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From Lithium–Sulfur to Lithium–ion: Strategies for Improved Battery Materials

A dissertation submitted in partial satisfaction
of the requirements for the degree

Doctor of Philosophy

in

Chemistry

by

Molleigh Bea Preefer

Committee in charge:

Professor Ram Seshadri, Chair
Professor Fred Wudl
Professor Galen Stucky
Professor Craig J. Hawker

September 2020

The Dissertation of Molleigh Bea Preefer is approved.

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May 2020

From Lithium–Sulfur to Lithium–ion: Strategies for Improved Battery Materials

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by

Molleigh Bea Preefer

To Princess Pixie Pie Preefer, PhD: she who keeps me sane.

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Curriculum Vitæ

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13. M. B. Preefer, J. Vinckevičiūtė, J. L. Kaufman, W. Zhang, K. E. Wyckoff, J. N. Weker, A. Van der Ven, R. Seshadri, NiNb_2O_6 : an Atypical Lithium Battery Conversion Material with Improved Capacity over Time, *manuscript in preparation (working title)*.
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Abstract

From Lithium–Sulfur to Lithium–ion: Strategies for Improved Battery Materials

by

Molleigh Bea Preefer

Improved battery materials are necessary to offset the intermittency of renewable energy sources such as wind and solar, to provide enhanced driving range and faster charging speeds for electric vehicles, and to make portable electronics lighter, faster, and longer lasting. There is a range of materials for next-generation batteries that fit can fit each of these needs. Lithium–sulfur (Li–S) batteries are one such technology that has the potential of increasing energy density for portable electronics while using an environmentally-conscious active material, elemental sulfur. All-solid-state batteries are another technology that has potential to increase energy density and also improve upon safety by removing flammable liquid electrolytes from the cell. Next-generation Li-ion batteries employing electrodes with 3-dimensional crystal structures have the opportunity to greatly increase the rate capabilities of batteries, which is especially important for electric vehicle applications.

These three next-generation battery technologies will be discussed in the context of detailed structure-property relationships of disulfide polymers as Li–S electrodes, lithium thiophosphate solid electrolytes for all-solid-state batteries, and oxide structures with highly connected metal-oxygen octahedra for fast-charging Li–ion batteries. I use different synthesis techniques including air-free solution synthesis and solid state synthesis to make materials and use a combination of electrochemical measurements, such as galvanostatic cycling, cyclic voltammetry, electrochemical impedance

spectroscopy to characterize the electrochemical properties of these materials. I also use a variety of *ex situ* and *operando* techniques, particularly Raman spectroscopy, X-ray photoelectron spectroscopy, XANES, X-ray diffraction, among others, to gain a detailed mechanistic understanding of the underlying chemistry and redox processes that drive the performance of these materials.

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Chapter 1

Introduction

1.1 Motivation for improved electrochemical energy storage

To relieve our dependence on fossil fuel as our main energy source, switching to relying upon renewable energy is becoming increasingly urgent. To make that a reality, energy conversion and energy storage must go hand-in-hand in offsetting reliance on fossil fuels.[12] The intermittent nature of wind and solar energy necessitate having to store the energy for the times of day when there is not enough wind or the sun is not visible.

Grid-scale energy storage is also only one piece to the battery puzzle. Different applications call for different battery technologies to take different metrics into account, such as energy density (the amount of energy stored per unit volume or mass), power density (the amount of energy that can be delivered in some measure of time), and the resources required to make different types of batteries.[13] For example, in the case of

grid-scale storage, the weight of the battery matters little, but the environmental cost matters greatly.[14] Therefore, batteries using chemistries involving earth-abundant and inexpensive elements are the preferred choice.[15] For portable electronics, the weight of the battery is going to take precedent, so maximizing the energy density will be important. For electric vehicles, both energy density and power density are priorities.[16] A Ragone plot can help rationalize the chemistries for different applications [Figure 1.1], such as Na-ion batteries being more ideal for grid-scale storage, versus Li-S batteries being more ideal for portable electronics. With all batteries, safety will play an important role.

Most of the types of batteries represented on this Ragone plot are not commercially viable yet, which necessitates the further research to make them a reality. Several of the challenges facing a few of these, namely Li-S, all-solid-state, and Li-ion batteries, will be discussed further.

1.2 Key terms and definitions for electrochemical energy storage

Electrochemical energy storage is rooted in the process of converting chemical energy to electrical energy using chemical reactions (and in reverse, in the case of rechargeable electrochemical energy storage). There are three main components in a battery: the anode, the cathode, and the electrolyte, which is contained in some kind of electrically insulating mechanical barrier. The electrically insulating nature of the electrolyte and separator act to isolate the flow of electrons from the anode to the cathode, such that they are forced to flow through an external circuit instead, which supplies

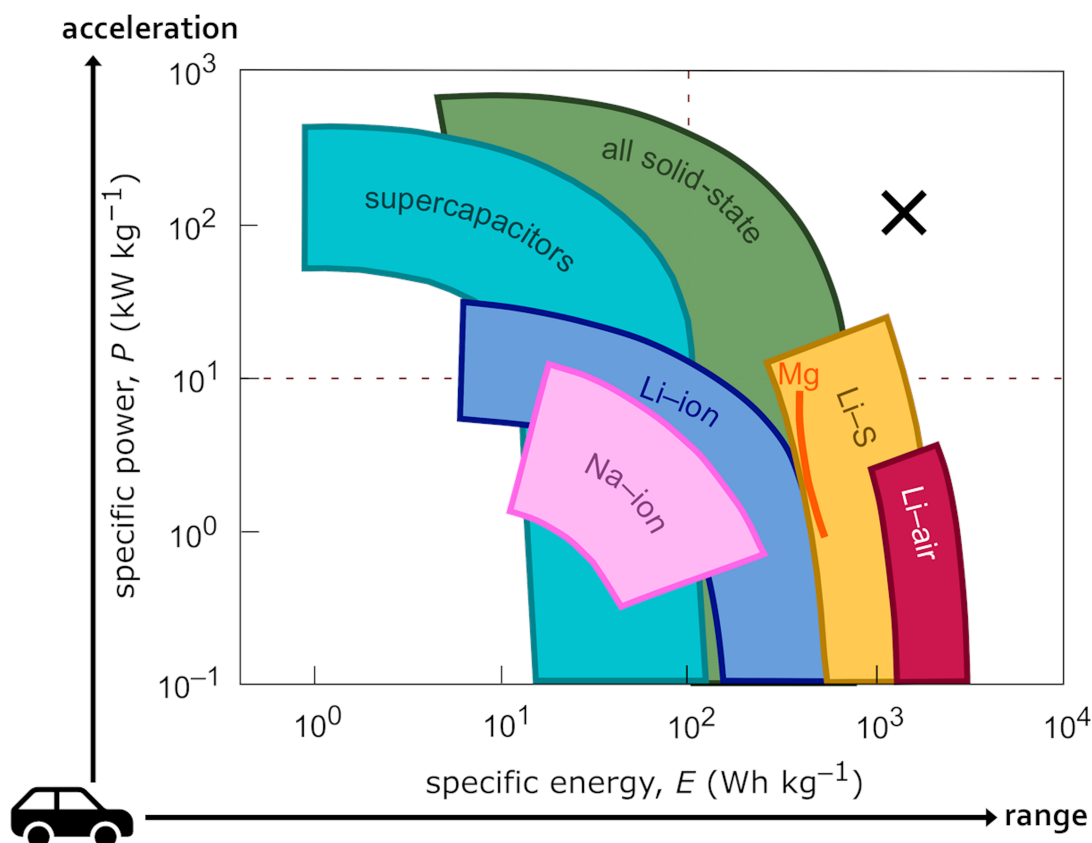


Figure 1.1: Ragone plot demonstrating the general regimes of energy density and power density within which current secondary battery (and adjacent) technologies lie. Taking electric vehicles as an example, specific power relates to the acceleration of the car (or the speed at which it can charge), and specific energy relates to the range the car can drive. The black $\times$ refers to the ideal quadrant for batteries, in which both specific power and specific energy are maximized. Figure adapted from [17].

energy to our devices. Additionally, the electrolyte's primary requirement is that it has high ionic conductivity. The anode, as applied to batteries, is the low voltage material, and the cathode is the high voltage material, where the higher the electrode's potential represents the difficulty of removing Li, for example, from the host structure.

One of the canonical examples of secondary Li-ion batteries is the lithium cobalt oxide (cathode) and graphite (anode) battery [Figure 1.2]. In the schematic shown, the anode contains layers of graphitic carbon, and the cathode contains layers of cobalt

oxide. The Li can be removed and inserted into these layers, a process called intercalation. The cell is discharged when Li is removed from graphite and intercalated into the cobalt oxide layers. The cell is charged when Li is removed from the cobalt oxide layers and is reinserted into the graphite layers. The electrons move around the external circuit to balance the charge, and the Li ions move through the electrolyte.

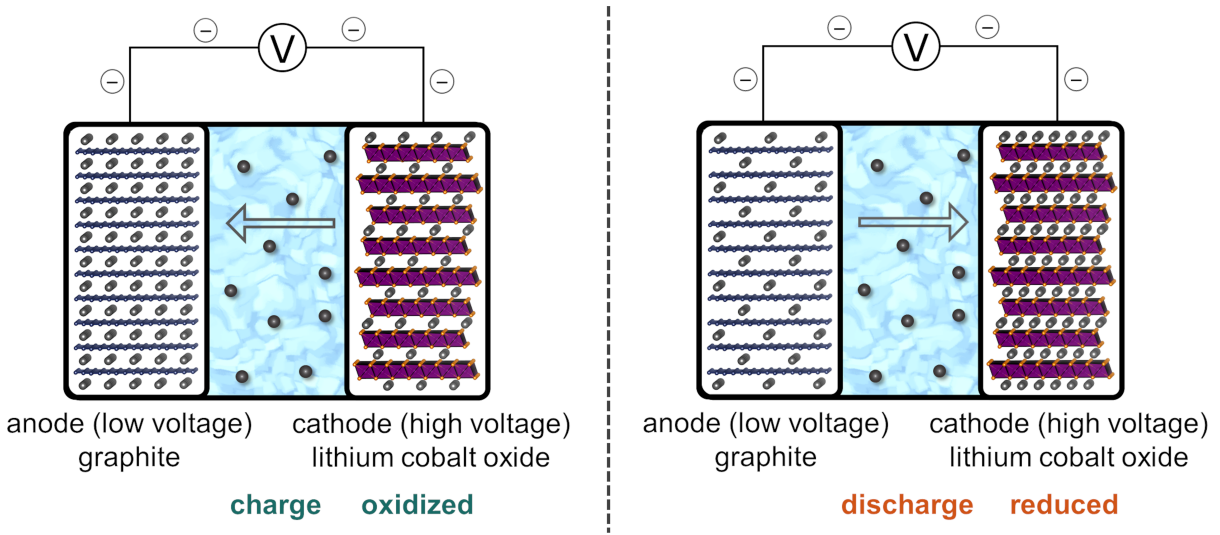


Figure 1.2: Pictorial representation of electrochemical lithium insertion (particularly intercalation in this example) in batteries. The anode is graphite, and the cathode is LiCoO_2 .

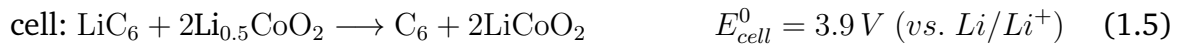
There are two key metrics that determine the specific energy of a cell (often given in units of Wh kg^{-1}). The first is the cell potential (measured in volts), E_{cell}^0 , which is the difference between the potentials of the anode and the cathode versus a chosen reference electrode), which stems from the Gibbs free energy:

$$\Delta G_{\text{cell}}^0 = \Delta G_{\text{cathode}}^0 - \Delta G_{\text{anode}}^0 = -nFE_{\text{cell}}^0 \quad (1.1)$$

in which n is the number of electrons, and F is Faraday's constant ($96485.3 \text{ C mol}^{-1}$).

$$E_{cell}^0 = E_{anode}^0 + E_{cathode}^0 \quad (1.2)$$

An example of this as applied to the given example of a LiCoO₂ cathode and graphite anode is as follows:



The positive cell potential indicates a thermodynamically favored reaction but by applying a potential, the reverse reaction occurs (charging the cell). Generally, Li batteries are referenced *versus* Li/Li⁺, which is offset from standard hydrogen electrode (SHE) by −3.04 V.

The second key metric is the capacity of the cell, or the amount of charge that can be stored, Q (units of C g^{−1}). The theoretical specific capacity for a given material can be found through the following relationship:

$$Q = \frac{F \cdot n}{M} \quad (1.6)$$

where F is Faraday's constant, n is the number of electrons per formula unit, and M is the molar mass of the material per formula unit. The common way to express specific capacity in battery literature, however, is in m A h g^{−1}. The conversion between these units is 1 m A h = 3.6 C.

For example, the theoretical capacity of LiCoO_2 is:

$$\frac{1 \text{ mol } e^-}{1 \text{ mol LiCoO}_2} \cdot \frac{96485.3 \text{ C mol}^{-1}}{97.87 \text{ g mol}^{-1}} \cdot \frac{1 \text{ m A h}}{3.6 \text{ C}} = 273.8 \text{ m A h g}^{-1} \quad (1.7)$$

The specific energy is therefore the product of the cell potential and the specific capacity:

$$E = Q \cdot V \quad (1.8)$$

Though so far everything has been normalized to mass, another way to normalize is through volume, which is arguably a more important metric for certain applications. For both ways of normalizing, there is an important gap to mention between what is regularly reported in academia versus what is salient in industry settings. Often the specific capacity or energy in academic papers refer to only the mass of the active material (*ie* only LiCoO_2) as opposed to the mass of the active material plus additives often used in cell design (*ie* conductive carbon and polymeric binders), and even the cell casings.[\[18\]](#)

One caveat to note, however, which is aptly illustrated through the example of LiCoO_2 , is that obtaining the theoretical capacity calculated is not always realistic. If more than about half of the Li are removed from the structure per formula unit, the reaction is no longer reversible. The remaining Li is structurally necessary to prevent collapse of the CoO_2 van der Waals layers. This is why in the half reactions listed, the reaction occurs between LiCoO_2 and $\text{Li}_{0.5}\text{CoO}_2$. While the predicted theoretical capacity in this case is $273.8 \text{ m A h g}^{-1}$, in practice it's closer to 150 m A h g^{-1} . On the other side, sometimes transition metals can accommodate more than 1 electron, known

as multielectron redox, as long as there's space in the host structure to accommodate the lithium. Therefore, the theoretical capacity is usually an assumption and should be clearly defined.

Beyond specific energy, another metric that is becoming increasingly important to future battery research is specific power (units of W kg^{-1}), which is a measure of how quickly a cell can be discharged or charged. Especially for electric vehicle applications, this is a crucial parameter to aim to maximize.

Power is the rate at which energy moves, and is related to energy by:

$$P = \frac{\partial E}{\partial t} = \frac{\partial Q}{\partial t} \cdot V = I \cdot V \quad (1.9)$$

where V is voltage, and I is current.

An indirect way of assessing the power of a particular material is through cycling cells at different rates. Rates are often defined in terms of C , which is the amount of current needed to galvanostatically discharge the cell to its theoretical capacity in 1 hour. Therefore, for example, a rate of $C/10$ is the amount of current needed to galvanostatically discharge the cell to its theoretical capacity in 10 hours. Alternatively, $10C$ is the amount of current needed to galvanostatically discharge the cell to its theoretical capacity in 6 minutes. Materials that are able to cycle faster while maintaining appreciable energy are batteries capable of high power. (Another related technology is supercapacitors, which are designed for extremely high power and lower energy, but they are outside the scope of this work.)

Cycle life is another measure of a cell's performance. Testing a material's cycle life give an idea of potential applications and failure modes. Often times, this is coupled with different forms of *operando*, *in situ*, and *ex situ* analysis to understand the mech-

anisms that either lead to high reversibility or failure. Hand-in-hand with cycle life testing, the energy efficiency of a cell can also be assessed. Coulombic efficiency, defined as the ratio between the charge put into the cell and the charge extracted from a cell within a cycle, is a measure of how efficiently electrons are transferred within the cell toward the intended reaction. Voltaic efficiency, also known as the voltage hysteresis, is associated with increased energy needed to reverse the reaction when charging. This overpotential can be caused by kinetic barriers, resistance relating to the cell design, concentration differences, among other reasons. Both high Coulombic efficiency and a small overpotential are desirable for highly reversible and efficient batteries.

1.3 Brief history of lithium secondary batteries

In 2019 the Nobel Prize in Chemistry was awarded to Stanley Whittingham, John Goodenough, and Akira Yoshino, after many years of anticipation, for the "development of the Li-ion battery," each for a different piece of the ubiquitous Li-ion secondary batteries prevalent in today's electric vehicles and portable electronics. The origin story of the Li-ion battery often begins with Stanley Whittingham's development of the first lithium battery using TiS_2 , a Li-Al alloy anode, and a LiClO_4 -based electrolyte, technology he developed at Exxon.[19–22] This was the first proven example of intercalation electrodes, the process of inserting Li atoms into a layered material, such that the structure can remain relatively unchanged, leading to high reversibility (rechargeable).[23, 24] This is a key electrochemical process at the center of many batteries commercially-available today. However, the specific example of TiS_2 was ill-fated and faced a number of stumbling blocks, including cost, safety, and performance. The safety concerns associated with using pure Li metal as an anode material are still highly

relevant to current research in the field.

The next major development in terms of intercalation chemistry was LiCoO_2 , which revolutionized the use of secondary batteries.[25, 26] Simultaneous with the development of LiCoO_2 , framework structures such as V_6O_{13} were being explored.[27] These framework structures are now having a resurgence and are showing promise for high rate capabilities.

While cathode chemistries were making huge strides, the anode was another barrier to overcome. The challenges of Li metal anodes prompted the first dual intercalation electrode battery, using a TiS_2 and a WO_2 anode.[28] While the use of WO_2 greatly decreased the energy density of the total cell, it demonstrated the ability to use an intercalation anode and cathode simultaneously. Shortly after, graphite was used successfully as an intercalation anode for the first time using a PEO solid electrolyte.[29] In 1985, the first prototype for a full cell with LiCoO_2 as the cathode and graphite as the anode was disclosed,[30] and this became the basis of commercialized cells by Sony in the 1990s, persisting through to cells we use today.

Since the discovery of LiCoO_2 , other cathode advances have been made to improve upon the energy density of Li-ion batteries. One such example first reported in 1997 is LiFePO_4 ,[31, 32] which has slow Li diffusion, but when nanosized can handle extremely fast cycling rates.[33] Another example is $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ($x + y + z = 1$), also known as NMC, which is a layered structure like LiCoO_2 with an average voltage of 3.6 V – 3.7 V.[34, 35] NMCs offer improved energy density over pure LiCoO_2 and are the most widely used cathode materials today in commercial Li-ion cells. The field continues to strive toward higher energy density, higher power capabilities, and the use of sustainable elements.

In 1980, Goodenough *et al* succinctly communicated all of the basic principles that

guides research for next-generation Li-ion batteries today:

“A larger negative free energy change for a reaction



is expected when A is small and electropositive, MX_n contains a metal atom M in a high oxidation state, and X is small and electronegative. Therefore, for a higher cell voltage, lithium is preferable to sodium, and oxides are preferable to sulphides. Moreover, a higher oxidation state of M is more likely to be thermodynamically stable as an oxide than as a sulphide. The problem is to prepare electronically conducting oxides containing M in a high oxidation state with structures suitable for fast-ion insertion.”[25]

1.4 Overview of topics covered: next-generation technologies

The brief history discussed only touches on the classical idea of a Li-ion battery, but there are other, "next-generation" secondary battery technologies that function through different chemical mechanisms. Beyond lithium, there are fields of work devoted to other Group 1 and 2 metals, for example, Na, K, Mg, and Ca; however, these will not be discussed herein. Examples of next-generation Li battery chemistries include conversion electrodes, such as Li-S, all-solid-state batteries that employ solid electrolytes in place of conventional liquid electrolytes, and 3-dimensional oxide host structures that can withstand exceptionally high power densities for fast-charging applications.

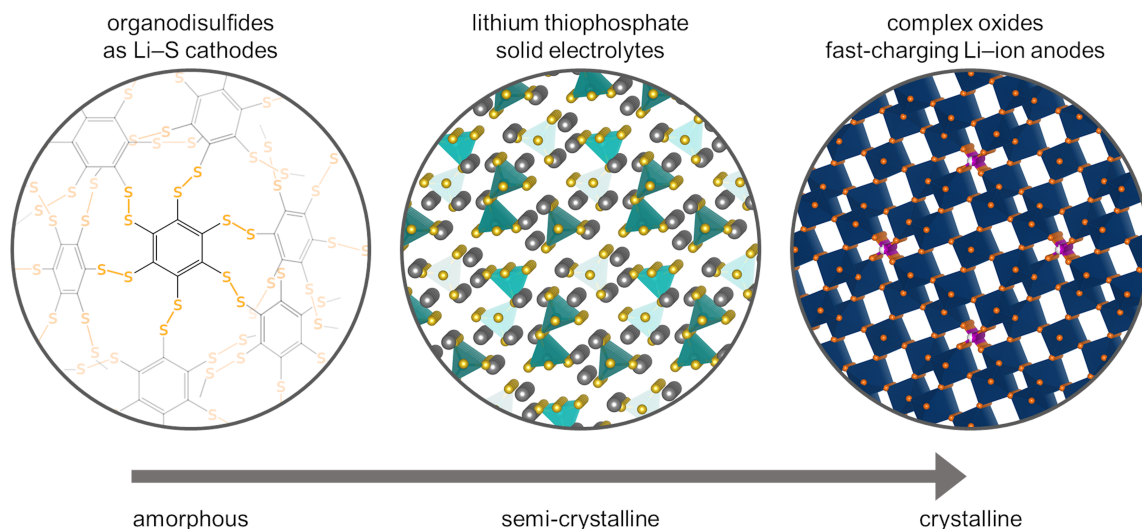


Figure 1.3: An illustrated overview of the topics covered within: the evolution from amorphous to crystalline materials in the form of Li-S chemistry, to fundamental studies of solid electrolytes, to next-generation oxide electrodes.

All of these next-generation materials are born from strategies to improve certain deficiencies in current, commercially available batteries. For Li-S batteries, the main improvements are capacity and environmental and monetary cost. All-solid-state batteries have the opportunity to improve upon safety, power density, and potentially full cell capacity. 3-dimensional oxide tunnel structures are already leading to promising applications for fast-charging. These different applications include a range of materials classes, including amorphous, pseudo-organic polymeric sulfur materials for Li-S batteries, inorganic sulfides of amorphous and crystalline natures for solid electrolytes, and highly crystalline inorganic oxides for fast-charging [Figure 1.3].

1.4.1 Lithium-sulfur

Lithium-sulfur batteries are promising in terms of high capacity, low cost, low toxicity (relative to Li-ion), and environmental considerations. They operate on the premise of fully converting elemental sulfur (commonly found as the orthorhombic polymorph

of S₈ rings) to Li₂S according to the following reaction:



This translates to a theoretical capacity of 1672 m A h g⁻¹ based on 2 e⁻ per S atom. While the capacity is exceptionally high, the voltage is lower than that of a LiCoO₂ cathode, for example, with multiple plateaux between 2.5 V and 1.7 V. A better metric for comparison is the theoretical specific energy, which for S₈ versus a Li metal anode is roughly 2,567 Wh kg⁻¹ (compared to LiCoO₂ versus graphite at 387 Wh kg⁻¹).^[36] Additionally, sulfur is relatively earth abundant, but its main environmental benefit is that there is already a plentiful supply generated as a side product of oil refining.

The barrier to its commercial viability is tied to its high theoretical capacity – the conversion reaction leads to poor reversibility and Coulombic efficiency. As previously discussed, electrodes such as LiCoO₂ accommodate Li in the host structure, but the host structure is relatively unchanged during intercalation and deintercalation of lithium. Sulfur reduction occurs through a completely different mechanism, such that the host structure converts into an entirely different structure, Li₂S upon lithiation [Figure 1.4]. Large structural changes can be associated with poor reversibility due to the difficulty to fully convert back to the original structure. Li-S batteries have an additional challenge: when S₈ reduces to Li₂S it also produces polysulfide intermediates that are soluble in the electrolyte. These soluble polysulfide species continue to oxidize at the cathode and reduce at the anode, which lowers the efficiency and consumes the active material in the cathode, leading to rapid capacity loss. This phenomenon and strategies used to combat the polysulfide shuttle will be discussed extensively in Chapters 2 and 3.

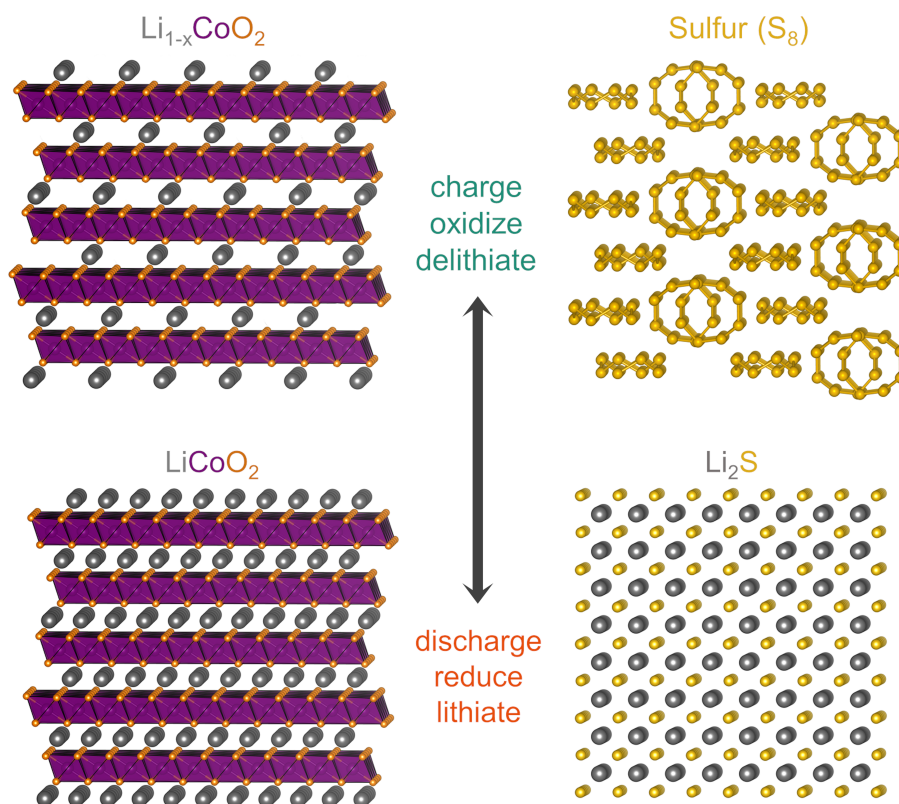


Figure 1.4: When elemental sulfur (S_8) is discharged versus lithium, the original structure is not maintained. Instead, the original structure of S_8 becomes Li_2S under complete conversion. Under ideal conditions, this process would be reversible and would lead to high capacity due to the amount of Li that can be stored per S (which is also very light).

1.4.2 All-solid-state batteries

One of the main reasons that all-solid-state batteries is attractive stems from the hope that solid electrolytes will make Li metal anodes tractable in practical or commercial applications [Figure 1.5]. There have been relatively fewer advances in anode chemistries as compared to cathode chemistries since commercialization of the LiCoO_2 | graphite cell. While graphite is still in widespread use, its specific capacity is limited at 372 mA h g^{-1} . The specific capacity of Li metal is 3860 mA h g^{-1} , which would significantly reduce the weight of the anode in a full cell.

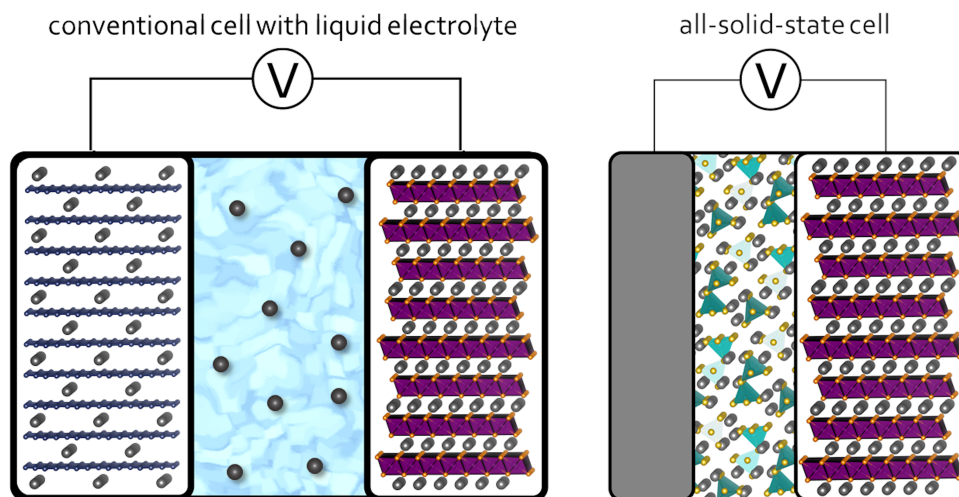


Figure 1.5: Pictorial representation of a conventional Li-ion battery, as described above, and a battery in which the electrolyte is replaced by a solid electrolyte, which is a lithium thiophosphate ceramic in this example. The hope for all-solid-state batteries is that the solid electrolyte makes a pure Li metal anode a feasible reality.

Lithium plating with conventional liquid electrolytes is a huge challenge that causes dendrites to form, especially at high current densities. Dendrites are atomically thin filaments of Li that can pierce through the separator and short-circuit the cell once it reaches the cathode. The short-circuit can lead to explosions due to a rapid release of heat from the direct contact of lithium with the cathode active material. This contributes to one of the largest safety concerns with Li-ion batteries. Solid electrolytes have the potential to eliminate the safety risks associated with liquid electrolytes, increase the energy density of the full cell, and possibly increase the power densities achievable without the same polarization effects that occur in liquid electrolytes.

The main challenges are finding materials with high enough lithium conductivity values to be competitive with liquid electrolytes, while maintaining a wide range of electrochemical stability between both the anode and the cathode, with which the electrolyte will be in direct contact. This is not a trivial pursuit. While oxides have relatively high stability windows against lithium, their near-room temperature ionic conductivity

values are too low (on the order of $10^{-5} \text{ S cm}^{-1}$ as opposed to 1 M LiPF₆ in EC/DMC which is on the order of $10^{-2} \text{ S cm}^{-1}$).^[37–39] Conversely, inorganic sulfide solid electrolytes have high room temperature conductivity values, some reported on the order of $10^{-2} \text{ S cm}^{-1}$, the electrochemical stability window is quite small. Engineering solutions such as depositing a thin oxide barrier between the sulfide and lithium metal have been explored to get the best of both worlds. Understanding the innate chemistry and conductivity properties of these materials is the first-order priority in order to design better materials, and this is the focus of chapters 4 and 5.

1.4.3 Fast-charging electrodes for Li-ion batteries

One other limitation with regards to graphite anodes not covered so far is the comparatively poor power delivery. Since the potential of graphite is so close to the potential at which Li plates (0.1 V *vs.* Li/Li⁺), often when cycling rates are increased, Li will plate instead of intercalating into the graphite layers, which leads to classic thermal runaway failure modes.^[40] Therefore, looking toward structures that have high lithium mobility and perhaps slightly higher potentials versus lithium is a better option for next-generation Li-ion batteries.

One such example that has been commercialized by Toshiba and Altairnano is the spinel Li₄Ti₅O₁₂. It's a 3-dimensional structure in which Li can insert into and deinsert out of the tunnels. This process is particularly reversible in this structure because it has near zero-volume expansion when Li inserts, so the structure does not change at different stages of lithiation. However, it only occurs quickly when the particles are nanosized because lithium conduction in spinels is generally slow.

Even more recently, a class of materials with crystallographic shear known as Wadsley-

Roth phases are seeing commercial success. The phase TiNb_2O_7 has also been commercialized by Toshiba as a high power anode material. Unlike the spinel, TiNb_2O_7 has high lithium mobility without the need to nanoscale the particles. The root of why this is the case is still being explored and is the topic of chapters 6 and 7.

As shown, there are many active areas of research in secondary Li batteries which aim to improve different performance metrics. By considering different chemistries across the cell, this document aims to present a multitude of pathways by which next-generation lithium batteries can achieve enhanced performance.

Chapter 2

Cathode Chemistries of Lithium–Sulfur Batteries

1

2.1 Introduction

Li-ion batteries are ubiquitous in our daily lives, from phones and computers to electric vehicles. The next-generation of batteries for portable electronics and electric vehicles must improve upon energy density and be environmentally conscious of the materials used for energy storage. Lithium-Sulfur batteries are an improvement upon current Li-ion batteries in both of these regards. Elemental sulfur boasts a large theoretical gravimetric capacity of 1672 mA h g^{-1} , derived from the $2 e^-$ reduction per S atom. Elemental sulfur is also earth-abundant, but perhaps most importantly, it is a side-product of oil refining, making it cheap and readily available to be repurposed.

¹This chapter includes contributions from Charles J. Hansen, Ram Seshadri, Kim See, and Fred Wudl.

2.1.1 Brief history of Li-S batteries

Sulfur was first demonstrated as a cathode material in a primary cell, in which lithium was the anode, sulfur was the cathode, with an amine-based electrolyte.[41] Soon after, a cell was patented with different organic electrolytes, including propylene carbonate, γ -butyrolactone, dimethylformamide, and dimethyl sulfoxide, demonstrating voltages between 2.35 V and 2.5 V.[42] The use of tetrahydrofuran as an electrolyte solvent was a marked improvement, in sulfur utilization.[43] In the 1980s, the first use of using ether-based electrolytes, specifically dioxolane, paved the way for the most effective electrolyte solvent for Li-S batteries yet to be discovered. The switch to ether-based electrolytes came with a tradeoff: ionic conductivity is about an order of magnitude higher in ether-based electrolytes over THF which allows higher current densities, but sulfur utilization in the first studies were about 45% lower.[44] Recently, most ongoing research accepts ether-based electrolytes as the "conventional" system for Li-S batteries. Since this early work, the landscape of Li-S battery research has evolved to include a rich library of different cathode composites, chemistries, and architectures.

2.1.2 Previous Li-S reviews

As the field of Li-S batteries has exploded to incorporate a broad range of chemistry and engineering approaches, it is important to discuss other reviews written about Li-S batteries that have targeted emphases of the range of subfields. Employing different carbon additives, for example, is a large subfield in Li-S literature.[45, 46] Also, different cathode architectures are widely employed as an engineering approach to inhibiting polysulfide shuttle and improve the kinetics of the system.[47, 48] An important area of focus is the effect different electrolyte focuses have on the redox chemistry of

sulfur.[49] In this review, we focus on the chemistry and redox mechanisms occurring in the cathode of Li-S batteries. This includes how additives, encapsulation, and unique chemical design affect reduction and reversible redox of sulfur.

2.2 Elemental sulfur cathodes

Sulfur comes in many forms and oxidation states but the primary focus of redox in Li-S batteries is the seemingly simple reduction of neutral sulfur to sulfide, S^{2-} . The most common allotrope of neutral sulfur, or elemental sulfur, is orthorhombic S_8 . Sulfur is easily purified *via* sublimation to form the orthorhombic phase. Most of the Li-S work uses commercially purchased sulfur in the form of platelets, powders, and needle-like crystals. The following discussion will focus on the use of neutral, elemental sulfur as the active material in Li-S cells. Unlike traditional Li-ion batteries, Li-S batteries operate on the premise of conversion reactions. The starting structure is completely consumed to form another structure as the discharge process. In an ideal world this would be a reversible process, but there are several barriers that hinder that for sulfur reduction and oxidation in a traditional liquid electrolyte setup.

The overall reaction of converting S_8 to Li_2S is the following:



As mentioned previously, this reaction most commonly occurs in a cell versus lithium with an ether-based electrolyte, usually in the form of 1 M LiTFSI in DOL/DME. In order for S_8 to convert to Li_2S , there are several intermediate steps. The galvanostatic discharge curve of sulfur shows two sloping plateaus at 2.25 V and 2.15 V. Several

studies prescribe the first plateau at 2.25 V to the formation of long-chain polysulfides, such as Li_2S_8 and Li_2S_6 , and the second plateau at 2.15 V to short chain polysulfides, such as Li_2S_4 , Li_2S_2 , and Li_2S .[\[36, 50, 51\]](#) The rationale for this mechanism being that the solubilized polysulfide species facilitate a cascading reaction from long chain to short chain to finally Li_2S .

There has been competing evidence, however, that suggests this is a simplified picture. Rather than the first plateau relating solely to long-chain to short-chain polysulfide formation, in reality there is formation of Li_2S within the first plateau, as well. ^7Li NMR shows the formation of Li_2S starting in the first plateau with increased formation of Li_2S in the second plateau.[\[52\]](#) Since a relatively small amount of Li_2S is formed initially, techniques such as X-ray diffraction are not sensitive enough to detect it, especially if it is nanosized.

Additionally, solid electrolyte interphase (SEI) formation, though not exclusive to Li-S batteries, can play an important role for understanding the redox mechanism of sulfur conversion. SEI is a complicated passivation layer comprised of salt and electrolyte degradation products that are established on the first several cycles, usually including LiF from salts such as LiTFSI and LiPF_6 . [\[53\]](#) For the most part, unmediated SEI formation does not affect the fundamental redox mechanisms of sulfur. It does, however, dictate whether Li ions are able to continue to access the active material within the surface of the particle. There is a large body of research devoted to electrolyte additives to inhibit either polysulfide formation or polysulfide shuttle if they are formed. One of the most researched electrolyte additives is LiNO_3 . With the addition of LiNO_3 a passivation layer is formed consisting of lithium sulfide and LiN_xO_y , which can be effective at slowing capacity fade by restricting the amount of polysulfides that can reach the Li surface after a few conditioning cycles.[\[54, 55\]](#)

2.3 Cathode additives

2.3.1 Conducting additives

Due to the low electrical conductivity of sulfur ($5 \times 10^{-30} \text{ S cm}^{-1}$), sulfur electrochemistry can only be evaluated in composite electrodes containing a significant mass percent of an electronically conductive matrix. Carbonaceous materials are commonly used to facilitate electronic conductivity of the electrode, and sulfur/carbon composite electrodes can achieve near theoretical capacity, at least on the first cycle.[56–58] Especially in the case of dense cathodes, maintaining the electrochemical contact to the active material is aided by intimate mixing and infiltration of sulfur into various carbon blacks such as acetylene black, Ketjen black, Super P, and others. The choice of carbon plays a significant role in the electrochemistry with variations on particle size, porosity, specific surface area, and micro- and nano-structures that not only modify the conductivity of the additive, but also the interaction of the carbon with sulfur. Importantly, Nazar and coworkers revitalized the Li-S field in 2009 by demonstrating high sulfur utilization and relatively low capacity fade upon infiltration of sulfur into a high surface area mesoporous carbon matrix.[59] The implications of this work and more generally micro- and nano-structured carbons for sulfur confinement will be discussed in detail later.

The activity of the carbon can go beyond enhancing electronic conductivity of the electrode by introducing heteroatoms into the carbon matrix and modifying the interactions between the carbon and sulfur, as well as dissolved lithium polysulfides. Introduction of S heteroatoms, for example, makes the interaction between polar dissolved polysulfides and the normally non-polar carbon surface more thermodynamically favorable as evidenced by isothermal titration calorimetry data. Other heteroatoms have

been shown to enhance the interaction between the carbon and dissolved polysulfides theoretically, including P and N. Experimental data also shows enhanced cyclability when heteroatoms are introduced. Arguably, much of the work in Li-S in the recent decade has focused on the development and understanding of the carbon in the carbon/sulfur composite electrode. However, carbons are not a focus of this review as others have reviewed the subject extensively.[45, 60–62]

2.3.2 Transition metal sulfides

Transition metal sulfides of the form M_xS_y are used in composite electrodes with S_8 for a variety of purposes including increasing the conductivity, enhancing polysulfide adsorption, and promoting reduction and oxidation. Although metal sulfides can have beneficial effects, addition of the metal sulfides can also convolute the electrochemistry as they are, in general, electrochemically active in the voltage range of the sulfur cathodes. Careful analysis is required to determine if the beneficial effects are due to the additional active material that must be accounted for when calculating gravimetric capacity, or the interaction between the metal sulfide and S_8 , or intermediate species.

A notable M_xS_y additive is layered TiS_2 and was first reported in S_8 composite electrodes by Garsuch *et al.* in 2012.[63] Layered TiS_2 is the canonical intercalation cathode reported by Whittingham[64] that led to the development of intercalation oxides and, of course, the Li-ion battery. Here, we focus on its use as an additive in sulfur composite electrodes. Addition of TiS_2 shows substantial enhancement in performance metrics including sulfur utilization and capacity retention at various discharge rates. Liu *et al.* showed that discharge of Li- TiS_2/S_8 cells begins with lithiation of TiS_2 followed by reduction of S_8 . [65] TiS_2 reduction to, eventually, $LiTiS_2$ is suggested to contribute to the discharge profile throughout the voltage range but the major character

is dominated by S_8 reduction. In cells with and without TiS_2 , the initial capacity is high ($\geq 1300 \text{ mAh g}_{sulfur}^{-1}$ at 0.3 C) and the Coulombic efficiency (CE) is 100% without $LiNO_3$ in the electrolyte. Addition of TiS_2 appears to reduce the capacity fade, however, with 97% retention at cycle 200 compared to 67% without TiS_2 .

To account for the capacity contributed by TiS_2 in the composite electrode, the capacity of TiS_2 was measured separately and subtracted from the capacity of the composite. Because TiS_2 is active in the voltage region of interest, the capacity should instead be normalized to the total mass of active material, in this case $TiS_2 + S_8$, and compared to that of an electrode with only S_8 to determine if the addition of TiS_2 is indeed beneficial. The comparison would be especially useful in this case because the electrode has a high content of the TiS_2 : 40% TiS_2 and 60% S_8 in a composite electrode with 70% $TiS_2 + S_8$, 20% C, and 10% binder. In general, the capacity normalized to the total mass of the electrode is seldom reported but is an important metric.

Other examples of metal sulfides used in composite electrodes with S_8 include VS_2 , [66] MoS_2 , [67, 68], WS_2 [68, 69] and in all cases, capacity fade is reduced. The addition of metal sulfides not only contributes to the Faradaic processes within the voltage window of the S_8 , as discussed above, but also modifies the interactions of the intermediate, dissolved polysulfides with the electrode. The interaction between the metal centers of the metal sulfides and dissolved lithium polysulfides depends on the metal. Surface interactions are very difficult to probe experimentally although the interactions of polysulfide species with transition metal sulfides has been probed experimentally through UV-vis analysis of solutions of nominal " Li_2S_x ." [68] The most data on the interactions is therefore computational. Binding energies are a useful proxy to understand the interactions, however, calculating the binding energy requires a input structure of the lithium polysulfide itself. Assuming a lithium polysulfide stoichiometry

of Li_2S_6 and a ring structure, the interaction between Li_2S_6 and a S-terminated metal sulfide surface is more favorable in $\text{VS}_2 > \text{TiS}_2 > \text{CoS}_2 > \text{FeS} > \text{SnS}_2 > \text{Ni}_3\text{S}_2$.^[66] Interestingly, the capacity retention appears to trend with the calculated binding energies, i.e. lower capacity fade for metal sulfides with more favorable binding energies with Li_2S_6 .^[66] We note, however, that contributions from a more reversible redox couple, such as lithiation of a metal sulfide, could artificially cause better capacity retention because the capacity is originating from both S_8 redox and the metal sulfide redox.

2.3.3 Transition metal oxides

Various metal oxides has been incorporated into composite cathodes with S_8 for similar reasons to metal sulfides - namely for the adsorption sites available due to the polar nature of the metal oxide. The shape of the discharge and charge profiles of the Li-S chemistry upon incorporation of mixed metal oxides such as $\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$ ^[70] and binary metal oxides such as Ti_4O_7 ,^[71] remain largely unchanged. Despite the apparent qualitative similarity of the electrochemistry measured on composite cathodes with and without the metal oxide, Li_2S precipitation was observed during the first plateau while S_8/C cathodes are suggested to form Li_2S during the second plateau. Li_2S precipitation was monitored by *operando* X-ray absorption at the sulfur K-edge in each chase.^[71]

Evidence for polysulfide adsorption to the metal oxide has been probed both experimentally and theoretically. A systematic study by Liang *et al.* across different metal oxides with redox potentials ranging from lower than sulfur redox (i.e. ≤ 2.0 V vs. Li/Li^+) to higher (i.e. ≥ 2.5 V vs. Li/Li^+) utilized X-ray spectroscopy to propose a modified reduction mechanism.^[72] The authors identified species in the sulfur 2p photoelectron spectrum indicative of thiosulfate (i.e. $[\text{S}_2\text{O}_3]^-$) and polythionate (i.e. $[\text{S}_x\text{-SO}_3]^-$ where $x \geq 1$) for sulfur composite electrodes with metal oxides whose first

reduction potential was slightly above that of sulfur (see Figure ??), suggesting that surface oxide groups effectively "trap" polysulfide species by chemical disproportionation reactions in a similar way to the Wackenroder reaction describing the reaction of H_2S with SO_2 in aqueous media.[73] The surface retention of the polysulfide and polysulfide-derived species (e.g. polythionates) has been proposed as a reason for the success demonstrated with materials such as MnO_2 , noted by the high Coulombic efficiencies (typically 95%-100%) and extended cycle life even at higher discharge rates (e.g. 1-2C). [74, 75] Despite the proposed modification to the conventional sulfur redox mechanism, however, CV and galvanostatic (dis)charge experiments show exceptionally similar behavior to conventional S_8/C composite cathodes. Since the mechanism appears to impact only the chemical disproportionation of polysulfides, it is possible that the electrochemical steps (those probed by the aforementioned techniques) are not affected, or at least not to noticeable degrees in the cases studied to date.

The adsorption of polysulfides to metal oxides has been probed theoretically to determine the energetics of the interfacial interactions. Probing the interfacial interactions with theory is beneficial as interfaces are extremely difficult to study, especially *operando*. With theory, the interaction between defined polysulfides with predicted structures and oxide surfaces provide insight into trends. For instance, the formation energy of adsorbed Li_2S_8 on oxides surfaces is predicted to be more stable on Al_2O_3 , followed by $\text{La}_2\text{O}_3 > \text{CeO}_2 > \text{MgO} > \text{CaO}$. [76] These trends, however, are not reflected in the cycling data with MgO composite electrodes showing the best cyclability. In fact, the Al_2O_3 shows the worst capacity fade which is ascribed to issues with electrodeposited Li_2S fracturing in the composite electrode.[76] Although the theoretical predictions are useful to visualize trends, the Li-S chemistry is too complex to use a

simple adsorption model to describe the affect of metal oxides on capacity retention.

2.3.4 Nitride additives

Many of the metal oxides studied (aside from Ti_4O_7) are rather insulating in nature, and in part have fueled the study of more conductive nitrides mixed with sulfur as a comparative class of composite cathodes. A variety of materials have been studied, from fairly insulating C_3N_4 , to conductive TiN and VN, among others.[77–81] The main contribution of the conductive nitrides is a coupled effect between their ability to supply electrons and the affinity of polysulfides due to the polar nature of the nitrides, similar to the metal oxides and sulfides described previously. In terms of simple composite mixtures of sulfur, carbon, a polymeric binder, and the additive, Jeong *et al.* demonstrated that TiN outperformed Ti_4O_7 and TiO_2 in terms of capacity, polarization, and cycle life at higher rates. The authors attributed this effect to a combination of the rapid supply of electrons facilitated by the highly conductive TiN (conductivity $> 10^3 \text{ S cm}^{-1}$ at room temperature) and the enhanced strength of Ti-S interactions due to significant undercoordination of Ti at TiN surfaces (supported by DFT calculations). The dramatic enhancement of S_8 binding, however, does not show substantial differences in terms of the sulfur redox mechanisms, and instead only imparts improved kinetics which are increasingly apparent at higher (dis)charge rates (e.g. $\geq 1\text{C}$).

2.3.5 Other inorganic solids

Materials other than conventional binary inorganic compounds have also been utilized in composite cathode architectures for Li-S cells. Some examples include S_8 composites with Prussian blues and MXenes. Prussian blue in its parent form is $\text{Fe}_4^{\text{III}}(\text{Fe}^{\text{II}}(\text{CN})_6)_3$,

with $\text{Fe}^{II}\text{-C-N-Fe}^{III}$ connectivity. [82, 83] Composite cathodes of S_8 /Prussian blue, studied by Peng *et al.*, show significantly enhanced redox kinetics compared to S_8/C composites, especially as the Prussian blue content in the composite increased towards a 9:1 ratio of S_8 to Prussian blue. Of note is the kinetic enhancement seen by the decreased polarization in the galvanostatic profiles at higher discharge rates (i.e. $\geq \text{C}/2$) and the improvement in charging reactions in terms of a shift of the oxidative peak in CV to lower potentials by ≥ 100 mV. [82] The redox mechanisms again appears similar to S_8/C composite cathodes; however, tight binding of S species to Fe(III) centers probed by XPS is suggested to mitigate effects of polysulfide shuttling. The retention of S species has also been suggested to maintain a more accessible distribution of S and reduced sulfides deposited on the cathode, promoting the oxidation as described previously.

MXenes are a class of two-dimensional transition metal carbides or carbonitrides, first reported by Naguib *et al.* in 2012, prepared by selectively etching the "A" layer from $\text{M}_{n+1}\text{AX}_n$ phases where M is a transition metal, A is aluminum or a similar species easily removed by common etchants, and X is carbon and or nitrogen. [84] The surfaces of the MXenes (specifically Ti_3C_2 , Ti_2C , and Ti_3CN) are often terminated by oxide, hydroxyl, or similar moieties, which has implications on their use in composite cathode materials beyond electronic conductivity. Multiple research groups in recent years have reported limited capacity fading and high CEs on MXene/ S_8 composite cathodes. [85–88] The oxygen-containing moieties on the surfaces have been proposed to contribute to this stabilization by a mechanism similar to that proposed on some of the oxide composite materials - conversion of polysulfide species to surface bound thio-sulfate and polythionate species based on sulfur 2p photoelectron spectra. [86, 88] DFT calculations have supported interactions of polysulfide species with the exposed

Ti sites after polysulfide reaction with the surface terminating groups as well as with the terminating groups themselves, largely based on Coulombic interactions between the sulfur and electropositive Ti or H atoms at the surface. [88, 89]

2.4 Encapsulated S₈

2.4.1 TiO₂

Efforts to reduce polysulfide shuttling using mechanical barriers within the electrode have given rise to encapsulated S₈ architectures. For instance, core-shell structures of S₈ encapsulated by porous TiO₂ have shown promising cyclability. TiO₂ is discussed herein separately from the composite oxide cathode section, however, similar concepts already invoked in the physical mixtures could also apply to the core-shell structures including adsorption through Ti-S interactions. Aside from conventional core-shell structures in which the core material fills the entire void created by the shell (S and TiO₂ here, respectively), Seh *et al.* also investigated the use of yolk-shell structures - that is where the material within the shell does not fill the entire void space leaving room for expansion. Upon reduction of S₈ to Li₂S, a volume expansion of approx. 80% is expected and the yolk-shell structures can theoretically accommodate it.[90] The authors propose that the high CE of over 98% after 1,000 cycles at C/2 and substantial sulfur utilization is a result of the retention of polysulfides within the cavities of the yolk-shell particles in part due to the small pore size of the TiO₂ itself (approx. 3 nm) and the Ti-S interactions and surface hydroxyl groups present. The fundamental reaction mechanism does not appear to change in the case of this amorphous TiO₂, or in the case of a similarly structured rutile TiO₂ mesocrystals that also showed

promising performance metrics. [91] In anatase TiO_2 , however, even in architected micro-structures, the redox processes become more complex as Li^+ also intercalates into anatase TiO_2 at c.a. 1.8 V vs. Li/Li^+ . [92, 93]

2.4.2 Graphene and other carbons

A variety of carbonaceous hosts have also been used to confine sulfur ranging from morphologies similar to the shelled TiO_2 described above to confinement in mesoporous carbon, graphene and carbon nanotubes (CNTs). Physical confinement of sulfur by melt-diffusion into mesoporous carbon (e.g. CMK-3) and confinement within carbon nanospheres (similar to the confinement in TiO_2) has shown significantly enhanced CE ($> 95\%$) and sulfur utilization beyond conventional mixtures of sulfur and conductive carbons. [59, 94] Additional functionalization to mesoporous carbons (e.g. introduction of S heteroatoms), increasing the wall thickness of the nanospheres, or forming hierarchical composites has additionally shown improvement on the cycle life or CE of such composite electrodes. [95–97] Confinement within graphene, conversely, suffers from substantial capacity fade without the addition of a polymeric coating such as Nafion or polyethelene glycol to potentially help trap polysulfides and maintain enhanced contact between the graphene sheets and the sulfur particles, where the confinement by graphene is ostensibly not as rigorous as that within enclosed spheres or mesoporous materials (e.g. in coating or sandwich-like geometries). [98, 99]

In general, the carbon encapsulation strategies enhance the electrochemical wiring of such cathodes and serve in some ways to retain polysulfide species closer to the electrode surfaces, but does not substantially alter the sulfur redox processes. However, when the carbon pore size becomes small enough, the redox processes appear to change. Xin *et al.* studied sulfur infiltrated into a porous carbon with a CNT core

consisting of pores < 1 nm in diameter based on N_2 adsorption measurements and transmission electron micrographs. [100] The authors suggest that due to the small pore size, smaller allotropes of sulfur than the thermodynamic orthorhombic S_8 crystallize within the pores of the carbon host after the typical melt-diffusion process. As a result, the typical voltage plateau at 2.3 V vs. Li/Li⁺ is not observed in the galvanostatic discharge profile, and using cyclic voltammetry between 3.0 V and 1.0 vs. Li/Li⁺, only a single pair of reduction and oxidation waves are observed at c.a. 1.7 V and 2.1 V vs. Li/Li⁺, respectively. The resulting CE and cycle life shows a initial capacity decay in the first five cycles at C/10 and rather stable operation through 200 cycles with little capacity fade (see Figure ??). The polarization, especially at higher rates (e.g. 5C) is significant, which would be unexpected based on the intimate contact between the active sulfur particles and the conductive carbon matrix especially at the low areal sulfur loading ($\leq 1 \text{ mg}_S \text{ cm}^{-2}$).

2.4.3 Metal organic frameworks (MOFs)

Another type of porous architecture with pores suitable for sulfur infiltration are metal organic frameworks (MOFs). Composed of repeating units of metal centers connected by different organic linkages, MOFs in general result in highly porous structures, often with tunable pore sizes based on the chemistry. Demir-Cakan *et al.* studied a Cr-based MOF known to be stable under sulfidizing conditions, chromium trimesate MIL-100(Cr), with cavities 3 nm wide connected by smaller "windows" ≤ 1 nm wide. [101] Upon sulfur infiltration by melt-diffusion into the MOF, the resulting hybrid structure exhibits several interesting characteristics that contribute to some of its unique performance features. Namely, sulfate species are noted in the sulfur 2p photoelectron spectrum in the material as synthesized, and a distinct melting point below 200 °C is

not observed (compared to the endotherm in the calorimetry experiment at 112 °C for a physical mixture of MIL-100(Cr) and sulfur). The sulfur reduction mechanism appears to be rather similar to S_8/C electrodes in this instance via galvanostatic cycling experiments aside from a small feature in the discharge profile near 1.4 vs. Li/Li^+ . However, the CE in this system is rather low (i.e. less capacity is recovered on charging the cell than was obtained on the previous discharge), which likely contributes to the substantial capacity fade over limited cycling. Other groups have utilized different metal centers and different linkages to construct MOFs of different pore sizes with varying impacts on the cycle life and CE. [102–104]

2.5 Reduced sulfur chemistries

Reduced sulfur chemistries include a variety of approaches mainly aimed towards inhibiting or eliminating polysulfide shuttle. The end goal of these approaches is to reduce the solubility of polysulfide intermediates through bonding sulfur to organic or inorganic linkers. While some amount of solubility is generally needed for the conversion mechanism to occur, too much solubility can lead to the inability to use the majority of active material for energy storage, as well as a high overpotential associated with polysulfide shuttle. Both inverse vulcanization and disulfide materials use organic linkers to create copolymers with sulfur, both of the linear and crosslinked varieties. While these are often considered under the category of Li-ion batteries, transition metal polysulfides offer unique insight on sulfur redox. Generally, they are extended solids, either crystalline or amorphous, containing disulfide or polysulfide bonds that undergo anionic redox, often in addition to transition metal redox.

2.5.1 Inverse vulcanization

One approach that has recently gained much attention to combat polysulfide shuttle in Li-S batteries is to create sulfur-carbon copolymers as the active material. Inverse vulcanization is a means of synthesizing such materials, taking advantage of covalent bonding between vinylic carbon monomers and sulfur biradicals to keep the sulfur bound in a polymer network.[105] It describes the process of ring opening molten liquid sulfur to create liquid sulfur diradicals and subsequently quenching the radical chain ends with dienes to make sulfur-carbon copolymers.[106] While technically the same process as the one used to make rubber tires, “inverse” suggests a higher sulfur-to-carbon ratio. The increased ratio of sulfur:carbon is desirable for application in Li-S batteries because higher sulfur content increases the gravimetric capacity possible in the cell and minimizes the mass of electrochemically inactive moieties.[107] One of the first reports of inverse vulcanization from Pyun *et al* exhibited the fast synthesis route to creating these copolymers, their tunable thermomechanical properties, and greater capacity retention over elemental sulfur cathodes.[108] One of the main benefits of these sulfur-rich polymers is that they use low-cost, abundant monomers and elemental sulfur and have been shown to be scalable on the order of kilograms in a one-step reaction, making them highly relevant for industrial application.[109] There are also many examples of using sustainable precursors, such as myrcene, diallyl disulfide, limonene, cardanol benzoxazine, squalene, and perillyl alcohol as the vinyl comonomer, many of which are naturally abundant or industrial side-products, much like sulfur.[110–113]

The most well-studied comonomer for inverse vulcanization as applied to battery materials is 1,3-diisopropenylbenzene (DIB).[105, 108, 109, 114] The straightforward synthesis of poly(sulfur-random-1,3-diisopropenylbenzene), or poly(S-r-DIB), involves

heating sulfur to 185° until the molten phase is formed, then adding DIB and stirring for 10 minutes to form a red glass once cooled. The first poly(S-r-DIB) polymers were made with a range of compositions, from 10-50 wt% DIB.[108] The 10 wt% DIB polymers demonstrated an initial specific discharge capacity of 1100 mAh g⁻¹ and maintained 823 mAh g⁻¹ at cycle 100 with a C/10 rate, calculated from the mass of sulfur content in the polymer (excluding the carbon-based comonomer). The effect of the varying weight percent of DIB on cycling performance versus lithium was further explored in a follow-up study, comparing galvanostatic profiles for 5%, 10%, 20%, 30%, and 50% DIB.[105]. They found the polymers containing 5, 10, and 15 wt% DIB were most effective at slowing capacity fade and argue this is due to the organosulfur units acting as “plasticizers” to the short chain polysulfides. With higher DIB content, the organosulfur discharge products reform longer polysulfides which solubilize into the electrolyte.

Even more recently, materials made by inverse vulcanization incorporating selenium along with sulfur have been explored as cathode materials. [115, 116] The synthesis starts with both elemental sulfur and elemental selenium to make a molten selenium-sulfur mixture, but is otherwise identical to the synthesis of poly(S-r-DIB) and yields a mixture of poly(SeS-DIB) and cyclic selenium sulfide molecules.[115] By comparing cyclic voltammetry of the pure poly(S-DIB) and poly(SeS-DIB), the electrochemistry of the poly(SeS-DIB) seems to include both the previously observed discharge mechanism of poly(S-DIB) and a new discharge mechanism that includes the incorporated selenium, though detailed *in situ* or *ex situ* analysis will need to be done to confirm the mechanistic details. The first reduction step at 2.3 V vs. Li/Li⁺ is attributed to creating the corresponding DIB thiolate and long-chain polysulfides, followed by a new reduction at 2.2 V vs. Li/Li⁺ creating long chain polysulfoselenide compounds.

The following two steps are reported to be the reduction of the long-chain polysulfides at 2.1 V to Li_2S and Li_2S_2 and the reduction of the polysulfoselenide compounds to Li_2Se and Li_2Se_2 at 1.9 V. At a rate of C/5, the initial gravimetric capacity is 880 mAh g^{-1} and show a 0.4% capacity loss per cycle, as compared to 0.6% observed in the pure poly(S-DIB) material.

One study took inverse vulcanization one step further by incorporating propylene-dioxythiophene (ProDOT-Sty) as a comonomer with 1,3-diisopropenylbenzene (DIB) with subsequent electropolymerization in order to increase the inherent electrical conductivity within the active material.[114] While there was no demonstrated electrochemical cycling in a Li-S cell, electrochemical impedance spectroscopy for poly(dibenzyl-ProDOT) thin films on ITO at 0.8 V vs. Ag/Ag^+ showed a 95% decrease in charge transfer resistance, as compared to the control polymer missing the conjugated poly(ProDOT) segments. This work aims to simultaneously improve upon one of the other main challenges of Li-S batteries, the electronically insulating nature of sulfur.

While the performance of many versions of these copolymers continues to be increasingly studied, a more fundamental understanding of the mechanism that leads to inhibited polysulfide shuttle is currently an unanswered question. Specifically, what properties, functional groups, or geometries make a specific comonomer successful over others, since some are susceptible to the same capacity fade as elemental sulfur, such as in the case using the comonomers bismaleimide and divinylbenzene, styrene, as well as 1,4-diphenylbutadiyne.[117–120] Future work in this field will look forward to a better understanding of these relationships, using many of the techniques previously used extensively in S_8 experiments, and hopefully *in situ* techniques to understand the intermediate chemistry during cycling.

2.5.2 Organodisulfides

In order to avoid polysulfide shuttle completely, organodisulfides provide a means to confine sulfur redox to ideally insoluble disulfide-containing compounds, preventing formation of polysulfides in the first place. In the context of a Li battery, the charged product is the fully bonded disulfide, $-R-S-S-R-$, and the discharge product is the corresponding thiolate, $2(-R-S-Li)$.^[121] The redox reaction can therefore store two electrons per disulfide moiety, generally represented as $n(-R-S-S-R-) + n(n(2e^-) \rightleftharpoons 2n(-R-S^-)$.^[122] In exchange for greater capacity retention and good Coulombic efficiency associated with eliminating polysulfide shuttle comes a reduction in the achievable gravimetric capacity, since the carbon framework adds electrochemically inactive mass. In some instances, such as in the case of many small molecules or too few crosslinks, this approach does not work because many are either readily soluble in ether-based electrolytes in their oxidized form or solubilize once the disulfide bond is cleaved.^[123? , 124] While this does not lead to the observance of the overpotential associated with the polysulfide shuttle mechanism, it results in rapid capacity fade due to the loss from the active material solubilizing into the electrolyte.

Having the disulfides bound to a polymer network, either through crosslinking or as pendent functional groups, can help prevent the dissolution of the discharged thiolate product. In the case of a polymer backbone with pendent disulfide groups, the mass of the electrochemically inactive carbon can greatly outweigh the mass of the active material, leading to much lower gravimetric capacities, for example with poly(2,5-dihydroxy-1,4-benzoquinonyl sulfide) (PDBS) and poly(5,8-dihydro-1H,4H-2,3,6,7-tetrathia-anthracene) (PDTTA).^[124, 125] The benefit, though, is that the thiolates continue to be tethered to the carbon backbone even after complete discharge. One example shows charge storage in a sulfur-linked tetrathionaphthalene (TTN) poly-

mer, where the redox occurs on the pendent disulfide groups between 3.8 and 4.1 V vs. Li/Li⁺ in 1.0 M LiPF₆ EC:DEC (1:3 volume ratio). The chosen potential range is higher than the potential at which the sulfur linking TTN to each other, so the integrity of the polymer stays intact while taking advantage of the pendant disulfide redox for energy storage.[126]

With crosslinked disulfide polymers, there is greater chance for much higher sulfur loadings, though still much lower than achievable with elemental sulfur. Crosslinked disulfides have the chance for the same fate as small molecules, where individual monomer thiolate units can solubilize into the electrolyte if the polymer is entirely reduced, especially if the charge-to-mass ratio is too low in the presence of conventional ether-based electrolytes.[122] Therefore, much of the seminal work in this field focused on the performance of crosslinked disulfides paired with polymer electrolytes. The discharged thiolate material cannot solubilize into the polymer electrolyte. The field of polymer electrolytes as applied to full cells is also still in relatively early research stages, so more progress can be expected in this area with the discovery of new highly conducting polymer electrolytes.

Electrode kinetics of organodisulfide redox polymers has also been explored through pulse polarization measurements and impedance spectroscopy to reveal the rate capabilities are dependent upon the substituents of the polymer backbone. Electron withdrawing heteroatoms in the α and β positions referenced to the disulfide facilitate faster redox processes, particularly N, S, and F.[122, 127]

One material in particular that has gained much attention is 2,5-dimercapto-1,3,4-thiadiazole (DMcT), which forms a linear polymer when electropolymerized to form disulfide linkages. The disulfide bonds are broken during reduction to form thiolates and can reversibly oxidize back to disulfides.[128] When slurry cast onto copper, the re-

duction of sulfur occurs between 3.4 V and 2.8 V and can handle relatively high current densities of 137 mA g^{-1} . When mixed with a conducting polymer such as PEDOT, the reduction of DMcT at room temperature is accelerated.[129, 130] Facilitating the redox reactions in organosulfur cathodes with electrocatalysts can be an effective tool to maximize observed capacity.

Crosslinked disulfides have also been observed to have highly stable cycling as a direct replacement for sulfur in Li-S batteries, using conventional ether-based electrolytes. A highly crosslinked network maximizes sulfur content while preventing the formation of polysulfide species in solution. The sulfur is instead bound, in once instance, to benzene rings, and reduces to thiolate species. Upon oxidation, they re-crosslink to form a polymeric network. The reduction and oxidation process was found to be highly reversible over hundreds of cycles.[9]

2.5.3 Transition metal polysulfides and sulfides

There is a wealth of studies on transition metal sulfides with a focus on cation redox, but there is also a building body of work aiming to understand anion redox of sulfur in transition metal sulfides, including polysulfides. While systems relying solely upon transition metal cation redox is outside of the scope of this review, it should be noted that intercalation systems of this type, such as TiS_2 , MoS_2 , VS_2 , among others, are prevalent. [131–133] However, anion and cation redox is not always mutually exclusive, and there are many systems based upon mixed cation and anion redox, particularly conversion materials.[134, 135] Some transition metal disulfides, such as the chalcopyrites CoS_2 and FeS_2 , fall into this category. Both are better known for use in primary cells, but have been studied in Li secondary cells due to the theoretical high gravimetric capacity, owing to both transition metal and disulfide redox.[136, 137] For

example, FeS_2 , can store 4 mol of Li per formula unit if completely reduced to Fe^0 according to the equation: $\text{FeS}_2 + 4\text{Li}^+ + 4e^- \rightarrow \text{Fe}^0 + 2\text{Li}_2\text{S}$, corresponding to a theoretical gravimetric capacity of 893 mA h g^{-1} . This high gravimetric capacity comes at a cost, however, because once Co^0 and Fe^0 are formed, the reactions are not electrochemically reversible. CoS_2 and FeS_2 are not recovered after the first discharge.[138, 139]

In some transition metal trisulfides, there are two distinct sulfur species: S^{2-} and the disulfide anion S_2^{2-} , where another way to write the formula is $\text{M}^{4+2-}\text{S}_2^{2-}$ in compounds such as TiS_3 , ZrS_3 , TiS_3 , NbS_3 , among others.[140] Another example of mixed redox is with VS_4 , in which all of the sulfur exists as S_2^{2-} . [141] Upon lithiation, vanadium oxidizes from V^{4+} to V^{5+} while sulfur reduces from S_2^{2-} to S_2 to form Li_3VS_4 . Further reduction forms Li_2S and V^0 , which is semi-reversible upon delithiation.

There are even fewer studies of the transition metal being redox-innocent in these materials. One such example is of an amorphous MoS_x chalcogel that contains, in the local structure, Mo_3S_{13} clusters linked by polysulfide chains.[142] The inorganic clusters act as linkers between the polysulfide chains, helping to limit polysulfide shuttle. Remarkably, the chalcogel can successfully cycle in both the traditional Li-ion carbonate-based electrolyte and the traditional Li-S ether-based electrolyte, owing to its hybrid nature. The Mo is proven to be redox innocent through *operando* Mo K-edge XANES. Successful reversible instances of anionic redox is often found when the transition metal center or cluster acts as an inorganic linker to the di-, tri-, or polysulfides, rather than when all sulfur bonds to the metal are broken.

2.6 Li_2S oxidation

2.6.1 Particle size

As many difficulties as are associated with cells fabricated in the charged state (i.e. with an S_8 cathode), cell fabricated in the discharge state (i.e. with a Li_2S cathode) in some cases show even more challenges, especially in the early cycle life of such cells. Yang *et al.* showed that the initial oxidation process, other factors remaining constant, is heavily dependent on particle size. [143, 144] Utilizing Li_2S and carbon composite electrodes from grinding with conventional carbons, ball-milling, and chemical reduction of sulfur-infiltrated mesoporous carbon, the authors showed that the kinetic overpotential to begin substantial oxidation of Li_2S decreased with decreasing particle size. Moreover, utilizing micrometer-sized Li_2S particles, after an initial activation to 3.5 V vs. Li/Li^+ , the oxidation plateau on initial charge returns to 2.5 V vs. Li/Li^+ and remains there for the majority of charge at modest charging rates (C/8), where larger Li_2S particles display a sloped galvanostatic charge profile with most of the oxidation occurring at voltages > 3 V vs. Li/Li^+ (see Figure ??). [144] Additional efforts at nano-structuring Li_2S with carbon nanotubes or nanoparticles have shown even lower overpotentials and reasonable sulfur utilization within conventional voltage windows (i.e. ≤ 3 V vs. Li/Li^+), but the electrochemical processes overall appear to be mechanistically consistent with S_8 cathode, based on redox processes identified in CVs. [145, 146]

2.6.2 Redox mediators

In contrast to using particle size to modulate oxidation kinetics, another prominent area of focus has been on the incorporation of redox mediators in the electrolyte solution. Redox mediators serve as additional routes for electronic access to the insulating Li_2S active material other than directly through the conductive carbon matrix. Mediator species can be oxidized at the electrode and, upon contact with Li_2S , facilitate the oxidation of Li_2S at the active material-electrolyte interface, after which they can effectively be reused and facilitate the oxidation process continually. Meini *et al.* demonstrated this concept across a range of metallocene-based mediators whose redox potentials varied from below that of Li_2S oxidation (2.3 V vs. Li/Li^+) to above.[147] The species with redox potentials below that of Li_2S , showed little difference from a conventional electrolyte, whereas those with higher redox potentials effectively reduced the overpotential for initial oxidation and demonstrated significant active material utilization shown by both galvanostatic experiments and powder x-ray diffraction. Other redox mediators have also shown substantially reduced overpotentials and consequently improved cycling life including InI_3 , P_2S_5 , and even polysulfide species. [144, 148, 149]

Chapter 3

High Sulfur Content Material with Stable Cycling in Li–S Batteries

1

3.1 Introduction

With increasingly widespread use of renewable energy from intermittent sources such as solar and wind comes a pressing need for improved energy storage devices. However, currently used lithium-ion batteries involve intercalation, specifically layered oxide cathodes with graphite anodes, which limit energy densities and specific capacities due to the relatively heavy host structures and state of charge limitations. One of the most promising systems to overcome this challenge is Li–S batteries,^[150] owing to its high theoretical gravimetric capacity based on a conversion redox reaction

¹The contents of this chapter have substantially appeared in reference 9: M. B. Preefer, B. Oschmann, C. J. Hawker, R. Seshadri, and F. Wudl. *Angew. Chemie - Int. Ed.*, 57(47), 15118 (2017). © 2017 Wiley, reprinted with permission.

(1675 mA h g^{-1} assuming reduction of S^0 to S^{2-}), making it especially attractive for applications in portable electronics and electric vehicles. Additionally, sulfur is non-toxic and an underutilized, abundant byproduct of oil refining, making it a sustainable alternative to toxic, expensive transition metals used in common intercalation materials.[151]

Major challenges of Li-S include the low electronic conductivity of sulfur,[152] leading to low utilization of active material and therefore low capacity. Additionally, volume changes during cycling result in the loss of electrical contact, leading to device failure.[153–155] Furthermore, when sulfur is cycled with commonly used ether-based electrolytes, soluble polysulfide intermediates form[52, 156] and create what is known as polysulfide shuttle.[157, 158] These soluble intermediates migrate between the anode and the cathode, cause rapid capacity fade and poor Coulombic efficiency, eventually short-circuiting the cell.

There have been many efforts to combat polysulfide shuttle, including nanostructured carbon-sulfur cathodes,[47, 51, 159, 160] polysulfide reservoirs,[161, 162] encapsulation in carbon[163–169] and TiO_2 ,[170] polysulfide mediators,[171, 172] and altering solvent conditions, [173–175] among others.[176–178] Our approach exploits the chemical functionality of disulfides to prevent the initial formation of polysulfides by only providing one point of electrochemical scission. De Jonghe *et al.* have shown impressive electrochemical reversibility using disulfide-containing solid-state cathode materials with polyethylene oxide electrolytes versus lithium, however the sulfur content of the active material is a maximum of 33 atom percent or less.[122, 179, 180] To address this challenge, we have designed a crosslinked disulfide with 50 atom percent sulfur content (C_6S_6 monomer containing roughly 50 mole-% S and 50 mole-% C) that operates using the conventional Li-S electrolyte system, bis(trifluoromethane)sulfonamide

lithium salt (LiTFSI) in dioxolane (DOL) and dimethoxyethane (DME). The new, highly stable Li-S cell we report has a theoretical gravimetric capacity of 609 mAh g^{-1} based on 6 moles of lithium per C_6S_6 monomer unit. The high sulfur content benefits the performance two-fold: there is potential for high gravimetric capacity and, if full conversion occurs, creates a highly charged discharged product. In its discharged state, the active material is expected to form $\text{C}_6\text{S}_6^{6-}$ with six Li^+ counter-ions, creating a highly-charged structure that is insoluble in the ether-based electrolyte. This allows the material to undergo a reversible redox reaction over hundreds of charge cycles without shuttle or capacity fade. Additionally, if full reduction does not occur, the monomer units will be bound in the crosslinked framework, also preventing dissolution into the electrolyte.

3.2 Methods

Preparation and characterization of disulfide active material Synthesis of hexakis(benzylthio)benzene: Hexakis(benzylthio)benzene was synthesized by a modified procedure reported by Harnisch and Angelici.[181] NaH (60 % dispersion in mineral oil), hexachlorobenzene (analytical grade), benzyl mercaptan (99 %), Li chips, and NH_3 were used as received from Sigma Aldrich. All solvents were dried at a solvent system before use. After washing 8.0 g of NaH (60 % dispersion in oil, 0.20 mol) with 3 x 20 mL of hexanes and with $2 \times 20 \text{ mL}$ of DMF, NaH was suspended in 150 mL of DMF and cooled to 0°C . Benzyl mercaptan (23.5 mL, 0.20 mol) was added slowly to the suspension followed by the addition of hexachlorobenzene (4.76 g, 16.7 mmol). The reaction mixture was stirred for 10 min at 0°C before it was allowed to warm to room temperature. The mixture was stirred at room-temperature overnight. 10 mL of

isopropyl alcohol was added to the reaction mixture and stirred for 15 minutes, followed by the addition of 75 mL of deionized water. The mixture was extracted with chloroform and dried with magnesium sulfate. The organic layer was concentrated to 200 mL using reduced pressure, and the product was precipitated with 400 mL of methanol. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.22 (m, 5H, Ar-H), 4.07 (s, 2 H, CH_2). ^{13}C NMR (500 MHz, CD_2Cl_2): δ 147, 138, 129, 128, 127, 42. FDMS TOF m/z : Calc'd for $\text{C}_{48}\text{H}_{42}\text{S}_6$ 810.16; Found 810.13.

Synthesis of crosslinked lithium benzene hexathiolate 496 mg of Li (71 mmol) was added to 70 mL of liquid ammonia at -78°C . A solution of hexakis(benzylthio)benzene (4.8 g, 6.0 mmol) in 15 mL of dry THF was added. After stirring for one hour at -78°C , 30 mL of degassed methanol were added and the reaction mixture was warmed to room temperature over 2 hours. 50 mL of degassed water were added and side products were removed by the extraction with diethyl ether. Lithium benzene hexathiolate (1.2 g, 65 % yield) was concentrated by freeze drying. The hexathiolate is extremely air-sensitive, so crosslinking was conducted immediately by dissolving lithium benzene hexathiolate (250 mg, 0.8 mmol) in water (10 mL) and by purging with air purified through a bubbler of sulfuric acid for 48 hours. The crosslinked material precipitated during purging. After 48 hours, the reaction mixture was centrifuged to isolate the precipitated material. The material was redispersed in water and centrifuged followed by two more redispersion and centrifugation steps. The final product was isolated by freeze drying over night with a yield of 180 mg (84 %).

Preparation and characterization of electrodes The active disulfide material and conductive carbon additive (AzkoNobel Ketjenblack EC-600JD) were mixed in an aqueous dispersion of carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR)

(CMC:SBR = 1:1 wt/wt) in a weight ratio of disulfide:KB:CMC/SBR = 50:35:15. The slurry was cast on carbon coated aluminium foil as the current collector (Toya-Carbo-50G01, Toyal) and dried at 60 °C for 12 h under vacuum. Disc electrodes with a diameter of 10 mm were punched after drying. Active material mass loadings were in the range of 0.8 mg and 1.2 mg per electrode. Average thickness of the electrodes was 30 μm .

Electrochemical measurements Galvanostatic cycling was conducted using 2032-type coin cell (MTI Corporation) with metallic Li as the counter electrode. 19 mm disks of polypropylene (Celgard 3501) were used as the separator, and the electrolyte was composed of 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in 1,3-dioxolane (DOL) and dimethoxy ethane (DME) with a volume ratio of 1:1 (Sigma Aldrich). All cells were assembled in an Ar glovebox starting from the negative case and crimped at 1200 psi using a MTI Corporation hydraulic crimping machine. Batteries were cycled on a Bio-Logic Variable Multichannel Potentiostat VMP3 in a voltage range of 1.0 V to 3.2 V (versus Li) with a rate of C/10 (where C/10 = Q/10 for one Li per CS molecular weight unit; specific current is 61 mA g^{-1}). Cyclic voltammetry was conducted between 1.0 V and 3.2 V with a scan rate of 0.1 mV s^{-1} . All electrochemical studies were performed at room temperature. Specific capacities are reported per gram of active disulfide material. Coulombic efficiency is reported as charge capacity divided by discharge capacity in per cent form.

Characterization, including NMR, Raman, and XPS ^1H nuclear magnetic resonance (NMR) spectra were recorded on a AVANCE500 Bruker 500 MHz (11.7T) narrow bore spectrometer. ^{13}C and ^7Li solid state NMR with magic angle spinning (MAS) at 16k Hz was measured using a Bruker AVANCE III Ultrashield Plus 800 MHz (18.8T) narrow

bore spectrometer. A Horiba Jobin-Yvon Lab ARAMIS instrument was used to measure Raman spectra with a 633 nm laser equipped with a confocal microscope and a 50x objective lens. Measurements were done using 500 μm aperture, 500 μm slit, and 600 gratings per mm, with exposure time of 1 s, averaged 10 times. Spectra of cast material was prepared by sealing a glass coverslip over the electrode such that it would remain air-free. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos Axis Ultra instrument loaded through an air-free transfer chamber with a monochromatic Al $K\alpha$ source at 14.87 keV. Photoelectrons at pass energies of 20 eV and 80 eV were detected with a multichannel detector. The spectra were fit by the least-squares method to Voigt functions with Shirley baselines using CasaXPS.

3.3 Results and discussion

The crosslinked disulfide polymer was obtained in a three-step synthesis described in Figure 3.1. $\text{C}_6(\text{SLi})_6$ was synthesized from a modified procedure previously reported by Harnisch and Angelici,[181] which was subsequently oxidized in purified air to obtain the crosslinked structure.

The thiol form of the intermediate structure, benzenhexathiol (BHT), is well-studied and is commonly used as a ligand in MOF and coordination polymer chemistry.[182, 183] Lithium was used as the counterion in the thiolate intermediate so that the starting material would be assembled in a partially discharged state for an Li-S cell if the material does not fully crosslink at every site.

Solid state ^{13}C NMR with magic angle spinning shows a signal at 127 ppm arising from aromatic C. The presence of a shoulder at 137 ppm [Figure 3.2a] and a ^7Li NMR signal at 0 ppm [Figure 3.5] suggest the presence of residual thiolate. However, the

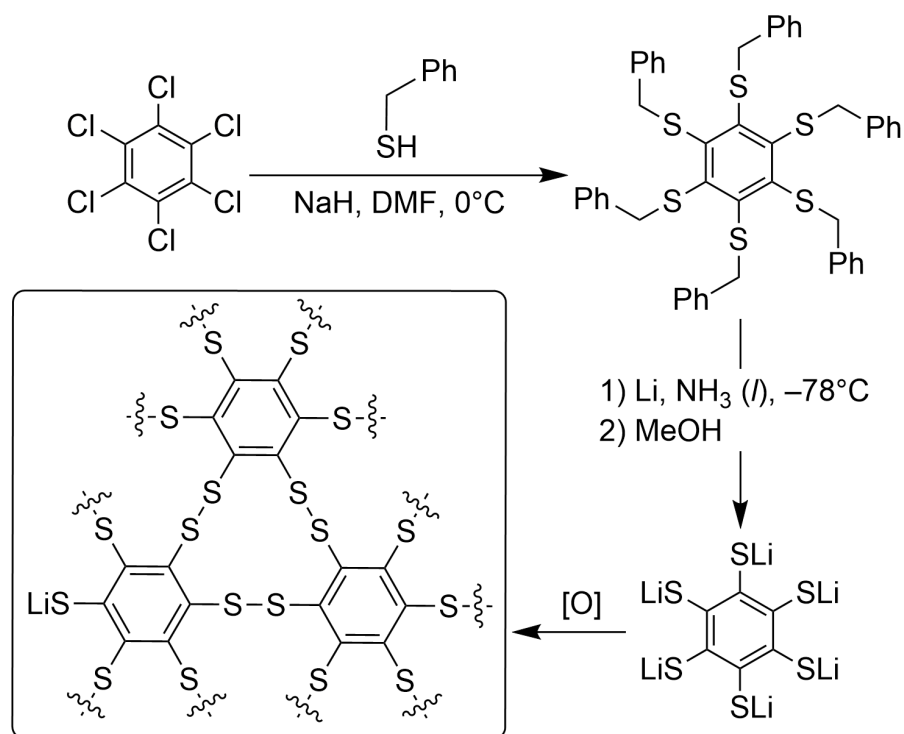


Figure 3.1: Synthesis scheme of crosslinked disulfide active material.

sulfur high-resolution X-ray photoelectron spectrum (XPS) indicates the presence of only one sulfur oxidation state [Figure 1c], and the lithium high-resolution spectrum shows no signal [Figure 3.2d]. Therefore, the disulfide active material is almost entirely crosslinked prior to cycling. Raman spectroscopy [Figure 3.2b] provides significant structural insight into the materials, both in the pristine state and at different states of charge. The pristine disulfide powder displays a strong disulfide peak at 480 cm^{-1} , assigned from previous literature.[184, 185] Also seen is a strong aromatic C—S mode at 1050 cm^{-1} , as well as an aromatic C—C mode at 1450 cm^{-1} [Figure 3.2b]. These three peaks signify the major structural components of the active material, notably benzene rings connected through disulfide bonds. Electrochemical testing of the disulfide material reflects stable cycling through both cyclic voltammetry (CV) and Galvanostatic cycling with potential limitation (GCPL) with lithium as both the anode and the refer-

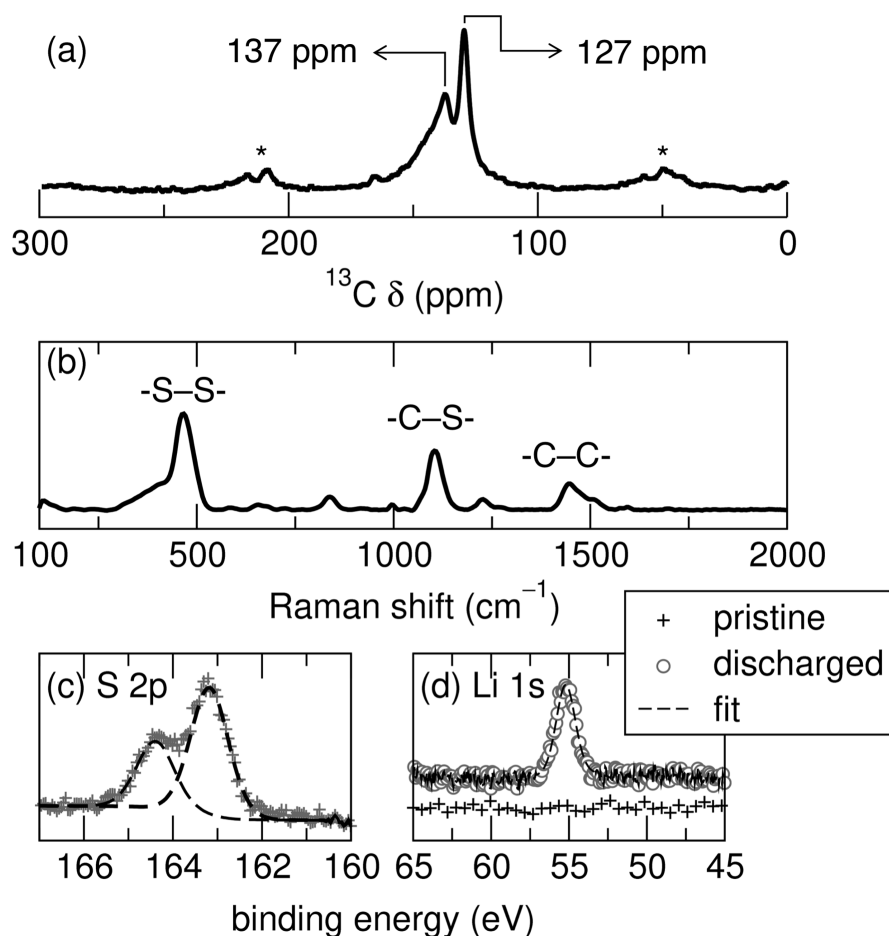


Figure 3.2: Characterization of the disulfide active material prior to electrochemical testing. (a) ^{13}C NMR spectrum with MAS at 16 kHz show two peaks in the aromatic region, and the asterisks label the spinning sidebands. (b) Raman spectrum with labelling of characteristic peaks. (c) High resolution XPS in the sulfur 2p region with fits for the $2p_{1/2}$ and $2p_{3/2}$ components of one oxidation state. (d) High resolution XPS in the lithium 1s region of the pristine material (no peak detected) and the discharged material at 1.0 V.

ence electrode. CV was performed in a coin cell at 0.1 mV/s and indicates reversibility is established after the first cycle [Figure 3.3a]. The main reduction occurs at 2.25 V with a less pronounced reduction at 2.18 V. There is a one-step oxidation at 2.5 V. GCPL also reflects the same redox potentials from the presence of plateaus at the corresponding potentials [Figure 3.3b]. The Galvanostatic cycling was performed with identical

coin cells for 200 cycles. The gravimetric capacity grows over the first 100 cycles and stabilizes through cycle 200 with 98 % capacity retention [Figure 3.3c]. The Coulombic efficiency nears 100 % for all cycles following cycle 1 [Figure 3.3d], suggesting the crosslinked disulfide material circumvents one of the most detrimental processes in classical Li-S batteries, parasitic polysulfide shuttle. All electrochemical testing was done without any additives to the electrolyte or the cathode material, demonstrating the exceptional stability of the disulfide material. Extended electrochemical testing is demonstrated with fewer cells to confirm its longevity.

Ex situ analysis provides confirmation for and insight into how the active material performs at the molecular level and microstructural level. Raman spectroscopy is particularly useful for confirming the mechanism by which redox occurs. The disulfide bond, which is the only electrochemically active part of the material, can be tracked by the peak at 480 cm^{-1} , starting in the pristine material. Once cast, the Raman spectrum shows the emergence of the graphitic bands at 1350 cm^{-1} and 1580 cm^{-1} from the Ketjen Black carbon additive [Figure 3.4a, shaded region]. Spectra were taken after 100 cycles at the most charged and discharged states, 3.2 V and 1.0 V, respectively. The charged product clearly shows a strong disulfide peak that even grows in intensity from the pristine material, suggesting an increase in crosslinking. The peak at 480 cm^{-1} recedes in the spectrum of the discharged product, and a new peak at 270 cm^{-1} emerges. By comparison with a less easily oxidized analogous material, lithium benzene-1,3,5-tris(thiolate), the peak at 270 cm^{-1} can be assigned to $-\text{S}-\text{Li}$ [Figure 3.6]. Therefore, the presence of the disulfide peak for the charged state and its suppression upon discharging indicate the electrochemical cleavage and reformation of the disulfide bonds in the network. A larger sampling of Raman spectra [Figure 3.7] suggests that complete conversion is not taking place during cycling, which is consistent

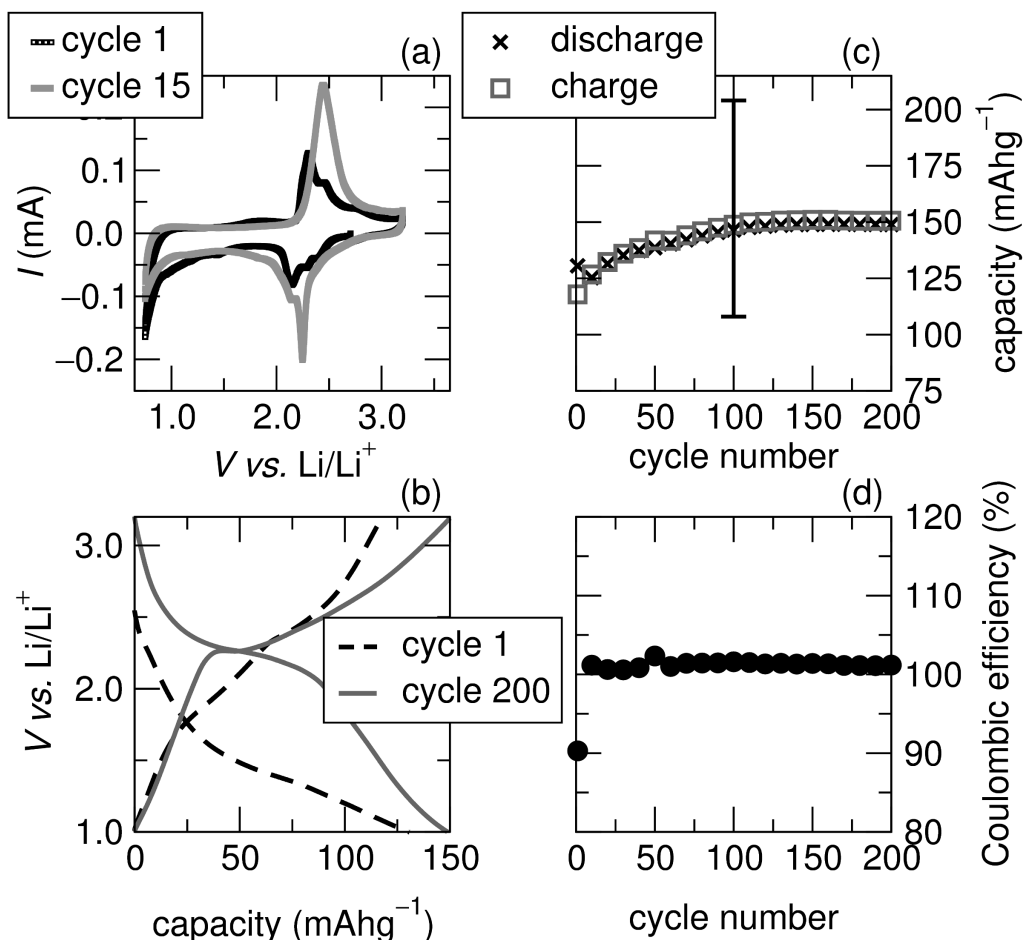


Figure 3.3: Electrochemistry of the disulfide material with LiTFSI in DOL/DME as the electrolyte system, and Li is both the anode and the reference electrode. (a) Cyclic voltammetry from 3.2 V to 0.75 V at a sweep rate of 0.1 mV s^{-1} . (b) Galvanostatic cycling with potential limitation (GCPL) at a rate of $C/10$ from 3.0V to 1.0V shown for 200 cycles. (c) Capacity for each cycle (charge and discharge) from GCPL increases through cycle 100 and maintains 150 mAh g^{-1} through 200 cycles. The error bar at cycle 100 represents the standard deviation of capacities observed over 10 different cells. (d) Coulombic efficiency, defined as charge divided by discharge capacity, hovers around 100% for all 200 cycles.

with the material not reaching theoretical capacity during cycling. Different regions in the electrodes display different extents of charge or discharge, suggesting not all particles undergo redox with every cycle.

Scanning electron microscopy (SEM) provides further understanding of the capac-

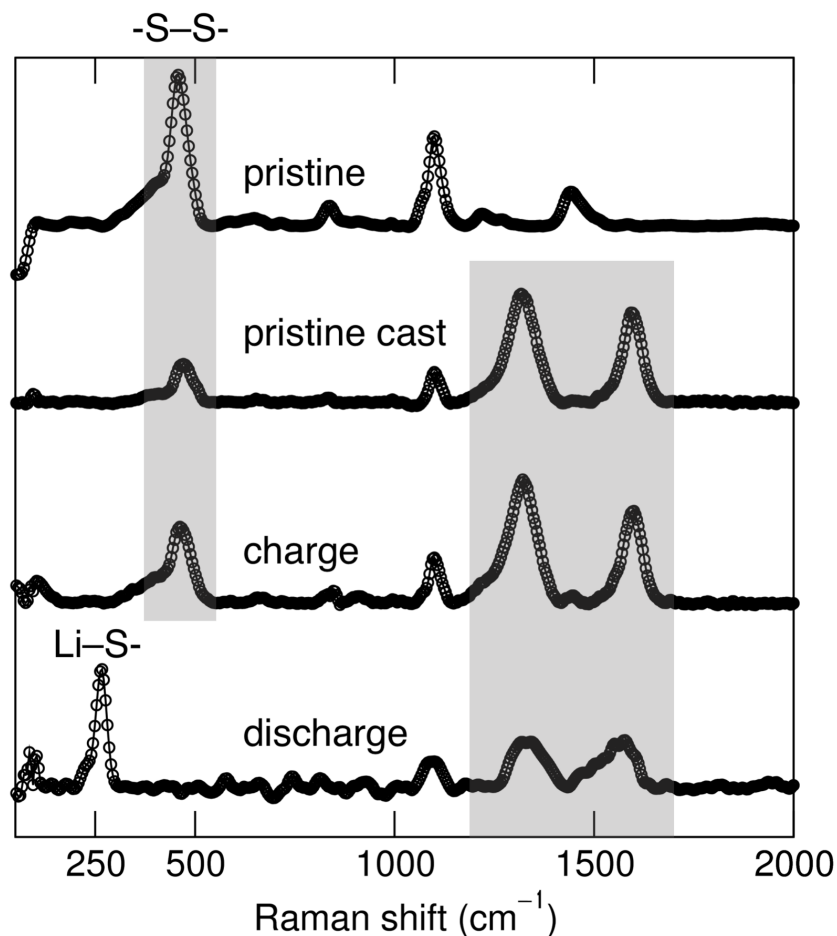


Figure 3.4: Raman spectroscopy of the pristine powder, pristine electrode, charge, and discharged products compare disulfide bonds breaking and reforming. The highlighted region from 1350 cm^{-1} to 1580 cm^{-1} indicates the graphitic contribution from the Ketjen Black additive.

ity gain over the first 100 cycles, which is an unexpected occurrence in the Li-S system. Comparing SEM images from the cast electrodes before and after cycling reveals the disulfide particles undergo self-microstructuring, creating porosity over many cycles [Figure 3.8]. The increased surface area may account for the capacity gain seen in the Galvanostatic cycling over the first 100 cycles, as lithium can access the densely-crosslinked active material more readily at the surface. Once the particles have undergone this microstructural change, the electrochemical performance reaches a steady

state, and the capacity does not change from cycle 100 through 200.

In summary, we report a new crosslinked disulfide material that exhibits stable cycling over hundreds of cycles and good Coulombic efficiency with no electrolyte additives and minimal device engineering. The use of a disulfide active material with maximized sulfur content prevents polysulfide shuttle by providing only one point of electrochemical scission, a crosslinked framework, and a highly charged discharged product. With increased optimization, particularly engineering the electrodes to incorporate improved ionic and electronic properties, the cathode material reported herein has potential for practical applications with capacities close to the theoretical amount.

3.4 Additional characterization and analysis

Since the hexa-substituted thiolate is extremely easily oxidized, it is difficult to isolate it through synthesis for Raman spectroscopy. In order to identify the emergence of a new mode at 270 cm^{-1} in the discharge product, ascribed to the S-Li moiety, a Raman spectrum of 1,3,5-benzenetrithiolate was measured. 1,3,5-Benzenetrithiolate was synthesized by reacting 1 equivalent of 1,3,5-Benzenetrithiol (TCI chemicals) with 3 equivalents of LiOH (Sigma Aldrich).

Different sampling spots over the total electrode suggest incomplete conversion upon charge and discharge. Particularly, regions in the discharged electrode (1.0 V) show remnants of the crosslinked product (Raman shift 480 cm^{-1}), which aligns with the observed electrochemical performance not achieving theoretical capacity.

In comparison to the pristine electrode, the active material particles post-cycling now show an increase in porosity (seen by the holes present). The difference in particle

size between the before and after SEM images are not indicative of and increase in particle size over cycling – the average particle size of the material remains on the order of $0.5\ \mu\text{m}$ to $2\ \mu\text{m}$ after cycling. These SEM images with these particular particles were chosen for clarity of the texture of the particles. The slight compressing of the Ketjen Black matrix (the smaller particles surrounding the larger active material particle) is likely due to wetting and compression once pressure is applied during the cell crimping process.

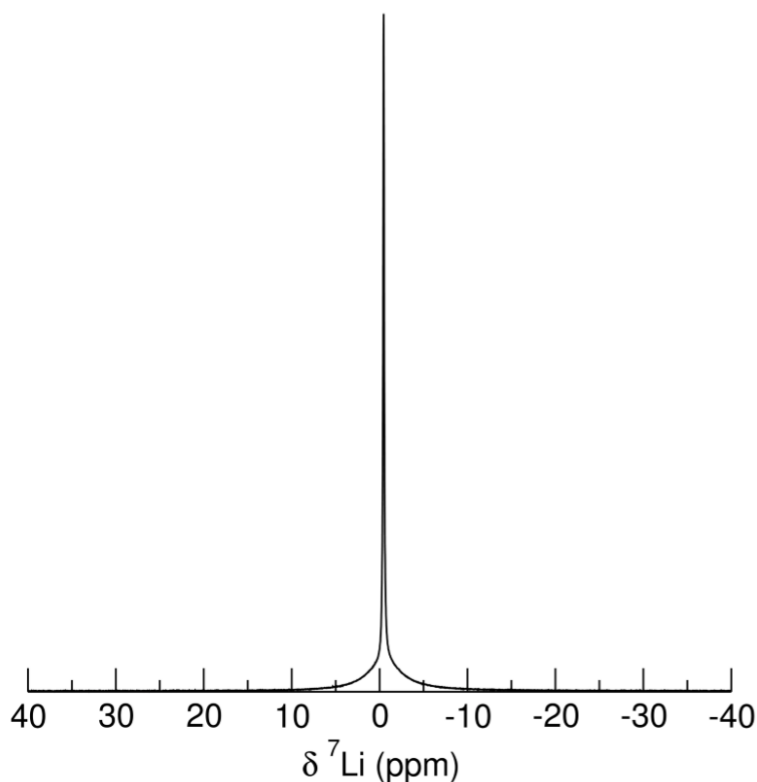


Figure 3.5: ${}^7\text{Li}$ NMR of crosslinked disulfide material. ${}^7\text{Li}$ NMR with magic angle spinning at 16 kHz shows a prominent peak at $-0.45\ \text{ppm}$. Though the presence of Li was below the detection limit by X-ray Photoelectron Spectroscopy, NMR suggests the presence of residual Li after the crosslinking. The cell is therefore in a negligibly discharged state prior to cycling. The spectrum was measured using a Bruker AVANCE III Ultrashield Plus 800 MHz (18.8T) narrow bore spectrometer.

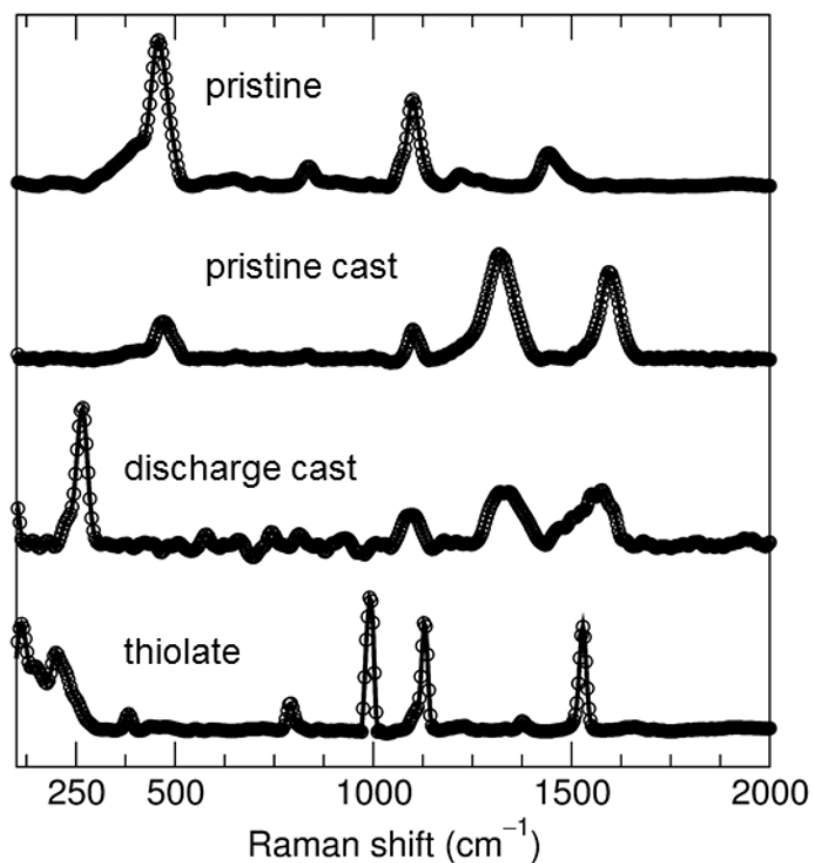


Figure 3.6: Raman spectroscopy of analogous 1,3,5-benzenetrithiolate. The pristine and pristine cast material show a peak at 480 cm^{-1} corresponding to the disulfide moiety. In the discharge product, the peak at 480 cm^{-1} recedes and a peak at 270 cm^{-1} emerges. The peak at 270 cm^{-1} can also be seen in lithium 1,3,5-Benzenetrithiolate, corresponding to the thiolate functionality. This material was measured as a powder, so it therefore does not have the graphitic carbon bands between 1350 cm^{-1} and 1580 cm^{-1} seen in the spectra of the cast materials.

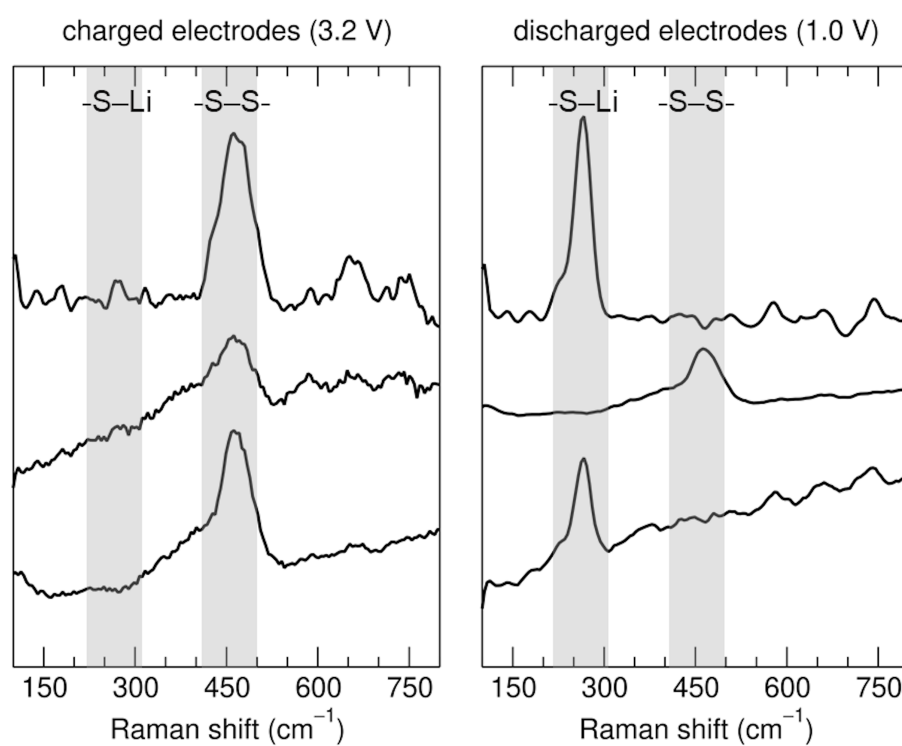


Figure 3.7: Raman spectra of spots focused across different parts of the electrode from both the charged electrode (left) and the discharged electrode (right).

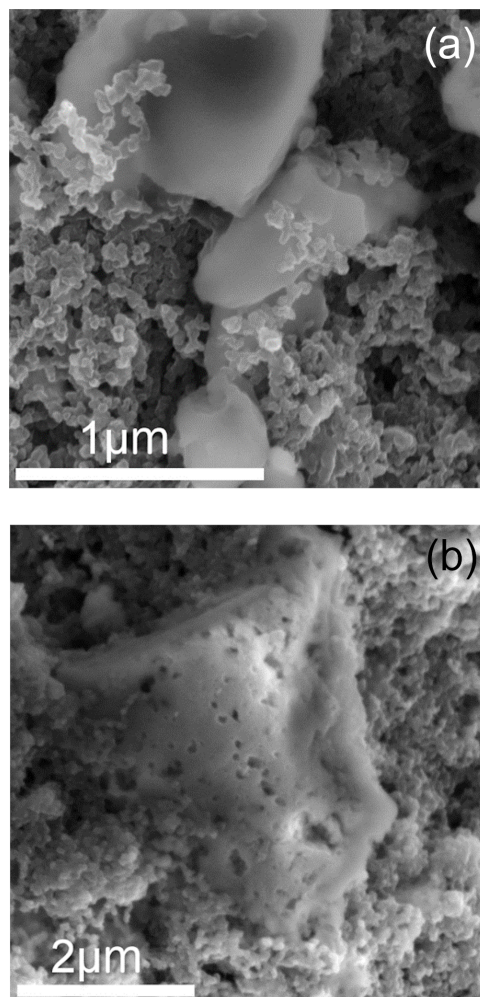


Figure 3.8: Scanning electron micrographs were acquired on a FEI Nova Nano 650 FEG Scanning Electron Microscope with a 5.0 kV beam voltage in immersion mode. Samples were prepared in the glovebox on a conductive carbon tape substrate and were quickly transferred into the high vacuum chamber to minimize air exposure. Micrograph of pristine electrode (top) shows large particles of the active disulfide material in a matrix of Ketjen Black carbon additive, which are the smaller, more spherical agglomerated particles. The active material particles are on the order of $0.5\ \mu\text{m}$ to $2\ \mu\text{m}$ and have a smooth surface. Micrograph of cycled electrode material after 100 cycles (bottom) shows particles of active material in a matrix of Ketjen Black carbon additive. Featured in the micrograph is a large active material particle on the order of $2\ \mu\text{m}$ surrounded by smaller particles of carbon.

Chapter 4

Rapid and Tunable Assisted-Microwave Preparation of Glass and Glass-Ceramic Thiophosphate $\text{Li}_7\text{P}_3\text{S}_{11}$ Li-ion Conductors

1

4.1 Introduction

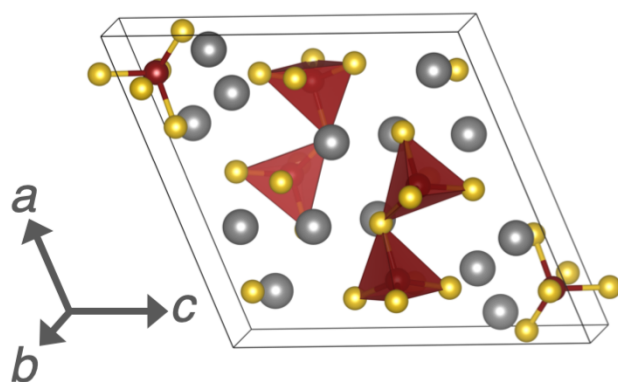
All-solid-state batteries are promising candidates to replace some current applications of lithium-ion batteries employing liquid electrolytes, and may potentially enable

¹The contents of this chapter have substantially appeared in reference 4: M. B. Preefer, J. H. Grebenkemper, F. Schroeder, J. D. Bocarsly, K. Pilar, J. A. Cooley, W. Zhang, J. Hu, S. Misra, F. Seeler, K. Schierle-Arndt, and R. Seshadri. *ACS Appl. Mater. Interfaces*, 11(45), 42280–42287 (2019). © 2019 American Chemical Society, reprinted with permission.

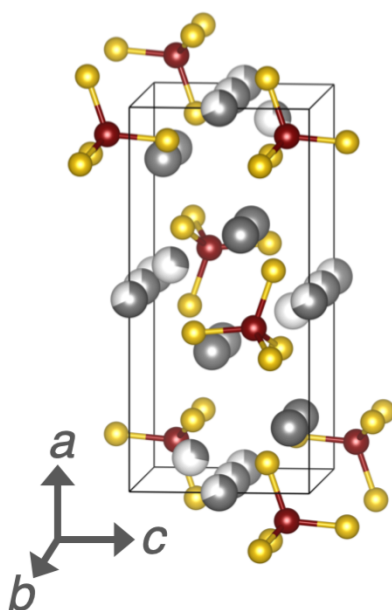
beyond Li-ion chemistries such as the conversion based Lithium-sulfur system.[186, 187] Crucial to enabling all-solid-state batteries is the ability to replace conventional liquid electrolytes with one that is solid, demonstrated to potentially include materials ranging from polymers to ceramic oxides and sulfides.[38, 188] Realization of all-solid-state batteries would avoid the hazards of flammable and corrosive liquid electrolytes, simplify construction of the cell by potentially eliminating the need for a separator, and may offer greater stability at higher voltages.[17, 189] Beyond improving upon these features of current Li-ion technologies, all-solid-state batteries also open new potential applications in more extreme environments because they can safely operate at higher temperatures, in fact often with improved performance.[190]

The fundamental requirements of a solid electrolyte include having high ionic conductivity (on the order of 1 mS cm^{-1} at room temperature), no electronic conductivity, and thermodynamic and kinetic stability versus the anode and cathode materials of choice. Lithium thiophosphates are some of the leading materials to realize all-solid-state batteries, due to their high ionic conductivity. There are many related materials within the family of lithium thiophosphate solid electrolytes, including the thio-LISICONs incorporating Ge[191–193], Sn,[194] and Si[195, 196], as well as argyrodites and other halogen-containing thiophosphates [197–200]. Within the pure Li–P–S phases, there are three main compositions studied both fundamentally and in battery applications: Li₇P₃S₁₁ [Figure 4.1(a)], Li₃PS₄ [Figure 4.1(b)], and Li₄P₂S₆ [Figure 4.1(c)], in decreasing order of room temperature conductivities.[201–203] In terms of their structure, Li₃PS₄ and Li₄P₂S₆ can be thought of as end-members, where Li₃PS₄ exclusively has PS₄^{3–} isolated tetrahedra, Li₄P₂S₆ exclusively has P₂S₆^{4–} dumbbells, and Li₇P₃S₁₁ has a mixture of PS₄^{3–} isolated and P₂S₇^{4–} corner-sharing tetrahedra. Of the three phases, Li₇P₃S₁₁ is the only metastable phase, and is therefore of-

(a) $\text{Li}_7\text{P}_3\text{S}_{11}$



(b) Li_3PS_4



(c) $\text{Li}_4\text{P}_2\text{S}_6$

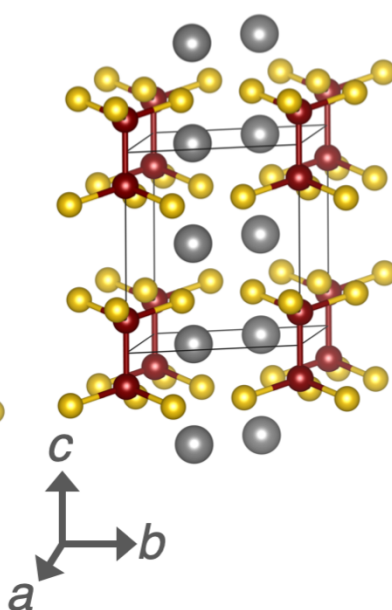


Figure 4.1: Crystal structures of related lithium thiophosphates (a) $\text{Li}_7\text{P}_3\text{S}_{11}$, (b) Li_3PS_4 , and (c) $\text{Li}_4\text{P}_2\text{S}_6$. $\text{Li}_7\text{P}_3\text{S}_{11}$ is the focus of this work, but this series demonstrates the increase in isolated tetrahedra with higher S:P content.

ten observed co-mingled with some percentage of the other two phases, especially Li₄P₂S₆.^[204] In addition, while the two end-member phases are crystalline, Li₇P₃S₁₁ forms as a glass-ceramic phase, which consists of domains of crystalline solid in an amorphous matrix.^[205] Li₇P₃S₁₁ has been reported to achieve conductivity values on the order of liquid electrolytes such as LiPF₆ in ethylene carbonate and dimethyl carbonate, although this is highly dependent on the processing conditions.^[39, 206] In relation to the last requirement listed, the intrinsic interfacial instability of lithium thiophosphates and lithium is well documented through electrochemical testing in symmetric cells versus lithium, but can be overcome through several engineering routes, including recent evidence of successfully incorporating surface layers onto the solid electrolyte that are stable to lithium.^[37, 206–211] There have been several examples to date of using the Li₇P₃S₁₁ solid electrolyte system to date in both Li-ion and Li-S cells.^[212–214]

Microwave-based methods provide convenient routes to generating a range of materials and have been successfully employed for preparing chalcogenide and pnictide compounds.^[10, 215–217] In a category of materials in which the balance between the degree of crystallinity will be a dictating factor in device performance, a tunable synthesis of this nature is highly desirable.^[218] The most common reported synthetic method for the 70 Li₂S–30 P₂S₅ glass has been melt quenching from greater than 700 °C in order to form an amorphous glass, which can then be subsequently annealed between 260 °C and 280 °C to form the glass-ceramic – that is, varying contents of Li₇P₃S₁₁ stabilized in the amorphous 70 Li₂S–30 P₂S₅ glass matrix.^[219–221] Alternatively, the glass-ceramic can be formed directly through melt quenching from 800 °C.^[222] These procedures often result in impurities from the less ionically conductive Li₄P₂S₆ phase, however.^[223–226] This is because the metastable Li₇P₃S₁₁ phase only forms in very

narrow temperature regimes, as detailed above. Other syntheses for the glass have involved mechanical milling or solution-phase methods, both requiring further annealing to precipitate crystalline Li₇P₃S₁₁ domains.[227–230]

Here we report assisted-microwave preparation wherein the glass can be made in 18 minutes, as well as a direct, one-step preparation of the the glass-ceramic in 28 minutes with extremely low to undetectable amounts of the undesirable, yet highly stable Li₄P₂S₆ phase. The highly varied nature of these glass-ceramic materials, comprising significant amorphous and crystalline components, makes a range of techniques essential in order to capture the average structure and crystallinity, as well as local structure information. Therefore, the samples are carefully characterized by a combination of synchrotron X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy, and solid state ⁷Li nuclear magnetic resonance spectroscopy in order to capture the structure-property relationships stemming from the combination of amorphous and crystalline materials.

4.2 Methods

Microwave preparation of 70Li₂S–30P₂S₅ glass and Li₇P₃S₁₁ glass-ceramic Li₂S and P₂S₅ were ground until homogeneous in a 70:30 molar ratio using an agate mortar and pestle in an Ar filled glovebox with H₂O and O₂ < 0.1 ppm. For the glass preparation, the powder was pressed into 250 mg 6 mm pellets, which were sealed in 3 inch long, 3/8 inch diameter fused silica ampoules under 0.25 atm of Ar. Two 275 mg pellets were sealed in 3.5 inch ampoules for the glass-ceramic preparation. Each ampoule was buried in the center of a 250 mL alumina crucible filled with activated charcoal (DARCO 12-20 mesh) held in a cylinder of alumina fiberboard insulation and placed

off-center in a 1200 W microwave oven (Panasonic NN-SN651B). This was heated at power 4 (*ie.* 40 % of the total power) for 18 min for the glass and power 4 for 28 min for the glass-ceramic, followed by removing the insulation assembly and sample from the microwave oven and quenching the sample tube in water. The longer heating times for the glass-ceramic allows the material to reach higher temperatures, which is in agreement with previous solid-state methods, in which the glass-ceramic can be formed by melt quenching from higher temperatures than for the glass. The conditions presented above were arrived at after extensive trial-and-error. An immediate noticeable advantage of employing microwaves is that since fused silica is a poor susceptor, and being transparent, absorbs convectional heat poorly, the walls of the container do not get very hot. Consequently, there is little or no reaction between the (corrosive-for-silica) contents and the ampoules, as observed from how clean and transparent the ampoules remain.

X-ray photoelectron spectroscopy X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra X-ray Photoelectron Spectroscopy system with a monochromatic Al source at 1.4 keV. Samples were prepared in an Ar glovebox using a sample holder with a cover that sealed with an O-ring. The entire sample holder was placed into the first vacuum chamber, and when the vacuum reached approximately 10^{-5} Torr, the cover was removed and the samples were pumped down to 10^{-8} Torr. Photoelectrons at pass energies of 20 eV and 80 eV for survey and high resolution spectra were detected with a multichannel detector. The spectra were fit by the least-squares method to Voigt functions with Shirley baselines using CasaXPS.

Raman spectroscopy Raman spectroscopic measurements were carried out under inert conditions using a Horiba LabRAM ARAMIS Raman spectrometer equipped with a

confocal microscope. Samples were prepared in an Ar-filled glovebox by sealing a glass cover slip over the powder sample on a glass microscope slide. Data was collected with a 633 nm laser, 500 μm hole, 500 μm slit, 1200 cm^{-1} grating, 2 second exposures, and 5 spectra averaged, centered at 450 cm^{-1} . To ensure no decomposition of the sample, a control sample was left in air for a day before measuring. No decomposition peaks were observed in the samples reported herein, the peaks of which have also been detailed in previous studies.[\[231\]](#)

Diffraction analysis of amorphous and crystalline components Laboratory powder X-ray diffraction (XRD) data was collected using a Panalytical Empyrean diffractometer with $\text{Cu K}\alpha$ radiation. Powders were protected from the atmosphere utilizing an air sensitive holder containing a zero background plate and a Kapton film window. High resolution synchrotron diffraction data was collected at room temperature at the Advanced Photon Source at Argonne National Laboratories, beamlines 11-BM-B (for the glass) and 11-ID-B (for the glass-ceramic) using an average wavelength of 0.414581 Å. Samples were loaded into kapton capillaries and sealed with epoxy. They were removed from inert atmosphere minutes prior to measurement. Control experiments were also performed on samples purposefully exposed to air prior to measurement to ensure the integrity of the air-free samples. Rietveld analysis was performed using Topas Academic v6. In order to quantitatively determine the crystallinity of the glass-ceramic phases, additional patterns were collected on samples that had been spiked with known quantities of crystalline Si (on the order of 10 wt.%). Multi-phase Rietveld refinement including all phases was performed on these patterns including the phases $\text{Li}_7\text{P}_3\text{S}_{11}$, $\text{Li}_4\text{P}_2\text{S}_6$, and Si. Based on the difference between the refined Si wt.% and the known spiked wt.%, the amorphous content of the sample was determined according to the following equations:

$$W_{\text{Li}_7\text{S}_3\text{S}_{11}} = \frac{W_{\text{Si,known}}}{W'_{\text{Si}}} \times W'_{\text{Li}_7\text{S}_3\text{S}_{11}} \times 100 \% \quad (4.1)$$

$$W_{\text{Li}_4\text{S}_2\text{S}_6} = \frac{W_{\text{Si,known}}}{W'_{\text{Si}}} \times W'_{\text{Li}_4\text{S}_2\text{S}_6} \times 100 \% \quad (4.2)$$

$$W_{\text{amorphous}} = 100 \% - W_{\text{Li}_7\text{S}_3\text{S}_{11}} - W_{\text{Li}_4\text{S}_2\text{S}_6} - W_{\text{Si,known}} \quad (4.3)$$

Here, $W_{\text{Si,known}}$ is the spiked weight percent of Si in the sample, and W'_{Si} is the apparent weight percent of Si from the Rietveld refinement. $W_{\text{Li}_7\text{S}_3\text{S}_{11}}$ and $W'_{\text{Li}_7\text{S}_3\text{S}_{11}}$ are respectively the true and apparent weight percents of crystalline $\text{Li}_7\text{S}_3\text{P}_{11}$, and $W_{\text{Li}_4\text{S}_2\text{S}_6}$ and $W'_{\text{Li}_4\text{S}_2\text{S}_6}$ are the true and apparent weight percents of the secondary $\text{Li}_4\text{S}_2\text{S}_6$ phase. $W_{\text{amorphous}}$ is the weight percent of the sample that is not crystalline, which is assumed to come solely from the glassy component of the $\text{Li}_7\text{S}_3\text{P}_{11}$ glass-ceramic. Based on this analysis, the percent crystallinity of the $\text{Li}_7\text{S}_3\text{S}_{11}$ can be determined.

Electrochemical impedance spectroscopy Electrochemical impedance spectroscopy was measured using a VMP3 Bio-logic potentiostat from 1 MHz to 1 Hz with a 200 mV sinus amplitude under inert conditions. The samples were sintered under approximately 180 MPa pressure at 90 °C for 12 h before being subject to variable temperature measurements. Equilibrium was ensured for all of the data reported here by repeating measurements in succession at each temperature until each spectrum aligned before proceeding with the next measurement. To ensure robust fits, data was collected from 20 °C to 90 °C in 5 °C increments using an environmental chamber. Spectra were also collected at 10 °C in order to clearly fit equivalent circuits to each sample, using ZFit in the ECLab software. The custom cell design used is described in detail in the Support-

ing Information. A vise and a force gauge (Omega) were used to press pellets *in-situ* and apply and monitor pressure throughout the measurements.

Nuclear magnetic resonance Pulsed-field gradient NMR was conducted on a 300 MHz (7.1 T) Bruker Avance NMR spectrometer with a Bruker diffusion probe capable of 3000 G/cm. A stimulated echo pulse sequence with bipolar gradient pulses was utilized to measure ⁷Li diffusion coefficients at a resonant frequency of 116.6 MHz. The sample temperature was varied from 25 °C to 80 °C in approximately 10 °C increments, with the sample temperature allowed to equilibrate for 20 min. between subsequent measurements. The pulsed-field gradient strength was set to 16 values between 50 G cm⁻¹ and 2800 G cm⁻¹ for each measurement. The observed signal attenuation was fit to the Stejskal-Tanner equation to obtain diffusion coefficients. ⁷Li MAS NMR spectra were acquired on a Bruker AVANCE III Ultrashield Plus 800 MHz (18.8T) NMR spectrometer. These experiments were conducted using a Bruker 2.5 mm HX MAS probe at a spinning speed of 30 kHz. The spectra are referenced to LiCl in H₂O and processed using Bruker TopSpin software. The recycle delay was optimized and found to be 3.2 s for quantitative analysis. Single pulse experiments were used to obtain quantitative spectra and a Hahn echo pulse sequence was used to apply a T_2 filter. Peak fitting was performed using the DMFIT software.[232]

4.3 Results and discussion

The microwave prepared glass and glass ceramic samples were characterized by a combination of X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and X-ray diffraction to understand their local and long-range structures. While XPS is a

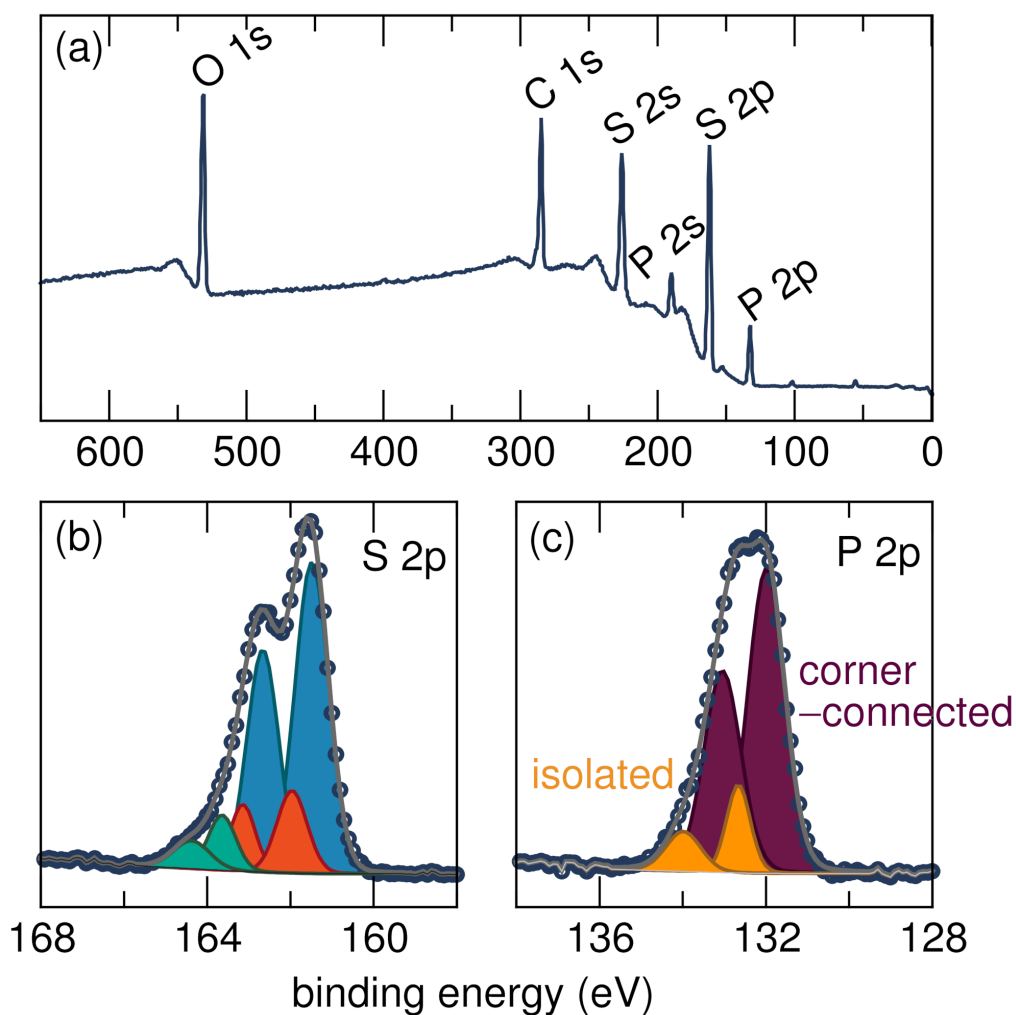


Figure 4.2: (a) XPS survey region showing elemental composition of a representative glass-ceramic sample. (b) High resolution spectrum in the S binding energy region and (c) high resolution spectrum in the P binding energy region, which shows a higher concentration of the corner sharing tetrahedra as compared to isolated tetrahedra.

surface technique and is therefore very sensitive to slight surface oxidation or surface inhomogeneities, the survey scan from 600 eV to 0 eV serves as an approximation for elemental composition in the samples. This range encompasses the characteristic S 2s, S 2p, P 2s, and P 2p energies, allowing quantitative ratios of S:P to be calculated [Figure 4.2(a)]. The ideal S:P ratio for the targeted Li₇P₃S₁₁ stoichiometry is 3.7:1. The glass and glass-ceramic samples synthesized via the one-step microwave preparation range in S:P ratios from 3.8:1 to 4.0:1 between multiple samples for each, which is within reasonable error extrapolating to the bulk material. While the survey scan shows evidence of the O 2p peak, this can be attributed to the stainless steel sample holder and that spectral region does not play a role in extracting the relative ratios of S:P. High resolution spectra of the S 2p [Figure 4.2(b)] and P 2p [Figure 4.2(c)] can be fit to analyze the nature of bonding in these structures. These results are consistent with previous reports and with the known structure of Li₇P₃S₁₁ in which there is a higher concentration of the corner-connected tetrahedral environments (seen in the P 2p region) centered at 133 eV to the isolated tetrahedral environments centered at 133.5 eV.[233] The high resolution spectra do not indicate any formation of phosphate species, which would be indicative of oxidation in these samples.

Raman spectroscopy corroborates this local bonding environment picture (Figure 4.3). The region of the spectrum from 350 cm⁻¹ to 450 cm⁻¹ includes the modes associated with the isolated PS₄³⁻ tetrahedra, corner-connected P₂S₇⁴⁻ tetrahedral pairs, and P₂S₆⁴⁻ dumbbells indicative of Li₄P₂S₆ impurity phase when present [Figure 4.3(b)]. The main modes attributed to the Li₇P₃S₁₁ structure are the stretching vibrations of the P-S bonds at 410 cm⁻¹ and 425 cm⁻¹ for the P₂S₇⁴⁻ and PS₄³⁻ anions, respectively. Assignments of these modes are in agreement with several previous reports on Li₇P₃S₁₁.[220, 234] The glass samples show no signatures of Li₄P₂S₆, and the glass-

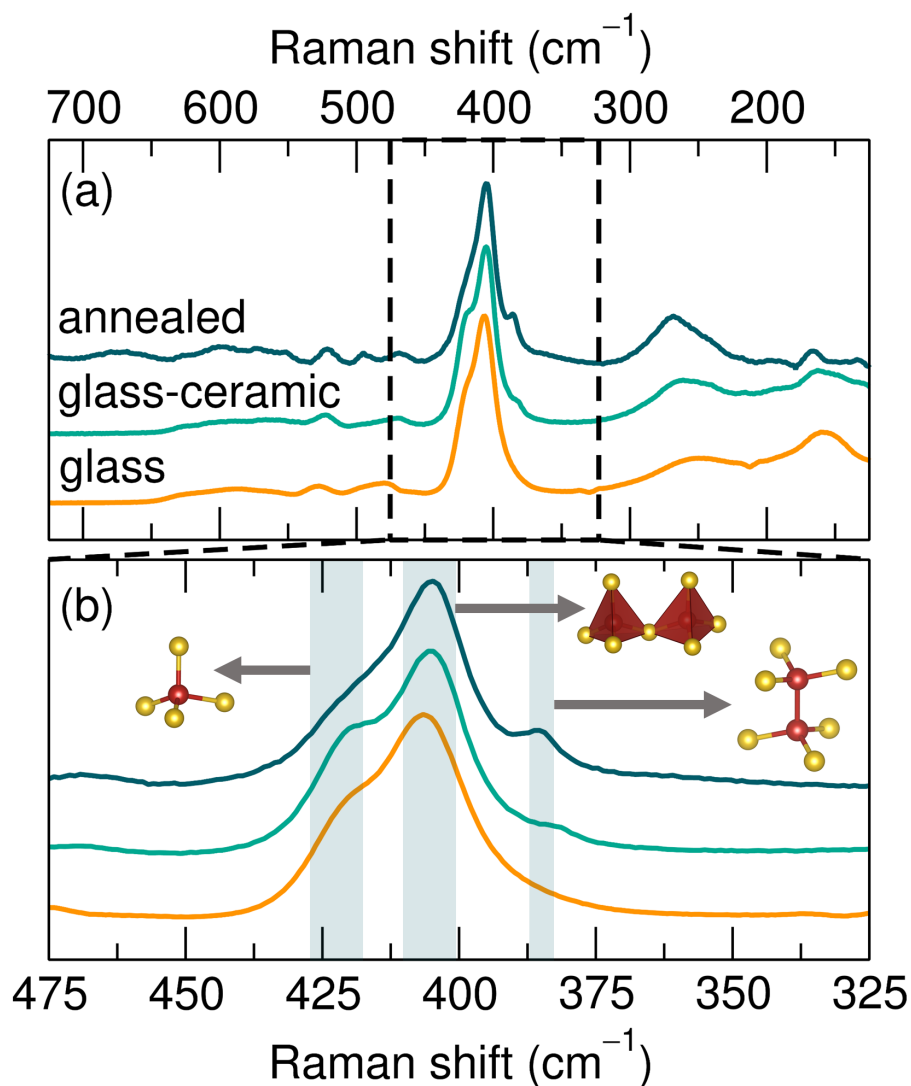


Figure 4.3: (a) Raman spectra of the glass and glass-ceramic made using assisted-microwave methods, and the subsequently annealed glass-ceramic sample over the full spectral range where peaks are observed. (b) Highlighted spectral region of the modes relating to isolated PS_4^{3-} tetrahedra, corner-sharing tetrahedra (as in $\text{P}_2\text{S}_7^{4-}$), and $\text{P}_2\text{S}_6^{4-}$ dumbbells.

ceramic samples show a hint of the P₂S₆⁴⁻ dumbbell centered at 390 cm⁻¹. The presence of the Li₄P₂S₆ in the subsequently annealed glass-ceramic is, however, more prominent.

X-ray diffraction yields crucial information about the crystallinity of the microwave-prepared samples, and furnace annealed samples in relation to their conductivities. Crystallization of the 70Li₂S-30P₂S₅ glass into the glass-ceramic is well documented to give superior lithium ionic conductivity, especially when processed in a hot-press setup.[39, 220, 233, 235] However, this is also usually accompanied by some degree of growth of the less-favorable Li₄P₂S₆ phase.

From laboratory Cu-*K*α X-ray diffraction, the ability to learn about the glass and glass-ceramic is somewhat limited (Figure 4.7). In contrast, high-resolution synchrotron X-ray diffraction reveals much more; that a range of states spanning from purely glassy to mostly crystalline is possible. Figure 4.4(a) shows a high-resolution synchrotron diffraction pattern of the microwaved glass form, showing a complex background with no diffraction peaks, indicating a fully amorphous sample with only short-range order. The microwaved glass-ceramic [Figure 4.4(b)], on the other hand, shows diffraction peaks for Li₇P₃S₁₁ as well as the amorphous background. In part, the diffuse scattering observed is due to the kapton capillary background, and the intensity of the complex amorphous background is much less than the crystalline component evidenced by the counts. Quantitative phase analysis of samples measured with internal Si standards reveal that the Li₇P₃S₁₁ is 33(6) % crystalline. The standard deviation on the last significant figure, presented within parentheses, are based upon three identically prepared samples. In these samples, the contribution from Li₄P₂S₆ is negligible. Upon further annealing at 280 °C for 2 h, the majority of the amorphous contribution is reduced [Figure 4.4(c)]. The crystallinity of the Li₇P₃S₁₁ increases to 76(3) wt.%, and 8.6(9) wt.% of Li₄P₂S₆ grows into the sample. Rietveld refinements for representative

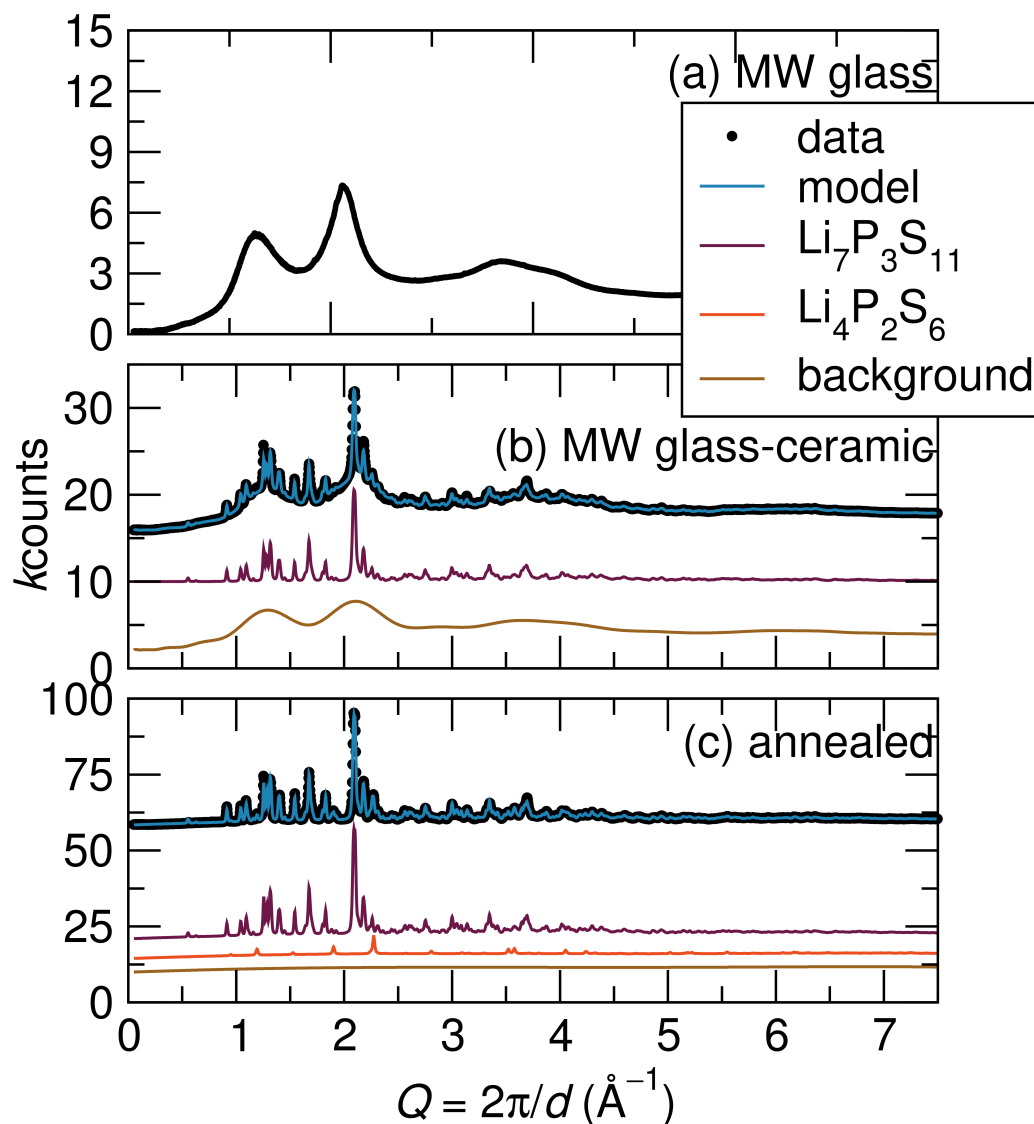


Figure 4.4: Rietveld refinements from high resolution X-ray diffraction of (a) the microwave-prepared glass, (b) the microwave-prepared glass-ceramic and (c) the microwave-prepared glass-ceramic subsequently annealed at 280°C for 2 h. The amorphous peaks in the microwave prepared glass and glass-ceramic are due to contributions from the kapton capillary background scattering. The y-axis denotes counts, which can be used to compare the much weaker scattering intensity of the amorphous backgrounds. While the microwave-prepared glass-ceramic sample has a significant amorphous component, the amorphous component significantly decreases in the annealed sample.

samples containing added Si for the quantitative analysis is shown in the Supporting Information (Figure 4.9), along with a table including the refinement results from several identically-prepared samples.

Since the heating time is much shorter using the microwave preparation and more uniform across the sample, there is less growth of the $\text{Li}_4\text{P}_2\text{S}_6$ phase in contrast to accessing the glass-ceramic by annealing glass in a furnace. The preparation methods employed here also allows for tuning between purely glass and highly crystalline $\text{Li}_7\text{P}_3\text{S}_{11}$ with significant amounts of $\text{Li}_4\text{P}_2\text{S}_6$ impurity. The moderate level of crystallinity from the microwave glass-ceramic synthesis also offers an ideal trade-off between favorable mechanical properties (more compliant and less grain boundaries) and higher conductivity values than only the pure glass.[218, 236]

The crystalline tuning through the microwave preparation is also reflected in the conductivity values observed through electrochemical impedance spectroscopy in these samples. Arrhenius relationships of the glass, glass-ceramic, and subsequently annealed glass-ceramic align with the percent crystallinity extracted from the Rietveld analyses [Figure 4.5(a)]. Room temperature conductivity of the microwave-prepared glass is $0.12(1) \text{ mS cm}^{-1}$, while this value is approximately doubled in the microwave-prepared glass ceramic to $0.210(2) \text{ mS cm}^{-1}$. When the glass-ceramic sample is further annealed, the room temperature conductivity increases by an order of magnitude to 1.1 mS cm^{-1} . This is in good agreement with the percent crystallinity doubling from the microwave glass-ceramic to its annealed counterpart.

The activation energies associated with the glass, glass-ceramic, and annealed glass-ceramic can be found through the following Arrhenius-type relationship:[237, 238]:

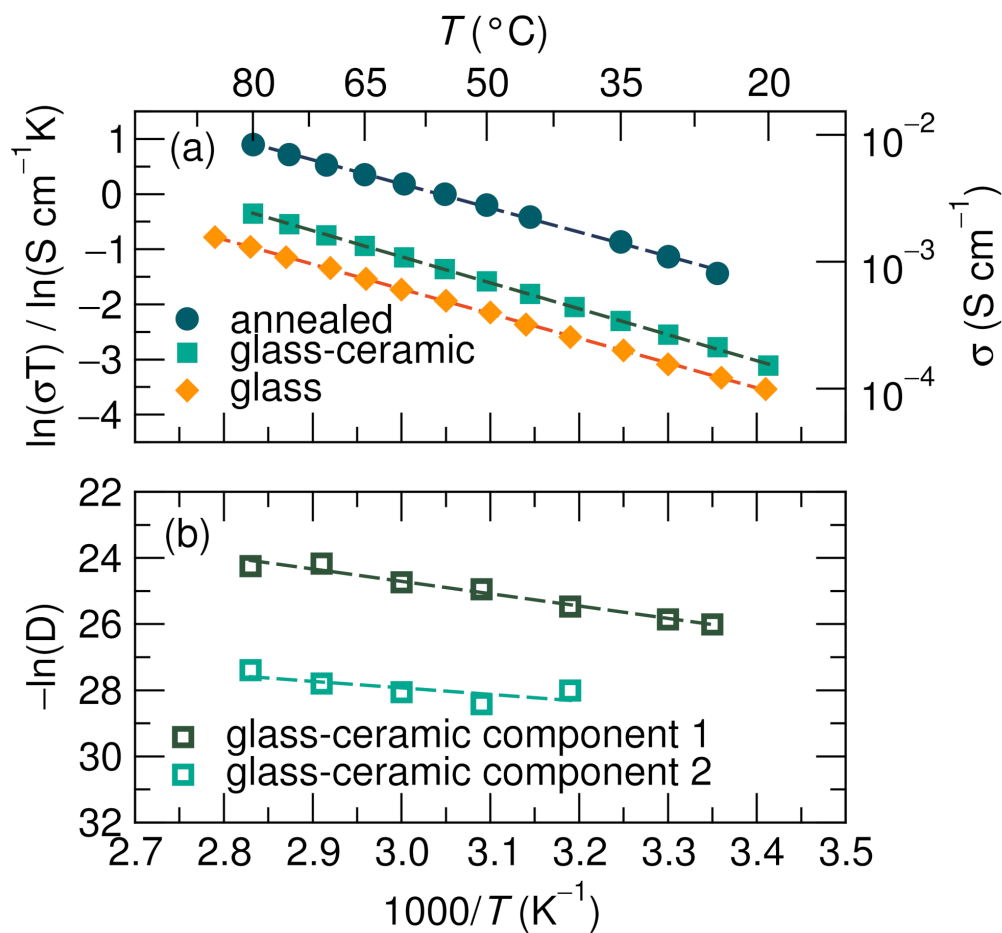


Figure 4.5: (a) Arrhenius plot of the microwave-prepared glass, glass-ceramic, and subsequently annealed sample, derived from electrochemical impedance spectroscopy at varying temperatures of each sample from 1 MHz to 1 Hz. (b) Arrhenius plot of the two components fit from temperature dependent ^7Li pulsed-field gradient NMR of the glass-ceramic, revealing a slower diffusing species and a faster diffusing species within the sample.

$$\sigma T = \sigma_0 \exp\left(\frac{-E_A}{k_B T}\right) \quad (4.4)$$

where E_A is activation energy, σ_0 is the pre-factor, and k_B is the Boltzmann constant. The Meyer-Neldel compensation rule is applied here due to the intrinsic conductivity of Li in the structure, which has thermally activated hopping (incorporated into the pre-factor term).^[239] The activation energies are consistent between the three levels of crystallinity reported here, where the glass is 378(11) meV, the glass-ceramic is 390(15) meV, and the glass-ceramic is 380 meV. The similar activation energies between the annealed glass-ceramic and the one-step microwave prepared glass-ceramic are likely a function of the $\text{Li}_4\text{P}_2\text{S}_6$ present in the annealed glass-ceramic increasing the activation energy in what otherwise should have a lower barrier to diffusion considering the high percentage of overall crystallinity in the samples.

The pulsed-field gradient ^7Li NMR of the glass-ceramic indicates that there are two different diffusion processes, one in which Li diffuses slower than the other by approximately an order of magnitude [Figure 4.5(b)]. This is consistent with previous studies using time-of-flight neutron diffraction to distinguish two lithium conduction pathways and previous temperature-dependent $^{6/7}\text{Li}$ studies.^[240, 241] At 40 °C, the first diffusion constant is $8.7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, while the second component has a diffusion constant of $6.8 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. The overall values are consistent with the electrochemical impedance spectroscopy, as the activation energy of the first component is 320(25) meV, and the activation energy of the second component is 330(22) meV.

By filtering chemical shift environments by T_2 relaxation delays, groupings of Li assignments can be determined experimentally, rather than purely by fitting the peaks to Gaussian curves [Figure 4.6(a)]. Despite spinning at 30 kHz using an 800 MHz

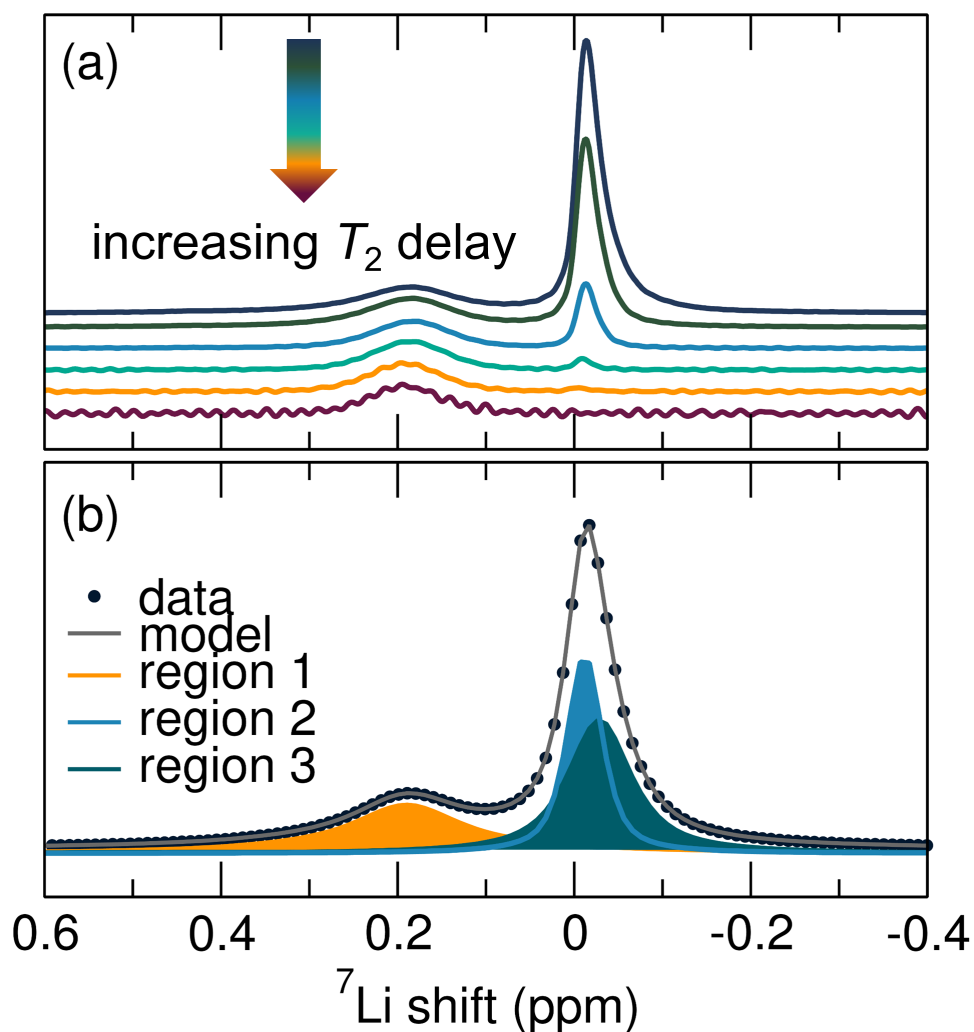


Figure 4.6: (a) ^7Li MAS NMR with varying T_2 delays filters chemical shift environments with similar ion mobilities, indicating the presence of three environments containing similarly behaving lithium sites. (b) ^7Li MAS NMR fit with the three discernible regions from the T_2 filter. While we know there are 7 crystallographic sites, they can generally be grouped into these 3 regions.

spectrometer, the narrow range of ⁷Li chemical shifts and line-broadening means the resolution is not sufficient to parse all 7 crystallographic sites. Even with the T_2 filter, only 3 general environments are observed experimentally [Figure 4.6(b)]. This suggests that the bonding environments in the structure are not vastly different from each other. Increasing T_2 is indicative of faster motion in these systems (and can be thought of as inversely proportional to line width). The most upfield peak at 0.2 ppm has the longest T_2 delay, though is obviously the broadest peak fit to the spectrum. This indicates that there are multiple Li sites encompassed within this larger peak, likely with sharper line widths, that are indistinguishable from each other in terms of their motion and only very slightly in how shielded they are. The two downfield peaks centered at -0.01 ppm and -0.04 ppm disappear as the T_2 delay increases. Though not certain, it is possible these two peaks correspond to the slower diffusing species identified from the PFG NMR, and the 0.2 ppm general environment corresponds to the faster diffusing species.

Microwave-based preparation methods provide a convenient route to preparing lithium thiophosphate solid electrolytes, especially in light of the inherent thermodynamic metastability of these materials. The synthesis can be tuned to achieve varied levels of crystallinity, and when paired with further annealing, opens a wide range of degree of crystallinity that lends flexibility and tunability of mechanical and ionic transport properties. As discussed in previous literature, this is highly consequential when considering building full cells, where the optimal balance of these properties is paramount. Furthermore, this work highlights the need for rigorous characterization using a multitude of techniques that yield insight into both the crystalline and amorphous components of solid electrolyte materials to fully understand the structure-composition-function-performance relationships in these materials.

4.4 Additional characterization and analysis

Table 4.1: Phase fractions and lattice parameters from Rietveld refinements of replicate samples of the glass (top) and glass-ceramic (bottom). These samples were used to calculate the standard deviations of the crystallinity percentages discussed in the main text.

sample	$\text{Li}_4\text{P}_2\text{S}_6$ wt.-%	$\text{Li}_7\text{P}_3\text{S}_{11}$ % crystallinity	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
MW glass ceramic									
1	0	25.6(4)	12.540(2)	6.0289(9)	12.531(2)	102.53(2)	113.42(2)	74.33(2)	830.6(3)
2	1.6(1)	22.9(3)	12.533(2)	6.0285(8)	12.527(2)	102.53(2)	113.38(1)	74.34(2)	830.0(2)
3	2.8(1)	35.5(3)	12.545(1)	6.0285(5)	12.532(1)	102.59(1)	113.456(9)	74.29(1)	830.4(2)
4 ^a	0	33.0(5)	12.522(2)	6.0264(7)	12.530(1)	102.58(1)	113.32(1)	74.44(1)	829.8(2)
5 ^a	0	40.7(5)	12.548(1)	6.0285(5)	12.528(1)	102.61(1)	113.358(9)	74.38(1)	831.2(2)
MW glass ceramic + 2 hr anneal									
1 ^b	5.4*		12.538(1)	6.0279(4)	12.5282(8)	102.666(7)	113.377(6)	74.385(8)	830.2(1)
2	8.6(2)	76(1)	12.529(1)	6.0271(5)	12.528(1)	102.626(10)	113.419(8)	74.360(10)	829.3(1)
3	10.5(2)	82(1)	12.533(1)	6.0261(5)	12.5272(9)	102.615(8)	113.419(7)	74.350(8)	829.4(1)

^a Samples 4 and 5 were not annealed. ^b Sample 1 was not measured with a Si standard after annealing, so percent crystallinity is not available. The weight percent of $\text{Li}_4\text{P}_2\text{S}_6$ is estimated from Rietveld of the standard-less diffraction data by assuming the $\text{Li}_7\text{P}_3\text{S}_{11}$ % phase is 79% crystalline.

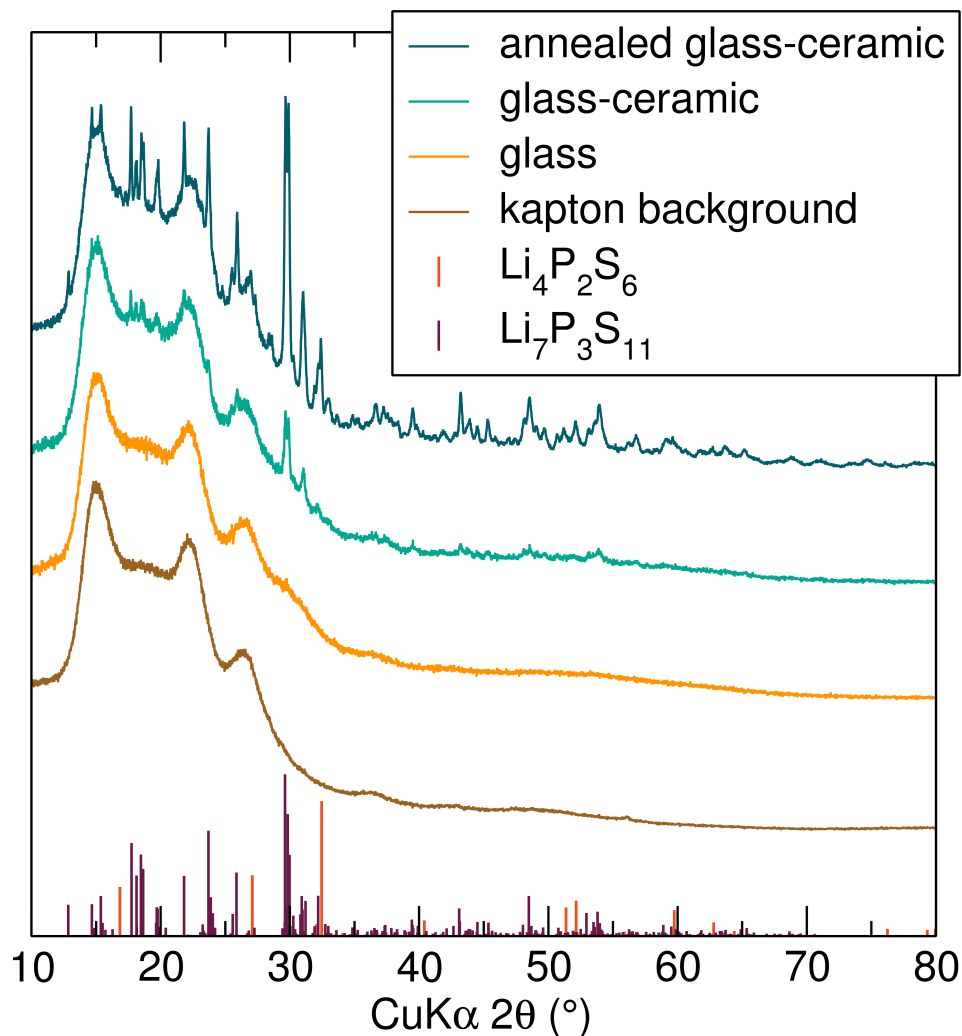


Figure 4.7: X-ray diffraction of the glass, glass-ceramic, and annealed glass-ceramic from a laboratory Cu $k\alpha$ radiation source in a kapton holder to maintain an air-free environment. The kapton background obscures the true nature of the background, but there is a clear progression from more amorphous (glass) to more crystalline (annealed glass-ceramic). However, to fully understand how crystalline the sample is, a key property relating to the conductivity in these samples, high energy X-ray diffraction must be used.

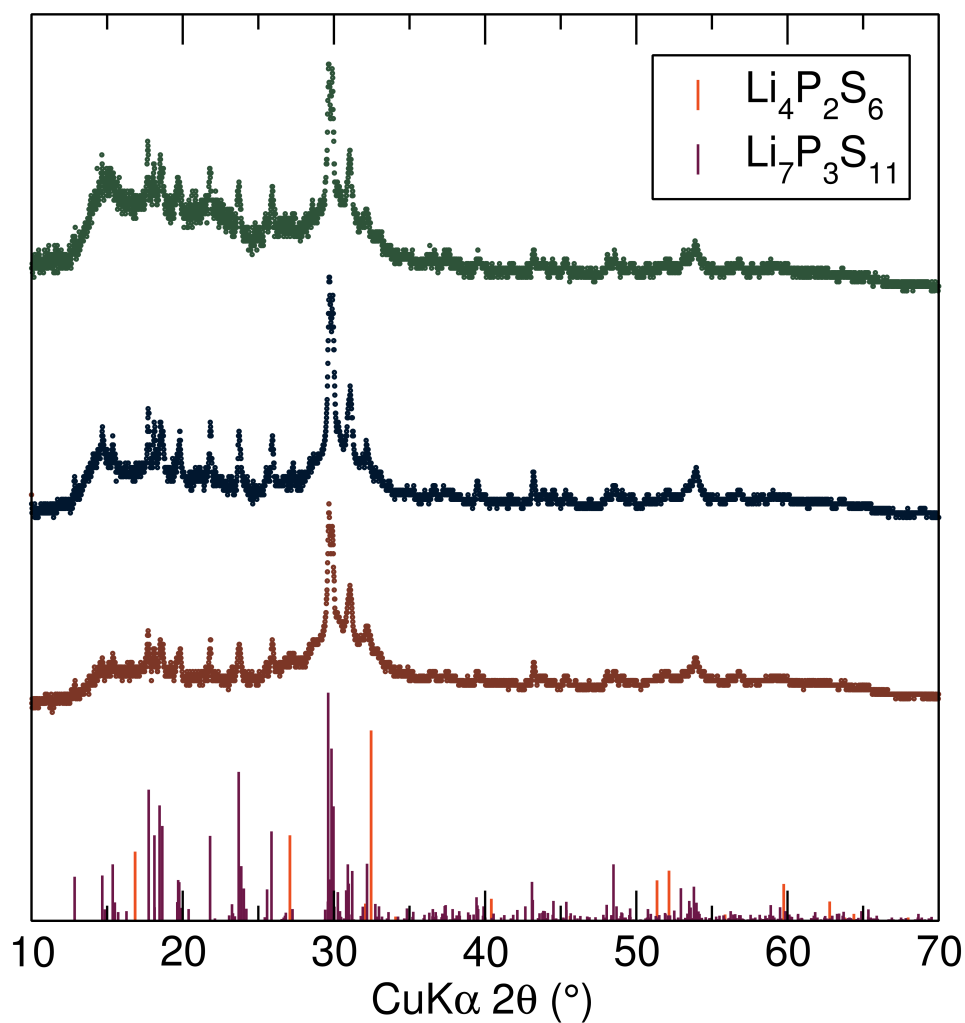


Figure 4.8: XRD patterns of three identically prepared glass-ceramic samples show similar patterns matching the reflections of $\text{Li}_7\text{P}_3\text{S}_{11}$ from the laboratory Cu $k\alpha$ radiation source.

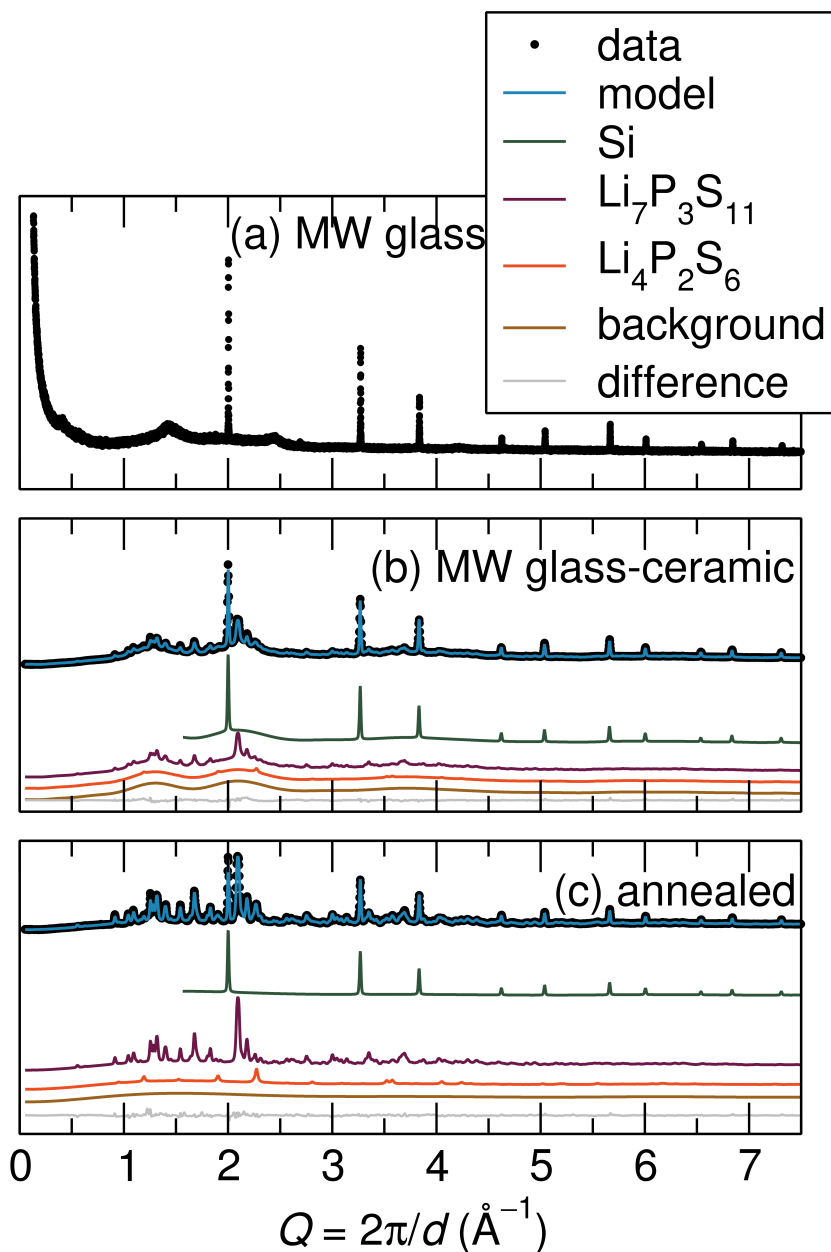


Figure 4.9: Synchrotron X-ray diffraction on (a) a microwave glass sample (from APS 11-BM at Argonne National Lab), (b) microwave glass-ceramic sample (from APS 11-ID-B at Argonne National Lab), and (c) annealed microwave glass-ceramic sample (from APS 11-ID-B at Argonne National Lab) with Si added for crystallinity analyses. The glass does not show any discernible crystalline peaks, so no crystallinity analysis was performed. The microwave glass-ceramic shows negligible $\text{Li}_4\text{P}_2\text{S}_6$ present in the sample ($<2\%$), while in the annealed sample the $\text{Li}_4\text{P}_2\text{S}_6$ grows to a significant proportion of the model.

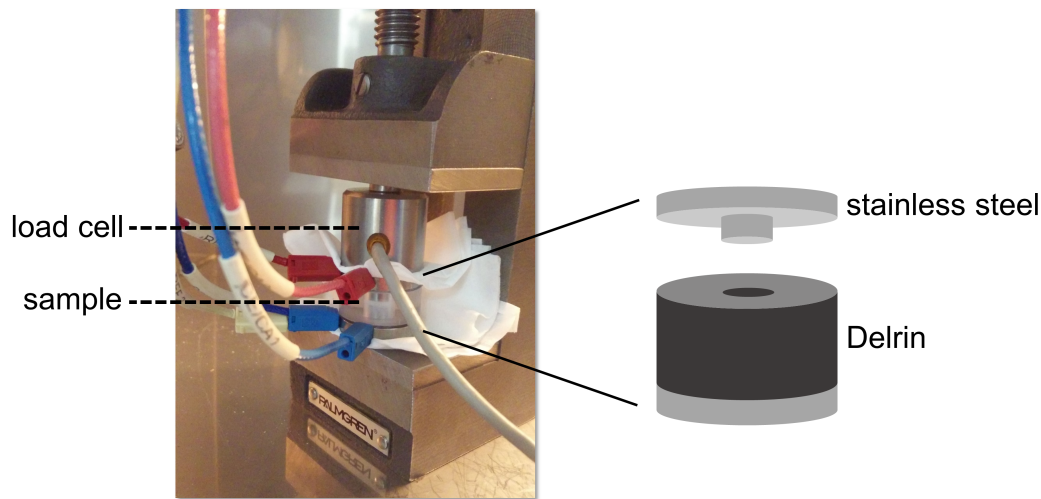


Figure 4.10: The photograph on the left shows the impedance cell, load cell, and vise used to apply pressure on the sample while keeping it air-free for the duration of temperature-dependent measurements. The entire apparatus was inserted into a temperature chamber and allowed to equilibrate fully between measurements to ensure steady-state processes were probed. The body of the cell is constructed from Delrin, and the end-caps were machined from 316 stainless steel to have a tight slip with the body (6 mm cavity). The samples were loaded in an Ar glovebox, and the end-caps were greased with vacuum grease. Once placed in the antechambers, the antechambers were evacuated to create a good seal between the end-caps and the body of the cell before being removed. Either kimwipes or sheets of acrylic were used to insulate the cell from the load cell and vise. The cells were allowed to sinter overnight at the highest temperature of measurement at 5 kN. The force would relax to roughly 4 kN. Before measurement, the vise was retightened to 5 kN and stayed stable at this force throughout the measurement.

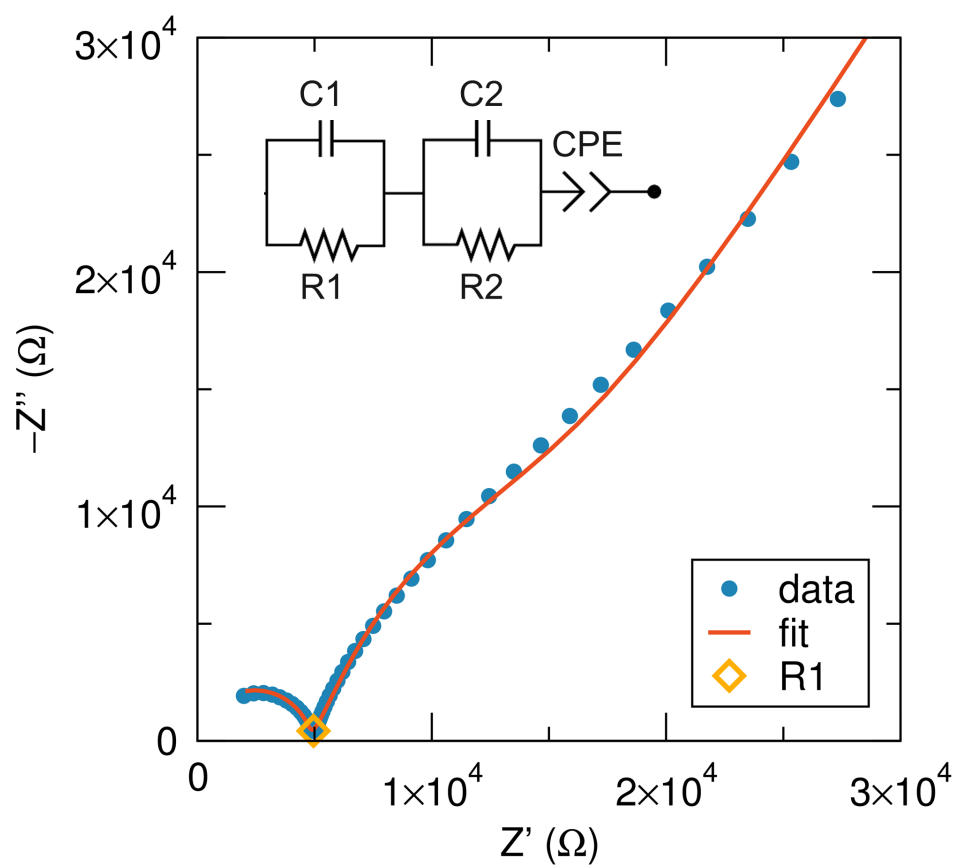


Figure 4.11: A representative Nyquist plot showing the equivalent circuit fit applied to all of the spectra. This single circuit fit all of the spectra from sample to sample as well as at different temperatures. The R1 value can be attributed to the defined semicircle, which is indicative of the ionic conductivity of the Li within the sample.)

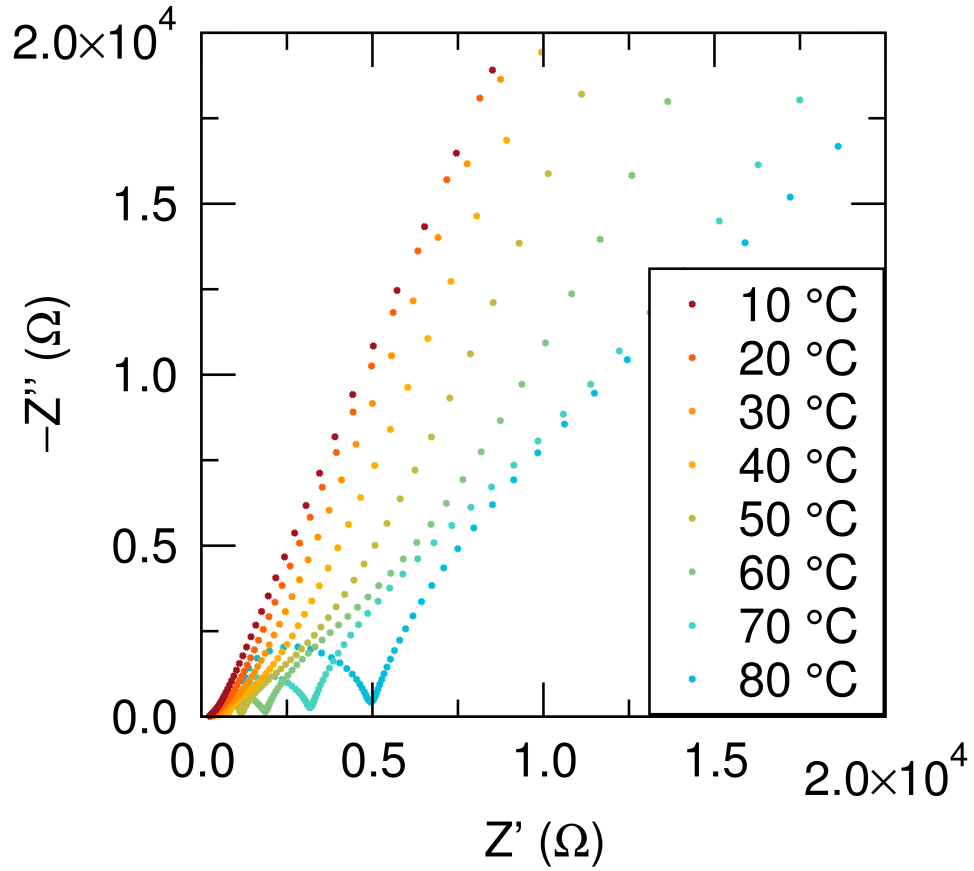


Figure 4.12: Nyquist plots presenting the temperature dependent data for the glass-ceramic (similar spectra were acquired for the glass and annealed glass-ceramic samples) from 10 °C to 80 °C. By fitting these spectra to the above equivalent circuit and extracting the resistance of the defined semicircle, we were able to calculate ionic conductivity values as a function of temperature, leading to the Arrhenius plots presented in the main text.)

Chapter 5

Local Structure Variation in Identically-Prepared Lithium Thiophosphate Glass Solid Electrolytes

1

5.1 Introduction

All-solid-state batteries are gaining momentum as a promising next-generation battery technology to relive many of the concerns and limitations of current Li-ion cells with liquid electrolytes.[186] Inorganic solid electrolytes are attractive because they have the potential to improve safety, simplify cell design, and potentially improve upon energy and power density.[38] However, there are many tradeoffs to consider in order

¹This chapter includes contributions from Jason H. Grebenkemper, Joya A. Cooley, Catrina Wilson, Margaux Everingham, and Ram Seshadri.

to identify materials that could be commercially viable.[242] There are many classes of inorganic solid electrolytes, including fluorides, oxides, and sulfides, among others. One of the main tradeoffs when comparing these three classes of materials is the electrochemical stability window versus lithium and the lithium conductivity at reasonable operating temperatures. While fluorides offer some of the widest stability windows against lithium, the lithium conductivity tends to be relatively poor. [37, 189] Oxides can also have reasonable stability windows against lithium, but conductivity is often still too low to be practical to replace liquid electrolytes. [189?] Sulfides have been shown to exhibit lithium conductivity values on the same order as liquid electrolytes, but the stability window against lithium is very narrow. [39, 208, 243] Therefore, there are many chemical design considerations moving forward to create sensible solid electrolytes for all-solid-state batteries. [244–246]

Since the sulfides do exhibit some of the most promising lithium conductivity values, they are studied widely. Within the lithium thiophosphate system $\text{Li}_2\text{S-P}_2\text{S}_5$, there are several stoichiometries and crystal structures explored in terms of synthesis, ionic conductivity, stability versus lithium, and mechanical properties, all parameters necessary to understand how these materials will perform in a cell. Especially within the $\text{Li}_2\text{S-P}_2\text{S}_5$ system, there are many stoichiometries that form glasses and glass-ceramics, which are crystalline domains stabilized within a glassy matrix. For $70\text{Li}_2\text{S-30P}_2\text{S}_5$, the glass-ceramic crystallizes into the $\text{Li}_7\text{P}_3\text{S}_{11}$ structure [Figure 5.1(a)], and the glass is composed of two main structural motifs present in the $\text{Li}_7\text{P}_3\text{S}_{11}$ structure: the isolated PS_4^{3-} tetrahedron, also known as *ortho*-thiophosphate and the corner-sharing $\text{P}_2\text{S}_7^{4-}$, also known as *pyro*-thiodiphosphate [Figure 5.1(b,c)]. Since $\text{Li}_7\text{P}_3\text{S}_{11}$ is metastable, sometimes the less conductive, thermodynamically-stable product $\text{Li}_4\text{P}_2\text{S}_6$ will form simultaneously, so the $\text{P}_2\text{S}_6^{4-}$ dumbbell, also known as *hypo*-thiodiphosphate can also

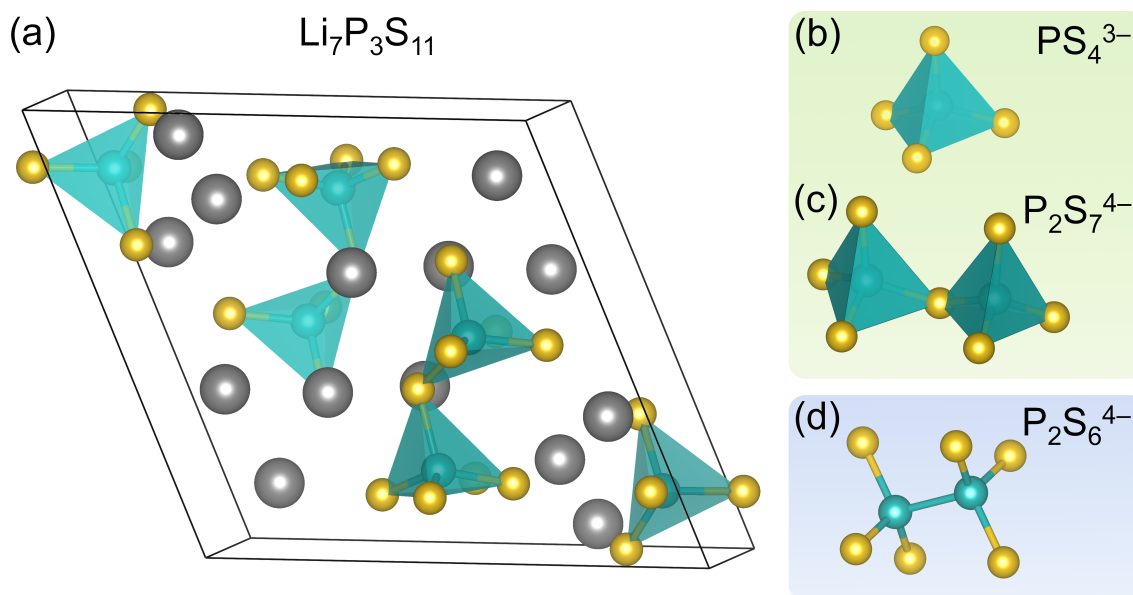


Figure 5.1: (a) Structure of $\text{Li}_7\text{P}_3\text{S}_{11}$, which crystallizes from the $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ glass in the $P\bar{1}$ space group (# 2). On the right, structural motifs observed in the $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ glass. (b) The isolated PS_4^{3-} tetrahedron, also known as *ortho*-thiophosphate. (c) The corner-sharing $\text{P}_2\text{S}_7^{4-}$, also known as *pyro*-thiodiphosphate. (d) The $\text{P}_2\text{S}_6^{4-}$ dumbbell, also known as *hypo*-thiodiphosphate, which is a signature of the thermodynamically-stable $\text{Li}_4\text{P}_2\text{S}_6$ structure that can crystallize from the $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ glass.

be present in the glassy structure [Figure 5.1(e)]. While high $\text{Li}_7\text{P}_3\text{S}_{11}$ content leads to higher conductivity, the glass component is desirable for its compliant mechanical properties, which is important when considering constructing a full cell.[218, 247, 248]

Beyond pure lithium thiophosphates, there are also the $\text{Li}_4\text{GeS}_4\text{-Li}_3\text{PS}_4$ system (LGPS), [192, 193, 249] Si substitution in LGPS, [195, 250] and argyrodites [198–200]. Even in systems that appear crystalline, there can still exist some fraction that is glassy. For example, the LGPS-like compound Li_7SiPS_8 has a crystalline diffraction pattern, but through quantitative phase analysis using both Rietveld refinements on the XRD patterns and integrating NMR spectra, Harm *et al* found between 5-9 wt% of an amorphous contribution depending on the synthesis conditions.[196] In many cases this glassy component would go undetected, but the local structure in these types of materials plays an important role. In order to fully understand the structure-property relationships in these materials, and therefore their function in all-solid-state cells, the entirety of the material must be carefully characterized.

Recently, an important inter-lab collaboration highlighted different conductivity results from measuring the same argyrodite samples, synthesized and shared amongst the labs.[251] Room temperature conductivity values had a relative standard deviation of up to 50%, and activation energies had a relative standard deviation of up to 15%, indicating different densification procedures and measuring methods can yield different conductivity results. We report a complementary study, in which identically made glassy LPS samples are measured using the same processing conditions and experimental setup. The samples are characterized comprehensively using a combination of high resolution synchrotron diffraction, Raman spectroscopy, XPS, and electrochemical impedance spectroscopy, relating the local structure to differences in activation energies.

5.2 Methods

Preparation of 70Li₂S–30P₂S₅ glass The assisted-microwave preparation has been previously reported.[4] Li₂S and P₂S₅ were ground until homogeneous in a 70:30 molar ratio using an agate mortar and pestle in an Ar filled glovebox with H₂O and O₂ < 0.1 ppm. The powder was pressed into a 6 mm pellets comprised of 250 mg, which was sealed in fused silica ampoules under 0.25 atm of Ar (3 inch long, 3/8 inch diameter). The ampoules were individually buried (1 per reaction) in the center of a 250 mL alumina crucible filled with 70g of activated charcoal (DARCO 12-20 mesh). The alumina crucible was then placed a cylinder of alumina fiberboard for insulation and placed off-center in a 1200 W microwave oven (Panasonic NN-SN651B). This was heated at power 4 (40 % of the total power) for 18 min followed by quenching the sample tube in water. This process was repeated for a total of 4 samples under identical conditions, including pellet size, mass, tube length, partial pressure, mass of charcoal, insulation, microwave conditions, and quenching. A previous procedure was followed for the melt-quench method.

X-ray photoelectron spectroscopy X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra X-ray Photoelectron Spectroscopy system with a monochromatic Al source K α (1.4 keV). Samples were prepared in an Ar-glovebox using a stainless steel sample stage with a cover that seals using an o-ring. Once transferred to the chamber, and the chamber was allowed to reach high vacuum, the cover was removed (inside of the chamber). Pass energies of 20 eV (survey scans) and 80 eV (high resolution scans) were detected with a multichannel detector. Dwell times were 80 ms and 5 scans were averaged. The spectra were fit by the least-squares method to pseudo-Voigt functions (Gaussian/Lorentzian 70/30) with Shirley baselines using CasaXPS. All spec-

tra were referenced to adventitious C 1s peak at 284.8 eV. The phosphorus $2p_{3/2}$ and $2p_{3/2}$ peaks were constrained to split by $\Delta = 0.87$ eV, with a relative area ratio of 2:1. Similarly, the sulfur $2p_{3/2}$ and $2p_{3/2}$ peaks were constrained to split by $\Delta = 1.16$ eV, with a relative area ratio of 2:1.

Raman spectroscopy Raman spectroscopic measurements were carried out under inert conditions using a Horiba LabRAM ARAMIS Raman spectrometer equipped with a confocal microscope. Samples were prepared in an Ar-filled glovebox by sealing a glass cover slip over the powder sample on a glass microscope slide. Data was collected with a 633 nm laser excitation, 500 μm hole, 500 μm slit, 1200 cm^{-1} grating, 2 second exposures, and 5 spectra averaged, centered at 450 cm^{-1} . For the crystallization study, a 532 nm laser excitation was used instead. Heating was executed using a TS1200 Linkam stage. Small glass crucibles were made to fit inside of the heating chamber, into which the powder was loaded in an Ar-filled glovebox. The top of the glass crucible was sealed with a 100- μm thick glass cover slip and high temperature epoxy (JB Weld). The laser was focused through the Linkam stage and the glass cover slip. Initial spectra were also acquired at 40 °C, 90 °C, and 190 °C to track the progression leading up to the crystallization temperature regime. Raman spectra were acquired from 240 °C to 310 °C in 5 °C intervals with 10 minute dwell times for equilibration. As a control, data was also collected on samples that were heated and exposed to air, and left in ambient conditions for several hours. This was done to ensure the samples did not degrade during the duration of the crystallization experiments.

Powder X-ray diffraction High resolution synchrotron diffraction data was collected at room temperature at the Advanced Photon Source at Argonne National Laboratories, beamline 11-BM-B using an average wavelength of 0.414581 Å. Samples were loaded

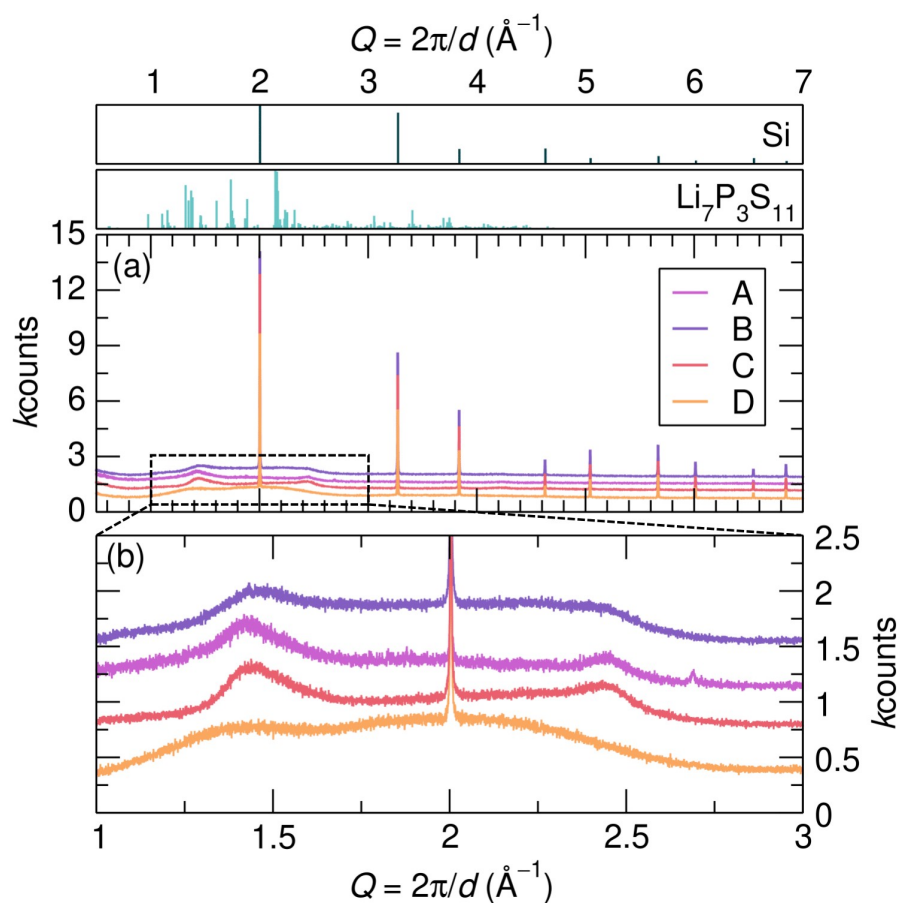
into kapton capillaries and sealed with epoxy inside of an Ar-filled glovebox. They were removed from inert atmosphere minutes prior to measurement. For the powder diffraction, approximately 10 weight percent crystalline silicon was added to each sample (with known exact masses) in order to quantify any crystalline components observed in the material. However, since only amorphous scattering was observed, we did not perform any further refinements. Laboratory powder X-ray diffraction (XRD) data was collected using a Panalytical Empyrean diffractometer with Cu $K\alpha$ radiation. Powders were protected from the atmosphere utilizing an air sensitive holder containing a zero background plate and a Kapton film window.

Electrochemical impedance spectroscopy Electrochemical impedance spectroscopy was measured using a VMP3 Bio-logic potentiostat from 1 MHz to 1 Hz with a 200 mV sinus amplitude under inert conditions. The samples were sintered under approximately 180 MPa pressure at 90 °C for 12 h before being subject to variable temperature measurements. Equilibrium was ensured for all of the data reported here by repeating measurements in succession at each temperature until each spectrum aligned before proceeding with the next measurement. To ensure robust fits, data was collected from 20 °C to 90 °C in 5 °C increments using an environmental chamber. Spectra were also collected at 10 °C in order to clearly fit equivalent circuits to each sample, using ZFit in the ECLab software. The custom cell design used has been described in detail in previous work.^[4] A vise and a force gauge (Omega) were used to press pellets *in-situ* and apply and monitor pressure throughout the measurements.

Comparison to prior literature results Prior literature results were digitized from the plots presented in each corresponding reference. For the data not processed with the Meyer-Neldel compensation, they were replotted such the y -axis reflects $\ln(\sigma T)$,

and the activation energy was calculated from the resulting slopes. In the example of Busche *et al*, the calculated activation energy matched the reported activation using the Meyer-Neldel compensation, giving confidence to the digitization and processing.[233]

5.3 Results and discussion



In order to understand how differences in local structure of identically-prepared samples correlate with their measured conductivity, first we set out to thoroughly characterize the structure of the materials. In order to confirm all of the glass samples are truly amorphous, high resolution synchrotron diffraction was used to characterize the long-range order in these materials [Figure 5.2]. In case any crystalline component was found, the samples were preemptively spiked with 10 wt% NIST standard Si, which would allow us to quantify the crystalline component, noticeably the sharp, high-intensity peaks in Figure 5.2(a). However, no crystalline component relating to $\text{Li}_7\text{P}_3\text{S}_{11}$, $\text{Li}_4\text{P}_2\text{S}_6$, or any of the known crystalline phases in the Li-P-S ternary system were found and therefore the materials are all deemed to be amorphous. In one sample, a very small, unidentified impurity at $2.7 \text{ \AA}^{-1}$ is noticeable, which may be an artifact from preparing the samples inside of the glovebox. It is interesting to note, however, that the amorphous background component in the different diffraction patterns, differ slightly [Figure 5.2(b)]. The patterns for samples **B** and **C** are closely related, which is a theme throughout the characterization.

Raman spectroscopy is a powerful tool to understand the structure in these materials. As a local structure probe, the modes corresponding to the two expected structural features in the glass can be identified. These modes are the strongest in the relevant spectral region, from 0 cm^{-1} to 750 cm^{-1} [Figure 5.3(a)]. Overall, the spectra between the 4 samples are markedly reproducible, exhibiting all of the same peaks at the same positions. A closer look at the region between 340 cm^{-1} and 475 cm^{-1} shows the fine details in intensity in these modes [Figure 5.3(b)]. From previous literature, the mode at 410 cm^{-1} can be assigned to the corner-sharing tetrahedra, and the mode at 423 cm^{-1} can be assigned to the isolated tetrahedron. The spectra were normalized to the intensity of the corner-sharing tetrahedra in order to clearly see how the ratios of

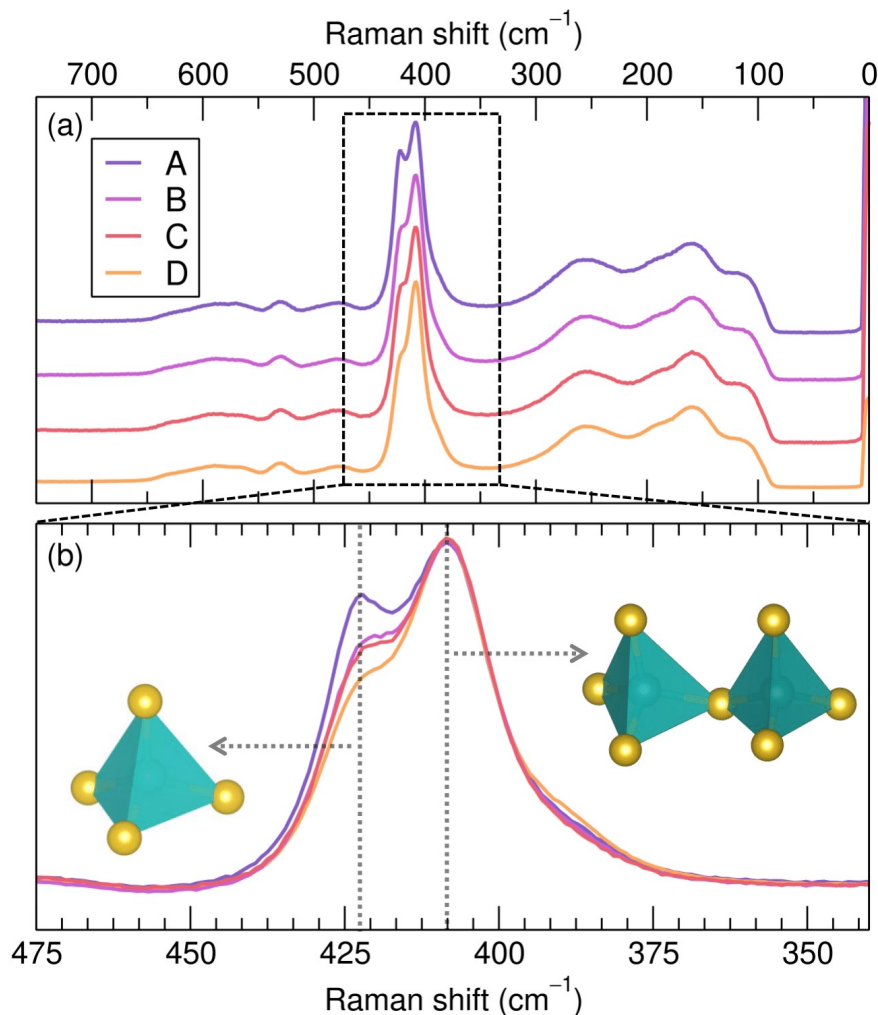


Figure 5.3: Raman spectroscopy is extremely sensitive to the local structure differences of the 4 identically-prepared 70Li₂S-30P₂S₅ glass samples. The spectra were all normalized to the highest intensity peak and strongest mode at 408 cm⁻¹. (a) The entire spectrum shows the same peaks exist for each sample, confirming they are structurally alike. (b) The peaks characteristic of the corner-sharing tetrahedra (408 cm⁻¹) and isolated tetrahedra (423 cm⁻¹) highlight the subtle local structure differences, in which the ratio of these structural features can vary significantly.

the corner-sharing tetrahedra and the isolated tetrahedra differ across the 4 samples. Sample **A** has the highest amount of the isolated tetrahedra. Samples **B** and **C** have very similar ratios, though **B** is slightly higher in the isolated tetrahedra. Finally, sample **D** has much less of the isolated tetrahedra, signaled by the clear decrease in the mode at 423 cm^{-1} . These are relatively large differences in intensity when compared directly that might otherwise go unnoticed. It is also pertinent to note that this is not simply an artifact of the assisted-microwave preparation conditions. We observe similar effects in samples prepared consistently with the melt quench method in an internal study [Figure 5.8]. Since the intensity of the modes differ based on selection rules, these local structure observations remain qualitative. However, XPS provides a quantitative route to characterizing the amount of each structural unit across the four samples.

The phosphorus $2p$ binding energy region is especially telling of the quantitative ratio of the isolated and corner-sharing tetrahedra. A single, convoluted peak-shape is observed for all 4 samples, consistent with previous reports for $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ glasses. The broad peak between 130 eV and 135 eV can be deconvoluted into 4 distinct peaks, which in turn correspond to 2 distinct P states due to the closely-spaced spin-orbit components ($\text{P } 2p_{3/2}$ and $\text{P } 2p_{1/2}$) [Figure 5.4]. The lower binding energy peak (132 eV) is assigned to the P environment within the corner-sharing tetrahedra ($\text{P}_2\text{S}_7^{4-}$) while the higher binding energy peak (132.7 eV) is assigned to the P environment within the isolated tetrahedron (PS_4^{3-}), extensively characterized in previous studies. For clarity, it's easiest to compare the $\text{P } 2p_{3/2}$ peaks against each other across samples (signified by the shaded peak fits in 5.4). Qualitatively, the spectra all appear to be similar, with less of the state corresponding to the isolated tetrahedra than the corner-sharing tetrahedra, as expected according to the composition of the material. The higher binding energy peak appears to decrease from sample **A** through sample **D**.

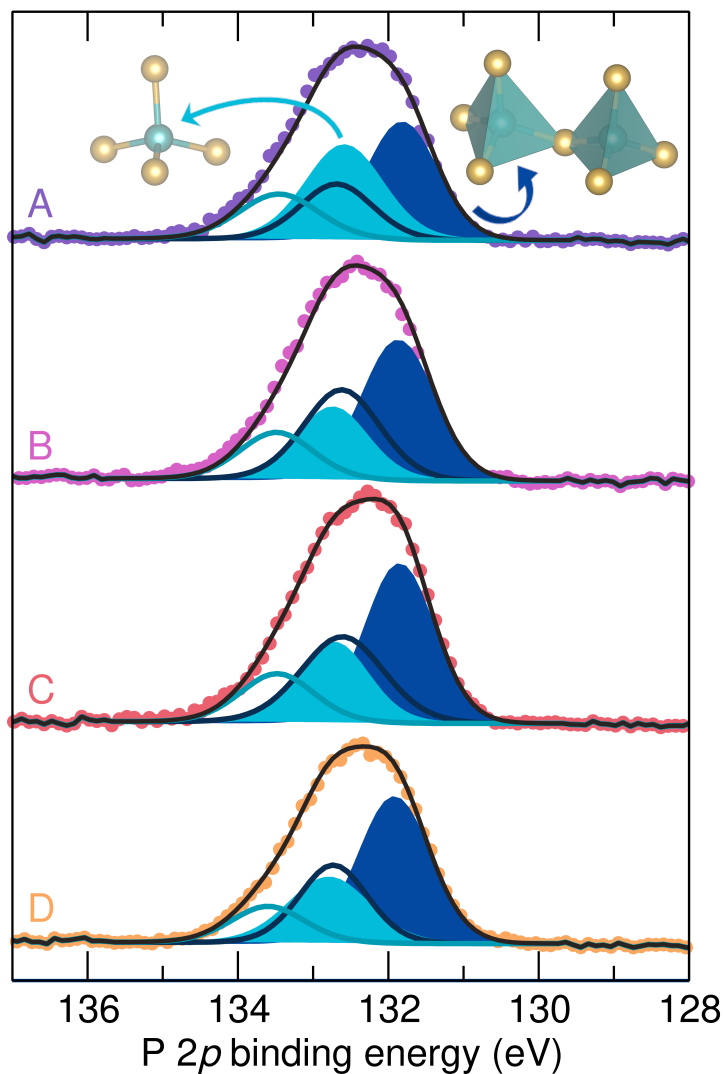


Figure 5.4: P $2p$ binding energy region from high resolution X-ray photoelectron spectroscopy of all four $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ glass samples. The lower binding energy $2p_{3/2}$ peak corresponds to the P in the corner-sharing tetrahedra environment (shaded dark blue), and the higher binding energy $2p_{3/2}$ peak corresponds to the P in the isolated tetrahedron (shaded light blue). The corresponding $2p_{1/2}$ peaks for both environments, shifted toward higher binding energies by $\Delta = 0.87$ eV, are not shaded (outlines only). Quantitative analysis was only performed using the results from the $2p_{3/2}$ peaks. The samples follow a consistent trend as seen in the Raman spectroscopy results.

Table 5.1: Quantitative fitting of the P $2p_{3/2}$ peaks in 70Li₂S-30P₂S₅ glass samples.

		$2p_{3/2}$ position (eV)	FWHM	area	% area	S:P ratio
A	corner-share	131.9	1.08	1130.2	53.0%	3.74:1
	isolated	132.8	1.20	1002.9	47.0%	
B	corner-share	132.0	1.11	1386.5	59.2%	3.71:1
	isolated	132.8	1.19	956.5	40.8%	
C	corner-share	131.9	1.07	1507.0	60.3%	3.70:1
	isolated	132.6	1.29	991.8	39.7%	
D	corner-share	131.9	1.11	1443.3	66.1%	3.67:1
	isolated	132.6	1.06	741.1	33.9%	

This can be described quantitatively by comparing the values corresponding to the peak areas, as reported in Table 5.1. These quantification results are consistent with the trends observed in the Raman spectroscopy, such that sample **A** has the highest concentration of the isolated tetrahedra, followed by samples **B** and **C** (which are very similar), and sample **D** has the lowest concentration of the isolated tetrahedra. The greatest difference, between sample **A** and **D**, is a 13% decrease in concentration of isolated tetrahedra in **D**. Additionally, the similarity between **B** and **C** observed in the XRD and Raman spectroscopy is persists in the XPS quantification. **B** has a slightly higher concentration of the isolated tetrahedra than **C** by 1.1%. The overall S:P ratio per sample can then be calculated based on the relative amounts of the two structural motifs. For the 70Li₂S-30P₂S₅ composition, the ideal S:P ratio is 3.67:1. While all of the samples are within a reasonable range, all of the samples besides **D** are slightly enriched in sulfur. This suggest that the “ideal” composition of the glass should contain approximately 66% corner-sharing tetrahedra and 34% isolated tetrahedra.

While we have established that there is a clear trend in the differences in the local structure between the identically-prepared samples, it is also important to understand how this affects the conductivity in this material. Electrochemical impedance spec-

troscopy was used to characterize the intrinsic Li conductivity in all of the samples (blocking electrode setup). Spectra were collected from 20 °C to 85 °C in 5 degree increments to also calculate the activation energy associated with the Li conductivity [Figure 5.5(a)]. Each spectra were fit to a modified Debye circuit in order to extract the bulk resistance [Figure 5.5(b)], which then was converted to conductivity values using the geometry of the densified sample.

The activation energies for the 4 glass samples were calculated using an Arrhenius-type relationship with the Meyer-Neldel compensation:[237, 238]

$$\sigma T = \sigma_0 \exp\left(\frac{-E_A}{k_B T}\right) \quad (5.1)$$

where σ_0 is the pre-factor, E_A is the activation energy, and k_B is the Boltzmann constant. The Meyer-Neldel compensation was used to take thermally-activated hopping into account (incorporated into the pre-factor term) for an intrinsic Li-ion conductor.[239]

The activation energies are particularly illustrative of how the variations described in the local structure are significant to the properties and function of the material [Figure 5.5(c)]. Sample **A** has the lowest activation energy of 364 ± 4 meV, and **D** has the highest activation energy of 364 ± 5 meV, suggesting a higher concentration of the isolated tetrahedra facilitates Li migration in LPS glasses. **B** also has a lower activation energy than **C** by 9 meV, the least difference between any other sample pair. This corresponds to **B** containing slightly more isolated tetrahedra than **C**, which has been consistent throughout all of the characterization described. The room temperature conductivities (298 K) of all of the samples are on the order of 10^{-4} S cm⁻¹. There are also slight variations between these values, with **A** having the highest room temperature conductivity. Interestingly, **D**'s conductivity is slightly higher than **B** and **C**. Since a sin-

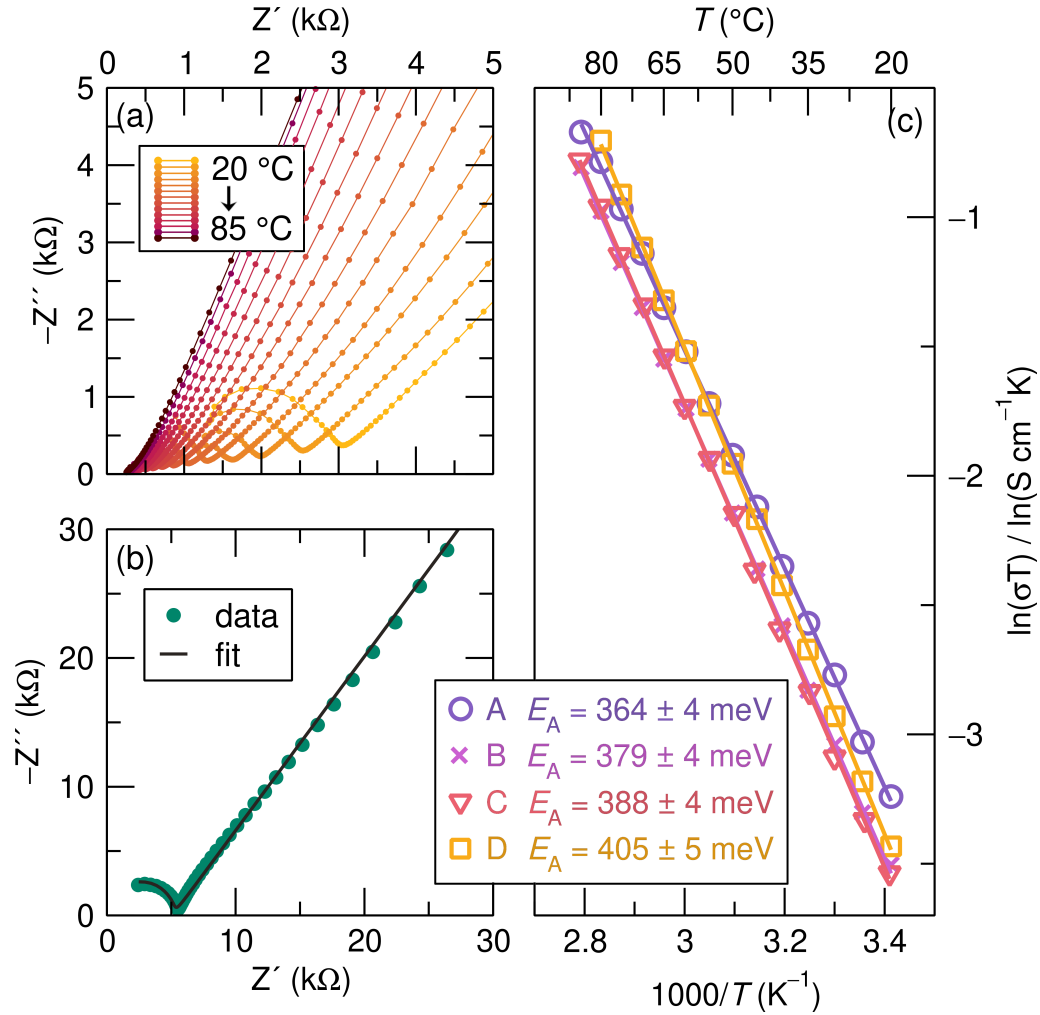


Figure 5.5: Electrochemical impedance spectroscopy in a blocking electrode (stainless steel) setup of the 70Li₂S–30P₂S₅ glass. (a) Representative series of spectra from one of the glass samples showing the evolution of the spectra as a function of temperature, from 20 °C to 85 °C. (b) A representative spectrum at 10 °C with the equivalent circuit fit overlaid. (c) The conductivity of the 4 glass samples as a function of temperature fit to an Arrhenius-type relationship with a Meyer-Neldel correction. The corresponding activation energies for each sample is listed in the legend in units of meV.

gle conductivity value is highly dependent on measurement conditions, the activation energies reported are much more indicative of the trends within the materials.

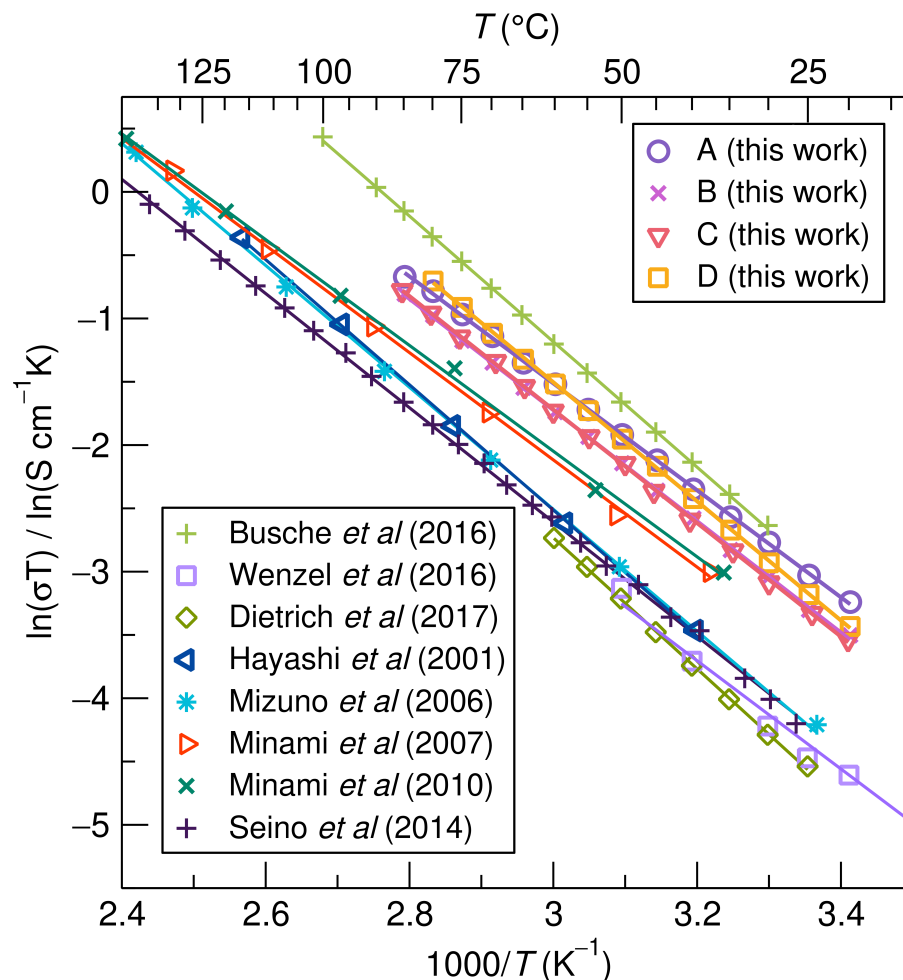


Figure 5.6: Arrhenius-type analysis with Meyer-Neldel compensation of the 4 glass samples presented in this work overlaid with similar samples from prior literature. All of the data corresponds to glass $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ samples, as described in each work, showing a distribution of results within the same glass lithium thiophosphate system. The data was digitized and, when necessary, replotted with the Meyer-Neldel compensation such that all of the datasets are treated identically. Each dataset is fit to a linear equation, and the slope of that equation was used to calculate activation energies. The activation energies calculated and room temperature conductivity values are reported in a subsequent table. Some data was truncated for clarity of comparisons, but the complete datasets can be found in the Supporting Information.

To put these values in context with previous results on this well-studied material, there is a considerable spread of reported values for reported $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ glasses

Table 5.2: Summary of the activation energies and room temperature conductivities found in each corresponding study, along with the preparation method for the 70Li₂S-30P₂S₅ glasses.

	preparation method	E_A (meV)	$T = 298 \text{ K } \sigma$ (S cm ⁻¹)
Busche <i>et al</i> [233]	mechanochemical	425	$1.86\text{E} \times 10^{-4}$
Wenzel <i>et al</i> [208]	mechanochemical	373	$3.83\text{E} \times 10^{-5}$
Dietrich <i>et al</i> [203]	mechanochemical	448	$3.58\text{E} \times 10^{-5}$
Hayashi <i>et al</i> [227]	mechanochemical	433	
Mizuno <i>et al</i> [234]	melt quench	415	5.00×10^{-5}
Minami <i>et al</i> [252]	melt quench	365	
Minami <i>et al</i> [222]	melt quench	360	
Seino <i>et al</i> [39]	melt quench	389	5.00×10^{-5}
A (this work)	assisted-MW	364	1.63×10^{-4}
B (this work)	assisted-MW	379	1.23×10^{-4}
C (this work)	assisted-MW	388	1.20×10^{-4}
D (this work)	assisted-MW	405	1.39×10^{-4}
standard dev		28.2	5.46×10^{-5}
average		395	1.01×10^{-4}

[Figure 5.6]. The conductivity data presented in this study is plotted concurrently with data mined from 8 other studies, specifically of the glass in this exact chemical composition. Since the data is reported inconsistently, where in some cases the Meyer-Neldel compensation is applied and in others a simple Arrhenius relationship is applied, the data was replotted to include the Meyer-Neldel compensation if not already in that form. It is immediately apparent that there are both differences in the activation energies (indicated by the slopes of the Arrhenius relationships) and the room temperature conductivities.

Table 5.2 lists the activation energy values in meV, the room temperature conductivity, and the preparation method for each glass sample. The comparison is based on the assumption that the samples prepared are truly glass samples, and not glass-ceramic samples that are partially crystalline. Given the room temperature conductivity values,

we believe this is a valid assumption. One important caveat to keep in mind while comparing these samples is that conductivity measurement conditions lab-to-lab can differ, which may also affect the spread in reported values.[251] However, the local structure variation that likely exists is also convoluted with the differing measurement conditions. This leads to an overall standard deviation of 28.2 meV for the activation energy of the 70Li₂S-30P₂S₅ glass, and the average activation energy is 395 meV.

Since more attention for practical applications is given to the superionic conductor glass-ceramic (Li₇P₃S₁₁) due to its higher conductivity, it is of interest to elucidate how these local structure effects propagate throughout the crystallization process. While there have been other studies previously on the crystallization process, specific emphasis here is placed on what happens to the ratio of the isolated and corner-sharing tetrahedra during annealing. Results from DSC and other crystallization experiments suggest the crystallization process begins around 240 °C, and many glass-ceramic samples are prepared by annealing the glass between 260 °C and 280 °C for 1 or 2 hours before a significant amount of the undesirable (and thermodynamically-stable) Li₄P₂S₆ forms. Therefore, a few spectra prior to the accepted crystallization regime were recorded – at 40 °C, 90 °C, and 190 °C [Figure 5.7(b)]. At these temperature points the spectra are reproducible, with the same ratios of the isolated and corner-sharing tetrahedra. When the sample reaches the crystallization regime, there is a noticeable shift in the peak positions toward lower wavenumbers, which is consistent with previous literature. Simultaneously, the intensity of the peak associated with the isolated tetrahedra begins to decrease (in this view where the peaks are normalized to the peak associated with the corner-sharing tetrahedra). This is notably before any discernible amount of the Li₄P₂S₆ phase begins to form, so inducing crystallization naturally decreases the ratio of the isolated:corner-sharing tetrahedra. After 255 °C, a detectable amount of the

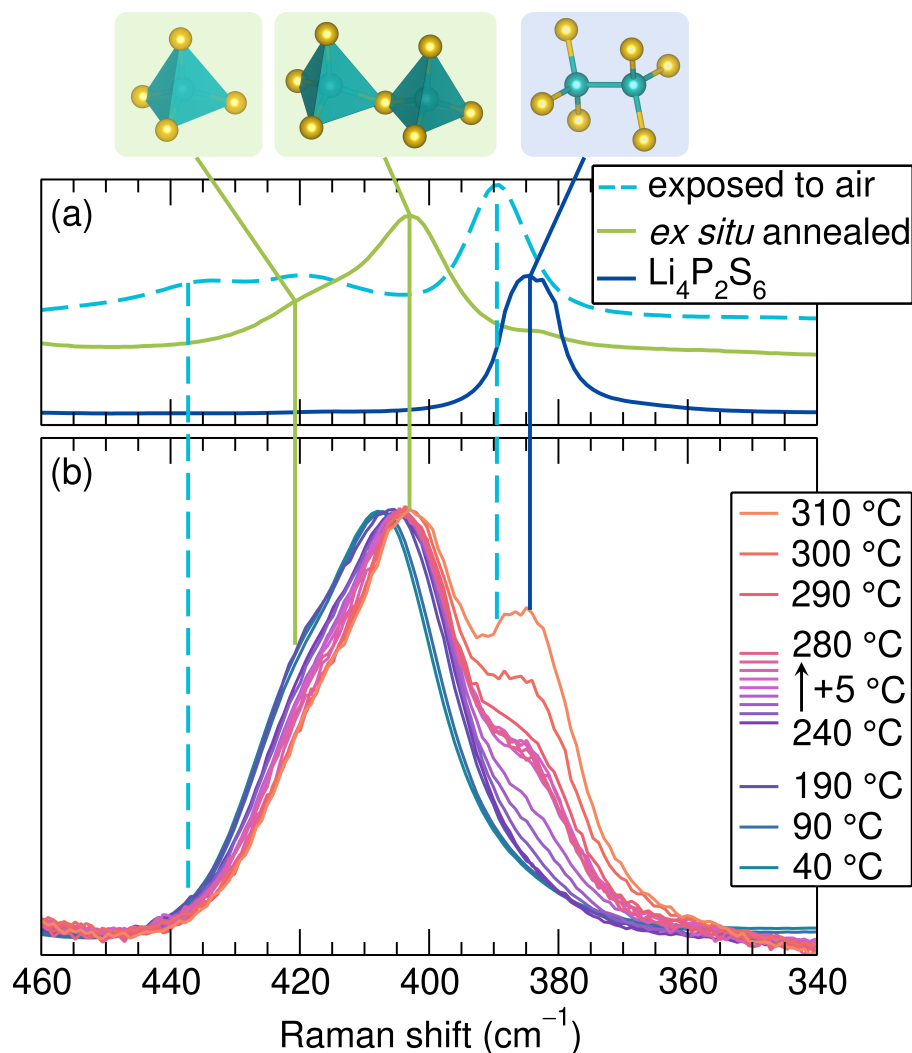


Figure 5.7: Raman spectroscopy of the glass as it is heated *in situ* from 40 °C to 310 °C, causing it to crystallize. (a) Standards and controls to understand the evolution of the spectrum as the sample is annealed. The significant structural features are depicted above, corresponding to the labeled peaks. The sample purposefully exposed to air, as a control, is plotted in dashed lines because we believe there is no evidence for air exposure throughout the experiment. (b) Spectra normalized to the corner-sharing tetrahedra peak at 410 cm^{-1} (average). Data was collected more densely between 240 °C and 280 °C, in the region that has previously been recorded to induce crystallization. The sample and laser were not adjusted during the annealing process, so signal-to-noise decreases steadily throughout, likely due to the transformations of the material. The significant changes observed are: a decrease in the peak intensity associated with the isolated tetrahedron (421 cm^{-1}), a shift in the peak associated with the corner-sharing tetrahedra toward lower wavenumbers (403 cm^{-1}), and an increase in the peak intensity associated with the $\text{P}_2\text{S}_6^{4-}$ dumbbell (385 cm^{-1}), a signature of the $\text{Li}_4\text{P}_2\text{S}_6$ structure.

$\text{Li}_4\text{P}_2\text{S}_6$ phase grows, and by 265 °C through 280 °C, the peak associated to the $\text{P}_2\text{S}_6^{4-}$ dumbbell remains a consistent intensity, along with the peak associated with the isolated tetrahedra. Above 280 °C, the $\text{Li}_4\text{P}_2\text{S}_6$ phase increases significantly. A control experiment was conducted for which a sample was heated and exposed to air in order to make sure the assignments were indicative of the local structure changing due to crystallization and not due to air exposure. The spectra collected for the crystallization study are indicative of a mixture of structural units comprising $\text{Li}_7\text{P}_3\text{S}_{11}$ and $\text{Li}_4\text{P}_2\text{S}_6$.

While many studies have highlighted the importance of processing conditions for tuning conductivity values in glass-ceramic solid electrolytes, *ie* hot-pressing versus cold pressing, or different synthesis conditions leading to different ratios of crystalline versus amorphous components, another factor to be cognizant of is sample-to-sample variation. The glassy nature of these materials lends itself to differences in the local structure, which in turn affect the conductivity properties.

In conclusion, the local structures of identically-prepared 70Li₂S-30P₂S₅ glass samples were studied through Raman spectroscopy and XPS, showing variation in the ratio of isolated to corner-sharing tetrahedra across the different samples. This translates to the activation energies calculated from EIS measurements, delineating that samples with higher amounts of the isolated tetrahedra have lower activation energies. This ratio of isolated to corner-sharing tetrahedra changes throughout the crystallization process, when the glass is heated through 280 °C. Especially when keeping in mind practical applications, this study highlights the need for in-depth understanding of the local structure in these materials, since they will affect the performance of all-solid-state batteries.

5.4 Additional characterization and analysis

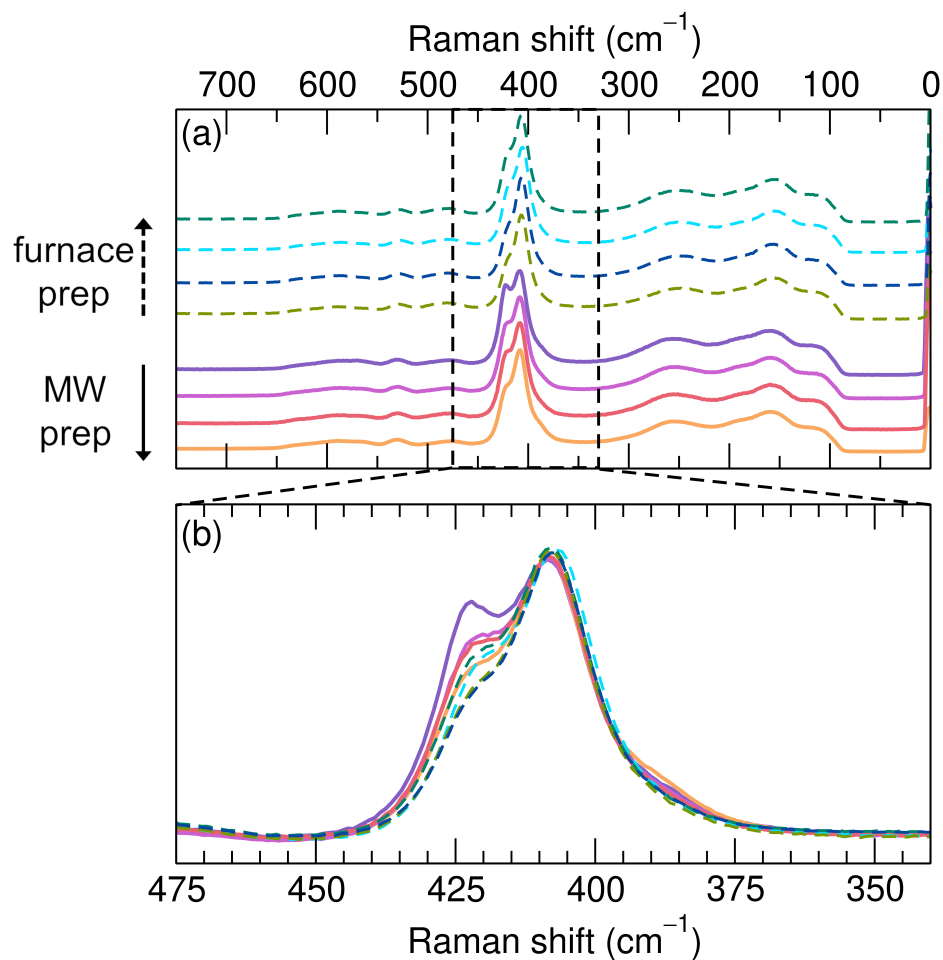


Figure 5.8: A comparison of the Raman spectra of 70Li₂S-30P₂S₅ glass samples prepared via the conventional melt quench method. An internal study reveals the melt-quench method shows the same variations in local structure, and likely all preparations of the glass do.

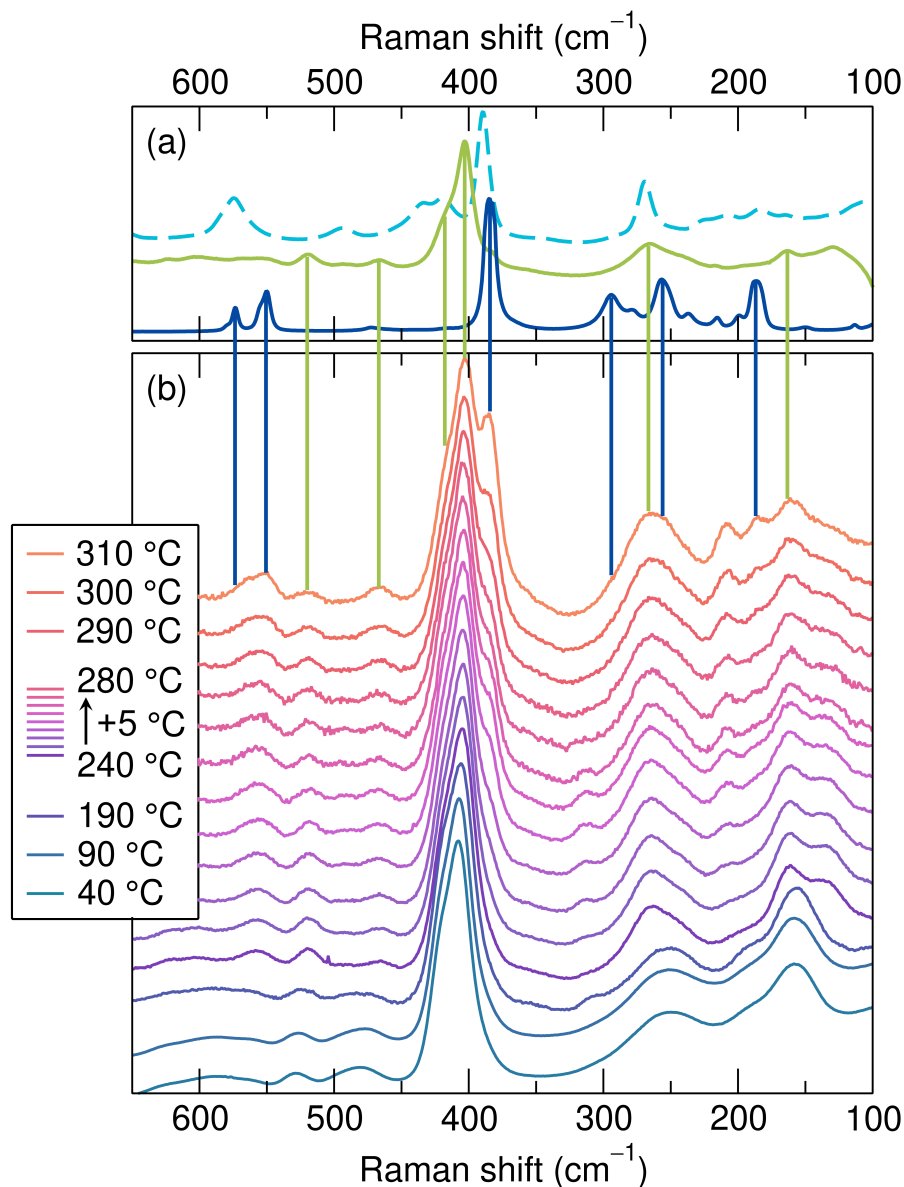


Figure 5.9: The full spectral range for the Raman spectra of the glass as it is heated *in situ* from 40 °C to 310 °C, causing it to crystallize. (a) Standards and controls to understand the evolution of the spectrum as the sample is annealed. The significant structural features are depicted above, corresponding to the labeled peaks. The sample purposefully exposed to air, as a control, is plotted in dashed lines because we believe there is no evidence for air exposure throughout the experiment. (b) Spectra normalized to the corner-sharing tetrahedra peak at 410 cm⁻¹ (average). The spectra are offset in the y-axis.

Chapter 6

Multielectron redox and insulator-to-metal transition upon lithium insertion in the fast-charging, Wadsley-Roth phase $\text{PNb}_9\text{O}_{25}$

1

6.1 Introduction

The next-generation of Li-ion batteries requires both higher energy density and higher power to overcome the challenges of breaking with fossil fuels, especially when

¹The contents of this chapter have substantially appeared in reference 2: M. B. Preefer, M. Saber, Q. Wei, N. H. Bashian, W. Zhang, G. Lee, J. Milam-Guerrero, E. S. Howard, R. C. Vincent, B. C. Melot, A. Van der Ven, R. Seshadri, and B. Dunn. *Chem. Mater.*, 32(11), 4553–4563 (2020). © 2020 American Chemical Society, reprinted with permission.

it comes to electric vehicles. Both increased range and faster charging times are critical to the widespread adoption of electric vehicles, which requires designing new electrode materials.[253] Current anode technology relies mostly upon the use of carbon-based materials (such as graphite), which are unsuitable to fast-charging applications for several reasons. Since the average potential of graphite versus lithium is 0.1 V, the anode faces increased unfavorable reactions with the electrolyte,[254, 255] as well as significant dendrite formation especially at high current densities.[256–258] While the former impacts long-term performance in the cells, the latter poses a significant safety issue that can lead to runaway heat generation and explosions.[259] Furthermore, volume expansion leads to significant particle fracturing, especially at high rates.[260] Therefore, anodes with higher voltages and small volume expansion are more suitable for high-power applications, with the compromise of slightly reduced energy density [255].

There has been a wealth of research on hierarchical and nanoscaled anode materials. Nanostructuring provides the most direct approach to reducing diffusion pathways for lithium to insert, therefore allowing higher rate cycling.[261–263] This approach has proven successful in a variety of materials, particularly TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. [264–266] With the example of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, there is almost zero volume change upon lithium insertion, allowing fast lithium insertion and deinsertion without the negative effects of particle fracturing that degrades the electrode material with repeated cycling, as well as an average voltage of 1.5 V, avoiding the aforementioned issues with cycling to low-voltage.[267, 268] However, in order to circumvent the low ionic conductivity in the delithiated and lithiated phases, the material must either be nanostructured or prepared with induced porosity to create short Li diffusion path lengths.[265] Despite starting as electronically insulating, the lithiated phase $\text{Li}_7\text{Ti}_5\text{O}_{12}$ is electronically con-

ductive, which allows for cycling of the material without the addition of conductive carbon additives at reasonably high rates.[268, 269] This is not the only example of a host electrode material undergoing an insulator-to-metal transition. The canonical intercalation material LiCoO_2 , popularized by Goodenough and coworkers and later commercialized,[26] undergoes an insulator-to-metal transition,[270, 271] which is highly favorable, especially when it comes to fast cycling when the transition metals are required to acquire and release electrons rapidly.

More recently, crystallographic shear phases derived from the ReO_3 structure — also known as Wadsley-Roth phases — have been popularized for their record-breaking rate-capabilities as electrodes in lithium batteries despite electrodes being prepared with particle sizes on the order of microns.[272–274] While few so far have been studied in-depth to understand the origin of their high rate capabilities, it is believed that the regions of edge-sharing octahedra are the key to success, providing delocalized pathways for electrons, and structural rigidity to suppress large changes in the structure upon lithiation.[3, 275] In the absence of crystallographic shear, as in the case of ReO_3 , the octahedra are allowed to freely rotate upon lithium insertion, which appears to degrade the material upon cycling.[276, 277] Additionally, many Wadsley-Roth phases are attractive electrode materials due to their high capacity as compared to conventional materials, arising from more than one Li ion inserted per transition metal. For example, TiNb_2O_7 , which is now commercialized, is able to accommodate 1.25 Li per transition metal at a rate of C/5,[3] in conjunction with a small unit cell volume expansion of 7 % when Li^+ is inserted, which is then almost entirely reversible.[278] In the same vein, $\text{PNb}_9\text{O}_{25}$ has previously been reported to have little lattice expansion upon lithium insertion by *operando* diffraction, about 7.5 %, suggesting promise as a high rate electrode material.[279] Additionally, both of these materials have demon-

strated high Li diffusion coefficients, with $\text{PNb}_9\text{O}_{25}$ three orders of magnitude higher than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, [280] further alluding to its promise as a high rate electrode material without nanostructuring.

The existence and preparation of such non-stoichiometric transition metal oxides, including bronze phases and Wadsley-Roth phases [281–284] have been known since the 1950s and 1960s. Chemical and electrochemical lithium insertion into these materials began in the 1980s. Seminal work by Murphy *et al.* [27, 285] and Cava *et al.* [286] introduced reversible lithiation in shear phases such as V_6O_{13} , TiNb_2O_7 , Nb_2O_5 , $\text{W}_8\text{Nb}_{18}\text{O}_{69}$, $\text{W}_{2.5}\text{V}_{0.5}\text{O}_7$, and $\text{VNb}_9\text{O}_{25}$. Through the amount of lithium inserted, and later through *ex situ* and *operando* diffraction, it was presumed that a common trait of these crystallographic shear structures is more than one Li inserted per transition metal. [279, 285, 287, 288]

$\text{PNb}_9\text{O}_{25}$ is an interesting model system to study in the realm of the Wadsley-Roth crystallographic shear structures, in that most of the structures contain only corner- and edge-sharing octahedra. First reported in 1965 by Roth *et al.*, [281, 289] the structure of $\text{PNb}_9\text{O}_{25}$ is created from shearing 3×3 blocks of ReO_3 -type metal-oxygen octahedra, leaving space for a tetrahedral bridging site between blocks (Figure 6.1), which has been refined to be half-occupied. [290] The phosphorus is incorporated in PO_4 tetrahedra and can also be substituted by redox-active vanadium, and presumably other elements that have affinities for tetrahedral environments, in the same crystal structure. While the small abundance of phosphorus and vanadium initially seems inconsequential, the difference between a redox active and redox inactive element in the tetrahedral site changes the fundamental redox mechanisms underlying the battery performance. This opens a wide range of chemical tuning to target electrochemical properties of interest in identical structures. Interestingly, incorporating vanadium actually leads to

a decrease in rate performance and capacity retention despite providing another redox active element. The comparison between $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ shows that small chemical changes within these structures can lead to disproportionately large electrochemical differences.

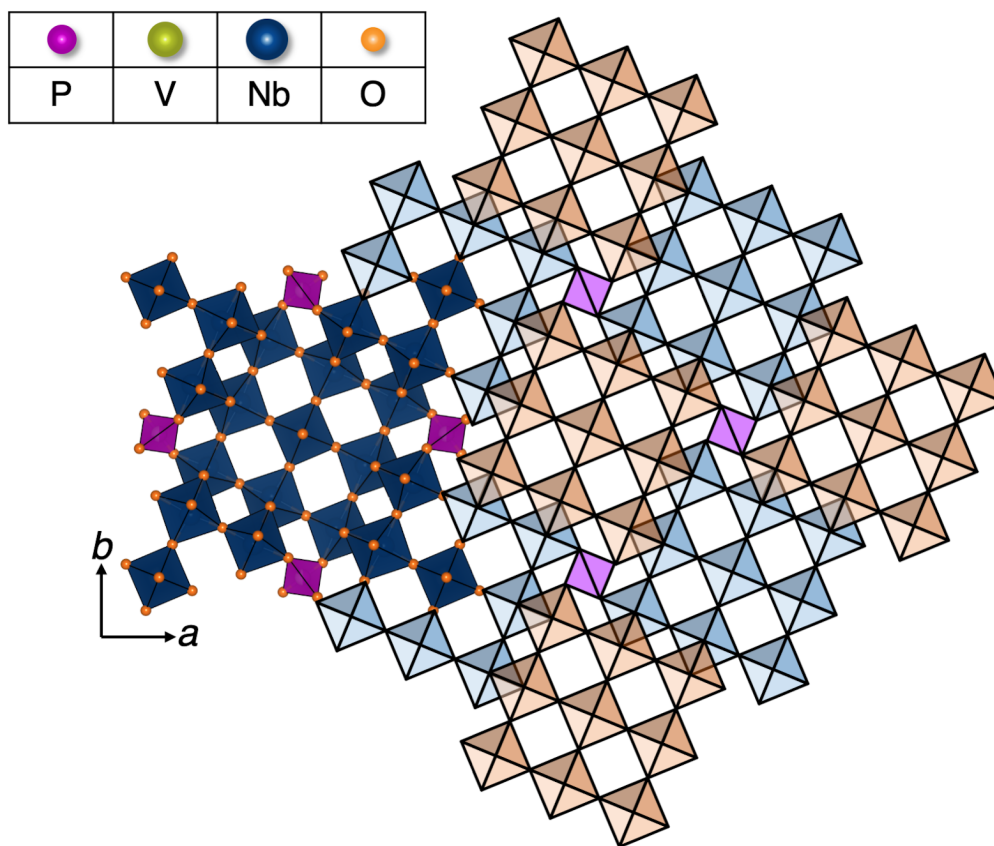


Figure 6.1: Crystal structure of $\text{PNb}_9\text{O}_{25}$ as derived from the ReO_3 structure. On the left is the real structure, and on the right, a scheme comprising $3 \times 3 \times 1$ blocks of Nb–O octahedra offset to create corner- and edge-sharing moieties. P (or V) bridge the offset Nb–O blocks with half-occupancy on the tetrahedral site. The distinct colors of the octahedral blocks on the right indicate their relative positions along the c direction. The space group is $I4/m$ (# 87).

We report for the first time fast, reversible cycling up to 60C in $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ on the order of microns, with greater capacity in $\text{PNb}_9\text{O}_{25}$ despite having fewer redox active elements, as well as high capacity retention over 500 cycles at a

rate of 2C. This motivates the practical use of $\text{PNb}_9\text{O}_{25}$ as a next-generation Li-ion electrode material that can be charged to 85% of its theoretical capacity in 30 minutes, even without much electrode optimization. Kinetic analysis shows the underlying difference in rate performance in $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ to be related to many redox reactions in $\text{PNb}_9\text{O}_{25}$ being surface-controlled versus bulk-controlled in $\text{VNB}_9\text{O}_{25}$. Additionally, X-ray absorption near-edge spectroscopy (XANES) and X-ray photoemission spectroscopy (XPS) provide direct evidence of multielectron redox in both materials and point to the fundamental cause for electrochemical differences in these isostructural electrode materials. Finally, through a combined experimental and computational approach we show direct evidence for an insulator-to-metal transition in $\text{PNb}_9\text{O}_{25}$, which likely is a larger feature of crystallographic shear structures with channels of edge-sharing octahedra, as suggested here from Density Functional Theory-based calculations of the electronic structure of pristine and lithiated $\text{PNb}_9\text{O}_{25}$.

6.2 Methods

6.2.1 Solid-state preparation of $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$

$\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ were prepared using bulk solid state methods, starting from stoichiometric ratios of Nb_2O_5 (Materion, 99.95%) and $(\text{NH}_4)_3\text{PO}_4$ (Sigma Aldrich, 98%) or Nb_2O_5 (Materion, 99.95%) and V_2O_5 (Materion, 99.9%), respectively, following previous procedures.^[279, 291] To prepare $\text{PNb}_9\text{O}_{25}$, a ground stoichiometric mixture of Nb_2O_5 and $(\text{NH}_4)\text{H}_2\text{PO}_4$ was pressed into a 6 mm pellet under 2.5 metric tons of force with a total mass of 500 mg. Pellets were annealed in an alumina crucible in air at 623 K for 20 h and subsequently annealed at 1523 K for 18 h before being allowed

to slow cool. To prepare $\text{VNb}_9\text{O}_{25}$ a ground stoichiometric mixture of Nb_2O_5 and V_2O_5 was pressed into 6 mm pellets under 2.5 metric tons with a total mass of 500 mg. Pellets were annealed in an alumina crucible in air at 1053 K for 48 h, and then allowed to slow cool. Purity was confirmed through powder diffraction data collected at the high-resolution beamline 11-BM at the Advanced Photon Source at Argonne National Laboratory for $\text{PNb}_9\text{O}_{25}$ ($\lambda = 0.457841$) and at the high-throughput beamline 17-BM for $\text{VNb}_9\text{O}_{25}$ ($\lambda = 0.4524 \text{ \AA}$). The patterns were refined using the Rietveld method using TOPAS Academic v6. Both patterns were well-refined within previously reported structures in the $I4/m$ (# 87) space group.[290, 292] A Crystallographic Information File is provided in the Supporting Information with the refined structure for $\text{PNb}_9\text{O}_{25}$.

6.2.2 Electrochemical testing

The active material was cast on copper foil in a ratio of 75% active material, 10% polyvinylidene fluoride (Solef), and 15% carbon black (TIMCAL Super P). First, the active material was ball milled for 30 minutes with the appropriate ratio of carbon black in a 2 cm³ canister. The active material/carbon mixture was then added to a mixing cup with PVDF dissolved in NMP. The slurry was mixed in a FlackTek speed mixer at 2000 rpm for 15 minutes. Approximately 1.5 cm³ of NMP was used for 100 mg of slurry. The slurry was cast onto copper foil using a 150 μm doctor blade, dried under vacuum at 90 °C, and punched into 10 mm diameter discs such that there is approximately 1.5 mg cm⁻². The cells were cycled in coin cell configuration (MTI parts, 2032 SS casings) using 1 M LiPF_6 in EC/DMC 50/50 v/v (Sigma Aldrich) versus a polished Li foil counter electrode with Celgard C480 polypropylene/polyethylene separators. Based on the number of pockets for Li to sit and the number of redox-active elements, 12 Li were assumed to insert into $\text{PNb}_9\text{O}_{25}$, and 14 Li were assumed to insert into $\text{VNb}_9\text{O}_{25}$ for

calculating C rates.

6.2.3 X-ray photoelectron spectroscopy

The same samples prepared for *ex situ* X-ray diffraction were used for XPS and were loaded onto an air-free sample holder in an Ar-filled glovebox. The powder was spread onto double-sided scotch tape attached to a stainless steel sample holder. A lid with an o-ring seal was secured onto the sample holder to transfer the samples into the XPS chamber. Once under vacuum, the lid was removed such that the samples were never exposed to air. The samples were measured using a Thermo Fisher Escalab Xi+ XPS equipped with a monochromated Al anode ($E = 1486.7$ eV). Survey scans were collected at 100 eV pass energy for 20 ms, averaged 2 times. High resolution scans were collected in the Nb $3d$, P $2p$, V $2p$, O $2p$, and Li $1s$ regions at 20 eV pass energy for 100 ms, averaged 15 times. All spectra were referenced to adventitious carbon at 284.8 eV. Fits were executed using CasaXPS: Shirley backgrounds, GL(30) peak shapes, and peaks within elemental regions with spin-orbit splitting were locked to their appropriate ratios and energy splitting according to the element.

6.2.4 Operando X-ray Absorption Spectroscopy

Pellet electrodes were fabricated with 60% active material, 10% acetylene black, 10% graphite powder (300 mesh) and 20% polytetrafluoroethylene (Sigma Aldrich, 1 μm average particle size), pressed in a 10 mm die under a hydrostatic pressure of 1 metric ton with approximately 20 mg total material. The pellet electrodes were cycled versus polished Li foil with glass fiber GF/D separators soaked in LiPF_6 in EC/DMC 50/50 v/v in AMPIX cells at Beamline 12-BM at the Advanced Photon Source, Argonne

National Laboratory. This method was adapted from Borkiewicz *et al.*[293] The cells were cycled at a C/10 rate. Simultaneously, the absorption was measured at the Nb K-edge (18.9 keV), calibrated using Nb foil. Data was collected in transmission mode over 8 minutes. Processing and analysis of the XANES region was done using ATHENA, an open source software package for XAS, and the edge position was determined by the zero-crossing of the second derivative.[294]

6.2.5 Electrochemical impedance spectroscopy

$\text{Li}_x\text{PNb}_9\text{O}_{25}$ at discrete lithiated states was prepared in 1.5 inch diameter Swagelok cells to accommodate approximately 100 mg of pure $\text{PNb}_9\text{O}_{25}$ powder in a thin layer without the addition of binder or carbon. The active material was cycled against polished Li metal using 1 M LiPF_6 in EC/DMC 50/50 v/v (Sigma Aldrich). The cells were discharged at a C/60 rate to the chosen potentials. The active material was extracted from the cells in an Ar-filled glovebox and ground with an agate mortar and pestle. In order to probe the intrinsic conductivity, the samples were washed three times with dimethyl carbonate in order to remove LiPF_6 from the electrolyte, centrifuged, and dried under vacuum. Approximately 60 mg of powder was pressed into a blocking electrode cell, using stainless steel plungers and a Delrin body (electrically insulating). A full description of the cell and setup has been previously reported.[4] The end caps are greased in order to maintain an air-free environment within the cell. The material was cold pressed to 10 MPa, then transferred to an environmental chamber and continuously pressed to approximately 100 MPa using a vise and a load cell for monitoring the force. Before measurements were started, the material densifies under these conditions for 15 hours. The conditions for the electrochemical impedance spectroscopy measurements are as follows: 1 MHz to 100 mHz at an amplitude of 25 mV to 100 mV,

depending on the signal from each sample, averaged twice per measurement, with 10 points per decade. Temperature was swept from 258.15 K to 318.15 K, and the samples were allowed to equilibrate for 45 minutes. in between each temperature point.

6.2.6 Nuclear Magnetic Resonance

Solid-state MAS ^{31}P NMR spectra were acquired on a Bruker AVANCE III Ultra-shield Plus 800 MHz (18.8T) NMR spectrometer equipped with a Bruker 2.5mm HX MAS probe. $\text{PNb}_9\text{O}_{25}$ was packed in a 2.5 mm zirconia rotor in air. $\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$ was prepared identically to the sample described for the corresponding EIS measurement (discharged to 1 V) and was packed in a 2.5 mm zirconia rotor in an Ar-filled glove-box. Both spectra were referenced to solid triphenylphosphine and processed using Bruker TopSpin software. The recycle delay was optimized and found to be 3.2s for quantitative analysis. Single pulse experiments were used to obtain the 1d spectra.

6.2.7 Magnetic susceptibility measurements

Magnetic susceptibility as a function of temperature was collected using a Quantum Design Magnetic Property Measurements System (MPMS-3). Measurements were performed on three powder samples with different levels of lithiations, prepared identically to the samples described for EIS measurements, such that there were no carbon or binder additives. The cells were discharged to 1.75 V, 1.4 V, and 1 V corresponding to $\text{Li}_{1.8}\text{PNb}_9\text{O}_{25}$, $\text{Li}_{8.0}\text{PNb}_9\text{O}_{25}$, and $\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$, respectively. Weighed, powdered samples were loaded into sealed polypropylene capsules within an argon glovebox and transferred to the magnetometer without exposure to air. From magnetization vs. field hysteresis loops at room temperature, all samples were found to contain small amounts

of a ferromagnetic impurity, which was traced back to the ball-milling process. In order to measure the true susceptibility of the bulk sample without the ferromagnetic impurity signal, magnetization measurements at each temperature were performed at two different fields which were chosen to be above the field at which the ferromagnetic impurity saturates. The differential magnetic susceptibility was then calculated from those data points. Details of this procedure are provided in the Supporting Information.

6.2.8 Electronic structure calculations

Density functional theory (DFT) calculations were performed with the Vienna *ab initio* Simulation Package (VASP)[295–298] using the Perdew-Burke-Ernzerhof (PBE) functional.[299] The plane wave basis energy cutoff was set at 550 eV. All relaxations were followed with static calculations. The fully relaxed energies of a total of 1130 different Li-vacancy orderings over octahedral sites of the $\text{PNb}_9\text{O}_{25}$ host were calculated. Benchmark calculations showed that spin polarization has a negligible effect of the energies, and subsequent relaxations were performed in the absence of spin polarization. For each of the calculated ground state configurations, the spin polarized electronic density of states was calculated. A k -point mesh of density $50 \text{ \AA}^3$ was employed. Charge density calculations were performed for bands beneath and within the range of the Fermi level. Gaussian smearing was used with a width of 0.1 eV. Visualization of the Nb t_{2g} state density on discrete lithiated states was done using VESTA.[300]

6.3 Results and discussion

6.3.1 Electrochemical properties

Understanding the electrochemistry of $\text{PNb}_9\text{O}_{25}$ is enhanced by comparing it to its closely related counterpart $\text{VNb}_9\text{O}_{25}$. Despite $\text{PNb}_9\text{O}_{25}$ and $\text{VNb}_9\text{O}_{25}$ being isostructural, varying the tetrahedral site atom immensely alters the electrochemistry and mechanism in which lithium inserts into the structure, particularly at varying rates and over long-term cycling. This is especially surprising given the low abundance of phosphorus or vanadium in the structure. The difference, however, lies in the fact that vanadium is redox active, whereas phosphorus is redox inactive, lending a clue into the importance of the surrounding pocket sites or pyramidally-coordinated sites available for lithium to insert. $\text{PNb}_9\text{O}_{25}$ exhibits more structure in its galvanostatic response, which can be observed in detail when cycled slowly at a C/20 rate [Figure 6.2(a)]. There is a small initial plateau at 1.95 V that incorporates about 0.3 Li experimentally, which leads into a sloped region until about 1.69 V for a total of 1.85 Li. The largest plateau at 1.69 V ends at about 4.5 Li, and then a large, undulating sloping region incorporates up to 10.3 Li total. Finally, there is a small plateau at 1.6 V, and a total of about 11.5 Li inserts into the structure. The capacity loss associated with the first charge is the largest, 1 Li, but thereafter is only small fractions of Li. The structure of the galvanostatic curve maintains its integrity throughout cycling, and the slopes and plateaus are highly repeatable.

The galvanostatic behavior from inserting Li into $\text{VNb}_9\text{O}_{25}$ shows a quite different profile [Figure 6.2(b)]. The first discharge has a large sloping region incorporating about 4 Li, a small plateau at 1.7 V inserting a total of 7 Li, and a large sloping region until about 13.5 Li. The subsequent charge is much less reversible – more than 3 Li are

not removed. This is in agreement with previous slow cycling results on both micron-sized and nano-sized particles.[279, 286, 301] Subsequent cycles do not exhibit the same large sloping region at the beginning of discharge. The capacity loss cycle-to-cycle is much more significant than with $\text{PNb}_9\text{O}_{25}$. For both materials, the lower voltage cutoff (1 V) was chosen to avoid convolution with Li storage in carbon, which can add anomalous capacity.[302]

When the rate is increased to 2C, the differences in electrochemistry are further exacerbated [Figure 6.2(c) and (d)]. The same plateau and structure are maintained in the $\text{PNb}_9\text{O}_{25}$ electrochemical curve, with slightly increased polarization. $\text{VNb}_9\text{O}_{25}$ still exhibits the large irreversible capacity on the first discharge and greatly increased polarization. When cycled at 2C long-term, both have high capacity retention over 500 cycles, though interestingly $\text{PNb}_9\text{O}_{25}$ maintains much higher capacity than $\text{VNb}_9\text{O}_{25}$ by almost a factor of two (190 mAhg^{-1} versus 100 mAhg^{-1} at the 500th cycle, respectively), as seen in Figure 6.1(e).

Cyclic voltammetry at varying rates makes the underlying kinetic differences more apparent. Multiple redox processes can be teased out in the CV curve of $\text{PNb}_9\text{O}_{25}$ from 1 V to 3 V, whereas there is only one distinct redox reaction revealed in the CV curve of $\text{VNb}_9\text{O}_{25}$. Varying the rates allow values of the exponent b to be calculated for each of these processes, which reveals which redox reactions are bulk- or surface-limited according to the power law relationship $I = av^b$, where I is the current, v the voltage sweep rate and a and b are fitting parameters.[303–305]

Values of the exponent b calculated for different peaks in the CV of $\text{PNb}_9\text{O}_{25}$ and $\text{VNb}_9\text{O}_{25}$ are presented in Table 6.1, and the calculations for these values in Figures 6.14 and 6.15. Both b -values calculated for the reduction and oxidation reactions in $\text{VNb}_9\text{O}_{25}$ are closer to 0.5, suggesting diffusion-limited processes are associated with the bulk

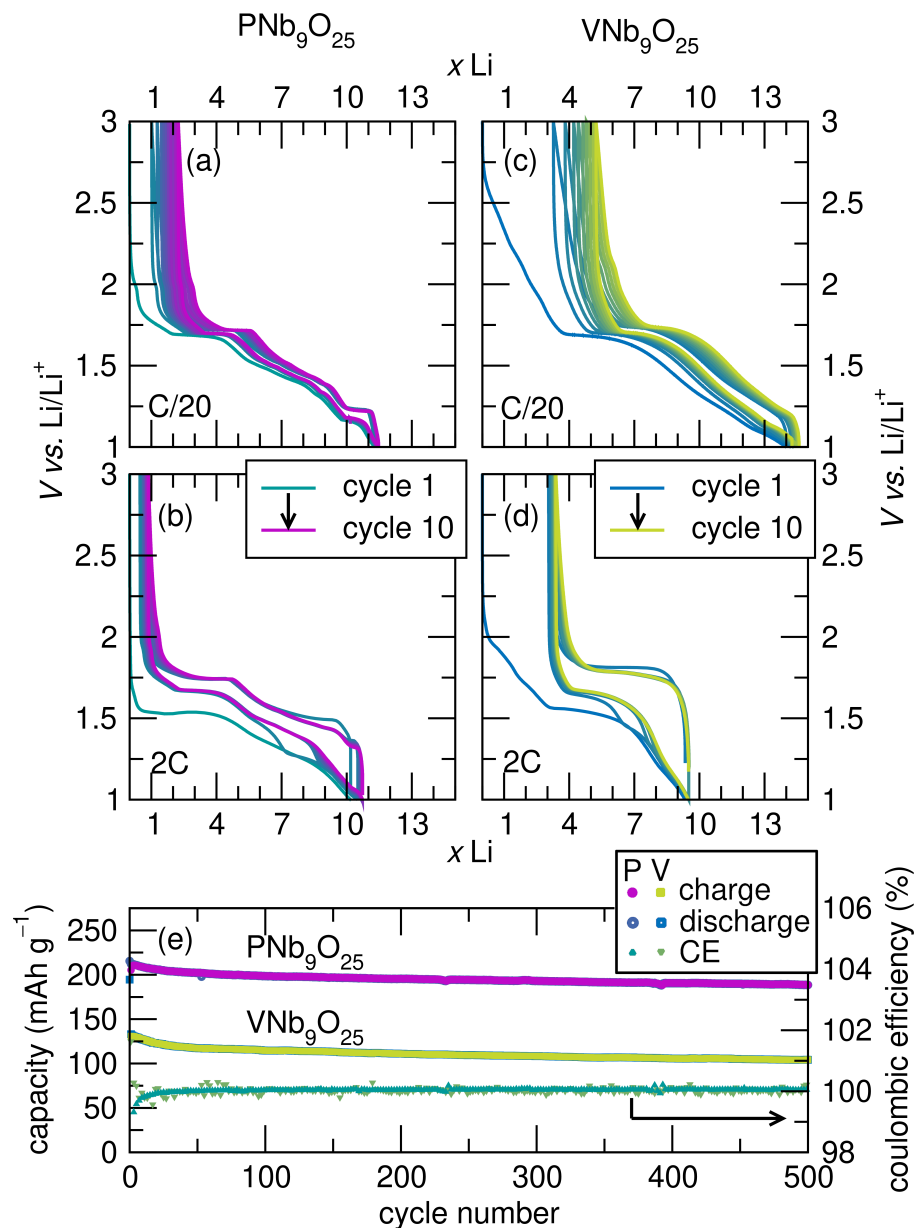


Figure 6.2: Cycling comparisons between $\text{PNb}_9\text{O}_{25}$ and $\text{VNb}_9\text{O}_{25}$ at slow and fast rates, as well as long-term cycling. (a) $\text{PNb}_9\text{O}_{25}$ cycled at C/20 over 10 cycles shows its distinct plateau and reversible cycling. (b) $\text{PNb}_9\text{O}_{25}$ cycled at 2C still maintains the same structure in the electrochemical curve with more polarization and slightly reduced Li incorporation. (c) $\text{VNb}_9\text{O}_{25}$ cycled at C/20 shows the irreversible capacity loss on the first cycle equivalent to about 4 Li, then less capacity fade thereafter. (d) $\text{VNb}_9\text{O}_{25}$ cycled at 2C still has the same capacity loss now equivalent to about 3 Li and a large increase in polarization. Li incorporation in $\text{VNb}_9\text{O}_{25}$ is significantly reduced at 2C. (e) Long-term cycling comparison between $\text{PNb}_9\text{O}_{25}$ and $\text{VNb}_9\text{O}_{25}$ at 2C. Both show relatively high capacity retention, though $\text{PNb}_9\text{O}_{25}$ maintains higher reversible capacity over 500 cycles.

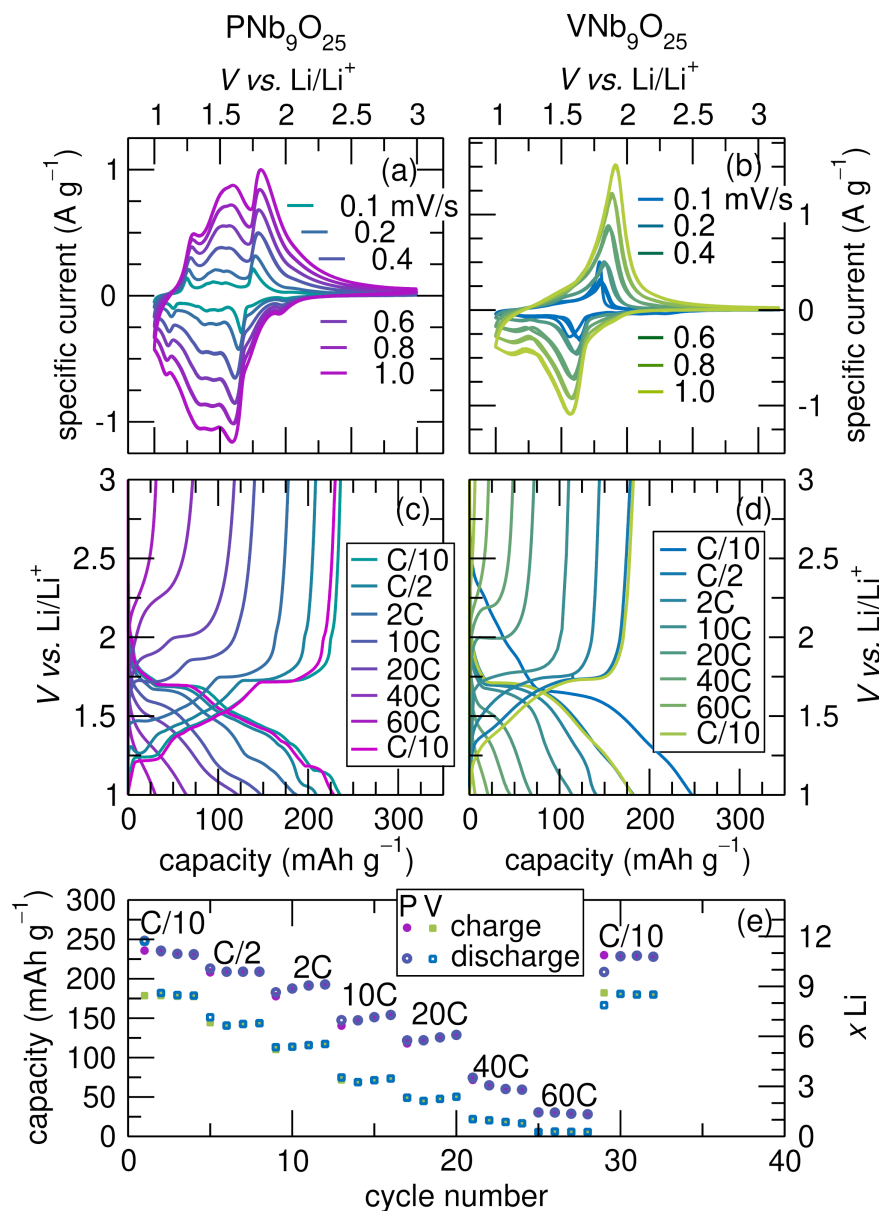


Figure 6.3: Variable rate electrochemistry comparison of $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$. (a) Cyclic voltammetry performed at sweep rates from 0.1 mVs^{-1} to 1.0 mVs^{-1} allows for analysis of the value of the exponent b for $\text{PNb}_9\text{O}_{25}$. (b) Cyclic voltammetry performed at sweep rates from 0.1 mVs^{-1} to 1.0 mVs^{-1} allows for b to be evaluated for $\text{VNB}_9\text{O}_{25}$. (c) $\text{PNb}_9\text{O}_{25}$ cycled galvanostatically from C/10 to 60C, and its recovery. The second cycle (out of four for each rate) is shown for clarity. (d) $\text{VNB}_9\text{O}_{25}$ cycled galvanostatically from C/10 to 60C, and its recovery. The first and second cycles are shown for C/10, but the second cycle is shown thereafter to see the evolution of the curves. (e) Cycle number versus capacity corresponding to the variable rate galvanostatic cycling depicted in (b) and (d). $\text{PNb}_9\text{O}_{25}$ consistently shows higher capacity after the first discharge. Both $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ recover to almost their starting C/10 capacities.

of the material. Conversely, $\text{PNb}_9\text{O}_{25}$ has four distinct redox reactions, and while the high voltage reduction and oxidation peaks suggest diffusion limitations in the bulk, the redox reactions between 1.37 V and 1.57 V appear to be associated with the diffusion-limiting steps associated with the surface. It is important to distinguish that both $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ behave as battery materials, and not pseudocapacitors, as evidenced through the phase changes that occur in their diffraction patterns during cycling (Figure 6.16).[279] Overall, the b -value analysis lends quantitative insight into the improved rate capabilities in $\text{PNb}_9\text{O}_{25}$ over $\text{VNB}_9\text{O}_{25}$.

Table 6.1: Quantitative insight into the kinetic variations between $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ is gleaned from varying the cyclic voltammetry sweep rate [Figure 6.3(a) and (b), and 6.14 and 6.15]. Values of the exponent b for the four distinguishable peaks in the $\text{PNb}_9\text{O}_{25}$ CV curve upon oxidation and reduction, and the one observable, reversible peak in the $\text{VNB}_9\text{O}_{25}$ CV curve are listed for comparison.

	reduction		oxidation	
	position	b	position	b
$\text{PNb}_9\text{O}_{25}$	1.11 V	0.80	1.28 V	0.56
	1.37 V	0.95	1.49 V	0.91
	1.46 V	0.97	1.57 V	0.94
	1.62 V	0.62	1.79 V	0.70
$\text{VNB}_9\text{O}_{25}$	1.56 V	0.59	1.93 V	0.69

Both compounds exhibit impressive rate capabilities, with measurable capacity up to 60C, and more than 99% recovery of capacity when the rate is reduced back to C/10. This demonstrates a wide range of practical applications for electric vehicles and portable electronics, in which one may wish to discharge their batteries slowly but charge them within minutes. In this instance $\text{PNb}_9\text{O}_{25}$ can reach 85% of its C/10 capacity in 30 minutes or 67% in 6 minutes. The surprising result from comparing the rate capabilities between $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ is that we would expect $\text{VNB}_9\text{O}_{25}$, if anything, to exhibit higher capacity given the higher ratio of redox active atoms per formula unit. However, the rate capabilities of $\text{PNb}_9\text{O}_{25}$ far exceed those of $\text{VNB}_9\text{O}_{25}$.

For example, at 2C, $\text{PNb}_9\text{O}_{25}$ exhibits an additional 77 mAhg^{-1} capacity than $\text{VNb}_9\text{O}_{25}$. Further, at 60C the capacity of $\text{VNb}_9\text{O}_{25}$ diminished to almost zero, while in $\text{PNb}_9\text{O}_{25}$ it is still 30 mAhg^{-1} . This wide range in performance given the very small chemical variations in these structures points to significant mechanistic differences in their redox properties.

6.3.2 Characterization of multielectron redox

Operando Nb K-edge X-ray absorption spectroscopy, especially the near edge region shown in Figure 6.4(a) and (c), lends insight into the reversibility of the niobium redox throughout the first cycle. The overall spectra and changes observed throughout the first cycle of $\text{PNb}_9\text{O}_{25}$ and $\text{VNb}_9\text{O}_{25}$ look similar, as expected for isostructural compounds. Both show a slight pre-edge feature in the pristine material centered at 18990 eV that is reversible once the material is re-oxidized. They both also show the same restructuring of the peak after the energy onset that shows a shift to lower energy upon reduction, which is restored to its position in the pristine state upon re-oxidation.

The relationship between composition and the associated change in energy yields mechanistic information about how niobium is reduced and oxidized in both structures and highlights their differences. With $\text{PNb}_9\text{O}_{25}$, both the reduction and oxidation result in a single linear relationship between the composition and energy. This is the expected result for a single redox active element, which is continually being reduced at the same rate throughout discharge and subsequent charge. $\text{VNb}_9\text{O}_{25}$ shows different trends, owing to the fact that vanadium is also redox active. While not probing the vanadium oxidation state directly, we can infer from the slow initial reduction of Nb up to $\text{Li}_5\text{VNb}_9\text{O}_{25}$ that vanadium is simultaneously being reduced during this stage of irreversible capacity loss. Interestingly, there is still some reduction in niobium until

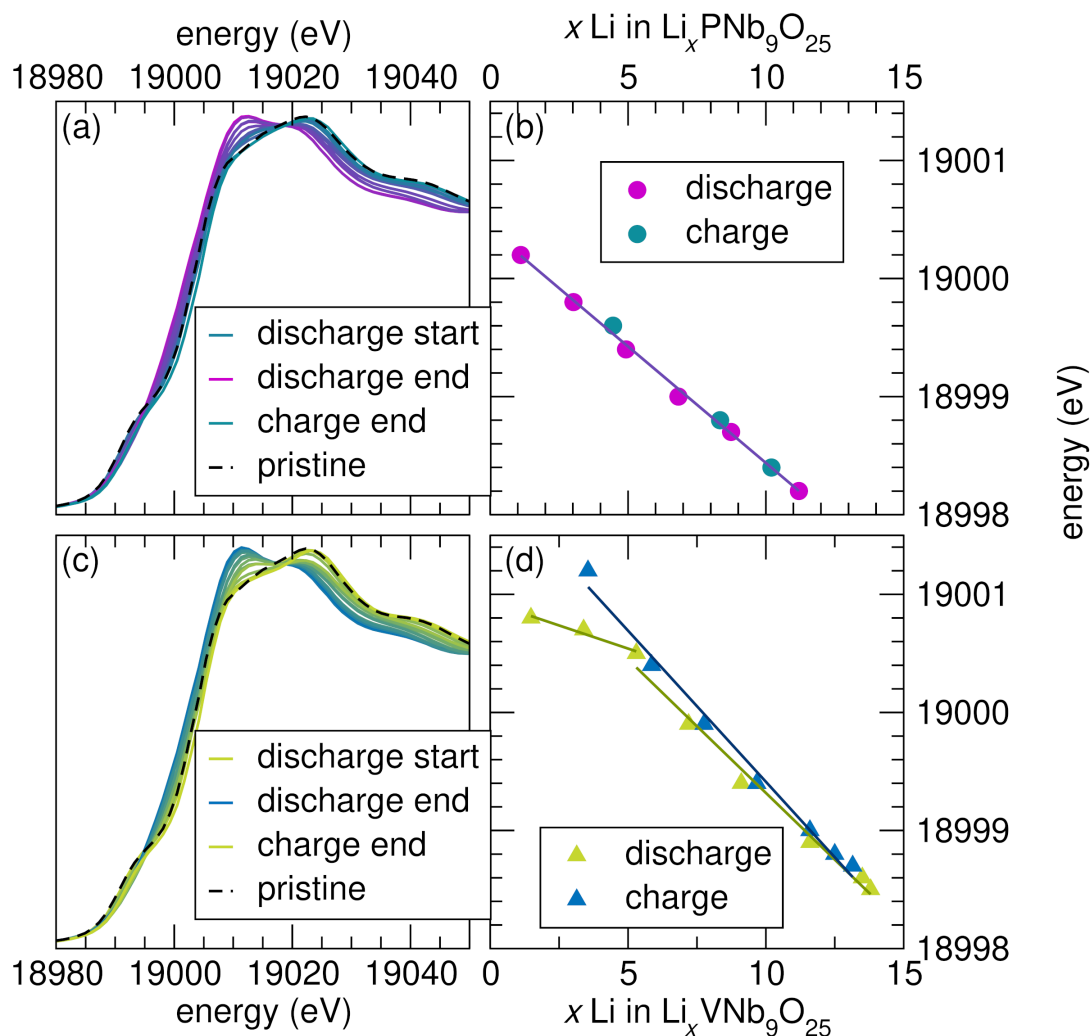


Figure 6.4: (a) Evolution of the XANES region of the Nb K-edge as $\text{PNb}_9\text{O}_{25}$ is reduced to 1 V and subsequently oxidized to 3 V (one full cycle). (b) The energy change of the onset after the pre-edge region as a function of composition as Li is inserted into $\text{PNb}_9\text{O}_{25}$. There is a linear relationship upon discharge and charge. (c) Evolution of the XANES region of the Nb K-edge as $\text{VNB}_9\text{O}_{25}$ is reduced to 1 V and subsequently oxidized to 3 V (one full cycle). (d) The energy change of the onset after the pre-edge region as a function of composition as Li is inserted into $\text{VNB}_9\text{O}_{25}$. In contrast with what is seen for $\text{PNb}_9\text{O}_{25}$, the initial change in energy $\text{VNB}_9\text{O}_{29}$ is slower upon discharge, marked by a linear relationship with a shallower slope.

this point, which differs from the hypotheses in previous reports. It was earlier believed that only vanadium is initially reduced, linked to the irreversible capacity loss observed in $\text{VNb}_9\text{O}_{25}$ in the first discharge. It is likely that the irreversible reduction of not only vanadium but also niobium is responsible for the diminished rate capabilities and capacity retention in $\text{VNb}_9\text{O}_{25}$.

We have employed *ex situ* XPS to quantitatively track the changes in oxidation states in niobium, phosphorus, and vanadium in both structures. The lithiated states were chosen based on clear changes in the galvanostatic response, such as before and after the discernible plateau [Figure 6.5(a) and (d)]. While XPS is quantitative and the measurements were done using air-free transfer from a glovebox, slight surface oxidation is still probable, skewing the results slightly toward Nb^{5+} . As expected, in the pristine state niobium only exists in the Nb^{5+} state [Figures 6.5(b), S13]. Even at the very beginning of lithiation with only 0.06 Li, 4% of niobium are converted to Nb^{4+} . This increases incrementally to 21% Nb^{4+} through $x=1.4$. At the end of the largest plateau, experimentally corresponding to $x=4$, 7% of niobium are converted to Nb^{3+} , but still a significant amount exists as Nb^{5+} . An interesting shift occurs in the sloping region between $x=4$ and $x=9.4$, in which the percentage of Nb^{3+} is almost 3 times that of Nb^{4+} (33% Nb^{3+} versus 13% Nb^{4+}). This indicates a complex mechanism in which either Nb^{5+} directly converts to Nb^{3+} or quickly reduces through Nb^{4+} to Nb^{3+} . Either way, Nb^{3+} is the favored reduced state toward the end of the discharge. After the final plateau at the end of discharge when $x=11.2$, an increase in Nb^{4+} is observed, such that 25% is Nb^{4+} and 29% is Nb^{3+} . Finally, upon charge, almost all of the niobium is oxidized back to Nb^{5+} , with only 2% remaining in the reduced Nb^{4+} state. Complete oxidation back to Nb^{5+} leads to the high capacity retention observed in $\text{PNb}_9\text{O}_{25}$.

To confirm that phosphorus does not participate in redox, high resolution XPS was

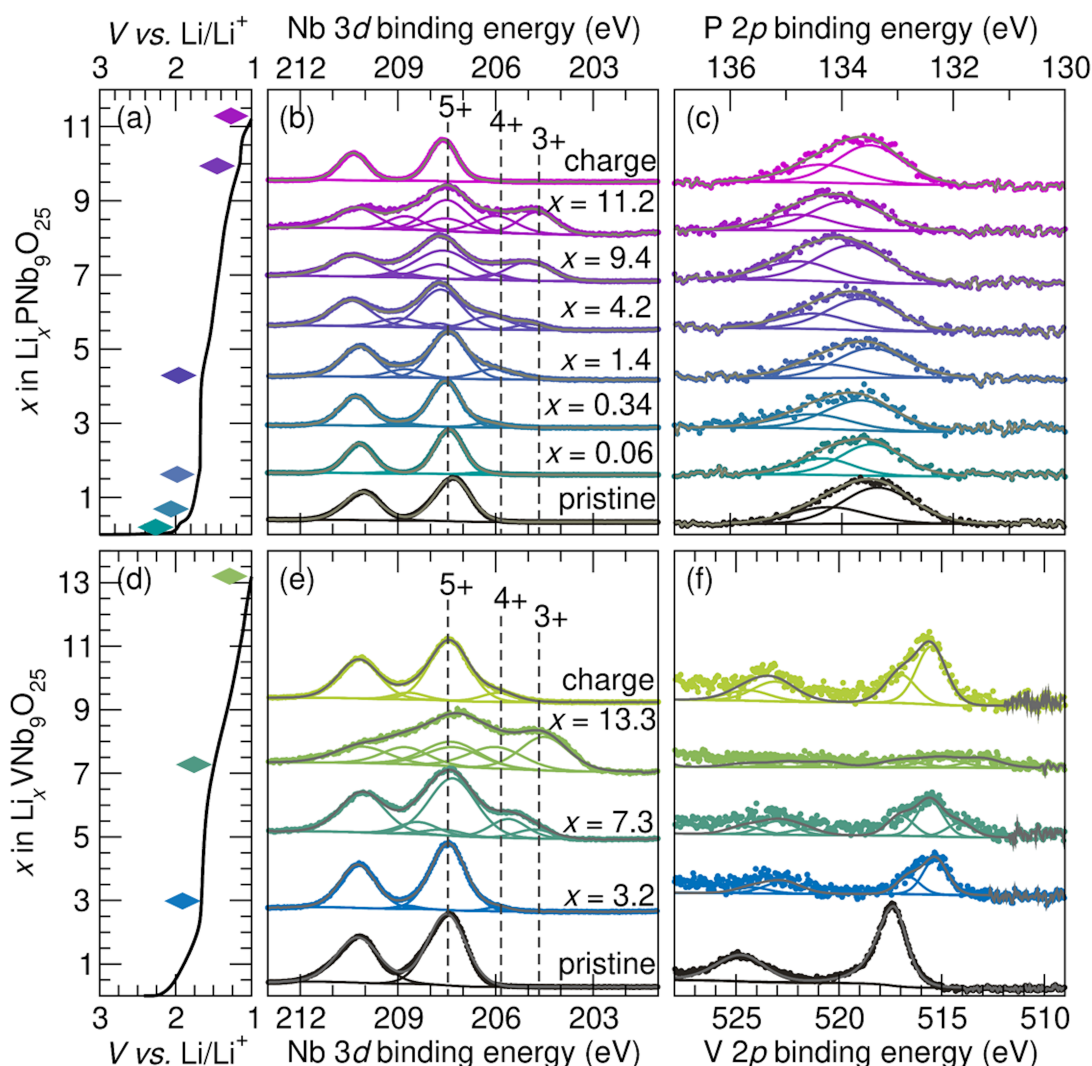


Figure 6.5: (a) The first galvanostatic discharge for Li insertion in $\text{PNb}_9\text{O}_{25}$ and the states of charge corresponding to the XPS spectra in the Nb 3d binding energy region (b) and P 2p binding energy region (c). Similarly, (d) is the $\text{VNB}_9\text{O}_{25}$ first galvanostatic discharge annotated to indicate the states of charge reflected in the Nb 3d region (e) and V 2p region (f). The oxidation state assignments were made using both literature references as well as Nb_2O_5 , NbO_2 , and NbO references collected on the same spectrometer. The duplication of peaks arises from spin-orbit splitting – the Nb 3d states split into Nb $3d_{5/2}$ (lower binding energy) and Nb $3d_{3/2}$ (higher binding energy). This is the case for V 2p and P 2p splitting into $2p_{3/2}$ (lower binding energy) and $2p_{1/2}$ (higher binding energy). For clarity, only the $3d_{5/2}$ and $2p_{3/2}$ peaks are marked. The grey line on each spectrum is the total fit arising from the peaks fitted to each oxidation state.

measured in the P 2p region as well [Figure 6.5(c)]. Though the signal-to-noise ratio is diminished due to phosphorus being lighter and in much lower abundance than niobium in the sample, there's no clear shift or emergence of new states to indicate that phosphorus is being reduced during discharge.

Table 6.2: Quantitative analysis of the evolution of oxidation states from fitting the high resolution spectra found in Figure 6.5.

$\text{Li}_x\text{PNb}_9\text{O}_{25}$				
x in $\text{Li}_x\text{PNb}_9\text{O}_{25}$	% Nb ⁵⁺	% Nb ⁴⁺	% Nb ³⁺	average
0.06	96	4	0	4.95
0.34	91	9	0	4.91
1.40	79	21	0	4.79
4.00	70	23	7	4.62
9.40	54	13	33	4.20
11.2	46	25	29	4.18
charged to 3.0 V	98	2	0	4.98

$\text{Li}_x\text{VNb}_9\text{O}_{25}$				
x in $\text{Li}_x\text{VNb}_9\text{O}_{25}$	% Nb ⁵⁺	% Nb ⁴⁺	% Nb ³⁺	average
3.50	96	4	0	4.96
7.30	72	19	9	4.38
13.3	32	29	39	3.93
charged to 3.0 V	88	12	0	4.88

High resolution XPS of $\text{VNb}_9\text{O}_{25}$ lends insight into the electrochemical processes in this crystal structure, as well. Previous reports have speculated through XRD and limited XPS of $\text{VNb}_9\text{O}_{25}$ that the irreversible capacity in the first discharge is due to irreversible reduction of V^{5+} to V^{3+} . However, this is only partly the case. There is irreversible capacity loss due to both incomplete oxidation of niobium back to Nb^{5+} and vanadium back to V^{5+} [Figures 6.5(e),(f) and S14 and S15]. Approximately 12% of the niobium remains as Nb^{4+} at the end of charge. The low signal-to-noise ratio of the vanadium binding energy region prevents the same quantitative analysis with confidence, especially at the bottom of discharge when the total intensity is broadened

by all three oxidation states, but a non-trivial fraction of vanadium oxidizes completely to V^{5+} . The largest fraction remains as V^{4+} , though this is still oxidized as compared to when $\text{VNb}_9\text{O}_{25}$ is most lithiated. Quantitative analysis of the percentages of oxidation states arising from fitting the spectra can be found in Table 2. It is likely that the irreversibility due to niobium is the driving force for the larger capacity loss over extended cycling, since niobium comprises the majority of the structure, though this is conjecture. When evaluated with the significant differences in the galvanostatic behavior between $\text{PNb}_9\text{O}_{25}$ and $\text{VNb}_9\text{O}_{25}$, the small chemical difference of replacing phosphorus with vanadium in low overall concentration leads to surprisingly large mechanistic deviations in an otherwise identical crystal structure, which has implications for future design of new complex oxides for electrode materials.

6.3.3 Evidence of insulator-to-metal transition in $\text{PNb}_9\text{O}_{25}$

While $\text{PNb}_9\text{O}_{25}$ is a d^0 compound and insulating to start, electrochemical lithium doping induces an insulator-to-metal transition, which may play a role in its fast rate capabilities. AC impedance spectroscopy in the solid state of pure $\text{Li}_x\text{PNb}_9\text{O}_{25}$ at different states of charge was used to find the temperature-dependent resistance. A comparison of Nyquist plots at an early stage of lithiation ($\text{Li}_{1.2}\text{PNb}_9\text{O}_{25}$) and a highly lithiated state ($\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$) demonstrates the transition from thermally-activated conductivity [Figure 6.6(a)] to thermally-impeded conductivity [Figure 6.6(b)].

The absence of a Warburg tail points to the conductivity measurements being overwhelmed by electronic conductivity, and only one semicircle could be fit in a simple equivalence circuit of a resistor and capacitor in parallel [Figure 6.6(a) and (b)]. Therefore, the total resistance found by fitting the circuit was used as an approximation for electronic conductivity. The resistance values were normalized to the resistance at

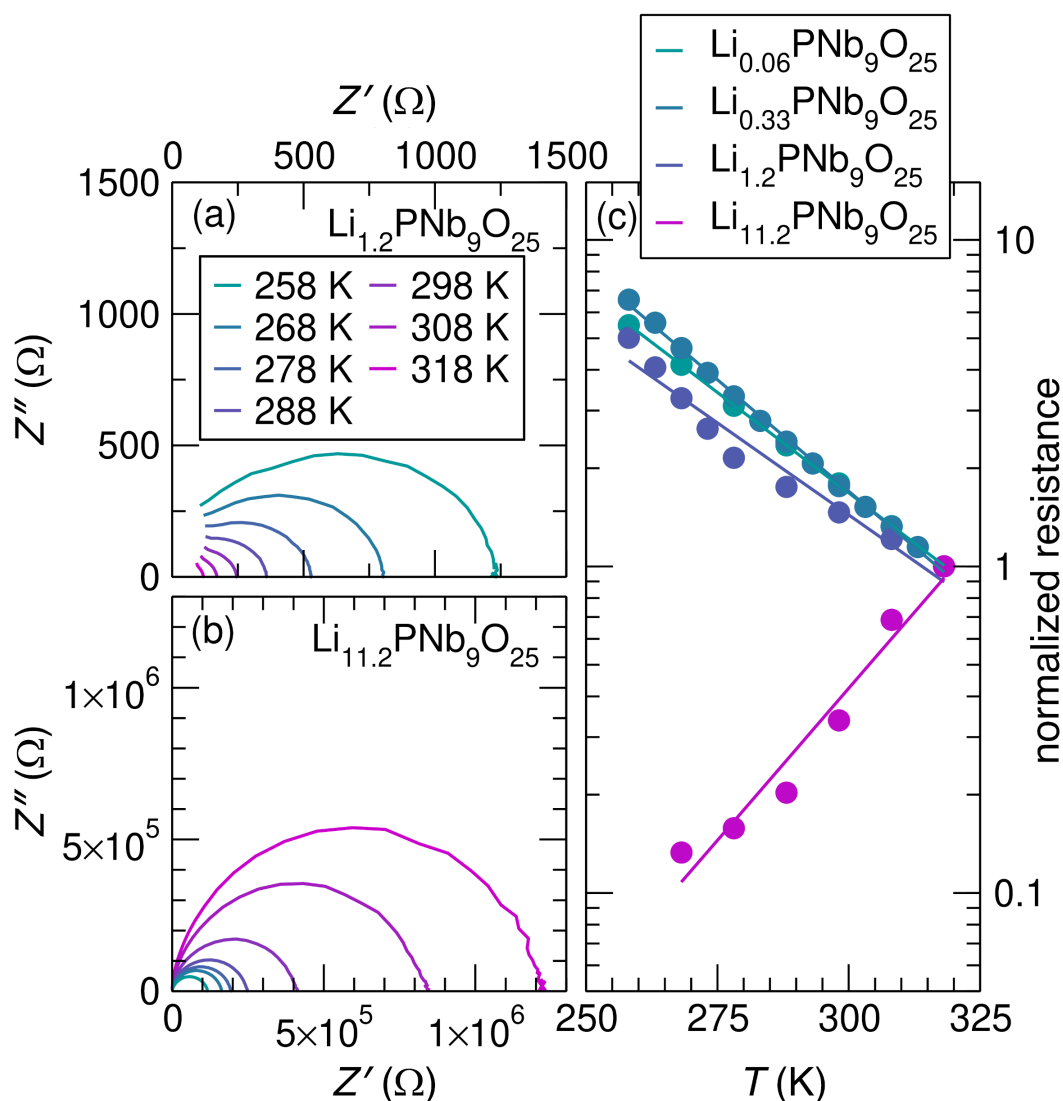


Figure 6.6: (a) Nyquist plot of $\text{Li}_{1.2}\text{PNb}_9\text{O}_{25}$ washed free of LiPF_6 from 256 K to 318 K such that only the intrinsic conductivity is measured. Resistance decreases with increasing temperature in low lithiated states. (b) Nyquist plot of $\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$ washed free of LiPF_6 from 256 K to 318 K. Resistance increases with increasing temperature in high lithiated states. (c) Resistance normalized to the highest temperature value for discrete states of lithiation follows an exponential trend. $\text{PNb}_9\text{O}_{25}$ goes through an insulator-to-metal transition at higher states of lithiation.

the highest temperature measured to remove the influence of sintering on the trends observed as lithium is inserted [Figure 6.6(c)]. At higher states of lithiation it is particularly challenging to densify the pellets sufficiently to ascertain the absolute value of the resistance. This is reflected in the Nyquist plots presented in Figure 6.6(a) and (b), in which the recorded absolute resistance for the highest lithiated state reaches the order of $\text{M}\Omega$ s. Additionally, some deviation from linearity can be attributed to small deviations in the thickness of the materials as they are heated and cooled. While there is constant pressure applied, the natural expansion and contraction of the sample slightly changes the force applied by as much as 0.5 kN as monitored by a load cell. These deviations are especially pronounced in the highly lithiated sample due to the densification challenges previously mentioned. However, the trends observed by comparing the slopes of the normalized resistance as a function of temperature on a semi-log scale are indicative of how the electronic conductivity changes throughout progressive lithiation. The reversal in slope from lightly lithiated samples to highly lithiated samples shows that $\text{Li}_x\text{PNb}_9\text{O}_{25}$ changes from semiconducting to metallic in nature.

The insulator-to-metal transition was further probed using solid-state NMR and magnetic susceptibility measurements. Figure 6.7(a) shows the 1D ^{31}P NMR spectrum of pristine $\text{PNb}_9\text{O}_{25}$ and fully-lithiated $\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$. The spectrum of $\text{PNb}_9\text{O}_{25}$ contains sharp, resolvable peaks at -16.5 ppm and -12.5 ppm, therefore reflecting the crystallographic structure since the P site in the $\text{PNb}_9\text{O}_{25}$ structure is half-occupied. The highest intensity peak, likely capturing the phosphorus site in which the nearest P site is unoccupied, spans 6 ppm. The spectrum of $\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$, however, is drastically different. The main chemical environment is shifted to 50 ppm and is much broader, spanning 75 ppm, suggestive of a Knight shift due to the delocalized electrons in the system (metallic), similar to what is observed upon delithiation in LiCoO_2 . [270] There

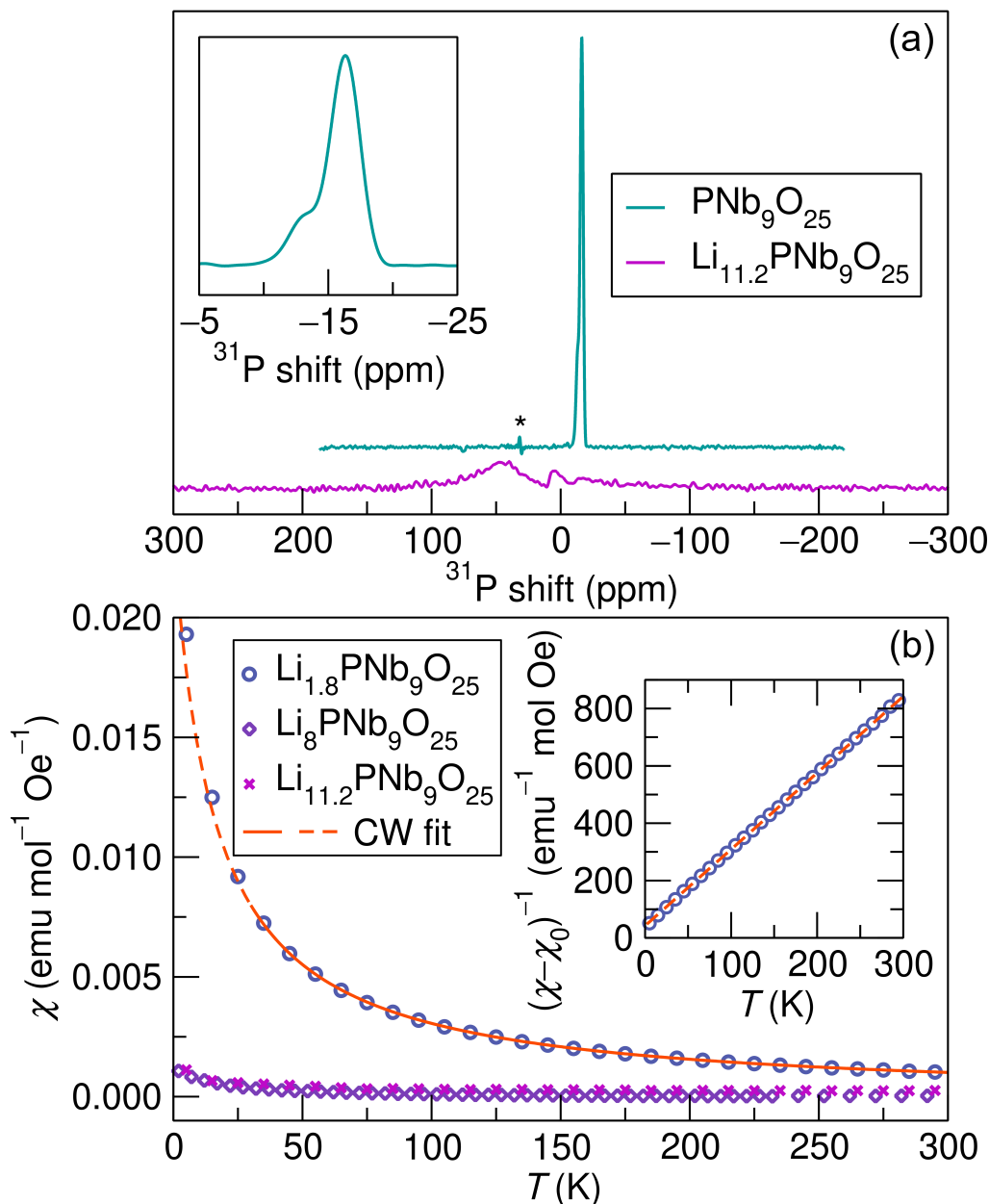


Figure 6.7: (a) ^{31}P NMR spectra of $\text{PNb}_9\text{O}_{25}$ before cycling and fully lithiated at $\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$ (cycled to 1 V) both referenced to solid triphenylphosphine. Inset expands upon the $\text{PNb}_9\text{O}_{25}$ spectra in a narrower chemical shift range to show the presence of (at least) 2 phosphorus sites. (b) magnetic susceptibility vs. temperature for three samples. $\text{Li}_{1.8}\text{PNb}_9\text{O}_{25}$, a lightly-lithiated sample, shows Curie-Weiss (CW) paramagnetism consistent with the localization of the Nb d -electrons into discrete magnetic moments. The Curie-Weiss fit shown is performed between 30 K and 300 K, and extrapolated to lower temperatures. The heavily-lithiated $\text{Li}_8\text{PNb}_9\text{O}_{25}$ and $\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$ samples, on the other hand, show much lower susceptibility and are not well-fit with the Curie-Weiss relation, consistent with delocalization of the d electrons.

is also a noticeable lower intensity and broadened peak at 5 ppm, which may reflect the new shift of the smaller peak observed in the original spectrum.

Figure 6.7(b) shows magnetic susceptibility as a function of temperature for $\text{Li}_{1.8}\text{PNb}_9\text{O}_{25}$, $\text{Li}_{8.0}\text{PNb}_9\text{O}_{25}$, and $\text{Li}_{11.2}\text{PNb}_9\text{O}_{25}$, expressed per mol formula unit. The lightly-lithiated sample ($x = 1.8$) shows a magnetic susceptibility χ that excellently follows the Curie-Weiss law:

$$\chi = \frac{C}{T - \theta} + \chi_0 \quad (6.1)$$

where C is the Curie constant, T is the temperature, θ is the Weiss temperature, and χ_0 is the temperature-independent proportion of the magnetic susceptibility. Fitting the susceptibility between 30 K and 300 K to this equation yields $C = 0.375 \text{ emu K mol}^{-1} \text{ Oe}^{-1}$, $\theta = -15.9 \text{ K}$, and $\chi_0 = -0.000177 \text{ emu mol}^{-1} \text{ Oe}^{-1}$. This C is consistent with a local paramagnetic moment $\mu_{\text{eff}} = 1.29\mu_B$ per inserted Li, which is in reasonable agreement for the theoretical value expected for a single Nb^{4+} ion ($\mu_{\text{eff}} = 1.55\mu_B$).^[306] Therefore, this susceptibility data suggests a picture where, for low levels of lithiation, the electrons introduced by adding lithium to $\text{PNb}_9\text{O}_{25}$ remain localized as discrete paramagnetic ion spins sitting on individual Nb atoms, rather than becoming delocalized into a metallic state. This mechanism can explain why the introduction of electrons to the Nb d -band *via* lithiations does not, for low levels of lithiation, result in a metal. Upon the introduction of larger quantities of Li ($x = 8.0$ and $x = 11.2$), this paramagnetic signal is greatly suppressed. Attempts to fit the susceptibility to the Curie-Weiss law resulted in poor fits with nonphysical parameters, and μ_{eff} values ≤ 0.2 per Li inserted. This loss of Curie-Weiss paramagnetism is consistent with the formation of metallic conducting state where the Nb d electrons now form a delocalized band instead of remaining in localized in paramagnetic moments. Furthermore, some temperature-independent paramagnetism is seen in these samples, consistent with the Pauli paramagnetism that

occurs in systems with metallic electrons. These susceptibility results are similar to those observed in the $\text{Li}_x\text{TiNb}_2\text{O}_7$ electrode system, which is also believed to become metallic upon lithiation.[3]

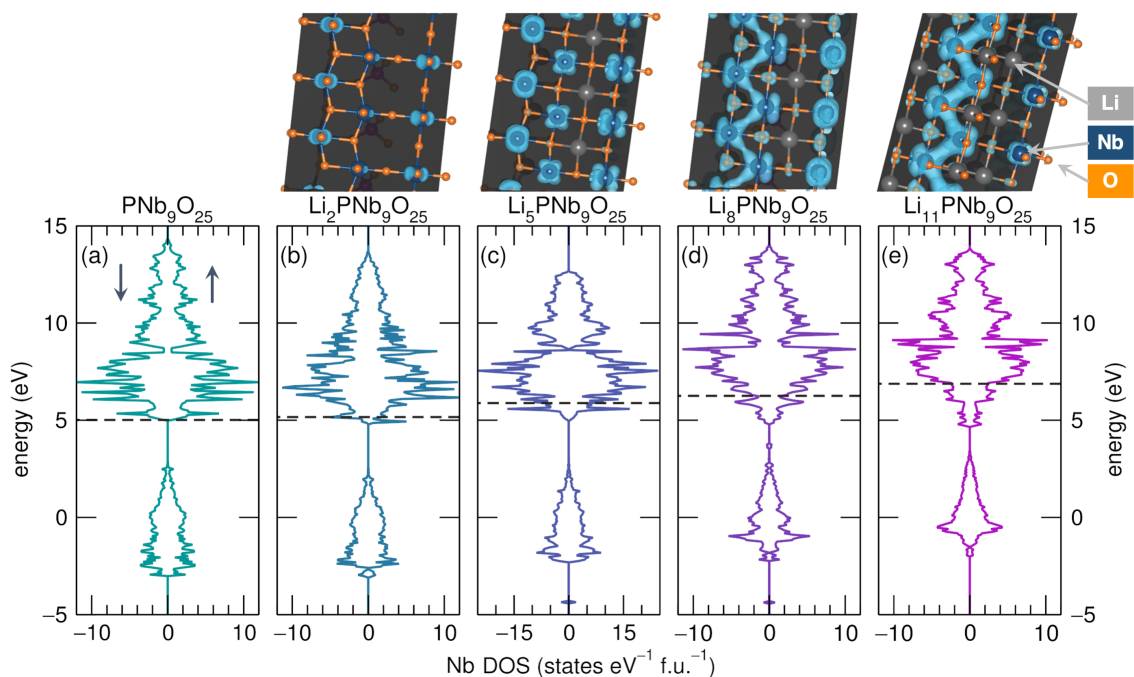


Figure 6.8: Nb partial densities of states (p DOS) across varying compositions of $\text{Li}_x\text{PNb}_9\text{O}_{25}$ and the corresponding structures, showing the Nb t_{2g} states (light blue), which are unfilled for the $\text{PNb}_9\text{O}_{25}$ case but become occupied as the compound is lithiated. Nb atoms are dark blue, O atoms are orange, Li atoms are grey, and in the background, P atoms are magenta.

Electron delocalization at high states of lithiation can be best visualized by separating the crystal structure into distinct regions of structural features and Nb t_{2g} state density. $\text{PNb}_9\text{O}_{25}$ has three symmetrically nonequivalent niobium in its unit cell. Two form NbO_6 octahedral units that are edge sharing with the octahedra in the blocks above and below them. These units merely differ by one octahedra sharing a corner with phosphorous and the other not. These octahedral units connect the blocks along the infinite axis through their edges forming a jagged network of NbO_6 octahedral

units. There is also a single niobium that forms an NbO_6 octahedra where the oxygens are shared only along octahedral vertexes. Edge- and vertex-sharing octahedra exhibit large differences in d -orbital overlap, and in both cases, the bonding changes dramatically with composition.

$\text{Li}_x\text{PNb}_9\text{O}_{25}$ starts as a d^0 band insulator prior to lithiation ($x = 0$). From the partial Nb t_{2g} state density plots (Figure 6.8), at low lithium composition we observe little d orbital overlap. This is a result of the electrons occupying t_{2g} orbitals, effectively preventing orbital overlap and therefore, delocalization. At this stage, we anticipate that electron-electron correlation (not described here) would be important, forcing the d electron to remain localized into discrete spins on Nb ions, as seen in the magnetic susceptibility data. In this picture, any electrical transport would require a hopping mechanism,[307] which results in the thermally-activated conduction observed in the impedance spectroscopy data. As lithium composition increases, d orbital overlap between the edge-sharing octahedra increases as electrons further fill t_{2g} orbitals. This occurs along the edge-sharing connections, allowing a network of electronic conductivity through the length of the crystal [Figure 6.8(d) and (e)]. The transition from no orbital overlap between the edge-sharing octahedra and electronic conductivity between them appears to initially occur at $\text{Li}_5\text{PNb}_9\text{O}_{25}$ [Figure 6.8(c)], and increases further in the $\text{Li}_8\text{PNb}_9\text{O}_{25}$ configuration, where the electronic density begins to emerge along the oxygen atoms [Figure 6.8(d)]. This effect is amplified when the composition reaches over $x = 11$ for the $\text{Li}_x\text{PNb}_9\text{O}_{25}$ system, where there is a large increase in the electronic density of the edge-sharing octahedra [Figure 6.8(e)].

Along the vertex sharing octahedra, there is charge localization on the niobium at low lithium compositions. Since electrons fill the t_{2g} orbital, there is no d orbital overlap with surrounding octahedra. The electron density in corner-sharing and edge-

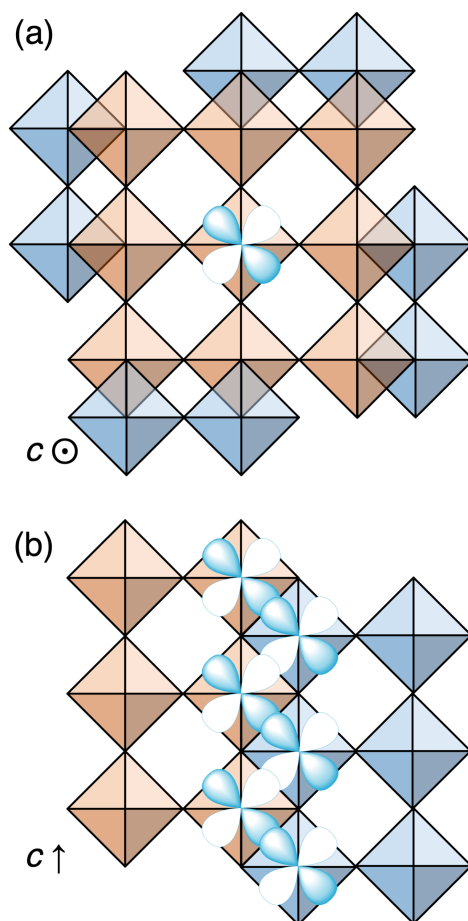


Figure 6.9: Schematic of (a) the initial localization of electron density on a t_{2g} orbital on an octahedron that is only corner-connected with other octahedra, and (b) delocalized electron density extended along edge-sharing regions as a result of t_{2g} being able to communicate with each other through the shared octahedral edges. This takes place at higher levels of lithiation.

sharing regions is conveyed with greater clarity in the schematic representation in Figure 6.9. Localization of electrons near the vertex-sharing octahedra was also found for other Wadsley-Roth structures including $\text{Nb}_{14}\text{W}_3\text{O}_{44}$, $\text{Nb}_{16}\text{W}_5\text{O}_{55}$, and $\text{Nb}_{12}\text{WO}_{36}$, [275] suggesting similarities in electronic conductivity and charge localization among crystallographic shear structures. For higher compositions, charge on the vertex-sharing octahedra decreases dramatically with increasing composition until charge is mainly present on the edge-sharing octahedra for lithium compositions over $x = 8$ for the $\text{Li}_x\text{PNb}_9\text{O}_{25}$ system.

6.3.4 Summary of the complex processes in $\text{PNb}_9\text{O}_{25}$

A summary of the discussed, complex processes occurring throughout the $\text{PNb}_9\text{O}_{25}$ discharge curve is shown in Figure 6.10. Niobium oxidation states are tracked using a combination of XANES and XPS. Initially, Nb is reduced from Nb^{5+} to Nb^{4+} as up to 2 Li are inserted. After the first extended plateau at 1.72 V, the evolution of Nb^{3+} is observed, signaling multielectron redox properties. Through the sloping region up to $\text{Li}_{10}\text{PNb}_9\text{O}_{25}$, there is a sharp increase in the percentage of Nb^{3+} , surpassing the amount of Nb^{4+} . This suggests that Nb^{5+} is being reduced to Nb^{3+} either directly or moving through Nb^{4+} . Finally, more Nb^{5+} is reduced through the end of discharge. Also mapped onto the discharge curve is where the expected insulator-to-metal transition occurs based on a combination of experimental conductivity measurements, NMR, magnetic susceptibility, the optical color change, and DFT calculations. At low levels of lithiation, the material remains insulating due to localization of the electron density. At full lithiation, the material becomes metallic, and the density maps of the Nb t_{2g} states reflect delocalization along the edge-sharing regions in the structure. From DFT, we can extrapolate that this delocalization occurs around $x = 5$. The color of the purely

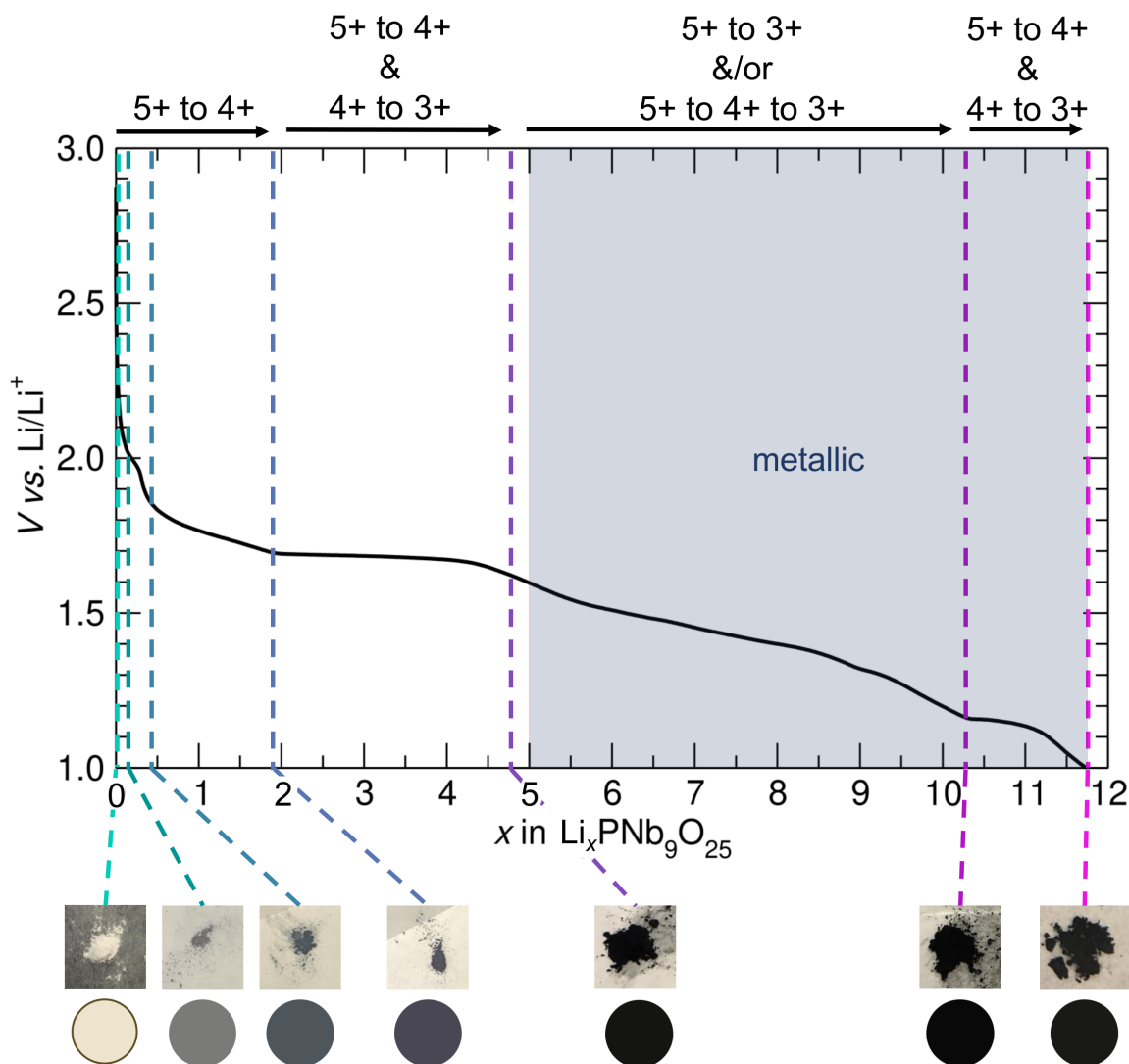


Figure 6.10: $\text{PNb}_9\text{O}_{25}$ goes through a complicated redox mechanism that involves multielectron redox on Nb and induces an insulator-to-metal transition. The conversion from Nb^{5+} to Nb^{3+} is summarized on top of the discharge curve, and the color evolution as Li is progressively inserted from white, to grey, to blue, to black is shown at the bottom.

lithiated samples (no carbon or binder additives) reflects these changes in the electrical conductivity. The material changes from white in its pristine state to grey at very low levels of lithiation ($x = 0.06$). By $x = 0.33$, the material is blue, and at $x = 2$ the color deepens to a dark blue. Thereafter, and first observed at $x = 4.75$, the material is black, coinciding with the expected insulator-to-metal transition as a function of composition.

Electrochemical comparisons of $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$, particularly the use of variable rate testing, indicate very small amounts of chemical substitution can dramatically influence electrochemical behavior, diffusion kinetics, and cycling performance in the high-performing Wadsley-Roth family of fast-charging electrode materials. $\text{PNb}_9\text{O}_{25}$ exhibits impressive rate capabilities with observed capacity up to 60C and more than 1 electron stored per transition metal, leading to its high capacity retention over hundreds of cycles. Additionally, we directly observe an insulator-to-metal transition in the material, which is highly desirable for applications and likely contributes to its fast rate capabilities in micron-sized particles. Irreversible reduction of vanadium and niobium in $\text{VNB}_9\text{O}_{25}$ results in lower capacity retention and contributes to its comparably sluggish rate capabilities as compared to $\text{PNb}_9\text{O}_{25}$, exemplifying that not all shear structures are created equally for Li insertion. Chemical tuning of this structure type and other structure types within the broader crystallographic shear structure family may allow for optimization of the electrochemical features observed.

6.4 Additional characterization and analysis

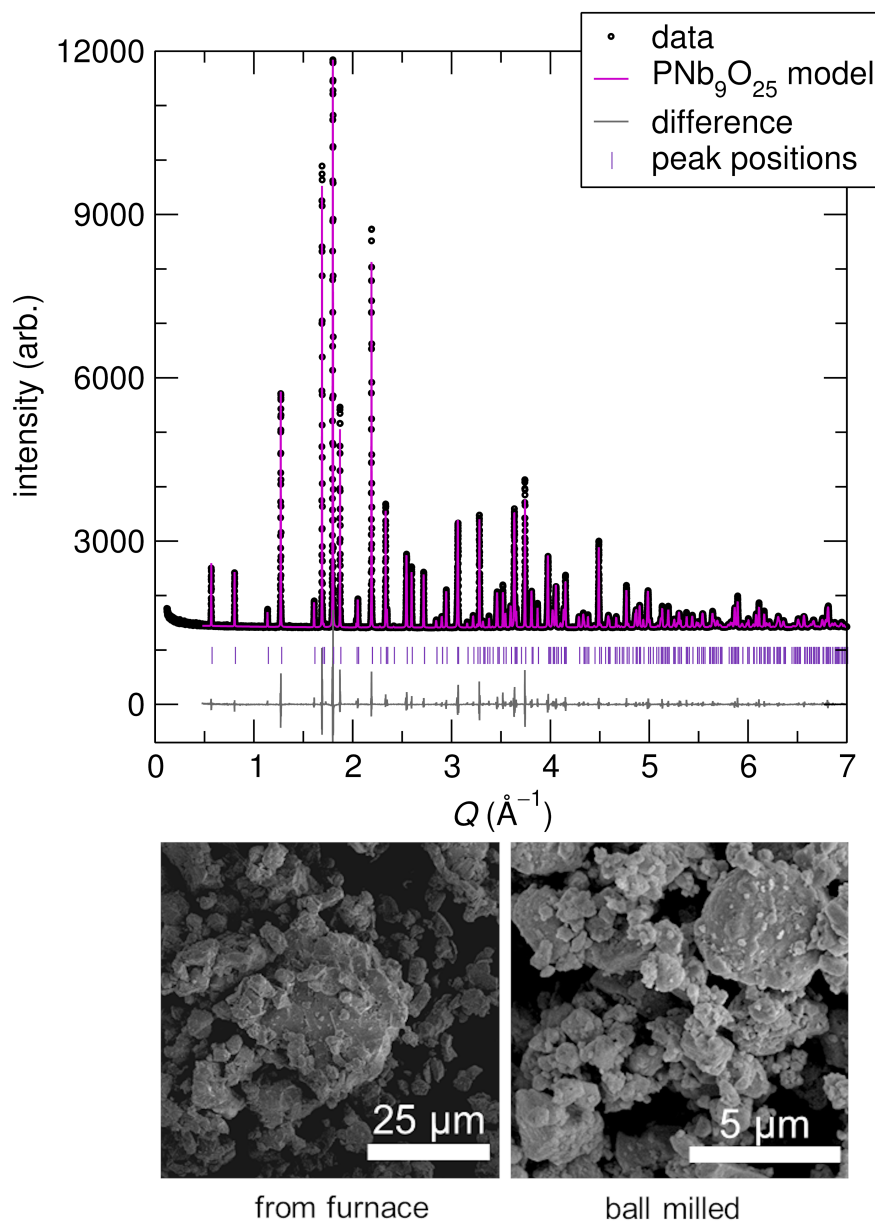


Figure 6.11: $\text{PNb}_9\text{O}_{25}$ was synthesized by solid state methods as described in the main text. Rietveld refinement of high-resolution synchrotron powder XRD from beamline 11-BM at the Advanced Photon Source revealed the sample to be single phase, and the Bragg reflections are shown below for reference. $R_{wp} = 15.1$, $R_{exp} = 10.3$, and $\text{GOF} = R_{wp}/R_{exp} = 1.46$. The refined structure is provided as a Crystallographic Information File. Additionally, the SEM images from the as-prepared sample and the ball-milled sample show that all of the electrochemistry and characterization has been done using micron-sized particles. Primary particles are on the order of $1\ \mu\text{m}$. Images were collected using a FEI Nova Nano 650 FEG SEM on uncoated pristine powder.

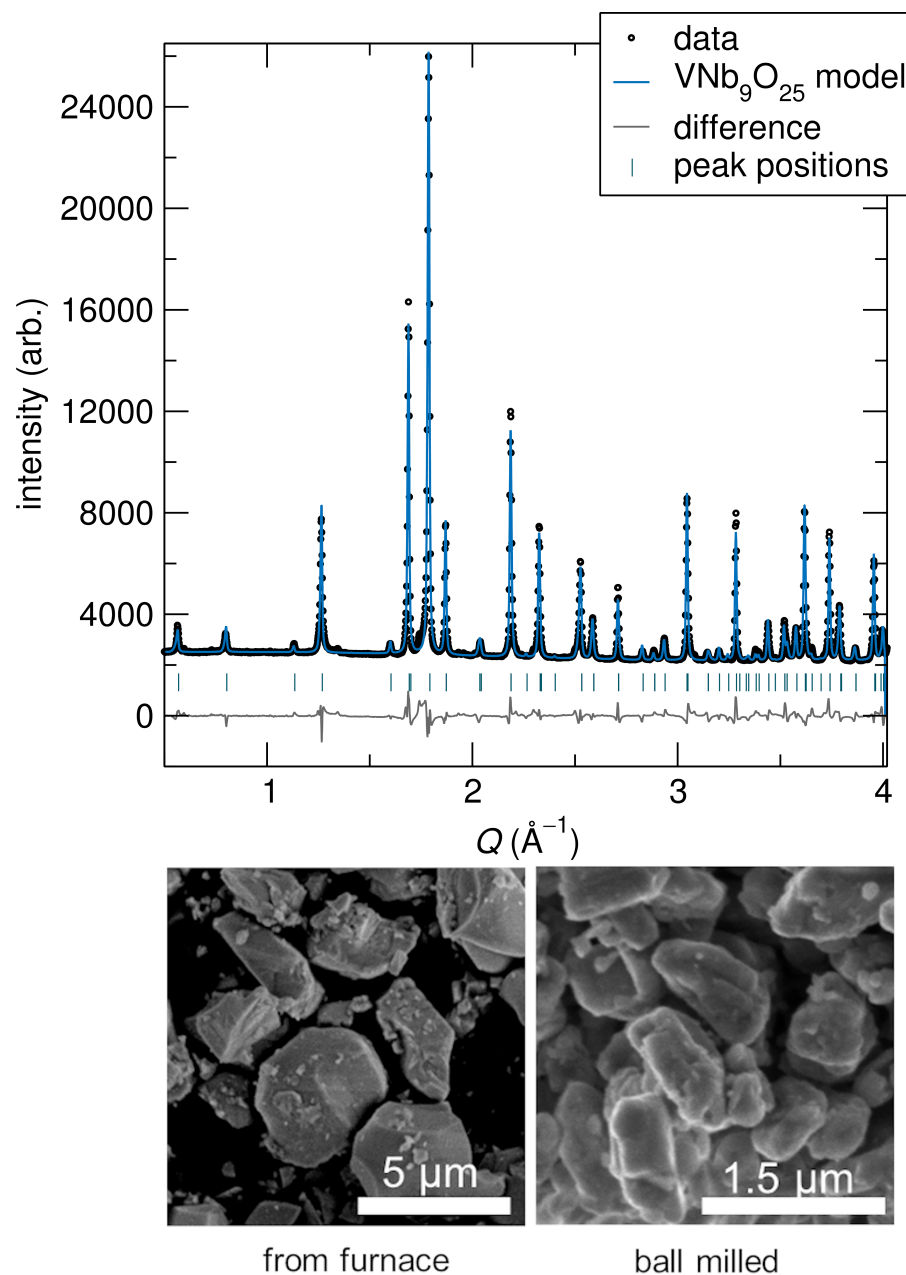


Figure 6.12: $\text{PNb}_9\text{O}_{25}$ was synthesized by solid state methods as described in the main text. Synchrotron powder XRD from beamline 17-BM at the Advanced Photon Source and subsequent Rietveld refinement confirm the successful synthesis of $\text{V Nb}_9\text{O}_{25}$. The obtained lattice parameters are $a = 15.7101(7)$ and $c = 3.8284(2)$. $R_{wp} = 4.00$, $R_{exp} = 1.88$, and $\text{GOF} = R_{wp}/R_{exp} = 2.13$. The sample was subsequently ball-milled, and SEM reveals the particle size of the primary particles is on the order of 1 μm . Images were collected using a FEI Nova Nano 650 FEG SEM on uncoated pristine powder.

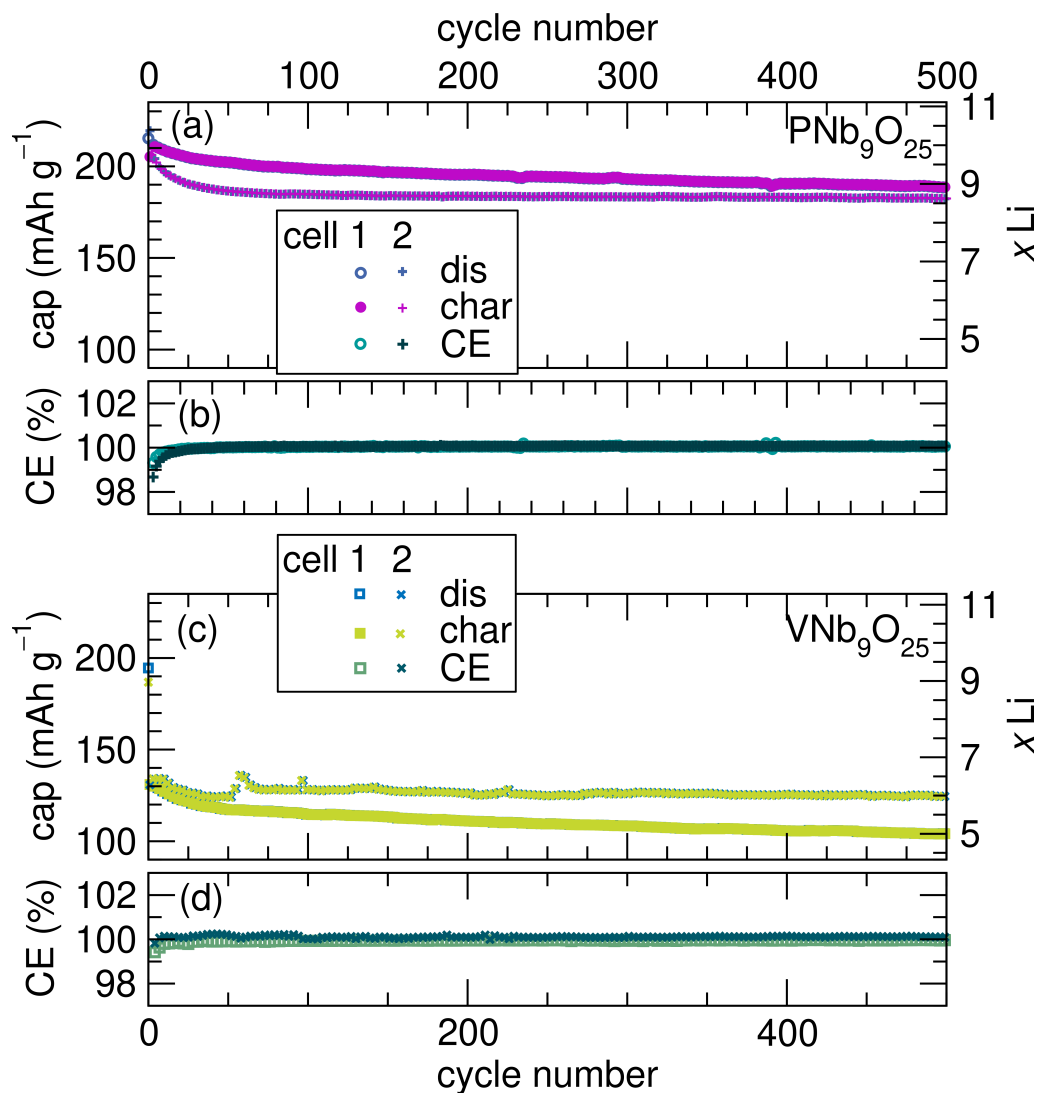


Figure 6.13: Replicate cells for $\text{PNb}_9\text{O}_{25}$ and $\text{VNB}_9\text{O}_{25}$ show similar behavior and capacities at 2C over 500 cycles. (a) Capacity as a function of cycle number for $\text{PNb}_9\text{O}_{25}$ in two distinct coin cells prepared according to the description in the main text and (b) the corresponding Coulombic efficiencies (CE) as a percentage. (c) Capacity as a function of cycle number for $\text{VNB}_9\text{O}_{25}$ in two distinct coin cells prepared according to the description in the main text and (d) the corresponding Coulombic efficiencies (CE) as a percentage. After the first 5 cycles across all cells and materials, the discharge and charge capacities within each cycle are roughly even.

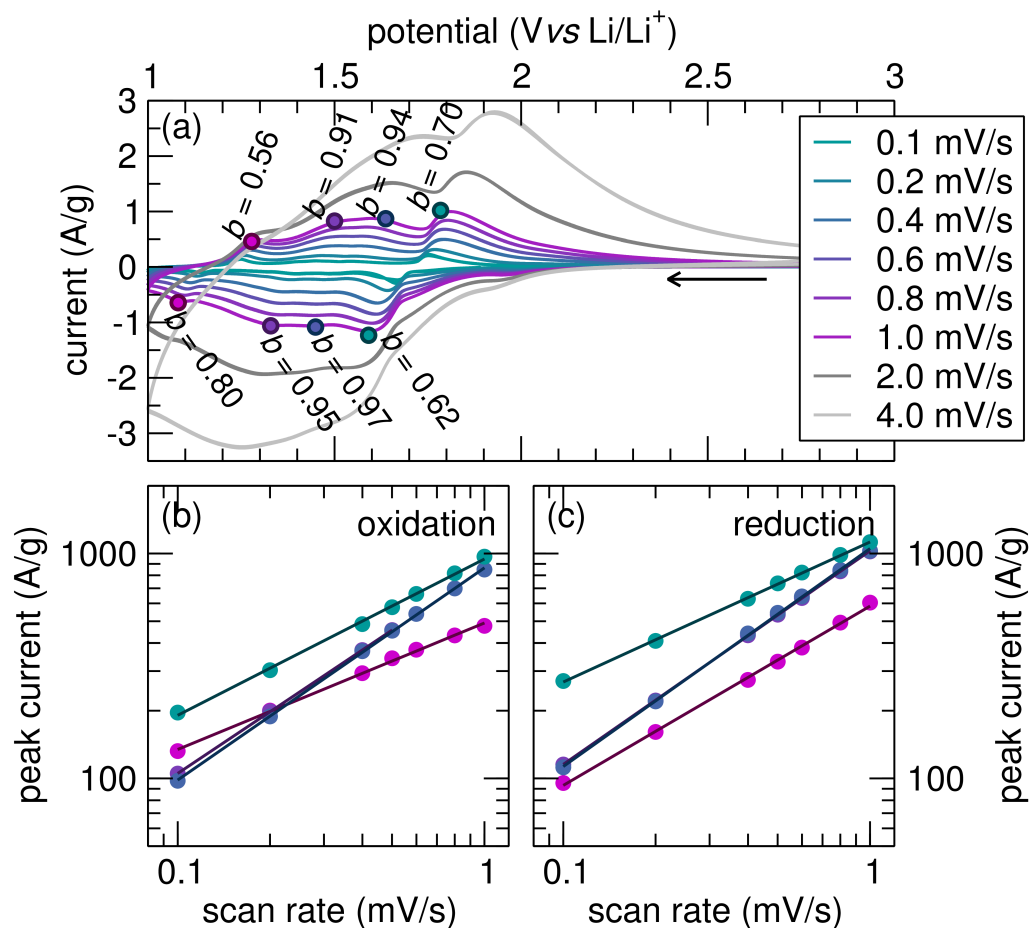


Figure 6.14: Cyclic voltammetry of $\text{PNb}_9\text{O}_{25}$ at varying sweep rates and the b-values overlaid at the corresponding redox peaks (a). Power law fits for each oxidation peak as a result of relating the scan rate and current (b). Power law fits for each oxidation peak as a result of relating the scan rate and current (c).

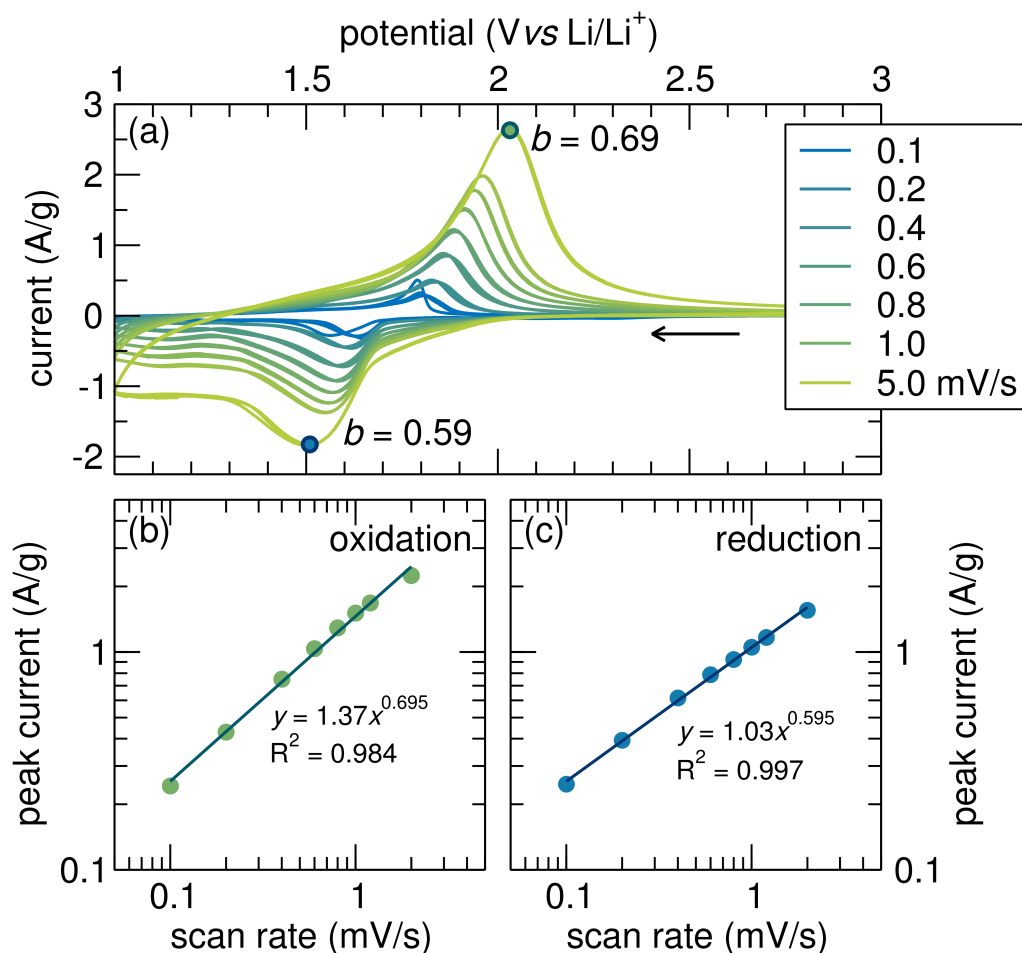


Figure 6.15: Cyclic voltammetry of $\text{VNb}_9\text{O}_{25}$ at varying sweep rates and the b -values overlaid at the corresponding redox peaks (a). Power law fits for each oxidation peak as a result of relating the scan rate and current (b). Power law fits for each oxidation peak as a result of relating the scan rate and current (c).

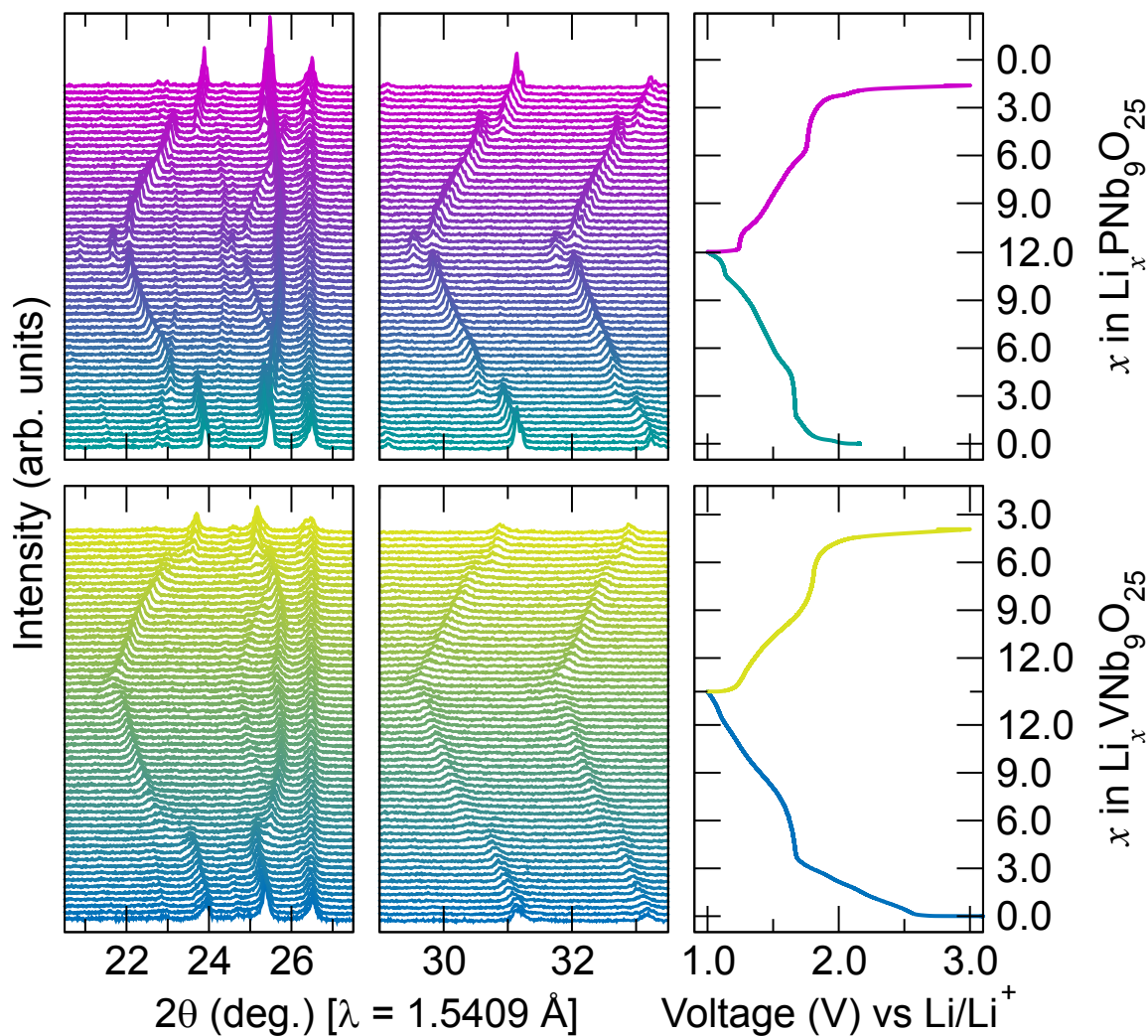


Figure 6.16: *Operando* XRD for $\text{PNb}_9\text{O}_{25}$ (top) and $\text{VNB}_9\text{O}_{25}$ (bottom) during the first galvanostatic cycle at a rate of C/10 shows the structural transformations as the materials are cycled. Both compounds have an initial unit cell expansion in common, corresponding to the discharge plateau at 1.7 V. After they get in formation, they both show reversible cycling, recovering the initial powder pattern prior to cycling. *Operando* XRD measurements were performed using a Bruker D8 diffractometer with a $\text{Cu } K_\alpha$ source ($\lambda_1 = 1.5406 \text{ \AA}$, $\lambda_2 = 1.5444 \text{ \AA}$), equipped with a Lynxeye XE-T detector. A modified Swagelok cell, with Be window serving as a current collector, allowed for diffraction patterns to be collected during electrochemical cycling. XRD scans were collected in a Bragg-Brentano geometry over a range of 20° , to 50° , 2θ with a total scan time of 20 minutes.

Chapter 7

NiNb₂O₆: an Atypical Lithium Battery Conversion Material with Improved Capacity over Time

1

7.1 Introduction

The main driving force for next-generation Li-ion batteries is improved energy density and power density. Especially for applications such as electric vehicles, it is increasingly important to increase the driving range and decrease the time to charge the battery. There are many chemical design routes to make this a reality, including exploring new crystal structures that can accommodate Li with a combination of mul-

¹This chapter includes contributions from Julija Vinckevičiūtė, Jonas L. Kaufman, William Zhang, Kira E. Wyckoff, and Ram Seshadri.

tielectron redox, high electronic conductivity, and high ionic conductivity. The combination of these properties can lead to high capacity, high power electrode materials. One example of this is the Wadsley-Roth crystallographic shear structures,[284] such as TiNb₂O₇,[3] PNb₉O₂₅,[279] and Nb₁₆W₅O₅₅[273]. The Wadsley-Roth structures have *M*-O octahedra both corner-connected and edge-sharing, which creates ideal channels for Li diffusion and, in some cases, electronic conductivity along the edge-sharing regions. They are almost entirely comprised of early transition metals, leading to low voltages between 1 V - 2 V, in the range of high voltage anode materials.

The columbite structure has some parallels with the Wadsley-Roth structures, in that there are both corner-connected and edge-sharing *M*-O octahedra. Unlike the Wadsley-Roth structures, they form with a combination of early and later transition metals, which can be a useful knob to increase the average voltage at which the redox reactions take place. Columbites have also been shown to have increased electronic conductivity when reduced. For example, introducing oxygen deficiency in MnNb₂O₆ increases the electronic conductivity,[308] which is also theoretically predicted for other columbites.[309] Therefore, upon Li insertion (reduction) they have the propensity to become electrically conductive, aiding in high power capabilities.

However, the ionic conductivity in structures like spinels and rutiles can be notoriously slow. The popular spinel anode material Li₄Ti₅O₁₂ has slow diffusion in the bulk but can be nanoscaled for high rate applications.[265, 266, 310, 311] Similarly, the rutile TiO₂ can be nanoscaled or made mesoporous to increase its rate capability, but innate Li diffusion in the bulk is slow.[312]

Previously, there have been some electrochemical insertion in columbite structures such as FeNb₂O₆, [313, 314] CrNb₂O₆, [313] CuNb₂O₆, [315, 316] CoNb₂O₆, [316] ZnNb₂O₆, [316] CdNb₂O₆, [316] CaNb₂O₆, [317] and MgNb₂O₆ [317]. Only the first

discharge and charge has been previously reported for NiNb₂O₆.[\[316\]](#) Out of all of the columbite structures tested, only CuNb₂O₆ and NiNb₂O₆ have significant discharge capacity on the first cycle between 3 V and 1 V, and CuNb₂O₆ was shown to undergo rapid capacity fade over 10 cycles between 3.5 V and 0.5 V. Some of the previous studies have a lower potential cutoff below 0.7 V, which is then convoluted by charge storage from carbon additives and harder to deconvolute.[\[302\]](#) Thus far, there has been no clear insight into why NiNb₂O₆, for example, can store more than 1 Li, but almost all of the other columbites store on average less than 0.25 Li on the first discharge. Additionally, understanding of what happens beyond the first cycle and the charge storage mechanisms have not been previously explored.

Through careful analysis using electrochemistry, Nb and Ni K-edge XANES, *operando* and *ex situ* powder diffraction, Raman spectroscopy, and DFT, we explore the unique charge storage mechanism of NiNb₂O₆ in contrast with MnNb₂O₆. We find that electrochemical lithium insertion into NiNb₂O₆ invokes a conversion mechanism. While often conversion leads to rapid capacity fade, the capacity instead increases over time.

7.2 Methods

7.2.1 Solid-state preparation of NiNb₂O₆ and MnNb₂O₆

The solid state syntheses of NiNb₂O₆ and MnNb₂O₆ have been previously reported.[\[318–320\]](#) Following these procedures, stoichiometric mixtures of Nb₂O₅ and NiO (for NiNb₂O₆) or MnCO₃ (for MnNb₂O₆) were ground together in an agate mortar and pestle on a scale of 2 grams. The ground powder starting materials were pressed into 13 mm diameter pellets under 2 tons and placed into alumina crucibles. For NiNb₂O₆, the reaction

mixture was annealed at 1000 °C for 20 hours with a ramp rate of 10 °C/min in ambient conditions and slow cooled, resulting in polycrystalline samples. For MnNb₂O₆, the reaction mixture was annealed initially at 800 °C for 2 hours, followed by 1050 °C for 20 hours in ambient conditions with a ramp rate of 10 °C/min, resulting in polycrystalline samples. NiNb₂O₆ and MnNb₂O₆ were each ball milled in a 2 mL stainless steel canister for a total of 30 minutes to reduce the particle size prior to electrochemical testing. Purity was assessed by synchrotron powder XRD at the high-resolution beamline 11-BM at the Advanced Photon Source at Argonne National Laboratory ($\lambda = 0.457841$). The samples were ground by mortar and pestle, packed in Kapton capillary tubes (1 mm OD), and sealed with epoxy. The patterns were refined using the Rietveld method using TOPAS Academic v6. Both patterns were refined within previously reported structures in the *Pbcn* (# 60) space group (R_{wp} NiNb₂O₆ = 10.9; R_{wp} MnNb₂O₆ = 7.4) and were found to have <5% impurities of NiO and Nb₂O₅.[\[321, 322\]](#)

7.2.2 Electrochemical testing

Composite electrodes were made with 70 % active material, 20 % conductive carbon (TIMCAL SuperP), and 10 % polyvinylidene fluoride (PVDF; Solef). The PVDF was dissolved in N-Methyl-2-pyrrolidone (NMP; Sigma Aldrich) in a FlakTek speedmixer at 2000 rpm for 5 minutes. The active material and carbon were ground together and added to the PVDF suspension and mixed at 2000 rpm for an additional 15 minutes. The slurry was cast onto aluminum foil with a doctor blade with a height of 150 μ m. The composite electrodes were dried under vacuum at 90 °C for 12 hours and punched into 1 cm diameter discs. Active loading per electrode is approximately 1 mg (1.25 mg/cm²). All electrochemical measurements were made using coin cells, except for samples for *ex situ* analysis described separately below, (MTI parts, 2032 SS cas-

ings) with polypropylene separators (Celgard 2500), 1 M LiPF₆ in EC/DMC electrolyte (Sigma Aldrich), and polished Li metal counter electrodes. All cells were assembled in an Ar-filled glovebox (H₂ < 0.1 ppm, O₂ < 0.1 ppm). Cyclic voltammetry was measured between 3 V – 1 V at 0.1 mV/s using a Bio-logic VMP-3 potentiostat. Galvanostatic cycling was measured between 3 V – 1 V at a C/10 rate, where for NiNb₂O₆, $C/10 = Q/10 = 340.5 \text{ mAh g}^{-1}/10 \text{ h} = 34.05 \text{ mA g}^{-1}$. Galvanostatic intermittent titration technique was executed similarly, with a rate of C/20 with rests of 90 minutes every 30 minutes. Separately, electrochemical impedance spectra were collected at the end of every discharge and charge over 20 cycles to monitor the evolution of the overall conductivity of the cell during cycling at a rate of C/10.

Ex situ samples were generated from loose powder (70 % active material ground with 30 % conductive carbon) in Swagelok cells with glass fiber separators (Whatman GF/D), 1 M LiPF₆ in EC/DMC electrolyte (Sigma Aldrich), and polished Li metal counter electrodes. Cells were cycled to the desired cycled number and voltage limit at a C/20 rate and moved back into an Ar-filled glovebox. The powder was isolated and washed three times with dimethyl carbonate, dried under vacuum, and subsequently ground with an agate mortar and pestle.

7.2.3 X-ray Absorption Spectroscopy

For *operando* XAS, thin pellet electrodes were fabricated from a ground mixture of 60% active material, 20% PTFE, 10% acetylene black, and 10% graphite. Approximately 20 mg of the composite electrode mixture was pressed into 10 mm pellets under 1 ton. The pellet electrodes were deposited directly onto a glassy carbon window of AMPIX cells, which have been previously described in detail.[293] Cell construction was completed in an Ar-filled glovebox. Glass fiber separators (Whatman GF/D) were

soaked with 1 M LiPF₆ in EC/DMC (Sigma Aldrich), and polished Li foil was used as the counter electrode. Measurements were completed in transmission mode ever 8 minutes while cells cycled at a rate of C/10. The absorption was measured at the Nb K-edge (18.9 keV), which was calibrated using Nb foil. *Ex situ* sample preparation is described above, and samples were harvested after 20 discharge cycles for Nb K-edge XAS and the first two discharges and charges for Ni K-edge XAS. Ni K-edge (8.3 keV) measurements were calibrated using Ni foil. *Operando* and *ex situ* Nb K-edge XAS was performed at beamline 12-BM at the Advanced Photon Source at Argonne National Laboratory, and *ex situ* Ni K-edge XAS was performed at beamline 6-2c at the Stanford Synchrotron Radiation Lightsources at SLAC. Processing and analysis of the XANES region was done using ATHENA, an open source software package for XAS.[\[294\]](#)

7.2.4 *Operando* X-ray diffraction

Operando XRD was collected using an electrochemical cell with a built-in Be window (127 μm thick). The slurry was prepared as described above but cast directly onto the Celgard separator. The composite electrode was placed directly onto the Be window, and the rest of the construction consisted of an additional glass fiber separator, 1 M LiPF₆ in EC/DMC (Sigma Aldrich), and a polished Li metal counter electrode. Diffraction patterns were collected using a Panalytical Empyrean powder diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in Bragg-Brentano geometry from $Q = 1.5 \text{ \AA}^{-1}$ to $Q = 3.75 \text{ \AA}^{-1}$. Scans were 13 minutes, repeatedly collected over the course of 1 galvanostatic discharge and charge cycle from 3 V – 1 V at a C/10 rate.

7.2.5 *Ex situ* X-ray powder diffraction

Ex situ samples for powder XRD were prepared as described above and harvested at the end of discharge (1 V) 1, 2, 5, 10, and 20, and at the end of charge (3 V) 1, 2, 5, and 10. The powders were loaded into a Kapton capillaries (1 mm OD) inside of an Ar-filled glovebox and sealed with epoxy on both ends. The capillaries were double sealed into air-impermeable bags inside of the glovebox and remained in inert atmosphere prior to data collection. Patterns were collected at the high-resolution beamline 11-BM at the Advanced Photon Source at Argonne National Laboratory ($\lambda = 0.457841$). The patterns were refined using the Rietveld method using TOPAS Academic v6.

7.2.6 Raman spectroscopy

Ex situ Raman spectra were collected using a Horiba LabRAM ARAMIS Raman spectrometer equipped with a confocal microscope and laser excitation wavelength of 633 nm. The powder samples were encased between two glass coverslips epoxied together inside of an Ar-filled glovebox. The spectrometer settings were as follows: 500 μm hole, 500 μm slit, 1200 cm^{-1} grating, 5 second exposures, and 10 spectra averaged, centered at 600 cm^{-1} .

7.2.7 Calculated Raman spectra

The off-resonance Raman spectrum was calculated using VASP via the vasp_raman.py program (A. Fonari and S. Stauffer, vasp_raman.py, <https://github.com/raman-sc/VASP/>, 2013.). Calculations used PAW pseudopotentials (Ni pv, Nb pv, O) and the PBE functional. A Hubbard correction with $U = 6.2$ eV was applied to Ni. Spin polarization was enabled,

with moments initialized ferromagnetically. Calculations used a plane wave energy cutoff of 640 eV and a Gamma-centered Monkhorst-Pack mesh with density 30 Å. The structure was first fully relaxed until all forces were less than 0.02 eV/Å. Phonons at the Gamma-point were then calculated from finite differences in VASP. A second order finite difference scheme with step size 0.005 Å was used to compute the activity of each mode, with the macroscopic static dielectric tensors calculated using density functional perturbation theory.

7.3 Results and discussion

NiNb₂O₆ adopts the columbite structure (*Pbcn*), consisting of corner- and edge-sharing Ni-O and Nb-O octahedra [Figure 7.1(a)]. Synthesis by solid state methods leads to particles on the order of 1–2 μm [Figure 7.1(b)]. When the bulk particles are cycled between 1 V and 3 V, a unique evolution of electrochemical features are observed. Cyclic voltammetry at a slow rate of 0.1 mV/s for 25 cycles shows the stark difference between the first cycle and subsequent cycles [Figure 7.2(a)]. There is a small pair of reduction and oxidation peaks at 1.7 V and 1.75 V, respectively, consistent with the small Nb₂O₅ impurity evident from the high-resolution XRD Rietveld refinement.[272, 323] The main reduction event on the first cycle between 1.25 V and 1.05 V is irreversible. There is a small oxidation peak at 1.45 V that increases in current over 25 cycles. Upon subsequent cycles, a reduction peak forms with maximum current at 1.4 V, forming a redox couple with the observed oxidation peak. Like the oxidation peak, the current grows over 25 cycles.

The galvanostatic cycling (C/10, based on one electron) reflects similar features [Figure 7.2(b)]. There is a very small plateau in the discharge at 1.7 V, which can

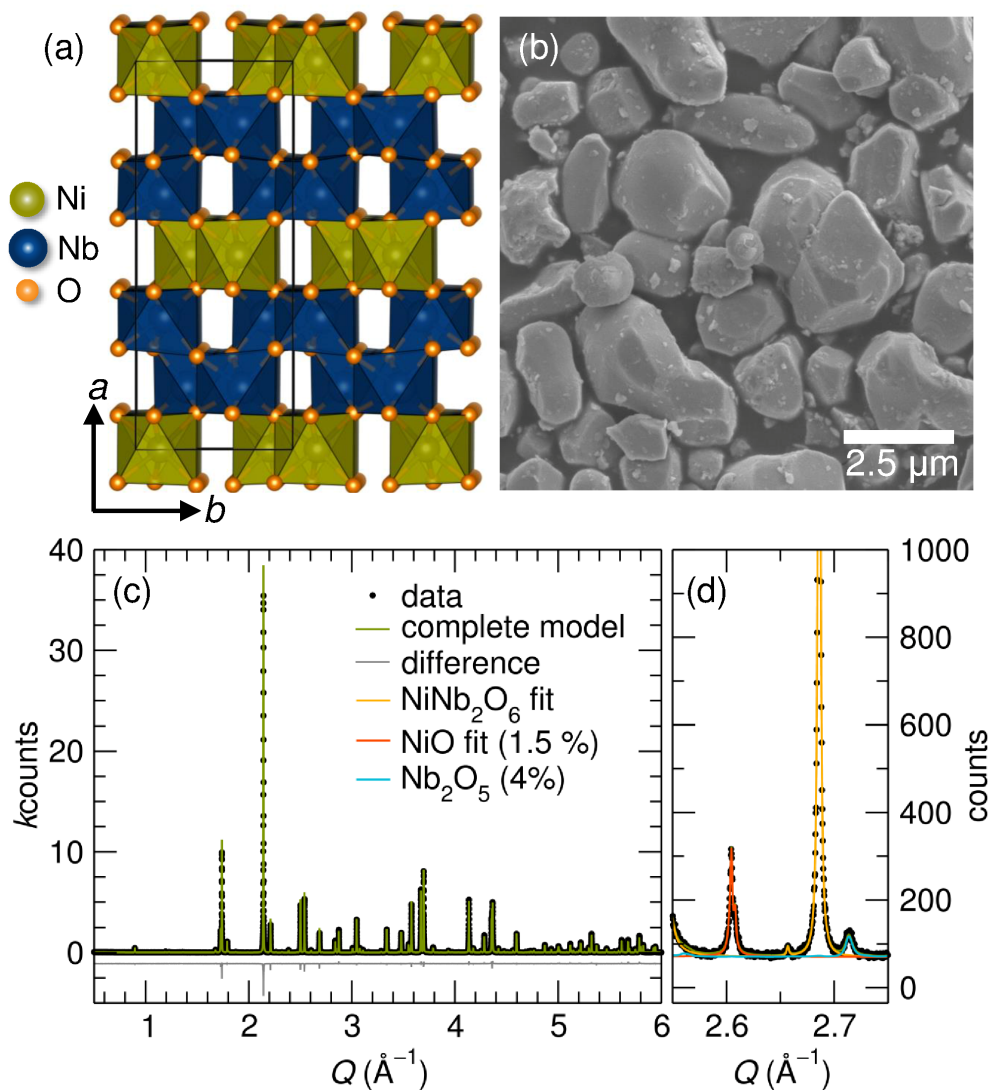


Figure 7.1: (a) The crystal structure of NiNb₂O₆ in the *Pbcn* space group (# 60). The Columbite structure consists of corner- and edge-sharing M-O octahedra. (b) SEM image of ball-milled particles (as used in battery slurries) show particle sizes on the order of 1–2 μm. (c) Synchrotron diffraction (11-BM at the APS) of the as-synthesized NiNb₂O₆. Rietveld refinements indicate a small amount of NiO (1.5 %) and Nb₂O₅ (4 %) impurities. (d) Evidence of the NiO and Nb₂O₅ impurities can only be visualized near the baseline of the pattern.

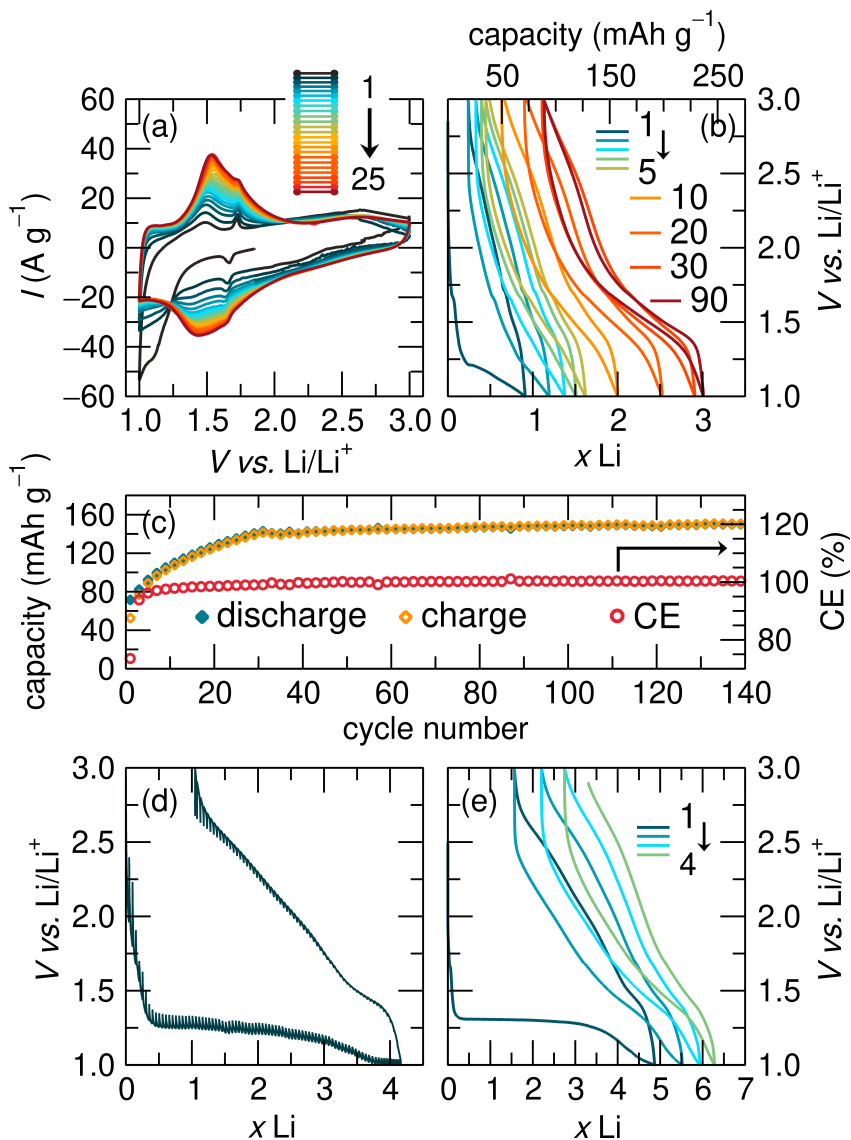


Figure 7.2: Electrochemical characterization of NiNb₂O₆ between 1 V and 3 V against Li metal. (a) Cyclic voltammogram at 0.1 mV s⁻¹. Every cycle between 1 and 25 is shown, and the specific current increases over time. (b) Galvanostatic cycling at C/10. Approximately 1 Li is inserted upon the first discharge, which increases to 1.5 Li over the first 30 cycles. (c) Specific capacity versus cycle number shows how the capacity increases over the first 30 cycles. It reaches a maximum capacity of 150 mA h g⁻¹. The Coulombic efficiency, as defined by the charge capacity divided by the discharge capacity, is poor in the first 5 cycles, but subsequently reaches nearly 100%. (d) Galvanostatic intermittent titration technique at C/20 with a 90 minute rest period every 30 minutes. (e) NiNb₂O₆ galvanostatically cycled slowly (C/50) at 40 °C shows almost 5 Li inserts on the first cycle, and about 4 thereafter, reflecting the thermodynamics of the system more closely. Additionally, the shape of the electrochemical curve matches the curve after many cycles when cycled at room temperature.

be attributed to the residual Nb₂O₅. Between 1.25 V and 1 V there is a long sloping plateau, resulting in a total of 0.9 Li inserting upon the first discharge. There is some cell-to-cell variation with how much Li inserts upon the first cycle, ranging from 0.9 Li to 2 Li, which could possibly arise from electrolyte wetting differences within the cell or ball milling conditions leading to slightly smaller particle sizes. The plateau observed on the first discharge does not exist in subsequent cycles. Instead, there is a sloping region between 3 V and 1 V. The shape of the galvanostatic curves changes over the first 30 cycles, as well. The voltage hysteresis toward lower potentials (between 1.7 V and 1 V) decreases after the second cycle, and a higher voltage sloping plateau is observed between 1.75 V and 1.3 V. Additionally, the amount of Li inserted per cycle increases to 1.5 Li. This evolution in electrochemical features is evidence of the material converting over time, and through an atypical means that leads to an increase in capacity.

This capacity increase can be observed more clearly by looking at the capacity as a function of cycle number [Figure 7.2(c)]. The first cycle shows a low discharge capacity of 75 mAhg⁻¹, and the charge capacity is even less at 53 mAhg⁻¹, such that some of the initial Li that's inserted is never removed. However, there is a gradual increase in capacity over the first 30 cycles, reaching a respectable capacity of 150 mAhg⁻¹ that's maintained through 140 cycles. The Coulombic efficiency starts very poor in the first few cycles but by cycle 30 reaches 100 %. This can also be observed from the discharge and charge capacities reaching equal capacities after the growth plateaus.

GITT was performed to gain a better understanding of the first cycle under near-equilibrium conditions [Figure 7.2(d)]. Similarly to the C/10 galvanostatic discharge, there is a sloping plateau between 1.3 and 1 V. However, the stark difference is now 4 Li inserts during the first discharge. The shape of the charge is also reminiscent of first charge at C/10, but 3 Li are removed. There is also a large change in the over-

potential (the difference between the potential with applied current and the potential at open circuit) from discharge to charge. The largest overpotential is at the very start of discharge, suggesting a kinetic barrier to Li inserting into the structure. There is a reduction in the overpotential, but still large, during the sloping plateau during the first discharge, suggesting a kinetically slow two-phase region. The overpotential dramatically decreases during charge, when the profile becomes sloping. The initial irreversible conversion is associated with leading to faster kinetics in the deinsertion process. Toward the end of charge, the overpotential increases again, likely related to full deinsertion becoming disfavorable.

The electrochemical behavior observed for NiNb₂O₆ is unique among other isostructural columbites with different transition metals substituted for Ni, such as FeNb₂O₆, CoNb₂O₆, and CuNb₂O₆. In order to probe this phenomenon with an internal study, and to compare and contrast to learn more about the NiNb₂O₆ we synthesized and cycled MnNb₂O₆. MnNb₂O₆ is also in the *Pbcn* space group and made on a bulk particle scale (1–2 μ m) [Figure 7.8]. Within the same voltage window of 1 V to 3 V, there is no evidence of Li insertion in MnNb₂O₆ [Figure 7.9]. (A small Nb₂O₅ impurity similar to what is seen in the electrochemical characterization of NiNb₂O₆ contributes to the only observable capacity.) This suggests that Ni plays a crucial role in the electrochemical performance in this structure.

Nb and Ni K-edge XANES lends credence to this idea. NiNb₂O₆ in its pristine state is comprised of Ni²⁺ and Nb⁵⁺. Since Ni is already in the 2+ state, intuition dictates that Nb would be reducing (first, at least). However, this is not what we observe in the XANES data [Figure 7.3]. Instead, *operando* Nb K-edge XANES throughout the first discharge and charge shows no change in the energy of the edge [Figure 7.3(b)]. Therefore, Nb is not being reduced in the first discharge. Only upon subsequent cycles

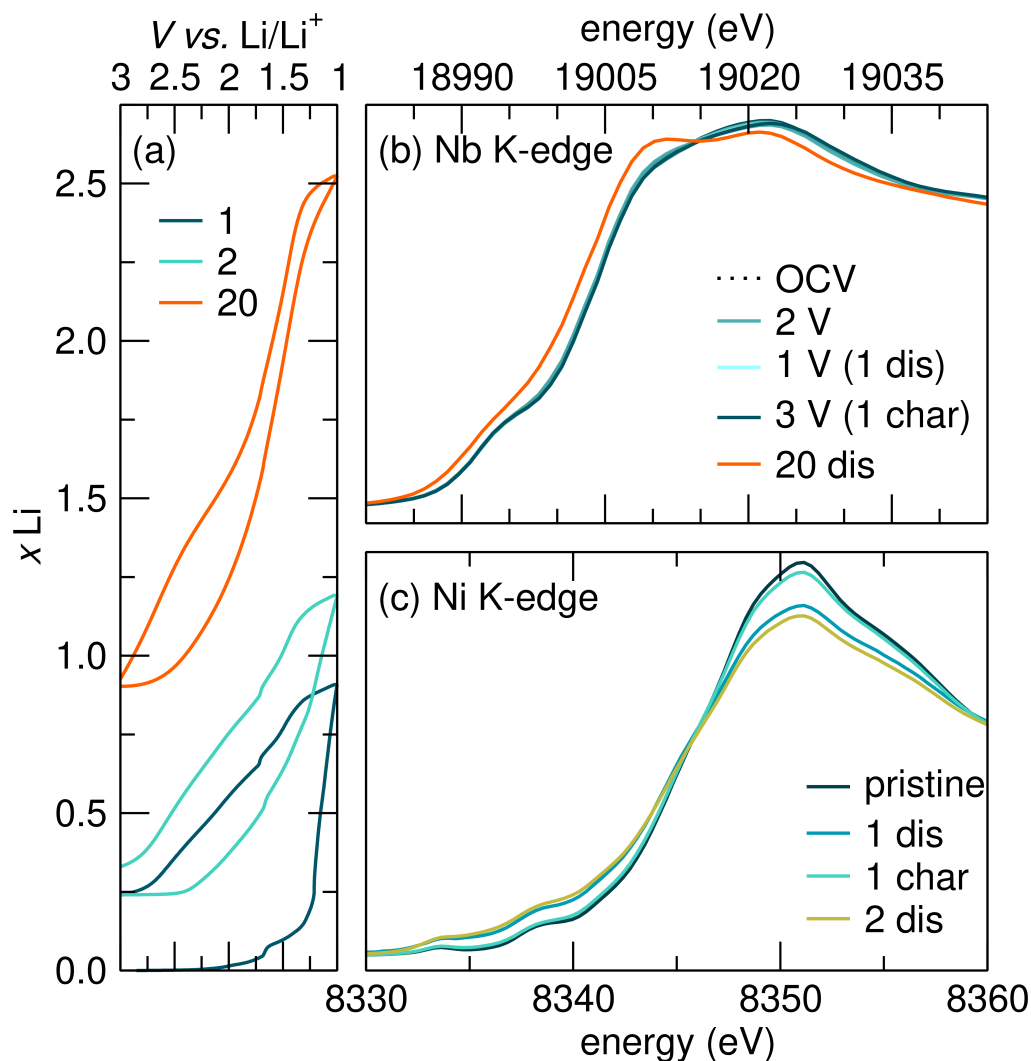


Figure 7.3: X-ray absorption near-edge spectroscopy lends insight into the evolution of redox processes across several cycles. (a) Relevant galvanostatic cycles of NiNb₂O₆ against Li metal. (b) *Operando* Nb K-edge XANES through the first discharge and charge shows no energy shift. *Ex situ* Nb K-edge XANES after 20 cycles (discharge) shows a substantial decrease in the edge energy (reduction). (c) *Ex situ* Ni K-edge XANES show the edge shifting to lower energies upon discharge 1 and 2 and a shift back to higher energies upon charge.

do we see reduction of Nb, evidenced by the shift in the edge to lower energies after the 20th discharge (1 V).

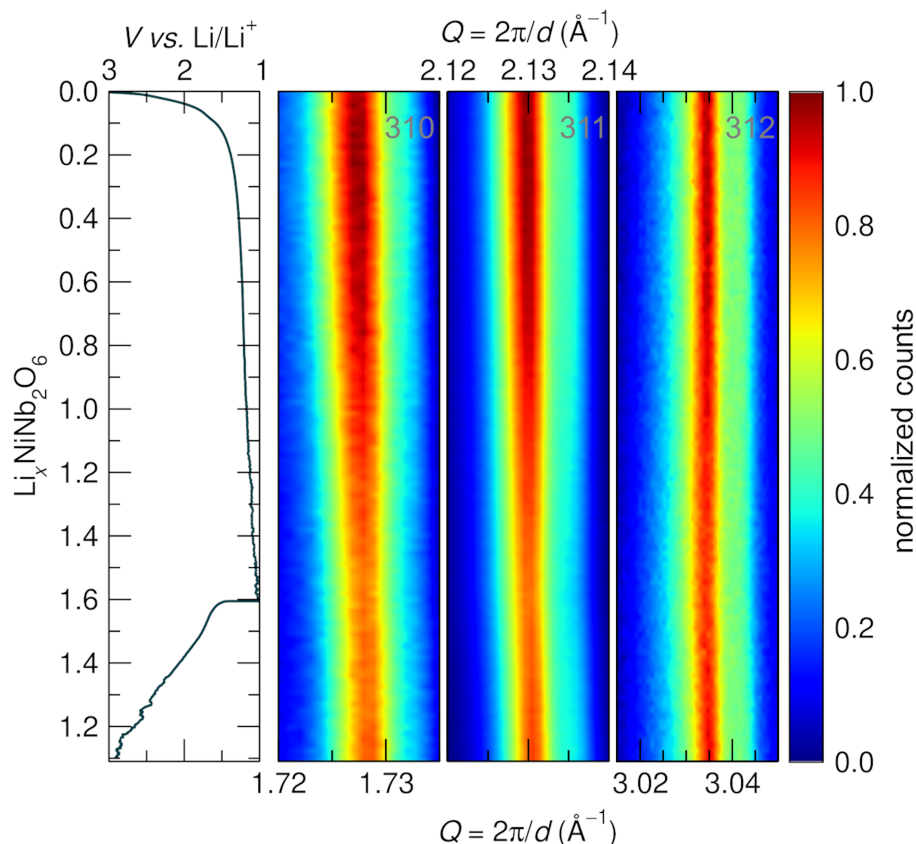


Figure 7.4: *Operando* powder XRD for the first discharge and charge (3 V – 1 V). The first discharge inserts 1.6 Li, and the charge extracts 0.5 Li. OCV is at the top of the heatmap, and depth of discharge increases going down. Select Q ranges are shown to highlight the changes in distinct peaks, mostly the loss of intensity that does not recover upon charge. The heatmaps are normalized to the highest intensity peak in each region, such that dark red reflects the highest intensity. A heatmap of the full Q range is provided in the Supporting Information.

There is direct evidence through Ni K-edge XANES that Ni initially reduces instead, and the process is semi-reversible. The edge shifts to lower energy at the end of the first discharge (1 V). When charged (3 V), the edge shifts back to the original energy in the pristine state, with lower intensity. The second discharge shows the edge decreasing in energy again, slightly more than observed in the first cycle and with lower intensity at

the top of the edge. Since the first charge resembles the energy of the pristine material, and the two discharges resemble each other, this Ni reduction process, at least in the first couple of cycles, is semi-reversible.

The change in long-range order is mostly the loss of intensity with increasing cycling. The changes in the first cycle are particularly subtle and were probed by *operando* powder XRD [Figure 7.4]. The first discharge inserted 1.6 Li, limited at 1 V. A detailed look at some of the prominent peaks in the pattern, the 310, 311, and 312 peaks, show a gradual decrease in intensity of those peaks through the end of discharge, but no peak shifting. There is also no evidence of new peaks emerging from the full diffraction pattern [Figure 7.10]. Upon charge, 0.5 Li is removed and there is a very slight contraction of the unit cell, which is also observable, perhaps more clearly, in the 510 and 021 peaks [Figure 7.11]. The 510 and 021 peaks also show a small increase in intensity at the top of the charge, but none of the peaks regain full intensity.

Ex situ high-resolution synchrotron XRD tracks the changes in long-range order for cycles 1, 2, 5, 10, and 20, when the majority of the significant changes occur according to the electrochemistry results [Figure 7.5(b-d)]. The same select Q ranges are shown for clarity. The decrease in intensity is even clearer over the 20 cycles comparing the discharge products, as well as the slight unit cell contraction. There is also a noticeable increase in amorphous background contributions starting from the 5th discharge that suggests there are more local structural changes occurring. Cycle-to-cycle there is some reversibility seen in the long-range order, since some of the intensity is recovered on each charge. The lower peak intensity over 20 cycles is consistent with *ex situ* SEM images that show particle cleaving and smaller particles after 20 discharges, which does not exist after just 1 discharge [Figure 7.5(e-f)].

Ex situ Raman spectroscopy lends insight into how the local structure changes over

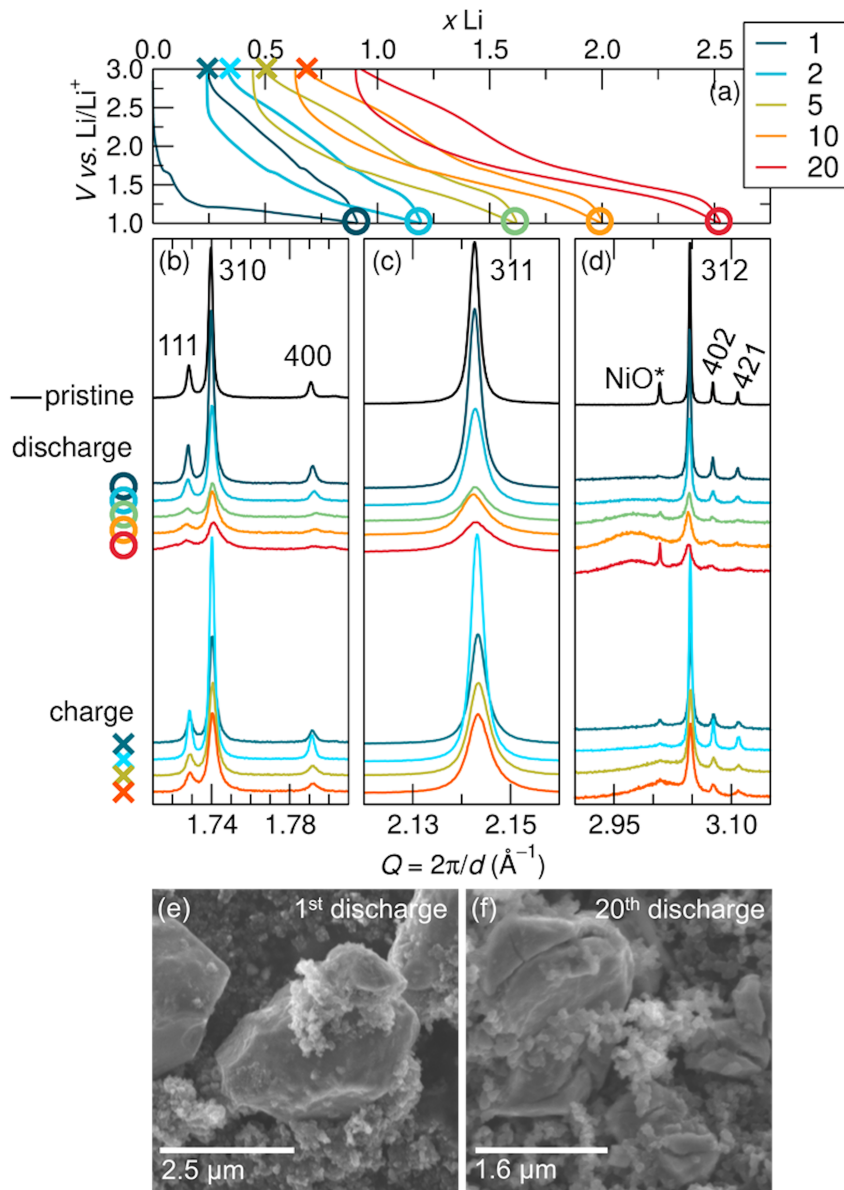


Figure 7.5: *Ex situ* synchrotron powder XRD at the end of discharge and charge across 20 cycles and *ex situ* SEM images of the particles after 1 discharge and 20 discharges. (a) Representative galvanostatic cycles marked at the sampling points (circles = discharge, crosses = charge). The patterns are divided into representative Q ranges to highlight the changes observed and peak intensities are consistent within each panel. Full patterns are provided in the Supporting Information. Discharge and charge patterns are grouped together to clearly see the trends. (b) $1.71 - 1.81 \text{ \AA}^{-1}$ shows a reduction in peak intensity over 20 cycles. (c) $2.12 - 2.16 \text{ \AA}^{-1}$ also shows a reduction in peak intensity over 20 cycles. (d) $2.9 - 3.15 \text{ \AA}^{-1}$ shows a similar decrease in peak intensity over 20 cycles and additionally the emergence of broad peaks within the background. (e) SEM image of the particles as cast within the composite electrode after 1 discharge. The large particles are the active material (on the order of $2 \mu\text{m}$) and the smaller particles are the SuperP carbon additive. (f) SEM of the particles after 20 discharges. The particles have become significantly smaller (on the order of $0.3 - 1 \mu\text{m}$) and are fractured.

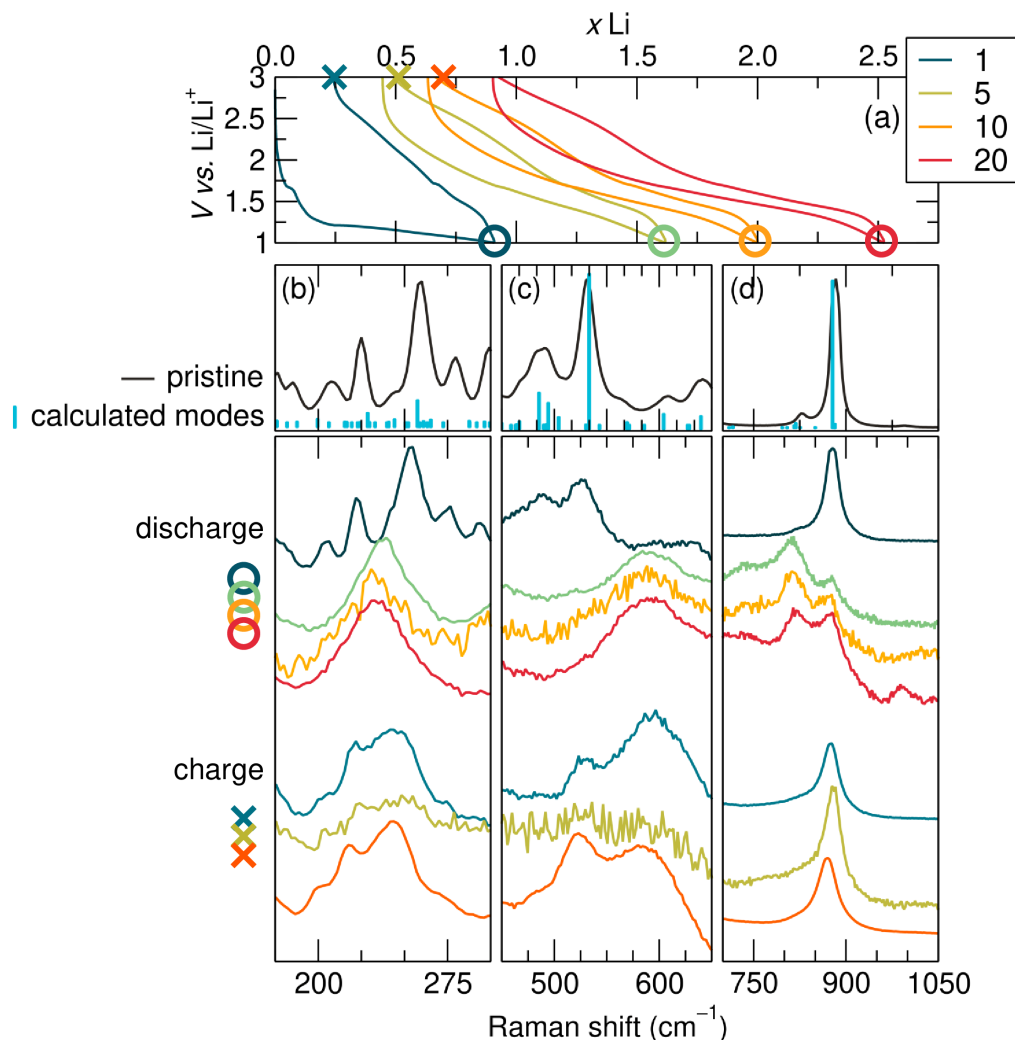


Figure 7.6: *Ex situ* Raman spectroscopy at the end of discharge and charge across 20 cycles. (a) Representative galvanostatic cycles marked at the sampling points (circles = discharge, crosses = charge). The spectra are divided into representative wavenumber ranges to highlight the changes observed. Discharge and charge spectra are grouped together to clearly see the trends. The pristine NiNb₂O₆ spectrum is grouped with the calculated modes at the top for each region. (b) 175 – 300 cm^{-1} , (c) 450 cm^{-1} – 650 cm^{-1} , and (d) 700 cm^{-1} – 1050 cm^{-1} . Full spectra are provided in the Supporting Information.

the first 20 cycles [Figure 7.6]. The Raman spectrum of pure NiNb₂O₆ was calculated using DFT in order to identify the symmetry elements changing as Li is inserted. The highest intensity mode, evident from the full spectrum, is at 879 cm⁻¹, which represents a wagging mode of the Ni–O bonds [Figure 7.13]. Another prominent peak at 534 cm⁻¹ represents a wagging mode of Nb–O bonds [Figure 7.13]. Tracking the changes in these modes in particular yields insight into the transformations of the Ni-O and Nb-O octahedra during cycling. The first discharge shows the least amount of change. Subsequent spectra at the end of discharge show very similar features. The mode at 879 cm⁻¹ diminishes greatly, but does not disappear completely. This suggests heavy interaction of Li with the Ni-O octahedra. This interaction is reversible, evidenced by the spectra recovering to the original peak upon charge. The transformations associated with Li interaction with the Nb-O octahedra appear to be much less reversible. After the first discharge, the main mode at 534 cm⁻¹ disappears in all of the other discharge spectra and a new broad peak emerges centered at 590 cm⁻¹. The charge spectra show a small recovery of the original Nb-O bond, but the new mode at 590 cm⁻¹ does not disappear. The Raman spectroscopy is indicative of the local structure transformations, which is likely what drives the capacity observed. After the first cycle, NiNb₂O₆ converts and becomes increasingly more amorphous. The added capacity is likely due to consumption of more of the material over time. An interesting study would be to compare the effects of nanosizing NiNb₂O₆, to understand if the mechanism of conversion stays the same or if a different evolution of redox processes occur.

7.4 Additional characterization and analysis

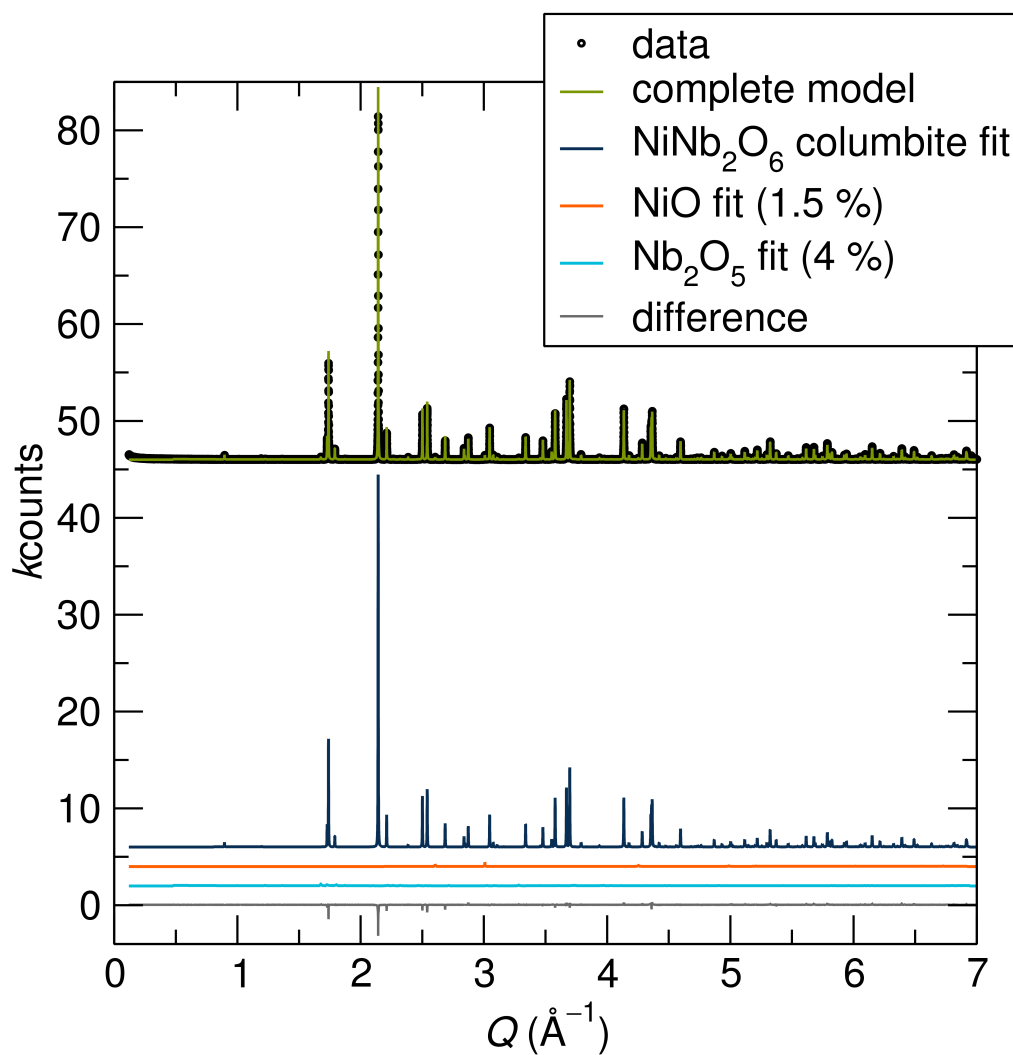


Figure 7.7: Rietveld refinement of NiNb₂O₆ with phase deconvolution, including less than 5 % impurities of Nb₂O₅ and NiO.

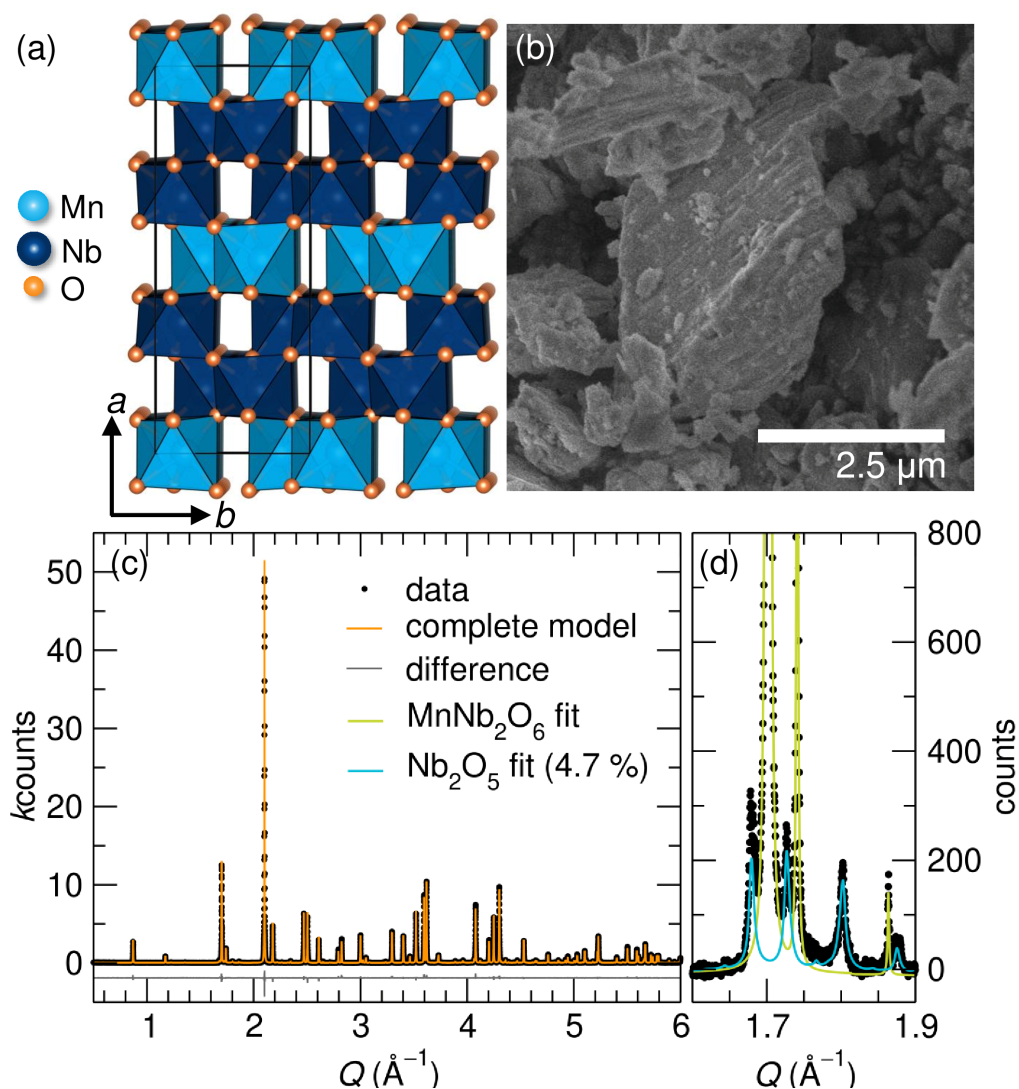


Figure 7.8: (a) The structure of MnNb₂O₆ is isostructural to NiNb₂O₆ and crystallizes in the *Pbcn* space group. (b) The particle sizes from the solid-state synthesis of MnNb₂O₆ after ballmilling are similar to those observed in NiNb₂O₆. They are bulk particles on the order of 1 μm to 2 μm. (c) A Rietveld refinement of high resolution synchrotron diffraction of MnNb₂O₆ reveals a 4.7% impurity of Nb₂O₅. (d) The deconvoluted fit in the *Q* = 1.6 Å⁻¹ - 1.9 Å⁻¹ range shows distinct Nb₂O₅ peaks, though much lower in intensity.

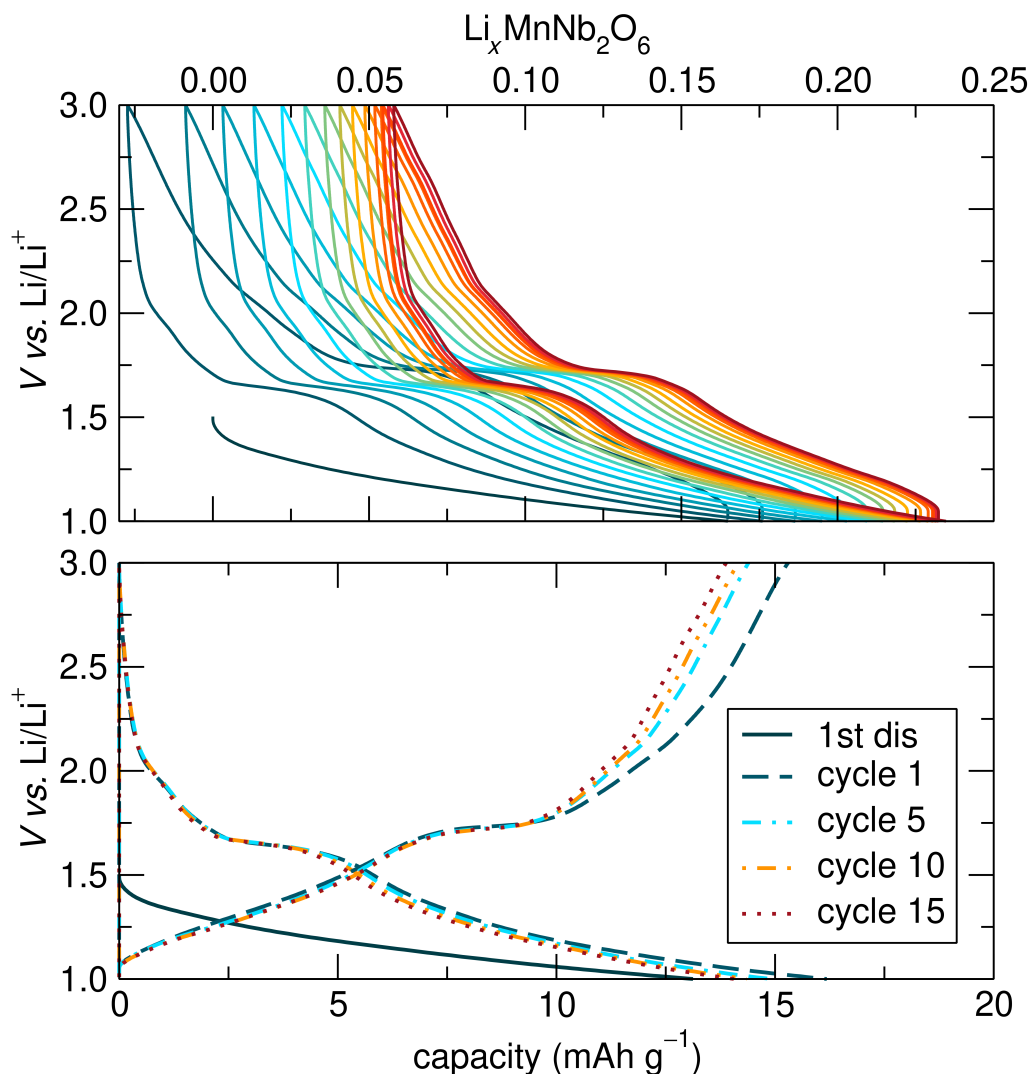


Figure 7.9: MnNb_2O_6 was cycled galvanostatically at a C/10 rate between the 1 V and 3 V, under identical conditions to NiNb_2O_6 . However, MnNb_2O_6 shows negligible capacity in this voltage range. The very small plateau is likely from the Nb_2O_5 impurity. The stark contrast to the galvanostatic cycling results for NiNb_2O_6 suggest Ni plays an important role in activating the redox in this structure.

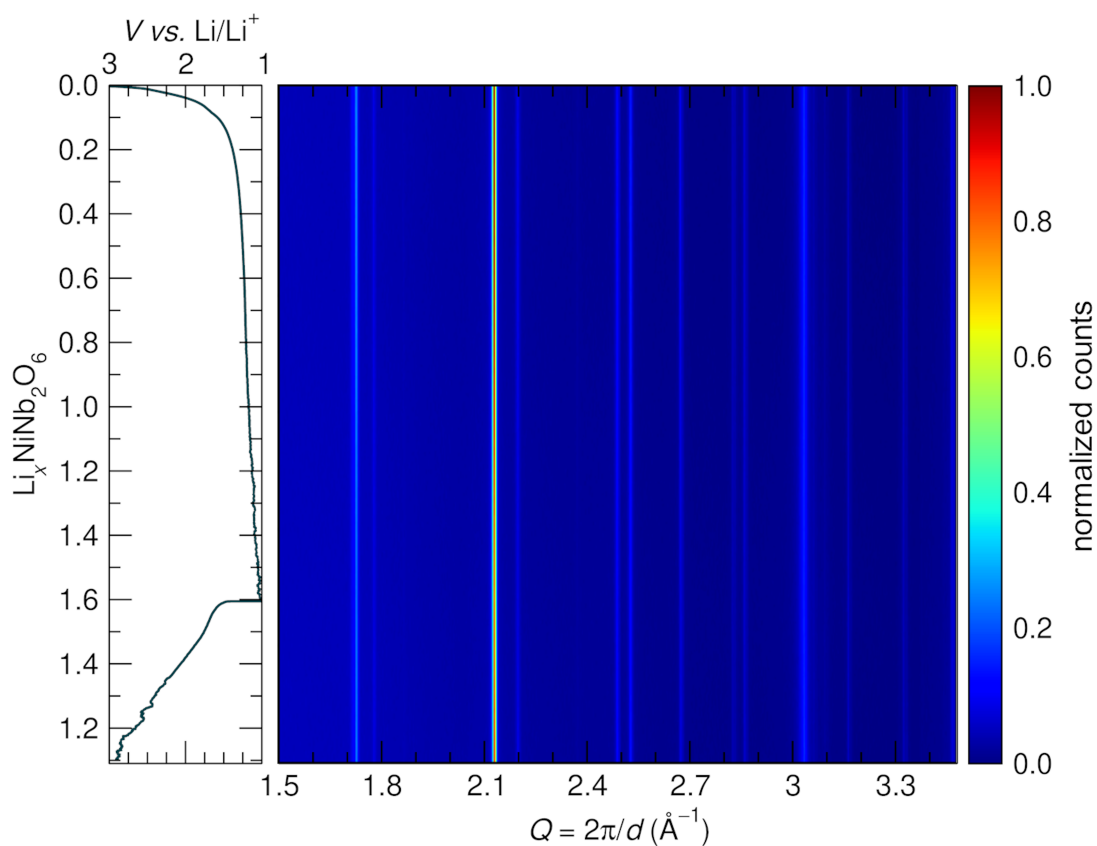


Figure 7.10: *Operando* X-ray diffraction in the full Q range measured from $1.5 \text{ \AA}^{-1}$ to $3.5 \text{ \AA}^{-1}$. There are no obvious changes when the entire Q range is represented, which highlights that many changes that occur within the first cycle are subtle.

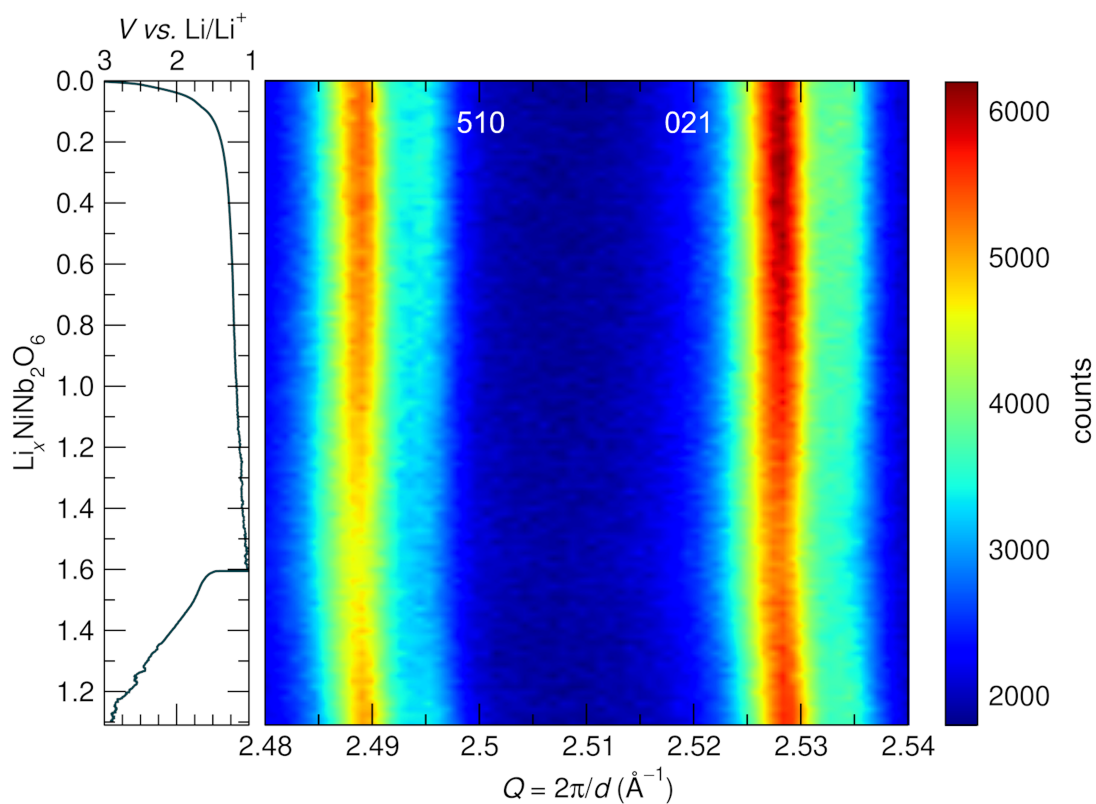


Figure 7.11: *Operando* X-ray diffraction in the Q range from $2.48 \text{ \AA}^{-1}$ to $2.54 \text{ \AA}^{-1}$ includes the 510 and 021 peaks. The changes seen in these peaks deviate slightly from the changes seen in most of the other peaks. The 510 peak especially slightly regains intensity upon charge. Both the 510 and 021 peaks show a small unit cell contraction upon charge, as well.

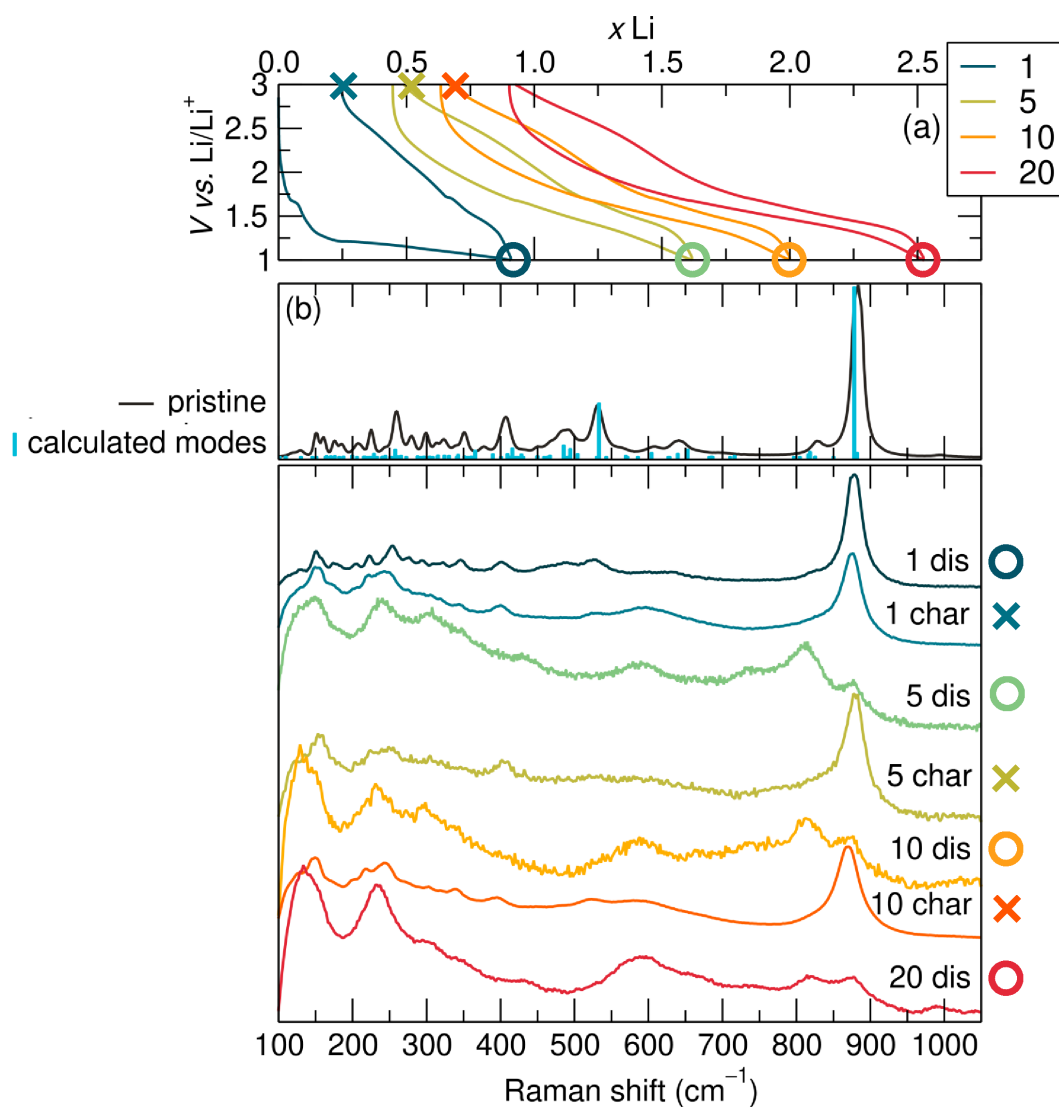


Figure 7.12: *Ex situ* Raman spectra at the end of discharge and charge across 20 cycles. (a) Representative galvanostatic cycles marked at the sampling points (circles = discharge, crosses = charge). The full spectral region shows the relative intensity of peaks within a single spectrum.

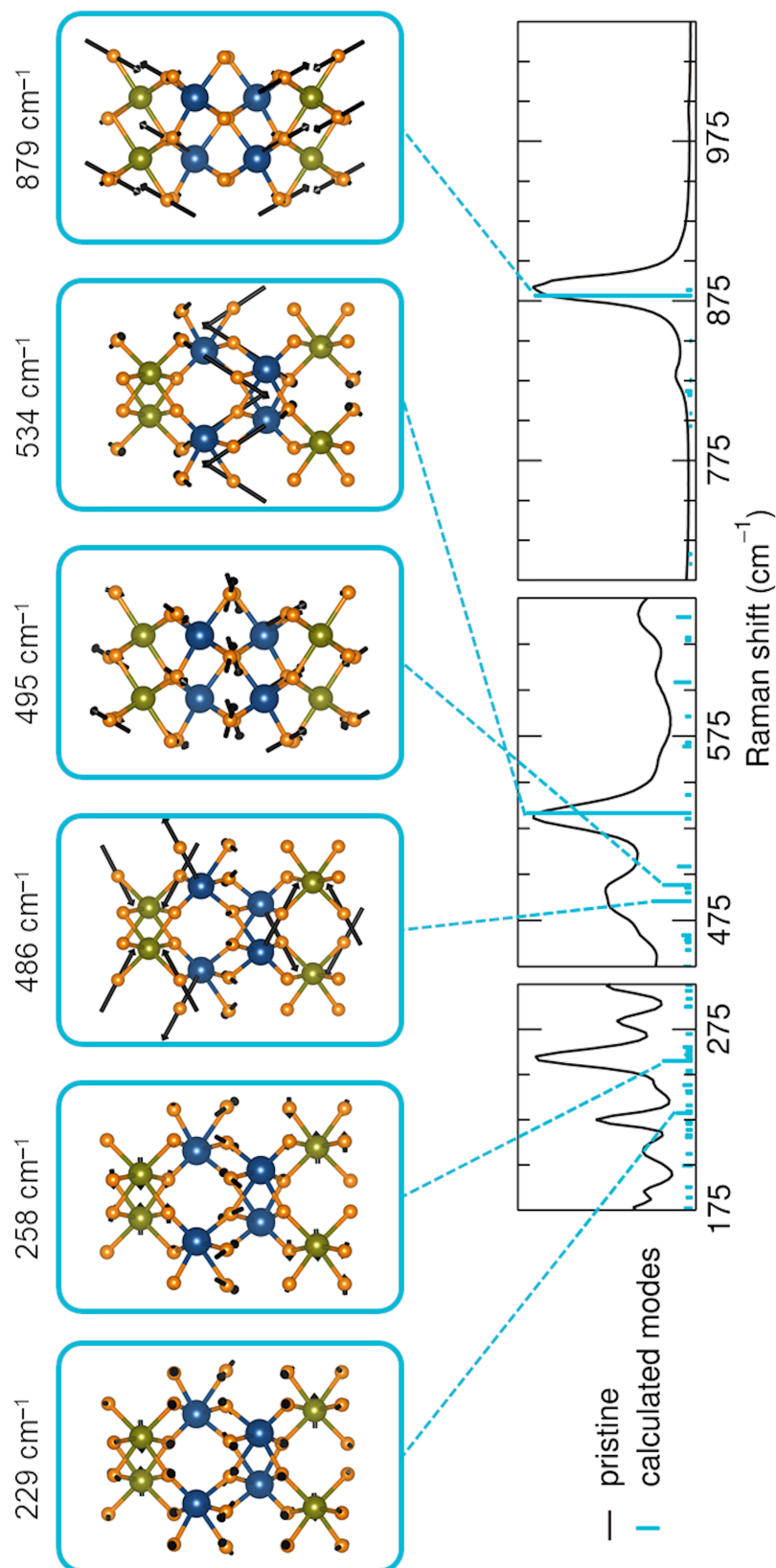


Figure 7.13: Vibrations corresponding to individual Raman modes calculated mapped onto the crystal structure of NiNb₂O₆. Arrows indicate the direction for motion of the bonds. Select modes were chosen according to intensity, how well they match to the experimental shifts, and if there are significant changes to those modes during cycling.

Appendix A

Design and implementation of an *operando* XRD and Raman spectroscopy electrochemical cell

A.1 Introduction

Detailed mechanistic understanding of the electrochemical reactions, particularly chemical and structural transformations, are necessary to improve battery performance. While *ex situ* measurements can lead to valuable insight, many times the electrochemical processes progress through metastable pathways. Therefore, *in situ* (within the native environment) or *operando* (during operation) measurements are ideal to capture the metastable reactions occurring within the cell.[324] *Operando* measurements have the added benefit of showing these transformations in real time. Each technique has its own set of challenges in terms of cell design to make feasible for *operando* measurements. Despite this, there have been dozens of unique cell designs to accommodate

different techniques, including but not limited to X-ray scattering and imaging,[325–328] neutron scattering and imaging,[329, 330] Raman spectroscopy,[323] UV-Vis spectroscopy,[331] NMR spectroscopy,[332–334] electron paramagnetic resonance,[335] and microscopy[336–338]. Many synchrotrons and neutron spallation sources have dedicated a lot of time and energy to accommodate *operando* electrochemistry,[293, 329, 339, 340] but there are also many custom cells built in lab settings.[337, 341] The main requirements for an electrochemical cell still stand. The ends must be electrically conductive, but they must be isolated by an electrically insulating body hosting the electrochemical stack. Often the challenge becomes maintaining good electrical contact to the electrodes and enough internal pressure for good electrochemical performance.

Two *operando* techniques that have a great deal of utility in a lab setting are X-ray powder diffraction and Raman spectroscopy, especially if they can be used in tandem. X-ray diffraction gives information of the long-range order of crystalline materials, while Raman spectroscopy yields information of the local structure through vibrational modes. For crystalline materials with Raman-active modes, these are therefore complementary techniques, though they can be used independently; for example, amorphous materials can greatly benefit from *operando* Raman spectroscopy. Since Raman spectroscopy requires an optical window and XRD requires an X-ray transparent window, adaptive cell designs usually do not intersect. The methods described within include a single cell, in which one of the components can be switched to adapt to either Raman spectroscopy or XRD.

A.2 Methods

Cell design and construction The cell was designed using the academic version of Autodesk Fusion 360 CAD (computer-aided design) software. Three parts were designed cohesively: the top of the cell (316 stainless-steel), the electrically-insulating spacer (PEEK), and the bottom of the cell (316 stainless-steel) with an opening left for an X-ray- or optically- transparent window to be inserted. Additionally, a stainless-steel cell holder was designed to snugly fit the cell with set screws as both an electrical contact to the cell top and as a way to center the cell and securely attach it with screws to either an XRD stage or a Raman stage. The X-ray transparent window is a pre-machined Be disc (Materion) 13 mm in diameter and 127 μm thick, which was chosen as an optimal thickness for mechanical robustness as well as X-ray transparency. The optically transparent window is a single-crystalline quartz disc (Ted Pella) 6 mm in diameter and 100 μm thick. The cell is 50 mm in diameter, and the cavity for the electrochemical stack is 20 mm in diameter within the confines of the PEEK spacer. Two chemical-resistant Viton fluoroelastomer o-rings on either side of the PEEK spacer allow for an inert atmosphere to be maintained. Flathead screws were chosen such that the top of the cell could lie flush with the centering piece with appropriate countersinking, and, to prevent short-circuiting, they are made from either PEEK or polycarbonate. A compromise between size and strength, the screws are size 6-32 and 0.5 inches long. A current collector for the Li metal is made from 316 stainless steel and is 19 mm in diameter and 0.5 mm thick. A stainless-steel conical compression spring (0.72 in diameter, 0.375 in length) provides internal pressure.

Building the electrochemical stack The cell is constructed from the bottom to the top. The PEEK spacer is inserted into the bottom of the cell, and the electrode of

interest is placed directly onto the window (either Be or quartz, depending on the application). A 20 mm diameter glass fiber separator (Whatman, GF/D) is placed on top of the electrode. (The oversize fit helps to keep the electrode in place). The remainder of the assembly takes place in an Ar-filled glovebox. 1 mL of 1 M LiPF₆ in EC/DMC (or electrolyte of choice) is added to the cell bottom, enough to soak the glass fiber separator. Lithium metal foil is polished, cut to 19 mm diameter, and adhered to the stainless-steel current collector, and subsequently added to the bottom of the cell (Li-side down). The conical compression spring is added on top of the stainless-steel current collector. The top of the cell is then added to the stack and secured using the four screws. The cell can then be flipped such that the window is on top and the bottom is secured to the cell holder with the set screws.

Electrode formulations For composite electrodes, there are two formulations that have been tested to perform with this cell geometry. The first formulation results in a thin pellet composed of the active material, PTFE binder, and carbon black additives in an average composition of 60% active material, 20% PTFE, and 20% carbon, though the active material can be increased for more signal by subtracting the amount of carbon added. An average total mass of 60 mg can be pressed into a pellet using a 15 mm diameter pellet die press under 1 ton of pressure. The fabricated electrode should encompass the entire area of the window and contact the surrounding stainless-steel bottom of the cell, which acts as the current collector. The second formulation results in a cast electrode adhered to a lithium-permeable separator. The electrode is composed of 70% active material, 10% PVDF binder, and 20% carbon black (though the same modifications can be made for this electrode type). PVDF is first dispersed in NMP and speed mixed for 5 minutes at 2000 rpm until dissolved. Carbon black and the active material are either ball milled for an intimate mixture or ground by hand in

an agate mortar and pestle. The carbon and active material are speed mixed together with PVDF and NMP until a uniform mixture is achieved. The dispersion is then cast onto polypropylene separator material of choice (McMaster Carr, Celgard) using a doctor blade with a 400 μ height and dried in a vacuum oven at 80 C for 3 hours. 19 mm discs are then punched from the overall cast and massed to know the exact mass of active material per electrode. Average active mass per electrode is 10 mg.

Data collection Collecting XRD patterns and Raman spectra will mostly depend on the material of interest. The centering plate can be affixed to both the sample stages for the Panalytical Empyrean powder diffractometer and the Horiba T64000 Raman spectrometer (specific to UCSB). Otherwise, a centering plate can be made to affix to any appropriate sample stage in order to ensure the cell is stable during electrochemical measurements and the beam or laser is maximized to measure the sample.

A.3 Results and discussion

Inspired by the AMPIX cell designed from Argonne National Laboratory, the cell consists of a 3-part construction that screws together to achieve an air- and liquid-tight seal by using o-rings [Figure A.1]. A PEEK spacer separates the top and bottom stainless steel cell casing, and PEEK screws are used to prevent short-circuiting. The electrochemical stack is typical of most cells – a spring to create ensure good contact between all of the parts, a stainless steel current collector, a lithium chip, the separator soaked in electrolyte, and the electrode of interest. The electrode of interest is in direct contact with the window. This makes it easier to focus on the sample for Raman spectroscopy and gives the best signal-to-noise for XRD.

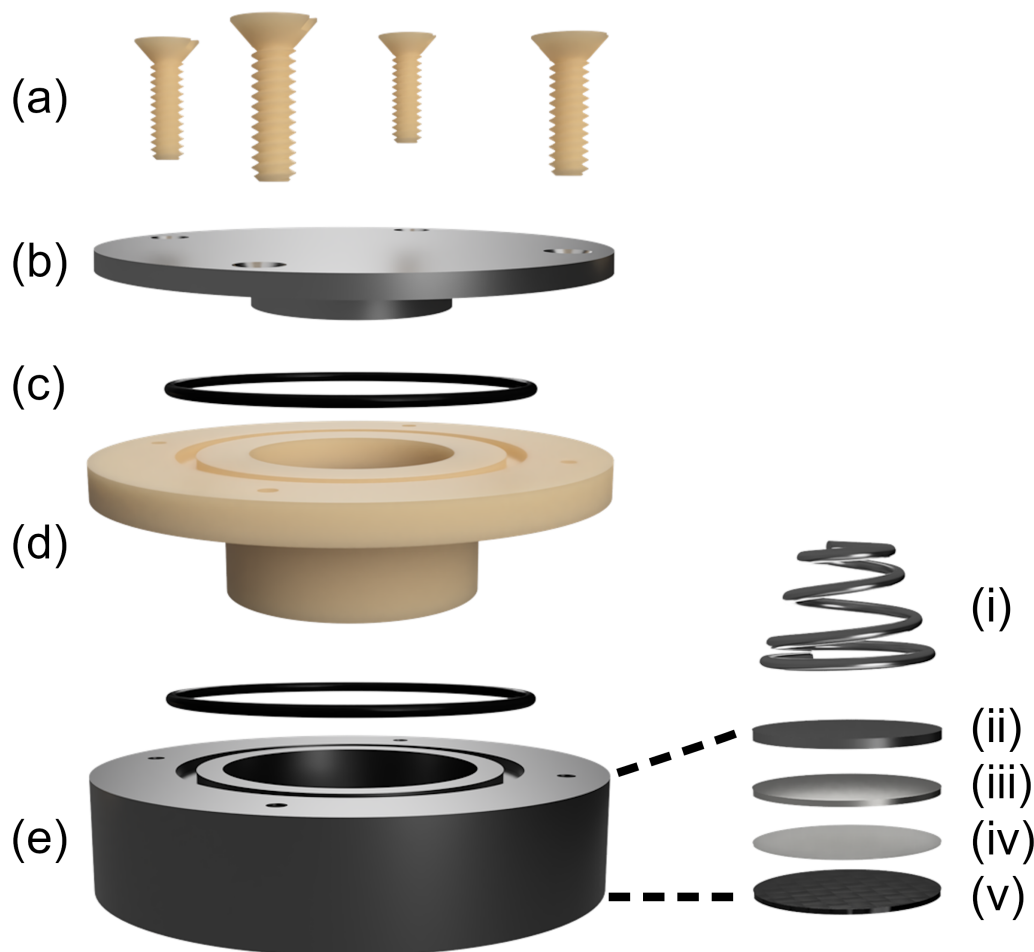


Figure A.1: Rendering of *operando* cell design (left) and electrode stack (right). (a) PEEK screws to prevent short-circuiting, (b) cell top (in order of assembly), (c) Viton fluoroelastomer o-ring to create an air- and liquid-tight seal ($\times 2$), (d) PEEK spacer to prevent short-circuiting (electronically insulating), (e) cell bottom (in order of assembly) that contains the X-ray or optically transparent window. The electrode stack consists of: (i) conical compression spring to apply internal pressure once the cell top is tightened, (ii) stainless steel current collector (also for providing mechanical rigidity against the spring), (iii) polished Li chip, (iv) separator material (usually glass fiber), (v) fabricated composite electrode of interest, such that the active material lies flush with the window of the cell bottom.

An important point is the electrode must also be in contact with the stainless steel bottom beyond the window because this acts as the current collector. Since the X-ray transparent Be window is 13 mm in diameter, the active electrode must have be

at least 14 mm in diameter to contact the stainless steel. The optically transparent window for Raman spectroscopy is only 6 mm, so any electrode size greater than 7 mm in diameter can be accommodated [Figure A.2]. Another consideration to be aware of is the possibility of a lithium concentration gradient, where the center of the electrode farthest from the stainless steel could be more deficient in lithium. The size of the windows were chosen by carefully weighing the tradeoffs.

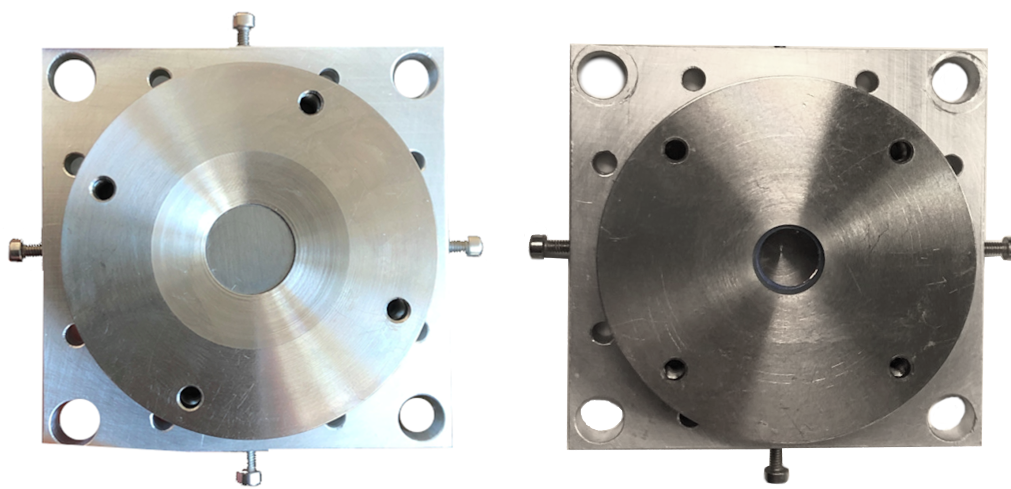


Figure A.2: Machined *operando* cells following the described design. View is of the bottom of the cell (looking down upon the window) as the cell is positioned in its centering holder. Left, *operando* X-ray diffraction cell with a Be disc window (13 mm diameter). Right, *operando* Raman spectroscopy cell with a quartz window (6 mm diameter). All parts of the cell are common between the two except for the bottom piece in which the window sits to accommodate different sizes for the different techniques.

For XRD, the larger sampling area translates directly to higher signal-to-noise and limits the amount of stainless steel in the beam without having to alter the beam size. The thickness of the window was also made as thin as possible to reduce the amount of Be signal but provide enough mechanical rigidity to hold up to the internal pressure of the spring. For Raman spectroscopy, the quartz window can be much smaller since the laser spot size is on the order of microns. Since quartz is electrically insulat-

ing, shrinking its size is highly necessary to avoid too much of a lithium concentration gradient. The 6 mm diameter window creates options to sample different spots sequentially during cycling, or to map the electrode surface during cycling to understand inhomogeneity across an electrode surface.

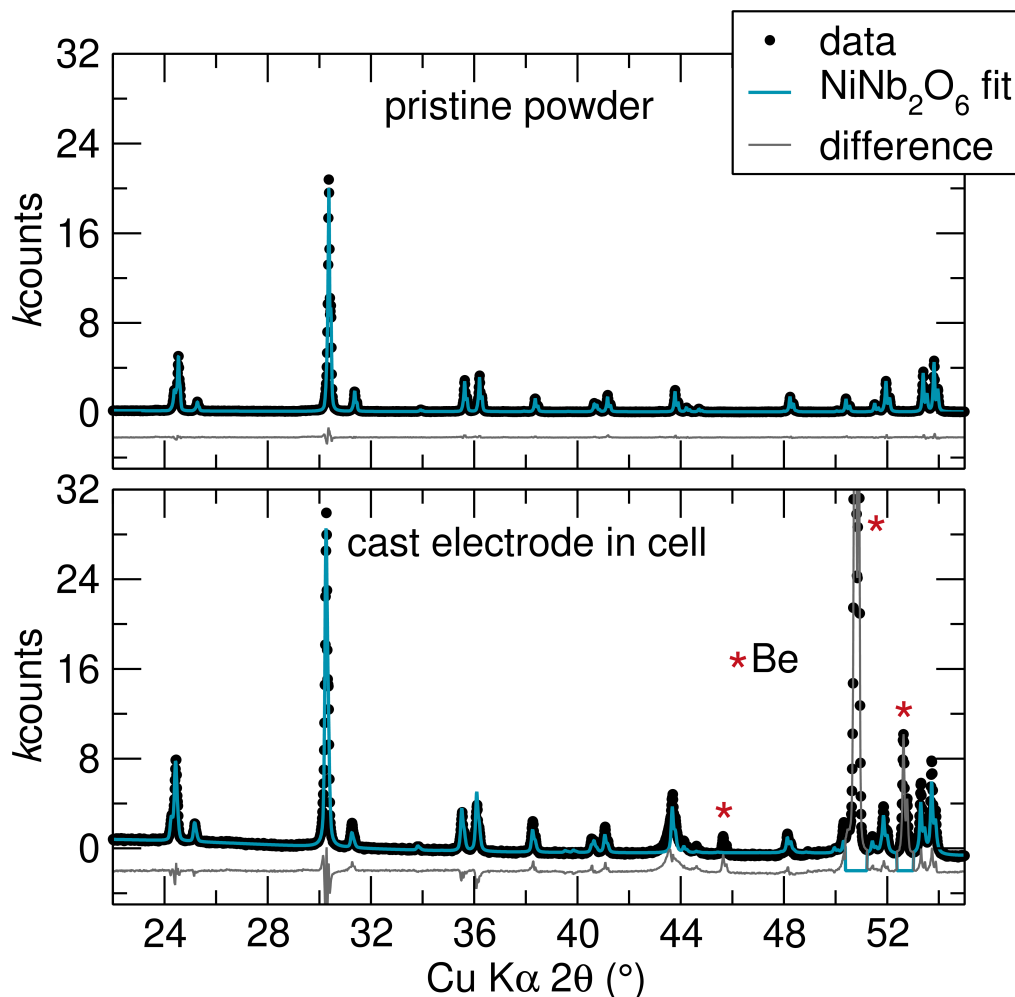


Figure A.3: Diffraction patterns of NiNb_2O_6 using a Panalytical Empyrean powder diffractometer equipped with a $\text{Cu K}\alpha$ source. (a) Diffraction pattern of pristine powder measured on a Si single crystal zero-background plate. (b) Diffraction pattern of composite electrode cast onto polypropylene (Celgard) separator material, cut into a 19 mm disc, and assembled into the cell. The sample height was adjusted to take the thickness of the Be window into account.

In terms of the electrode fabrication, there are two general options. The first is

a composite pellet electrode that includes a mixture of the active material, conductive carbon, and PTFE pressed into a free-standing electrode. The second is a slurry composite electrode cast onto polypropylene separator material. The advantage of the pellet electrode is quick, simple fabrication only needing about 30 mg of active material. The advantage of the cast electrode is less active material per electrode, and it is easier to keep centered in the cell when constructing it. The cast electrode also yields excellent counts on the diffractometer equipped with a Cu K α source [Figure A.3]. The specific recipes for both types of composite electrodes are highly customizable depending on the active material of interest.

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