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Worcester Polytechnic Institute

Developing a Low-Cost Methodology for Fabricating All-Solid-State Lithium-Ion Battery

A Major Qualifying Project Submitted to the Faculty of
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Abstract

Lithium-ion batteries, rechargeable batteries widely used in laptop computers, cell phones, and electric vehicles, utilize liquid electrolyte solutions. Using liquid electrolytes requires the use of additional materials and poses inherent fire hazard. All-solid-state lithium-ion batteries utilize solid electrolytes and are much safer and efficient, but are much more expensive to produce. This project made an effort to develop a low cost method for fabricating all-solid-state lithium ion batteries. $LiCoO_2$ cathodes were prepared using high temperature sintering. Different methods of $LiCoO_2$ sol and $LiLaTiO_3$ sol deposition were tested for removing surface pores from cathode disks. $LiLaTiO_3$ solid electrolyte was prepared using sol-gel reaction and was deposited on $LiCoO_2$ cathode disk via spin-coating. The effectiveness methodology was tested by evaluating the condition cathode-solid electrolyte system and testing an all-solid-state battery.

Executive Summary

Lithium-ion batteries are used in wide range of electrical devices, from laptop computers and cell phones to electrical vehicles. Just like every other battery, lithium-ion batteries have three major components – cathode, anode, and electrolyte. Most commercial lithium ion batteries utilize lithium cobalt oxide (LCO), $LiCoO_2$, as the cathode material, liquid solution of lithium salt in an organic solvent, and graphite as the anode.

The cathode is a source of lithium ions. The electrolyte provides a medium for lithium ion transfer between the cathode and the anode. The anode stores lithium ions during charging. Electrical power is provided as lithium ions transfer from the anode to the cathode through the electrolyte and electrons flow through and outside circuit, recombining with the lithium ions at th cathode side.

However, the use of liquid electrolyte poses several problems. The cathode and the anode have to be separated in order to avoid short-circuit of the battery. The liquid electrolyte cannot provide such a separation and separators have to be used. These separators increase the weight of the battery. In addition, the liquid electrolyte can leak through the containment walls of the battery and can catch on fire. This is a serious safety issue for commercial lithium ion batteries.

In all-solid-state lithium ion batteries the components are all in the solid phase. Solid electrolytes are being used not only to provide medium for lithium ion transfer but also to physically separate the cathode from the anode, eliminating the need for separators. In addition, solid electrolytes cannot leak out of the battery and cause fire, enhancing the safety properties of the battery. A promising material for solid electrolyte is Lithium Lanthanum Titanium Oxide, LLTO, providing good electrochemical properties, high ionic conductivity and low electronic conductivity.

Fabricating all-solid-state lithium ion batteries is an expensive endeavor. Thin film of the solid electrolyte has to be developed to provide low resistance for lithium ion transfer. Costly methods such as pulsed-laser deposition, atomic layer deposition, vacuum deposition, are used in laboratory environments. The cost of these methods does not allow for scaling up the process and commercial production.

The goal of this project was to develop a cheaper methodology for all-solid-state lithium-ion battery fabrication. The goal was separated in three objectives: developing high-relative density Lithium Cobalt Oxide cathode, filling surface pores on a cathode disk, and deposition of a thin film of Lithium Lanthanum Titanium Oxide solid electrolyte.

Lithium Cobalt Oxide cathode disks were prepared via cold-pressing $LiCoO_2$ powder and subsequent high temperature sintering. The disks were polished to a reflective surface to allow for better solid electrolyte deposition. During polishing pores appeared on the surface of the cathode disk. Methodology to remove these pores included evaporation of LCO sol, evaporation of LLTO sol, spin-coating LLTO and LCO sol on a cathode disk. Thin film of solid electrolyte was developed by spin-coating LLTO sol followed by heat treatment.

The relative density of the LCO cathode disks was satisfying for assembling a battery. Electrochemical testing of cathode disks showed that the cathode had to be thin in order to allow faster lithium ions to transfer between the anode and the cathode.

Evaporation of LCO sol from LCO cathode disk surface proved effective in eliminating surface pores. Evaporation of LLTO sol also showed great results in eliminating surface pores. Spin-coating LCO sol and LLTO sol did not have the same success as the other two methods.

Spin-coating LLTO sol on LCO cathode disks followed by heat treatment was effective in developing thin film solid electrolyte. The thickness of the electrolyte was approximately 1 micrometer, just as desired by the research group.

Testing of all-solid-state battery proved inconclusive. Three batteries were assembled. Of the three only two showed voltage of 2V and 0.9 V for a short period of time. All three batteries fail as short-circuit occurred when the cathode contacted the anode. The reason for the contact was not an imperfection of the LLTO solid electrolyte film, but of the cathode-solid electrolyte system sinking in the lithium metal anode. The contact occurred in the periphery of the disks.

The results were inconclusive in evaluating the effectiveness of the methodology tested. Further testing is recommended to evaluate the potential of the methods used in this project.

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1. Introduction

There is a lot of effort and research put into discovering and developing new energy sources and technologies. Most of the current demand for energy is satisfied by fossil fuels (coal, oil, and gas). However, fossil fuels are limited energy source and, although widely debated when, eventually they will run out and will not be able to satisfy the world's energy demand.[1] Alternative energy sources, such as solar, wind and tidal energy sources, and biofuels, have been introduced as technologies to replace the fossil fuels.[2],[3] As for now, alternative energy resources cannot satisfy completely the demand for electric power, as shown in the figure below.

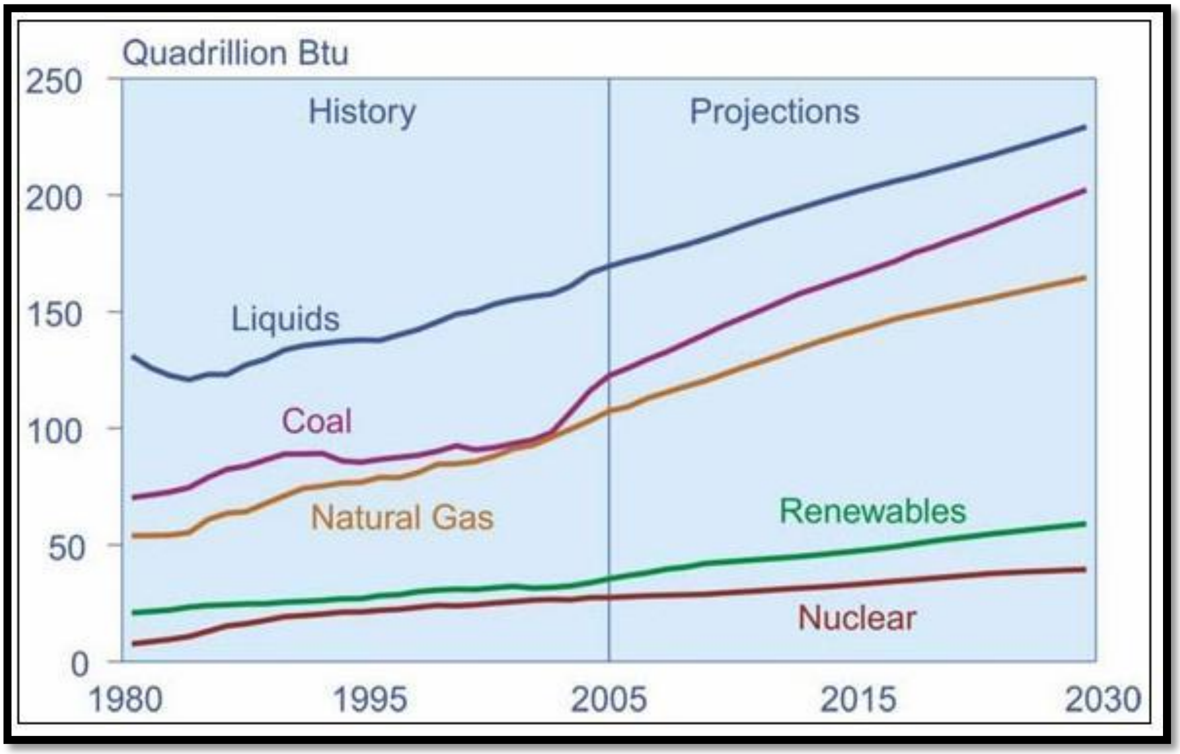


Figure 1 Historical and Projected energy demand of different energy sources[10]

In addition, the energy supplied by wind and solar power cannot always be used at the moment of production. Furthermore, portable devices such as cameras, laptop computers, cell phones, etc., cannot constantly be connected to the power grid when used. For these purposes electrochemical devices that store energy are used. Electrochemical cells, commonly known as batteries, are such devices that store energy for use at a later moment.

Batteries can be primary and secondary, depending on whether they can be recharged. Primary batteries are used only once, while secondary batteries can be used multiple times when recharged. Currently, the most widely used secondary batteries include NiCd (nickel cadmium), NiMH (nickel metal hydride), Lead-Acid, and Lithium-ion batteries.[4] From these batteries the lithium-ion battery has the highest capacity. Lithium-ion batteries can be smaller and lighter and provide higher capacity than the rest of the rechargeable type batteries.

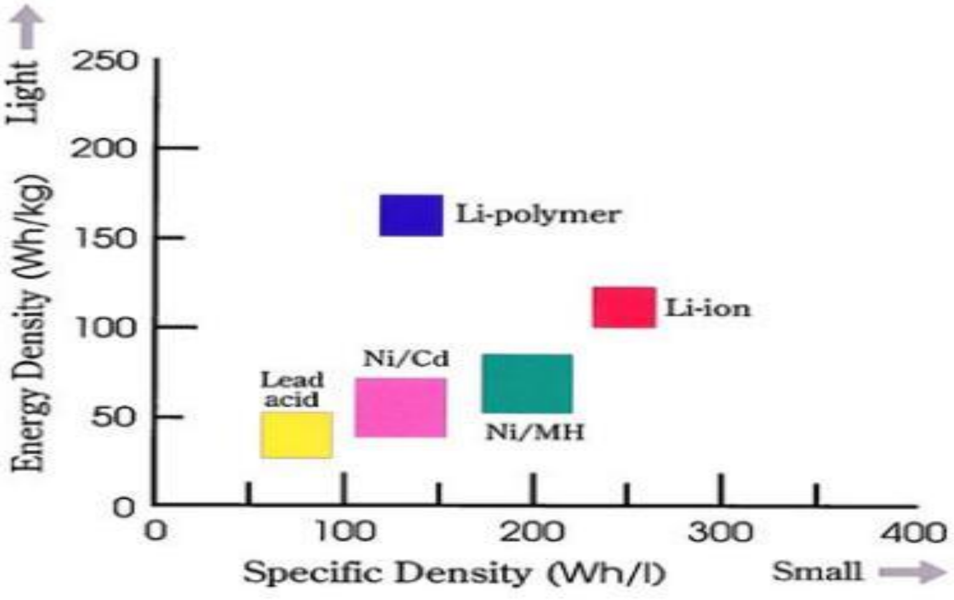


Figure 2 Mass-based and volume-based energy density of different types of batteries [5]

In addition to their higher capacity, lithium-ion batteries are also more expensive than the rest. Their wide use, however, and the research involved in their development have caused the lithium-ion battery cost to decrease significantly. Cost of the different types of batteries is presented in the figure below. In addition to the high cost, lithium-ion batteries have safety issues. There are cases of lithium ion batteries catching on fire due to liquid electrolyte leaking out of the cell.

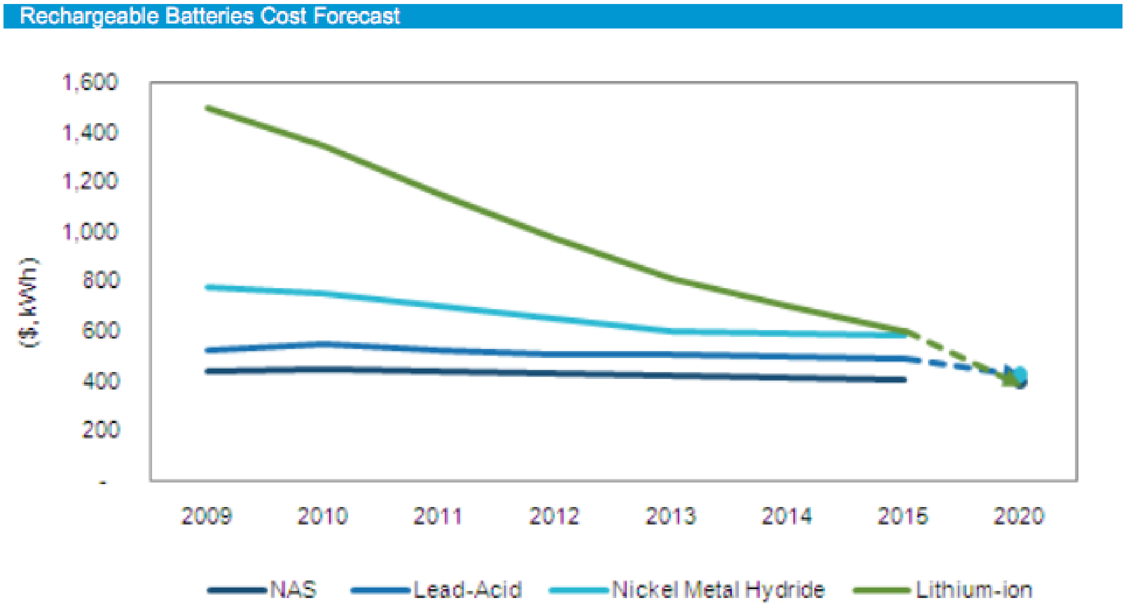


Figure 3 Cost of rechargeable batteries (S/kWh) over the last few years[6]

Lithium-ion battery consists of anode, electrolyte, and cathode, just like every other battery. The anode stores lithium ions during charging. The cathode supplies lithium ions during charging and accepts them back during discharging. The electrolyte provides medium for lithium ion transfer between the cathode and the anode and can be either a liquid or a solid.[7] Most lithium-ion batteries use liquid electrolyte, i.e. an organic solution of lithium salt. A polymer separator is used to physically separate the cathode and the anode and should be permeable to the liquid electrolyte solution, in the lithium-ion batteries that use liquid electrolyte. In addition, a binder is necessary to contain the liquid electrolyte and to hold all components of the battery together.[7] Electric power is provided by the flow of electrons though an outside circuit and recombination with the lithium ions at the cathode, during discharging.

The use of liquid electrolyte, separator and binder increases the weight of the lithium-ion battery, thus decreasing the power per unit mass delivered. In addition, the safety issues, mentioned above, result from solution leaking out of the battery, due to binder deformation or breaking, and catching on fire.[8] Also, the cathode and anode materials degrade much faster because of liquid solutions. Lithium-ion batteries that use solid electrolyte do not pose such a threat. The solid electrolyte acts both to allow medium for lithium ion transfer and to physically separate the cathode and the anode of the battery.[7] The solid electrolyte has to be a thin film in order to reduce the internal resistance of the battery, cause from mass transfer resistance of the lithium ions. Lithium-ion batteries using solid electrolyte are much smaller and lighter than the lithium-ion batteries using liquid electrolyte.

Such a battery would be very attractive for the consumer market. Not only the safety issues are solved, but also the decreased size allows for lighter and smaller portable devices. However, all-solid-state lithium ion batteries are very costly to produce. Developing a thin film of the solid electrolyte is done by expensive methods such as spark plasma sintering, atomic layer deposition, etc.[9] A cheaper production method would decrease the cost of a lot of portable devices and electric vehicles, considering that he lithium-ion battery is contributes a considerable fraction of the cost of the final product. A lot of research in the recent years has been directed towards developing all-solid-state lithium-ion batteries.

The goal of this project is to develop a low-cost method for all-solid-state lithium-ion battery fabrication. The focuses of the research are methodologies for cathode development and solid electrolyte deposition. Providing that the experiments involved provide promising result, a battery will be assembled and tested in order evaluate the potential of the procedures used to fabricate an all-solid-state lithium-ion battery.

2. Background and Literature Review

Lithium-ion battery is an electrochemical cell in which lithium ions, Li^+, are exchanged between positive and negative electrodes, flowing through an electrolyte. Electrons flow through an outer circuit to provide electric power and recombine with the positive lithium ions at the anode. Lithium-ion batteries are secondary batteries, that is, they undergo cyclic charging and discharging and can be used multiple times, unlike primary batteries which cannot be used further after they are discharged.[7] Such batteries are used in wide range of electronic devices from laptop computers and cell phones to electric vehicles. Currently, research is focusing on developing better materials to be used for cathodes, anodes, and electrolytes, in order to increase the power storage and life cycle of the lithium-ion batteries, to satisfy the energy demand.

2.1. Historical Development

Batteries, or electrochemical cells, were invented in the late 18th century. During the next hundred years the lead-acid battery and the nickel-cadmium (NiCd) battery were invented by Gaston Plante and Waldmar Jungner respectively.[10] Both of these batteries were rechargeable and had such an impact on the electrochemical industry and consumption that they are still used today.

During the 1960s and 1970s a large amount of portable electronic goods became available on the market.[10] These electronics required small and light energy source. Lead acid and NiCd were too big and too heavy to power small electronic devices. The introduction of primary lithium batteries, using lithium metal as one of the electrodes, proved to be successful by providing higher energy density, thus, reducing size and weight.[10] The next step was to make lithium batteries rechargeable.

In the 1970s M.S. Whittingham developed a lithium battery using lithium as the anode, TiS_2 as the cathode, and liquid organic electrolyte.[11] The battery was able to charge and discharge multiple times making it a secondary type cell. The discharging process, represented by the equation $xLi + TiS_2 \rightarrow Li_xTiS_2$, proceeded by lithium intercalation within Titanium Sulfide, TiS_2 , lattice crystal with approximately 10% expansion of the structure. It was able to withstand more than 1100 cycles and retain almost 70% of its theoretical capacity.[11]

Lithium metal was used as the cathode for its high specific capacity. However, there were inherent safety concerns for its use, since lithium is very reactive with water. In the late 70s Samar Basu discovered lithium intercalation within graphite.[10] Rachid Yazamy used graphite as anode material and solid electrolyte to show reversible lithium intercalation.[13] The governing equation that represents the process is as follows: $C + x \cdot Li^{+} + x \cdot e^{-} \rightleftarrows Li_xC$, where the forward reaction represents discharging and the backwards reaction - the charging process. Graphite is still used and is the most common material for the anode.

The safety issues were overcome by the introduction of the graphite anode. However, with the elimination of the lithium metal, the need for a material that would act as lithium source emerged. The properties of the material should be such that it allows reversible movement of lithium in and out of its structure in order to allow the electrochemical process.[7] The material that met these characteristics was Lithium Cobalt Oxide, $LiCoO_2$, introduced by Goodenough in the 80s. Akira Yoshino concluded the efforts of research and development by assembling a cell using $LiCoO_2$ and a carbonaceous anode (carbon fiber) to produce a working rechargeable lithium ion battery in 1985. [15] The safety improved significantly as no metallic lithium was used. After many years of research, discoveries, and development the lithium-ion battery was finally commercialized in 1991 by Sony and in 1992 by Toshiba.[7], [15]

2.2. Advantages and Disadvantages of Lithium-Ion Batteries

Portable devices have grown smaller and lighter during the years and the batteries have also followed that trend. This means that batteries need to have higher energy density - that is provide more energy per unit mass or volume. Since their inception, lithium ion battery use and demand has increased considerably. The main reasons for that are its advantages compared to the other rechargeable batteries.

The major advantage of the lithium ion battery is the higher energy density. High specific energy (240 Wh/kg) and energy density (640 Wh/L) significantly outperform the rest of the rechargeable batteries.[7] Lithium-ion battery have long cycle life and low self-discharge rate, meaning the batteries can be used multiple times for a long period without losing their charge while not being used.[17]

Nickel Cadmium (NiCd) batteries have to be fully discharged before recharging. Otherwise, they start to lose capacity; this is known as the memory effect. Unlike them, the Li-ion batteries don’t have that problem.[7] Other advantages include high terminal voltage (4.2 V), rapid charge capability, wide temperature range of operation, and design flexibility due to different chemistries available for transport and intercalation of lithium ions.[7]

However, lithium-ion batteries are not perfect and have some drawbacks. Overcharging the cell can lead to thermal runaway. This can cause fire and explosions. A protective circuitry is required to avoid overcharging. Cathode and anodes degrade when the battery uses liquid electrolytes. Furthermore, this type of battery has the highest cost among all secondary batteries, as mentioned before.[7],[17]

Despite its disadvantages the lithium-ion battery is the most widely used battery. However, the consumer market requires a cell that provides power for a long time without any risks of malfunction.

2.3. Applications and Demand

Lithium-ion batteries are used in a lot of portable electronic devices, such as laptop computers, cell phones, cameras, notebook, etc.[18],[19] They have also been introduced in the automotive industry as a power source for electrical vehicles. Basically, the demand for lithium-ion batteries is closely related to the demand for electronic devices and as the availability of such products increases the power requirements for batteries will tend to rise. The lithium-ion battery market have a considerable share of the battery market with $11.7 billion for 2012.[18] The figure below shows the development of lithium-ion battery market for different consumer electronic devices.

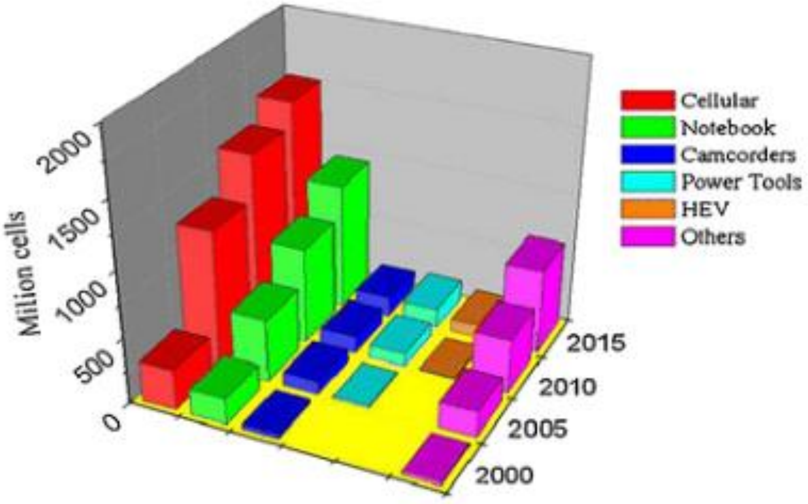


Figure 4 Lithium-Ion battery market development[10]

2.4. All-Solid-State Lithium-Ion Batteries

Every battery has three major components: an anode, a cathode, and an electrolyte. All-solid-state batteries use electrolytes that are in the solid phase, unlike the lithium-ion batteries that use liquid electrolytes for medium of positive lithium ions transfer. In addition, the cathode and anode are also solids. Using solid electrolytes eliminates the need for plastic separators and liquid solutions, which considerably increases the safety feature of the battery. However, solid electrolytes do not have high ionic conductivities compared to liquid electrolytes. That is, they have higher resistance to positive lithium ion transfer between the anode and the cathode. In addition, the interface of contact between the solid electrolyte and the anode or cathode has high contact resistance which further inhibits flow of lithium ions.[20] Therefore, materials with high ionic conductivity and low electronic conductivity are needed to allow for better lithium ion transfer. This would allow easier and faster transfer of lithium ions and would inhibit electrons exchange between the anode and the cathode through the electrolyte.

2.5. Electrochemical Overview

In lithium-ion batteries lithium ions delithiate from the cathode, transfer through the electrolyte, and lithiate in the anode when charging, and vice versa when discharging. The electrons that provide electric power flow from an outside circuit and recombine with the lithium ions at the cathode to provide electric neutrality.

2.5.1. Lithium Intercalation

The process of insertion and exiting the cathode and the anode is called intercalation.[7] Intercalation occurs when a guest species (atom or ion) inserts itself between the layers of ionic or covalent layered material. Whittingham and Yazami discovered intercalation of lithium in different compounds. [11],[14] Research has shown lithium intercalation in different compounds with layered or tunneled structure.[21],[22]

The process of intercalation of lithium within the electrodes during charging and discharging is presented visually in the figure below.

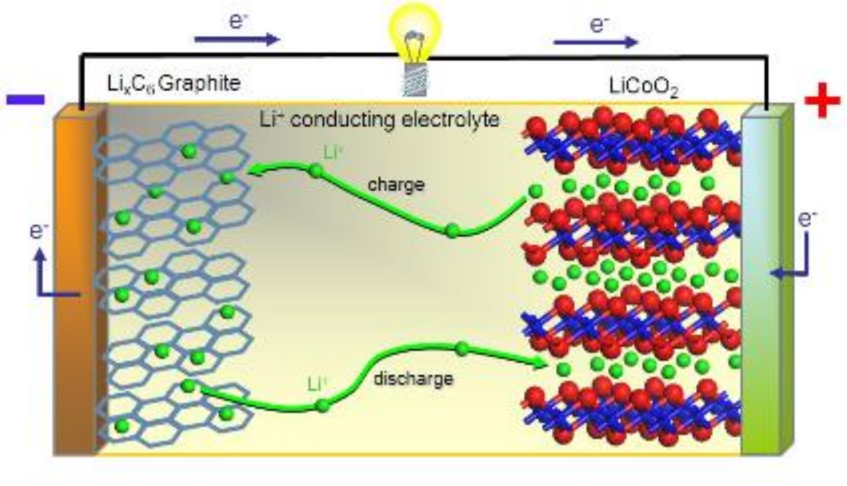


Figure 5 Intercalation of lithium with graphite as the anode and LiCoO2 as the cathode[23]

During charging positive lithium ions deintercalate from the cathode, diffuse through the electrolyte, and intercalate in the anode. During discharging the opposite happens, lithium deintercalates from the anode, diffuse through the electrolyte, and intercalate in the cathode. [23]

Structural changes of the host species occur during intercalation. Therefore, it is necessary that the material that accepts lithium ions do not undergo significant changes in its structure. The amount of electricity produced depends on the amount of lithium ions flowing between the anode and the cathode. Thus, the material that hosts the lithium ions should be able to allow easy insertion and removal of lithium ions from its structure.

Also, lithium ions should be able to diffuse easily through the electrolyte. Thus, to allow that, the electrolyte needs to have high ionic conductivity and low electronic conductivity, to prevent rapid self-discharge.[7]

2.5.2. Cathode Materials

The cathode provides the battery with lithium ions. Therefore, it should be able to hold a large amount of lithium ions in order to provide high battery capacity.[24] In addition, the material should react reversibly with the lithium ions without changing structure as more lithium ions are added. If the reaction with the lithium ion is faster during both intercalation and removal of lithium, this would allow faster charging and discharging rates. The material needs to be a good ionic and electronic conductor since the overall process involves removal of positive lithium ions and electrons from the cathode. Stability of the material is also a preferable feature for a proper battery function.[24] Degrading of material during overcharging or overdischarging decreases its capabilities to store and transfer lithium ions, thus, the ability to withstand such severe conditions is preferable. Last but not the least, the cost of the material plays an important role for its usability as a cathode.

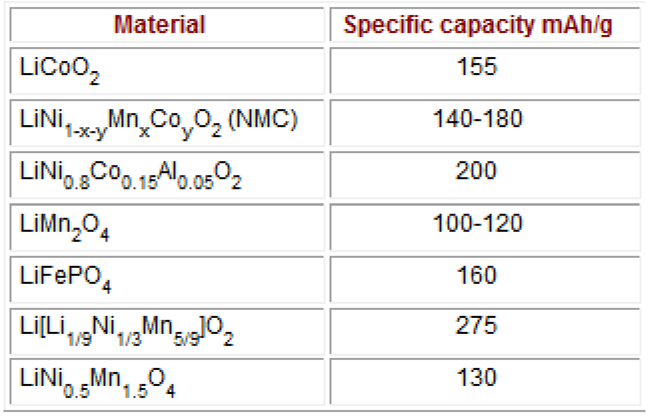
Usually, cathodes of lithium-ion batteries are lithium metal oxides that have structures allowing lithium intercalation and deintercalation. Lithium Cobalt Oxide, $LiCoO_2$, commonly abbreviated as LCO, is the most widely used cathode material. It has high specific energy and gravimetric capacity of 137mAh/g, which is a result of its layered structure.[25] However, LCO is relatively expensive due to the high cost of Cobalt. In addition, it degrades of fails during overcharging, which results in decrease in capacity. Nevertheless, its high capacity makes it suitable for cathode use.

Another cathode material is Lithium Manganese Oxide, $LiMn_2O_4$. It has a three dimensional spinel structure which allows for less resistance of lithium ion transfer.[4] The lower resistance increases the rate of charging and the current during discharging. The structure provides higher material stability and safety and is less expensive than LCO. However, it has a lower capacity than $LiCoO_2$ and the phase change that occurs during cycling decreases the lifespan.[25]

The olivine structure of $LiFePO_4$, in which the lithium ions form one-dimensional chains, provides a good electrochemical performance and low resistance.[4],[25] In addition, lithium iron phosphate is safer and has longer cycle life compared to $LiCoO_2$. However, $LiFePO_4$ has a lower voltage which reduces the power obtained from it. This also reduces the specific energy density. Furthermore, phosphate batteries have high self-discharge ratio which seriously speeds up the aging of the battery.

Other cathode materials have also been developed. Vanadium oxide is a layered compound that provides a high capacity, but a relatively low voltage.[25] $LiMnPO_4$ and $LiCoPO_4$ have higher voltages, but have low capacities. $LiNiCoAlO_2$ has high specific energy and power density, which makes it very attractive cathode material for use in electrical vehicles.[25] Different cathode materials and their specific capacity are summarized in the table below.

Table 1 Summary of cathode materials and their specific capacity



Material	Specific capacity mAh/g
$LiCoO_2$	155
$LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC)	140-180
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	200
$LiMn_2O_4$	100-120
$LiFePO_4$	160
$Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$	275
$LiNi_{0.5}Mn_{1.5}O_4$	130

The research efforts are for producing cathode materials with high capacity, specific power, and specific energy that withstand long cyclability and are safe to use.

2.5.3. Anode Materials

The anode in a lithium-ion battery acts as a storage for positive lithium ions. During charging, lithium ions intercalate in the anode, and they deintercalate during discharging. The anode, just like the cathode, needs to have ability to store large amounts of lithium to provide high capacity. The anode should have a low voltage in order to provide a high overall voltage across the cell. This would ensure a high driving force for the lithium ions to transfer between the electrodes and, thus, provide higher battery power.[4]

The amount of lithium ions that the anode can hold is highly dependent on the structure of the anode. The first anode material used in lithium-ion batteries was lithium metal. It had high specific capacity and produced a good performance.[4] However, its high reactivity and cases of batteries catching on fire cause the lithium anode to be abandoned as an anode material.

The layered structure of the graphite allows for lithium ions intercalation. However, it has relatively low capacity. Despite that graphite is the most widely used anode due to its low voltage and its ability to withstand long number of cycles.[26] In addition, graphite expansion during lithium ion intercalation is just 10% further favoring it over other materials. Graphite could also possess flexibility in manufacturing as its structure can be controlled to provide different ordering of its layers. In addition, it could also be coated or mixed with other materials to improve its capacity and oxidation properties.[26]

In addition to graphite there are other carbonaceous materials used as anodes. Soft carbon is material that possesses disordered structure, suitable for lithium intercalation. Soft carbon is fabricated by organic precursors, such as petroleum pitch and coal tar pitch.[27] Hard carbon, just like soft carbon materials, also has a disordered structure. However, hard carbon retains its disordered structure after heat treatment, unlike soft carbon. Hard carbon possesses high reversible capacity, compared to graphite and soft carbon. However, it is not as widely used due to problems with low density, hysteresis between charge and discharge periods, and large irreversible capacity.[27]

Lithium Titanate ($Li_4T_5O_{12,}$ LTO) is another anode material used in lithium ion batteries. LTO has a gravimetric capacity of 175mAh/g, which is lower than the graphite materials.[28] In addition, its poor lithium and electronic conductivity limit its rate capabilities. However, LTO possesses a spinel structure that gives it a considerable stability during lithium intercalation and extraction.[4],[28] Structural changes during charging and discharging are minimal. This results in a long cycle life and enhanced safety performance.[28]

Other anode materials with better capacity, low voltage, and safety performances are being developed, but the ones mentioned above are the most widely used in commercial applications.

2.5.4. Electrolyte Materials

The electrolyte’s function is to provide medium for lithium ion diffusion between the cathode and the anode. It should have high ionic conductivity and low electronic conductivity in order to prevent the battery from self-discharging and shorting out.

Liquid electrolytes utilize a lithium salt dissolved in organic solvents.[4] For proper functioning of the battery and good performance the solvent needs to have certain properties. It needs to dissolve the lithium salt to a high extent, which means it needs a polar group and high dielectric constant.[29] It needs to operate in wide temperature range in order to remain liquid and retain relatively low viscosity for proper lithium ion transfer.[4] Last but not the least it should not react with the rest of the battery materials (electrodes, separator, etc.).

At an early developmental stage of the lithium-ion batteries propylene carbonate (PC) was the choice for organic solvent. Lithium salts dissolve to a large extent in propylene oxide.[4] High viscosity of propylene oxide hinders lithium transfer. Nowadays, mixtures of solvents are used. In addition, it intercalates in carbon anodes causing less lithium ions to be stored in the anode.

Usually, solvents in lithium-ion batteries consist of three to five different solvents. Some of the most widely used organic solvents are ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC).[4] The table below summarizes the solvents and their properties.

Table 2 Organic solvents and their properties

Solvent	**EC**	**PC**	**DMC**	**EMC**	**DEC**
BP (° C)	248	242	90	109	126
MP (° C)	39	-48	4	-55	-43
Viscosity(cP)	1.86	2.5	0.59	0.65	0.75
Dielectric Constant	89.6	64.4	3.12	2.9	2.82

It can be seen that no single solvent has the perfect properties. Solvents with high dielectric constant (dissolving lithium salts better), have high viscosity, thus, limiting lithium transfer. Solvents with low viscosity have low dielectric constant, thus, dissolving less lithium and limiting capacity. That is why mixtures are preferred.

Despite the requirement for chemical inactivity towards the rest of the materials, there is a reaction that occurs between the electrolyte and the anode during the first cycling. Lithium from the electrolyte reacts with the anode forming a passivation layer called solid electrolyte interface (SEI).[4], [29] This layer contains inactive lithium which causes irreversible loss of capacity. Despite that the SEI is still able to let lithium ions diffuse through it and intercalate in the anode.

The most common salt used in lithium-ion batteries is $LiPF_6$. Its properties include high lithium transference number (0.35) and high ionic conductivity (10^{-2} S/cm).[4],[30] $LiBF_4$ has higher ionic conductivity than $LiPF_6$. However, both salts react with water to form HF. Thus, they require dry environment and careful handling when used. Carbonate salts do not react as readily with water and have received considerable attention in lithium-ion battery research.[29],[30]

Solid electrolytes are not as common in lithium-ion batteries as liquid electrolytes. However, they have some advantages. Using solid electrolyte does not require additional materials for separators, solvents, and salts. The solid electrolyte contacts both the anode and the cathode and physically separates them. This can significantly decrease the weight of the battery if thin film of the solid electrolyte is prepared, thus, increasing the energy per unit weight of battery obtained. In addition, solid electrolytes offer higher safety, since there is no risk of liquid leaking out of the battery and catching on fire.

Different materials providing different conductivities can be used for solid electrolytes.[31] Polymers, ceramics, and glass materials have been studied for construction of all solid state batteries.[31],[32] Solid electrolytes offer lower conductivities than liquid electrolytes. One of the most promising solid electrolytes is Lithium Lanthanum Titanium Oxide (LLTO).

LLTO has a relatively high ionic conductivity, between 10^{-3} to 10^{-5} S/cm. The Li/La ratio in the ionic structure significantly affects the conductivity. It has been reported that composition of $Li_{0.35}La_{0.55}TiO_3$ provides the best ionic conductivity of the material.[31],[33] For laboratory purposes LLTO is usually prepared by simple sol-gel reactions.[33]

LLTO has electrochemical stability, which gives it long cycle life. However, being a ceramic material it poses difficulties for developing a thin film in all-solid-state batteries. [31]

2.6. All-Solid-State Batteries Using LLTO as a Solid Electrolyte

All-solid-state batteries are composed of materials that are all in solid phase. The solid electrolyte is developed as a thin film between the anode and the cathode. The lower the thickness of the solid electrolyte the faster the lithium ions can diffuse through it. This results in increased current density and faster charging and discharging rates. However, in laboratory environments expensive equipment and procedures are used.

Methods such as spark-plasma sintering, atomic layer deposition, and pulsed laser deposition have been used to develop LLTO thin films in laboratories.[34],[35],[36] However, these methods and the equipment are too expensive to allow for competitive commercialization. Vacuum deposition is a commercial method used for developing atomic layers, but it also uses expensive machinery, which results in high cost.[37] If a simpler method, which does not require expensive equipment, is invented, the cost could be brought to a level that can increase the demand and utilization of all-solid-state batteries.[37]

3. Methodology

Every lithium ion battery has three major components: cathode, electrolyte, and anode. In the all-solid-state battery all the components are in the solid phase. This eliminates the need of liquid electrolytes, separators, and binders. The main focus of the project was the development of a cathode with a solid electrolyte layer. The materials chosen for this purpose were Lithium Cobalt Oxide (LCO), $LiCoO_2$, for the cathode and Lithium Lanthanum Titanium Oxide (LLTO) for the solid electrolyte. Lithium metal was used for the anode part when assembling a battery.

Due to the time limitations, the advancement of the project work highly depended on success of each individual experimental step. The project chronology was divided in the three objectives presented in the figure below. Each of these three objectives was achieved by stepwise procedures. Lack of success in the achieving of any of the objectives meant that development of the methodology and testing a battery were precluded. This section will describe the experimental procedures in developing a low cost production method. Each sub-section describes the considerations behind the experiments, the exact experimental procedures, difficulties faced before or after the described procedure.

Figure 6 Project development

3.1. Lithium Cobalt Oxide ($LiCoO_2$) Cathode Development

Lithium Cobalt Oxide has high theoretical capacity, 137 mAh/g, and is widely used in lithium ion batteries as a cathode material. For this reason, and because of the convenience of a being a material already used in the laboratory, it was chosen for making a cathode. The overall goal of the following experiments was to prepare a cathode disk with a high relative density. Higher relative density meant low porosity. The porosity of the cathode could affect the transfer of lithium ions and thus, increase the internal resistance of the battery.

Much of the methods used to prepare the lithium cobalt oxide cathode were replicated from the previous group's attempts. Additional attempts were made to further improve and develop the procedures used.

3.1.1. Cold-Pressing and High Temperature Sintering of Lithium Cobalt Oxide Powder

Usually, procedures for producing all-solid-state thin film batteries involve expensive methods such as RF magnetron sputtering, pulsed-laser deposition, vapor deposition, etc. This project utilized a simpler and cheaper methodology that if successful, could be easily implemented for a commercial manufacturing. The preparation of LCO cathode involved cold pressing and subsequent high-temperature sintering.

Lithium cobalt oxide powder was prepared by a previous research team at WPI, and was out of the scope of this project. The powder was prepared by ball milling of stock LCO powder, achieving a particle size of 5 to 30 micrometers in diameter.

Approximately 0.3 grams were measured and were put into a steel mold with a diameter of 1 centimeter. The powder was then pressed in a cold press for two minutes under 10000 psi of pressure. The pressure applied made the individual particles stick together. Higher pressure would cause formation of cracks and lower pressure would not press the particles tight enough. Although it was not determined whether 10000 psi is the optimum pressure, it was deemed acceptable for disk formation.

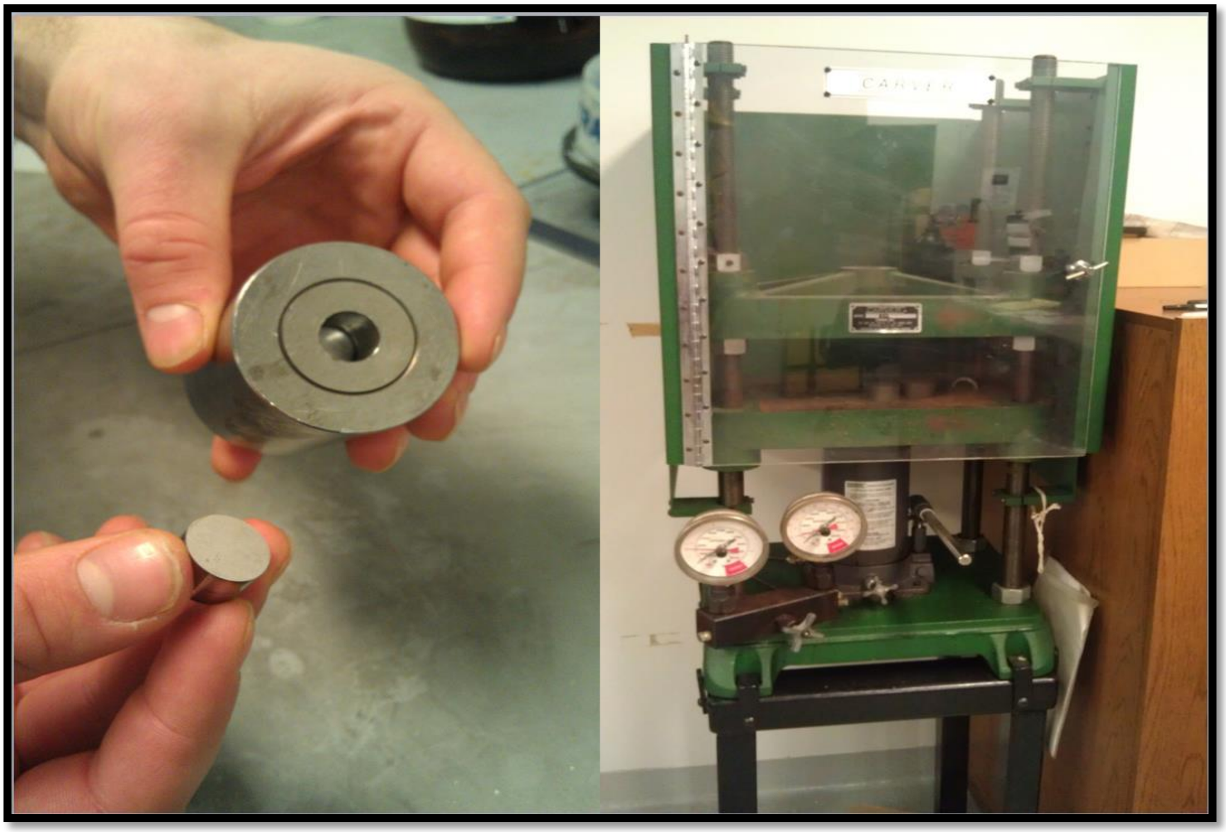


Figure 7 Mold and Cold press

A ceramic plate was covered with stock lithium cobalt oxide powder and the resulted disk was put on it. In order to achieve uniform crystallization, retain the shape of the disk, and prevent lithium from escaping the crystal structure of LCO, the disk was also covered with stock powder.

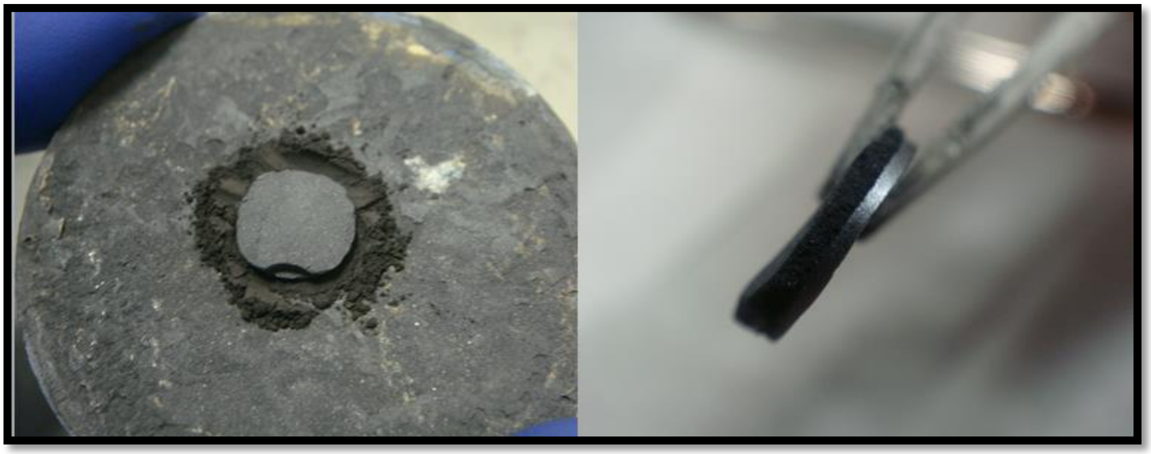


Figure 8 LCO Cathode disk before (left) and after (right) Sintering

Several sintering temperatures and times were used. First, the LCO disk was put in a furnace to sinter at 1200° C (degrees Celcius) for 24 hours with a heating rate of 9° C per minute. After the sintering procedure was finished the disk was recovered from the powder using combination of razor blade and polishing paper. This procedure did not produce a disk with the desired properties. During heating the disk had shrunk creating large number of pores. Although, individual particles had fused together, which meant that there would be no surface resistance in lithium ion transfer, the density was too low and the disk was not appropriate for solid electrolyte deposition. In addition, the disk had fused so much with the covering powder that it was very difficult to recover and the uncovering process caused extreme stress on the disk and it would often break.

Figure 9 Furnace used for sintering LCO disks

To increase the relative density, avoid disk shrinking and pore formation and the difficulties associated with its recovery, the temperature was decreased to 1100° C. The time the disk was kept in the furnace remained the same. The disk was recovered easily from the powder and was polished. After polishing the density was measured using Archimedes' method.

An experiment was made to determine whether the time spent in the furnace would affect the relative density. The pressing procedure was repeated but the heat treatment was set at 1100° C for 15 hours. Similar procedure was used by the previous research team. Longer heat treatment would allow for longer diffusion through each particle's surface. However, it was hypothesized that the time difference of nine hours would not produce large differences in the density. The shorter amount of required would allow for quicker cathode production. The time saved was spent for other procedures. The relative density measured was the same despite the different amount of time the disks spent in the furnace.

During the polishing process, the disks sintered at 1100° C would break or disintegrate into powder before achieving the desired thickness. The disks sintered at 1200° C could be polished below the desired thickness, but were not used because of their low density. An attempt was made to improve the strength of the LCO cathode disks. The same preparation procedure was repeated, but the sintering temperature and time were set to 1150° C and 15 hours respectively. The resulted disk had lower density than those sintered at 1100° C without a significant increase of its strength. Therefore, it was determined to improve the polishing procedure.

3.1.2. Polishing of Lithium Cobalt Oxide Cathode Disks

After the heat treatment, the LCO disks had to be polished to a thickness of no more than 100 micrometers and a smooth surface. Larger area was needed to increase the transfer rate of lithium ions and lower thickness was desired to decrease mass transfer resistance, thus, internal resistance of the battery. This would result in higher charging and discharging rates. Smooth surface would have allowed for better deposition of the solid electrolyte during spin coating. The smoother the surface the thinner and the more uniform film of solid electrolyte could be prepared. For the polishing process sand paper with different fineness of the grit was used. The polishing was done manually without using polishing equipment.

The first step was to decrease the thickness of the disk. 320-grit sand paper was used to polish the cathode from one millimeter to about 300 micrometers. The disk was thickness was then decreased to approximately 150 micrometers with sequential polishing with 400 and 600 grit paper. It was then polished to a mirror surface with a 2400 grit paper.

It was observed that after polishing with 2400 grit sand paper. Small pores and holes were visible on the surface with diameter of 10 micrometers. It was hypothesized that these have resulted from the preceding rough polishing treatment. To eliminate these pores or holes visible on the surface the polishing approach was changed. Sequential polishing with 320, 400, 600, 800, 1200, 2000, and 2400 grit was carried on to polish to a reflective surface. Scanning the surface with electron microscope showed that the pores have not disappeared.

Surface pores and holes affected the lithium lanthanum titanium oxide (LLTO) solid electrolyte film development. The large number of pores caused formation of cracks in the LLTO film. These cracks would have resulted in short-circuiting of the battery. Different procedures were employed in order to eliminate surface pores, as will be presented later in this section.

During the polishing, uneven pressure from the manual operation would break the disk at thickness lower than 300 micrometers. The polar structure of $LiCoO_2$ made it brittle, therefore, the polishing required utmost care and exactness. Attempts were made to improve the strength of the disk, which did not resolve the problem of disk breaking. To achieve desired thickness without compromising its integrity, the disk was attached to a surface with a double tape and one side of it was polished manually. This process proved better as the disk was successfully polished.

After each polishing procedure the disk was washed in ethanol. In addition, it was washed in a sonic cleaner to remove any particles stuck on it during polishing.

The polishing procedure was finalized by additional improvement. After the disk was recovered from the furnace, one of the sides was polished to a mirror surface with paper with increasing grit. After that, the other side was polished with a rougher sand paper to decrease the disk to the desired thickness. Later that proved useful, as it was easily distinguishable which side was smooth and covered with solid electrolyte.

After the lithium cobalt oxide disk was prepared, it was ready to be spin coated with solid electrolyte. The overall and finalized procedure for cathode development is represented visually in the figure below.

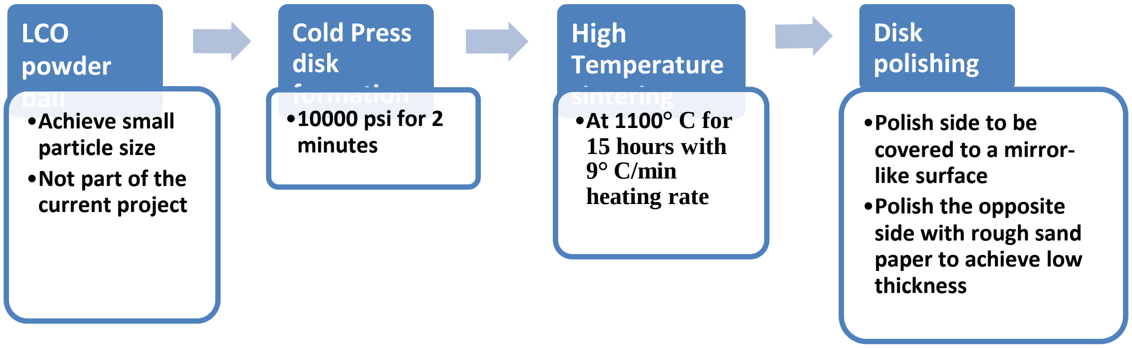


Figure 10 LCO cathode development procedure

3.2. Lithium Lanthanum Titanium Oxide Solid Electrolyte Thin Film Development

Usually, lithium ion batteries utilize lithium salt dissolved in organic solutions for highly conductive electrolyte. However, solid-state batteries utilize materials that conduct lithium ions and that do not need to be dissolved in organic solutions. As already discussed Lithium Lanthanum Titanium Oxide, LLTO, is a fast lithium ion conductor with bulk conductivity of $1x10^{-3}$ S/cm. LLTO thin films have been prepared using sol-gel reactions. Sol-gel LLTO deposition was being utilized by the graduate students working in the same laboratory. After reviewing studies on an effective electrolyte, the group determined that LLTO sol solution would be the best solid electrolyte for the team's project. The team created the solution with the help from PhD student at WPI, Zhangfeng Zheng.

3.2.1. Lithium Lanthanum Titanium Oxide Sol-Gel with High Concentration of Polyvinylpyrrolidone Binder Preparation

As an initial process, two different types of solutions were prepared by mixing different chemicals. Solution A was created by mixing LiAC (Lithium Acetate Dihydrate), $La(AC)_3$ (Lantahnum Acetate Hydrate), Acetic acid, and Propionic acid. Measured amount of solid chemicals, LiAC and $La(AC)_3$, were added to liquid chemicals, acetic acid and propionic acid, then stirred on the heating pot (90~100˚C) for 15 minutes.

A second solution was prepared by mixing Titanium isopropoxide, Acetic acid, Isopropyl alcohol, and Polyvinylpyrrolidone (PVP). As a first step, titanium isopropoxide and acetic acid were mixed using micropipette, and stirred for about 15 minutes. Since titanium isopropoxide is a chemical that evaporates easily in air, this process was carried out in an argon hood glove box. After 15 minutes, measured amount of isopropyl alcohol and PVP were added to the solution, causing the solution to change its color into yellow, then stirred for another 20 minutes. Once both solutions were prepared, solution A was added to solution B drop-wise over a period of time on the stirring pot in order to create LLTO sol solution. Each drop was approximately one to three cubic millimeters. The prepared solution was stirred for additional two hours to allow for perfect mixing and avoid precipitation of LLTO particles. The recipe of the exact amounts of each chemical used are presented in the table and figure below.

Table 3 Composition of solutions A and B

Chemical	**Amount**
Solution A	
LiAC (Lithium Acetate Dihydrate)	0.0804 g
$La(AC)_3$ (Lanthanum Acetate Hydrate)	0.4356 g
Acetic Acid	0.6800 g
Propionic Acid	1.6800 g
Solution B	
Titanium Isopropoxide	0.69 ml
Acetic Acid	1.30 ml
Isopropyl Alcohol	2.7045 g
PVP (Polyvinylpyrroliodine)	0.3750 g

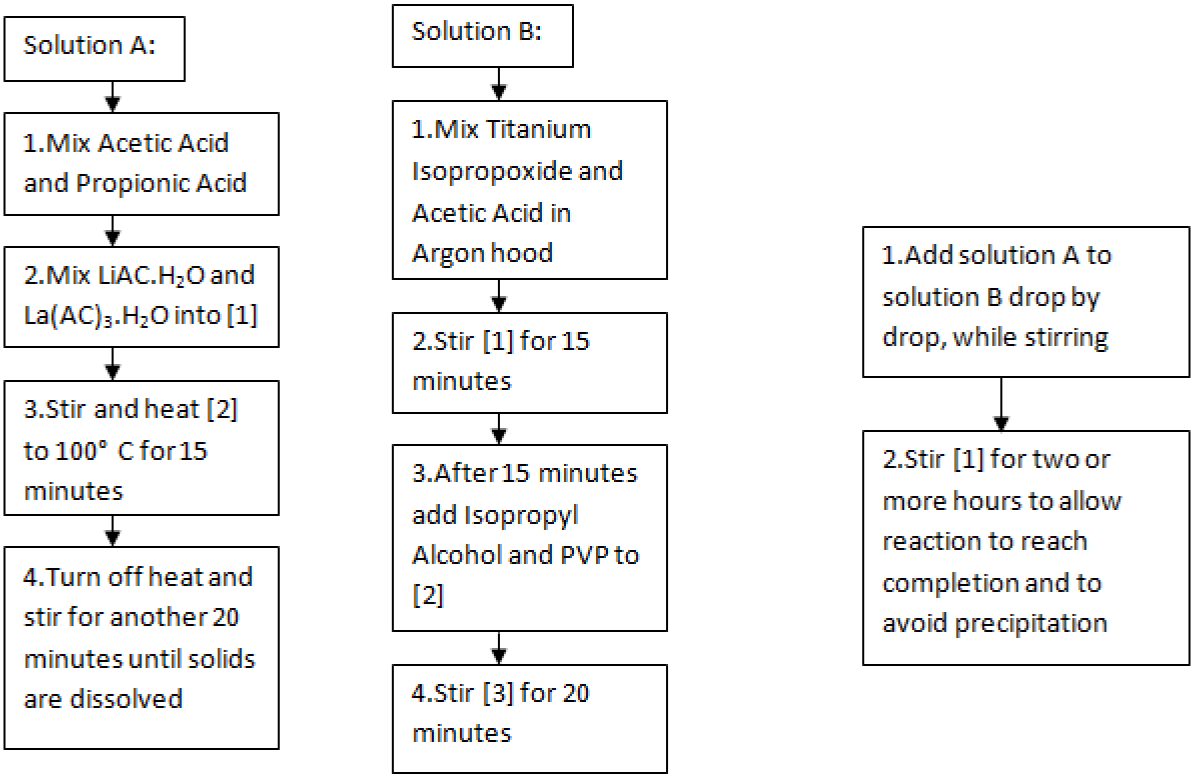


Figure 11 LLTO sol step-by-step preparation

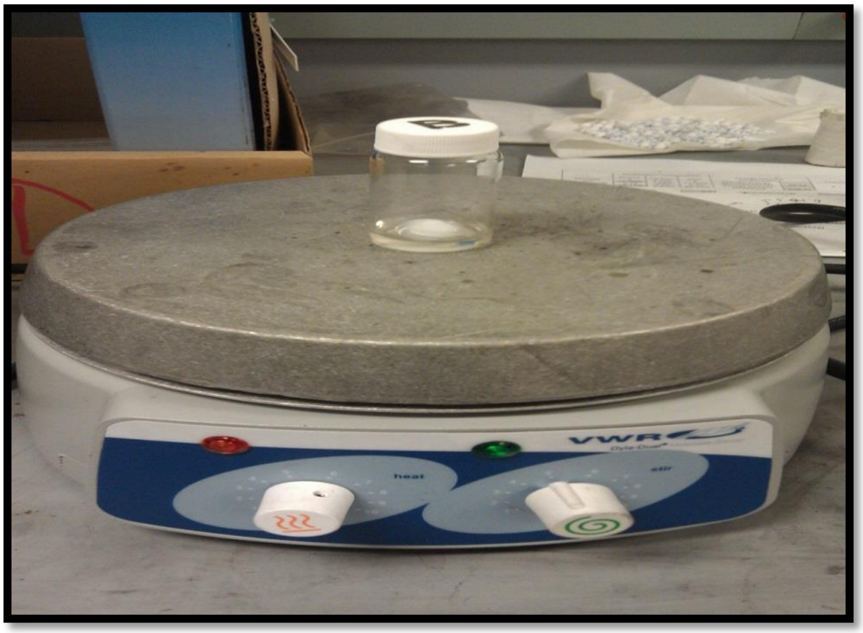


Figure 12 Solution B stirring prior to mixing with solution A

The relative composition of Lithium Lanthanum Titanium Oxide achieved with this sol-gel process was approximately $Li : La = 0.35 : 0.56$. As described in the background section, at this approximate composition LLTO shows its highest ionic conductivity.

The concentration of LLTO in the solution was 5.1% by mass and the PVP binder concentration was 4.7% by mass. The PVP binder was used to increase solution viscosity and for better adhesion to the LCO substrate. This would have reduced the spinning iterations required to produce a thin and uniform LLTO film.

The solution could be stored and used for 2-3 weeks. After that time precipitation of LLTO particles was observed, which changed the overall LLTO concentration; the solution was no longer used and was discarded.

3.2.2. Low Concentration of Lithium Lanthanum Titanium Oxide Sol-Gel

The results from the heat treatment of the LLTO sol-gel cracks and pores would form in the layer. It was decided to use a procedure to cover these cracks and pores. For that reason a low concentration LLTO sol-gel without PVP binder was needed. The lack of PVP would decrease the viscosity of the solution and would allow it to penetrate pores on the surface of the $LiCoO_2$ cathode disk.

The preparation procedure was similar to the one already described. The only difference was that Acetic Acid and Propionic Acid in solution A were substituted with water. In addition, no PVP binder was used. The concentration of the LLTO in this solution was 3.78% by mass. Table 2 presents the amounts of each chemical used.

Table 4 Compositions of solutions A and B for low LLTO concentration sol

Chemical	**Amount**
Solution A	
LiAC (Lithium Acetate Dihydrate)	0.0804 g
$La(AC)_3$ (Lanthanum Acetate Hydrate)	0.4356 g
H_2O (Distilled Water)	5.6 g
Solution B	
Titanium Isopropoxide	0.6935 g
Acetic Acid	1.3613 g
Isopropyl Alcohol	2.7045 g

3.3. Spin-Coating Deposition of LLTO Sol-Gel on LCO Cathode Disks

Once the cathode disks were prepared (polished to a smooth reflective surface) the LLTO sol could be deposited on their surface. The method chosen for that was spin-coating. Spin-coating allows for a uniform film deposition; thickness of the film can easily be controlled by regulating angular speed. The spin-coater device used had the adjusting the speed of rotation as desired.

The desired thickness of solid electrolyte film was one micrometer. The thicker the film the longer it would take for lithium ions to transfer between the cathode and the anode of the battery. If the film was too thin it could break due to stress during handling and electrochemical testing and would short the battery. Although it was recognized that the optimum thickness of the solid electrolyte film depended on set of factors, it was agreed that one micrometer would allow for proper functioning of the battery.

Several different procedures were experimented until the desired uniformity and thickness were obtained. The Lithium Cobalt Oxide disk was attached to the center of the spin-coater with a double-side heat release tape.

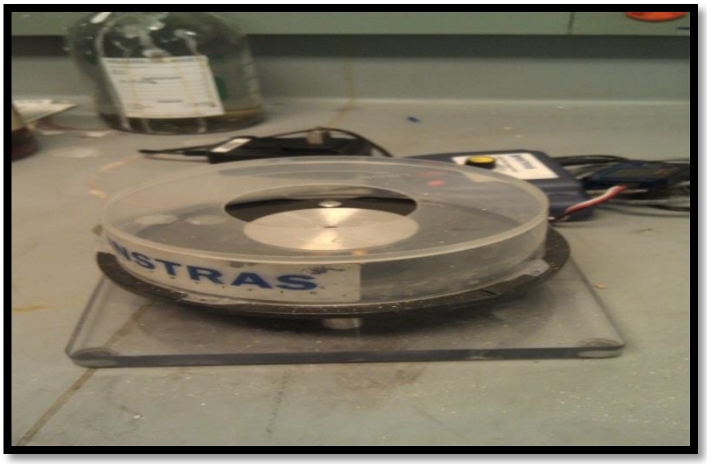


Figure 13 Spin-coater with speed regulator and display (visible in the back)

The first spin coating procedure involved depositing LLTO solution during spinning. The disk was accelerated to 3000 revolutions per minute. After this, solution was deposited with a micropipette drop by drop. Each drop was 5 seconds apart and 20 drops in total were deposited. It was observed that large volume of the liquid was expelled outwards, flying off the disk and sticking on the protective cover. The covered disk was dried on a hot plate at temperature of 170° C for five minutes. After this, the disk with the LLTO film was heat treated. Heat treatment procedures will be explained in the next section. The spin-coating procedure was repeated for total of five times to allow achieving desired thickness. The figure below represents the overall process.

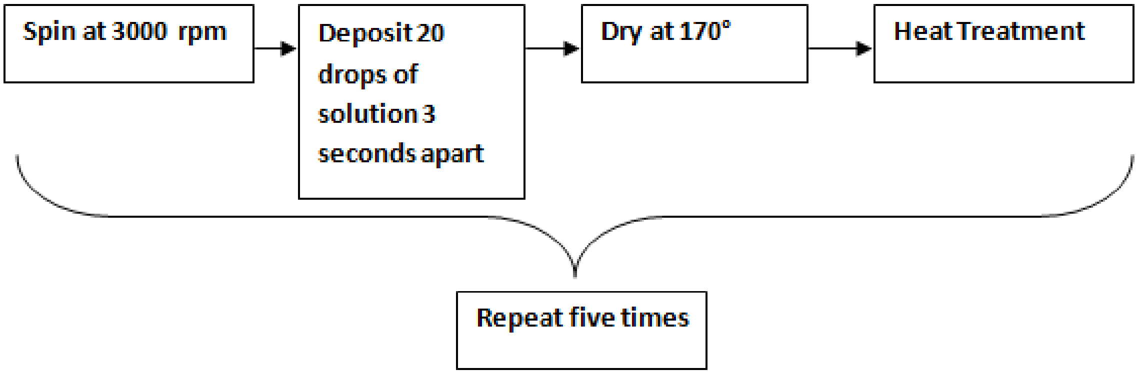


Figure 14 Procedure of solution deposition while spinning

Figure 15 LCO cathode disk covered with LLTO Sol

The results showed that the film was not developing properly. At places there was no coverage whatsoever and where there was LLTO large cracks were observed. In addition large amounts of solution were propelled off the disk, which meant serious loss of material. Also, after heat treatment LLTO particles were observed on scanning electron microscope analysis. Such particles resulted from the sol-gel reaction and could affect the formation of the solid electrolyte film during spinning.

Different method was used in order to improve the coverage, decrease the loss of solution, eliminate particles, and to result in a better overall film. First, the solution was placed in a syringe with a filter attached to it. The role of the filter was to remove large particles from the solution. Second, the after the disk was attached to the spin-coater, it was covered with solution prior to spin-coating. To avoid spills and large exhaust amount of liquid, the disk was slowly accelerated do 3000 rpm. It was rotated for 30 seconds to allow for uniform film formation. The covered disk was then dried at 170° C for five minutes and then was heat treated in a furnace. The whole procedure was repeated from three to seven times.

It was observed that the liquid film was slowly getting thin with accelerating the rotation speed. Also, areas of thicker coverage were observed on the edges of the disk. These areas were not a concern as they were cut after heat treatment. The figure below presents the overall process.

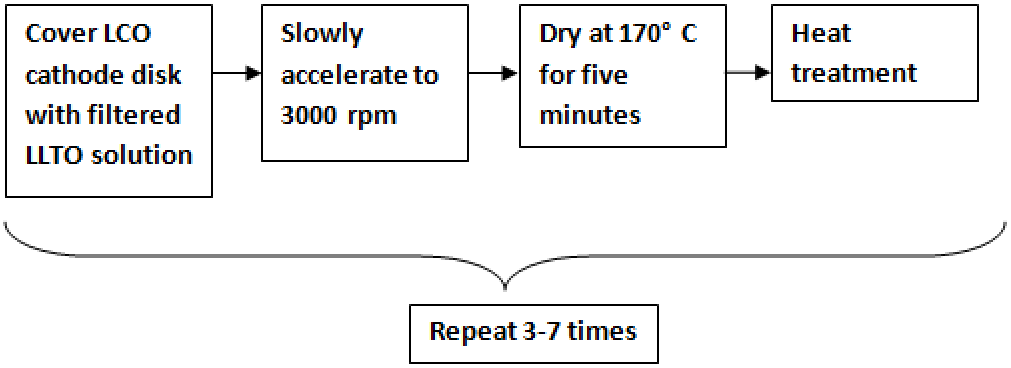


Figure 16 Filtered LLTO deposition prior to spinning

The results were satisfying and that procedure was employed throughout the project. The thickness and uniformity will be discussed in the next section.

3.4. Heat Treatment of LCO-LLTO Cathode-Electrolyte Disks

To fully form the Lithium Lanthanum Titanium Oxide solid electrolyte film, heat treatment was required to evaporate all organic components. In addition, the film had to be annealed to achieve the LLTO amorphous structure for a good ionic conductivity. The parameters that could be changed for heat treatment were temperature, time spent annealing, and heating and cooling rate. Considerations about the heat treatment process involved too high temperature, too long exposure, too quick heating rate.

Lithium Lanthanum Titanium Oxide would react with Lithium Cobalt Oxide at temperature higher than 700° C. Thus, the temperature of annealing was set to 600° C. Too long exposure to that temperature could have resulted in the formation of cracks in the film. Such cracks could result in battery short-circuit. Too fast heating rate could also cause the film to shrink very quickly and, thus, result in cracks. These variables were changed until a film without cracks formed.

After the disk was dried, it was put in a ceramic plate and was put in a furnace. In the first experiment the temperature was set to 600° C; the time for the sample to stay at that temperature was set to two hours and the heating rate was set to 9° C per minute. The results showed the formation of large cracks, which depth reached the LCO disk. It was hypothesized that the cracks were due to the long exposure time.

The time was decreased to just thirty minutes with the temperature and the heating rate at the same values. Again, large cracks were observed at the end of the overall solid electrolyte film procedure. Although it was recognized that some of the cracks were due to substrate's surface pores, the large number of them indicated that at least some were formed due to severe stress from heat treatment. This lack of integrity of the film could result in short-circuiting of the battery. The lithium metal anode would grow and form dendrites, penetrating within the cracks and reacting with the $LiCoO_2$ cathode, rendering the battery useless.

Another heat treatment procedure involved heating the disk to 350° C for 30 minutes at 5° C per minute heating rate. Each time the disk was spin coated and dried it was heat treated at that set-up. After the last heat treatment at 350° C the disk was cooled and then placed in the furnace to anneal at 600° C for 30 minutes with heating rate of 5° C per minute. The results were satisfying as the number of cracks had decreased significantly and were observed only where the LCO substrate had pores.

Simultaneously with the upper method, heat treatment that kept the temperature at 600° C after each spinning and the time at 30 minutes, but used different heating rate - 5° C, was used. This procedure also provided good results. Eventually, the method of heat treating the disk at 350° C first and then at 600° C was used. Table 4 presents each heat treatment and its effectiveness.

Table 5 Different heat treatment techniques

Procedure	Temperature	Time	Heating rate
1	600° C	2 hours	9° C / minute
2	600° C	30 minutes	9° C / minute
3	350° C after each spin-coating, 600° C final annealing	30 minutes for both temperatures	5° C / minute for each temperature
4	600° C	30 minutes	5° C / minute

3.5. Eliminating Pores from LCO Cathode Disk Surface

The importance of the smooth surface of the LCO disk was implied in the previous sections. As mentioned before, SEM scans revealed small pores and holes on the Lithium Cobalt Oxide cathode disk surface. These pores affected the spin-coating and heat treatment of LLTO sol processes and resulted in the formation of holes and cracks within the solid electrolyte film. This meant that the battery would short-circuit if the lithium metal anode penetrated within them.

3.5.1. Lithium Cobalt Oxide Sol-Gel Reaction Preparation

Sol-gel reaction could also be used to produce thin film $LiCoO_2$. It is used in the fabrication of micro-batteries. It was decided to employ such a method in an attempt to produce a smooth cathode surface acceptable for spin-coating.

$Co(CH_3COO).4H_2O$ was dissolved in Acetic Acid and stirred for 20 minutes. Then, in an argon hood $Li(OC_3H_7)$[i] was dissolved in Acetic Acid and was stirred until all solid particles were dissolved. The first solution was then added to the second solution drop-wise with 1 drop per 5 seconds, while stirring, until completely mixed. The resulting solution was then left to stir for 12 hours to avoid precipitation and had a dark purple color. The goal was to deposit this LCO sol on the cathode surface in order to penetrate and fill the surface pores. Therefore, the viscosity needed to be low and no PVP was added. Table 4 presents the amounts of chemicals used for this reaction.

Table 6 Compositions of solution A and B for LCO sol

Chemical	**Amount**
Solution A	
$Co(CH_3COO).4H_2O$	0.6225 g
Acetic Acid	4.503 g
Solution B	
$Li(OC_3H_7)^i$	0.165 g
Acetic Acid	1.501 g

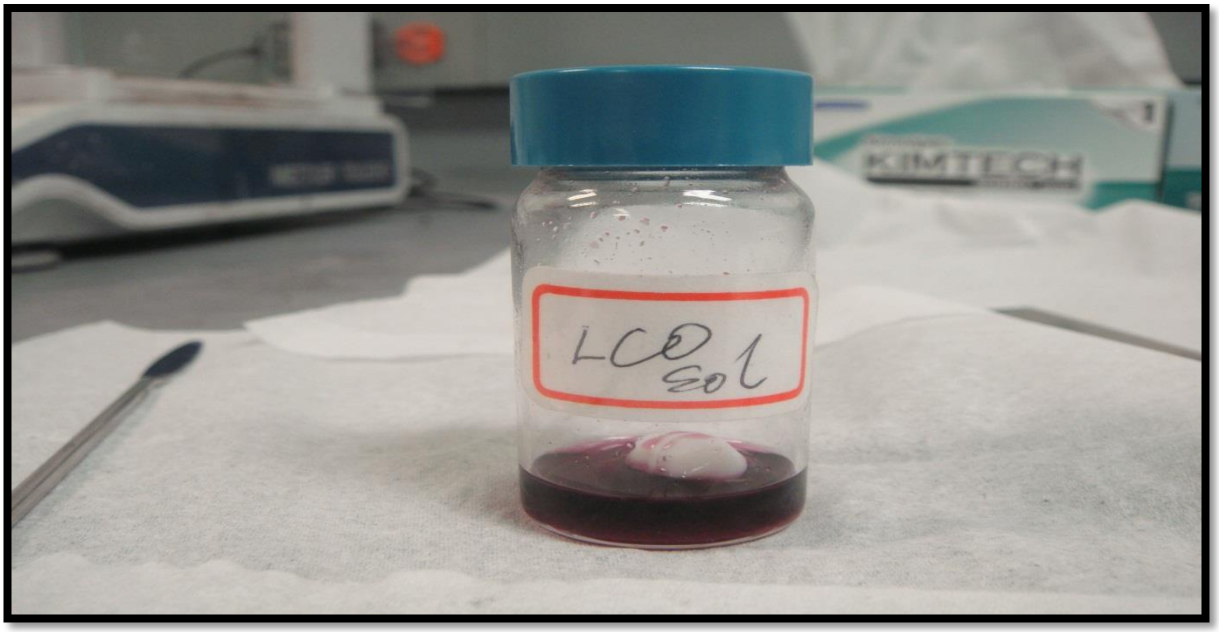


Figure 17 Lithium Cobalt Oxide Sol Solution

3.5.2. Evaporative Deposition of Lithium Cobalt Oxide Sol to Fill Surface Pores

The LCO cathode disk was placed on a glass dish. It was covered with LCO sol and was left in a fume hood. After approximately 20 hours the liquid content of the solution had evaporated and the disk had a solid purple cover. It was removed from the dish and was heat treated. The heat treatment involved annealing at 600° C for 30 minutes. After retrieving the disks from the furnace a dark black powder was observed on the surface of the cathode. This was $LiCoO_2$ formed during the reaction. The surface of the disk was then polished with a fine sand paper (2400 grit). SEM scan was taken to analyze the effectiveness of this method. The results showed that the pore had been filled effectively and only one evaporative procedure was necessary. The figure below shows disks covered with LCO sol prior to heat treatment.

After polishing, the disk was covered with LLTO sol enhanced with PVP binder using the spin-coating method as described in the previous sections.

Figure 18 Evaporative LCO sol deposition (right), spin-coating deposition (left)

3.5.3. Spin-Coating Cathode Disks with LCO Sol to Fill Surface Pores

Another procedure for pore removal involved spin coating. The aim was to deposit $LiCoO_2$ sol on the surface of the cathode disk, allow some tome for solution to penetrate pores, and spin-coat to remove excess LCO sol and provide a smooth surface.

LCO sol was deposited, left for 5 minutes before spin-coating, spun at 3000 rpm and then dried at 170° C. After this the same heat treatment followed – at 600° C for 30 minutes at 5° C heating rate. After the heat treatment similar result was observed. Black powder has formed on the surface of the disk. The disk was carefully polished with 2400 grit polishing paper. This process was not very effective in covering the pores. Therefore, several spin-coating procedures were needed to provide a smooth surface.

3.5.4. Evaporation of Low Concentration LLTO Sol to Fill Surface Pores

As described before low concentration LLTO sol without PVP was prepared. The lack of PVP decreased the viscosity of the solution and allowed it to penetrated surface pores.

A cathode disk was boiled in ethanol for 30 minutes. It was then dried and put in 0.02M water solution of Dodecylbenzenesulfonic acid sodium salt. This measure was done to improve the wettability of the disk for $LiLaTiO_3$.

Immediately after removal from the water solution, the cathode disk was put in a glass dish and was covered with the LLTO sol solution. It was then put in a fume hood to allow for evaporation. After 15 hours the disk was removed. The timing of the disk removal was crucial. If the disk was left for too long, the whole LLTO solution would have evaporated and the disk would get trapped under the solid residue. This made it almost impossible to remove the disk and retain its integrity. The perfect moment for removing the disk was when there was a solid layer of LLTO on its upper surface, but the solution had not evaporated under it. This allowed removing the disk from the dish using razor blade, without affecting the disk or the LLTO layer. The figure below shows a disk covered with LLTO prior to heat treatment.

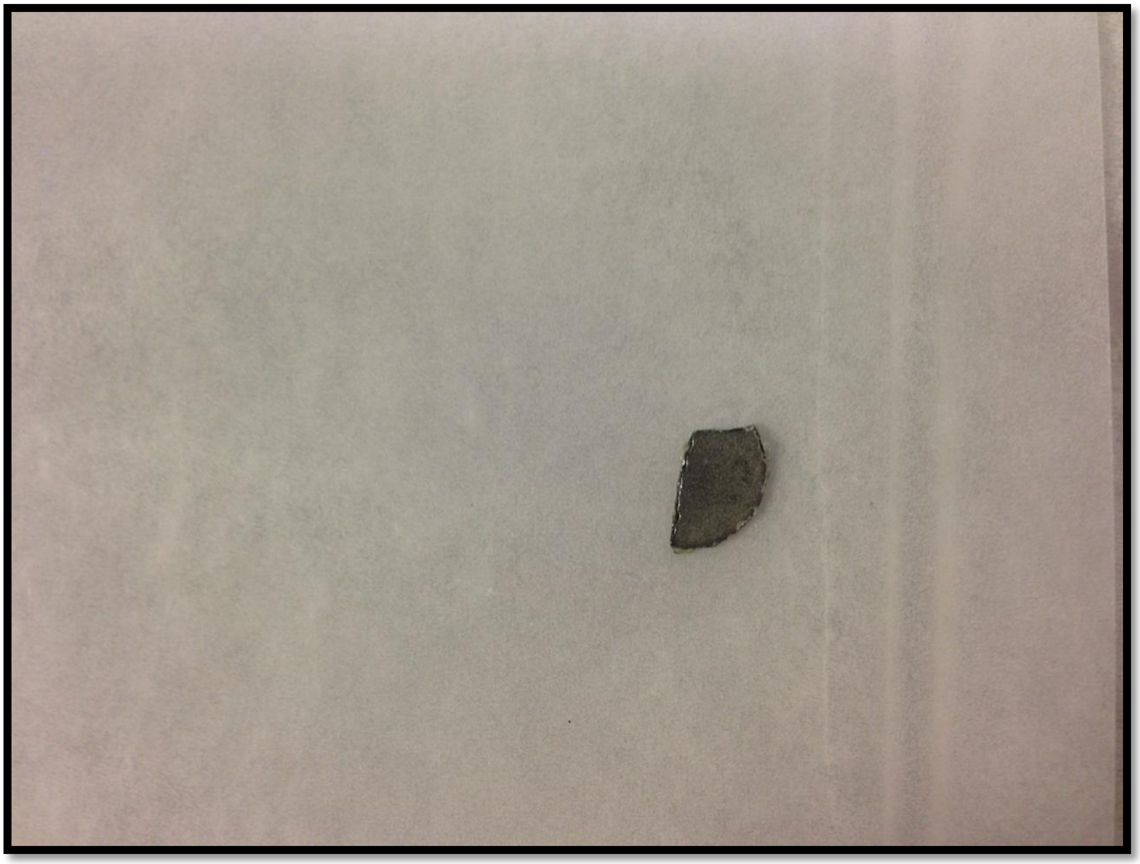


Figure 19 Cathode disk after LLTO sol evaporation

After the disk was recovered from the dish, it was heat treated using the following procedure: first, 350° C for 30 minutes with 5° C per minute heating rate, then cooled to room temperature; second, heat to 600° C for 30 minutes with 5° C per minute heating rate, then cool to room temperature. After heat treatment a thick film of LLTO was formed, approximately 100 micrometers. To remove the excess of LLTO the disk surface was polished with 2000 grit paper. The results were satisfying and only one evaporation procedure was needed to fill the pores.

After the pores were covered with this method it was spin-coated using the methodology already described.

3.5.5. Spin-Coating Low Concentration LLTO Sol on an Already Covered LCO Cathode Disk

The last effort to remove surface pores and cracks from the film was to spin coat a disk that was already covered with LLTO sol with PVP binder. This time, however, the disk was covered with the low concentration LLTO sol on top of the already formed LLTO film.

The spin-coating procedure was the same as described before. The disk was attached to the spin-coater, covered with LLTO sol, accelerated to 3000 rpm and kept rotating for 20 seconds, and then dried at 170° C before heat treated. The heat treatment was the same – first at 350° C for 30 minutes with 5° C per minute heating rate and cooled to room temperature, then heated to 600° C for 30 minutes with 5° C per minute heating rate.

The results were not very promising and several spin coating procedures were necessary. The advantage was that no additional polishing was necessary.

A final process was formulated from the methods described above. Three sample disks were prepared using the three methodologies for pore filling. The figure below presents the process for preparing each sample.

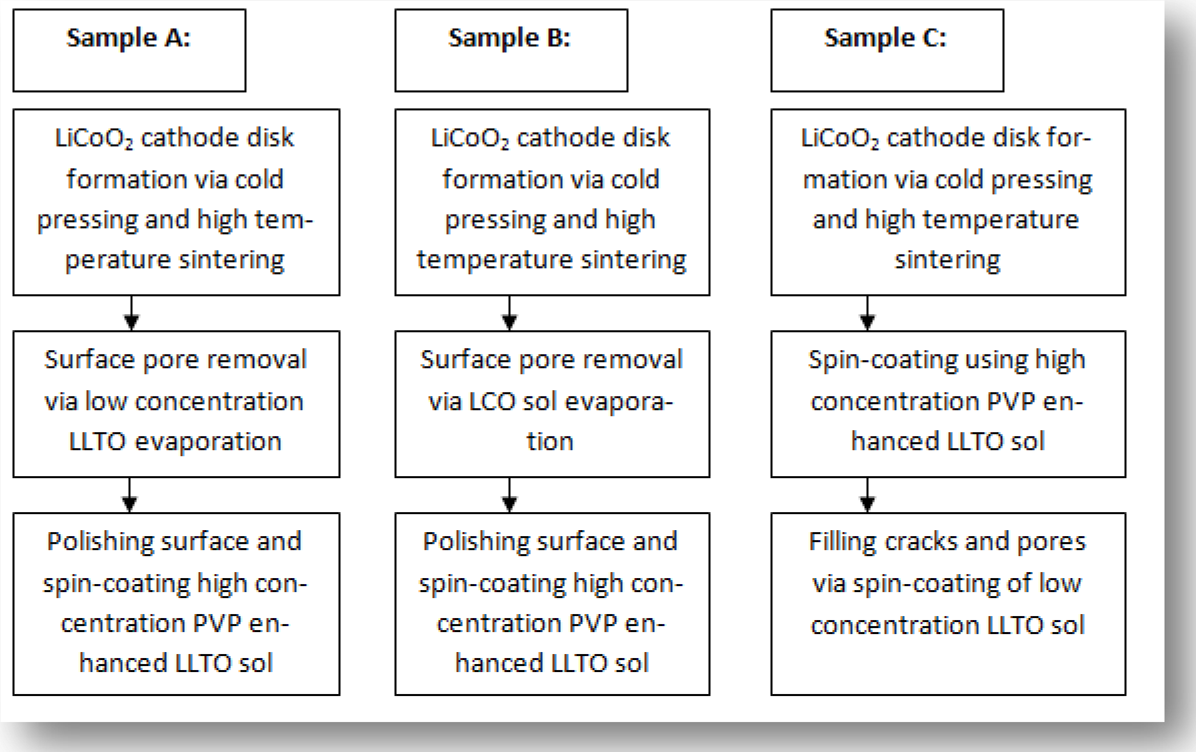


Figure 20 Final Procedures for all-solid-state cathode-electrolyte system preparation

3.6. Battery Assembly and Testing

The last stage of fabricating an all-solid-state lithium ion battery was the actual assembling and testing the battery. First, the battery was assembled and then the samples were set for electrochemical testing using VMP3 Electrochemical Tester. Two types of batteries were tested. One battery used liquid electrolyte and tested the capacity of $LiCoO_2$ high density cathodes. The second type was an all-solid-state battery testing the samples prepared by the methods described above.

3.6.1. Swagelok Cell Assembling

Swagelok cells were used to produce a battery. The cell consisted of three main parts: main body, anode current collector, and cathode current collector. The current collectors were attached to the main body using screws and were isolated from the environment using two isolating rings for each collector. The anode current collector consisted of hollow metal cylinder into which a spring was inserted. A metal plate was attached to the spring. The cathode current collector consisted of just solid metal cylinder.

To assemble a battery first a piece of lithium metal anode was cut from a strip of stock lithium metal. The circular anode was put in the middle of the anode current collector plate. A piece of separator was cut and was placed on top of the lithium anode. Then, the separator and the anode were pressed with the cathode current collector. That way the lithium stuck to the anode current collector. The hollow part of the anode current collector cylinder was filled with liquid electrolyte. The liquid electrolyte used was 1M $LiPF_6$ solution in ethylene carbonate, diethyl carbonate, and dimethyl carbonate with solvent ratio of 1 : 1 : 1. Two pieces of separator were placed on top of the lithium anode and were soaked in liquid electrolyte. The lithium cobalt oxide cathode was placed on top of the separators. Then, holding the battery with the cathode on top to avoid spilling the electrolyte, the screws were slowly rotated until tight grip. All of the above procedure was carried out in an argon hood to avoid moisture reacting with the lithium metal.

When assembling the all-solid-state lithium-ion battery, the hollow cylinder of the anode current collector was not filled with liquid electrolyte. After the lithium metal was placed on the current collector, a drop of liquid electrolyte was spread on it. This was done to decrease the surface resistance of lithium ion transfer between the solid electrolyte and the lithium anode. The solid electrolyte-cathode disk was then placed on the lithium metal anode. The battery was then screwed. The full assembling procedure is presented step-by-step in the appendix.

3.6.2. Electrochemical Testing

After a battery was made it was ready to be electrochemically tested. Each disk was measured prior to testing. Its weight allowed for calculating the current necessary to charge to theoretical density.

First, only LCO cathodes were tested. For educational purposes a cathode disk with thickness of 350 micrometers was tested and was charged with 1C. On theory the higher thickness would impose higher mass transfer resistance and the high charging rate would not allow enough time for lithium transfer. The results supported theoretical expectations.

Then the thickness was decreased to 250 micrometers. At that time, polishing the cathode to desired thickness was still a problem. The battery was charged with rate of C/50 to allow enough time for lithium transfer, considering the thick cathode. Third LCO cathode, this time polished to

100 micrometers (± 10 micrometers), was tested using C/30. The results are presented in the results and discussion section.

The three samples prepared with LLTO solid electrolyte were with thickness of approximately 100 micrometers. They were set to charge at C/20 as working of concept was desired rather than performance. The results were not as desired and the batteries short-circuited. Unfortunately, due to time limitations at the time of writing this project the procedure was not retested. Table 5 presents each sample and its charging rate. The results are presented in the next section.

Table 7 Samples and their charging rate

Sample	Disk Thickness	Charging rate
A (no LLTO film)	350 micrometers	1 C
B (no LLTO film)	250 micrometers	C/50
C (no LLTO film)	100 micrometers	C/30
D (surface pores covered with low concentration LLTO sol evaporation)	100 micrometers	C/20
E (surface pores covered with LCO sol evaporation)	100 micrometers	C/20
F (pores and cracks covered with low concentration LLTO sol spin-coating)	100 micrometers	C/20

The overall methodology for preparing all-solid-state batteries is presented in in the figure below. Sample F had a preparation procedure different from the rest of the samples.

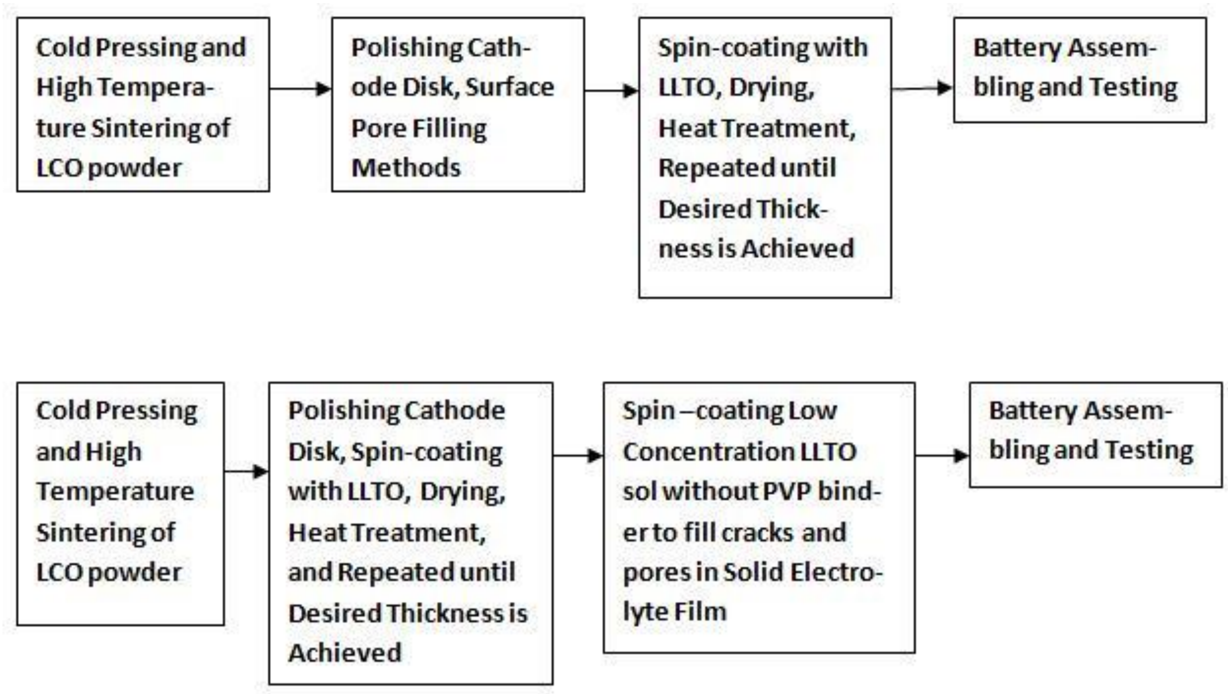


Figure 21 Overall methodology for preparing all-solid-state battery (top), procedure for Sample F (bottom)

4. Results and Discussion

The overall goal of the project was to fabricate an all-solid-state battery and its testing. The success of that goal depended on achieving smaller objective: high density Lithium Cobalt Oxide cathode and Lithium Lanthanum Titanium Oxide electrolyte film development. During the course of the project an additional objective emerged from the experiments. Methods had to be used to remove surface pores from LCO cathode disk, which appeared after sintering and polishing.

Although some experiments were unsuccessful, important knowledge was attained for further research and development of a methodology for low cost all-solid-state lithium ion battery production. This section will discuss the results from each set of experiments, successes and failures of the methods used, and the extent to which the goal was achieved.

4.1. Lithium Cobalt Oxide Disk

Lithium Cobalt Oxide cathode disks were prepared by cold-pressing LCO powder and subsequent high temperature sintering. That procedure was carried out to achieve a high relative density cathode. This meant low internal porosity that would allow for proper lithium ion transfer and storage by reducing internal resistance of the battery. Therefore, a capacity close to the theoretical could be achieved.

The disks sintered at 1200° C did not produce the desired results. The higher temperature and longer exposure cause the disk to shrink and created a lot of internal pores. Although the individual particles had fused together, it was determined that the disk is not appropriate for further experimentation, mainly because the pores would affect the development of the solid electrolyte layer. The relative density measured was less than 73%. The cross sectional view of the disk presented, made by scanning electron microscope (SEM) in the figure below shows the abundance of the pores.

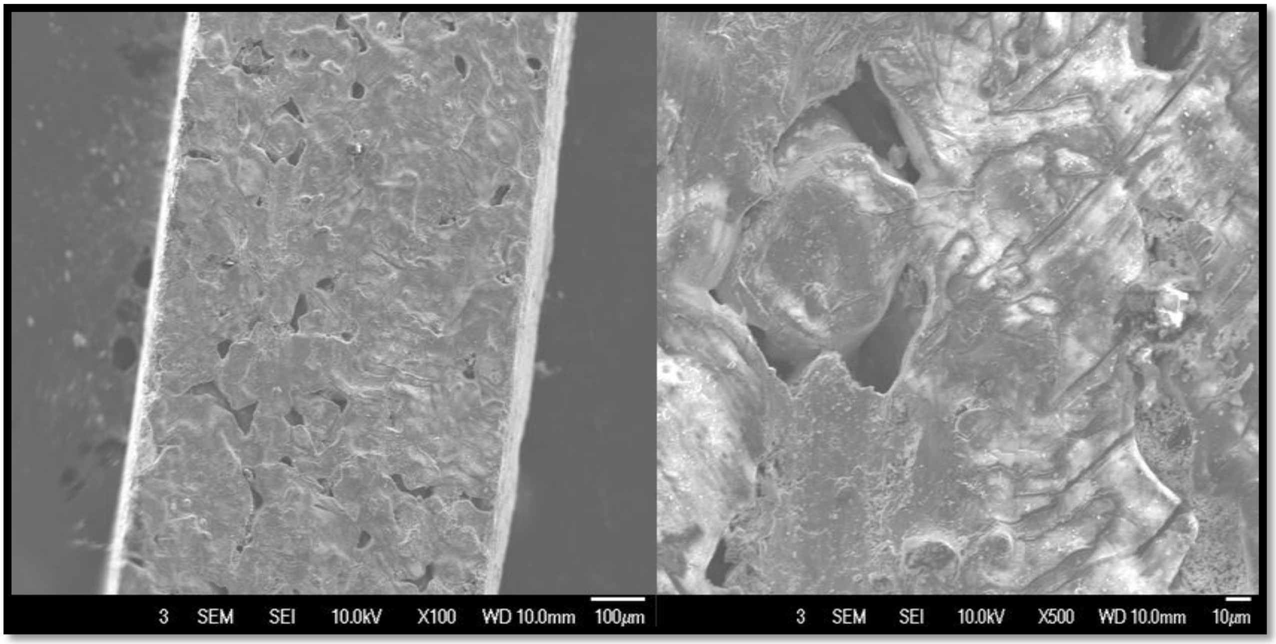


Figure 22 Cross-sectional view of disk sintered at 1200 C

The reasons for the large number of pores were not investigated. Instead, the temperature was changed to 1100° C. The disks sintered at that temperature showed considerable improvement of the density. No internal pores were observed. The relative density had increased significantly to the value of 96% of the density of $LiCoO_2$. The figure below shows a cross sectional view of the disk sintered at 1100° C.

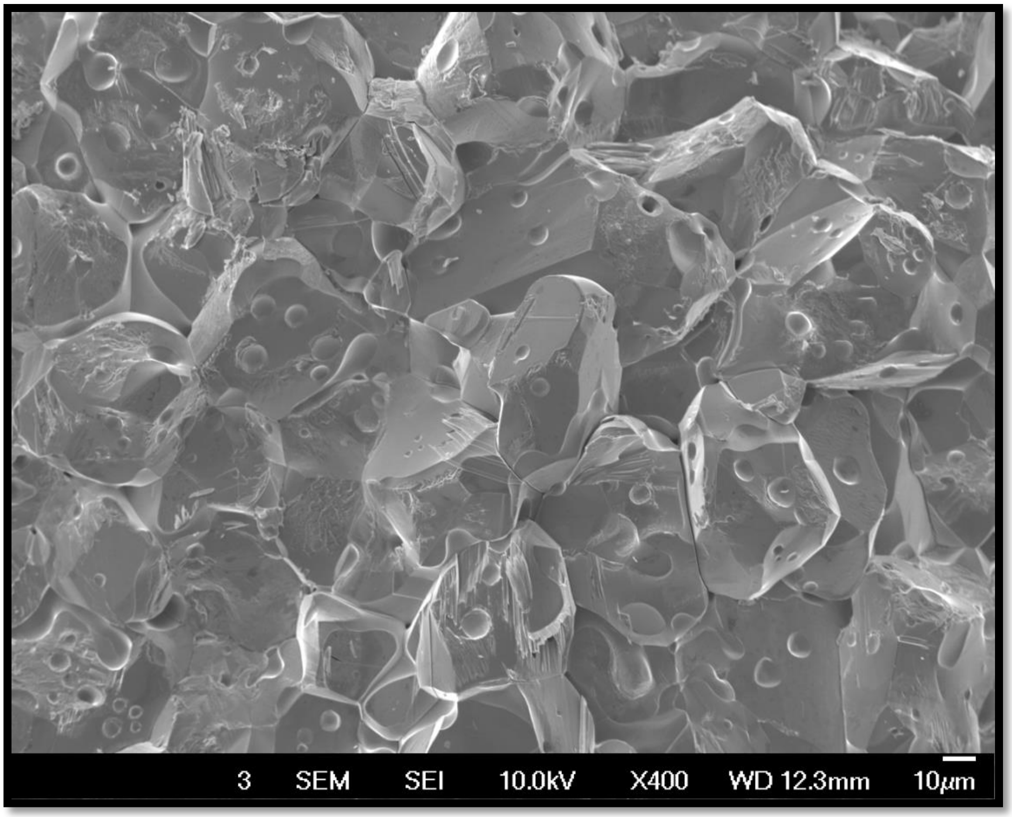


Figure 23 Cross-sectional view of cathode sintered at 1100 C

Despite the 96% measured density it was hypothesized that it was actually a little lower due to formation of closed internal pores, which could not be detected on the SEM scans or during the density measurements.

During polishing, the disk would become very brittle and it was extremely difficult to achieve the desired thickness of 100 micrometers. Attempts were made to improve disks strength by sintering at 1150° C for 15 and 24 hours. The results proved fruitless as the density decreased without an increase of disk strength. To achieve desired thickness the polishing procedure was improved.

The polishing of the disk was carried out until the disk was thin and its surface smooth enough. The surface was polished until the disk reflected light. However, during SEM scans, taken after spin-coating with LLTO sol, pores and holes appeared on the surface. It was hypothesized that these had appeared during the polishing process. The disk was polished consecutively with finer polishing paper. Grits of 600, 800, 1200, and 2000 were used. The surface was scanned and is compared in the figure below.

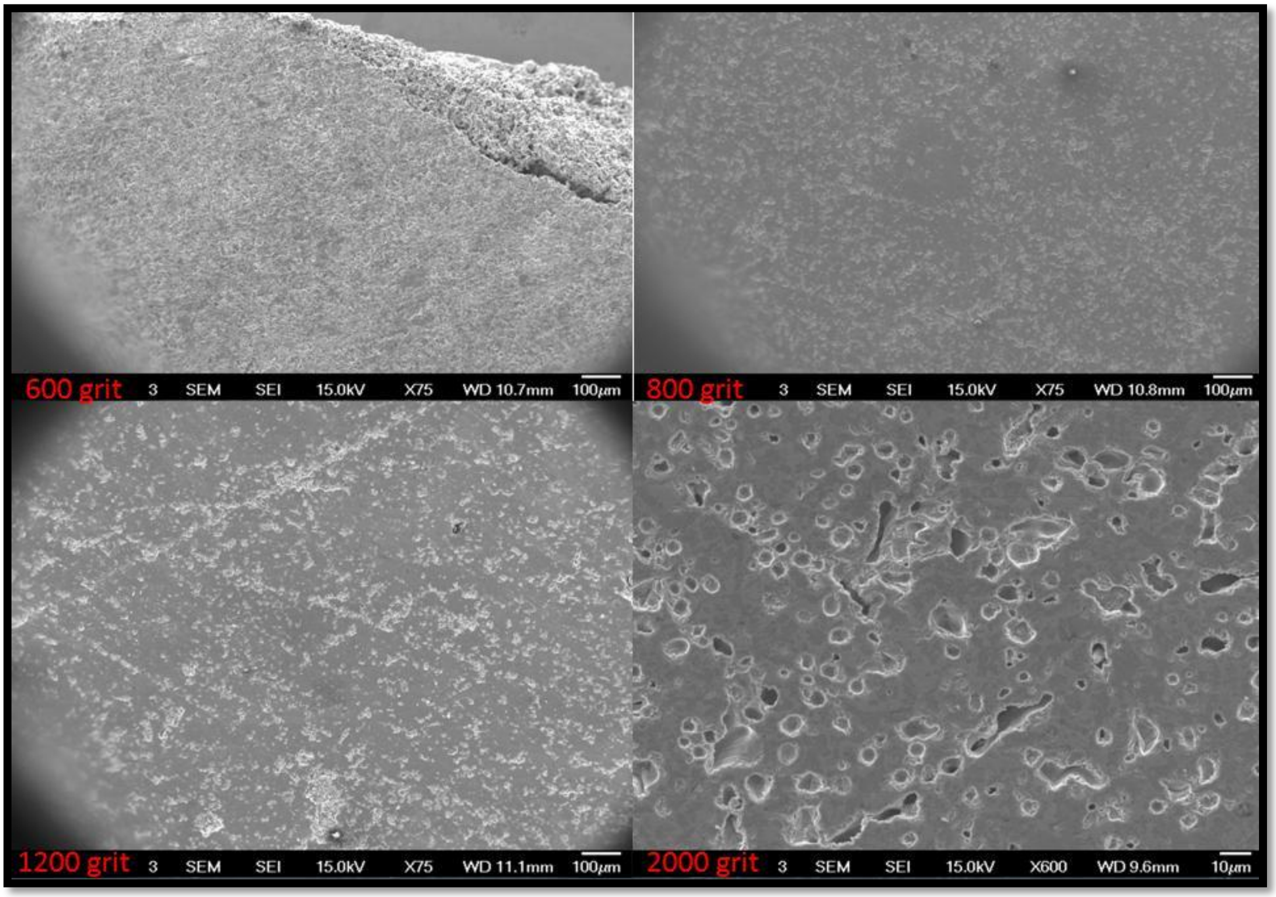


Figure 24 Surface scans of disks polished with different polishing paper

Finer polishing methods did not remove surface pores. Initially, the pores could not be recognized on the surface of disks polished with 600 grit paper. They appeared as the polishing got finer. It was hypothesized that these were a result of uncovering internal pores. It was important to achieve a smooth surface in order to allow for proper development of smooth and uniform LLTO film during spin coating.

4.2. LLTO Solid Electrolyte Thin Film Development

The spin-coating procedure was carried out once the disks were prepared. Assuming that the disk was smooth and that the speed of rotation was high enough, the centrifugal force would spread the solution evenly in the radial direction. After heat-treating the resulted solid-electrolyte layer should have been ready for battery assembly. The objective was to achieve smooth film with 1 micrometer of thickness. This section presents the results after the spin-coating and the subsequent heat treatment.

4.2.1. Deposition of LLTO Sol Solution While Spin-Coating and Heat Treatment at 600° C

Depositing LLTO sol solution, while spinning, did not provide good coverage of the cathode disk. As mentioned in the Methodology section, large amount of the solution was propelled outwards and flying off the disk. The subsequent heat-treatment was provided too severe stress for the thin film and caused it to shrink and crack. The figure below shows an SEM scan of the LLTO film developed by this method.

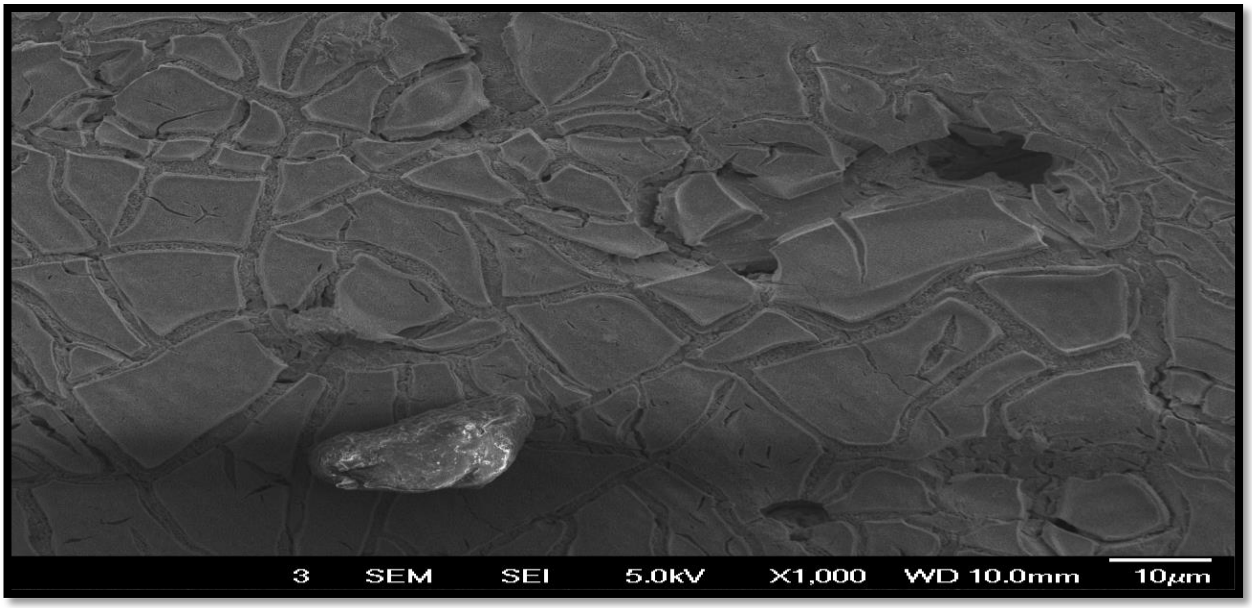


Figure 25 LLTO Layer developed by deposition of LLTO sol during spinning (5 spinning iterations)

Larger particles of LLTO were observed on the SEM scans. This called for the use of filters during LLTO sol deposition. Also, the severe heat treatment had to be changed by decreasing the time of annealing.

4.2.2. Deposition of LLTO Sol Prior To Spin-Coating and Heat-Treatment at 600° C for 2 hours

In this procedure the solution was deposited prior to spin coating, to avoid loss of material. This change appeared to improve the film development. The film cracks had decreased in size (from 5 micrometers wide to 1-3 micrometers wide) and the five iterations provided a thin film almost exactly 1 micrometer.

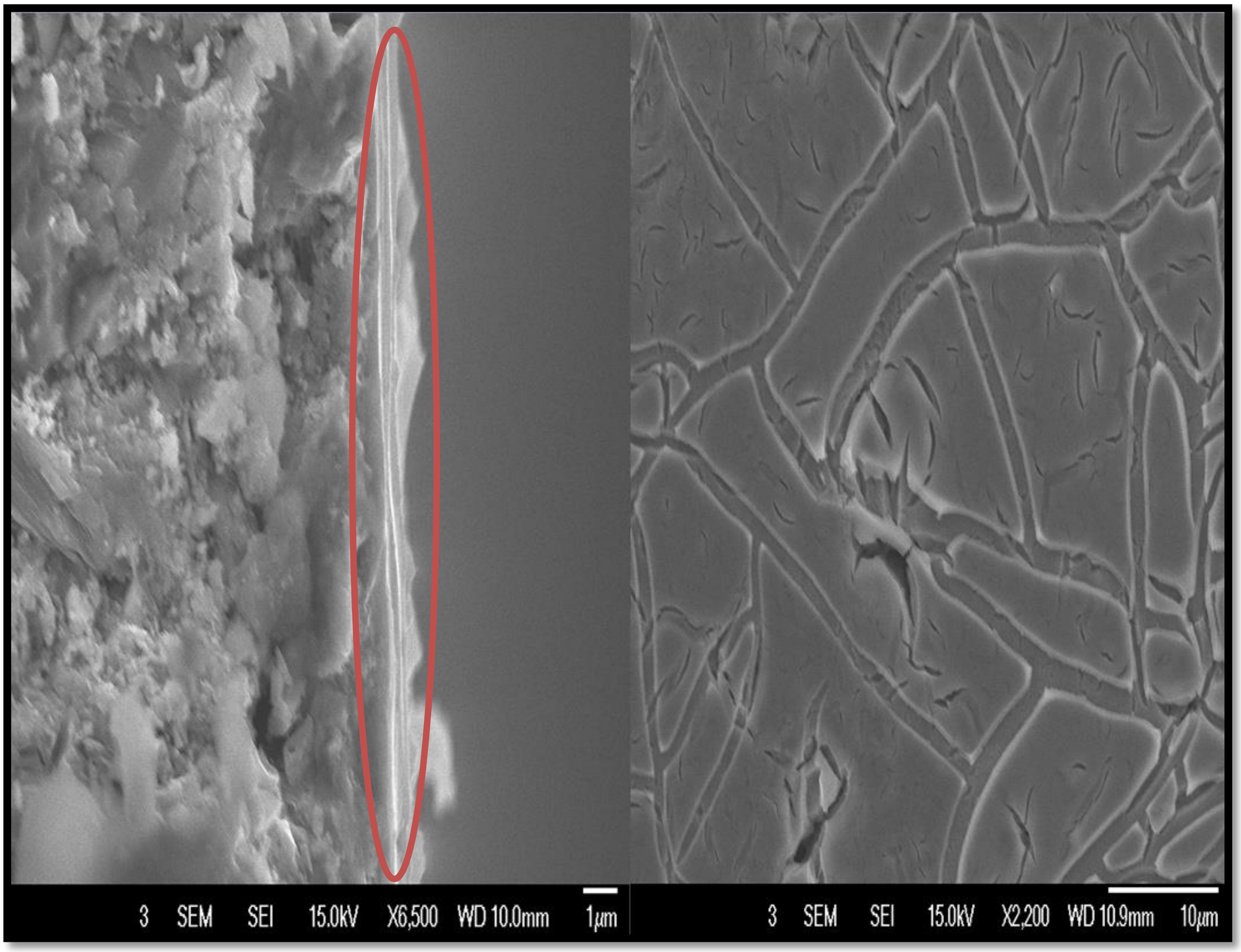


Figure 26 Film thickness and surface after 5 spinning iterations and heat treatments

The desired thickness was achieved (the pale grey strip on left picture), but the problem of cracks remained unsolved. It was determined that the lithium metal can grow within these valleys, by forming dendrites, and short-circuiting the battery after long operation. Different heat-treatment procedures were tried, as described in the Methodology section.

4.2.3. Different Heat Treatments

As described in the methodology, three heat treatment procedures were carried out. The first one consisted of annealing the LLTO film at 600° C for 30 minutes. The decrease of annealing time was expected to decrease the stress caused by the contraction during heat treatment. An SEM scan of the LLTO film resulting from this procedure is presented in the figure below.

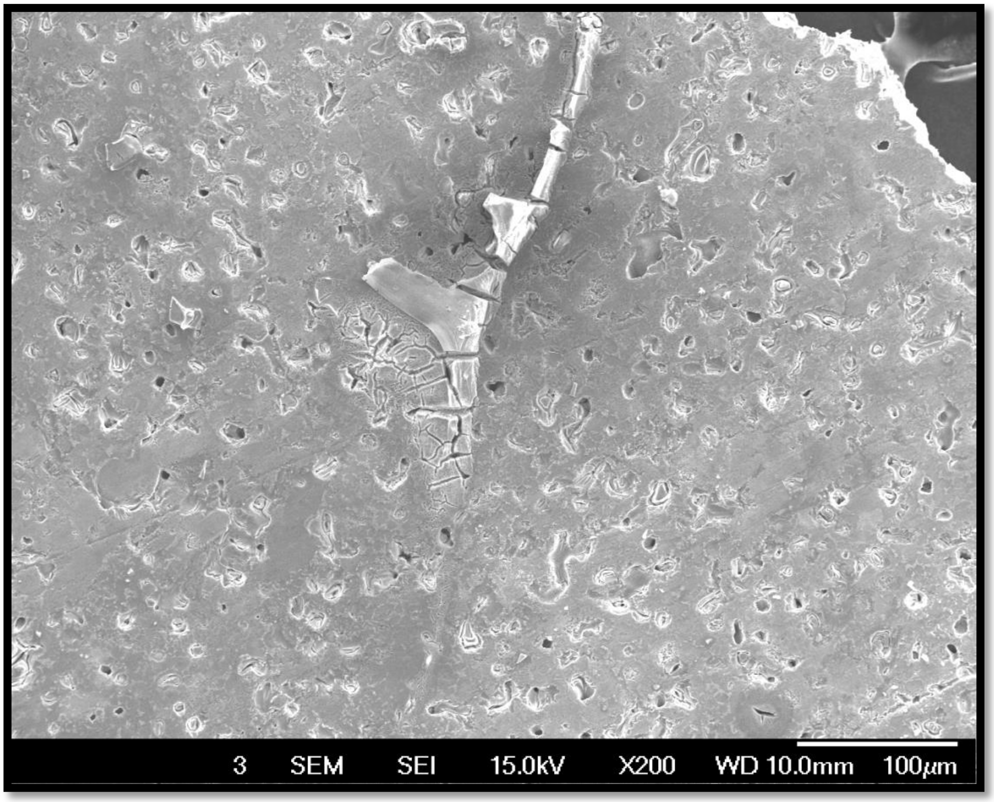


Figure 27 LLTO film surface after 600 C for 30 minutes heat-treatment

The resulted film exhibited almost no cracks. However, at that point of time the presence of surface pores was realized. The LLTO film was too viscous to penetrate the pores during spin-coating. Possibly, the pores contained air trapped under the LLTO film that expanded during heat-treatment, rupturing the LLTO film. In addition, due to the lack of substrate under these particular areas the LLTO film shrank during heat treatment exposing the pores. The results from the methods used to eliminate surface pores will be presented later.

4.2.4. Heat Treatment at 350° C after Each Spinning Iteration and Final Annealing at 600° C

The heat treatment was further improved. In this procedure the film was annealed at 350° C for 30 minutes with 5° C per minute heating rate after each spin-coating procedure. A final annealing was done at 600° C for 30 minutes with 5° C per minute heating rate. This procedure cause less heat stress on the LLTO film. It was observed that were significantly lower in number and width and that they were forming predominantly around the surface pores. The figure that is following presents the surface SEM scan of the LLTO film.

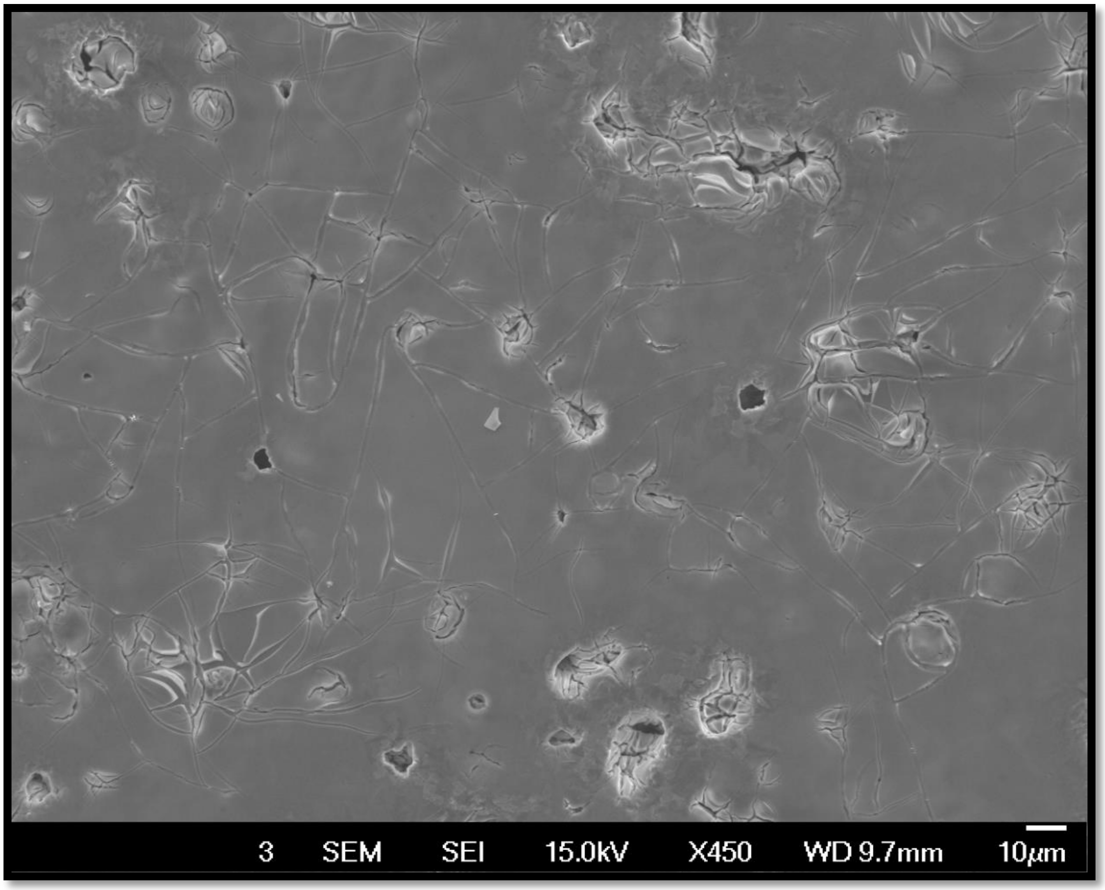


Figure 28 LLTO film after heat-treatment at 350 and 600 C (surface view)

4.2.5. Heat Treatment at 600° C for 30 Minutes with 5° C per Minute Heating Rate

This procedure had similar results to the previous heat-treatment. Since the presence of pores could not be eliminated by changing the heat treatment, and because of the usefulness of the previous procedure, this procedure was abandoned.

After altering the heat-treatment settings, the LLTO film improved significantly. The pores in the LLTO film were investigated and it was concluded that their bottom reached the lithium cobalt oxide cathode and that they were wide enough for the lithium anode to grow in them and short-circuit the battery. Therefore, they had to be removed in order to produce a uniform thin film of solid electrolyte.

4.3. Eliminating Surface Pores

The development of the cathode disks with this high relative density was partially successful. The appearance of surface pores was considered a drawback that had to be overcome. As described in the Methodology section four different procedures were experimented.

The process of filling surface pores to achieve smooth disk surface was carried out after spin-coating results were obtained. The time limitations did not allow for extensive SEM scanning and the surface after each procedure was checked with an optical microscope. After filling the pores, the resulted disks were spin-coated with high concentration of LLTO sol enhanced with PVP binder. The resulted films were also observed with an optical microscope.

4.3.1. Low Concentration LLTO Sol Evaporation

Removing pores with evaporation of low concentration of LLTO sol without PVP binder proved very successful. As described before, the sol was evaporated and the disk was heat treated. The disk was then polished to remove excess LLTO. In the figure below the LLTO is visible as a white layer on the cathode disk.

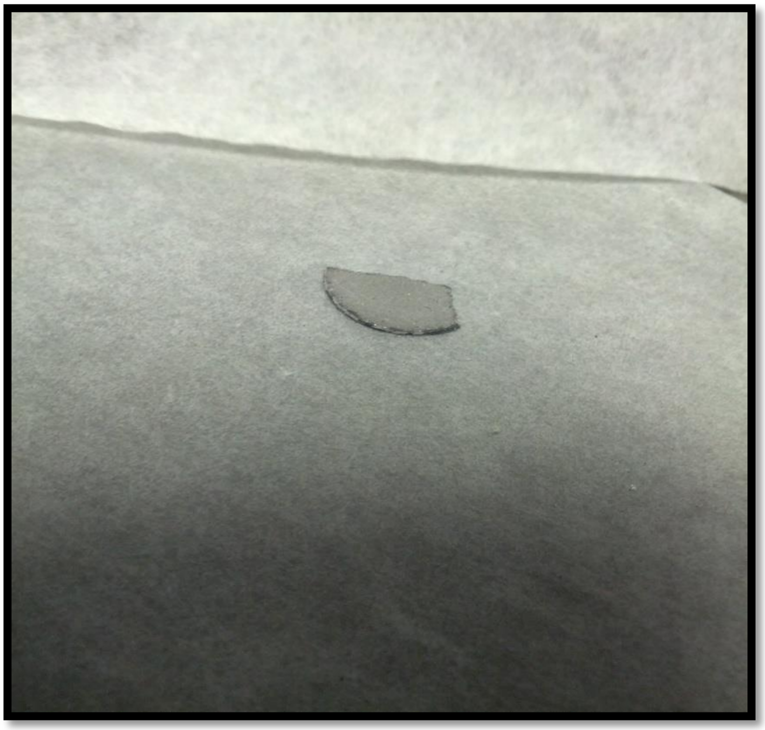


Figure 29 LLTO sol evaporation disk after heat treatment

The SEM scans in the figure below of the surface after polishing with 2000 grit paper, did not reveal any pores. The light grey shapes were hypothesized to be the areas where the pores were. It was thought that the procedure could be repeated once more, to make sure that these areas are also smooth enough. However, it was determined that they do not represent concern for short-circuiting since they were already filled with LLTO, and the disk was ready to be spin-coated with LLTO sol enhanced with PVP binder.

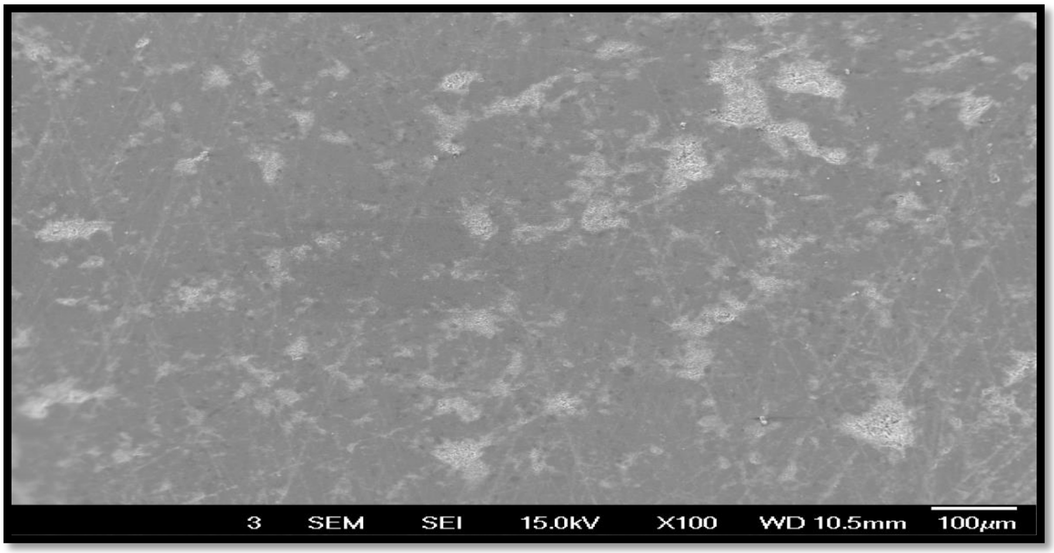


Figure 30 Disk's surface after LLTO evaporation

The spin-coating procedure was repeated five times and the surface was checked with an optical microscope. Observations did not reveal any pores on the LLTO solid electrolyte film.

4.3.2. Evaporation of LCO Sol

As described in the Methodology section, this procedure involved evaporation of LCO sol covered disk. After the solution had evaporated the disk was treated and then polished.

The results of this method are presented in the figure below. The procedure of LCO evaporation also showed great results. Small lithium cobalt oxide particles were visible on the surface, which could be removed with very fine polishing. The pores were successfully filled and, after fine polishing, the surface was smooth. The disk was then spin-coated with LLTO sol enhanced with PVP.

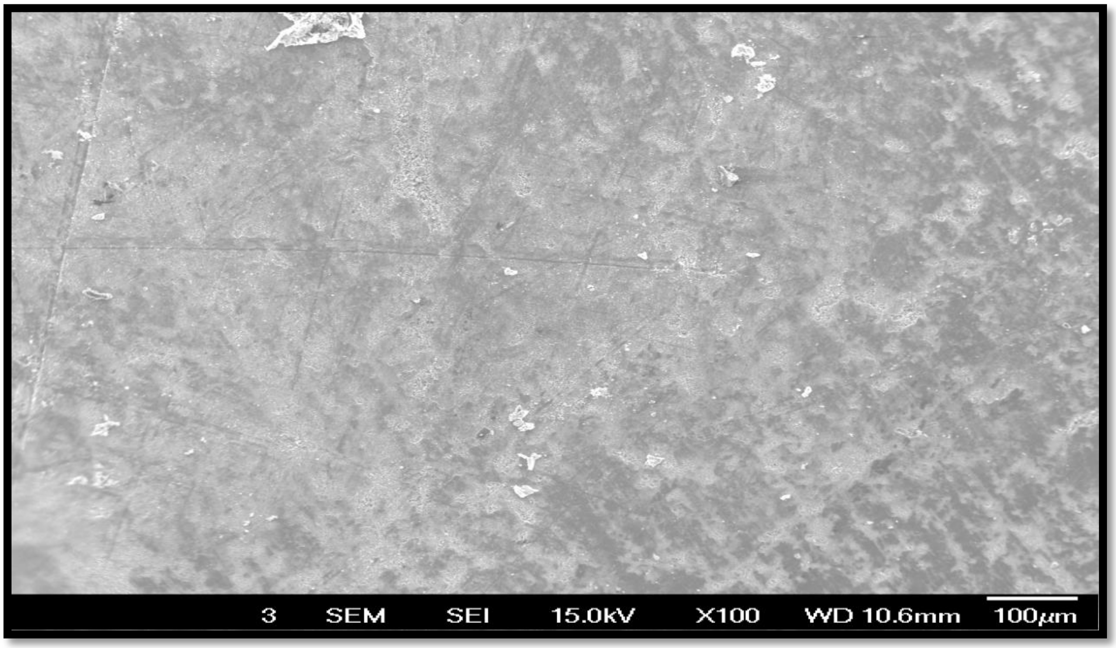


Figure 31 Disk surface after LCO sol evaporation

After spin-coating the LLTO film was observed with optical microscope and was determined to be acceptable for all-solid-state battery fabrication.

4.3.3. Spin-Coating Low Concentration LLTO Sol on a Disk Already Covered with LLTO Layer

This procedure involved an attempt to fill pores and cracks not in the LCO cathode disk, but in the LLTO film that resulted from spin-coating high concentration LLTO enhanced with PVP binder. Low concentration LLTO sol was spin-coated on top.

The results were checked with optical microscope. The pores appeared to be filled, but minor cracks were observed in the film. Nevertheless, it was assumed that these cracks would not result in short-circuit, since there was another LLTO layer beneath them. Despite the fact that this procedure was not as effective as the first two procedures, a battery was constructed and was tested.

4.3.4. Spin-Coating LCO Sol on LCO Cathode Disk

This attempt to fill surface pores did not prove to be as effective as the other three methods. After five spin-coating iterations and subsequent heat treatments, the LCO disk was checked using optical microscope. The observations revealed that the pores were not covered. In addition, annealing had caused additional crack formation the LCO film that was spin-coated. Because of lack of success that procedure was abandoned.

The pore filling procedures had different efficiency. However, the end result allowed proceeding to spin coating. Each procedure and its effectiveness of creating a smooth surface acceptable for spin-coating is presented in table 8.

Table 8 Effectiveness of different methods used to fill surface pores

Method	Difficulties	Pore Removal Results
LCO sol evaporation	Problems with removing disk from glass dish after evaporation	Highly effective
Low concentration LLTO sol evaporation	Problems with removing disk from glass dish after evaporation	Highly effective
Low concentration LLTO sol spin-coated on LLTO film	None	Effective
LCO sol spin-coating	None	Not effective

4.4. Battery Testing

The main goal of the project, as mentioned before, was to assemble and test a battery. All samples prepared for testing utilized LCO cathode disks sintered at 1100° C for 24 hours. Six different samples were tested in total. Three of them were only $LiCoO_2$ cathodes and utilized liquid electrolyte. The other three were samples that had thin film of $LiLaTiO_3$ solid electrolyte.

4.4.1. Lithium Cobalt Oxide Cathode Electrochemical Testing

The first cathode was polished to 350 micrometers. At the time of the testing this was the optimal thickness that resulted after the polishing process. It was tested using 1 C charging and discharging rates. The battery was charged to 4.2 volts. Figure 26 shows the voltage as a function of time for this sample.

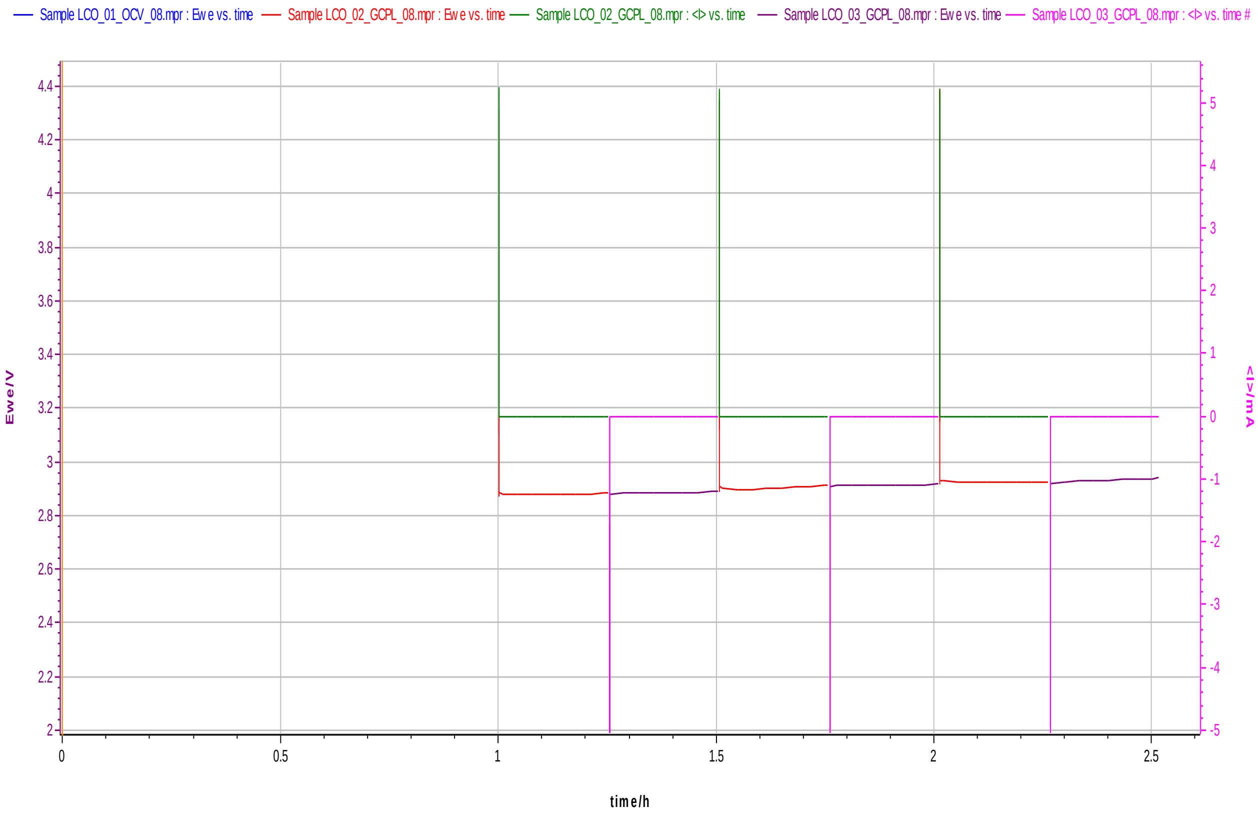


Figure 32 Voltage as a function of time graph for 350 micrometers thick sample

The test of this sample was purely educational. It was expected that because of the quick charging and discharging rate and the thick cathode the lithium ions would not have transferred from the cathode to the anode. As the graph shows, there is almost no capacity.

Another sample tested was polished to 250 micrometers and was charged with C/50 charging rate and was charged to 4.2 volts. This sample charged and discharged for approximately 16 hours. The total capacity was 37 mAh/g (32% of the theoretical capacity). Despite lower charging rate, the thickness was still too high to achieve higher capacity.

The last LCO cathode tested was polished to 100micrometers (±13 micrometers). The battery was set to C/20 charging rate, but to 4.3 volts. This allowed for higher than theoretical capacity to be obtained, as well as to overcome the resistance due to the thickness of the cathode disk. Figure 27 presents the voltage as a function of time.

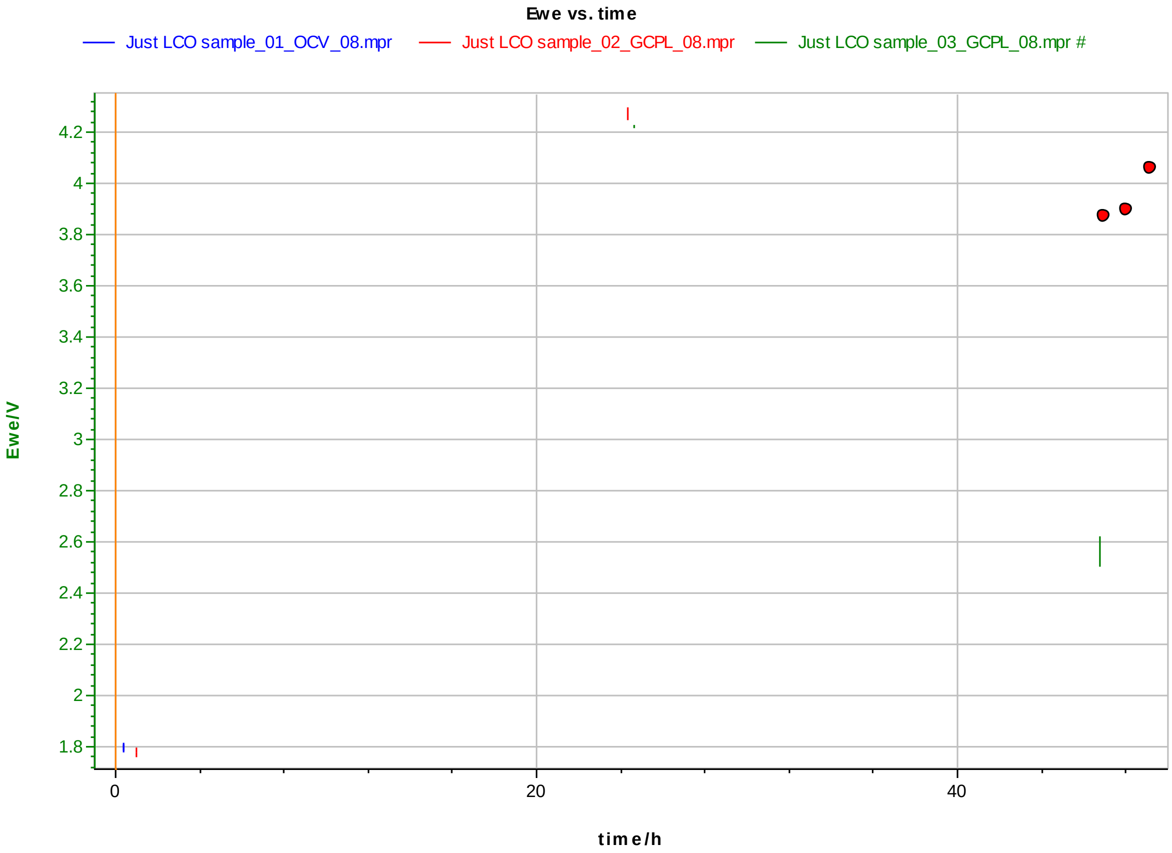


Figure 33 Voltage as a function of time for 100 micrometers thick cathode

Figure 27 shows a good charging and discharging curve. The charging and discharging processes lasted almost 23 hours each. The higher voltage caused the battery to charge more quickly than the 30 hours it was set to. The capacity was calculated to be 151 mAh/g, (10% higher than the theoretical capacity). This was expected as the voltage the battery was charged to

4.3 volts, above the usual charging voltage of 4.2 volts. Due to time limitations, the battery was not cycled multiple times.

Table 9 Results for the electrochemical testing of each LCO cathode

Sample	Thickness (in micrometers)	Charging/Discharging rate	Charging/discharging time (in hours)	Capacity (mAh/g)
A	350	1 C	1	~ 0
B	250	C/50	16	37
C	100	C/20	23	151

4.4.2. Electrochemical Testing of Samples with Thin Film of LLTO Solid Electrolyte

Three samples that had solid electrolyte layer were prepared. They differed only in the way the pores on the surface of the cathode were filled. All samples had the same thickness of 100 micrometers.

The first sample utilized low concentration LLTO sol evaporation to cover the pores. The battery was assembled and was connected to the electrochemical tester. Before the open circuit voltage was recorded the battery showed a voltage of 2 V. The settings of the electrochemical testing procedure were set to charging to 4.2 volts with C/20 charging rate. Seconds after the program was run, the battery short-circuited and stayed flat at approximately 0 volts. T

This was considered a partial success. Even though the battery failed, for few seconds it had voltage of 2 V. The battery was disassembled, but the disk disintegrated before it could be recovered for investigation. It was noticed that the anode disk had a footprint of the sample.

The second sample had its surface pores covered with LCO evaporation. After the evaporation, spin-coating was performed. The same procedure of battery assembly and electrochemical testing was employed. The program was set to the same settings of 4.2 volts and C/20 charging rate. This time the battery did not show any voltage. It was flat at 0 volts right after connecting to the electrochemical tester. The same footprint in the lithium metal anode was observed.

The third sample did not fail right away, but did not work properly either. It was a sample that was spin-coated with high concentration LLTO sol enhanced with PVP five times, and the spin-coated with low concentration LLTO sol another five times, to fill pores and cracks in the layer. The battery was set to charge to 4.2 volts and C/20 charging rate. This was the only sample which could experience any charging. Figure 28 shows the voltage as a function of time for this sample.

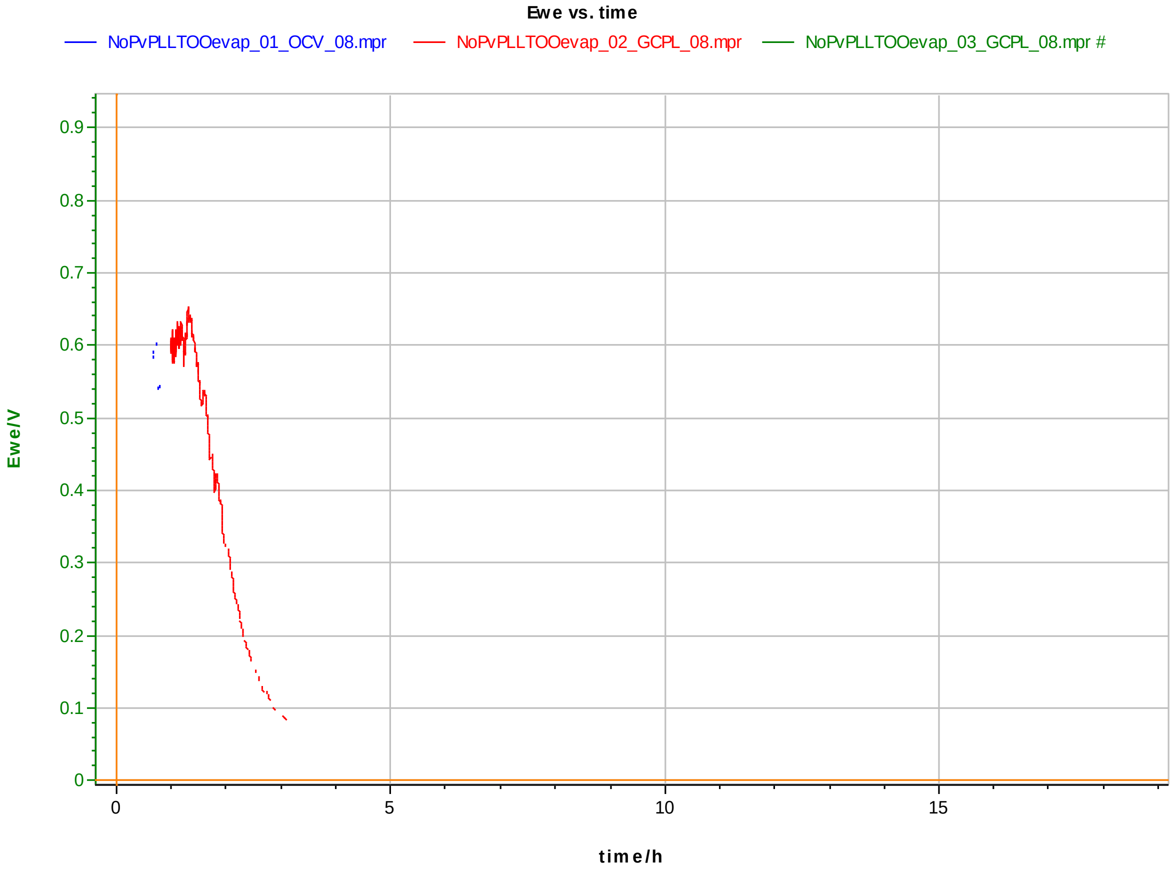


Figure 34 Sample with LLTO film spin coated with two different LLTO sol solutions

The battery did not fail immediately after connecting to the electrochemical tester. The open circuit voltage on figure 28 (the blue line) showed that the battery had a voltage of 0.9 volts that slowly dropped to 0.5 volts. After that the battery started charging. This by itself can be considered a success since the battery showed potential to work. However, after charging for almost an hour the voltage started decreasing rapidly, indicating short-circuit.

When the battery was disassembled, the same phenomenon was observed as with the other batteries. The lithium metal anode had a footprint on it resembling the LCO/LLTO disk.

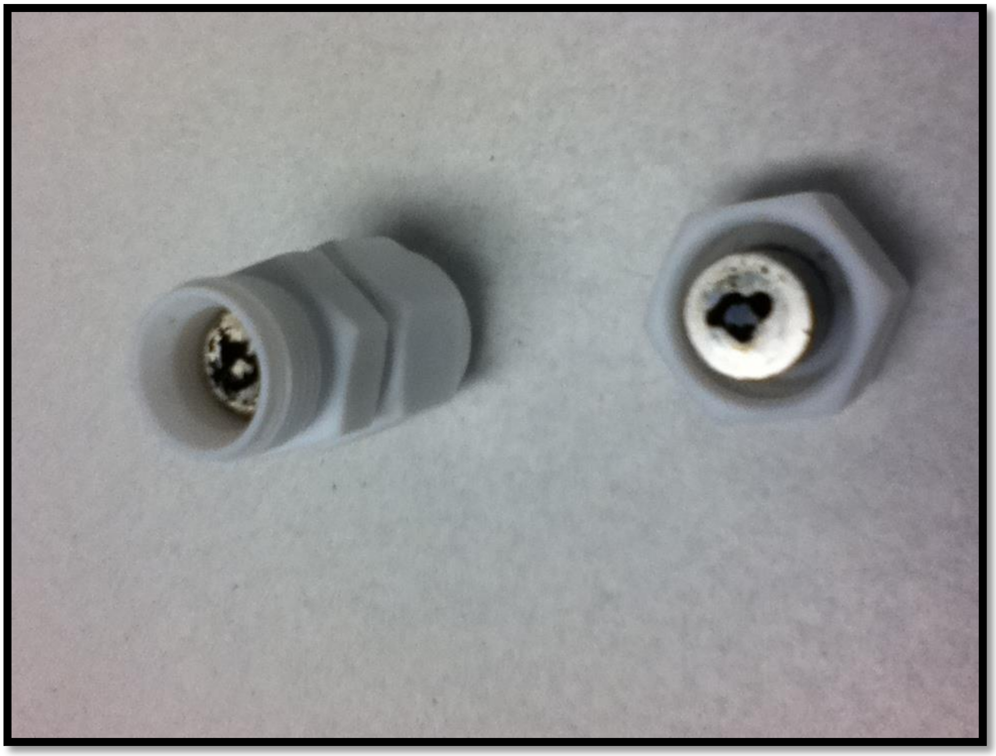


Figure 35 Disassembled battery after electrochemical testing

On the figure above it can be observed that the sample had not shorted out in the middle. This meant that the reason is not in the LLTO solid electrolyte thin film, rising hopes to potential future success of the process. The reason for the battery to fail was determined to be in the force the cathode is pressed against the anode. Lithium metal is soft and the solid electrolyte film is only 1 micrometer thick. When pressed the lithium metal has “engulfed” the cathode/electrolyte disk, going around the LLTO solid electrolyte layer and reacting with the lithium cobalt oxide cathode.

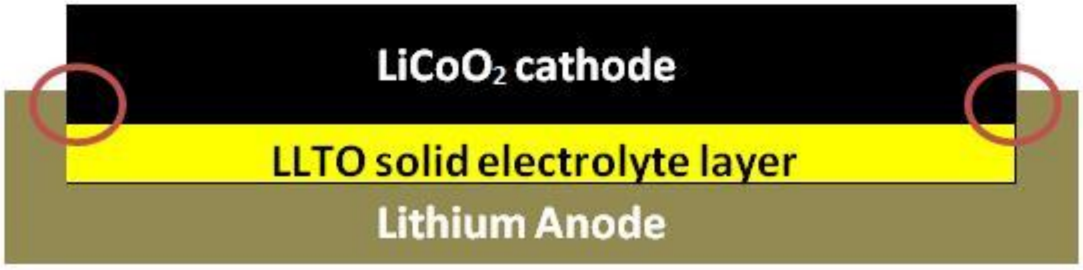


Figure 36 LCO/LLTO system sinking in lithium metal anode

The figure above visually represents the contact between the anode and the cathode. The red circles represent the points where short-circuit occurred.

5. Conclusion

The overall goal of this project was to establish a methodology for fabricating an all-solid-state lithium ion battery. The objectives were to prepare a high-density $LiCoO_2$ cathode, deposit a thin film of $LiLaTiO_3$ solid electrolyte, and assemble and test an LCO/LLTO/Lithium battery. The time of 14 weeks allocated for this project and the problems faced with the presence of surface pores on the LCO cathode disk severely limited the development of the methodology. Nevertheless, the results can be considered a partial success for achieving the goal.

High temperature sintering of $LiCoO_2$ powder proved to be a good method for developing a high-density cathode. This method and the powder, initially developed by a previous research group, resulted in a LCO cathode with 96% relative density. During the polishing process, surface pores were discovered. It was hypothesized that during polishing closed internal pores were uncovered, but this was not proven.

The experiments that were carried out to fill the pores on the cathode disk surface were quite effective. Evaporation of LCO sol and LLTO sol produced a smooth cathode disk surface. It is worth noticing that if there is a methodology that can produce a cathode with smooth surface, then these procedures are not needed. Nevertheless, they allowed for spin-coating with high concentration LLTO sol.

The spin-coating and subsequent heat-treatment procedure was very effective in developing a thin-film of LLTO solid electrolyte. A film with thickness of 1 micrometer was produced and, after removing pores from the cathode surface, uniformity was achieved.

The results, however, remain inconclusive due to failure of all of the three all-solid-state batteries assembled with the cathode-solid electrolyte samples. Two of those samples did not short out immediately, showing voltage of 0.9 and 2 V for a small amount of time, and raised hopes that the overall methodology could be effective in fabricating an all-solid-state lithium ion battery using $LiCoO_2$ as the cathode and $LiLaTiO_3$ as the anode.

6. Recommendations for Future Research

The procedure developed in this project appears to be much simpler and cheaper from the methods used for fabricating an all-solid-state battery. However, further research is necessary for its evaluation as a potential commercial process. Here are some recommendations for future studies.

6.1. Preparing High-Density $LiCoO_2$ Cathode Using Hot-Press

The cold-pressing/high temperature sintering of LCO powder provided good results for fabricating a cathode. The two steps involved in this procedure meant multiple handling of the disk. This could damage the fragile cathode. To avoid this, and to achieve better results in terms of density, disk strength, and better particle adhesion and fusion, a hot-press can be used. This not only combines two procedures into one and avoids multiple handling of the cathode, but also provides for better particle interaction during the sintering stage. In addition, it was hypothesized that using hot press can eliminate the formation of surface pores.

6.2. Polishing LCO Cathode Disks

It is easier to know which side of the cathode disk has been covered with LLTO solid electrolyte if the two sides are different. If the one cannot distinguish which side is covered, assembling and testing of the battery might not work. We recommend polishing one side to a smooth, light-reflecting surface before polishing to the desired thickness. Then polish the other side with rough polishing paper until the desired thickness is achieved. There will be an obvious difference that can serve for recognizing the covered side. Also, if the disk is polished to the desired thickness and then to the desired smoothness, there is a high risk of the disk disintegrating. Therefore, this can be avoided with the recommended procedure.

Roughly polished side

Side polished to a reflective surface

Figure 37 Cathode disk sides polished to different smoothness

6.3. Evaporation of Low Concentration LLTO Sol

This procedure was used for filling surface pores. Previous researchers have used it to develop a thin film of the solid electrolyte. This procedure proved to be much simpler and quicker than the spin-coating. It also meant less handling of the disk. However, when performing this procedure it is imperative to monitor the evaporation of the LLTO sol. If all of the solution has evaporated, then removing the cathode disk without damaging it becomes impossible. The amount of time for evaporation depends on the amount of the sol deposited. Ideally, the sol would have evaporated and solidified on the top surface of the disk and would remain gel-like on the bottom surface. This state allows for easier removal of the cathode disk.

6.4. Anode Preparation for Battery Assembly

In this project the all-solid-state batteries failed due to cathode contacting the lithium anode. The lithium anode disk was much wider than the LCO/LLTO disk. Since the lithium metal is soft it allowed for the cathode-solid electrolyte to sink in and short-circuit the battery. A better way to test the battery and avoid short-circuit is to prepare a cathode disk that is wider than the anode. Also, cutting a smaller piece of lithium metal that fits in the interior of the cathode would prevent battery failure. The recommendation is visually presented in the figure below. On the other hand, to avoid the contact between the anode and the cathode, graphite anode could be used.

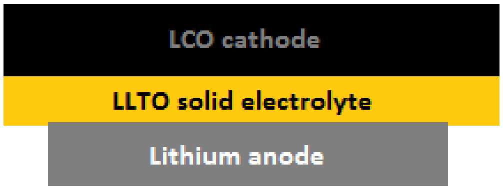


Figure 38 Recommendations for Anode Preparation

6.5. Repeating Methodology for Verification and Validation

Since the methodology developed in this project showed inconclusive results, we recommend its repetition. Repeating the procedures and avoiding or solving the problems that this project faced could show results that either support or reject this methodology. If the batteries assembled and tested work, then further research can improve and develop the process to achieve better performance.

6.6. Cost-Benefit Analysis of the Methodology

The goal of this methodology was to develop a low cost method for fabricating all-solid-state lithium ion batteries. However, cost-benefit analysis was not carried out due to time limitations. We recommend calculating the use of materials for fabricating a single battery, then comparing the cost with the methods that are currently used for fabrication of all-solid-state batteries. Only such analysis can resolve whether this method is suitable for commercialization.

7. Reflections on Major Qualifying Project Experience

The Major Qualifying Project (MQP) is designed for students to apply the knowledge they gained throughout their undergraduate studies in a real life engineering application or problem and is a required for obtaining a degree. It is often completed in the course of one to four seven week terms under the guidance of one or more professors. Quite often it is carried out in parallel with other classes. That being said, MQP is not a typical research project as its time restrictions often do not allow for an exhaustive scientific study.

In addition to the time constraints, very often there were also equipment limitations. In this project the laboratory space was shared with other students. Quite often the equipment was unavailable because it was occupied by somebody else. The equipment was not highly sophisticated and this exactly matched the goal of the project – to develop a low cost production method for all-solid-state lithium ion batteries. The devices used were hydraulic press, high temperature furnace, spin-coater, argon hood glove box, and an electrochemical tester. Last but not the least the research was carried out by two undergraduate students, which meant lack of human capacity for quick progress of the project work.

The above mentioned limitations not only delayed the project work, but also provided the researchers with valuable experience for their future work and careers. One of the most important lessons learnt was that time is a valuable resource and managing it wisely will provide a good foundation for achieving project results. In this particular project too much time was spent on developing the lithium cobalt oxide cathodes. This slowed down the work and severely limited the amount of time left for other experiments.

The main delay was caused by the formation of pores on the cathode surface. Surface pores were discovered after spin coating with LLTO sol and SEM scanning. The team drew the wrong assumptions that with changing the sintering temperature the cathode disk would result in no pores. The continuous effort to develop a high relative density cathode disk did not provide satisfying results. The procedures for filling surface pores came at a late stage of the project. Although successful, not enough time was left for testing the battery. Were they implemented at an earlier point in time, more time could have been spent on battery testing and performance.

The team recognized the need to be more result oriented with the experiments done. Trying to achieve the overall goal proved fruitful as more ideas emerged during the thinking process. Group members also noted that the time allocated for the project did not allow for testing the effect of one variable at a time.

Valuable experience and knowledge was gained through communication with professors and graduate students. The team members learned that effective communication with other researchers can give rise to ideas or sharing of knowledge that can be beneficial for both sides of the contact.

Evaluating the mistakes and the successes of this project, the team made a retrospect as how the project could have been done in a more efficient manner. Summarizing the experience and the lessons learnt from this project – time is the most valuable resources; communication with other people can provide valuable feedback and give rise to ideas that would prove useful in project work; gaining knowledge of the matter involved in the experiments and predicting possible outcomes to allow for further problem solving.

Although those conclusions seem obvious, they were the result of experience that the research group had never faced before in their studies. This valuable experience would serve in the future endeavors and work of each of the research group members.

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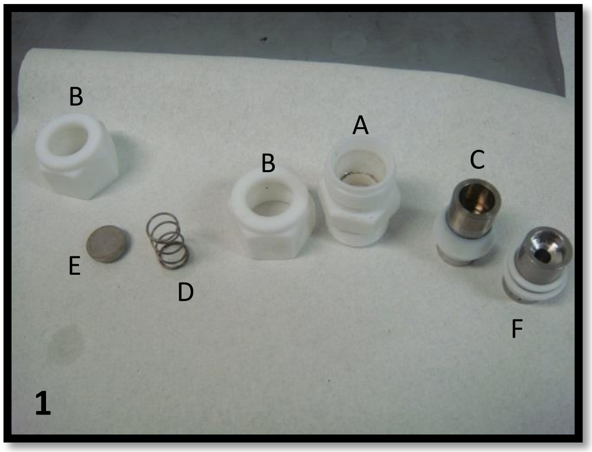
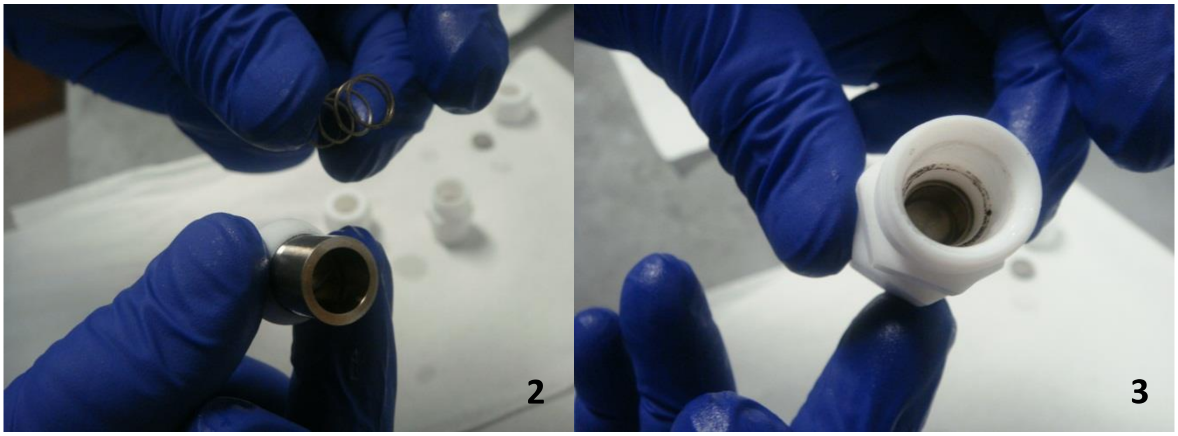
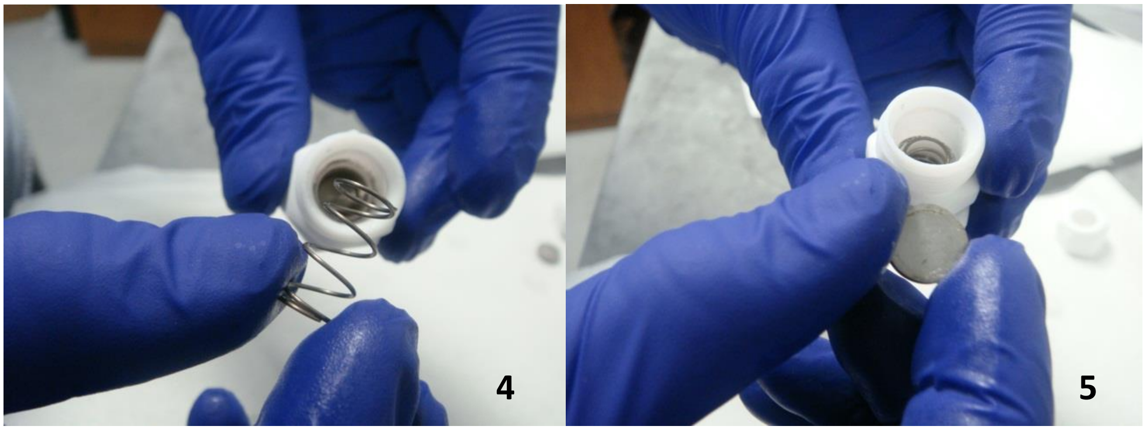
Appendix A: Swagelok Cell Assembling



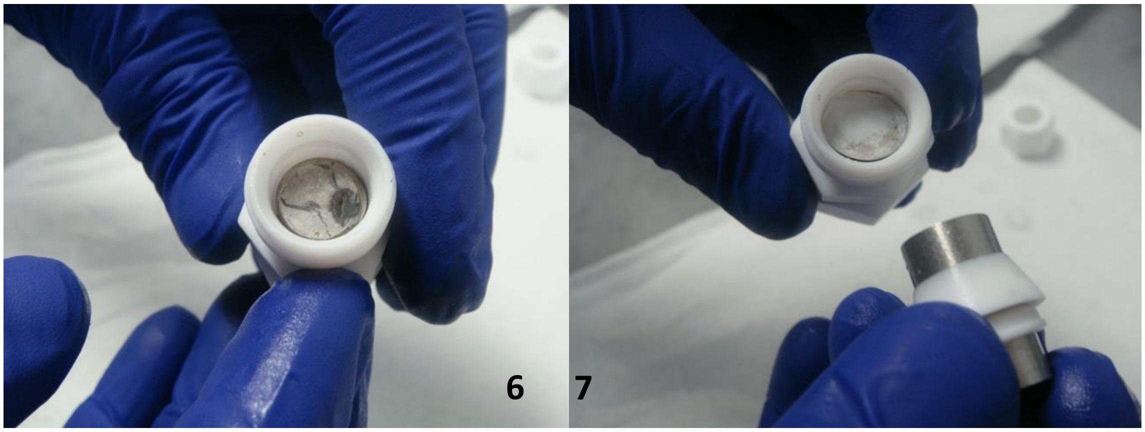
Step 1: Wash battery parts in water, distilled water, and ethanol, and dry for 24 hours; Battery parts: A - main body of the battery; B - screws; C - hollow cylinder for anode current collector; D - spring inserted in the hollow cylinder for anode current collector; E - anode current collector plate; F - cathode current collector.



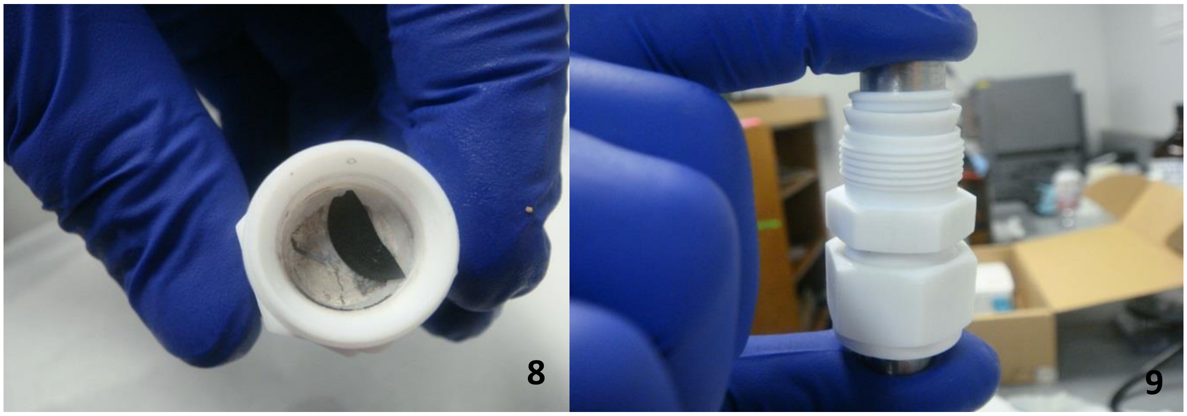
Steps 2 and 3 Insert hollow cylinder in the main body of the battery and attach with one of the screws.



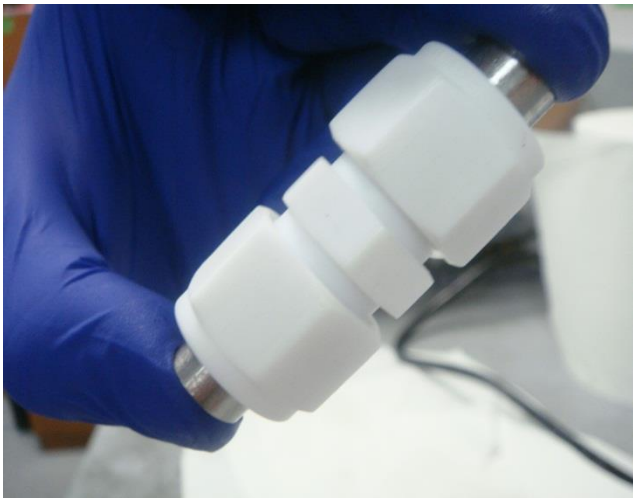
Steps 4 and 5 Insert spring in the hollow cylinder and place anode current collector plate on top



Steps 6 and 7 Place a piece of lithium metal on the anode current collector; Place a plastic separator on the lithium metal and press with the cathode current collector to attach the lithium metal to the plate



Step 8 and 9 Place 2 pieces of plastic separator on the lithium anode and fill the battery with electrolyte and place the LCO sample on the separators (if constructing all-solid-state battery do not use separators; instead put a drop of liquid electrolyte on the lithium metal); press with the cathode current collector



Step 10 Slowly finalize the battery with the last screw. Battery is ready to use

Appendix B: LLTO Sol Solution

LLTO Sol Solution with High Concentrated Polyvinylpyrrolidone (PVP)

Solution A	
Chemical	**Amount**
LiAC (Lithium Acetate Dihydrate)	0.0804 g
La(AC)$_3$ (Lanthanum Acetate Hydrate)	0.4356 g
Acetic Acid	0.6800 g
Propionic Acid	1.6800 g

Solution B	
Chemical	**Amount**
Titanium Isopropoxide	0.69 ml
Acetic Acid	1.30 ml
Isopropyl Alcohol	2.7045 g
PVP (Polyvinylpyrroliodine)	0.3750 g

Low Concentration LLTO Sol Solution without Polyvinylpyrrolidone (PVP)

Solution A	
Chemical	**Amount**
LiAC (Lithium Acetate Dihydrate)	0.0804 g
La(AC)$_3$ (Lanthanum Acetate Hydrate)	0.4356 g
H_2O (Distilled Water)	5.6000 g

Solution B	
Chemical	**Amount**
Titanium Isopropoxide	0.6395 g
Acetic Acid	1.3613 g
Isopropyl Alcohol	2.7045 g

Preparation of LLTO Sol

Solution A

1. Mix measured acetic acid and propionic acid.
2. Mix measured LiAC and $La(AC)_3$ into [1].
3. Stir [2] on the heating pot that is heated to 90-100˚C for 15 minutes.
4. Turn off the heat, then let it stir for another 20 minutes until all the solid chemicals are dissolved.

Solution B

1. In the argon hood, mix measured amount of titanium isopropoxide and acetic acid using a micropipette.
2. Stir [1] for 15 minutes.
3. After 15 minutes, add isopropyl alcohol and PVP into the solution (this will cause the solution to change its color into yellow).
4. Stir [3] for another 20 minutes.

LLTO Sol Solution with High Concentrated PVP

1. Add solution A into solution B, drop by drop, while stirring.

2. Stir [1] for 2 hours.
3. Let the solution sit for a day before use.

Appendix C: Preparation of LCO Sol

Chemical	Amount
Solution A	
$Co(CH_3COO).4H_2O$	0.6225 g
Acetic Acid	4.503 g
Solution B	
$Li(OC_3H_7)^i$	0.165 g
Acetic Acid	1.501 g

Procedure:

1. Prepare Solution A and stir for 20 minutes
2. Prepare Solution B and stir until all solids are dissolved
3. Mix drop by drop (1 drop every 5 seconds) solution A into solution B and stir for 12 hours