# DEVELOPMENT OF 3D PRINTING TECHNIQUES FOR SOLID-STATE LITHIUM BATTERIES

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# Abstract

The goal of this internship was to develop a solid polymer electrolyte with a suitable ionic conductivity and mechanical properties and integrate it with 3D printed cathode for solid state lithium batteries. While liquid electrolytes will have much higher conductivities and therefore higher power densities than solid electrolytes, batteries with such electrolytes suffer from extreme dendritic growth, short-circuiting, and general failure. Typically, batteries prevent this by including a solid yet porous separator somewhere between the anode and cathode to suppress dendritic growth. Solid polymer electrolyte acts as the conductive medium between electrodes as well as the separator that prevents failure from short-circuiting. The specific system explored is a vinyl ethylene carbonate (VEC) and polyethylene glycol diacrylate (PEGDA) mixed polymer solution using both 2,2'-azobis(2-methylpropionitrile) (AIBN) and Irgacure 819, respectively as thermal and photo- initiators. Electrochemical and rheological techniques were used to determine the optimal polymer solution and curing conditions. Through this research, multiple new pathways of exploration have been determined to create a usable solid polymer electrolyte through a combination of varying cure intensities and initiator concentrations.

# Introduction

Solid polymer electrolytes such as poly(ethylene) oxide (PEO) - lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) [1] have been intensively investigated for commercial applications in solid state batteries, although the ionic conductivity is still not satisfying. This project has the final objective of using additive manufacturing to deposit a solid polymer electrolyte on top of a 3D printed $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (referred to as NMC811). A new system is a composite polymer electrolyte used by Wang et al. [2] that involves using hydrophilic silica as a cross-linker and 2,2'-azobis(2-methylpropionitrile) (AIBN) as a thermal initiator in vinyl ethylene carbonate (VEC). Despite showing a high conductivity of $2*10^{-3}$ S/cm at 25°C, we could not synthesize it with our given materials. The electrolyte was still viscous and so it was suggested that a second photosensitive polymer be introduced to aid in the solidification of the polymer, namely polyethylene glycol diacrylate (PEGDA).

My interest in this project comes with increasing my understanding of solid polymer electrolytes for use in energy and power intensive systems such as vehicles, as is the target and main objective of the Department of Energy's Vehicle Technologies Office. Already for my own PhD, I study the design and additive manufacturing of cathode and anode materials, and so the opportunity to study solid polymer electrolytes allows me to obtain a full overview of battery design.

# Research Project

The purpose of this internship is to develop a solid polymer electrolyte that can be used in all solid-state lithium batteries. For lithium and lithium-ion batteries, their conductivity and power density are dependent on the ability of lithium ions to diffuse through the electrolyte medium. With traditional electrolytes, they are composed of lithium salts dissolved in organic

solvents, such as LiTFSI in PEO with conductivity on the order of $10^{-3}$ S/cm [3]. However, the main issue with these electrolytes is that lithium anodes can grow dendrites upon cycling and cause a short-circuit. As such a separator would be needed to prevent dendrites from reaching the cathode and short circuiting the battery. Solid polymer electrolytes combine the function of separators and electrolytes; as a solid, the electrolyte suppresses dendritic growth, yet it is still conductive due to the inclusion of a lithium salt, such as LiTFSI. By developing a solid polymer electrolyte, we would therefore simplify battery construction and increase the safety of lithium batteries for use in higher power and voltage applications.

The initial goal of this project is to create a full lithium battery using a direct-ink write 3D-printed NMC811 cathode and solid polymer electrolyte in order to control the amount of material being used, therefore the first checkpoint is to synthesize a solid polymer electrolyte and test its conductivity in a symmetric stainless-steel configuration, as well as confirm that it has fully solidified. The solidification can qualitatively be tested any number of ways, such as by touch, using a tweezer to poke or deform the electrolyte, etc. Once confirmed a solid, the polymer is then cured into the shape of a dogbone so it can be used for quantitative mechanical testing. Simultaneously, the electrolyte is to perform electrochemical impedance spectroscopy to determine the electrolyte's conductivity. Once the electrolyte has solidified and displays a conductivity of $10^{-3}$-$10^{-5}$ S/cm, it will then be assembled into a cell with a 3D printed or thin film electrode and a lithium metal anode, and more electrochemical characterizations will be performed. During the development of the polymer resin, an NMC811 ink is simultaneously being developed for 3D printing, and also to be used to qualify the performance of newly obtained film casters.

# Electrode Manufacturing

In this project, I first aided in the optimization of electrode thin film and 3D printed lattice manufacturing. This occurred in three parts, 1) establishing a relationship between the newly purchased thin film casters and the final cast films – their actual thickness and mass loading, 2) rheology of NMC811 inks, and 3) improving dimensionality of 3D printed inks.

Three different ink compositions were used – 8% by weight PVDF dissolved in NMP, 10%, and 12.6%, with NMC811 and C65, the latter which has been previously 3D printed. When cast, each of these inks were cast at four different thicknesses and then dried (overnight room temperature drying, and then overnight 80°C vacuum drying). After drying, the mass loading and actual thickness of the film were determined and compared to the theoretical thickness of the cast film. The interesting result is that regardless of the initial ink composition, the final mass loading is directly proportional to the dried film thickness (Figure 1). As a result, the desired mass loading can be directly related to the caster thickness as there is also a one-to-one relationship between the cast thickness and final film thickness (Figure 2).
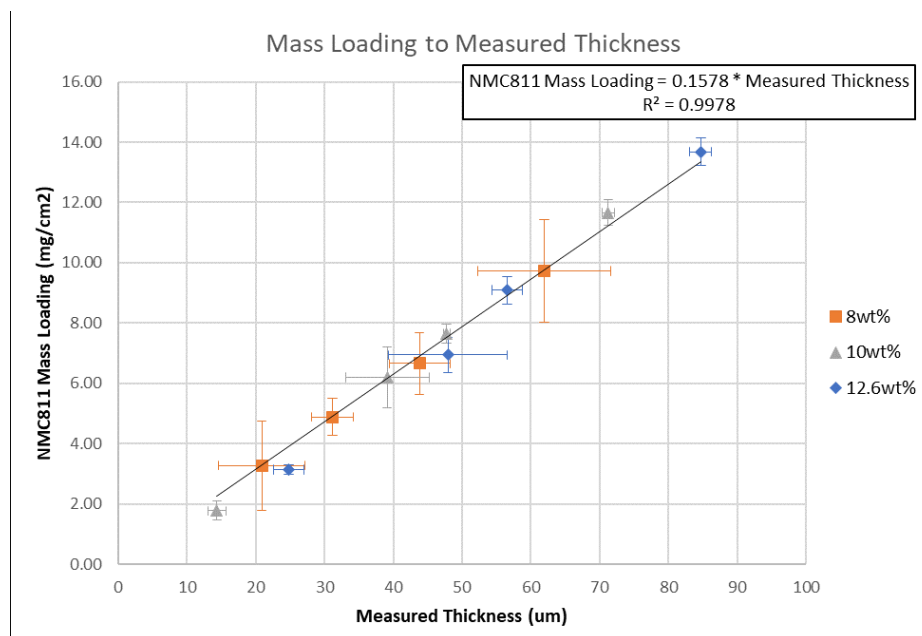
*Figure 1 Mass loading graphed against measured film thickness for each ink composition, error bars for both measurements*
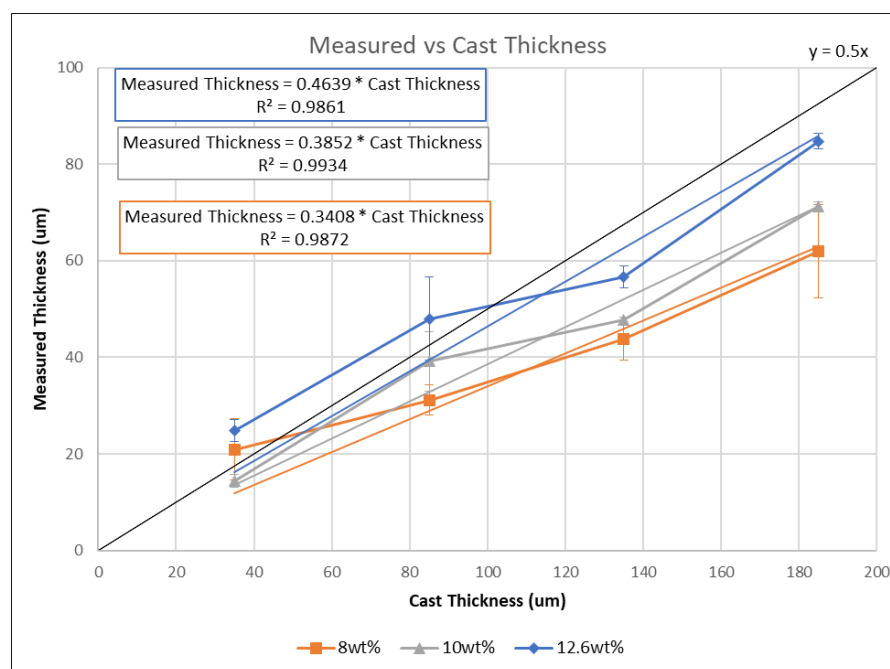
*included.*



*Figure 2 Relationship between the cast film thickness and measured film thickness, with error bars in the measured thickness.*
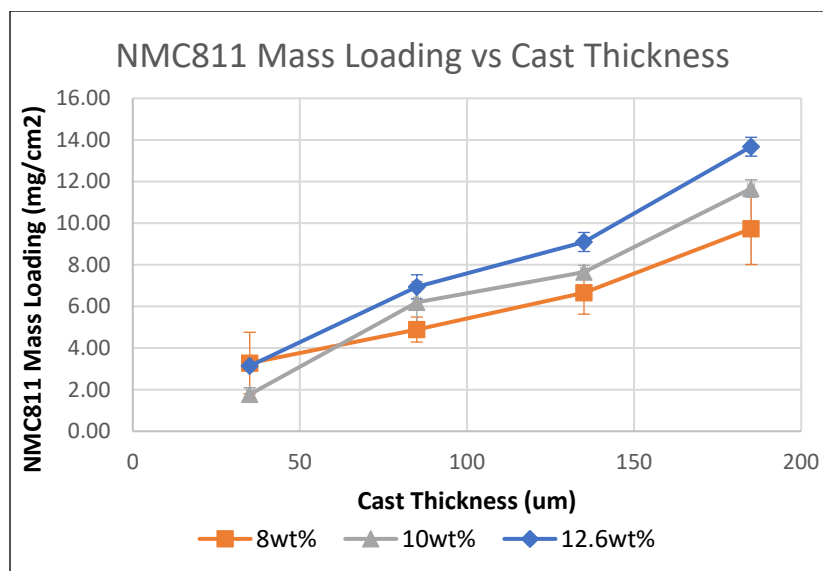
*Figure 3 Relationship between the casting thickness and the mass loading for each of the three inks.*

Rheology experiments were performed on the three aforementioned ink compositions to further characterize them and determine their suitability for 3D printing. The storage and loss moduli were measured along with each inks' viscosity. As expected, the viscosity of the ink decreased with the decreased solid content (Figure 4).
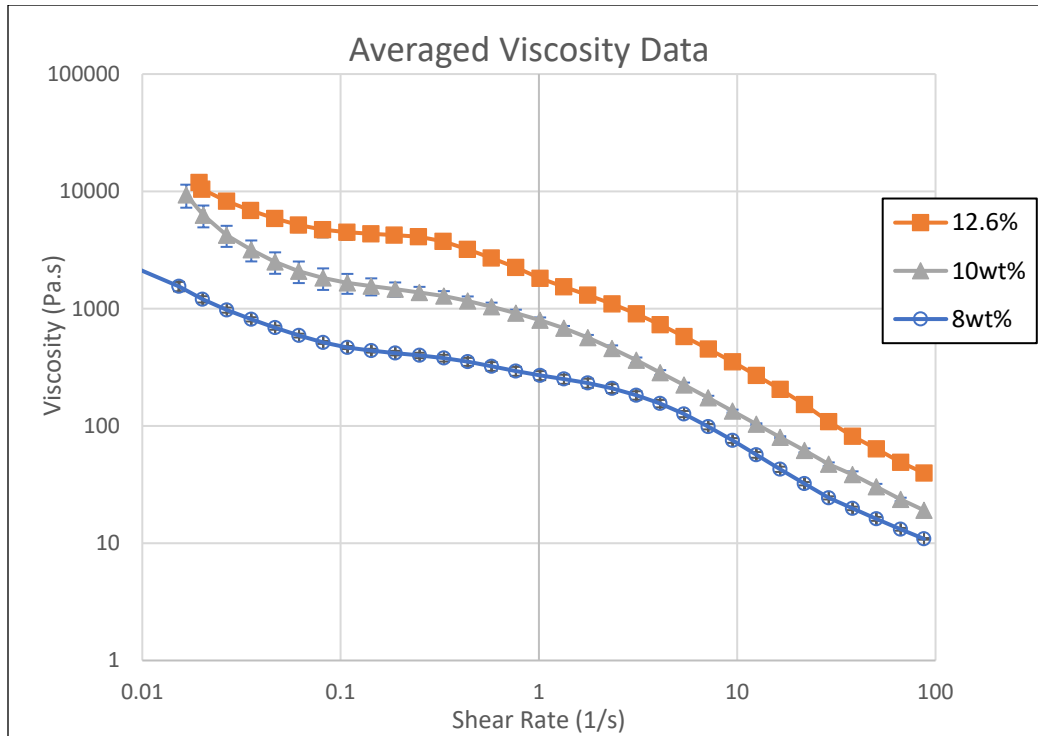
*Figure 4 Viscosity of the three ink formulae, with error bars.*

Looking at their storage and loss moduli, it was found relatively generally that all the inks could be used for 3D printing, as they all display shear-thinning behavior, where the storage modulus crossed under the loss modulus at high shear rates (Figure 5). However, the moduli shows unusual rheological artefacts, so more measurements are required to obtain the viscoelastic properties of each ink more accurately. Yet, similar to the viscosity data, the moduli of the inks decrease with composition.
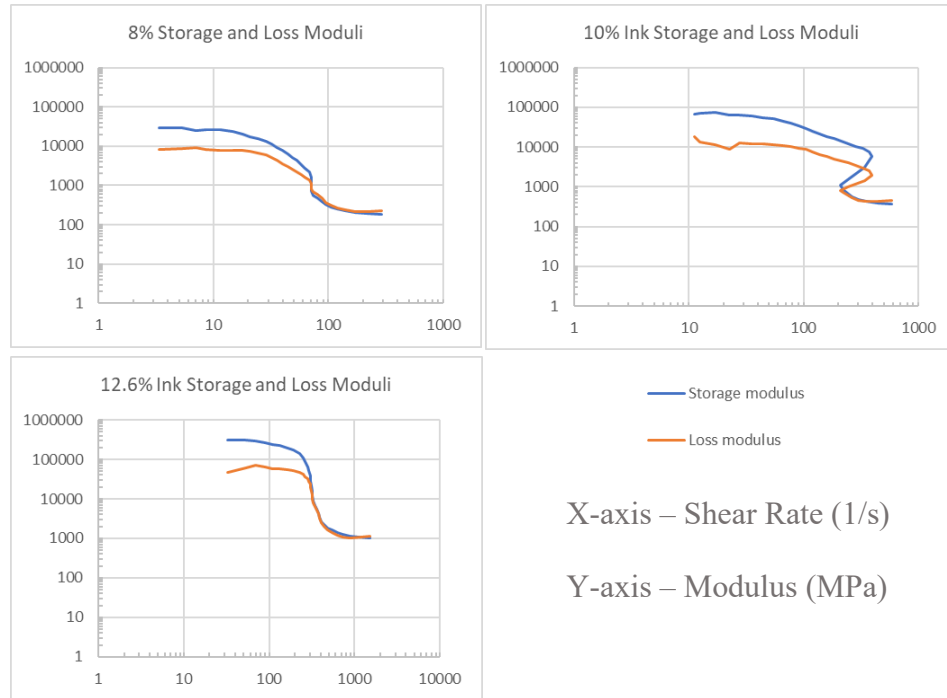
*Figure 5 Storage and loss moduli data for the 8%, 10%, and 12.6% ink. Rheological measurements were taken at the time as if they were to be cast or printed.*

Using only the 12.6% PVDF ink for 3D printing NMC811 lattices, the only parameters changed were the spaces in between the lattice rods, 200um, 150um, and 100um. The easiest to accomplish is the 200um gap spacing, with the height of the nozzle not leading too much difficulty in printing clean lattices with defined void spacing (Figure 6). The situation is the same with printing of 150um gaps. However, when printing 100um gap spacing, the height becomes very critical, because if the nozzle is too high, then there will be poor adhesion with the Aluminum foil, but too low and the lines will bleed too much and close the lattice gaps (Figure 8).
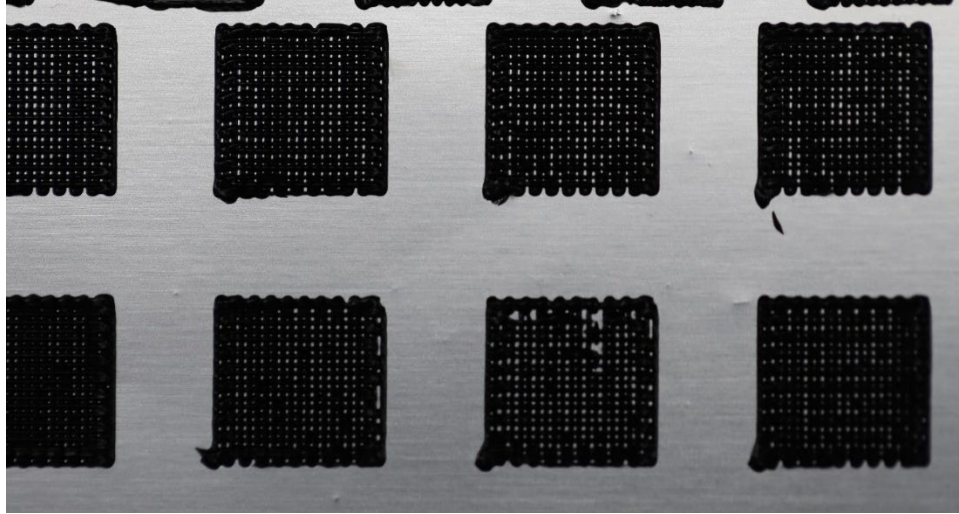
*Figure 6 200um line width and 200um gap. Because the Hyrel printer can change its height during printing, it is difficult to achieve uniform void spacing across different prints.*
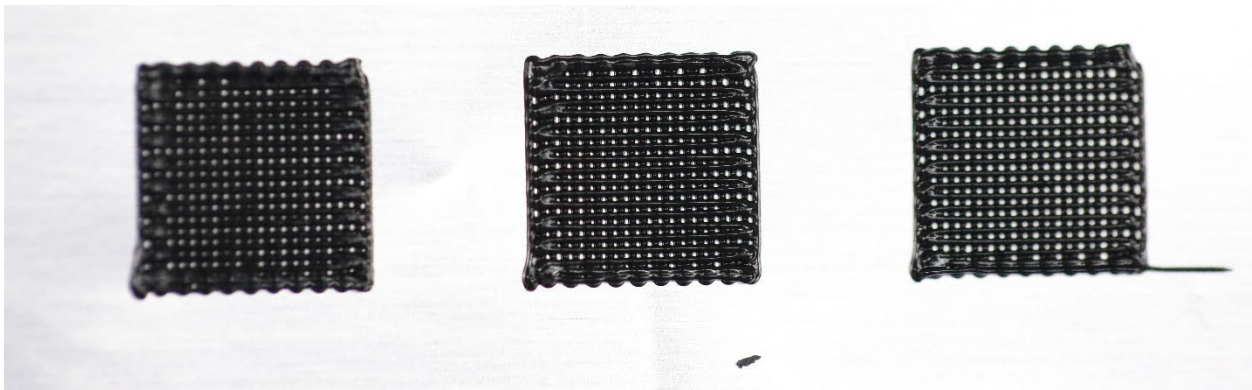


*Figure 7 200um line width and 150um gap. Because the Hyrel printer can change its height during printing, it is difficult to achieve uniform void spacing across different prints.*
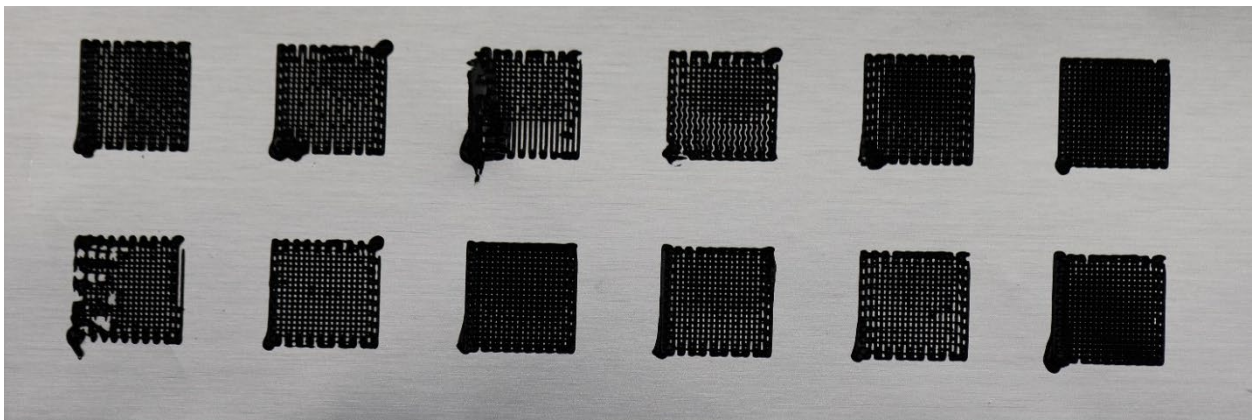


*Figure 8 200um line width and 100um gap. Because the Hyrel printer can change its height during printing, it is difficult to achieve uniform void spacing across different prints.*

## Electrolyte Material Selection

The original objective of this internship was to utilize additive manufacturing to controllably deposit the amount of thermally curable electrolyte resin onto the electrode – important for the manufacturing of solid polymer electrolytes around a 3D printed electrode. However, this was not achieved because the electrolyte resin itself was not fully developed. Initially, the resin was based on research completed by Wang et al. [2], but upon replication, the resin could not thermally cure. As a result, multiple different kinds of resins were tested. Specifically, polyacrylates were added to mix with the VEC and LiTFSI salt, and the $SiO_2$, as used by Wang et al., was removed for simplicity as it was initially believed not to contribute significantly to the solidification of the resin. Additionally, photoinitiators were added as it was believed that they would aid in the solidification of the acrylates, PEGDA and PEGMEA. Once the resin has been mixed, they were then assembled into symmetric stainless steel coin cells to have their conductivity measured by electrochemical impedance spectroscopy.

Very soon, PEGMEA was ruled out as a viable mixture because it could never solidify into a solid electrolyte either by UV-curing, thermal curing, or both. The most successful mixture involved using 8% by weight PEGDA with Irgacure819 as a photoinitiator and AIBN as a thermal initiator, which displayed a conductivity of $2.29*10^{-4}$ S/cm with reasonable solidification after photocuring and thermal curing. Another possible mixture is 10% PEGDA, which has a lower conductivity of $10^{-5}$ S/cm but greater solidification.
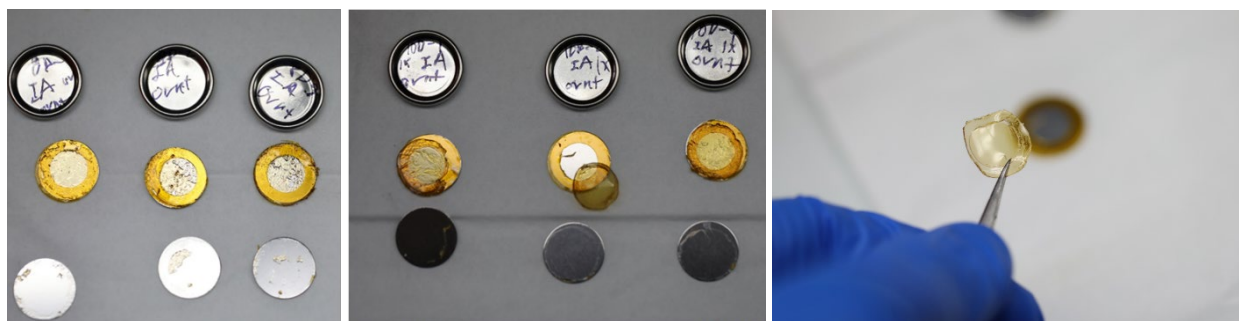
*Figure 9 Left, disassembled coin cell containing 8% PEGDA mixture cured resin. Center, disassembled coin cell containing 10% PEGDA mixture cured resin. Right, 10% PEGDA cured resin held up with a pair of tweezers.*

While these electrolytes do show promise, their solidification is inconsistent, and the conductivities can be improved and/or simplified. As a result, photorheology was performed to determine the best UV-curing conditions of each the electrolytes. Through these experiments, two surprising results were obtained. Firstly, the combination of AIBN and Irgacure819 resulted in the formation of bubbles in the electrolyte (Figure 10), whereas this does not exist in resin with just Irgacure819. Based off of the polymerization scheme of AIBN (shown in Figure 11), these bubbles are likely nitrogen gas. However, infrared spectroscopy is needed to confirm that hypothesis, as well as to be used to determine if the acrylate actually polymerized.
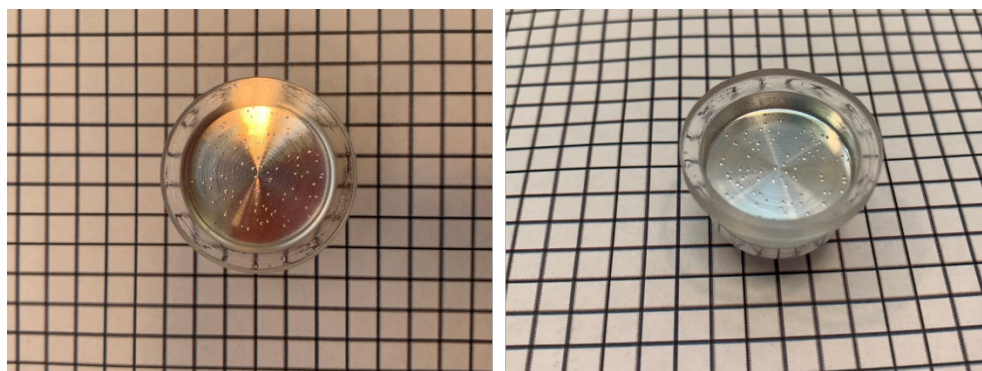


*Figure 10 8% PEGDA + Irgacure819 and AIBN + LiTFSI resin drop-cast in between a quartz piece and DHR attachment stub and UV-cured for 10 min. at an intensity of 21mW/cm2. Both are the same image, but at different angles.*
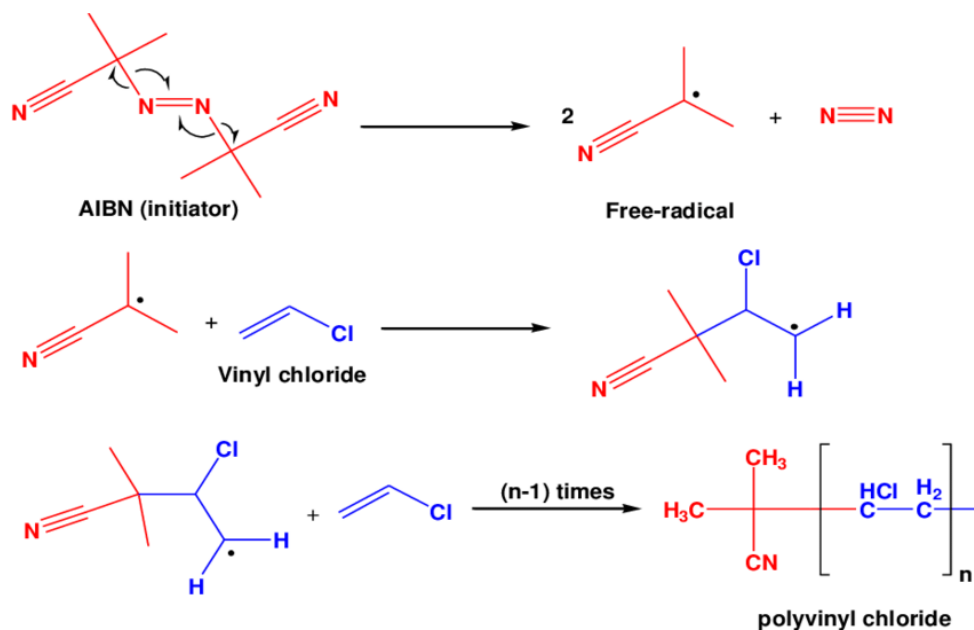
*Figure 11 Reaction scheme of AIBN (in red) with a vinyl chloride (in blue). Nitrogen is produced as a byproduct (top row), and the vinyl chloride is polymerized into polyvinyl chloride (bottom row). Obtained from Dena et al. [4].*

Secondly, increasing intensity does not improve solidification of the resin. It was initially assumed that with increasing intensity, the ink would have higher moduli. However, as seen in Figure 12, not only does increased intensity not increase the moduli, but it does also not even reach the moduli reached by the low intensity curing. Furthermore, the graph does not even indicate that the resin solidified, since the loss modulus was higher than the storage modulus. As a result, the next set of photorheology experiments was performed at a lower strain rate.
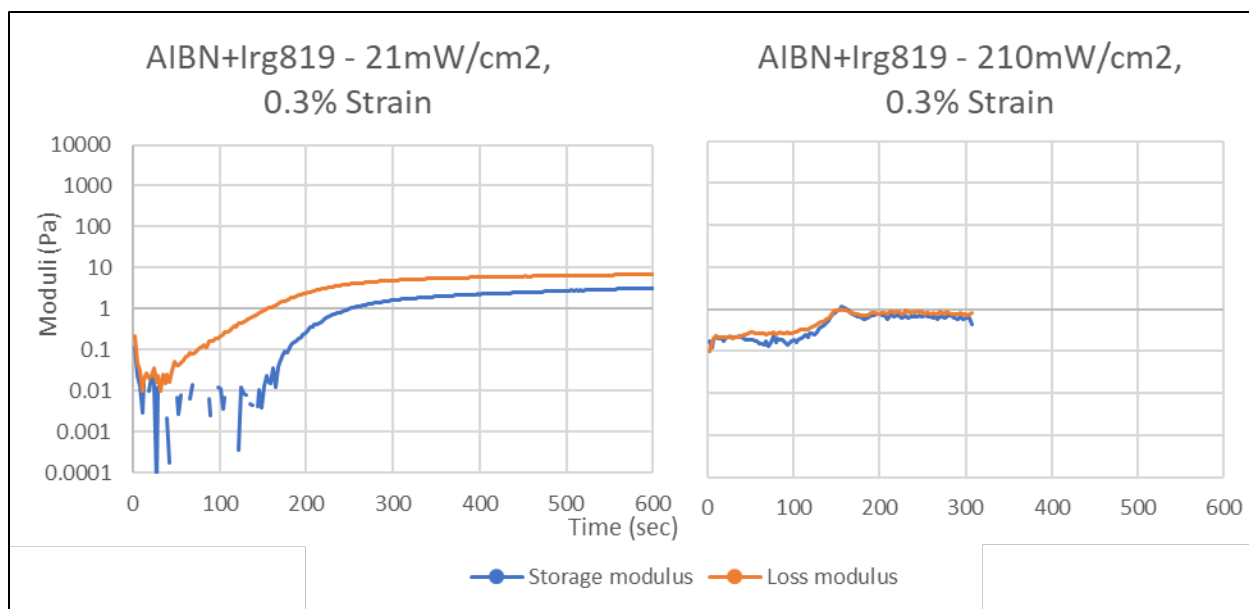
*Figure 12 Curing of 8% PEGDA + 1wt% AIBN + 1wt% Irgacure819, with LiTFSI. Left, curing performed at 21 mW/cm², right, curing performed at 210 mW/cm². The full 10 minutes of curing was not completed for the higher intensity condition because the moduli were not changing significantly.*

Because there is an unusual interaction between AIBN and Irgacure819, the AIBN was removed to better obtain the relationship between the curing intensity and solidification. In Figure 13, the low intensity light cures the resin to a higher moduli and with the storage modulus crossing over the loss modulus. Compared to high intensity light, it appears as though the resin does not cure at all. Upon qualitative testing of the electrolytes by scraping it off of the metal stub (as can be seen in Figure 10), and the low intensity cured resin is much more solid and maintains its shape when handled softly.
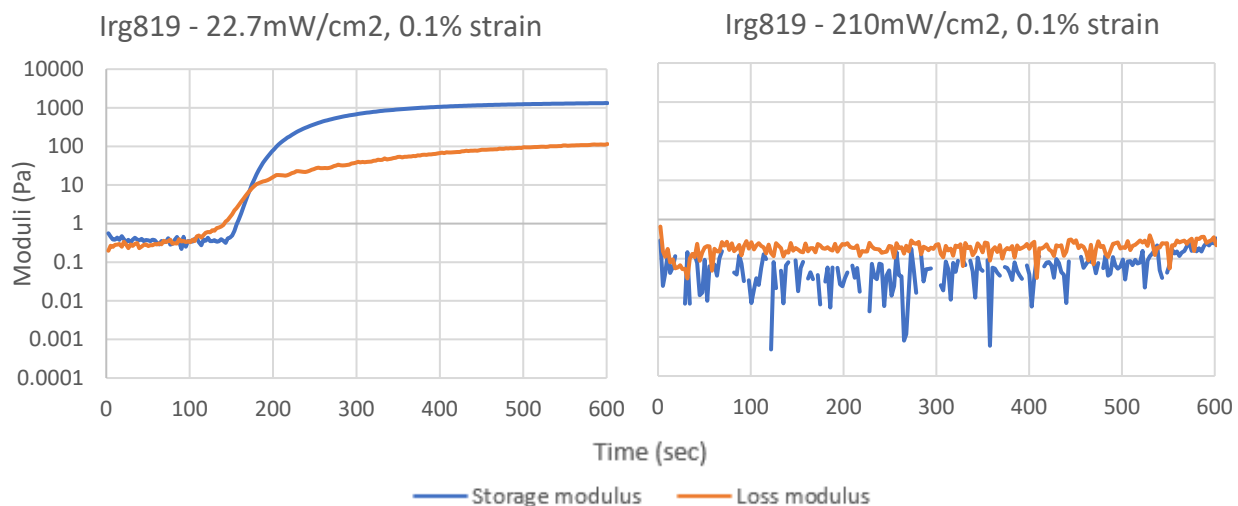
*Figure 13 Curing of 8% PEGDA + 1wt% Irgacure819, with LiTFSI. Left, curing performed at 22.7 mW/cm², right, curing performed at 210 mW/cm².*

Although this ink did not continue on to further electrochemical testing, including interactions with the NMC811 electrode and as a 3D printing ink, the information obtained here has provided valuable insight into future manufacturing or solid polymer electrolytes.

## Conclusion

The manufacturing of electrode thin films is important as it allows a fair comparison between the electrochemical properties of the films and that of 3D printed structures (at similar mass loadings). With a new series of thin film casters which have a predefined thickness, there is a clear established relationship between the thickness of the caster and the final dried film thickness and mass loading. The properties of the ink itself is also important to characterize, as it then aids in determining the final mass loading of the cast or printed inks. Finally, being able to reliably 3D print the inks into a woodpile lattice is crucial to making steps toward higher rate performances as expected of 3D electrodes. Similarly, solid polymer electrolyte is also important as it helps to create safer batteries during their operation. Although the final goal of the project to

3D print the electrolyte could not be achieved, the troubleshooting gone through material selection of the resin still provided insight on the manufacturing of solid polymer electrolytes. All of these contribute to advancing the technologies involved in addressing the energy and environmental challenges faced by humanity.

Through this internship, I was able to quickly be introduced to many technical skills and equipment used by professionals in the industry, including a 3D printer, rheometers, and various electrode and electrolyte manufacturing techniques. Additionally, I obtained many soft skills used by pioneers in the battery field to troubleshoot, innovate, and communicate, all of which will aid me in my own academic pursuit of my PhD as well as future professional developments in the field of battery manufacturing and renewable materials.

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