Advanced AFM-Based Techniques for Understanding and Engineering the
Fundamental Properties of Materials for Energy Storage and Catalysis Applications

by

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Applications of lithium ion batteries (LIBs) are expanding rapidly from electronic devices to electric vehicles and many other markets. To further improve their energy storage capacities and durability, scientists have dedicated much efforts on investigating the least understood part of the batteries, the solid electrolyte interphase (SEI). SEI is the reductive decomposition product of the electrolyte of LIBs (the solvent and Li ion salts), deposited on the surface of the electrodes, during the charge/discharge process. The properties of SEI dramatically influences or even determines the capacity, charging/discharging rate, and cycle life time of a battery. In the case of graphite-based LIBs, one of the most important causes of the capacity loss is due to the irreversible co-intercalation of the solvent into the graphite layers. This unwanted co-intercalation of the solvent causes blister formation and exfoliation in the graphite electrode. To prevent this co-intercalation, scientists have been trying to alter the commercially used battery electrolyte or to introduce additives to grow a stable SEI that prevents the co-intercaalton of the solvent.

In chapter 2, for the first time, without altering the most commonly used commercial LIB electrolyte (LiPF$_6$ in ethylene carbonate and dimethyl carbonate) or introduction of any
additives, we aimed to prevent the co-intercalation of the solvent by only applying a new electrochemical method as a pre-treatment of charge/discharge processes. Different from the commonly used constant current charging method, which always associates with a large voltage jump applied to the electrodes, this pre-treatment applied a slow changing voltage, which gradually decreases from OCV to 0.2 V vs Li/Li⁺. The voltage pattern instigates a different double layer structure near the electrode, which in turn leads to different SEI structures. The unique structures efficiently prevent blister formation and graphite exfoliation, therefore can be used to largely minimize the irreversible capacity loss of graphite based LIB electrodes.

In Chapter 3, we focus on the most promising alternative anode materials for the LIBs, silicon (Si). Si as an anode has 10 times higher the maximum theoretical capacity of the-state-of-the-art graphite anode materials. Si is also the second-most abundant element in the earth's crust and is environmentally benign. Large (>10 µm) Si microparticles (SiMP) are especially attractive, due to a low production cost. However, the dramatic volume expansion of silicon (~280%) during battery operation leads to mechanical fracture, inducing loss of the interparticle electrical contact and exposure of the highly reactive fresh Si surface to electrolyte, which leads to continuous (SEI) growth, electrolyte consumption resulting in a low Coulombic efficiency (CE). The SEI formed from the currently used carbonate electrolytes can tolerate only a small volume change (~12%) of graphite but is not robust enough to accommodate 280% of volume change of SiMP. Hence, SiMP anodes exhibit an extremely fast capacity drop to less than 60% of the initial value in the first 20 charge/discharge cycles in contrast to the microsized graphite anodes that achieve cycling CE (CE) >99.9% after 10 cycles, ensuring 1000 cycle life. With collaboration with Dr.
Wang and Dr. Chen from University of Maryland we demonstrate that the rationally designed electrolyte provides a simple and practical solution to current battery technology without any modification of binder and fabrication methods. A LiF SEI with high interfacial energy in contact with SiMP is key for accommodating deformation of the lithiated Si during cycling. The LiF layer thickness was directly measured for the first time and compared to the commercially available LIB electrolyte SEI layer thickness. Also, the thickness and the roughness of the soft organic SEI layer was measured and compared to the commercially available electrolyte after charge/discharge to find that the new electrolyte enhances the homogeneity of the SEI layer and decreases the thickness of both inorganic and organic sublayers’ thickness.

In chapter 4, we established a standard protocol for measuring the mechanical properties of complicated samples, such as SEI layers, by using AFM technique. We addressed the details and factors impacting on measuring the mechanical properties of SEI via AFM both by calculations and by using standard samples with known mechanical properties. This protocol which is based on contact mechanics, solves the issues related to discrepancies that are observed in the scientific reports about the mechanical property measurement of SEI.

In the following chapters, we explored the correlation between the intrinsic physical properties, in particular, the work function of nanomaterials with their catalytic activities (both as catalysts themselves/or as catalyst supports) in chemical catalysis and electrochemical-catalysis. There are many reported cases on enhancing/altering the catalytic activity of materials by heteroatom doping. However, physical properties of the material such as work function before and after doping has not been well-studied in many
cases. The research efforts have been devoted to shed more light on this fundamentally/practically important aspect of the catalysts in areas, taking advantage of our AFM-based work function measurement (Kelvin Probe Force Microscopy, KPFM).

In chapter 5, in a joint experimental and computational study, we aimed at shedding light on the electronic properties of the most industrially used catalyst support, γ-Al₂O₃. Combined with a variety of surface characterization techniques, as well as simulations based on Density Functional Theory (DFT) by Prof. Pavanello’s group, we studied and compared the structure and electronic properties of phosphorus doped γ-Al₂O₃ and non-doped γ-Al₂O₃ nanoparticles to fundamentally understand how phosphorus doping could fine tune the surface structure and electronic properties of γ-Al₂O₃ nanoparticles. Our experimental results combined with the theoretical calculations agree in finding that P doping of γ-Al₂O₃ leads to a significant decrease in its work function. The computational models show that this decrease is due to the formation of a new surface dipole, providing a clear picture of the effect of P doping at the surface of γ-Al₂O₃. In this study, we uncover a paradigm for tuning support-catalyst interaction that departs from details of the chemistry and intimately involves the electrostatic properties of the doped γ-Al₂O₃ surface specifically, the surface dipole. Our findings open a new pathway for engineering the electronic properties of metal oxides’ surfaces.

In chapter 6, inspired by our findings about the correlation between the work function and the catalytic activities of our newly synthesized P-doped graphitic carbon (PGC), we aimed at using this compound to explore its possible catalytic activities towards the electrochemical reduction of CO₂. CO₂ is the major cause of global warming and its lifetime in the atmosphere is between 100 to 800 years. The amount of CO₂ in the
atmosphere is at its highest ever (over 400 ppm) and it is likely to continue to rise in the future. The most sustainable image that scientists have for removing the CO₂ is to recycle it through renewable energy via electrochemical reactions. The combination of our designed electrochemical cell and our catalyst, resulted in the selective production of iso-propanol with the highest Faradaic efficiency reported (by 70%). Phosphorus configuration in the catalyst was identified through XANES characterization with collaboration with Dr. Lockard’s lab. Troubleshooting the reproducibility issue is undergoing. Inductively coupled plasma - optical emission spectrometry (ICP-OES) measurement shows a large concentration of Iron in the catalyst’s raw material. Iron has a low catalytic activity towards CO₂ reduction and if any, it can produce the gas products and not the iso-propanol.
Preface

Chapter 3, a large portion of this material has been submitted to Nature Energy Journal. All the figures and text of this future publication are reprinted in this chapter with permission from Ji Chen1, Xiulin Fan, M. Reza Khoshi, Sooyeon Hwang, Long Chen, Xiao Ji1, Chongyin Yang, Huixin He, Dong Su, Oleg Borodin, and Chunsheng Wang.

Chapter 5, a large portion of this material has been published as a full journal article in Physical Chemistry Chemical Physics Journal. All the figures and texts of this published article are reprinted in this chapter with permission from Muhammed Acikgoz, M. Reza Khoshi, Jaren Harrell, Alessandro Genova, Rupali Chawla, Huixin He and Michele Pavanello. (Tuning the electronic properties of the γ-Al2O3 surface by phosphorus doping." Physical Chemistry Chemical Physics 21(27): 15080-15088.)
Dedication

For my parents, who brought me to life.

For my grandmother, who nurtured me with the purest love.

For my sister, who has always been there for me, since the day one.
Acknowledgement

First and foremost, I would like to thank my PhD dissertation adviser, professor Huixin He, for allowing me to achieve the most valuable goal of my life, so far. Since day one, I have felt welcomed and cared in her research group. Her ambition and love for knowledge and doing great research, in addition to her kindness and motherhood towards the group members, have made us a family. A family that its members are in touch with each other for years after graduation and they care for one another and treat each other with love and respect. There has not been a time that I needed any help which I did not receive, from her or our other group members. For the past 7.5 years of being privileged to be a member of Dr. He’s research group, I have gained a great deal of knowledge and experience in my most favorite field of science, all of which would not happen if it was not for her patience and constant guidance, and there is no way that I can put any price on that. Every second of my PhD was a moment of growth for me. I have learnt from her not to give up, ever!, to go after my dreams, to become mentally stronger, to be able to pass through obstacles that one faces on his path. If I ever had a choice of going back in time and start over, there would not be any other group that I would choose over Dr. He’s group.

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I am also truly grateful for my collaborators for their efforts to make us great scientific teams and for their valuable insights and great works: Dr. Pavanello, Dr. Acikgoz and the rest of Dr. Pavenello’s group members for their valuable works on the
computational side of our collaborative work; Dr. Wang and Dr. Chen for their amazing collaborative work on battery testing and materials characterizations, as well as offering their state-of-the-art new electrolyte for our battery projects together; Dr. Brukh for his constant help with the departmental instrumentations (SEM, EDAX, etc.); Dr. Kakalis for his help in solid and liquid NMR and also training me for advanced NMR techniques; Dr. Lockard, Dr. Kucheryavy and Mikhail Solovyev for their help with XANES characterizations.

I would also like to sincerely thank my research group members, Dr. Pui Lam Chiu, Dr. Ruiming Huang, Dr. Mehul Patel Dr. Keerthi Savaram, Bowei Li and Qingdong Li. Their help and support was another reason that I could accomplish my degree and I am forever thankful to them.

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Chapter 1: Introduction

1.1 In-situ and operando Electrochemical Atomic Force Microscopy-Peakforce Quantitative Nano-Mechanical Property Mapping (EC-AFM-PF-QNM) of Lithium Ion Battery (LIBs) to Enhance its Performance

1.1.1. Lithium Ion Batteries

Lithium ion batteries (LIBs) have been successfully commercialized due to their large energy density and long lifespan.[1] It is now one of the most sought after choices for power source of portable and rechargeable applications.[2] Applications of LIBs have been expanding rapidly from consumer electronics to electric vehicles, renewable energy storage systems, defense and military applications, and many other markets.[3-8] The desirable LIBs for practical applications requires high energy density, coulombic efficiency, good cyclability, excellent safety and low self-discharge. [9] It is expected that LIBs will continue to drive large market shares, and that new applications of LIBs such as powering electric and hybrid electric vehicles will flourish after a series of improvements resulting from current research efforts.

The conventional commercial Li-ion batteries consists of graphite based anode, [10] an organic electrolyte that acts as an ionic path between electrodes and separates the two electrode materials, and a transition metal oxide (such as LiCoO$_2$, [11] LiMn$_2$O$_4$, [12] and LiNiO$_2$ [13])
cathode. Graphitic carbon anodes have a theoretical specific capacity of only 372 mAh g$^{-1}$, due to the limited number of intercalation sites for Li$^+$ ions within the host lattice. Although there have been many efforts to increase the capacity of the batteries by altering the anode materials (i.e. phosphorus based materials, [14, 15] metal oxide materials, [16-18] tin-based materials, [19, 20] and Silicon based materials [21-23]), there is an inevitable part of every battery that plays a vital role in its performance and cyclability, which was found years after the development of batteries: the solid electrolyte interphase (SEI)

1.1.2. Solid Electrolyte Interphase (SEI)

One of the most impressive advancements in the chemistry beneath LIBs is the understanding of the electrodes surface chemistry. The graphitic anode in state-of-the-art LIBs operates at potentials ($-3.03$ V vs SHE) where nearly no organic electrolyte molecule is thermodynamically stable against electrochemical reduction. For reversible Li$^+$ intercalation/deintercalation with graphitic anodes, electrolyte solvents are chosen to maximize lithium salt solubility and Li$^+$ conductivity. More importantly, the electrolyte molecules (the salt and the solvent molecules) should have the ability to stabilize the electrolyte/graphite interface by in-situ formation of a new subcomponent on the electrode surface, which is known as solid electrolyte interphase (SEI). This layer, was named SEI layer by Peled [24] and it is a determinant factor on the performance of LIBs since the SEI nature and behavior determines the safety, power capacity, morphology of the lithium deposits, shelf life, and cycle life of the battery. [25-28]

An ideal SEI layer should be able to passivate the electrode materials and prevent continuous electrolyte decomposition. At the same time, it must remain conductive to Li ions.
The structure and properties of the SEI layer not only ensure the reversibility of Li+ (cycle life stability of the battery) but also influence the kinetics of Li+ transport across the electrolyte–electrode interface, which dictates the rate capability and power density of the battery.

1.1.3. SEI Characterizations

The onset potential of SEI formation is not a fixed value. Literature offers values such as 2 V, [29] 1.7 V, [30] or 1 V, [31] but 0.8 V [32, 33] is the most widely adopted practical value. SEI formation may also continue up to few cycles. However, this parameter cannot be normalized because it depends on a number of factors like nature and composition of electrolyte, nature of additives used in the electrolyte, [34] sweep rates, [35] etc. It is desirable to have complete SEI formation before Li-ion intercalation begins (>0.3 V [36]).

SEI is a very complicated layer comprising of inorganic components which are normally salt degradation products and organic components which are partial or complete reduction products of the solvent of the electrolyte. [35] The thickness of the SEI may vary from few Å to tens or hundreds of Å. [33, 37] It is difficult to distinctly measure the SEI thickness as some of the components are partially soluble in the electrolyte. [38] But as formation of a new phase between active material and the electrolyte modifies the interphase resistance, the average thickness was estimated using electrochemical impedance spectroscopy (EIS). [39] The picture of a real SEI inside the battery has always been unclear. Models of the SEI on graphite were proposed by Peled et al., [27] Aurbach, [36, 39] and Edström et al. [33, 40] They all suggest SEI to be a dense layer of inorganic components close to the carbon, followed by a porous
organic or polymeric layer close to the electrolyte phase. Sometimes crystals of LiF are also detected. [41]

As mentioned, SEI has been the least understood component in the batteries, due to its in-situ and complex formation and evolution mechanisms. Many efforts have been devoted to understand the SEI formation and the co-intercalation of the solvent in graphite based LIBs.[24, 27, 35, 42-45] However, numerous aspects of the SEI and intercalation are still not well understood, including its electrochemical formation potential, or if these components are arranged in a homogeneous manner or distributed hierarchically in a multilayer structure, etc. Most such studies rely on ex-situ instrumentation, such as X-ray photoelectron spectroscopy (XPS), [46-48] Fourier transform infrared or Raman spectroscopy (FTIR, FT-Raman),[34, 49-51] and scanning or transmission electron microscopy (SEM, TEM), [52] which provide rich information about interfacial chemistry, however, they inevitably introduce significant disturbances to the delicate SEI, due to exposure to environment (SEI components are highly sensitive towards water and oxygen in ppm level) or high energy beams, as well as mechanical/chemical deterioration through sample preparation and handling.

1.1.4. Electrochemical Controlled Atomic Force Microscopy (EC-AFM)

In situ/operando analysis by electrochemical controlled atomic force microscopy (EC-AFM) in an Ar-filled glovebox (with water and oxygen level of <0.1 ppm) allows direct probing of SEI formation and structure, while maintaining conditions that closely simulate real-life Li ion devices with the least destructive impact. The quantitative nature of AFM provides the capability to directly monitor morphology evolution and mechanical
properties in nano-scale level anode surface evolution as a function of applied electrochemical potentials or electrolyte compositions/additives. Therefore, AFM is not only an in-situ imaging tool, but also potentially a standard diagnostic method to evaluate the quality of SEI thus formed. There are several reports on conducting in-situ EC-AFM for studying batteries. [53-57]

To study the EC-AFM, the EC cell of Dimension Icon AFM system from Bruker was used. As it is illustrated in figure 1.1, the EC cell (Fig. 1.1. b) mimics the real battery assembly of a coin cell (Fig.1.1.A) with an opening on the top for the AFM probe to scan the surface of the working electrode. The EC cell make a semi-closed environment once the AFM head is submerged into the electrolyte and sealed the opening, preventing the electrolyte solvent evaporation and/or contamination from the environment.

![Figure 1.1.](image)

**Figure 1.1.** (A) Illustration of a coin cell battery (Jan Petter Maehlen) vs. (B) the electrochemical cell for EC-AFM studies that mimics the battery system (Bruker EC-AFM cell)

All the working electrodes studied in the following chapters act as cathode since they are in a cell against lithium metal, which has the lowest reduction potential. These working
electrodes, are in fact anode materials in the real batteries once they are against the cathode materials such as metal oxides. The lithium metal is placed under the glass top (Figure 1.2.) and connected to a Ni wire which works as the conductor and it connects to the potentiostat terminal.

Figure 1.2. Lithium metal is placed under the glass top and is connected to a Ni wire

The assembly for the cathode is more time-consuming than the anode (Li foil) in the EC cell. To make the electrical connections for the electrochemical process, we designed a new way of assembling the cell to decrease the internal resistivity between the current collector (copper foil) and the electrode (Fig.1.3)

Figure 1.3. Assembly of the electrode and electrical connections for in-situ EC-AFM studies.
The electrode was glued to a Teflon small EC cell adapter by Torr Seal Low Vapor Pressure Resin Sealant (Agilent Technologies) and was conductively glued to the copper wire-which is used as the conductor between the electrode and the potentiostat’s terminal- with conductive carbon glue (Pelco®). Both the resin and the conductive glue were cured within 24 hours at room temperature. After that, the sample was assembled into the EC-cell and transferred into the glovebox.

1.1.5. Quantitative Nano Mechanical mapping (QNM)

Solid electrolyte interphase can play a very important role in accommodating the anode materials expansion, preventing the constant pulverization and rupture of the electrode. A mechanically strong SEI layer can increase the capacity of the anode materials by accommodating the volume expansion and shrinkage, preventing the rupture of the anode particles. Hence, the mechanical properties of the SEI is an important characteristic for the battery performance and quality. Scientist have been trying to measure the mechanical properties of this layer. To assess the mechanical properties of the SEI, researchers have been using AFM-based methods. [9, 58-63] However, the application of this AFM method for the SEI layer mechanical property mapping is relatively new and scientists often have made significant errors in this measurements that can be proven to be more than 50%.

Chapter 4 explains the studies of the mechanical property measurement, based on AFM methods. In this chapter, the factors that need to take into consideration for measuring the accurate and repeatable mechanical properties for the SEI are presented and studied.
1.2. Synergy of the Work Function with Catalytic Activities of Chemical/ Electrochemical Catalysts and a Catalyst Support

1.2.1. Background of KPFM method

KPFM measures topography concurrently with surface potential mapping, using an AFM tip. Kelvin probe force microscopy, or KPFM, was used as a tool to measure the local contact potential difference between a conducting atomic force microscopy (AFM) tip and the sample, thereby mapping the work function or surface potential of the sample with high spatial resolution as first introduced by Nonnenmacher et al. in 1991. [64] KPFM is primarily based on the instrumentation of an AFM system.

Using a gold-leaf electroscope in 1898, Sir William Thomson, later known as Lord Kelvin, observed that plates of copper and zinc mounted on insulating shafts created charge when they were brought into electrical contact and then moved apart. His discovery can now be explained in terms of work function differences. The work function is the minimum energy (or work, usually measured in eV), needed to remove an electron from a solid, to a point immediately outside the solid surface (or energy needed to move an electron from the Fermi level into vacuum). When two different conductors are brought into electrical contact, for example via an external wire contact, electrons will flow from the one with lower work function to the one with higher work function, equalizing the Fermi energies. If they are made into a parallel plate capacitor, equal and opposite charges will be induced on the surfaces. The
potential established between these two surfaces is called the contact potential difference (CPD), contact potential, or surface potential, which equals the work function difference of the two materials. Measuring the CPD is thus simple. An external potential (also called the backing potential) is applied to the capacitor until the surface charges disappear. At this point, the external potential equals the CPD. The various Kelvin probe techniques developed thus far differ mainly only on how this charge free state is detected.

In general, the electrostatic force between an AFM tip and a sample is given by:

\[ F_{es} = \frac{1}{2} \frac{dc}{dz} \Delta V^2 \quad \text{(eq. 1.1)} \]

Where \( C \) is the tip-sample capacitance, \( z \) is the tip-sample separation, and \( \Delta V \) is the potential difference between the tip and the sample. The contact potential difference is defined by:

\[ V_{cpd} = \frac{\phi_{tip} - \phi_{sample}}{-e} \quad \text{(eq. 1.2)} \]

Where \( \Phi \) is the work function of the target material and \( e \) is the electron charge. Thus, if we apply both a \( V_{dc} \) and \( V_{ac} \) (at a frequency of \( \omega \)) between the tip and sample, the total voltage difference is given by:

\[ \Delta V = V_{dc} - V_{cpd} + V_{ac} \sin (\omega t) \quad \text{(eq. 1.3)} \]

Inserting this into equation 1 (eq. 1), would result in three frequency components which are the following equation:
\[ F_{dc} = \frac{dC}{dz} \left[ \frac{1}{2} (V_{dc} - V_{c_{pd}})^2 + \frac{1}{4} V_{dc}^2 \right] \]  
\text{(eq. 1.4)}

\[ F_\omega = \frac{dC}{dz} [V_{dc} - V_{c_{pd}}] V_{ac} \sin (\omega t) \]  
\text{(eq. 1.5)}

\[ F_{2\omega} = \frac{1}{4} \frac{dC}{dz} V_{ac}^2 \cos (2\omega t) \]  
\text{(eq. 1.6)}

The \( \omega \) component of the force, \( F_\omega \), is what is used in KPFM; we can clearly see that when \( V_{dc} = V_{c_{pd}} \), \( F_\omega \) is zero. By controlling \( V_{dc} \) with the KPFM feedback loop such that \( F_\omega = 0 \), we achieve \( V_{dc} = V_{c_{pd}} \) and thus \( V_{c_{pd}} \) can be measured.

Once the \( V_{c_{pd}} \) is measured by the instrument, by knowing the work function of the AFM tip, one can calculate the work function of the desired sample. Although the conductive KPFM tips is made of metals or silicon, their individual work function can vary, thus, the work function of each AFM tip needs to be measured by using a standard sample, such as gold or highly oriented pyrolytic graphite (HOPG)

\subsection*{1.2.2. KPFM Applications}

KPFM has been used extensively as a unique method to characterize the nano-scale electronic/electrical properties of metal/semiconductor surfaces and semiconductor devices.[65] Recently, KPFM has also been used to study the electrical properties of organic materials/devices, [66-68] biological materials, [69, 70] corrosion studies of alloys, [71-73] and photovoltaic effects on solar cells. [74-76]. By using KPFM, scientist have been also making efforts to fundamentally understand the catalytic activity of the materials and correlate it with
their physical properties, such as work function. [77-81] In this regard, KPFM has been a strong and sensitive method for not only understanding the fundamental properties of the catalysts, but it also helps to engineer better materials for specific applications.

The KPFM that is integrated into the Dimension Icon system in an Ar-filled glovebox gives us a unique advantage over most KPFM measurements, since the work function measurement is not be influenced by the water layer that inevitably covers the sample’s surface in air. The inert environment helps us to obtain more accurate measurements, since the dipole moment of any absorbed species can directly induce a difference in contact potential and, subsequently, a phase shift of our samples.[82]

In chapter 5, KPFM method, along with other characterization techniques, was used to understand and compare the fundamental properties of non-doped and P-doped alumina which are both used as catalyst supports, commercially. It was then confirmed that their difference in work function is coming from the difference in their dipole moment, which is caused by P-doping. This collaborative work with the computational research group at Rutgers University-Newark (Dr. Pavanello’s group) led to a publication.[83]

This valuable method was also used to study two of our lab products in terms of work function and to correlate that with their catalytic activities, which has led to another collaborative publication. [78] Encouraged by our findings about the work function of our materials, another research project was initiated and established to explore and investigate the catalytic activity of these materials for the electrochemical reduction of carbon dioxide, which is briefly explained on chapter 6 and it is an on-going project in Dr. He’s research group.
1.3. References

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Chapter 2: Enhancement of Charging Cycles for Graphite-Based Lithium Ion Batteries by a New Electrochemical Pre-Treatment Approach

2.1. Introduction

Applications of LIBs have been expanding rapidly from consumer electronics to electric vehicles, renewable energy storage systems, defense and military applications, and many other markets.[1-6] The desirable LIBs for practical applications requires high energy density, coulombic efficiency, good cyclability, excellent safety and low self-discharge. [7] One of the major reasons of the capacity loss in graphite-based LIBs is due to the irreversible co-intercalation of the solvent molecules into the graphite layers upon anode lithiation reaction, which leads to exfoliation of the graphite layers (Figure 2.1. C) and blister formation (Figure 2.1. D). [8]
**Figure 2.1.** Exfoliation and blister formation process. (A) Intact graphite layers before lithiation, (B) Beginning of solvent co-intercalation in graphite, (C) Exfoliation and reductive decomposition of the solvent molecules, (D) Blister formation. The last two layers on the bottom of graphite in all figures were kept intact for comparison.

For a reversible Li$^+$ intercalation/deintercalation in graphitic anodes, electrolyte solvents are chosen to maximize lithium salt solubility and Li$^+$ conductivity. More importantly, the electrolyte’s salt and solvent should have the ability to stabilize the electrolyte/graphite interface by in-situ formation of a new subcomponent on the electrode surface, which is known as solid electrolyte interphase (SEI). An ideal SEI layer should be able to passivate the electrode materials and prevents continuous electrolyte decomposition. At the same time, it must remain conductive to Li ions. The structure and properties of the SEI layer not only ensure the reversibility of Li$^+$, but also influence the kinetics of Li$^+$ transport across the electrolyte–electrode interface. SEI is the key factor which determines the safety, power capacity, morphology of the lithium deposits, shelf life, and cycle life of the battery. [9-12]
The charging methods for batteries have been studied in many different ways, such as constant current (CC), constant voltage (CV), and constant current constant voltage (CCCV), etc.[12-14] For conducting research and development of new batteries, similar charging methods of as CC have been utilized, which one can take advantage of, to calculate the capacity and the capacity loss of the battery with. During this conventional charge/ discharge process, depending on the desired charging rate, a constant current is applied on the anode to lithiate it (Figure 2.2.A. part 2). Then, the same amount of current, but opposite sign is applied to delithiate it. (Fig.2.2.A. part 3). The combination of these two parts are considered as one charge/discharge cycle. The amount of the applied current depends on the desired time for cycling and also the capacity of the battery materials (in this case, graphite). Applying constant current on the anode causes a dramatic voltage drop within seconds and since this time period is negligible in comparison with the total cycling time, for a long time, its existence and also its possible influence on the battery’s chemistry and its cycling life has been ignored. At the very beginning of applying the constant current and the associated drastic and rapid change in electrode potential (Fig 2.1.B ) resemble the scenario of chronopotential voltammetry technique commonly used in electrochemistry studies[15], influence the interfacial chemistry and the double layer structure of the active surfaces (electrodes), however, to our knowledge, the influence of this phenomenon on the SEI formation has not been thoroughly studied, especially in-situ and operando conditions.
One of the most important indications of the battery performance is its capacity. Battery capacity is the amount of charge that a battery can store and deliver. The typical charge/discharge process is plotted based on potential vs. time (Fig 2.2.B). Then based on the time, applied current, and the amount of the anode materials used (in grams), one can calculate the capacity of the battery in mAh/g unit. The following figure shows a typical charge/discharge characteristics of the graphite anode in LIBs:
As we see in Fig 2.3, the amount of charge consumed during the first charging was not fully recovered during the following discharging, meaning the stored energy could not fully discharge and is wasted. The capacity that cannot be recovered (notated as “x” in Fig 2.3.) is called the “irreversible capacity” \(Q_{irr}\), which is generally believed to be consumed by SEI formation. [8] The irreversible capacity loss for the graphite based LIBs is coming from two difference sources: Co-solvent intercalation of the electrolyte into the graphite layers and also and unstable SEI layer.

There are several reports on conducting in-situ EC-AFM for studying batteries. [30-34] However, in most of these works, the electrode potential was controlled either with a constant voltage or a changing voltage with a constant and slow changing rate. The latter is known as cyclic voltammetry (CV), which is widely used in fundamental electrochemical studies, but seldom used for charging/discharging a practical battery. Rich information has been obtained in understanding the SEI formation as a function of electrolyte composition and the properties of electrode materials. However, to our
knowledge, there has been no report applying the constant current method to really mimic the actual charge/discharge cycles of batteries to understand how the associated large voltage jump at the very beginning of the charging/discharging process influences the formation of SEI, therefore the performance, and the cycle life of a battery.

This chapter aimed at addressing this overlooked issue, which is both fundamentally important and practically critical. For the first time, EC-AFM is applied to in situ/in operando monitor the morphological change of the electrode under constant current charging, mimicking the real charging situation of a battery. Surprisingly, when we found that the constant current charging protocol was not capable to lead to the formation of a high quality SEI layer on a HOPG electrode. Instead, it induced a large amount of blister formation (co-intercalation of Li ions with the associated solvent molecules). With a higher charging rate, not only do the blisters become larger, but they also creep deeper inside of the galleries of the graphene layers, which leads to irreversible exfoliation of the graphite layers, dramatically shortening the lifetime of a battery. We systematically studied the SEI formation and Li ion intercalation (blister formation) under both slow voltage changes with a constant rate (CV) and fast voltage change (pulse voltages). We found that CV leads to SEI formation preferentially along the edges, consistent with the widely reported results.[35] We also found that the preferential growth along the edges efficiently blocks Li-solvent co-intercalation into the inner graphene galleries of graphite (blister formation). On the other hand, pulse voltages not only promote blister formation, but also SEI deposition on the basal planes of the graphite surfaces, with observation of no prereferral growth along the edges. A hypothesis was proposed to understand these discoveries. Based
on these discoveries, a new charging protocol is suggested to largely avoid these issues, to reduce capacity lost during cycles, and subsequently to extend the lifetime of a battery.

2.2. Result and Discussion

To understand how the commonly used CC charging protocol affects the morphology of the HOPG, one cycle of charge and discharge with a 0.1 mA current was applied within the potential range of 5 mV to 3 V vs. Li⁺/Li. A dramatic morphological distortion was observed upon one cycle of charge/discharge (Fig 2.4).

![Figure 2.4](image)

**Figure 2.4.** Morphology change upon constant current charging: (A) Before the first cycle at open circuit potential (OCV), (B) After the first cycle.

The two layer-thick graphite (0.66 nm) on the top part of image A in Fig. 2.4. was intercalated and exfoliated to the height of ~ 2.5 μm. This dramatic change is due to the swift potential drop which caused a large electrical field gradient between the lithium metal and the surface of the HOPG. To our knowledge, this is the first time that in-situ /operando EC-AFM was used to directly observe the effect of commercially used CC charging protocol on graphite based LIBs.
To explain this phenomenon, we look at it with two different points of view. Firstly, the large negative electric field on the anode (HOPG) not only enhances the molecular interaction between Li ions and the neutral solvent molecules, due to swift repulsion of lithium counter ions (PF₆⁻) [36], it also increases the overall Li ion diffusion rate. If we look at the initial seconds of the charging process, we can model the electrochemical method to the pulse current/potential. It has been reported that the pulsed electric fields may significantly enhance the diffusion of Li⁺, which is larger than that in a static electric field or in the control case, where no electric field is applied.[37] This can be evidence to prove that the initial process of the CC is very crucial to the electrochemical reactions on the surface of the electrode. The second way to explain this dramatic morphological change is through the huge potential gradient in a short time frame. When the potential gradient is large, the amount of electric force that the charged lithium ion senses would dramatically increase. As a result, the accelerating energy of the Li ion would be much higher in comparison to a similar event with lower potential gradient:

\[
F_{el} = \frac{V}{d} \quad (F: \text{electric field}; \ V: \text{potential}; \ d: \text{distance}) \quad \text{(eq. 2.1)}
\]

\[
F = ma \quad (F: \text{mechanical force}; \ m: \text{mass of the object}; \ a: \text{acceleration}) \quad \text{(eq. 2.2)}
\]

\[
\frac{V}{d} = ma \quad \text{(eq. 2.3)}
\]

Since the edges are not yet protected and are electrochemically active, the accelerated Lithium ions can travel further into each layer of the graphite, and by opening up the path through further intercalation of the layers, they increase the probability of exfoliation and blister formation. As a result of a high applied potential, more solvent
molecules with the Li ions co-intercalate deeper into the inner gallery of graphene layers and are reductively decomposed or dimerized there.[35]:

\[
\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow 2\text{HF} + \text{POF}_3 + \text{LiF}
\] (A)

\[
\text{HF} + \text{Li} \rightarrow 0.5\text{H}_2 + \text{LiF}
\] (B)

\[
\text{EC} \quad \begin{array}{c}
2e^- \\
\leftrightarrow \\
\text{LEDCA}
\end{array}
\]

\[
\text{O}^\text{-Li}^+ \\
\text{Li}^+ \quad \begin{array}{c}
e^- \\
\leftrightarrow \\
\text{COO}^- + 0.5\text{C}_2\text{H}_6
\end{array}
\]

**Scheme 2.1.** Chemical reactions proposed by Liu, T., et al., In situ quantification of interphasial chemistry in Li-ion battery. Nature Nanotechnology, 2019. 14(1): p. 50-56

In the following anodic scanning during discharging process, even if some of the dimers decompose and go back into the solution, there will still be decomposed and dimerized products left within the graphite layers, providing a reason for the observed dramatic thickness increase after the first cycle of charging/discharge.

If this assumption is correct, we hypothesize that using cyclic voltammetry, which can slowly apply a voltage to the electrodes, will minimize the electric field effect. Accordingly, the interaction between the neutral solvent molecules will be decreased and the interaction with the salt, LiPF\(_6\) will be back to almost the original level. As a consequence, not only are there fewer solvent molecules co-intercalated into the inner gallery of graphene, the double later structure also changed, as it contains more of the salt molecules. This double layer structure would
facilitate the salt molecules reduction to deposit more LiF as the SEI, the desired component of SEI (Scheme 2.1.). Furthermore, since the reaction rate can be controlled by the applied potential, the reduction products can selectively deposit along the edges and block the co-intercalation sites for when a large current (high electric field) is applied during CC charging.

In the second set of experiments, to slow down the potential drop and decrease the electrical field on the surface of HOPG, a cyclic voltammetry (CV) method was used in the potential window of OCV to 0.2 V with a scan rate of 1mV/s. So rather than dropping the potential within few seconds, in the CV method it took 3,000 seconds (50 mins) to lower the potential to 0.2V, the reported potential for SEI growth on the edges of the graphite electrode and intercalation. (Fig. 2.5.)

![Cyclic voltammogram from OCV to 0.2 V vs Li+/Li, with a scan rate of 1mV/s and an initial negative polarization.](image)

**Figure 2.5.** Cyclic voltammogram from OCV to 0.2 V vs Li+/Li, with a scan rate of 1mV/s and an initial negative polarization.
While the CV was underway, the morphology evolution of the HOPG electrode was monitored by in-situ EC-AFM (Figure 2.6. and Figure 2.7.)

**Figure 2.6.** Morphology evolution of the HOPG surface during CV from OCV to 0.2 and back to 0.367 V

**Figure 2.7.** Morphology evolution of the HOPG surface during CV from OCV to 0.2 and back to 0.367 V.
The figures above, show that at the potentials close to 0.2 V, the uniform SEI layer was formed along the edges of the HOPG. It has been reported that sweeping to the oxidative potentials will generate more inorganic SEI layers by oxidizing the organic solvated lithium ions to lithium oxides. [35] We used this insight to tune the edges of the HOPG surface in a way to block these intercalation sites from co-solvent intercalation. To test this idea, after running one CV from OCV to 0.2 V, the same charge discharge CC protocol with the same current was used. The result was consistent with the hypothesis (Figure 2.8)

Figure 2. 8. Morphology change upon constant current charging after edge blockage: (A) Before the first cycle, (B) After the first cycle.

As observed in Fig. 2.8, the blocked edge did not get exfoliated and lifted microns away from the HOPG surface, as it did in fig. 2.4, where there was no pre-treatment of cyclic voltammetry prior to the charge/ discharge. The schematic comparison of the un-treated and pre-treated graphite upon lithiation is shown below.

Figure 2. 9. Schematic comparison between the un-treated (A) and treated (B) graphite upon lithiation.
To mimic the very beginning of the CC charging protocol, the same potential window from the CV was used and the potential was pulsed from OCV to 0.2 V within in less than a second and was set at 0.2 for 5 seconds (Figure 2.10.)

Figure 2.10. Pulse potential sweep. A: electrochemical method. B: morphology of the HOPG at OCV, C: morphology evolution upon one potential pulse.

As one can see in figure 2.10., upon a pulse potential from OCV to 0.2V, the formation of blisters are observable throughout the whole HOPG surface. We believe that these small blisters are the active sites for further exfoliation of the graphite upon further lithiation. After this pulse potential, a conventional CC charging protocol was applied to the electrode, identical to the previous CC throughout this chapter to give us an insight about the capacity loss.

The following figure is the comparison between the CC in these three different electrochemical approaches (Fig. 2.11):
Figure 2.11. Coulombic Efficiency Comparison and Qirr measurement summary, by applying 0.1 mA constant current, first on the cathode (HOPG) to charge, and then on the anode (Li metal)

As shown in fig.2.11, the pre-treatment approached decreases the irreversible capacity loss by 30%, whereas without the pre-treatment, the capacity loss is close to 100%.

2.3. Conclusion

For the first time, without altering the most commonly used LIB electrolyte or addition of any additives, and only with an electrochemical approach, we developed a pre-treatment protocol for preventing the blister formation and exfoliation of graphite based LIBs, by applying a cyclic voltammetry with a slow scan rate. This pre-treatment method can significantly decrease the irreversible capacity loss as it blocks the exfoliation sites. This method is cost effective, and can save time and effort for the research and development of new electrolytes. We hope that by further investigation, we could introduce this new method, as a cyclic voltammetry constant current (CVCC) charging protocol as a competitor protocol for other existing approaches for increasing the capacity of the batteries, as well as their life time.
Morphology, SEI evolution, roughness and mechanical properties of the SEI on the edges and the basal plane were accurately measured and compared. Electrochemical methods were used to mimic the charge/discharge processes and the irreversible capacity loss have been calculated. By applying the pre-treatment method, the irreversible capacity loss of the battery was largely minimized. By taking advantage of electrochemical impedance spectroscopy, we also compared the ionic diffusion of the SEI and concluded that the electrochemical pre-treatment enhances the ionic diffusion, as well. Based on other studies and our new findings we hypothesized that the pre-treatment is enhancing the growth of the inorganic SEI layer.

2.4. Experimental:

2.4.1 Sample Preparation/Cell Assembly

Highly oriented pyrolytic graphite (HOPG) was used as a model electrode for graphite anode of the LIB systems. HOPG used in this series of experiment was purchased from Bruker AFM Probes, with 12mm x 12mm, 2mm thick and ZYB grade. Pyrolytic Graphite (PG) is a unique form of graphite manufactured by decomposition of a hydrocarbon gas at very high temperature in a vacuum furnace. The result is an ultra-pure product which is near theoretical density and extremely anisotropic. Mechanical, thermal, and electrical properties are generally far superior to conventional graphites. HOPG with its high conductivity and atomically flat surface allows the observation of the SEI evolution and surface morphological changes within its layers.

HOPG consists of two major morphological components: Edges and basal planes (Fig. 2.6).
Figure 2. 12. a: HOPG morphology and b: zoomed in morphology of the rectangular area in a. The thickness of the layer in b is 1.33 which is equivalent of 4 graphene layers.

When we use scanning tunneling microscopy (STM) to observe the morphology of the basal plane, we can observe the following in a relatively small scan scale, where we can observe the bonds between the carbon atoms.

Figure 2. 13. STM image of the HOPG’s basal plane
To make the electrical connections for the electrochemical process, we developed a new way of assembling the cell to decrease the internal resistivity between the current collector and the electrode (HOPG). The HOPG was glued to the Teflon small EC cell adapter by Torr Seal Low Vapor Pressure Resin Sealant (Agilent Technologies) with curing time of 24 hours at room temperature. After the glue was cured, the HOPG was cleaved at least 5 times to remove the residuals from previous experiments/the interfacial reactions of the HOPG with air which would affect the following experiments. After cleaving the HOPG, the sample was inserted to the EC-cell and transferred into the glovebox (Figure 1.3.)

2.4.2 AFM/PF-QNM Technique:

The EC-AFM was conducted by using the Bruker Dimension Icon system in an Ar-filled glovebox with the water and oxygen levels of less than 0.1 ppm, each. The small antechamber of the glovebox that contained the EC-cell went under vacuum level of -1 atm and kept at that pressure for 5 minutes, then it was refilled from the globe box atmosphere (Ar). This process was repeated 3 times to make sure that the adsorbed water and oxygen on the EC cell parts were removed, before entering to the main glovebox.

To use the EC-AFM, the EC-chuck was installed. This chuck has a marked reference position (blind engage position) to mount the EC-cell on it, since the movement of the probe is limited in the EC-cell and the crashing of the tip should be prevented from happening. The limit for the movement of the probe in the EC-cell is $\pm 2470$ m. Also this
chuck has the electrochemistry related terminals for the working, reference and the counter electrodes. Once the EC-chuck is installed, the X, Y, Z of the blind engage position was updated into the software. The last piece of the cell assembly which was installed in the glovebox is the glass top cover. The lithium foil that is stored in the glovebox was smeared under the glass cover, then the cover was sealed on the top of the cell. Then the cell was ready to be mounted on the chuck and to be electronically connected to the potentiostat. The EC cell was mounted on the quardopole magnet that were evenly distributed around the blind engage position to assure that the cell is exactly mounted at the center of the blind engage position. The blind engage position was updated again, since the Z position of it is now changed, due to the thickness of the substrate and the additional thickness of the cell. Then the cell position was secured and the electronic connections were connected, approximately 1.7 mL of the electrolyte was added to the cell and then the cell was navigated to the blind engage position, where the probe was then submerge into the electrolyte. Since the electrolyte had a different refractive index than argon gas and also because of the difference in the interfacial tension between the tip of the probe and the electrolyte, the tip position and the laser position were slightly change. The X direction of the laser was turned counter clockwise to bring the laser spot back on the tip, then the horizontal and vertical of the photo diode sensor were zeroed. The OCP vs. time was immediately run to observe the OCP changed upon time, while the PF-QNM in liquid calibrations were on going. The potentiostat connected to the AFM is CH Instrument 760 E, which is one of the most advanced versions of the potentiostats produced by the CHI company. The lithium was both the counter and the reference electrode, while the HOPG was the working electrode in our experiments. Once the sum signal was set to the maximum
and the photodiode was set to zero for the horizontal and vertical, the rest of the PF-QNM calibration was conducted. Deflection sensitivity of the cantilever depends on the Probe, laser alignment, instrument and the media (i.e. air, liquid). Thus, when the probe was submerged into the electrolyte, the deflection sensitivity was calibrated in the new medium. However, the spring constant of the probe remained the same, regardless of the experiment’s medium. By using the thermal tune in the liquid, the deflection sensitivity of the probe in the electrolyte was obtained and used for the QNM measurements. Also the sync distance QNM and the peak force amplitude were calibrated based on the peak force frequency that was used to obtain the mechanical properties of the sample. The surface of the HOPG was then characterized by in-situ AFM, to obtain the morphology of the substrate and also to make sure that the substrate is intact before starting applying any potential to the system.
2.4. References


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Chapter 3: Enabling High Performance Microsized Si Anodes for Li ion Batteries via Electrolyte Design

3.1. Introduction

Si is a promising anode material for next-generation lithium-ion batteries (LIBs), having low average voltage and nearly ten times the theoretical capacity of state-of-the-art graphite anodes (3579 mAh g\(^{-1}\) for Li\(_{1.5} Si_4\) vs. 372 mAh g\(^{-1}\) for LiC\(_6\)). [1] Si is also the second-most abundant element in the earth's crust and is environmentally benign. Large (>10 µm) Si microparticles (SiMP) are especially attractive due to a low production cost and high gravimetric capacity. However, the large volume expansion of silicon (~280%) during battery operation leads to mechanical fracture and rupture of Si particles, inducing loss of the inter-particle electrical contact and exposure of the highly reactive fresh lithiated Si surface to electrolyte. This leads to continuous solid electrolyte interphase (SEI) growth, electrolyte consumption and isolation of the pulverized Si particles, resulting in a low cycling Coulombic efficiency (CE). The SEI formed from reduction of currently used carbonate electrolytes can tolerate a small volume change (~12%) of graphite but is not robust enough to accommodate 280% of volume change of SiMP. Consequently, microsized SiMP anodes exhibit an extremely fast capacity drop to less than 60% of the initial value in the first 20 deep galvanostatic charge/discharge cycles[2] in contrast to the microsized graphite anodes that achieve initial CE (iCE) >90% in the first cycle and cycling CE (cCE) >99.9% after 10 cycles, ensuring 1000 cycle life.
Attempts to improve SiMP electrode performance by optimizing electrode fabrication[3, 4] and cycling condition[5] have only limited success. In a meantime the Si nanoengineering showed great promise because nano-sized Si particles (<150 nm) and Si wires (<250 nm) do not fracture during (de)lithiation cycles. [6, 7] Concepts such as one-dimensional Si nanowires, [8] core-shell nanowires, [9] hollow particles, [10] tubes, [11] porous Si, [12] SiC [13, 14] and SiC/MXenes composites[15] have been reported to effectively improve cycling stability at half- cell level. However, the complex fabrication and associated high cost of nanostructured Si powders make it less appealing for practical applications. Recently, functional binders with strong adhesive and elastic properties were reported to keep the pulverized micro-size silicon particles coalesced without disintegration,[16-19] reducing the reaction of pulverized silicon particles with electrolytes, enabling the 1-3 µm SiMP to be stably charged/discharged in half-cell configuration for 150 cycles with iCE of 91% and cCE of 99.8% after 22 cycles, and Si/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 full cell for 50 cycles.[17] Another effective method to avoid an electrolyte reacting with a pulverized Si is to encapsulate 1-3 µm SiMP with a conformal multilayered graphene cage, where SiMP can expand and fracture within the cage, while the electrolyte is blocked by a stable SEI formed on the graphene cage surface.[19] The graphene- encapsulated SiMP exhibits iCE of 93.2%, increasing to 99.5% after the first five cycles. [20] However, the relatively low cCE of < 99.7% for Si requires significant excess of Li to be introduced via costly pre-lithiation step or usage of the oversized cathodes leading to lower energy density. Figure S1 shows the effect of cCEs on the capacity retention of the full cell, which emphasizes that the electrodes with cCEs below 99.9% do not meet battery requirements for electric vehicles and many portable electronics
applications. Unfortunately, to the best of our knowledge, the large (>10 µm) SiMP anodes with cCE > 99.9% at practical loading but without costly processing has not been reported up to date.

Development of an electrolyte that forms a thin and robust SEI to yield high CE is the most attractive, yet elusive option for enabling SiMP due to complexity of SEI formation and evolution mechanisms. Carbonate electrolytes with fluoroethylene carbonate (FEC) and vinylene carbonate (VC) additives currently yield the best performance for Si anodes,[20] yet a thick, inhomogeneous, and uneven SEI formed on Si is not robust enough to tolerate the volume change of Si, resulting in the continuous consumption of the lithium, electrolyte and loss of active Si. [21-23] Inspired by the significantly enhanced iCE (>90%) and cCE (>99.9%) of Sn micro-particles (SnMP) anode in Na-ion battery, which has similar volume change to SiMP anode in Li-ion battery, through a simple change of the carbonate to more stable ether solvent in Na-ion electrolytes,[24] we initiated a rational electrolyte search that forms a thin uniform inorganic SEI on SiMP. We demonstrate that a designed SEI with low adhesion to a lithiated Si enables the SiMP to provide 2800 mAh g⁻¹ with long cycling life of >300, high iCE of >90%, and cCE of >99.9% for large (>10 µm) SiMP anodes (without any pre-treatment), in sharp contrast to previous values of cycle life of ~20, iCE of ~80%, and cCE of <97%. This finding opens new avenues for practical application of SiMP anodes.
3.2. Results and discussion

3.2.1. Critical role of Li_xSi|LiF interface in enhancing cycling stability and CE of Si anodes

Traditional electrolyte design focused on graphite anodes, with the main consideration of inhibiting co-intercalation and decomposition of solvents inside graphite layers. The SEI formed on graphite from EC-based electrolyte features an organic-inorganic mixed structure that has a strong bond with graphite to withstand the ~12% volume expansion upon full lithiation. However, the ~30 times higher volume change of Si than graphite results in the complete failure of organic-inorganic SEI formed from EC-based electrolytes for the Si anode, as presented by the extremely low CE of only ~90%, calling for a paradigm change in the electrolyte design approach. The main obstacle for achieving stable cycling of Si anodes is the breaking/reforming of SEI layer during repeated expansion/shrinkage cycles combined with high lithiated Si electrochemical/chemical reactivity to the electrolytes. Strong bonding between the organic-rich SEI and Si surface puts additional constrains on the Si evolution during lithiation/delithiation cycling by restricting Si slip at the Si|SEI interface, thus the SEI suffers from a high deformation, leading to breakage and eventual formation of isolated particles covered with thick SEI (Figure 3.1a). The non-uniform mixed organic-inorganic SEI also induces high stresses due to non-uniform lithiation/delithiation, further enhancing the SEI and lithiated Si cracking. The reformation of organic-inorganic SEI in Si cracks due to electrolyte penetration eventually isolates lithiated Si. In order to reduce the deformation of the SEI layer, it is desirable to form a layer with low affinity to lithiated Si, so that a lithiated Si can slip at the interface to accommodate the volume changes (Figure 3.1.b). Among the
known components in SEI, LiF possesses high interfacial energy with the Li$_4$SiO$_4$ (fully lithiated surface oxide) and Li$_x$Si surface at various lithiation degrees (Figure 3.1c), suggesting that Li$_4$SiO$_4$ and Li$_x$Si can slip easily without damaging the LiF SEI shell as lithiated Si volume changes. In addition, considering its wide bandgap and high electronic blocking effect that significantly reduces the thickness of SEI (increasing iCE), high shear modulus of LiF creates a robust shell that suppresses the Li$_x$Si pulverization. Not surprisingly, the most successful electrolytes for SiMP cycling contain FEC that presumably leads to a denser, LiF-rich SEI with an extremely low electronic conductivity, [21, 22, 25, 26] improving CE to about 99.7% from 99.0% for the conventional carbonate electrolytes. However, significant organic SEI components also form during FEC reduction in addition to LiF, thus increasing adhesion of SEI to Si surface and facilitating SEI deformation and rapture during Li$_x$Si expansion.

Figure 3. 1. The effect of SEI and electrolyte properties on the Si anode particles. (a,b) Schematic of the cycled Si with (a) organic-low interfacial energy, non-uniform and (b) inorganic, high interfacial energy and uniform Li$_x$Si|SEI interface. (c) Electron localized function (ELF) and work of separation (W$_{sep}$) for the a-Li$_x$Si|LiF interfaces. (d)
Comparison of the extent salt aggregation and Li$^+$ solvation shell composition for the mixTHF:LiPF$_6$ and EC:DMC:LiPF$_6$ electrolytes from MD simulations. (e) Reduction potentials of key electrolyte components predicted from quantum chemistry (QC) calculations.

3.2.2. Electrolyte design to form the Li$_x$Si|LiF interface

We strive to further increase the LiF fraction and uniformity in the SEI by selecting a highly fluorinated LiPF$_6$ salt that preferentially reduces to LiF without organic by-products and combine it with the solvents that only undergo reduction after full expansion of lithiated Si, thus ensuring easy and uniform expansion of lithiated Si under LiF SEI during lithiation. In order to increase the potential of LiPF$_6$ reduction, it is important to realize that the LiPF$_6$ reduction potential depends on the extent of ionic aggregation.[27-29] A higher number of Li$^+$ bound to (PF$_6$)$^-$ leads to stabilization of an excess electron near the anion making reduction and LiF formation energetically favorable at higher potentials.[29] Thus, counterintuitively, our target electrolyte needs to have high degree of salt aggregation and low reduction potential of solvents.

For conventional EC-based carbonate electrolytes, solvent separated ion pairs (SSIP) dominate ~60% of the solvation structure with 38% of ions being contact ion pairs (CIP) (Figure 1d). Quantum chemistry (QC) calculations predict that reduction of LiPF$_6$ CIP in EC:DMC solvents occurs at ~1.0 V vs Li/Li+, which is lower than the initial reduction potential of linear carbonates at 1.5 V, [30] but is higher than main reduction of EC and DMC occurring at ~0.6 V (Figure 3.1.e). Thus, because reduction of all electrolyte components in LiPF$_6$ EC:DMC occur in a similar potential range and LiF segregates in the reduced carbonates matrix, a heterogeneous mixed organic and inorganic SEI with large
separate domain forms.[31] Linear and cyclic ethers have much lower thermodynamic reduction potentials than those of esters, making them good solvent candidates for supporting preferential fluorinated salt decomposition (Figure 3.1. e). Tetrahydrofuran (THF), and 2-methyl THF (MTHF) and TEGDME (G3) solvents have very low reduction potential near 0.0V. Salt aggregation and CIP formation progressively increased in the sequence of 1M LiPF$_6$ in G3 < 1 M LiTFSI in mixTHF < 1 M LiPF$_6$ in mixTHF (Figure S5). Importantly, high degree of LiPF$_6$ aggregate (AGG) in the mixTHF:LiPF$_6$ electrolyte (Figure 3.1. d) pushes the onset reduction potential of LiPF$_6$ to a high value of ~1.5 V, which is substantially higher than the reduction potentials of THF and MTHF around 0.0V (Figure 3.1. e). Thus, a highly uniform LiF SEI layer is expected to form on Si during lithiation of Si above 0.1V and only minor organic component formed from reduction of mixTHF solvents on the LiF surface at near end of Si lithiation in the LiPF$_6$ mixTHF electrolyte in contrast to the mixed organic-organic SEI in EC:DMC. Low mixTHF solvent viscosity and poor LiF solvation in mixTHF solvents further enhance kinetics of LiF salt aggregation after LiPF$_6$ reduction. These modeling predictions are in accord with the observation that monodentate THF and MTHF molecules have the lowest solvation ability with Li$^+$ because of the absence of chelating effect.

To further validate predictions from MD simulations, we performed a systematic Raman spectroscopy characterization of esters and ethers solvation (Fig. 3.2). We compared the solvation ability of monodentate THF, and MTHF with typical multidentate ethers such as DME (G1), DEGDME (G2), TEGDME (G3) by acquiring the Raman spectra of 1M LiTFSI salt in these solvents (LiPF$_6$ salt is incompatible with most ethers, so LiTFSI was used instead). Solvation structure information was derived from Raman band shift of
TFSI⁻ anion (740 cm⁻¹, expansion/contraction of the entire anion) and CH₂ stretching mode of solvent molecules. The TFSI⁻ anion Raman band is a known marker for the TFSI⁻···Li⁺ cation coordination. Firstly, we compared the Raman shift of TFSI⁻ anion band at ~740 cm⁻¹ in various ether electrolytes. The Raman peak blueshift increases in the following order: G3≈G2, G1, THF, MTHF (blue line in Figure 3.2.), indicating the increasing ionic association between Li⁺ and TFSI⁻ anion. We also compared the blueshift of Raman solvent band upon addition of 1M LiTFSI, which decreases in the sequence of G3≈G2>G1>THF≈MTHF, indicating the decreasing in solvent solvation. Consequently, THF and MTHF have the lowest solvation ability and stand out as solvents to support preferential salt reduction forming LiF, while THF and MTHF themselves will be reduced at a much lower potential. In addition, the low solvation ability also improved the chemical compatibility with LiPF₆ salt. While G1 and G2 will immediately polymerize once mixed with LiPF₆ salt; the 1:1 mixture of THF and MTHF is chemically stable.

Figure 3.2. Raman spectra of 1 M LiTFSI in different ether solvents, and the peak shift trend of CH2 stretch and S-N-S bending mode.
Since the local Li$^+$ concentration around anions controls the salt reduction potential, we compared the solvation structure, namely SSIPs, CIPs, and AGGs in the mixTHF and carbonate-based electrolytes (Figure 3.1.d). It is clear that in 1 M LiPF$_6$ solutions, SSIPs decreased from ~60% in carbonate to ~8% in mixTHF, while CIPs increased from ~38% in carbonate to 87% in mixTHF (Figure 3.1.d). A small fraction of the Li$^+$PF$_6^-$Li$^+$ AGGs (~5%) is observed in 1 M LiPF$_6$ in mixTHF, further increases to 10% as the LiPF$_6$ salt concentration increases to 2M. Higher salt concentration has three benefits, 1) upshift the salt decomposition potential to ~1.5V, facilitating LiF formation due to higher aggregation; 2) suppress the solvent reduction to lower potentials, inhibiting formation of organic component in SEI during Si expansion; 3) diminishes electrolyte oxidation as a fraction of free solvent decreases. Thus, in this electrolyte the dominant LiPF$_6$ reduction forms an initial LiF SEI and repairs it by LiF during Si lithiation from the preferred LiPF$_6$ reduction. Only when the voltage goes very low at fully lithiated Si state, solvent starts to decompose, providing an organic shell outside of the LiF layer. Such homogeneous organic/LiF bilayer SEI formed after full Si lithiation is expected to be thin and to hold the lithiated Si together as it allows underneath lithiated Si to shrink through its elastic and plastic deformation during delithiation due to the high interfacial energy at LiF/Si interface, thus maintaining integrity of SiMP during expansion/shrinkage (Figure 3.1.b). Therefore, LiF organic/SEI bilayer SEI functions as robust shell that strongly holds ruptured/flowed Si together rather than insulating ruptured Si by organic-dominated SEI formed in traditional electrolytes (Figure 3.1.a).
3.2.3 Electrochemical performance of SiMP in LiPF\textsubscript{6} in THF/MTHF (1:1 by volume, mixTHF) electrolytes

The commercial bulk SiMP of \textasciitilde325 mesh was used as received without any treatment. It is \textgtrsim10 \mu m in size, as revealed by scanning electron microscope (SEM) in Figure 3.3.

\textbf{Figure 3. 3.} SEM image, and XRD pattern of SiMP.

The sharp diffraction peaks of the bulk SiMP in the X-ray diffraction (XRD) pattern are characteristic for crystalline Si. The SiMP electrode is composed of 60 wt\% of SiMP, 20 wt\% of Ketjen Black, and 20 wt\% of Lithium polyacrylic acid (LPAA), and produced by hand milling and blade-coating of the slurry onto Cu foil. The Si electrode processing is the same to that of commercial graphite electrodes without any additional pretreatment or pre-lithiation. Developed electrolytes enable a simple drop-in replacement for current graphite anode fabrication technology, ready to be integrated in a current battery production line for commercialization.
Figure 3.4. Cycling of SiMP electrodes in half cells. (a-d) Typical charge/discharge profiles of SiMP electrode cycled in different electrolytes, (a) 2 M LiPF$_6$ mixTHF, (b) 1 M LiPF$_6$ EC/DMC. (c) Charge/discharge curves at different rates of Si cycled in 2 M LiPF$_6$ mixTHF. (d) Rate performance comparison. (e) Cycling stability and CEs of SiMP cycled in 2 M LiPF$_6$ mixTHF and 1 M LiPF$_6$ EC/DMC electrolytes, the rate is C/5.
The electrochemical performance of SiMP in the LiPF$_6$ mixTHF electrolyte was evaluated by galvanostatic charge/discharge from 0.06 to 1.0V in 2032 coin cells using Li as a counter electrode. The Si mass loading was ~2.0 mg cm$^{-2}$ corresponding to a high areal capacity of 5.6 mAh cm$^{-2}$, which is about 2 times of the areal capacity for the commercial cathodes. The reversible capacity of the SiMP reached ~2,800 mAh g$^{-1}$ at a current density of C/5 (1C = 3579 mA g$^{-1}$) in the LiPF$_6$ mixTHF electrolyte (Figure 3.4. a). The achieved capacity is a little lower than the theoretical value because of the stress-induced overpotential during lithiation. The high cycling stability is demonstrated by the almost unchanged capacity during the first 20 cycles and overlapped charge/discharge curves after the 2nd cycle (Figure 3.4.a). The capacity retention was 100.0%, 96.3% and 94.4% after 20, 50 and 100 cycles, respectively. Even after 300th cycle, capacity retention is still 90.0% (Figure 3.5).

![Figure 3.5](image)

**Figure 3.5.** (a) Typical charge/discharge profiles and (b) Cycling stability and CE of SiMP electrode cycled in 2 M LiPF6 mixTHF. The rate is C/5 then C/2.

The high and stable specific capacity indicates that SiMP is fully utilized and remains electrically well connected during repeated electrochemical lithiation/delithiation.
The CE of > 10 µm SiMP reaches 90.6% in the first cycle and jumps to > 99.9% at the 7th cycle and remains > 99.9% in the following cycles (Figure 3.4.e, Figure 3.5), which is even higher than the CE of small SiMP (1-3µm) confined by graphene cage or using elastic binder. In sharp contrast, for the Si electrodes cycled in conventional 1M LiPF₆ EC/DMC electrolyte, ~40% of capacity is lost within 20 cycles (Figure 3.4.b), while only ~8% of the capacity can be maintained after 50 cycles. The CEs are as low as 96- 97% in the first several cycles, and only hover around 98.0% after 50th cycles with low specific capacity of 200 mAh g⁻¹, which is consistent with previous reports.[32] In addition to cycling stability difference, it was found that the rate capability of Si electrode in LiPF₆ mixTHF electrolytes also far exceeds that in standard 1 M LiPF₆ EC/DMC electrolyte. As shown in Figure 3.4. c and 3.4. d, at a discharge rate of 1C (3.58 A g⁻¹), Si electrode in 2 M LiPF₆ mixTHF can retain over 2400 mAh g⁻¹, corresponding to over 87% of the capacity at 0.1C; while only 1098 mAh g⁻¹, 54% with respect to 0.1C, is achieved in standard 1 M LiPF₆ EC/DMC electrolyte. Even at an extremely high current density of 3C (10.7 A g⁻¹), the Si electrode in 2 M LiPF₆ mixTHF can still maintain a capacity of 1,580 mA h g⁻¹, nearly three times of that (539 mA h g⁻¹) in 1 M LiPF₆ EC/DMC electrolyte. Without the interference from conductive carbon and binder, the rate capability difference is only attributed to the low SEI resistance in LiPF₆ mixTHF electrolyte.

Importantly, unlike SiMP cycled in carbonates, SiMP also shows an outstanding low temperature performance in LiPF₆ mixTHF electrolyte (Figure 3.6.).
Figure 3.6. Typical charge/discharge curves of SiMP cycled in different electrolytes as denoted in panels at different temperatures.

As temperature decreases from 20 to 0, −20, and −40 °C, the SMP electrodes in LiPF$_6$ mixTHF electrolyte achieve reversible capacities of 2922, 2547, 2304, and 1475 mAh g$^{-1}$, respectively, while only 2221, 1802, 658, and 0 mAh g$^{-1}$ were reached for SiMP in LiPF$_6$ EC/DMC electrolyte at the same temperatures. The capacity value at −40 °C in LiPF$_6$ mixTHF is 224% that of the capacity at −20 °C in LiPF$_6$ EC/DMC, demonstrating the outstanding performance at low temperatures. The super low-temperature performance of Si at −40 °C is unique for LiPF$_6$ mixTHF electrolyte, and can only be achieved in designed electrolytes by scarifying other performance.

Such superior anode performance of pristine Si particles with large size of >10 µm in LIBs has never been reported before. All the cycling performance, rate capability, CE and low-temperature behaviors achieved in LiPF$_6$ mixTHF are the best as yet reported for SiMP. This unique solvation structure as well as stable organic/LiF bilayer SEI developed in LiPF$_6$ mixTHF electrolytes enables the highly stable cycling of the large (> 10 µm) SiMP, and most importantly substantially improved the cCE to >99.9%. Since all the
electrode configurations are exactly the same, the distinct electrochemical difference of Si electrode in the above electrolytes should be mainly attributed to the property of their corresponding SEI layers.

Figure 3. 7. SEI chemical composition of Si anodes. (a) XPS characterization of the SEI formed on Si cycled using 2MLiPF6 in mixTHF or 1MLiPF6 in EC/DMC. The C1s, O1s, Si2p, and F 1s spectra are displayed in columns, with corresponding depth profiling results in columns, with corresponding depth profiling results in columns. (b) CryoTEM images and corresponding EDX line scan of elemental composition using 2 M LiPF6 in mixTHF or 1 M LiPF6 in EC/DMC.
3.2.4. Characterization of SEI on cycled Si thin film in LiPF$_6$ THF/MTHF electrolytes

The unprecedented SEI performance merits in-depth examination of its morphology and chemical composition. The latter is examined via X-ray photoelectron spectroscopy (XPS) with Ar$^+$ sputtering depth profiling. We sputtered Si on Cu foil as a working electrode to exclude the elemental interference of conductive carbon and binder and enable the monitoring of thickness depth dependent SEI information. Experimentally, the Li||Si half cells were disassembled in the delithiated state after 50 lithiation-delithiation cycles to examine the SEI on Si surface. Samples were transferred into the XPS chamber under Ar protection to avoid any contaminations of the air.

First, we analyzed the composition of SEI on Si formed in LiPF$_6$ mixTHF electrolyte. The top surface of the SEI consists of both organic (RCH$_2$OLi) and inorganic (Li$_2$O, LiF) components. However, the inner part of the SEI film is more important to the cycling stability of Si electrode, XPS elemental analysis after different Ar$^+$ sputtering time shows that the content of carbon, which is indicative of organic decomposition product, decreases with increasing sputtering time to less than 10% only after 120s (Figure 3.8).
Figure 3.8. Atomic compositions (Black: C, Red: O, Blue: F, Purple: S or P, Green: Li, Navy: after 0, 120, 300, 600, 900, 1500s of Ar+ sputtering. Si) of Si electrode cycled in (a) LiPF6 mixTHF and (b) LiPF6 EC DMC electrolytes.

Specifically, in Si spectra, \( \text{Li}_4\text{SiO}_4, \) Si, and Li-Si alloy dominate the Si spectra, with the Li-Si alloy signal reaches about ~50% of all Si signal at 600s sputtering, which is assumed as the interface between SEI and Si. The C 1s signal drops to noise level after 600s sputtering, accompanied by the decrease in carbon related \( \text{O}^-\text{C}=\text{O} \) signal in O 1s spectra. Meanwhile, LiF signal is still strong at the interface of SEI|Si, and persists throughout the whole sputtering process of 1500s, indicating that inorganic ceramic without any organic reduction species are on the surface Si film, consistent with the proposed organic/LiF bilayer SEI structure in Figure 1b although minor LiF also exist in organic layer of SEI. In addition, the signals of \( \text{Li}_4\text{SiO}_4 \) in both O 1s and Si 2p spectra reach its maximum at the SEI|Si interface (600 s sputtering). The absence of SiO\textsubscript{x} peak for Si cycled in LiPF\textsubscript{6} in mixTHF electrolyte further confirms a complete and homogeneous lithiation of surface.
oxide layer due to uniform SEI. This Li$_4$SiO$_4$ layer on Li-Si alloy is also beneficial to the integrity of Si electrode because it has been demonstrated to be elastic [33] and prevents the electrode from pulverization. In sharp contrast, the top surface of SEI formed in LiPF$_6$ EC/DMC electrolytes consists of both organic reduction products (lithium alkyl carbonates; RCH$_2$OCO$_2$Li) and inorganic products (LiF). The carbon and LiF signals persist, while no Si and Li$_x$Si peaks appear in whole 1500s of sputtering, indicating the SEI is made up of mixed organic/inorganic compounds from the surface to inner part, and this SEI layer is much thicker compared with those generated in LiPF$_6$ mixTHF electrolyte. The LiF signal intensities in F 1s spectra are lower compared with those collected from SEI in LiPF$_6$ mixTHF (before 600 s sputtering), indicating less LiF generated in LiPF$_6$ EC/DMC electrolyte despite the overall higher decomposition degree. This can be anticipated because carbonates are prone to reduction at higher reduction potentials thus contribute more to the SEI compared to glymes. [34] In addition, the O 1s spectra of SEI formed in LiPF$_6$ EC/DMC also exhibit less Li$_2$O content, indicating insufficient lithiation of the surface oxide layer on SiMP. Moreover, in Si 2p spectra, the original SiO$_x$ peak (104 eV) emerges after sputtering for 300 s in the case of carbonate electrolyte, but never in LiPF$_6$ in mixTHF electrolyte. This remaining SiO$_x$ indicates incomplete lithiation of surface oxide, and leads to higher inhomogeneity and resistance to Li$^+$ diffusion and consequent low kinetics. The non-uniform lithiation due to a non-uniform organic-inorganic SEI also induces a high stress and strain at places where expansion is highly inhomogeneous, which easily breaks the weak mixed organic-inorganic SEI. Consequently, repeated breaking/reforming of SEI leads to low CE and poor stability.
The elemental composition of bilayer SEI was also verified by CryoTEM with EDX line scans (Figure 3.7 b). The Si sputtered on Cu was also used as electrode to eliminate the interference of carbon and oxygen signals from conductive carbon and binder. From the line scans it can be clearly seen that the content of F increases before the increase of Si and O, while other elements remain constantly low for Si cycled in the LiPF$_6$ mixTHF electrolyte, indicating the LiF layer is coated on Si surface (with SiOx on Si surface), which is consistent with the XPS result. For Si cycled in LiPF$_6$ EC/DMC electrolyte, C and O increase before the increase of Si, indicating organic component dominates the SEI in this case, which also confirms the result from XPS analysis. With all the experimental evidence discussed above, it can be concluded that the uniqueness of LiPF$_6$ mixTHF electrolyte is that the organic/LiF bilayer SEI, substantially different from the traditional organic based SEI.

Figure 3.9. Morphology of Si anodes after cycling. (a) Typical EC-AFM surface roughness comparison at the lithiated and delithiated states, area 2×2 µm, (b) SEM images of SiMP electrode after 100 cycles of operation in different electrolytes before and after electron beam irradiation. Electrolyte: LiPF6 mixTHF (row 1) or EC DMC (row 2).
The roughness and thickness of the SEI on Si during dynamic lithiation/delithiation was studied by in situ electrochemical atomic force microscope (EC-AFM). This technique allows the in-situ accurate measurement of the SEI without disassembly of the electrochemical cell. Crystalline Si wafer with super smooth surface (~0.18 nm roughness at open circuit voltage, Figure 3.10) was used to monitor the surface morphology evolution of Si during lithiation/delithiation process. For Si cycled in LiPF$_6$ mixTHF electrolyte, the roughness increased to ~1.78 nm at lithiated state, and reduced to ~1.01 nm after delithiation (1 cycle), much smaller than the corresponding values from LiPF$_6$ EC/DMC electrolyte, 3.87 and 4.06 at lithiated and delithiated states (Figure 3.9. a).

**Figure 3. 10.** EC-AFM image of the Si substrate
Figure 3.11. (a,b) Schematic of SEI thickness formed in LiPF$_6$ mixTHF measured using EC- AFM by scraping off with a (a) soft tip or (b) hard tip-brushed area, and (c) corresponding EC- AFM images from SEI generated in electrolyte

The different roughness is consistent with XPS Si 2p spectra that surface oxide is uniformly and fully lithiated in LiPF$_6$ mixTHF electrolyte and partially lithiated with SiO$_x$ remaining in LiPF$_6$ EC/DMC electrolyte. The 4 times as much roughness in LiPF$_6$ EC/DMC electrolyte than that in LiPF$_6$ mixTHF electrolyte indicates ~400% strain applied to the SEI layer by lithiated Si, which can break the SEI much easier. In addition, the decreased roughness during delithiation in LiPF$_6$ mixTHF electrolyte reflects that the organic/LiF bilayer SEI suppresses the irregular volume expansion and hold the Si together, which cannot be achieved by the mixed organic-inorganic SEI from LiPF$_6$ EC/DMC electrolyte (roughness increases after delithiation). Both of these characteristics of SEI in LiPF$_6$ mixTHF electrolyte benefit stable cycling and high CE.

Two layer thickness of SEI in LiPF$_6$ mixTHF electrolyte was further characterized by scraping off the soft and hard SEI components on Si. Two sets of tips were used to apply different forces to remove SEI component with different mechanical properties: 1) soft tip
to remove surface layer with modulus only in MPa range, which is regarded as soft SEI and mainly consist of organic component; 2) hard tip designed for removing sample with higher modulus in GPa range, mainly inorganic component such as Li$_2$O and LiF. By sequential scarping off the top layer with the soft and hard tip after the first cycle, we were able to distinguish the soft (Figure 3.11.a) and hard (Figure 3.12.b) part of the SEI layer. The thickness of the soft SEI generated in LiPF$_6$ mixTHF electrolyte was 2.50 nm. The thickness and roughness of the hard SEI in LiPF$_6$ mixTHF electrolyte are 0.37 and 0.44 nm, respectively (Figure 3.11.c).

The high interfacial energy between LiF SEI and lithated Si and Li$_x$SiO$_4$ (Figure 3.1.c) allows lithiated Si to freely expand/shrink forming core/shell structure in LiPF$_6$ mixTHF electrolyte (Figure 3.1.b), which is confirmed by SEM (Figure 3.9.b). Since the organic out layer and LiF inner layer in SEI are sensitive to electron beam, selected area electron beam irradiation is applied to gradually remove the electron beam sensitive SEI layer on SiMP. After electron beam irradiation of SEI for different times, the underneath belt-like Si (or lithiated Si) are gradually exposed more clearly. It is obvious that the bulk SiMP evolved into belt-like integrity coated with a smooth SEI layer after a hundred deep lithiation/delithiation cycles in the LiPF$_6$ in mixTHF electrolyte. This is the result of repeated plastic flow of soft lithiated Li$_x$Si with the help of stiff but less interacted LiF SEI which holds Si together and limits the rupture. The lithiation of silicon is known to undergo an amorphous Li-Si alloy (a-Li$_x$Si) route(1), and is accompanied by an elastic softening of the as-formed a-Li$_x$Si. [35] Theoretical simulation indicated that the shear moduli of a-Li$_x$Si reduces to <30 GPa when Li fraction increases to >0.2. [35] Si lithiation experiment also confirmed that the Li$_x$Si alloy undergoes plastic deformation at a stress of ~1 GPa after
the elastic stress reaches its maximum of 1.7 GPa at a low lithiation degree of 325 mAh g\(^{-1}\) (9% of its full capacity).\[36\] LiF has a much high shear modulus of \(~50\) GPa, \[37\] thus can withstand elastic stress of \(Li_xSi\) and avoid the soft \(a-Li_xSi\) from penetrate into LiF SEI. Instead, its deformation will be restricted underneath the LiF SEI layer. Better than the inorganic LiPON-based artificial SEI, \[38\] the LiF-rich stiff SEI constrains Si expansion and can be quickly self-healed by new formed LiF (without weak organic component) if broken during lithiation, leading to development of the mulberry-configuration integrity after cycling without any pulverization with connected Si domains well protected under SEI. Such bend lamellar morphology of Si allows expansion in the direction perpendicular to lamellar that requires creation of a relatively small new (self-healed) SEI surface to accommodate \(Li_xSi\) growth during lithiation. Moreover, a stiff LiF SEI is likely to withstand stress and prevent void collapse during delithiation making these voids available to accommodate \(Li_xSi\) expansion during the next cycle. In addition to the mechanical properties, the LiF SEI layer is known to possess high ionic to electronic conductive ratio, \[39\] thus a thin layer is sufficient to inhibit the unwanted side electrochemical/chemical reactions between SiMP and the electrolyte. On the contrary, the organic component in the SEI formed in LiPF\(_6\) EC/DMC electrolyte has low interfacial energy with lithiated Si, thus strongly bonds to lithiated Si surface and experiences the same degree of deformation with lithiated Si when volume changes, as demonstrated by the similar pulverized particle morphology before and after electron beam irradiation (Figure 3.9.b). In addition, shear modulus of the organic carbonate-based SEI is an order of magnitude lower than LiF, \[40\] which is unable to withstand the large elastic stress before the plastic deformation, resulting in the pulverization of Si. The formation of organic-rich SEI in the pulverized Si further
isolates the broken Si. Consequently, in the LiPF$_6$ EC/DMC electrolyte, the Si electrode after cycling becomes pulverized to nanoparticles and is covered by thick SEI layer (Figure 3.9.b). Since the SiMP in in LiPF$_6$ mixTHF electrolyte gradually evolved into a mulberry-configuration integrity after cycling without any pulverization ensuring high Coulombic efficiency of >99.9%, while the Si lithiation in conventional carbonate electrolytes accompanies with significant breakage and growth of thick SEI layer resulting in the continuous pulverization of the SiMP and a low Coulombic efficiency (<99%). This electrolyte-enabled super SiMP anode provides opportunity to commercialize high-volume expansion alloy anode and guide the design of next generation high-energy batteries.

3.2.5. Criteria of salt and solvent selection for electrolytes.

Formation of the organic/LiF bilayer SEI is critical for achieving a stable cycling for SiMP. To form LiF SEI inner layer, the salts and solvents have to meet several requirements. For the salts, the reduction product of salts should be reduced at a high potential and form solely LiF without organic co-products. The solvent should have low thermodynamic reduction potential and low solvation ability with salt to kinetically reduce the solvent decomposition. We conducted two series of experiments to verify the above rules. Firstly, LiTFSI is both thermally and chemically more stable than LiPF$_6$, and it does not trigger the polymerization of ether solvents at all. Moreover, theoretical simulation confirms that the CIPs (71%) dominate the solvation structure, reducing the possibility of solvent reduction, similar to the case of LiPF$_6$ mixTHF electrolyte. However, the LiTFSI mixTHF electrolyte is unable to stabilize SiMP during cycling. The capacity drops to 70% at 20 cycles, and further to 38% and 24% after 50 and 100 cycles, while the CE keeps at
97.4% in the first 15 cycles, and slightly rises to ~98.9% after 30 cycles when the specific capacity has dropped below 1100 mAh g\(^{-1}\).

Figure 3. 12. Cycling of the LiFePO\(_4\)–SiMP full cells. (a) The initial, 5th, 10th and 20th charge-discharge profile of the LiFePO\(_4\)–SiMP full cell at 0.33 C (1 C = 2.4 mA cm\(^{-2}\)), (b) comparison of capacity retentions after 30 (first blue) and 100 cycles (second blue), and average CE (red) from 6th cycle to 80% capacity retention, and (c) full cell cycling performance at 0.33 C, along with the CEs.

LiPF\(_6\) mixTHF electrolyte also enable lithium iron phosphate (LFP) cathode to achieve exception cycling stability at a high area capacity of 2.3 mAh cm\(^{-2}\). By coupling LFP cathode with SiMP anodes that have the unprecedentedly high CEs of > 99.9%, we are able to construct a practical Si/LFP full-cell battery (Figure 5). No pre-cycling of anode or cathode, nor pre-lithiation of SiMP anode are performed, with all processes same as in the LIB industry. The full cell exhibits stable cycling (93.6% and 80.8% capacity retention after 30 and 100 cycles) and high CE (approaching 100% after the fifth cycle) at practical
values of current density (0.8 mA cm$^{-2}$) and areal capacity (> 2.0 mAh cm$^{-2}$). Moreover, no increase in the overpotential was observed in the voltage profiles at various cycle numbers (Figure 3.11. a), indicating that both electrodes and their electrode/electrolyte interfaces remain stable during cycling. In sharp contrast, full cells cycled in traditional LiPF$_6$ EC DMC only retained 56.3% and 4.5% after 30 and 100 cycles respectively (Figure 3.9. b and 3.9. c), with average CE only 91.1%. Even with the addition of the state-of-the-art additive FEC in LiPF$_6$ EC DMC electrolytes, the capacity retention only slightly increases to 80.8% and 6.18% after 30 and 100 cycles, with only limited improvements on average CE (93.64%). The severe capacity decay is due to the continuous SEI growth on the SiMP anode, which leads to both low CE and increasing hysteresis. This unprecedentedly stable full-cell with large (>10 µm) microsized Si as anode materials which has never been achieved to cycle stably (even in half-cell configurations) with the highest cycling CE of > 99.9% demonstrates the effectiveness of our newly developed LIB electrolyte. The thin and effective SEI formed in our electrolyte enables us to address the most stringent issues of micro-Si anode material, and will provide insights in future electrolyte design directions.

3.3. Conclusions

A rationally designed 2M LiPF$_6$ mixTHF electrolyte enables selective formation of an organic/LiF bilayer SEI on SiMP anodes, which allow SiMP to undergo elastic and plastic deformation due to the high interfacial energy at LiF/Si interface. Large (>10 µm) SiMP in 2M LiPF$_6$ mixTHF provide a high gravimetric capacity of 2800 mAh g$^{-1}$ and areal capacity of 5.6 mAh cm$^{-2}$ for 300 cycle with initial CE of 91% and cycling CE of >99.9%.
The Si/LiFePO$_4$ full cell exhibits 100 cycle life with high cCE approaching 100% at practical areal capacity of $>2.0$ mAh cm$^{-2}$. This report suggests a simple drop-in replacement for graphite anode via a simple electrolyte modification is leading to high energy SiMP anode-containing batteries operating at practical areal capacity and charge-discharge rates.

3.4.1. Experimental method

The in-situ electrochemical atomic force microscopy (EC-AFM) was conducted with a Dimension ICON AFM setup, inside of an Argon-filled-glove box, where both H$_2$O and O$_2$ levels were below 0.1 ppm – coupled with a CH Instrument 760 E potentiostat. For all the topographical mappings, ScanAsyst fluid plus probe (Bruker AFM Probes) was used with a nominal spring constant of 0.7 N/m, composed of silicon nitride cantilever with a sharp silicon tip. This probe was also used to remove the soft SEI layer. RTESPA-525 probe (Bruker AFM Probes) with a nominal spring constant of 200N/m was used to remove the hard SEI layer from the substrate, which is composed of antimony doped silicon with a silicon tip. The cycling was conducted against Li metal foil, in an electrochemical cell designed for lithium-ion battery materials and sealed during the AFM operation.

To measure the thickness of the soft SEI layer, first the contact mode was operated with ScanAsyst fluid plus, with a contact force of 20 nN, to remove the soft SEI layer in a 1.5x1.5 cm$^2$ scanning area. Higher contact forces were also applied to assure that there is no softer SEI layer to be removed. Afterward, the same probe was used to conduct peak force tapping mode for imaging the morphology in a 5x5 cm$^2$ area, including the brushed region. This topography mapping compares the height between the brushed and un-brushed
regions to measure the thickness of the soft SEI layer. For measuring the hard SEI thickness, RTESPA-525 probe was used with a contact force of 3.0 µN to remove all the SEI layers from the Si substrate. Higher forces were also applied to make sure that there is no more SEI layer left on the substrate. (Knowing the Young’s modulus of Si to be over 100 GPa, this probe was chosen, since it can only penetrate through surfaces with maximum 20-30 GPa)

3.4.2 Experimental (AFM sample preparation)

The substrate used for the EC-AFM measurements is a polished Boron doped Silicon (University Wafer), with the resistivity of 0.001-0.005 ohm.cm. The substrate was cut to almost 1 cm² surface area, the surface area was then accurately measured for charge discharge applied current of 20 µA/cm². Then it was rinsed with water and was submerged into a freshly made Piranha solution (H₂SO₄:H₂O₂ 3:1) for 3-5 mins. After that, the substrate was thoroughly rinsed with excess amount of ultrapure deionized water (18.2 Mohm.cm) and was dried with 99.998% Nitrogen gas. The backside of the substrate was scratched to get to the pure Si (more conductive) part and then was conductively glued to a thin copper foil as a conductor, by using Pelco conductive carbon glue. The borders of the substrate were then glued to a Teflon adaptor by using Torr Seal Sealant (Varian vacuum Technologies) and was left for more than 24 hours for both the conductive glue and the sealant to cure. The substrate was then assembled to the Bruker EC cell and was kept under vacuum over night before inserting to the glove box for the EC-AFM measurements.
3.5. References


Chapter 4: Standard Protocol for Measuring the Nano-scale Mechanical Properties of Complicated Samples of Solid Electrolyte Interphases

4.1. Introduction

As mentioned in the previous chapters, the solid electrolyte interphase (SEI) plays a vital role for the battery’s life, its performance and its safety. During the charging process, the anode materials undergo volume expansion due to the lithiation. In the case of graphite-based LIBs as the most commercially used LIBs, the volume expansion is due to the Li ion intercalation in the graphite layers to form LiC₆ (at its maximum capacity, equation 1), causing about 10-12% of volume expansion.[1]

\[ xLi^+ + 6C \rightarrow Li_xC_6 \]  \hspace{1cm} (eq. 4.1)

The maximum amount of lithium ion that is stored in graphite is equivalent to x=1 (LiC₆). However, The lithiation process of Si is different from the interaction process of Li in graphite, where Li ions are intercalated between the graphite sheets during the charging cycle and removed during discharge with minimal structural change in volume. Si experiences large structural changes upon lithiation and de-lithiation. In the case of Si anodes, the expansion is due to the chemical reaction and bonding between the Li and Si
to form Li$_{15}$Si$_4$, when is completely lithiated. [2, 3] The expansion rate of Si upon lithiation is over 300%. [4]

$$15Li^* + 4Si \rightarrow Li_{15}Si_4$$ (eq. 4.2)

The anode cases mentioned above are the two most promising and practical anode materials that have been used in LIBs. The constant volume expansion and shrinkage phenomenon from continual charging and discharging leads to a drastic morphological change and rupture of the anode materials which in the case of Si anode, it causes pulverization and destruction of the electrode.[5-7] In the case of Si anodes, there have been numerous attempts to solve this issue by engineering the structure of the anode materials. [8-28] However, none of these efforts allow the Si to reach its maximum capacity for a long time. Another way to approach this issue is by engineering the solid electrolyte interphase, by introducing additives or using unconventional electrolytes. [29-39]

Solid electrolyte interphase can play a very important role in accommodating the anode expansion, preventing the constant pulverization and rupture of the electrode. As mentioned in the previous chapter, a mechanically strong SEI layer can increase the capacity of the Si anode by accommodating the volume expansion and shrinkage, preventing the rupture of the large Si anode particles. Since the mechanical properties of the SEI is an important characteristic for the battery performance and quality, scientists have been trying to measure the mechanical properties of this layer. To assess the mechanical properties of the SEI, researchers have been using AFM-based methods. [40-46]
Measuring the mechanical properties are based on contact mechanics science, which can produce results with large amount of errors on the Young’s modulus measurements, if the prior calibrations and the right mathematical models are not taken into considerations.

Measuring mechanical properties of the materials by using AFM-based methods has been well-established. However, when it comes to the SEI mechanical property measurements the complex nature of the SEI has been misleading the scientist. To measure the mechanical properties of a material, depending on the mathematical model that is used, certain amount of indentation into the substrate is needed. Most samples that have been studied for their mechanical properties, by using AFM-based methods, have a uniform chemical structure in the Z range, hence the AFM tip experiences a uniform composition of the sample in the indentation range (which can be from nm to \( \text{m} \) range). However, in the case of SEI, it is well established that it has an inhomogeneous structure, ranging from in homogenous inorganic layer- that is closer to the electrode- mostly organic layer that is closer to the interphase between the electrolyte and the SEI. Hence, while indenting the SEI layer, the AFM tip experiences multiple chemical compositions and layers which introduces a great error in measuring its mechanical properties. This fact has been ignored in all the mechanical property measurement reports, related to the SEI.

In this chapter we shed light on this totally ignored issue when it comes to the SEI mechanical property measurement. Several standard samples with known mechanical properties were used to point out the importance of using an indenter (AFM tip) with the right spring constant for samples with different mechanical properties.
4.2. Theory of mechanical property measurement

Young modulus is a mechanical property that measures the stiffness of a solid material. It defines the relationship between stress (force per unit area) and strain (proportional deformation).

\[
E = \frac{(F/A)/\Delta L/L_0}{FL_0/(A\Delta L)} \quad \text{(eq. 2)}
\]

Where \(E\) is the Young’s modulus, \(F\) is the force exerted on the object under tension, \(A\) is the area where the force is applied on, \(L_0\) is the original length of the object, and \(\Delta L\) is the length change of the object under the applied force. It is important to note that Young’s modulus measurement is only applicable in a material in the linear elasticity regime of a uniaxial deformation. As mentioned before, SEI does not have a uniaxial chemical composition, hence its deformation in the Z range is not uniform either. Also not all parts of the SEI are made of elastic materials. Our measurements have shown that SEI can be plastically deformed, which we will discuss in the following sections.

Figure 4.1. demonstrates what happens when the modulated AFM tip interacts with the surface.
Figure 4.1. Force and piezo Z position as a function of time, including (B) jump-to-contact, (C) peak force, (D) adhesion

The top (dashed) line represents the Z-position of the modulation as it goes through one period plotted as a function of time. The lower line (solid) represents the measured force on a probe during the approach (blue) of the tip to the sample, while the red part represents the force while the tip moves away from the sample. Since the modulation frequency is about 2 kHz in the current implementation, the time from point A to point E is about 0.5 ms. When the tip is far from the surface (point A) there is little or no force on the tip. As the tip approaches the surface, the cantilever is pulled down toward the surface by attractive forces (usually van der Waals, electrostatics, or capillary forces) as represented by the negative force (below the horizontal axis). At point B, the attractive forces overcome the cantilever stiffness and the tip is pulled to the surface. The tip then stays on the surface and the force increases until the Z position of the modulation reaches its bottom-most position at point C. This is where the peak force occurs. The peak force (force at point C) during the interaction period is kept constant by the system feedback. The probe then starts to withdraw and the force decreases until it reaches a minimum at point D. The adhesion is given by the force at this point. The point where the tip comes off
the surface is called the pull-off point. This often coincides with the minimum force. Once the tip has come off the surface, only long range forces affect the tip, so the force is very small or zero when the tip-sample separation is at its maximum (point E). As the system scans the tip across the sample, the feedback loop of the system maintains the instantaneous force at point C at a constant value by adjusting the extension of the Z piezo.

Figure 4.2. shows the same data as figure 4.1. but with the force plotted as a function of the distance.

![Figure 4.2. Force as a function of the distance](image)

Since we control the Z position of the modulation as a function of time and we measure the deflection of the cantilever as a function of time, it is possible to eliminate the time variable and plot the force against the Z-position. These plots can then be compared directly with the force-distance curves that have been used for decades by researchers interested in measuring mechanical properties of their samples with SPM, but at a several orders of magnitude faster measurement speed. The oscillation is more pronounced for
softer levers. Peak Force Tapping control has the ability to identify the repulsive force and respond to this interaction only, regardless of the magnitude of the snap-off ringing.

To obtain the Young’s Modulus, the retract curve is fit (the bold green line in fig. 4.3.) using the Derjaguin–Muller–Toporov (DMT) model. [47]

![DMT fit for modulus](image)

**Figure 4.3.** Force vs. separation where the separation is calculated from the Z piezo position and the cantilever deflection

\[ F = \frac{4}{3} E^* \sqrt{R(d - d_0)^3} \]  

(eq. 3)

F is the force on the cantilever relative to the adhesion force, R is the tip end radius, and d – d₀ is the deformation of the sample (indentation depth, δ). This model is valid for when the a is much smaller in comparison to R (Figure 4.4.)

![Indenter geometrical model](image)

**Figure 4.4.** Indenter geometrical model
The result of the fit is the reduced modulus $E^*$. If the Poisson’s ratio is known, we can calculate the Young’s Modulus of the sample ($E_s$). This is related to the sample modulus by the equation:

$$E^* = \left[ \frac{1 - v_s^2}{E_s} + \frac{1 - v_{tip}^2}{E_{tip}} \right]^{-1} \quad (eq. 5)$$

We assume that the tip modulus $E_{tip}$ is infinite, and calculate the sample modulus using the sample Poisson’s Ratio ($v$). The Poisson’s ratio generally ranges between about 0.2 and 0.5 (perfectly incompressible) giving a difference between the reduced modulus and the sample modulus between 4% and 25%. Since the Poisson’s ratio is not generally accurately known, many publications report only the reduced modulus.

One can re-write the eq. 3 in the form of Force vs. Young’s modulus:

$$F = \left( \frac{4}{3} \right) \frac{E}{1 - v^2} R^{1/2} \delta^{3/2} \quad (eq. 6)$$

In order to measure the Young’s modulus, we need to have the information about the force that is applied from the AFM tip to the sample, the tip radius and the indentation depth. To measure the force:

$$F = D * D_s * k \quad (eq. 7)$$

Where $D$ is the cantilever deflection, $D_s$ is the cantilever deflection sensitivity, and $k$ is the cantilever spring constant. By using the deflection sensitivity, one can translate the cantilever’s deflection from millivolt to nanometer. Once we obtain the deflection of the cantilever in terms of nm, by multiplying it by the spring constant of the cantilever, we can measure the force.

Now that we can calculate the force, the next parameter to measure is the indentation depth ($\delta$).
When the scanner moved down towards the sample, upon the tip-sample contact, if the sample is relatively very hard in comparison with the cantilever, the AFM tip will deflect. In this case, the Z scanner movement would be equal to the cantilever’s deflection (D). However, if the sample is relatively soft, upon applying more force on the sample, the cantilever will indent the sample and it might deflect as well. In this case the Z scanner movement would be equal to the combination of the deflection (D) and the indentation (\( \delta \)). Since the Z scanner movement value is known from the instrument, and the deflection can be calculated to nm by using the deflection sensitivity, the indentation can be calculated as well.

\[
Z = \delta + D
\]  
(\text{eq. 8})

To accurately measure the Young’s modulus, there are three parameters that need to be precisely calibrated: (1) Deflection sensitivity, (2) spring constant, and (3) tip radius. To measure the deflection sensitivity of an AFM tip, a very hard sample, such as sapphire is used to make sure that there would not be any indentation through the sample, which in this case the Z scanner movement would be equal to the deflection and the deflection sensitivity can be calibrated.

To evaluate how the error in the deflection sensitivity measurement can affect the indentation depth, here we introduce a relative error to the deflection sensitivity and based
on the following calculation, we find the error that this will cause on the amount of the indentation depth. Based on the eq. 8:

\[ Z = (1+x) + (1+e)D \]

\[ x = -e \left( \frac{D}{e} \right) \]

Therefore, the error that is introduced to the indentation depth measurement, is equal to the error in the deflection measurement multiplied by the ratio of the deflection over the indentation. Hence, if this ratio is more than 1, it can introduce a large error to the indentation depth measurement. As an example, if we assume that \( Z = 21 \) nm, \( D = 20 \) nm and the deflection sensitivity error is only 5%, then the indentation depth would be zero. In this case, if the indentation depth is zero, based on the DMT model calculation for finding the Young’s modulus, \( E \) would be equal to infinity, which means infinite error.

4.3. Results and Discussion

In one set of experiments, the following values were obtained, which a ScanAsyst air probe with a nominal spring constant of 0.4 N/m was used. The calibrations resulted in the following values: Deflection sensitivity: 41.11 nm/V, Spring constant (k) = 0.4245 N/m. The result of the mechanical property measurements for two different standard samples are as follows:
Figure 4.6: Mechanical mapping measurements for two standard samples.

As it is shown in Figure 4.6, the mechanical mapping shows an infinite amount of Young’s modulus which in this case and for this software, it is 60 GPa. This evidence confirms the fact that if a relatively soft AFM tip is used to measure the mechanical properties of a hard sample, since the ratio of the deflection over the indentation will be very large, the measured Young’s modulus will have a great error. In this case the error is about 1600%. However, with the same AFM tip if a soft enough sample is used, we can measure its mechanical properties with a very high accuracy (only 3.2% error), because the ratio of the deflection over the indentation is minimal in this case.

This is one of the most concerning discrepancies in the mechanical property measurement for SEI. Since SEI is not homogeneous on the Z range, the apparent deformation might come from the error in the photodiode of the instrument, if the lower
layers of the SEI are much harder than the AFM tip, which will cause the minimal or no indentation but all deflection. As an example, it was reported that by applying 150 nN on a 0.6 N/m cantilever an indentation of ~20nm was obtained. By using the nominal deflection sensitivity of ~40 nm/V:

\[
\frac{150 \text{ nN}}{0.6} = 250 \text{ nm deflection}
\]

\[
\frac{250 \text{ nm}}{-50 \text{(def sens.)}} = 6.25 \text{ V vertical move (error in photodiode reading)}
\]

Reported \( \approx 20 \text{ nm} \)

\[
D/ = \frac{250}{20}=12.5
\]

Error on \( = 5\% \times 12.5= \approx 62\% \Rightarrow 62\% \text{ error on Young’s modulus result JUST coming from this error.}

Another potential source of error is from the AFM photodiode limitation on the linear window. As an example, on the following figure, a large force was applied to obtain 600 nm in deflection on a relatively soft tip. The substrate that was used here is sapphire with a very high Young’s modulus. In the range of small deflection, no indentation was observed on the separation diagram. However, when a large force is applied the deflection is too high that it surpasses the linear range detection limit of the photodiode and it shows a large indentation on the sample, even though we know that there cannot be any indentation on the sapphire, by using this soft AFM tip with ~0.6 N/m spring constant.
4.4. Conclusion

While indenting the SEI layer for measuring the mechanical properties, the AFM tip experiences multiple chemical compositions and layers which introduces a great error in measuring its mechanical properties. This fact has been ignored in all the mechanical property measurement reports, related to the SEI. In this chapter we shed light on this totally ignored issue when it comes to the SEI mechanical property measurement. We have also shown by mathematical evidence how much error we introduce to the final mechanical property measurements if we ignore the important factors on calibration and using the right AFM tips for the measurements.
4.5. References

Chapter 5: Tuning the electronic properties of alumina

5.1. Introduction

Alumina has been one of the most famous catalyst supports for decades and has been doped with variety of elements such as N, [1, 2] F[3] B [4] Si [5] for variety of applications from CO₂ adsorption and Nitrogen adsorption[6] to fluid catalytic cracking process. [7] Metal oxides and their surfaces find extensive use in numerous fields of materials science, such as chemical catalysis, photocatalysis, and photovoltaics, among others.[8, 9] Thus, engineering the electronic properties of the oxide surfaces is crucial for a broad application of the materials, as well as for the improvement of their current applications[10] As of today, however, serious limitations affect the extent of this control, mainly for two reasons. First, most synthetic methods yielding well defined doped surfaces are limited to academic use (small scale)-which are not cost effective for industrial applications - or the products are not stable in those operational conditions of most industrial processes.[11] Secondly, the ceramic processes typically employed in industry to engineer oxide-containing materials result in complex morphologies [12] and a priori unpredictable behavior of the generated materials.
In this work, our primary goal is to generate phosphorous doped alumina surfaces, by employing simple ceramic processes and characterizing their electronic properties. We aim at shedding light on three major points: (1) theory-experiment correlation to inspect the average or the most likely surface morphology (we consider an array of possible location of P on $\gamma$-Al$_2$O$_3$ surfaces); (2) finding a structure-function relationship between the electronic properties and surface morphology. This can be exploited when metal oxides are engineered; (3) determining the degree of stability for various possible surface terminations, as well as P locations in the P-doped $\gamma$-Al$_2$O$_3$ ($P\gamma$-Al$_2$O$_3$).

Our study focuses on an atomic-level understanding of the morphology and the structure-property relationships of realistic (hydroxylated) surfaces of $P\gamma$-Al$_2$O$_3$ nanoparticles. $\gamma$-Al$_2$O$_3$ has been widely used as adsorbent and catalysts,[13] and also it is perhaps the most important nanomaterial used as a support for metal catalysts.[14] The properties of Al$_2$O$_3$ can change during chemical operations, which include chemical contamination, thermal stress leading to loss of surface area, pore blockage, and undesired crystal phases.[15-17] It has been empirically observed that dopants improve the overall performance of catalysts acting as crystal phase and/or surface area stabilizers.[18-20] For example, studies have been reported that treating the surface of $\gamma$-Al$_2$O$_3$ with phosphates could largely promote the performance of the catalysts in hydrodesulphurization (HDS).[20-22] Also, doping of $\gamma$-Al$_2$O$_3$ is commonly used for tuning its mechanical[23, 24] and optical properties.[25, 26] Many dopants such as metal, silica, and heteroatoms, have been used to modify the surface and bulk $\gamma$-Al$_2$O$_3$ during fabrication.[27-30] Phosphorus is our choice of dopant, because it has variety of atomic coordinations and
multiple electronic states. Also, it is known that phosphorus can covalently bind to Al\textsubscript{2}O\textsubscript{3}, thus making a stable catalyst support.[31, 32]

Experimentally, we characterized the structural and chemical properties of both P-doped and non-doped γ-Al\textsubscript{2}O\textsubscript{3} nanoparticles by utilizing Fourier transform infrared spectroscopy (FT-IR), solid-state magic-angle spinning nuclear magnetic resonance (MAS-NMR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Peak Force Kelvin probe force microscopy (PF-KPFM) techniques. On the theoretical side, we carried out several DFT simulations accounting for an array of surface and doping morphological models. Electronic properties were characterized by computing the density of Kohn-Sham states (DOS), surface work function and surface dipole moment; as well as IR and NMR of P-doped and non-doped γ-Al\textsubscript{2}O\textsubscript{3}.

5.2. Results and Discussion

The morphologies of γ-Al\textsubscript{2}O\textsubscript{3} and P-γ-Al\textsubscript{2}O\textsubscript{3} nanoparticles were probed by scanning electron microscopy (Hitachi S-4800 Field Emission Scanning Electron Microscope, FE-SEM, Hitachi Co.Ltd.). High resolution images were obtained by coating the samples by gold, using an ion beam coater (Gatan, IBC 681). The SEM images, Figure 5.1, show how complex the morphology of these particles is.
Figure 5.1. SEM images of (a,b) γ-Al2O3 and (c,d) P-γ-Al2O3 nanoparticles. The samples were coated with a gold layer for obtaining higher resolution images.

We see that the sample is a rough aggregate of several nanoparticles. Although, due to the different length scales probed, it is difficult to relate the SEM images to the DFT simulations or to the other characterization techniques. Nevertheless, the images give a glimpse to the systems measured by the experiments. And particularly, they highlight the need to carry out simulations of grain boundaries and sintering sites – a line of work we have already embarked on for γ-Al2O3 particles and plan to report in a future publication.

To investigate the P content in the doped γ-Al2O3 structure, EDS was conducted, using EDAX coupled with FE-SEM Hitachi S-4800. As EDAX microprobe analysis is semi-quantitative, analysis of several samples was carried out and averaged values are presented in Table 5.1.
<table>
<thead>
<tr>
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<tr>
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<tr>
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Table 5.1. The results of EDS analysis for the P-γ-Al2O3 samples.

We perform DFT calculations (see the Computational details section) where γ-Al2O3 and P-γ-Al2O3 surfaces are presented for two different essential surface models, namely oxygen terminated and 100% hydroxylated (OH terminated). We considered single-atom doping as well as two-atom doping (i.e., two interacting and independent P atoms in the simulation cell). Each structure underwent geometry optimization. Although we carried out the simulations on two cell sizes (a small bulk unit containing 40 atoms and a supercell containing 160 atom bulk) the presented results are based on the simulations of the larger, more realistic cell, unless otherwise stated. Both slab models consist of five cation layers (tetrahedrally and octahedrally coordinated Al atoms). A vacuum thickness of 15 Å above the surface was added between two periodically repeated slabs. We placed P on one surface of the slab. The bottom 40% of atoms in each slab was kept fixed at their optimized positions throughout the simulations. We consider four different positions for the P atoms in two categories:

- models **sub/surf**: P locates to a subsurface/surface site substituting an Al atom;
- models **md/bd**: P is in a phosphate-type ligand with mono/bidentate complexation to a surface Al atom;
Throughout the manuscript, we use abbreviations to identify each surface model of the relevant termination (e.g., O-sub and OH-sub are for subsurface location of P on O-terminated and OH-terminated surfaces, respectively).

In the simulation, we choose the (001) surface of γ-Al₂O₃ in the spinel-like bulk morphology proposed by Gutierrez et al.[33], Pinto et al.[34], and Taniike et al.[35] This structure compares favorably to known crystallographic and physical properties of γ-Al₂O₃.[36] In Figure 5.2, we depict the computed morphology (a and b) for the O-terminated γ-Al₂O₃ model as well as its associated DOS, plot (c). Not surprisingly, this surface termination activates the material. Although it is known that this termination is only detectable at very high temperatures, we present it here as a model for Oxygen-rich surface islands.

![Figure 5.2](image)

**Figure 5.2.** Computed morphology, both top view (a) and side view (b), and associated DOS (c) of non-doped O terminated γ-Al₂O₃ surface. Those of the 100% hydroxylated γ-Al₂O₃ surface are given in (d), (e), and (f), respectively. Fermi energy placed at zero for DOSs.

As our picture of γ-Al₂O₃ is that of a heterogeneous material with OH-rich and O-rich domains, we also present a depiction of the 100% hydroxylated surface termination of
the supercell in Figure 5.1. (d and e) alongside the associated DOS plot (f). From the mentioned figure, it is clear that, as expected, hydroxylated $\gamma$-Al$_2$O$_3$ is an insulator and electronically stable.

Experimentally, the P-doped $\gamma$-Al$_2$O$_3$ was synthesized by impregnation of phosphoric acid and commercially available $\gamma$-Al$_2$O$_3$, followed by a simple and commonly applied ceramic process, i.e. high temperature annealing process in air (see the experimental details section). By optimizing the ratio of $\gamma$-Al$_2$O$_3$ and the molarity of H$_3$PO$_4$, we are able to tune the doping level of P. In Figure 5.3, we show the atomic-level surface morphologies, resulted from the DFT simulations and the corresponding PDOS. When considering phosphate chemisorption, it can be realized through a monodentate or bidentate ligand configuration. Additionally, here we consider two types of slabs: one that is stoichiometric with a P(+5) oxidation state, and one that is consistent with a P(+3) oxidation state. This was accomplished by the addition of an electron donor to the bottom of the slab. The relevant computed morphologies and associated PDOSs show that the phosphorous coordination and overall local geometry and surface PDOS are slightly affected by the overall stoichiometry of the slab. This indicates that the chosen slab model is sufficiently thick that the surface properties are resilient to the chemistry occurring at the other end of the slab.

In the models O-sub/O-surf and OH-sub/OH-surf, the doping P atom was introduced at a tetrahedral Al site. The theoretical prediction delivers a clear picture for O-sub: a planar configuration is assumed for P consistent with an effective double oxidation (+3 oxidation state). For this model, we also explore the O terminated subsurface doped with two P atoms at the three tetrahedral doping sites. The three resulting models show
how the location of the second P atom introduces significant changes to the shape of the conduction band (CB). As there are unoccupied orbitals with P character, therefore similarly to the previous O terminated P-doped model (O-sub) one or both subsurface P atoms have +3 oxidation state character. When the P atom is located on the surface (model O-surf), it causes surface reorganization and distortions across the surface O atoms to form an O-dimer (see the relevant structure in Figure 5.3.a). The computed PDOS of this model has a band gap of 4 eV and it shows that the Fermi level lies at the top of the valence band. The computed PDOS plots display no significant changes either in monodentate (O-md) or bidentate (O-bd) configuration models, even though the surface morphology in O-bd was affected by several distortions of surface O atoms.
Figure 5.3. Models of O terminated and OH terminated P-γ-Al2O3 surfaces (a) and their associated surface PDOSs (b). The P atom is placed at various positions as defined before, particularly at the spinel defect site for O-sub and OH-sub models. In the PDOSs, the Fermi energy is set to zero.

When doping the OH terminated surface, we obtain the morphology/DOS depicted in Figure 5.3. In model OH-sub, the P atom is now non-planar, maintaining the lone pair as a partially filled state. At the same time, the P atom is sheltered in a sub-surface site. The surface P atom doping (OH-surf model) at the tetrahedral Al site causes the
neighboring octahedral Al to become five coordinated. In this situation, the surface P atom becomes three coordinated. When considering the phosphate models (OH-md and OH-bd), we notice that the surface largely maintains its non-doped surface morphology (low reorganization), but the DOS profile changes, displaying clear gaps with no P states on the band edges.

We further investigate the subsurface P doping and also consider higher concentration doping (i.e., two independent P atoms in the same simulation cell). The idea behind this set of simulations is to inspect the extent of nonadditivity/cooperation in the electronic behavior of the surfaces after P-doping. We achieved this by replacing another tetrahedral Al with P. The second P was inserted at three of the different, available and inequivalent tetrahedral Al locations and considered both the OH and O terminated surfaces. For the OH terminated surface, we found two local minima of the potential energy surface. The first structure features one P atom four-coordinated with three subsurface oxygen atoms and one surface hydroxyl group. The second P location is 3 coordinated with its lone pair still on P and pointing in the direction of the spinel defect site. In the second local minimum structure, the P closer to the surface moved toward the bulk expelling a water molecule. When the O-terminated surface is considered, the two P atoms achieve a planar tri-coordinated geometry. Conceivably, this is an indication that the oxidation state of P atoms is now +3.

The PDOS of these surfaces showed largely the same trend as for singly-doped surfaces. For the O-terminated surfaces, P doping induces a narrowing of the gap and the appearance of states with P character at the band edges. The OH-terminated surfaces are more resilient to the doping and maintain a large gap. However, as for the case of the
singly-doped surface, the valence band (VB) edge has a strong P character. Thus, we do not find a significant cooperative effect between P sites.

Our next set of investigations regard the simulations and measurement of the work function (WF or \( \phi \)) of P doped and non-doped \( \gamma \)-Al\(_2\)O\(_3\) nanoparticles. To understand the influence of P doping on the work function of \( \gamma \)-Al\(_2\)O\(_3\) nanoparticles, PeakForce Kelvin probe force microscopy (PF-KPFM™) in an Argon-filled glovebox is conducted for both doped and non-doped \( \gamma \)-Al\(_2\)O\(_3\) nanoparticles. PF-KPFM measurement is carried out on several nanoparticles with similar dimensions for each sample (Figure 5.4.).

![Figure 5.4](image)

**Figure 5.4.** (A and C) Topography and (B and D) potential mapping images of \( \gamma \)-Al\(_2\)O\(_3\) and P-\( \gamma \)-Al\(_2\)O\(_3\), respectively.

The average measured WF of the \( \gamma \)-Al\(_2\)O\(_3\) is 4.88±0.04 eV, while the average measured WF of P-\( \gamma \)-Al\(_2\)O\(_3\) is 4.16±0.06 eV. Our results show that doping of \( \gamma \)-Al\(_2\)O\(_3\) by phosphorus, has lowered its WF by almost 15% (Figure 5.5.a).
Figure 5.5. (a) Experimentally determined WFs for non-doped and P-doped \( \gamma \)-Al2O3. (b) Comparison of the experimentally and theoretically determined WF differences (\( \Delta WF \)) between non-doped and P-doped structures for supercell models of O-terminated and OH-terminated surfaces. Here, the negative \( \Delta WF \) denotes the increase in WF after P-doping as opposed to experimental results. (c) Surface stability diagram of P doping in terms of the chemical potential for both O-terminated and OH-terminated surfaces. (d) Surface stability diagram of P doping (O-sub and OH-sub models) in terms of the chemical potential. 2P\(_1\), 2P\(_2\), and 2P\(_3\) are for three different available tetrahedral Al sites.

We employ and compare GGA with GGA+U for the calculation for the WFs of all surface models. In performing GGA+U we derive suitable U values for O (1.11 eV) and P (1.77 eV) by employing the Cococcioni-de Gironcoli linear response method[37] to the small surface structures (40 atoms). DFT+U is chosen here to remove the spurious self-interaction present in semilocal (GGA) exchange-correlation functionals[38] and is particularly suited to improve the ab-initio description of surfaces and interfaces.
It is seen that for all surface models except OH-md and OH-bd, the computed WFs agree with the experiment in that WF is reduced as a result of P-doping. The reason for the fact that OH-md and OH-bd models stand out is complex and it involves two observations: (1) the surfaces do not rearrange significantly from the non-doped case, and (2) the P-OH contribution to the surface dipole is to increase it. Specifically, comparing the P-OH angle and OH direction in O-md and O-bd with the OH-counterparts from Figure 2, we notice that the hydroxylated surfaces see a P-OH pointing upward, while the O-terminated surfaces see a P-OH pointing downward. Thus, when the phosphates are added to the surface, the dipole is depleted for the O-terminated surfaces and enhanced for the OH-terminated ones. This observation is especially important for the OH-bd system. When we inspect the effect of doping by two independent P atoms (higher concentration) on the WF for the various structures of subsurface (O-sub and OH-sub) models, we notice that the addition of the second P atom further decreases the WF. Thus, theory and experiment semiquantitatively agree that on average P-γ-Al₂O₃ has a lower WF than non-doped γ-Al₂O₃, with the chemisorbed phosphate models going against the trend and increasing the WF values when the OH-terminated surfaces are considered.

To understand the reasons for the WF reduction by P doping we present in Figure 5.5.b the WF differences (Δϕ) between the non-doped and P-doped surfaces of each structural model, providing us with a comparison of theory and experimental results. It shows that all the O-terminated surfaces are in accordance with the experiment by yielding lower WF after P-doping (Figure 5.5.b). Whereas, the dentate models (OH-md and OH-bd) increase WF values.
The size of the surface dipole contribution to \( \phi \) (\( \phi_d \)) estimated by computing the difference between the left and right vacuum levels\([39]\) exhibits a clear trend that \( \phi_d \) reduces linearly with the increase in the number of P dopant for the O-terminated surfaces whereas it conversely rises for the OH-terminated surfaces.

Our analysis is substantiated by characterizing the energetic stability of the O-/OH-terminated surfaces in terms of chemical potentials, \( \mu \), (see Figure 5.5.c) reveal that dentate attachment models on both O- and OH-terminated surfaces (O-md/OH-md and O-bd/OH-bd) are quite less stable compared to other surface models (O-sub/OH-sub and O-surf/OH-surf). Also, O-terminated surfaces are more stable than OH-terminated ones by providing O-sub models as the most stable ones among all possible configurations (Figure 5.5.d).

Furthermore, to get a structure-function relationship among various surface models of P-\( \gamma \)-Al\(_2\)O\(_3\) discussed here, we plot a correlation between the WF and \( \phi_d \) (Figure 5.6.), which demonstrate the behavior of the electronic structure against the various P location on \( \gamma \)-Al\(_2\)O\(_3\) surfaces.
Figure 5.6. Plot of WF vs surface dipole $\phi_d$ for supercell models of (a) O-terminated surfaces and (b) OH-terminated surfaces models. Those for small cell models are (c) and (d), respectively.

Figure 5.6.a shows that there exists a clear linear correlation between $\phi$ and $\phi_d$ for the models of O-terminated surfaces, whereas less correlation for $\phi$-$\phi_d$ occurs for OH-terminated surfaces of supercell (Figure 5.6.b). However, the similar plots for the small cell models (O- and OH-) (see Figure 5.6. c&d) display a less linear correlation for O-terminated surfaces but a relatively good correlation for OH-terminated ones. This shows the importance of sizable finite size effects and surface relaxation effects on modeling of $\gamma$-Al$_2$O$_3$ surfaces. [40] Upon inspection of the Bader charges of the P atom in OH-md (+0.14) and OH-bd (+0.15), we further confirm that the reduction in the WF witnessed in our simulations is due to a change in dipole moment orientation rather than to charge transfer.
In order to obtain more detailed information about the structure and change in the chemical environment after P doping, the Al-NMR spectra were obtained for three samples; the as received γ-Al₂O₃, P doped γ-Al₂O₃ and heated γ-Al₂O₃, which was obtained by annealing the γ-Al₂O₃ at the same temperature as applied for P doped γ-Al₂O₃, just without H₃PO₄ source. (Figure 5.7.a). The spectrum of as-received γ-Al₂O₃ sample (in black) shows two peaks which are corresponding to AlO₄ at around 70 ppm and to AlO₆ around 12 ppm with an about 1:2 integration ratio, which is consistent with the literature reported values.[18, 41, 42] In the case of P-γ-Al₂O₃, the peak positions for AlO₆ and AlO₄ remain unchanged. While a new sharp peak appeared at 42.3 ppm and a shoulder to the octahedral Al peak at around 4 ppm. The peak at 42.3 ppm has been assigned to AlO₅ bonding. It is worth to mention that the AlO₅ surface units have been considered as selective anchoring sites for Pt catalysts.[41] The upshifted shoulder is possibly caused by the coupling of P with the AlO₆ units to form Al-O-P in the local environment of the surface AlO₆ units.[18]
Figure 5.7. (a) $^{27}$Al magic-angle spinning (MAS) NMR spectra of P-$\gamma$-Al2O3 (top), heated $\gamma$-Al2O3 (middle), and as received $\gamma$-Al2O3 (bottom). Theoretical predictions of solid-state Al-NMR spectra computed on a bulk model supercell including 40 independent atoms and plotted with dashed lines; (b) Non-doped $\gamma$-Al$_2$O$_3$, (c) P-doped $\gamma$-Al$_2$O$_3$. (d) Experimental IR spectra of the non-doped and P-doped $\gamma$-Al$_2$O$_3$ nanoparticles. Calculated IR spectra (e) for subsurface (O-sub) and surface (O-surf) P-doped O-terminated surface models and (f) for subsurface (OH-sub) and surface (OH-surf) P-doped OH-terminated surface models.

To assure that these structural changes are not due to a simple high temperature annealing effect, a control experiment was conducted, where the as-received $\gamma$-Al$_2$O$_3$ was heated to 550°C for 4.5 hrs (the same heating condition as in P-doping process, without the phosphorus source). As shown in Figure 5.7.a, the heated $\gamma$-Al$_2$O$_3$ shows the similar NMR spectrum to the as-received one,[41] suggesting that the P-doping process promoted the structural rearrangement for the formation of so-called pentahedral coordination units (AlO$_5$) and possible Al-O-P structures.

Additional evidence supporting the experimental measurements for Al-NMR is provided by the theoretical calculations. Computations of bulk $\gamma$-Al$_2$O$_3$ (carried out with GIPAW[43] on bulk $\gamma$-Al$_2$O$_3$), reproduce the experimental spectrum of the clean non-doped $\gamma$-Al$_2$O$_3$ nanoparticles with remarkable accuracy (Figure 5.7.b). The computational spectra (Figure 5.7.c) assign the peak at 42.3 ppm to either distorted tetrahedral or distorted octahedral-coordinated Al atoms. Our work, thus, improves upon recent theoretical results[44], which could only tentatively assign the 42.3 ppm peak to pentacoordinated Al atoms. We further find that the pentacoordinated Al atoms, depending on the nature of the bonding (length and angles) give rise to NMR peaks upfield (not shown) compared to the octahedral Al atoms explaining the presence of the shoulder peak. It should be noted that our DFT calculations for the NMR of the P-doped surface structures did not converge. Our works regarding a comprehensive NMR computation of P-doped $\gamma$-Al$_2$O$_3$ surface structures to
accurately understand the shoulder at 0 ppm and the additional sharp peak at 42.3 ppm are in progress and will be published elsewhere.

To gain more information about the chemical bonds, both non-doped and P-doped \( \gamma \)-Al\(_2\)O\(_3\) nanoparticles were characterized with FT-IR spectroscopy (Figure 5.7.d). Also, we computed the vibrational frequencies for the models of O-terminated (Figure 5.7.e) and OH-terminated (Figure 5.7.f) \( \gamma \)-Al\(_2\)O\(_3\) surfaces. The experimental spectrum of \( \gamma \)-Al\(_2\)O\(_3\) show a wide peak between 3000-3800 cm\(^{-1}\), which is assigned to O-H stretching and the hydrogen bond between the OH groups existing on the surface of Al\(_2\)O\(_3\). [45, 46] The computational spectra of all OH-terminated surface models and dentate models of O-terminated surfaces (O-md and O-bd) confirmed that the peaks in this region are due to asymmetric stretching mode of O-H. The EDAX measurement indicated that the P loading in the P-\( \gamma \)-Al\(_2\)O\(_3\) was around wt. 8.5\% (atomic 5.6\%), which is much higher than those required to react all the surface hydroxy groups on the surface of \( \gamma \)-Al\(_2\)O\(_3\). [47, 48] However, this peak still exists, even though it is weakened in P-\( \gamma \)-Al\(_2\)O\(_3\). At the same time, the peak intensity is increased in P-\( \gamma \)-Al\(_2\)O\(_3\) at 1639 cm\(^{-1}\), which has been assigned as the bending moment of adsorbed water molecules. [49] The remaining weak peak is assigned to the hydroxy group stretching from surface phosphate groups formed upon P doping and/or from water molecules adsorbed on the P-\( \gamma \)-Al\(_2\)O\(_3\). [47] On the other hand, the weak peak with the high P doping level also suggested that either some of the phosphate groups were dehydrated and/or some of the phosphorus was incorporated into the lattice of Al\(_2\)O\(_3\) (and not on the surface of the alumina). In the spectra of OH-surf model similar peaks, an intense peak around 2000 cm\(^{-1}\) as well as a relatively very small peak around 1650 cm\(^{-1}\), are reproduced due to the asymmetric stretching mode and inplane bending moments of O-
A similar O-H bending mode is seen around 2200 cm\(^{-1}\) for OH-md model.

Indeed, a significant peak at 1100 cm\(^{-1}\) was shown up in P-\(\gamma\)-Al\(_2\)O\(_3\), which was considered as the identification of different P-O stretching, especially for ideal tetrahedron [PO\(_4\)]\(^3\) groups. However, our computational analysis shows that OH-non-doped model also indicates such a peak and the peaks in this region result from the O-H bending mode for OH-terminated surface models of P-\(\gamma\)-Al\(_2\)O\(_3\). Only O-sub model has a peak due to P-O stretching in this region. For the other models, the vibrational modes of P appear between 800 and 1000 cm\(^{-1}\) as P-O bending mostly. This finding, in combination with the unexpected small peak of the hydroxy group of phosphate in the range of 3000-3800 cm\(^{-1}\), supports our hypothesis that P is either in the form of surface phosphate groups, which did not carry hydrogen atoms, and/or some of P dopant incorporated inside the lattice or network of Al\(_2\)O\(_3\).

It was reported that absorption in the range of 400-900 cm\(^{-1}\) corresponding to the Al–O stretching related to the octahedral (AlO\(_6\)) and tetrahedrons (AlO\(_4\)) units in the network of \(\gamma\)-Al\(_2\)O\(_3\). Both FT-IR spectra of \(\gamma\)-Al\(_2\)O\(_3\) and P-\(\gamma\)-Al\(_2\)O\(_3\) show absorptions in this range. More specifically, they all show peaks at 500 cm\(^{-1}\) and two shoulders at 720 and 776 cm\(^{-1}\). The intensity of the peaks significantly decrease in P-\(\gamma\)-Al\(_2\)O\(_3\), while the peak positions do not change very much. It was reported that Al-O stretching in AlO\(_6\) and AlO\(_4\) units were around 500-750 cm\(^{-1}\) and 750-850 cm\(^{-1}\), respectively. The peak position may change significantly dependent on the fabrication methods and existence of defects and dopants in the lattice of \(\gamma\)-Al\(_2\)O\(_3\). On the other hand, Du et al. reported that the band at 523 and 570 cm\(^{-1}\) related to the stretching mode of Al–O in the AlO\(_6\) and AlO\(_4\),
respectively. The bands at 734 and 774 cm$^{-1}$ related to the symmetric stretching vibration of the AlO$_4$ tetrahedron. [51] Boumaza et al. reported that Al-O stretching in AlO$_6$ was 491 cm$^{-1}$. [53] Based on these literatures, the peak at 500 cm$^{-1}$ is assigned for Al-O stretching in the octahedral units (AlO$_6$)[53, 54] and the shoulders at 720 cm$^{-1}$ and 776 cm$^{-1}$ are related to the symmetric stretching vibration of the AlO$_4$ tetrahedron.[51, 55] The relative decrease in these peaks upon P doping in this range might be due to the decrease of their population upon introducing phosphorus to the Al$_2$O$_3$ lattice or due to the formed PO$_4$ species covered on the surface, which decreases the detectable absorption of these bands. These results are confirmed by the presence of some P related vibrational modes seen at around 700 cm$^{-1}$ and 500 cm$^{-1}$ in both O/OH-terminated surface models. Overall, our computational approach is able to reproduce the main features of the experimental spectra, especially for OH-sub and OH-surf models.

5.3. Conclusion

In conclusion, employing experimental and computational methods, we have shown that the electronic properties of metal oxide surfaces can be manipulated via Group 5A doping (P atoms in this work). The surfaces can be made electron-rich in the sense that they have a lower work function than the undoped ones. The main reason for the work function lowering is the introduction of a surface dipole after doping. Interestingly, we find that the OH groups of thermodynamically stable mono- and bi-dentate Phosphate surface ligands cooperate with the surface by damping its dipole thereby decreasing the work function. Substitutional P-doping leads to nonsymmetric arrangements of P (tri- and four-
coordinated) with an added dipole that once again dampens the work functions. The reduced coordination of the P atom correlates with the reported higher catalytic activity of P-doped alumina surfaces. With this study, we paved the way to using group 5A doping as a tuning knob for engineering electrostatic properties of metal oxide surfaces with catalytic applications.

5.4. Materials and Methods

**Preparation of samples.** Doping γ-Al₂O₃ (Sigma Aldrich, gamma phase aluminum oxide nanopowder) with P was achieved by impregnation of γ-Al₂O₃ with phosphoric acid (with the ratio of 14g of γ-Al₂O₃ per 100mL of 1.0M phosphoric acid, Sigma Aldrich, 85 wt. % in H₂O) for 7 hrs while stirring to reach equilibrium adsorption.[56] After impregnation, the sample was dried at 100°C overnight, then it was placed in an oven at 550°C for 4.5 hrs. The product was then sonicated and dispersed in ultrapure water and centrifuged 5 times at 5,000 rpm for 8 mins, to make sure there is no free phosphoric acid in the sample. The final product was then dried at 100°C overnight.

**Characterization.** PF-KPFM measurements on the alumina samples were conducted with a Dimension ICON AFM setup inside an Argon-filled glove box where both H₂O and O₂ levels were below 0.1 ppm. The probes used were PFQNE-AL (Bruker AFM Probes), composed of a silicon nitride cantilever with a sharp silicon tip. The highly inert environment helped us to conduct more accurate measurements. P-γ-Al₂O₃ and γ-Al₂O₃ particles were first dispersed into ethanol, using bath sonication for 3 minutes. Then the samples were prepared by drop casting the dispersion of P-γ-Al₂O₃ and γ-Al₂O₃ particles
onto a boron-doped silicon substrate. Solid state $^{27}$Al (130.2 MHz) magic-angle spinning (MAS) NMR spectra were acquired at a magnetic field of 11.74T with a Bruker Avance III HD spectrometer equipped with a 4mm solid-state broadband probe (Bruker Biospin, Billerica, MA). One-pulse spectra were recorded with 45 deg pulse of 1 µs and 0.4 sec relaxation delay, collecting 1K data points over 104 KHz with the sample spinning at 10 KHz in a 4mm zirconia rotor, in which the finely powdered samples were packed. FT-IR spectra of $\gamma$-Al$_2$O$_3$ and P-$\gamma$-Al$_2$O$_3$ were acquired with a Thermo-Nicolet iS5 spectrometer (Thermo-Electron Corp., Madison, WI), using iD7 ATR accessory with diamond crystal plate, in the range of 400 to 4000 cm$^{-1}$. The spectra were recorded after 16 scans with a resolution of 4 cm$^{-1}$.

**PF-KPFM measurement:** To understand the impact of phosphorus doping on the work function of $\text{Al}_2\text{O}_3$, we have conducted PeakForce Kelvin probe force microscopy (PF-KPFM™). PF-KPFM™, the combination of PeakForce Tapping mode and frequency modulated KPFM (FM-KPFM), integrates the benefits and capabilities of PeakForce Tapping and the superior spatial resolution and accuracy of FM-KPFM. PF-KPFM has the highest performance of KPFM working in a dual-pass fashion$^1$. By utilizing KPFM method, one can obtain the local surface potential of materials in nanoscale level, while imaging their topography. Since KPFM measures the potential required to nullify the work function ($\phi$) difference between the conductive tip and the sample or vice versa, (depending on whether the potential was applied to the sample or the probe), the contrast in the contact potential difference (CPD) window is equivalent to the local work function difference of the sample and the supporting substrate ($\phi_{\text{substrate}} - \phi_{\text{sample}}=\text{CPD}$). Therefore, the local
surface potential can be used to calculate the work function of the sample, if the work function of the substrate is known.

PF-KPFM measurements on the alumina samples were conducted with a Dimension ICON AFM setup inside an Argon-filled glove box where both H₂O and O₂ levels were below 0.1 ppm. The probes used were PFQNE-AL (Bruker AFM Probes), composed of a silicon nitride cantilever with a sharp silicon tip. The highly inert environment helped us to conduct more accurate measurements, since the dipole moment of any absorbed species can directly induce a difference in contact potential and, subsequently, a phase shift of our samples. To measure the work function of P- Al₂O₃ and Al₂O₃ with PF-KPFM, we first disperse P- Al₂O₃ and Al₂O₃ particles into ethanol using bath sonication for 3 minutes. Then the samples were prepared by drop casting the P- Al₂O₃ and Al₂O₃ particles onto a boron-doped silicon substrate. Because the P- Al₂O₃ and Al₂O₃ particles only partially cover the Si substrate, the measured work function value of doped Si substrate can be used as the reference to calculate the work functions of P- Al₂O₃ and Al₂O₃ (ϕ_substrate − ϕ_sample=CPD).

Knowing the work function of the PFQNE-AL probe from previous experiments on a freshly cleaved HOPG (with a known work function of 4.68 eV), we calculated the work function of the doped-Si substrate to be 4.56 eV. The CPD for Al₂O₃ and P- Al₂O₃ were -312.6 mV and 397.3 mV, respectively, from which we calculated the work function of Al₂O₃ as 4.88 eV, which is 720 mV higher than that of P- Al₂O₃ (4.16 eV). Note that the dark contrast observed in the CPD image indicates their work function is higher than the Si substrate used in this work.
**Computational Details.** Our simulations relied on Density Functional Theory (DFT), and specifically we employ the Quantum ESPRESSO software. In the calculations, the PBE functional and Projector Augmented Wave (PAW) Pseudopotentials were employed with a kinetic energy cutoff of 50 Ry for the wavefunctions kinetic energy and 500 Ry kinetic energy cutoff for the charge density and potential. A Gaussian smearing to the occupations of the KS states was used, with a width (sigma) of 0.0001Ry. The self-consistent field calculations featured a Broyden mixing beta of 0.15. A k-point sampling on a 2x2x1 grid of points for geometry optimizations and an 4x4x1 grid for all single-point computations were set. Additional non-self consistent field (NSCF) was employed to generate smoother DOS plots.

The NMR calculations were carried out on the optimized bulk $\gamma$-Al$_2$O$_3$ structures by first performing a self consistent field (SCF) calculation with pw.x. Computation of NMR spectra have been carried out using DFT GIPAW (The Gauge-Including Projector Augmented Wave) method using norm-conserving PPs (e.g. Al.pbe-tm-gipaw-dc.UPF) with the PBE functional.

IR spectra calculations were computed with PHONON to generate vibrational frequencies carried out with fixed occupations (no smearing). In these calculations we first performed a SCF calculation with pw.x, second, we calculated the vibrational frequencies (normal modes/phonons) with ph.x and finally using dynmat.x we resolved the phonon information from ph.x output. The wavefunction kinetic energy cutoff for phonon calculation was 50 Ry on a 4x4x1 k-point grid with a 1.0 x $10^{-14}$ threshold.

The chemical potentials ($\mu$) were calculated as follows:
For P-doped and surface models (\textbf{O-sub}, \textbf{O-surf}, \textbf{OH-sub}, and \textbf{OH-surf}): 

\[ \mu_{\text{P-doped/surface}} = E_{\text{P doped-\(\gamma\)Al}_2O_3} - E_{\gamma Al_2O_3} + (E_{Al} - E_{P}) \]

(1)

For monodentate (\textbf{O-md}, and \textbf{OH-md}) and bidentate models (\textbf{O-bd}, and \textbf{OH-bd}): 

\[ \mu_{\text{monodentate}} = E_{\text{P doped-\(\gamma\)Al}_2O_3} - E_{\gamma Al_2O_3} - E_{H_3PO_4} + E_{H} + E_{O} \]

(2)

\[ \mu_{\text{bidentate}} = E_{\text{P doped-\(\gamma\)Al}_2O_3} - E_{\gamma Al_2O_3} - E_{H_3PO_4} + 2E_{H} + 2E_{O} \]

(3)

where the energy values were computed using the same cell for all species.
5.5. References


Chapter 6: Electro-reduction of CO$_2$ with Non-metal Doped Carbon-based Nano-materials to Selectively Produce Valuable Fuels

6.1 Introduction

CO$_2$ is the most important anthropogenic greenhouse gas and the increase of its concentrations in the atmosphere is believed to be the primary cause of global warming. [1, 2] CO$_2$ concentrations in 2016 have exceeded the historical 400 parts per million (ppm). [3] Another destructive impact of increasing CO$_2$ concentration in atmosphere is that an estimated 30–40% of CO$_2$ gas from human activity released into the atmosphere dissolves into oceans, rivers and lakes, causing ocean acidification. [4] In the last 150 years, the pH of the oceans has dropped by ~0.1 units and modelling predicts that the pH of the oceans will fall by 0.2 to 0.4 units by the year 2100. [5] This pH change will have significant effects on marine organisms, especially those with calcareous skeletons such as echinoderms. In an experimental report, acidification by only 0.2 units induced 100% larval mortality within 8 days, while control larvae showed 70% survival over the same period. [6] A recent report on the future of carbon dioxide emission predicts that in the coming few decades (by 2060), ~496 giga tones of CO$_2$ will be produced because of fossil fuel combustion by existing infrastructure. [7] This huge amount of CO$_2$ can be considered as a
destructive waste or it can be considered as a raw material for producing fuels and commodity chemicals. [8, 9]

CO₂ conversion has been proposed as a potential way to maintain balance in the carbon cycle and develop a sustainable society, and many kinds of technologies, such as photocatalytic reduction and Fischer–Tropsch synthesis have been already applied in this area. [10-14] A better and more sustainable alternative is the electrochemical reduction of CO₂ to hydrocarbons using renewable energy, which has been an attractive topic, due to its high conversion efficiency and desirability of the hydrocarbon-based products that can be obtained.[15-18] Electroreduction of CO₂ supplied by renewable energy is the most sustainable way to convert this disastrous waste to valuable products. Many electrocatalysts including metal and molecule pyridine catalysts have been investigated for CO₂ reduction in the past few decades.[19-29] Of all the metals examined hitherto, only copper (Cu) has shown a unique ability to produce hydrocarbons with reasonable faradaic efficiency (FE).[30] All the other metals in the same media produce carbon mono oxide or formate, or they promote the competitive reaction, hydrogen evolution reaction (HER). [31] Nevertheless, the overall selectivity of copper catalysts towards hydrocarbons is still very limited.[32] Copper has shown to produce over 20 different product in aqueous media, from the electro-reduction of CO₂ which brings up the challenge of product selectivity of this metal.[33]

As an alternative approach to the metal catalysts, researchers have been developing non-metal catalysts for the electrochemical reduction of CO₂.[18, 29, 34] Most non-metal doped catalysts for the electroreduction of CO₂ are nitrogen doped carbon materials that
are limited in their faradaic efficiencies.[35] One of the highest Faradaic efficiencies reported for conversion of CO\(_2\) to 2 carbon hydrocarbons (ethylene and ethanol, combined) is \(~\text{45}\%\) max.[36]

Electroreduction of CO\(_2\) is one of the most challenging electrochemical catalysis reactions of all, since there are so many factors playing a role in the FE of this complex reaction. Extensive works have shown that the selectivity and activity of all of these catalysts (metal or non-metal catalysts) can be modified by alloying, [37] surface restructuring, [38, 39] surface functionalization, [40] solvent, [41, 42] and electrolyte composition, [43, 44] pH,[45] as well as temperature,[46, 47] pressure [48] and CO\(_2\) flowrate. [49]

One of the most important factors in the electroreduction of CO\(_2\) is the reaction media. Since the saturated concentration of CO\(_2\) in water is relatively low, there are many reports showing a successful electro-reduction of CO\(_2\) in other media such as ionic liquids [47, 50, 51] or acetonitrile.[52, 53] At the same time, the reaction media can be a limiting factor in obtaining various products from the reduction reaction, as hydrogen from the aqueous media can promote the production of different types of hydrocarbons, which is not the case in a medium such as acetonitrile (CO\(_2\) reduction products in acetonitrile are limited to carbon monoxide, carbonate and oxalate.

For the first time, we have reported an impressive electrocatalytic activity of P-doped graphitic carbon (PGC) for the CO\(_2\) reduction reaction to a 3 carbon chain oxygen containing hydrocarbons. Not only is our catalyst the first one in the family of P-doped carbon based materials for CO\(_2\) reduction, but also we have shown that it can convert CO\(_2\)
selectively to iso-propanol, which has been always a minor product (if any) in electroreduction reaction in all the reports. We also have made our own electrochemical cell to promote the catalytic reaction by optimizing the electrolyte volume over the catalyst surface area ratio and the headspace and the electrolyte space ratio. In contrast to other carbon-based electrocatalysts for CO2 reduction that take hours and days to be synthesized, [34] our catalyst can be synthesized as extremely fast as 45 seconds. However, this amazing catalyst comes with a price of reproducibility issue which is under investigation.

6.2 Result and Discussion

Our recent collaborative project on this synthesis and fundamentally characterizing the P-doped graphitic carbon (PGC),[54] shows that PGC has an oxophylic property which we hypothesized to be useful for the electrochemical reduction reaction of CO2. We hypothesize that since P is an oxophylic element it may stabilize side-on bindings of the CO2•• intermediate which is well-established established to be the first intermediate in the chain chemical reactions of CO2 reduction. [55]

Also the following SEM images show the porous structure of PGC with two different angles. These images were taken by SEM, Hitachi S-4800. The porous structure of the PGC makes it a great candidate for catalytic reactions as it offers a large surface area.
To gain more information about the component of the synthesized PGC, Energy-Dispersive X-ray Spectroscopy (EDS) was also conducted, which its results are as follows.

<table>
<thead>
<tr>
<th>PGC components</th>
<th>Elements</th>
<th>Ave. W%</th>
<th>Ave. atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>83.19</td>
<td>87.97</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>13.35</td>
<td>10.60</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>3.44</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Table 6.1. EDS table of PGC elemental contents

The PeakForce Kelvin probe force microscopy (PF-KPFM) measurements of the PGc catalysts were conducted using a Dimension ICON AFM setup inside a nitrogen-filled glove box where both H2O and O2 level were below 0.1 ppm. The tips used were PFQNE-AL (Bruker AFM Probes), composed of a silicon nitride cantilever with a sharp silicon tip. (Figure 6.2)
To conduct the electrochemical reaction, a custom electrochemical cell made from polycarbonate and fitted with Teflon coated silicon O-rings (McMaster-Carr) was employed for CO₂ electrolysis experiments (Fig. 6.3.). The electrochemical cell employed was designed to have a large electrode surface area to electrolyte volume ratio to maximize the concentration of liquid phase products in the electrolyte. The cell maintained the working electrode (on cell part D) parallel to the counter electrode (on cell part A) to achieve a uniform voltage. An cation exchange membrane (Nafion 114) was used to separate the working and counter electrode compartments to prevent the oxidation of reduced CO₂ products. The Nafion 114 was chosen, after the control experiment with copper foil as the working electrode with anion exchange membrane (Selemion AMV, AGC Inc.) caused the migration of negatively charged ions to the anolyte, such as formate. The cell was designed to have a large electrode area (3.14 cm²) and a small electrolyte volume (~4 mL) in each of the two compartments, along with a gas headspace of approximately 1.5 mL above the electrolyte on each side of the membrane. CO₂ (Airgas, 99.9% purity), regulated by a rotameter (Omega Instruments) at 10 sccm, flowed through the cell during electrolysis. The flow rate of 10 sccm was chosen to ensure sufficient CO₂
transport to the surface while preventing interference from gas bubbles striking the surface. The CO\textsubscript{2} was humidified with water by passing it through a bubbler before it entered the electrolysis cell in order to minimize the evaporation of volatile liquid phase products. For each electrolysis experiment the cell was assembled with PGC film on titanium foil as the working electrode and platinum as the counter electrode. A Saturated Calomel electrode (SCE) (CH Instrument) was used as the reference. The distance between the working and reference electrodes was kept small to reduce solution resistance. A 0.1 M solution of KHCO\textsubscript{3} (Sigma-Aldrich, 99.99% metals basis) was prepared with 18.2 MΩ deionized water from a Millipore system and used as the electrolyte. The pH of the electrolyte purged with CO\textsubscript{2} was 6.8. The electrolyte was purged for 30 prior to the electrolysis.

**Figure 6.3.** Schematic drawing of the designed sandwich electrochemical cell.

Figure 6.4. shows the chronoamperogram (electrolysis) of PGC film in 0.1M aqueous KHCO\textsubscript{3}, purged with CO\textsubscript{2} at -1.0 V vs. RHE.
Liquid phase products were quantified using 1D 1H NMR (600 MHz, Varian Inova). Standard curves were made using purchased chemicals over the concentration range of interest, with the internal standards DMSO and phenol, in 0.1 M KHCO$_3$. The water peak was suppressed by a presaturation sequence. NMR parameters used (see the experimental section) were identical between collected spectra to make standard curves and in the subsequent quantification of products in the electrolyte. 700 µL of the catholyte containing CO$_2$ reduction products after 10 mins electrolysis was mixed with 35 µL of a 10 mM dimethyl sulfoxide (DMSO) and 50 mM phenol for use as internal standards in D$_2$O for NMR analysis. The ratio of the area of the iso-propanol peak to the area of the DMSO peak area was compared to standard curves to quantify its concentration. The coulombs needed to produce that concentration of each product was calculated and divided by the total coulombs passed during the chronoamperometry to determine the current.

**Figure 6.4. CO$_2$ reduction electrolysis at -1.0V vs. RHE**
efficiency. 1H NMR allowed for quantification of all of the liquid phase products identified in this study.

After the electrolysis and identification and quantification of the liquid product by using NMR (Figure 6.3.), the faradaic efficiency of the reaction was calculated to be ~ 70% at -1.65 V vs. saturated calomel electrode (SCE) at pH 6.8 (-1.0 V vs RHE), towards iso-propanol production.

![Figure 6.5](image)

**Figure 6.5.** H1 NMR diagram of the past-electrolysis solution

<table>
<thead>
<tr>
<th>CO₂ Reduction Products</th>
<th>Chemical Shift</th>
<th>H splitting</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.2</td>
<td>t</td>
<td>phenol</td>
</tr>
<tr>
<td></td>
<td>6.86</td>
<td>t</td>
<td>phenol</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>d</td>
<td>phenol</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>p</td>
<td>Iso-propanol</td>
</tr>
<tr>
<td></td>
<td>3.53</td>
<td>q</td>
<td>Ethanol</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>d</td>
<td>iso-propanol</td>
</tr>
<tr>
<td></td>
<td>1.06</td>
<td>t</td>
<td>Ethanol</td>
</tr>
</tbody>
</table>

**Table 6.2.** The CO₂ reduction products based on HNMR
To obtain more insights about the configuration of phosphorous atoms in the PGC structure, X-ray absorption near edge structure (XANES) was conducted (Figure 6.4.) XANES result shows the resemblance of the energy of phosphorus with the standard chemical of triphenylphosphate, which means that the P atoms are in a phosphate configurations on the top of the carbon structure.

![Figure 6.6. The XANES diagram of PGC and Triphenylphosphate](image)

Although the reduction result is truly promising, the catalyst suffers from reproducibility issue. Trace metal contamination is a great concern in electrochemical reduction of CO2 as it promotes Hydrogen evolution reaction (HER), which is a competitor reaction of CO2RR in aqueous media or in case of trace amount of copper, it can enhance the electrochemical CO2 reduction activity.[56] The product selectivity of metal electrodes is often severely affected by the presence of extremely small amount of adatoms on the surface. [31] To assess the metal contamination issue for the electrolyte salt and the raw materials for PGC, inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted. The electrolyte has no tracible metal contamination, however, the phytic acid which was used to synthesize PGC has ~ 500 ppm concentration and zinc has 7.6 ppm
contamination. This result was obtained from the semi-quantitative analysis of the ICP software. 500 ppm in the raw material can be the answer to the reproducibility issue of our catalyst, even though the synthesized pgc undergoes filtration, the trace amount of iron can stick to PGC and cause the severe irreproducibility issue. This project is ongoing and is transferred another graduate student, since it is worth to put more effort to it as the catalyst can reduce the CO₂ to iso-propanol to the higher FE ever reported with the highest selectivity.

6.3 Conclusion

For the first time, we have reported an impressive electrocatalytic activity of P-doped graphitic carbon (PGC) for the CO₂ reduction reaction to a 3 carbon chain oxygen containing hydrocarbons. Not only is our catalyst the first one in the family of P-doped carbon based materials for CO₂ reduction, but also we have shown that it can convert CO₂ selectively to iso-propanol, which has been always a minor product (if any) in electroreduction reaction in all the reports. We also have made our own electrochemical cell to promote the catalytic reaction by optimizing the electrolyte volume over the catalyst surface area ratio and the headspace and the electrolyte space ratio. In contrast to other carbon-based electrocatalysts for CO₂ reduction that take hours and days to be synthesized, [34] our catalyst can be synthesized as extremely fast as 45 seconds. However, this amazing catalyst comes with a price of reproducibilty issue which is under investigation.

6.4 Experimental
**PGC synthesis:** PGC was made The phytic acid (Sigma Aldrich, 50 w/w% in water, 1 mL) was placed in 35 mL Pyrex glass vessel (CEM, #909036) and then closed with Teflon lined cap (CEM, #909235). This closed glass vessel was kept in 500 mL beaker and then the whole assembly was covered with watch glass before transferring to a domestic microwave oven (1100 W, Sanyo-EM-S9515W, 2.45 GHz). A microwave irradiation was applied for 40 seconds which results into black carbonized material. After microwave treatment, the glass tube was left in a fume hood for a few minutes to remove any gas generated during microwave reaction and then dispersed in ethanol by bath sonication (5 minutes). The resulting dispersion is filtered by 0.8 µm polycarbonate filter paper (Millipore, ATTP 04700) and washed with water (~800 mL) and ethanol (~400 mL).

**Electrode preparation:** The dried PGC was mixed with carbon black and PVDF as the binder with the ratio of 7:2:1 in 0.5 mL of N-Methyl-2-pyrrolidone (NMP). The mixture was grinded by mortar and pestle for 30 mins, until a uniform slurry was obtained with no observable granule in it. The Ti foil (99.99% Alfa Aesar) surface was thoroughly cleaned with ethanol and wiped and air dried. The 120 m PGC film was made on the Ti foil by using MSK-AFA-2- Automatic thick film coater, from MTI Corporation. The sample was then placed into a vacuum oven for 24 hours at 60°C. After the sample was fully dried, the film was cut to circular pieces to get assembled into the cell for the electrochemical reaction.

**Product Analysis:** 1D NMR spectrum on a sample of 0.1 M KHCO₃ containing a mixture of products. The spectrum was acquired on a 600 MHz Varian Inova with a 0.5
s prescan delay, 5 s presaturation of the H₂O resonance, 45 degree read-pulse, over an 8000 Hz spectral width, 4 s acquisition time, centered on the water peak, for 52 scans. The change in the baseline near the middle of the spectrum corresponds to the location of the suppressed water peak.

**PF-KPFM measurement of PGc catalysts:** To understand the mechanism of the alcohol oxidation reaction catalyzed by PGc materials, we have conducted a PeakForce Kelvin probe force microscopy (PF-KPFM™). PF-KPFM™, the combination of PeakForce Tapping mode and frequency modulated KPFM (FM-KPFM), integrates the benefits and capabilities of PeakForce Tapping and the superior spatial resolution and accuracy of FM-KPFM. PF-KPFM has the best performance of KPFM working in a dual-pass fashion. By using KPFM, one can measure the local surface potential of nanoscale materials, concurrently imaging their topography. Since KPFM measures the voltage required to nullify the work function (φ) difference between the conductive tip and the sample (φ_{tip} − φ_{sample}) or vice versa, depending on whether the potential was applied to the sample or the probe) the contrast in the contact potential difference (CPD) is equivalent to the local work function variation of the sample on a supporting substrate. So the local surface potential can be used to calculate the work function of the materials, if the work function of the tip is known. KPFM has been widely used to investigate the influence of dopants or atomic scale defects on the variation of work function. It has also been used to study the work function of graphene as a function of number of layers and heteroatomic doping. PF-KPFM measurements on the PGc materials were conducted with a Dimension ICON AFM setup inside an Argon-filled glove box where both H2O and O2 levels were
below 0.1 ppm. The probes used were PFQNE-AL (Bruker AFM Probes), composed of a silicon nitride cantilever with a sharp silicon tip. The inert environment helped us to obtain more accurate measurements, since the dipole moment of any absorbed species can directly induce a difference in contact potential and, subsequently, a phase shift of our samples. To ascertain the accuracy of our surface potential measurements, the CPD measurement was first conducted for a piece of freshly cleaved highly ordered pyrolytic graphite (HOPG) in the glove box. The average CPD value of 0.60 V (with the standard deviation of 0.02 V) was obtained from the measurements at four different spots on the same HOPG. Knowing the work function of the probe tip from previous experiments (4.08 eV), the average work function $\phi$ of HOPG was calculated to be 4.68 eV. This value is in agreement with the literatures.

To measure the work function of PGc with PF-KPFM, we first break the monolith of PGc to small particles and disperse them into water or ethanol using bath sonication for 3 minutes. Then the samples for CPD measurements were prepared by drop casting the PGc particles onto a doped silicon (Si) substrate with 50 nm SiO$_2$ layer. Because the PGc or particles only partially covers the Si substrate, the measured CPD value of Si substrate can be used as the reference value to calculate the work functions of PGc. We calculate the work function of PGc is 4.87 eV.
Figure 6. 7. Calibration curve of isopropanol peak vs. DMSO

\[ y = 0.4545x - 0.0149 \]
\[ R^2 = 1 \]

Figure 6. 8. Cell assembly for Pt foil (applicable for the PGC foil on the cathode side as well)
6.5. References

1. The Intergovernmental Panel on Climate Change. 2013.
2. Forster, P., et al., Changes in Atmospheric Constituents and in Radiative Forcing Chapter 2. 2007, United Kingdom: Cambridge University Press.