spectra of the synthesized poly-EC collected from a suspension in CDCl$_3$-$d$. As the molecular structure shows (Scheme 4-2), the polymerized form of EC is actually a copolymer of alkyl carbonate and ethylene oxide functional groups. The triplet at 3.63 ppm represents a $-\text{C(O)}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-$ substructure, and the triplets at 3.72 and 4.31 ppm correspond to $-\text{C(O)}-\text{O}-\text{CH}_2-\text{C}_\text{H}_2-$ and $-\text{C(O)}-\text{O}-\text{CH}_2-$ substructures, respectively (Figures 4.1(c)). Peak area integration further confirmed the former substructures with a proton ratio of 1:1:1. Although poly-EC was extensively washed to remove the residual monomers and initiator, a small amount of the monomer was left on the product, as indicated by the signal at 4.57 ppm, assigned to the $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ substructure of the EC monomer. $^{13}$C NMR identified four non isotropic $^{13}$C nuclei located at 66.22 ppm ($-\text{C(O)}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-$), 66.81 ppm ($-\text{C(O)}-\text{O}-\text{CH}_2-\text{CH}_2-$), 69.13 ppm ($-\text{C(O)}-\text{O}-\text{CH}_2-$), and 152.23 ppm ($-\text{C(O)}-\text{O}-\text{CH}_2-$) (Figure. 4.1(d)). The $-\text{C(O)}-$ carbon at 155.23 ppm shows a relatively lower abundance than the other carbons because it is an $sp^2$-hybridized carbon peak. All chemical shifts of $^1$H and $^{13}$C nuclei are given in Table 4.1.
Table 4.1 Chemical shifts in $^1$H and $^{13}$C NMR spectra of synthesized DEDOHC and poly-EC collected from a suspension in CDCl$_3$-$d$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^1$H (ppm)</th>
<th>$^{13}$C (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDOHC</td>
<td>4.31 (t, 4H), 4.18 (q, 4H), 1.28 (t, 6H)</td>
<td>154.6, 65.1, 64.8, 14.2</td>
</tr>
<tr>
<td>poly-EC</td>
<td>4.31 (t, 2H), 3.72 (t, 2H), 3.63 (2H)</td>
<td>152.2, 69.1, 68.8, 66.2</td>
</tr>
</tbody>
</table>

Figure 4.2 FTIR spectra of synthesized (a) DEDOHC, and (b) poly-EC.

Figures 4.2(a) and (b) show FTIR spectra of synthesized pure DEDOHC and poly-EC, respectively. To aid the interpretation of the spectra, vibrational frequencies of the compounds were obtained from $ab$ $initio$ quantum chemical calculations. Calculated and experimental frequencies of pure DEDOHC and poly-EC are given in Tables 4.2 and 4.3, respectively.
Tables 4.2 Comparison of experimental and calculated vibrational frequencies of DEDOHC.

![Diagram of DEDOHC molecule]

<table>
<thead>
<tr>
<th>Experimental (cm⁻¹)</th>
<th>Relative intensity(a)</th>
<th>Calculated (cm⁻¹)</th>
<th>Relative intensity(b)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2986</td>
<td>vww</td>
<td>3004</td>
<td>0.02</td>
<td>C(7)H₂ asymmetric stretch</td>
</tr>
<tr>
<td>2944</td>
<td>vww</td>
<td>2968</td>
<td>0.045</td>
<td>C(1)H₂ and C(2)H₂ asymmetric stretch</td>
</tr>
<tr>
<td>2913</td>
<td>vww</td>
<td>2930</td>
<td>0.046</td>
<td>C(1)H₃ asymmetric stretch, C(2)H₂ symmetric stretch</td>
</tr>
<tr>
<td>2878</td>
<td>vww</td>
<td>2863</td>
<td>0.015</td>
<td>C(1)H₃ symmetric stretch</td>
</tr>
<tr>
<td>1744</td>
<td>m</td>
<td>1696</td>
<td>0.76</td>
<td>C(4)=O(5) stretch</td>
</tr>
<tr>
<td>1447</td>
<td>w</td>
<td>1419</td>
<td>0.015</td>
<td>C(1)H(1) bending stretch (umbrella)</td>
</tr>
<tr>
<td>1379</td>
<td>w</td>
<td>1340</td>
<td>0.04</td>
<td>C(4)H(3) wagging</td>
</tr>
<tr>
<td>1278, 1234</td>
<td>s</td>
<td>1244</td>
<td>1.00</td>
<td>O(3)–C(4)–O(6) asymmetric stretch, C(2,7)H₂ wagging</td>
</tr>
<tr>
<td>1092</td>
<td>vww</td>
<td>1102</td>
<td>0.16</td>
<td>O(3)–C(4)–O(6) symmetric stretch</td>
</tr>
<tr>
<td>1031, 1006</td>
<td>w</td>
<td>1010</td>
<td>0.13</td>
<td>C(1)–C(2) stretch</td>
</tr>
<tr>
<td>857</td>
<td>w</td>
<td>850</td>
<td>0.05</td>
<td>O(6)–C(4)–O(5)–O(3) out-of-plane bending</td>
</tr>
</tbody>
</table>

(a) The relative intensity in the experimental spectrum is denoted as very weak (vww), weak (w), medium (m), and strong (s).

(b) The relative intensity in the calculated spectrum is obtained by normalizing with the strongest peak signal.
Table 4.3 Comparison of experimental and calculated vibrational frequencies of poly-EC.

<table>
<thead>
<tr>
<th>Experimental (cm⁻¹)</th>
<th>Relative intensity(a)</th>
<th>Calculated (cm⁻¹)</th>
<th>Relative intensity(b)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2948</td>
<td>w</td>
<td>2914</td>
<td>0.15</td>
<td>C(7)H₂ and C(8)H₂ asymmetric stretch</td>
</tr>
<tr>
<td>2872</td>
<td>w</td>
<td>2872</td>
<td>0.11</td>
<td>C(7)H₂ and C(5)H₂ symmetric stretch</td>
</tr>
<tr>
<td>1743</td>
<td>m</td>
<td>1700</td>
<td>0.2</td>
<td>C(1)≡O(2) stretch</td>
</tr>
<tr>
<td>1453, 1392, 1352</td>
<td>w</td>
<td>1394</td>
<td>0.066</td>
<td>C(4,5,7,8)H₂ wagging</td>
</tr>
<tr>
<td>1259</td>
<td>s</td>
<td>1276</td>
<td>1</td>
<td>O(3)–C(1)–O(3′) asymmetric stretch, C(4,5)H₂ wagging</td>
</tr>
<tr>
<td>1103 (wide)</td>
<td>m</td>
<td>1120</td>
<td>0.78</td>
<td>C(5)–O(6)–C(7) asymmetric stretch</td>
</tr>
<tr>
<td>1092</td>
<td>w-m</td>
<td>1105</td>
<td>0.02</td>
<td>O(3)–C(1)–O(3′) symmetric stretch</td>
</tr>
<tr>
<td>948</td>
<td>w</td>
<td>940</td>
<td>0.074</td>
<td>C(10)–C(11) stretch and C(4)–O(3) stretch</td>
</tr>
<tr>
<td>859</td>
<td>w</td>
<td>840</td>
<td>0.06</td>
<td>O(6)–C(4)–O(5)–O(3) out-of-plane bending</td>
</tr>
</tbody>
</table>

(a) The relative intensity in the experimental spectrum is denoted as very weak (vw), weak (w), medium (m), and strong (s).

(b) The relative intensity in the calculated spectrum is obtained by normalizing with the strongest peak signal.

Table 4.4 Characteristic vibration frequencies of DEDOHC and poly-EC and corresponding group frequency assignments

<table>
<thead>
<tr>
<th>Group frequency assignment</th>
<th>Wavenumber (cm⁻¹)</th>
<th>DEDOHC</th>
<th>poly-EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkyl asymmetric or symmetric stretch</td>
<td>2986, 2944, 2913, 2878</td>
<td>2948, 2872</td>
<td></td>
</tr>
<tr>
<td>C=O stretch</td>
<td>1744</td>
<td>1743</td>
<td></td>
</tr>
<tr>
<td>O–C–O asymmetric stretch</td>
<td>1278, 1234</td>
<td>1259</td>
<td></td>
</tr>
<tr>
<td>C–O–C stretch (ether structure)</td>
<td>–</td>
<td>1103 (wide)</td>
<td></td>
</tr>
<tr>
<td>O–C–O–O out-of-plane bending</td>
<td>857</td>
<td>859</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.4 gives characteristic vibrational frequencies and corresponding group frequency assignments. The vibrational mode at ~1744 cm$^{-1}$ is characteristic of the delocalized carbonyl group C=O stretch mode, whereas vibrational modes at ~1234, 1278, and 1259 cm$^{-1}$ are attributed to the O–C–O asymmetric stretch mode. The small peaks at 2986 and 2948 cm$^{-1}$ are assigned to the CH$_2$ asymmetric stretch, whereas the peak at 2872 cm$^{-1}$ is due to the CH$_2$ symmetric stretch. The weak vibrational mode at ~857 cm$^{-1}$ originates from the out-of-plane bending mode of the carbonate O–C–O–O group. All of these stretch modes are common to DEDOHC and poly-EC; however, what mainly distinguishes the FTIR spectra of these two compounds is the ether structure C–O–C vibration stretch at 1103 cm$^{-1}$, which is only present in the FTIR spectrum of the poly-EC.

4.3.2 Analysis of the solvation effect on the DEDOHC and poly-EC FTIR spectra

The FTIR spectra of the synthesized standard compounds are of great importance to the identification of the electrolyte decomposition products under both in-situ and ex-situ experimental conditions. The spectra of organic compounds can be significantly affected by solvents and ions of the battery electrolyte, collectively referred to as the solvation effect. To investigate this effect on the FTIR spectra of the reference compounds, DEDOHC and poly-EC were introduced in the electrolyte, and FTIR spectra were acquired under conditions identical to those of in-situ and ex-situ experiments. FTIR spectra of DEDOHC, DEDOHC/LiPF$_6$, DEDOHC/EC/LiPF$_6$, and DEDOHC/EC/DEC/LiPF$_6$ in the ranges of 2700–3100 and 800–2000 cm$^{-1}$ are respectively shown in Figures 4.3(a) and (b). A salient peak at ~840 cm$^{-1}$ is observed for all electrolytes containing the LiPF$_6$ salt except for pure DEDOHC.

Quantum mechanical calculations show that free perfluorate anion (PF$_6^-$) with O$_6$ symmetry gives rise to two IR active modes at 860 and 540 cm$^{-1}$ and the PF$_6^-$ vibration in the electrolyte is sensitive to the solvent environment (for the EC-based electrolyte, the PF$_6^-$ vibration is observed at ~840 cm$^{-1}$). Additional spectral features attributed to the presence of LiPF$_6$ are the carbonyl group (C=O) stretching mode at ~1718 cm$^{-1}$ and the shifting of the peaks at 1316 and 1238 cm$^{-1}$ (O–C–O stretch). Compared to the FTIR spectrum of Li ion-free DEDOHC, Li solvation weakens the C=O bond and strengthens the C–O bond, resulting in red and blue shifting of the C=O and O–C–O vibrational stretches, respectively. The change in bond energy may be due to different factors, including electron redistribution, Coulombic interaction, and mechanical renormalization. Collectively, the spectral features attributed to the addition of the LiPF$_6$ salt into the DEDOHC reflect interactions between solvent molecules and ions, which are consistent with the findings of previous studies of electrolyte solvents. The addition of both EC and LiPF$_6$ in DEDOHC causes the O–C–O stretch to shift to a higher wavenumber, i.e., from 1238–1316 cm$^{-1}$ to 1253–1316 cm$^{-1}$ ranges, which may be attributed to co-solvation of EC and DEDOHC by Li ions. Because of the similarity of the DEDOHC and DEC spectra, it is difficult to distinguish the DEDOHC peaks in the spectrum of DEDOHC/EC/DEC/LiPF$_6$; however, the variation of the relative intensity may be used as an indicator because IR is linear vibrational spectroscopy.
The effect of Li-ion solvation on the FTIR vibration spectrum of poly-EC was investigated by adding poly-EC to EC/DEC/LiPF₆, EC/LiPF₆, and LiPF₆. Figures 4.3(c) and (d) show FTIR spectra of pure (i) poly-EC, (ii) poly-EC/LiPF₆, (iii) poly-EC/EC/LiPF₆, and (iv) poly-EC/EC/DEC/LiPF₆. Changes in the poly-EC spectra include vibrational frequency shifts due to the solvation effect, similar to those observed with DEDOHC, such as a new band on the low-frequency side of the carbonyl group C=O vibration at 1720 cm⁻¹ and the high-frequency side of the carbonate group O–C–O asymmetric stretch at 1302 cm⁻¹. An additional change in the FTIR spectrum of poly-EC containing the LiPF₆ salt is the blue shift of the alkyl group of the C–H stretch at 2887 cm⁻¹. Poly-EC/EC/LiPF₆ demonstrates the same shifts as poly-EC/LiPF₆, only the relative intensity is different; however, poly-EC/EC/DEC/LiPF₆ shows a combination of Li ion solvation and co-solvent effects.

![Figure 4.3 FTIR spectra of (a, b) DEDOHC and (c, d) poly-EC for different Li-ion solvation conditions. (i) pure compound (i.e., DEDOHC or poly-EC); (ii) compound with 1 M LiPF₆; (iii) compound mixed with EC/LiPF₆; (iv) compound mixed with EC/DEC/LiPF₆. (The wavenumbers given correspond to the neighboring peak positions indicated by dashed lines.)](image)

Figure 4.3 FTIR spectra of (a, b) DEDOHC and (c, d) poly-EC for different Li-ion solvation conditions. (i) pure compound (i.e., DEDOHC or poly-EC); (ii) compound with 1 M LiPF₆; (iii) compound mixed with EC/LiPF₆; (iv) compound mixed with EC/DEC/LiPF₆. (The wavenumbers given correspond to the neighboring peak positions indicated by dashed lines.)

Figures 4.4 shows that the intensity of the peak at 1744 cm⁻¹ is much higher than that of the two neighboring C=O vibration peaks in the DEDOHC/EC/DEC/LiPF₆ spectrum compared to the EC/DEC/LiPF₆ spectrum, indicating the presence of DEDOHC. This
indicator provides an important and unique means of *in-situ* FTIR distinction of the DEDOHC from the DEC.

![FTIR spectra](image)

Figures 4.4 FTIR spectra of DEDOHC, DEC, EC/DEC, EC/DEC/LiPF$_6$, and DEDOHC/EC/DEC/LiPF$_6$. (Wavenumbers given correspond to neighboring peak positions indicated by dashed lines.)

### 4.3.3 Analysis of surface species on Sn and Ni electrodes

The Sn electrode was swept from 2 to 0 V at a scan rate of 1 mV/s for two cycles in 1 M EC/DEC/LiPF$_6$ electrolyte with EC:DEC = 1:2 v/v. Cyclic voltammetry results are shown in Fig. S3 (Supporting Information). Figure 4.5 shows FTIR spectra of electrolyte decomposition species formed on the Sn foil. The product on the Sn foil surface is mainly DEDOHC with Li ion solvated (1744 and 1316 cm$^{-1}$), although residual electrolyte EC/LiPF$_6$ is also detected (doublet peaks at ~1804 and 1769 cm$^{-1}$ in the spectrum shown in Figure 4.6. Details about the absorption bands of the residual electrolyte, including complete assignments, can be found elsewhere.\(^{21}\) Li solvation causes the O–C–O vibration peak in the DEDOHC spectrum to shift from 1278 cm$^{-1}$ to 1316 cm$^{-1}$, which matches the new surface species feature on the Sn electrode. Moreover, a recent *in-situ* FTIR study\(^{30}\) has shown a progressive intensification of the peak at 1744 cm$^{-1}$ (characteristic of the DEDOHC) in the Sn electrode spectrum, which is consistent with the result of the present study derived from *ex-situ* FTIR analysis. These findings confirm that the unstable product detected on the Sn electrode surface in previous studies is DEDOHC.\(^{29,30}\) Without considering the Li ion solvation effect, it would be difficult to identify DEDOHC as an electrolyte decomposition product by IR techniques.
Figure 4.5 FTIR spectra of (a) C–H, and (b) C–O region of a Sn electrode cycled between 0 and 2 V as well as reference spectra of (i) DEDOHC, (ii) DEDOHC/LiPF$_6$, and (iii) DEDOHC/EC/LiPF$_6$. (The potentials are referred to the Li/Li$^+$ redox couple. The wavenumbers given correspond to neighboring peak positions indicated by dashed lines.)

Figure 4.6 FTIR spectra of EC/LiPF$_6$ and EC. (Wavenumbers given correspond to neighboring peak positions indicated by dashed lines.)

In a previous study,$^4$ a Ni electrode was swept from an open circuit voltage (OCV) of 2.9 V to a voltage of 0.5 V, followed by a reverse scan from 0.5 to 2.5 V at a scan rate of 1 mV/s in a 1.2 M EC/EMC/LiPF$_6$ (with EC:EMC = 3:7 w/w) electrolyte. From a comparison of the FTIR spectrum of the Ni electrode cycled between 0.5 and 2.5 V (Ni(1)
spectrum in Figure 4.7) to that of synthesized lithium ethylene dicarbonate (LiEDC), the main surface species identified on the Ni electrode is LiEDC (1663 cm$^{-1}$).

Because Li metal deposition does not occur in this potential range, it may be inferred that LiEDC is a product of the electrochemical reduction of EC in the electrolyte, not a product of the chemical reaction of EC with freshly deposited Li. When the lower potential of cycling was changed to −0.5 V to induce the deposition of metal Li, the same product was observed but with a higher intensity (Ni (2) spectrum in Figure 4.7). However, after a total of nine cycles of scanning between −0.5 and 2.5 V (Ni(3) spectrum in Figure 4.7), the FTIR spectrum of the Ni electrode shows a broadening of the peak at ~1103 cm$^{-1}$, a shoulder at 1302 cm$^{-1}$, and dramatic changes in the multiple C–H stretching bands in the 2800–3200 cm$^{-1}$ range, which can be attributed to the formation of poly-EC after long-term cycling. Although the synthesized poly-EC may not have exactly the same ratio as the electrolyte decomposition products and the ratio of the carbonate to ethylene oxide segments could affect the relative intensities of the C=O and C–O stretches, the positions of the vibrational frequencies will be essentially the same. The kinetics of EC polymerization may be expected to be much slower than the kinetics of LiEDC reduction, as indicated by these experimental results (i.e., relative changes among Ni(1), Ni(2), and Ni(3) spectra in Figure 4.7). In the previous study from which the ex-situ IR spectra of the Ni electrode were obtained, poly-EC could not be identified as a product because a reference spectrum was not available, although it was clear that another product (besides LiEDC) was produced after extended cycling.

Figure 4.7 FTIR spectra of (a) C–H and (b) C–O region of Ni electrodes (Ni(1): electrode cycled between 0.5 and 2.5 V; Ni(2): electrode cycled between −0.5 and +2.5 V, and Ni(3): electrode cycled nine times between −0.5 and +2.5 V), LiEDC, and poly-EC/LiPF$_6$. The potentials are referred to the Li/Li$^+$ redox couple. Ni(1), Ni(2), and Ni(3) spectra are reproduced from raw data obtained from another study. The wavenumbers given correspond to neighboring peak positions indicated by dashed lines.
4.4 Conclusions

EC-based electrolyte decomposition was investigated by ATR-FTIR vibrational spectroscopy and the decomposition products were identified by matching their corresponding FTIR spectra to those of synthesized reference compounds. Reference FTIR spectra of DEDOHC and poly-EC compounds were obtained and peak assignments were made based on quantum chemical (Hartree-Fock) calculations. The solvation effect was studied by introducing the synthesized compounds into various electrolyte environments (i.e., LiPF₆, EC/LiPF₆, and EC/DEC/LiPF₆). Significant peak shifts and broadening of the FTIR spectra were induced by the solvation effect.

By analyzing the surface species formed on a Sn electrode, the unstable product was detected to be DEDOHC, whereas poly-EC was found to form on a Ni electrode after extended cycling in conjunction with the previously identified product LiEDC. These examples demonstrate the importance of including the solvation effect in the identification of electrolyte decomposition products using ex-situ FTIR spectroscopy, which is also important for in-situ FTIR spectroscopy and other vibrational spectroscopy analysis of electrolyte decomposition process.

4.5 References

(22) Zhang, G. V.; Ross, P. N. Electrochem. Solid-State Lett. 2003, 6, A136.
Chapter 5 – A catalytic path for electrolyte reduction in lithium-ion cells revealed by in-situ attenuated total reflection-Fourier transform infrared spectroscopy

Although controlling the interfacial chemistry of electrodes in Li-ion batteries (LIBs) is crucial for maintaining the reversibility, the electrolyte decomposition process has not been fully understood. Electrolyte decomposition on model electrode surfaces (Au and Sn) was investigated in this chapter by in-situ attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy. Simultaneously obtained ATR-FTIR spectra and cyclic voltammetry measurements show that lithium ethylene dicarbonate and lithium propionate form on the Au electrode at 0.6 V, whereas diethyl 2,5-dioxahexane dicarboxylate and lithium propionate form on the Sn electrode surface at 1.25 V. A non-catalytic reduction path on the Au surface and a catalytic reduction path on the Sn surface are introduced to explain the surface dependence of the over-potential and product selectivity. This represents a new concept for explaining electrolyte reactions on the anode of LIBs. The present study shows that catalysis plays a dominant role in the electrolyte decomposition process and has important implications in electrode surface modification and electrolyte recipe selection, which are critical factors for enhancing the efficiency, durability, and reliability of LIBs.

5.1 Introduction

Rechargeable lithium-ion batteries (LIBs) are widely used in energy storage, portable electronics, and electric vehicles.1 It is well known that the electrolyte of LIBs is thermodynamically unstable in the operating potential range, i.e., the electrolyte is reduced and oxidized on the anode and cathode surfaces, respectively. The decomposed electrolyte forms a film on the electrode surfaces, referred to as the solid-electrolyte interphase (SEI), which passivates the electrodes, inhibiting further parasitic reactions while allowing the conduction of the Li+ ions. Because of the significant impact on the stability and durability of LIBs,2 the composition, properties, and formation mechanism of SEI on inactive (e.g., Au),3,4 active (e.g., Li),5 and carbon6 electrodes have been extensively studied. SEI components include both carbonaceous (e.g., (CH2OCO2Li)2, ROCO2Li, Li2CO3, and polycarbonates) and non-carbonaceous (e.g., LiF, Li2O, and LiOH) compounds.7-10 However, because most of the aforementioned studies used ex-situ techniques, the reported results have been inevitably compromised due to electrolyte residue, operation uncertainty, and air sensitivity of the SEI.11 To better understand the electrolyte decomposition process and growth mechanism of the SEI, it is necessary to perform in-situ studies of the electrode-electrolyte interface.

Previous studies have indicated that the formation mechanism and composition of the SEI greatly depend on the type of electrolyte and additive used.7,12 It was postulated that cyclic carbonate (e.g., ethylene carbonate (EC)) dominates the primary Li+ solvation sheath and ultimately most of the reduction product is a signature of the cyclic carbonate reduction
by an electron transfer reaction. However, recent studies\textsuperscript{13–14,15} have shown a surface dependence of both reduction potentials and products, suggesting that the electrochemical reduction of the electrolyte solvent is an electrocatalytic process with kinetics strongly dependent on the electrode materials.\textsuperscript{16} Therefore, a thorough understanding of the roles of the primary Li-ion solvation sphere structure and electrode material on the electrolyte decomposition process is essential.

\textit{In-situ} attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy (see Supporting Information for details) was developed and used to systematically study the electrolyte reduction process. Considering the complexity of surface functional groups on real battery electrodes, two simple model electrode materials were chosen for study, namely Au as a metal electrode without any functional groups and Sn as an electrode material with oxygen functional groups that can be controlled and/or identified.\textsuperscript{17–20} As a noble metal, the Au surface is relative inert and barely interacts with aprotic electrolyte solvent, whereas Sn, as a typical active metal surface, forms a native oxide layer upon exposure to the atmosphere. When such active metal is introduced into a polar aprotic electrolyte solution, its oxygen spices will first react with the electrolyte solvent.

5.2 Experimental

5.2.1 Electrochemical half-cell test

The electrolyte consisted of 1 M LiPF\textsubscript{6}/ethylene carbonate (EC): diethyl carbonate (DEC) (1:2 v/v) (Novolyte Technologies, BASF). Dimethyl carbonate (DMC) (>99.9\%, HPLC grade, Sigma-Aldrich) was used as the rinsing solvent. A single compartment Teflon cell with two electrodes was used in the electrochemical experiments (Figure 5.1). The counter and reference electrodes were made of Li, whereas the working electrodes consisted of Au or Sn foil (99.99\%, Sigma-Aldrich). All potentials reported in this work are referred to the Li/Li\textsuperscript{+} redox couple. All electrochemical tests were set up in an Ar-filled glove box (H\textsubscript{2}O and O\textsubscript{2} contents <10 ppm). A potentiostat (WeveNow, Pine Research Instrumentation) was used for potential/current control.
5.2.2 In-situ and ex-situ FTIR spectroscopy measurements

In-situ ATR-FTIR experiments were performed with an electrochemical cell having three electrodes, i.e., Au and Sn foil as working electrodes and Li foil as both reference and counter electrodes. The working electrodes were pressed against a 45°-cut Ge prism (Figure 5.2). A thin layer of electrolyte was formed by adjusting the electrode camshaft against the prism. The cell is made of Teflon, while all O-rings consist of chemically stable Kalrez compound. To examine the potential dependence on the reduction chemistry, the anode was discharged (Li alloying) from its open circuit potential (OCP) to various potentials ranging from ~2.9 to 0.2 V for the Au electrode and ~2.8 to 0.75 V for the Sn electrode and potentiostatically held at each potential for 2 h. These threshold potentials were chosen before lithium plating. For a sufficiently low potential, the total signal of the electrolyte increased with the commencement of lithium plating, and the absorption intensity decreased when the lithium was dissolved.
All of the in-situ ATR-FTIR measurements were carried out inside a small glove box under N\textsubscript{2} atmosphere using a Thermo-Nicolet Nexus 670 spectrometer (GMI) equipped with a mercury-cadmium-telluride (MCT) detector. The focal point of the incidence beam was adjusted on the surface of the working electrode. All spectra were acquired with a resolution of 4 cm\textsuperscript{-1}. Each spectrum was obtained by adding a total of 512 scans. The FTIR spectra are presented in the form of absorbance $A = \log(1/T) = -\log(R_e / R_{ref})$, where the reference spectrum is the single-beam spectrum of the electrode/prism system without electrolyte.

In the ex-situ ATR-FTIR experiments, the Au or Sn working electrode in the Teflon cell was discharged under the same conditions as in the in-situ experiments. The spectra were obtained in ATR mode directly on the electrode surfaces immediately following DMC rinsing. After the evaporation of the volatile electrolyte component DEC in the glove box and rinsing with DMC to remove the residual electrolyte, the anode was transferred directly to the N\textsubscript{2}-filled spectrometer for ATR-FTIR analysis.

### 5.2.3 X-ray photoelectron spectroscopy

The formation of the SnO\textsubscript{2} layer was identified by X-ray photoelectron spectroscopy (XPS) performed with a PHI 5400 ESCA/XPS system (Physical Electronics) equipped with an Al-K\textalpha\ X-ray source of energy 1486.6 eV. For each point, the energy resolution was 0.1 eV. The binding energy was calibrated to the C1s core-level peak. The Sn 3d\textsubscript{5/2} core-level XPS spectrum of the Sn foil used as working electrode in the present study is shown in Figure 5.7.
5.3 Results and discussion

5.3.1 Electrochemical characterization of Au and Sn

Figure 5.3(a) and (b) show cyclic voltammograms (CVs) of Au and Sn electrodes in 1 M LiPF₆ electrolyte (EC:DEC = 1:2 v/v). The potential was swept from 2 to 0 V (all potentials are referred to the Li/Li⁺ redox couple) at a scan rate of 1 mV/s. On the Au electrode, in addition to the features associated with under-potential deposition of Li below 0.2 V and the two anodic peaks at ~0.3 and ~0.5 V corresponding to Li dissolution, a reduction (cathodic) peak of ~25 μA/cm² is observed at ~0.6 V in the first cycle but not in the second cycle (see inset of Figure 5.3(a)). The disappearance of this peak in the second cycle is attributed to the formation of a stable reduction product, which passivates the surface from further electrolyte reduction. Conversely, on the Sn electrode, in addition to the features below ~0.5 V associated with Sn lithiation and the features above 0.5 V in the anodic sweep indicating Sn delithiation, a reduction peak consistently appears at ~1.25 V, indicating that the reduction products do not passivate the electrode surface from further electrolyte reduction after lithiation and delithiation. Considering the identical experimental conditions, the different electrolyte reduction potentials reveal different reactions on each electrode material.

**Figure 5.3** Cyclic voltammograms of (a) Au and (b) Sn electrodes in 1 M LiPF₆ electrolyte for 1 mV/s scan rate. The inset in (a) is a magnified plot of the CV region revealing the formation of SEI.

5.3.2 In-situ ATR-FTIR measurements

*In-situ* ATR-FTIR spectroscopy was used to study the surface chemistry associated with these different reaction paths on the Au and Sn electrodes. The electrode potential was changed from the open circuit potential (OCP) to various potentials before Li deposition and held at each potential for 2 h while spectra were acquired.

Figure 5.4(a) and (b) show the potential dependence of *in-situ* ATR-FTIR spectra of Au and Sn electrodes, respectively, in EC/DEC 1 M LiPF₆ electrolyte. The dashed lines...
indicate new peaks encountered at different potentials. The spectrum of the EC/DEC 1 M LiPF₆ electrolyte at OCP is similar to that obtained in previous studies;²²-²⁴ more details about the peak assignment can be found in Figure 5.5 and Table 5.1. Five new peaks (2920, 2851, 1576, 1557, and 1115 cm⁻¹) appear in the spectrum of the Au electrode at 0.6 V potential, which is the electrolyte reduction potential, as shown by the CV of the Au electrode (Figure 5.3(a)). These peaks are assigned to lithium ethylene dicarbonate (LiEDC) (1115 cm⁻¹) and lithium propionate (2920, 2851, and 1565 cm⁻¹). The spectrum of dissolved sodium propionate (Figure 5.4(c)) indicates that the doublet peak at 1576 and 1557 cm⁻¹ in the in-situ ATR-FTIR spectra (Figure 5.4(a) and (b)) is due to the formation of lithium propionate (peak at 1565 cm⁻¹). The splitting of the peak at 1565 cm⁻¹ (pure lithium propionate) to a doublet peak (1576 and 1557 cm⁻¹) is due to the solvation of EC, as explained in the Figure 5.6.

The C=O stretch at 1663 cm⁻¹ corresponding to LiEDC is not visible in the spectrum shown in Figure 5.4(a) due to the strong background signal of the electrolyte. A possible reason is that the C=O and C–O stretch intensities vary with the orientation of bond dipoles and the electric field vector, making a certain vibration frequency region invisible. Another possibility is that the synthesized bulk LiEDC exists in dimer form, whereas the LiEDC formed on the Au surface may be in a different form (e.g., monomer or mixture state). Thus, the typical C=O stretch may accordingly shift. Alternatively, the C=O stretch is observed in the ex-situ ATR-FTIR results presented below (in these tests most of the bulk electrolyte was rinsed off).

New features are also observed in the spectra of the Sn electrode (Figure 5.4(b)), but in a higher potential range compared to the Au electrode. The peaks at 2920, 2851, 1576, and 1557 cm⁻¹ appearing at a potential of 1.4 V are assigned to lithium propionate, whereas the peak at 1744 cm⁻¹ is assigned to diethyl 2, 5-dioahexanedicarboxylate (DEDOHC). Since the FTIR spectra of DEDOHC and DEC are very similar because of their similar chemical structure, a reference spectrum (Figure 5.7) is used to validate the assignment of the peak at 1744 cm⁻¹ to DEDOHC. Further details about the characterization of DEDOHC can be found elsewhere.²⁵ The intensity of the peak at 1197 cm⁻¹ (assigned to the –C–O– stretch of Li-solvated EC) decreases with the potential concurrently with the formation of DEDOHC. A possible explanation is a change in the near-surface EC solvation state at these potentials. In brief, lithium propionate is identified as a reduction product on both Au and Sn electrodes, whereas the reduction products LiEDC and DEDOHC are detected only on the Au and Sn electrode surfaces, respectively.

The presence of different chemical species is direct evidence that the electrode material surface exhibits a catalytic effect on both the selectivity and kinetics (over-potential) of electrolyte reduction.
Figure 5.4 *In-situ* ATR-FTIR spectra of (a) Au electrode obtained after applying a potential of open circuit potential (OCP), 0.6, 0.4, and 0.2 V, and (b) Sn electrode obtained after applying a potential of OCP, 1.4, 1.0, and 0.75 V (both electrodes are in EC/DEC 1 M LiPF₆ electrolyte), (c) ATR-FTIR spectra of sodium propionate (reference spectrum for lithium propionate), DEDOHC, and LiEDC.
Figure 5.5 ATR-FTIR spectra of pure DEC, EC/LiPF$_6$ (1:5 v/v), EC/DEC (1:2 v/v), and EC/DEC(1:2 v/v)/LiPF$_6$.

Table 5.1 Summary of main peak assignment for EC/DEC (1:2)/LiPF$_6$.

<table>
<thead>
<tr>
<th>Vibration mode</th>
<th>C=O stretch (cm$^{-1}$)</th>
<th>C–O (cm$^{-1}$)</th>
<th>C–H (cm$^{-1}$)</th>
<th>P–F (cm$^{-1}$)</th>
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</thead>
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<tr>
<td>EC/LiPF$_6$</td>
<td>1799,1769</td>
<td>1071</td>
<td>3001,2935</td>
<td>841</td>
</tr>
<tr>
<td>DEC</td>
<td>1748</td>
<td>1267</td>
<td>2986</td>
<td>–</td>
</tr>
<tr>
<td>EC/DEC (1:2)</td>
<td>1806,1774 (EC)</td>
<td>1257 (DEC)</td>
<td>2986 (DEC)</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1744 (DEC)</td>
<td>1074 (EC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC/DEC (1:2)/LiPF$_6$</td>
<td>1806,1774 (EC)</td>
<td>1262(DEC)</td>
<td>2986 (DEC)</td>
<td>843</td>
</tr>
<tr>
<td></td>
<td>1744( DEC),1717 (DEC solvated)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1302(DEC solvated)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1076 (EC)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.6 ATR-FTIR spectra of Na propionate dissolved in EC/LiPF₆ (1:5 v/v), Na propionate, and EC/LiPF₆. Under EC solvation conditions, the characteristic peak of Na propionate at 1565 cm⁻¹ splits into two peaks at 1576 and 1557 cm⁻¹.

Figure 5.7 ATR-FTIR spectra of DEDOHC, DEC, EC/DEC, EC/DEC/LiPF₆, and DEDOHC/EC/DEC/LiPF₆ (1:5 v/v). With the addition of DEDOHC to the EC/DEC/LiPF₆ control electrolyte, the intensity of the peak at 1744 cm⁻¹ increases, whereas that of the peak at 1197 cm⁻¹ decreases.

5.3.3 Ex-situ ATR-FTIR measurement

Many of the new features in the in-situ ATR-FTIR spectra are barely observable above the background signal of the bulk electrolyte. Thus, to better resolve these features and determine which is associated with less soluble products, ATR-FTIR analysis was performed ex situ in which the bulk electrolyte was rinsed off using a previously developed
method. Ex-situ ATR-FTIR spectra were collected from electrodes subjected to the same experimental conditions (i.e., constant potential of 0.2 or 0.75 V applied for 2 h to the Au and Sn electrodes, respectively, both in EC/DEC 1 M LiPF₆ electrolyte). As expected, none of the features assigned to lithium propionate were observed ex situ due to its IR absorbance sensitivity and solubility in the rinsing solvent (dimethyl carbonate). In the spectra shown in Figure 5.8, the peaks at 1799 and 1769 cm⁻¹ are assigned to the C=O stretch of EC in 1 M LiPF₆ electrolyte. The peaks at 1663 and 1318 cm⁻¹ confirm the presence of LiEDC as a stable product precipitating on the Au electrode (thus, an SEI component), and the peaks at 1744 and 1278 cm⁻¹ confirm the assignment of DEDOHC as a reduction product on the Sn electrode, consistent with the in-situ results. Since the organic salts (e.g., LiEDC) are less soluble than the organic compounds (e.g., DEDOHC) in the electrolyte, LiEDC precipitates on the Au electrode during the first cycle, preventing further decomposition of the electrolyte. In contrast, the Sn electrode is not passivated by the more soluble DEDOHC; therefore, electrolyte decomposition continues to occur in each cycle. This explains the CV curves shown in Figure 5.3(a) and (b), which indicate that different products of catalysis forming on the Au and Sn electrodes may affect the SEI stability during cycling.

Figure 5.8 Ex-situ ATR-FTIR spectra of (a) LiEDC and SEI formed on the Au electrode surface obtained after applying a constant potential of 0.2 V for 2 h, (b) DEDOHC and SEI formed on the Sn electrode surface obtained after applying a constant potential of 0.75 V for 2 h (both electrodes are in EC/DEC 1 M LiPF₆ electrolyte).

5.3.4 Catalytic versus non-catalytic paths in Li-ion batteries

The CV curves and FTIR spectra of the Au and Sn surfaces show that both the over-potential and the selectivity exhibit clear surface dependence during electrolyte reduction. The non-catalytic (Au) and catalytic (Sn) reduction paths shown in Scheme 5.1(a) and (b), respectively, can be used to explain the over-potential and selectivity surface dependence. The EC molecular reduction potential is ~0.9 V vs. Li/Li⁺, which mainly depends on the solvation condition of EC. The electrolyte reduction potential on the Au surface is equal to ~0.6 V, which is close to that of a graphite electrode (~0.75 V) and lower than the theoretical value (0.9 V), suggesting that the reduction path on the Au surface is non-catalytic. On the contrary, the reduction potential on the Sn surface is much higher (~1.25
revealing a typical catalytic reduction process and can be attributed to the much stronger interaction of the Sn surface with the solvent molecules that lowers the barrier for subsequent electron transfer steps. Furthermore, the reduction selectivity of the Au electrode differs from that of the Sn electrode. On the inactive Au surface, the main electrolyte reduction product is LiEDC, which, according to the “solvation sheath” argument, is a signature EC-reduction product. Such product has also been found on graphite and Ni electrodes. As shown in Scheme 5.1(a), in the absence of a strong interaction between the Au electrode and the electrolyte solvent, the solvated molecule is reduced by an electron, yielding the thermodynamically favorable product LiEDC.

On the active Sn electrode, which is covered by oxygen spices, the main reduction product is DEDOHC. The Sn 3d_{5/2} core-level XPS spectrum of the Sn foil used as working electrode in the present study is shown in Figure 5.9. As a trans-esterification compound of the electrolyte, the formation mechanism of DEDOHC has been systematically investigated. Ethyl oxide radical is an important intermediate catalyst during the formation of DEDOHC. As shown in Scheme 5.1(b), the strong interaction between DEC and Sn oxide produces ethyl oxide, which trigger the decomposition of EC and the formation of DEDOHC. Control experiments confirmed the role of DEC in the formation of DEDOHC.

Scheme 5.1 Proposed formation mechanisms of reduction products. (a) A non-catalytic path leads to the formation of LiEDC on the Au electrode surface. The inactive electrode
primarily serves as a current transfer medium; thus, the state of ion solvation is the dominant factor in the electrolyte decomposition process. (b) A catalytic path leads to the formation of DEDOHC on the Sn electrode surface. The active electrode surface strongly interacts with the co-solvent molecule DEC, whereas the effect of ion solvation state is secondary; therefore, electrolyte reduction follows a catalytic path and electrolyte decomposition demonstrates surface dependence.

The Sn electrode was tested under the same conditions in pure 1 M LiPF$_6$ EC electrolyte using ex-situ ATR-FTIR, and only LiEDC signal was detected (Figure 7.10). Without DEC, the radical ethyl oxide does not exist; hence, the proposed catalysis path on the Sn surface does not occur. To summarize, the electrolyte decomposition exhibits clear surface dependence. The inactive Au electrode barely interacts with the electrolyte solvent and the state of ion solvation mainly determines the electrolyte reduction; thus, the Au electrode primarily serves as current transfer medium and electrolyte reduction follows a non-catalytic path. Conversely, the active Sn electrode strongly interacts with the solvent molecules and the state of ion solvation is secondary; thus, the Sn electrode serves as catalyst and electrolyte reduction follows a catalytic path.

![Figure 5.9 Sn 3d$_{5/2}$ XPS spectrum of Sn foil. Open circles are raw data, while curves present the results of a Gaussian deconvolution.](image-url)
Figure 5.10 Ex-situ ATR-FTIR spectra of reference compound LiEDC and SEI formed on the Sn electrode obtained after 2 cycles of potential cycling between 0 and 2 V at a scan rate of 1 mV/s in 1 M LiPF$_6$ EC electrolyte.

5.4 Conclusions

Standard Li-ion electrolyte reduction on two metal electrode surfaces (Au and Sn) was investigated by in-situ ATR-FTIR spectroscopy. A pronounced surface dependence of the over-potential and reduction products was observed in CV tests and confirmed by ATR-FTIR spectral analysis. It was found that relatively insoluble LiEDC forms on the Au electrode at ~0.6 V, whereas relatively soluble DEDOHC forms on the Sn electrode at ~1.25 V. As another reduction product, lithium propionate exists on both electrode surfaces. Two different reaction mechanisms were introduced to explain the observed surface dependence, i.e., a non-catalytic reaction path (Au electrode) and a catalytic reduction path (Sn electrode). The catalytic role of the electrode material surface in the electrolyte decomposition process demonstrated in this study may play a more general role in LIBs than heretofore recognized.

5.5 References


(8) Ross, P. N. ECS Trans. 2006, 1, 161.

(9) Aurbach, D. J. Power Sources. 2000, 89, 206.


(22) Akita, Y.; Segawa, M.; Munakata, H.; Kanamura, K. J. Power Sources. 2013, 239, 175.


Chapter 6 – In-situ attenuated total reflection-infrared (ATR-IR) investigation on electrolyte decomposition on single-crystal silicon in Li-ion batteries

Despite of its extraordinary energy density, the main drawback of Si anodes is the significant irreversible capacity fading over cycles due to both chemical and mechanical degradation of the electrode. Chemical degradation is mainly caused by surface passivation with electrolyte during the first cycle and the formation of unstable solid electrolyte interphase (SEI) with extended cycling. To better understand the surface chemistry of Si electrodes during battery cycling, a novel in-situ ATR-FTIR spectro-electro-chemical cell was developed, which allows the probing depth in vibrational spectra of molecules to be tuned near the electrode surface. It is shown that the main product produced on the SiO$_2$ is DEDOHC, whereas the reduction product on freshly exposed Li$_{15}$Si$_4$ is LiEDC. The effect of reaction kinetics on the chemical composition of the SEI, revealed in this chapter, should be beneficial to future studies of Si electrode surface modification and treatment to form an SEI with desirable characteristics, and can also be applied to other electrode materials.

6.1 Introduction

Advanced rechargeable batteries with high energy density, good cyclability, and minimal capacity degradation are critical to various industrial applications, including large-scale/long-term energy storage, power supplies for portable electronics, and electric vehicles. Due to the high energy capacity, alloy host anode materials, such as Si and Sn, are considered as leading candidates for next-generation anode materials.\(^1\) Compared with the graphite anode, where every six C atoms host one Li atom, a Si anode can host 3.75 Li atoms per Si atom. This yields a significant increase in theoretical capacity, from 372 mAh/g for graphite to 4008 mAh/g for Si. However, this remarkable capacity increase implies a huge volume expansion (~300%) of a fully charged Si electrode, and irreversible capacity loss is always observed after extended cycles. It is believed that the source of irreversible capacity loss is mechanically-induced electrode cracking, followed by the continued reduction of the electrolyte and the formation of a solid electrolyte interphase (SEI) on the freshly exposed electrode surface. This process continuously builds up an interphase resistance, consumes the limited source of Li, and eventually disables the cell. Therefore, a key factor for achieving high capacity and long durability of Si or other alloy hosts of Li ions at the battery anode is a chemically and mechanically stable interphase.

There is no evidence that the chemical composition of the SEI forming on a Si electrode differs significantly from that of SEIs forming on other electrode, such as graphite. Thus, graphite and Si electrodes demonstrate markedly different SEI characteristics. First, the potential for SEI formation on graphite and Si is equal to ~0.6 V and ~1.5 V, respectively, indicating different electrolyte reduction reaction. Second, while the SEI is chemically stable on the graphite electrode, it is difficult to be stabilized on the Si electrode, which suggests different chemical properties. Although the formation
mechanism of the SEI on Si is still under debate, it is highly possible the process is quite different for the following reasons: (1) the reductive reactions on the Si surface are mediated by the SiO$_2$ native film existing on most Si materials and (2) the Si electrode experiences irreversible changes in surface morphology during the first lithiation cycle from crystalline to amorphous and the large volumetric changes during subsequent lithiation/delithiation cycles.\textsuperscript{2} Accurate characterization of the chemical composition, structure, and formation and degradation mechanisms of the SEI is in general limited by insufficient interfacial sensitivity of conventional spectroscopies and limited capability for simultaneous information collection of \textit{ex-situ} instruments.

In this chapter, the chemical composition of SEI is investigated by advanced \textit{in-situ} attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy. By tuning the probing depth in vibrational spectra of molecules near the electrode surface, the dependence of the SEI chemical composition on the applied potential can be investigated and the correlation between the incidence angle and the Li ion solvation gradient from the interface to the bulk to be determined. The experimental results indicate that soluble species form on the single-crystal Si surface covered by its native oxide, which might be related to the chemical instability of the SEI, and contribute to the early failure of the Si anode. In addition, the reaction of electrolyte on Li$_{15}$Si$_4$ is shown to be responsible for the cracking of the freshly exposed surface during long-term cycling. This knowledge can be used to develop and tailor SEI films for Si anodes exhibiting less irreversible capacity loss, improved long-term stability, and cyclability for vehicular applications.

6.2 Experimental

6.2.1 Electrochemical experiments

The electrolyte was 1 M LiPF$_6$/ethylene carbonate (EC): diethyl carbonate (DEC) (1:2 v/v) (Novolyte Technologies, BASF). Dimethyl carbonate (DMC) (Aldrich, 99.9+\%, HPLC grade) was used as rinsing solvent. A p-type Si(100) wafer (5-10 $\Omega \cdot$cm) was cut into 25.4 x 25.4 mm$^2$ pieces of 100 $\mu$m thickness, double polished, and thoroughly cleaned, which were used as reference of the working electrode (apparent area 1.93 cm$^2$). A single-compartment Teflon cell with two electrodes was used in the \textit{ex-situ} measurements. Lithium metal was used as both counter and reference electrodes. All the potentials reported here refer to the Li/Li$^+$ redox couple. All the electrochemical cells were assembled in an Ar-filled glove box (water and oxygen contents <10 ppm).

6.2.2 \textit{In-situ} and \textit{ex-situ} FTIR spectroscopy measurements

The FTIR spectra were taken with a fast-scan Nicolet Nexus 670 FT-IR spectrometer equipped with a MCT detector cooled with liquid nitrogen. Polarization discrimination was not used. The spectral resolution was set to 4 cm$^{-1}$. A total of 256 interferograms were co-added for each spectrum, unless otherwise stated. The spectra are presented in the form of absorbance $A = \log(1/T) = -\log(R_s / R_{ref})$, where the reference spectrum is the single-beam spectrum of the electrode/prism system without electrolyte. All of the spectra have been processed with ATR correction.
The *in-situ* ATR-FTIR setup is schematically shown in Figure 6.1. A hemicylindrical prism of ZnSe crystal was used as the primary ATR element. The double-polished Si wafer was pressed against the reflecting plane of the ZnSe prism. Si(100) served as both a combined ATR element and a working electrode. The thickness of the water interlayer was controlled to be <1 µm by tightening four screws of a clamping apparatus against the PEEK cell with an O-ring used to seal the electrolyte. The interference from the Si absorption between 1300 and 900 cm⁻¹ was found to be negligible in the current setup.³ It is very important to ensure the LiPF₆ in the electrolyte can be identified because the P-F stretching frequency of PF₆⁻ is in this range. An ultrathin Cu foil was used to connect the silicon electrode to the potentiostat (Wave-now, Pine Research Instrument).

![Figure 6.1 Schematic diagram of the in-situ ATR-FTIR configuration with single-crystal Si serving both as the IR transport window and the working electrode.](image)

In the *ex-situ* ATR-FTIR experiments, the Si(100) electrodes in the Teflon cell were discharged under the same conditions as in the *in-situ* experiments. The spectra were obtained in ATR mode directly on the electrode surfaces immediately after DMC rinsing. After the evaporation of the volatile electrolyte component DEC in the glove box and rinsing with DMC to remove the residual electrolyte, the anode was transferred directly to the Ar-filled spectrometer for ATR-FTIR analysis. Both *in-situ* and *ex-situ* assembly and rinse treatment were performed in the glove box. Details about the *ex-situ* ATR-FTIR analysis can be found elsewhere.⁴-⁷

### 6.3 Results and discussion

#### 6.3.1 *In-situ* ATR-FTIR cell design and calibration

The *in-situ* ATR-FTIR cell used to analyze the chemistry of the electrolyte reduction at the surface of a p-type Si(100) is shown in Figure 6.1. The advantage of internal reflection mode ATR is to minimize the signal from the electrolyte. However, a pure Si prism suffers from strong IR absorption at frequencies lower than 1200 cm⁻¹, preventing the observation of important spectral fingerprints in this region, hence compromising the structural and mechanistic elucidation at silicon electrodes. To overcome this limitation,
we combined a thin Si component with ZnSe prism as the ATR window, which is adopted from surface-enhanced IR absorption spectroscopy cell.\textsuperscript{3,8} Because penetration of evanescent waves into the interface is related with the incidence angle and the wavelength of the IR beam, with this hemi-cylindrical prism it was possible to smoothly change the incidence angle, vary the penetration depth of the IR radiation, and analyze both near-surface (<0.5 µm) and diffuse layer (<3 µm) regions, thus gaining depth resolution along the silicon/electrolyte interface. Because the SEI layer has reduced dimensionality and is also non-homogenous,\textsuperscript{9,10} such variability is valuable.

Figure 6.2 shows the effect of incidence angle on FTIR spectra of Si(100) interface in the wavenumber range of 3100-800 cm\textsuperscript{-1} at open circuit potential (OCP). According to the penetration equation, the depth of chemical species detected at 65° incidence angle is shallower (i.e., closer to surface) than at 40° incidence angle. The spectra obtained at 40° incidence angle is consistent with previous literature according to which, in the C–O vibration region, Li solvation causes the DEC C=O bond to red shift from 1744 to 1714 cm\textsuperscript{-1}.\textsuperscript{11-13} However, this solvation shoulder gradually diminishes with the increase of the incidence angle to 65°, which means probes close to surface solvent absorption according to the double layer structure. In the C-H vibration region, the 2991 cm\textsuperscript{-1} peak is typical of C-H bond in the DEC molecule, and the signal disappears as the beam grazes the interface. The P-F vibration from the PF\textsubscript{6} anion in the electrolyte salt exists below 800-900 cm\textsuperscript{-1}. The peak is typically around 841 cm\textsuperscript{-1} in the EC/DEC electrolyte, and the P-F vibration energy is very sensitive to the anion solvation conditions.\textsuperscript{14} The P-F bond shifts from 838 to 841 cm\textsuperscript{-1} upon approaching the electrode surface. As a result, for an incidence angle of 65°, we gained most close to surface condition; therefore, in the following \textit{in-situ} measurement, the incidence angle is set at 65° for best resolution of surface detection.

![Figure 6.2 ATR-FTIR spectra for various incidence angles (40°–65°) on the Si(100) interface in the EC/DEC/LiPF\textsubscript{6} (1:2 v/v) electrolyte at open circuit potential.](image)

\textbf{6.3.2 \textit{In-situ} ATR-FTIR with CV}

The electro-chemical curves corresponding to the initial formation of the SEI and associated \textit{in-situ} FTIR spectra from the near surface region were analyzed. Figure 6.3(a)
shows cyclic voltammograms (CVs) of a p-type boron-doped Si(100) electrode in 1M LiPF₆ electrolyte (EC/DEC = 1:2 v/v). The potential was swept from 3 to 0.005 V at a scan rate of 1 mV/s. In the first cycle, the first reduction current peak was observed at ∼1.5 V corresponding to the onset of SEI formation. The current continued to decrease until the second occurrence of current decrease at ∼0.1 V, attributed to the initial alloying of crystalline silicon with lithium. In the second cycle, the lithiation reduction peak shifts to ∼0.3 V. The two anodic peaks at ∼0.3 and ∼0.5 V are associated with Li dissolution.¹⁵,¹⁶

_In-situ_ spectra from the near-surface region (65° incidence angle) changed when different potentials were applied (Figure 6.3(b)). At a potential of 1 V, three new features appeared at 1760, 1274, and 2997 cm⁻¹, and the intensities of these peaks continued to increase as the potential decreased to 0.4 V. However, no further change was observed below 0.4 V, even the potential scan to lithiation state and scan back to open circuit potential. It has been reported that the DEC strongly interacts with oxygen species on the Sn electrode to form DEDOHC.¹³ The surface functional groups on Si are very analogous to those on Sn, suggesting that the SEI formation mechanism may also be similar. In addition, new species on the Si surface appeared at ∼1.25 V, which is also consistent with a Sn surface. Therefore, these new features are attributed to the strong interaction of DEC with native SiO₂ oxide layer and the formation of DEDOHC. Compared with other electrode surfaces that do not have a native oxide film (e.g., Au and graphite), the oxide functional groups on Si electrodes clearly change the electrolyte decomposition path with the sweeping potential. Thus, the reactivity of the native SiO₂ layer with the electrolyte during cycling has important implications on Si electrode modification and electrolyte recipe selection.
Figure 6.3 (a) Cyclic voltammograms and (b) in-situ ATR-FTIR spectra of Si(100). The in-situ CV scan rate is 1 mV/s, the ATR-FTIR incidence angle is 65°, and the electrolyte is EC/DEC/LiPF$_6$ (1:2 v/v).

6.3.3 In-situ CA

As mentioned previously, due to excessive volume expansion/contraction, the Si electrode is often cracked over cycles and freshly lithiated Si is exposed to the electrolyte. Therefore, it is of importance to understand the formation of SEI on Li$_x$Si$_y$. A constant potential of 5 mV was applied for 1 h to pre-lithiate the Si electrode. Then, various incidence angles were used to vary the penetration depth in SEI product probing. As shown in Figure 6.4, three new peaks appear as the probing depth decreases (i.e., incidence angle increases). The peaks at 2975, 1664 and 1310 cm$^{-1}$ are visible above 50° incidence angle. According to previous literature, the peaks at 2975, 1664, and 1310 cm$^{-1}$ are assigned to lithium ethyl dicarbonate (LiEDC) and the peak at 940 cm$^{-1}$ to Si-F vibration. As the IR beam probes deeper into the electrolyte (40° and 45° incidence angle), the SEI signal diminishes and the electrolyte signal dominates. So far we have seen that the SEI layer on Li$_x$Si$_y$ is different from that on native SiO$_2$ oxide (or SEI is sensitive to applied
potential/chemical potential) and have confirmed that the SEI layer is non-homogenous, based on the IR depth profile.

Figure 6.4 *In-situ* ATR-FTIR spectra of a Si electrode obtained after applying a potential of 5 mV for 1 h in EC/DEC/LiPF$_6$ (1:2 v/v) electrolyte. The incidence angle was adjusted to 40°, 45°, 50°, 55°, and 65°.

### 6.3.4 SEI component comparison with various condition: *Ex-situ* measurements

The adsorption signals of electrolyte decomposition products on the electrode surface observed in the *in-situ* ATR-FTIR spectra in previous sections provide evidence for the mechanism of initial SEI formation. To better understand the long-term SEI degradation mechanism and validate it with the synthesized reference compound, *ex-situ* ATR-FTIR analysis was performed in which the bulk electrolyte was rinsed off using a previously developed method.\textsuperscript{5} *Ex-situ* ATR-FTIR spectra were collected from electrodes subjected to the following experimental conditions: CV cycled for 1 and 5 cycles between 5 mV to 2 V; applied 5 mV for 1 h on Si(100) electrodes; all tests performed in EC/DEC 1 M LiPF$_6$ electrolyte. As shown in Figure 6.5, after the first cycle, the formed SEI mainly consists of DEDOHC because the native SiO$_2$ layer covers the electrode surface. After 5 cycles, while the DEDOHC remains, the LiEDC product emerges (3308, 2975, 2961, 1664, 1310 cm$^{-1}$). This is because cracking of the electrode surface after extensive cycling results in the exposure of freshly lithiated surface, leading to the reduction of EC on the Li$_2$Si$_y$ and, consequently, the formation of LiEDC. Moreover, none of Li$_2$CO$_3$ signal (1400-1500 cm$^{-1}$) is visible in both in-situ and ex-situ measurement, which is a main product on silicon reported in other literatures.
Figure 6.5 Ex-situ ATR-FTIR spectra of (a) reference compound DEDOHC, (b) SEI formed on the Si electrode surface obtained after CV cycled for 1 cycles, (c) CV cycled for 5 cycles between 5mV to 2V, and (d) applied 5mV for 1 h on Si (100) electrodes, respectively (all tested in EC/DEC 1 M LiPF₆ electrolyte). (e) reference compound LiEDC.

6.3.5 Discussion of SEI formation mechanism on Si electrodes

The presented CV curves and FTIR spectra of Si electrode surfaces suggest that the electrolyte reduction product strongly depends on the applied potential and closely relates to the evolution of the electrode morphology (e.g., surface cracking). Based on the SEI chemical composition detected under different conditions, the following SEI formation mechanism on Si electrodes is proposed (Figure 6.6). When the reduction potential is above 1 V, both SiO₂ and Si remain intact and the SEI component is mainly DEDOHC, which passivates the electrode surface upon its formation, preventing any other reaction to occur, as evidenced by the in-situ result in Figure 6.3. If the reduction potential is directly set to 5 mV, the SiO₂ is converted to lithium silicate and pristine Si underneath converts to Li₁₅Si₄ immediately; as a result, LiEDC is the dominant reduction product, as shown in the Figure 6.4. When the Si electrode is subjected to several cycles (e.g., 5 cycles), surface cracks form on the electrode and the electrolyte can access the SiO₂ in the first few cycles and the exposed fresh LiₓSiᵧ surface in subsequent cycles leading to the formation of two different reduction products.
6.4 Conclusions

Li-ion battery electrolyte reduction on single-crystal Si(100) electrodes was investigated by in-situ ATR-FTIR spectroscopy. DEDOHČ was observed to form at ~1.25 V on the electrode surface covered with a native oxide (SiO₂) layer during potential sweeping, thus suppressing any other reduction reactions. LiEDC was detected as the main reduction product when the potential was directly set to and held constant at 5 mV on the lithiated silicon (Li₁₅Si₄) surfaces. The SEI chemical composition varied with penetration depth – inorganic compound Si-F only exists near the electrode surface, while organic compound dominates beneath the electrode surface. The SEI degradation mechanism over extended cycles was tracked by ex-situ FTIR of the cracked surface of the Si electrode. The reduction product LiEDC increased with cycling, even though the original electrode surface was passivated by DEDOHČ. This clearly indicates that SEI formation on electrode surface is determined by the combined effects of mechanical degradation (electrode fracture) and chemical reaction (electrolyte reduction). This work represents the first attempt of in-situ vibrational spectroscopy experiment to explore SEI formation on Si electrodes. The electrolyte reduction mechanisms revealed at different potentials and cycling conditions have important implications for future electrode and electrolyte recipe design.

6.5 References


(9) Bertrand Philippe; Rémi Dedryvère; Mihaela Gorgoi; Håkan Rensmo; Danielle Gonbeau; Edström, K. J. Am. Chem. Soc. 2013, 135, 9829.

(10) Bertrand Philippe; Rémi Dedryvère; Mihaela Gorgoi; Håkan Rensmo; Danielle Gonbeau; Edström, K. Chem. Mater. 2013, 25, 394.


Chapter 7 – Failure mechanisms of single-crystal silicon electrodes subjected to electrochemical lithiation/delithiation in lithium-ion batteries

Chemical/electrochemical experiments, microstructure characterization, and finite element analysis were used to explore the fracture mechanism of single crystal Si electrode over cycles. Cracks were found initiated perpendicularly at electrode surface, propagated in the vertical direction and deflected along the lithiation boundary, causing material peeling-off. While crack initiation and propagation both occurred during delithiation, they were essentially driven by irreversible plastic deformation accumulated in lithiation. Once the crack tip approached the lithiation boundary, the low fracture toughness of crystalline and amorphous silicon interface makes itself the “weakest” microstructural path for crack deflection. The current investigation provides a comprehensive understanding on the failure mechanism of silicon electrode and helpful guidance for electrode material selection and design optimization.

7.1 Introduction

Despite significant research devoted to the exploration of new types of batteries,1-3 lithium ion batteries (LIBs) remain the most extensively used power source for various applications, such as portable electronics, electric vehicles, and long-term energy storage. In common with traditional batteries, LIBs have two electrodes which reversibly host Li ion insertion and extraction.4 Novel electrode materials, such as silicon, have been proposed as a promising upgrade for the current graphite carbon-based electrodes because of their improved gravimetric energy density.5 However, the larger capacity density implies that the silicon electrode must host more insertion and extraction of lithium ions during lithiation/delithiation cycling. As a result, the silicon electrode experiences excessive volume expansion and contraction cyclically, which induces irreversible electrode deformation and fracture. Consequently, the mechanical degradation of the silicon electrode results in severe capacity and power fade, thereby greatly limiting the battery’s long-term durability for critical applications, such as power systems of electric vehicles. Accordingly, here we seek to provide a fundamental understanding of the failure mechanisms of silicon electrodes in LIBs over extended cycles, in order to provide guidance for new and improved electrode design with minimal capacity decay.

It has been suggested that decreasing electrode material size to nanostructures in the form of nanoparticles, nanowires, or nanotubes is a promising strategy for preventing electrode failure.5-7 In addition, critical sizes of “fracture-free” nanoparticle and nanowire electrodes have actually been proposed.5,9 The delicate nanostructured silicon electrodes, however, are still not ready for commercialization due to several reasons. First, the columbic efficiency of these nanostructures in the first cycle is naturally very poor because their high surface-to-volume ratio causes more lithium ions to be trapped in the solid
electrolyte interphase (SEI). Second, the much higher manufacturing cost of nanostructured electrodes may offset the competitive advantages associated with their presumed improved capacity. Third, the size of silicon particles that commercial vendors can manufacture with reasonable control is still larger than the estimated “fracture-free” size. Consequently, the salient mechanisms controlling the fracture and hence the lifetime of silicon electrodes of LIBs remains an unavoidable issue that must be understood. To this end, various theoretical models have been developed and experimental studies performed to elucidate the fracture mechanisms of both crystalline and amorphous silicon electrodes.\textsuperscript{10-13} However, there have been few attempts to investigate the physical mechanisms underlying fracture behavior of these electrodes at more realistic larger scales (from micrometers to centimeters), especially during long-term cycling.\textsuperscript{14}

In this chapter, we combine chemical/electrochemical experiments with fracture mechanics/finite element method (FEM) analysis to investigate the electrochemical and mechanical response of single-crystal silicon electrodes subjected to long-term cycling. Single-crystal silicon was chosen because it provides an ideal model surface and bulk material; moreover, as standard electrochemistry measurements can be readily made, it is possible to track the development of a crack in the electrode and, most importantly, identify its trajectory over extended cycles. The simulated stress/strain contours and predicted progress of the crack paths are shown to be consistent with experimental observations. Specifically, with increasing number of cycles, perpendicular cracks initiate at the electrode surface, propagate in the vertical (thickness) direction, and eventually deflect along the lithiation boundary causing delamination. We believe that these results have significant implications to the understanding of the progressive failure of silicon electrodes and provide guidance for the development of design strategies that can mitigate the degradation and failure of silicon electrodes in LIBs.

7.2 Experimental

7.2.1 Electrode fabrication

In this chapter, p-type boron-doped Si(100) wafers (MTI) of 100 mm (4 in.) diameter and 0.001 Ω·cm electrical resistivity were used as electrodes. The native oxide film was removed by first treating with diluted 5% HF and then rinsing with ultra-pure water (18.2 MΩ·cm) for 2 min. Silicon micropillars were fabricated by dry etching the wafers using photolithography (Figure 7.1). The cross-sectional area and height of the pillars were precisely controlled to be 3 × 3 μm\(^2\) and 8 μm, respectively. Before performing the photolithography, the mask was aligned with two \(<110>\) notches at the wafer side. The pillars were fabricated with their \{110\} lateral surfaces exposed and their round corners in the \(<100>\) direction (Figure 7.1(b)).
Electrochemical experiments were performed in a single-compartment Teflon cell (Figure 7.2). An electrolyte consisting of 1 M LiPF₆/ethylene carbonate (EC): diethyl carbonate (DEC) (1:2 v/v) (Novolyte Technologies, BASF) was used in all the electrochemical tests. Dimethyl carbonate (DMC) (>99.9%, HPLC grade, Sigma-Aldrich) was used as the rinsing solvent. The counter and reference electrodes were made of Li, whereas the working electrodes were 2 × 2 cm² pieces that were cut from Si(100) wafers with or without vertically standing Si micropillars. The potentials reported here are referred to the Li/Li⁺ redox couple. All the electrochemical tests were performed inside a glove box filled with Ar gas (H₂O and O₂ contents <10 ppm). A multi-channel potentiostat (Multistat 1480, Salartron Analytical) was used for potential/current control.

Surface morphology characterization

After electrochemical treatment, the Si samples (both with and without micropillars) were rinsed in DMC to remove the residual electrolyte. The samples were then transferred to a scanning electron microscope (SEM) (JSM-6700F, JEOL) for imaging. The electrode microstructure was observed with a focused ion beam (Nova 600i Dual Beam, FEI). The cycled electrodes were cross-sectioned with a Ga⁺ ion beam and observed with the SEM.
7.2.4 Secondary ion mass spectrometry

Secondary ion mass spectrometry (SIMS) measurements of the lithiated electrodes were obtained with a SIMS system (Evans Analytical Group). The Cameca IMS 4f mass spectrometer was operated at a pressure of $2.67 \times 10^{-7} \text{ Pa} \left(2 \times 10^{-9} \text{ Torr}\right)$. A 3-keV Cs$^+$ sputtering beam with $200 \times 200 \mu\text{m}^2$ sputtering area was used in all the SIMS measurements. Elemental concentration depth profiles were obtained by analyzing the positively charged CsLi and CsSi secondary ions. The Cs$^+$ current was typically equal to 10 nA. The sputtering depth was determined from the depth of the sputtering craters measured with a profilometer. Data acquisition and post-processing analysis were performed with the SIMS view software of the SIMS system. The lithiated samples were sealed in a glove box and transferred to the SIMS spectrometer within 1 min before exposure to the ambient.

7.3 Finite element modeling

The finite element method (FEM) code ABAQUS/Standard (6.14 version) was used to determine the in-plane stress and strain fields due to anisotropic lithiation/delithiation and to study crack initiation, propagation, deflection, and, eventually, delamination on a silicon electrode subjected to multiple lithiation/delithiation cycles. The unlithiated (crystalline) silicon ($c$-Si) was modeled as an isotropic elastic material with an elastic modulus of 185 GPa and a Poisson’s ratio of 0.23. Although $c$-Si is not strictly an isotropic elastic material, because its elastic modulus may vary by 10% among different crystalline orientations, this variation is considered to be secondary due to the strong orientation-dependence of the Li$^+$ ion diffusion rate. The lithiated (amorphous) silicon ($a$-Si) was modeled as an isotropic elastic-perfectly plastic material. Depending on the Li$^+$ ion
concentration, the elastic modulus and yield strength of the lithiated silicon assume values in the range of 50–102 GPa and 0.5–3.0 GPa, respectively.\textsuperscript{13}

7.3.1 Finite element model for in-plane stress/strain analysis

Figure 7.3 shows the plane-strain FEM model of a Si micropillar with four \{110\} edges and four \{100\} edges all 2 \(\mu\)m in length, representing the four sides and four round corners in the top-view SEM image shown in Figure 7.1(b), respectively. The equilateral octahedral FEM model consists of 56,800 four-node linear isoparametric elements of uniform size equal to 0.02 \(\mu\)m. The total number of nodes is 57,201. All the edges are exposed to Li\(^+\) ion diffusion. The rate of Li\(^+\) ion diffusion \(D\) depends on the crystal orientation, i.e., \(D_{\{110\}} = 6.4D_{\{100\}} = 6.1D_{\{111\}}\).\textsuperscript{10} In the present analysis, lithiation is modeled as a quasi-static diffusion process. As such, the stresses and strains are determined by the relative rate of Li\(^+\) ion diffusion in different crystal orientations, not the absolute diffusion rate. By using a homogeneous initial temperature field and a constant thermal expansion coefficient, the ingress of Li\(^+\) ions is simulated by a temperature front moving at different speeds in different directions. Thus, lithiation-induced volume expansion and associated stress field are equivalently represented by thermal expansion and thermal stress distribution.

To prevent rigid body movement in the simulations of the unconstrained micropillar “unit cell”, the center node of the FEM model (shown in red in Figure 7.3) was fully constrained against in-plane displacement and rotation. In the simulations of the constrained micropillar “unit cell”, the nodes on all the edges (shown by red lines in Figure 7.3) were constrained against in-plane displacement and rotation, to model the constraint induced by the surrounding material.

Figure 7.3 Plane-strain FEM model of a Si micropillar “unit cell” with four \(<110\> edges and four \(<100\> edges.
7.3.2 Finite element model for fracture analysis across electrode thickness

Figure 7.4(a) shows the plane-strain FEM model used to study crack initiation, propagation, deflection, and delamination through the thickness of the Si electrode. The model consists of 43,235 four-node linear elements comprising 46,018 nodes. The element size in the vicinity of the potential crack path is equal to 0.05 µm, gradually increasing to 4 µm in the region away from the lithiated region. The left and right boundaries of the mesh are constrained against displacement in the x-direction, while the bottom boundary is constrained against displacement in the y-direction. Multiple interfaces (shown with colored lines in Figure 7.4(b) are modeled with a bilinear cohesive zone model, which can be used to simulate crack initiation and growth by allowing the interfaces to separate from each other. Figure 7.4(c) shows a schematic of the bilinear traction-separation law of the cohesive interface, where \( \sigma \) is the interfacial stress (either normal or parallel to the interface), \( \delta \) is the interface separation, \( \sigma_c \) is the cohesive strength, \( \delta_c \) is the interface separation for crack initiation, \( \delta_0 \) is the interface separation for failure (i.e., delamination), and \( G_c \) is the interface work of adhesion (fracture energy), represented by the area (OAB), i.e.,

\[
G_c = \frac{1}{2} \sigma_c \delta_0 \quad (7-1)
\]

In the present analysis, it is assumed that \( \delta_c, \delta_0, \sigma_c, \) and \( G_c \) are the same in both normal and shear directions. In all the FEM simulations, (on the order of the interatomic distance) is fixed, while\( \delta_0(\approx 5\delta_c) \) varies with \( \sigma_c \) and according to Eq. (7-1).

Crack initiation and complete failure are, respectively, controlled by the following relations:

\[
[\sigma_n^2 + \sigma_s^2]^{1/2} = \sigma_c \quad (7-2)
\]

\[
G_n + G_s = G_c \quad (7-3)
\]

Where, subscripts \( n \) and \( s \) denote the normal and in-plane shear directions with respect to the crack plane, respectively.

Thus, the stress-separation law at the interface can be expressed as:

\[
\sigma = \begin{cases} 
\frac{\delta}{\delta_c} \sigma_c & (0 < \delta \leq \delta_c) \\
\frac{\delta_0 - \delta}{\delta_0 - \delta_c} \sigma_c & (\delta_c < \delta < \delta_0) \\
0 & (\delta \geq \delta_0)
\end{cases} \quad (7-4)
\]

For \( \delta \leq \delta_c \), the interfacial stress increases linearly with the separation, implying purely elastic stretching at the interface, while for \( \delta_c < \delta < \delta_0 \), the interfacial stress decreases linearly from \( \sigma_c \) to zero as the crack propagates. Crack growth leads to a different unloading path (CO) from the loading path (OA). Complete failure occurs when \( \delta \geq \delta_0 \), resulting in a locally stress-free interface.

The present FEM model contains three types of interfaces: (1) \( c \)-Si/\( c \)-Si interface with \( G_c = 9 \text{J/m}^2 \left( K_{IC} = 1.3 \text{ MPa}\sqrt{\text{m}} \right) \) and \( \sigma_c = 5 \text{ GPa} \); (2) \( a \)-Si/\( c \)-Si interface at different
lithiation/delithiation cycles with $G_c = 1 \text{ J/m}^2$ ($K_{IC} \approx 0.3 \text{ MPa}\sqrt{\text{m}}$) and $\sigma_c = 1.5 \text{ GPa}$, and (3) $a$-Si/$a$-Si interface with $0.5 \leq G_c \leq 3 \text{ J/m}^2$ ($0.14 \leq K_{IC} \leq 0.5 \text{ MPa}\sqrt{\text{m}}$) and $0.25 \leq \sigma_c \leq 1.5 \text{ GPa}$, depending on Li$^+$ ion concentration. In the first cycle, the red line ($y = 1 \mu$m) represents the $a$-Si/$c$-Si interface. The cohesive interface above the $a$-Si/$c$-Si interface (part of the blue line) is $a$-$a$-Si/$a$-Si interface, whereas the cohesive interface below the $a$-Si/$c$-Si interface (part of the blue, yellow, and red lines) is $a$-$c$-Si/$c$-Si interface. As the lithiation depth increases with the lithiation/delithiation cycles, the $a$-Si/$c$-Si interface moves to the second ($y = 2 \mu$m), third ($y = 3.5 \mu$m), and fourth ($y = 5 \mu$m) red line and the cohesive interface above and below the $a$-Si/$c$-Si interface is accordingly updated.

Figure 7.4 (a) Plane-strain FEM model of a Si electrode. The left and right boundaries are constrained in the $x$-direction, while the bottom boundary is constrained in the $y$-direction; (b) A magnified view of the FEM mesh in the vicinity of potential cohesive interfaces. The yellow line represents the $c$-$c$-Si/$c$-Si interface, the blue line represents the $c$-$c$-Si/$c$-Si interface initially, which later becomes $a$-$a$-Si/$a$-Si interface as the lithiation depth increases, while the red line represents the $c$-$c$-Si/$c$-Si interface initially, which later changes to $a$-$c$-Si/$c$-Si interface with the increase of the lithiation depth; (c) Schematic of a bilinear cohesive zone model describing the relation between interfacial stress $\sigma$ and interface separation $\delta$. A surface separation greater than $\delta_c$ leads to crack initiation and propagation, accompanied by a decrease in cohesive strength $\sigma_c$ and interface work of adhesion (fracture energy) $G_c$ until complete failure ($\delta = \delta_0$).
7.4 Results and discussion

Figure 7.5(a–c) shows cyclic voltammetry curves of a p-type boron-doped Si(100) electrode subjected to 30 cycles between voltages of 2.0 and 0.01 V at a scan rate of 0.1 mV/s. The onset of the reduction current is observed in the first cycle at ~0.1 V, corresponding to the initial alloying of the crystalline silicon with lithium, while in the second cycle the lithiation reduction peak shifts to ~0.3 V (Figure 7.5(a)). The two anodic peaks at ~0.3 and ~0.5 V are associated with Li dissolution. The magnitude of the oxidation and reduction peaks increases with the number of cycles (Figure 7.5(b)), which can be attributed to the continuous increase of the amount of electrochemically-active silicon in each cycle.

The kinetics of lithiation in silicon is analogous to the model of SiO\textsubscript{2} layer formation on silicon. During the initial cycles (Figure 7.5(a–b)), the increase in active silicon is controlled by the lithiation reaction rate; thus the current density increases with the number of cycles (i.e. lithiation time). Both the lithiation depth and the time needed for lithium to transport from the surface to the reaction front increase with cycling. After 30 cycles, the time for lithium transport approaches the cycle time and the cyclic voltammetry curve stabilizes (Figure 7.5(c)). With continued cycling of the silicon electrode, the redox current area begins to decrease, indicating the loss of active silicon material.

Here, we characterize the evolution of the surface morphology of the silicon electrode using top-view scanning electron microscope (SEM) images obtained after 3, 8, and 50 cycles (Figure 7.5(d–f)) and magnified SEM images of the electrode surface obtained after 30 cycles (Figure 7.5(g–i)). The dominant feature is the development of surface cracks in two orthogonal directions, resulting in isolated small squares, which form a regular repetitive pattern on the electrode surface. These crack patterns further account for the formation of square cavities (Figure 7.5(f)). Apparently, the damage to the electrode surface is not a rapid and catastrophic process, but occurs in a gradual and cumulative fashion. While damage of the electrode surface is insignificant during the first few cycles, shallow surface cracks initiate after a critical number of cycles and propagate with further cycling, eventually causing delamination at the electrode surface.
Figure 7.5 Cyclic voltammetry curves of a Si(100) electrode cycled between 2.0 and 0.01 V at a scan rate of 0.1 mV/s for (a) 1–3, (b) 4–8, and (c) 30 successive lithium/delithiation cycles. Top-view SEM images of the electrode surface obtained after (d) 3, (e) 8, (f) 50, and (g–i) 30 cycles.

To explain the origin of these orthogonal surface cracks, we need to consider that lithiation in single-crystal silicon is a strongly orientation dependent process. In particular, lithiation preferentially occurs in the <110> direction, while it is relatively slow in the <100> and <111> directions. Figure 7.6 shows a top-view SEM image of 3 × 3 × 8 µm³ micropillars fabricated by photolithography on a Si(100) substrate with exposed {110} lateral surfaces and round corners in the <100> direction. With increasing lithiation, the straight edges of the micropillars preferentially expand in the <110> directions (Figure 7.6(b–c)), while the round corners expand significantly less. This anisotropic expansion causes the “rotation” of the micropillars in the <100> direction to vanish (Figure 7.6(d–e)) and the neighboring micropillars to merge (Figure 7.6(f)). If a micropillar is presumed to represent a “unit cell” of the solid Si(100) electrode, the volumetric expansion during cycling will be confined by the surrounding material, resulting in the development of a compressive force at the micropillar edges. Because of the significantly higher lithiation
rate in the <110> directions than the <100> directions, the “unit cell” is subjected to a higher compressive force on all the {110} planes, which, in turn, induces a high shear stress and plasticity along the ±45° directions (i.e., along the {100} planes).

Figure 7.6 SEM and FEM results of the anisotropic in-plane expansion and cracking of single-crystal silicon micropillars and a Si(100) electrode subjected to lithiation. (a–f) Square micropillars fabricated on a p-type Si(100) wafer at various lithiation stages (the size of the red solid squares is 3 × 3 µm²). In-plane equivalent plastic strain $\bar{\varepsilon}_p$ distributions in (g) lithiated (unconstrained) micropillar and in (h) lithiated and (i) delithiated (constrained) octahedral “unit cell” of the silicon electrode. (j) Crack pattern on the surface of a lithiated silicon electrode showing crack formation in the <100> directions.

To validate the above hypothesis, a planar octahedral model of the “unit cell” of the silicon electrode was developed and analyzed with the finite element method (Figure 7-6(g)). Lithiation-induced volumetric expansion was simulated as a thermal expansion process. A moving temperature field was applied to represent the diffusion and migration of lithium into the silicon electrode. The unlithiated (crystalline) silicon (c-Si) was modeled as an isotropic elastic material of elastic modulus $E = 185$ GPa and Poisson’s ratio $\nu = 0.22$, whereas the lithiated (amorphous) silicon (a-Si) was modeled as an elastic-plastic material with material properties depending on lithium ion concentration (i.e., $E = 50–102$ GPa, $\nu = 0.22$, and yield strength $Y = 0.5–3.0$ GPa). Because the pillar height is much larger than its in-plane dimensions, plane-strain conditions were assumed in all the simulations. Figure
7.6(g) shows the deformed configuration of a fully lithiated micropillar, including contours of equivalent plastic strain. Due to the anisotropic lithiation rate (ion diffusion in the (110) direction is 6.4 times faster than that in the (100) direction\textsuperscript{11}, the expansion is asymmetric, in agreement with our experimental observations (Figure 7.6(b-c)) and those of others.\textsuperscript{10,18} Figure 7.6(h) shows the equivalent plastic strain in a “unit cell” of the electrode after full lithiation. Because volumetric expansion of the “unit cell” is fully constrained by the surrounding material, large plastic strains develop along the (100) edges, contributing to the formation of perpendicular stress bands along the <100> directions. Figure 7.6(i) shows equivalent plastic strain contours after full delithiation, which indicate that during delithiation the locations of large plastic strain continue to accumulate plasticity. The perpendicular bands of large plastic strain encountered in the simulation agree well with the experimental observation of repeated perpendicular surface cracks at different length scales.

After the formation of cracks perpendicular to the electrode surface (Figure 7.5(e, g–i)), small squares of electrode material defined by these surface cracks begin to delaminate (Figure 7.5(f)). To understand the origin of this process, it is necessary to consider how these surface cracks form and progressively propagate with cycling before causing electrode material to delaminate. This can be accomplished by analyzing the experimental evidence of surface crack growth during the first 50 lithiation/delithiation cycles. Figure 7.7(a–d) (left column) shows cross-sectional SEM images across a typical surface crack after 3, 8, 30, and 50 cycles, respectively. The crack initiates at the electrode surface (Figure 7.7(b)), consistent with the fracture of single-crystal silicon nanopillars\textsuperscript{20} propagates in the depth direction with further cycling (Figure 7.7(c)) and, finally, it is laterally deflected at a depth of ~5–8 µm (Figure 7.7(d)). The lateral deflection of neighboring cracks after prolonged cycling is the reason for the formation of square delamination fragments of electrode material (Figure 7.5(f)).

Two samples were examined with SIMS: a reference sample obtained by discharging a Si(100) electrode at 5 mV for 2 days and a half-cycle lithiated Si(100) sample obtained by a linear sweep from the open current potential (OCP) to 5 mV at a rate of 0.1 mV/s. Figure 7.7 shows depth profiles of Li, Si, and Li/Si ratio obtained with SIMS. The vertical dashed line at a Li/Si ratio equal to 3.75 indicates the boundary between the solid electrolyte interface (SEI) and the lithiated Si. The significantly higher Li/Si ratio near the surface is attributed to Li trapped in the SEI and residual electrolyte which is almost free of Si. The Li/Si ratio reaches a steady-state of ~3.75 at depths ≥2 µm (Figure 7.7(a)). This region is identified as the Li\textsubscript{15}Si\textsubscript{4} phase, and the 3.75 value was used to calibrate the Li/Si ratio (Figure 7.7(b)). The results clearly show a higher Li concentration at the electrode surface than the bulk and a fairly linear Li concentration distribution through the lithiated Si region. Therefore, a linear distribution of Li concentration was adopted in all the FEM simulations.
Despite the clear evidence from cross-sectional SEM images of the observed crack trajectories, the question that remains is the physics and mechanics underlying such behavior; specifically, why do cracks initiate at the electrode surface and why do such initially vertical cracks deflect laterally? To seek answers to these questions, we analyzed the lithiation/delithiation-induced stress and strain fields in the cross-section of the silicon electrode over multiple cycles. A cohesive zone model was used to represent multiple interfaces, which were allowed to separate at a critical stress and thus simulate crack initiation and growth. These interfaces are characterized by the cohesive strength $\sigma_c$ and the interface work of adhesion $G_c$ (fracture energy). An approximately linear lithium concentration profile (Figure 7.7) was simulated by the gradual advancement of the lithiation boundary with increasing lithiation/delithiation cycles.

As shown in Figure 7.8(a) (middle column), after 3 cycles both the lithiation depth $d$ (~1µm) and plastic deformation are mainly confined to the electrode surface. With continued cycling, the lithiation depth increases with more plasticity accumulating below the surface owing to further lithium insertion. During the subsequent delithiation, the tensile residual stresses generated in the large plastic region cause face separation along the cohesive interface, resulting in the initiation and propagation of vertical cracks (Figure 7.8(b–c), right column). When the crack tip approaches the lithiation boundary, the crack is abruptly deflected laterally and continues to propagate along the $\alpha$-Si/$c$-Si interface (Figure 7.8(d), right column), which is consistent with the experimental evidence (Figure 7.8(d), left column).

Such a marked deflection in crack trajectory can be interpreted in terms of the mutual competition between the direction of maximum mechanical driving force and the weakest microstructural path. Specifically, from a mechanics perspective, cracks in nominally brittle (elastic) materials follow the path of maximum strain energy release rate.
Figure 7.8 Cross-sectional SEM images and corresponding FEM results of a Si(100) electrode obtained after (a) 3, (b) 8, (c) 30, and (d) 50 lithiation/delithiation cycles. The SEM images (left column) show crack growth through the electrode thickness followed by crack deflection and propagation along the lithiation boundary (lithiated/unlithiated interface). The FEM results (middle and right columns) show the equivalent plastic strain $\varepsilon_p$ after lithiation and the maximum principal stress $\sigma_{\text{max}}$ after delithiation, illustrating crack initiation, propagation in the thickness direction, and lateral deflection along the lithiation boundary versus cycles.

This is essentially consistent with a $K_{II} = 0$ crack trajectory, where $K_{II}$ is the stress intensity factor for in-plane shear crack displacement, although this is mitigated in real materials by the nature of the microstructure encountered by the crack. In the current system pertaining to silicon electrodes in LIBs, although the elastic modulus of $c$-Si (185 GPa) is higher than that of $a$-Si (50–102 GPa), its fracture toughness $G_c \approx 9$ J/m$^2$ ($K_{IC} \approx 1.3 \text{MPa} \sqrt{m}$) is an order of magnitude higher than that of the $a$-Si/$c$-Si interface in the $<100>$ direction, whose estimated fracture toughness is $G_c \approx 1.0$ J/m$^2$. 
accordingly, the crack is deflected along the $a$-Si/$c$-Si interface as this is both energetically more favorable and the weakest microstructural path.

Such deliberations of the behavior of cracks impinging on dissimilar (elastic) material interfaces can be explained in mechanics terms by the He and Hutchinson analysis,\textsuperscript{22} which provides a quantitative criterion to predict whether a singular crack will penetrate through or deflect along a linear-elastic bimaterial interface. As depicted in Figure 7.9, the crack path depends on two principal factors, namely the elastic modulus mismatch across the interface, described by the Dundurs’ parameter $\alpha = (E_1 - E_2)/(E_1 + E_2)$, where $E_1$ and $E_2$ are the respective elastic moduli of material 1 and 2, and the ratio of the toughness (critical strain energy release rate) of the interface to that of the material beyond the interface $G_{c,\text{int}}/G_{c,2}$. By substituting the material and interfacial properties of the present system (given in the preceding paragraph) into this analysis, we can calculate that the modulus mismatch $\alpha$ for the lithiated/unlithiated $a$-Si/$c$-Si interface is approximately equal to $–0.4$ with a toughness ratio of $G_{c,\text{int}}/G_{c,2} \approx 0.11$ (red square point in Figure 7.9). Accordingly, it is clear from Figure 7.9 that, from a mechanical driving force perspective, the crack will definitely deflect along the $a$-Si/$c$-Si interface.

![Figure 7.9 Linear-elastic solution of the ratio of the interface toughness to the toughness of the material beyond the interface $G_{c,\text{int}}/G_{c,2}$ versus Dundurs’ parameter $\alpha = (E_1 - E_2)/(E_1 + E_2)$](image)

Figure 7.9 Linear-elastic solution of the ratio of the interface toughness to the toughness of the material beyond the interface $G_{c,\text{int}}/G_{c,2}$ versus Dundurs’ parameter $\alpha = (E_1 - E_2)/(E_1 + E_2)$. Where $E_1$ and $E_2$ are the elastic modulus of material 1 and 2, respectively, for a normally incident crack impinging onto a biomaterial interface.\textsuperscript{22} Whether the crack penetrates through the interface or is deflected along the interface depends on the elastic modulus mismatch (represented by the Dundurs’ parameter) and the ratio of the interface toughness to the toughness of material 2 ($c$-Si). For the $a$-Si/$c$-Si interface, $\alpha \approx –0.4$ and $G_{c,\text{int}}/G_{c,2} \approx 0.11$ (red square point). The theory predicts that a crack growing in the $a$-Si will not propagate into the $c$-Si, but will be deflected along the $a$-Si/$c$-Si interface.
7.5 Conclusions

By establishing a mechanistic explanation for the root cause of the premature failure of silicon electrodes in LIBs following prolonged lithiation/delithiation cycles, this chapter provides a basis for the future development of more robust and durable batteries from the following aspects:

(i) **Surface modification (artificial SEI design).** Recent Fourier transform infrared spectroscopy studies\(^{23-25}\) have shown that the main components of SEI forming on silicon electrodes have high solubility in the electrolyte and very weak mechanical strength. A thin protective film of enhanced chemical stability and mechanical strength can prevent crack initiation by minimizing surface plasticity.

(ii) **Electrode material selection.** Despite its high capacity, the silicon electrode material is naturally brittle and prone to fracture. Emerging ductile electrode materials (e.g., silicon-metal alloy) and structurally optimized electrode materials (e.g., porous/hollow structure) may substantially reduce the risk of electrode fracture.

(iii) **Charging profile optimization.** Secondary ion mass spectrometry (SIMS) shows an approximately linear decrease in lithium concentration through the electrode thickness (Fig. S3b, Supplementary Information). By tuning the charging profile, we can obtain the same capacity with a uniform lithium distribution through the electrode thickness. This would allow a lower surface lithium concentration, thereby reducing surface plasticity, which is a key factor for suppressing crack initiation and propagation.

The present work provides a mechanistic explanation of the root cause of premature silicon electrode failure in LIBs following prolonged lithiation/delithiation cycling. Based on this insight, we demonstrate how electrolyte additives can heal electrode cracks and improve the electrode fracture resistance. In addition, we propose other strategies including surface modification, electrode material development, and charging profile optimization to increase the material ductility and suppress high surface stress. We consider the knowledge of the failure mechanisms of silicon electrodes gained from the present study as a foundation for future design improvements and the aforementioned strategies as main paths toward the development of more robust and durable electrodes for next-generation LIBs.

7.6 References


(13) Berla, L. A.; Lee, S. W.; Cui, Y.; Nix, W. D. J. Power Sources. 2015, 273, 41.


Chapter 8 – Summary and outlook

8.1 Summary

This dissertation focuses on the electrochemical and mechanical processes at surfaces and interfaces of energy devices, covering issues from process characterization, underlying mechanisms, to implications in practical applications. Several important topics were examined in this dissertation, such as electro-catalytic processes (hydrogen, carbon monoxide, methanol oxidation, and oxygen reduction reactions) in fuel cells, electrolyte passivation processes in SEI of the anode of LIBs, and material failure processes on Si anodes of LIBs. The main findings and key conclusions of the work included in this dissertation can be summarized as following:

(1) Two different strategies (addition of oxygen vacancies and fluorine doping) were used to modify the electronic structure the TiO$_2$ substrate with a Pt nanoparticle surface catalyst. The electrochemical activity was examined to identify how catalysis can be affected by changes in the support material electronic structure. Among the reactions investigated, only hydrogen evolution reaction was insensitive to the changes in the electronic structure of the TiO$_2$ substrate. Methanol oxidation showed an increase in activity and stability by a factor of 1.75 and 2.7, respectively, the CO oxidation peak exhibited a negative shift by 0.12 V, implying enhanced anti-poisoning capability, and the oxygen reduction potential showed a positive shift by 0.07 V, compared with Pt nanoparticles on pristine TiO$_2$ support. Experimental observations were interpreted in the context of an electronic structure model showing that the electrochemical activity increases when the Fermi level of the support material in Pt/TiO$_x$ systems is close to the Pt Fermi level and the redox potential of the reaction. The in-depth understanding of the substrate effect on electro-catalysis obtained from this work provides important guidance for the selection of support materials for Pt/TiO$_x$ systems.

(2) EC-based electrolyte decomposition was studied by ATR-FTIR spectroscopy and the decomposition products were identified. Peak assignments were made on reference FTIR spectra of the DEDOHC and poly-EC compounds, based on quantum chemical (Hartree-Fock) calculations. Significant peak shifts and broadening of the FTIR spectra were found to occur due to the solvation effect. By analyzing the surface species formed on a Sn electrode, the unstable product was detected to be DEDOHC, whereas poly-EC was found to form on a Ni electrode after extended cycling. These examples reveal the importance of including the solvation effect in the electrolyte decomposition product identification using ex-situ FTIR spectroscopy. This finding should be helpful in studies based on in-situ FTIR spectroscopy and any other vibrational spectroscopy analyses of electrolyte decomposition processes.
(3) Standard Li-ion electrolyte reduction reactions on two metal electrode surfaces (Au and Sn) were first investigated by in-situ ATR-FTIR spectroscopy. The over-potential and reduction products showed clear surface dependence. It was found that relatively insoluble LiEDC forms on the Au electrode at ~0.6 V vs. Li/Li⁺, whereas relatively soluble DEDOHC forms on the Sn electrode at ~1.25 V vs. Li/Li⁺. Another common reduction product, lithium propionate was detected on both electrode surfaces. To explain the surface dependence observed in these studies, two different reaction mechanisms were proposed: a non-catalytic reaction path for the Au electrode surface and a catalytic reduction path for the Sn electrode surface. The catalytic role of the electrode material surface in the electrolyte decomposition process demonstrated in this dissertation may play a more general role in LIBs than heretofore recognized.

(4) The underlying physics and fracture mechanics of single-crystal silicon electrodes over multiple lithiation/delithiation cycles were investigated in the light of electrochemistry experiments, linear-elastic fracture mechanics analysis, and finite element modeling. It was found that crack initiation at the electrode surface is induced by surface plasticity due to excessive volumetric strain. Due to anisotropic in-plane lithium diffusion, the surface cracks were aligned perpendicularly. Driven by a high tensile stress field, the cracks propagated into the electrode up to the amorphous/crystalline interface, where they were deflected latterly, eventually resulting in electrode delamination. Based on the understanding of the failure mechanism, electrolyte additives were used to effectively arrest electrode surface cracks, preventing them from propagating deep into the electrode material and causing delamination. In addition, other strategies were proposed to increase the electrode fracture resistance, including surface modification, electrode material development, and optimization of the charge profile. The knowledge of the electrode failure mechanism gained from this work provides a theoretical foundation for future electrode design improvements, while the aforementioned strategies pave the way toward the development of more robust and durable electrodes for next-generation LIBs.

8.2 Outlook

Energy storage devices represent an emerging field full of challenges and opportunities. Basic understanding of chemical and mechanical processes at surfaces and interfaces is of paramount importance for the successful development of future fuel cells and batteries. To overcome the many challenges ahead, joint efforts from various research fields, e.g., electrochemistry, materials science, and mechanical engineering, are necessary because of the highly interdisciplinary nature of the required research. “One mission” project needs insight into the generic interactions between the coupling and independent issues in one device.

Beyond the work of this dissertation, the following topics are viewed as interesting and important to explore in future studies.

(1) Cathode electrode performance improvement: Although tremendous research has been focused onto the anode performance, the cathode is actually the “shortest board” in
LIBs. The chemical composition of its interphase is even less understood compared to the anode. The increasing trends for higher operation voltage are expected to bring the cathode interphase problem in the frontline. The increase of the cathode capacity will makes it more prone to fracture due to the profound increase of the volumetric strain. Therefore, both chemical and mechanical degradation mechanisms at the cathode must be thoroughly understood to enable further evolution of high-energy-density LIBs.

(2) **Advanced battery systems free of an ion-hosting system:** Metal-based, rechargeable lithium and sodium batteries have recently emerged as promising platforms. Unlike other “host-guest” electrodes, such as those of LIBs, metal anodes rely on ion deposition/stripping instead of ion insertion/extraction. This means that there is no dead weight/volume in the electrochemical reactions; therefore, the energy density can be further increased. However, the main challenges with this kind of system are chemical passivation and dendrite growth/mechanical deformation on electrode interfaces.