

ADVANCES AND DEVELOPMENT OF ALL-SOLID-STATE LITHIUM-ION BATTERIES

by

JAMES EDWARD TREVEY

B.S., University of Colorado, 2007

M.S., University of Colorado, 2010

A thesis submitted to the

Faculty of the Graduate School of the

University of Colorado in partial fulfillment

of the requirement for the degree of

Doctor of Philosophy

Department of Mechanical Engineering

2011

This thesis entitled:

Advances and Development of All-Solid-State Lithium-Ion Batteries

written by James Edward Trevey

has been approved for the Department of Mechanical Engineering

Se-Hee Lee

Conrad R. Stoldt

Date_____

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Trevey, James E. (Ph.D., Mechanical Engineering)

Advances and Development of All-Solid-State Lithium-Ion Batteries

Thesis directed by Associate Professor Se-Hee Lee

Lithium-ion battery technologies have always been accompanied by severe safety issues; therefore recent research efforts have focused on improving battery safety. In large part, the hazardous nature of lithium-ion batteries stems from the high flammability of liquid electrolytes. Consequently, numerous researchers have attempted to replace liquid electrolytes with nonflammable solid electrolytes in order to avoid potential safety problems. Unfortunately, current solid electrolytes are incapable of performing as effectively as liquid electrolytes in lithium-ion batteries due to inferior electrochemical capabilities. While some “all-solid-state” batteries have found niche application, further technological advancement is required for large scale replacement of liquid-based batteries.

The goal of this research is to develop all-solid-state batteries that can outperform liquid batteries and understand the mechanisms that dictate battery operation and behavior. This involves fabrication of highly conducting solid electrolytes, production and analyzation of batteries employing state-of-the-art electrode materials, and generation of high power and high energy density lithium batteries.

In this dissertation, the first objective was to manufacture highly conducting solid electrolytes that are stable in contact with lithium metal. Numerous characterization techniques were used to gain understanding of physical and chemical properties of solid electrolytes, as well as mechanisms for fast ion conduction. A new process for production of highly conducting and

stable solid electrolytes is developed and materials are used to evaluate performance of electrodes in an all-solid-state construction.

The second objective of this work was to research the performance of both positive and negative electrodes incorporating solid electrolyte. Evaluation of electrochemical results allowed for a good understanding of reaction mechanisms taking place within composite battery materials and at electrolyte/electrode interfaces. Variation of solid electrolyte make-up and composite electrode architecture reveals numerous advantages of solid state batteries over liquid batteries.

The third and final objective of this work was to demonstrate high energy/power density all-solid-state rechargeable batteries. Electrode materials with fast lithium diffusion and kinetic properties were investigated. Alteration of particle size and testing temperature exposed the capability of solid state batteries to achieved high performance, comparable to that of liquid electrolyte batteries.

DEDICATION

To my darling fiancé, Kristie, for supporting me and believing in me always.

To my life-long friend, Paul, for always helping me stay in the game and stay on track.

To my amazing family, who's proud and encouraging words helped keep me motivated.

ACKNOWLEDGEMENTS

I am grateful to my advisor, Prof. Se-Hee Lee, for his help and guidance throughout the course of this investigation. Without him, I would never have perused this degree.

Extra thanks to Dr. Leah Riley, my friend and lab mate, for being a large source of encouragement, motivation, and as she says “friendly competition”. Discussions with her and my other friend and lab mate Isaac Scott were invaluable to my overall understanding of electrochemistry. I would also like to extend my great appreciation to Dr. Yoon Seok Jung, who, during my earlier graduate years helped develop the foundation for my later work, and whose expertise helped me to grasp the knowledge and perspective I needed to succeed in my field.

Special thanks to Prof. Conrad Stoldt for interim advising and guidance. The outcome and success of my PhD would not have happened without his management and motivation.

The assistance given to me by faculty, Victor Bright and Martin Dunn, for their insight and wisdom, as well as staff of the Mechanical Engineering department of the University of Colorado Boulder, namely Sharon Anderson, for keeping me on track and helping me get through the fine print.

I would also like to thank my undergraduate assistants for their help. This work could not have been completed without them. Special thanks to Sean Miller for help in compiling the references for this dissertation.

The author is grateful for financial support from DARPA/DSO.

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1. Introduction

1.1 Motivation

The technological revolution of the past few centuries has been fuelled almost entirely by various deviants of the common combustion reaction, resulting in nearly depleted fossil fuel reserves as well as global climate change as an outcome of carbon dioxide emissions. A more sustainable means of energy production must be adopted in order to continue supplying the growing energy needs of technological improvement as well as an ever-increasing population. Electrochemical energy production and conversion/storage is under serious consideration as a more sustainable and environmentally friendly alternative for providing energy to the rising needs of today's society. Current systems under investigation for mass energy conversion/storage include batteries, fuel cells, and electrochemical capacitors.

Rechargeable lithium-ion batteries are widely accepted as power sources for portable electronics and telecommunications equipment [1]. They are being increasingly researched for larger-scale applications such as power supply of plug-in hybrid electric vehicles (PHEV) and electric vehicles (EV) [2] as well as energy storage for renewable applications such as wind and solar in an effort to reduce carbon emissions and prevent the rapid depletion of fossil fuels [3]. While lithium-ion batteries are well suited for the relatively small-scale applications of portable electronics, their large-scale application has revealed a number of issues regarding safety of operation.

1.2 Why Solid State?

Currently, liquid electrolytes are the dominant electrolyte for use in lithium-ion batteries as they maintain a number of advantages such as high ionic conductivity, excellent contact area with high capacity electrodes, and accommodation of size changes of electrodes during charge and discharge cycles. However, liquid electrolytes are extremely flammable and hazardous and have the potential to fuel thermal runaway within batteries. Thermal runaway of liquid-based lithium-ion batteries can result in explosion; therefore it is necessary for batteries containing liquid electrolytes to contain extra safety layers and devices in order to enclose the liquid safely and to prevent safety issues. These extra safety layers and devices tax the overall energy density of batteries as additional weight. Furthermore, liquid electrolyte batteries typically exhibit solvent leakage and rapid self discharge, especially in elevated temperature environments. Liquid-based batteries are also susceptible to decomposition of the electrolyte with electrode materials which can result in poor performance. Current batteries of today contain these hazardous liquid electrolytes regardless of their safety drawbacks as their performance is unparalleled. In order to construct batteries with a higher degree of safety, liquid electrolytes must be replaced with non-flammable solid electrolytes.

Recent research has revealed solid electrolytes as a viable means of replacing flammable liquid electrolytes for lithium-ion batteries. Solid electrolytes possess a number of advantages over liquid electrolytes such as excellent chemical and physical stability as well as excellent shelf life. Most importantly, they are non-flammable and non-conductive to thermal runaway enabling them for general use as well as larger scale applications. Additionally, batteries employing solid electrolyte do not require the extra safety layers and devices, allowing the overall energy density of batteries to remain high after production. Moreover, only lithium ions are

mobile in solid electrolytes, reducing the number of undesirable side reactions and decomposition of the electrolytes that can result in performance loss or safety issues. Unfortunately, current solid state electrolytes cannot perform comparably with liquid electrolytes due to lower achievable conductivity and poor contact area.

The challenge for materials scientists and battery researchers alike is to develop a battery architecture that is safe, low cost, and yields high energy density while maintaining scalability. This thesis studies solid electrolytes and their integration with state-of-the-art (SOA) positive and negative materials in all-solid-state lithium-ion batteries. The physical, kinetic, and electrochemical properties of solid electrolytes and electrode materials are examined with various analytical tools and the results are analyzed.

1.3 Goal

It was the goal of this work to demonstrate functional all-solid-state batteries as well as to understand the mechanisms of electrochemistry as they apply to battery technologies. This work includes developmental research on solid-state electrolytes regarding manufacturing methods and characterization, as well as integration with SOA electrodes.

The first objective was to synthesize highly conducting solid electrolytes and characterize their physical and chemical properties. Understanding mechanisms for fast ion conduction through solid materials is the key to fabrication of all-solid-state batteries. Second, electrochemical performance of both anodes and cathodes incorporating solid electrolyte was investigated. A good understanding of reaction mechanisms taking place within composite battery materials and at electrolyte/electrode interfaces is gained from analysis and evaluation of electrochemical

performance of electrodes in an all-solid-state construction. The third and final objective of this work was to demonstrate high energy/power density all-solid-state rechargeable batteries. Enhanced kinetic properties of electrode materials resulting from reduced particle size are confirmed by electrochemical titration techniques and observation of improved battery performance.

References

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2. Background

2.1 Concept of a Battery

Rechargeable lithium-ion batteries (LIBs) involve the exchange of lithium ions between two electrodes upon charging and discharging. The lithium insertion and extraction process occurs with a flow of ions through the electrolyte, accompanied by a reduction and oxidation (redox) reaction of the host matrix enabled by the flow of electrons through an external circuit. This is called a “rocking-chair” design because the lithium ions “rock” back and forth between the positive and negative electrode. Lithium is the most favorable mobile ion species for batteries as it is the lightest of all metals and has the greatest electrochemical potential, providing the largest energy density for weight. The performance of LIBs in comparison to other rechargeable batteries is shown in Figure 2.1 [1].

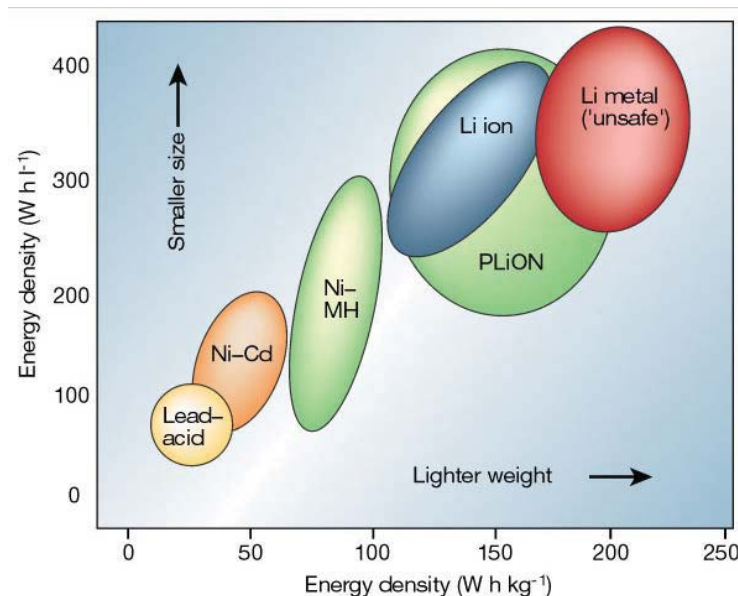


Figure 2.1: Comparison of the different battery technologies in terms of volumetric and gravimetric energy density [1].

The principal problem of using conventional batteries such as lead-acid and Ni-Cd batteries as power sources for consumer electronics or electric vehicles is low specific energy density compared with other batteries. This low specific energy density is typically a result of low voltage. Over the voltage or specific charge alone, the most critical feature of a battery is high energy density. Second most important is how this energy is supplied: the potentials should be as constant as possible. Operatively, having no flex in the “*Potential vs. Capacity*” curve it is ideal, which will be shown in Section 2.3.5. The presence of flexes indicates that the energy is furnished at different potentials. Of course, this potential can be stabilized easily by an appropriate electronic component, but with additional costs and weight. That is why it is preferable to have a no-flex discharge shape. The principle advantages and disadvantages of LIBs are listed in Table 2.1.

Table 2.1: Strengths and drawbacks of LIBs.

Advantages	Disadvantages
High Energy/Power density Good Cycle life Coulombic efficiency Low Self-discharge rate No memory effect	High Cost Unstable at high temperature Unstable at Overcharging High internal resistance Safety

For large batteries, i.e. electric vehicle batteries, high voltage is an additional advantage because it reduces the number of cells required to achieve the desired voltage thereby reducing the complexity of the battery management system [2]. The present specific power and energy density for commercial lithium-ion batteries stands at approximately 200 W kg^{-1} and 150 Wh kg^{-1}

¹, respectively. High power lithium-ion cells can reach power densities of 10000 W kg^{-1} , but there is a tradeoff with a lower energy density of 60 Wh kg^{-1} . A Ragone plot (Figure 2.2) shows the superior performance of the lithium ion battery cells [3].

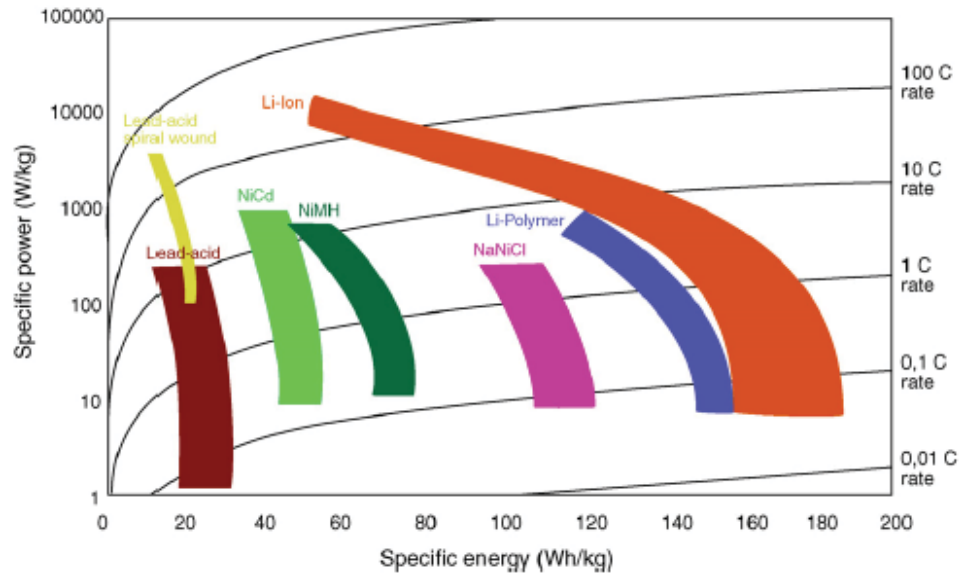


Figure 2.2: Ragone plot for performance of leading battery technologies [3].

For all intents and purposes, production of large cell sizes that would be put together into battery packs for electric vehicles (EVs) and hybrid electric vehicles (HEVs) can be scaled from smaller consumer electronics. However, the cost of producing small cells is far too high for such batteries to be used economically in mass-market vehicles. Therefore, considerable research and development (R&D) work has been devoted to lowering the costs of Li-ion batteries to improve their competitive position for potential long-term development in the vehicle market. While there is a concentrated effort on reducing the extremely high cost of cathode materials, efforts to reduce other cost components are being examined too. Mass market production of electric

vehicles would require large scale production or importing of several materials, with the impact on price depending on the material. For less abundant materials such as cobalt, supplies could eventually be constrained, driving up the price. Therefore, research on material cost reduction is critical if mass development of EV's and HEV's is to be realized in the near future.

2.1.1 Components

Electrochemistry covers all reactions in which a chemical change is the result of electric forces and in the reverse case, where an electric force is generated by a chemical process [4]. A galvanic cell is an electrochemical cell that generates electricity as result of the spontaneous reaction occurring within the cell. It consists of two dissimilar electronically conducting electrodes (the anode and the cathode) separated with an ionically conducting electrolyte in between. At the interface between electronic and ionic conductors the passage of electrical charge is coupled with a chemical reaction known as a redox reaction, where there is a transfer of electrons from one species to another. The two half reactions of the anode and cathode involve oxidation (removal of electrons) and reduction (addition of electrons), respectively.

A battery consists of one or more electrochemical cells, connected in series or parallel, or both, depending on the desired output voltage and capacity. The electrochemical cell generally consists of only a few major components:

1. The anode/negative electrode/reducing electrode, which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.
2. The cathode/positive electrode/oxidizing electrode, which accepts electrons from the external circuit and is reduced during electrochemical reaction.

3. The electrolyte or the ionic conductor and electron insulator, which provides the medium for transfer of electrons, as ions, inside the cell between the anode and cathode. The electrolyte is typically a liquid (an organic solvent, such as EC-DMC), with dissolved salts (such as LiPF₆) to impart ionic conductivity. Some batteries use solid electrolytes, of which high ionic conductivities at room temperature have been recently obtained, making them viable for commercialization.
4. The separator, which is a porous sheet that serves to keep the positive and negative electrodes apart. Batteries employing a solid electrolyte do not need a separator as the solid electrolyte itself is the barrier between the positive and negative electrodes.

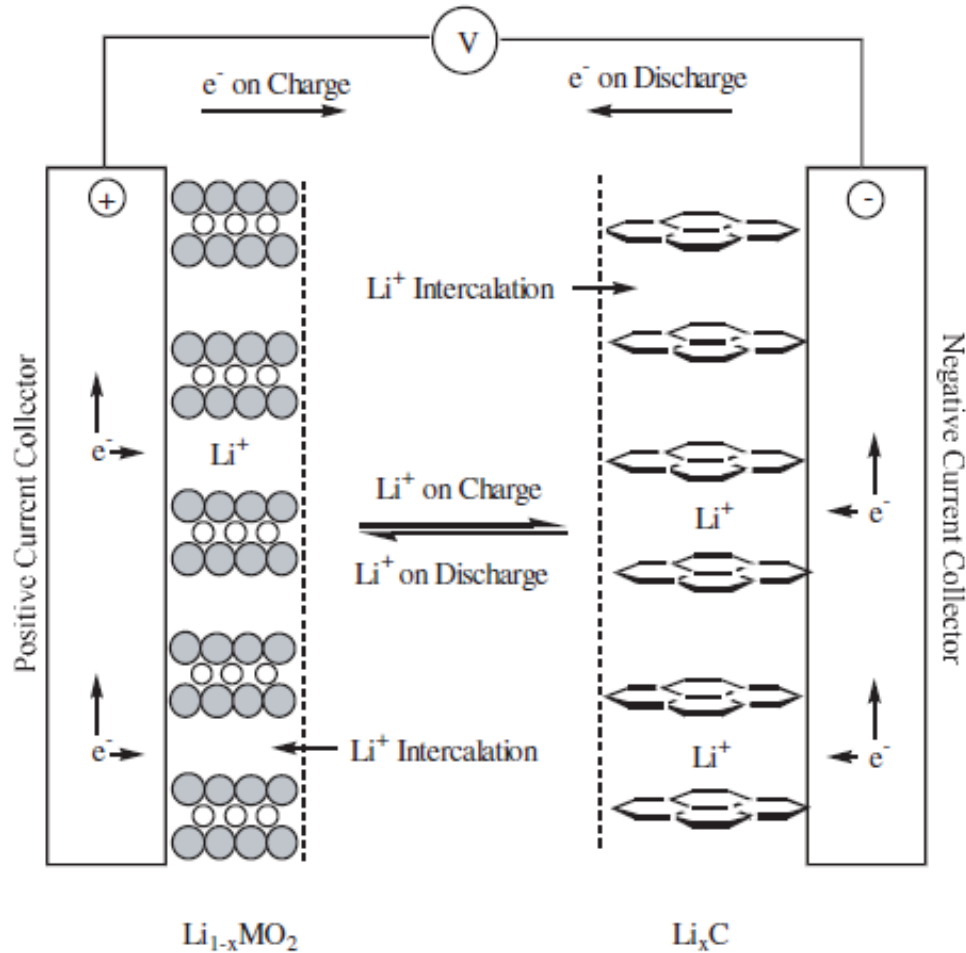
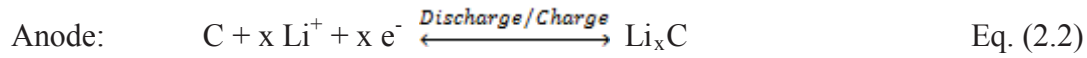


Figure 2.3: Schematic of the electrochemical processes in a rechargeable lithium ion battery [5]. Positive electrode materials for lithium-ion batteries are typically a metal oxide with a

layered structure such as lithium cobalt oxide (LiCoO₂) or a material with a tunneled structure such as lithium manganese oxide (LiMn₂O₄), on a current collector of aluminum foil. The representative negative electrode material in the leading technologies of LIBs is selected as a carbon based material like graphite on a copper current collector. In the charge/discharge process, lithium ions are inserted or extracted from interstitial space between atomic layers within the active materials. Figure 2.3 presented the schematic of the discharge process of the lithium containing metal oxide cathode with a graphite anode. The reactions of this cell can be described by Equations (2.1), (2.2) and (2.3).



In the discharge process, the cell is connected to an external load, electrons flow from the anode, which is oxidized, through the external load to the cathode, where the electrons are accepted and the cathode material is reduced. The electric circuit is completed in the electrolyte by the flow of anions (negative ions) and cations (positive ions) to the anode and cathode, respectively. Upon

charging, the positive material is oxidized and the negative material is reduced. In this process, lithium ions are de-intercalated from the positive material and intercalated into the negative material.

The voltage of a battery is defined as the difference of chemical potentials between the cathode and anode divided by Faraday's constant, F shown in Equation 2.4. The chemical potential of the cathode, Eq. (2.5), and the anode, Eq. (2.6), results from lithium ion movement from the cathode to the anode or vice versa resulting in a lithium chemical potential between the cathode and anode. The lithium chemical potential of the respective electrodes are defined in terms of the lithium chemical potential in its standard state and the activity of lithium in the cathode material.

$$V_{oc} = \frac{\mu_{Li}^c - \mu_{Li}^a}{F} \quad \text{Eq. (2.4)}$$

$$\mu_{Li}^c = \mu_{Li}^0 + RT \ln a_{Li}^c \quad \text{Eq. (2.5)}$$

$$\mu_{Li}^a = \mu_{Li}^0 + RT \ln a_{Li}^a \quad \text{Eq. (2.6)}$$

A relationship between voltage and activity is derived, Eq. (2.7), and is known as the Nernst Equation.

$$\Delta\mu = -nFE \quad \text{Eq. (2.7)}$$

Thermodynamic stability considerations require the redox energy of the cathode and the anode to lie within the bandgap of the electrolyte, so that no undesirable reduction or oxidation of the electrolyte occurs during the charge/discharge process. Thus electrochemical stability requirements impose a limitation on the cell voltage as:

$$eV_{oc} = \mu_{Li}^c - \mu_{Li}^a < E_g \quad \text{Eq. (2.8)}$$

This is shown in the schematic energy diagram of the LIB in its open circuit state (Figure 2.4). The open circuit voltage (V_{oc}) is determined by the energies involved in both the electron transfer and the Li ion transfer. The energy involved in electron transfer is related to the work functions of the cathode and anode which depend on the crystal structure and the coordination geometry of the sites into/from which Li ions are inserted/extracted [6].

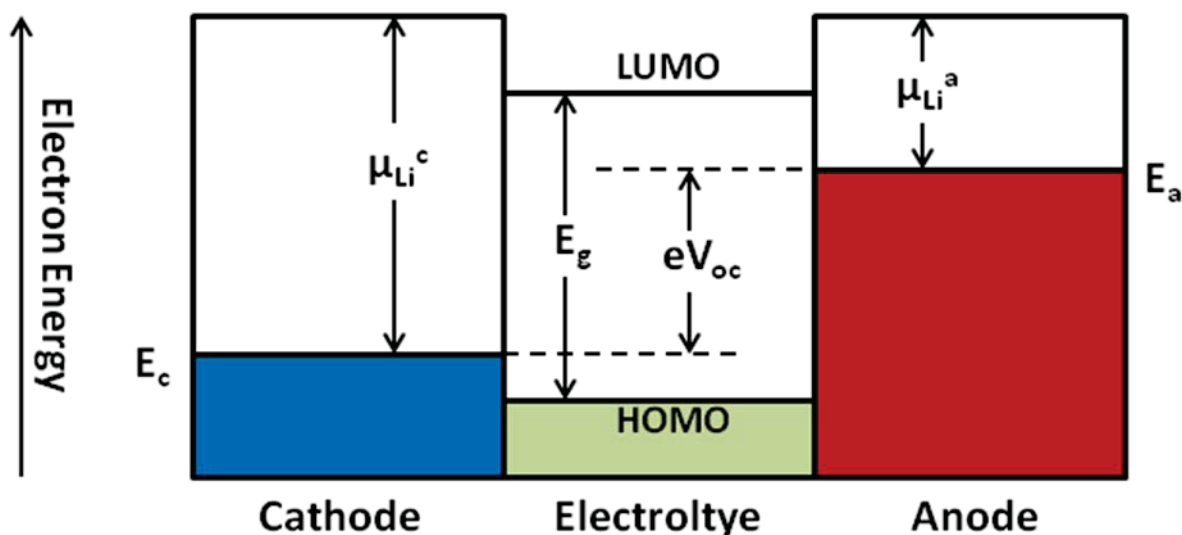


Figure 2.4: Energy diagram of a LIB in open circuit state [7] with labeled lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO).

2.1.2 Metrics

No single LIB is capable of meeting all of the demands of the large variety of applications for LIBs. Therefore individual applications and technologies can be targeted by changing the architecture and chemistries of LIBs. Depending upon which elements and architecture are chosen for a LIB, various performance metrics can be achieved at the cost of others. Therefore, it is necessary to have standard techniques to evaluate the performance of LIBs for practical application. For several of the performance criteria of electrochemical power sources, a distinction must be made between the theoretical values and the practical values. Theoretical values are calculated from the thermodynamics of the electrochemical cell reaction. Practical values are related to the total mass of the complete battery, including the mass of the electrolyte, the separators, the current collectors, the terminals, and the cell housing [4]. In this work, the specific capacity always refers to the weight of the active material component only. Key performance indicators are summarized next.

2.1.2.1 Standard free energy and electromotive force

Reactions take place at both the cathode and the anode in the reaction sites situated at electrode-electrolyte interfaces of Li-ion cells. Thermodynamically, the reduction reaction at one electrode can be represented by



where a molecules of A take up n electrons e to form c molecules of C . Simultaneously the other electrode undergoes oxidation that can be described by



The overall reaction in the cell is given by addition of these two half cell reactions.



Then, the change in the standard free energy, ΔG° of this reaction is expressed as

$$\Delta G^\circ = -nFE^\circ \quad \text{Eq. (2.12)}$$

where, F is the faraday constant, 96487 coulombs, and E° is the standard electromotive force.

The free energy of the reaction from Eq. (2.11) is defined by

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad \text{Eq. (2.13)}$$

where, a , R , T is activity of relevant species, gas constant, and absolute temperature, respectively. Inserting Eq. (2.12) into Eq. (2.13) gives the cell voltage which is described by Eq. (2.14), known as the Nernst Equation.

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad \text{Eq. (2.14)}$$

The change in the standard free energy, ΔG° , of a cell reaction is the driving force which enables a Li-ion battery to deliver electrical energy to an external circuit. Together with activity coefficients, equilibrium constants, and solubility products in the reaction processes, measurement of the electromotive force makes available data on changes in free energy, entropies and enthalpies. The standard electromotive forces of half reactions for either oxidation or reduction

are summarized in Table 2.2 with respect to the “zero” reference electrode H_2/H^+ [8]. As it is impossible to measure individual electrode potentials in an absolute sense, they are each measured with reference to another electrode, which is used as standard electrode. The electrode normally used for this purpose is the standard hydrogen electrode (SHE), where the temperature is equal to 25°C , the pressure is equal to 1 bar, and all species are at unity activity.

Table 2.2: Standard potentials in aqueous solutions at 25°C [5].

Electrode reaction	E^0 , V	Electrode reaction	E^0 , V
$\text{Li}^+ + e \rightleftharpoons \text{Li}$	-3.01	$\text{Tl}^+ + e \rightleftharpoons \text{Tl}$	-0.34
$\text{Rb}^+ + e \rightleftharpoons \text{Rb}$	-2.98	$\text{Co}^{2+} + 2e \rightleftharpoons \text{Co}$	-0.27
$\text{Cs}^+ + e \rightleftharpoons \text{Cs}$	-2.92	$\text{Ni}^{2+} + 2e \rightleftharpoons \text{Ni}$	-0.23
$\text{K}^+ + e \rightleftharpoons \text{K}$	-2.92	$\text{Sn}^{2+} + 2e \rightleftharpoons \text{Sn}$	-0.14
$\text{Ba}^{2+} + 2e \rightleftharpoons \text{Ba}$	-2.92	$\text{Pb}^{2+} + 2e \rightleftharpoons \text{Pb}$	-0.13
$\text{Sr}^{2+} + 2e \rightleftharpoons \text{Sr}$	-2.89	$\text{D}^+ + e \rightleftharpoons \frac{1}{2}\text{D}_2$	-0.003
$\text{Ca}^{2+} + 2e \rightleftharpoons \text{Ca}$	-2.84	$\text{H}^+ + e \rightleftharpoons \frac{1}{2}\text{H}_2$	0.000
$\text{Na}^+ + e \rightleftharpoons \text{Na}$	-2.71	$\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$	0.34
$\text{Mg}^{2+} + 2e \rightleftharpoons \text{Mg}$	-2.38	$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e \rightleftharpoons 2\text{OH}^-$	0.40
$\text{Ti}^+ + 2e \rightleftharpoons \text{Ti}$	-1.75	$\text{Cu}^+ + e \rightleftharpoons \text{Cu}$	0.52
$\text{Be}^{2+} + 2e \rightleftharpoons \text{Be}$	-1.70	$\text{Hg}^{2+} + 2e \rightleftharpoons 2\text{Hg}$	0.80
$\text{Al}^{3+} + 3e \rightleftharpoons \text{Al}$	-1.66	$\text{Ag}^+ + e \rightleftharpoons \text{Ag}$	0.80
$\text{Mn}^{2+} + 2e \rightleftharpoons \text{Mn}$	-1.05	$\text{Pd}^{2+} + 2e \rightleftharpoons \text{Pd}$	0.83
$\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}$	-0.76	$\text{Ir}^{3+} + 3e \rightleftharpoons \text{Ir}$	1.00
$\text{Ga}^{3+} + 3e \rightleftharpoons \text{Ga}$	-0.52	$\text{Br}_2 + 2e \rightleftharpoons 2\text{Br}^-$	1.07
$\text{Fe}^{2+} + 2e \rightleftharpoons \text{Fe}$	-0.44	$\text{O}_2 + 4\text{H}^+ + 4e \rightleftharpoons 2\text{H}_2\text{O}$	1.23
$\text{Cd}^{2+} + 2e \rightleftharpoons \text{Cd}$	-0.40	$\text{Cl}_2 + 2e \rightleftharpoons 2\text{Cl}^-$	1.36
$\text{In}^{3+} + 3e \rightleftharpoons \text{In}$	-0.34	$\text{F}_2 + 2e \rightleftharpoons 2\text{F}^-$	2.87

2.1.2.2 Theoretical potential

The standard potential of the LIBs is determined by the type of active materials contained in the battery and can be calculated from the electrode potentials (reduction potentials) of the

half reactions. The overall *theoretical cell voltage*, ΔE^o is obtained by subtracting the negative electrode potential, $E^{o,(-)}$, from the positive electrode potential, $E^{o,(+)}$:

$$E^o = E^{o,(+)} + E^{o,(-)} \quad (2.15)$$

The maximum accessible energy is simply the free energy of reaction, ΔG . Consequently, high energy results from the choice of electrode materials. This can be achieved by the selection of electrodes with the greatest difference of electrochemical potential, μ [9]. The cell voltage can be derived from the standard Gibbs free energy (Eq. 2.12) of the equivalent chemical reaction reorganized as:

$$E^o = \frac{-\Delta G^o}{nF} \quad (2.16)$$

For example, in the reaction of a Li metal/graphite cell, the theoretical voltage is calculated as the sum of the oxidation potential of the reaction from Li metal to Li cation and electron (=3.08V) and the reduction potential of the reaction from carbon, Li cation, and electron to LiC_6 (= -2.80V). According to Eq. (2.5) and (2.6), the theoretical voltage of Li metal/graphite cell is 0.28V.



Figure 2.5 compares the electrochemical potential ranges of popular lithium insertion compounds vs. lithium metal schematically, with cell voltages as high as 5 V vs. lithium metal possible with variations of $\text{Li}_{1-x}\text{CoMnO}_4$ and $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

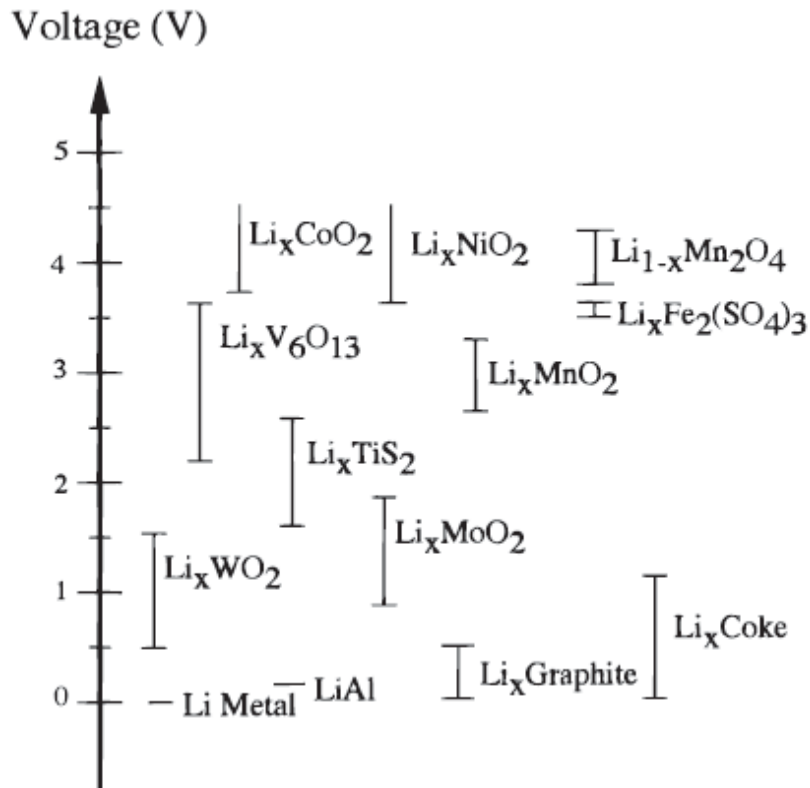


Figure 2.5: Electrochemical potential ranges of common lithium insertion compounds in reference to metallic lithium [10].

2.1.2.3 Theoretical capacity

The theoretical capacity of an electrochemical cell is based only on the amount of active material present and participating in the electrochemical reaction, calculated from the equivalent weight of the reactants. It is expressed as the total quantity of electricity involved in the electrochemical reaction and is defined in terms of coulombs or ampere-hours (Ah). The ampere-hour capacity of a battery is directly associated with the quantity of electricity obtained from the active materials. Theoretically 1 gram-equivalent weight of material will deliver 96,487 C or 26.8 Ah. In general, 1 gram-equivalent weight is the atomic or molecular weight of the active material in grams divided by the number of electrons involved in the reaction. Similarly, the ampere-hour capacity on a volume basis can be calculated using the appropriate data for ampere-hour per cubic centimeter. The theoretical specific charge capacity, q_{th} (Ah kg⁻¹), can be expressed by the amount of charge per kg of reactants, m_i , calculated from the stoichiometry of the overall cell reaction (Eq. 2.19):

$$q_{th} = \frac{nF}{\sum_i m_i} \quad (2.19)$$

2.1.2.4 Energy density and power density

The capacity of a LIB can also be expressed in terms of energy, taking both the voltage and the quantity of electricity into consideration. This theoretical energy value is the maximum value that can be delivered by a specific LIB system and it is calculated as the product of voltage (V) and capacity (Ah) into units of watt-hour (Wh):

$$(Wh) = (V) \times (Ah) \quad (2.20)$$

Energy density is calculated as the energy per unit mass ($Wh\ kg^{-1}$) and is expressed with respect to either the weight of the active material only, the composite electrode weight, the weight of the inter-battery components (anode, cathode, electrolyte/separator), or the entire cell with packaging included. The value for energy density decreases with additional weight of inactive components of a battery and is therefore always less than the theoretical energy density. Additionally, there are inevitable energy losses that become more significant at high charge discharge rate.

Power is defined as the rate at which energy is delivered from or to a battery, the maximum power of which a battery delivers or accepts is determined by the highest rate at which the LIB can be cycled without any failure. The maximum power is governed by kinetic processes of the complete battery system. In practice, the charge/discharge rate is expressed in terms of C-rate and defined as:

$$I = M \times C_n \quad \text{Eq. (2.21)}$$

where, I = dis(charge) current, [A]

C = numerical value of rated capacity of the LIB, [Ah]

n = time for which rated capacity is declared, [hr]

M = multiple or fraction of C

For example, $C/37$ refers to a dis(charge) time of 37 hours, or a full cycle time of 74 hours based on the amount and theoretical capacity of the active material. Likewise, $10C$ represents a cell being dis(charged) in 6 minutes, with a total discharge-charge time of 12 minutes. With increasing active material capacity, the absolute current being applied will increase while the C -rate stays constant, so care must be taken in consideration of comparing various materials. The power (W) can then be calculated as:

$$(W) = (V) \times (Ah) \times C\text{-rate (hr}^{-1}\text{)} \quad \text{Eq. (2.22)}$$

Similar to calculation of energy density, power density is calculated relative to the desired components for the most meaningful result and can be expressed in watts per kilogram ($W \text{ kg}^{-1}$) or in terms of volume ($W \text{ m}^{-3}$).

2.1.2.5 Cycling behavior and coulombic efficiency

In many applications a secondary battery is expected to maintain its major properties over many discharge/charge cycles. This can be a serious practical challenge, and is often given a lot of attention during development and optimization of rechargeable batteries. Cycling behavior depends on the coulombic efficiency, defined as the fraction of the prior charge capacity that is available during the following discharge. It can be observed that even minor inefficiency per cycle can have important consequences (Figure 2.6). For example, a half percent loss per cycle causes available capacity to drop to only 78% of the original value after 50 cycles. After 100 cycles only 61% remains at that rate. The cycling behavior degrades rapidly for even lower coulombic efficiency [5].

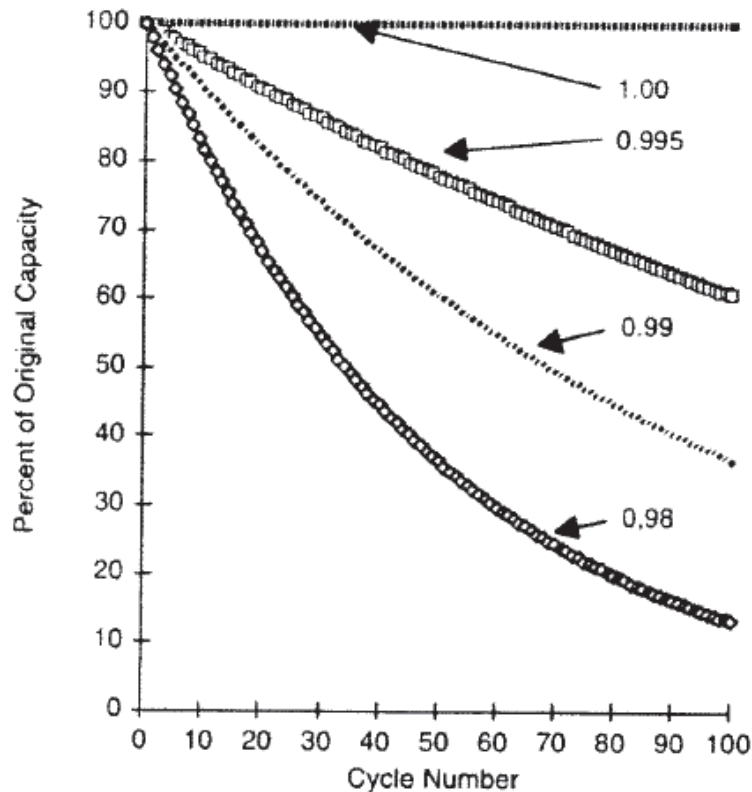


Figure 2.6: Capacity decrease with respect to coulombic efficiency in LIBs [5].

2.1.2.6 Self discharge

Another property of importance in practical cells is self-discharge, or, the reduction in available capacity with time, even without energy being taken from the LIBs by passage of current through the external circuit. This is also relevant to the shelf-life of practical cell or batteries and is a serious practical problem in some system of LIBs.

As previously discussed, the capacity is a property of the electrodes and its value at any time is determined by the remaining extent of the chemical reaction between the neutral species in the electrodes. Any self-discharge mechanism that reduces the remaining capacity must involve either transport of neutral species or concurrent transportation of neutral combinations of charged species, through the cell. The transport of neutral species can occur such that individual neutral species can move across from one electrode to the other such as transporting through an adjacent vapor phase, cracking the solid electrolyte, or dissolving the gas in a liquid electrode. Since the transport of charged species is not involved, these processes produce chemical self-discharge. Concurrent transportation of neutral combinations of charged species involves the transport of charged species, and therefore is called electrochemical self-discharging. Self discharge can also be a result of impurities within the constituent electrodes reacting with the electrolyte, reducing the available capacity over time.

2.1.3 Lithium vs. Lithium-ion Batteries

A popular misconception among the general public is the difference between lithium and lithium-ion batteries. Figure 2.1 showed the energy density potentials of respective batteries with differentiation between lithium and lithium-ion batteries, showing higher achievable energy

density from lithium batteries. Simply, lithium batteries contain lithium metal, and lithium-ion batteries do not.

Lithium metal batteries are desirable because lithium is the most electropositive metal and therefore yields a high potential as an electrode against high voltage cathodes. They provide for high energy density, good charge retention, and low self-discharge. Unfortunately, lithium batteries exhibit low cycle life and present numerous safety issues, especially in liquid electrolyte based systems due to its extreme reactivity. Lithium-ion batteries involve two electrode materials, one of which contains lithium within, such as LiCoO_2 . During discharge, lithium ions are removed from the LiCoO_2 and travel through the electrolyte into the anode (typically graphite). The battery cycling occurs by the movement of lithium ions, without the presence of metallic lithium. These systems are typically safer than lithium battery systems and also exhibit a very high energy density, good cycle life, and low self-discharge rates. Lithium-ion batteries are however expensive, and sensitive to degradation and/or thermal runaway at high temperature.

Typical laboratory testing procedures involve the manufacture and testing of lithium “half cells” in order to properly evaluate performance of individual electrode materials. A half cell is essentially a lithium battery, utilizing lithium metal as a negative electrode. However, this configuration is used to test typical low voltage negative electrodes such as graphite and silicon as well, which does not constitute a battery. With lithium as the “anode” these low voltage materials comprise the “cathode”, however the low voltage of these cells prevents their use as batteries, and therefore must be referred to as half cells.

2.2 Electrode materials

The terms “intercalation” and “de-intercalation” are often used for reactions involving the insertion and extraction of guest species for the specific case of host materials that have layered-type crystal structures. On the other hand “insertion” and “extraction” are more general terms. Reactions of this type are most likely to occur when the host has an open framework or layered type of crystal structure, so that there is space available for the presence of additional small ionic species. Since such reactions involve a change in the chemical composition of the host material, they can also be called solid solution reactions.

Insertion reactions are generally topotactic, with the guest species moving into, and residing in, specific sites within the host lattice structure. These sites can often be thought of as interstitial sites in the host crystal lattice that are otherwise empty. The occurrence of a topotactic reaction implies some three-dimensional correspondence between the crystal structures of the parent and the product.

2.2.1 Negative electrode materials

Graphitic carbons are currently the most employed material for negative electrodes due to their low cost, excellent cyclability and reliability, and non-toxicity [1, 11, 12]. Compounds for negative electrodes can be divided into two major categories: *carbonaceous* and *non-carbonaceous* materials. Present research is moving towards replacing carbonaceous anodes with non-carbonaceous anodes, as with metal-alloys, silicon-based materials, and transition metal oxides. The driving force behind this research trend is to obtain a new generation of anode

materials with higher specific capacities ($> 372 \text{ mAh g}^{-1}$), while retaining the good properties of carbonaceous materials such as cyclability, cost, and safety.

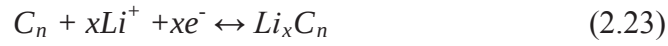
2.2.1.1 Carbonaceous material

Carbonaceous-based materials are the most attractive and widely investigated materials for use as anode in Li-ion batteries [1, 12]. This has been mainly due to the following reasons:

- low cost,
- high safety for people and the environment,
- low Li-ion insertion potential ($\sim 0.1 \text{ V}$ vs. Li/Li^+) very close to that for metallic lithium,
- good cycling stability due to the high mechanical integrity (compared to metal alloys) of the electrode even after 500 charge-discharge cycles, and
- relatively high specific charge when compared to transition metal oxides.

The insertion of lithium into carbon is referred to as *intercalation*, with intercalation being formally described as the insertion of a guest species into a layered host structure, without any major resulting structural changes [12]. In half-cell reactions against metallic lithium, lithium-ion

intercalation into carbon is referred to as the discharge step, while the de-intercalation process is the charge step.



At ambient temperature, graphitic carbon intercalates one lithium atom per six carbon atoms to form the compound, LiC_6 [12]. The maximum attainable specific charge capacity of the LiC_6 electrode is 372 mAh g^{-1} (based on the carbon weight only). Graphite is comprised of sp^2 -hybridized carbon atoms arranged in a planar “honeycomb-like” network of “graphene” layers (Figure 2.7). Weak cohesion of the graphene layers provided by Van der Waals forces result in the layered graphite structure. The intercalation reaction between lithium and carbon proceeds via the prismatic surface but occurs only at defect sites throughout the basal plane. Upon the insertion and extraction of lithium, the interlayer distance between graphene layers increases by the stacking order shift from AB to AA and total volume change of graphite is calculated as 10.3%.

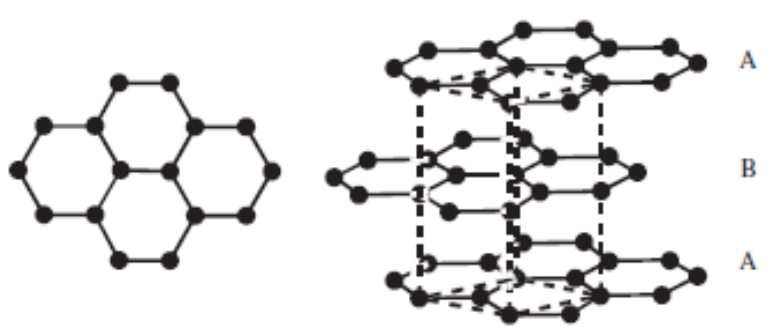


Figure 2.7: The hexagonal structure of a carbon layer and the structure of hexagonal graphite [5].

When the structure disorder becomes dominating among crystallites, the carbonaceous material can no longer be considered graphite and must be regarded as non-graphitic carbon. Non-graphitizing carbon and graphitizing carbon can be separated based on whether or not it can be formed as graphite by heat treatment. Since non-graphitizing carbons are mechanically harder than graphitizing ones, it is common to divide the non-graphitic carbons into soft and hard carbons. Hard carbons have shown to exhibit high capacity as a result of lithium absorption on both sides of single graphene layers but results in high irreversibility and poor cycling stability [13-15]. In contrast, graphitizing (soft) carbons have a more disordered structure which offers a lower number of sites for lithium intercalation as compared to graphite [12,16]. Additionally, cross-linking of carbon layers in disordered carbons hinders shifting to AA stacking, which is necessary for the accommodation of a higher lithium amount into graphitic sites [17-19] and therefore lower capacities of less than 200 mAh g^{-1} are observed for soft carbons.

Recent discovery of new crystalline forms of carbon including single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) with dimensions of less than 100 nm in tube diameter have attracted considerable attention. As a result of high ion mobility, nanotubes exhibit an increased capacity as an active material and highly improved cyclic characteristics as additives to anode materials [20-30]. For example, current research is showing that it is possible to charge SWCNTs up to one lithium for every three carbon atoms and higher [31]. Frackowiak and Beguin as well as Yang et al. have shown lithium capacities of crude material to exceed 600 mAh g^{-1} [26,32]. A maximum reversible capacity of 1000 mAh g^{-1} for SWCNTs mechanically milled to enable filling of the nanotube cores has been reported [21]. However, a large irreversible capacity typically observed with increased reversible storage capacity, absence of a voltage plateau during discharge, and large hysteresis in voltages between

charge and discharge [21,26] currently limit energy density and efficiency as compared to other carbonaceous materials.

2.2.1.2 Lithium metal and alloys

Lithium metal is studied as an anode for its high potential and extremely high theoretical specific charge capacity (3860 mAh g^{-1}) [5]. Batteries developed using lithium as an anode in conjunction with intercalation cathodes exhibit attractive energy densities, excellent storage characteristics, and reasonable cycle life. However, difficulties associated with the use of metallic lithium stem from its reactivity with the electrolyte and changes that occur after repetitive charge-discharge cycling. When lithium is electroplated, during recharge, onto a metallic lithium electrode, it forms a mossy and in some cases a dendritic deposit with a larger surface area than the original metal, corresponding to increased reactivity.

Lithium alloys have been studied since the early 1970's in order to reduce the lithium activity at the surface of electrode for suppressing the dendrite growth. Lithium alloy materials typically exhibit higher capacity than carbonaceous materials as well as high operation voltage and good stability with some electrolytes (Table 2.3). However, lithium alloys are typically brittle and therefore cannot be extruded, making them difficult to scale up. Some alloys have also been shown to exhibit large volume changes when lithium is either incorporated or removed, resulting in mechanical stress and cracks during cycling which leads to electrochemically inactive particles and thus poor cycle stability. In spite of these drawbacks, lithium alloy materials are some of the candidates in consideration to replace the carbonaceous materials due to their

high energy density. Recently, good cycling performances have been obtained using shallow lithium insertion or the composite materials with inactive oxides.

Table 2.3: Theoretical capacities and volume changes of different elements [34].

Material	Lithiated Phase	Capacity in mAh/g	Capacity in mAh/ml	Volume change in %
Li	LiC ₆	372	833	12
Al	Li ₉ Al ₁₄	2235	6035	238
Si	Li ₂₂ Si ₅	4200	9800	400
Sn	Li ₁₇ Sn ₄	994	7000	257
Bi	Li ₃ Bi	385	3773	115

As it is low cost, physically abundant on earth, and has the highest known theoretical capacity (4200 mAh g⁻¹), silicon appears to be a superior anode material for high energy-density Li-ion batteries [1, 34-36]. However, severe capacity fade found during initial cycling is a highly limiting issue for Si anodes. During the last decade, intensive research has been conducted to understand the reasons for this poor capacity retention, and several methodologies have been proposed to overcome the problem.

Although Si has a theoretical capacity of more than 10 times that of graphite, it has yet to be successfully commercialized as an anode material due to its significant volume expansion upon lithiation[37,38]. Pure Si can accommodate up to 4.4 Li atoms per Si (Li_{4.4}Si), which results in approximately 400% volume expansion[39,40]. Stresses created in the anode from expansion exceed the breaking stress of Si, resulting in particle cracking and the unavailability of progressive amounts of Si for further Li insertion and extraction due to loss of interparticle electronic contact. In addition, when Si is charged to potentials less than 0.03 V versus Li/Li⁺,

formation of a two-phase system occurs, leading to higher internal stresses in the anode material [12]. Several methods have been attempted to improve the capacity retention of Si anodes: (i) the use of a conductive additive (inactive or active) to act as a buffer for volume expansion and to aid in maintaining contact between pulverized Si particles[41-46]; (ii) the limitation of voltages over which the material is cycled, thereby reducing the extent to which pulverization occurs and extending cycle life at the expense of capacity[47,48]; (iii) the reduction of particle size of Si particles to the nanometer range in the anode, which reduces mechanical stress and fading during cycling[35,49-57]. Implementation and optimization of the aforementioned techniques could lead to the near term commercialization of all-solid-state batteries with a Si anode.

As metallic Sn can be alloyed similarly to Si with 4.4 moles of lithium resulting in a theoretical capacity of 994 mAh g⁻¹ it has attracted much attention as an alternative to carbonaceous anode materials. However, Sn, like Si, undergoes pulverization from volume expansion upon lithiation and delithiation which causes rapid capacity fade. Many efforts to mitigate this pulverization have been investigated with a focus on embedding Sn into a conductive matrix to maintain high electron transport capabilities and compensate for volume expansion.

2.2.1.3 Transition metal oxides

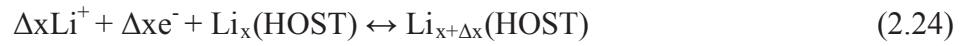
One of the main design challenges of Li-ion batteries is ensuring electrodes maintain their integrity over many discharge-charge cycles. Although promising electrode systems have been proposed [58-60], their lifespans are limited by Li-alloying agglomeration [61] or the growth of passivation layers [62], which prevent the fully reversible insertion of Li-ions into the negative electrodes. Transition metal oxides with a layered structure favorably permit lithium

(de)intercalation. Nevertheless the potentials at which this process takes place is far above the Li/Li⁺ couple and significantly lower 4 V positive electrode materials, therefore a greatly reduced voltage is obtained resulting in low energy densities for these systems [12]. Among the metal oxides explored, nano-sized anatase structured TiO₂ and spinel Li₄Ti₅O₁₂ have received much attention. While they both maintain a potential over 1.5 V resulting in low overall voltage and energy density, they are under serious consideration as negative electrodes for high-power application. High chemical diffusion coefficients and good stability allow for high rate performance of batteries employing these materials.

Poizot et al. [63] were the first to demonstrate electrodes made of nano-sized transition-metal oxides (MO, M = Co, Ni, Cu or Fe) with electrochemical capacities over 700 mAh g⁻¹, 100 % capacity retention for up to 100 cycles, and high charging rates. The mechanism of Li reactivity differs from the classical Li-alloying processes as the formation and decomposition of Li₂O accompanies the redox reaction of metal nanoparticles. As will be discussed in Chapter 4, it is expected that the use nanoparticles to enhance surface electrochemical reactivity will lead to further improvements in the performance of lithium-ion batteries.

2.2.2 Positive electrode materials

A wide range of materials can be used as positive electrodes for Li-ion batteries, the best of which are those with little to no structural modification during cycling. Typical insertion or intercalation compounds are therefore preferred candidates because removal and subsequent insertion of lithium-ions in the host lattice precedes *topotactically* (without change in the structure). The reaction at the positive electrode can be described as follows:



where (HOST) is an insertion cathode material. There are several key requirements that must be considered carefully when choosing a cathodic compound:

- high free energy of reaction with lithium,
- wide range of x (amount of Li-ion insertion),
- a reasonably low mass and volume per Faraday charge stored,
- small structural changes on reactions,
- rapid diffusion of lithium within the host lattice,
- good electronic conductivity,
- non-solubility in electrolyte, and
- ease and low cost of synthesis.

Some popular cathode materials and their corresponding characteristics are shown in Table 2.4. The compounds for positive electrodes are generally divided into four major categories: the *layered transition metal oxides*, the *spinel oxides*, the *olivines*, and lithium-free compounds such as the *transition metal dichalcogenides*.

Table 2.4: Characteristics of representative positive electrode materials for lithium batteries [5].

Negative electrode material	Molecular weight		Density [kg/L]		Theoretical specific charge [Ah/kg]	Theoretical charge density [Ah/L]
Li (primary)	6.94		0.53		3862	2047
Li ₄ (secondary)	27.76		0.53		965	511
LiC ₆ (graphite)	79.00	(72.06)	2.24	(2.25)	339	(372)
LiAl	33.92	(26.98)	1.75	(2.70)	790	(993)
Li ₂₁ Sn ₃	739.31	(593.55)	2.55	(7.28)	761	(948)
LiWO ₂	222.79	(215.85)	11.30	(12.11)	120	(124)
LiMoO ₂	134.88	(127.94)	6.06	(6.47)	199	(209)
LiTiS ₂	118.94	(112.01)	3.06	(3.22)	225	(239)

2.2.2.1 Layered transition metal oxides

The general formula LiMO₂ with M = V, Cr, Co and Ni defines the group of cathode materials known as layered transition metal oxides. Typically the materials crystallize with a layered rock salt structure having strongly bonded MO₂ layers. Li⁺ and M³⁺ ions occupy alternating (111) planes to give a layered O-Li-O-M-O sequence along the c axis (Figure 2.8). LiCoO₂ is the most popular of the layered structure materials used for cathodes and was first proposed by Mizushima et al. in Ref. [64]. Good cyclability and stability as well as a high voltage of ~4V has allowed it to become the most widely used positive electrode material in commercial lithium-ion batteries [1,4,12,65]. However, alternative positive electrode materials are being investigated due to high toxicity and low natural abundance of LiCoO₂.

The α -NaFeO₂ structure of LiCoO₂ is built up from a cubic close-packed oxygen array [12,64,66,67]. LiCoO₂ crystallizes in the space group $R\bar{3}m$ with the lithium and transition metal atoms distributed in the octahedral interstitial sites in such a way that CoO₂ layers are formed, consisting of edge sharing (CoO₆) octahedra. Between these layers lithium resides in octahedral holes, which give LiO₆ coordination [68]. Although the theoretical capacity of LiCoO₂ is 248 mAh g⁻¹, the material delivers only around 137 mAh g⁻¹ since a new phase appears near $x = 0.5$ in Li_xCoO₂. Lithium-ions reversibly intercalate into or out of van der Waals gaps between the CoO₂ layers. Generally the a -axis changes slightly, but the c -axis changes from 14.1 to 14.6 Å with lithium de-intercalation [69].

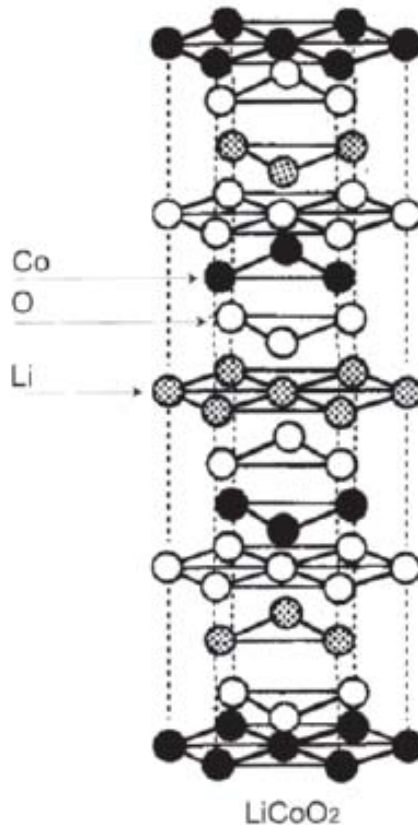


Figure 2.8: Crystal structure of LiCoO₂ having O₃ layered structure [5].

2.2.2.2 Spinel oxides

Lithium manganese oxide (LiMn_2O_4) of the general formula LiM_2O_4 ($\text{M}=\text{Ti, V, and Mn}$) has a cubic spinel structure (Fig. 2.9). It can be expressed as a cubic close-packed oxygen array with the oxygen anions on the crystallographic $32e$ sites of the $Fd3m$ space group. The manganese cations reside in half of the octahedral interstitial sites, $16d$, and the lithium cations in one eighth of the tetrahedral sites, $8a$. The interstitial space in the Mn_2O_4 framework corresponds to a diamond-type network of tetrahedral $8a$ and surrounding octahedral $16c$ sites. These vacant tetrahedral and octahedral sites are interconnected with one another by common faces and edges to form 3D diffusion pathways for the lithium ions [12,65,70,71]. The anionic lattice of LiMn_2O_4 is closely related to the $\alpha\text{-NaFeO}_2$ layered structure, differing only in the distribution of the cations amongst the available tetrahedral and octahedral holes.

Spinel LiMn_2O_4 was the focus of a concentrated research effort by Thackeray et al. [72] in the 1990's for its lower cost relative to using Co or Ni, larger thermal stability domain, higher discharge voltage, and less severe environmental impact. However, it exhibits a lower specific capacity of only 148 mAh g^{-1} , potentially lower power density compared to layered materials (LiCoO_2 and LiNiO_2), and rapid capacity fade with cycling, especially at higher temperature. Several strategies have been employed to overcome the capacity fade resulting from a number of factors including Jahn-Teller distortion, a geometric distortion to minimize overall energy that removes degeneracy, formation of two phase regions, loss of crystallinity, and development of micro-strain during cycling [73]. Current efforts are focused on substitution of other metals, surface modification by coating, and use of different electrolytes to minimize manganese dissolution [74-77]. Regardless of capacity fading issues, LiMn_2O_4 is explored continuously by

researches as it is low cost and environmentally benign compared to other cathode materials [78].

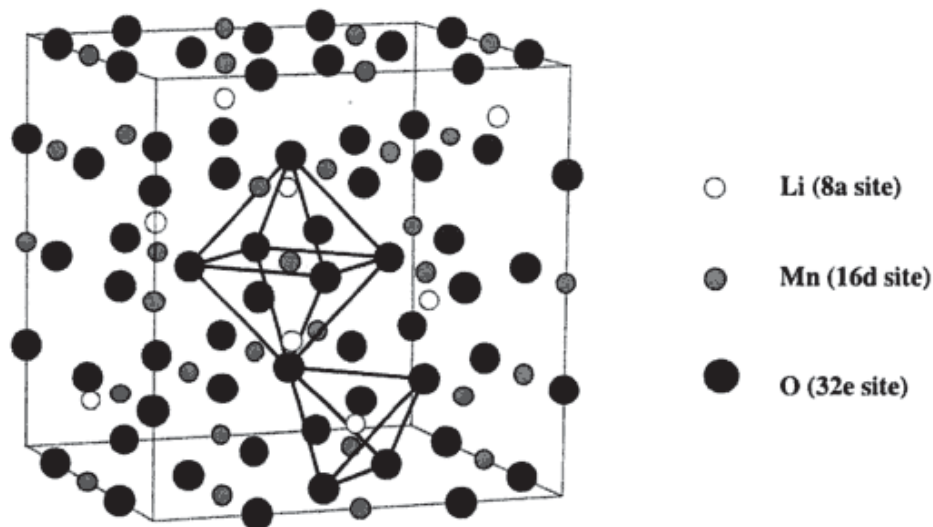


Figure 2.9: Crystal structure of spinel LiMn_2O_4 [7].

2.2.2.3 Olivines

A promising cathode material which has attracted a considerable attention over the past decades is lithium iron phosphate (LiFePO_4). While pure LiFePO_4 has a very low conductivity on the order of $10^{-9} \text{ S cm}^{-1}$ [79], it can be utilized very effectively with particle sizes less than $1 \mu\text{m}$, as well as at low current densities and high temperature. Reversible cycling of $\sim 90\%$ of its theoretical charge capacity (165 Ah kg^{-1}) at a steady voltage of around 3.4 V [80], has been achieved by electrodes that possess a well dispersed conductive carbon matrix [81,82]. This olivine compound is inexpensive and uses non-toxic Fe as opposed to Ni or Co [83]. LiFePO_4 has the olivine structure, which consists of corner sharing FeO_6 octahedral and PO_4^{3-} tetrahedral anions (Figure 2.10), with lithium occupying the octahedral holes. LiFePO_4 , which has the same

generalized AB_2O_4 formula as the spinel structure, has a hexagonal-close-packed oxygen array, in which the octahedra share both edges and faces. The cation arrangement in $LiFePO_4$ differs significantly from that in the layered (e.g. $LiCoO_2$) and spinel (e.g. $LiMn_2O_4$) structures. There is no continuous network of FeO_6 edge-sharing octahedra that might contribute to electronic conductivity; instead, the divalent Fe^{2+} ions occupy corner-sharing octahedra. The phosphorus ions are located in tetrahedral sites, and the lithium-ions reside in chains of edge-sharing octahedra [79].

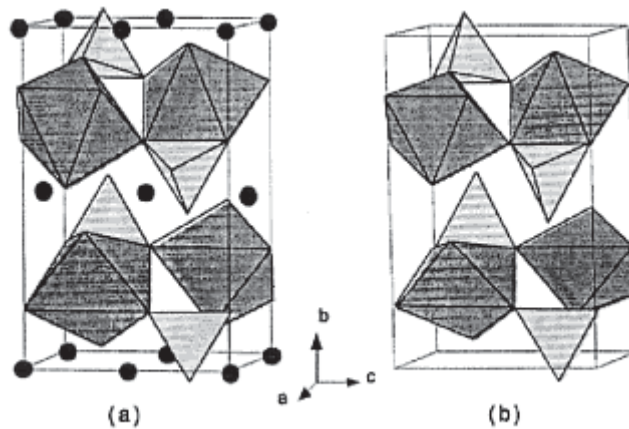


Figure 2.10: Crystal structure of olivine (a) $LiFePO_4$ with circles referring to lithium ion and (b) $FePO_4$ consisting of FeO_6 octahedra and PO_4 tetrahedra

2.2.2.4 Transition metal dichalcogenides

The elements that form transition metal dichalcogenides are shown in Figure 2.11 [84]. The unit building blocks of the disulfides consist of two hexagonally close-packed chalcogen layers between which reside transition metal ions. The metal ions are found either in sites of

Li	Be											B	C
Na	Mg											Al	Si
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb



Figure 2.11: Periodic table of the elements showing those that form layered sulfides or selenides with the metal on octahedral or trigonal prismatic coordination [84].

octahedral symmetry (group IVB) or in ones of trigonal prismatic symmetry (group VIB) with niobium and tantalum are found in both. Building units can be stacked together to form the overall unit cell, the particular ordering of which units is not necessarily maintained on formation of an intercalation compound. Titanium disulfide (TiS_2) has been widely studied as an intercalation material for lithium batteries as it more than satisfies the conditions for a positive electrode material listed in section 2.3.2. It has the 1T structure shown in Figure 2.12 which can accommodate some excess titanium in the van der Waals layer without structural change. The reaction $\text{Li} + \text{TiS}_2$ takes place with a high free energy of reaction, 206 kJ mol^{-1} , and with little change in free energy over the composition range. A single phase over the entire composition range also exists, so no energy is expended in nucleating a new phase. Additionally the lattice expands only by 10% which should not cause substantial mechanical degradation problems. TiS_2 is also a good electronic conductor with high lithium ion diffusivity, sufficient to permit high current density and hence good power density.

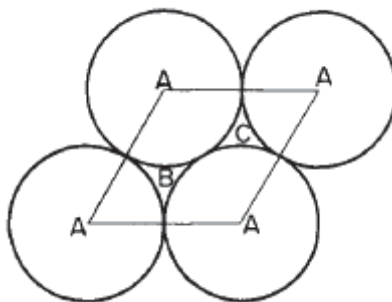


Figure 2.12: (001) sections of lattice showing atomic positions for ABC notation. The relative positions of all atoms in the layered hexagonal structures can be described by the letters A, B, C to notify the anion, a, b, c for the transition metal and [a], [b], [c], the intercalated species. Thus the 1T structure of LiTiS_2 can be written as AbC[b]AbC[b] [84].

For its exceptionally high conducting properties and high lithium diffusion rates, TiS_2 has been studied extensively for use in lithium batteries. It is also the lightest and cheapest of all group IVB and VB layered dichalcogenides and exhibits a high theoretical specific capacity of 239 mAh g^{-1} [85]. Whittingham et al. performed considerable research on TiS_2 as an electrode material for lithium batteries, however, while TiS_2 delivered exceptionally well as a cathode material, it required a lithium battery construction due to a low potential of approximately 2.1 V against lithium, which was not viable due to safety problems with liquid electrolytes [86]. TiS_2 was later shown to be compatible in a thin-film solid state construction but was never fully explored in an all-solid-state bulk-type construction. The introduction of layered oxides by Goodenough et al., lithium-ion “rocking chair” batteries by Murphy et al. and Scrosati et al., and development of the first lithium-ion batteries by Sony in the 1990’s deterred further exploration of TiS_2 lithium batteries [86].

2.3 Materials characterization and analytical techniques

Numerous characterization and analytical techniques have been established as a means of quantifying and describing the various changing properties of materials upon fabrication and electrochemical cycling. Some of the most applicable techniques to this research will be briefly discussed here.

2.3.1 AC Impedance Spectroscopy

If a potential (voltage) is applied across an electrochemical cell a current is caused to flow through the cell, with a value determined by the mechanisms of the reaction taking place. The reaction is the formation of new chemical species resulting from the movement of ions through the electrolyte as we previously discussed. The ionic movements are caused by the applied potential difference, and constitute a flow of electric current. If the applied potential is a sinusoid ($\Delta E \sin \omega t$) then the subsequent current will also be sinusoidal, with a value $\Delta i \sin (\omega t + \phi)$, of which harmonics of this current ($2\omega, 3\omega \dots$ etc.) will also flow. The relationship between the applied potential and the current flow is known as the impedance, which is analogous to the resistance-current-potential relationship of a dc circuit. The impedance (Z) has a magnitude ($\Delta E / \Delta i$) and phase (ϕ) and is thus a vector quantity. If a sinusoidal potential is applied across a pure resistance of magnitude R , then the magnitude of the impedance $Z = R$ and the phase $\phi = 0$ for all frequencies. This is shown on a plot of the real (a) and imaginary (jb) components as a point on the real axis in Figure 2.13.

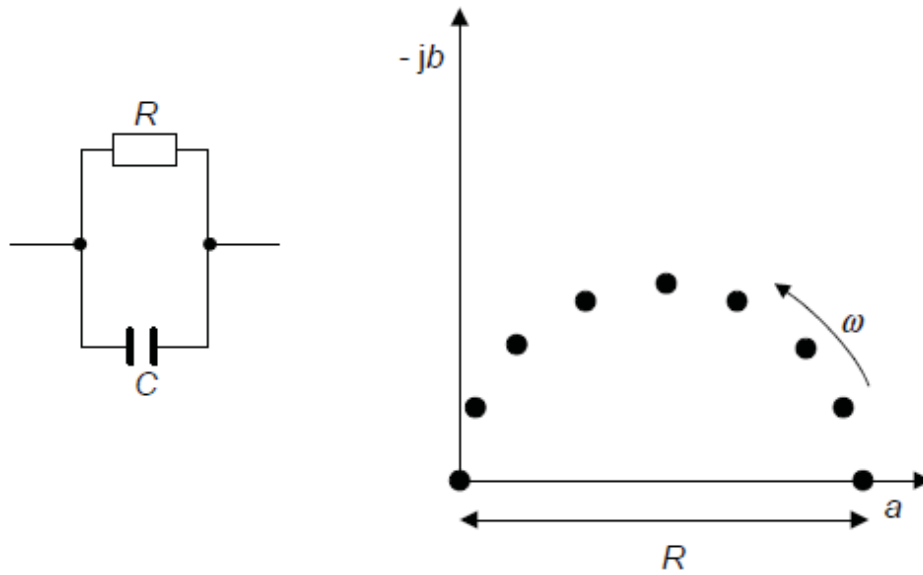


Figure 2.13: Complex plane impedance spectrum – resistance.

If the sinusoid is applied across a pure capacitance, the impedance becomes dependent upon the frequency by the relationship $Z = 1/\omega C$ with a phase angle of 90° . As the frequency increases the magnitude of the impedance decreases, as shown in Figure 2.14.

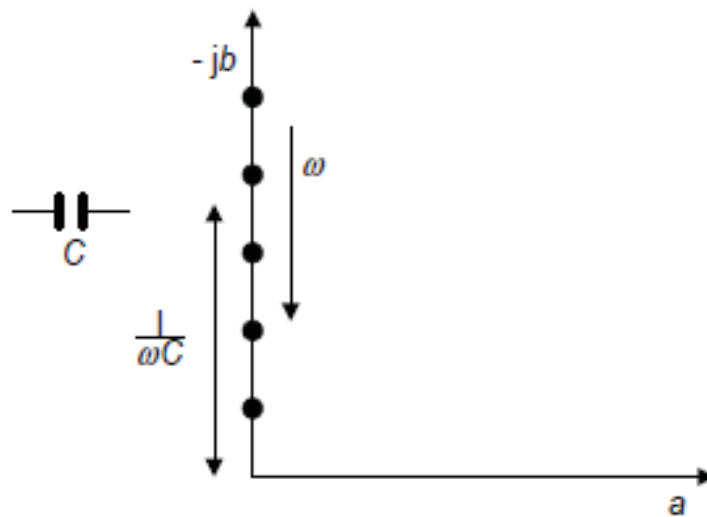


Figure 2.14: Complex plane impedance spectrum – capacitance.

The result of combining the two basic circuit components of Figure 2.13 and 2.14 in parallel can be easily deduced, shown in Figure 2.15, for a parallel resistance and capacitance.

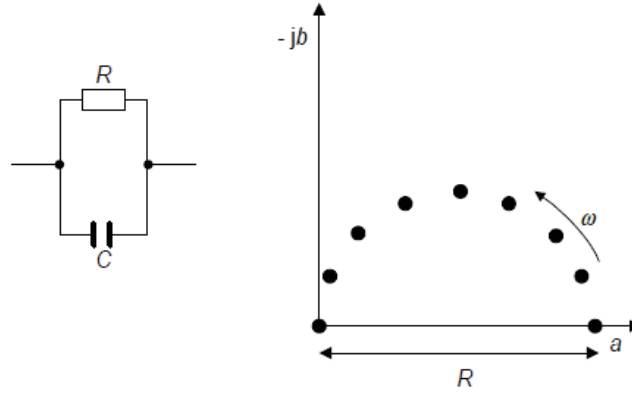


Figure 2.15: Complex plane impedance spectrum – parallel resistance, capacitance.

An electrochemical cell can be represented by a network of resistors and capacitors - known as an equivalent circuit. From an impedance spectrum, (plotted in the real/imaginary plane) it is possible to deduce the equivalent circuit and determine the significance of the different components. The equivalent circuit of an electroactive species is shown in Figure 2.16 as proposed by Randles et al. [87]. R_t is the uncompensated ohmic resistance of the electrolyte and electrode, C_{DL} is the double layer capacitance of the electrode-electrolyte interface (the electrode has surface charge of electrons that is balanced by oppositely charged ions in the electrolyte), θ is the charge transfer resistance (determined by rate of the reaction, in this case lithium migration through electrolyte), and Z_w^* is a complex impedance arising from the diffusion of the electroactive species and is often known as Warburg impedance [88].

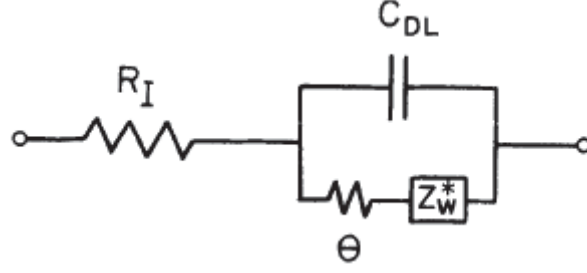


Figure 2.16: Equivalent circuit for the ac response of a system with charge transfer and diffusion of the electroactive species in Reference [89].

For this case of semi-infinite diffusion,

$$Z^*_w = A w^{-1/2} - j A w^{-1/2} \quad \text{Eq. (2.25)}$$

where, w is the radial frequency, $j = \sqrt{-1}$, and A is a constant which contains a concentration independent diffusion coefficient. The charge transfer resistance, θ , is related to the exchange current density, I_0 , through a linearization of the Butler-Volmer equation for small overpotential, δE ,

$$\Theta = \frac{\delta E}{i} = \frac{RT}{nF I_0}, \quad \delta E \ll \frac{RT}{F} \quad \text{Eq. (2.26)}$$

The frequency response of the Randles equivalent circuit will be governed by the relative importance of charge transfer and diffusion in determining the current. Since Z^*_w is a function

of frequency and Θ is not, then an electrode reaction rate is controlled by diffusion at low frequencies and by charge transfer at high frequencies.

For solid state applications, impedance spectroscopy is commonly employed to observe mass and charge transfer effects of electrochemical cells as well as the ionic conductivity of solid electrolytes. In the determination of solid electrolyte conductivity, an equivalent circuit including both bulk mass transfer and interfacial resistance effects is shown in Figure 2.17. The frequency translates to impedance that is described using an electrical circuit model. At high frequencies, the double layer capacitance (C_{DL}) conducts readily, effectively eliminating the charge transfer resistance. As the frequency decreases, the conduction of the capacitance becomes reduced and the interfacial resistance is observed. As the frequency approaches zero, the capacitor ceases to conduct and the cell impedance is a function only of R .

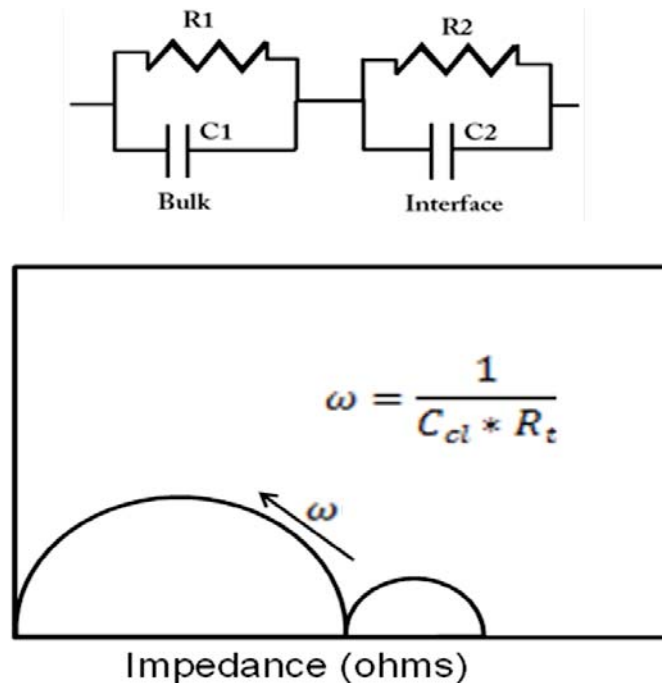


Figure 2.17: A typical equivalent circuit including both bulk mass transfer effects of the solid electrolyte as well as interfacial resistance effects.

The ionic conductivity can be readily calculated from the value of the resistance recorded by impedance spectroscopy. As the value of the resistance for the bulk electrolyte can be directly inferred from the value of Z in the complex plane, the conductivity can be calculated as the thickness of the electrolyte divided by the area of the cell and the recorded resistance:

$$\sigma = \frac{L}{A * R} \quad \text{Eq. (2.27)}$$

where, σ = conductivity (S cm^{-1})

L = thickness of electrolyte layer (cm)

A = planar area of the electrolyte layer (cm^2)

R = resistance from impedance measurement (Ω)

2.3.2 Cyclic Voltammetry (CV)

If we assume that concentrations at the surface of electrodes are governed by the Nernst equation, the concentration of the oxidized species at the surface will decrease as the potential becomes more negative. Assuming that the electron transfer rate is very rapid, the current i that is measured as the potential is decreased will be directly related to diffusion rate of oxidized species to the electrode surface:

$$i = nFAJ \quad \text{Eq. (2.28)}$$

where, n is the number of electrons

F is Faraday's constant

A is the area of the electrode surface

J is the flux of the oxidized species to that surface.

The flux is governed by Fick's law:

$$J = -D \left(\frac{dC}{dx} \right)_{x=0} \cong D \frac{(C^* - C_{x=0})}{\Delta x} \quad \text{Eq. (2.29)}$$

where, D is the diffusion coefficient of the species

x is the distance from the electrode surface

$(dC/dx)_{x=0}$ is the concentration gradient at the surface

C^* is the concentration of the oxidized species in the bulk solution

$C_x=0$ is its concentration at the surface.

It is observed that the greater the concentration gradient, the greater the flux J and therefore by Eq. (2.28), the greater the cathodic current. The change in the concentration gradient for the cathodic portion of the cyclic voltammogram is shown in Figure 2.18.

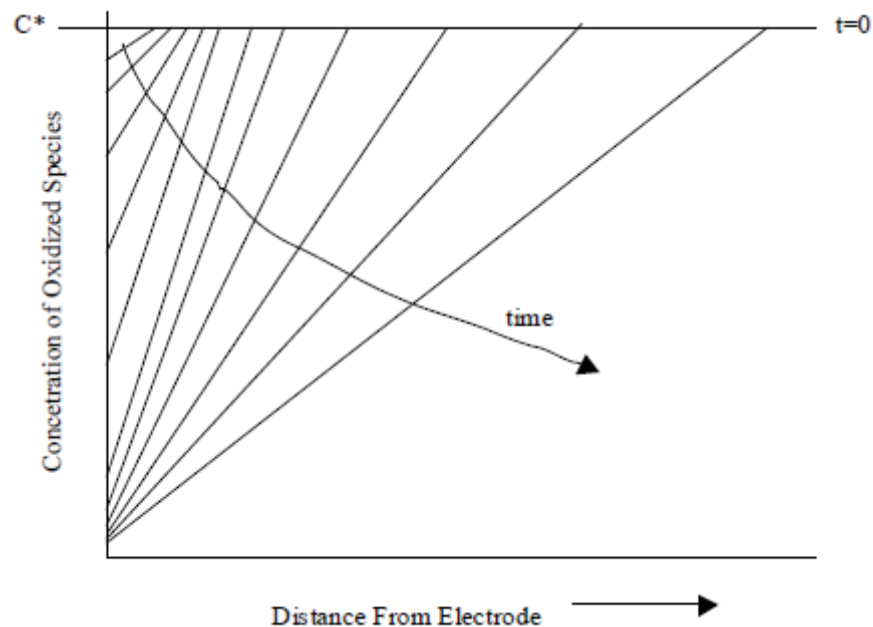


Figure 2.18: Crude concentration profiles at different time in a CV experiment (only the negative scan shown).

Before a potential is applied to the electrode ($t=0$), there is no concentration gradient, and the solution has the uniform bulk concentration C^* . As the potential is applied, the concentration of the oxidized species is depleted at the surface. This lower concentration at the surface gives a higher concentration gradient (at least initially) so according to Fick's law of diffusion Eq. (2.29), there will be more flux to the surface and hence a higher cathodic current. As the potential becomes more negative, the concentration of the oxidized species at the surface will eventually go to zero. Simultaneously, the volume in the solution that is depleted of the oxidized species will increase and the concentration gradient will begin to decrease. As the concentration gradient decreases, there will be less flux to the surface and current will begin to decrease. All of this will result in a current-voltage curve that looks like the forward scan in Figure 2.19 with i_{pc} as the peak cathodic current, i_{pa} as the peak anodic current, and $E_{p/2}$ as the point where current is half that of E_p .

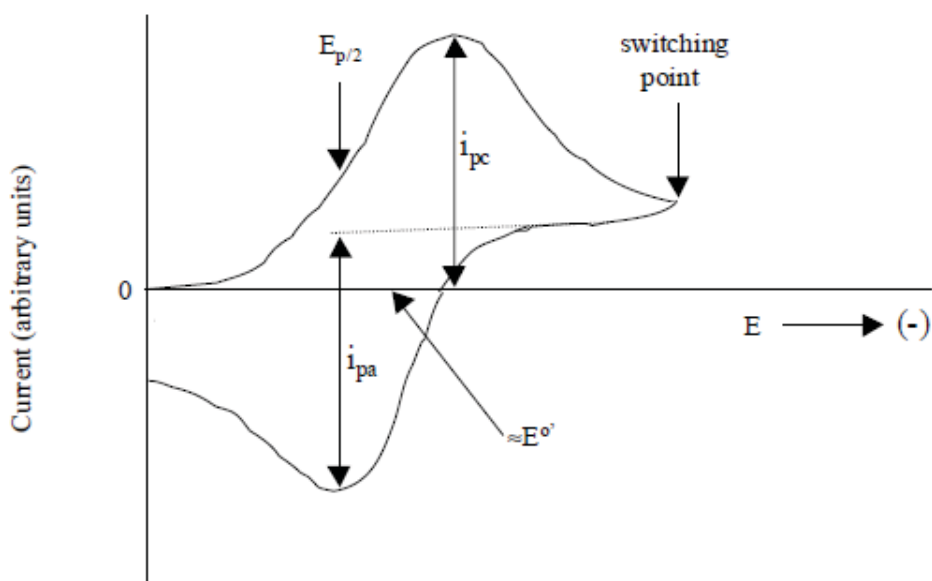


Figure 2.19: Shape of a cyclic voltammogram for a Nernstian electrochemical reaction.

Reversal of the voltage scan, will have a layer depleted of the oxidized species, but the surface concentration begins to rise so current decreases further. Finally, a region is reached where anodic current begins to dominate. Then similar concentration profiles for the reduced species appear. A peak negative current will be achieved and then the current will decrease in magnitude as the depletion layer for the reduced species increases.

Qualitatively, CV is used to identify species and mechanisms of reactions, as well as determination of rate constants and reaction rates, capacitive current due to double layer charging, and oxidation/reduction reactions of electroactive species. A reversible system has been discussed, but irreversible and quasi-irreversible systems can also be analyzed.

2.3.3 X-ray diffraction (XRD)

Solid matter can be described as being either amorphous, atoms arranged in a random way similar to the disorder found in liquids, or crystalline, atoms arranged in a regular pattern where a volume element (smallest in a material) that by repetition in three dimensions describes the crystal. This smallest volume element is called a unit cell, the dimensions of which are described by three axes: a , b , c and the angles between them α , β , γ (Figure 2.20) [90].

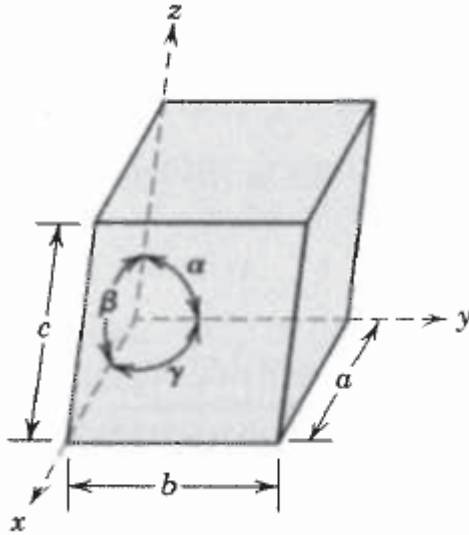


Figure 2.20: A unit cell with x , y , and z coordinate axes showing axial lengths (a , b , and c) and interaxial angles (α , β , and γ) [90].

An electron in an alternating electromagnetic field will oscillate with the same frequency as the field. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. For amorphous materials, there will be destructive interference in all directions, that is, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern, and therefore yield constructive interference in some directions (Figure 2.21) [90].

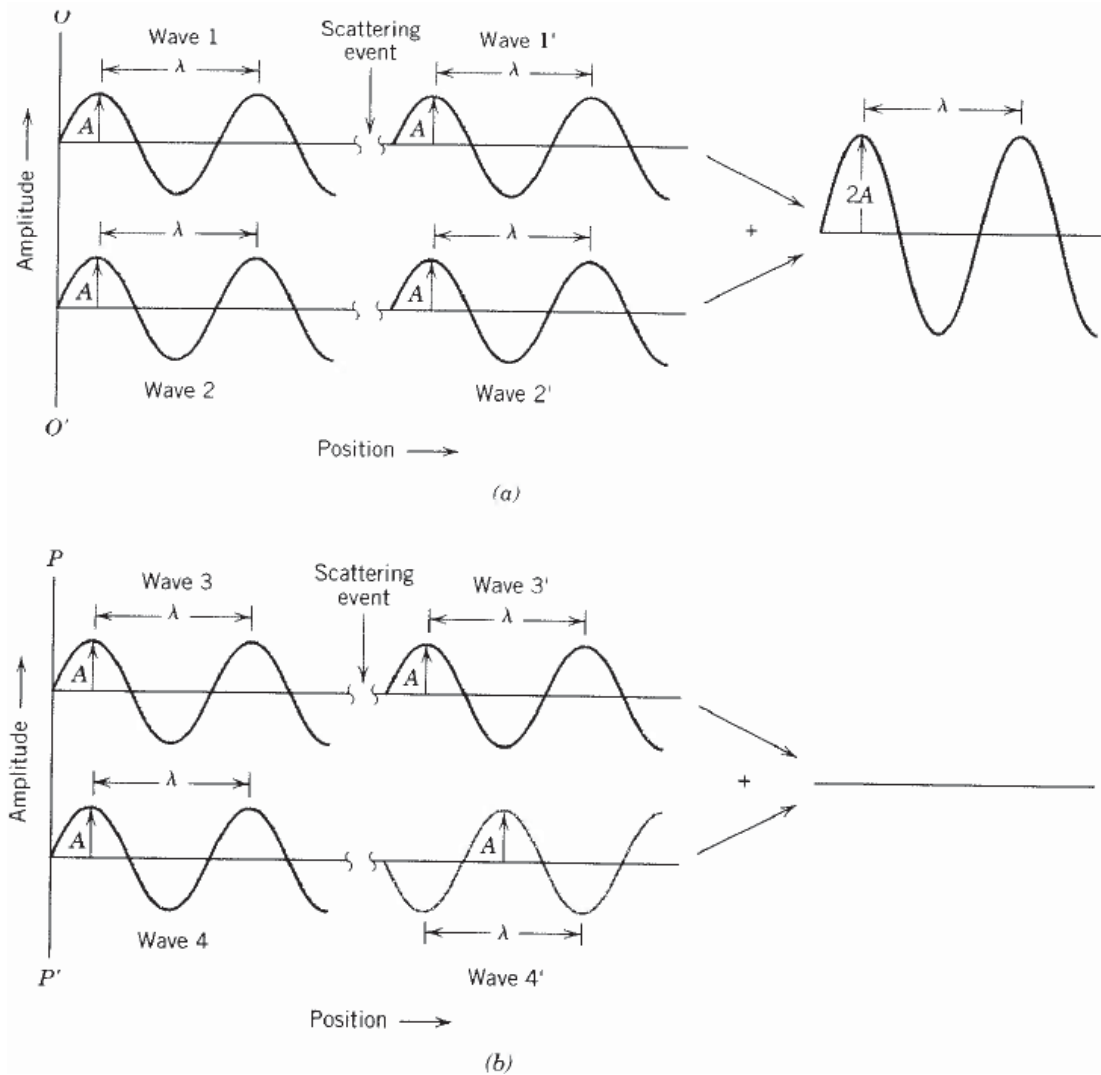


Figure 2.21: (a) Demonstration of how two waves (labeled 1 and 2) that have the same wavelength λ and remain in phase after a scattering event (waves 1' and 2') constructively interfere with one another. The amplitudes of the scattered wave add together in a resultant wave. (b) Demonstration of how two waves (labeled 3 and 4) that have the same wavelength and become out of phase after a scattering event (waves 3' and 4') destructively interfere with one another. The amplitudes of the two scattered waves cancel one another [90].

The waves will be in phase and there will be well defined X-ray beams leaving the sample. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another.

X-ray reflections originate from series of parallel planes inside the crystal: the orientation and interplanar spacing's of these planes are defined by the three integers h , k , l called Miller indices. A given set of planes with indices h , k , l cut the a -axis of the unit cell in h sections, the b axis in k sections and the c axis in l sections (Figure 2.23). A zero indicates that the planes are parallel to the corresponding axis. E.g. the $(2,2,0)$ planes cut the a - and the b - axes in half, but are parallel to the c - axis.

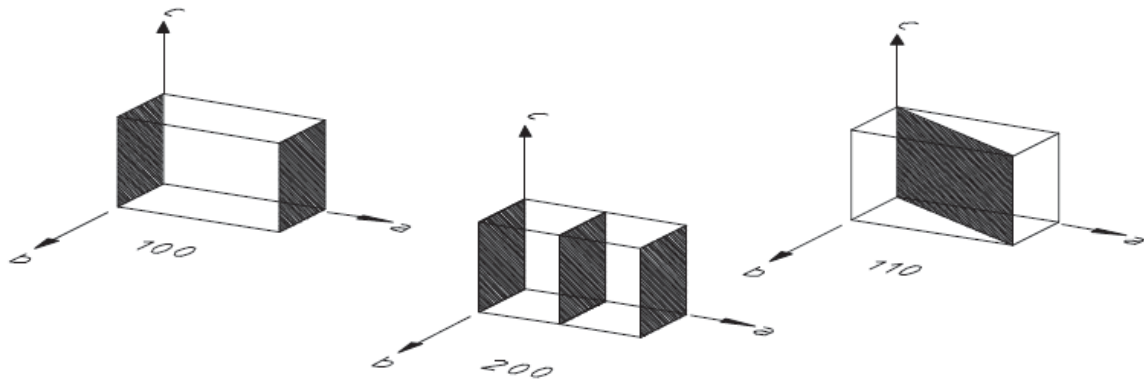


Figure 2.22: Example planes sections for respective h , k , l indices.

As mentioned, the indices values are used to calculate interplanar spacing d_{hkl} , which for a crystal structure of cubic symmetry for example, can be calculated according to Eq. (2.30).

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{Eq. (2.30)}$$

in which a is the lattice parameter (unit cell edge length). The interatomic spacing, in conjunction with the angle of the diffracted beam and the incident wavelength upon the planes are related through Braggs law, Eq. (2.31).

$$n\lambda = 2d_{hkl} \sin \theta \quad \text{Eq. (2.31)}$$

where n is the order of reflection which may be an integer (1, 2, 3, ...) consistent with $\sin\theta$ not exceeding unity.

Powder XRD is one of the most widely used x-ray diffraction techniques for characterizing materials. While samples are generally analyzed in powder form, consisting of fine grains of single crystalline materials, the technique is also used widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials). As powder, the crystalline domains are randomly oriented in the sample, therefore when the 2-D diffraction pattern is recorded it shows concentric rings of scattering peaks corresponding to the various interatomic spacing's in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. For example, the diffraction lines of graphite are different from diamond even though they both are made of carbon atoms. This phase identification is important because the material properties are highly dependent on structure. Likewise, the diffraction patterns for doped xerogels show a transition from amorphous to crystalline with heat treatment.

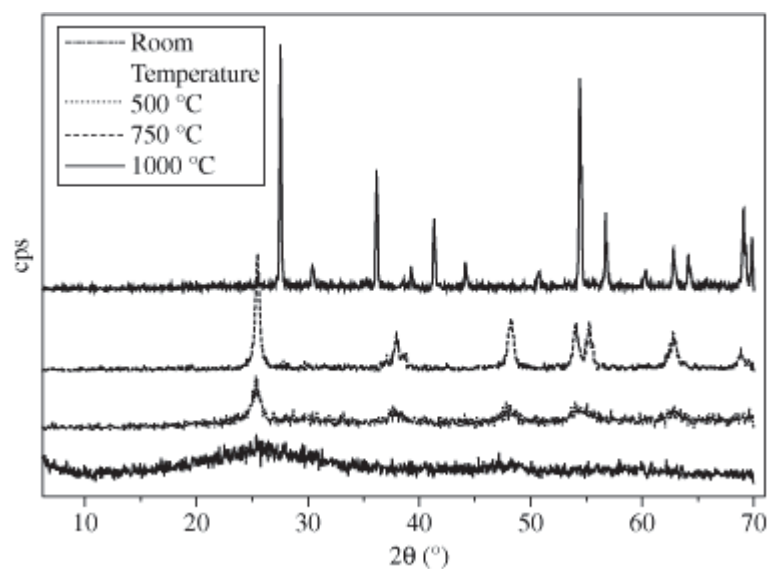


Figure 2.23: X-ray diffraction of xerogels doped with 0.3% mol of europium and heat-treated at different temperatures displaying the transition from amorphous to crystalline material [91].

2.3.4 Raman Spectroscopy

Like XRD, Raman spectroscopy provides information on chemical structures and physical forms to identify substances from the characteristic spectral patterns (“fingerprinting”). When light interacts with matter, the photons which make up the light may be absorbed or scattered, or pass straight through it without interacting. If the energy of an incident photon corresponds to the energy gap between the ground state of a molecule and an excited state, the photon may be absorbed and the molecule promoted to the higher energy excited state. It is this change which is measured in absorption spectroscopy by the detection of the loss of that energy of radiation from the light. However, it is also possible for the photon to interact with the molecule and scatter from it, in which case there is no need for the photon to have an energy matching the difference between two energy levels of the molecule. The scattered photons can be observed by collecting light at an angle to the incident light beam, and provided there is no absorption from any elec-

tronic transitions which have similar energies to that of the incident light, the efficiency increases as the fourth power of the frequency of the incident light [92].

Radiation is often characterized by its wavelength (λ), however in spectroscopy the interaction of radiation with states of the molecule being examined are discussed in terms of energy, therefore frequency (ν) or wavenumber (ω) are generally used as they are linearly related with energy (E). The relationships between these scale are given in Eq. (2.32), Eq. (2.33), and Eq. (2.34).

$$\lambda = c/\nu \quad \text{Eq. (2.32)}$$

$$\nu = \Delta E/h \quad \text{Eq. (2.33)}$$

$$\omega = \nu/c = 1/\lambda \quad \text{Eq. (2.34)}$$

Energy is therefore proportional to the reciprocal of wavelength allowing characteristic intense scattering frequencies to be used as fingerprint values to determine or confirm the presence of various materials. An example of a Raman scattering for different carbon hydrides can be observed in Figure 2.24.

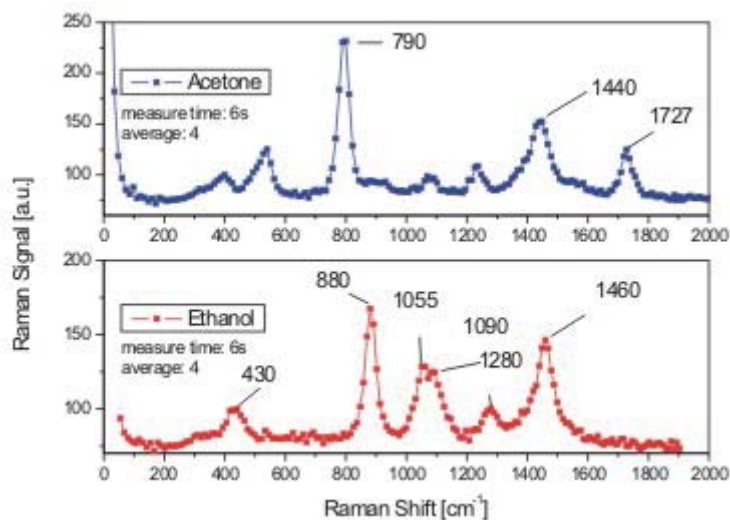


Figure 2.24: Raman scattering “fingerprints” for both acetone and ethanol.

2.3.5 Electrochemical measurement

Electrochemical measurements can be taken as “continuous” or “intermittent” by controlling either the current or voltage, or both. Information can be collected by electrochemical measurement regarding chemical reactions taking place within battery electrodes and kinetic properties of battery components, which aid in explaining practical reaction voltages and characteristic discharge-charge behavior and deviation from theoretical performance. Typical testing procedures involve constant-current (CC) cycling or constant-current-constant-voltage (CCCV) cycling in order to understand electrochemical properties of cycling batteries. CC cycling requires that current remain constant for the duration of discharging and charging, but does not require that both the currents be equal. Likewise for CCCV cycling, but a voltage hold takes place at the upper cut-off voltage for a pre-set time interval or low current cut-off. Utilization of a voltage hold allows for equilibration of mobile species into an electrode.

One method of presenting and analyzing information is through use of discharge and charge curves, in which the cell voltage is plotted as a function of the state of charge. The

relationships for a single material can vary significantly depending upon the rate at which the energy is extracted from, or added to the cell. Likewise, curves vary extensively for different materials. Figure 2.25 shows an example of a discharge curve for various types of materials.

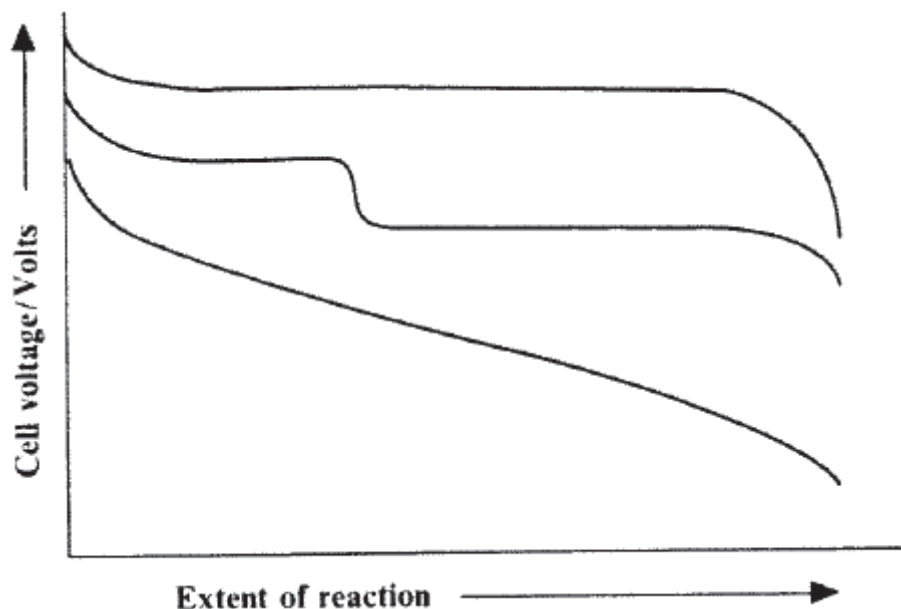


Figure 2.25: Schematic representation of three different types of discharge curves: one that is flat, one that has more than one flat curve, and a slanted/stretched S-shaped curve with a relatively large slope [5].

The flat plateaus represent multiphase reactions with potentials that are essentially independent of the state of charge of the cell. A sloping plateau allows for potential misinterpretation as it could be the result of undesirable reactions between two or more components of the battery, such as the electrolyte and active material.

The information obtained from electrochemical measurements is not only limited to observation of reaction voltages, but is useful for observation of polarization losses (Chapter 4), the maximum rate at which cells can maintain a high capacity (Chapter 6), and kinetic properties

of materials (Chapter 6). Electrochemical measurements are also used to show cycle life through repeated cycling, and in the case of degradation, explain the mechanisms for reduced capacity (Chapter 4).

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3. Solid Electrolyte

3.1 Introduction

Recent popularization of various kinds of portable electronic devices has driven the importance of energy devices like secondary batteries, fuel cells, and capacitors to new heights. It is widely understood that all-solid-state energy storage is most promising for improving safety and reliability of these devices [1]. As a key material of all-solid-state energy devices, solid electrolytes have been extensively studied in the fields of materials science and electrochemistry. Many research efforts have focused on preparation of solid electrolytes with a broad spectrum of materials and manufacturing methods.

For any rechargeable lithium battery, the electrolyte material must permit the repeated and rapid transfer of Li^+ between the anode and cathode over a predetermined set of operating conditions (voltage, temperature, and current), without significant deterioration. Ideally, an electrolyte material would be electronically insulating, ultra-thin, lightweight, free of hazards and inexpensive. Inorganic solid electrolytes offer both advantages and disadvantages over liquid and organic polymer electrolytes. For the required rapid transport of Li^+ across the electrolyte, the product of the resistivity and electrolyte thickness must be minimized (Arrhenius Equation, Section 3.2.1). Typical room temperature conductivities are on the order of $10^{-1} \text{ S cm}^{-1}$ for liquids, 10^{-3} - $10^{-6} \text{ S cm}^{-1}$ for various gel and solvent-free (dry) polymers [2], and 10^{-3} - $10^{-8} \text{ S cm}^{-1}$ for typical glass and glass-ceramic solid electrolytes [3]. One of the principle advantages of the inorganic solid electrolytes is that these materials are generally single ion conductors, meaning that only the Li^+ ions have an appreciable mobility, while the anions and other cations form a rigid framework. This has many beneficial consequences such as eliminating the anionic concentration gradient across the electrolyte, which may help suppress undesirable side reactions or

decomposition of the electrolyte. The single ion conductor expands the choice of electrode material and permits operation at higher voltages. Few polymer electrolytes mimic this single ion behavior and they are usually associated with a higher resistivity [4]. Similarly, a negligible electron transport across the electrolyte is necessary to prevent self-discharge of the battery. For a shelf life of months or years, the electrolyte must be an excellent insulator with an electronic conductivity $<10^{-12} \text{ S cm}^{-1}$ [5]. Conductive electron paths may be formed along lithium dendrites of liquid or polymer electrolytes, while grain boundaries, pores, or cracks may become electronic paths in glass and ceramic electrolytes. Establishment of these conductive paths has resulted in explosions among liquid electrolyte batteries in the past, which is the primary motivation for developing all-solid-state batteries that, while susceptible to electron path formation, are not prone to thermal runaway and therefore operate at a more preferable level of safety.

While it is important to develop solid electrolytes with high “bulk” conductivity, the resistance of the solid electrolyte-electrode interface is just as important as the bulk resistivity of the electrolyte. One might assume that ion exchange across the solid electrolyte-electrode interface would be more resistive than that with a liquid or soft polymer electrolyte. However, this is not necessarily the case due to the formation of a “solid electrolyte interphase” (SEI) reaction layer (Discussed in section 5.1.2), which adds to the interface resistivity for most liquid or polymer electrolytes. The solid electrode-electrolyte interface has the added advantage of providing a dense, hard surface that maintains its integrity and inhibits roughening of the microstructure that leads to mossy or dendritic deposits. Without good adhesion however, stresses may cause a rigid interface to form permanent cracks or voids. It is therefore the goal of many research groups to establish a good interface between the solid electrolyte and electrode in order to minimize resistance as well as potential for cracks and voids.

The nature of highly active lithium battery chemistry places severe electrochemical requirements on the electrolyte. The organic electrolytes invariably rely on the formation of a protective SEI layer to limit the reaction or decomposition rate. And while many of the glass and glass ceramic electrolytes in the literature decompose under high voltages or react with lithium, some have shown to be thermodynamically stable and viable for all-solid-state battery construction.

As previously mentioned, liquid electrolytes currently dominate among the lithium-ion battery industry due to their exceedingly high ionic conductivity and highly optimized properties. While their replacement with solid electrolytes is sought as a means of increasing the operation safety, relatively low ionic conductivity and poor interfacial contact of solid electrolytes stand in the way of commercial integration with SOA electrode materials. Solid electrolytes must exhibit a high ambient temperature ionic conductivity over $1 \times 10^{-4} \text{ S cm}^{-1}$ in order to effectively compare to liquid-electrolyte batteries. Ideally, an ionic conductivity of solid electrolytes over $1 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature would make all-solid-state batteries feasibly commercializable; however achievement of such high conductivities for solid electrolyte is difficult.

In this chapter we will focus on sulfide-based lithium conductors of two structurally different classes, glass and glass-ceramic materials. Glassy materials are typically preferred over crystalline materials because they exhibit higher conductivities as a result of isotropic properties, no grain boundaries, and easy control of properties with changing chemical compositions [4]. Crystalline glass-ceramic electrolytes have an inherently lower density, higher defect concentration, space charge polarization, and segregated impurities which may form resistive barriers for Li^+ but fast paths for other species, increasing the likelihood of an internal short circuit, a precipitated Li metal dendrite, or breakdown related to electrochemical stress. However, sulfide-based

glass-ceramic solid-electrolytes have been shown to exhibit extremely high conductivities over $10^{-3} \text{ S cm}^{-1}$ [6,7]. In some cases, the glass-ceramic shows a higher conductivity than its equivalent glass counterpart as a result of highly conducting crystal formation [8]. Conventional solid electrolyte production techniques such as melt quenching are discussed; however this work focuses on mechanochemical synthesis techniques for production of both glass and glass-ceramic solid-electrolytes. The benefit of mechanochemistry and the properties of the obtained glasses are demonstrated. Finally, the effects of crystallization on conductivity of glassy materials are discussed.

3.2 Background

3.2.1 Solid electrolytes

In general, ions cannot migrate in a solid, since the constituent cations and anions are necessary to maintain the rigid skeletal structure. In some solids however, only one ion species is able to migrate with a low energy barrier, and these have high ionic conductivities comparable to those of molten and aqueous electrolytes. Such solids are called “solid electrolytes” [9]. Put simply, a solid electrolyte is a fast ion conductor composed of a rigid framework within which ions move through voids in the crystal lattice structure.

Frenkel [10] and Schottky [11] developed the classical microscopic models showing how ionic hopping among vacant or interstitial lattice sites can result in long range ionic migration in a rigid lattice (Figure 3.1a). Frenkel defects, ions promoted to interstitial sites from normal lattice positions, are the typical mechanism employed by solid electrolytes as proposed by Kharkats et al. [12]. Schottky defects, anion-cation vacancy pairs, occur more typically in alkali halides and

alkaline-earth oxides over alkaline sulfide solid electrolytes. Both Frenkel and Schottky defects can arise from intrinsic and extrinsic sources. Intrinsic defects occur in thermodynamic equilibrium with a crystal's lattice. The driving force for their creation is the lattice disorder produced. Extrinsic vacancies occur to compensate the charge of impurities of different valence. Often the number of defects is dominated by impurities at lower temperatures and intrinsic equilibrium at higher temperatures [13].

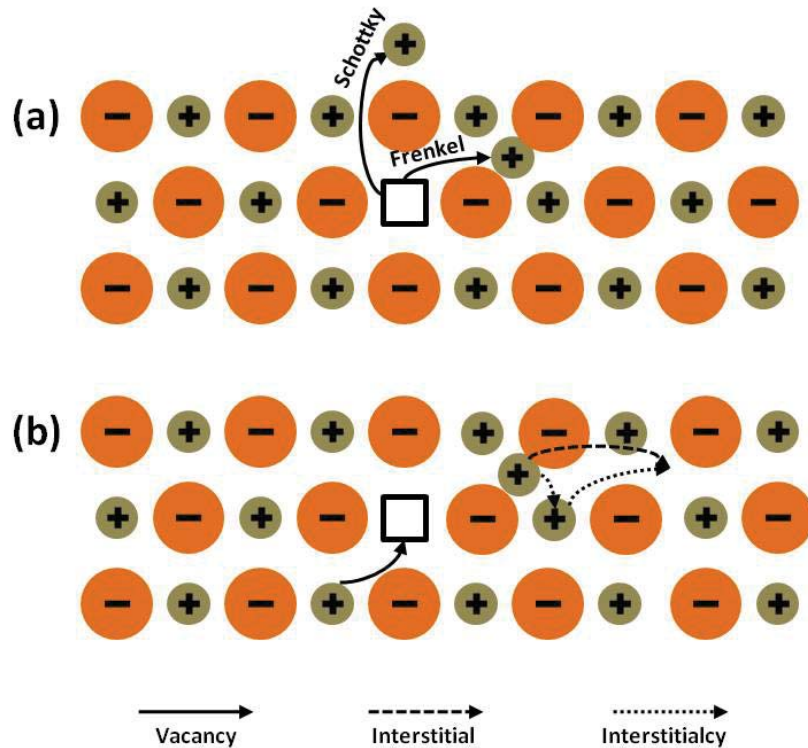


Figure 3.1: (a) Frenkel (interstitial) and Schottky (vacancy) models of lattice defects that can result in ionic conductivity. (b) Three classical mechanisms for ionic conductivity in crystalline solids [13].

Ionic transport in crystals is described classically by the vacancy, interstitial, and interstitialcy models (Figure 3.1b). The vacancy mechanism involves the motion of a vacancy through a lattice by successive ion hops in the direction opposite to vacancy motion. In the interstitial model an ion moves through a series of interstitial sites. The interstitialcy mechanism involves cooperative motion in which a lattice ion hops to an interstitial site and an interstitial ion fills the remaining vacancy. For all these mechanisms, ion conductivity, σ , in crystals can usually be described by the Arrhenius equation:

$$\sigma = \frac{\sigma_0}{T} \exp^{E_A/kT} \quad (3.1)$$

in which σ_0 is a function of the ionic charge, concentration of mobile ions, and their attempt frequency and the jump distance; E_A is the activation energy for defect formation and motion, and k and T are the Boltzmann constant and temperature, respectively. Ionic conductivity is extremely sensitive to the value of E_A . In many materials conductivity falls into intrinsic and extrinsic temperature regimes, depending on the dominant mechanism of defect formation. In Figure 3.2 the line corresponding to low temperatures (right side) is due to the extrinsic vacancies: at low temperatures the concentration of intrinsic vacancies is so small that it can be ignored because it is dominated by the defects created by the impurity. At higher temperatures

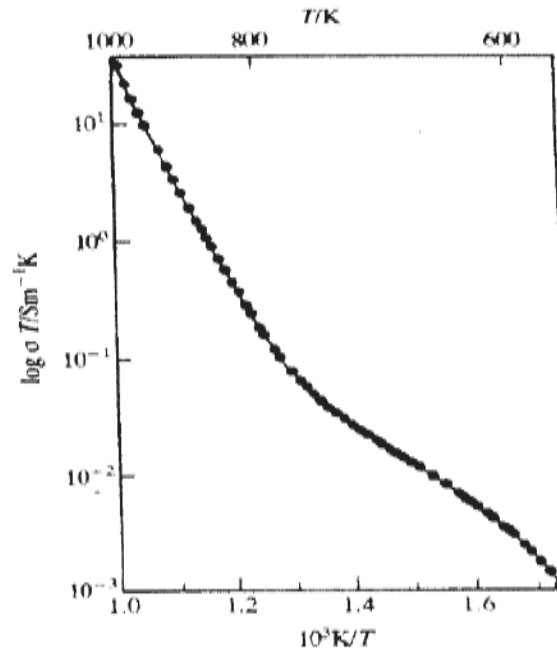


Figure 3.2: Ionic conductivity of NaCl plotted against reciprocal temperature revealing two slopes [15].

(left side) the concentration of intrinsic defects has increased to such an extent that it is now similar or greater than the concentration of extrinsic defects [14].

For a solid to have high ionic conductivity at temperatures much lower than its melting point, it must maintain a rigid, three dimensional cation-anion network having three main characteristics: a high concentration of vacancies or interstitial sites, a high concentration of potential charge carriers, and low activation energy for ion hopping from filled to unfilled sites. More recently, it has been shown that utilization of large, highly polarizable framework ions results in significant improvement of ionic conductivity. Highly polarizable framework ions (usually anions) can deform to stabilize transition state geometries of the migrating ion through covalent interactions. Basically, the formation of strong covalent bonds between the anions of the framework orients the charge density away from the interstitial ions reducing interference from the framework. Ion mobility is governed chemically by the bonding energy between the

mobile ions and the network anions as well as physically by the size of the bottlenecks (gaps between interstitial positions) between the interstitial alkali-ion positions. The shortest diameter of the bottlenecks should be larger than twice the sum of the mobile-ion and anion radii (so a larger radii means larger bottlenecks) [15]. With knowledge of the previously mentioned characteristics of solid electrolyte, we will now review some of the most wide spread solid electrolytes being researched.

3.2.1.1 Lithium phosphorus oxynitride (LIPON)

As previously stated, the requirements for the battery electrolyte layer are most stringent. The material must have a good Li^+ conductivity, be electrochemically stable with both the cathode and anode material at high cell potentials, and have a negligible electronic conductivity to minimize the self-discharge of the cell. The electrolyte must tolerate volume changes of the anode and cathode and the high lithium ion flux without developing lithium filaments along cracks or other flaws which makes glassy materials preferable to polycrystalline films which have internal boundaries prone to form leakage paths. The only single-phase electrolyte currently known to meet all these criteria is an amorphous lithium phosphorus oxynitride, first synthesized by Bates in 1992 at Oak Ridge National Laboratories, with a composition near $\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.46}$. This material, known as "Lipon" forms a uniform conformal coating free of grain boundaries and cracks, and can be deposited at near ambient temperatures. Electrical measurements by Yu have demonstrated Lipon films stable in contact with lithium metal, and cathode potentials up to 5.5V [16]. While the Li^+ conductivity is only on the order of $10^{-6} \text{ S cm}^{-1}$, that for electronic carriers is $10^{-14} \text{ S cm}^{-1}$ [5]. If formed as a very thin film of less than about $1\mu\text{m}$, even a relatively

resistive material may compete favorably when compared to a much thicker cast polymer or liquid-filled porous separator membrane. An ultra-thin electrolyte also provides a considerable savings in terms of volume and mass for the battery, if not offset by the need for thick inactive support material. Cells with the Lipon electrolyte have demonstrated excellent cycle life over 70000 cycles between 4.3 and 3V and shelf lives of at least 3 years with no significant self-discharge. However, Lipon is an example of a material that cannot be achieved readily by bulk synthesis with the high lithium content; Lipon composition is outside of the normal glass-forming region. As the ionic conductivity is very low, this electrolyte is predominantly useful only in a ‘thin film’ configuration with solid electrolyte layer thicknesses around $\sim 1\mu\text{m}$. The thin film construction of batteries employing Lipon electrolyte limits overall capacity and therefore limits commercial application to small medical devices and MEMS devices. Furthermore, the slow rate at which solid electrolyte layers can be actively coated impede production on a large scale.

3.2.1.2 Lithium super ionic conductor (LISICON)

Development of the LISICON structure came from attempts to create a 3D rigid framework for mobile alkali ions to move through interstitial space. LISICON electrolytes employ the formula $\text{Li}_x\text{M}_2\text{M}'_3\text{O}_{12}$, where M and M' are typically metals and represent network cations that are, respectively, octahedrally and tetrahedrally coordinated to the O^{2-} ions ($\text{Li}_8\text{Mg}_2\text{Si}_3\text{O}_{12}$ for example) [15]. All three network cations, particularly the Li^+ , form strong covalent bonds to O^{2-} ions that polarize the oxygen charge density away from the interstitial ions. This effect is especially important because each O^{2-} ion is bonded to four network cations, leaving none of its sp^3

orbitals available for covalent bonding to the interstitial Li^+ ions. The essential structural feature of highly conducting solid electrolytes is a rigid, three dimensional, cation-anion network having an interconnected interstitial space that is partially occupied by mobile alkali ions. As ion mobility is governed physically by the size of the bottlenecks between the interstitial alkali-ion positions and chemically by the bonding energy between the mobile ions and the network anions, the shortest diameter of the bottlenecks should be larger than twice the sum of the mobile-ion and anion radii and the covalent bonding between the mobile ion and the anion should be as weak as possible, which may be achieved if the anion forms a strongly covalent complex with the network cations. Essentially, larger ions enlarge bottlenecks to Li-ion transport and therefore improve conductivity, for example using $\text{M}=\text{Si}$ instead of Ge in the above example. Although there are two inequivalent types of interstitial sites, both are partially occupied, indicating that the difference in potential energy between the sites is not large enough to prevent easy transfer of Li^+ ions from one to the other. The mobility of the interstitial Li^+ is increased because the interaction between these ions and the O^{2-} ions forming the bottlenecks is reduced by the chemical bonding between the O^{2-} ions and the cations of the three-dimensional network. In short, high conductivity LISICON electrolyte is achieved by enlarging bottlenecks and utilizing highly polarizable oxygen to create strong covalent bonding of a rigid network to orient charge density away from interstitial ions.

3.2.1.3 Thio-LISICON

Thio-LISICON electrolytes share the principles of LISICON electrolytes employing a large polarizable anion; however thio-LISICON's differ by utilizing larger and more polarizable

sulfur as the anion over oxygen. The higher polarizability and larger ionic radius result in higher mobility of Li^+ and therefore higher conductivity. Thio-LISICON electrolytes have the general formula $\text{Li}_x\text{M}_{1-y}\text{M}'_y\text{S}_4$ ($\text{M}=\text{Si}$, Ge and $\text{M}'=\text{P}$, Al , Zn , Ga , Sb) with the framework structure of the $\gamma\text{-Li}_3\text{PO}_4$ type and conductivities on the order of 10^{-7} - 10^{-3} S cm^{-1} [17]. The ionic conduction properties are strongly dominated by size and polarizability of the constituent ions, or interstitial-vacancy character caused by the substitutions. The sulfide based electrolytes also exhibit a high decomposition potential at room temperature. Thio-LISICON is the first example of an ionic conductor with high ionic conductivity and high decomposition potential at room temperature, and is a promising candidate as a solid electrolyte for lithium secondary batteries.

Among the thio-LISICON family of solid electrolytes a special case exists where no metal elements are included, resulting in the Li-P-S system made from combining Li_2S and P_2S_5 . The Li-P-S system has exhibited high conductivity and stability in all-solid secondary battery configurations at room temperature [18]. The amorphous glass electrolyte has been produced by numerous methods (Section 3.3) and exhibited high conductivity at room temperature. Interestingly, it can be treated to form a crystalline material with higher conductivity than comparable glass electrolyte. For example, the highly conducting crystal $\text{Li}_7\text{P}_3\text{S}_{11}$ obtained from the Li-P-S system yields a higher conductivity than its amorphous glass counterpart [9]. While it demonstrates good stability against Li metal, the electrolyte undergoes significant reactions with high voltage cathodes. This has stimulated a large research effort to stabilize the Li-P-S electrolyte with high voltage cathodes, and will be discussed further in Chapter 5.

3.2.2 Solid electrolyte fabrication methods

Solid electrolytes have been synthesized by a number of different techniques throughout the past that express a variety of different attributes. Initially, solid electrolytes were prepared by melt quench methods where both glass and crystalline materials with high conductivity can be produced. These electrolytes showed ionic conductivity on the order of $10^{-3} \text{ S cm}^{-1}$ and expressed good electrochemical stability [19]. More recently however, mechanochemical milling of solid electrolytes has been adopted for production of solid electrolytes as it is a room temperature, low cost, and less time consuming process. These techniques will now be discussed in detail.

3.2.2.1 Melting and quenching

While numerous variations of the melting and quenching process exist, only one procedure is discussed here as an example of general procedure. Starting powders are initially mixed by mortar and pestle and then placed into a carbon coated quartz tube. The tube is then sealed under vacuum to obtain an ampoule containing the starting materials. In order to prepare glasses, the ampoule is heated to 750°C for 10 hours to obtain a single phase melt with uniform chemistry and then quenched in ice water to suppress diffusion and produce a room temperature solid solution. Crystalline materials are prepared by heating the glasses at temperatures above the crystallization temperature (T_c) and then cooling at different rates in order to obtain different crystals. In the case of crystallization from the melt, the ampoule can be heated at 750°C for 10 hours and then the melt held for 48 hours at various temperatures lower than 750°C in order to

promote nucleation and crystal growth from the melt [9]. Figure 3.3 shows a simple phase diagram for a Li-P-S electrolyte fabricated by this method.

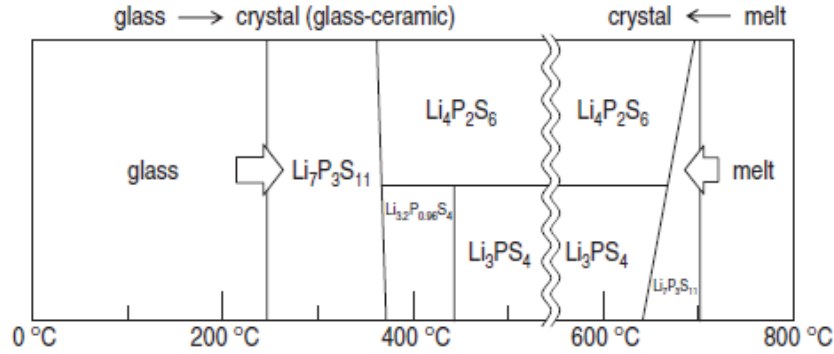


Figure 3.3: Simple phase diagram of the 70Li₂S-30P₂S₅ (mol%) composition based on the XRD results of crystals precipitated from the glass and melt [9].

3.2.2.2 Ball milling

While melt and quench methods for $x\text{Li}_2\text{S} \cdot (100-x)\text{P}_2\text{S}_5$ binary systems have produced promising results in the past, ball milling has emerged as a more enticing method for solid state electrolyte development because it is relatively lower cost and less time consuming [20]. Conventional ball milling techniques have proven useful for generating ultra-fine amorphous materials at room temperature. Fine powders function well for achieving high ionic conductivities as well as close contact between electrolytes and electrode materials for all-solid-state cells [21,22]. Ball milling has also proven effective for enlarging the compositional region in which amorphous materials are obtained, beyond that of conventional melt-quenching methods [23,24]. Ball milled amorphous powders are often heat treated to attain a crystalline structure capable of even higher conductivities than those reached by amorphous powders [25,26]. Potentially, ball

milling can produce a large range of nanoscale materials, including nanocrystalline materials, nanoparticles, and nanocomposites.

Mechanical milling embraces a complex mixture of fracturing, grinding, high-speed plastic deformation, cold welding, thermal shock, and intimate mixing. The mechanical energy created by the milling can also induce chemical reactions of the reactants at room temperature [27]. This mechanical treatment can also introduce a large number of crystal defects and increase the specific surface area of compounds, thought to be one of the main reasons for increased reactivity of milled materials [28,29]. Any chemical interaction between solids proceeds neither in the entire volume of the reacting compounds nor on their entire surface but rather exclusively in the contact areas between the particles [30]. Thus the total number of such contacts between reacting particles plays the decisive role at the initial steps of a solid-state reaction. This means that it is always desirable to grind and mix components in such a way as to prevent the aggregation of particles of the same component (this dramatically decelerates the reaction) [31].

High energy ball milling (HEBM) and planetary ball milling are popular and powerful milling techniques for producing amorphous materials. Both techniques involve similar materials concepts for the mechanism of producing alloys with only some variation in mixing apparatus and dominant pulverization technique. HEBM is typically done with shaker mills that rotate on a pivoted axis which cause balls to impact the walls and each other. While effective, this method of milling can produce inconsistent results as a consequence of poor rotary control. Essentially, the extremely high energy causes fast instrument wear and therefore inconsistent production of material. Planetary milling involves more of a high attrition grinding motion for milling but with some impact, as well as maintains relatively good control and high scalability. Vertically set chambers rotate in a planetary motion on a base disk which operates under a controlled rate.

During milling, material particles are repeatedly flattened, fractured and welded. Every time two steel balls collide or one ball hits or rolls against the chamber wall, they trap some particles between their surfaces. The high-energy impacts severely deform the particles and create atomically fresh, new surfaces, as well as a high density of dislocations and other structural defects [32]. Such a high defect density can accelerate the diffusion process [33]. Furthermore, the deformation and fracturing of particles cause continuous size reduction and leads to reduction in diffusion distances. This can at least reduce the reaction temperatures significantly, even if the reactions do not occur at room temperature [34–36]. As mentioned previously, ball milling can produce smaller grain size, possibly higher surface area and disordered structure, which should all contribute a reduced reaction or vaporization temperature and a higher chemical reactivity in comparison with samples without the milling treatment. The ball-milled powders are often metastable and have higher chemical reactivity's, thus new reactions could take place during the subsequent annealing with the formation of various nanostructures as the end products [37].

Heat treatment of ball milled electrolytes has been shown to have adverse effects on the conductivity and morphology of materials. For instance, researchers have found heating ball milled materials beyond their glass transition temperature can result in highly conducting crystalline solid electrolytes [9]. While the same can be done with melt quenching, production by ball milling is a room temperature, less time consuming and less costly procedure. As will be discussed in Chapter 5, heat treating can also be used to modify and improve solid electrolyte performance by treating with elemental additives. Because fragmentation of crystallites during milling can lead to a microcrystalline structure, a problem of ball milling is determining if the new disordered material is only microcrystalline or actually amorphous, particularly for alloys synthesized by ball milling since the evolution of the disordered structure often involves the

broadening of diffraction lines with milling time [38,39]. The appearance of a glass transition temperature T_g however, and therefore crystallization, is strong evidence for a liquid-like and therefore truly amorphous structure [34].

Other emerging ball milling techniques beyond planetary (attrition milling) or HEBM (impact milling) include cryogenic milling/grinding (cryomilling), and jet milling. Cryomilling takes advantage of both the cryogenic temperatures and conventional mechanical milling. It involves cooling or chilling a material for low temperature milling to achieve reduced particle size of “soft” materials that are difficult to grind to small particle sizes at ambient temperatures due to material adhering in lumpy masses and/or agglomeration. The extremely low milling temperature suppresses recovery and recrystallization and leads to finer grain structures and more rapid grain refinement. Jet milling is a fairly new technique that involves no grinding media, but near sonic velocity jets. Typically used more for size reduction, it is becoming increasingly popular for use to combine materials. Size reduction and material combination is the result of the high-velocity collisions between particles of the process material itself. Interior of chambers are designed to allow recirculation of over-sized particles, enhancing the incidence and the effect of these collisions. As particles are reduced in size and progressively lose mass, they naturally migrate toward the central discharge port, making precise classification both automatic and precisely controllable. The process involves no moving parts or screens and is suitable for virtually any friable or crystalline materials, even materials that are very abrasive. And, since contamination can be avoided and no excess heat is produced, jet pulverizers are suitable for materials that must remain ultra-pure and those that are heat sensitive. Even cryogenic applications can be accommodated. Further, by precise metering of the product input and air or steam velocity, highly predictable and repeatable graduation and classification of the finished particles is possible.

3.3 Single step ball milling (SSBM)

While ball milling with subsequent heat treatment has proven effective, the multi-step process is time consuming and inefficient. More importantly, the post heat treatment usually results in glass-ceramic materials with larger particle size of which morphology may not be desirable for use in all-solid-state Li-ion batteries. A single step ball milling (SSBM) procedure where ball milling and heat treatment are performed simultaneously is proposed in this work. We report on the glass-ceramic $x\text{Li}_2\text{S} \cdot (100-x)\text{P}_2\text{S}_5$ binary system produced by a the SSBM process in terms of its structural and electrochemical characteristics.

3.3.1 Experimental

Reagent-grade powders of Li_2S (Aldrich, 99.999%) and P_2S_5 (Aldrich, 99%) were used as starting materials for mechanical ball milling. Appropriate concentrations of materials were combined into a zirconia vial (Spex) at a net weight of one gram with 2 zirconia balls (1x 12mm, 1x15mm in diameter) for grinding. High energy ball milling (Spex2000) took place for 20 continuous hours in an Ar filled glove box at 55 °C. Ambient temperature was maintained by use of a temperature controller connected to a heater within the glovebox where ball milling took place. Ball milled vials were paused periodically to measure the vial temperature and adjust the ambient temperature accordingly to achieve desired vial temperature. A direct correlation was developed for the discrepancy between ambient and vial temperature and vials were then milled without pausing. High energy ball milling was also performed at room temperature. In order to maintain room temperature, vials were milled in 30 minute intervals. By milling for 30 minutes and resting for 30 minutes repeatedly, temperatures can be held below 32 °C for the 20 hour

milling time. Materials ball milled at room temperature were amorphous and their conductivity values were consistent with previously reported data [21]. Materials are then cold pressed (5 metric tons) into pellets 13mm in diameter and 1mm thick in a titanium die.

The obtained samples were characterized by X-ray diffraction measurements with Cu-K α radiation. Sample materials were sealed in an airtight aluminum container with beryllium windows and mounted on the X-ray diffractometer (PANalytical, PW3830). Diffraction measurements were observed for all starting materials as well as significant compositions between 10 and 40 degrees. Ionic conductivities were measured by AC impedance spectroscopy (Solartron 1280C) for all SSBM sample materials. Weighed materials are cold pressed at 8 metric tons, before lithium metal plates are pressed to both sides of the pellet at 1 metric ton to serve as electrodes. The impedance of selected cells was measured from 20 MHz to 100 mHz at room temperature and the conductivity was determined using complex impedance analysis.

3.3.2 Characterization

Figure 3.4 shows the X-ray diffraction (XRD) spectra of the glass-ceramic samples in the composition range $70 < x < 80$ for $[x\text{Li}_2\text{S} \cdot (100-x)\text{P}_2\text{S}_5]$. Sharp diffraction peaks are observed among all compositions due to the crystalline material structure formed under the SSBM method. For concentrations of $x=77.5$ and $x=80$ electrolytes sharp diffraction peaks are observed near

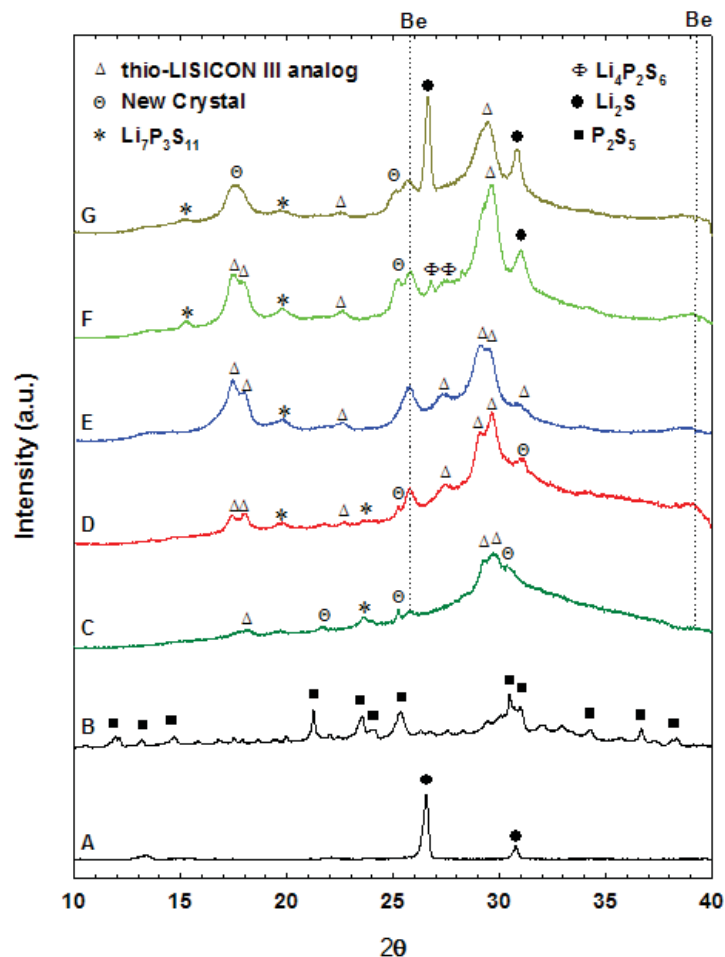


Figure 3.4: XRD patterns for all tested electrolytes, (A) Li_2S , (B) P_2S_5 , (C) $x=70$, (D) $x=72.5$, (E) $x=75$, (F) $x=77.5$, and (G) $x=80$.

25.5° and 31° due to excess Li_2S content in the sample [22,40]. The diffraction patterns for SSBM samples show a trend of increasing intensity of crystalline peaks up to $x=77.5$ at which point only the Li_2S peaks intensifies for $x=80$. Formation of a new crystalline phase similar in structure to that of thio-LISICON II analog can be observed by similarly positioned peaks throughout the composition range [22]. Individual properties of compounds such as the low melting temperature of P_2S_5 may be a factor in the crystallization of materials during SSBM. It is proposed that the crystalline structure observed for SSBM material is a result of microcrystal-

line formation from the rapid recovery and recrystallization of particles during ball milling. In essence, ball milling at high ambient temperature has an opposite effect to that of cryomilling.

Figure 3.5 shows the stability window for samples tested with titanium rod and lithium foil as the working and counter electrodes, respectively. Measurements were carried out from the rest potential to the cathodic direction and then the anodic direction up to 5 V vs. Li^+/Li and down to -0.5 V vs. Li^+/Li . No reactions were observed in these voltammograms except for lithium deposition ($\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$) and dissolution ($\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$) reactions between -0.5 and 0.6 V, up to 5 V vs. Li^+/Li , suggesting that the SSBM materials have a wider electrochemical window than 5 V [23].

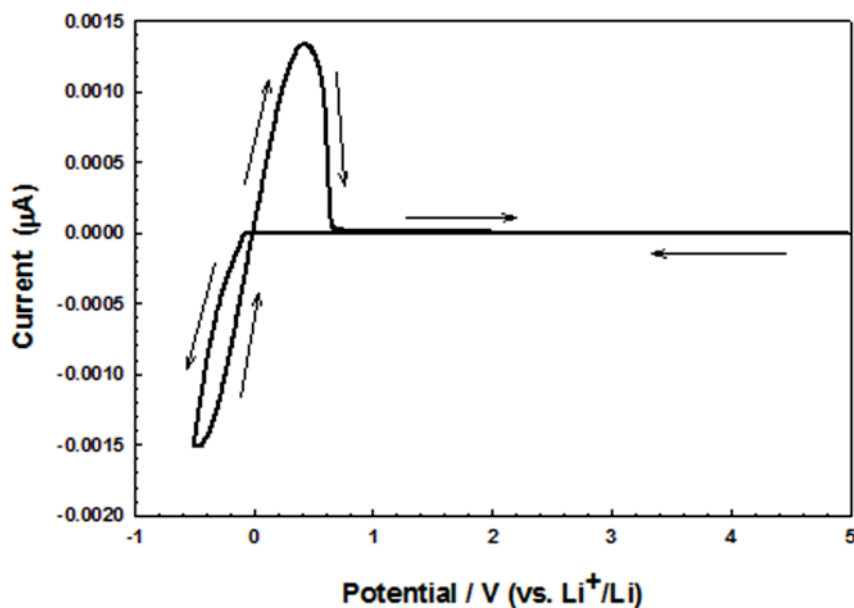


Figure 3.5: The stability window for the first cycle of tested SSBM glass-ceramic sample $x=72.5$. Glass-ceramic samples containing larger concentrations of Li_2S are not shown but follow a similar trend as the other samples with a maximum recorded current of $.0144 \mu\text{A}$ for $x=80$. Repeated cycling shows a negligible difference in the stability windows of all samples.

3.3.3 Conductivity

Figure 3.6 shows a conductivity map comparing the conductivity values attained from our amorphous glass and SSBM glass-ceramic electrolytes with Tatsumisago groups' amorphous glass and two step glass-ceramic samples. Standard two step heat treatment shows increased conductivities over glass electrolytes caused by formation of new highly conductive crystalline structures [26]. For the SSBM glass-ceramics, enhancement in conductivity by crystallization was due to formation of a highly conductive crystalline phase during the ball milling process, analogous to the thio-LISICON phase $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ ($0.6 < x < 0.8$) defined by a unique monoclinic superstructure exhibiting high conductivities over $10^{-3} \text{ S cm}^{-1}$ [41]. We found that the values for conductivity attained by SSBM were higher by approximately one order of magnitude than all glass electrolytes and were as high as or higher than those values for glass-ceramics by standard two step heat treatment for all but the compositions at the extremes of our range [26]. The SSBM glass-ceramic sample with $x=70$ was not as high as standard two step glass ceramics, but the SSBM glass-ceramic sample with $x=80$ was comparably close in conductivity to the standard two step glass-ceramic sample. We attribute this discrepancy in conductivities for $x=70$ to the lower temperature at which SSBM samples are exposed in comparison to standard heat treating. We speculate the entire SSBM conductivity curve can rise as a result of higher ball milling temperatures. More systematic studies on the effect of the ball milling temperature on ionic conductivity are in progress. The simplicity of the SSBM process and high ionic conductivity of SSBM samples make the SSBM method superior for development of solid state electrolytes for all-solid-state battery production. Furthermore, the SSBM with no post heat treatment required, completely eliminates any potential grain growth of as-ball-milled fine powders.

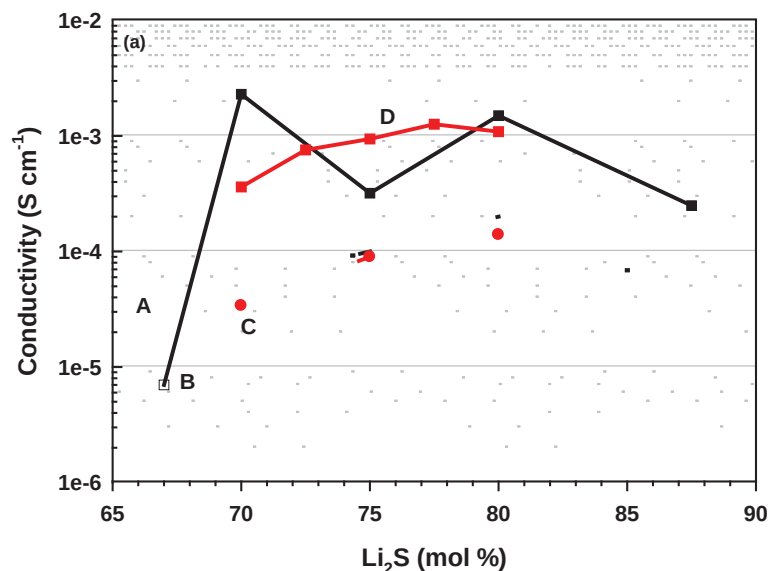


Figure 3.6: (a) Conductivity map for $[x \cdot \text{Li}_2\text{S} - (100-x) \cdot \text{P}_2\text{S}_5]$ (mol%) for $70 < x < 80$ (A) glass [26], (B) glass-ceramic [26], (C) our glass, (D) SSBM glass-ceramic.

3.4 Conclusion

Glass-ceramic solid state electrolytes were prepared from high energy ball milling of the $[x\text{Li}_2\text{S} - (100-x)\text{P}_2\text{S}_5]$ system with simultaneous heating called SSBM. While ball milling typically results in amorphous materials and subsequent heat treatment in crystalline material, we have shown that crystalline solid electrolyte can be produced in a single high temperature ball milling step. Electrolytes of the concentration $77.5\text{Li}_2\text{S} - 22.5\text{P}_2\text{S}_5$ mol% proved to have the best overall conductivity, displaying an ionic conductivity of $1.27 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. The data obtained from XRD measurement provided validation for the production of a crystalline glass-ceramic electrolyte from a one step process.

3.5 Summary

We have defined solid electrolytes and discussed the fundamental mechanisms behind fast ion conduction. Frenkel defects were described as the typical mechanism for fast ion conduction in solid electrolytes. It was shown that temperature has a significant effect on conductivity through control of the dominant mechanism for defect formation. Common types of solid electrolytes are briefly examined and some of their applications mentioned. The leading methods for generating solid electrolytes are disclosed with an emphasis on ball milling as a means of producing materials.

A technique combining the two step process of ball milling with subsequent heat treatment into a single step procedure called single step ball milling (SSBM) was proposed and tested and the results analyzed. It was discovered that SSBM could successfully generate highly conducting crystalline material (as opposed to amorphous material) in one step by ball milling in a high ambient temperature environment. High conductivity for solid electrolytes was observed over $10^{-3} \text{ S cm}^{-1}$, and good stability against lithium metal was observed up to 5V using cyclic voltammetry. Crystallinity of solid electrolytes was confirmed by x-ray diffraction.

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4. Anode

4.1 Introduction

In the previous chapter solid electrolyte materials and fabrication techniques were discussed and the single step ball milling (SSBM) procedure was explored for production of Li-P-S electrolyte. SSBM $77.5\text{Li}_2\text{S-P}_2\text{S}_5$ will be used as the solid electrolyte for the rest of this work unless otherwise stated. In Chapter 2, graphite was revealed to have a relatively low capacity of 372 mAh g^{-1} compared to the capacity of Si at 4200 mAh g^{-1} . For its extremely high capacity, Si has been investigated in this work as an anode material for all-solid-state batteries. In this chapter, research focuses on the electrochemical behavior of Si as it performs in a half cell configuration with lithium metal as the counter electrode. As we know, the exceedingly high capacity of Si is accompanied by an extreme volume expansion of up to 400% upon lithiation which prevents Si from successful commercialization as an anode material. In this chapter, we investigate the aforementioned methods of accommodating the large Si volume expansion (Section 2.2.1.2): (i) the use of a conductive additive; (ii) the limitation of voltages over which the material is cycled; (iii) the reduction of particle size of Si particles.

An investigation into 3-D nanostructured Si electrodes for solid state integration is also detailed. Recent technological advancements have realized improved battery performance by reconfiguring electrode materials from the typical 1-D battery design of commercial technology into 3-D architectures [1,2]. Such battery configurations more effectively utilize the highly limited space on board of MEMS and CMOS devices by increasing the power capabilities of batteries without increasing their footprint. We discuss the procedures for fabrication of 3-D Si electrodes as well as their performance in the lithium half cell configuration.

4.2 Experiments

Composite electrodes were prepared by mixing as-received crystalline nano-silicon (n-Si) powder (50-100nm, Sigma-Aldrich) or as-received bulk silicon (B-Si) powder (1-5 μ m, Alfa-Aesar), solid-state electrolyte (SE) 77.5Li₂S-22.5P₂S₅ (mol%) prepared by the single step ball milling procedure described previously, and as-received multi-walled-carbon-nanotubes (MWCNTs) (Nanocyl Inc., NC7000 series) at a weight ratio of 1:5:1 respectively. We have replaced the conventionally used conductive additive, acetylene black, with MWCNTs because of the increased surface area (350 m² g⁻¹) over acetylene black (75 m² g⁻¹) (Figure 4.1 A and B)

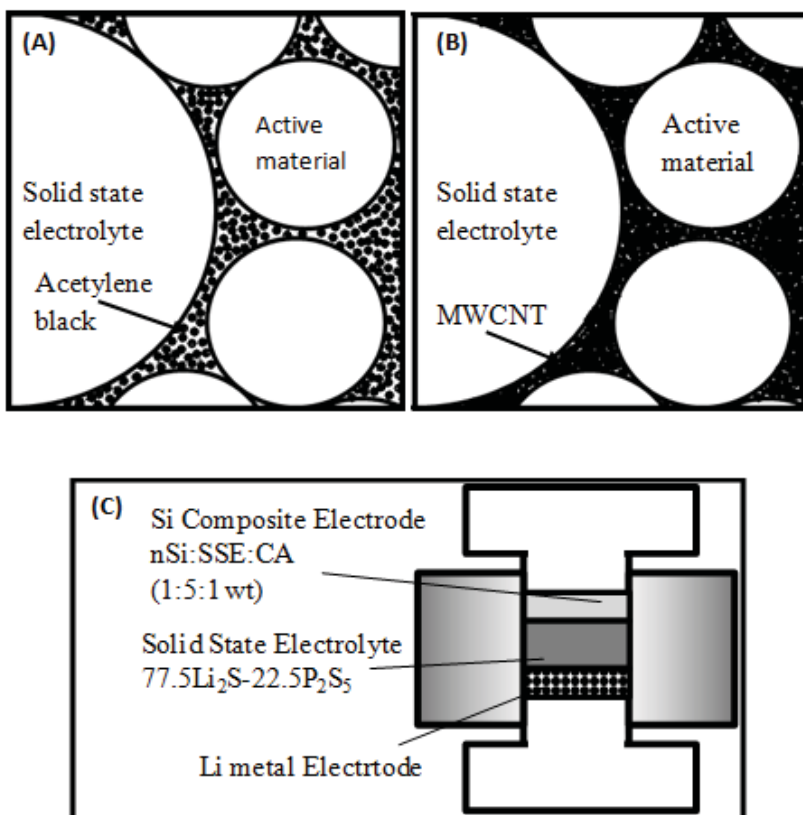


Figure 4.1: (A) Acetylene black in composite anode. (B) MWCNT in composite anode. (C) Ti test die schematic (not to scale) of the all-solid-state lithium battery.

and the improved conductive properties. A bilayer pellet is formed by pressing 2mg of composite electrode powder on top of 200mg of the solid state electrolyte powder at 5 metric tons. Li foil is then attached to the solid electrolyte at 1 metric ton. A schematic of the cell assembly in Figure 4.1.C shows an all-solid-state lithium battery cell. All pressing and testing operations are carried out in a polyaryletheretherketone (PEEK) mold ($\phi = 1.3$ cm) with Ti metal rods as current collectors for both working and counter electrodes. All assembly and testing was carried out in an Ar-filled glove box. Galvanostatic charge-discharge cycling took place for various potential ranges at a current density of 120 mA/g at room temperature using an Arbin BT2000 galvanostat. SE samples were characterized by XRD measurement with Cu-K α radiation. Samples were sealed in an airtight aluminum container with beryllium windows and mounted on the X-ray diffractometer (PANalytical, PW3830).

4.3 Electrochemical Investigation

4.3.1 Liquid vs. Solid

Using the glass-ceramic electrolytes produced by the SSBM technique, silicon nanoparticles were evaluated as anode material for use in all-solid-state Li-ion batteries. Figure 4.2a shows the charge and discharge curves of all-solid-state cells fabricated using Si nanoparticles as the anode material and $x\text{Li}_2\text{S} \cdot (100-x)\text{P}_2\text{S}_5$ ($x=77.5$) as solid electrolyte. The battery cell was cycled between 0.005 and 1.5V versus Li^+/Li at a current density of 210 mA g $^{-1}$ at room temperature. The first discharge and charge capacities of Si nanoparticles were found to be 3127 mAhg $^{-1}$ and 1367mAhg $^{-1}$, respectively. During the first cycle (Figure 4.2a), the potential rapidly drops to 1.0 V, stays at $\sim 1.0\text{V}$ showing a small plateau, and then gradually drops to 0.005V.

After the first cycle, the charge and discharge capacities in the subsequent cycles are highly reversible as shown in Figure 4.2b.

4.2b compares the cycling performance of solid state and liquid electrolyte systems employing Si nanoparticles. The charge capacity of solid glass-ceramic electrolyte system decreases very slowly from 1420 to 950 mAh/g up to the 40th cycle. The Si nanoparticles in

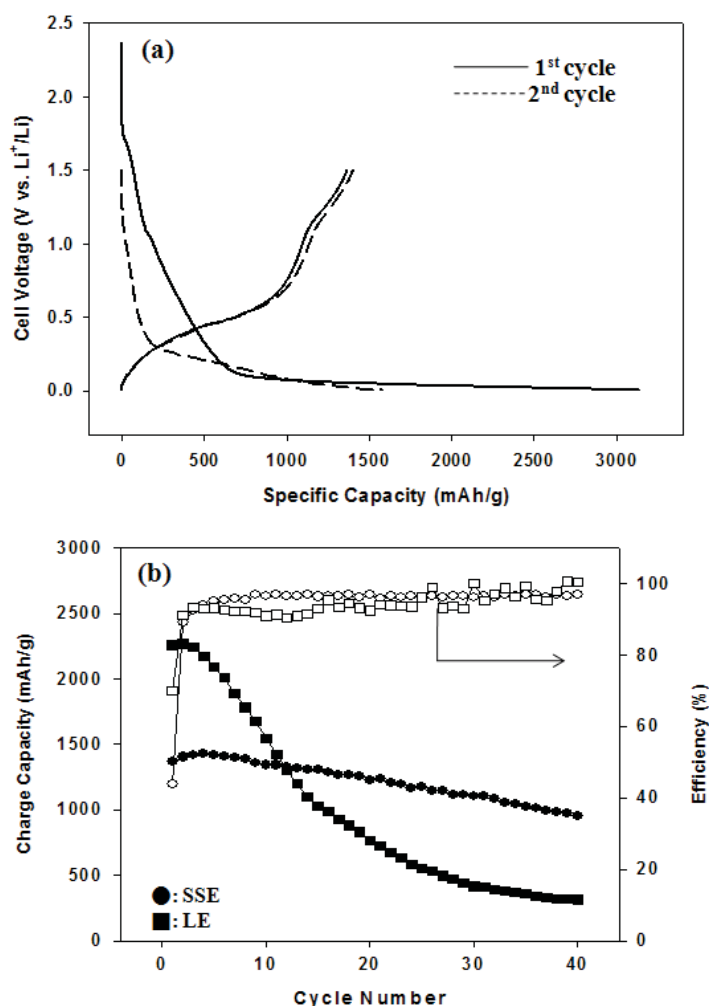


Figure 4.2: (a) Charge/discharge curves of all-solid state cell fabricated with n-Si as anode material. Cells were cycled between 0.005 and 1.5 V at a current density of 210 mA g^{-1} . (b) The cycle performance of solid state electrolyte (SSE, ●) and liquid electrolyte (LE, ■) lithium battery cells fabricated using Si nanoparticles. Open circle (○) and rectangle (□) correspond to the coulombic efficiencies of solid state electrolyte and liquid electrolyte cells, respectively.

solid-state battery configuration exhibited a capacity retention of 66.9% after 40 charge-discharge cycles in the 0.005- 1.5 V (vs. Li/Li^+) range. In contrast, the Si nanoparticles in conventional liquid electrolyte cell displayed only 14% capacity retention. This difference in capacity retention with respect to cycling is related to the volume expansion during Li accumulation. It is well known that the volume change of Li-Si alloy is approximately 400% when 1 mol Si absorbed 4.4 mol Li in lithium secondary battery with a liquid electrolyte [3-5]. In contrast, it is believed that the volume change as well as cracking of the Si nanoparticles in solid-state lithium battery cell could be much less than liquid electrolyte lithium batteries because of the pelletized active mixture and strong built-in pressure in the solid-state cell [6]. Fig. 4.2b also shows the coulombic efficiency of the two systems. The decrease in efficiency during the 1st and 2nd cycles is due to the irreversible alloying reaction. The coulombic efficiency of the solid-state cell shows stable values near 98% after 3 cycles. On the other hand, the liquid electrolyte cell shows unstable values in the range of 91% to 95%.

4.3.2 Conductive additive modification

Figure 4.3 illustrates the enhanced performance of composite n-Si cells using MWCNT over that of cells using AB, under galvanostatic charge-discharge cycling between 0.005 and 1.5 V (vs. Li/Li^+). It is customary to report specific capacity as a function of the mass of the active material (i.e., n-Si) in the electrode composite; however the lithium intercalation capacity of MWCNTs or AB can significantly contribute to the overall specific capacity of the electrode composite. Therefore, the capacity contribution of the conductive additives was measured in a cell using only MWCNTs or AB as the active material (i.e., without n-Si). The specific capacity

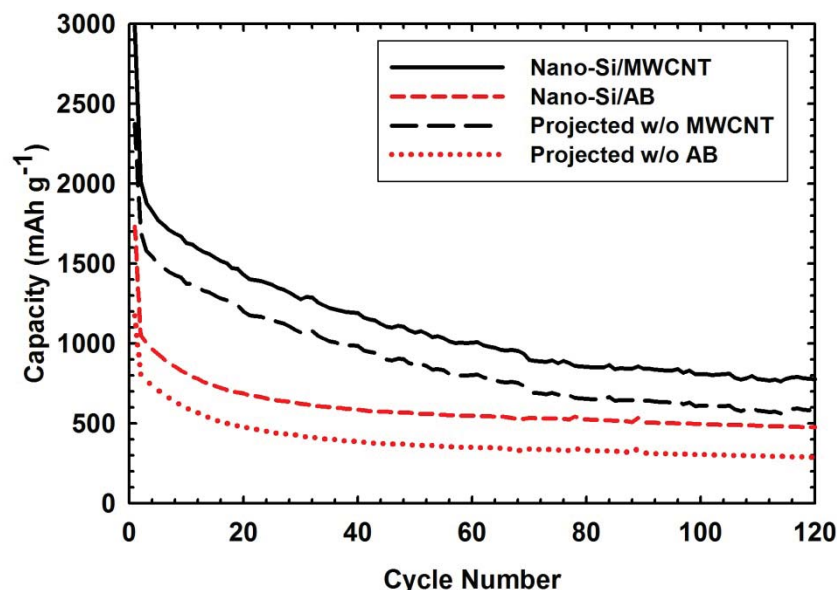


Figure 4.3: Comparison showing superior performance of MWCNT as a conductive additive for all-solid-state lithium batteries over acetylene black.

contribution of these anodes (MWCNTs or AB only) was then subtracted from the capacity data for the corresponding composite n-Si anodes in order to provide direct evidence that the use of MWCNTs instead of AB shows a significant increase in the specific capacity performance of the n-Si. This result is expected due to the dramatic increase in specific surface area of the MWCNTs over AB, and the MWCNTs ability to flex in order to maintain electrical contact with the n-Si particles as they expand and contract upon cycling [7]. As shown in Figure 4.3, solid state lithium batteries employing n-Si and MWCNTs as a conductive additive maintain a capacity approximately 100% higher than batteries using n-Si and AB. MWCNTs were shown to improve cycling capacity in all-solid-state lithium batteries over acetylene black as a conductive additive.

4.3.3 Voltage range variation

Figure 4.4 shows n-Si/MWCNT cells under galvanostatic charge-discharge cycling for ranges of 0.005-1.5V, 0.005-1.0V, and 0.05-1.0V. Cells cycled within the widest voltage range of 0.005-1.5V demonstrated the highest initial discharge capacity of 2013 mAh g⁻¹ for the second cycle and the fastest rate of capacity fade in later cycles, with 64% retention after 50 cycles, and negligible capacity loss from cycle 105 to cycle 120. The intermediate range of 0.005-1.0V resulted in a reduced initial discharge capacity of 1744 mAh g⁻¹ for the second cycle, but an increased capacity retention of 75% after 50 cycles, and negligible capacity loss from cycle 100 to cycle 120. The narrowest voltage range of 0.05-1.0V, resulted in the lowest initial discharge capacity of 1278 mAh g⁻¹ for the second cycle, the highest capacity retention of 91% after 50 cycles, and negligible capacity loss from cycle 80 to cycle 120. The reasons for the faster stabilization of the c-Si/AB cell are not fully understood at this time. We speculate that

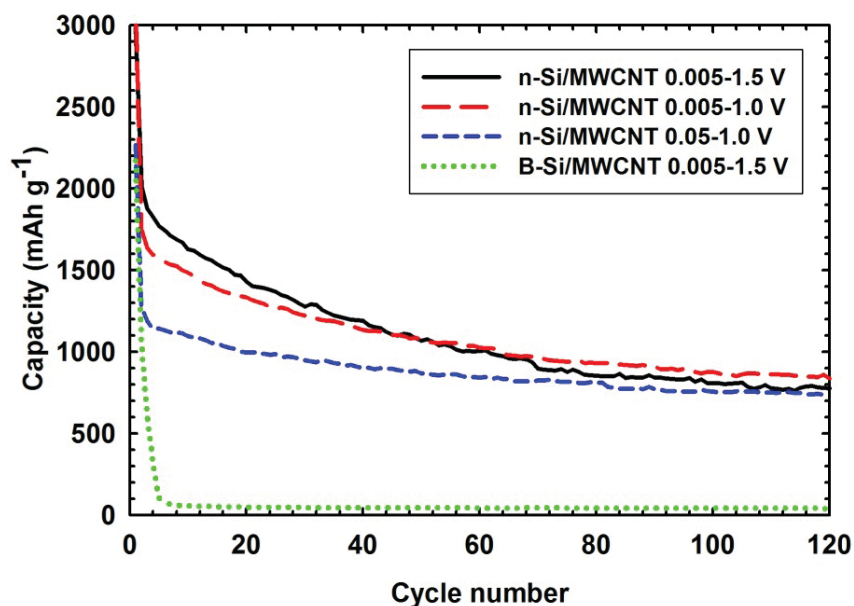


Figure 4.4: Discharge profiles for n-silicon for the range 0.005-1.5 V.

decomposition of the SSE is accelerated in the anodes containing MWCNTs as a result of the increased interfacial area and consequent increased kinetics for surface reactions. Regardless of voltage range, all three cells using MWCNTs as a conductive additive eventually stabilize and cycle without further loss at a specific capacity of approximately 800-900 mAh g⁻¹. For both MWCNT and AB cells, the columbic efficiency was almost 100% after the first cycle. n-Si lithium batteries using MWCNTs as a conductive additive showed a stable cycling capacity twice that of cells using AB as a conductive additive.

For comparison, a B-Si/MWCNT cell was cycled within the widest voltage range of 0.005-1.5V, demonstrating an initial capacity of 3091 mAh g⁻¹, a capacity retention of less than 9% after 10 cycles, and a capacity of approximately 200 mAh g⁻¹ for all remaining cycles. We conclude that the 200 mAh g⁻¹ capacity of the remaining cycles has no contribution from Si, but is instead the capacity derived from MWCNTs in the composite electrode. Consistent with Graetz and Fultz et al., we find that the bulk material has a high first cycle capacity but decays quite rapidly to a nominal capacity within 10 cycles [8] while all of the n-Si samples maintain relatively high capacities for over 100 cycles. We speculate that decomposition of the SSE is accelerated in the anodes containing MWCNTs as a result of the increased interfacial area and consequent increased kinetics for surface reactions.

Electrochemical potential spectroscopy (EPS) is the study of differential capacity as a function of the applied potential and was performed to obtain information relevant to the structural transformations that take place during lithiation and delithiation of solid state n-Si/MWCNT cells. EPS spectra and capacity curves are shown together in Figure 4.5 to highlight structural and capacity changes in the n-Si composite electrodes. For all voltage ranges tested, the EPS data obtained during the first cycle is remarkably different than that from all subsequent cycles, which

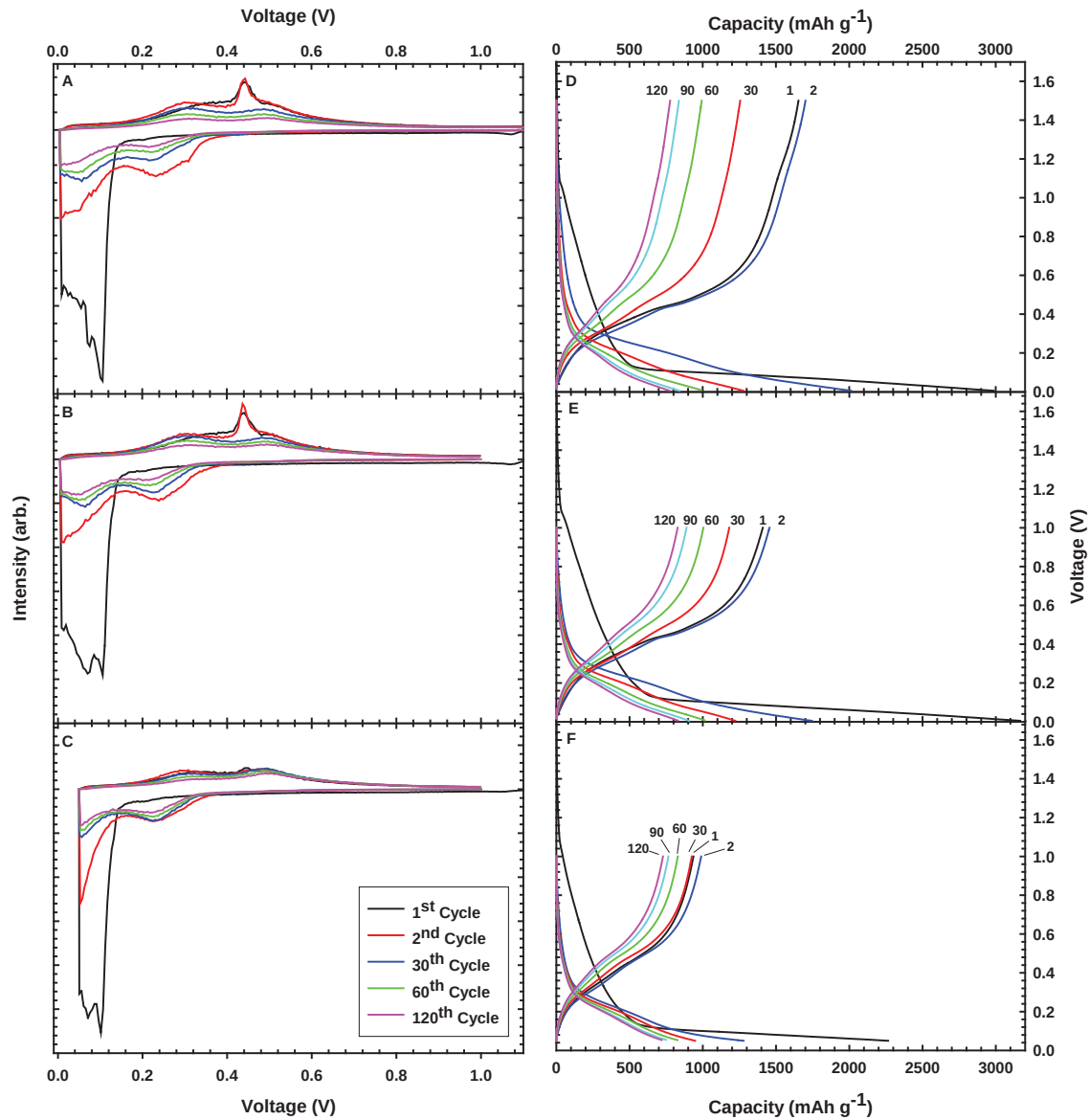


Figure 4.5: dQ/dV vs. Voltage (A-C) and Capacity vs. Voltage (D-F) plots for comparison between structural transformation, capacity, and cycle life. (A,D) 0.005-1.5V, (B,E) 0.005-1.0V, (C,F) 0.05-1.0V.

we attribute to crystalline Si (c-Si) transformation to amorphous silicon (a-Si) upon lithiation. In this work, we observe phase similar phase transitions as detailed by Obrovac and Krause [9] for c-Si as an active material in a composite electrode. At 0.1V is a two-phase region where c-Si reacts with Li to form an amorphous lithium silicide, a-Li_xSi of which we observe a long sloping

plateau in the Capacity vs. Voltage plots. In the model proposed by Obrovac and Krause, it is during this transformation that particles move to two phases, where c-Si exists at the core of particles with a-Si at the edges. In accordance with Obrovac and Krause as well as Chan and Cui group [10] high cut-off voltages above 0.05-0.07V will not see total lithiation of n-Si and will therefore avoid formation of the c-Li₁₅Si₄ phase. We show that cycling below 50 mV results in formation of the c-Li₁₅Si₄ phase [11,12] revealed by the small delithiation peak at 0.44V (Figure 3). The cell with voltage range 0.05-1.0V shows no formation of the c-Li₁₅Si₄ phase and therefore does not undergo as severe of volume expansion, which allows it to maintain higher capacity retention. Long term cycling shows the degradation of the amorphous single phase regions for cells cycling below 0.05V. A relation between initial reversibility and voltage range is made obvious by the Capacity vs. Voltage plots showing the extensive degradation of cells with larger voltage windows over the cell with a 0.05V cut-off voltage, having essentially no capacity loss for the first 30 cycles. Cycling below 0.05V in a lithium battery with a n-Si composite electrode containing a MWCNT conductive additive results in fast capacity fading as a result of formation of a high volume crystalline lithium silicide phase (Figure 4.5). However, while maintaining a low cutoff voltage above .05V does result in less relative degradation, we observe that all test sample capacities converged to the same approximate value regardless of voltage range. This is an important observation because it shows that our nSi/MWCNT configuration is capable of utilizing Si as an active material at almost a 1000 mAh g⁻¹ capacity for long term cycling. We show that MWCNT's are a sufficient buffer for mitigating Si volume expansion in solid electrodes and can maintain high capacity for over 100 cycles for numerous voltage ranges.

4.3.4 Micro vs. Nano

Reducing the grain size of a material below certain limits results in the appearance of either new or changed properties of the material due to: inherent crystalline grains approaching the size of the characteristic physical lengths of the relevant properties, an increase in the proportion of interface defects and their impact on dependent properties, and the appearance of new structural properties that characterize the grain boundaries of the material [13]. For example, a material comprised of spherical crystalline grains 3 nm in diameter might find approximately half of its atoms positioned at grain surfaces, which implies more pronounced reactivity of the system. However, a decrease in grain size, equivalent to an increase in the specific surface area of the system, indicates not only increased reactivity but also that those physical properties are no longer dominated by the physics of the bulk matter. In this light, many active electromaterials previously rejected because they did not fulfill the criteria as classical intercalation hosts for lithium, are now under reconsideration.

Physical properties such as electrical conductivity, micro-hardness, coercivity, and permittivity decrease in proportion to the average particle size of a material. Mechanical failure of a material frequently takes place through crack migration processes along grain interfaces, so the fact that materials with nanosized grains (down to ~ 10 nm) are stronger compared with their bulk counterparts implies significant modifications of strength and toughness mechanisms as a result of the transition from bulk to the nanoscale [14]. The formability of ceramics for instance, is known to improve with the reduction of grain size towards the nanoscale. Some advantages and disadvantages of nanomaterials are listed in Table 4.1.

Table 4.1: Advantages and disadvantages of nanomaterials.

Advantages	Disadvantages
New reactions not possible with bulk material	Potentially complicated synthesis
Large electrode-electrolyte contact area	Difficult handling of nanosized powder
Short path lengths for Li^+ and e^- transport	Potential unknown health and safety hazards
Stable cycling performance	Low production rate with existing technology

Most important for utilization of nanomaterials are the capability to generate new reactions, which can lead to higher specific capacity, and larger electrode-electrolyte surface area, which can lead to higher charge-discharge rate. Also, shorter path lengths are desirable among materials used for electrodes because they can permit operation even with very low electronic or ionic conductivity, broadening the capabilities of material once thought impossible for battery fabrication.

4.3.4.1 Si particle size reduction

A new nano-silicon powder (Melorium, 30 nm) referred to as M30 in this work, is now introduced for further investigation of Si particle size effects on electrochemical performance of half cells. The experimental set-up as depicted in Section 4.2 applies for the newly added Si powder, as cells were constructed with the same ratio of materials and the same composite weight. A comparison of the long term cycling capacity of comparable cells using the widest voltage window 0.005-1.5 V discussed earlier, with variation of Si particle size is shown in Figure 4.6a The very large B-Si particles exhibit complete degradation after only 5 cycles, while the Sigma-Si (previously n-Si) retains a capacity of approximately 800 mAh g^{-1} after 120 cycles

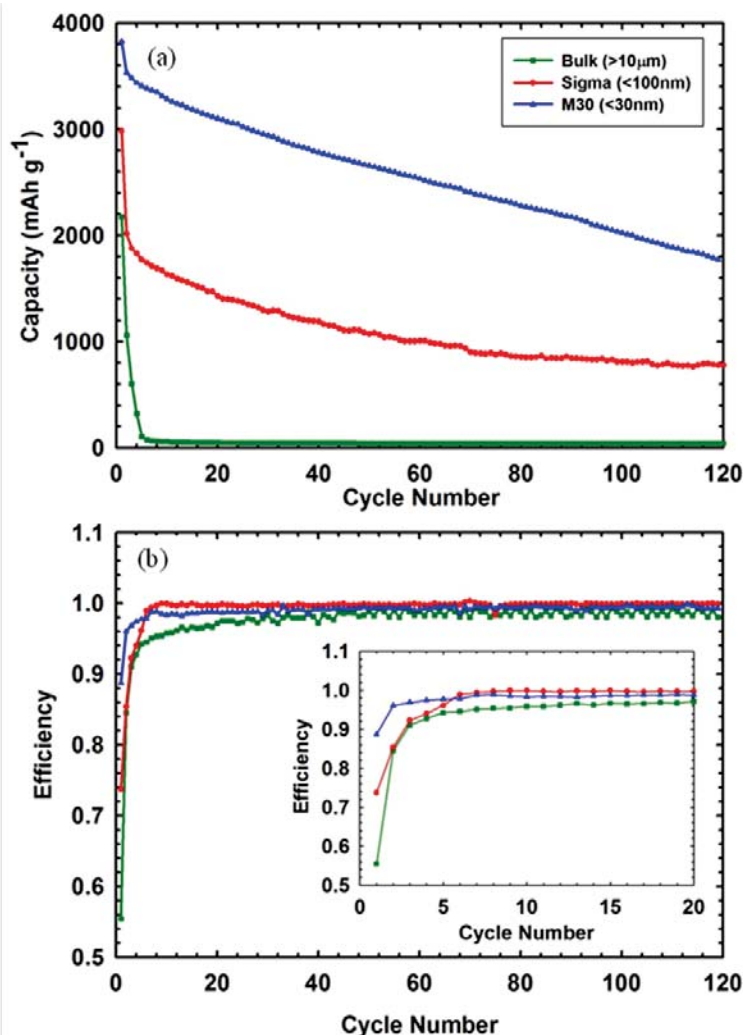


Figure 4.6: Size comparison between bulk 10μm particles, 100nm particles, and 30nm particles for (a) capacity and (b) coulombic efficiency.

and the M30-Si maintains a capacity above 1800 mAh g⁻¹ for 120 cycles. It is observed that degradation for the M30-Si is very consistent whereas the degradation for the Sigma-Si wanes slowly up to ~100 cycles. Utilization of smaller particle size of Si in this experiment results in better long term cycling behavior of lithium half cells but does not resolve degradation. The inset of Figure 4.6B reveals an increase in first cycle reversible capacity for using reduced particle size of Si. This result is attributed to the reduced particle size better accommodating the strain of the

large expansion [15]. Both nano-sized Si cells show consistent long term cycling degradation which is recognized as a result of the relatively low coulombic efficiency (charge capacity/discharge capacity) of the cells, shown in Figure 4.6b. The first cycle efficiency for cells is approximately 55%, 74%, and 88% for B-Si, Sigma-Si, and M30-Si respectively. Extended cycling reveals average efficiencies for the Sigma-Si and M30-Si of 99.7% and 99.2%, which, as previously discussed in Chapter 2 (Figure 2.6) is not sufficient for long term cycling. The half cell construction of our cells reduces degradation from that portrayed in Figure 2.6 because the relative “unlimited” supply of Li from the Li metal electrode allows replenishment of any Li trapped in the Si.

Low efficiency roughly translates to Li trapping in the electrode composite, reducing the amount of active material available for later cycles and resulting in lower capacity. Sigma-Si has a higher efficiency than M30-Si which agrees with the capacity data, as the capacity of M30-Si is higher but the Sigma-Si degrades less quickly. This behavior could be the result of inserting and extracting far less Li per cycle, and therefore less expansion and contraction in the Sigma-Si. The M30-Si allows for a larger capacity of Si that could result in faster capacity fade.

4.4 3-D Nanostructured Array

4.4.1 Introduction

Mounting electric energy sources on semiconductor chips is highly attractive due to rapid growth of electrical and mechanical integration technologies such as wireless telecommunications and emerging integrated optoelectronic circuits. Planar solid-state thin film batteries are widely used as an energy source in current MEMS and CMOS devices but are incapable of

meeting growing power demands [1]. Recent technological advancements have realized improved battery performance by reconfiguring electrode materials from the typical 1-D battery design of commercial technology into 3-D architectures [2]. Such battery configurations more effectively utilize the highly limited space on board of MEMS and CMOS devices by increasing the power capabilities of batteries without increasing their footprint. Here, we show that silicon rod structured battery electrodes circumvent the pulverization issues as they can accommodate large strain with minimal pulverization, providing good cycle life and relatively high coulombic efficiency.

4.4.2 Producing 3-D arrays

In this work we investigate the fabrication and use of 3-D integrated all-solid-state lithium batteries with structured Si rod electrodes and powder solid-state electrolyte (Figure 4.7). Using a n-type (Sb doped) single side polished, 3 inch diameter silicon wafer (<100> cut, 350 μm thick, 0.008~0.02 Ωcm), Si micro-rods are obtained by deep reactive ion etching (DRIE: STS Pegasus DRIE system), and made thinner by subsequent RIE (Plasmatherm 540/540 Dual Chamber RIE system). The fabrication process of the rod array is shown in Figure 4.8. After spin coating and photo-

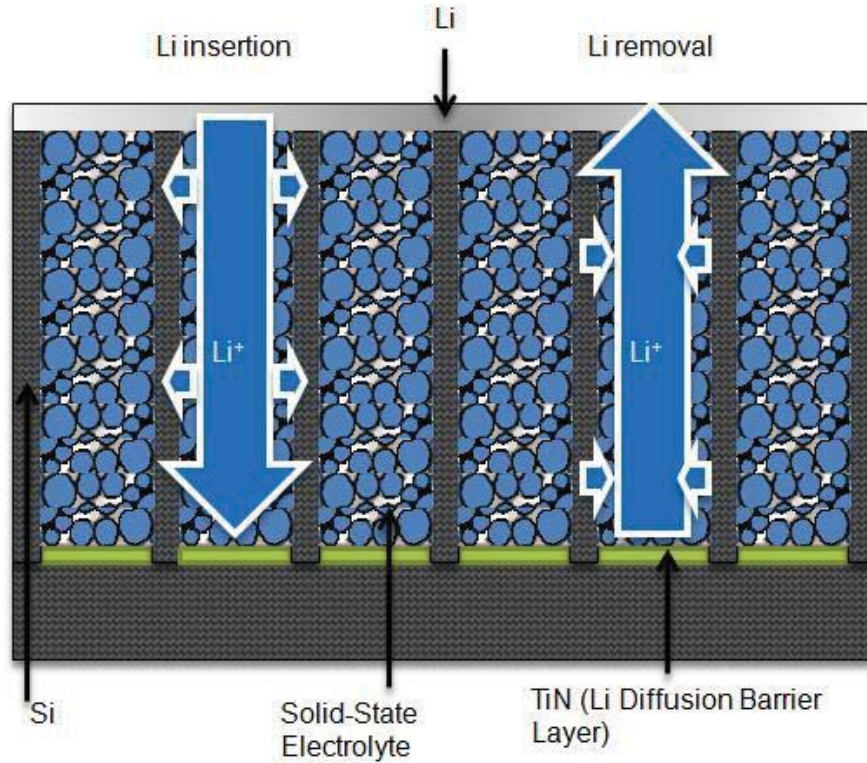


Figure 4.7: Cross-section view of our 3D integrated all-solid-state battery.

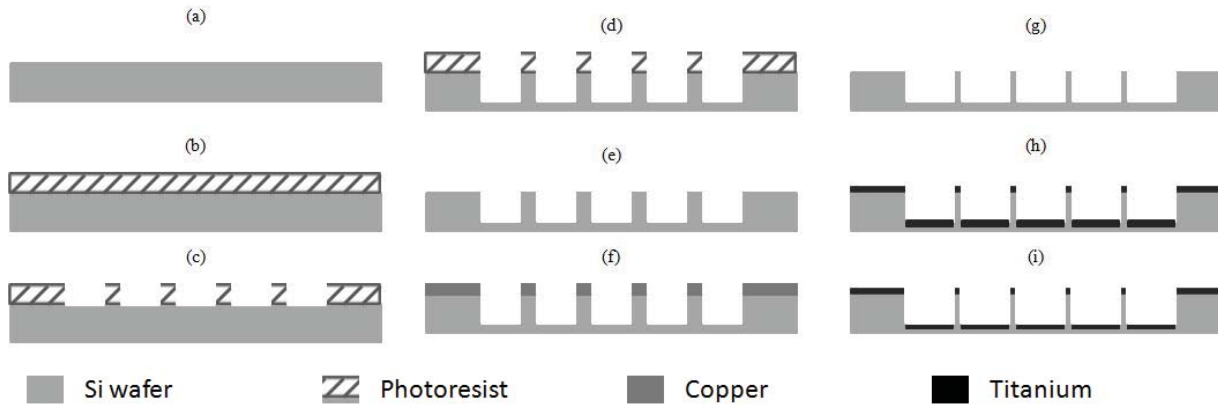


Figure 4.8: Fabrication process for creating Si rod array. (a) Silicon wafer (n-type, Sb-doped, 100 cut, 350 μm thick 0.008~0.02 ohm-cm) (b) Spin coating 2.5 μm Photoresist (AZ 4210) on Silicon wafer (c) Photo lithography and PR hard baking (d) DRIE for 8 mins (etching rate 3 $\mu\text{m}/\text{min}$) (e) Remove PR and clean the sample (Acetone, API clean first, then Plasma clean) (f) Thermal evaporate metallic mask (Copper) (g) SF_6 RIE and remove Copper (h) Thermal evaporate Ti and heat the sample in N_2 atmosphere (i) SF_6 RIE.

lithography, the photoresist (AZ 4210) is hard baked in a vacuum oven for 10 minutes before using DRIE to obtain the Si rod array. The diameter of the rods can be controlled to within the range of 300-800 nm by using different masks. Following DRIE, rods are made thinner by subsequent SF_6 RIE at an etching rate of 400-600 nm min⁻¹. At this step, 400 nm copper is thermally evaporated (3L-TEC MED 020 Coating System) onto the sample as a metallic mask layer for the RIE process. After RIE, the copper layer is removed by copper etchant and then a 70 nm layer of Ti is evaporated on top of the Si substrate and the rods. Ti is turned into a TiN barrier layer by heating the sample in N_2 for 1 minute at 800 °C. Due to the high aspect ratio of the gap, the TiN barrier will only cover the substrate and the top of the rods but not the side wall as proved by Figure 4.9.

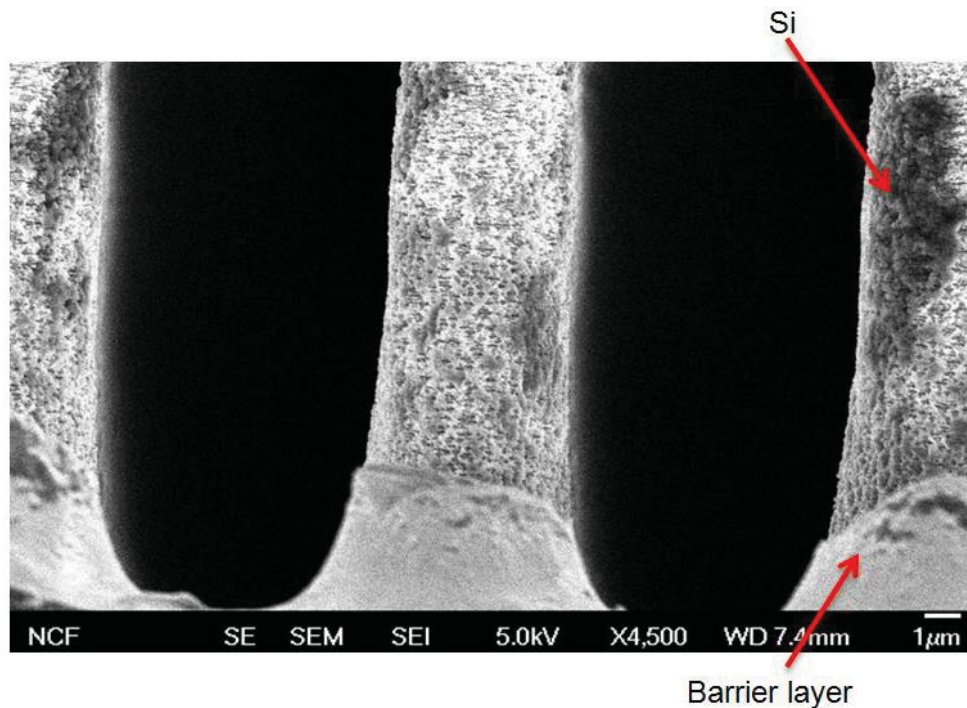


Figure 4.9: SEM image of Si rods with TiN barrier layer coated on the substrate but not the side wall of the rod.

A TiN Li diffusion barrier layer is formed on the Si substrate for the purpose of preventing lithiation of Si substrate, in order to avoid mechanical failure of the bulk Si substrate during the cycling [16]. After the TiN barrier layer is coated, SF_6 RIE is used again to obtain the desired dimension of rods. The diameter of the rods is controlled by the etching time of RIE. Figure 4.10

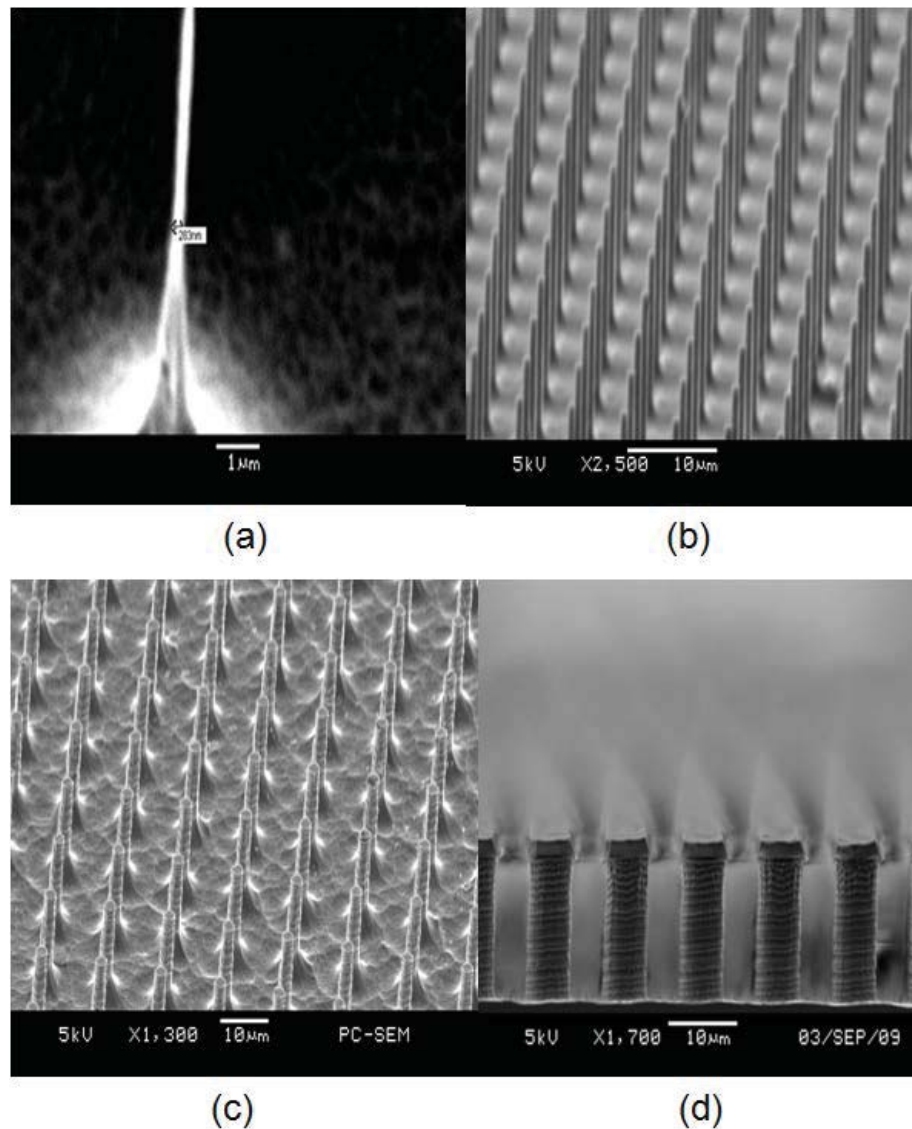


Figure 4.10: SEM image of Si rods with the diameter in the range of 300nm~8000nm on Si substrate. The diameters of the rod from (a) to (d) are respectively 300 nm, 750 nm, 2000 nm and 8000 nm.

shows the final result of a fabricated rod array. From (a) to (d), the diameters of the rods are respectively 300 nm, 750 nm, 2000 nm and 8000 nm. The gap between the rods can also be controlled by using different masks in the lithography process.

4.4.3 Modeling of Electrochemical Insertion

Lithium batteries are developed and tested in this study. The rechargeable batteries are simple in design, as well as safe and robust. The all-solid-state construction prevents lithium dendrites from growing through the electrolyte, as happens with liquid-based electrolyte systems, thereby enhancing the operation safety. We integrated various sizes and dimensions of structured rod arrays into solid state batteries to study the effects of dimensioning on pulverization of the Si. In order to help understand the interplay between the size of the silicon rods, the charge/discharge current, and the mechanical integrity of the electrodes, we modified a recently-developed model of lithium insertion into (extraction from) silicon particles proposed by Golmon et al. to simulate the development of stresses in silicon rods as lithium is inserted [17]. The model consists of a silicon rod embedded in an electrolyte as shown schematically in Figure 4.11

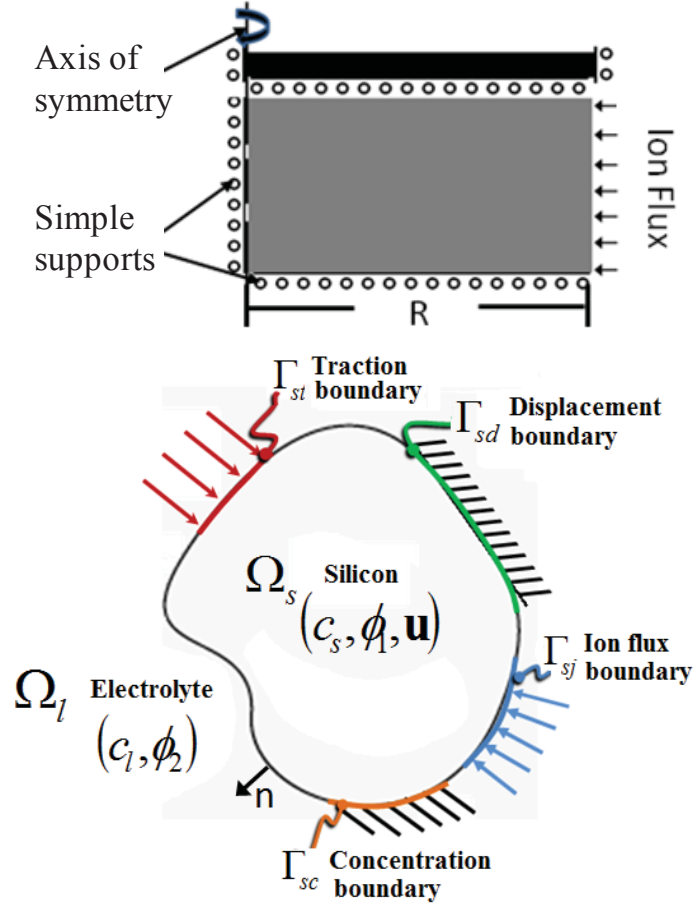


Figure 4.11: Simulation domain for the insertion of Li into a silicon rod.

In general the electrochemical reactions at the rod/electrolyte interface generate a flux of Li ions into the Si rod. As Li ions diffuse through the lattice, a series of phase transitions occur that result in the formation of various LiSi alloys. The nature of the final state during Li insertion is a subject of debate in the literature, but the most conservative view is that it culminates in $\text{Li}_{22}\text{Si}_5$ where each Si atom accommodates 4.4 Li atoms. This process results in straining of the Si rod and due to the heterogeneous nature of this strain, stresses develop. These stresses can cause cracking and pulverization of Si electrodes that lead to loss of electrical contact and capacity fade during cycling.

Within the rod we model the full (two-way) coupling between diffusion of Li and the evolution of stresses. We assume the mechanical response is much faster than the diffusion response, so mechanical equilibrium can be represented by:

$$\nabla \cdot \boldsymbol{\sigma} = 0 \quad \text{Eq. (4.1)}$$

Diffusion of ions within the electrode particle is described by the standard diffusion equation.

$$\frac{\partial c_s}{\partial t} + \nabla \cdot \mathbf{j} = 0 \quad \text{Eq. (4.2)}$$

The coupling between stress and diffusion is represented in the constitutive and kinematic equations:

$$\boldsymbol{\sigma} = \mathbf{C} : \tilde{\boldsymbol{\varepsilon}} = \mathbf{C} : (\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_{cs}) \quad \text{Eq. (4.3)}$$

$$\boldsymbol{\varepsilon} = \frac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^T) \quad \text{Eq. (4.4)}$$

$$\boldsymbol{\epsilon}_{cs} = c_s \frac{\Omega}{3} \boldsymbol{\delta} \quad \text{Eq. (4.5)}$$

$$\mathbf{j} = -D \left[\nabla c_s - \frac{\Omega c_s}{RT} \nabla \sigma_h \right] \quad \text{Eq. (4.6)}$$

The displacement and ion concentration ($\mathbf{u}$ and c_s) fields are coupled in two ways. Ion concentration affects the mechanical response through the strain due to diffusion ($\boldsymbol{\epsilon}_{cs}$), and diffusion is coupled to the displacement field through the hydrostatic stress gradient (σ_h). The ion flux into the particle can be modeled as a constant concentration at the surface, a constant surface ion flux, or by modeling the surface reaction kinetics with the popular Butler-Volmer equation. In the experiments discussed, power electronics are used to keep the boundary ion flux nearly constant, so in our model we take the boundary ion flux to be constant. The top and bottom of the Si rods are insulated from ion flux and the rod is taken to be much longer than the rod diameter so the rod is effectively an infinite cylinder.

We solve the coupled stress-diffusion problem using the finite element method with axisymmetric elements. The infinite cylinder is simulated by applying simple supports to the bottom face and multi-point constraints to the top face, keeping it flat. Surface ion fluxes, $\mathbf{j}$, are calculated for the $\Delta t = 2$ and 10 hour charge times as per our experiments,

$$j = \mathbf{j} \cdot \mathbf{n} = \frac{1}{\Delta t} c_{s \max} \frac{V}{A} = \frac{1}{\Delta t} c_{s \max} \frac{\pi R^2 h}{\pi 2 R h} = \frac{1}{\Delta t} c_{s \max} \frac{R}{2} \quad \text{Eq. (4.7)}$$

Listed in Tables 4.2 and 4.3 are all of the variables, the material properties, and constants used for the simulations.

Table 4.2: List of symbols.

Mechanical Variables			Diffusion Variables		
Sym- bol	Name	Type	Sym- bol	Name	Type
u	Displacement	1 st order tensor	c_s	Ion concentration in particle	Scalar
σ	Stress	2 nd order tensor	$c_l = c_{l0}$	Ion concentration in solution	Scalar
C	Linear elasticity tensor	4 th order tensor	$\Phi_1 = \Phi_{10}$	Potential in solid	Scalar
ε	Total strain	2 nd order tensor	$\Phi_2 = \Phi_{20}$	Potential in liquid	Scalar
ε_{cs}	Diffusion strain	2 nd order tensor	j	Ion flux	1 st order tensor
δ	Kronecker delta	2 nd order tensor	j	Surface ion flux	Scalar
σ_h	Hydrostatic stress	Scalar	Δt	Charge time	Scalar

Table 4.3: List of material properties and constants.

Material Properties and Constants		
Symbol	Name	Value
E	Young's modulus of elasticity	121 GPa
ν	Poisson's ratio	0.28
$c_{s\ max}$	Ion concentration in particle	311053 mol/m ³
D	Diffusion coefficient	1.124e-11 Pa
Ω	Partial molar volume	4.265e-6 m ³ /mol
R	Gas constant	8.314 J/(K mol)
T	Temperature	300 K

The results of the model yield a prediction for the electrochemical-mechanical interactions of the structured rod array lithium batteries. Figure 4.12 show the resulting radial stress profile during Li insertion. Overall, we find that smaller rod diameters maintain lower radial stresses in comparison to larger rod diameters and that lower applied currents result in lower radial stress concentrations. The data reveals an almost linear relationship between applied current and maximum radial stress, with approximately a factor of 5 difference between relative 2 hour (Figures 4.12a and 4.12c) and 10 hour (Figures 4.12b and 4.12d) simulations. The maximum stress within samples is reached almost immediately, happening between the first 20 and 90 seconds of operation.. After the maximum stress is achieved the stress concentration decreases quite rapidly for the 2 hour simulations and remains rather constant with the 10 hour simulations. We observe that the 10 hour simulations show an overall stress that is much lower than respective 2 hour simulations and maintains a fairly steady stress profile with respect to time. The accelerated pulverization and loss of electrical contact in the 2 hour experiments could potentially be driven by this stress field during rapid repeated stress fluctuations. In the 10 hour

simulations, the observed constant stress profile is consistent with the observed longer cycle life in lower applied current tests, as less severe stress concentrations occur. We found that our simulations support that smaller silicon rods and lower applied currents result in lower overall stress and stress variation which can lead to longer cycle life and higher capacity.

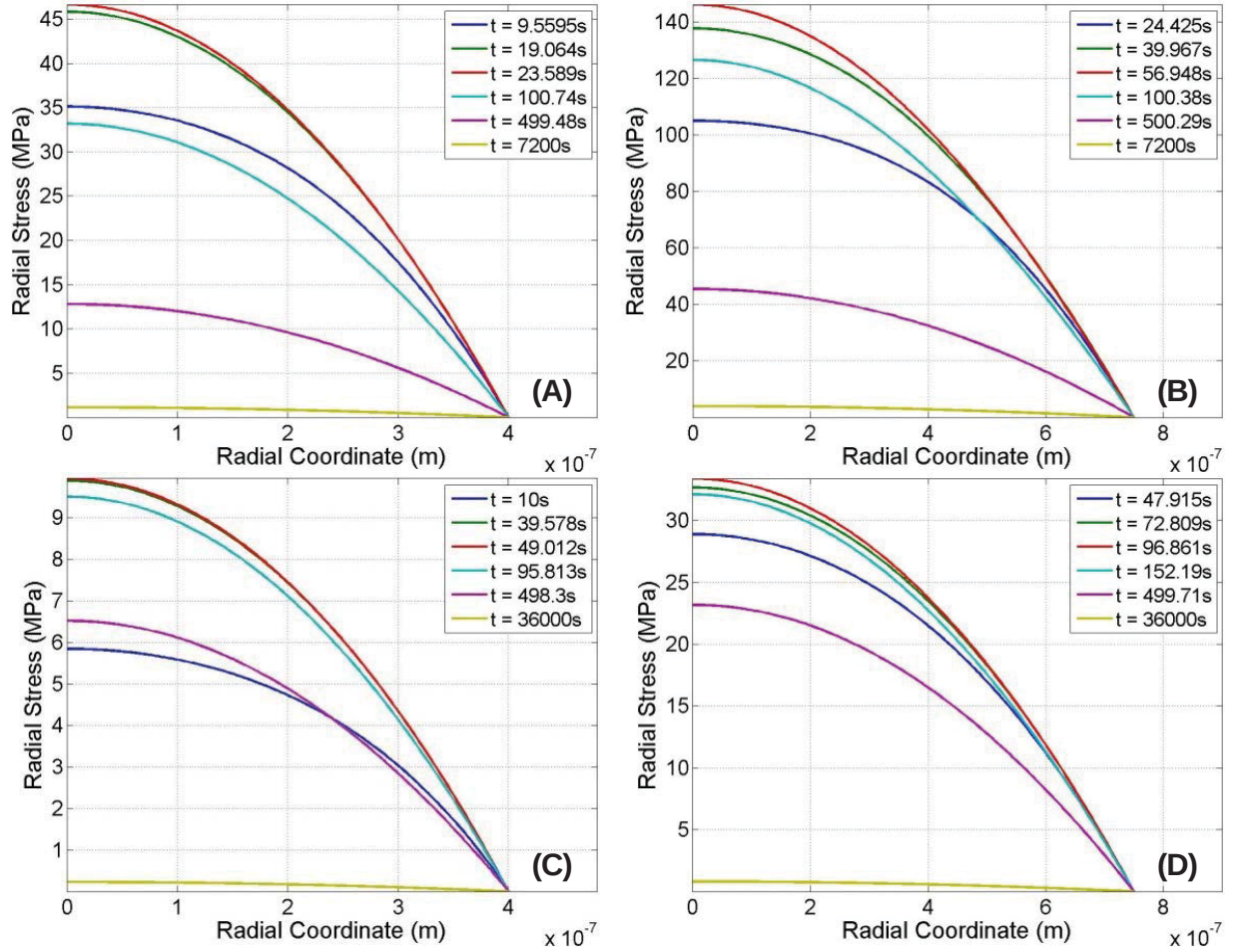


Figure 4.12: Plots of the radial stress profile of silicon rod arrays for changing rod diameter and applied current. (A) Diameter 800nm, current rate $C/2$, (B) Diameter 1500nm, current rate $C/2$, (C) Diameter 800nm, current rate $C/10$, (D) Diameter 1500nm, current rate $C/10$.

4.4.4 Battery Assembly and Testing

A cross-sectional schematic of the battery assembly process composed of two electrodes separated by an electrolyte cavity can be seen in Figure 4.13. In the lithium battery, the bottom electrode is comprised of just the silicon wafer and rod array while the top electrode is simply lithium metal, both in contact with titanium current collectors. The lithium batteries are formed by first attaching the silicon substrate to a titanium current collector with a conductive silver paste to ensure good contact. After the conductive paste has cured, solid electrolyte is weighed and poured into the die. The silicon wafer and solid electrolyte are pressed together in the die at

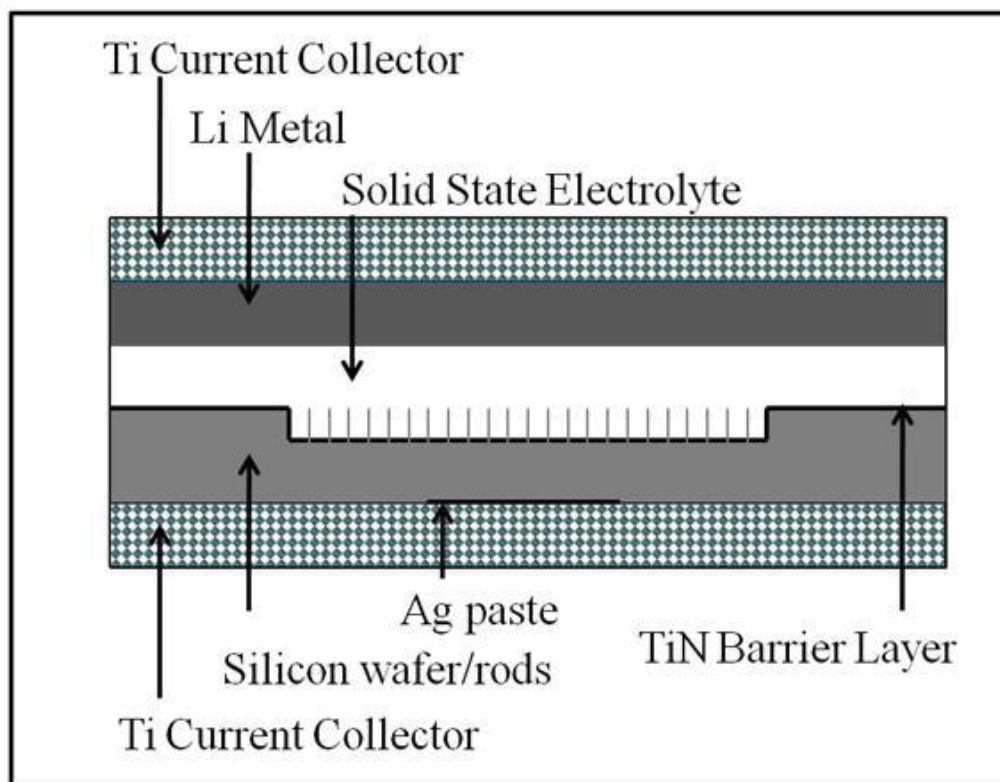


Figure 4.13: Schematic of battery construction. The lithium battery employing the silicon wafer/rods in a cathode design.

5 metric tons for approximately 5 minutes. A lithium foil is then attached to the solid state electrolyte at a pressure of 1 metric ton.

Batteries were characterized by using galvanostatic cycling to observe their charge-discharge behavior. Batteries were cycled at varying current densities to observe performance and degradation. Most commonly, batteries are charged and discharged between preset voltage limits, called constant voltage cycling. We employed constant capacity cycling limits for discharging so that structured silicon rods were lithiated to a capacity correlating to the room temperature theoretical capacity of Si as an electrode material in all solid state batteries. In general, constant capacity cycling is used to determine materials' potential limits for the first few cycles and will be followed by constant voltage cycling to observe degradation. Our experiments, using continued constant capacity cycling, perform the same task but allow for closer observation of structural transformations and degradation of materials.

4.4.5 Results

Figure 4.14 shows the electrochemical data for our 3-D integrated all-solid-state lithium battery for the first 20 cycles and data for a comparable state-of-the-art 1D battery for comparison [12]. The coulombic efficiencies of the first cycle of structured 3D batteries are 70% and 82% at an applied current of $1250 \mu\text{Ah cm}^{-2}$ and $250 \mu\text{Ah cm}^{-2}$ respectively (Figure 4.14a). The high value of the coulombic efficiency of the first cycle is most fascinating because the generally accepted value for the coulombic efficiency of batteries with Si based electrodes is closer to 35% due to the excessive pulverization of electrode material. Coulombic efficiency is a reading of how well a battery is transporting lithium. 100% coulombic efficiency implies that all of the

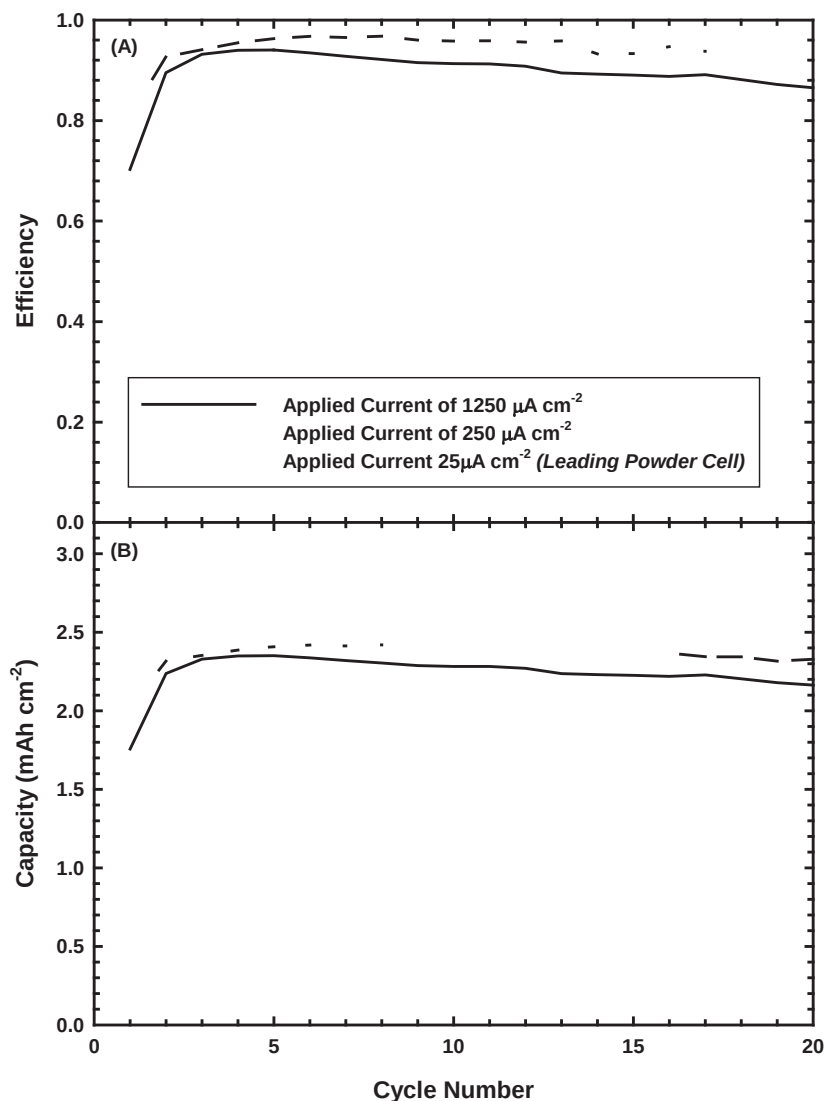


Figure 4.14: (A) Electrochemical data for our 3D integrated all-solid-state battery and comparison with state-of-the-art battery, coulombic efficiency versus cycle number at different applied currents. (B) Electrochemical data for our 3D integrated all-solid-state battery and comparison state-of-the-art battery, capacity versus cycle number at different applied currents.

lithium that was transported from the lithium metal to the silicon electrode is transported back to the lithium metal. In the case of low coulombic efficiency, some lithium is being trapped in the electrode through the loss of electrical contact between particles. Continued cycling revealed a relatively stable coulombic efficiency that indicates lithium trapping and degradation in the Li_xSi

electrode is minimal during cycling. Figure 4.14b shows again a comparison of our all-solid-state lithium batteries verses a current state-of-the-art battery, except for capacity at various applied currents instead of coulombic efficiency. An approximate 8 fold improvement in capacity is observed for our rod structured battery over the leading technology. We have shown significant improvement of not only the overall capacity of potential on-board batteries but we have achieved high coulombic efficiency on the first cycle of a Si based electrode.

Si Micro/Nano rod structures were found to exhibit a longer cycle life than bulk Si [18]. Our rod-structured battery displays constant capacity with minimal degradation for over 20 cycles. As lithium trapping and pulverization isolate Si upon cycling, lithium diffuses deeper into the rods for conducting Si with which to react. As more Si becomes isolated, a larger resistance is observed. Figure 4.15 shows the increasing resistance with a decreasing low cut-off voltage of

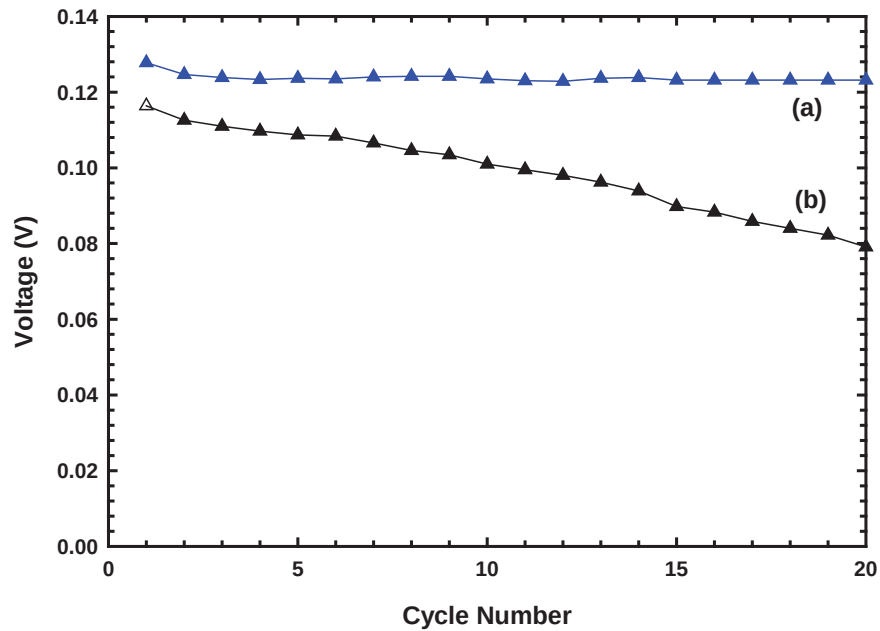


Figure 4.15: The low cut-off voltage of each discharge cycle for (a) 800nm and (b) 1500nm.

each cycle, following Ohms law. The structured nature of the rod array electrodes allows for minimal resistance layer build-up, as the rods can accommodate large strain with minimal pulverization [19]. We see that by reducing the rod size we can stabilize cycling so that we don't see the continued build up of a resistance layer.

We observe degradation as a function of rod diameter and applied current load in Figure 4.16. With the application of different current loads upon rod-arrays of varying diameter we can essentially observe degradation as a function stress as we proposed in our model. Higher current rates allow less time for lithium diffusion through Si and therefore cause higher stress concentrations. We use C-rates to draw comparison between the different sizes of rod diameter. C/10 represents a battery that is discharged in 10 hours whereas C/2 represents a battery that is reduced crystal size and lower currents result in lower stress concentrations, leading to better cycle life and higher capacity.

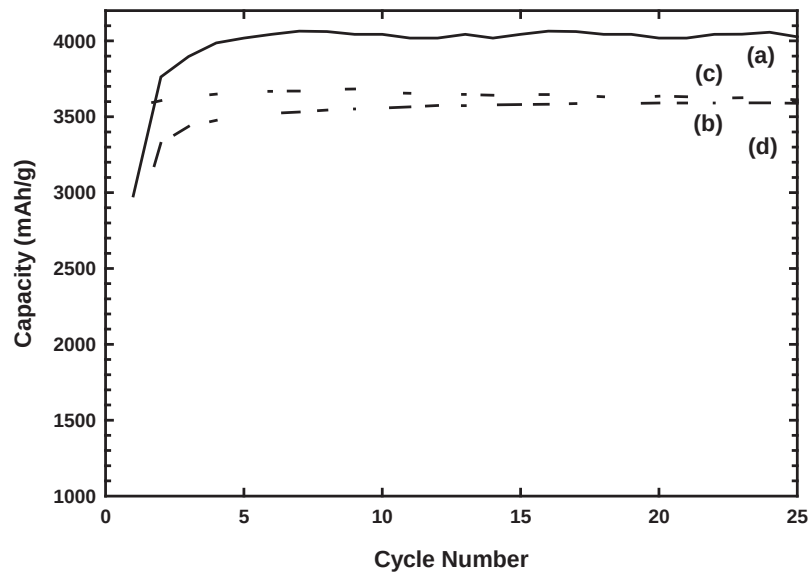


Figure 4.16: Capacity vs. Cycle Number for tested samples with varying rod diameter and applied current. (a) 800 nm rods with C/10 applied current, (b) 800 nm rods with C/2 applied current, (c) 1500 nm rods with C/10 applied current, (d) 1500nm rods with C/2 applied current.

discharged in 2 hours. It is typical to see a decreased capacity and faster capacity fade with higher applied currents, as we saw in our model. In our study, we observe this behavior for the rod size of 1500nm, showing more rapid degradation of the C/2 sample as compared to the C/10 sample, which agrees with Figure 4.12b and 4.12d. However, for the 800 nm rod diameter we observe only a decrease in capacity, and show no excess degradation corresponding to the increased current. This could be a result of the behavior predicted by our model in Figure 4.12a, that, even though we are applying a high current, the overall stress is low enough in the 800 nm rods to prevent pulverization. In a similarly structured experiment, Teki and Koratkar et al. claim the mechanism behind lower stresses in Si nanowires is due to the increased space between nanowires accommodating the volume change associated with the alloying and de-alloying of Li [20]. This may also be the case in our experiment as the 800 nm rods have larger gaps between them than do the 1500 nm rods. We find that our experimental results agree with our model in that

Rechargeable lithium batteries were produced and tested in this work with a fair degree of repeatability. Inconsistencies arose with imperfections in our method of manufacturing rod arrays as well as battery assembly. Rod array dimensions were difficult to fabricate with accuracy of less than 100 nm of the target dimension. We speculate that the TiN coating was partially ineffective towards preventing lithiation of the Si substrate, which would explain the high capacities observed in units of mAh g^{-1} in Figure 4.16. Future work will focus on repeatability of size dimensioning of rod arrays and of battery assembly, as well as TiN coating effectiveness. Extended cycling of the electrode under realistic conditions would yield more commercially viable results, as well as evaluation of full lithium-ion cells using known cathode material systems over significantly larger number of cycles.

Processes for developing all-solid-state batteries of the form depicted in this work are far from being industrially scalable. Excess solid-electrolyte and lithium metal layers fabricated by cold pressing techniques were used in this work to facilitate testing of 3-D Si rod-arrays as anodes. Successful commercialization will require more than bulk-type cold pressing methods such as advanced coating technologies, capable of handling sulfide-based solid-electrolytes and electrodes composed of large particles and more than one material. However, fabrication of Si rod-arrays is not entirely out of reach for industrial fabrication. While patterning techniques such as e-beam lithography are inapt for covering areas larger than square millimeters, DRIE and RIE processes could be readily scaled to accommodate sheets of Si as opposed to individual wafers. Moreover, DRIE is a relatively cost effective means of nano-fabrication in comparison to other scalable patterning techniques such as x-ray lithography [21]. Therefore, it is determined that industrialization of all-solid-state 3-D integrated lithium-ion batteries is not limited by processes regarding the production of Si rod-arrays but by the processes involving battery fabrication.

4.5 Conclusion

To the best of our knowledge this is the first demonstration of Si nanoparticles as an anode material for lithium-ion batteries, and as such, optimization of liquid and solid state electrode composition and construction is ongoing. Further studies are required to fully understand and overcome the irreversible capacity loss during the initial cycle. The inclusion of MWCNTs in solid-state n-Si based lithium batteries showed higher reversible capacities than batteries using AB as the CA. MWCNTs in composite electrodes allowed for approximately a 100% increase of capacity over those made with AB. Specifically, a stable capacity of 800 mAh

g^{-1} was measured for n-Si electrodes employing MWCNT for over 100 cycles. Analysis of electrochemical potential spectroscopy measurements demonstrates capacity fade as a function of c-Si formation beyond the c- $\text{Li}_{15}\text{Si}_4$ phase. Maintaining a low-voltage cutoff above 0.05-0.07V reduced capacity fading and resulted in stable cycling. We showed that all test cells stabilized at approximately 800 mAh g^{-1} regardless of voltage cycling limits. MWCNT's are shown to be a superior CA for Li batteries with a solid-state construction and Si nanoparticles are shown to demonstrate improved reversible cycling over bulk Si anode material. Successful employment of Si nanoparticles allowed for reversible cycling beyond that of bulk (micron) sized Si particles.

3-D MEMS-fabricated lithium batteries incorporating structured silicon rods were designed, fabricated and tested. A simple, quick, and repeatable micro/nano rod array fabrication process for the battery anodes was developed by our group using traditional MEMS technology. The testing results of the 3-D lithium battery showed a fair degree of repeatability and revealed that structured silicon rod arrays achieve a high first cycle as well as high continued cycling coulombic efficiency. High capacity with high reversibility was observed for lithium batteries. Rod diameter showed to have a significant effect on degradation as a function of applied current and overall stress on the Si rods. Our results for cycle life and capacity were directly supported by the data from modeling the stress in Si rods under an applied current. Long cycle life with little capacity fading was achieved by using rod-structured electrodes.

Further exploration of Si in solid state is required to resolve degradation issues. Numerous methods have been proposed for mitigation Si degradation, of which: integrating elemental Ni as a highly electronically conducting buffer, growing Si particles in a highly ordered carbon matrix, and optimization of nanostructured electrodes have all shown promising results.

4.6 Summary

Si was demonstrated as an electrode material for fabrication of all-solid-state half cells. It was shown that utilizing Si in an all-solid-state construction resulted in an improved electrochemical performance over liquid-based cells. Utilization of nano-sized silicon with the substitution of carbon black with higher surface area MWCNT, and a narrow voltage range showed that Si degraded less than 9% over 50 cycles while maintaining over 1160 mAh g⁻¹. This result is remarkable, as standard liquid cells typically degrade completely within the first 50 cycles, as was observed. Furthermore, study of the size of Si particles in composite electrodes revealed greater initial reversible capacity from smaller particles. While degradation was consistent throughout all sample sizes, the smallest material, M30-Si, was able to maintain a reversible capacity over 1800 mAh g⁻¹ for 120 cycles.

3-D nanostructured Si rod arrays were also produced and used as electrodes in all-solid-state batteries. It was proposed that the large volume expansion/breakage could be mitigated by use of structured rods. Using a DRIE process, Si arrays were constructed and tested resulting in extremely high capacities, but low repeatability as a result of potential insufficient TiN blocking of lithiation of the Si wafer. A model was developed to confirm the experimental results with great success. As predicted, thinner rods exhibited less stress degradation and better performance at high rate as compared to thick rods.

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5. Cathodes

5.1 Introduction

While all-solid-state batteries have a number of advantages over liquid-based cells, they remain rate-limited which inhibits their potential for commercialization. Recently developed solid electrolytes have exhibited high ionic conductivities on the order of $10^{-3} \text{ S cm}^{-1}$, comparable to the ionic conductivity of commonly used liquid electrolytes. Therefore it must be that the rate-limiting step of all-solid-state batteries is not the bulk conductivity, but the interface between the electrode and electrolyte material. A large disadvantage of all-solid-state batteries is the difficulty of forming an effective electrode-electrolyte interface. In all-solid-state battery systems using sulfide-based solid electrolytes, high interfacial resistances between the positive electrode and the solid electrolyte have been observed during the initial charging process when LiCoO_2 was used as the electrode active material [1,2]. It is believed that the high resistance is caused by degradation of the interface between the LiCoO_2 and the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte [3]. There exists two methods of resolving issues of the electrode-electrolyte interface in all-solid-state batteries; 1) Incorporation of framework electrolyte additives to increase ionic conductivity and stabilize the electrolyte in contact with the electrode, and 2) Forming a favorable electrode/electrolyte interface by interfacial modification. It has been shown that by adding second network formers such as GeS_2 and SiS_2 to the $\text{Li}_2\text{S-P}_2\text{S}_5$ system, researchers have not only obtained higher conductivities for solid electrolytes but observed better stability of the electrode/electrolyte interface [4]. These second network formers maintain elements with large ionic radii and high polarizability that allow for enhancement of mobility of conducting ions as well as improved framework of the electrolyte [5]. Incorporation of the electrolyte additives has also shown to reduce the large chemical potential difference between the sulfide electrolyte and

oxide electrode in this work (Section 5.3.3). Forming a favorable electrode/electrolyte interface by interfacial modification has also shown to effectively decrease the interfacial resistance, such as with coatings of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ on LiCoO_2 particles [6]. Also recently shown is the use of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to prevent dissolution [7]. The coating aids in preventing diffusion of the LiCoO_2 into the electrolyte while providing a medium for mitigating the large chemical potential difference between the sulfide electrolyte and oxide electrode.

In this work, we have focused our interfacial improvement investigation on electrolyte additives for the purpose of enhancing the stability of electrolytes in contact with electrode materials while increasing the conductivity of respective electrolytes. We detail GeSe_2 as a network forming additive to increase the conductivity and stabilize the electrolyte as well as GeS_2 . In conjunction with GeS_2 , elemental sulfur is used as an additive to aid in stabilization of the electrolyte with the high voltage cathode. Lastly, we use the lithium-containing additive Li_2O in a specific effort to increase the stability of the electrolyte/electrode interface by decreasing the potential difference between the oxide cathode and sulfide electrolyte.

5.1.1 Solid electrolyte interphase (SEI) and space charge

Typically, lithium-ion batteries employ liquid electrolytes that must be stable at both the anodic and cathodic potentials found in Li-ion cells, 0 V to 4.2 V vs. lithium. No practical solvents have been found to be thermodynamically stable with lithium or low anode potentials near 0 V, however many solvents can undergo a limited reaction to form a passivation film on the electrode surface. This film spatially separates the solvent from the electrode in liquid-based batteries, yet is ionically conductive, and thus allows passage of lithium ions. The passivation

film is termed the solid electrolyte interphase (SEI) and imparts extrinsic stability to the system allowing the fabrication of cells that are stable for long periods of time without significant degradation [8]. When the SEI is formed, lithium is incorporated into the passivation film of which process is irreversible and is thus considered as a loss of capacity, generally on a cell's first cycle. The amount of irreversible capacity is dependent on the electrolyte formulation and the electrode materials. As the reaction occurs at the particle surface, materials with low specific surface area typically offer lower irreversible capacity. Unfortunately, the film is electrically insulating and its growth can eventually lead to loss of electrical contact between cathode particles, resulting in cell failure [9]. Much research on liquid-electrolyte modification has been done to control SEI formation and has resulted in great advances among lithium-ion battery technologies. For all-solid-state chemistries, similar SEI formations are observed but result in different effects on electron/ion conduction and stability. While the formation is still observed primarily on the first cycle, it has been observed in this work (Figure 5.1) to continue formation on further cycling depending upon the solid-electrolyte being employed. While formation of the SEI in solid-state does result in some added stability, the continued formation during cycling is evidence of on-going chemical reaction between the electrolyte and electrode. Furthermore, it is found that in contrast to the liquid-based batteries, formation of an SEI in a solid-state configuration results in an ionically insulating layer. In this work, SEI formation is investigated as a function of electrolyte variation, in that electrolytes are modified through the addition of secondary network formers to create a more stable interface.

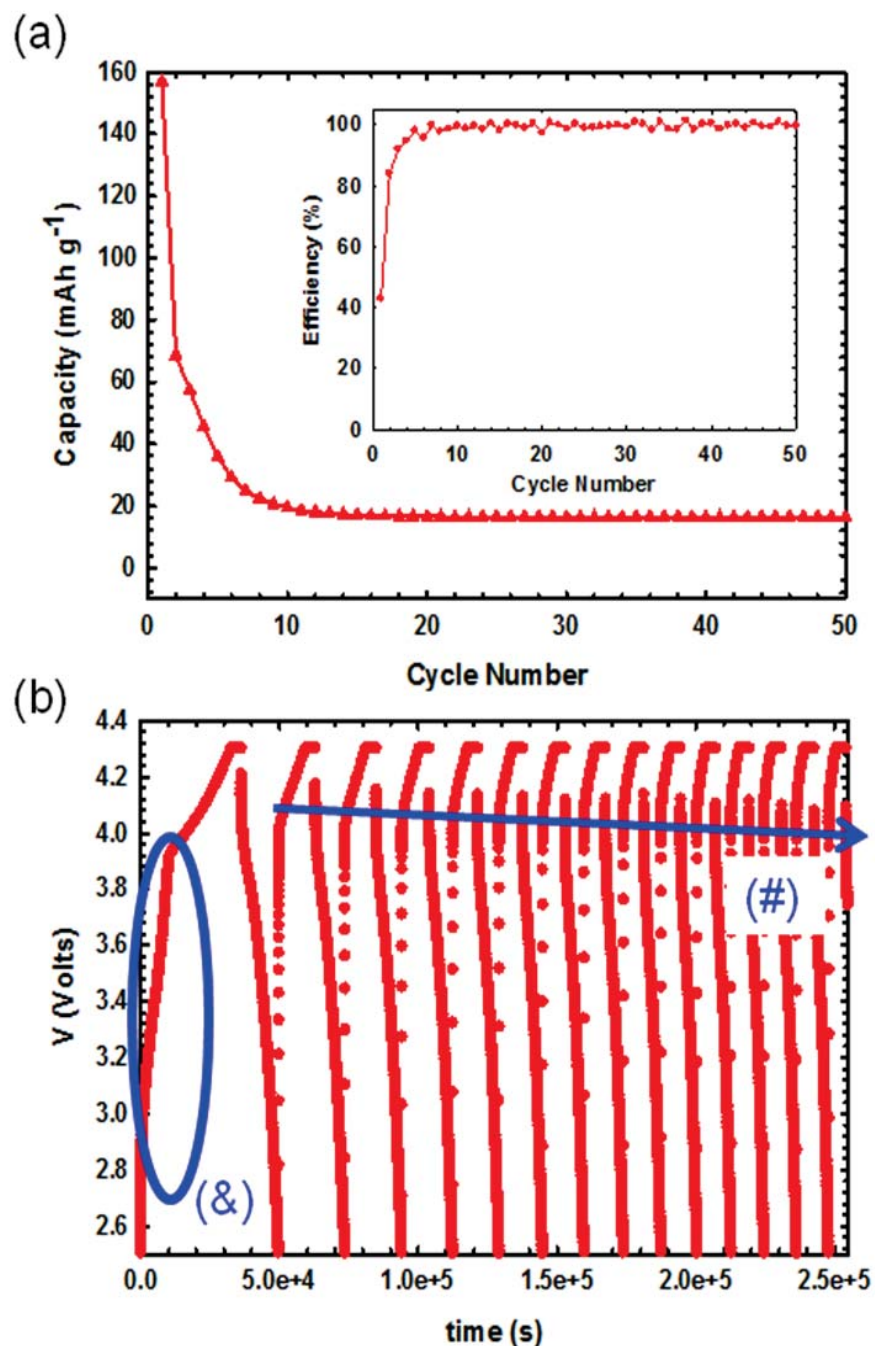


Figure 5.1: (a) Cycling performance and coulombic efficiency of binary electrolyte with a LiCoO₂ cathode. (b) The side reaction observed during the first cycle below the reaction potential of 3.9 V for the LiCoO₂/SE/Li half cell (&) as well as increasing resistance during further cycling is shown (#).

The increasing resistance within solid state batteries during cycling has also been described as the development of a depletion region, or space charge layer. A space charge layer is an insulating region within a conductive material where the mobile charge carriers have diffused away or been forced away by an electric field. A space charge layer (as it applies to all-solid-state Li-ion batteries in this work) results from the large chemical potential difference between the electrolyte and electrode (Figure 5.2a) which drives Li^+ ions to transfer from the sulfide electrolyte to the oxide based electrode. As the electrode material is typically oxide based and a mixed conductor, the space-charge layer on the oxide side of the interface should vanish because the electronic conduction will resolve any concentration gradient of the Li^+ ions. Consequently, Li^+ ions will additionally transfer from the sulfide in order to reach equilibrium, further developing the space-charge layer on the sulfide side and resulting in a very large interfacial resistance (Figure 5.2b) [10].

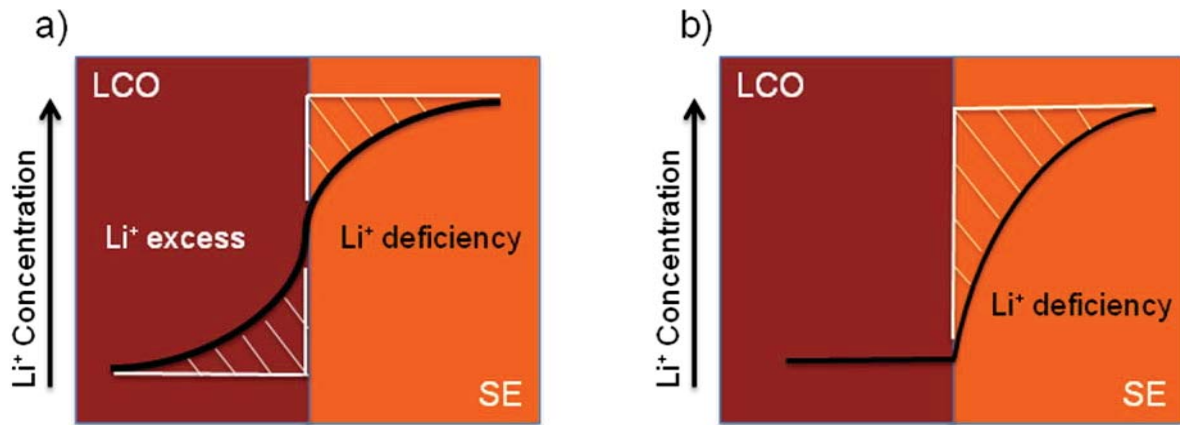


Figure 5.2: (a) The chemical potential drives Li^+ transfer from the solid electrolyte to the oxide based electrode (e.g. LiCoO_2) and space charge layers develop on both sides. (b) Electrical conduction of the LiCoO_2 brings electrons to neutralize Li^+ ions resolving the space charge, further developing the space charge in the solid electrolyte.

5.2 Experimental procedures

5.2.1 Electrolyte fabrication

Li_2S - GeS_2 - P_2S_5 electrolytes were prepared using the SSBM procedure previously discussed in Chapter 3 [11,12]. Reagent-grade powders of Li_2S (Aldrich, 99.999%), P_2S_5 (Aldrich, 99%), and GeS_2 (City Chemical, 99.99%) were used as starting materials. Appropriate concentrations of materials were combined into a zirconia vial (Spex) at a net weight of 1 g with two zirconia balls (1×12 mm, 1×15 mm in diameter) for grinding. High energy ball milling (Spex8000) took place for 20 continuous hours in an Ar-filled dry box. Heat treatment of SSBM SSE powders was performed by first mixing sulfur and SSE powders in mortar and pestle and pelletizing the powders at 8 metric tons in a stainless steel die ($\phi = 1.3$ cm) with 400 mg of starting material. Extracted pellets were placed in a sealed glass container and heated on a hot plate to 240°C at approximately $10^\circ\text{C min}^{-1}$ for 16 hours. With the starting time corresponding to the point when the hot plate reached the desired temperature, finished pellets were removed from the hot plate and placed on a cooling rack. The heat-treated pellets were then ground in a mortar with pestle and used for solid battery production with no further modifications. All pelletization and heat treatment processes were performed in a dry Ar filled glove box. Li_2S - GeSe_2 - P_2S_5 ($\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$) electrolytes were prepared similarly with GeSe_2 (Strem, 99.999%) instead of GeS_2 and HT was performed for 240°C , 360°C , and 480°C .

5.2.2 Electrode fabrication with bilayer electrolyte

Composite electrodes were prepared by mixing LiCoO_2 powder (Sigma-Aldrich) as the active material, SSE Li_2S - GeS_2 - P_2S_5 powder for fast lithium ion conduction, and acetylene

black (Alfa-Aesar, 50% compressed) for electron conduction at a weight ratio of 20:30:3 respectively. Bilayer electrolyte pellets are formed by hand pressing 100 mg of $\text{Li}_2\text{S-GeSe}_2\text{-P}_2\text{S}_5$ or $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ SE on top of a 100 mg hand pressed layer of 77.5 $\text{Li}_2\text{S-22.5P}_2\text{S}_5$ (mol %) SE prepared by the SSBM procedure. The purpose of the bilayer construction method will be discussed in section 5.3. A 10 mg layer of the composite cathode material is then carefully spread on the top of the $\text{Li}_2\text{S-GeSe}_2\text{-P}_2\text{S}_5$ or $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ electrolyte layer and the cell pelletized by cold pressing (5 metric tons) for 5 min. Li foil (Alfa-Aesar, 0.75 mm thick) is then attached to the 77.5 $\text{Li}_2\text{S-22.5P}_2\text{S}_5$ (mol %) SSE face at 2 metric tons. All pressing and testing operations are carried out in a polyaryletheretherketone (PEEK) mold ($\phi = 1.3$ cm) with Ti metal rods as current collectors for both working and counter electrodes. All processes were carried out in an Ar-filled dry box. Galvanostatic charge-discharge cycling took place at first cycle cut off voltages of 4.1 and 2.5 V while the remaining cycles were run from 2.5-4.3 V at a $50 \mu\text{A cm}^{-2}$ current density at room temperature using an Arbin BT2000. Schematic diagrams for the Li/SSE/LiCoO₂ cells and AC impedance cells can be seen in Figure 5.3a and 5.3b, respectively.

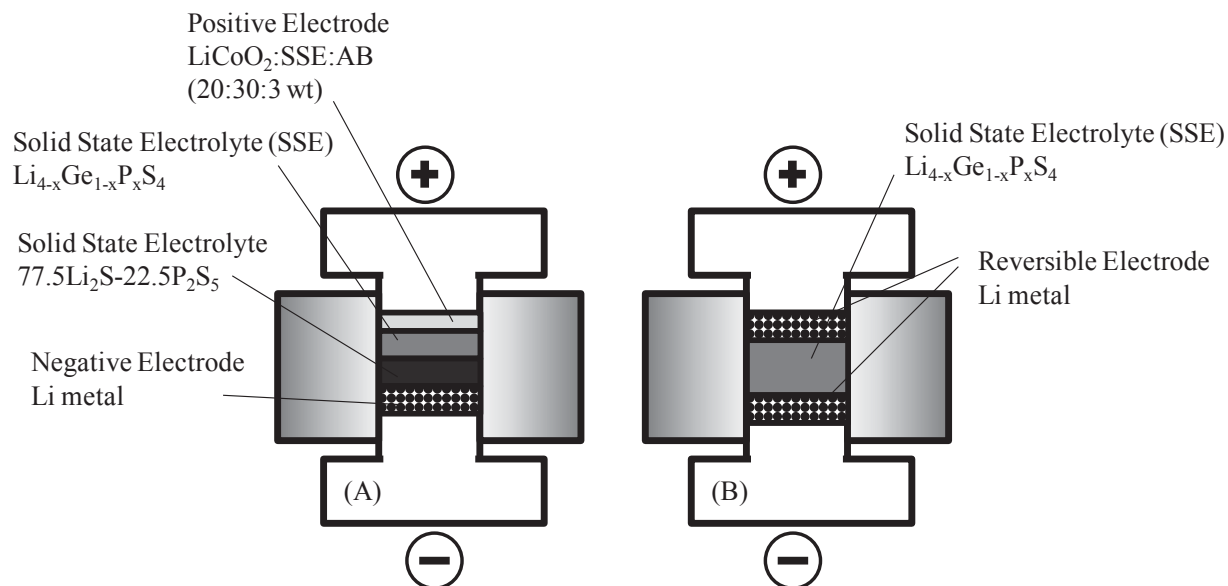


Figure 5.3: Schematic diagram of Ti test die with Li_2S - GeS_2 - P_2S_5 electrolyte for a) the all-solid-state battery and b) measuring conductivity of SE.

5.3 Electrochemical Investigation

5.3.1 GeS_2 with sulfur

We have prepared sulfide-based lithium ion conducting SSE by the single-step ball-milling (SSBM) procedure [12], which combines ball-milling and heat treatment (HT) into one step. The Li_2S - GeS_2 - P_2S_5 glass-ceramic electrolytes produced by SSBM exhibit high conductivities over $1 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature. The all-solid-state cells with these SSE were confirmed to work as lithium secondary batteries. We also report on the inclusion of elemental sulfur into the Li_2S - GeS_2 - P_2S_5 system which showed improved cycling stability and first cycle coulombic efficiency of Li/LiCoO_2 all-solid-state cells. While it is well known that sulfur is highly insulating and its incorporation into electrolytes typically shows decreased ionic conductivity, it has a highly polarizable character that has potential to improve stabilization of electrolyte in contact with the electrode. Elemental sulfur was chosen for enhancing the cycling

stability of the electrolyte for its highly polarizable character, as high polarizability of anions is well known to aid the formation of strong covalent bonds between the anions of the framework, effectively orienting charge density away from the interstitial ions and improving ion conduction [13].

A schematic diagram for ternary component $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ is shown in Figure 5.4. As x in $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ increases, GeS_2 decreases and P_2S_5 increases with relatively small changes of Li_2S , and finally $x = 1.00$ corresponds with $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ (mol %).

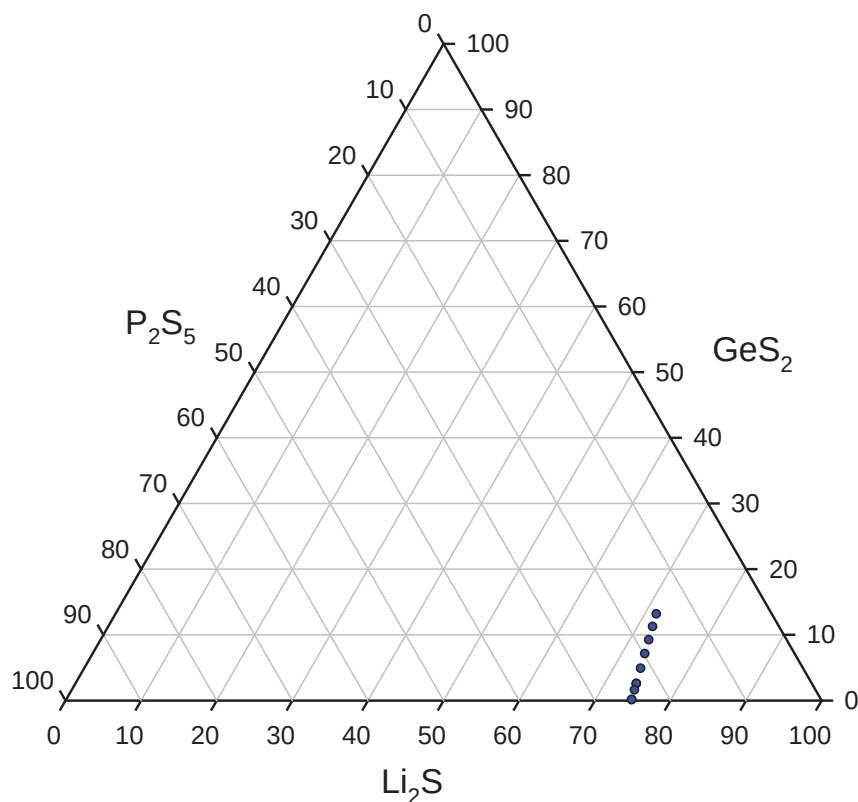


Figure 5.4: Diagram for ternary components of $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ which is also expressed as $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$.

Figure 5.5a shows the recorded conductivities of the $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_5$ ($\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$) electrolyte in the range of $0.70 < x < 1.00$. We show that the SSBM procedure is superior to conventional ball-milling by approximately a factor of two for achieving extremely high conductivities when compared to the results obtained by Yamamoto et. al. [14]. High conductivities

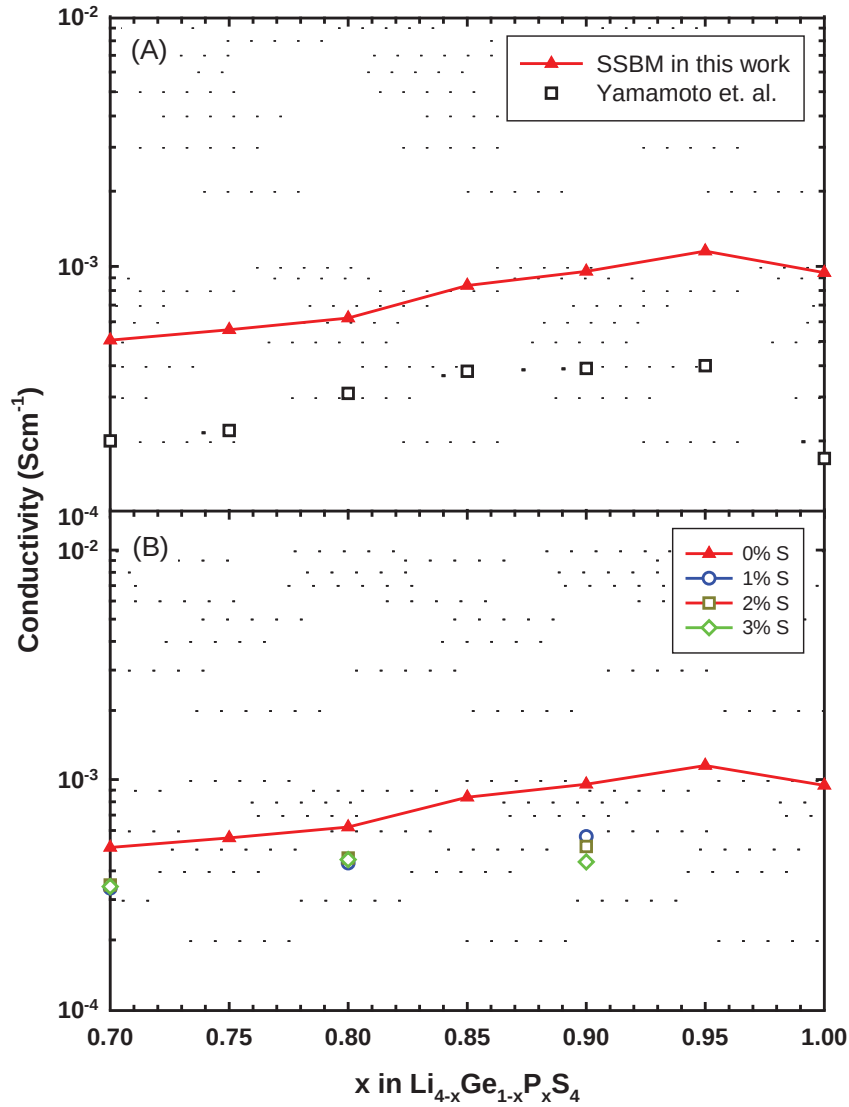


Figure 5.5: (A) Conductivity of ball milled $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ in this work and solid electrolyte produced by Yamamoto et.al. [14]. (B) Conductivity of ball milled $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ with different amount of elemental S.

were observed for the entire range of compositions with values ranging from $5.0 \times 10^{-4} \text{ S cm}^{-1}$ at the lowest and $1.2 \times 10^{-3} \text{ S cm}^{-1}$ at the highest but with most values recording around $1 \times 10^{-3} \text{ S cm}^{-1}$ as shown in Table 5.1. The highest recorded value for conductivity corresponds to the

Table 5.1: Conductivity of $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_{2(1+x)}\text{S}_{2(1-x)}$.

x	Conductivity / S cm^{-1}
0.70	5.1×10^{-4}
0.75	5.6×10^{-4}
0.80	6.2×10^{-4}
0.85	8.4×10^{-4}
0.90	9.5×10^{-4}
0.95	1.2×10^{-3}
1.00	9.4×10^{-4}

composition of $x = 0.95$, which corresponds to the molar composition of constituent compounds as $74.4\text{Li}_2\text{S}-2.4\text{GeS}_2-23.2\text{P}_2\text{S}_5$. This composition is that of the highest recorded conductivity for the $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ system studied by Yamamoto et. al. as well. We attribute the high ionic conductivities of this system to the mixed-anion effect which involves the mixing of two kinds of network-forming sulfides P_2S_5 and GeS_2 , and the presence of a large concentration of Li in the glass-ceramic materials [14]. The mixed-anion effect typically results in a higher ionic conductivity due to the introduction of more polarizable anions that can deform to stabilize transition state geometries of the migrating ion through covalent interactions between anions [13]. The high ionic conductivities may also be due to the larger ionic radii of Ge atoms which improve the mobility of the conducting species [15]. As we received our highest conductivity from the composition $x = 0.95$, we began our study using this material but found that the composition $x = 0.70$ ($71.7\text{Li}_2\text{S}-13.0\text{GeS}_2-15.2\text{P}_2\text{S}_5$) performed better for our Li/LiCoO_2 cells in terms of

cycling stability as well as initial coulombic efficiency. Therefore, we used the material with $x = 0.70$ exclusively for heat treatment studies with adding elemental sulfur. Other compositions were initially considered and tested but did not yield significantly comparable results to that of $x = 0.70$ when heat-treated with adding elemental sulfur, which proved to be optimal for our Li/LiCoO₂ cells.

Ball milled powders were heat treated with numerous weight concentrations of elemental sulfur, the most significant of which are specified in Table 5.2 with corresponding recorded conductivities. Data were taken for 1%, 2%, and 3% wt. to observe the effects of sulfur composition on conductivity. Fig. 3b shows a conductivity map for samples heat treated with elemental sulfur where the conductivity remains high in spite of increasing amounts of sulfur. A decreased conductivity is more pronounced with increased sulfur for samples correlating to $x = 0.90$ in Li_{4-x}Ge_{1-x}P_xS₄. An overall trend of decreasing conductivity can be observed for increased amounts of added sulfur, as we expected.

Table 5.2: Conductivity of Li_{4-x}Ge_{1-x}P_xS₄ with added sulfur.

x	S (%)	Conductivity / S cm ⁻¹
.70	1	3.4×10^{-4}
.70	2	4.3×10^{-4}
.70	3	5.6×10^{-4}
.80	1	3.5×10^{-4}
.80	2	4.6×10^{-4}
.80	3	5.1×10^{-4}
.90	1	3.4×10^{-4}
.90	2	4.5×10^{-4}
.90	3	4.4×10^{-4}

Fig 5.6 shows the XRD patterns of the SSBM glass-ceramic electrolytes for the compositional range of $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ powders for $0.70 < x < 1.00$ without HT. The gradual negative shift of the “thio-LISICON III analog” peaks (circle) starting from $x = 0.95$ and ending at $x = 0.75$ is noticeable. This could be explained by larger ionic size of Ge [15], which can enlarge the whole $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ lattice. One of the reasons for the increased conductivity by adding small amount of

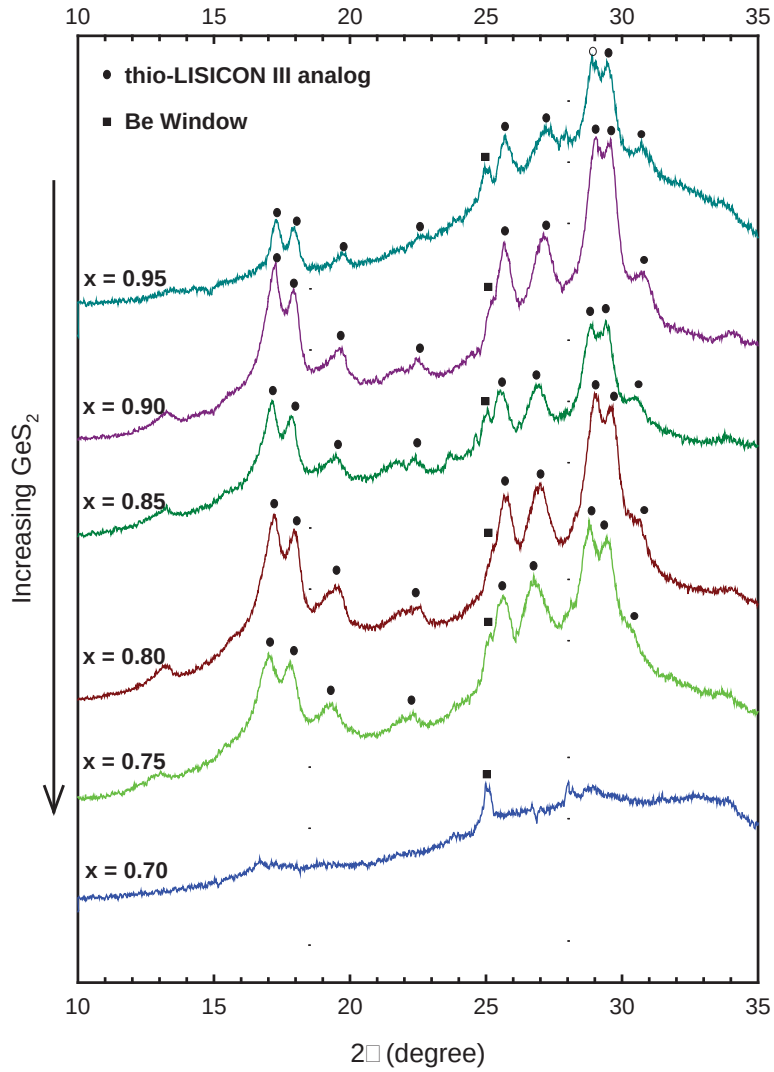


Figure 5.6: XRD patterns of SSBM $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$.

GeS_2 ($x = 0.95$) in $0.75\text{Li}_2\text{S}-0.25\text{P}_2\text{S}_5$ ($x = 1.00$) may be explained by more open structure for better Li^+ transport by the inclusion of GeS_2 . The most interesting point, however, is the close correlation that can be drawn between the changing crystal structures and the variations in electrochemical performance. The composition with the lowest conductivity among the tested compositions corresponded to the only amorphous phase of material which also represents the sample with a large overall change in the dominant crystal structure as well as the best stability and performance, especially with the inclusion of elemental sulfur. These results closely correlate to our previous findings using GeSe_2 as a second network former [11].

Figure 5.7 shows the typical charge-discharge voltage profiles of LiCoO_2/Li cells using $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid-state electrolytes. The columbic efficiency for the first cycle

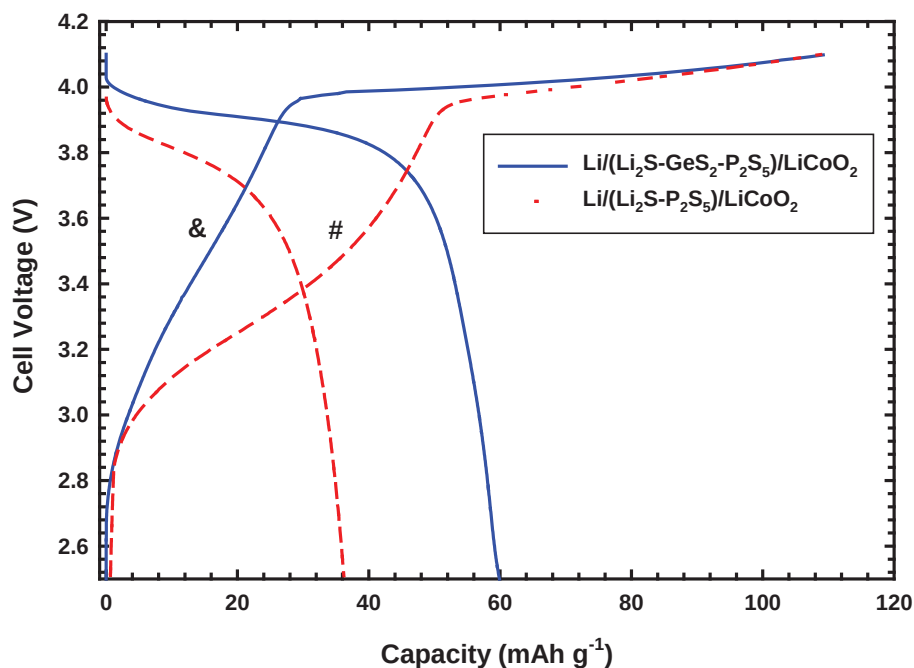


Figure 5.7: First cycle voltage profiles for (a) $\text{Li}/(\text{Li}_2\text{S}-\text{P}_2\text{S}_5)/\text{LiCoO}_2$, (b) $\text{Li}/(\text{Li}_2\text{S}-\text{P}_2\text{S}_5/\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5)/\text{LiCoO}_2$ double layer pellet, and (c) $\text{Li}/(\text{Li}_2\text{S}-\text{P}_2\text{S}_5/\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5)/\text{LiCoO}_2$ double layer pellet with 1% wt. elemental sulfur heat treated into the $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ solid electrolyte. of the samples is poor, which we attribute to the severe side reaction observed by the sloping plateau ('#') for $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ and ("&") for $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ between 2.8-3.9 V. The LiCoO_2 should ideally create a charge/discharge reaction voltage plateau at ~ 3.9 V. We observe that for the electrolyte containing GeS_2 , the first cycle side reaction is far less severe than that of the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ electrolyte. The inclusion of GeS_2 reduced the fraction of side reaction constituting the first cycle charge capacity from 48% for the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ electrolyte down to 26% for the $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$ electrolyte. A side reaction at the interface between $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ SSE and active material may be creating a larger resistance barrier than that for $\text{Li}_2\text{S}-\text{GeS}_2-\text{P}_2\text{S}_5$. When the sulfide and oxide ion-conducting species are in contact, there is a transfer of Li^+ ions forms a space-charge layer in both materials that in turn leads to interfacial resistance [10,11]. We speculate that the inclusion of GeS_2 prevents excessive side reaction by stabilizing the large chemical potential difference between the sulfur based electrolyte and the oxide based active

material. While the inclusion of GeS_2 results in approximately a 50% reduction of side reaction when compared to the $\text{Li}_2\text{S-P}_2\text{S}_5$ system, further exploration is needed to resolve the large fraction of side reaction that remains. Current efforts for reduction of the side reaction revolve around improved mixing procedures for composite cathodes and utilization of size-reduced electrolyte materials. No significant side reactions were observed for subsequent cycling. However, some degradation was observed for both cells which we attribute to the increasing interfacial resistance.

Figure 5.8a depicts capacity of Li/LiCoO_2 cells as a function of cycle number depending on the SSE configuration – single layer or bilayer. Previously we have shown that SSBM $77.5\text{Li}_2\text{S-22.5P}_2\text{S}_5$ is stable in contact with Li metal [9]. However, the $77.5\text{Li}_2\text{S-22.5P}_2\text{S}_5$ is not stable in contact with LiCoO_2 as seen in the fast capacity fading (circle) after several cycles, which drove exploration of second network formers for stabilization. Utilization of the GeS_2 -

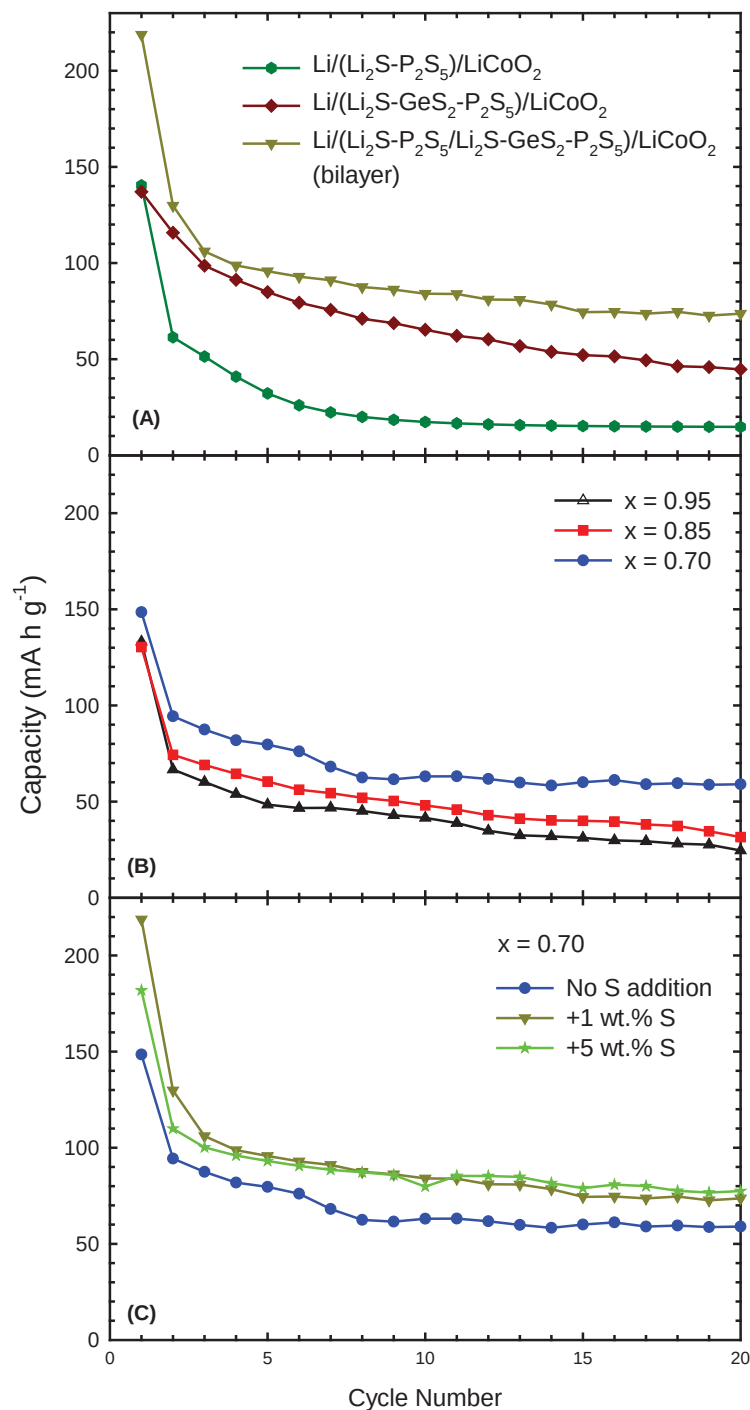


Figure 5.8: (A) Charge capacity of Li/LiCoO₂ as a function of cycle number depending on configuration of the SE layers (single layer or bilayer) of 0.775Li₂S-0.225P₂S₅ and/or Li₂S-GeS₂-P₂S₅ (x = 0.70 in Li_{4-x}Ge_{1-x}P_xS₄ with 1 wt.% sulfur addition). (B) Effects of the amount of GeS₂ and (C) addition of sulfur on Li₂S-GeS₂-P₂S₅ on the cycle performance of Li/LiCoO₂ cell using bilayer SE consisting of SSBM 0.775Li₂S-0.225P₂S₅ and Li₂S-GeS₂-P₂S₅ (Li_{4-x}Ge_{1-x}P_xS₄) electrolytes.

based electrolyte ($\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$, $x = 0.70$ in $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ with adding 1 wt.% sulfur) leads to the improvement of the capacity and cycle performance. However, it still shows capacity fading, which we found to be due to the instability of $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ in contact with Li metal. Consequently we constructed a bilayer electrolyte with cell configuration, $\text{Li}/(\text{Li}_2\text{S-P}_2\text{S}_5/\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5)/\text{LiCoO}_2$. Figure 5.8a shows that the bilayer SSE construction (triangle) is superior to the single layer SE ones (circle and diamond), which is attributed to the stable interfaces of both $\text{Li}/\text{Li}_2\text{S-P}_2\text{S}_5$ and $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5/\text{LiCoO}_2$.

The cycling performance of Li/LiCoO_2 cells using SSBM electrolytes using bilayer electrolytes, $77.5\text{Li}_2\text{S-22.5P}_2\text{S}_5/\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ ($\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$) with three different amounts of GeS_2 in $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$, agrees well with the observation that addition of GeS_2 in $\text{Li}_2\text{S-P}_2\text{S}_5$ system enhances the stability of $\text{LiCoO}_2/\text{SSE}$ interface (Figure 5.8b). Increasing the amounts of GeS_2 leads to increase the capacity and improve the cycle retention. Cells cycled at the smallest concentration of GeS_2 ($x = 0.95$) demonstrated a charge capacity of 66 mA h g^{-1} for the second cycle and the fastest rate of capacity fade in the following cycles, with only 36% retention after 20 cycles. The highest concentration of GeS_2 ($x = 0.70$), resulted in the highest second cycle charge capacity of 94 mAh g^{-1} , and the highest capacity retention of 64% after 20 cycles. The first cycle coulombic efficiency, which we define as the charge capacity divided by the discharge capacity, increased for larger amounts of GeS_2 , going from approximately 49% for $x = 0.95$ up to 62% for $x = 0.70$ shown in Table 5.3.

Table 5.3: First cycle efficiency (Charge/Discharge) of $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_{2(1+x)}\text{S}_4$ based systems.

Sample (x)	Efficiency
0.70	0.63
0.75	0.57
0.80	0.56
0.85	0.55
0.90	0.52
0.95	0.49
1.00	0.42
0.70+1%S	0.70
0.70+2%S	0.65
0.70+3%S	0.63
0.70+5%S	0.60

Finally, in Fig. 5.8c, we show that incorporation of elemental sulfur at various compositions can have significant effects on the cycling stability and first cycle coulombic efficiency. The cell with 1 wt.% added sulfur (triangle) shows the best performance with a second cycle capacity of 129 mA h g^{-1} , a 20th cycle capacity of 75 mA h g^{-1} and a first cycle coulombic efficiency of 70%. When we increased the amount of added sulfur past 1 wt.% (star), we began to see a decline in first cycle coulombic efficiency down to 60% for 5 wt.% added sulfur (Table 5.3), and no improvement in cycling behavior. When more than 5% wt. sulfur was added, cycling capacity degraded quite rapidly.

5.3.2 GeSe_2

Motivated by larger ionic size and more polarizability of selenium than sulfur we report on the inclusion of GeSe_2 as the second network former into the $\text{Li}_2\text{S-P}_2\text{S}_5$ system which showed great improvement of ionic conductivity. We attribute the conductivity improvement to

the large ionic radius of Ge and Se and the more polarizable character of Se ions improving the mobility of the conducting species [15]. A schematic diagram for ternary component Li_2S - GeSe_2 - P_2S_5 is shown in Figure 5.9. As x in $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$ increases, GeSe_2 decreases and P_2S_5 increases with relatively small changes of Li_2S , and finally $x = 1.00$ corresponds with $75\text{Li}_2\text{S}$ - $25\text{P}_2\text{S}_5$ (mol %).

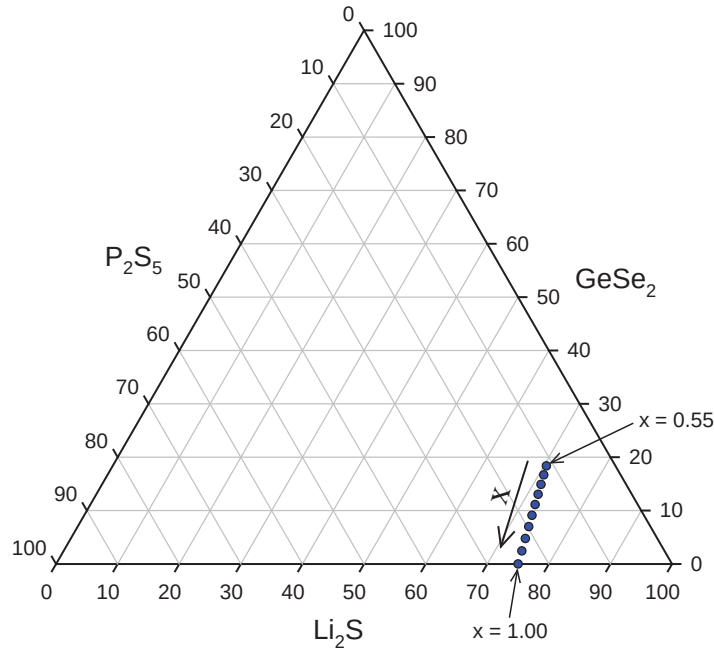


Figure 5.9: Diagram for ternary components of Li_2S - GeSe_2 - P_2S_5 which is also expressed as $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$.

Figure 5.10a shows the recorded conductivities of the $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$ in the range of $0.55 < x < 1.00$. Relatively high conductivities were observed for the entire range of compositions with values ranging from $5.1 \times 10^{-4} \text{ S cm}^{-1}$ at the lowest and $1.4 \times 10^{-3} \text{ S cm}^{-1}$ at the highest but with most values recording above $1 \times 10^{-3} \text{ S cm}^{-1}$ as shown in Table 5.4. We

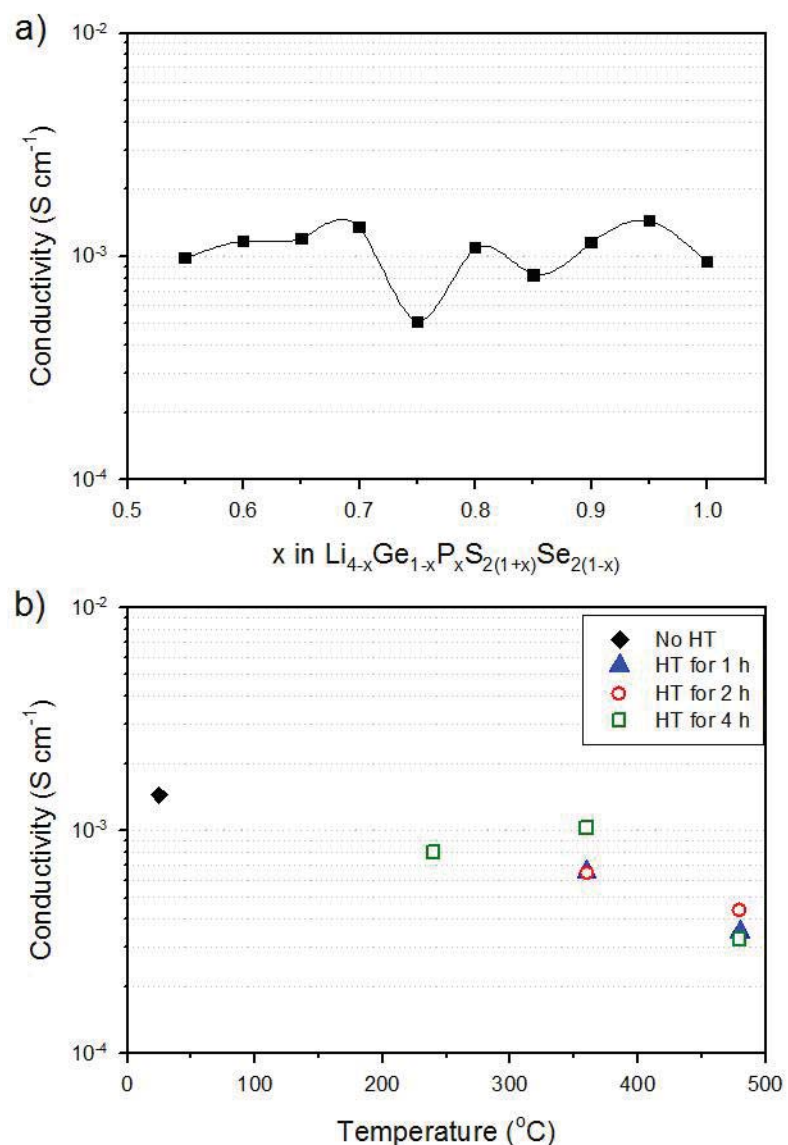


Figure 5.10: a) Electrical conductivity of ABM for $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$. (b) Conductivity map of PHT series for $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$ with $x = 0.95$.

observed a typical activation energy of 30-32 kJ mol⁻¹ over the entire compositional range following a plot of the Arrhenius equation where the slope of $[\ln(\sigma) \text{ vs. } 1/T]$ is equal to $(-E_a/R)$, where σ is the conductivity, T is the thermodynamic temperature, E_a the activation energy for conduction, and R the gas constant [16,17]. Comparatively, typical values for activation energy

Table 5.4: Conductivity of $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_{2(1+x)}\text{S}_{2(1-x)}$.

x	Conductivity / S cm^{-1}
0.55	9.8×10^{-4}
0.60	1.2×10^{-3}
0.65	1.2×10^{-3}
0.70	1.4×10^{-3}
0.75	5.1×10^{-4}
0.80	1.1×10^{-3}
0.85	8.2×10^{-4}
0.90	1.2×10^{-3}
0.95	1.4×10^{-3}
1.00	9.4×10^{-4}

for similar systems include 35-40 kJ mol^{-1} for $\text{Li}_2\text{S-GeSe}_2\text{-P}_2\text{S}_5$ [14] and 35-45 kJ mol^{-1} for $\text{Li}_2\text{S-P}_2\text{S}_5$ [18], which places our SE among some of the best thus far. The highest recorded value for conductivity corresponds to the composition of $x = 0.95$, which relates to the molar compositions of constituent compounds as 74.4 Li_2S -2.4 GeSe_2 -23.2 P_2S_5 (mol %). This composition is closely related to that of the highest recorded conductivity for the $\text{Li}_2\text{S-GeSe}_2\text{-P}_2\text{S}_5$ system studied by Yamamoto group [14]. We attribute the high ionic conductivities of this system to the mixed-anion effect which involved the mixing of two kinds of network-forming sulfides P_2S_5 and GeSe_2 , and the presence of a large concentration of Li in the glass and glass-ceramic materials [14]. The high ionic conductivities may also be due to the larger ionic radii of Ge and Se atoms which improve the mobility of the conducting species [17]. As we received our highest conductivity from the composition $x = 0.95$, we used this material exclusively for PHT studies. Other compositions were initially considered and tested but did not yield significantly comparable results to that of $x = 0.95$, which proved to be optimal for our research.

Figure 5.10b shows a conductivity map for all PHT samples. A trend of decreasing conductivity with increased PHT temperature is observed among all samples. ABM powder was heat treated to seven different conditions specified in Table 5.5 with corresponding recorded conductivities. Data were taken for 1, 2, and 4 hours to observe the effects of time on conductivity and crystal structure. PHT time variation showed slight changes in conductivity. A single 4 hour measurement is shown for the sample heated to 240 °C due to insignificant changes from the ABM starting material conductivity. For samples heat treated to 360 °C and 480 °C we observe similar traits for the different HT times with one exception. Comparison of the 1 h HT, 2 h and 4 h HTs shows slight variation of conductivities respectively with the exclusion of the sample heat treated to 360 °C for 4 h reaching a high ionic conductivity above $1.0 \times 10^{-3} \text{ S cm}^{-1}$. The overall trend of decreasing conductivity with higher HT temperatures disagrees with the generally observed behavior of the $\text{Li}_2\text{S-P}_2\text{S}_5$ system which shows a trend of increasing conductivity. Though, with the exception of the $\text{Li}_2\text{S-P}_2\text{S}_5$ system, generally crystallization of glassy materials results in lower ionic conductivity [18-21].

Table 5.5: Conductivity of $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_{2(1+x)}\text{S}_{2(1-x)}$ with $x = 0.95$.

Heat treatment Temperature / °C	Time / h	Conductivity / S cm^{-1}
ABM		1.4×10^{-3}
240	4	8.0×10^{-4}
360	1	6.5×10^{-4}
360	2	6.4×10^{-4}
360	4	1.0×10^{-3}
480	1	3.5×10^{-4}
480	2	4.4×10^{-4}
480	4	3.3×10^{-4}

The small amount of GeSe_2 that is added to the $\text{Li}_2\text{S-P}_2\text{S}_5$ system has a significant effect on the conductivity and the behavior under HT conditions. The chemical composition dependence on concentration of GeSe_2 yields a non-significant change in the amount of Li_2S and instead, GeSe_2 essentially replaces P_2S_5 (Figure 5.9). Because the conductivity of Li^+ ion conducting materials is known to be determined mainly by the lithium concentration in the glasses [22], and we have a somewhat unwavering amount of Li contribution from the Li_2S , we observe only small changes in the high conductivity of the $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ system over its wide compositional region. We achieved high ionic conductivities for both ABM material with varying chemical compositions and PHT material with varying temperatures and times.

In order to show the dominant trends among the compositional range of ball milled materials, XRD patterns of the $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$ powders for $0.55 < x < 1.00$ without HT are shown in Figure 5.11. Several interesting trends are observed over the large range of tested compositions. Foremost the gradual negative shift of the “thio-LISICON III analog” peaks (triangle) starting from $x = 1.00$ and ending at $x = 0.75$ is noticeable. This could be explained by larger ionic size of Ge and Se, which can enlarge the whole $\text{Li}_2\text{S-P}_2\text{S}_5$ lattice. In spite of two exceptions for $x = 0.75$ and 0.85 , one of the reasons for slightly increased conductivity by adding GeSe_2 might be more open structure for better Li^+ transport than $\text{Li}_2\text{S-P}_2\text{S}_5$ system ($x = 1.00$). With further decreasing x we observe a totally different crystalline structure for ABM materials (‘*’) from that of $\text{Li}_2\text{S-P}_2\text{S}_5$ compounds. Surprisingly, the new structure represents even higher conductivities than $\text{Li}_2\text{S-P}_2\text{S}_5$ system ($x = 1.00$) (Table 5.5). The most interesting point, however, is the close correlation that can be drawn between the changing crystal structures, and the variations in ionic conductivity. The composition with the lowest conductivity among the tested

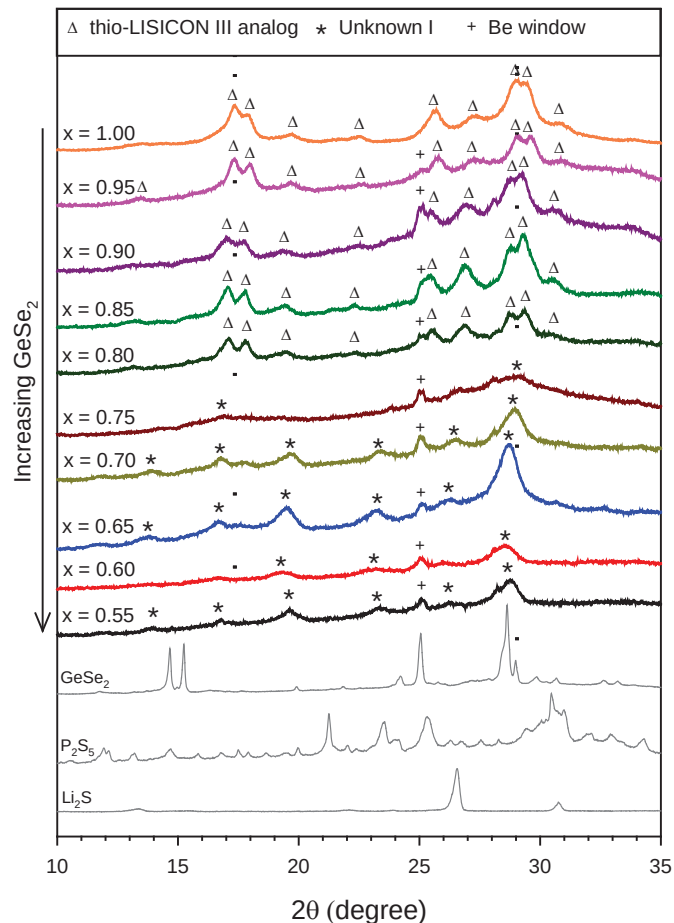


Figure 5.11: XRD patterns of ABM for $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$. XRD patterns for the precursor powders (Li_2S , P_2S_5 , and GeSe_2) are shown for comparison.

compositions corresponded to the only amorphous phase of material which also represents a turning point for large overall changes in the dominant crystal structure.

XRD patterns of heat treated samples are shown in Figure 5.12 where we see the progression of ABM material go from slightly crystalline to highly crystalline as the HT temperature is increased, with HT time constant at 4 h. First of all, the peak positions of thio-LISICON III analog do not change much for HT below 360 °C. In the case of HT at 480 °C (Fig. 5.12c) however, we not only see changes of crystallinity but also a negative shift of peaks are observed, which may be indicative of significant structural change. By comparison to the conductivities of

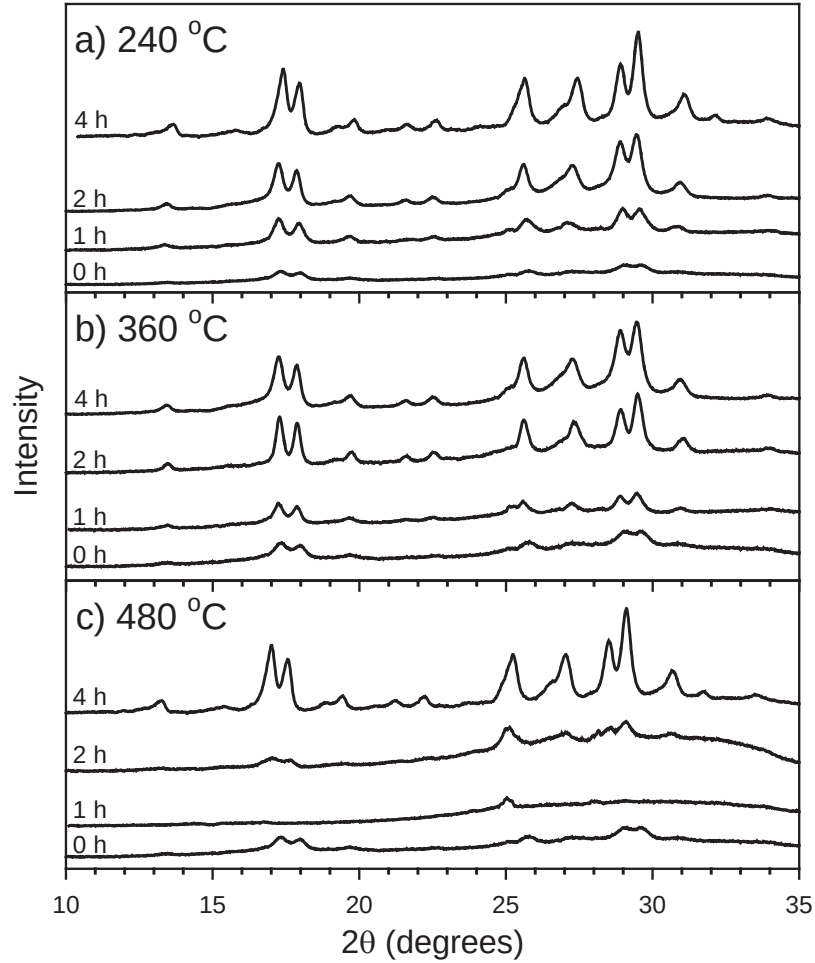


Figure 5.12: XRD patterns of ABM and PHT series of $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$ with $x = 0.95$ heat-treated at a) 240 °C, b) 360 °C, and c) 480 °C. Heating time is indicated on the left for each pattern.

PHT samples below 360 °C, we can say there is a close relation between the degree of crystallinity and conductivity, with conductivity decreasing with increased crystallinity with one exception of HT at 360 °C for 4 h. We attribute this decrease in conductivity to the changing intergranular resistance with crystallization of the material [23]. Presumably as we heat treat materials, the crystal growth or phase change induces grain boundary reconstruction towards a structure with higher activation energy and therefore higher resistance. Figure 5.12b depicts the progression of HT of ABM powders at a constant temperature of 360 °C but for increasing HT

times of 1, 2, and 4 h. We see a largely increasing degree of crystallinity with increasing HT time, but do not observe the same relationship as that of increasing temperature and constant time that we do with conductivity. In the case of increasing time at constant temperature (Fig. 5.12b, 360 °C) we see an initial decrease in conductivity with increased crystallinity, but then observe an increase in conductivity when heat treated to the maximum time of 4 h. We attribute this rise in conductivity to the completion of reaction in the PHT pellets. We observed color gradients within broken PHT pellets for lower times, but a consistent color throughout when heat treated for 4 h. Because the temperature is highest on the outside of the pellet, the crystallization works inwards over time when held at a high temperature. Another explanation for the material gradient we observed could be due to the semi-rapid cooling the samples undergo after HT. By placing the PHT pellets on a cooling rack we have essentially quenched the material of which process could be responsible for the amorphous structure we see for the sample heat treated to 480 °C for 1 h (Fig. 5.12c).

Figure 5.13a shows the typical charge-discharge voltage profiles of LiCoO₂/Li cells using Li_{4-x}Ge_{1-x}P_xS_{2(1+x)}Se_{2(1-x)} (x = 0.95, heat-treated at 480 °C for 1 h). Table 3 summarizes the electrochemical performance of ABM and heat-treated samples. The columbic efficiency for the first cycle of all samples is poor, but rapidly increases to almost unity by the 10th cycle. The low coulombic efficiency mainly comes from a sloping plateau (‘#’) between 2.8-3.9 V indicates that a severe side reaction takes place on first charge process, which is also the case for all other cells using ABM and heat-treated SEs. We use differential capacity curves in Figure 5.13b to show the differences in degradation of PHT materials. The LiCoO₂ should ideally create a charge reaction voltage plateau at 3.93 V and a discharge reaction plateau at 3.90 V which varies with

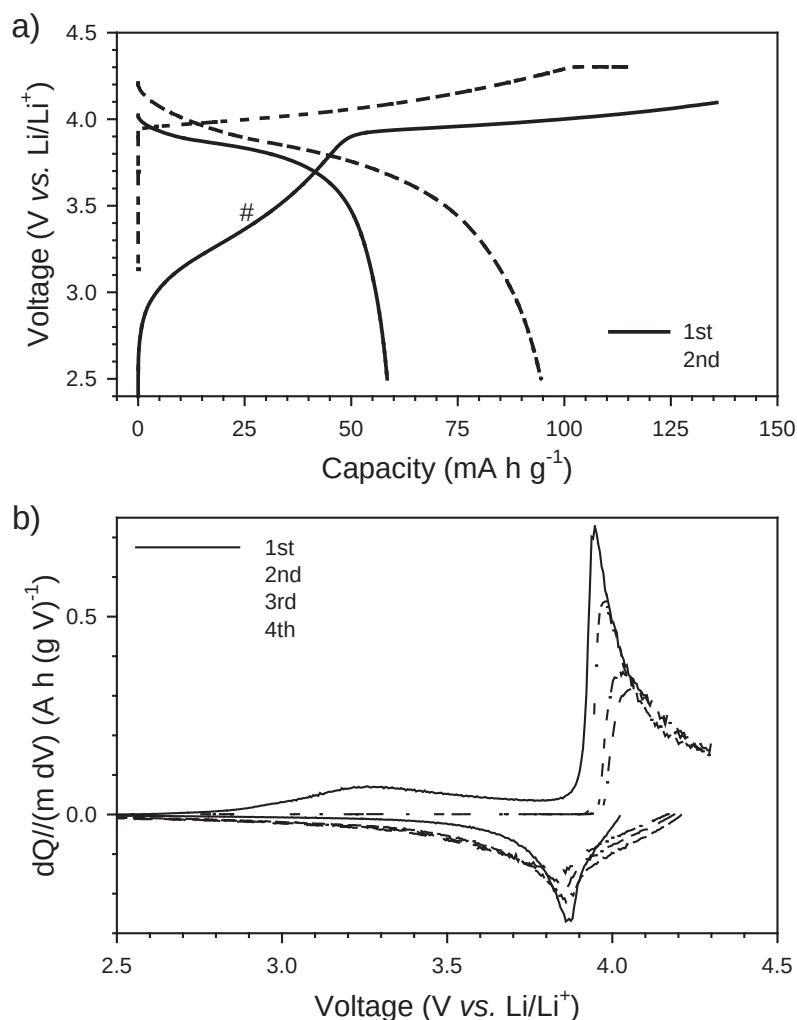


Figure 5.13: a) Charge-discharge and b) differential charge-discharge capacity profiles for $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$ with $x = 0.95$ heat-treated at 480 °C for 1 h.

dependence on electrolyte material and inconsistencies within a cell. Another noticeable theme in Figure 5.13b is the progression of reaction voltage away from ideal which could be the result of a space-charge layer developing at the SE interface with the electrode. It is also obvious that the specific capacity decreases with increased cycling which may also be due to a charge-layer build up. A reaction at the interface of SE and active material may be creating a resistance barrier that causes the reaction voltage to shift towards a larger polarization. We speculate that under applied current, the lithium in the SE within the composite as well as at the electro-

lyte/composite interface may be undergoing lithiation and delithiation. It is possible that a lithium deficiency in the SE may be the cause of lithium trapping in the composite electrode, and be responsible for the enormous side reaction on the first cycle. Such a process could result in a number of inconsistencies that would result in degradation due to stress, lithium trapping, or charge layer build up. We also consider that the poor discharge efficiency could be the result of Li corrosion in contact with the SE. A reaction between the interface of the SE and the Li metal could also be responsible for a charge layer build up. For all SE listed in Table 5.6, we found the sample heat-treated at 480 °C for 1 h shows the best performance; the smallest side reaction and the least capacity fade. Interestingly, the sample displaying the smallest first cycle side reaction and the best cycling performance is the only sample that has an amorphous structure.

Table 5.6: Electrochemical performance of $\text{LiCoO}_2/\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_{2(1+x)}\text{S}_{2(1-x)}$ with $x = 0.95/\text{Li}$ cells.

Heat-treatment		Capacity / mA h g^{-1}				
Temperature / °C	Time / h	1st		2nd		10th
		Charge	Discharge	Charge	Discharge	Discharge
ABM		141	33	94	63	17
240	4	126	46	103	82	39
360	1	138	60	123	96	29
360	2	154	53	113	88	41
360	4	162	60	122	96	38
480	1	136	58	115	95	62
480	2	124	53	112	89	34
480	4	136	58	115	95	33

In spite of the achievement of extremely high bulk conductivities comparable to that of liquid electrolytes, we can conclude that the inferior capabilities of all-solid-state cells lie with

interfacial discontinuities and reactions as well as chemical instability [23]. To improve the performance of all-solid-state batteries it is necessary to reduce resistances, in particular to improve the interface between electrodes and electrolytes to engender lower interfacial resistance [2,24,25].

5.3.3 Li₂O

Li₂S-Li₂O-P₂S₅ solid electrolytes produced by SSBM are shown to exhibit high conductivities over $1 \times 10^{-4} \text{ S cm}^{-1}$ at ambient temperature and all-solid-state cells with these SEs were confirmed to work as lithium secondary batteries. As was previously discussed, sulfide based solid electrolyte (thio-LISICONs) are preferable over oxide based solid electrolytes (LISICONs) for their high polarizability and large ionic radius that allow for higher conductivity. However, as discussed previously, sulfide based electrolytes are not completely stable against oxide based cathode materials such as LiCoO₂ due to the large potential difference. It is proposed in this section that incorporation of an oxide based lithium conductor, Li₂O, into the binary Li-P-S electrolyte will mitigate the potential difference between the oxide-based cathode and sulfide based electrolyte, thereby reducing any side reactions that may result in increased internal resistance within the cell. As it is well known that incorporation of oxygen into the sulfide electrolyte will reduce ionic conductivity, the benefits resulting from increased stability of the contacting oxide and sulfide species are projected to outweigh the conductivity losses.

Figure 5.14 shows the conductivity of two systems, $x\text{Li}_2\text{S}-(80-x)\text{Li}_2\text{O}-20\text{P}_2\text{S}_5$ (mol%) (20P₂S₅) and $x\text{Li}_2\text{S}-(70-x)\text{Li}_2\text{O}-30\text{P}_2\text{S}_5$ (mol%) (30P₂S₅). High conductivities over $1 \times 10^{-4} \text{ S cm}^{-1}$

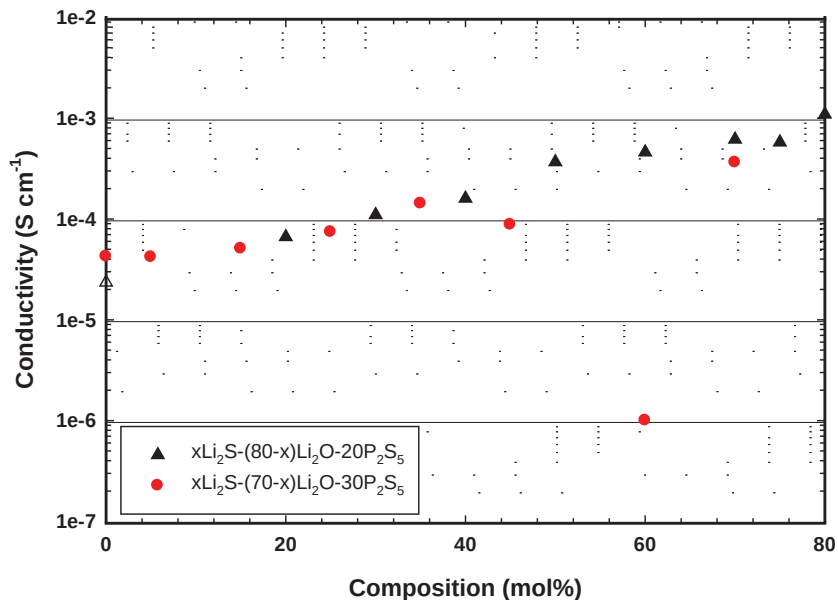


Figure 5.14: Conductivity map for the $x\text{Li}_2\text{S}-(80-x)\text{Li}_2\text{O}-20\text{P}_2\text{S}_5$ (mol%) and $x\text{Li}_2\text{S}-(70-x)\text{Li}_2\text{O}-30\text{P}_2\text{S}_5$ (mol%) systems.

are observed for the $20\text{P}_2\text{S}_5$ system above $x=30$, and above $x=35$ for the $30\text{P}_2\text{S}_5$ system, with maximum conductivities of $6.2 \times 10^{-4} \text{ S cm}^{-1}$ and $3.7 \times 10^{-4} \text{ S cm}^{-1}$ for the $20\text{P}_2\text{S}_5$ and $30\text{P}_2\text{S}_5$ systems respectively. In the $30\text{P}_2\text{S}_5$ system, an interesting trend is observed in which a sharp decrease in conductivity down to $1 \times 10^{-6} \text{ S cm}^{-1}$ is observed for the composition $x=60$. This could be due to some large structural transformation in the electrolyte causing lower ionic conductivity.

A binary system of the formula $x\text{Li}_2\text{O}-(100-x)\text{P}_2\text{S}_5$ was also investigated, and its conductivity map is shown in Figure 5.15. Interestingly, it is found that without Li_2S , only a single composition of $x=60$ maintains a conductivity above $1 \times 10^{-4} \text{ S cm}^{-1}$. The observed lower conductivity of the whole system is attributed to the relative absence of highly conducting sulfide anions. As we expected, incorporation of less polarizable and smaller ionic radius oxygen into the sulfide system greatly reduced ionic conductivity.

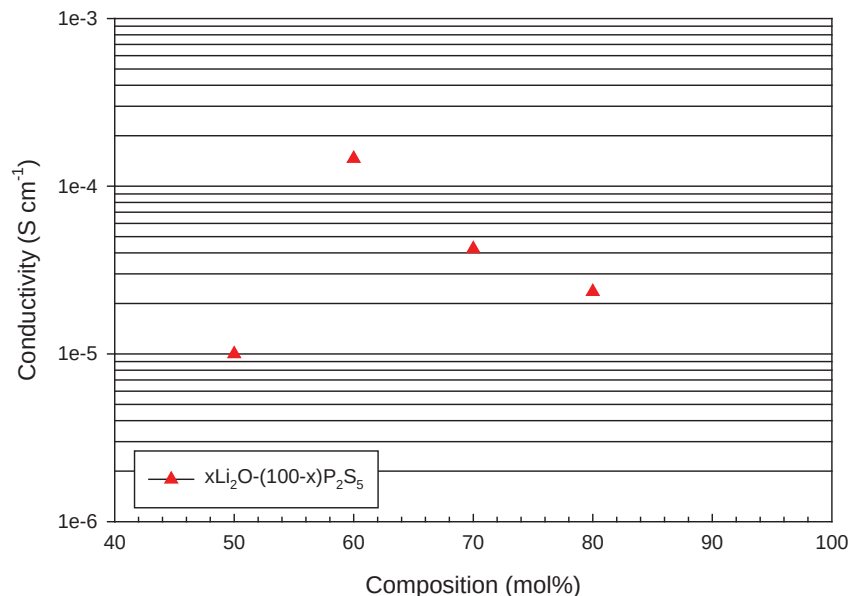


Figure 5.15: Conductivity map for the binary $x\text{Li}_2\text{O}-(100-x)\text{P}_2\text{S}_5$ system.

While conductivity of Li_2O containing solid electrolytes was lower by almost an order of magnitude from the binary Li-P-S and GeS_2 modified systems, electrochemical measurements revealed improved cycle stability (Figure 5.16a). Li_2O electrolytes were employed similarly to the GeS_2 system as with double layer electrolytes due to the irreversible reaction between oxygen and lithium metal. As was discovered previously, the highest conductivity electrolyte did not necessarily yield the best results, in regard to cycling behavior. Utilization of 40 Li_2S -40 Li_2O -20 P_2S_5 , with a conductivity just above $1 \times 10^{-4} \text{ S cm}^{-1}$ showed the best results. An initial reversible capacity over 120 mAh g^{-1} was observed with a LiCoO_2 cathode in a lithium battery configuration. While degradation remains a problem for the Li_2O system, a reversible capacity of approximately 70 mAh g^{-1} for 100 cycles is recorded. Inconsistency is observed for the entirety of cycling, which is a result of temperature variation in the testing environment. Rapid stabilization of the electrolyte within the first 10 cycles is observed, for after the first 10 cycles,

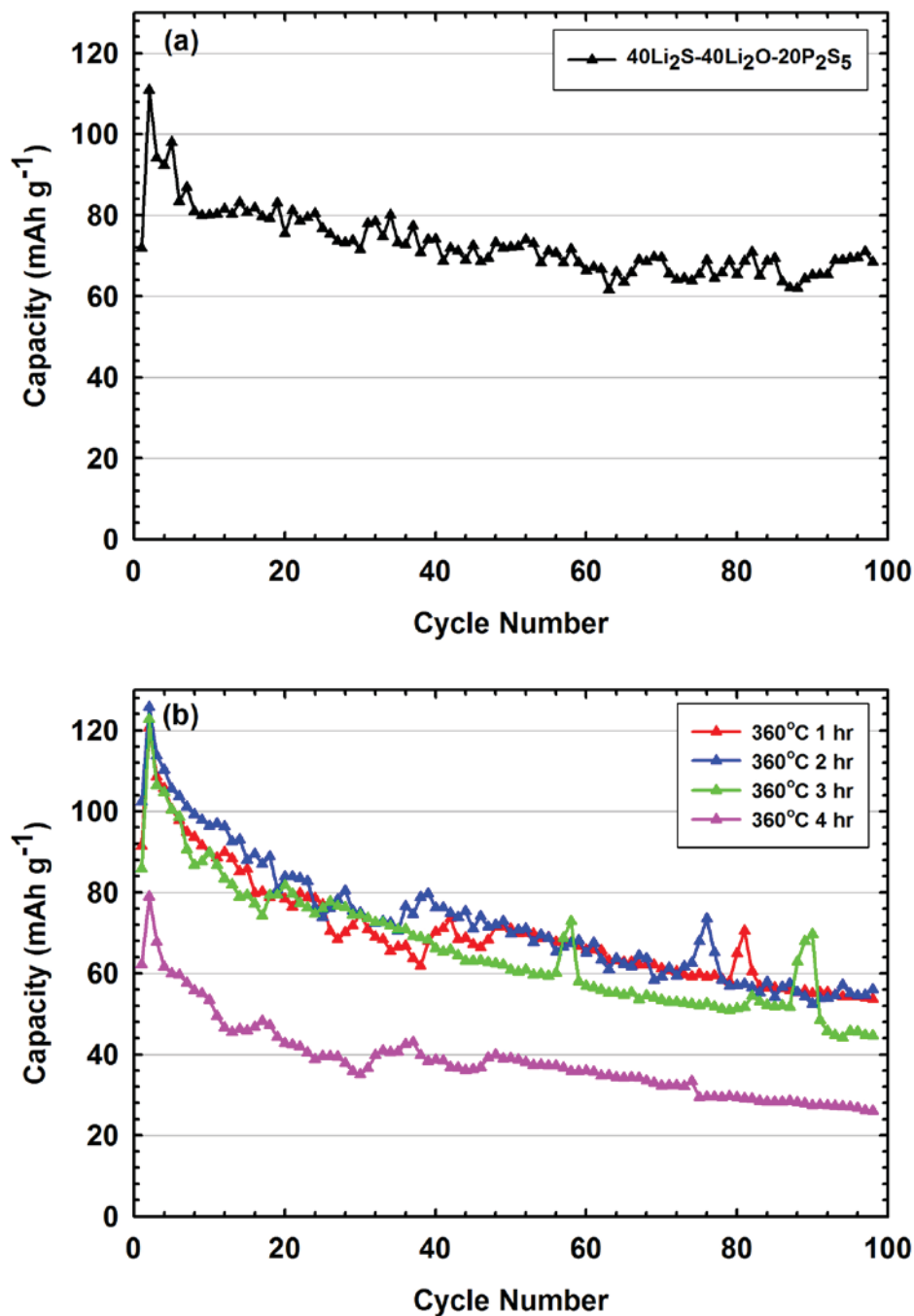


Figure 5.16: (a) Cycling stability of the LiCoO₂/40Li₂S-40Li₂O-20P₂S₅/Lithium cell. (b) Comparison of cells employing various heat treated 40Li₂S-40Li₂O-20P₂S₅ electrolytes.

we see only a ~12% decrease in reversible capacity up to 100 cycles. Other compositions of Li₂O electrolytes corresponding to the compositions shown in Figure 5.14 and 5.15 for

conductivity were examined electrochemically, but revealed less desirable performance compared to the $40\text{Li}_2\text{S}-40\text{Li}_2\text{O}-20\text{P}_2\text{S}_5$ electrolyte.

Similar to the GeSe_2 experimentation, heat treatment was performed on the most favored electrolyte and the resulting electrochemical performances were measured and compared. It was found that heat treating the electrolyte did not benefit electrochemical cycling, and in fact resulted in decreased performance, as shown in Figure 5.16b. A comprehensive scheme of heat treatment temperature and time was employed in generating heat treated $40\text{Li}_2\text{S}-40\text{Li}_2\text{O}-20\text{P}_2\text{S}_5$ samples, however only a single series is disclosed. For electrolytes heated at 360°C in the range of 1-4 hours, no large differences in performance are observed, unlike the results of the GeSe_2 study.

5.4 Conclusion

Glass-ceramic and glass $\text{Li}_2\text{S}-\text{GeSe}_2-\text{P}_2\text{S}_5$ ($\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$) electrolytes with various compositions from $x = 0.55$ to $x = 1.00$ were prepared by a simple SSBM process. The $\text{Li}_2\text{S}-\text{GeSe}_2-\text{P}_2\text{S}_5$ showed high conductivities of maximum $1.4 \times 10^{-3} \text{ S cm}^{-1}$ for $x = 0.95$ in $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$. Structural analysis showed that inclusion of GeSe_2 leads to the increased lattice followed by occurrence of new phase. All-solid-state LiCoO_2/Li cells using $\text{Li}_2\text{S}-\text{GeSe}_2-\text{P}_2\text{S}_5$ system showed a high specific capacity of over 100 mAh g^{-1} for the second cycle. HT of the ABM resulted in lower overall conductivities but better cycling performance and electrochemical stability. Especially, the sample heat treated at 480°C at 1 h for $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_{2(1+x)}\text{Se}_{2(1-x)}$ with $x = 0.95$ resulted in an amorphous structure that exhibited the best performance among all samples. With the observation of relatively high conductivities comparable to

that of liquid electrolytes, we can conclude that the inferior capabilities of all-solid-state cells lie with interfacial reactions and chemical instabilities.

Glass-ceramic $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ ($\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$) electrolytes with various compositions from $x = 0.70$ to $x = 1.00$ were prepared by a simple SSBM process. The $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ SE showed high conductivities of maximum $1.2 \times 10^{-3} \text{ S cm}^{-1}$ for $x = 0.95$ in $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$. Structural analysis showed that inclusion of GeS_2 leads to the enlarged lattice structure followed by occurrence of amorphous structure. HT of the SSBM material with 1 wt.% elemental sulfur resulted in increased capacity (129 mA h g^{-1} at the second cycle), better cycling performance and electrochemical stability of all-solid-state LiCoO_2/Li cells. Instability problem of the $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ in contact with Li was solved by using bilayer electrolyte configuration ($\text{Li}/(\text{Li}_2\text{S-P}_2\text{S}_5/\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5)/\text{LiCoO}_2$). With the observation of ionic conductivities comparable to that of liquid electrolytes, we can conclude that the inferior performances of all-solid-state cells lie with interfacial reactions and chemical instabilities.

Multiple solid electrolytes systems containing Li_2O were prepared by a simple SSBM process. A maximum conductivity of $6.2 \times 10^{-4} \text{ S cm}^{-1}$ for the $x\text{Li}_2\text{S-(80-x)Li}_2\text{O-20P}_2\text{S}_5$ (mol%) system and $3.7 \times 10^{-4} \text{ S cm}^{-1}$ for the $x\text{Li}_2\text{S-(70-x)Li}_2\text{O-30P}_2\text{S}_5$ (mol%) system was observed. While its conductivity was only $1 \times 10^{-4} \text{ S cm}^{-1}$, the $40\text{Li}_2\text{S-40Li}_2\text{O-20P}_2\text{S}_5$ electrolyte exhibited the best overall cycling performance maintaining $\sim 70 \text{ mAh g}^{-1}$ for 100 cycles. Heat treatment of the $40\text{Li}_2\text{S-40Li}_2\text{O-20P}_2\text{S}_5$ electrolyte did not result in any benefit to cycling performance. Cycle stability was improved by incorporating an oxygen containing species, Li_2O , into the sulfide electrolyte. However, further investigation is required as interfacial reactions and chemical instability continues to cause degradation of cell performance.

Using the best electrolytes (for electrochemical cycling) made by SSBM, the electrochemical cycling data for respective $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$, and $\text{Li}_2\text{S-Li}_2\text{O-P}_2\text{S}_5$, and binary $\text{Li}_2\text{S-P}_2\text{S}_5$ electrolytes are compared (Figure 5.17a). With regard to the electrolyte additives, a significant

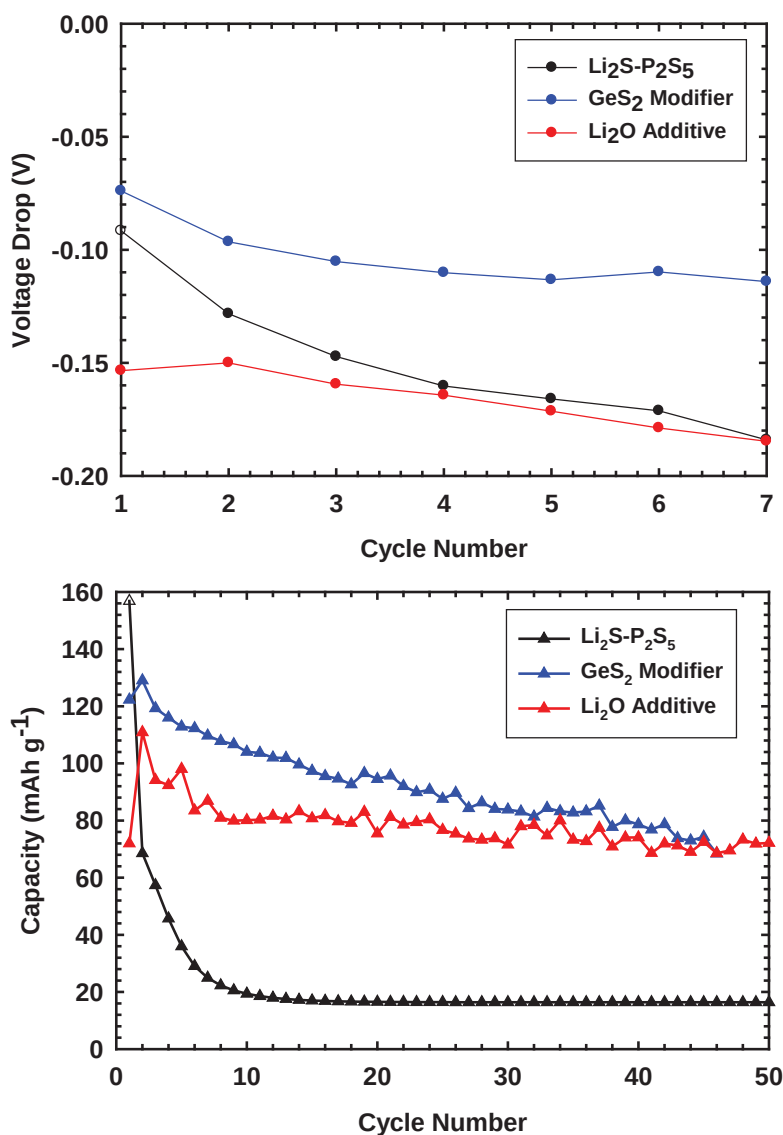


Figure 5.17: (a) A comparison of the cycling performance of the best performing GeS_2 and Li_2O electrolytes previously discussed vs. the performance of binary Li-P-S electrolyte. (b) Observa-

tion of the stability of electrolytes as a function of increasing voltage drop resulting from side reactions causing higher resistance within $\text{LiCoO}_2/\text{SE}/\text{Li}$ cells (See Figure 5.1).

improvement in cycling performance is observed over the binary electrolyte. The GeS_2 electrolyte exhibits much higher capacity initially, but degrades quite rapidly when compared to the Li_2O electrolyte. While initial capacity is lower for the Li_2O electrolyte compared to the GeS_2 electrolyte, slower degradation allows it to maintain a higher capacity after 50 cycles. Figure 5.17b shows a comparison of the development of higher resistance within the cell resulting from side reactions. While the value for the voltage drop of the Li_2O electrolyte is larger, simply as a result of lower conductivity of the electrolyte, the rate at which the voltage drop increases is significantly lower than the GeS_2 and binary electrolytes. This is a clear indication of the improvement in cycling stability and reduction of side reactions as a result of electrolyte additives for obtaining better cycle stability of all-solid-state batteries containing sulfide-based solid electrolyte.

5.5 Summary

In this chapter we discussed the utilization of LiCoO_2 in all-solid-state batteries. It was found that a highly resistive layer forms at the interface of the electrolyte and electrode material causing losses in cycle performance. In this work, we used electrolyte additives enhance the conductivity and stability of the sulfide electrolytes to prevent excess reactions between the electrolyte and electrode materials, thereby reducing capacity fade.

Incorporation of large, sulfide containing additives resulted in improved ionic conductivity of electrolytes. In the system $\text{Li}_2\text{S}-\text{GeSe}_2-\text{P}_2\text{S}_5$, high conductivities over $1 \times 10^{-3} \text{ S cm}^{-1}$ were

obtained, with a maximum of $1.4 \times 10^{-3} \text{ S cm}^{-1}$. While implementation of GeSe_2 resulted in a high conductivity electrolyte, it exhibited poor electrochemical cycling performance with a LiCoO_2 positive electrode. The $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ SE showed similarly high conductivities with a maximum $1.2 \times 10^{-3} \text{ S cm}^{-1}$. GeS_2 electrolytes with sulfur integration showed high conductivity and improved electrochemical cycling, with a second cycle capacity of 129 mAh g^{-1} and better cycle stability. As expected, inclusion of an oxide modifier, Li_2O , into the $\text{Li}_2\text{S-P}_2\text{S}_5$ system reduced conductivity, however high conductivity of $\text{Li}_2\text{S-Li}_2\text{O-P}_2\text{S}_5$ electrolytes over $1 \times 10^{-4} \text{ S cm}^{-1}$ were achieved, with a maximum of $6.2 \times 10^{-4} \text{ S cm}^{-1}$. While introducing an oxide into electrolytes reduced conductivity, electrolytes containing Li_2O exhibited the best cycle stability of all tested materials with a reversible capacity of $\sim 70 \text{ mAh g}^{-1}$ for 50 cycles was achieved. Additives for solid electrolytes were successfully employed to improve the conductivity of electrolytes but more importantly improve the stability of sulfide based-solid electrolytes against oxide-based LiCoO_2 .

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6. High Power/Energy Density All-Solid-State Batteries

6.1 Overview and introduction

Lithium-ion batteries have the highest energy density of all commercialized rechargeable batteries [1-3]. In order to employ Li-ion batteries (LIBs) in next generation electric vehicles (HEVs and PHEVs), LIBs must satisfy many requirements: electrodes with long lifetimes, stability over a wide temperature range, high energy density, and high rate capability [4-8]. However, large scale utilization of lithium-ion battery technology has been limited due to safety issues associated with liquid electrolytes and the low specific capacity of typical positive electrode materials such as LiCoO_2 (137 mAh g^{-1}) [3,9,10].

Liquid-containing rechargeable lithium-ion batteries have exhibited major safety issues in the past owing to the hazardous and flammable nature of commercialized liquid electrolytes [11-13]. Furthermore, liquid electrolyte decomposition with the electrode material has shown to significantly decrease battery performance [14,15]. Use of a nonflammable solid electrolyte in lithium-ion batteries offers the possibility of avoiding the safety issues associated with conventional lithium-ion batteries containing combustible liquid electrolytes [16-18]. Simply, construction of an all-solid-state rechargeable lithium battery using solid electrolyte inherently resolves a large majority of the safety issues associated with lithium battery technology [19]. Unfortunately, all-solid-state lithium batteries typically exhibit lower power density, which is attributed to the positive electrode, in regard to large interfacial resistances, poor kinetics, and unwanted reactions with the solid electrolyte [18,20-23].

Despite its high cost and limited capacity, lithium cobalt oxide (LiCoO_2) is widely accepted as a positive electrode material for rechargeable lithium-ion batteries due to its high energy/power density capabilities [24]. Its capacity for highly reversible intercalation of lithium

as well as long cycle life have proven LiCoO_2 highly suited for use in liquid-based rechargeable lithium-ion batteries [25,26]. However, implementation of LiCoO_2 into all-solid-state batteries has resulted in high interfacial resistances between the electrode and electrolyte as a result of incompatibility of LiCoO_2 with solid electrolytes relating to the high oxidation potential of the oxide-based electrode materials [20]. This large interfacial resistance not only leads to poor reversibility and cycle life, but prevents all-solid-state rechargeable lithium-ion batteries from performing at high rates [27,28]. Characteristically, a more effective cathode material for solid state integration would have an oxidation potential close to that of the electrolyte in order to prevent the formation of a highly resistive interface.

Titanium disulfide (TiS_2) is a well-known electrode material that exhibits high energy density and high power in lithium batteries [15,29]. Since its inception as a prospective intercalation compound in the 1970's, its physical and electrochemical properties have been studied extensively [30]. At the time, TiS_2 was considered the most promising electrode material because it expresses exceedingly high conductivity and lithium diffusion rates, as well as being the lightest and cheapest of all group IVB and VB layered dichalcogenides [31]. Whittingham et. al. performed considerable research on TiS_2 as an electrode material for lithium batteries and revealed it to be a very stable and high capacity electrode material that exhibits long cycle life [32]. However, while TiS_2 performed exceptionally well as a cathode material, it required a lithium battery construction that was not viable due to safety problems with liquid electrolytes [9]. TiS_2 was later shown to be compatible in a thin-film solid state construction but was never fully explored in an all-solid-state bulk-type construction. The introduction of layered oxides by Goodenough et al., lithium-ion “rocking chair” batteries by Murphy et al. and Scrosati et al., and

development of the first lithium-ion batteries by Sony in the 1990's deterred further exploration of TiS_2 lithium batteries [9].

In this work we demonstrate TiS_2 as a suitable cathode material for construction of all-solid-state lithium batteries. The fast kinetic and conductive properties as well as lower electrode potential enable its successful use in solid state batteries. As proposed by Whittingham et al., we demonstrate that no conductive additive is required in constructing the composite cathode, as the electronic conductivity of TiS_2 is sufficiently high for fast electron transport through the composite electrode to the current collector [25,29]. We reduce particle size of TiS_2 as a way to effectively increase utilization of active materials and improve the power density [8]. While batteries tested at room temperature revealed better electrochemical cycling behavior for size reduced material, the ionic conductivity of the solid electrolyte was found to be limiting for our observation of enhanced kinetics. Testing at an elevated temperature of 60°C allowed sufficient ionic conductivity of the solid electrolyte for observation of enhanced kinetics of size reduced materials, as well as better utilization of active materials.

6.2 Experimental

6.2.1 Preparation of the TiS_2 active materials

TiS_2 (Sigma-Aldrich, 99.9%) was ball milled in a 100mL agate vial (Across International) at a net weight of 500 mg. Large-ball-milled (LBM) material was prepared using 10 agate balls (10mm diameter) and small-ball-milled (SBM) material with 50 agate balls (6mm diameter) for grinding. Ball milling (Across International PQ-N4) took place for 2 continuous hours for

LBM material and 5 continuous hours for SBM material in an Argon environment before the material was recovered and used without further modification.

6.2.2 Preparation of the Solid-State Electrolyte TiS_2 Composite Cell

$\text{Li}_2\text{S-P}_2\text{S}_5$ electrolyte prepared by planetary ball milling was used as the solid-electrolyte (SE) [33]. Milling resulted in amorphous electrolytes with room temperature and elevated temperature conductivity of $9.32 \times 10^{-4} \text{ S cm}^{-1}$ and $2.54 \times 10^{-3} \text{ S cm}^{-1}$ respectively. Composite electrodes were prepared by mixing our ball milled and non-ball-milled TiS_2 powders with SE in a mortar at a ratio of 1:2 respectively. For composites including acetylene black (AB) (Alfa-Aesar, 50% compressed) as a conductive additive, a ratio of 10:20:1 was used for the TiS_2 , solid electrolyte, and acetylene black respectively. Battery pellets are formed by cold-pressing (5 metric tons) 10 mg of the composite cathode material on top of 200 mg of SE for 5 min. Li foil (Alfa-Aesar, 0.75 mm thick) is then attached to the SE surface at 2 metric tons. All pressing and testing operations are carried out in a polyaryletheretherketone (PEEK) mold ($\phi = 1.3 \text{ cm}$) with Ti metal rods as current collectors for both working and counter electrodes. All processes were carried out in an Ar-filled glove box.

6.2.3 Cell Testing

Galvanostatic constant-current-constant-voltage (CCCV) charge-discharge cycling took place between 1.5 and 3.0 V at room temperature (25°C) and high temperature (60°C) using an Arbin BT2000 with a one hour voltage hold at 3.0 V after charging. The Galvanostatic Intermit-

tent Titration Technique (GITT) used 0.5C discharging for both discharge of the cell, and pulse measurement. Rest time for GITT testing was 2 hours, and the pulse time was 30 seconds, with a 30 second rest after the pulse before resuming discharge. Ball milled powder samples were characterized by XRD Cu-K α radiation (Scintag XGEN-4000) measurement and Raman spectroscopy (Jasco NRS-3100).

6.3 Nanostructured materials characterization

In recent years, high energy ball milling has been shown to be a very effective means of particle size reduction [34]. In addition, it is a room temperature process that is relatively fast and low cost [33]. The high energy attrition process involves grinding between two surfaces, the ball and the inner surface of containing jar, that results in particle breakage. It has been shown that smaller ball size will maintain a smaller contact area for grinding and result in reduced particle size [34]. In this respect, we used different size balls during ball milling to achieve a range of sizes for materials.

Field emission scanning electron microscope (FESEM) images of the various sizes of TiS₂ materials are shown in Figure 6.1. As-received TiS₂ with no ball-milling modification has been classified in this work as non-ball-milled TiS₂ (NBM) for simplicity. NBM exhibits a very large particle size distribution and an average particle size of approximately 10 μ m. The layered structure of TiS₂ is very obvious among the NBM plate-like particles, of which layers we found to be approximately 100 nm thick through further imaging. We fabricated two sizes of ball-milled material using different size balls, large and small. The material produced with the large

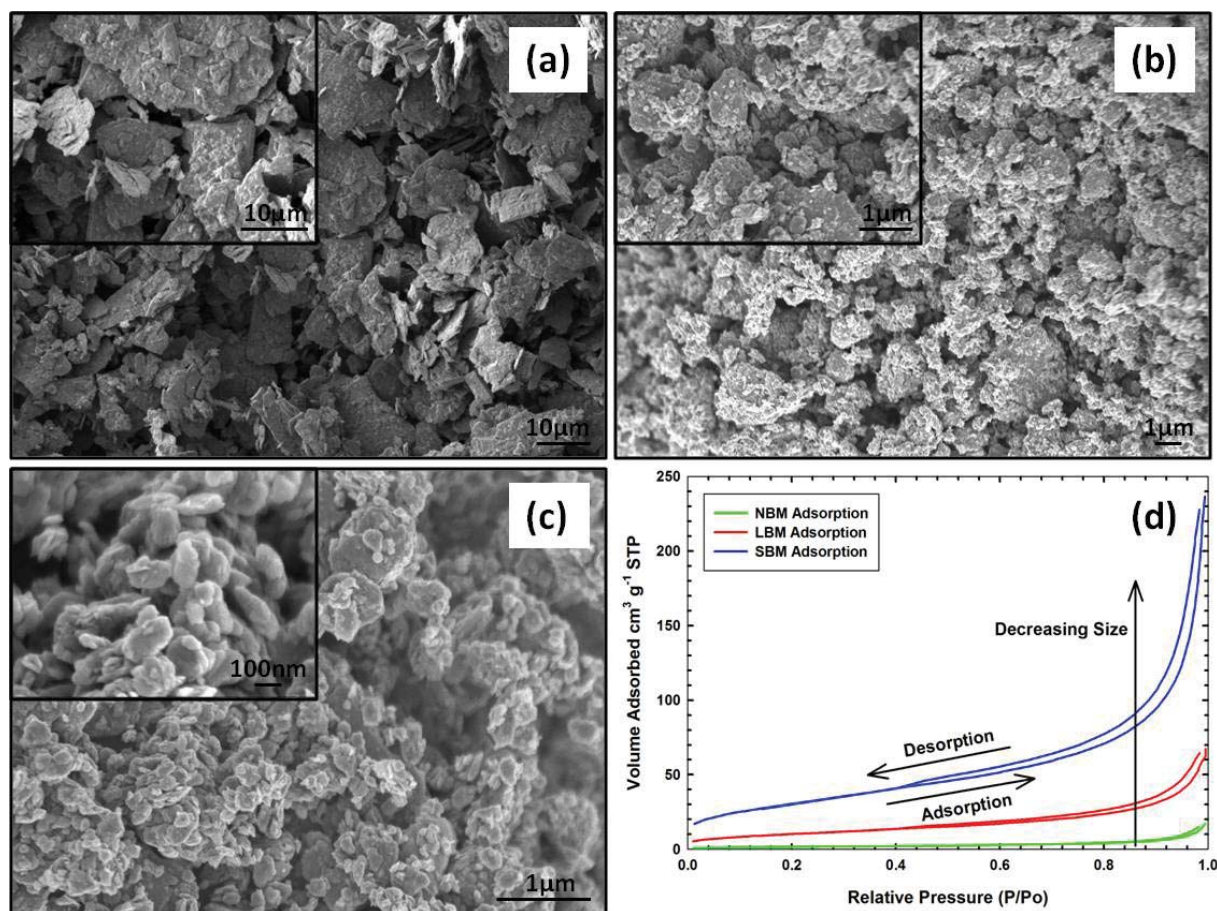


Figure 6.1: FESEM micrographs of (a) NBM, (b) LBM, and (c) SBM particles, showing a reduction in particle size of two orders of magnitude from NBM to SBM. (d) BET isotherms for NBM, LBM, and SBM showing significant increase in adsorption for size reduced materials.

balls is referred to as large-ball-milled TiS_2 (LBM) and the material produced with smaller balls is referred to as small-ball-milled TiS_2 (SBM). The FESEM imaging reveals that LBM has an average particle size near 1 μm , and the SBM to have a particle size of approximately 100 nm. However agglomeration of the SBM is observed as a result of the high surface energy of nano-particles. We were able to successfully reduce the particle size of TiS_2 by two orders of magnitude to an average size of 100 nm by ball milling.

In order to confirm particle size and distribution of our materials we measured the specific surface area using Brunauer-Emmett-Teller (BET) adsorption. Figure 6.1d shows the isotherms collected for all three sizes of materials. The BET method involves the determination

of the amount of the adsorbate or adsorptive gas required to cover the external and the accessible internal pore surfaces of a solid with a complete monolayer of adsorbate. This monolayer capacity can be calculated from the adsorption isotherm. For NBM we obtain a specific surface area of $5.63 \text{ m}^2 \text{ g}^{-1}$ and for the LBM and SBM, 36.44 and $107.12 \text{ m}^2 \text{ g}^{-1}$ respectively. These values confirm that we are effectively increasing the surface area of particles by reducing their size. A non-linear trend of increasing specific surface area is observed for particles due to the change in overall shape of particles with size reduction, as shown in Figure 6.1. As we reduce the particle size to the nanoscale, we see more cylinder-like than plate-like particles. Broad size distribution, agglomeration, and changing particle geometry attribute to inconsistencies between the FESEM estimated particle sizes and corresponding BET specific surface area, however there is good agreement in the overall trend between the two sets of data.

While ball milling is a proven technique for reducing particle size of materials, the process is also capable of changing the structure of materials [35]. To verify we have not changed the structure of TiS_2 in reducing particle size, we show the Raman spectra for all three materials in Figure 6.2a. We see no significant changes in structure as the characteristic frequencies for all materials are consistent. Raman spectra of our TiS_2 show strong scattering at 334 cm^{-1} with a shoulder at 380 cm^{-1} and a very shallow scattering peak in the region of 227 cm^{-1} , which agrees well with previous literature [36-38]. To further verify the structure of our size reduced materials, we show x-ray diffraction (XRD) patterns for all materials in Figure 6.2b. Collected data is consistent with HCP 1T- TiS_2 powder reported in the previous literature [39-41]. The NBM exhibits all of the signature peaks of TiS_2 with good relative intensity while the LBM and SBM resulted in intensity reduction and/or complete vanishing of the (00l) planes (basal

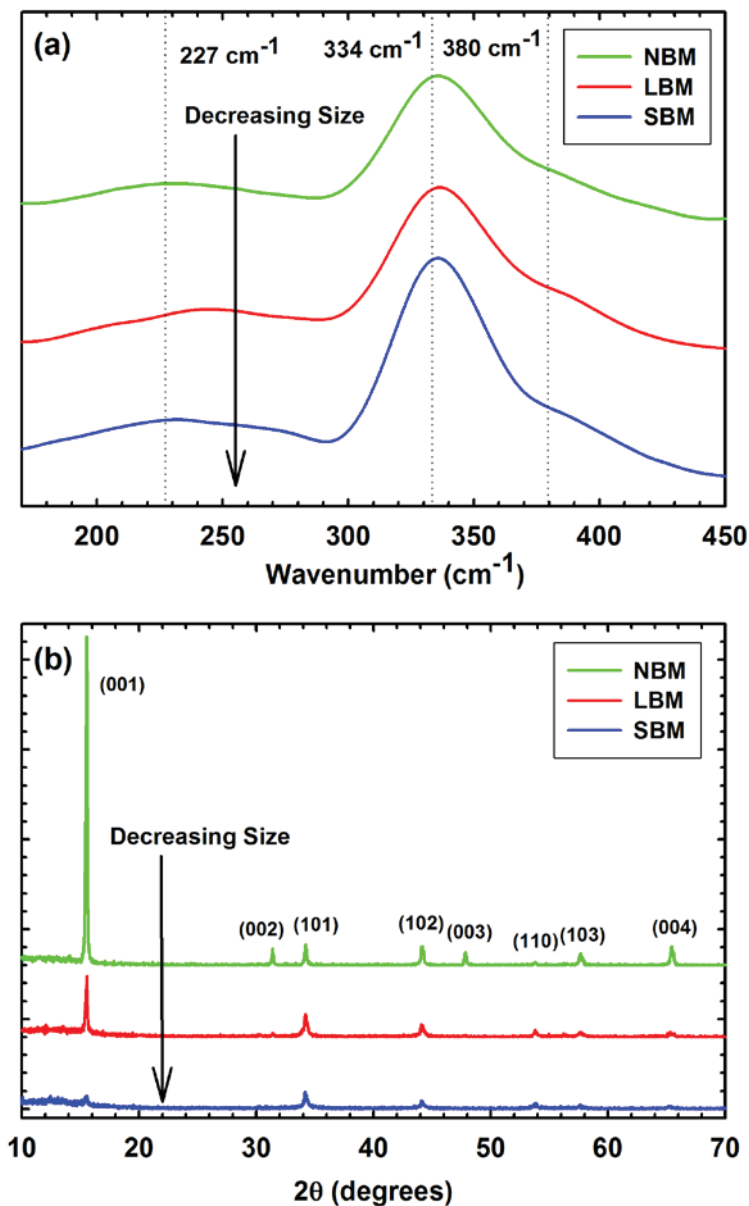


Figure 6.2: (a) Raman spectra for NBM, LBM, and SBM show no significant change in micro-structure as particle size decreases. (b) X-ray diffraction patterns for all three TiS₂ materials revealing no significant structural changes related to ball milling of TiS₂ to reduce particle size. Basal plane indexes fade as particle size is reduced and the structure of TiS₂ is changed from plate-like to cylinder-like.

plane) peaks. This result is consistent with the FESEM micrographs in Figure 6.1 through observation of the plate-like structure of NBM and the more cylinder-like particles of LBM and

SBM. Because we have eliminated the very long range order of the micrometer-sized layered particles we observe a marked decrease of intensity for respective peaks. We also observe the overall reduction of peak intensity as a result of reduced particle size [42]. Raman spectroscopy and XRD measurements confirm that TiS_2 powder maintains structural stability as particle size is reduced by high energy ball-milling.

6.4 Electrochemical measurement and analysis

In order to examine the capabilities of the composites when used as cathode materials for rechargeable batteries, composite/solid-electrolyte/lithium cells were fabricated and characterized. Initial efforts focused on determination of an ideal cathode composite construction regarding the ratio of active material to solid electrolyte. Based upon observation of highest obtainable capacity, cycle life, and coulombic efficiency at relatively low rates and at room temperature, we determined an ideal ratio of 1:2 of active material and solid electrolyte respectively, for constructing our composite cathodes. Incorporation of a conductive additive (acetylene black) at the various tested composite compositions showed insignificant changes regarding capacity, cycle life, and efficiency and confirmed best results using a ratio of 1:2 for active material and solid electrolyte respectively.

After determination of ideal composite construction, battery characterization was focused on achieving high power density from our cathode. Figure 6.3a shows the rate performance of NBM at room temperature with and without a conductive additive. We see a comparison of the typical discharge profiles for both samples showing little difference in performance at low rates.

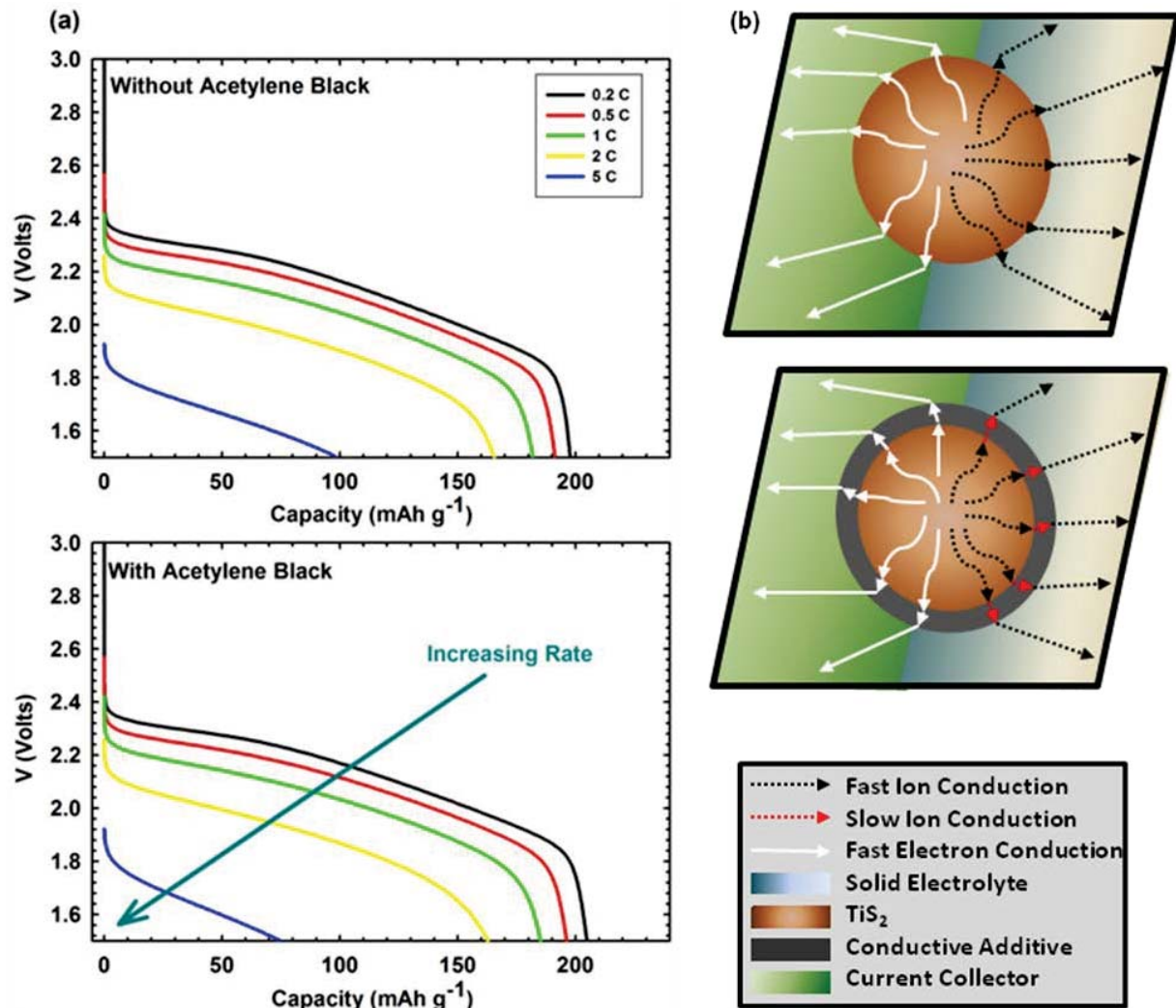


Figure 6.3: (a) Effect of conducting additive (AB) on the electrochemical rate capability of TiS₂ composite electrodes. The horizontal axis indicates the specific capacity that was calculated on the basis of the weight of the active material. (b) Mechanistic diagram of slowed ion conduction as a result of conductive additive blocking. Fast electron conduction is maintained through the AB but mass transfer is restricted as a result of poor ion conducting properties.

This result indicates that no conductive additive is necessary for use with a TiS₂ based electrode due to its mixed conducting properties. In particular electronically conducting properties are high enough to sustain fast electron transport through the composite to the current collector [25,29]. Furthermore, we find that at high rate, incorporation of a conductive additive into the composite cathode actually decreases performance significantly. When cycled at a rate of 5C, a 23%

decrease in achievable capacity has been observed for batteries with an addition of only ~3% acetylene black. Further addition of acetylene black showed a continued trend of decreasing cell performance. Testing with ball-milled materials as well as testing at elevated temperatures yielded similar results, with an overall observation of decreased performance with the addition of conductive additive to composite cathodes at high rates. This drop in high rate performance is attributed to the conductive additive blocking of ion conduction from the active material TiS_2 particles. As we depict in Figure 6.3b the acetylene black is essentially acting as an ionically insulating layer around the active material particles, effectively limiting the capacity at high rates. At low rates, this barrier effect is not observed because the transport capabilities of TiS_2 are beyond what is required for the applied current. TiS_2 maintains a high electrical conductivity in solid state composite cathodes and is sufficient enough for electron transport without the use of a conductive additive.

In order to examine the practical power density capabilities of the composites when used as cathode materials for rechargeable batteries, the composite/solid-electrolyte/lithium cells were discharged at various current rates ranging from .2C up to 10C with a charging rate of 0.5C. Figure 6.4a shows the voltage discharge profiles from electrochemical testing of all three sizes of material at room temperature with increasing rates. We observe significantly better results from ball-milled materials over the NBM material, with only slight variation in performance between the ball-milled samples. We attribute the increased capacity of ball-milled materials at high rates to the reduced particle size of TiS_2 . Smaller particles have shorter lithium diffusion paths and better kinetic properties that allow for better utilization of active materials [43,44]. We observe only slight variation of performance between the ball-milled samples which is attributed to the

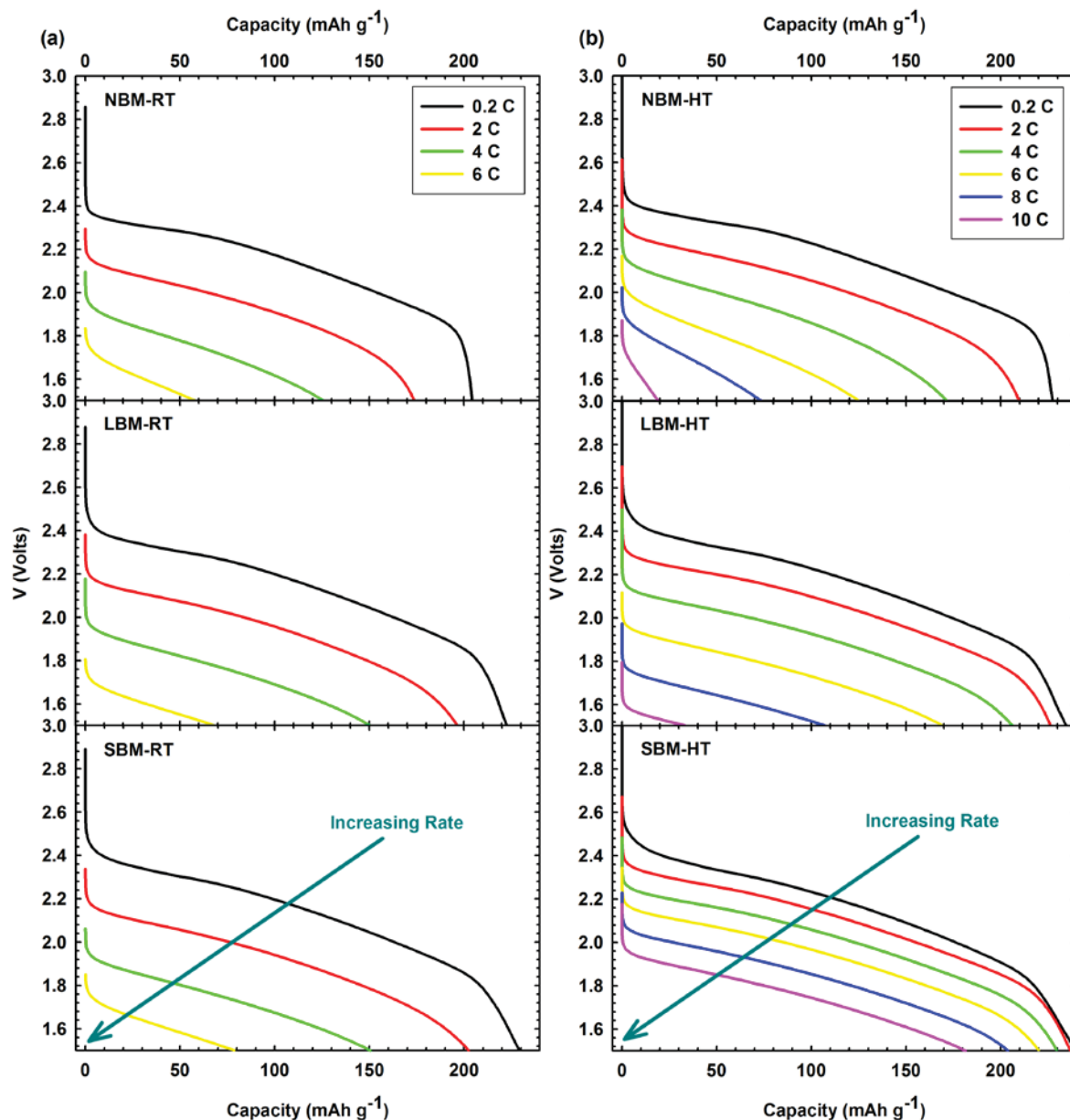


Figure 6.4: Electrochemical rate testing of all three materials at (a) room temperature and (b) elevated temperature showing superior rate performance of SBM. The notation (-RT) indicates samples tested at approximately room temperature 25°C, while the notation (-HT) denotes samples tested at high (elevated) temperature tested at approximately 60°C. Room temperature rate testing succeeded at current densities up to 6 C while the rate testing of elevated temperature samples succeeded at current densities up to 10 C.

limited ionic conductivity of the solid electrolyte at room temperature. Due to a relatively low bulk conductivity of the solid electrolyte at room temperature, observation of the kinetic benefit

associated with reduced particle size is difficult to recognize. As the conductivity of the electrolyte is limiting at room temperature, we tested batteries at 60°C under the same conditions as the room temperature cells, which is reported in Figure 6.4b. At elevated temperature, the ionic conductivity of the solid electrolyte is no longer limiting and we can clearly observe a difference in kinetic behavior with changing material size. One obvious effect is the high rate capability at elevated temperature. For room temperature samples we observe an appreciable capacity up to only 6C, whereas at elevated temperature we successfully cycle at 10C. We observe a marked enhancement of high rate performance from cells at elevated temperature, especially for the SBM material. The SBM material exhibits a discharge capacity of 180 mAh g⁻¹ at 10C when cycling at elevated temperature. It shows no loss in capacity ranging from 0.2C up to 2C, maintaining almost theoretical capacity for TiS₂ at 239 mAh g⁻¹. Increasing the applied current from 0.2C up to 10C for all materials at elevated temperature we see a 92% decrease in capacity for NBM composites and 86% decrease for LBM composites, but observe only a 25% decrease in achievable capacity for SBM materials. We attribute this excellent capacity retention to the reduced size of particles. The size reduced particles allow for improved Li ion kinetics resulting in a more effective utilization of active material.

A synopsis of the power capabilities of the different materials at both room and elevated temperature is shown in Figure 6.5. The Ragone plot shows the relationship between the energy density and the average power density of cells cycled at various current densities. We see that high temperature samples show an excellent improvement in power over room temperature samples, with SBM material exhibiting over 1000 W kg⁻¹ at 10C. In comparison to current state-of-the-art (SOA) power density of liquid cells, we see that the power density of our SBM material at 60°C is beyond the current state-of-the-art capabilities [20].

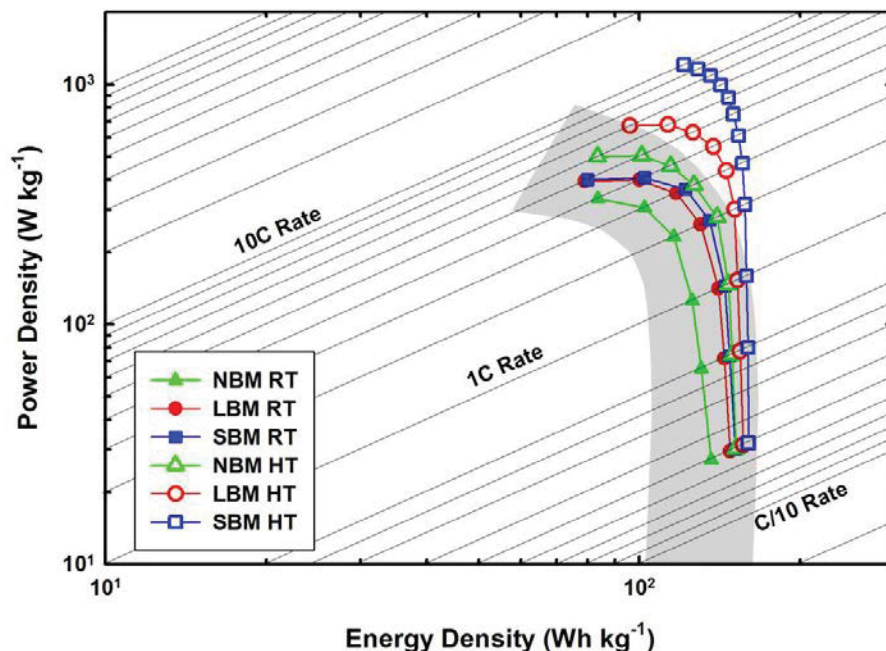


Figure 6.5: Ragone plot summarizing the power/energy density of TiS_2 materials vs. the state-of-the-art Li-ion technology. The plots for the present battery are based on weight of cathode composite only and derived from the discharge curves in Figure 6.4. The shaded area indicates the energy and power densities of commercialized lithium-ion batteries reported in literature [20].

We used the galvanostatic intermittent titration technique (GITT) as a means of evaluating the increased effective surface area within composite electrodes resulting from reduced particle size. This technique as described by Weppner and Huggins combines both transient and steady-state measurements to obtain kinetic properties of solid mixed-conducting electrodes [45]. Generally, the physical quantities of a material and electrochemical measurements can be used to calculate the chemical diffusion coefficient of a material. However, calculation of the diffusion coefficient requires knowledge of the effective surface area of your electrode material, which is a considerably difficult value to measure for a composite mixture. Assuming a constant chemical diffusion coefficient for our structurally consistent materials we compute the effective surface area of our electrodes to show increased surface area for size reduced TiS_2 electrodes, thereby

confirming enhanced kinetic properties corresponding to smaller particles. The equation for the calculating the surface area S (cm^2) was derived by Weppner and Huggins:

$$D_{\text{Li}} = 4/\pi (V_{\text{M}}/SF)^2 \times [I^0 (\delta E/\delta x)/(\delta E/\delta t^{1/2})]^2 \text{ at } t \ll \tau \quad \text{Eq. (6.1)}$$

where D_{Li} is the chemical diffusion coefficient ($1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) [30], V_{M} is the molar volume ($36.11 \text{ cm}^3 \text{ mol}^{-1}$), S is the effective contact area between electrolyte and active material, F is the Faraday constant (96486 C mol^{-1}), I^0 is the applied constant electric current ($4.0 \times 10^{-4} \text{ A}$), $\delta E/\delta x$ is the slope of the coulometric titration curve, and $\delta E/\delta t^{1/2}$ is the slope of the short time transient voltage change for a material.

The coulometric titration (CT) curves for both room temperature and elevated temperature samples can be seen in Figure 6.6a, which represent the evolution of the equilibrium potential vs. x in Li_xTiS_2 . We observe the slopes for all samples at $\text{Li}_{0.5}\text{TiS}_2$ are similar. The point $\text{Li}_{0.5}\text{TiS}_2$ is used for calculation because the voltage is relatively constant over a large concentration of x , whereas at $\text{Li}_{1.0}\text{TiS}_2$ the voltage changes dramatically and is therefore not a suitable point for estimation. An increasing voltage for $\text{Li}_{1.0}\text{TiS}_2$ at elevated temperature for the different materials indicates the better utilization of active material. As the size of particles is reduced, the relaxation time and potential difference between dynamic and equilibrium curves decreases, which agrees with the reduced time constant of particles exhibiting shorter diffusion paths. Figure 6.6b shows the transient voltage slopes for all samples collected from the

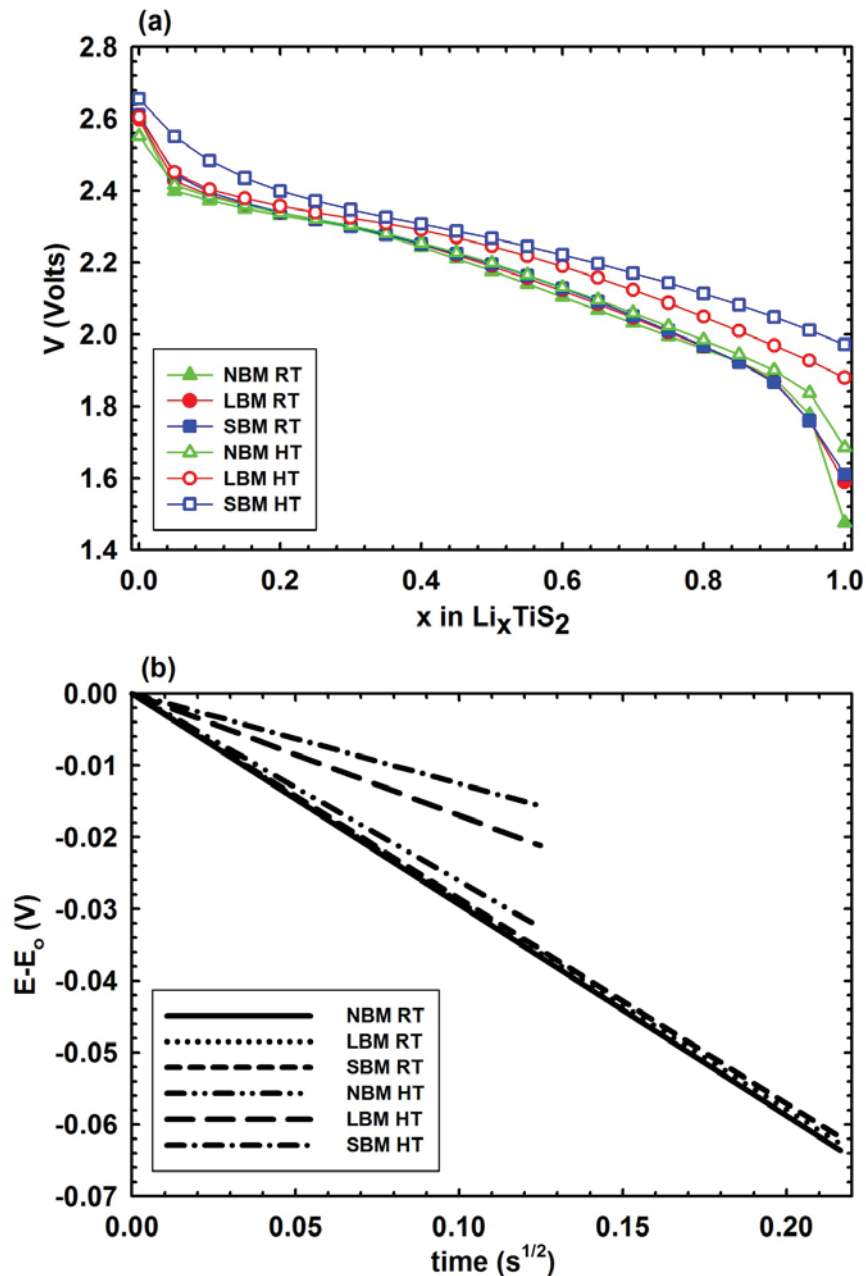


Figure 6.6: (a) Quasi-equilibrium potential vs. Li in Li_xTiS_2 as a function of stoichiometry x for both room temperature (RT) and elevated temperature (HT) samples. While potentials vary for different materials and temperatures, very similar slopes are observed for all samples in the region of $x = 0.50$. (b) Representation of the transient voltage of the GITT pulse as a function of square root of time for $\text{Li}_{0.5}\text{TiS}_2$ for all room temperature and elevated temperature samples. A significant change in slope is observed for elevated temperature samples while no change is observed for room temperatures samples.

galvanostatic pulse as a function of the square root of the time for $\text{Li}_{0.5}\text{TiS}_2$. No difference is observed for room temperature samples; however a large difference in slope for the elevated temperature samples is apparent. As previously discussed, the effects of relatively low ionic conductivity of solid electrolyte dominate kinetics at room temperature invalidating the equation developed by Weppner and Huggins. At high temperature however, we observe a very significant change in slope, verifying the faster kinetics of the size reduced materials. Using the slope of the transient-voltage GITT curves and the slope of the equilibrium-voltage CT curves in Table 6.1 we calculate the active surface area of the composite electrodes. The effective surface area of LBM is 152% higher than the area of NBM while the increase in area from NBM to SBM is an astonishing 298%. We have confirmed an increased contact surface area up to 300% for the size reduced materials and shown that relatively low bulk solid electrolyte conductivity at room temperature prevents the accurate measurement of kinetic benefits resulting from size reduction.

Table 6.1: Electrode surface area for elevated temperatures.

	NBM	LBM	SBM
CT Slope ($-\text{V } \delta x^{-1}$)	7.71×10^{-1}	7.65×10^{-1}	7.47×10^{-1}
GITT Slope ($-\text{V s}^{-1/2}$)	2.66×10^{-1}	1.70×10^{-1}	1.07×10^{-1}
Surface Area (cm^2)	1.78	2.71	5.31

As stated, solid electrolyte effects dominate at room temperature which prevents measurement of kinetic properties, invalidating the equation proposed by Weppner and Huggins for calculation of the chemical diffusion coefficient. Using electrochemical impedance spectroscopy

(EIS) we show that only resistance for the bulk solid electrolyte layer is obtainable at room temperature in Figure 6.7. No appreciable difference for decreasing interfacial resistance with smaller active material particles is observed as a result of the large solid electrolyte resistance effects at room temperature. At elevated temperature however, we see a clear distinction between the interfacial resistances for the various sizes of materials. While extrapolation of the actual interfacial resistance cannot be made, it is clear from the magnitude of resistance corresponding to the various sizes of materials in Figure 6.7 that a significantly lower interfacial resistance exists.

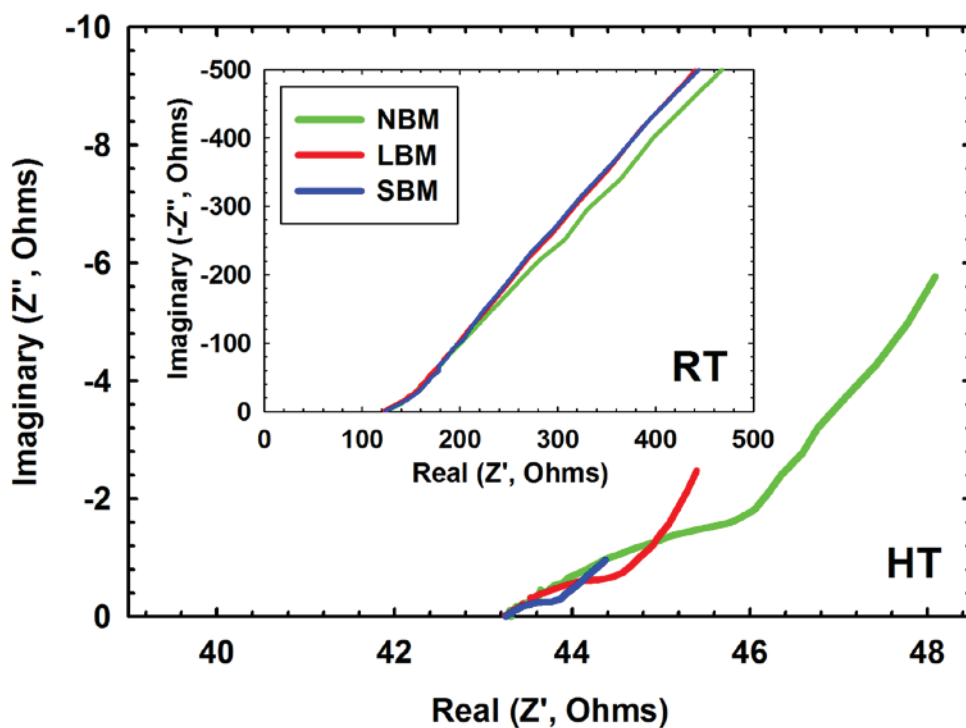


Figure 6.7: Electrochemical impedance spectroscopy measurements for both room temperature and high temperature batteries at $\text{Li}_{0.50}\text{TiS}_2$. Room temperature testing exhibits no change in kinetics as a result of increased surface area, whereas high temperature testing reveals the enhanced interfacial kinetics. The bulk conductivity for all samples is the same while we see a marked difference in interfacial resistance between the NBM, LBM, and SBM samples.

In order to show the high rate cycle life of TiS_2 in solid state we cycled the composite/solid-electrolyte/lithium batteries with a discharge rate of 2C and a charge rate of 0.5C. The first cycle of cells was discharged and charged at a rate of 0.2C. Figure 6.8a and 6.8b show the room temperature and elevated temperature high rate cycle life for all three sizes of materials respectively. We observe an average reversible capacity over 90% of the initial capacity after 50 cycles for all samples. There is an approximate 20% increase in capacity for ball-milled materials at room temperature, with an additional 15% increase in reversible capacity for the relative elevated temperature samples. The increase in capacity at room temperature is a result of smaller size and better utilization of materials. The increase in capacity for samples at high temperature is a result of increased surface area and utilization, as well as improved kinetics that result in a higher reversible capacity. The SBM material exhibits a theoretical capacity of 239 mAh g^{-1} assuming a complete reaction $\text{TiS}_2 + 1\text{Li} \rightarrow \text{Li}_1\text{TiS}_2$. In general, testing at elevated temperatures results in more pronounced undesired side reactions between the electrode material and the solid electrolyte. In the case of TiS_2 however, we observe negligible degradation for material tested at elevated temperature vs. testing at room temperature. This speaks highly to the stability of TiS_2 in a solid state configuration with a sulfide electrolyte as this suggests no increased reactions in the electrode as a result of an elevated temperature environment.

With the intention of demonstrating TiS_2 as a long lasting and high power electrode material for solid state batteries that can outperform current state-of-the-art batteries, we applied a rigorous testing procedure with a discharge rate of 10C to observe cycle life at extremely high rate. Again, using a first cycle discharge/charge rate of 0.2 C and a continued cycling charge rate of 0.5C we observe the cycle life of the best performing material, SBM TiS_2 . Figure 6.8c shows the cycling behavior of the SBM cell cycled at elevated temperature. We see an initial capacity

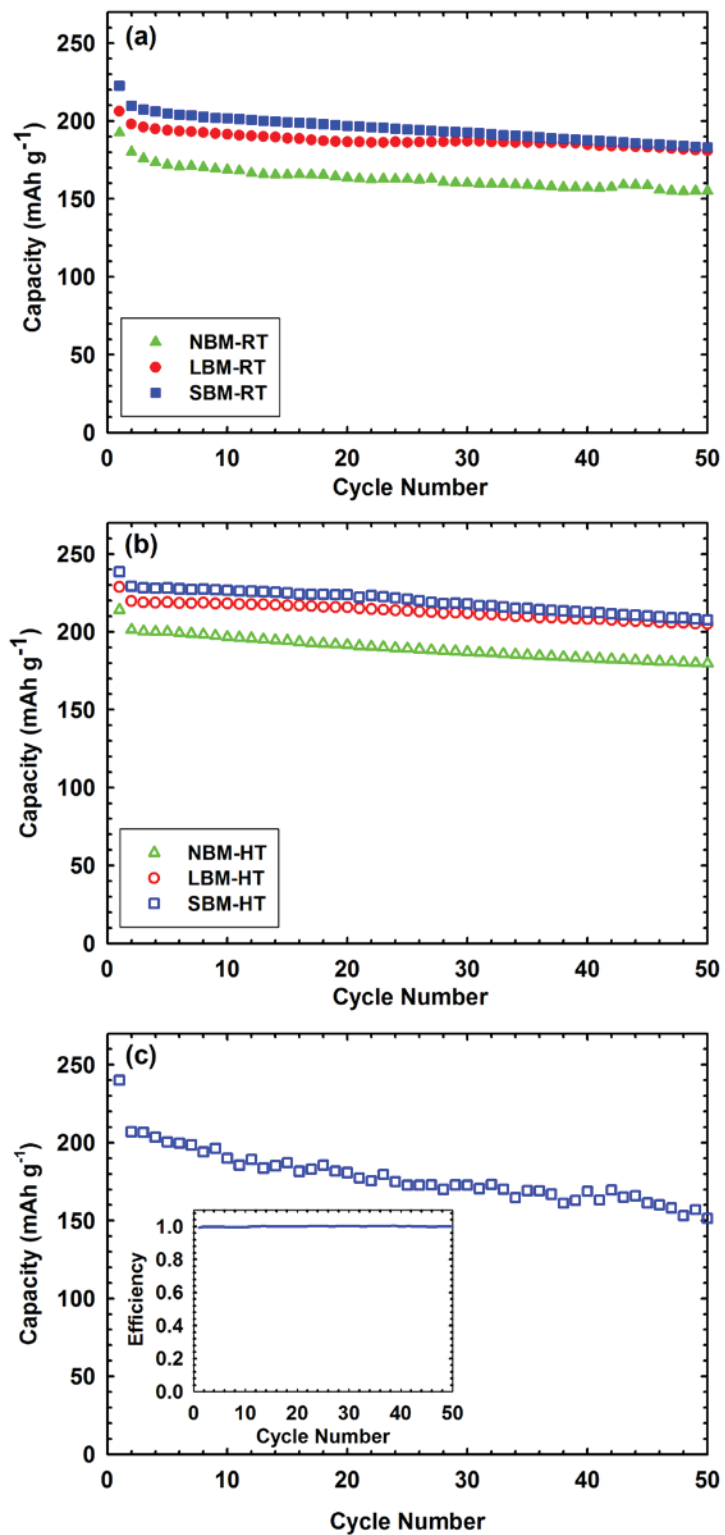


Figure 6.8: Reversible capacity increases for reduced particle size for both (a) room temperature and (b) elevated temperature cycling at 2 C-rate, and (c) SBM at 10 C-rate showing that the size reduced TiS₂ composite is capable of maintaining a high power density over 1000 W kg⁻¹ for over 50 cycles.

of the 2nd cycle at 208 mAh g⁻¹ and maintain a capacity over 150 mAh g⁻¹ for 50 cycles. This translates to an initial power density of almost 1400 W kg⁻¹ and a maintained power density over 1000 W kg⁻¹ for 50 cycles. This high rate cycling result is noteworthy because typically high rate cycling in solid-state results in fast capacity fade and low overall capacity. We see a high first cycle efficiency over 97% and continued cycling at almost unity. We do observe some minor capacity losses as a result of extremely high rate cycling. We achieved a maximum power density of the composite over 1400 W kg⁻¹ and maintained over 1000 W kg⁻¹ for 50 cycles at a rate of 10C.

6.5 Achieving higher energy density batteries

In order to achieve high energy density batteries, it is critical to meet two requirements: utilization of a high capacity electrode material, and minimization of the weight of inactive materials and components. In Chapter 2, it was mentioned that energy density can be calculated based on the numerous different weights, the most important of which is the weight of the entire cell, including all components and the casing. Until now, values for capacity, power density, and energy density have been given with regard to the weight of either the active material only (for capacity) or the weight of the composite (power density and energy density). It is the intent of the following work to present concepts for improving energy density of all-solid-state batteries, show preliminary results confirming these concepts, and discuss future directions to satisfy both of the requirements mentioned previously for maximizing energy density.

6.5.1 A novel concept

While elemental sulfur has a potential vs. lithium of only ~ 1.9 V, it exhibits the highest energy density of all known cathode materials due to its high capacity and relatively low weight. Sulfur however, is inherently insulating, both electronically and ionically [46], and therefore has become the center of much research only recently, due to technological advances. Current issues with fabrication of lithium-sulfur batteries revolve around rapid degradation of reversible capacity resulting from formation of highly resistive Li_2S and loss of active material in the form of soluble polysulfide reaction products [46] in liquid-based batteries.

While it was previously shown in this work that utilization of sulfide-based solid electrolytes in batteries inherently resolves numerous issues regarding capacity fade in liquid-based batteries resulting from internal reactions (Chapter 4), simple fabrication of all-solid-state lithium/sulfur batteries in all-solid-state does not resolve the poor performance. This is a direct result of the highly resistive nature of elemental sulfur as an electrode limiting the capacity and reversibility of cells. Even utilization of carbon for fast electronic transport does not resolve the cycling issues until only little sulfur remains in the electrode composite.

TiS_2 was shown previously to exhibit excellent power capabilities as an electrode for all-solid-state lithium batteries due to its fast lithium diffusion and high ionic and electronic conducting properties. In an effort to increase the energy density of TiS_2 -based all-solid-state lithium batteries, it is proposed to incorporate high capacity elemental sulfur into TiS_2 active materials. The highly conducting properties of TiS_2 are intended to off-set the highly insulating properties of sulfur, while the addition of sulfur greatly increases the capacity and therefore energy density of composite electrodes. An investigation as to the potential for success of this TiS_2/S active material for solid state batteries is begun and the preliminary results analyzed.

Lithium battery cells were fabricated similar to the previously discussed procedure in Section 6.2.1. TiS_2/S active materials were prepared by ball milling appropriate weight ratios of TiS_2 and S together. Planetary ball milling took place for 2 hours using 12x10mm agate balls in an agate vial sealed in an argon environment in order to effectively mix materials. Collected materials were then used as a single active material for fabrication of electrode composites using the same ratio 1:2 of active material and solid electrolyte, respectively. As the incorporation of more sulfur into the composite would result in higher capacity, preliminary research focuses on variation of the $\text{TiS}_2:\text{S}$ ratio to achieve both high capacity and good cycle life. Table 6.2 shows the theoretical capacity for TiS_2/S active materials.

Table 6.2: Theoretical capacity of TiS_2/S active materials.

Composite Active Material Ratio		
TiS_2	S	Theoretical Capacity (mAh g^{-1})
1	0	240
0.9	0.1	383
0.8	0.2	527
0.7	0.3	670
0.6	0.4	813
0.5	0.5	956
0.4	0.6	1100
0.3	0.7	1243
0.2	0.8	1386
0.1	0.9	1530
0	1	1673

Titanium forms a trisulfide (TiS_3) as well as the disulfide previously discussed as reported by Whittingham [47]. As TiS_3 was shown to exhibit highly irreversible cycling behavior and reduced conduction properties in comparison to TiS_2 , it is important that ball milling TiS_2 and elemental sulfur does not generate a different titanium structure. This is the reason for only a two hour ball milling period. The presence of elemental sulfur within a TiS_2 structure is shown using Raman spectroscopy in Figure 6.9. With increased amounts of added sulfur, isolated Raman peaks emerge which demonstrate the existence of elemental sulfur within TiS_2 , and not different structures.

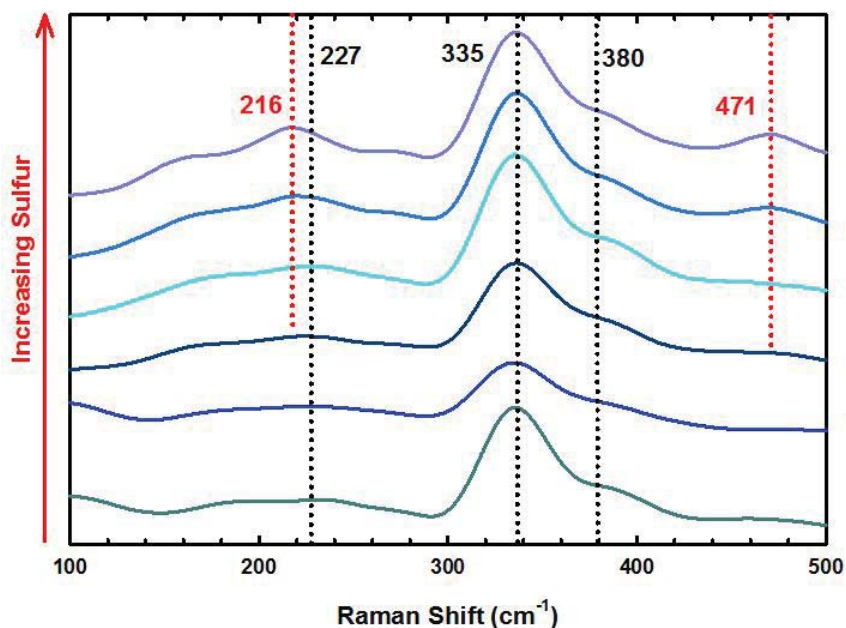


Figure 6.9: Raman measurements showing TiS_2 (227 cm^{-1} , 335 cm^{-1} , and 380 cm^{-1}) with the increasing presence of elemental sulfur (216 cm^{-1} and 471 cm^{-1}).

Electrochemical cycling results of TiS_2/S active materials are shown in Figure 6.10. Previously discussed results for low rate TiS_2 -only electrodes are shown for comparison, labeled for cells without acetylene black (TiS_2) and with acetylene black (TiS_2/M). Active material composites made with 10% sulfur without and with acetylene black are labeled $\text{TiS}_2/\text{S1}$ and

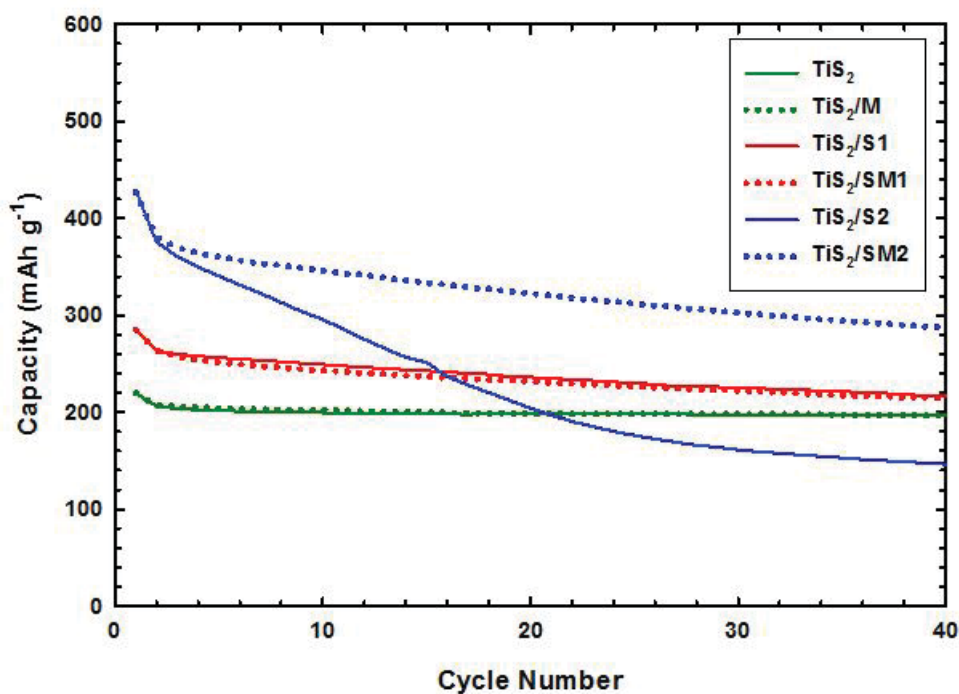


Figure 6.10: Cycling performance of cells with sulfur containing active materials. Cells were made with and without a conductive additive with the ratio of either 1:2 or 10:20:1 respectively of active material, solid electrolyte, and acetylene black.

$\text{TiS}_2/\text{SM1}$ respectively, and similarly for active material composites made with 20% sulfur without and with acetylene black as $\text{TiS}_2/\text{S2}$ and $\text{TiS}_2/\text{SM2}$ respectively. While the capacity is significantly increased, sulfur containing cells without conductive additive exhibit faster capacity fade than pure TiS_2 -only cells. $\text{TiS}_2/\text{S1}$ cells with added sulfur showed relatively reversible

capacity with only 15% capacity fade over 40 cycles, and no significant improvement in reversible capacity retention as a result of acetylene black incorporation. Rapid degradation of the TiS_2/S_2 cell is observed by a decrease of reversible capacity of nearly 60%. However, when acetylene black was added to the composite, degradation slowed significantly and cells maintained almost 80% of their initial capacity with respect to the second cycle capacity. This remarkable improvement in reversible capacity for sulfur-added composites shows that significantly decreased electronic conductivity as a result of embedded elemental sulfur can be mitigated by the addition of a conductive additive. Further addition of sulfur resulted in high initial capacity but rapid capacity fade. However, with only a 20% addition of elemental sulfur to the TiS_2 electrode, reversible capacity was remained almost 50% higher even after 40 cycles.

Observation of the charge/discharge profiles for the pure, and sulfur added TiS_2 composites reveals a distinct voltage plateau for increasing amounts of sulfur in Figure 6.11. It is obvious that sulfur is not being fully utilized in the electrode, as the maximum capacity reached on the first discharge for samples containing 10% and 20% sulfur was 283 mAh g^{-1} and 425 mAh g^{-1} respectively, instead of 383 mAh g^{-1} and 525 mAh g^{-1} . However, the addition of 20% sulfur more than doubled the first cycle discharge capacity. While inclusion of elemental sulfur into TiS_2 increases capacity, it results in faster capacity fade and the need for a conductive additive. Further investigation is required in order to fully understand the mechanisms for electrochemical cycling and reduce capacity fade.

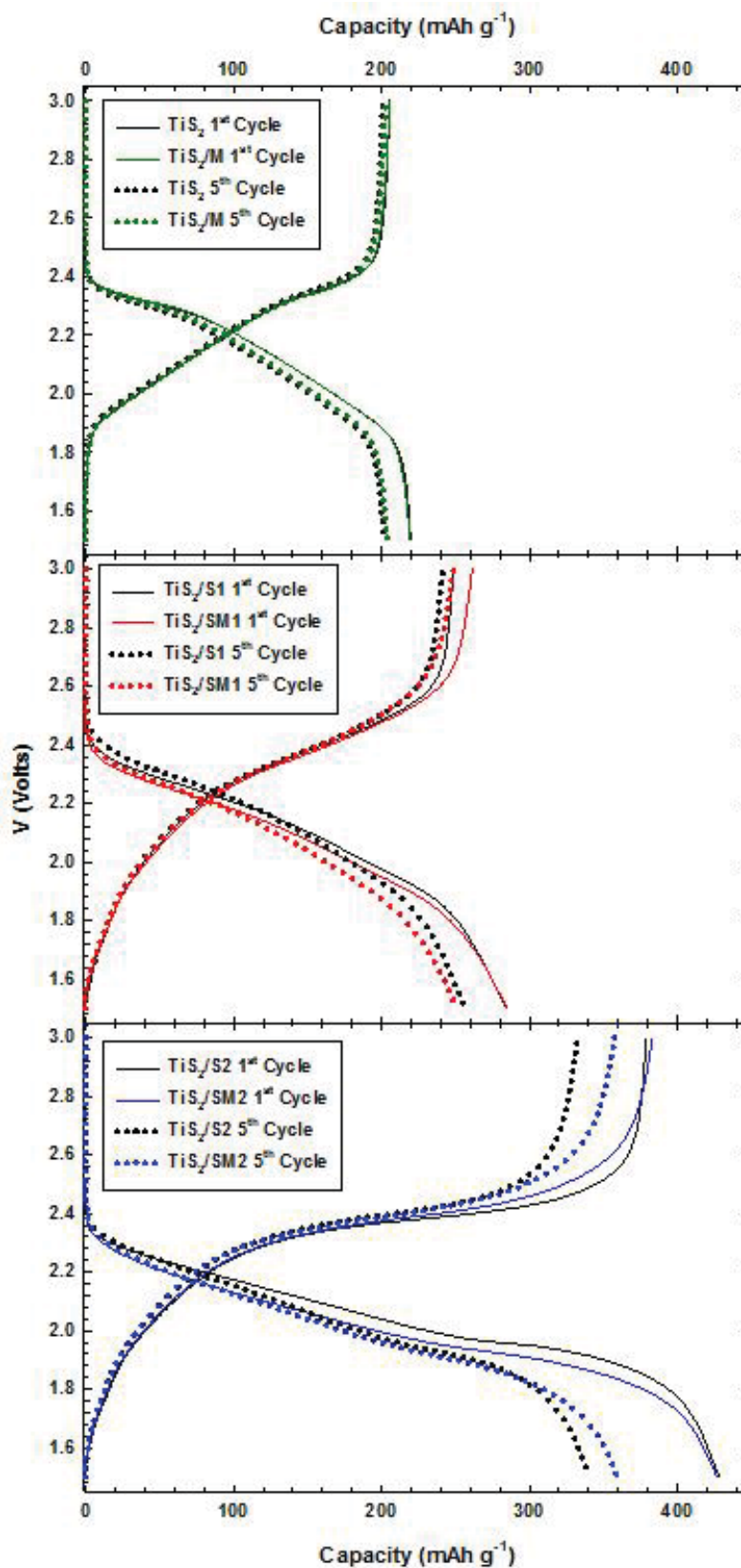


Figure 6.11: Charge/discharge profiles for pure TiS₂-only cells and sulfur added cells.

6.5.2 Future directions

Development and utilization of high capacity electrode materials has been discussed, however it is just as crucial to minimize the weight of inactive materials and components within batteries to maximize energy density. There are 3 general inner components of a solid state battery: the two individual electrodes, and the electrolyte. The most simple approach to maximizing energy density is to focus on keeping the percent of the total weight the active material comprises in the battery as high as possible.

A flow diagram for a generalized approach to maximizing the energy density of all-solid-state lithium batteries is shown in Figure 6.12. On the left, 5 labeled levels are observed (descending): Level 1 proposes the increase of active material (AM) content in the composite electrode, Level 2 involves the enhancement of active material for higher capacity, Level 3 involves the thickening of the positive electrode layer, Level 4 depicts reduction of the amount of material in the solid state electrolyte (SSE) layer, and Level 5 shows the reduction of the lithium electrode layer. On the right, theoretical calculations for energy density relative to the first and last values on the left side are observed. Level 2 was discussed previously in section 6.5.1, and can be essentially coupled with Levels 1 and 3 into a single cathode composite optimization step.

A computerized model for determining the best combination of the first three levels using thermodynamic calculations and physical properties of materials is most appropriate. However, without a model, basic conceptual arguments can be made to aid in the design of experiments. Based on the results of section 6.4, it is predicted that Level 1 will lead to decreased utilization of material, and therefore lower capacity, but higher energy density as a result of more AM in the composite. With regard to section 6.5.1, it is known that sulfur leads to increased capacity and faster capacity fade, however could result in stable high capacity behavior with further research.

Increasing the thickness of the electrode composite can result in greatly increased energy density as shown by the calculations on the right and side. However, it is expected that increasing the thickness of the cathode will have a negative impact on reversible capacity as a result of increased internal resistance and lithium ion migration distance. Testing of Levels 1-3 at elevated temperature is anticipated to yield significantly improved results over testing in a room temperature environment.

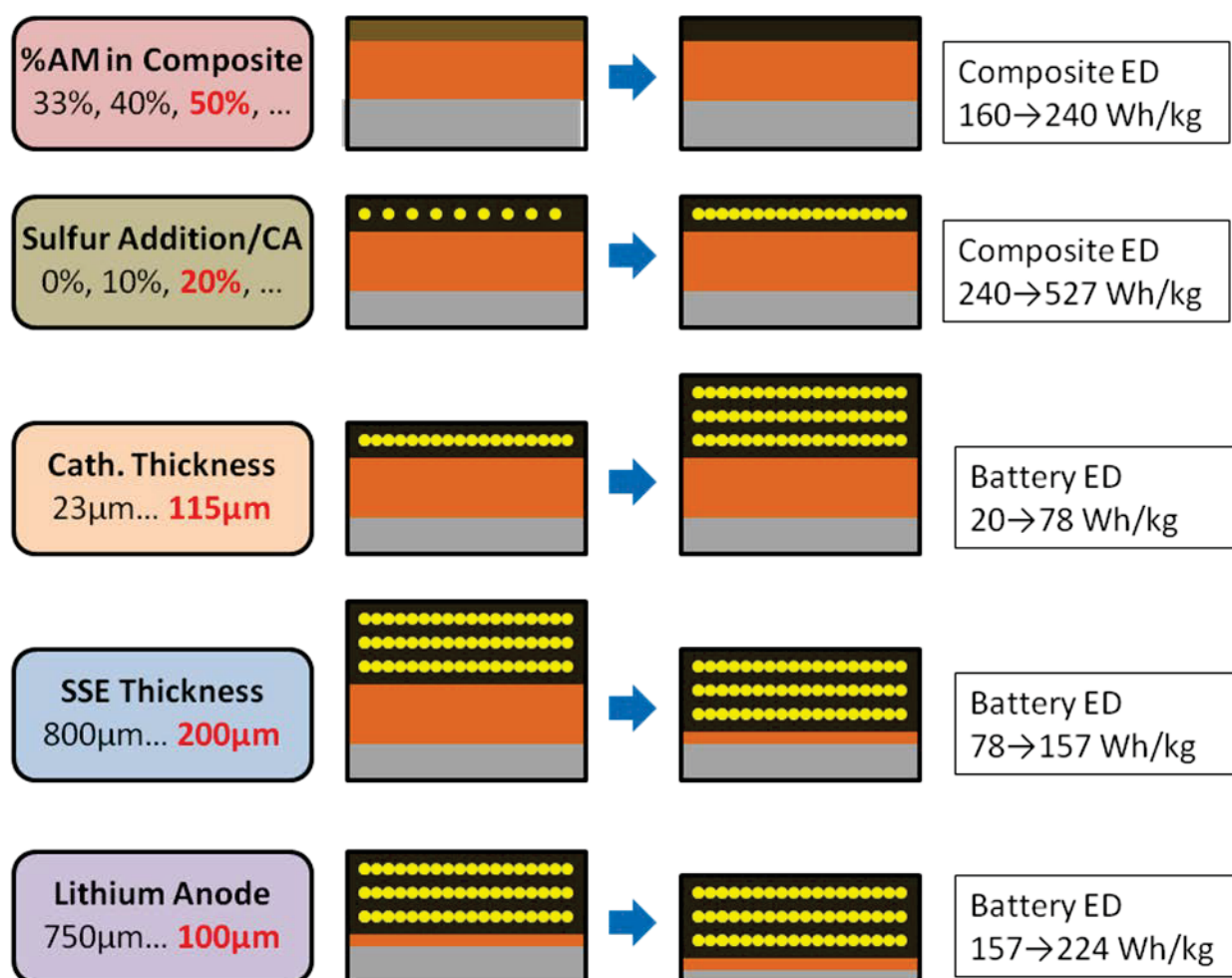


Figure 6.12: Schematic flow chart summarizing the steps to increasing energy density of all-solid-state lithium batteries. Composite energy density (ED) refers to energy density calculated based on the composite cathode weight only, while Battery ED refers to energy density calculated based on the weight of the composite cathode, solid electrolyte, and lithium metal anode.

Current “crude” battery fabrication techniques involving pressing operations limit the capability to construct batteries with a thin electrolyte layer. In fact, the solid electrolyte layer is the thickest part of the battery in this research, and it should be the thinnest. However, if it were possible to reduce the thickness of the electrolyte layer by a factor of 4, the battery energy density would double. The current battery fabrication techniques also restricts the size of the lithium metal anode. Cells are constructed using a large excess of lithium due to limited material availability. Reducing the amount of lithium down to only the amount required by the cathode composite for successful cycling to the desired capacity would put this particular example of an all-solid-state battery into a competitive commercialization perspective with a potential energy density for the entire battery above 200 Wh kg^{-1} .

For future testing, a number of potential composite and battery fabrication techniques can be used to maximize energy density and achieve successful commercialization. For instance, mixing cathode composites by ball milling instead of mortar and pestle grinding could achieve intimate contact between electrolyte and electrode materials leading to improved performance. Furthermore, successful generation of composites by ball milling would greatly improve repeatability and scalability of all-solid-state batteries as ball milling parameters can be controlled very accurately and ball milling equipment can be used on a very large scale. If commercial all-solid-state batteries are to be realized in the future, a serious look into coating techniques must be considered. For example, if it were possible to use one or more processes to coat any or all of the battery layers (composite, solid electrolyte, and/or lithium) to very precise thicknesses, fast and efficient battery fabrication with maximum energy density would be possible. A lithium battery fabricated with a high capacity electrode and ultrathin electrolyte layer, that can be made in a fast and reliable fashion would dominate the rechargeable battery market.

6.6 Conclusion

Durable and extremely high power rechargeable all-solid-state Li batteries are constructed using TiS_2 nanocomposites. Particle size of TiS_2 is reduced by high energy ball-milling and enhanced performance of nanocomposite cathodes in solid-state Li batteries is observed. The better utilization of active material and fast kinetics resulting from the size reduction of TiS_2 allows for highly reversible capacity in both room temperature and elevated temperature environments. Nanocomposite electrodes with better overall kinetics can be constructed without a conductive additive as the use of acetylene black is shown to degrade performance at high rate. Average capacity fade for all cells is less than 10% over 50 cycles while excellent reversible capacity for room temperature batteries and near theoretical capacity for elevated temperature batteries was observed. High power all-solid-state batteries were constructed with nano-sized TiS_2 and demonstrated high power density over 1000 W kg^{-1} for over 50 cycles, with a maximum power density of almost 1400 W kg^{-1} .

A method for production of high capacity electrode materials was proposed. TiS_2 and elemental sulfur were combined to create an active material with both high capacity and good conduction and kinetic properties. Cells utilizing 20% wt. sulfur in TiS_2 showed a high initial capacity over 400 mAh g^{-1} , and a 40th cycle capacity of $\sim 300 \text{ mAh g}^{-1}$. While capacity of cells was increased, so was the capacity fade. Future possibilities for improvement of active materials and increased energy density of batteries were discussed. Manufacturing techniques for improving overall battery energy density were mentioned, with the conclusion that coating techniques could allow all-solid-state batteries to reach commercialization.

The drawback to using TiS_2 as an electrode material is the relatively low voltage compared to conventional lithium-ion batteries. However, with further optimization of electrode

composites and manufacturing methods, these batteries could find potential for automotive applications in elevated temperature environments. Further developments with TiS_2 electrodes will focus on increasing the energy density.

6.7 Summary

TiS_2 nanoparticles generated by planetary ball milling of active material were tested in an all-solid-state lithium battery configuration. It was shown that TiS_2 maintains its highly conductive properties when mixed with solid electrolytes for a composite cathode, so much that a conductive additive is not required to allow electron migration through composites. Furthermore, it was shown that the addition of a conductive additive decreased performance of batteries when tested at high rates. Composite cathodes employing nanosized TiS_2 were revealed to cycle better at high rates and with a higher reversible capacity than composites made with large micron sized particles. Enhanced kinetics resulting from the reduced size of particles was measured by impedance spectroscopy, and it was confirmed that solid electrolyte conductivity was limiting to achievable capacity at room temperature. Elevated temperature testing showed further increased reversible capacity for TiS_2 cathodes, especially at high rates with nanoparticle active material, and showed a remarkably high power density.

A novel concept for increasing the capacity and energy density of TiS_2 lithium batteries was proposed. Utilizing the highly conducting properties of TiS_2 and the high capacity of elemental sulfur, TiS_2/S active materials with high potential for large capacities and good conduction were produced by ball milling. Preliminary results showed that adding sulfur to TiS_2 greatly increased capacity, but resulted in faster degradation of capacity during cycling. Acety-

lene black was added to electrode composites and resulted in a reduced capacity fade for sulfur added cathodes. Also, a plan for future development of solid batteries was discussed with an emphasis on improvement of manufacturing techniques. It was concluded that utilization of coating techniques for fabrication of all-solid-state batteries could result in commercializable batteries.

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7. Summary of Dissertation Work

This dissertation reviewed advances and development of all-solid-state batteries. Special attention was paid to the development and modification of solid electrolytes for increased ionic conductivity and enhanced stability with electrode materials. Interactions between solid electrolytes and both positive and negative electrode materials were studied and the results analyzed. Finally, lithium batteries were researched and fabricated with electrode composites capable of high power.

The motivation and purpose of this study was discussed in Chapter 1, with a focus on development of all-solid-state batteries for improving the overall safety of batteries. Chapter 2 reviewed pertinent literature on the basis of electrochemistry and lithium-ion batteries. The fundamental concepts of battery operation were summarized and the key metrics by which rechargeable batteries are evaluated were examined. A review of state-of-the-art electrode materials and their performance in both lithium and lithium-ion liquid battery configurations was conducted. Numerous characterization techniques used for quantifying the performance of batteries such as impedance spectroscopy, voltammetry, x-ray diffraction, and electrochemistry were also discussed.

Chapter 3 began with a detailed background on the history and fast ion conduction mechanisms associated with solid electrolytes. The most widespread solid electrolytes for use in lithium-based batteries were revealed and relative properties compared. Solid electrolyte fabrication methods were then discussed with a focus on ball milling techniques. A single step ball milling (SSBM) procedure was developed in this work as a means of generating solid electrolytes for all-solid-state battery fabrication. Properties of electrolytes produced by SSBM were

determined by various analytical techniques and the procedure was accepted for long term utilization and further exploration of solid electrolyte materials.

Chapter 4 focused on the use of high capacity silicon as an anode for all-solid-state batteries employing SSBM binary electrolyte. It was shown initially that substitution of a high specific surface area conductive additive, multi-walled-carbon-nanotubes, over a low specific surface area conductive additive, acetylene black, provided a better means of maintaining high capacity in silicon anodes. Testing of the voltage range within which silicon electrodes are cycled revealed that a narrow voltage of 0.05-1.0 V could result in a very minor capacity fade of the electrode. Utilization of reduced particle size of silicon showed that smaller particles maintain a larger first cycle coulombic efficiency and highly reversible capacity, but do not solve the issue of continued degradation. Exploration of silicon 3-D nanostructured arrays also revealed that smaller size correlates to higher capacity retention and better cycling at high rate.

LiCoO_2 as a cathode material for all-solid-state batteries was investigated in Chapter 5. It was shown that LiCoO_2 does not cycle well with binary $\text{Li}_2\text{S-P}_2\text{S}_5$ electrolyte made by SSBM and in fact, had rapid capacity fading as a result of side reactions at the electrolyte-electrode interface. The approach of modifying electrolytes to enhance stability against LiCoO_2 was perused to obtain high performance of LiCoO_2 in all-solid-state. Addition of GeSe_2 to the $\text{Li}_2\text{S-P}_2\text{S}_5$ system resulted in increased conductivity, but no significant improvement in capacity or cycle life. Inclusion of GeS_2 into the binary electrolyte also resulted in increased conductivity. Treatment of the $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ electrolyte with elemental sulfur resulted in significantly improved cycling stability and overall reversible capacity. Finally, experimentation with Li_2O as an additive yielded lower capacity, but was found to exhibit the best cycle stability of all electrolyte additives.

In Chapter 6, research on TiS_2 as a high power electrode material for all-solid-state lithium batteries was discussed. It was shown that TiS_2 has high enough conducting properties to eliminate the need for a conductive additive in electrode composites, and that use of a conductive additive at high rates actually decreased electrochemical performance. Particle size was reduced by ball milling and electrodes using smaller particles were shown to exhibit better electrochemical cycling as a result of enhanced kinetic properties. High power lithium batteries were demonstrated with electrodes containing TiS_2 nanoparticles, with high reversible capacities up to 6C at room temperature and up to 10C at elevated temperature. Testing of TiS_2 electrodes at high temperature showed higher achievable capacity of electrodes as a result of increased conductivity of the solid electrolyte. In an effort to achieve high energy density all-solid-state batteries, elemental sulfur was used to increase the capacity of TiS_2 electrodes. Preliminary results showed successful enhancement of capacity, but accelerated capacity fade. Lastly, a design plan was discussed to reduce the amount of inactive materials of a battery and achieve optimal energy density.

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