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Novel Methods for Fabricating All Solid State Lithium Ion Batteries

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Low Cost, Novel Methods for Fabricating All-Solid-State Lithium Ion Batteries

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A Major Qualifying Project Submitted to the Faculty of

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the

Bachelors of Science in Chemical Engineering

Submitted by

James Davison

James Boyce

Submitted on

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Approved:

Professor Yan Wang, Advisor

Professor Ravindra Datta, Co-Advisor

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Abstract

To further the advancement of safer, more cost effective lithium ion batteries, the effectiveness of all-solid-state lithium ion battery systems using $LiCoO_2$ sintered electrodes and LLTO solid state electrolyte was evaluated through electrochemical testing. The rapid advancement of power consumption by mobile devices and the high demand for more efficient electric vehicles calls for a novel battery with higher energy density, longer cycle life, and more dependable safety and construction. The research described here helps to advance the field of solid state lithium ion batteries and provides an avenue for future work and exploration.

Acknowledgements

We would like to start by thanking the two PhD students working in Professor Yan Wang's laboratory, Zhangfeng Zheng and Qina Sa. They both played an instrumental role in the completion of our MQP by assisting us with laboratory techniques, guiding us in our project, and aiding in the access and use of various laboratory equipment. Additionally, we appreciate all of the graduate students working in Professor Yan Wang's laboratory for all of their feedback throughout the duration of this project.

We would like to extend our gratitude to Professor Boquan Li for allowing us access to his scanning electron microscope, as it played a vital role in determining the effectiveness of the various methods used to apply our electrolyte material. Similarly, we would like to thank Rita Shilansky for working diligently on obtaining laboratory access for our group members.

Finally, we are very grateful to our advisors, Professor Yan Wang and Professor Ravindra Datta, for continually providing feedback and guidance throughout the duration of the MPQ process, as well as opening our eyes to the world of research in academia.

Executive Summary

In recent news the General Motors Chevrolet Volt has come under fire, literally and figuratively, for the problems that has occurred with the lithium ion battery contained inside the vehicle. Reports of the Volt catching on fire during testing have caused consumers to question if they trust driving themselves and their families in this car[1]. As if the safety issues were not enough of a setback, the price of the Volt is a tremendous problem in obtaining potential buyers. The car is listed at \$41,000 prior to a United States tax credit of \$7500, which brings the price down to \$33,500. A large part of this high price is the substantial price of the lithium ion battery, costing \$8000 per battery[2]. Excluding the battery price, the cost of the Volt is reduced to \$25,500 which gives the vehicle a competitive sticker price compared to similar cars available to consumers in the market. If the price of manufacturing a lithium ion battery can be reduced, and if the safety issues of these batteries are solved, the popularity and use of these electrochemical cells will become feasible for everyday applications.

In conventional lithium ion batteries, a liquid electrolyte is utilized to facilitate lithium ion transfer between the cathode and anode of the battery. If a hole is punctured in the frame of the cell, the liquid can leak out into the surrounding environment and possible be set on fire. A solid electrolyte can be created and placed between the two electrodes, eliminating the possibility of the electrolyte leaking out of the cell and igniting. Unfortunately, the manufacturing of solid electrolyte batteries is mainly performed through a physical vapor deposition method which is a costly endeavor. In Professor Yan Wang's laboratory in the Materials Science Department at Worcester Polytechnic Institute, faculty and students are diligently researching next generation lithium ion batteries and electrochemical processes to conquer the problems facing these technologies. The objectives of this project were to create an all-solid-state lithium ion battery using a low cost fabrication method to deposit the solid electrolyte and then test the cell using standard electrochemical testing methods.

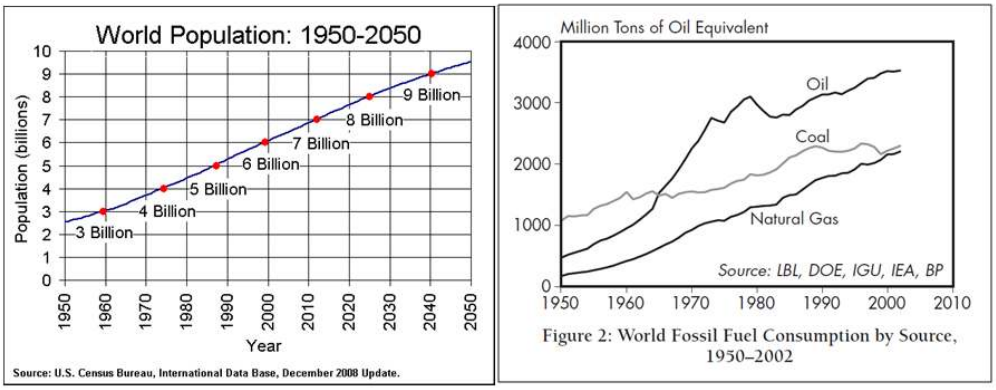
While creating an all-solid-state lithium ion cell, the first task undertaken was to develop a high performing lithium cobalt oxide ($LiCoO_2$) cathode with a high density so that a small thickness could be obtained. At first, a disk of approximately 88% density and a thickness equalling 100 microns was obtained through hand milling and the use of a polymer binder. Utilizing a ball mill installed in the laboratory, a 96% dense cathode with a thickness of 50 microns was achieved without the aid of a binder. The increase in density and decrease in thickness yielded a significantly higher performing cathode material. The next step commenced was the application of a solid electrolyte through low cost means. A lithium lanthanum titanium oxide (LLTO) sol solution was formed and applied via two methods; evaporation deposition and spin coating. Using the evaporation method, an electrolyte layer was able to be formed on top of a cathode disk with an achieved open circuit voltage of approximately 3.7 volts. This served as a proof of concept that this electrolyte can be applied to a $LiCoO_2$ cathode to yield a functioning battery. The spin coating work performed in this project lead to complete cathode coverage by a uniformly thick layer of LLTO. This should allow for adequate charging and discharging of the cell without the occurrence of a short circuit.

Currently, the spin coating method in which a LLTO sol solution is applied to a $LiCoO_2$ cathode disk is being tested for electrochemical performance. Since there is complete coverage of the cathode, as shown by the spin coating work, and a voltage drop can be obtained in the presence of a LLTO layer, evident from the evaporation method, the testing should come back with positive results. Further research will be necessary to perfect the method in which a lithium ion cell is fabricated using the low cost methods described throughout this report. The following recommendations should serve as a basis in which further work can be performed to increase the effectiveness of these methods and the resulting battery.

1. Throughout the process, the cathode disk would flip over while transporting it from one piece of equipment to another. A distinct feature should be cut into the disk to allow the user to instantly know if the deposited LLTO layer is facing in the correct direction.
2. Keeping the cathode disk on one surface during the entire spin coating or electrolyte evaporation process would be beneficial as the electrode would never encounter the opportunity to flip over.
3. Experimenting with the LLTO sol solution to find the ideal properties of the solution will be vital in creating the most effective electrolyte layer on the cathode.

1.0 Introduction

In recent years, scientists and engineers have poured large sums of money and time into researching and developing methods to reduce energy consumption in the world. Due to increased population and major advances in technology, energy consumption has reached new heights[3]. The majority of this energy is created through the combustion of fossil fuels such as coal, petroleum, and natural gas. While these substances are able to generate massive amounts of energy, they are limited resources and will be completely depleted if no major changes occur in the world's energy uses[4]. This fact has brought about the revolution of renewable energy sources, including hydroelectric power, wind turbines, and solar power. Though these sources are theoretically infinite, the energy harnessed from them has to be stored for latter use, presenting a potential issue[5]. Batteries can be used as a device to store power from an energy source, whether it is produced from a fossil fuel or renewable resource, until it is needed at some point in the future. Secondary batteries, also referred to as rechargeable batteries, are becoming especially popular due to their ability to be charged and discharged multiple times, eliminating the need to buy new batteries every time a device needs to be charged[6].



Source: U.S. Census Bureau, International Data Base, December 2008 Update.

Figure 1: The graph on the left shows the increase in world population. The data represent actual figures until 2008, and then is the projected population until 2050[7]. The graph on the right portrays the actual world fuel consumption for various fuel types until 2002, and then project fuel consumption afterwards[4].

Lithium ion batteries are an emerging secondary battery that show promise to be used in numerous applications in society. First produced in the 1970s, lithium ion cells are comprised of two electrodes, one positive cathode and a negative anode, and an electrolyte that facilitates the transfer of lithium ions between electrodes[8]. One reason for the popularity of such devices is the increased energy density compared to its leading competitors, such as nickel cadmium batteries, shown in Figure 2[9]. The reason for the range in the lithium ion battery values arises from the various materials comprising the cell, and the two types of lithium ion batteries; liquid electrolyte and solid electrolyte. A liquid lithium ion cell is characterized by the liquid electrolyte utilized to facilitate ion transfer between the electrodes. The liquid electrolyte consists of an organic solvent, a lithium salt, and a polymer separator. These materials are usually dimethyl carbonate, lithium hexafluorophosphate, and polypropylene, respectively[31]. The solvent and salt facilitate lithium ions across the cell while the separator is impermeable to electrons, keeping the cell from short circuiting. Though these cells are more efficient and can put out more power than most other batteries, all-solid-state lithium ion batteries have emerged as an even better alternative to their liquid counterparts.

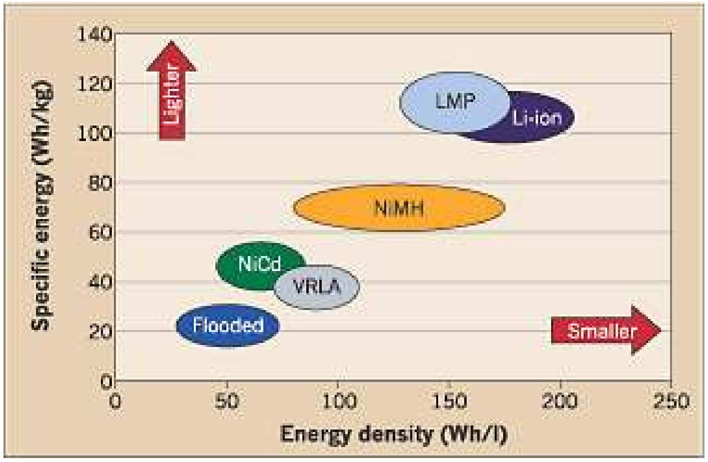


Figure 2: Energy density and specific energy data for various battery types[9]. Batteries become smaller moving to the right along the x axis and lighter moving up the y axis.

The major visual difference in a solid lithium ion battery is that the electrolyte is a solid material as opposed to the solvent, salt, separator combination used in a liquid battery. This electrolyte layer is often very thin, on the order of 1 micron, and allows only lithium ions to transfer across it, eliminating the need for a polymer separator to keep electrons from transferring across the cell[8]. This decreases the materials necessary to create a battery as well as the overall volume of the cell. This lower volume and lighter weight battery contains higher energy output since they can transfer lithium ions between the electrodes more efficiently. Due to the lack of a liquid, electrodes degrade at a significantly slower rate resulting in longer cycle lives for solid batteries[8]. In addition, solid electrolyte batteries have a much higher intrinsic safety level. Since no liquid is able to leak out of the cell, and all part are solid, explosions and fires are unable to occur[8].

The higher energy output provided by such batteries, as well as the safety, size, weight, and materials involved, makes them a great prospect to be used in applications such as cell phone and laptop batteries, cardiac pacemakers, and electric vehicles[10]. One major problem that researchers are facing regarding all-solid-state lithium ion batteries is the manufacturing cost. Many of these cells are created using expensive physical vapor deposition methods such as magnetron sputtering, making it difficult to mass produce and make the cells affordable in every day applications[8]. By creating a low cost method to apply a solid electrolyte to a cell, major growth in production of these cells will be plausible. The focus of this research is to create a low cost, simple application method that will allow for relative ease in manufacturing an all-solid-state lithium ion battery.

2.0 Background and Literature Review

Lithium ion batteries are a special type of secondary (rechargeable) battery) developed in which lithium ions transfer between a positive and negative electrode through electrolytic materials during charging and discharging[11]. Currently, lithium ion batteries populate consumer electronics markets around the world. The growth of the technology has eclipsed the once-used and hugely popular nickel cadmium and newly developed nickel metal hydride cells[12]. The success of the materials and technology associated can be attributed to: increased energy density, longer cycle life, and enhanced safety features. Improvements being made to lithium ion technology, both on an academic and industrial scale only help it maintain and expand its dominant status[13].

2.1 A Brief History

Battery research and development is a relatively slow-moving field. When compared to the high speed advancement of the consumer electronics industry, military applications, and aviation requirements that battery systems seek to fulfill, progress in battery research and development is almost unnoticeable at times[14]. In fact, only a handful of major technologies have been highlighted since the French-led development of lead-acid battery systems in the late 19th century. The pace of battery development is best exemplified by the fact that lead-acid batteries are still the most produced worldwide – over 100 years after their commercial inception[14].

Before the development of lithium ion battery technology, much of the recent consumer electronics industry was powered by nickel-cadmium based cells. As the energy density of materials became much more important, NiCd cells were challenged by two competing technologies: Li-Ion cells and NiMH cells. The two new, more capable technologies held many advantages over NiCd cells, including the lack of a "memory effect" and higher energy density[15].

Relatively unsuccessful at first, Li-Ion technology emerged from a long research effort challenged with developing secondary lithium-metal-based battery systems. Actual research of Li-Ion cells began at least 25 years before the first commercially developed cells. Hindrances of Li-Ion research started with difficulties in finding reliable materials that provided adequate and reversible lithium ion transfer. Most prominently, the general disregard of carbon (graphite) as a candidate for anode materials was a detriment to the research process. Its relatively low specific capacity (370 mAh/g vs. 3860 mAh/g) when compared to lithium metal and material deconstruction associated with solvent co-insertion deterred early researchers[14]. It was not yet known that, as shown in Figure 3, lithium ions could intercalate directly into the layered carbon structure, generating only a 10% volumetric increase upon intercalation virtually eliminating the original material deconstruction[16].

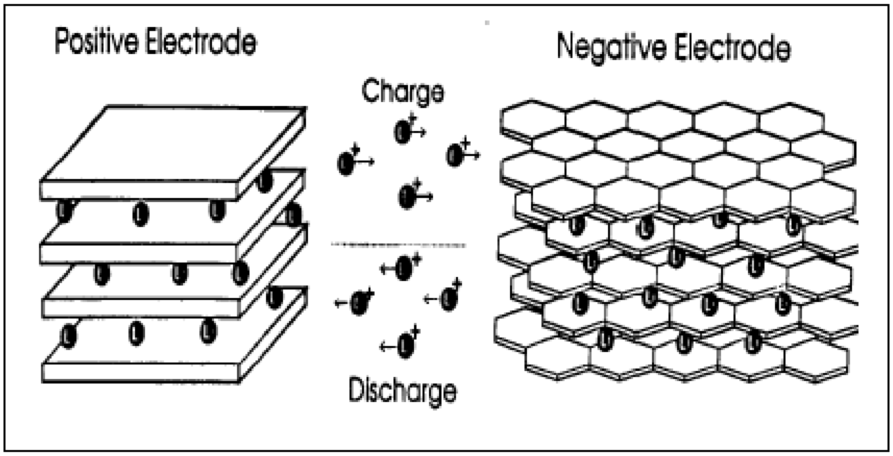


Figure 3: Lithium Ion Intercalation between cathode and anode materials during charging and discharging[17].

As a result of these discoveries the first lithium ion anode technologies (based on the layered structure of graphite) made use of Li Ion intercalation rather than ion exchange with lithium metal. This improved battery cycle life and eliminated the formation of short-circuit-causing dendrites that often bridged between anode and cathode materials in lithium metal batteries[18].

Despite its higher costs, Li Ion batteries emerged as the winning technology over NiMH cells. Despite the advantages of competitors, high operating voltage, high specific energy, and high energy density made lithium ion batteries more appealing. Figure 4 shows the energy density of difference battery technologies used in recent times. The evolution of popular battery technology over time essentially follows the same trend.

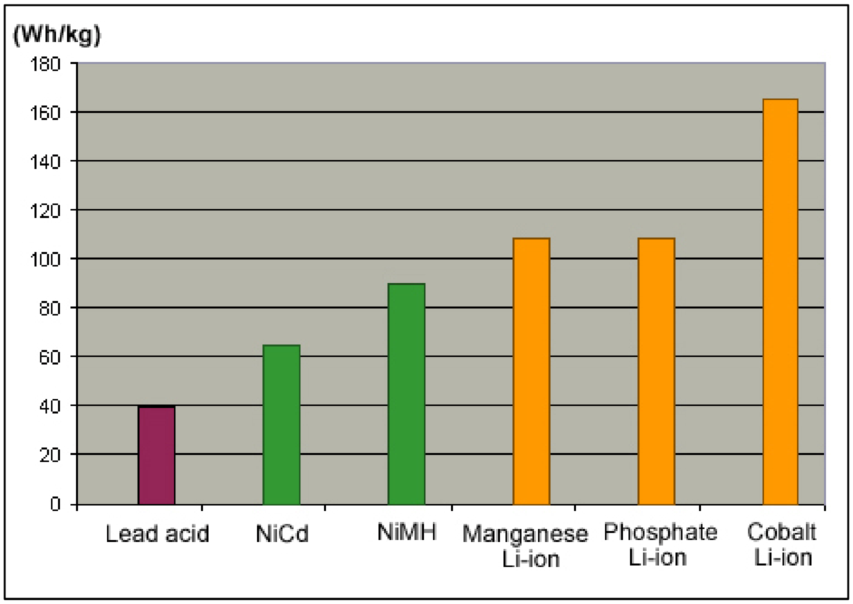


Figure 4: Specific Energies of Different Battery Cathode Materials[13]

After supporting research conducted by J. Goodenough and R. Yazami in the early 1980s on the capabilities of LiCoO2, the first lithium ion batteries were developed commercially in the early 1990s[17]. As shown in Figure 5, production increased dramatically in the first decade after the introduction of Li Ion technology. This production increase was a reaction to a higher demand for lightweight, portable electronics[17]. In 2003, just one decade later, Li Ion technology already had a 3 billion dollar worldwide market[19].

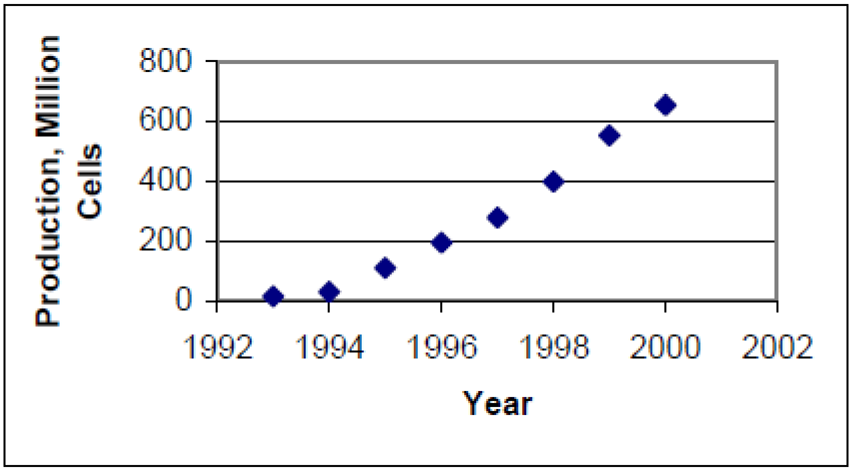


Figure 5: Increase in Production of Li Ion Cells after the Start of Commercial Production[17]

2.1.1 The Advantages and Disadvantages of Lithium Ion Battery Systems

As noted, one of the major advantages of Li Ion cells comes in the form of a relatively high energy density and specific energy. Since available space is one of the largest hurdles to overcome in today's ever-smaller personal electronics market, the higher the energy density and specific energy, the more desirable the product. Less necessary active material in a cell allows electronics developers to eliminate volume and weight in their product by adopting new battery advancements[19].

Equally important, lithium ion batteries require virtually no maintenance on the user's part. Unlike NiCd cells, there is no memory effect and manual charge cycles are not required by the user to prolong a cell's lifespan[13]. Because consumers expect products to work as effectively as they are marketed, a battery system that requires zero input "out of the box" generates an undeniable marketing advantage. Compared to other battery technologies, lithium ion batteries also possess rapid-charge capabilities and long shelf lives without extensive time-driven material decay[11].

Despite the advantages that have allowed Li Ion technology to propel to the forefront of the portable electronics power scene, the technology is not without its disadvantages. The cost of materials is relatively high when compared to alternative technologies. The high voltages provided by the cell systems also require protective circuitry to enable safe charge transfer through the electronics, and overcharging the cells can lead to dangerous thermal runaway[11]. Additionally, the traditional "cylindrical" design of batteries that is common in digital cameras, calculators, flashlights, and other consumer electronics can suffer from low power density when compared to NiMH or NiCd cells[11].

2.1.2 Funding Organizations and Outside Interests

All important research requires funding and interest from outside organizations. While research grants from academic institutions and government funded programs can propel small scale laboratory based research in order to develop a new product, capital from businesses is required. One of the most successful lithium ion battery companies is A123 systems, headquartered in Massachusetts[20]. The company produces conventional lithium ion battery cells, packs, and large scale battery systems. A123 claims that an investment of 1 billion dollars in capacity expansion research is planned to improve on existing lithium ion technologies.

While companies like A123 are well established, startup companies looking to improve on existing technology are also investing heavily in newer types of technology, most prominent of which are focusing on all-solid state battery development. Planar Energy, born out of the National Renewable Energy Laboratories (NREL), has been working on scaling up a development process for all-solid state lithium ion batteries. If successful, the process will represent a groundbreaking development that could change the way lithium ion batteries are manufactured[21].

2.1.3 Newer, Safer Types of Lithium Ion Battery Technology

Because the technologies that batteries power evolve so quickly, it is important for any changes allow battery technology to keep pace. Currently, the bulk mass and volume of conventional batteries is consists mostly of inactive materials. Liquid electrolyte systems require separators, containment spaces, and additional reinforcement to prevent leaks. All-solid-state battery systems are the most logical step toward a more compact, powerful, and safe electronic world.

Solid state batteries are generally defined by their electrolyte phase, composition, and formation methods. Of the four electrolyte types (liquid, gel, polymer, ceramic), only polymer and ceramic electrolytes can accurately be called all-solid-state because they are both liquid and solvent free[1]. In a solid state battery, the need for a separator is eliminated – the solid electrolyte layer acts to both separate the anode and the cathode (preventing short circuits), and facilitate lithium ion transfer during charging and discharging. Currently, one of the newest and most popular types of of solid state Li Ion battery research focuses on thin film battery systems – flexible, paper-thin cells primarily employing LiPON as an electrolyte material[22].

2.1.4 Evaluating the Current State of All-Solid-State Lithium Ion Technology

Research is often categorized as either: exploratory, incipient, or mature. Lithium ion battery technology as a whole could be classified as a matured technology, with several decades "experience" in research and industrial applications. However, all-solid-state systems are significantly less mature, and have not yet been met with commercial success. Materials engineering behind all-solid-state systems has succeeded thus far – producing several electrolyte and cathode candidates. However, industrial and commercial production methods remain in a very exploratory phase.

2.2 Chemical Technology Overview

All-solid-state lithium ion batteries rely, as all battery systems do, on five essential components: cathode, anode, electrolyte, and two current collectors. As the name implies, in all-solid-state systems, all of these components exist as a solid, lattice structure. This alters the chemistry associated with lithium ion transport and electrolyte interfaces. Understanding these mechanisms and the materials associated with them is essential to developing more reliable solid-state lithium ion battery systems.

2.2.1 Lithium Ion Transport Mechanism

Unlike liquid electrolyte lithium ion batteries, in which a liquid is utilized to facilitate lithium ion transfer across the cell, solid electrolyte batteries rely on solid diffusion mechanisms in order charge and discharge a cell. As the cell charges, lithium ions deintercalate from the cathode material, diffuse across the electrolyte, and intercalate into the anode[23]. Likewise, during cell discharge the ions deintercalate from the anode, diffuse through the solid electrolyte, and intercalate into the cathode. Since the electricity generated by the cell is proportional to the amount of lithium diffusing through these sections of the battery, it is important to understand how the ions move through the material.

The two main solid mass diffusion mechanisms that occur in solid state lithium ion cells are vacancy and interstitial diffusion[13]. Vacancy diffusion occurs when an atom in a lattice position of a solid moves into a neighboring empty lattice position[8]. As shown in Figure 6, the atom jumps from its original position to fill a void found in an adjacent point of the structure. As an ion moves from one point to another, its original position is then left unoccupied. This allows another lithium atom to jump from its original position and fill the new vacancy. This creates a continuous process in which ions move from one point to another allowing its original position to be filled as the ions move across the cell. In some electrode materials, lithium ions are able to diffuse on multiple axes while others only allow for migration on a single plane.

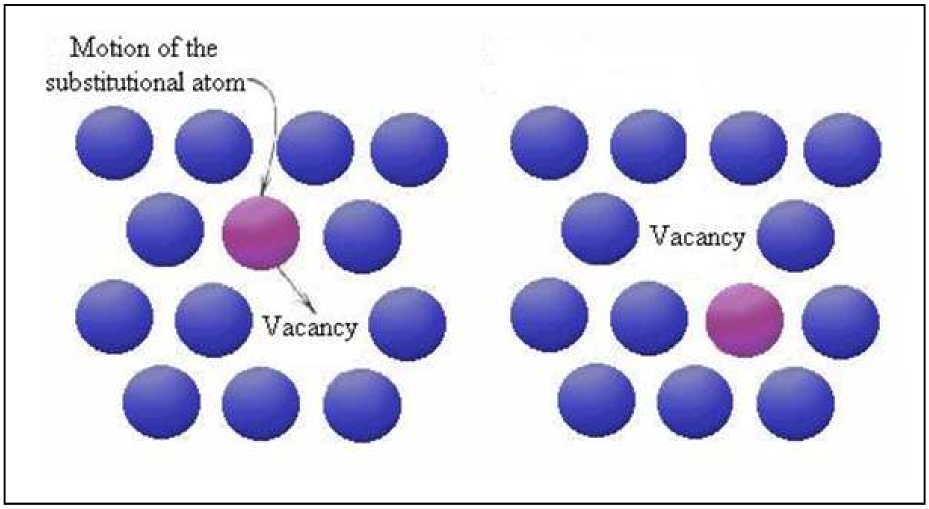


Figure 6: Presentation of generalized vacancy diffusion mechanism[54]

The other prominent type of solid diffusion occurring in solid state lithium ion cells is interstitial diffusion. During interstitial diffusion, an atom or ion inserts itself into an interstitial site in the solid material[8]. Once in the solid, the ion will continue to transfer from one interstitial site to another as it migrates across the cell (as illustrated in Figure 7). As with vacancy diffusion, some structures allow for diffusion on multiple axes while others are only able to support migration on one axis. This type of diffusion requires that the ion be sufficiently small in diameter in order to fit inside of the interstitial site[24]. If the particle is too large, it will not be able to enter and thus, diffusion will not occur via this mechanism. During diffusion, the structure of the solid will be distorted as it encounters a deviation from its normal cubic lattice. This type of diffusion, along with intercalation, contributes to the volumetric change seen in charging and discharging a cell.

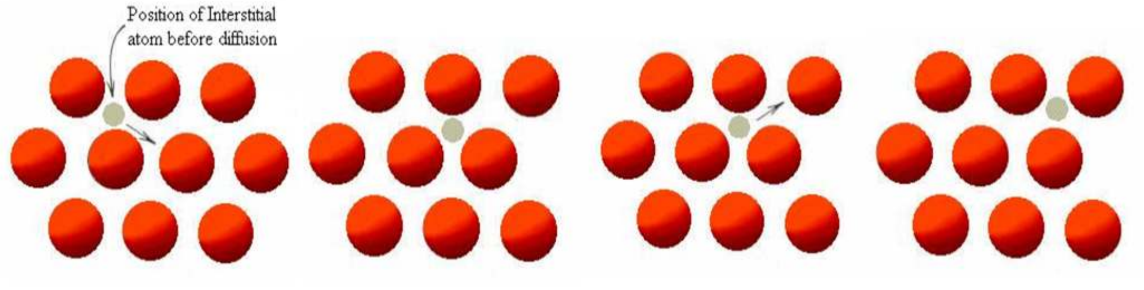


Figure 7: Presentation of Generalized Interstitial Diffusion[54]

In general, interstitial diffusion contains lower migration energy and thus predominates over vacancy diffusion in lithium ion batteries[23]. Interstitial migration is only able to occur when the circumstances allow for it; particles small enough to fit in the interstitial sites can migrate through the cell through this mechanism. Lithium ions transfer across a cell through vacancy diffusion, interstitial diffusion, and intercalation, allowing for the cell to charge and discharge. Optimizing the electrode-electrolyte interface geometry in all-solid-state lithium ion batteries becomes important to prevent material breakdown, and to improve the efficiency of diffusion pathways.

2.2.2 Cathode Materials

The function of the cathode in a lithium ion battery is to store lithium transferred during discharge so that it migrate back to the anode during cell charging. The materials used must meet certain basic requirements. These ideal parameters include[25,26].

- The ability to hold a large amount of lithium in order to provide the cell with a high capacity.
- Minimal irreversible changes to the structure of the material during lithium ion intercalation to ensure good reversibility.
- High electronic and ionic conductivity to facilitate high ion and electron transfer. Also, this will provide high rate capability in the cell.
- Structural and chemical stability over the range of voltage being applied to the cell.
- Low cost and easily manufactured
- Non-toxicity
- High voltage to ensure low oxidation potential and a sufficient cell voltage across the cell

Cathode materials exists in many forms, however, the most common ones are present in lithium ion batteries as a lithium-metal oxide. The lithium metal included in the electrode allows for a sufficient amount of lithium to be present in the cell to generate power. Metal oxides are chosen to be paired with lithium since they contain high voltages and are able to withstand reversible lithium intercalation to a high degree in general[25,26]. Explored here in detail are lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMn_2O_4$), and lithium iron phosphate ($LiFePO_4$). These cathodes represent the most common industrial candidates for use in all-solid-state lithium ion cells.

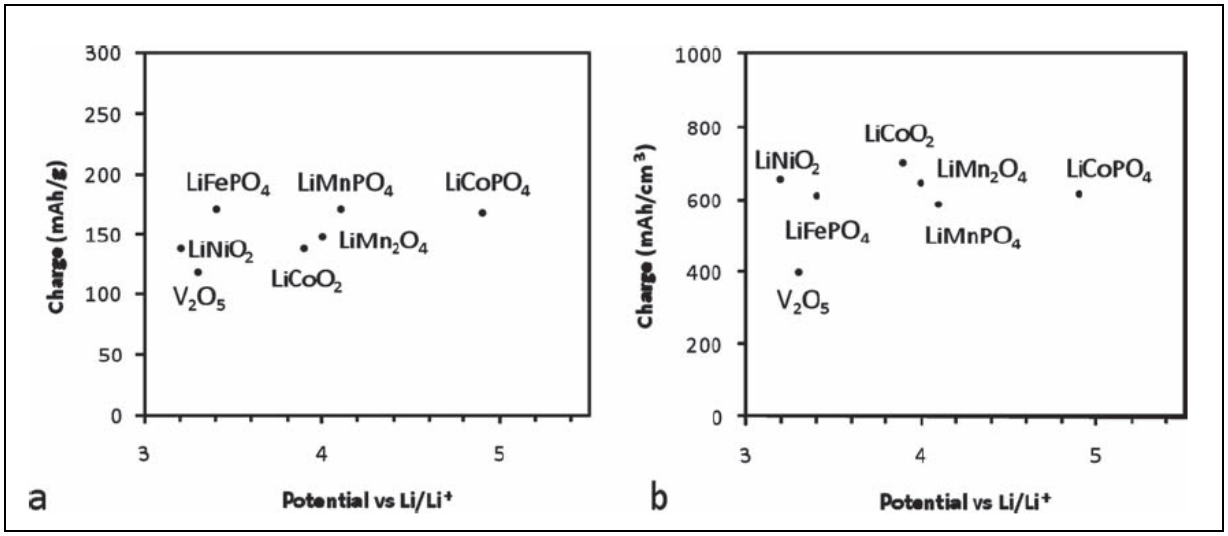


Figure 8: Comparison of Various Solid-State Cathode Candidates for use in All-Solid-State Lithium Ion Batteries[27]

2.2.3 Lithium Cobalt Oxide ($LiCoO_2$)

$LiCoO_2$ is present in lithium ion cells in a high temperature layered hexagonal structure and a low temperature spinel structure[27]. The layered hexagonal structure allows lithium ions to enter and exit the structure in between layers, resulting in one-dimensional diffusion in the electrode. Unlike the high temperature material, the spinel $LiCoO_2$ structure lets ions transfer occur in multiple directions within the material causing greater diffusion. In general, LiCoO2 has a potential of 3.9 V vs Li/Li^+ and is capable of reversible cycling with $0.5 < x < 1$ in Li_xCoO_2. This yields a gravimetric charge capacity of 137 mAh/g, which corresponds to a volumetric charge capacity of 700 mAh/cm^3 [26,27]. As shown in Figure 8, the gravimetric capacity is low compared to other common materials, but the volumetric capacity is among the highest. Despite the popularity of $LiCoO_2$, cobalt's innate rarity makes it expensive, making the search for alternative materials a priority[26]. Additionally, observable negative environmental impacts of cobalt acquisition and disposal have spurred a desire to search for alternate cathode materials

2.2.4 Lithium Manganese Oxide ($LiMn_2O_4$)

$LiMn_2O_4$ exists as a spinel structure, which is a three-dimensional cubic structure that allows for diffusion of lithium ions in multiple directions[17]. Since the migration of ions can occur on multiple axes, more lithium is able to travel into and out of the structure allowing for more power generation. $LiMn_2O_4$ is electrochemically stable at 4 V vs Li/Li^+ corresponding to reversible cycling of $0 < x < 1$ in $Li_xMn_2O_4$26. Due to the spinel structure, intercalation of lithium ions in this amount results in only a small volume change, which leads to a longer cycle life of the cathode. The high voltage in which $LiMn_2O_4$ operates is also desirable since it allows for a larger cell voltage to be obtained in the battery. The disadvantage to using this cathode is that, like $LiCoO_2$, the gravimetric charge capacity is low as it equals 148 mAh/g[27]. On the other hand, $LiMn_2O_4$ has a high volumetric charge capacity which can lead to smaller batteries.

2.2.5 Lithium Iron Phosphate ($LiFePO_4$)

As shown in Figure 8, with a gravimetric capacity of 170 mAh/g, $LiFePO_4$ has a high capacity compared to other common cathodes[27]. When looking at the volumetric charge capacity, the value is lower than that of $LiCoO_2$ and $LiMn_2O_4$ with a value equal to 610 mAh/cm^3. The olivine cubic structure of $LiFePO_4$ allows for diffusion to occur in a single direction, unlike $LiMn_2O_4$[28]. One major drawback to this cathode material is its low voltage, which is only 3.4 V vs Li/Li^+[26]. Due to this low value, the power that is able to be generated by the cell is limited. At this voltage, the positive electrode is able to reversibly cycle for values of $0.1 < x < 1$ in Li_xFePO_4. One advantage $LiFePO_4$ has over many other materials is the ease of forming it from a powder[27]. Commercial production of this cathode can utilize its ability to be formed from a powder in order to cut down the costs of expensive deposition techniques such as sputter and pulsed laser deposition. Because economies of scale have such a negative impact on the plausibility of laboratory techniques, any advantage in cost reduction results in a positive step for all-solid-state lithium ion batteries.

2.2.6 Other Common Cathodes

Despite the popularity and success of the aforementioned materials, many other alternative cathode materials exist that can provide reliable secondary solid-state cells. Of the substances listed in Figure 8, $LiCoPO_4$ and $LiMnPO_4$ have the largest potential to create powerful lithium ion batteries. Both have high gravimetric charge capacities of 167 mAh/g and 171mAh/g, respectively[27]. In addition, Li_xCoPO_4 is able to be reversibly cycled from $0 < x < 1$ at a voltage of 4.9 V vs Li/Li^+ while Li_xMnPO_4 experiences the same reversibility at 4.1 V vs Li/Li^+. This means that both of these orthorhombic crystal structured materials have good rate capabilities, due to the high capacity, as well as high cell power from their high voltages. As with all high-voltage materials, this requires extra circuitry protection and cell reinforcement.

Less desirable alternatives include: $LiNiO_2$ and LiV_2O_5. These found in cathode materials as layered structures which only allow one-dimensional ion diffusion unless deposited in a specific arrangement[27]. This lack of three-dimensional diffusion causes the reversibility of these materials to be limited, ultimately decreasing the rate capabilities. $LiNiO_2$ and LiV_2O_5 have capacities of 140 mAh/g and 118 mAh/g, respectively[27]. These low rates coupled with low operation voltages between 2.7 and 3.4 V vs Li/Li^+ cause these cells to have low power generation. These materials do not seem to show the potential to be relevant in future lithium ion batteries due to these serious disadvantages. Nickel-based battery systems can provide cheaper, easier to produce alternatives that rule out low-performance lithium materials.

2.3 Anode Materials

As with cathode materials, anode substances have very similar requirements that allow for the cell to function properly. These ideal parameters are the same as those presented in Chapter 2.2 with one exception. The last parameter states that a cathode should have high voltage to ensure low oxidation potential and a sufficient voltage across the cell. Unlike the cathode, the anode should have low voltage, resulting in high oxidation potential to develop a high voltage across the cell[25]. This is extremely important since cell voltage is proportional to the power generated in the battery.

The function of the anode in a lithium ion cell is to store lithium until electricity needs to be generated through electrochemical reactions. Once this occurs, lithium breaks into lithium ions and electrons. The lithium ions deintercalate from the anode and intercalate into the cathode during the discharge of the cell[1]. The structure of the material is important since it will determine how much lithium can be stored and what the storage reversibility is. These factors control how much capacity is available in the anode. Though most conventional batteries make use of solid-state anode materials, comparing anode compounds still shows how differences in materials affect the performance of an all-solid-state cell.

2.3.1 Graphite

Graphite is composed of sheets of stacked graphene creating a layered structure susceptible to the intercalation of a single lithium ion held between adjacent graphene layers[28]. This structure allows for one-dimensional diffusion since ions are not able to pass through neighboring carbon layers, as seen in many cathode materials. Graphite holds a few advantages over other anode materials including its low volume expansion of roughly 10% during lithium intercalation and its low voltage of 0.15 V vs Li/Li^+ [21]. This allows for the anode to be cycled reversibly with minimal structural damage and for the cell to have a high voltage and generate a lot of power. The major drawback of using graphite as an anode is the low capacity and thus poor rate capability of the material. The gravimetric charge capacity is equal to 372 mAh/g, significantly lower than many other anode materials. Its reliability, ease of production, and low cost still makes graphite the staple for commercial battery production.

2.3.2 Lithium Titanate ($Li_4Ti_5O_{12}$ or LTO) and Titanium Dioxide (TiO_2)

Titanium oxides do not possess high gravimetric capacities; TiO_2 and LTO are 168 mAh/g and 175 mAh/g, respectively[28,29]. This leads to poor rate capability in the cell when compared to other anode materials such silicone and lithium metal. One advantage that they do possess is their electrochemical stability during charging and discharging. LTO only experiences a 0.2% volume change, making it have a long cycle life. Both materials cycle reversibly between 1.5 and 1.8 V vs Li/Li^+, making them ideal for generating a lot of power[27]. The anatase structure of TiO_2 and the spinel structure of LTO can be largely credited with the good performance metrics of these anode materials since they allow for mulit-direction ion diffusion and multiple points for lithium ion storage.

2.3.3 Group IV b Elements and Lithium Metal

The collection of anodes that experience some of the largest capacities is the fourth group of the periodic table and lithium metal. Lithium metal, silicon (Si), germanium (Ge), tin (Sn), and lead (Pb) contain capacities of 3860 mAh/g, 4008 mAh/g, 1565 mAh/g, 963 mAh/g, and 1900 mAh/g, respectively[27,16]. Due to the high capacities of these materials, they have great rate capabilities and they require a small amount of material in a lithium ion cell to be paired with a cathode. One major problem, especially concerning the group IV b metals, is the low cycle life due to the high volume expansion encountered during lithium ion intercalation. Silicon in particular experiences a 300% volume change when lithium is intercalated in the cubic structure of the solid[16]. Ge, Pb, and Sn also observe similar expansion issues, decreasing the cycle life of these substances. In many cases these materials are being combined with substances containing low volume expansion, such as carbon, in order to obtain the benefits of the high capacity of these metals with the lower volume expansion of other materials. Lithium metal experiences another problem; an irreversible reaction with oxygen to form lithium oxide Li_2O. When this reaction occurs, the lithium in the anode is depleted causing the anode material to cease to be effective. Unfortunately, this problem takes away from the positives of lithium metal as an anode due to the lack of anode material after cycling.

2.4 Electrolyte Materials

The electrolyte in a solid state lithium ion cell has two main functions. First, it must act as a separator between the anode and cathode. If the two electrodes touch, the cell will short circuit and become electrochemically useless. In order to ensure that the material is a sufficient separator, it must be nonporous and contain no pinholes that could allow dendrite formation between the electrodes. Secondly, the electrolyte facilitates ion transfer from the cathode to anode during charging and from the anode to cathode while the cell discharges[27]. From these two essential functions, it is clear that the two most important properties of the electrolyte are the ionic and electronic conductivities. The ionic conductivity needs to be high to facilitate lithium ion transfer while the electronic conductivity should be low in order to keep electrons from passing through the cell. The physical nature of these properties is surmised in the transference number of the electrolyte, t_+, which is a measure of the fractional transference of lithium ions.

Transference is generally considered to have a value of 1 for solid state electrolytes due to their negligible electron transfer compared with their ionic conductivity[29,30]. Two promising candidates for commercial all-solid-state lithium ion batteries are LIPON and LLTO.

2.4.1 LIPON and Lithium Phosphate (Li_3PO_4)

Lithium Phosphate exists at room temperature as γ-Li_3PO_4, which is an orthorhombic crystal structure[23]. In this solid state, diffusion occurs via both mechanisms discussed in Chapter 2.1. Results show that interstitial diffusion dominates ion transfer with a migration energy barrier of 0.21 eV or 0.35 eV, depending on the path taken inside of the crystal[13]. Vacancy diffusion has an energy barrier of 0.56 eV, which is sufficiently higher and causes more resistance for ions to migrate in this manner[23]. Interstitial diffusion allows for Li_3PO_4 to have an ionic conductivity equal to 3×10^{-7} S/cm in bulk form and 7×10^{-8} S/cm in thin film materials[27]. As seen by the units of conductivity, S/cm, as the electrolyte becomes thinner the ionic conductivity increases due to the lower resistance in the material.

LIPON was first created in the 1990s when Li_3PO_4 was sputtered with nitrogen as the gas agent[27]. The two substances reacted and deposited on the substrate, creating the LIPON thin film electrolyte. As with the discovery of many materials, this accidental formation of electrolyte proved useful due to the excellent properties LIPON possesses. The ionic conductivity increased from Li_3PO_4, to 3×10^{-6} S/cm, while the electronic conductivity is measured to equal 8×10^{-13} S/cm, significantly lower than many other solid state electrolytes[17]. Also, the addition of nitrogen in LIPON adds increased electrochemical stability to the electrolyte, making it more durable during cycling and increasing its cycle life. Steps need to be taken to allow solid electrolytes to compete with conventional liquid electrolytes, which often have ionic conductivities three orders of magnitude higher than LIPON.

2.4.2 Lithium Lanthanum Titanium Oxides (LLTO)

The most attractive property of LLTO electrolytes is their high ionic conductivity. Studies have shown that LLTO is capable of existing in a state with an ionic conductivity of 10^{-3} S/cm, which is comparable to liquid electrolytes[27]. Other work has been done, where the electrolyte was made via pulsed laser deposition, yielding a value of 10^{-5} S/cm, which is still much higher than most other solid electrolytes. In addition to the high ionic conductivity of the material, LLTO is electrochemically stable and able to withstand hundreds of cycles. With all of these positive attributes, a few negatives do arise when using this electrolyte. The electronic conductivity is higher than most other materials, having a value between 10^{-8} and 10^{-9} S/cm. While this does not seem to present a pertinent threat to the material, given its high ionic conductivity, its ability to withstand processing does present an issue. LLTO requires a high annealing temperature, over 1000 ºC, which has been shown to break thin films[27]. Also, at this temperature lithium can react irreversibly with oxygen to form lithium oxide, Li_2O, which reduces the usefulness of the material. This renders a sintered LiCoO2/LLTO system useless, because sintering temperatures cannot be achieved without activating the associated chemical reaction.

2.4.3 Liquid Electrolyte Batteries

In liquid lithium ion batteries, a nonaqueous solvent is combined with a lithium salt to facilitate lithium ion transfer across the cell. In general, these types of batteries are far less efficient than solid electrolyte batteries due to their lower transference numbers, larger size, and poorer cycling.

Solvent

The liquid solvent used in liquid electrolyte lithium ion batteries must meet the following requirements[31]:

1. Have a high dielectric constant so that it can dissolve salts to a sufficient level.
2. Have a low melting temperature and a high boiling point. These properties allow the organic material to remain a liquid over a wide range of temperatures.
3. Maintain a low viscosity to allow for simple ion transfer.
4. Be nonreactive to all cell components including the salt, separator, both electrodes, and the cell casing.
5. Contain polar group that allow for the material to dissolve the salt more readily.

By observing these qualities of solvents, it can be determined if a liquid will be sufficient in a liquid lithium ion battery before the material is used. Some of the properties of common solvents are listed in Table 1.

Table 1: Comparison of liquid electrolyte solvents for use in lithium ion batteries[31]

Solvent	Molecular Weight (g/mol)	Melting Temperature (°C)	Boiling Temperature (°C)	Viscosity (cP)	Dielectric Constant
EC	88	36.4	248	1.90	89.78
PC	102	-48.8	242	2.53	64.92
DMC	90	4.6	91	0.59	3.107
EMC	104	-53	110	0.65	2.958

Observing propylene carbonate (PC), it can be seen that it contains a high dielectric constant and wide temperature range, making it seem to be a strong solvent material. Also, PC is able to dissolve a high amount of lithium salts and has high static stability with lithium[31]. Its viscosity, on the other hand, is high causing limitations in the ion transfer across the electrolyte. In addition, batteries using this substance experience poor cycle life due to a capacity fading caused by dendrite generation[31]. Formation of dendrites in a lithium ion cell can result in short circuiting as well as the occurrence of chemical side reactions.

With the limitations of PC, a large amount of research was poured into other solvent materials including ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC). EC has a higher dielectric constant than PC, while DMC and EMC are both an order of magnitude lower. In addition, DMC and EMC have small temperatures windows while EC is comparable to that of PC. EMC and DMC due, however, contain much lower viscosities than that of EC and PC, creating an upside for these solvents. Due to the non-ideality of certain properties within each solvent, they are often combined with each other to generate a better solvent[1]. Combing these solvents, in the presence of various salts, the transference numbers found in liquid electrolyte lithium ion batteries are 0.24 – 0.505, which are much lower than solid state electrolyte batteries[32].

Salt

The salt used in a liquid electrolyte lithium ion battery, like the solvent, has certain requirements it must meet[31]:

1. Completely dissolve and dissociate into the solvent to a sufficient concentration.
2. Move with high mobility within the electrolyte to facilitate ion transfer.

3. Be stable against oxidative decomposition at the cathode to ensure cell life.
4. Be inert to the solvent, both electrodes, and the cell packaging.
5. Stable against thermal induced reactions with the solvent and cell components.
6. Be nontoxic.

Commonly used salts in lithium ion liquid electrolyte batteries and their properties are listed in Table 2.

Table 2: Comparison of electrolyte salts for use in lithium ion batteries[31]

Salt	Molecular Weight (g/mol)	Melting Temperature (^oC)	Decomposition Temperature (^oC)	σ (mS/cm) in PC	σ (mS/cm) in EC/DMC
$LiBF_4$	93.9	293	>100	3.4	4.9
$LiPF_6$	151.9	200	80	5.8	10.7
$LiAsF_6$	195.9	340	>100	5.7	11.1
$LiClO_4$	106.4	236	>100	5.6	8.4

The most widely used salt in lithium ion cells is lithium hexafluorophosphate ($LIPF_6$). Partially available from Table 2, it can be seen that $LiPF_6$ does not have the highest values in every category important to performance in the cell. It does, however, contain moderate to good values in these properties which is the main reason it was used in commercialization of lithium ion batteries[31]. Many other salts exist with great properties, but they contain vital flaws unlike $LiPF_6$.

2.4.4 Other Electrolytes

Aside from the two popular solid electrolytes mentioned in the above sections, numerous other options exist in the field of solid state lithium ion batteries. These options include $LiNbO_3$, $LiTaO_3$, and Li-V-Si-O, which have ionic conductivities between 10^{-5} and 10^{-8} S/cm[27,33]. With these ionic conductivities, and electronic conductivities around 10^{-11} S/cm, these materials have comparable properties to LLTO and LIPON. In addition to these substances, a large group of polymer electrolytes exist that are able to contain very competitive ionic conductivities, as high as 10^{-3} S/cm. In these solid polymer electrolytes, as well as in $LiNbO_3$ and Li-V-Si-O, it was experimentally determined that amorphous structures contain higher ionic conductivities than crystalline structures [27,33]. In many cases, an amorphous material has a value between three and five orders of magnitude higher than its crystalline counterpart. One possible reason for the increase in ionic conductivity is that the unordered, amorphous material allows for diffusion to occur across multiple axes. This would give the ions far more diffusion directions than a crystalline solid and ultimately would lead to high ionic conductivity. The determination of high ionic conductivity in amorphous materials could potentially lead to increased use of these electrolytes in solid state lithium ion batteries.

2.5 All-Solid-State Li Ion Battery Cell Overview – Construction Current Technologies

Much of the current challenges associated with solid-state battery development involve high material and production costs coupled with an inability to efficiently produce all-solid-state cells on a large scale. The following discusses the difference between laboratory procedures commonly used to produce successful all-solid-state lithium ion batteries and proposed methods of mass-production.

2.5.1 Laboratory Production Methods

Laboratory production of all-solid-state Li Ion batteries is often successful because of how controlled and precise experiments can be. Because the ionic conductivity of solid electrolytes is less than that of liquid electrolytes (often 3 or more order of magnitude less), it is essential that the thickness of the electrolyte layer be reduced to reduce the resistance imposed by a less conductive and denser electrolyte substance. Figure 9 presents a generalized model for all-solid-state lithium ion battery construction[34].

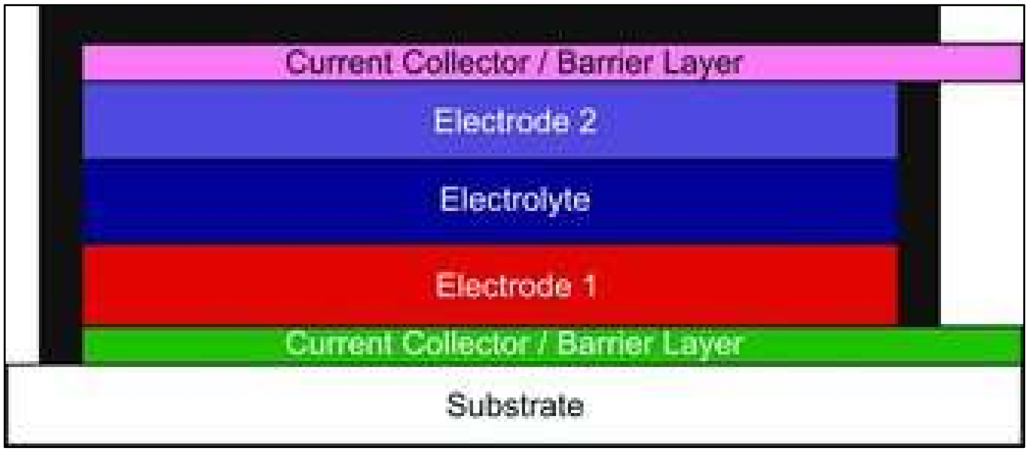


Figure 9: Demonstration of a Generalized Construction of All-Solid-State Li Ion Batteries[34]

It is important to note that, as mentioned, the solid electrolyte layer eliminates the need for an additional separator layer. However, it is imperative during construction that the solid electrolyte completely covers the electrode materials to eliminate the possibility of short circuits[27]. Different techniques are employed in the laboratory to achieve this layered and highly-compact structure. Presented in this review are examples of: magnetron sputtering, aerosol deposition, and pulsed laser deposition. Additionally, more practical, industrially oriented techniques are presented that hope to revolutionize and produce all-solid-state cells on a large, consumer-friendly and economic scale.

2.5.2 All-Solid-State Cells Developed Through Magnetron Sputtering

One of the most popular laboratory techniques for depositing solid films of cathode, anode, and electrolyte materials is known as magnetron sputtering. During magnetron sputtering, a target material is bombarded with microwaves during discharge, which ionizes and vaporizes the target material[35]. This technique allows for "ionizes physical vapor deposition" (IPVD) to take place on a surface, allowing for uniform, dense coatings of materials.

Because the energy density and transfer efficiency of all-solid-state lithium ion batteries can be greatly increased by increasing the density of the cathode, anode, and electrolyte materials, magnetron sputtering is a useful laboratory tool to accomplish cell construction. Magnetron sputtering is particularly useful for all-solid state systems because it allows for increased control over solid electrolyte deposition. Researchers at Beijing Institute of Technology have shown that, through magnetron sputtering and subsequent IPVD, it was possible to produce dense Li-Ti-Si-PO thin films[36]. While this research did not focus on battery implementation, Figure 11 demonstrates the capability of magnetron sputtering to form thin, dense films of electrolyte layers, while Figure 10 shows the competitive ionic conductivity of the resulting film at different temperatures.

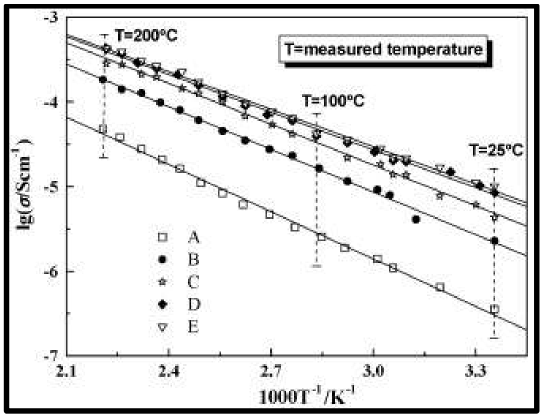


Figure 10: Plots of Ionic Conductivity of Li-Ti-Si-PO [36]

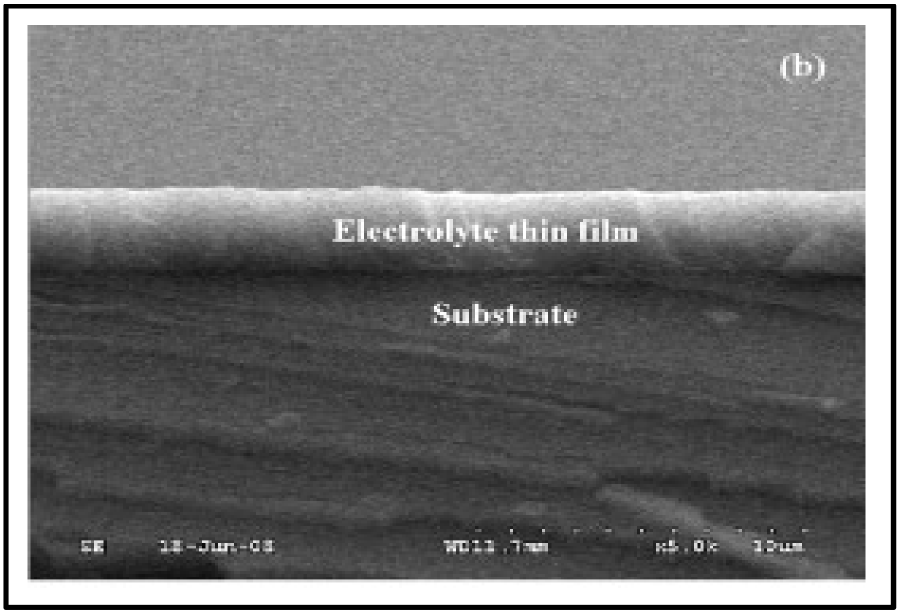


Figure 11: Li-Ti-So-PO Thin Film Solid Electrolyte Layer [36]

2.5.3 Applications of Pulsed-Laser Deposition in Li Ion Batteries

Because so much of battery technology focuses on operating at higher and higher energy densities and inside of thinner and thinner devices, being able to fabricate high-active material, high capacity batteries is essential to modern research and development. Pulsed-laser deposition (PLD) is an accurate and reliable way to deposit extremely thin (down to 1.2 nm thick) films on top of a chosen substrate[37]. The technology was originally developed to produce thin-film supercapacitors, but has since been adopted by the battery industry. The ability to produce such fine films allows for relatively easy laboratory-based thin film battery research.

When considering all-solid-state systems, the most important consideration is the application of the solid electrolyte. It must completely prevent contact between the anode materials and the cathode material without inhibition lithium ion transfer. Pulsed laser deposition has the advantage of having a fairly simple mechanism, in which a powerful laser "ejects" particles away from a solid or liquid surface[38]. Because of this, the technology can be used to transplant virtually any material (cathode, anode, electrolyte, current collector) from a bulk solution into a surface film. Using PLD to construct entire thin-film batteries is relatively new, first explored in 2004 by researchers at Tohoku University. The team sought to construct a thin-film battery modeled after the schematic seen in Figure 12.

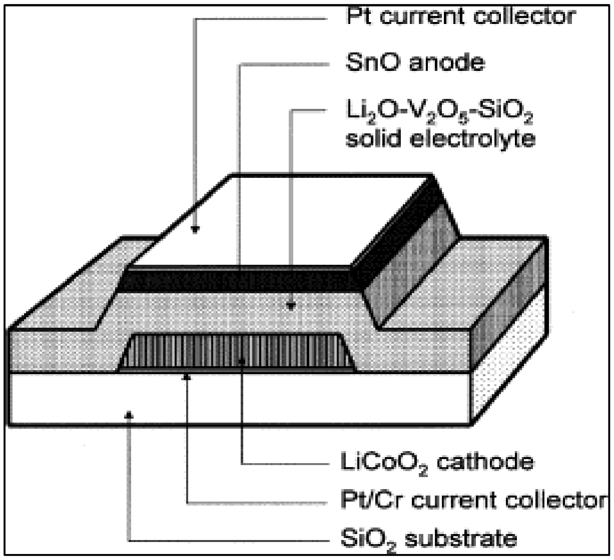


Figure 12: Thin Film Application to a Glass Substrate via pulsed laser deposition[39]

The materials for the project were prepared via various starting methods (including sintering and pressing), but all layers of the thin film were applied via PLD[39]. The team adhered a film of platinum onto a glass substrate and subsequently applied a $LiCoO_2$ cathode film onto the platinum current collector. The sintered LVSO electrolyte material was applied as a thin film through PLD, and on top of that the SnO anode and opposing platinum current collector. The cell achieved a thickness of just over 2 microns, and managed relatively high capacity and a cycle life approaching 100 cycles.

2.5.4 Solid-State Electrolyte Layers Developed Using Aerosol Deposition

One of the major complaints about pulsed-laser deposition and magnetron sputtering are that they require expensive environments for operation (vacuum, inert, etc…) and that the deposition rate is generally low, requiring a large amount of time to establish a relatively thin layer of material[40]. Additionally, in solid-state battery systems, the aforementioned technologies do not always allow for adequate interface contact between cathode and electrolyte, causing the cell to suffer from high resistance and lower overall ion transfer across the material boundary.

Researchers at Hayang University have attempted to circumvent these traditional problems by employing a technique known as aerosol flame deposition. In this technique, an electrolyte solution is aerosolized and fed to an extremely hot oxygen-hydrogen flame which deposits a layer of "glass soot" on a chosen substrate or electrode material[41].

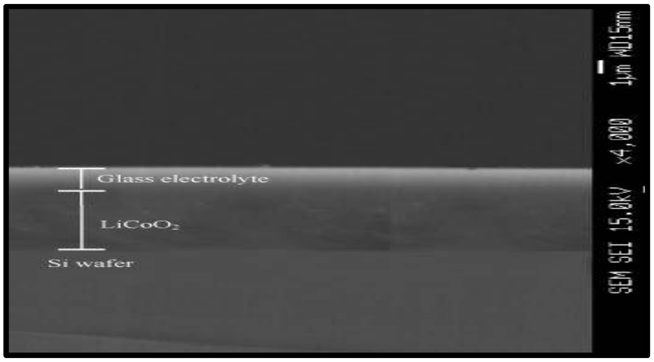


Figure 13: SEM of Solid-State Electrolyte Layers Deposited Through Aerosol Deposition[40]

The soot is then heat treated to remove lithium impurities and can be employed for electrochemical testing. This method allows for much higher rates of deposition (up to 3 microns/minute) than competing techniques, and as Figure 13 shows, when combined with high-density sintering, can generate reliably thin and integrated cathode and electrolyte layers[41].

The benefit of small scale, effective laboratory procedures is that they allow researchers to observe the full potentials of the materials that are being investigated. Deposition techniques involving expensive lasers, or costly nitrogen or vacuum environments allow for virtually perfectly dense and uniform material deposits to be formed. Unfortunately, economic and scaling issues have not allowed laboratory technologies, such as aerosol deposition and pulsed-laser deposition, to be adopted as standard industry practices, leaving all-solid-state lithium ion batteries from achieving mass commercial success. However successful in research and academic practices, the technology described is either expensive or not refined for industrial use.

2.5.5 Spin Coating Application in Battery Research Environments

Spin coating is an application method in which a thin film of material can be deposited onto a solid substrate. The use of spin coating as a deposition method for solid electrolyte batteries is not popular, but when utilized, it has been proven to be an effective means of creating an electrolyte layer[42]. Cheol-Ho Park and his research team have created a solid polymer electrolyte battery prepared by spin coating the electrolyte material onto the cathode[43]. In this work, the battery was cycled at a rate of 6C up to 100 times with a capacity fade to 85% of the initial capacity. The high rate in which the battery can charge and discharge, as well as the low loss of capacity over the cycle life, shows great promise in this method of solid electrolyte deposition.

Dunbar P. Birnie states that there are four main stages that occur during the spin coating process, with the first being the deposition of the fluid on the solid substrate[44]. In this step, the fluid is put on the target in excess to ensure a thick enough layer is formed and complete coverage of the material is obtained. The second step in spin coating occurs when the substrate is accelerated up to the final rotational speed used in the process. This step can be characterized by the expulsion of fluid from the surface of the solid substrate. A large portion of the liquid is spun off of the material, but a thin layer remains on the target. Next, in stage three, the fluid thinning is dominated by fluid viscous forces while the target spins at a constant rate. The force that pushes the liquid from the center of the material to the outer portion, and eventually off, the target overcomes the liquid viscosity during this step. This gives a uniform thickness across the solid substrate. The final stage occurring during the spin coating process is the solvent evaporation dominating liquid thinning while the substrate spins at a constant speed. Here, viscosity is too high for the force generated by the spinning of the substrate to move the liquid, so the viscous forces no longer effect the thinning of the liquid layer. Thus, the evaporation of the solvent liquid begins to dominate the thinning process until the disk is dry, with the exception of a small amount of liquid that may still remain. Often, the substrate with the newly formed layer is fired to remove any remaining volatiles from the material.

While the general list of stages occurring in the spin coating process is detailed above, deviations do exist. The main distinction that can be made between spin coating processes deals with when the liquid material is deposited onto the solid substrate. In the first spin coating style, a pool of liquid is placed on top of the target, completely covering the surface, and then the material is spun at a high rate, usually around 3000 rpm. The other method for application is to apply the solution as the target spins at a low rate, around 500 rpm. In this process, the film is created by adding droplets of the solution periodically to the spinning substrate. It has been found that this deposition method results in less waste of the solution material, since there is not a thick layer of liquid being spun off of the target[45].

One of the reasons that spin coating is starting to be utilized in laboratory experiments is the ability to control the thickness of the deposited film. Some of the parameters that affect the film thickness include spin speed, spin time, fume exhaust, and acceleration. The speed at which the substrate spins controls the multiple factors that play a role in the deposition of the film. As the target spins, the fluid experiences radial force that pushes the liquid to the edge and off of the substrate. In addition, the velocity and Reynolds number of the air above the spinning solid material is greatly affected by the spinning speed. Both the radial force and the flow of air above the material greatly determine the thickness of the film during the spinning stage of spin coating. Differences of ±50 rpm can lead to a difference of ±10% in the film thickness, proving that spin speed plays a substantial role in determining the film thickness.

Acceleration also plays a large role in the film thickness due to the evaporation of the solvent during the beginning of the process. Up to 50% of the solvents can be lost during the first few seconds of the spinning process, which is the time period when the substrate is taken from its initial resting point to its final spin speed. Another large factor in the thickness of the film during spin coating is the fume exhaust. The quality of the air surrounding the spin coating apparatus greatly affects the drying rate of the solvent being deposited on the substrate. Temperature and the flow of the air, turbulent or laminar, change the thickness by adjusting the natural evaporative rate of the solvent in the resin. Ideally, these parameters should be controlled to yield a slower drying rate as this results in a more controllable fluid viscosity. Aside from the previously listed factors, the spin time also plays a role. Longer spin times cause the liquid to experience longer thinning periods and ultimately yields a thinner film.

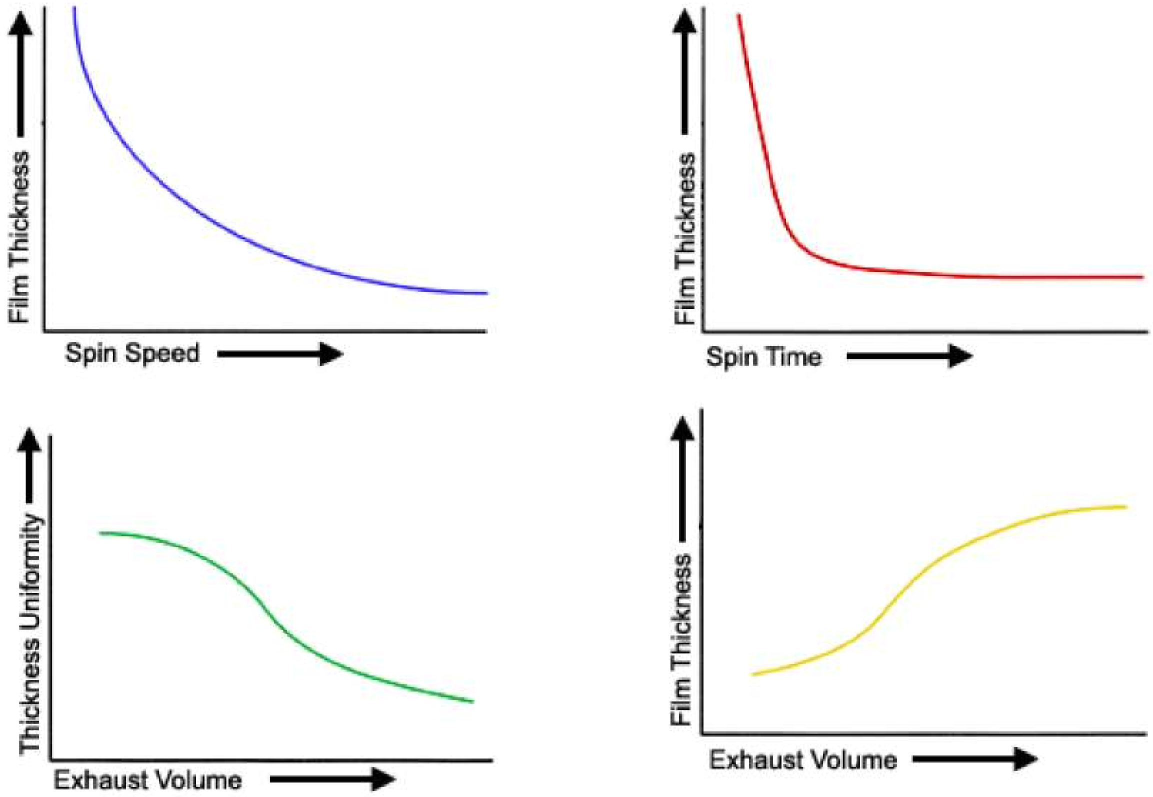


Figure 14: Graphical characterization of the various parameters of spin coating and their effects on film thickness and the uniformity of the film thickness[45].

While the thickness of the film can be controlled via spin coating, many problems involving the quality of the layer can occur. These problems, along with possible causes of these issues, are detailed below.

- Deposited Film is too thin
    - Spinning speed is too high
    - Spinning time is too long
- Deposited film is too thick
    - Spinning speed is too low
    - Spinning time is too short

    - Exhaust volume is too high
- Air bubbles on film
    - Air bubbles exist in the fluid prior to depositing
    - Dispense tip is cut unevenly or contains burrs or defects
- Streaks from the center to the edge of the film are visible
    - Fluid dispense rate is too high
    - Exhaust rate is too high
    - Resin sits on the substrate too long before the spinning begins
    - Spinning speed and acceleration are too high
    - Particles exist on the substrate before the liquid is dispensed
    - The fluid is not dispensed at the center of the substrate
- Swirl patterns are visible on the film
    - Exhaust rate is too high
    - Fluid is deposited off the center of the substrate
    - Spinning speed and acceleration are too high
    - Soin time is too low
- Uncoated areas on the substrate
    - Low dispense volume of the fluid
- Pinholes visible in the film
    - Air bubbles in the fluid
    - Particles exist in the fluid
    - Particles are on the substrate prior to the fluid dispensing

2.6 Industrial Manufacturing of All-Solid-State Lithium Ion Batteries

In order to harness the power of newly developed battery technology, to improve the safety of battery systems, and to take the next step in portable power supplies, all-solid-state cells must be able to be manufactured on a large scale. Laboratory practices that allow for solid electrolyte to be applied as thin films also limit the thickness of the cathode and anode materials, limiting the overall capacity of individual cells. This limits the potential of the technology to small scale systems.

Planar Energy, an all-solid-state battery startup company based out of Orlando, Florida has developed a method for printing solid-state lithium ion cells based off of printing technology[46]. The company has managed to develop solid electrolytes that are able to be applied through roll-to-roll technology with properties that mirror the performance of liquid electrolyte[21]. Normally, roll-to-roll processes are avoided, but chemical preparation in Planar Energy's pre-roll process (electrode and electrolyte slurries) allow for the development of cells that rival the performance of those formed with more reliable and consistent vapor deposition methods.

2.7 Directly Competing Technologies – PEMFC, SOFC, and Flow Batteries

Disregarding conventional battery technology, the most direct competitors to all-solid-state lithium ion batteries come from developments made to portable fuel cell technologies in the form of PEMFC and SOFC. Both proton exchange and solid oxide fuel cells convert a fuel stream into electricity rather than storing chemical energy and releasing it, as battery systems do.

PEMFC and SOFC differ in their construction, and the fuels that they are able to accept. PEMFC require, to operate efficiently, hydrogen as a fuel[47]. Ideally, this is an excellent strategy, as hydrogen burns to create water and no harmful byproducts. However, hydrogen is prohibitively expensive, dangerous to store, and difficult to transport. SOFC, on the other hand, are able to convert current, fossil fuel based hydrocarbons into electricity at a much higher efficiency than an internal combustion engine[48]. In the fuel cell market, SOFC are the most direct competitors for all-solid-state batteries, because much of the solid-state-electrolyte research is split between the two technology fields.

Flow battery systems is another competing type of battery in which liquid electrolyte that contains dissolved electroactive species goes into an electrochemical cell, which converts the chemical energy created into power. Specifically for redox flow batteries, when energy needs to be discharged, the analyte solution goes through an electrode and generates electrons that go through a circuit[41]. The charge carriers then go to an ion exchange membrane in order to separate the analyte and catholyte solutions. Two separate electrolytes are used to make sure the potentials at each electrode are relatively close to the reversible potential of the half-cell reactions. An example of this in action is shown in Figure 15. The energy losses in this system are attributed to moving the mass and charge in the electrolyte and separator[49].

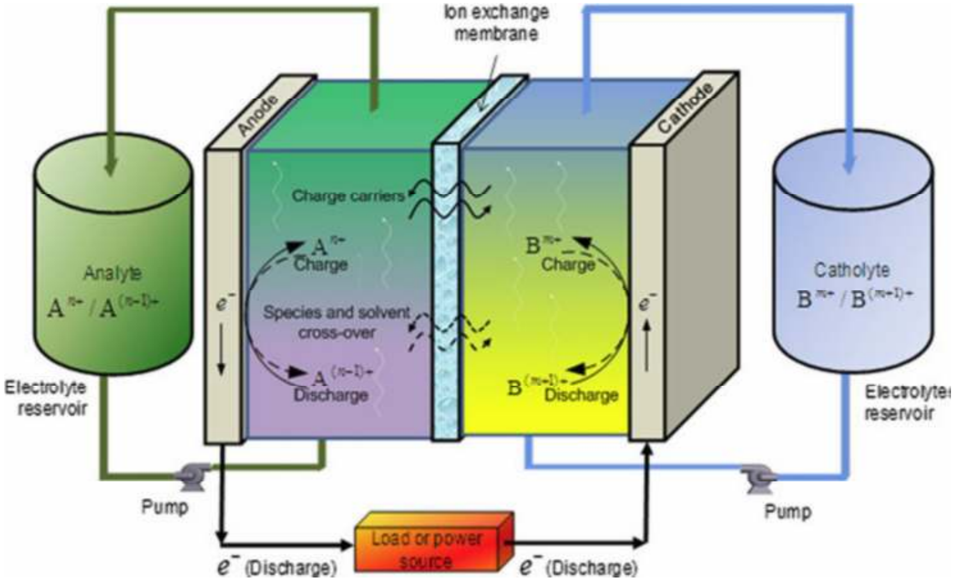


Figure 15: Theoretical Flow Battery Diagram[49].

One benefit of redox flow batteries is that there is no transfer of material across the electrode. The material (the analyte and catholyte) is transferred from outside the electrode into the electrode, which is useful for stationary applications. Some other advantages redox flow batteries have are that they have high efficiencies, low cost per kWh, more environmentally friendly that other sources, and long cycle lives[53]. Some types of materials for redox flow batteries that are currently being studied include iron/chromium, bromine/polysulfide, vanadium, and vanadium/bromine. Some factors that need to be studied further for this technology in the future are charge transport and the electrochemical reaction near the electrode surface, the mechanics behind transporting electrolyte through various cell architectures, and also performance degradation as the materials being used start to degrade[49]. Overall redox flow batteries sound promising, but there is much work that needs to be done to determine their validity.

2.8 Applications

Solid State Lithium Ion Batteries recently have had many applications due to its high temperature performance and long cycle lives. Unlike liquid electrolyte lithium ion batteries, solid electrolyte batteries are also intrinsically safe in design and therefore can be used in more applications. If the battery is punctured, the solid electrolyte will not leave the battery unlike liquid electrolytes which can flow out of the battery and cause a fire hazard. Because of these traits, solid state lithium ion batteries have many applications in the consumer, industry, and academic fields.

2.8.1 Consumer Applications

The main application solid state lithium batteries would have for consumers is in batteries and in battery operated appliances such as hybrid or electric vehicles. Solid state lithium batteries can store more energy safely than liquid lithium batteries which will eventually lead to lower costs for hybrid and electric cars. Specifically, Planar Energy, a company that creates lithium batteries, mentions that solid state Lithium batteries can store 2-3 times more energy at the same weight of liquid Lithium batteries. Planar Energy also claims they will also be able to last tens of thousands of cycles for only a third of the cost to create them[50]. With these advantages, solid state lithium batteries have the potential to replace liquid lithium batteries completely and eventually consumers could possibly have battery operated devices with only solid state lithium batteries in them.

2.8.2 Industrial and Manufacturing Applications

In industry, innovators have found many uses to the new technology of solid state Lithium batteries. For example, solid state Lithium batteries are used for medical devices such as implants and electronic pills, in which the latter can function as an imaging device or for controlling drug delivery in the body. These batteries need to be of a small size while keeping safety a priority, which is why solid state lithium batteries are essential. Solid state lithium batteries can also be used as an excellent storage mechanism for the energy photovoltaic cells absorb. An example of this is shown below using a 3D solid state battery. They can also store energy efficiently for piezoelectric, thermoelectric and electrostatic energy scavenger[27]. Other industry applications include RFID tags, wireless sensors, memory backup power and batteries for extreme high and low temperatures[51]. The safer solid state Lithium batteries allows for companies to provide more applications where consumer safety is important.

Smart cards are also being developed and they are powered using thin film Lithium batteries, a variation of solid state Lithium batteries in which the electrolyte is Lipon, an amorphous polymer. They can be used for a multitude of purposes, from being a combination of ATM, credit and debit cards, to holding healthcare files. Other uses would be to give authorization on documents, check out books, or even as keys for hotels and cars. The manufacturing process of these smart cards introduces the power supply to around 140ºC of heat and 200 N/cm^2 of lamination, which currently only thin film Lithium batteries can withstand and remain charged. Other types of batteries such as conventional liquid Lithium ion batteries cannot be processed at the high temperature and pressure. Even if the battery survives, leakage from the liquid electrolyte could cause problems with the rest of the device[52].

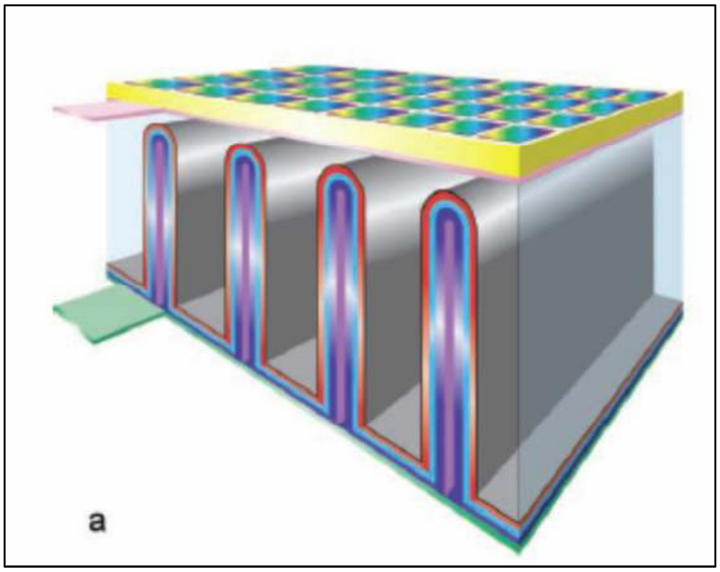


Figure 16: 3D solids state Lithium ion batteries with photovoltaic cell scavenger[52]

2.8.3 All-Solid-State Battery Systems in Academic Environments

Finally, in academics, the introduction of solid state Lithium batteries allows not only a further understanding of batteries but also stimulates research in the field. Due to the creation of solid state Lithium batteries, many universities have taken the steps to research ways to further increase the properties such as strength and energy capacity while lowering the size of the battery. In the last 5 years, research on these batteries has led to hundreds of publications being written. Some current research topics will be introduced in the following Chapter[51].

2.8.4 Future Potential

Although solid state lithium ion batteries are very efficient as is, many researchers have looked into ways to improve the design further for the future. One way is to create a 3D solid state battery, which increases the volumetric energy density of the battery while using the same amount of packaging and substrate material when the 3D geometry is created[27]. Some discussed geometries are based off of a membrane template, pyrolysed photoresist microrods, porous aerogels or micelle structures, microchannel plates and anisotropically etched micro-structures. An example of a 3D thin-film battery which uses microchannel plates is shown below in Figure 17.

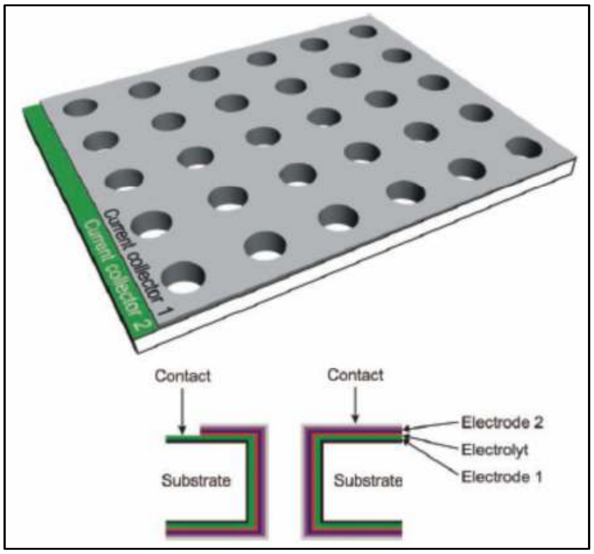


Figure 17: 3D thin film solid state Lithium ion battery based off of microchannel plates[52]

One application 3D solid state batteries will be used in is SAND or Small Autonomous Networked sensor Devices which use functions such as wireless communication, on board sensing and energy harvesting. Because wireless communication needs high peak currents, 3D solid state batteries can offer high currents and high energy densities while having a low volume. The storage potential of 3D solid state batteries is also an important factor for SAND's. Although this does sound promising, further testing must be done for 3D solid state batteries[27].

2.9 Current Technological Conclusions

Overall, solid state Lithium ion batteries have a great deal of potential and provide many advantages that conventional batteries currently cannot. The origins and advantages of solid state Lithium ion batteries were discussed as a background into the batteries, as well as the diffusion processes and types of materials used for solid state Lithium batteries. The construction of the cells and the current and competing technologies were also discussed to understand the current market and interest in solid state Lithium batteries. Finally, the applications and potential for the future of solid state Lithium batteries can show how solid state Lithium batteries can help and improve the lives of consumers and companies in the industry. With further work into solid state Lithium ion batteries, reliance on fossil fuels to power transportation vehicles has the potential to decrease due to the steady improvement of batteries. The focus on reducing reliance on finite energy sources is only a recent endeavor but with focus in research and application on improving energy sources such solid state Lithium batteries, future generations will not have to deal with this issue when it is too late.

3.0 Methodology

The scope of a project like this, in which an attempt is made to develop or enhance newly forming technologies in the field of lithium ion batteries could be considered beyond the scope of a generic Major Qualifying Project. The amount of time available to dedicate to a project such as this, considering technological setbacks, equipment delays, and the formulation of experiments and development strategies exceeds one year barring an excess of luck and efficiency on the part of the team completing the project. A project of this magnitude had the definite possibility of taking more than the 21 school-weeks allotted for it. Despite the best efforts of the group, the innovative, rather than replicative, nature of the project generated numerous setbacks which required further study and understanding in order to learn from and improve upon those experimental failures.

For this reason, the methodology and intent behind each individual step is of utmost importance for the success of this project. This section details the approach to each step of the process of developing $LiCoO_2$ cathode, LLTO solid electrolyte, and lithium metal anode based all-solid-state lithium ion batteries. It emphasizes the importance of each step of experimentation, and can be used as a way to repeat experiments performed during the project process. Figure 18, shown below, attempts to graphically demonstrate the thought process that drove this process.

Additionally, each section will explain the development and synthesis of: materials synthesis, battery construction, and experiment set-up. Specific details include: materials required, initial approach considerations, exact procedures, and resulting and supporting images and diagrams. Ideally, by studying Section 3 and Section 4 of this report, an informed reader should be able to replicate the experiments performed, and be able to avoid the pitfalls encountered during this specific project's timeline. The specific steps taken are mirrored in

Section 4 (Results and Discussion) to elaborate on the successes and failures of each approach taken during the experimentation and synthesis process.

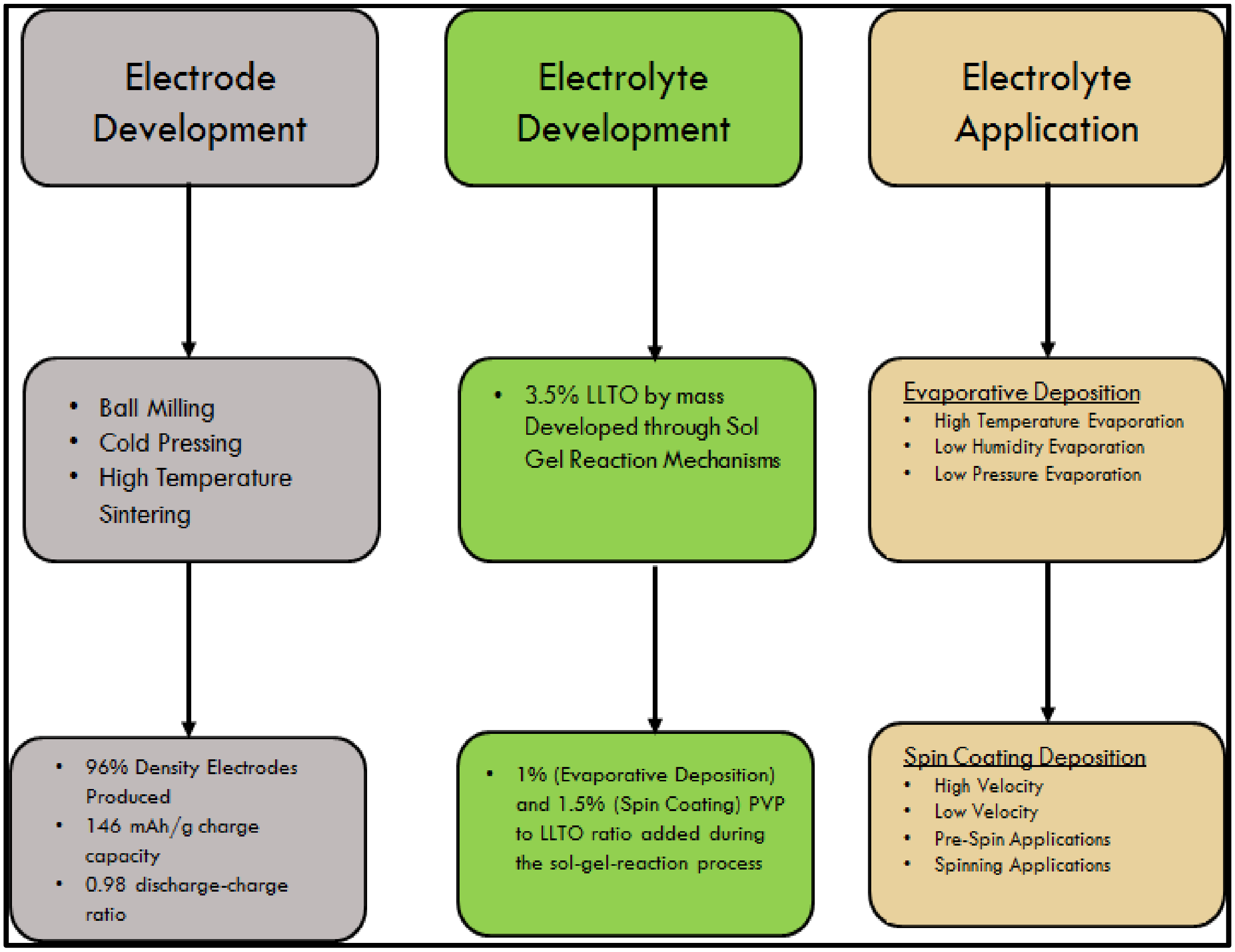


Figure 18: A pictorial representation of the though process behind this project, showing the three categories that were examined independently and together to produce new all-solid-state lithium ion battery construction methods

3.1 $LiCoO_2$ Electrode Development Process

Section 2 discussed the importance of areal energy density when constructing anodes and cathodes for all-solid-state lithium ion batteries. In order to increase the areal energy density of the cathodes developed during the course of this project, a less-common method of cold pressing followed by high-temperature sintering was employed. This allowed for increased thickness to be used while retaining relatively high density.

Generally, in a laboratory environment, common all-solid-state techniques include expensive equipment (pulsed-laser deposition, vapor deposition, etc…) to produce thin film batteries, as demonstrated by Wu and Kuwata[38, 39]. By using a simpler, more materials-based construction process, if successful, this electrode development would allow for a cheaper process more easily reproducible manufacturing process on a large production-based scale.

3.1.1 Large-Particle Medium Density $LiCoO_2$ Sintered Cathodes

Initial electrode development began with the procession of "stock" $LiCoO_2$ powder. This powder consisted of relatively-high particle size $LiCoO_2$, so additional processing considerations needed to be considered to develop successful cathodes. Because large particle sizes prevent particles from sticking together during cold-pressing, the "stock" $LiCoO_2$ powder was mixed at a 1:1 mass ration with a solution of 1% by mass polyvinyl alcohol in deionized water. These materials were mixed together into a slurry, and subsequently baked at 70° C to evaporate any water or other organics contained in the mixture.

After baking, this solid mixture was hand milled in a mortar and pestle for 30 minutes until fine and smooth. Approximately 0.6 grams of powder was then poured into a mold and cold-pressed under 5000 PSI for 2 minutes using a hydraulic press. The particles were then carefully removed from the mold (to avoid damage to the fragile pressed-powder electrode forms) and prepared for sintering. In order to achieve a uniform crystallization, the $LiCoO_2$ patties were laid on a ceramic sintering plate dusted with stock $LiCoO_2$. After arranging the samples to be sintered with ample room between (to allow for even heat distribution), the samples were then coated with stock $LiCoO_2$ powder. After preparation was completed, the samples were placed in a box furnace at 1100 C for 15 hours under a heating and cooling rate of 9 C per minute.

Once cooled and removed from the furnace, the samples were “cleaned” of unprocessed $LiCoO_2$ used to coat the samples using a razor blade, and the samples were polished as thin as possible to a reflective surface using high-grit sand paper. Progressive levels of grit were used for polishing, in order to achieve a mirror surface on the face of the electrode. The electrodes were then tested for density using volume-based density calculations. After completion, these electrodes were tested in a number of ways described in Section 3.4.

3.1.2 Ball-Milled Small Particle $LiCoO_2$ Sintered Electrodes

After acquiring a ball mill for use in the lab, it was possible to develop higher density $LiCoO_2$ patties by milling the stock $LiCoO_2$ powder for extended periods of time in the ball mill. The chosen milling jar was filled half way with aluminum oxide milling balls and 50 grams of stock $LiCoO_2$ powder. The ball mill was then run for 7 days at 100 rpm to produce low-particle-size $LiCoO_2$ for use in cold-press sintering.

After the powder was sifted and removed from the milling jar, the powder was immediately cold pressed in the same mold described in Section 3.1.1. In this case, because the particle size of the powder was much smaller than the initial construction process, no PVA was added before cold pressing, and no baking or hand-milling was necessary. The samples were again pressed at 5000 PSI for 2 minutes, subsequently sintered at 1100 C for 15 hours, and the samples were handled and polished as described in Section 3.1.1. Because of the smaller particle size, it was also possible to cut the amount of material required for cold pressing in half from 0.6 grams to 0.3 grams. The major difference in this case was the increase in density (approximately 8%, discussed further in Section 4), which allowed for polishing to a thinner electrode profile.

3.1.3 Ball-Milled Small Particle $LiCoO_2$ Sintered Electrodes Pressed with PVA Binder

Issues arose concerning the molding and cold-pressing of the $LiCoO_2$ patties during the polishing process several times throughout this project. During the polishing process, large cracks would appear traversing the length of the electrode. It was determined that these cracks were not a result of overly-aggressive polishing procedures, rather that they were produced during the cold press phase. The sintering phase was ruled out by taking cross sectional SEM of the samples and determining that the crystallization taking place during sintering was desirable while also taking into account the higher density.

In an attempt to rectify these issues, the ball-milled small particle $LiCoO_2$ powder was mixed into slurry form with 1% by mass PVA dissolved in water, baked until dry, and hand-milled as described in Section 3.1.1. This powder was then cold pressed, sintered, and polished in the same manner as described in Section 3.1.1 and 3.1.2. The temperature of the sintering was also dropped to 1050 C to determine if the initial 1100 C was promoting a change in the crystallization structure of the smaller particles, causing them to become brittle. The results of this attempt can be found in Section 4.

3.1.4 Ball-Milled Small Particle, Large Mold $LiCoO_2$ Electrode Development

In an attempt to produce cathodes with a larger working surface area to facilitate the proposed spin coating process described in Section 3.3.2, it seemed most logical to change the way that the electrodes were physically formed. The properties of the materials that were developed through sintering were acceptable, but the actual areal real estate was too small. There were two different attempts to make large exposed surface areas on which to work: large mold production and free form pressing. Both used additional ball-milled $LiCoO_2$ powder (1 gram, up from 0.3 grams) and the same hydraulic press.

The first attempt made use of a larger mold, approximately 1.5 times the diameter of the standard mold used for electrode development. A pressure of 10,000 PSI was applied to offset the increased amount of $LiCoO_2$ powder used to fill the mold and the increase in the cross sectional area of the mold to an acceptable level. The formed patty was then carefully transferred and coated with stock $LiCoO_2$ powder and sintered at 1100 C for 15 hours.

The second attempt to produce a larger working surface area made use of no mold, and instead, 1 gram of ball-milled powder was pressed between two sheets of wax paper. This strategy attempted to exploit the ability of the extremely fine powder to pack into a relatively strong cold-pressed patty. It was postulated that the increased surface area would produce more friction during spin coating and allow for a more even and complete distribution of solid electrolyte on the surface of the electrode (discussed further in Section 3.3.2).

3.2 LLTO Sol Solution Development and Storage

Once the development of the $LiCoO_2$ sintered, high-density electrodes was finished, time and resources were also dedicated to the research and fabrication of an acceptable solid-state electrolyte. As noted in Section 2, in order to be an effective electrolyte, the chosen material must have high ionic conductivity and low electronic conductivity. This facilitates the transfer of lithium ions from the cathode to the anode during charging, and vice versa during discharging while avoiding the possibility of a short circuit between the two current collectors.

LLTO was determined to be the solid electrolyte best suited for this project's overall progression and development, but it was important to determine the appropriate application method. As noted in Section 2, thin layers of solid electrolyte are generally applied via expensive pulse laser or electron sputtering deposition techniques in laboratory environments.

Without access to this equipment, it was determined that using a sol gel facilitated reaction to synthesize the LLTO, followed by either spin coating or evaporative deposition would be the most accessible paths to take.

During the development of this LLTO sol solution, several different chemical mixtures were employed in an attempt to improve the integrity of the film formed during the drying and sintering application process associated with the all-solid-state battery construction. These different development methods are described in the following sub-sections, and complete recipes are detailed in Appendix A.

3.2.1 LLTO Sol Solution Developed through Sol Gel Reaction in an Alcoholic Environment

Initially, with the help of WPI PhD student Zhangfeng Zheng, an LLTO suspension (sol solution) was generated through a sol gel reaction between two different solutions. Lithium Acetate Dihydrate and Lanthanum (III) Acetate Hydrate were dissolved in deionized water to form the first solution, and isopropyl alcohol, acetic acid, and Titanium (IV) Isopropoxide were mixed to form the second solution. The first solution was added drop wise over 30 minutes to ensure a complete reaction and dissociated throughout the final solution.

The final product was a semi-clear liquid with opaque particles floating throughout. The LLTO in the solution made up 3.5% by mass. It should be noted that due to solvency issues of Lanthanum (III) Acetate Hydrate in deionized water, it proved extremely difficult to increase the solution concentration of the LLTO sol solution throughout the course of the project. It became necessary to regulate the amount of LLTO applied by varying the amount of solution used concerning a particular sample.

3.2.2 LLTO Sol Solution Strengthened with addition of post-reaction Polyvinylpyrrolidone (PVP)

Because the strength and coverage of the original LLTO film being formed post-sintering (see Section 3.3 for details), changes needed to be made to improve the strength of the pre and post sintering of the applied LLTO sol solution. Drawing from US Patent 2009/0004371, which employed PVP to great success as a binding agent, new LLTO solutions were formulated.

Initially, it seemed that there was no immediate reaction taking place between the LLTO sol solution being generated. As such, the steps described in Section 3.2.1 and Appendix A were followed to generate the standard LLTO sol solution. Additionally, an extra solution of PVP in ethanol (ethanol chosen due to high solubility at standard temperatures and pressures), consisting of 1% PVP in ethanol by mass was formulated. This third solution was added to the LLTO solution drop wise at a 1:10 ratio resulting in a final solution of LLTO and PVP in organic solvents with approximately 3% LLTO by mass and 0.1% PVP by mass.

As an additional exploration, this LLTO, PVP, Ethanol final solution was also added at a 7:10 ratio of ethanol solution to PVP solution. As described further in Section 4, these increases in binder proved fruitless, because the low solubility of PVP in the ethanol, acetic acid, and isopropyl alcohol mixture.

3.2.3 LLTO Sol Solution with Reaction Dependent addition of Polyvinylpyrrolidone

Because of the inherent instability found when mixing PVP into LLTO post sol gel reaction, a different approach was necessary. This time, exactly following the recipe given in US Patent 2009/0004371, described further in Appendix A, a final LLTO solid state electrolyte sol solution was generated to be used throughout the rest of the project's life.

In this method, three independent solutions were generated. Solution A was the same as described in Section 3.2.2, where Lithium Acetate Dihydrate and Lanthanum (III) Acetate Hydrate were dissolved in deionized water. Solution B consisted of PVP dissolved in Isopropyl alcohol, and Solution C consisted of Titanium (IV) Isopropoxide dissolved in acetic acid. Solutions B and C were mixed together, and then solution A was added dropwise into the mixture of B and C.

Upon further investigation of the results of spin coating and evaporative deposition of LLTO on the surface of $LiCoO_2$, it became necessary to increase the amount of PVP dissolved in the LLTO solution from approximately 1% to 1.5%. By increasing the amount of PVP dissolved in solution, it was postulated that better adhesion would allow for a more complete and denser coverage of LLTO on the $LiCoO_2$ electrode surfaces.

3.3 LLTO Application Methods and Solid State Battery Construction

After successful development and testing of the $LiCoO_2$ cathodes and LLTO sol solution, the next, arguably the most important step in the process was the LLTO application and assembly of the all-solid-state cell. Without acceptable LLTO coverage, one of two things would happen. First, if there was not adequate coverage (100% of the $LiCoO_2$ surface), there would be a very high probability of short circuits. The lithium metal anode would be able to press directly against the $LiCoO_2$ cathode, allowing electrons to flow freely from one side of the cell to the other, causing a short circuit through the battery. Secondly, if adequate coverage was present to prevent the cell from short circuiting, there was the possibility that an uneven or excessively thick solid electrolyte layer would prevent the transfer of lithium ions from cathode to anode and vice versa. This limitation would prevent the cell from being charged and discharged, rendering it effectively useless.

During this project, three different LLTO deposition methods were employed in an attempt to establish a satisfactory layer of solid electrolyte to separate the $LiCoO_2$ electrode and lithium metal anode and facilitate a relatively high rate of lithium ion diffusion across the cell. These methods included: evaporative deposition, high velocity spin coating, and cold-press sintering. Each method was performed on a successfully sintered and polished $LiCoO_2$ electrode. Those methods, along with complications experienced, are described in the following sections.

3.3.1 Evaporative Deposition of LLTO on $LiCoO_2$ Sintered Electrodes

Given that one of the goals of this project was to produce safe, effective, low-cost all-solid-state lithium ion batteries, one of the most immediately evident ways to accomplish these goals was through evaporative deposition. Because the sol solution was stable and well distributed, it seemed that evaporation would provide a thin and even layer of solid electrolyte which could then be sintered on top of the $LiCoO_2$ disks.

In order to facilitate the evaporation of the LLTO sol solution, several methods were employed. First, a polished $LiCoO_2$ disk was placed in a glass dish and covered with approximately 2.5 mm of LLTO sol solution. This dish was then placed under a fume hood (to facilitate faster and more complete evaporation via a dehydrated environment) for 24 hours. After 24 hours one of two things happened. Either the sample was removed from the dish with a razor blade and preserved in a disposable glass bottle, or the evaporation was performed again. After either removing the sample or completing the extra evaporations (up to 3 times), the sample was placed into a box furnace at 650 C for 6 hours.

Occasionally, depending on the number of evaporations performed, or the size of the sample, it became difficult to remove the electrode from the glass dish without compromising the LLTO film or the electrode's physical properties. To remedy this, a flexible container was made out of aluminum foil which could be readily broken down after the evaporation was completed. This theoretically allowed for a more reliable method of recovering the $LiCoO_2$ disks used in the final battery construction.

After the addition of PVP to the LLTO sol solution, it became increasingly more difficult to recover by the $LiCoO_2$ disks after performing evaporative coating. The PVP would plasticize into a rigid and tacky film as the organic solvents dried, and the electrode proved time and again to be impossible to remove. To combat these difficulties, a strategy was proposed which involved performing the evaporations direction on top of a stainless steel current collector. Then, to avoid oxidation, the current collector covered by the electrode and solid state electrolyte film would be sintered in a tube furnace. This strategy would allow one to avoid excessive handling of the electrodes after applying the electrolyte, which could potentially damage the surface of the film, rendering it useless.

In order to remedy the irreversible damage experienced by the $LiCoO_2$ electrodes, a partial-evaporation method was proposed and tested. During partial-evaporation, a set of open containers were filled with LLTO sol solution and exposed to the atmosphere under a fume hood for varying amounts of time. Depending on the amount of time the mixture was allowed to evaporate, the thicker and more viscous it became. The ideal viscosity was between that of oil paint and honey; the mixture needed to be viscous enough to have high surface tension and be self-contained, but liquid enough to allow for easy spreading and to preserve the desired high-density coverage. These mixtures, exposed to evaporation for different amounts of time, were then “painted” onto the electrodes in an attempt to enhance the concentration of LLTO and improve the surface targeting of the evaporative method.

After the “painting” was completed, the mixture was allowed to dry completely and form a solid LLTO film on top of the electrode. This combination was then sintered in a furnace as the same specifications given previously, and the electrodes were subsequently tested and inspected using an electron microscope.

3.3.2 Spin Coating of LLTO on $LiCoO_2$ Sintered Electrodes

During evaporative coating, because of the low concentration of LLTO in the original sol solution, areas were occasionally left barren and devoid of any LLTO covering. Other areas were subsequently covered with much more LLTO than was necessary (10 -20 microns as opposed to the desired 1-2 microns), albeit being 100% dense and well formed. In order to solve this problem, the most viable and cost-effective solution appeared to be spin coating. Spin coating, as described in Section 2, aims to effectively and uniformly distribute the suspended solid in a solution through high velocity spinning and rapid drying.

The spin coating process was attempted with all LLTO mixtures to determine the effectiveness of each iteration of LLTO sol solution. Two main spin coating techniques were attempted – applying solution while spinning, and spinning after applying the solution to the substrate surface. Initial attempts involved the application of PVP-free LLTO while the substrate was spinning. Initial tests to determine the potential effectiveness of this method (to avoid wasting large quantities of LLTO sol solution and $LiCoO_2$ electrodes) involved spinning a piece of aluminum foil at 3000 RPM and applying the solution drop-wise. A thin film (visible to the naked eye) appeared to form, so this method was subsequently tested on actual electrodes.

A sintered $LiCoO_2$ electrode was polished and cleaned in ethanol, and subsequently attached to the spin coater surface with double sided tape. The sample was then spun at 3000 RPM and solution was applied drop wise (one drop per 10 seconds) for two minutes. The sample was allowed to dry under a fume hood, and was checked for the formation of a film once the drying was complete. Though the film was not visible, it was assumed that it might be too thin to see with the naked eye, so the sample was sintered at 650 C for 6 hours and re-checked. SEM results shortly thereafter revealed that the solution was not depositing properly, so this method was abandoned in search of a more effective spin coating method.

It was postulated that the method was not necessarily what failed to apply the LLTO film, but perhaps it was the LLTO solution itself. As described in Section 3.2.4, PVP was added to the LLTO sol solution in an attempt to increase the capability of the particles suspended in the solution to bind to the surface the of the $LiCoO_2$ substrate. In addition to using the new LLTO sol solution, the spin coating technique used involved applying the sol solution before spinning and only by spinning in short bursts.

Initial attempts to use PVP infused LLTO sol solution (lower relative concentration of PVP by mass) were conducted as follows. As described before, individual electrodes were polished to a mirror surface and washed with ethanol and subsequently attached to the spin coater with double sided tape. Enough PVP infused LLTO sol solution was then applied to the top of the $LiCoO_2$ electrode to cover the surface. The electrode was then spun at 3000 RPM for 10 seconds. After spinning, the tape was removed from the spin coater and placed inside of a furnace at 130 C. This precaution was taken to increase the drying rate of the film, and to prevent damage to the electrode when attempting to remove it from the surface of the tape.

Once the glue had been deteriorated by high temperature exposure, the sample was allowed to cool and was removed from the remaining plastic. The sample was then placed in a ceramic crucible and sintered at 650 C for 6 hours, with stepwise temperature increases of 1 degree per minute to 450 degrees, and 9 degrees per minute from 450 to 650 degrees. After the sintering was completed, the entire process was repeated up to seven times. Samples were retained for further testing and SEM imaging at 1 layer, 3 layers, 5 layers, and 7 layers, assuming one layer was formed per application cycle.

After testing and imaging this spin coating strategy, another was devised and implemented in an attempt to produce better results than those obtained through the steps described. This final spin coating strategy made use of the LLTO sol solution with increased amounts of PVP, as described in Section 3.2.4 and Appendix A. After preparing the new, higher concentration LLTO sol solution, the solution was strained through sterile filter paper to remove any large particles of PVP or LLTO in suspension. The idea behind the filtering was to avoid imperfections encountered in the initial spin coating attempts that resulted in peaks and valleys forming on the surface of the electrodes after sintering.

As before, the electrodes were sintered, polished to a mirror surface, washed in ethanol, and affixed to the spin coater with double sided tape. Enough LLTO solution was applied drop-wise to the cover the surface of the electrode, and the sample was spun at 3000 RPM for 15 seconds. The tape was removed from the spin coater, and the samples were placed on a hot plate at 170 C to dissolve the glue holding the sample to reduce the risk to the integrity of the film being formed during cathode handling. Because of the proposed thinness and uniformity of the film being formed, the electrodes were only sintered for 2 hours at 600 C to avoid forming cracks in the LLTO film caused by higher temperatures and longer exposure times.

Between the filtering of the LLTO, the higher PVP content, the low sintering time, and the rapidity with which the sample was spun, it was hypothesized that a very thin film (100-500 nanometers) would be formed over the entirety of an electrode that was 95% dense or higher. In order to achieve the desired thickness (1-2 microns), this process was repeated 6 times before assembling a cell. After the application process was completed, SEM images were taken to determine the thickness and integrity of the LLTO film and cells were assembled to assess the charge/discharge capability of the proposed system to determine the validity of the solid state spin coating method.

3.3.3 Powder-Based LLTO Cold Press and Sintering Solid State Electrode Coating

Ideally, the easiest way to manufacture an all-solid-state battery system through low cost methods would be to consolidate as many steps as possible into simple, easy to execute maneuvers. Because the electrodes were being developed mechanically though ball milling, cold pressing, and sintering, the most logical step was to continue layering and cold pressing and sintering until an acceptable design was producible. During these attempts, the only LLTO sol solution that was used contained no PVP.

The LLTO sol solution was prepared as described in Section 3.2.2 and Appendix A. After preparing the solution, approximately 10 ml were transferred to a beaker and placed in an oven at 70 C for 48 hours to evaporate the remaining organic components of the sol solution. This left a white powdered residue at the base of the beaker. This powder was scraped from the glass using a razor blade and collected for further use.

Because it was too difficult to cold press the powders together into a stable formation, a completed, sintered $LiCoO_2$ disk was prepared, polished, and washed. The electrode was then placed into a mold and covered with 0.2 grams of LLTO powder. This powder was then pressed at 10,000 PSI for 2 minutes. After the pressing was completed, the resulting disk was removed from the mold and sintered in a box furnace for 6 hours at 950 C. When the sintering was completed, the new, completed disk's properties were inspected, which are discussed in Section 4.

3.3.4 All-Solid-State Cell Construction Using MIT Swagelok Cells

After applying the solid state electrolyte to the prepared sintered $LiCoO_2$ disk targeted for cell assembly, a research-oriented Swagelok cell designed by the electrochemistry labs at the Massachusetts Institute of Technology was employed. Assembling the cells with easy-to-use Swagelok cells allowed for more focus on the orientation and preservation of the materials (cathode and anode), rather than the actual physical construction of the cell. Given the nature of the electrodes and electrolyte covering (thin and brittle), it was important to limit the risk imposed by the actual cell construction. Two types of construction were attempted throughout the process: liquid electrolyte based construction, and all-solid-state cell construction.

The assembly method used for liquid electrolyte cells is illustrated as follows. The most important aspect of this assembly was to maintain the correct liquid electrolyte levels while keeping the electrode (sans solid electrolyte) centered and separated from the lithium metal anode. Failure to do so has been shown to result in poor ionic conductivity or short circuits.

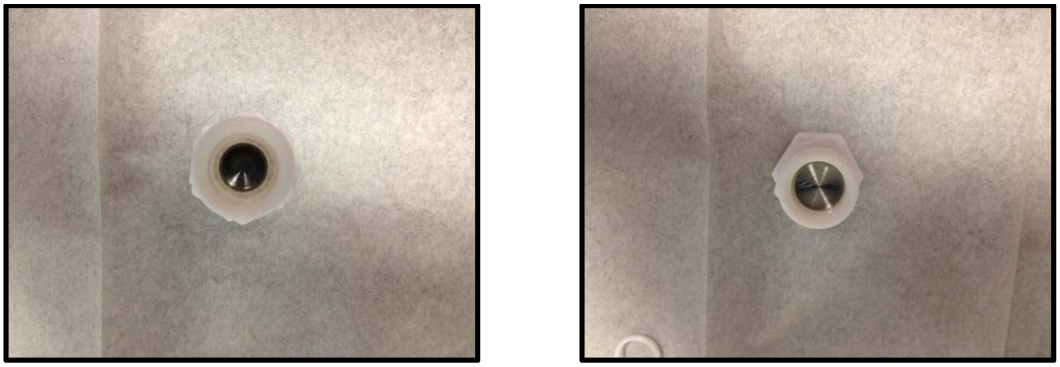


Figure 19: Electrolyte well (left) and inserted current collector disk (right). It was important to note that the liquid electrolyte needed to be filled to just under the position of the compressed spring underneath the current collector (see Appendix B)

The assembly method used for all-solid-state cells was considerably simpler than the assembly method for liquid electrolyte based batteries. Though the same Swagelok technology was used, less "moving parts" made it easier to handle the delicate parts required.

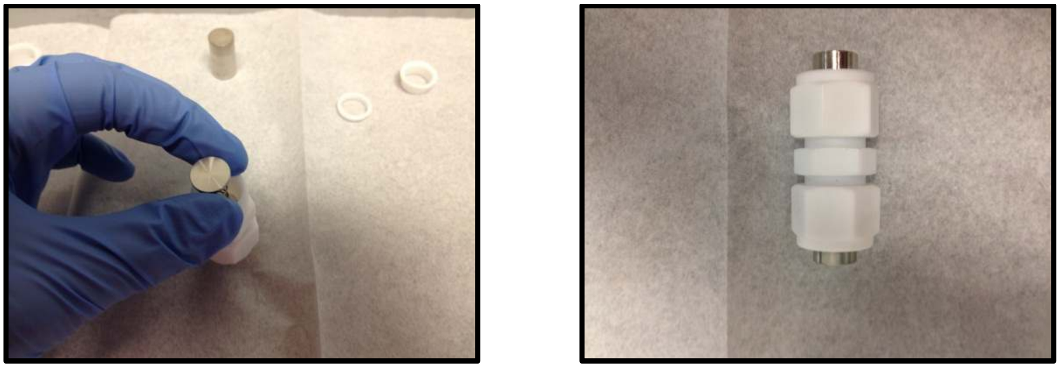


Figure 20: Current collector insertion (left) and completed cell (right). In an all solid state battery, there is only one, immovable surface to worry about. In a liquid electrolyte, liquid must fill the spaces not occupied by cathode and anode.

3.4 Battery Testing and Experimentation

After the physical cell assembly was completed, the cells needed to be tested both qualitatively and quantitatively, to determine the success of the assembly. EC Lab developed the program and equipment of choice for this testing. Qualitatively, it was important to determine whether or not the cells short circuited, which would indicate a failure of either the solid state electrolyte or of the mechanical assembly. Quantitatively, it was important to determine the batteries' abilities to perform via cycle testing and rate capability testing.

All qualitative examinations were performed immediately upon initialization of the EC Lab tester. By attaching the two applicable wire leads to the Swagelok cell, one was immediately able to observe whether or not a voltage drop was registered across a cell. The voltage difference between cathode and anode represents one of the fundamental principles of a battery system. Without a voltage drop, the cell cannot be charged or discharged, because no resistance moves across a cell. In cases where there was no voltage across a cell, a voltammeter was used to measure the resistance of the system to determine if the EC Lab reading was indeed accurate.

After determining whether or not a voltage drop was established across the cell, several tests were run to determine the effectiveness of the cell. Primarily, the cells were charged and discharged at a constant current, and from the data produced, the actual charge and discharge capacities were calculated and compared to the theoretical capacity of $LiCoO_2$ as a ceramic and ionically and electronically conductive cathode material.

Due to initial difficulties in which the resistance inside of the cell was too great to allow for adequate charging and discharging (producing forced short circuits), a tiered strategy was developed in order to test the cells. First, the current was set to a charging rate of C/100, to allow the materials to slowly adapt to the expansion and contraction experienced during the lithium ion transfer process. $LiCoO_2$ is a ceramic material, and the cold press sintering process made use of no organic binders, meaning that there was the potential for the materials to be affected by electrochemical stresses.

After one charge and discharge at C/100, the charge and discharge current was increased to C/50 and allowed to run for two cycles. After ensuring stability, the charge and discharge currents were increased to C/20 and C/10 respectively, and run until the battery showed signs of weakness or overuse. At this point, the batteries were disassembled, inspected to determine the cause of failure, and then the same $LiCoO_2$ electrode was used to reassemble a new cell. By recycling the older electrode, it was possible to determine whether the cathode/electrolyte combination was the cause of the failure, or if the lithium metal anode expiration was to blame. If the recycled cathode produced another working cell, the last charge and discharge current was tested again to establish the battery's failure point.

3.5 All-Solid-State Lithium Ion Battery Modeling Work

This area of research was noted from the beginning of the project as a "stretch goal." Ideally, had the battery construction process gone as planned, this portion of the project would have been able to analyze the differences between predicted battery behaviors and actual charge and discharge behaviors for all solid state lithium ion battery systems. Electrochemical models can be used to predict the behavior or product changes or enhancements before they happen, and can help determine if proposed changes might be beneficial to the enhancement of technology as a whole.

After developing reliable electrodes with high strength, density, and acceptable discharge to charge capacity ratios and testing the cells as described in Section 3.4.0, the trends in the data gathered were compared to the trends of popular liquid electrolyte lithium ion batteries. After establishing the potential viability of these models (based on qualitative comparisons of data trends), the parameters from the actual experiments conducted were used as inputs for the models. The generated data points from the model were then compared to the actual empirical data gathered from the EC Lab experiments conducted.

The main model focused on was drafted by Professor Ravindra Datta of Worcester Polytechnic Institute. The model involves a theory that lithium ions are distributed through a growing “ash layer” on a presumed spherical particle. Because the electrodes formed were essentially 100% dense (for the sake of the model), the volumetric calculations were adjusted to fit the situation, and the electrode was treated as one large particle for the purposes of the model. The success of these attempts is discussed in Section 4, and further recommendations are discussed in Section 5.

While the research done on the potential models associated with lithium ion batteries was limited, the future implications of this research are immense. After successful development of all-solid-state lithium ion batteries using low cost methods, determining whether or not they are comparable to and competitive with current liquid electrolyte lithium ion batteries will be essential to future research. If the current models are applicable, more research time can be dedicated to improving the quality of lithium ion transfer, solid state electrolyte contact, and other mechanical features of the cells. In addition, studying current models can reduce the amount of time that it takes to develop improved electrolyte mixtures, solutions, application methods, and testing methods.

4.0 Results

This section aims to highlight the successes and failures encountered during the course of this project. Though not all initial objects of the project were completed, all parts of the process provided valuable data and learning experiences that have the potential to be applied during future iterations of this research. The results of this project are most easily broken down into three main categories: electrode development, electrolyte development, and electrolyte application. In order for a wholly successful all-solid-state lithium ion battery to be developed, all three areas of research needed to synergize.

The most successful contribution of this research came in the form of the handling and processing of $LiCoO_2$ and its manipulation as a cathode material. As will be described further, $LiCoO_2$, with no organic binder, is a ceramic material that expands and collapses upon lithium ion intercalation. The ability to process this material with relative ease, to establish circumstances that generated low-cost processing methods, and to yield a product that is able to be charged and discharged repeatedly without material failure was a great accomplishment on its own.

Additionally, though a number of difficulties were encountered while attempting to produce and apply the LLTO electrolyte solution, strides in understanding and process development were made throughout the project. From gathering a better understanding of the properties of LLTO and $LiCoO_2$ and the way the materials interact, to developing improved methods for applying and handling the finished product, this project has paved the way for successful follow-up research and development. This section describes in detail both the qualitative and quantitative analyses of the results obtained during the research process. Additionally, Section 4 discusses the implications of these results and the impact that they may have upon future research into cost efficient all-solid-state lithium ion batteries.

4.1 Large-Particle Medium Density Hand Milled $LiCoO_2$ Sintered Cathodes

By and large, these initial attempts at developing low-cost, high energy density $LiCoO_2$ electrodes were a success. The resulting disks were strong, able to be polished to a relatively smooth surface on a thin plane, and could be charged and discharged without producing physical splintering or noticeable deformations. After polishing, the final density of the pieces was measured at 88% using Archimedes method, and the surface was able to be polished to the point where it would reflect light at approximately 100 +/- 13 microns of thickness.

Figure 21: Left: electrodes are able to be polished to a shiny, but not reflective surface. Right: the electrodes are thin, but still able to be handled manually with tweezers.

The electrodes were then tested in a Swagelok cell for charging and discharging capabilities. The assembly was done as detailed in Section 3 and Appendix B using a liquid electrolyte consisting of $LiPF_6$ and DMC. Initially, this cell was charged at C/10, and the charging was a failure. Upon initialization, there was a massive spike in resistance, and the voltage limit set on the EC Lab testing apparatus was exceeded. In response to this failure, the charging rate was reduced to C/100, and the voltage ranged was altered to a 4.3 V charging maximum and a 2.0 V discharging minimum. The results of this charging and discharging were much more favorable, and are detailed in Figure 22.

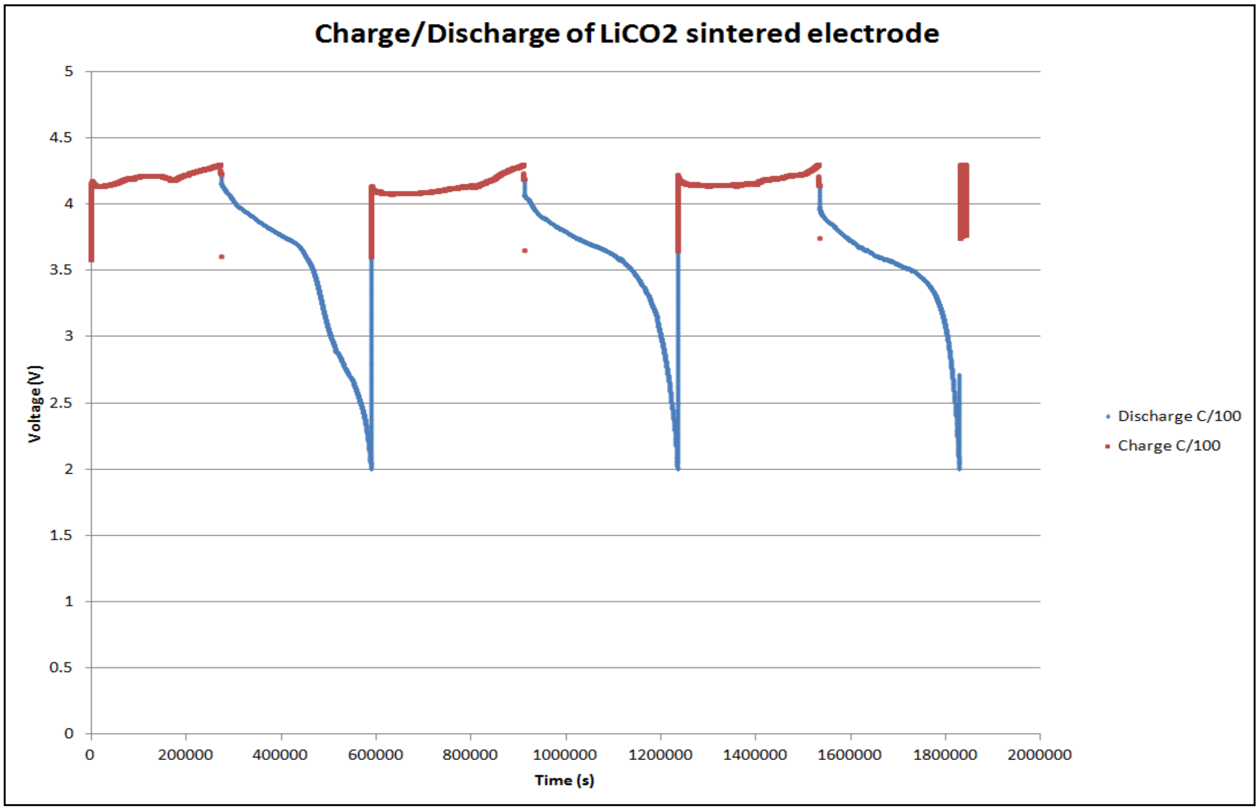


Figure 22: Low density (88%) charge and discharge curves. Constant current was applied to increase the voltage over time. The smooth curves indicate that no soft-short-circuits were encountered during the charge/discharge process

The charge and discharge curves for these three cycles were relatively smooth, with charging times hovering around 100 hours, and discharge times approximately equal. The charge and discharge capacities were also favorable, producing approximately 90% of maximum charge capability, and a 0.90 discharge to charge ratio. Table 3 illustrates the evolution of the three cycles.

Table 3: Charge time and capacity evolution of low density (88%) $LiCoO_2$ sintered electrodes

Cycle	Charge Time	Charge Capacity	Discharge Capacity
1	96 hrs	124 mAh/g	110 mAh/g
2	94 hrs	122 mAh/g	108 mAh/g
3	88 hrs	114 mAh/g	103 mAh/g

Unfortunately, after the third cycle, the resistance across the cell spiked to uncontrollable levels, and it was no longer able to be charged and discharged. The cell was disconnected, allowed to sit for one day, reconnected, and charging was attempted again. The result was the same – a massive spike in resistance followed by a failure to charge. In order to determine the cause of failure, the cell was disassembled and the components (anode, cathode, separator) were all inspected for defects or physical abnormalities. Figure 23 shows the results of the physical inspection.

Figure 23: Left: $LiCoO_2$ cathode extracted after disassembly of cell, intact and reusable. Right: exhausted lithium metal anode preventing addition charging and discharging.

The left image demonstrates that the electrode was completely intact, and the separator had not become saturated with lithium particles. The image on the right, however, shows a clearly spent piece of lithium, with a blackened surface (showing an exact blackened imprint of the $LiCoO_2$ cathode), most likely causing the high resistance and contributing to the cell's inability to charge and discharge. The most likely cause for this deterioration (rapid in terms of the number of cycles completed) can be attributed to the low charge and discharge rate and the high voltage ceiling. A large amount of stress was put on the lithium metal (which, once spent, de-intercalation cannot be reversed) over a long period of time because each cycle took approximately 200 hours to complete.

To attempt to remedy this, a higher charge rate was employed. A charging rate of C/50 and C/20 were both tested. Unfortunately, due to the relatively low overall density of the sintered $LiCoO_2$ cathodes, the resistance across the entire cell was simply too high at any appreciable charge and discharge rate. It was determined that, in order to positively affect the charge and discharge capability of the cells, the density of the $LiCoO_2$ cathodes needed to be increased.

4.2 Ball-Milled Small Particle High Density $LiCoO_2$ Electrodes

Post ball milling, additional $LiCoO_2$ electrodes were fabricated using the highly refined powder. As noted in Section 3, no binder was added during these fabrication attempts. A considerable increase in density was noted after sintering was completed with the ball-milled powder. After testing as described in Appendix C, it was determined that the density of the electrodes was approximately 96%. This 8% increase was hugely substantial, although the numerical increase might not seem considerable from an outsider's perspective.

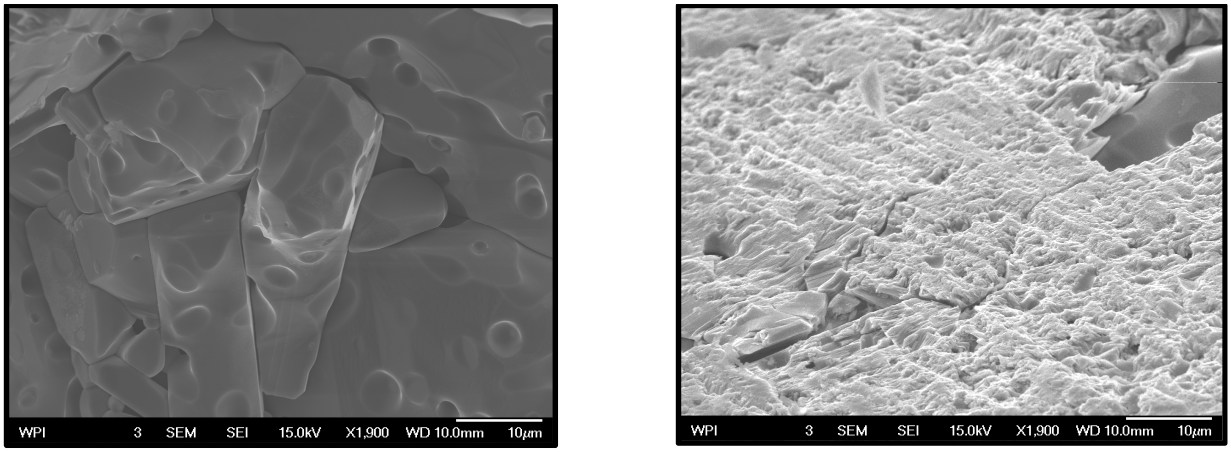


Figure 24: Left: SEM cross section of high density $LiCoO_2$ disk. Small pores indicate high density and low porosity. Right: surface image of high density $LiCoO_2$ disk after rough polishing.

The SEM images displayed in Figure 24 demonstrated the high density of both the surface and cross sectional makeup of the cathode. The left image, representing the cross section, demonstrates that in a sample that is 100 microns thick and polished to a reflective finish, the pore size did not exceed 1 micron. This would prove to be particularly important during charge/discharge testing, because higher density and lower pore size allowed for better lithium ion transfer rates, and lower overall cell resistance figures. Additionally, it was important to look at the surface of the electrode after polishing. The smoother the surface, the more acceptable it became for solid electrolyte application. While there were some surface imperfections, the pores produced were no larger than one micron in diameter, which were not large enough to inhibit the solid electrolyte application to the surface of the $LiCoO_2$ electrodes.

The electrodes were then tested in the same way as the medium density electrodes at a constant current. Because the higher density electrodes were able to be charged at a higher rate, testing was commenced at C/20 and continued until cell failure. Figure 25 demonstrates the results of this testing process.

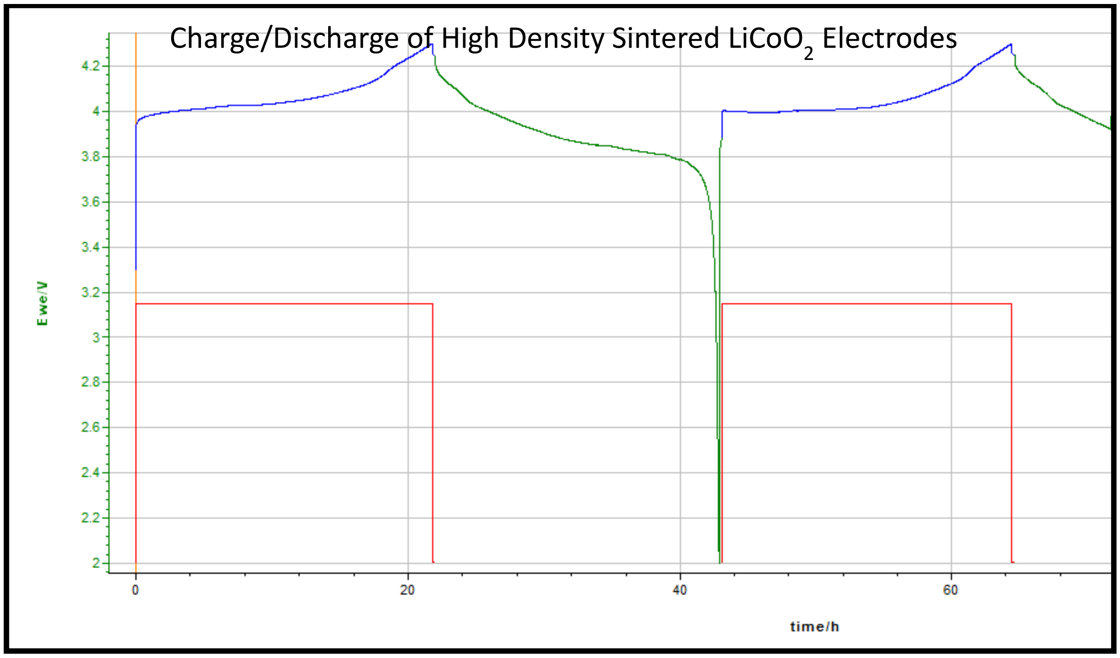


Figure 25: Charge/discharge curves of high density $LiCoO_2$ electrodes. Smooth curves indicate that applying a constant current over time raised voltage and led to controlled charging and discharging, not soft-short-circuits

The cell behavior represented a marked improvement over the initial testing. Besides the ability to charge and discharge the cells at rates of up to ten times those of the 88% density cells, the charge and discharge capacity actually exceeded the expected theoretical capacity of 137 mAh/gram. The ability for the cell to exceed the expected capacity can be contributed to the high voltage ceiling allotted to the cell. Normally, in a commercial grade battery, the voltage should not exceed 4.0-4.2 volts. The tests run on the high density $LiCoO_2$ electrodes were set at a 4.3 volt ceiling, allowing the total capacity to exceed the expected capacity because of the high ionic conductivity and density of the sintered cathodes.

Table 4: Charge time and capacity comparison of high density (96%) sintered lithium ion electrodes

Cycle	Charge Time	Charge Capacity	Discharge Capacity
1	18 Hours	149 mAh/g	144 mAh/g
2	18 Hours	144 mAh/g	140 mAh/g
3	Lithium Anode Failed	N/A	N/A

4.3 LLTO Solution Synthesis through Sol Gel Reactions

The four different LLTO sol solutions generated through the course of this project each had their own uses, and their own respective successes and failures. These four types, detailed in Section 3, included: basic LLTO sol solution, LLTO sol solution developed with post-reaction PVP, LLTO sol solution developed with reaction dependent PVP, and increased PVP added to LLTO sol solution developed with reaction dependent PVP addition. Each iteration of the sol solution was tested for stability, application dependability, and ease of use after application. Table 5 illustrates the important parameters that were observed, either qualitatively or quantitatively, in each solution fabricated.

Table 5: LLTO solution composition qualitative performance and stability

Solution Type	Stability	Application Dependency	Ease of Use
LLTO Sol Solution	3 Weeks	Evaporative – Highly Effective Spin Coating – Highly Ineffective	Brittle but easy to remove after evaporation. No ability to adhere during spin coating, difficult to use.
Post Reaction PVP	2 Days	Evaporative – Highly Effective Spin Coating – N/A	Must be used quickly or it falls out of solution. Spin coating not tested.
1.0% PVP Reaction Dependent	1 Month	Evaporative – Moderately Effective Spin Coating – Moderately Effective	Difficult to use when evaporating, moderately easy to use while spin coating.
1.5% PVP Reaction Dependent	1 Month	Evaporative – Moderately Effective Spin Coating – Highly Effective	Extremely difficult to use when evaporating, moderately easy to use while spin coating.

To further illustrate the important to add PVP during the sol gel reaction sequence, the following image shows the difference between a sample of post-reaction PVP and intra-reaction PVP addition.

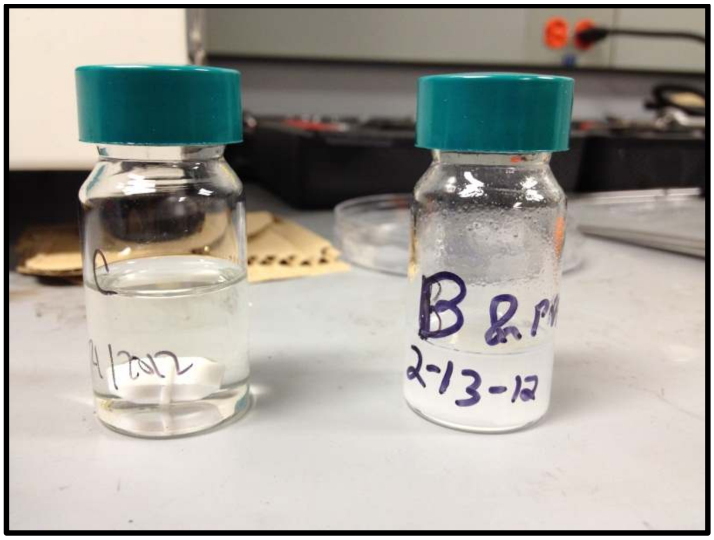


Figure 26: Comparison of PVP enhanced LLTO sol solution during the sol gel reaction sequence (left) and after the sol gel reaction sequence (right). Notice that the right vial has a thick precipitate and the left is clear.

The sample on the right, which had been mixed with post-reaction PVP, was one day old, and was already falling out of solution, forming a milky white precipitate that persisted throughout the contents of the vial. The sample on the left was nearly clear, which demonstrated the stability found by adding PVP during the sol gel reaction sequence.

Finally, as noted in Section 3, attempts were made to use partial evaporation to thicken the intra-reaction PVP based LLTO sol solution. These efforts were supposed to allow the material to become easier to work with. Initially, when evaporated for 3 hours under the low-humidity environment of a fume hood, the results were promising. The solution thickened while remaining clear and it looked as if a manual, painting-like application strategy may be possible.

However, after sealing the container and letting it sit for 12 hours, the solution began to rapidly dissociate. Figure 27 shows the precipitate forming, leaving only a semi-plastic solution devoid of LLTO.

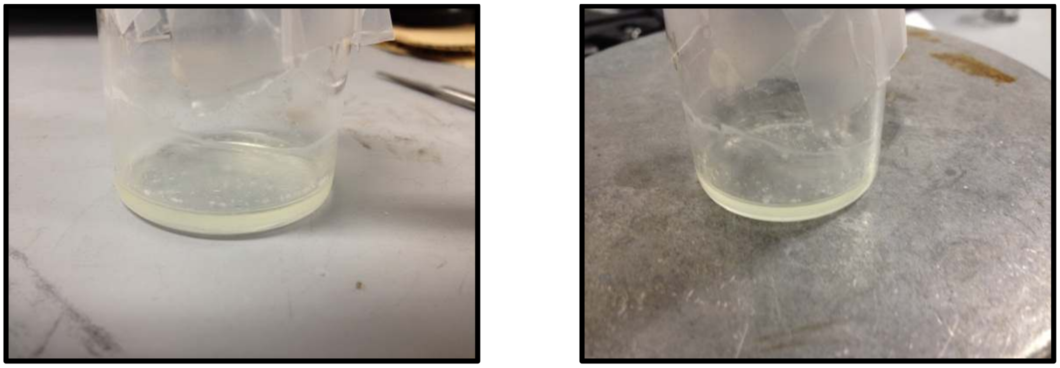


Figure 27: PVP enhanced LLTO sol solution thickened through partial evaporation. A thick slime and large particles are dissociated, indicating that partial evaporation is not stable enough to use for LLTO coating.

Because the solution was unable to remain stable for any extended period of time, it was not an acceptable solution to the problems being encountered. A solution that takes upwards of 7 hours to prepare, but cannot last for more than 4 hours was unacceptable for any realistic applications to be studied effectively.

4.4 LLTO Sol Solution Application Methods

As noted in Section 3, three main sol solution application methods attempted were: evaporative deposition, spin coating, and powder pressing combined with sintering. Each system had its own merits and drawbacks that were observed during the research process. Each method was evaluated by: the consistency of the solid electrolyte coverage, the ability to produce a voltage drop across a cell, and the charge and discharge capability of the completed cell.

4.4.1 Powdered, Cold Pressed, and Sintered LLTO Application

During the initial stages of the project, one of the main concerns was the strength potential of the solid electrolyte. Initial attempts at coating indicated that the electrolyte layer was not strong enough to withstand any appreciable abuse. To test whether or not a strong LLTO formation could be produced, a cold press, sintering method was used that was similar to the method used to develop the sintered $LiCoO_2$ electrodes.

After the heat treatment, in which a thin layer of LLTO powder was sintered on top of an already processed $LiCoO_2$ disk, it was observed that a hard, ceramic like disk was formed. However, despite its rigidity, the disk became curved and deformed, and a vigorous reaction took place between the LLTO and the $LiCoO_2$ as it was transformed into the crystalline phase under high temperature and standard pressure. Figure 28 shows the physical results of the sintering attempts associated with LLTO powder.

Figure 28: Flat, pre-heat treatment cold pressed LLTO powder on top of $LiCoO_2$ disk. Right: Deformed post-heat treatment LLTO disk with $LiCoO_2$ cathode removed.

The left image shows the pre-sintering geometry of the LLTO powder disk, and the right image shows the post-heat-treatment deformation that occurred because of the properties of the LLTO crystallization process, as well as the discoloration caused by the reaction between LLTO and $LiCoO_2$. Because of the irreversible chemical reaction that occurs, it was determined that this method of LLTO coating wasn't feasible for all-solid-state cell construction. Additionally, the layer that was formed was approximately 100 microns thick, which, considering the goal thickness of 1 micron, represented an insurmountable obstacle to battery construction.

4.4.2 Evaporative Deposition of LLTO Sol Solution onto $LiCoO_2$ Sintered Electrodes

As noted in Section 3, evaporative deposition was initially chosen because of the ease of implementation and use of the method. It required no additional equipment, and no additional labor on the part of those conducting the tests. Once the samples were coated with LLTO sol solution, they could be left for a virtually unlimited amount of time if necessary before being heat treated and subsequently tested in an assembled cell.

Each type of sol solution (PVP, no PVP, varying concentrations, etc…) was tested as a candidate for effective evaporative deposition. From an ease of use point of view, the LLTO sol solution without any additional binder proved to be the preferred mixture. As shown in Figure 29, when applied, the solution formed a smooth, even coating, and the samples were easy to remove from the surface upon which the evaporation was done.

Figure 29: PVP-less all solid state electrolyte coverage during coating process (left) and pre heat treatment (right)

Unfortunately, the ease of use and application was not without its downsides. After coating the samples, it was necessary to heat treat the solid electrolyte to transform it into the amorphous phase, and to eliminate all remaining organic components of the LLTO sol solution. This was done at 600 C for 6 hours. Initially, the results were remarkable – the surface was smooth and completely covered. Unfortunately, the film that had formed had no real strength behind it, and could be removed by any type of shear contact. Essentially, the surface had been reduced to a layer of fine sand instead of a solid, continuous LLTO film. Figure 30 shows the sample when it was pulled from the furnace, and after being handled.

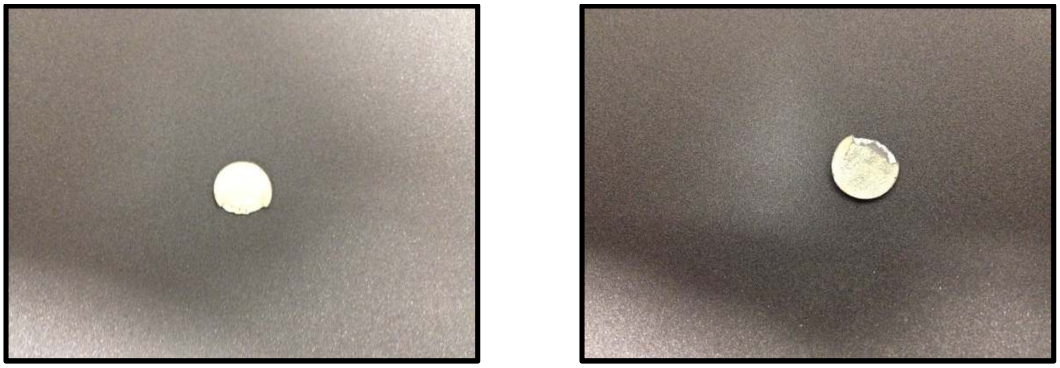


Figure 30: Left: solid electrolyte coverage post heat treatment. Right: solid electrolyte coverage post handling. Handling rubbed the solid electrolyte off because it had the consistency of fine sand instead of a film.

This deterioration of surface quality was unacceptable, as any break in the solid electrolyte film can result in a short circuit through the cell. These results were reproduced numerous times, to rule out the possibility that the heat treatment or handling of the surface was done incorrectly. After ruling out the possibility of evaporative deposition with the standard LLTO sol solution, the research focus shifted to binder-assisted LLTO sol solutions.

Unfortunately, these solutions proved to be much more difficult to work with. The evaporation process was still simple, where the solution was applied and left to dry in a dehydrated environment for 24 hours. However, upon attempting to remove the samples from the surfaces upon which the evaporation took place, it was noted time and again that the PVP in the LLTO sol solution had plasticized the surface of the film to such an extent that any attempt to remove the electrode would result in its destruction. Unfortunately, all organic solvents that could be used to assist in the removal of the $LiCoO_2$ disk would subsequently destroy the electrolyte layer.

The scraps that were able to be salvaged were too small to be used to construct actual all-solid-state cells, but they were large enough to obtain SEM images of. The results were very consistent for single applications of LLTO sol solution with PVP. Figure 31 shows the results of the SEM images that were taken of the remnants of the evaporative deposition on high density (96%) $LiCoO_2$ disks.

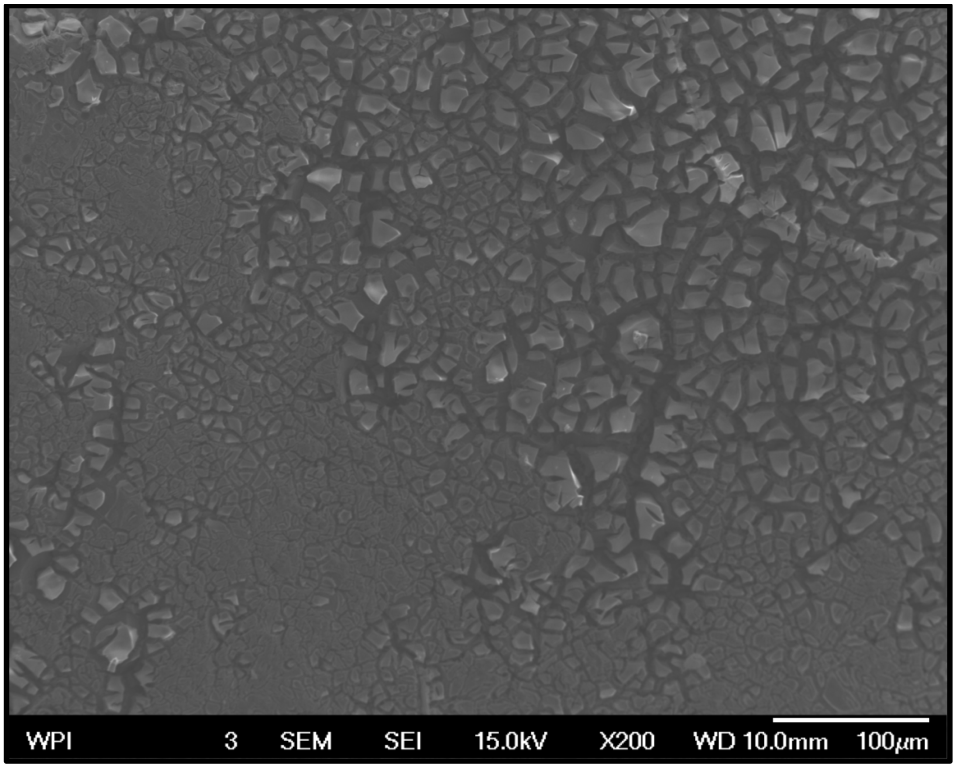


Figure 31: Wide-view SEM image of solid electrolyte coverage applied to the surface of a $LiCoO_2$ disk through evaporative deposition of LLTO sol solution

The distribution of LLTO across the surface was clearly uneven. In the bottom left of the image, there is a scarce coating of LLTO which barely registered on the EDS scan for titanium and lanthanum. Consequently, some areas were covered by cracked by thick and highly dense areas of LLTO coverage. Though the net coverage was only approximately 50%, the areas that were covered were very densely and evenly coated.

This 50% distribution could theoretically be solved with repeated applications of LLTO sol solution. However, the destruction of the cathode materials upon extraction from the evaporation surface made this nearly impossible to reproduce. Theoretically, it should have been possible to layer multiple times before heat treating without damaging the integrity of the layer formed. Previously, when working with LLTO sol solution with no PVP added, there was a considerable amount of crystallization that occurred when layers were added without heat treating. This caused a number of problems because the crystallization enabled height to be added to specific sections of the electrode surface without actually adding surface area. Figure 32 shows the results of these previous attempts.

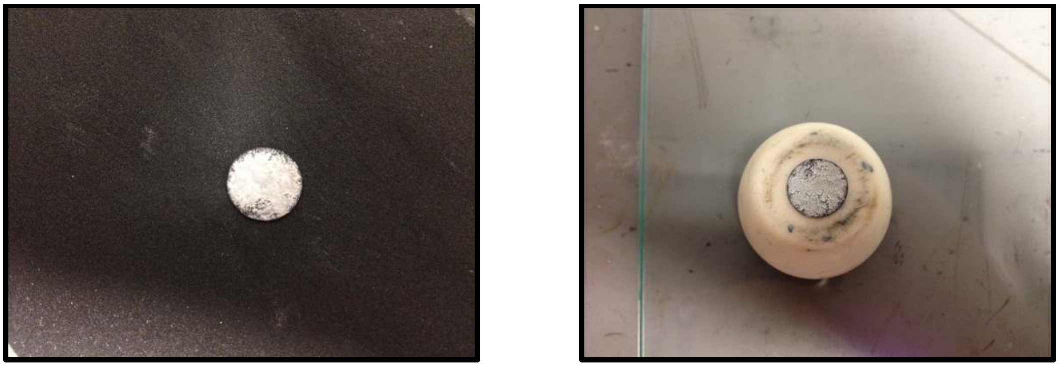


Figure 32: Multiple pre-heat treatment evaporative applications. Large crystals formed on the surface both pre and post heat treatment, resulting in poor overall surface coverage.

The crystallization that formed before heat treatment caused intense cracks to form along the surface of the solid electrolyte layer. When cell assembly was attempted, there was no voltage drop across the cell, meaning that a short circuit occurred. This method was repeated three times, applying different amounts of LLTO sol solution each time, but the results remained the same.

In order to solve the electrode destruction problem, and to remedy the damage to the solid electrolyte layer caused by over-crystallization, it was proposed that the LLTO sol solution be applied to the electrode while the electrode rested upon the current collector. This would ensure an effective seal, preventing a direct short circuit between anode and current collector, and would prevent damage to the cathode, because it would never need to be removed from the current collector during application and heat treatment. Unfortunately, in order to accomplish heat treatment under these conditions, a tube furnace, not a box furnace was required. If the stainless steel current collectors were sintered at 600 C to treat the solid electrolyte layer, oxidation of the steel would have occurred, and the cell would be rendered useless.

The accommodations for this research did not provide a tube furnace for use, so improvisation was required. In order to provide proof of concept and the possibility of a successful battery formation, the LLTO sol solution, including PVP binder, was applied carefully over the course of a week to a high-density $LiCoO_2$ electrode resting on top of a stainless steel current collector. Only trace amounts of LLTO were added at a time, and only to proper areas that had not yet been exposed to attempt to cover the surface evenly. Figure 33 shows the results of the coverage.

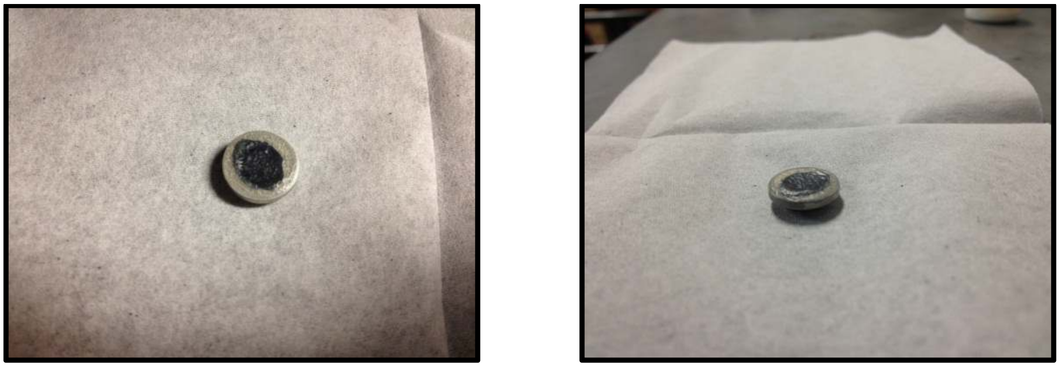


Figure 33: Semi-plastic coverage of PVP enhanced LLTO sol solution through evaporative deposition used in proof of concept experiment to determine the effectiveness of LLTO solid electrolyte film

It is important to note the relatively uneven nature of the surface. Had heat treatment been an option, the organic components of this semi-plastic coating would have been burned off, and the LLTO would have theoretically been allowed to settle into a fine film. While applying the solution, it was important to note that the LLTO tended to settle on the outside of the electrode first, and subsequent applications were required to cover the center of the surface. This was a behavior frequently observed, where new LLTO particles would attract to existing, settled LLTO particles, and was difficult to control under any application environment.

After repeated (5) evaporative applications, a cell was then assembled and tested for voltage drop and charge/discharge capability. The cell produced a voltage drop of approximately 3.6 – 3.7 volts, which falls within the range expected for a cell assembled with $LiCoO_2$ as a cathode to a lithium anode. While the open circuit voltage indicated that there was no hard short circuit through the cell, it was still incapable of charging and discharging. For a short period of time (15 minutes charging at approximately C/100), the cell appeared to be charging. However, after that time period, the voltage began to change erratically, and even spiked to 11.4 volts, indicating that there was a soft short circuit through the cell. Figure 34 demonstrates the observed behavior.

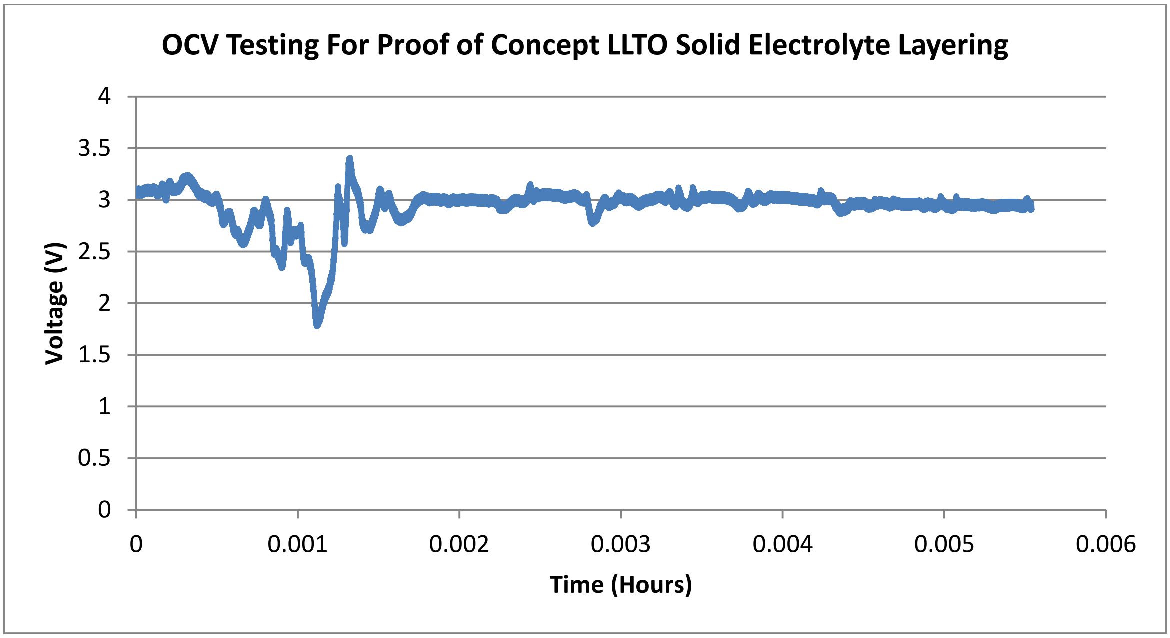


Figure 34: OCV testing to determine whether or not the cell was capable of holding a registered voltage for any appreciable time. Unfortunately, the cell was unable to hold a charge when constant current was applied.

Upon disassembly, it was noted that the electrode and electrolyte layer were both entirely intact. The electrode was recycled and prepared to be coated again by bathing the entire current collector in ethanol. This allowed for the semi-plastic electrolyte film to dissolve and for the $LiCoO_2$ electrode to be freed without damaging the surface. When rebuilt to test the integrity of the electrode, it proved to maintain its ability to charge and discharge, which indicates that without heat treatment, LLTO sol solution application does not change the integrity of the actual electrode.

4.4.3 Spin Coating Deposition of LLTO Sol Solution on Sintered $LiCoO_2$ Electrodes

Much like the evaporative deposition methods researched during the course of this project, spin coating deposition was attempted with all formulations of LLTO sol solution.

Ideally, spin coating would produce a completely uniform, thin film of LLTO to facilitate lithium ion transfer while inhibiting electron transfer across the barrier. Initial spin coating attempts were undertaken using the LLTO sol solution developed without the inclusion of PVP as a binder. Unfortunately, the solution was not viscous enough without the inclusion of a binder, and the spin coating yielded no film being formed on top of the electrode.

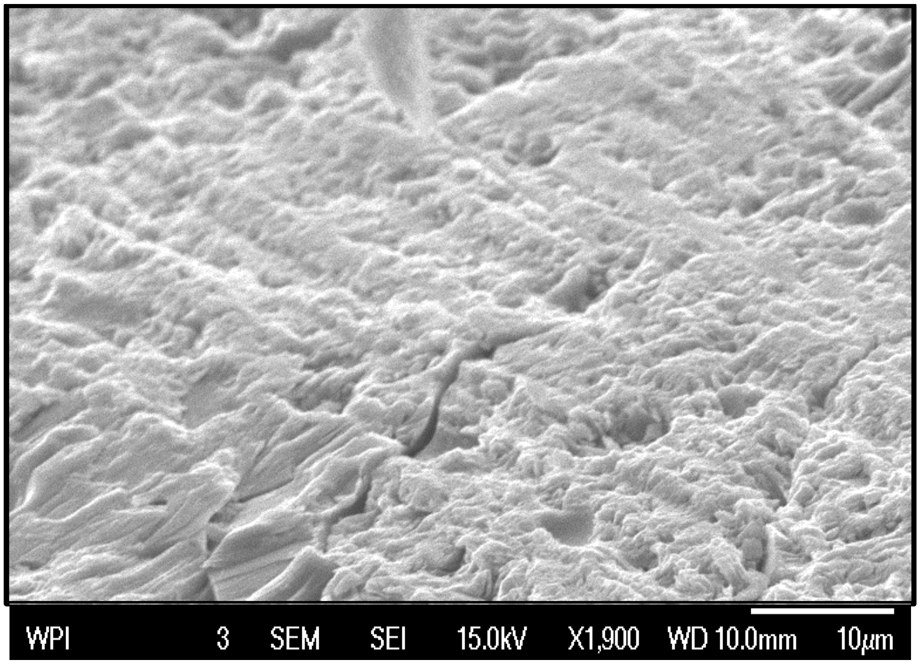


Figure 35: $LiCoO_2$ surface SEM image before LLTO application

In order to force the application of the LLTO film through spin coating, the low-concentration PVP solution (described in Appendix A) was employed. The different electrodes that were tested at one, three, and five spin cycles exhibited remarkably similar behavior. Figure 36 displays the behavior at the center, and edge of each spin cycle (except for one spin, which was only imaged in the center).

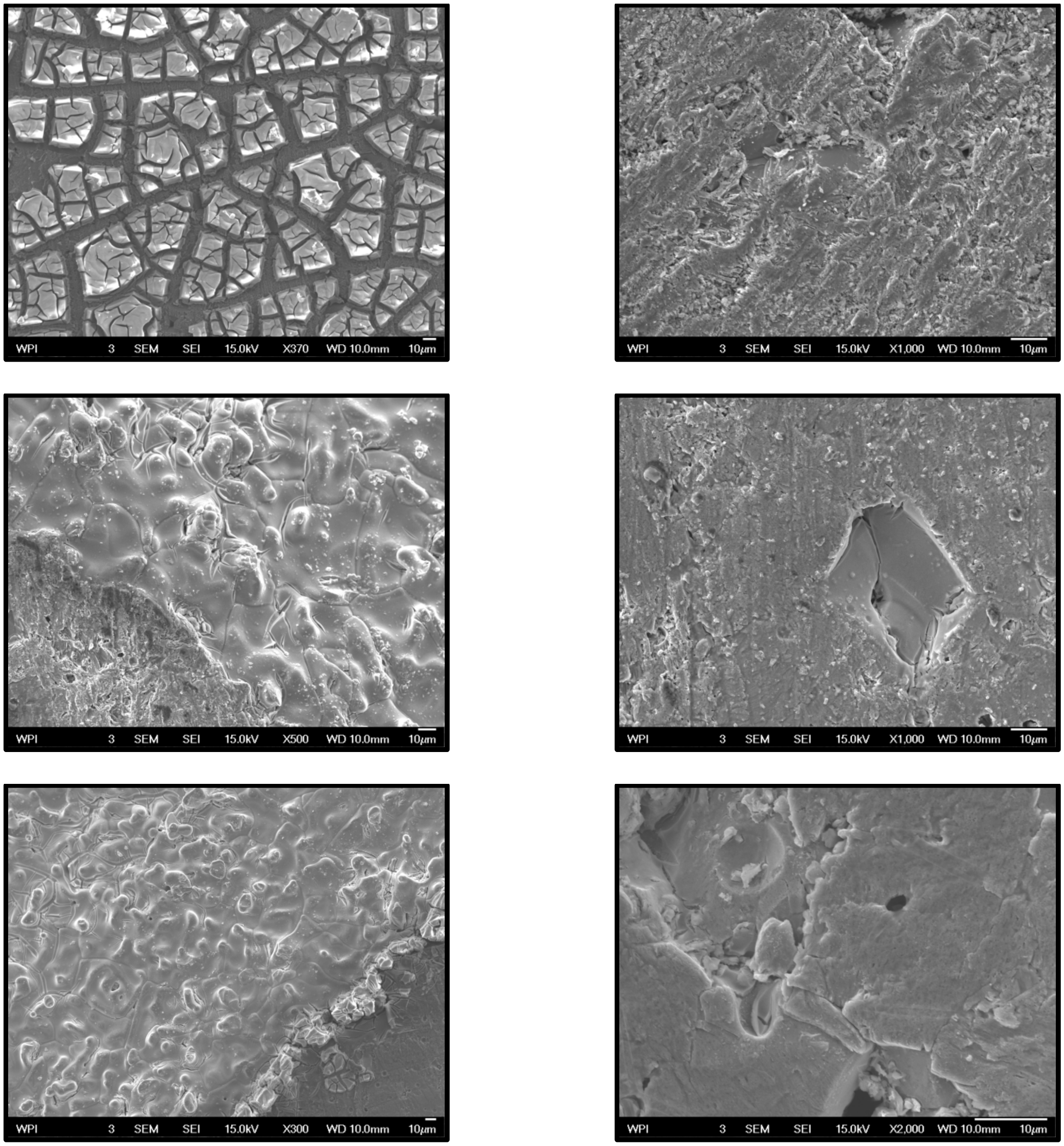


Figure 36: Top Left: Evaporative Deposition. Top Right: 1x Spin Center Coating. Middle Left: 3x Spin Edge Coating. Middle Right: 3x Spin Center Coating. Bottom Left: 5x Spin Center Coating. Bottom Right: 5x Spin Center Coating.

For reference, the top left image demonstrates the coating achieved through a single application of evaporative coating using the same LLTO sol solution. Through careful observation and EDS at different areal and specific points on the sample, it was determined that there was no detectable LLTO present on the single spin sample. Even the brightened spots on the SEM image were simply raised peaks of $LiCoO_2$. However, this cannot be counted at 100% fact. The sample was extremely small, and it was physically impossible to tell which side was correct, because there were no distinct markings on the sample. There is a chance that the wrong side of this sample was imaged.

The second row shows the edge (left) and center (right) of a sample that had undergone three cycles of spin coating. It is important to note that the edge has a uniform, thin LLTO film covering the $LiCoO_2$ electrode surface. The center, on the other hand, contains areal traces of LLTO, and large quantities of LLTO contained in individual large-size particles that are visible on the surface using the SEM. Between the central, sparse deposits of LLTO particles and the edge-oriented LLTO film, there was a barrier of LLTO approximately 10 microns high. This barrier was formed from large LLTO particles sticking together as they slowed down due to friction as spinning occurred.

The final row of images shows the results at the edge and center of an electrode that had been exposed to five spin cycles. As the images show, at the edges, the coverage was even more extensive than the coverage observed after three spin coating cycles. Additionally, a majority of the cracks prevalent throught the coating in the single and triple spin edge coatings had been sealed in by the extra spin cycles. The center of the electrode, while still sparsely covered, mostly by large particles, began to show signs of improved coating. Areal EDS examinations revealed lanthanum and titanium across the surface of the electrode. However, in these cases, the amount of cobalt detected was high enough to suspect that if a cell was constructed using one of these spin coated electrodes, it would short circuit due to a lack of uniform and complete coverage.

It was hypothesized that the smooth film was able to form towards the edge because of a "wave" like effect that was orchestrated by the LLTO barrier. As the large LLTO particles settled due to friction, it was entirely possible that only the fine LLTO film was able to settle past the barrier, creating a smooth, uniform surface. Unfortunately, with the situation at hand, it was virtually impossible to create a cell with the electrode-electrolyte layering that had been produced. Because of the sparse electrolyte coverage in the middle of the $LiCoO_2$ disk, all attempts to create actual, testable cells resulted in hard short circuits.

The LLTO spin coating application process was improved upon by increasing the ratio of PVP to LLTO sol solution. Additionally, the material was filtered before application in order to eliminate some of the large particles that would group up and form solid electrolyte barriers on the surface of the $LiCoO_2$ disk. The reduced heat treatment time also allowed for more even settling of the solid electrolyte, enabling more effective film coverage and reducing the risk of "clumping" materials. Figure 37 shows both central and edge surface images of the high PVP concentration LLTO sol solution coverage through spin coating deposition.

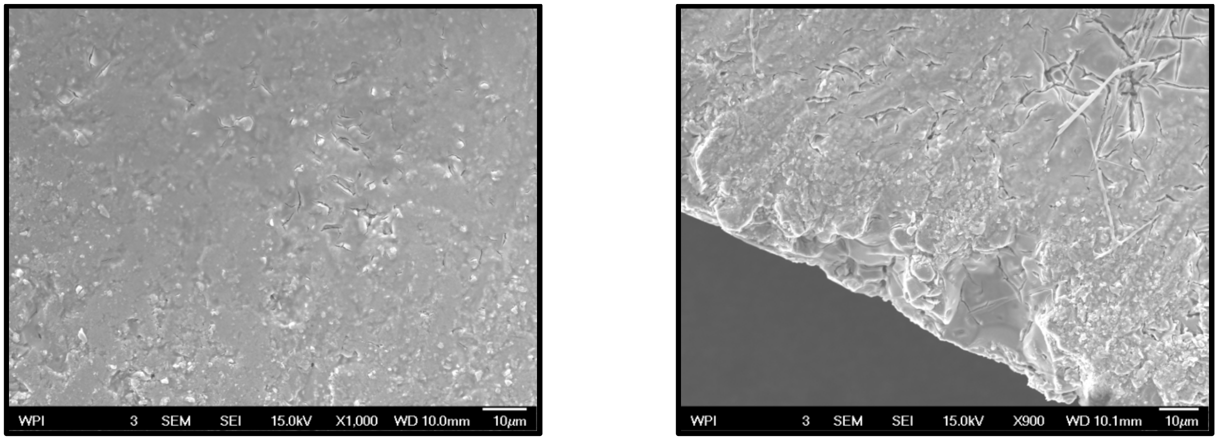


Figure 37: SEM images of center (left) and edge (right) of 3x spin coating with high concentration PVP enhanced LLTO sol solution

One can see that there is almost complete coverage on the surface of the $LiCoO_2$ disk, which, pending electrochemical testing, could mean that these electrodes could be used in the manufacturing of all solid state lithium ion batteries. While at the time of this writing, no cross sectional SEM imaging was done, it was estimated that the thickness of each application was between 100 – 200 nanometer, meaning that the images shown here, which represent three spin cycles, should have an LLTO layer of approximately 300 to 600 nanometers.

4.5 Sintered $LiCoO_2$ Cathode Behavior Modeling

As noted in Section 3, battery behavior modeling was investigated during the course of this project but not focused on. Inspiration was drawn from a paper written by Professor Ravindra Datta, and attempts were made to at least replicate the trends found in the paper. In order to do this, parameters of the low density (88%) electrodes were measured in the laboratory and plugged into the following equation:

$$V = V_0 - \frac{RT}{\vec{\alpha}_A F}\sinh^{-1}\left\{\frac{1}{2}\left(\frac{i/i_{A,0}}{1 - i/i_{A,L}}\right)\right\} - \frac{RT}{\vec{\alpha}_C F}\sinh^{-1}\left\{\frac{1}{2}\left(\frac{i/i_{C,0}}{1 - i/i_{C,L}}\right)\right\} - i\left(\frac{L_B}{\sigma_B}\right) - i(R_I)$$

In this case, resistance across the cell was ignored and assumed to be zero. Percent of maximum theoretical capacity was varied to alter the voltage and the results were plotted. The plots showed a downward trend where voltage decreased as the percent of the theoretical capacity increased. Figure 38 shows these results and compares them to results demonstrated in the description of the model.

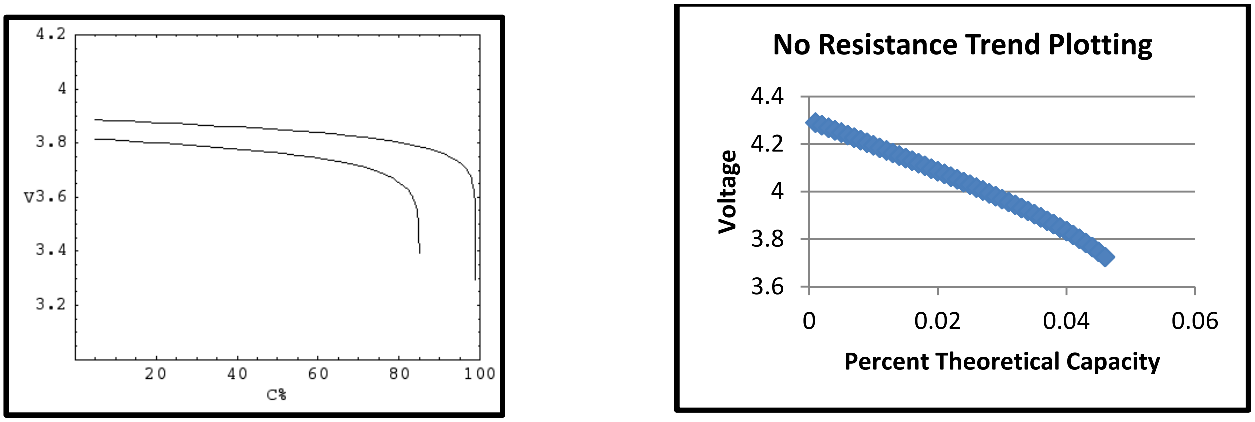


Figure 38: Comparison of theroretical and actual data as a source of trend comparison for lithium ion battery models.

The trends were remarkably similar with one major exception. In the proposed model, the voltage dropped off as the percent capacity approached 100%. In the model developed from the real electrochemical data gathered from the low density $LiCoO_2$ electrodes, the model could handle almost no theoretical capacity before breaking. After examining the parameters, it was determined that, because the entire electrode was considered to be one solid particle through which a lithium ion “ash layer” would develop, the area and volume were too large and broke the formula.

5.0 Discussion of Overall Results and Research Progress

The original goals upon inception of this project were to establish a construction method for a $LiCoO_2$/LLTO/Li all-solid-state lithium ion battery, and then to evaluate the lithium ion transfer rate across the LLTO electrolyte layer at various application temperatures and methods. During the course of the project, various setbacks caused the goals of the research to change, and an overall focus was set much more on electrode development and cell construction. It proved to be much more difficult than initially expected to layer LLTO effectively on top of $LiCoO_2$ for a number of reasons including: poor film generation without the addition of polymer binders, inability to sinter at high temperatures because of reactions between LLTO and $LiCoO_{2,}$ and difficulties in physically handling the fragile electrode/electrolyte samples.

However, even with the difficulties encountered during the project, the results that were generated were still important and allowed for advancements in the understanding of sintered cathode materials and inexpensive methods of solid electrolyte deposition. The $LiCoO_2$ cathodes that were generated were solid, dense ceramic materials with no additional polymer binder. The fact that they could be charged and discharged multiple times at a relatively high rate with little to no loss of physical structure or strength was remarkable. Normally, ceramic materials have issues with expansion and contraction during lithium ion intercalation and de-intercalation. The fact that these electrodes did not experience this physical degeneration as a step forward in producing high areal energy density sintered cathodes. Additionally, these materials achieved densities of over 96% using cost efficient methods, requiring only a hydraulic press and a furnace capable of reaching 1100 C.

Most of the project's life was spent researching and experimenting with the development of and application of LLTO as a solid electrolyte. Despite the many difficulties encountered, towards the end of the experimentation cycle, a consistent, uniform, and thin surface coverage was achieved using spin coating with PVP enhanced LLTO sol solution deposition. These electrodes are currently pending electrochemical testing to determine whether or not the layer is consistent enough to prevent short circuits. However, it is also important to note that during the course of this project, it was proven that it was possible to establish a voltage drop between lithium metal and $LiCoO_2$ by layering pre-heat treated LLTO through evaporative deposition. This method did not allow for adequate charging and discharging of the samples, but it was possible to prove that, with refinement, the materials could be properly implemented.

At the end of the project's life, it was evident that success was imminent concerning the development of the proposed all-solid-state lithium ion cell construction. Once this is accomplished, it will be important to study and consider the effects of different heat treatment and application methods on the lithium ion transference rate throughout the cell. The healthy performance of the $LiCoO_2$ cathodes and standard reliability of lithium metal anodes leaves three areas of focus for future research. First: the boundary between LLTO and $LiCoO_2$; if this boundary is not properly established, low contact will not allow for high levels of lithium ion transfer. The boundary between LLTO and the anode must also be considered, especially when more effective anode materials than lithium metal are considered, because they may be more difficult to work with. Finally, the structure, morphology, and layering of the LLTO solid electrolyte film will be instrumental to effective charging/discharging rates and cycle life.

6.0 Recommendations

After experimenting with a new fabrication method for creating an all-solid-state lithium ion battery throughout the duration of this project, one major problem that frequently occurred is the difficulty in handling the materials. Often, a cathode disk would flip upside down or break when being moved from one piece of equipment to another. The difficulty in using these disks arises from how small they are, especially in respect to their thickness. Multiple recommendations have been developed that are believed to allow for easier handling and transporting of the materials used in the battery.

A distinct marking must be made on the cathode disk to ensure that it is known which side is the bottom and which side is the top. Often when transferring the disk during the spin coating process, the cathode would be dropped from a razor blade or tweezers. Once dropped, it is very difficult to determine which side has an LLTO electrolyte layer deposited on it due to the film being so thin. This can lead to a guessing game in which the handler must use their best judgment to decide which side has the layer on it, and then place this side upwards for further spin coating. In order to maintain a clear understanding of which side is the top, two options arose as potential methods. First, a scratch could be made on the bottom side of the cathode prior to any spin coating. This would ensure the correct side is face up throughout the whole process, as long as the handler can not see the scratch. A more distinguishable method is to keep track of some deformity in the geometry of the disk. If a distinct, nonsymmetrical cut is made in the cathode it would allow the experimenter to quickly realize if the cathode is facing the correct way. As shown in Figure 38, a nonsymmetrical mark will not look the same when facing upwards as compared to the layer without LLTO facing upwards.

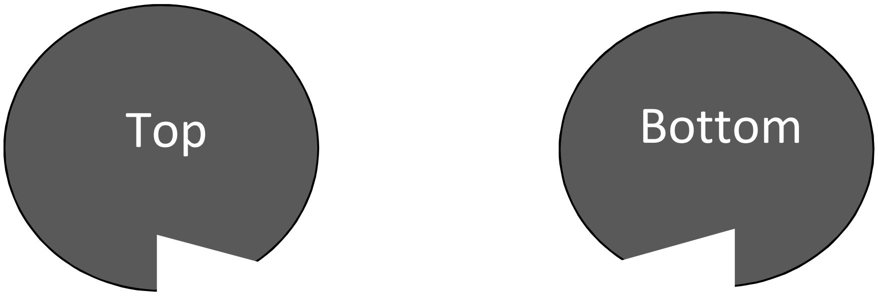


Figure 39: A cathode disk with a distinguishable, nonsymmetrical mark cut into the disk. This will allow for the handler to clearly determine if the disk is facing the correct way.

While making a distinguishable mark on the cathode disk can allow for the experimenter to keep track of which side should stay facing upwards, keeping the disk on one surface throughout the duration of the spin coating process would ensure that LLTO is applied to only one side. Besides flipping over during handling, the cathode disks often break when being transferred from one surface to another in the spin coating process. In the current electrolyte application method, the disk is held onto the spin coating platform with double sided tape. Often the cathode disk becomes stuck to the tape and breaks upon being peeled off. Additionally, the disks will sometimes break when they are dropped from the razor blade or tweezers. If the disk is kept on a single surface, such as a current collector, the need to continually move the electrode is eliminated. The electrode could be attached to the current collector by some kind of conductive paste to allow electron transfer between the current collector and cathode. If the cathode is attached to the stainless steel current collector used in the swage lock cell, the sintering of the LLTO layer would have to be accomplished in a furnace with a nonoxygen atmosphere, such as nitrogen, so the current collector does not oxidize. One consideration to be made with this method is the ignition of PVP. Since PVP needs to be burned off of the LLTO layer, oxygen needs to be present. It could be possible to burn off the PVP at one temperature in an oxygen environment and then sintered in a nonoxygen atmosphere to transform the LLTO layer into the amorphous region. Further research should be done in regard to this topic.

When creating the LLTO layer, it is imperative to use the correct amount of PVP in the solution. PVP plays a large role in the viscosity and the strength of the LLTO film that is formed on the cathode disk. Further experimentation with varying amounts of PVP should be done to determine what ratio of PVP to the other chemicals yields the ideal solution for spin coating.

Since the evaporation method for applying the LLTO solution is simple and requires minimal effort, further experiments should be done with this application process. This method only requires that the LLTO solution is pooled on top of the cathode disk and left to evaporate. One major problem encountered through this method was the strength of the film formed on top of the disk. When the PVP solution used for spin coating was applied via the evaporation process, a strong plastic film formed over the cathode and it was nearly impossible to remove from a flat surface. Attempting to evaporate a film on top of a cathode in a manner which will allow for its easy removal is highly recommended since it does not require a large amount of work. Also, since sintering causes cracks to form in the LLTO film a gel like substance could be created via the evaporation method to create a working battery. It has been proven that a battery manufactured in this way can obtain a voltage drop across it. This shows promise for the fabrication of an all-solid-state lithium ion battery via the evaporation method.

The final recommendation for this project is to create a cathode slurry that can be pasted onto a current collector. If this can be done, the need to move a disk during the spin coating process would be eliminated. Also, an electrolyte slurry and an anode slurry could be applied right on top of the cathode. By developing such a method, it would be easy to ensure constant contact between all layers of the cell without having to apply a large amount of pressure to the current collectors. Additionally, this would eliminate the need to move any of the materials used in the lithium ion battery.

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Appendix A: Recipes and Formulations

LLTO (NO PVP)

Solution A

Lithium Acetate Dihydrate	0.0804g
Lanthanum (III) Acetate Hydrate	0.4356g
H2O	5.700g

Solution B

Titanium (IV) isopropoxide	0.6395g
Acetic Acid	1.3613g
Isopropyl alcohol	2.7045g

Combine Li and H2O and stir for 10 min
Combine Ti and Ac and stir for 10 min
Add La to LI/H2O and stir for 30 min
Add Iso to Ti/Ac and stir for 30 min

Drop A into B slowly, 30 min of dropping time.

Stir for 2.5 hours

LLTO with PVP

Solution A

Lithium Acetate Dihydrate	0.0804g
Lanthanum (III) Acetate Hydrate	0.4356g
H2O	5.690g

Solution B

Iso	2.7045g
PVP	0.25g

Solution C

TI	0.6395g
Ac	1.3613g

Mix Li and H2O for 10 min
Add La to Li/H2O and stir 30 min

Stir B for 15 min
Stir C for 15 min
Mix C and B for 15 min

Drop A into C/B drop by drop, then stir for 2 hours

LLTO with High-Concentration PVP

Solution A

Lithium Acetate Dihydrate	0.0804g
Lanthanum (III) Acetate Hydrate	0.4356g
H2O	5.690g

Solution B

Iso	2.7045g
PVP	0.375g

Solution C

TI	0.6395g
Ac	1.3613g

Mix Li and H2O for 10 min

Add La to Li/H2O and stir 30 min

Stir B for 15 min
Stir C for 15 min
Mix C and B for 15 min

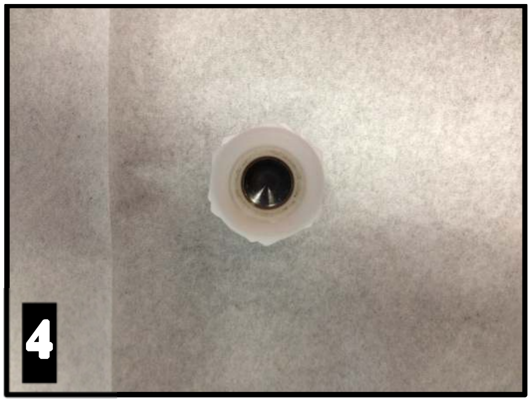
Drop A into C/B drop by drop, then stir for 2 hours

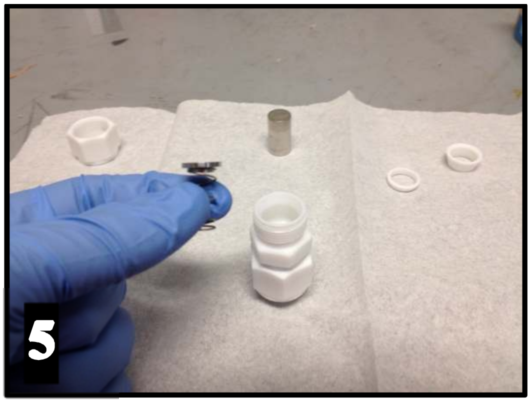
Procedure for Forming a Lithium Cobalt Oxide Cathode

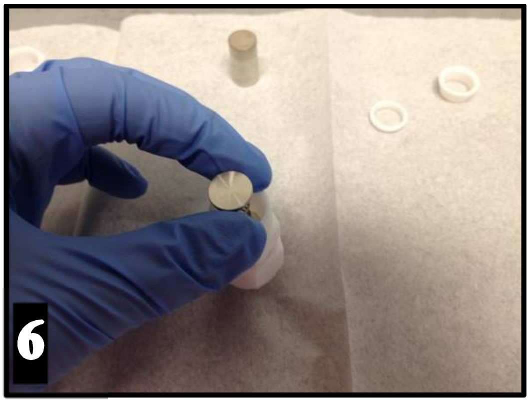
When forming a lithium cobalt oxide ($LiCo_2$) cathode patty, the first part of the procedure involves using the ball mill to reduce the grain size of the powder. Fill a plastic container approximately half way with a mixture of $LiCoO_2$ powder and aluminum oxide mixing balls. After sealing the cover to keep the contents from spilling out, place the plastic container on the ball mixing station. Set the roller to turn at the desired speed and leave the powder to mix for seven days, which will significantly reduce the powder grain size so that it becomes extremely fine. After the ball milling, the powder needs to be separated from the aluminum oxide mixing balls. This can be accomplished by pouring the contents into a beaker and picking the balls out of the beaker. Residual amounts of powder will remain on the balls, so they can be put back into the plastic container, vigorously shaken, and picked out of the powder that is left over.

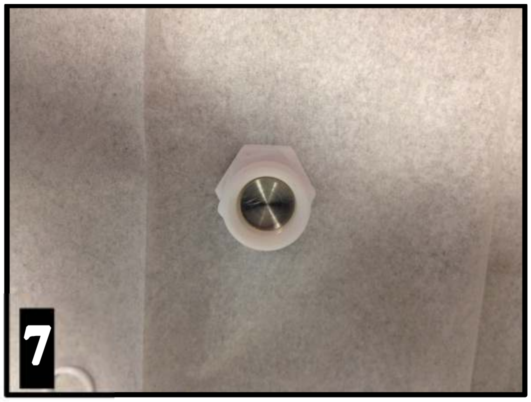
Now that the powder is isolated, the formation of the $LiCoO_2$ cathode disks can begin. A specified amount of powder is measured to be placed in the press, 0.3 grams in the batteries used in this project. Take the measured amount of powder and pour it into the molding used for cold pressing materials. After sealing the die, it is placed into the press at 5000 lbs for two minutes. Upon removing the cathode patty it is placed on a layer of $LiCoO_2$ powder and then covered with another layer of $LiCoO_2$. The cathode is placed in the furnace and sintered at a temperature of 1100°C for 15 hours with a heating and cooling rate of 9°C/min. The final high density product can be polished to a desired thickness by sand paper with increasingly fine grit.

Appendix B: Swagelok Cell Assembly Methods









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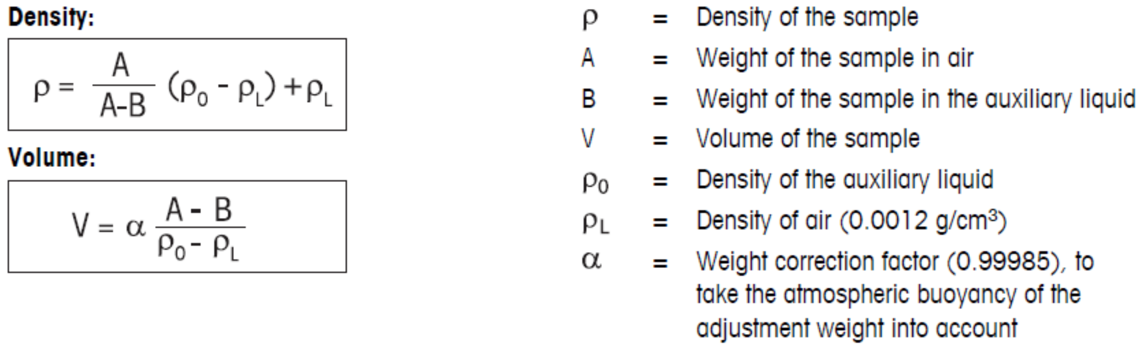
Appendix C: Density Measurements for Sintered Electrodes

To measure the density of the cathode disks, the density kit must be assembled on top of the mass balance according to the procedure provided by Mettler and Toledo’s operating instructions. After putting the density kit together, the glass jar should be filled to an adequate level with ethanol. To take the density measurement of the sample, the disk should be placed on one of the weighing plates to obtain the weight in air, A. Then the disk is placed in the solid basket inside of the ethanol filled jar to find the weight in the auxiliary liquid, B. Since the density of ethanol is known, as long as the temperature of the liquid is taken, and the density of air is given, the actual density of the sample can be found using the following equation.



Density:

$$\rho = \frac{A}{A-B}(\rho_0 - \rho_L) + \rho_L$$

Volume:

$$V = \alpha \frac{A-B}{\rho_0 - \rho_L}$$

ρ = Density of the sample
A = Weight of the sample in air
B = Weight of the sample in the auxiliary liquid
V = Volume of the sample
ρ_0 = Density of the auxiliary liquid
ρ_L = Density of air (0.0012 g/cm^3)
α = Weight correction factor (0.99985), to take the atmospheric buoyancy of the adjustment weight into account

All of this information, including more detailed instructions in density kit assembly, can be found in the instruction manual accompanying the equipment.

Appendix D: Equipment List, Descriptions, and Safety Precautions

Ball Mill

The ball mill is used is grind powder into a finer material to reduce grain size. By reducing the grain size of the powder, $LiCoO_2$ in this project, the density of the disk formed during cold pressing increases. This increase in density allows for the patty to be polished to a smaller thickness. Dry powder of the desired material and solid balls, made of aluminum oxide in this project, are placed in a plastic container until it is 50 percent is full. The cover of the container is screwed on tight to ensure no material is able to spill out of the container. The container is placed between two rollers, one of which is attached to a motor. A specified speed is selected which causes the roller attached to the motor to spin at a constant rate. The contents are left on the ball mill for a desired time so that a certain grain size can be obtained.

Hotplate/Stirrer

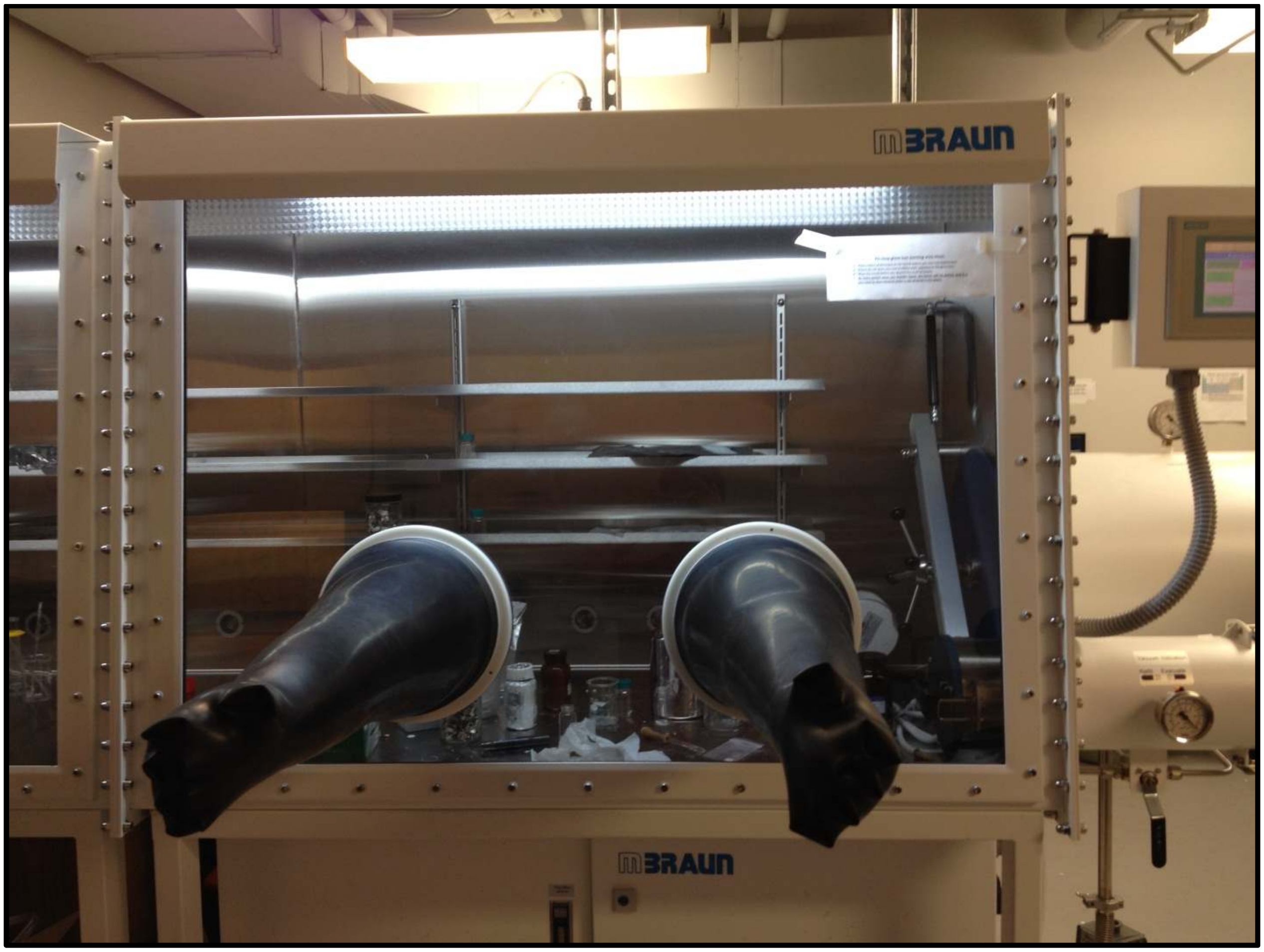
The hotplate/stirrer can be used to mix materials into a uniformly dispersed solution, heat up a substance, or a combination of the two functions. Both the heater and stirrer have controllers that allow for a range of temperatures and spin speeds to be selected. In this project, the unit was mainly used to create the LLTO sol solution for electrolyte deposition. If a material is being heated, it is important to know the temperature of the sample. If it is too hot, the user may need to use some form of personal protection so no burns occur. Also, if a vile is being stirred and heated with a sealed cap, the increase in temperature can cause the pressure to rise. If the pressure rises too high the vile could burst sending glass shards flying across the lab, along with potentially hazardous chemicals.

Density Kit

The density kit is assembled on a mass balance and functions by utilizing Archimedes' principle and the bulk density of the material to yield the actual density of the solid. Ethanol is used as the auxiliary liquid in which the sample is emerged to obtain the wet mass of the material. The wet mass, mass in air, density of ethanol, and density of air are combined to yield the actual density of the porous solid. Similarly, the volume of the sample is found using the mass in air, mass in ethanol, density of air, density of ethanol, and weight correction factor (0.99985). This piece of equipment is vital since the cathode disks are formed from a powder material and therefore are not 100 percent dense. The porosity of a cathode material plays a large role in the performance of an electrochemical cell.

Hydraulic Press

The press is used to compact materials to obtain a desired thickness and density. In this project, $LiCoO_2$ powder is placed in a die that is compressed at 5000 lbs. The plates in the press are hydraulically forced together to create a pressure that can be read from an external pressure gage. Since the press can apply a large amount of pressure, certain safety precautions should be taken into consideration. First, all body parts should be kept outside of the area where the two plates compress to ensure that no injuries occur. Secondly, there is a piece of plexiglass that provides protection from any shards of material that may shoot out of the press while it is operating. The shield should be closed at all times during the compressing of materials.

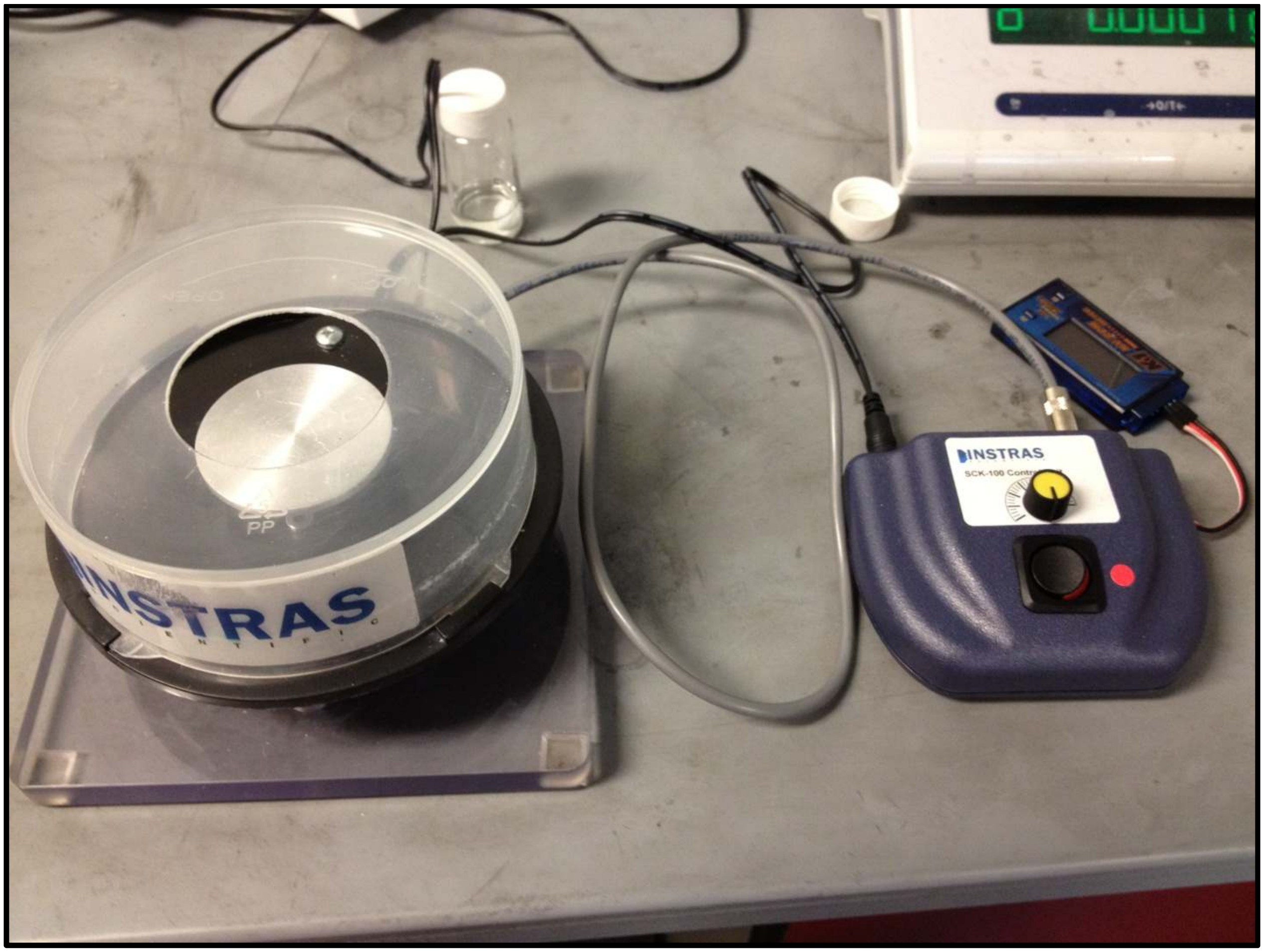


Glove Box

The glove box is a large piece of equipment that allows a person to handle materials in an atmosphere of any desired gas, usually one that is inert. The unit is completely sealed so that no gas can escape or leak into the contained area, allowing for complete control over the purity of the atmosphere. Four gloves are attached to the glass face of the unit so that the user can handle materials inside the container with relative ease. In this project, argon is the inert gas inside the container and is chosen because so the lithium used in fabrication of a cell will oxidize if exposed to air. The necessary pieces, including the swage lock cell, electrode and electrolyte materials, separators, and handling equipment are placed into a chamber that allows for air to be evacuated before transferring the contents into the main chamber. The user can then assemble the cell and remove it from the main container via the same evacuation chamber. When using the glove box, it is imperative to monitor the pressure inside of the unit. If the pressure increases too high, it becomes difficult to operate. If it drops too low, it is an indication that there is a leak somewhere in the system that must be fixed.

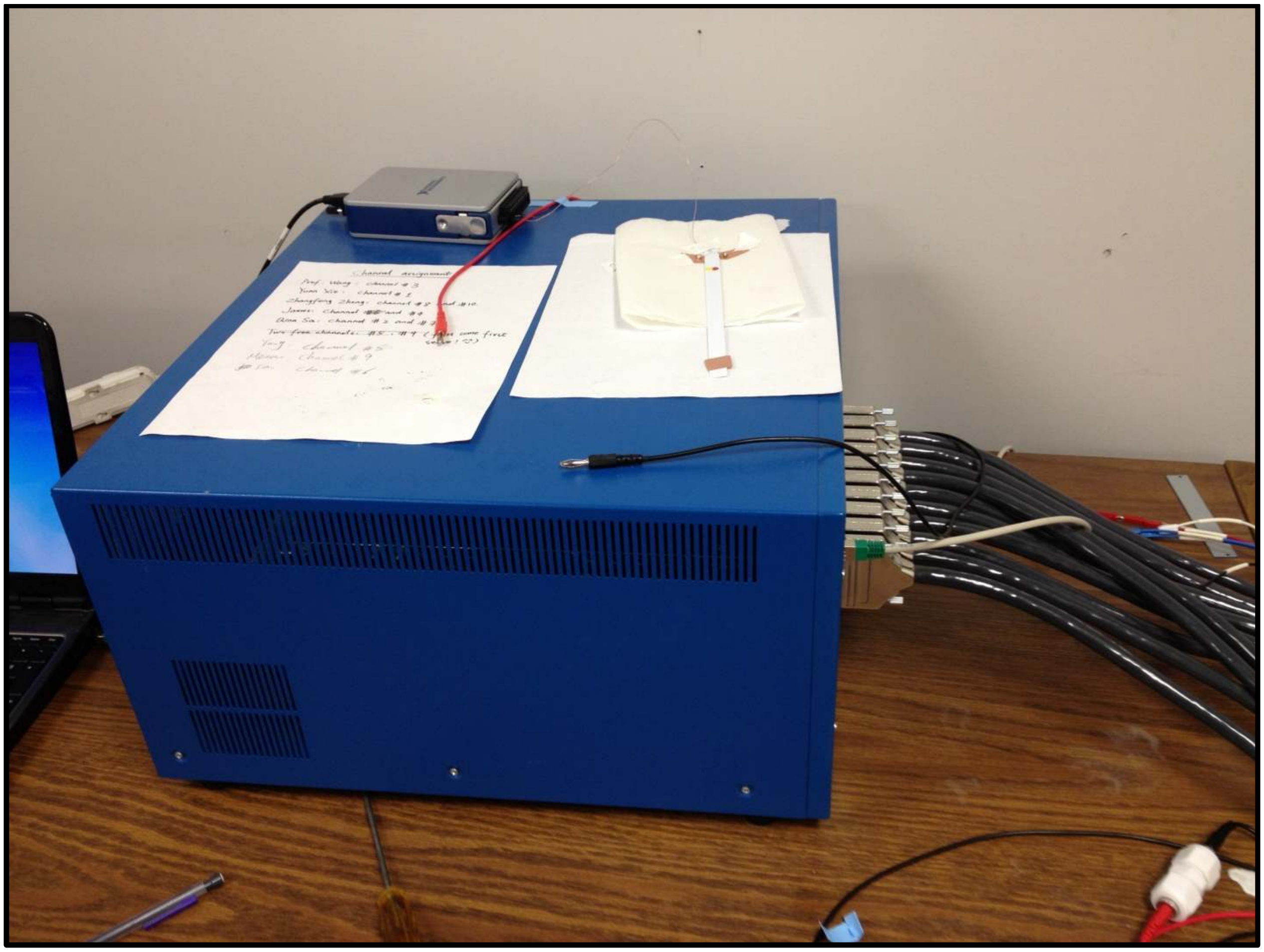
Furnace

The furnace was used to heat up materials to temperatures that could not be achieved by the hotplate/stirrer. High temperatures, up to 1100°C, were achieved in order to sinter the $LiCoO_2$ cathodes and LLTO layers of electrolytes. Controlling the temperature was easily accomplished by using the electronic interface on the front of the unit. Temperature ramp rate, for controlling how fast the temperature was increased and decreased, and dwell time were able to be controlled in these experiments. The most important safety precaution is handling the materials after they come out of the furnace. Depending on the temperature when they are removed, the contents may be too hot to touch with bare hands or while wearing nitrile gloves. When the materials are this hot, one must use insulated gloves or tongs to remove the contents from the furnace.



Spin Coater

Spin coating is used to uniformly distribute a thin layer of liquid on top of a substrate by rapidly spinning the substrate while a pool of liquid sits on top of it. The unit consists of two parts; the motor that rotates a metal platform and the controller that allows the user to manage how fast the platform spins. The user places the substrate material on the metal platform via double sided tape so that it can remain on top of the platform throughout the process. Once liquid is deposited on top of the wafer, the user selects a spin speed from the controller and allows the process to occur for a desired amount of time. Once the time has ended, the user sets the spin speed to zero so that the platform will cease rotating and the substrate can be removed from the platform. A plastic cover is included with the unit to catch any liquids that are wicked from the substrate during the spin coating process. This eliminates any damage that could be caused by the liquid being deposited on the substrate.



VMP3 Electrochemical Tester

The VMP3 electrochemical tester provides the user with a variety of options in testing of batteries. Multiple channels can be plugged into the VMP3 to allow for multiple batteries to be tested simultaneously. These tests allow the user to measure parameters such as voltage, current, impedance, and capacity to fully understand the effectiveness of the electrochemical cell being tested. The unit is attached to a computer in the lab that has EC-Lab software installed on it to obtain a digital output of the testing values. This valuable piece of equipment is the center stone of the research done on battery testing in the laboratory.