Study on SPEEK based electrolytes for Lithium ion conduction in batteries

By

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Abstract

The current increase in the installation of renewable energy and the transition from fossil fuels to more sustainable options has made the role of energy storage vital to the success of this shift. Batteries are going to have a major role in this and especially lithium batteries, which has been dominating the market for years now because of their high energy densities. With the increased use of lithium batteries in various applications, safety concerns have been raised, because of short-circuiting, dendrite formation thus demanding a more reliable and safe battery technology. Even though the use of metal anodes is the next step to provide higher energy density, they are currently held back because of dendrite growth which in turn cause short-circuits. Polymer electrolytes pose as a promising alternative to these issues as they are more stable and can be used as protective coatings, can be used as electrolytes (coating, film, liquid electrolyte), are cheaper and safer than the currently used liquid electrolytes.

In this thesis, the feasibility of Sulfonated Poly Ether Ether Ketone (SPEEK) as an electrolyte is explored. A proof of concept for the use of SPEEK mixed with other lithium salts and ionic liquids is done along with conductivity analysis. This SPEEK is then lithiated and used as an electrolyte coating, as a film (Lithiated SPEEK Film) and as liquid (Lithiated SPEEK liquid electrolyte). The conductivity range from 10^{-5} S/cm for a coating and film to 10^{-3} S/cm for liquid electrolyte is within the margin for commonly used polymer electrolyte systems.

All these composite electrolytes were investigated with Copper-Lithium, Lithium-Lithium, NMC/LTO-Lithium systems. In a Lithium-Lithium system, it is observed that over time, the lithium erodes due to stripping and plating activity, effecting the performance of the system. Intercalation materials like NMC and LTO were used and preliminary tests show positive result in terms of conductivity, which are comparable to the standard liquid electrolyte (EC:DEC). Keeping these positives in mind, further research can be done, using lithiated SPEEK with intercalation materials.

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1 Introduction

With the increasing demand of renewable energy in the form of solar, wind and EV the role of batteries is going to be significant, improving the concept of energy storage both short term and long term is the goal going forward. In the present age, lithium batteries have dominated the market because of their high energy densities. However, their flaws in safety concerns causing short circuits, dendrite formation and the lower stability of the regularly used liquid electrolyte has prompted the increased research in lithium batteries to improve their safety and performance.

The use of polymer electrolytes has come to the surface as one of the ways in which lithium batteries can improve their performance and ensure the safety aspect as well. There are several advantages of using polymer electrolytes, like apart from the fact that they have transport properties comparable to the regularly used liquid electrolytes. They are transparent, they can be solvent free, they are light weight, we can obtain flexible thin films, cheap and can be easily processed [1]. In case of polymer electrolytes they are several ways in which their ionic conductivity can be improved, polymer blending can be done, combo-branch copolymers, using dopants, addition of salts, ionic liquids, inorganic fillers, plasticizers and nanomaterials. [1]

One such popular polymer is Sulfonated Poly Ether Ether Ketone (SPEEK) is use as a fuel cell membrane but in this thesis its used as an electrolyte as it has shown ion conducting properties in batteries along with other lithium salts and also by lithiating it.

1.1 Polymer Electrolytes

A discussed earlier polymer electrolytes have shown a lot of promise as they can be used as liquid polymer electrolytes, gel polymer electrolytes, films and coatings along with various ways to improve their conductivity. It is important to understand the working principle of polymer electrolytes and their properties that need to be identified to improve their performance.

In a polymer electrolyte the polymer host material acts as a ionic transport medium, the chain segmental motion and rearrangement of the host polymer material cause the ion transport mechanism. In this thesis lithium salts are the source of Li^+ ions for conduction. The polymer is used a gel polymer/liquid plolymer electrolyte when dissolved in a liquid electrolyte solvent along with the lithium salts and in the absence of the liquid electrolyte solvent is acts as a solid electrolyte/film [2] [3] [1].

These composite polymer electrolytes need to have certain characteristics in order to perform as a suitable electrolyte. In them having high ionic conductivity is important which is dependant on the glass transition temperature of the material and ideally a low glass transition temperature is desired to have high ionic conductivity.[3] Polymer groups that allow easy dissolution of salts providing Li^+ ions for conduction are also desired.

A polymer electrolyte must have good interface contact, that reduces the interface resistance. The performance of the Li-ion battery also depends on the lithium transference number which is defined as the current carried by the Li^+ ions in the system. The lithium transference number of a Li-ion battery must be as close to 1 as possible, a higher number would increase the rate at which the dendrites are formed. [3][4]. These are some of the characteristics that needs to be there in a good polymer electrolyte and SPEEK is one such promising polymer material.

1.1.1 Sulfonated Poly Ether Ether Ketone (SPEEK)

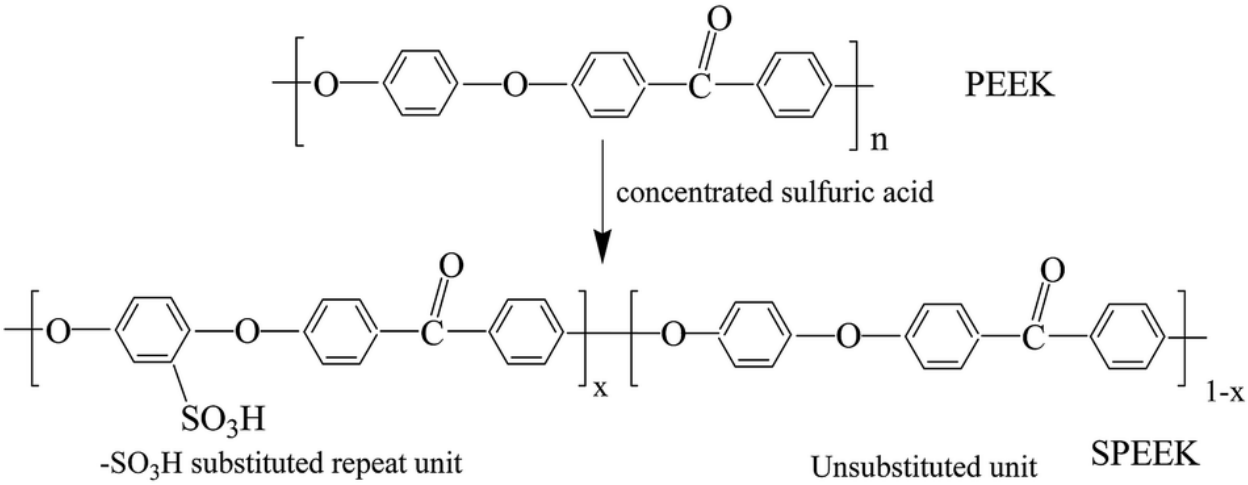


Figure 1.1: Chemical Structure of SPEEK [5]

SPEEK as we can see in Figure 1.1 is an ionomer (a single ion conducting polymer) where the anionic group is covalently bonded to the polymer. Thus as discussed earlier the free anion movement needs to be reduced to keep the transference number close to 1 allowing an increases in the conductivity which is possible in an ionomer, where the anion is covalently bonded to the polymer[6][7][5].

SPEEK can not just be used in fuel cells but also in batteries because of their mechanical, chemical and thermal properties. The preparation of SPEEK is explained in detail in [8]. 80-85% sulfonated PEEK is used for experiments in this thesis. The degrees of sulfonation are important to understand the performance of the material. It is observed that SPEEK becomes more hygroscopic with increase in the degrees of sulfonation, which means that it absorbs more water/moisture causing membrane instability, which is crucial in Li-ion batteries performance. Whereas when the degrees of sulfonation are below 50%, the ionic conductivity is significantly affected, jeopardizing the performance of the battery. Thus optimizing the degrees of sulfonation are important to have better performance of the battery[8][6][7][9].

The following experiments are performed using SPEEK dissolved in Dimethyle Sulfoxide (DMSO) along with other lithium salts and ionic liquids and also lithiating the SPEEK to increase the lithium ion conduction[10].

1.2 Scope of Work and Research Question

This Study aims to understand the use of SPEEK and Lithiated SPEEK as electrolyte in a lithium system. With preliminary studies already conducted and ongoing, this thesis aims at improving the electrolyte resistance of the system by the addition of lithium salts in varied concentrations, lithiating the base material (SPEEK) and also using the material in the form of film, liquid electrolyte and coating and trying to understand which combinations provide the best results.

The research questions can be framed in two categories.

I. Can SPEEK be used to make composite polymer electrolyte?
   YES!
   - There is improvement in the conductivity amongst the combinations tried.
   - Conductivity improve with addition of salts and conductive liquids.
   - Conductivity improve with increase in the temperature.
   - Conductivity values are in the range of commonly used polymer electrolyte systems.

II. Can Lithiated SPEEK be used as an electrolyte?
   YES!
   - Lithiation of SPEEK improve the conductivity.
   - Lithiated SPEEK as film improve the interface resistance showing similar conductivity values.
   - There an improvement in the conductivity by using 3hr Lithiated SPEEK than using Room Temperature Lithiated SPEEK.
   - Using Lithiated SPEEK as liquid electrolyte improve the conductivity of the system.
   - Lithiated SPEEK liquid electrolyte with intercalation materials like NMC and LTO gives impressive conductivity values comparable to standard electrolytes (ECDEC).

2 Methods and Material

In section will summarize about the lab cell used in which all the experiments were performed and also the characterization techniques used to analyze the performance of the battery. Methods of preparing the samples and how the battery was assembled is also explained here.

2.1 LAB Cell

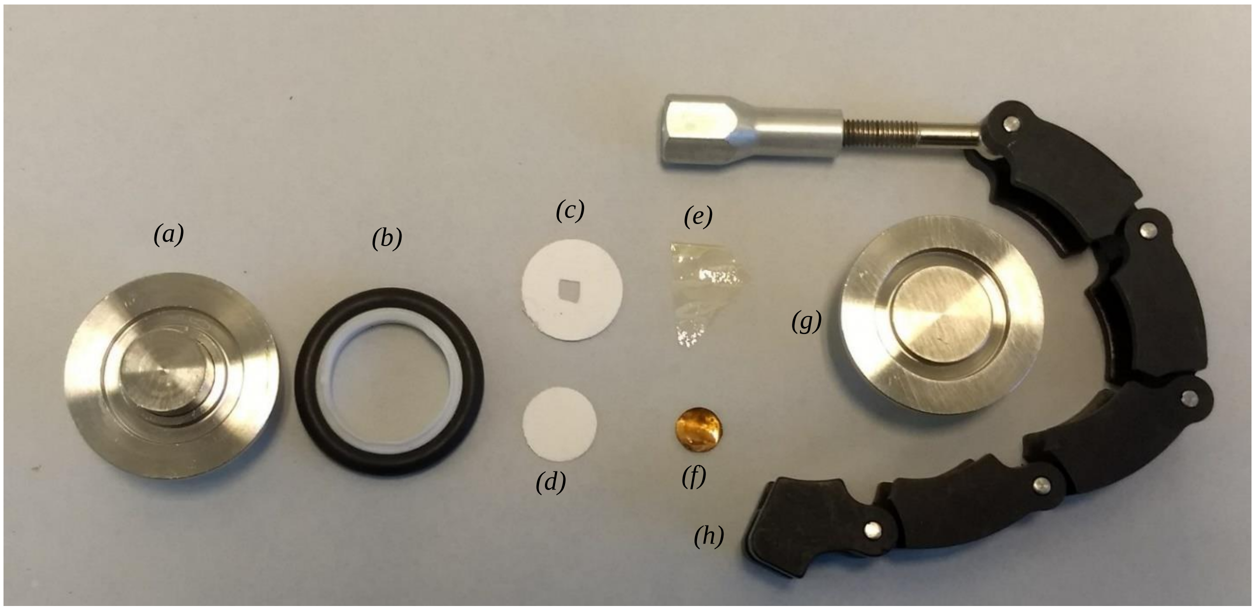


Figure 2.1: Components of a LAB Cell and the electrolytes used.

Figure 2.1 shows the components of a LAB Cell, along with the samples, used to make the battery. In the figure (a) and (g) are the two stainless steel electrode holders, on whom the electrodes are placed. (b) is the rubber seal, (h) is the clamp used to close the cell after assembly. Coming the actual components used to make the battery, (c) was used for coating assemblies as a separator, (d) was use as a separator in liquid electrolytes, and (e) is the lithiated SPEEK film used between the two electrodes. (f) Coating of the prepared electrolyte on copper.

Figure 2.2 Shows the way the cell is assembled for a coating (image 1) and for a film (image 2). Where in image 1, (a) is the coated copper substrate; (b) is the lithium, (c) Glass fiber separator. In image 2, (d) is the electrode and (e) is the Lithiated SPEEK film.

Figure 2.3 Shows the Coated copper substrate, Where (a) is the bare copper substrate, (b) is the lithiated SPEEK coating, (c) Composite SPEEK electrolyte coating.

In all the cases, the copper substrate was 9.52mm diameter (0.71cm^2) and the lithium was approximately 0.25cm^2.

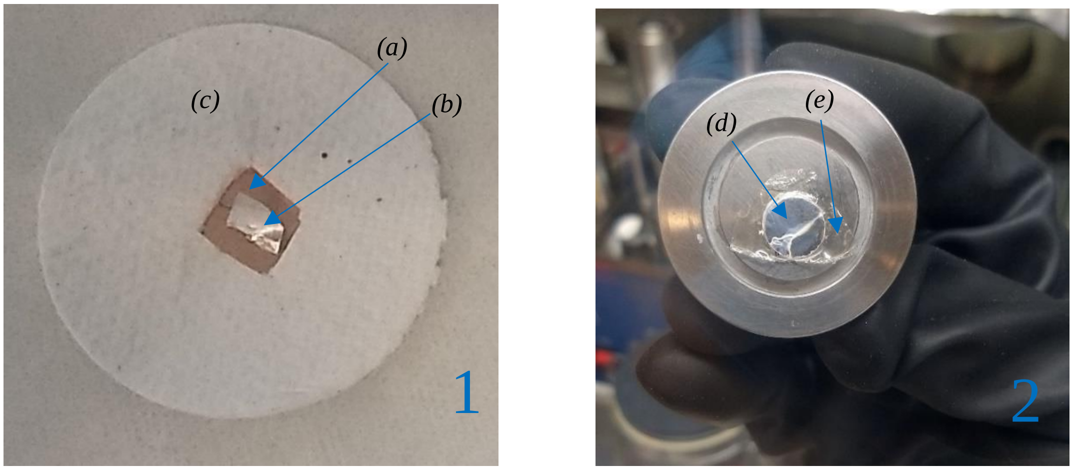


Figure 2.2: Image 1, shows the cell assembly for a coating. Image 2 shows the cell assembly for a film.

Figure 2.3: Copper substrate coated with electrolyte.

2.2 Characterization

EIS- Electrochemical Impedance Spectroscopy.

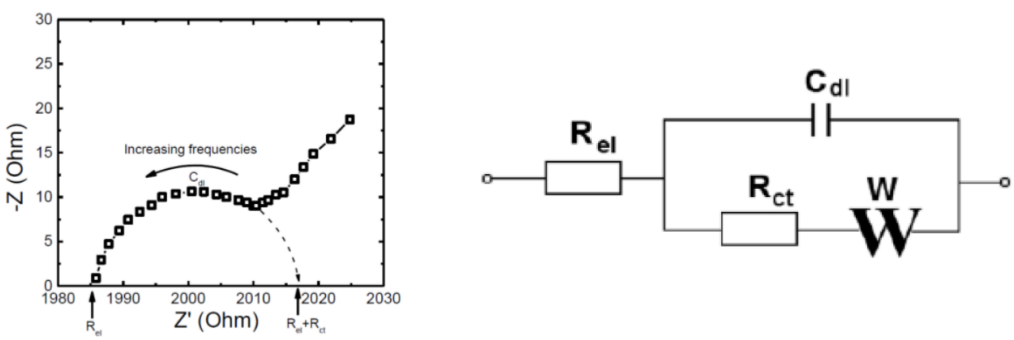


Figure 2.4: Nyquis plot for EIS of NMC | LiSPEEK LE | LTO and equivalent circuit. [11][12]

EIS is used to characterize the electrochemical behavior of a system. EIS studies the systems response to the application of a periodic small amplitude ac signal. These measurements are carried out at different ac frequencies. This analysis provides information about the interface, its structure and the reactions taking place. The EIS data is represented in a Nyquist plot and bode plot providing information about the resistance at high and low frequencies. Figure 2.2 shows the nyquis plot of EIS where R_{el} is the first touchdown point of the measurement at high frequencies indicating the electrolyte resistance, where as R_{ct} is the charge transfer resistance where as the W is the Warburg impedance which indicated the mass transfer in the electrode-electrolyte interface. The R_{el} is used to calculate the conductivity values of the electrolyte. Where σ is the conuctivity value of the electrolyte, d is the thickness of the electrolyte membrane (could be a coating, a film, or liquid electrolyte on a separator). S is the area of lithium in contact with electrolyte and the other electrode. R is the resistance value of the electrolyte[11]. Check appendix A1 to understand conductivity calculation.

$$\sigma = \frac{d}{S\text{x}\, R}\ \text{S/cm} \qquad (2.1)$$

CV: Cyclic Voltammetry

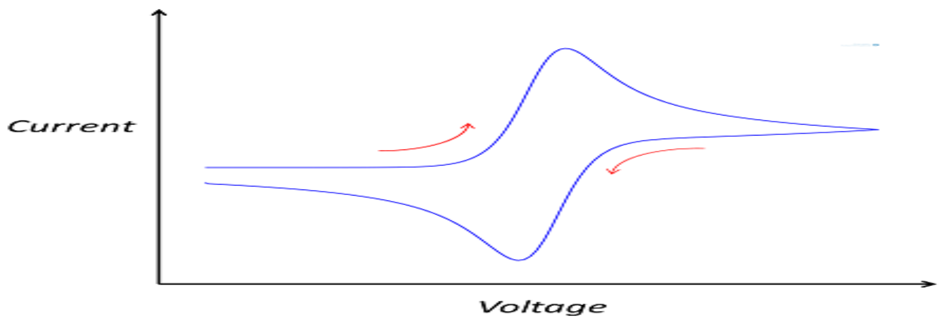


Figure 2.5: Representation of a CV curve[13]

CV measurements were done by applying a voltage sweep to the battery and the resulting current is measured over a period. CV is used to identify the redox potentials of the battery along with information like if the reactions are reversible and about other electrochemical reactions[13], [14].

XPS: X-ray photoelectron spectroscopy

Device: Thermo Scientific K-Alpha

XPS is used to analyses the surface chemistry of the material, XPS can measure the elemental composition of the material the type of bonds and electronic state of the elements in the material. XPS spectra is obtained by irradiating the material to be examined with a beam of X-rays and simultaneously measuring the kinetic energy and electrons emitted from the top 1-10nm of the material. A spectrum is recorded with the electron kinetic energy emitted by the material showing the elemental composition of the material and the intensity of the peaks of the spectrum indicate how much of the element is present.[15]

2.3 Preperation of SPEEK and Lithiated SPEEK

In sub section, we will look at the type of SPEEK used, the way the composite electrolytes were prepared for SPEEK. We will also look at the way the SPEEK was lithiated and how a film was casted and how it was used as a coating or liquid electrolyte. All the electrolytes were prepared and assembled inside the glove box at 0.1 ppm H_2O and 0.1 ppm O_2.

2.3.1 SPEEK Composite Electrolyte

The SPEEK used in this this thesis is 80-85% sulfonated [9][8], which was used to make composite electrolytes along with DMSO which is a common solvent used to dissolve SPEEK. There were three samples made using the SPEEK with different salt ratios. The performance and the analysis of these samples is explained in section 3.1

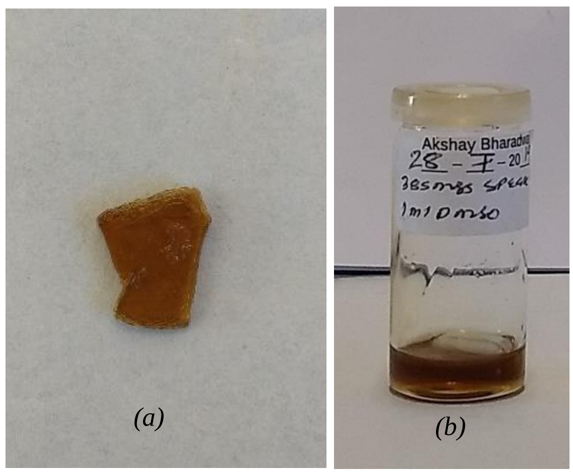


Figure 2.6: (a) SPEEK Crystal and (b) 385mgs SPEEK in 1ml DMSO

385mgs of SPEEK was dissolved in 1ml of DMSO as shown in figure 2.6 (b), creating a highly viscous solution and then adding the corresponding slats in their ratios, to this solution.

i) In the first case LiTFSI was added to the solution in the ratio (SPEEK: LiTFSI 5:1) [9].
ii) In the second case ionic liquid was added in the ratio (SPEEK:IL 7:2) along with LiTFSI in the ratio (SPEEK: LiTFSI 5:1) [9] [16].
iii) In the third case LAPG was added in the ratios (SPEEK:LAGP 3:1) along with LiTFSI in the ratio (SPEEK:LiTFSI 5:1) and ionic liquid (SPEEK:IL 7:2) [9] [16].

Each of these composite electrolytes were then drip coated on a copper substrate and then dried in a vacuum oven overnight. These coatings were then use to make the cell as assembled in figure 2.1, Image 1. The average thickness of these coatings was ~125microns, this value is then used to calculate the conductivity of the battery.

2.3.2 Preparation of Lithiated SPEEK

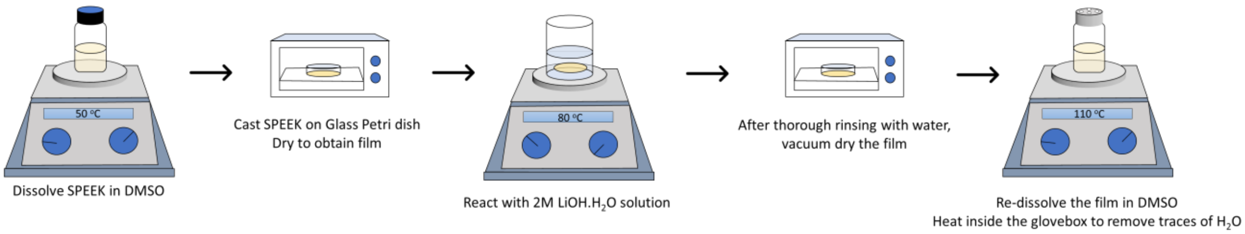


Figure 2.7: Preperation of Lithiated SPEEK

Figure 2.7 show the way the SPEEK is lithiated, where the SPEEK is first dissolved in DMSO and then is casted on a petri dish to obtain a film after drying. This film is then lithiated in 2M $LiOH.H_2O$ solution for different types (overnight at room temperature, and 3hr Lithiation at 80 ˚C).This lihtiated SPEEK is then rinsed and dried to remove all the moisture in it. The film itself is used as an electrolyte membrane see figure 2.2 Image 2, and its dissolved in DMSO so it can be used as a coating or used as liquid electrolyte. The performance and the analysis of these samples is done in section 3.2

2.4 3hr Lithiated SPEEK Preparation with Lithium

The 3hr Lithiated SPEEK was prepared with lithium in three ways

i. In the first case 3hr LiSPEEK film is dissolved in DMSO and is coated on 15mm diameter lithium disc and then kept in the antechamber to dry at 80℃. The approximate thickness of the coating was 85microns.
ii. In the second case 3hr LiSPEEK film is used directly with little DMSO between the film and the lithium electrode. The approximate thickness of the film was 45microns.
iii. In the third case 3hr LiSPEEK film is dissolved in DMSO and used a liquid electrolyte. This liquid electrolyte is then dripped on a separator and used an electrolyte between two lithium electrodes. The approximate thickness of the glass fiber separator used was 342 microns.

2.5 Preparation of NMC and LTO electrodes.

This section explains the preparation of NMC and LTO electrodes used to make the battery. The performance and analysis of these samples is done in section 3.5 of this report

2.5.1 Preparation of NMC

For the preparation of the NMC (Lithium Nickel Manganese Cobalt Oxide) electrodes. $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ was used along with PVDF and Carbon Black where NMP is used as the solvent. The ratios for NMC:PVDF:CB was 8:1:1, looking at the ratios we can tell that NMC is the active material with the highest concentration. After the slurry was prepared, it was casted on an aluminum foil, which was taped on a glass slab. Doctor Blade 200 was used to cast the slurry on the aluminum foil. After which it was rested over night to dry and the next day placed in a vacuum oven at 80˚C to ensure that the coating has completely dried. The dried coatings are then pressed under pressure to smooth the surface. These pressed electrodes are then measured for weight and thickness, which is use to calculate the capacity of the electrode. In case of NMC 0.160 mAh/mg is used as theoretical capacity [17].

2.5.2 Preparation of LTO

For the preparation of the LTO (Lithium Titanium Oxide) electrodes where LTO is the active material. $Li_4Ti_5O_{12}$ was used along with PVDF and Carbon Black where NMP is used as the solvent. The ratios for LTO:PVDF:CB was 8:1:1, looking at the ratios we can tell that LTO is the active material with the highest concentration. After the slurry was prepared, it was casted on an aluminum foil, which was taped on a glass slab. Doctor Blade 200 was used to cast the slurry on the aluminum foil. After which it was rested over night to dry and the next day placed in a vacuum oven at 80˚C to ensure that the coating has completely dried. The dried coatings are then pressed under pressure to smooth the surface. These pressed electrodes are then measured for weight and thickness, which are used to calculate the capacity of the electrode. In case of LTO 0.175mAh/mg is used as theoretical capacity [17].

3 Performance of SPEEK and Lithiated SPEEK electrolyte.

Summary

In this section, the performance analysis of all the experiments is done. After preparing the samples and assembling them using the LAB cell inside the glove box, EIS at increasing temperatures is done (20, 40, 60, 80℃). These EIS resistance values are then used to determine the conductivity of the sample calculations in appendix A1. After which the battery is charged and discharged at 80℃ at increasing current values ($1x10^{-4}$, $1x10^{-5}$, $1x10^{-6}$, $1x10^{-7}$ Amperes at 80℃).

3.1 SPEEK Electrolyte Coating

In this section, preparation of various SPEEK composite electrolytes is analyzed by examining the conductivity charts, to determine the best combination.

3.1.2 Analysis of SPEEK Electrolyte Coating

The SPEEK composite electrolyte was prepared and assembled as explained in chapter 2 of this report. For the analysis of all the prepared samples, we will examine the conductivity chart in figure 3.1. Where the conductivity is in 10^{-5} S/cm and increases with increase in temperature, the conductivity of commonly used polymer systems are in the range of 10^{-2} to 10^{-5} S/cm for a gel, dry or composite polymer electrolyte, so there values are well within the range [9] . We can see that the increase in temperature increases the conductivity. This gradual increase in the ionic conductivity is because of the small molecules in the polymer matrix, the motion of charge carriers could be strongly coupled to the segmental motion of the polymer, and the coating here involves the ion polymer segment coupling as observed in conventional polymers [2].

From the figure 3.1, we can infer that SPEEK with LiTFSI IL and LAGP salt coating gives the best conductivity as compared to the other coating combinations. The addition of ionic liquid and LAGP to the original combination of only LiTFSI with SPEEK has shown improvement.

Eventhough these conductivity values can be comparable to the commonly used polymer electrolyte systems, they are not enough to be used in a battery for regular use so the issue of improving the conductivity of the electrolyte needs to be addressed. Also looking at the EIS curves of these combinations in figure 3.2 and others attached in the appendix A2 we see, that there is a very high interface resistance that effects the performance of the battery.

In an attempt to improve the electrolyte conductivity, the SPEEK can be lithiated and a similar series of experiments can be tried. The interface resistance can be improved by using a conductive liquid from the outside on the coating to improve the contact between the two electrodes. These experiments can also be tried with intercalation materials like NMC and LTO instead of using Copper - lithium (dummy cell).

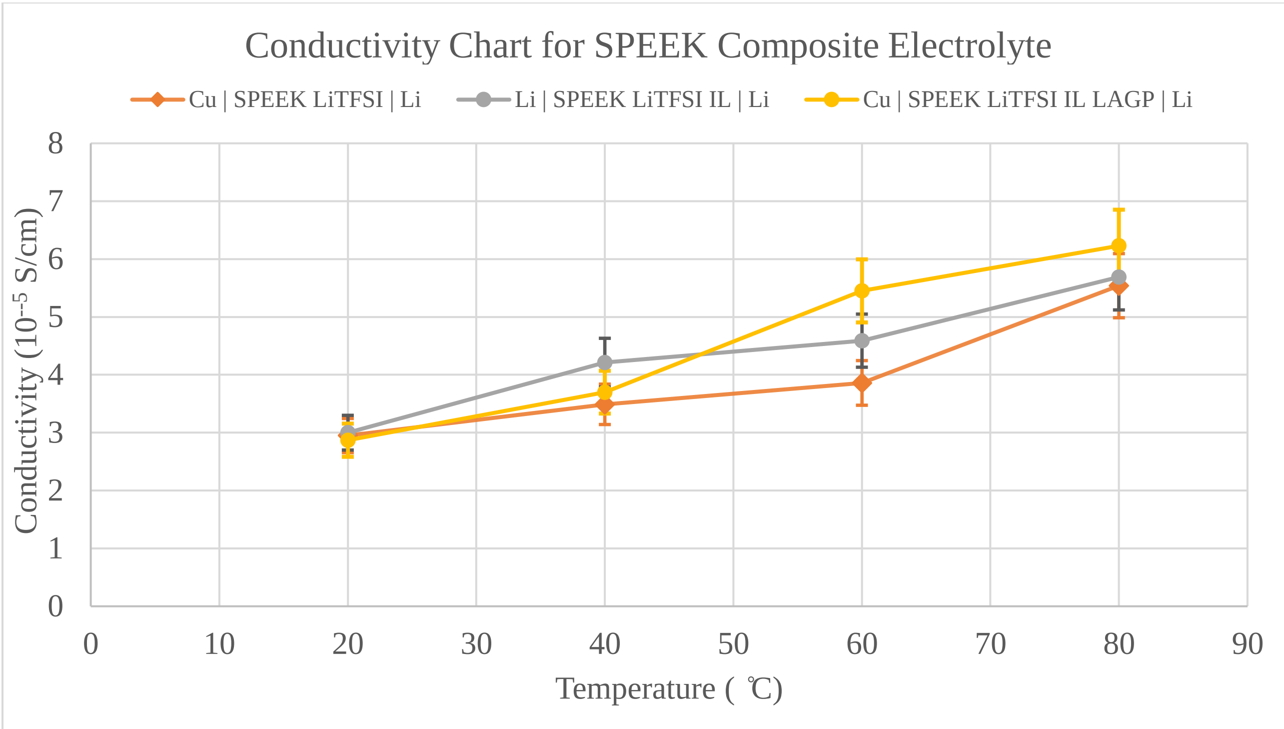


Figure 3.1: Conductivity chart in 10^{-5}S/cm for SPEEK composite Electrolyte

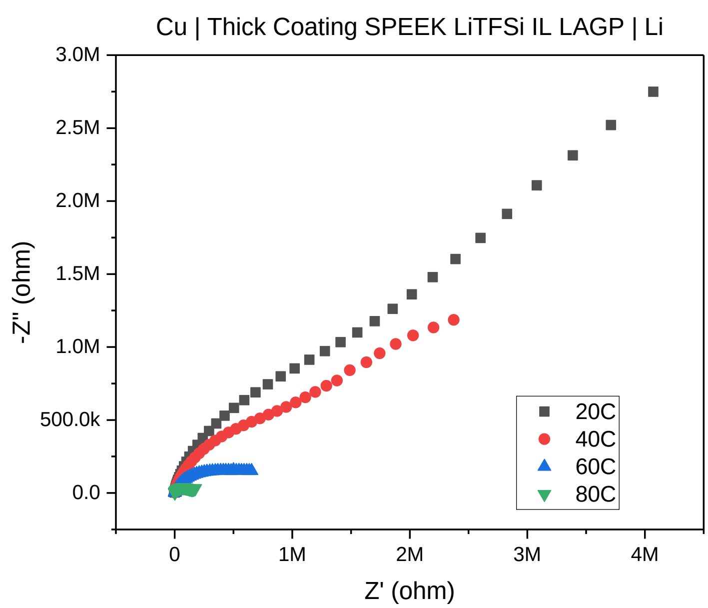


Figure 3.2: EIS of SPEEK LiTFSI IL LAGP

A few positives from these experiments is that we could dissolve a polymer (SPEEK) and a conductive liquid (ionic liquid) along with salts (LiTFSI and LAGP) in one solvent (DMSO). The ionic conductivity calculated in these experiments as at par with conventional polymer electrolyte systems [9] .

3.2 Lithiated SPEEK Electrolyte

Looking at the results from the previous section indicate that in order to improve the conductivity SPEEK can lithiated. Which is done by soaking the SPEEK film in a 2M $LiOH.H_2O$ solution over night at room temperature. This lithiated film can then be dissolved again in DMSO and used for coatings. Here we will look at the use of room temperature LiSPEEK as a film.

3.2.1 Lithiated SPEEK Film with NMC

In an attempt to improve the conductivity and also interface resistance of the battery. The lithiated SPEEK is first coated on NMC electrode and then dried overnight in the anit-chamber of the glove box and then during the assembly of the cell along with the film very less amount of DMSO was dropped on the outside, to improve the adhesion of the film with the electrode and thus improve the interface. Figure 2.2, Image 2 shows how the cell looks after assembly.

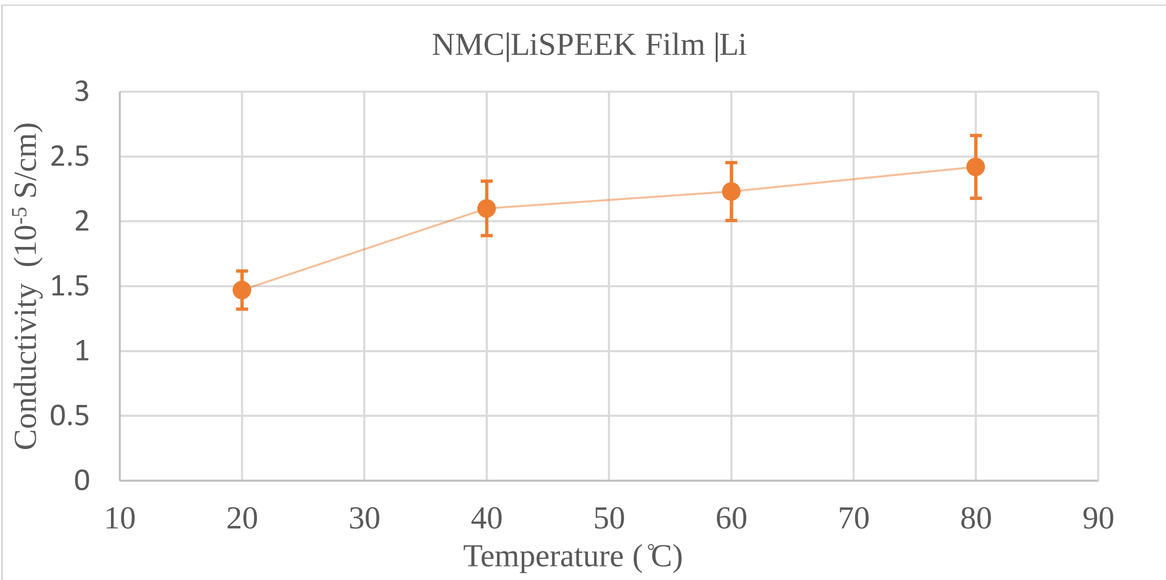


Figure 3.3: Conductivity of LiSPEEK Film with coated NMC and Lithium.

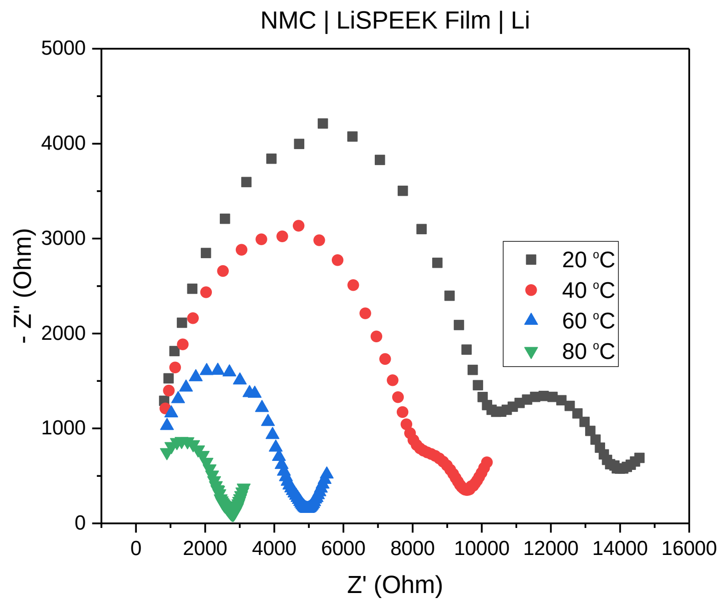


Figure 3.4: EIS of LiSPEEK Film with coated NMC and Lithium

Figure 3.3 shows the conductivity of the lithiated SPEEK Film with coated NMC and Lithium, where the NMC electrode was first coated with LiSPEEK electrolyte and dried in the anti-chamber of the glove box after which the LiSPEEK film was used along with very little DMSO and Lithium electrode. The conductivity does not improve much as compared to the earlier case, but the interface resistance improves a lot as can be seen in the figure 3.4.

The coating of NMC with some LiSPEEK electrolyte and drying it has caused the improve in the interface as some amount of electrolyte is now already part of the electrode and infused inside it. Moreover, when the film was placed along with some DMSO the point of contact of the film with the electrode could have improved because of the already present electrolyte on the surface of the electrode and the presence of DMSO.

Despite the use of NMC and lithiating the SPEEK the electrolyte resistance does not improve much but still remaining in the range of commonly used polymer electrolyte systems [9]. The positive is that the interface resistance was improved by the use of the film along with some DMSO on the outside.

In order to further improve the electrolyte conductivity the lithiation process can be improved and the electrolyte can be used as a liquid electrolyte to improve both the interface resistance and also the electrolyte conductivity.

3.3 Comparison of Room Temperature and 3hr Lithiation Summary

The primary method of lithiation remains the same where the SPEEK film is soaked in 2M LiOH solution. In the lithiation method used till now the SPEEK film was soaked overnight at room temperature, where as in an attempt to improve the lithiation process the SPEEK film was soaked in 2M LiOH solution for 3 hours at 80℃. EIS and XPS were used to analyse these methods.

3.3.1 Analysis of Room Temperature and 3hr Lithiation of SPEEK.

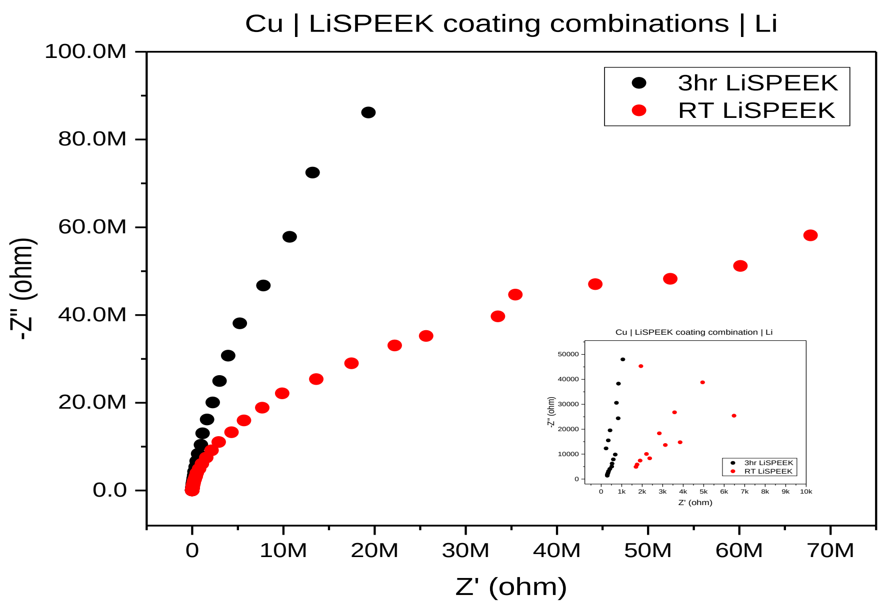


Figure 3.5: EIS at Room Temperature for different lithiation methods (3hrs LiSPEEK at 80℃ and Room Temperature LiSPEEK)

Figure 3.5 shows the EIS curves at room temperature for overnight lithiated SPEEK at room temperature and 3hr lithiated SPEEK at 80℃. The EIS was taken for a coating on copper after the respective lithiated films were dissolved in DMSO. The EIS plot in figure 3.5 shows that both the electrolyte resistance and the interface resistance of 3hr LiSPEEK is significantly better than the originally used room temperature over-night lithiated SPEEK.

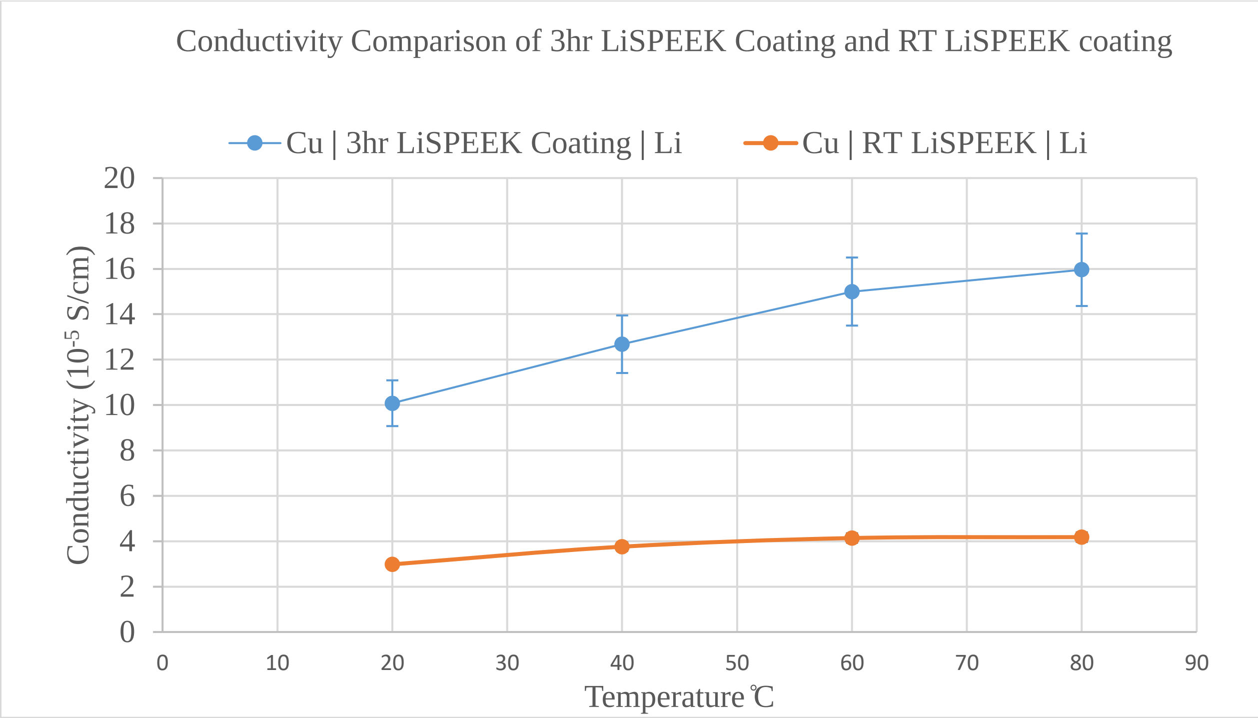


Figure 3.6: Conductivity chart in 10^{-5} S/cm for 3hr LiSPEEK and RT LiSPEEK coating on copper.

The conductivity chart for 3hr LiSPEEK and RT LiSPEEK coated on copper shown figure 3.6. Both the EIS curve in figure 3.5 and the conductivity chart show that the 3hr lithiation method was a better than the overnight room temperature lithiation method. The conductivity values of the 3hr LiSPEEK coating has been better than any other combination tried, which is a big positive. In order to verify that the film is being lithiated and also to find out if there was any difference in the amount of lithium in the samples, a XPS was conducted at PTG Eindhoven.

The XPS survey was done for regular SPEEK film along with the room temperature lithiated SPEEK film and 3hr lithiated SPEEK film at 80℃. The XPS survey in figure 3.7 shows that the 3hr lithiated SPEEK film has 6.72 % lithium as compared to the room temperature lithiated SPEEK, which has 0.32% of lithium. The increase in lithiation clearly shows that the 3hr LiSPEEK has improved resistance values as compared to the room temperature lithiated SPEEK. Despite the positive outcome XPS still remains a surface analysis method (only examining the first few nanometers of the sample) and so a more specific elemental analysis needs to be done to completely understand the lithiation.

A few positives out of the these tests is that the SPEEK film is indeed been lithiated, with the degrees of lithiation still under scrutiny. Another positive is that now lithiation of SPEEK can be done at a faster rate and so more time is saved. Also the conductivity of 3he LiSPEEK is now the best combination which can be made in a shorter period of time with fewer components. Which is an advantage looking from the business point of view.

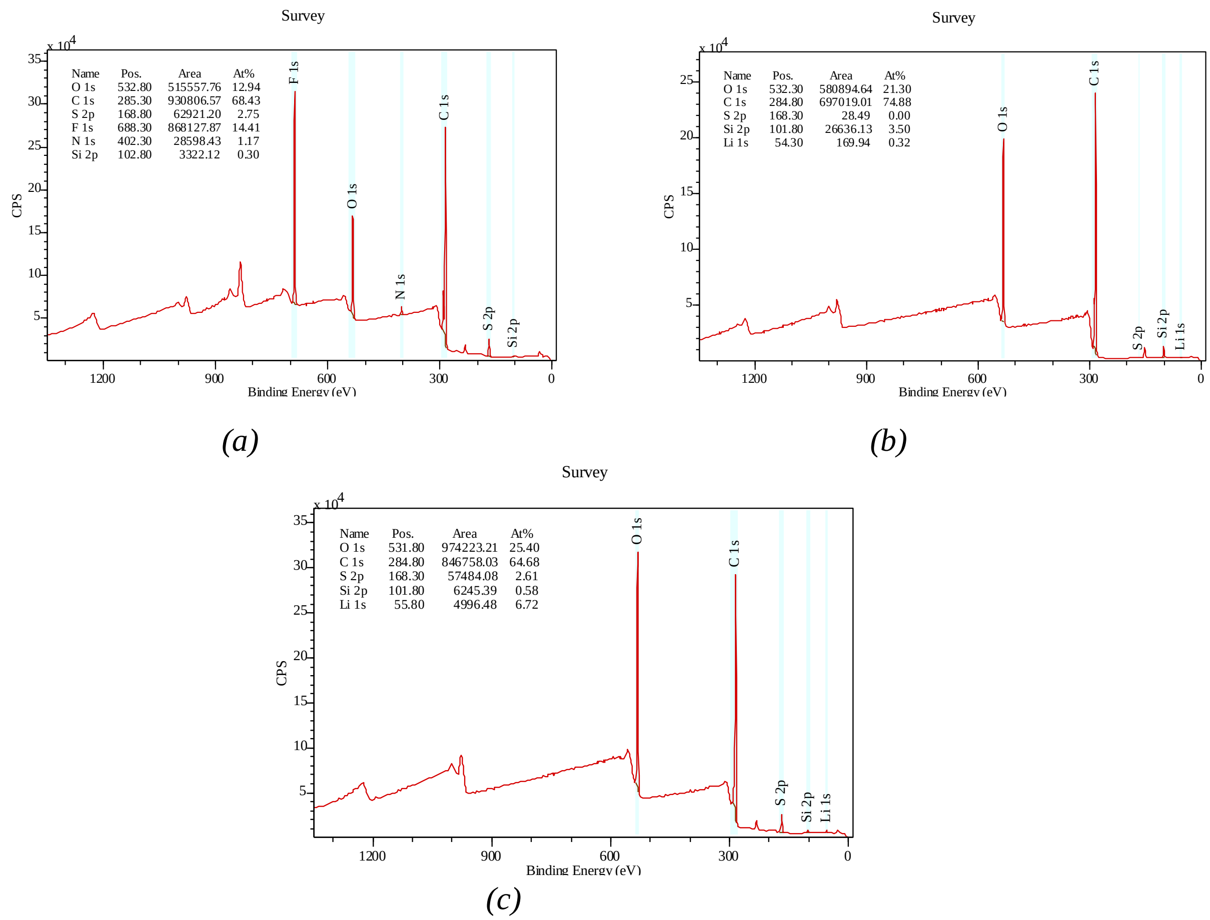


Figure 3.7: XPS Plots for (a) Regular SPEEK Film (b) Room Temperature overnight Lithiation Film (c) 3hr Lithiated SPEEK Film.

3.4 3hr Lithiated SPEEK with Lithium

From the experiments and analysis in section 3.3 its clear that 3hr LiSPEEK provides better conductivity and so in this section 3hr LiSPEEK will be tested with lithium electrodes as coating, film and liquid electrolyte. The preliminary results seem to be promising

3.4.2 Analysis of 3hr Lithiated SPEEK

The analysis for these experiments were done by computing the resistances for each of the cases and then using them to calculate the conductivity values. The thickness of the electrolyte and the area of contact between the two electrodes were considered along with the resistance values.

The figure 3.8 shows EIS comparison at room temperature for 3hr lithiated SPEEK liquid electrolyte with coating and film. We can see that the coating has high electrolyte and interface resistance as compared to the liquid electrolyte. Same is the case with the film where we can see that both the electrolyte and interface resistance is higher than that of the liquid electrolyte.

Figure 3.9 shows the conductivity chart for both 3hr LiSPEEK used as a liquid electrolyte in image *(a)* and as a film in *(b)* the EIS plots for these cases are attached in the appendix A5. Image *(b)* in the figure 3.9 shows the conductivity in 10^{-5} S/cm for the 3hr LiSPEEK film with lithium electrodes. The use of the film shows better conductivity values compared to the coating on lithium and the interface resistance and electrolyte resistance is improved. Despite this the conductivity values are similar to the previous other combinations and so in that way there is not much improvement.

Image (a) in figure 3.9 has conductivity values in 10^{-3}S/cm; the liquid electrolyte combination with lithium electrodes gives impressive results in terms of conductivity values and the resistances. This is the best possible conductivity values obtained until now. Its also clear from the figure 3.8 where the resistances comparison of the coating, film, is done with the liquid electrolyte, that there is substantial increase in the electrolyte resistance when used as a coating as compared to when used a liquid electrolyte. This also makes sense as the mobility of the ions is better in a liquid as compared to a solid coating and so there is improved conductivity as well.

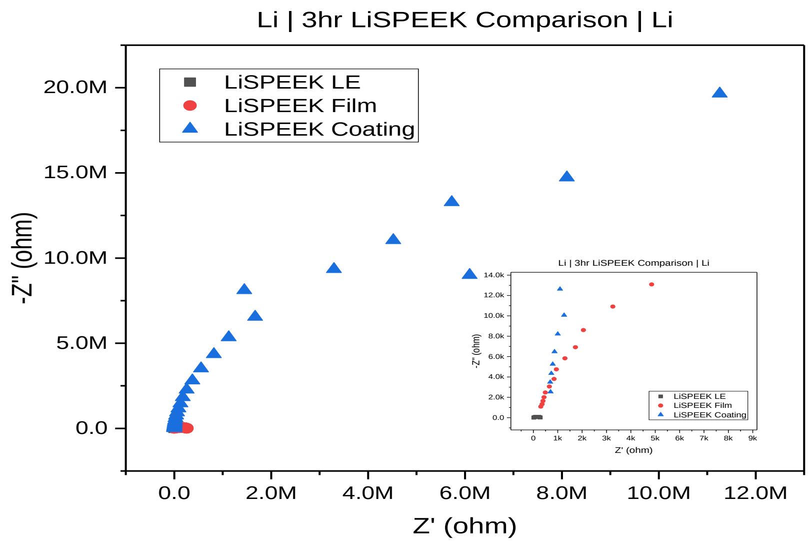
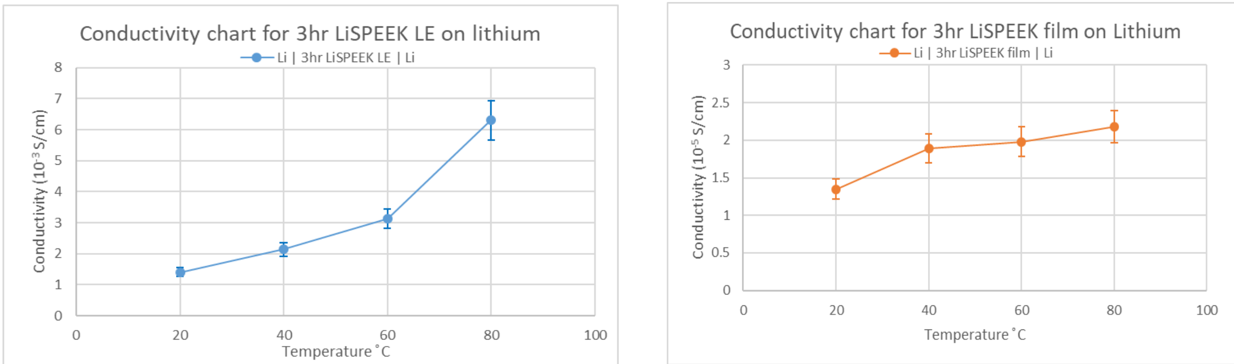


Figure 3.8: EIS comparison at room temperature for 3hr lithiated SPEEK liquid electrolyte with coating and film.



(a) *(b)*

Figure 3.9: (a) Conductivity charts in 10^{-3} S/cm for 3hr LiSPEEK liquid Electrolyte in a lithium lithium cell. (b)Conductivity charts in 10^{-5} S/cm for 3hr LiSPEEK Film in a lithium lithium cell.

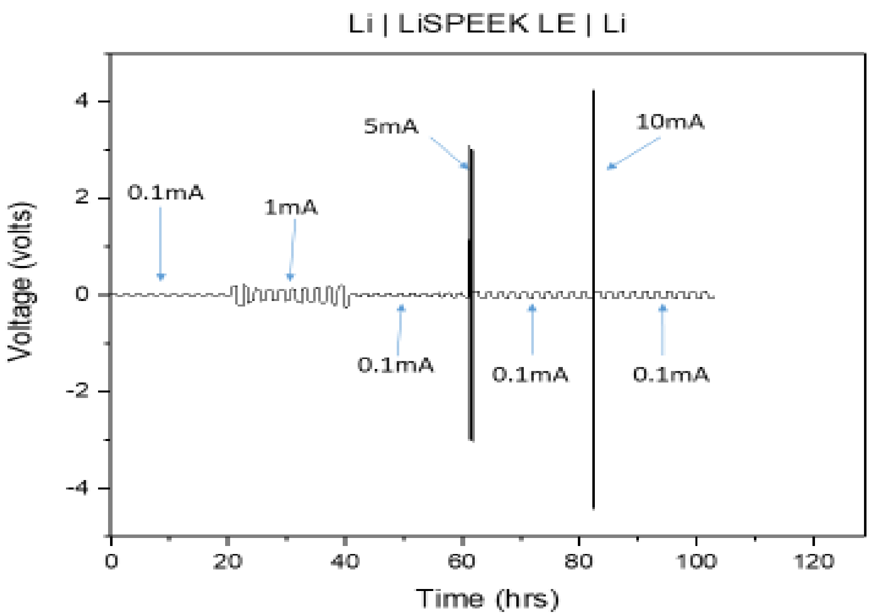


Figure 3.10: 3hr LiSPEEK LE shows stripping and plating of lithium at different currents.

Figure 3.10 shows the stripping and plating of lithium in 3hr LiSPEEK liquid electrolyte. In principle, the overall battery voltage should be zero volts as it is a symmetric cell but in this case, we did manage to strip and plate the cell for different current values thus showing some promise. Figure 3.11 shows the use of lithium metal over time will deteriorate and cannot be subjected to higher cycling time and the formation of dendrites and the erosion of the lithium metal need to be addressed in order to fully exploit the use of lithium metal in batteries. [18]

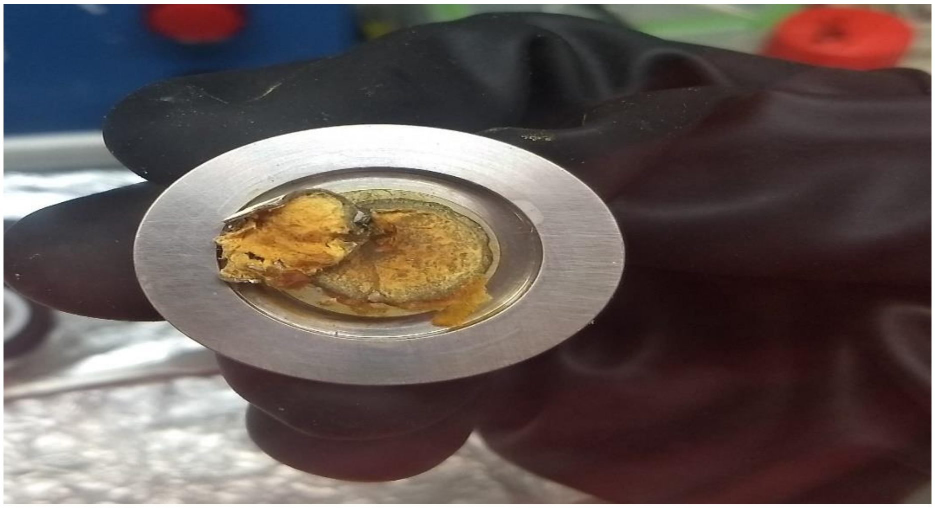


Figure 3.11: Lithium-Lithium battery with LiSPEEK Liquid Electrolyte

Moving forward by understanding that the 3hr LiSPEEK cells work best in liquid electrolyte form. The aim is now to use it with intercalation electrodes like NMC and LTO as half and full cells.

3.5 3hr LiSPEEK liquid electrolyte with NMC and LTO Summary

All experiments until now have been about optimizing the electrolyte, which is by addition of salt, conductive liquid. Using the lithiated SPEEK in different forms (i.e coating, film, liquid electrolyte). Improving the lithiation method and then trying it in different forms. All these gradual iterations have given us the best possible electrolyte in 3hr LiSPEEK as liquid electrolyte. The aim is now to use this 3hr LiSPEEK with NMC and LTO in half and full cells, and examine their performance.

3.5.2 NMC and LTO with 3hr LiSPEEK liquid electrolyte and Lithium

Figure 3.12 (a) shows EIS curve for NMC with LiSPEEK liquid electrolyte and Lithium metal. After curve fitting of the EIS to obtain the resistance, conductivity value is found to be 1.3 mS/cm for 1.26 cm^2 NMC-Lithium electrodes and the thickness of the galss fiber separator was 0.0342cm.

Figure 3.12 (b) shows the EIS curve for LTO with LiSPEEK liquid electrolyte and Lithium metal. After EIS curve fitting, the conductivity is found to be 1 mS/cm for 0.71 cm^2 LTO-Lithium electrodes and the thickness of the glass fiber separator is 0.0342cm.

Figure 3.12 (c) shows the EIS curve for NMC with LiSPEEK liquid electrolyte and LTO. After EIS curve fitting the conductivity is found to be 1.4 mS/cm for 0.71cm^2 LTO-NMC electrodes and thickness of the glass fiber separator is 0.0342cm.

Figure 3.12(d) shows the base case of NMC with ECDEC liquid electrolyte and LTO gives conductivity values of 7 mS/cm for 1.26 cm^2 NMC-LTO with a glass fiber separator thickness of 0.0342cm.

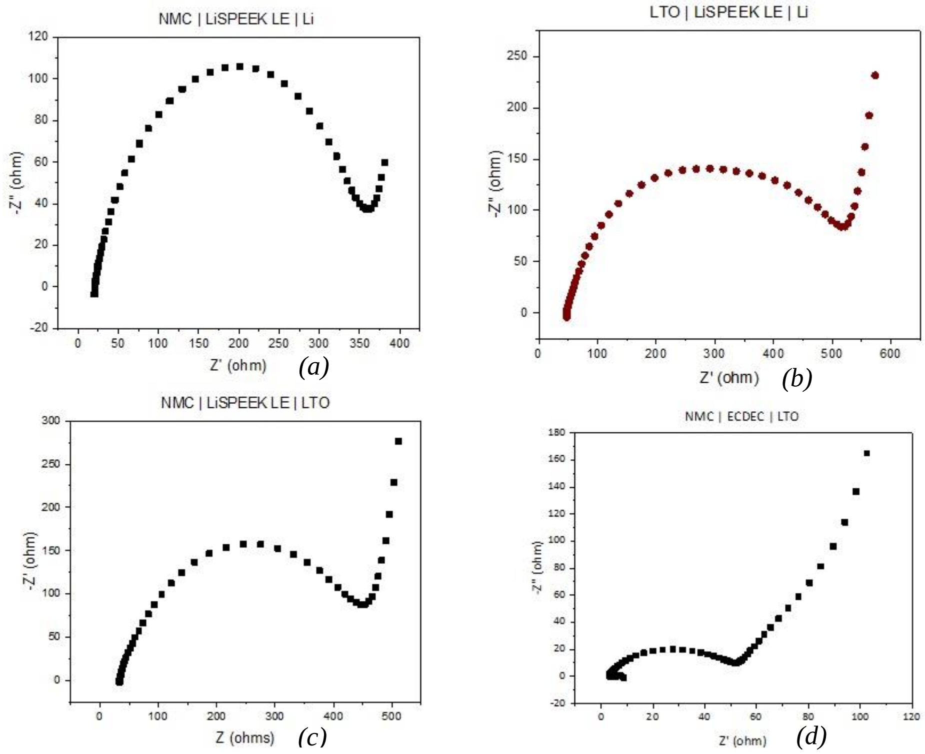


Figure 3.12: EIS curves for (a) NMC | LiSPEEK LE | Li (b) LTO | LiSPEEK LE | Li (c) NMC | LiSPEEK LE | LTO (d) NMC | ECDEC | LTO

Looking at these results, the conductivity values of the LiSPEEK liquid electrolyte combinations are very much in the range of the standard electrolytes and thus show a lot of promise for further experimentation with other intercalation materials. As stated earlier the problems of lithium metal in batteries, these positive results encourage more research for the use LiSPEEK with intercalation electrodes.

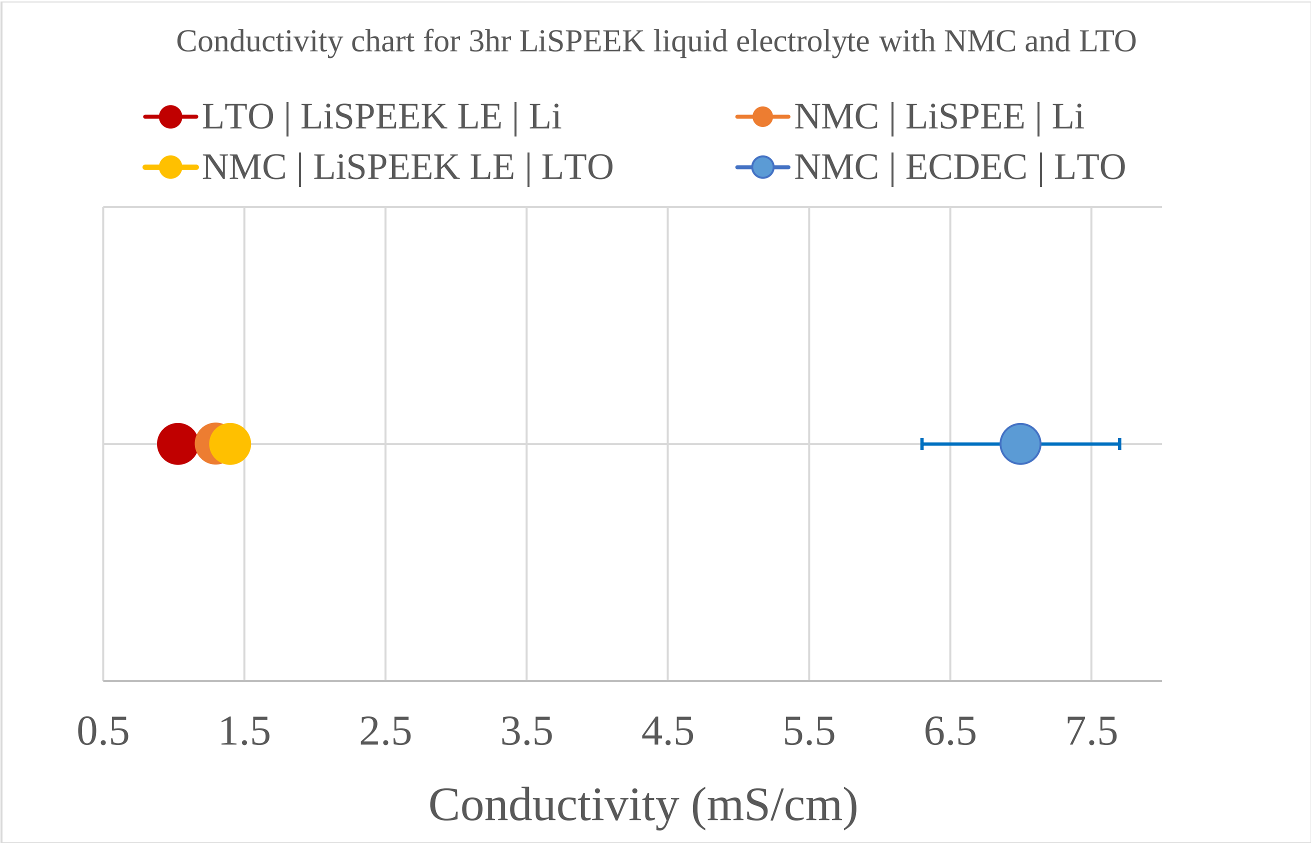


Figure 3.13: Conductivity chart for, NMC and LTO electrodes with LiSPEEK LE and ECDEC

4 Conclusions

Electrochemical performance of SPEEK and Lithiated SPEEK was studied. The goal of this thesis was to improve the electrolyte conductivity by using SPEEK along with other lithium salts and conductive liquids. Lithiated SPEEK was used as coatings, films, liquid electrolyte. Conductivity values were calculated for performance analysis of the batteries.

In case of SPEEK, SPEEK with LiTFSI, ionic liquid and LAGP was the best result with conductivity values in 10^{-5} S/cm, which is in range with the commonly used polymer electrolyte systems.[9][10] additionally the use of Lithiated SPEEK as a film showed improved interface resistance. The comparison of Overnight Lithiation at Room Temperature and 3hr Lithiation at 80 ˚C showed that the 3hr lithiation method provided better electrolyte conductivity.

In case of a lithium electrodes system with 3hr LiSPEEK as liquid electrolyte, provided the best result amongst all combinations, showing stripping and plating at 1mA/cm^2 current densities. These results are promising, but the use of lithium metal has its own shortcomings, dendrite growth and over a period the lithium electrode erodes and causes loss in capacity and performance in long term.

In order to mitigate the above-mentioned problems of lithium, intercalation electrodes like NMC and LTO were used. These electrodes along with LiSPEEK liquid electrolyte have shown promising conductivity values comparable to standard liquid electrolytes (EC:DEC).

In conclusion, LiSPEEK in DMSO as liquid electrolyte seems to be the best possible electrolyte amongst all combinations investigated in this thesis, thus reducing the cost of making the electrolyte (i.e without the addition of other salts and air sensitive materials) . The conductivity values of all the experiments were in the range of 10^{-2} to 10^{-5} S/cm for a gel, dry or composite polymer electrolyte, which is in the margin for commonly used polymer electrolyte systems, thus making it a feasible polymer for electrolytes [9]. If lithium metal is to be used in batteries then research must be done to protect the lithium from eroding by using coatings or other methods. The use of intercalation materials, NMC and LTO have shown a lot of promise in terms of conductivity and further research into such avenues need to be explored.

5 Recommendations

- Most of the combinations were copper-lithium along with the electrolyte. In all the cases the coating was on copper. A recommendation would be to try similar series of experiments with the coating on lithium and perform EIS to determine the conductivity, also intercalation materials like NMC, LTO can also be used.
- Other polymer materials like PVDF can also be used along with SPEEL/LiSPEEK with additional salts and a similar comparative study can be conducted.
- Another recommendation would be to use the LiSPEEK as a binder for intercalation materials and a comparative study can be done by changing the ratios of the LiSPEEK as binder to examine its performance. The use of LiSPEEK as a binder will be interesting to study as it can conduct ions as well.
- The use of LiSPEEK liquid electrolyte with NMC and LTO has shown promising conductivity values, an electrochemical study with other intercalation materials can be done to understand which material works best with LiSPEEK. The operando microscopy setup can be used to completely understand the interactions of the electrodes with the electrolytes.
- Apart from XPS, NDP can also be done to thoroughly examine the lithiation at the bulk of the film, as XPS itself is a surface examination method.

6 Bibliography

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Appendices

Appendix

A.1 Conductivity Calculation

Conductivity calculations were done by using the resistance values obtained after the EIS curve fitting done on AUTOLAB (the device/software used for measurements). Because of the high interface, resistance observed on the EIS and also the main goal of the thesis being the improvement of the electrolyte resistance the interface resistance (second touchdown point in the curve fitting) was not considered.

The Conductivity was calculated using the formula

$$\sigma = \frac{d}{S\text{x}\,R}\ \text{S/cm} \quad \text{(A1)}$$

Where the σ is for the conductivity measure in S/cm, d is the thickness of the electrolyte which is different in each type of electrolyte measured in cm. S is the area of lithium in contact with the electrode and electrolyte, measured in cm. R is the resistance value obtained from the curve fitting using AUTOLAB of the EIS.

As the electrolyte thickness keeps changing with the form of electrolyte used, in each calculation the corresponding thickness values are used. Also the area of lithium in contact with the electrolyte changes with the type of electrolyte used.

3hr LiSPEEK electrolyte coating on Copper.

i. 3hr LiSPEEK coating on copper d = 85microns (0.0085 cm), S = 0.25cm^2 , R(20̊ C) = 337Ω

   Using the equation A1 along with the data provided in i, gives $\sigma = 10$x 10^{-5} S/cm.

Similar calculations are done at (20̊ C, 40̊ C, 60̊ C, 80̊ C) for each combination using their corresponding electrolyte thickness and are of lithium in contact with the electrode and electrolyte.

A.2 SPEEK Composite Electrolyte EIS and Cycling plots.

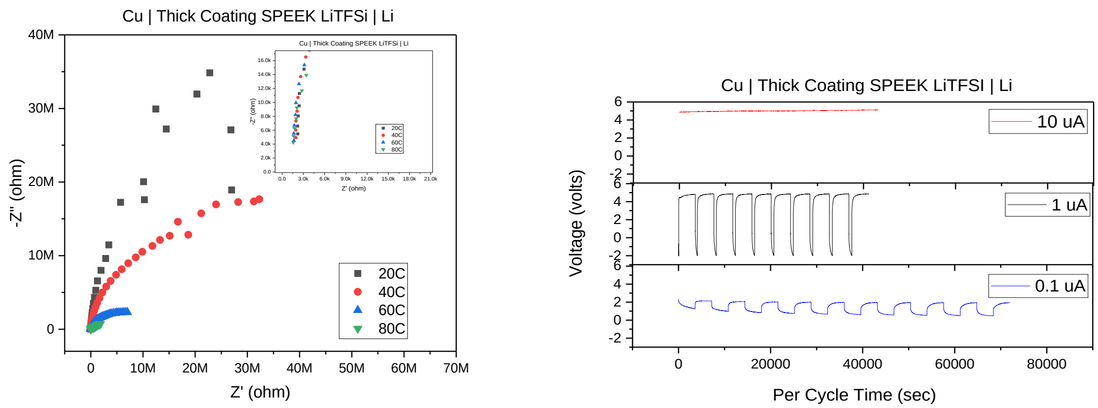

Figure A2.1 SPEEK with LiTFSI EIS and Cycling curves

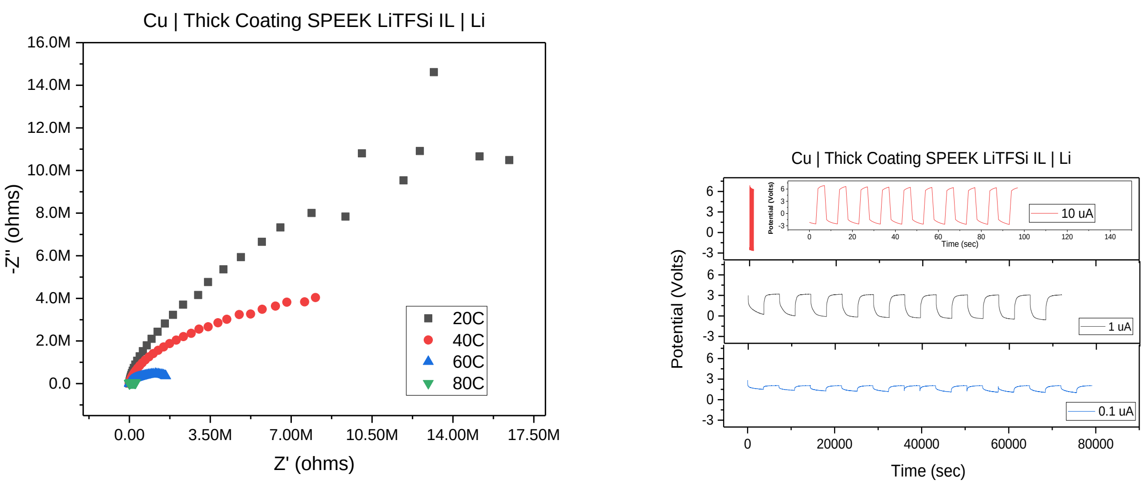

Figure A2.2 SPEEK with LiTFSI and IL EIS and Cycling curves

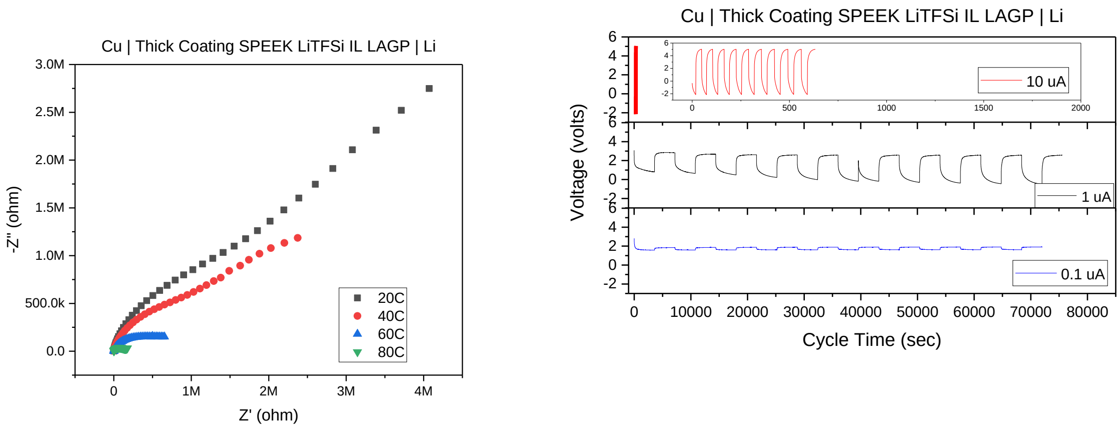

Figure A2.3 SPEEK with LiTFSI and IL and LAGP EIS and Cycling curves

A3 RT Lithiated SPEEK electrolyte

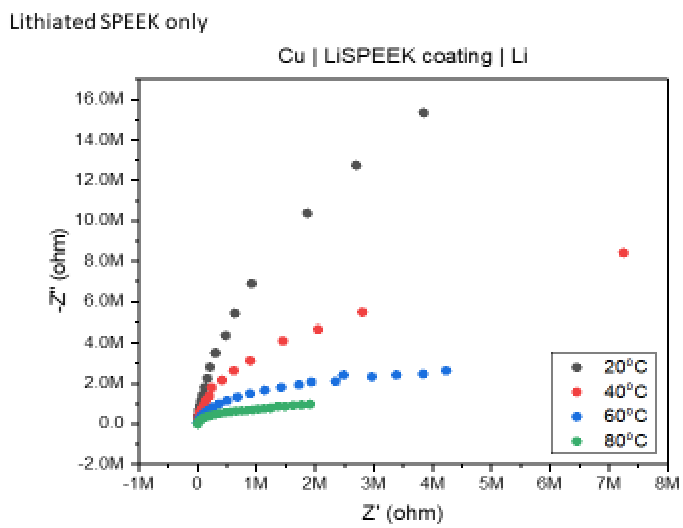

Figure A3.1 RT LiSPEEK EIS

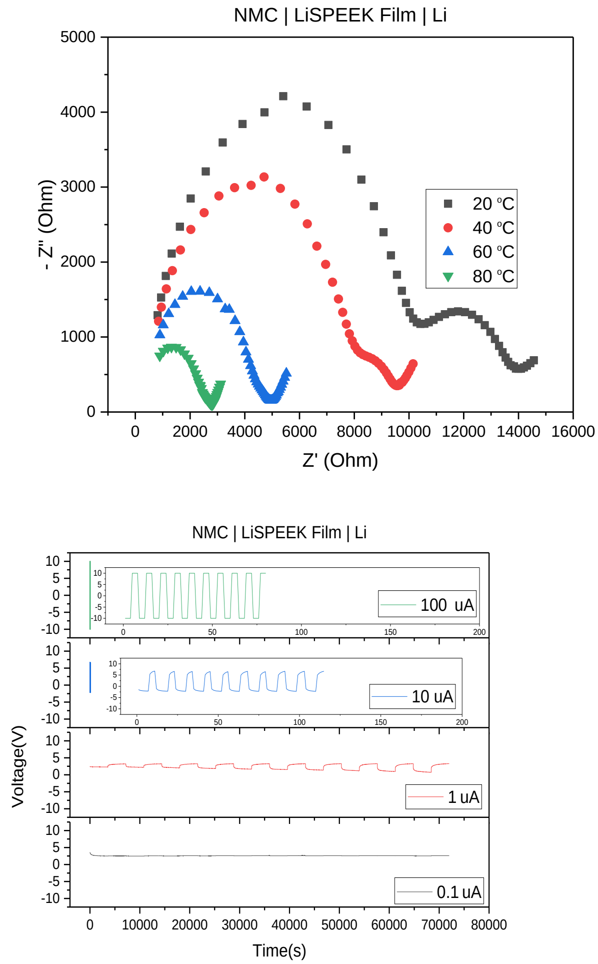

Figure A3.1 SPEEK with LiTFSI and IL and LAGP EIS and Cycling curves

A4 3hr Lithiated SPEEK

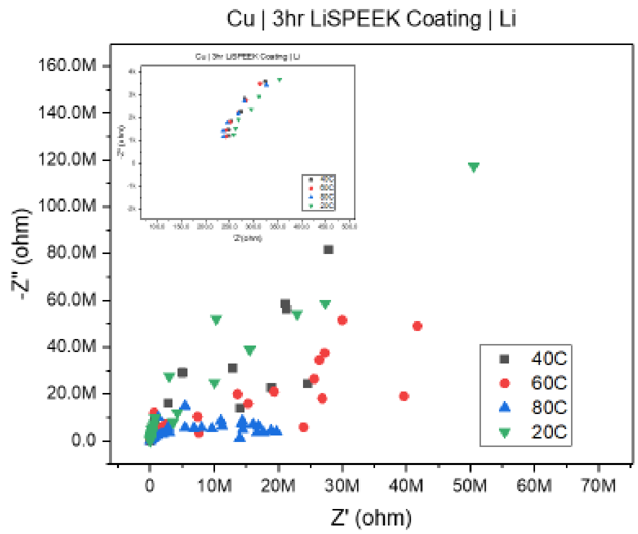

Figure A4.1 3hr LiSPEEK EIS

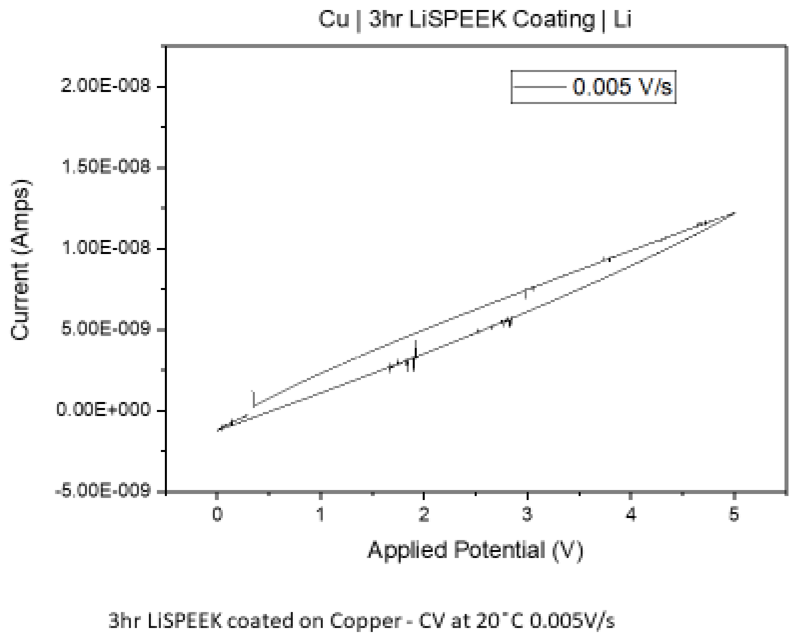

Figure A4.1 3hrLiSPEEK CV

A5 3hr Lithiated SPEEK with Lithium

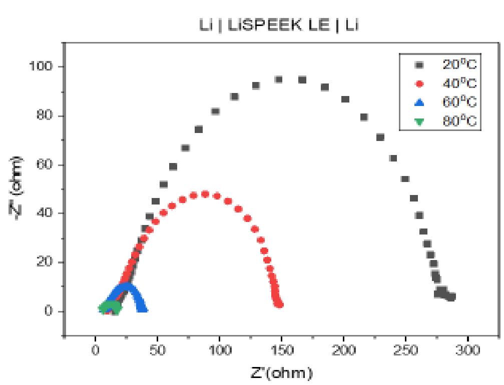

Figure A5.1 3hr LiSPEEK LE with Lithium electrodes EIS

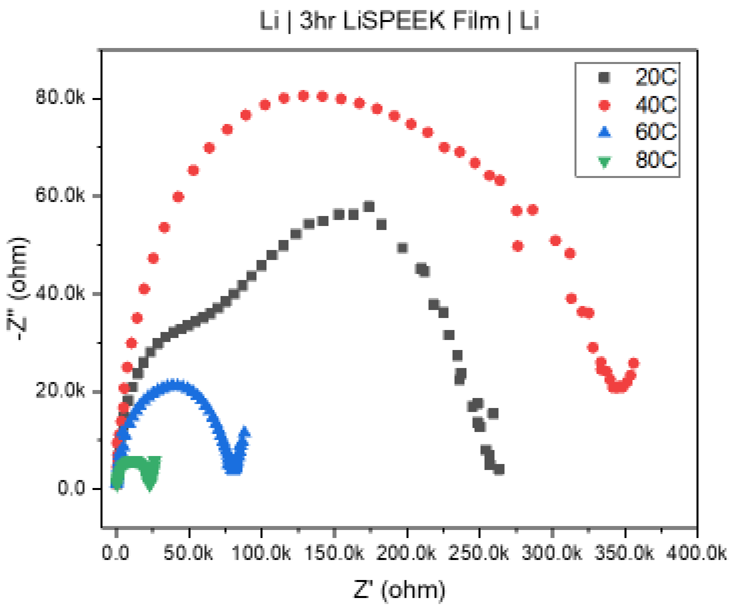

Figure A5.2 3hr LiSPEEK film with lithium electrodes EIS