

**An Analysis of the Effect of Absorbent Membranes on Electrochemical
Stability in Aqueous Li-ion Cells**

A Thesis

Presented to the Faculty of the Graduate School
of Cornell University

In Partial Fulfillment of the Requirements for the Degree of
Master of Science in Materials Science & Engineering

by

Sonya Sokhey

May 26, 2019

Copyright © 2019

Sonya Sokhey

All Rights Reserved

Abstract

Batteries have come a long way in terms of safety, portability, and energy density. Lithium-ion batteries are highly prevalent today and touted for their high energy density and rechargeability. One of the major drawbacks of lithium-ion systems are that they tend to be flammable. Since they are usually operated outside of their stability limits, flammability leads to catastrophic failure. Currently, almost all commercially available lithium-ion batteries are based on these systems. Water is a good solvent to use to bypass flammability. Water poses its own issues with stability such as its limited electrochemical stability window of 1.23V. A recent study from *Science* observed highly concentrated LiTFSI salt in water increased the stability window drastically, up to ~3.0V. One of the reasons this worked so well is because this salt is highly soluble in water. Using the principles of water affinity, in this study, we hypothesize that highly hydrophilic membranes with a lower salt concentration would yield an increase in stability window in a similar system. We found that a high molecular weight super absorbent membrane soaked in electrolyte with a swelling ratio of 14 on average, is able to increase the stability window of 5m LiTFSI by ~1.2V. Similarly, membranes of moderately high swelling ratios (~4–7) were also able to significantly increase the stability window of 5m LiTFSI. It was also found that a small addition of LiF to the electrolyte used in parallel with a membrane of moderately high swelling ratio is able to improve the stability window to a level on par with a high molecular weight membrane alone.

Biographical Sketch

Sonya Sokhey was born in Syracuse, NY to parents who lived in Ithaca, NY at the time. She was raised in Dayton, OH where she attended Northmont High School until 2012. Sonya attended the University of Cincinnati for a short while before enrolling at Wright State University. She interned at the university's terahertz & millimeter wave laboratory, and later, was a part of the additive manufacturing research group. In 2017, Sonya graduated with a Bachelor of Science in Physics & Mathematics. After an internship with the Air Force Research Institute at Wright Patterson Air Force Base, she moved to Ithaca, NY for graduate school at Cornell University where she pursued Materials Science & Engineering.

This work is dedicated to my father, Avtar Sokhey,
for whom I owe all my hopes, accomplishments, and dreams to.
He would say that knowledge is a gift to those who are humble enough to receive it.
You were right.
Thank you, dad, this is for you.

ਸਚਹੁ ਓਰੈ ਸਭੁ ਕੇ ਉਪਰਿ ਸਚੁ ਆਚਾਰੁ ॥

Acknowledgments

I would like to like to thank my advisor, Dr. Lynden Archer of the Robert Frederick Smith School of Chemical and Biomolecular Engineering at Cornell University. I am grateful to Dr. Archer for his patience. He became a true mentor of mine, and I learned so much from him. I would like to thank him for believing in me.

I would like to extend my deep gratitude to Sanjuna Stalin, whom without I would have not been able to complete this work. I would also like to thank Yue Deng, Qing Zhao, Shuke Li, and Snehashis Choudhury for their insurmountable help. Furthermore, I would also like to acknowledge the rest of the Archer Group for their support.

Finally, I must express my very profound gratitude to my mother and my sister for their love and support throughout my years at Cornell. I owe a special thanks to Megann Robinaugh who helped me make it this far.

Thank you.

Table of Contents

Abstract.....	iii
Biographical Sketch.....	iv
Dedication.....	v
Acknowledgments.....	vi
Table of Contents.....	vii
Introduction.....	1
Membrane Composition.....	7
Methods.....	13
Results & Discussion.....	19
Conclusion.....	26
References.....	27
Appendix.....	29

Introduction

One of the first descriptions of a battery was a capacitor-like device invented by Alessandro Volta. The invention was called an electric pile, which consisted of a stack of zinc and silver plates repeated up to forty times atop one another and separated by materials soaked in an alkaline salt or sodium chloride solution [1]. This was one of the first cases of such a device where it held its charge without external electricity applied, for it resulted in an output voltage until the water evaporated from the soaked material [1,2]. This is widely known as the first electrolytic cell, although it was a variation of a parallel-plate capacitor [2]. A parallel-plate capacitor is similar to a battery in which an electrically resistive material is placed between two charged conducting plates in that sense Batteries are mediums by which to store energy. A good analogy is a parallel-plate capacitor, Once removed from the circuit, it can transmit energy. Batteries are somewhat similar to a parallel-plate capacitor such that the electrolyte medium should not necessarily be a good electrical conductor, yet it should be able to store the electrical energy well. In fact,

Batteries have come a long way since Volta's time and several batteries with higher specific energy and power have been more available. The demand for miniaturization of technology was driven greatly by the need for portability and convenience. This demand took off after the silicon transistors were first incorporated into integrated circuits in the 1950s, and ever since, batteries have had to keep up with the miniaturization of such circuits [3]. For this reason, researchers looked for alternatives to polluting batteries that could also be made compactly, which led to the invention of the lithium metal battery in the 1970s. Concurrently, lithium-ion batteries were being

researched and became commercially available in the 1980s, and have been wildly popular ever since for their high energy densities of about $\sim 110\text{Wh/kg}$ as well as their energy efficiency of about 90% [2,11].

In lithium metal batteries the lithium metal itself is one of the electrodes and plates itself on either the cathode or anode depending on charging or discharging. Lithium-ion batteries differ from lithium metal batteries such that lithium ions are stored within the electrodes within intercalating layers [10]. This opens up doors for the use of materials that could otherwise not be available in lithium metal batteries, due to the reactivity of lithium. Lithium-ion batteries are particularly good at storing energy and they are touted for their ability to be rechargeable. The dielectric constant is a good indicator of how well a material can store electrical energy. Solvents with a high dielectric constant are generally more polar and therefore excellent mediums for ion transport [13]. Materials to create such a battery electrolyte are generally optimized to achieve the best possible conditions for a high dielectric constant, adequate energy density, specific density, and safety [24].

A stability window is the voltage range at which neither oxidation nor reduction occurs. A solvent with a wide stability window allows for the use of more energy dense electrodes which are the foundation of powerful batteries.

Common liquid electrolyte Li-ion batteries contain organic carbonate solvents for their high conductivities and their higher electrochemical stability window. An example such a battery is 1M LiPF_6 in a 1:1 ratio of ethylene carbonate (EC) to dimethyl carbonate (DMC) has a typical voltage stability window of about 3.7V and a conductivity of 10mS/cm [7]. Despite providing a large stability window, organic solvents like these have very low

flash points and are considered flammable. They are, therefore, a great deal more dangerous to use should a short circuit occur and ignite it [7]. Although lithium-ion batteries have a far lower environmental impact than alkaline batteries, the flammability of the aforementioned organic solvents are highly temperature dependent [11,12]. Should the cell overheat, thermal runaway leads to exothermic reactions such as fires and explosions. Furthermore, the breakdown of the common LiP_6 and EC:DMC electrolyte lead to the formation of other flammable substances and highly toxic alkyl fluorophosphate, which in the event of catastrophic failure, could spread to the surrounding area [12].

Because of the negative environmental impact of several current batteries, water-based aqueous electrolytes are an attractive option to avoid these issues. Additionally, water provides several advantages for use as a solvent. Unlike flammable organic solvents, water is non-flammable. It is a good choice because of its high dielectric constant, 80F/m, which indicates that it's extremely good at breaking ionic bonds [13]. Furthermore, it is a polar molecule which allows it to keep ions apart effectively through its ability to surround around them. Water also produces virtually no environmentally hazardous waste products, and would, therefore, make battery recycling far more efficient. Lithium itself is highly reactive with water, but in a lithium-ion system, water can be used as an effective solvent without a high risk of lithium fires. Catastrophic failure with water as a solvent is unlikely, but if occurred, would be far less hazardous than organic solvent containing cells. Finally, water is one of the most cost-effective solvents available, as it is readily available and easy to deionize.

The biggest downside to using water is that it is electrochemically unstable, as it has an extremely narrow stability window of 1.23V. Beyond this window, hydrogen and oxygen evolution begins to occur at the cathode and anode respectively. In order to truly make water a viable option in commercial Li-ion batteries, the stability window must be increased to accommodate more energy dense electrodes.

This work is motivated by a fascinating work in which water-based lithium-ion batteries were able to resist hydrogen evolution, the biggest pitfall of using water as a solvent in batteries. The authors showed the effectiveness of a “water-in-salt” electrolyte, where the ratio of salt to solvent was much higher than normal, as opposed to a salt-in-water electrolyte where the majority of the molecules are water. The “water-in-salt” cell study seemed only to be effective with a very high concentration of LiTFSI, or Lithium bis(trifluoromethanesulfonyl)imide, in water, and neither Li_2SO_4 nor LiNO_3 was effective, even at their highest possible concentrations in water respectively. Their maximum concentrations in water were ~3m and ~12.5m respectively, and even at the relatively high concentration of LiNO_3 , the highest stability window achieved was ~2.5V. Typical aqueous rechargeable batteries can only reach a stability of less than 2V [15]. Breaking through this limit, the authors found that in a near saturated aqueous solution of 21m LiTFSI produced a voltage stability window of 3.0V [14].

The authors suggested two reasons why this highly concentrated electrolyte worked so well. First, it is likely that the high solubility limit of LiTFSI (around ~606.9g/100ml) allows it to outnumber water molecules. This lowers the hydration number, therefore allowing the solvation shell and TFSI⁻ system is more likely to react at an electrode to form favorable molecules. LiTFSI forms a unique aggregate under

reduction at such a high concentration, such that one of its byproducts is LiF, a highly insoluble salt [in water], forms a thin SEI on the anode-electrolyte interphase. An anode-electrolyte interphase is useful because, in this case, it prevents water from reacting and destabilizing the battery. According to the authors' DFT calculations, salt-in-water electrolytes aggregate very differently under high concentration in comparison to low concentration. At low concentration, in the salt-in-water case, the TFSI⁻ ion reduces at a potential of 1.4V, whereas in high concentration, in the water-in-salt case, the TFSI⁻ ion aggregates with Li⁺ to form $\text{Li}_2(\text{TFSI})(\text{H}_2\text{O})_x$, which reduces at a much higher potential of 2.9V and consequently produces LiF, as mentioned before [14]. The significance of this is that since hydrogen evolution is already suppressed, $\text{Li}_2(\text{TFSI})(\text{H}_2\text{O})_x$ pushes that limit by simply being higher, but furthermore by forming a LiF SEI upon reduction [14].

According to "Water-in-salt," a high concentration of LiTFSI salt in water can lower the activity of water by reducing the water's presence in the solvation sheath. However, the main issue with this method is that the concentration required to achieve this effect is costly therefore financially inefficient means to utilize aqueous lithium salts in batteries. The purpose of this work is to further lower the activity of water in an LiTFSI-water electrolyte. The method to achieve this is by using superabsorbent membranes. Superabsorbent membranes are able to hold on to large quantities of water, up to several times their own weight. Using a hydrophilic polymer with a much lower concentration of LiTFSI may allow the same effect water-in-salt has on preventing water from reacting at electrodes.

In this work, an important topic is water affinity for a substance is when it is thermodynamically and electrochemically favorable for the substance be surrounded by

water. Water has the added bonus such that it is a polar molecule. Unlike dissolving nonionic solids where water simply breaks the relatively weak intermolecular bond, it has a high propensity to break much stronger ionic bonds. With ionic substances particularly, water surrounds and tears individual ions away from each other in a shell known as a solvation sheath. This solvation sheath effectively neutralizes the ion. This is important because, at the electrode interfaces, fewer water molecules will make contact with it, and would significantly reduce the onset of hydrogen evolution.

The opposite side of this argument is that perhaps the major source of stability wasn't the water-loving nature of the LiTFSI, but rather the SEI. A high concentration of LiTFSI in water produces a small amount of LiF, lithium fluoride, under potential difference. LiF is highly insoluble in water, soluble only up to about 0.13g/100mL in water. Suo et al found evidence that their 21m cells produced LiF and may have created anode-electrolyte interphase that prevented water from crossing it, thereby improving the stability [14].

Using superabsorbent membranes, a question we seek to answer in this paper is that can we exploit the diffusivity of the system to explore the possibility that higher diffusive boundary could yield similar results at a lower concentration. As a supplementary study to this, we will investigate the presence of lithium halides (LiX) in a lower concentration of LiTFSI to explore whether it can provide the same SEI effect that 21m LiTFSI does.

Membrane Composition

The membrane backbone was composed of poly(ethylene glycol) dimethacrylate (PEGDMA), as depicted in figure 1c. PEGDMA is a difunctional polymer that is easy to crosslink, and it also happens to be water-soluble. Its water solubility makes it easy to process and ensures fewer impurities are in the final product. Furthermore, its water-solubility indicates that water is attracted to it on a molecular level, therefore it was more likely to be absorbent.

The base polymer used was of molecular weight 3400 g/mol, and was prepared in house. First poly(ethylene) glycol ($M_n=3400$) (purchased from MP Biomedicals) was vacuum dried just below 60°C overnight to remove excess moisture. The dry PEG was dissolved in 150ml anhydrous dichloromethane in a round bottom flask under an inert argon environment. Then, triethylamine and methacryloyl chloride were sequentially added slowly via pipette. A rubber stopper was used to secure the system and the mixture was stirred at room temperature overnight. The mixture was transferred to a separator funnel and was washed by 2M K_2CO_3 solution several times. After allowing the layers to separate overnight, the organic layer was isolated, dried by anhydrous $MgSO_4$ and filtered. The filtrate was precipitated in diethyl ether and washed several times, vacuum filtered and vacuum dried overnight. The resulting powder was the PEGDMA used in the majority of the membranes. Additionally, 8000 g/mol PEGDMA was used alone and will be denoted polymer E (purchased from Polysciences). All polymers mentioned were crosslinked using a water-soluble crosslinker, 2,2'-Azobis(2-methylpropionamidine) dihydrochloride, 97% (purchased from Sigma Aldrich).

To prepare the uncrosslinked polymer solution, the dry polymer blends¹ were dissolved in water at a concentration of about 1g of blend per 1.2mL of water at ratios denoted in table 1. It was then mixed with ~0.75% crosslinker. To form even membranes, the uncrosslinked solution was dropped onto glass slides that had been wiped with a thin layer of polydimethylsiloxane, or silicone oil, to prevent sticking, and was sandwiched with another oiled glass slide, separated with spacers of a known thickness. Silicone oil was used because it is highly hydrophobic and it does not contain the necessary methacrylate functional groups to interfere with membrane crosslinking. To remove the excess silicone oil from the membrane, it was submerged in water and gently scraped with forceps several times before being left to soak in water for several hours to allow the remaining silicone oil to float to the top. All samples were crosslinked under 400nm UV light. This process was used for all iterations of polymers.

The goal was to create a polymer that was as absorbent as possible and compare this against the others in terms of swelling ratio, where the swelling ratio is the ratio of water absorbed to the dry mass. However, it was quickly noted how brittle and weak the swollen membranes were. The fragility becomes a problem when sealing coin cells, as pressure must be applied to do so. Although some damage will occur to the membranes during sealing no matter what, an additional goal became to create a polymer that absorbs a lot of water, but without as much fragility.

Polymer A was used as a baseline to compare against any improvements on its swelling abilities, where polymer A PEGDMA of molecular weight (MW) 3.4K.

¹ See appendix for complete ratios of polymers used in each blend.

Polymer B was utilized partially functionalized 10K PEGDMA, to create larger pores in the membrane that would take in more water. This membrane increased swelling with respect to polymer A by about 30%, as shown in Figure 1.

Based on Jian Ping Gong's work on double networks, polymer C included 50% by weight of Poly(2-Acrylamido-2-methylpropane sulfonic acid) solution that was 15wt% in water (purchased from Sigma Aldrich)². This polymer is abbreviated PAMPS. Gong first created the double network in 2010 [16,17], where she used a primary network of a rigid backbone polymer that would make up the main structure of the network, and a secondary network of a loose and ductile polymer. Double networks have been shown to be significantly stronger than ordinary hydrogels, even when swollen, and are able to extend the swelling ratio of the backbone polymer [16]. For this reason, this method was chosen for polymer C and D. In polymer C, PEGDMA was the rigid component and PAMPS was the ductile component as it only ionically crosslinks with itself. Polymer C had a swelling percent of about 60% greater than that of polymer A, and was able to hold up to an average of 8.24x its own weight but as much as 9.58x its weight [17].

The final polymer, denoted polymer D, contains a zwitterionic salt with an acrylic group. The salt itself is called [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide in its entirety, but abbreviated DMAPS and is also a part of a larger group of zwitterionic salts called sulfobetaine methacrylates. Sulfobetaines are heavily used in the biomedical field to improve medical device adhesion and prevent bacterial and mold growth, as well as in nautical applications as antifouling agents. It is

² See appendix for table 1 for more information.

also known for being hydrophilic [18,19,20]. In its ionic form, it contains a positive and negative charge on the same molecule in the form of nitrogen and oxygen atom respectively. This is desirable because, in theory, it increases the absorption of water if it can be attached to the walls of the polymer, which it can due to its methacrylate group. The reason water absorption occurs is due to capillary action, where the electrostatic attraction between water molecules and the inner surface of the polymer is stronger than that of the attraction between water and itself. However, the results indicate that the swelling behavior of polymer D is quite similar to that of C. This may be due to the decreased availability of methacrylate groups for the zwitterion to bond with.

When overserved in Fourier-transform infrared spectroscopy (FTIR), the profiles for each membrane are not very different from one another. However, there is a clear difference in swelling ability, so the bonds expected, but missing from the FTIR, *must* be there. The reason many of the bonds may not present themselves in FTIR is that in respect to PEGDMA, there isn't very much of any other type of polymer. In the case of polymer D where it contains both DMAPS and PAMPS, the expected sulfur-oxide bonds don't show up because the vast majority of the bonds are carbon-based bonds, and in a tangled polymer such as polymer C and D, reading a clear transmitted frequency without noise or obstruction is difficult.

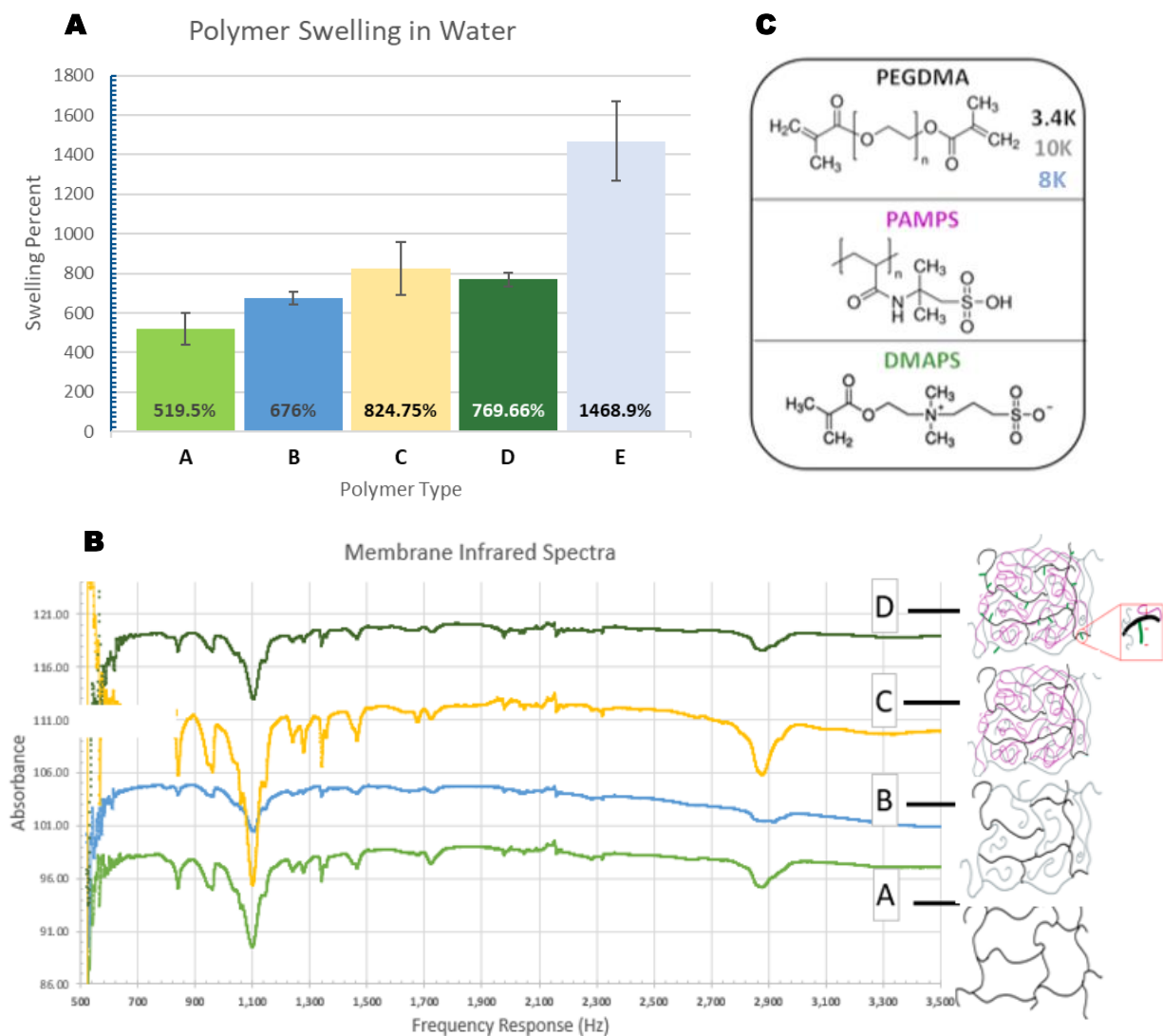


Fig. 1 (a) Swelling ratio of membranes used in water. (b) Infrared spectra of membranes and their corresponding structure. (c) Molecular structures of primary membrane components (*Molecular structures courtesy of Sigma Aldrich*), and legend to diagrams in figure 1b.

Polymer E performed the best out of all other polymers because it contains the longest polymer chains. The swelling ability of a polymer is intrinsically limited by the shortest chain length. When submerged in water, water diffuses into the membrane with ease because there is a lot of pores, and PEGDMA itself is hydrophilic. The water exerts a force on the polymer chains, prompting them to stretch to accommodate it. Eventually,

the polymer chains can no longer uncoil any further because the shortest chains are already fully uncoiled. The purpose of double networks is to reinforce otherwise rigid structures that would place all the stress of solvent swelling onto the shortest chains. The secondary network in the double network allows some of the stress that water absorption causes on the rigid PEGDMA polymer chains to be alleviated by the long and ductile PAMPS chains. This allows *all* of the chains to fully stretch, as they are no longer limited by the shortest chain, thereby allowing more water into the system.

Ultimately, an absorbent polymer's ability to intake solvent is limited by its molecular weight, and more accurately, its chain length [16]. The longer the chain the more water a fully crosslinked 10K PEGDMA matrix could intake, in theory. In practice, functionalizing long polymers requires a longer time and larger amount of photoinitiator to ensure the final product works.

These membranes are holding somewhat more liquid than would a standard battery separator, and that in and of itself would increase the ion density. For example, polymer A holds about 4.55g of 10m LiTFSI per centimeters cubed, whereas polymer E holds about 15.9g of LiTFSI per centimeters cubed, but both compared to a paper separator of similar diameter, holds only ~0.1414g per centimeters cubed on average. Compared to absorption in just water, these polymers never absorb more than 300mg of fluid at their current size.

Methods

In order to observe the stability windows of the system, linear sweep voltammetry (LSV) was performed on all samples. LSV works by stepping the voltage at a chosen rate and measures the current response at the working electrode. It is similar, in that regard, to cyclic voltammetry. In this case, the scan rate was chosen to be 10mV/s for consistency of comparison with other works that chose this rate. 10mV/s is a moderate scan rate that does well at controlling oxidation and reduction speed, ensuring reactions do not occur too quickly nor too slowly. For this purpose, symmetric steel cells were used. A steel symmetric cell limits the effects of the electrodes on the electrolytes so that the electrolyte can be studied essentially independently of the electrodes. Steel does not participate in reactions with the chosen electrolytes, but it is an adequate current collector for this study.

Each membrane-free electrolyte sample was soaked into a thin (0.18mm) cellulose paper separator with a pore size of $\sim 11\mu\text{m}$. For electrolyte-soaked membranes, the membrane itself was used in place of the paper separator. The main purpose of conducting linear sweep was to determine the stability window of the electrolyte. The electrochemical stability window from LSV graphs present themselves as a nearly zero current flat line between where neither oxidation nor reduction occurs. The arbitrary nature of measuring the stability window makes it difficult to decide where stability occurs. A common way of deciding the stability window is through the use of a cut-off current in which a current above and below are set such that voltages outside of it are considered unstable. As stated by Mousavi, this method “assumes the current arises exclusively from electrolyte decomposition,” which is not always realistic to assume [21]. The method described in Mousavi et. al known as the linear-fit method in which linear fit lines are

drawn between the stable edge and oxidative or reductive drop-offs respectively. The point at which the two lines meet is considered the start or end of the stability window. This method is repeated for the derivative $\frac{di}{dV}$ of the plot and the comparison between the two decides where stability ends and begins. Since this was the most quantitative approach, it was used in this work to determine the stability window.

Using the linear-fit method, within the plot derivatives of membrane-containing cells, there is occasionally an aberration that can only be described as a “bump”, at around -1V where some reaction takes place but the cell does not react completely at the electrode yet. If this bump were to be considered unstable, the stability window would hover around ~0.15V higher than the stability limit of the respective no-membrane system. The reason for the existence of the bump in the derivative plot is likely due to the thickness of the membrane. The conductivities of the soaked membrane samples are generally in tandem with a higher $\tan(\delta)$, in comparison with those without membranes. $\tan(\delta)$ here is a measure used to find conductivity that describes how electrically lossy the system is. This is an indicator that the polymer membranes themselves are insulting, or rather have a low dielectric constant [23]. The thick membrane between the metal electrodes may be yielding capacitive current because diffusion is not as steady through the membrane than it is without [13,21]. Furthermore, a vast majority of the derivatives did not do this as the phenomena were only observed in 21m membrane cases. For this reason, the upper stability estimate was not ignored, considering only extreme current spikes unstable.

Before any further tests were conducted, the conditions in the original paper were replicated, such that 1m, 5m, 10m, and 21m LiTFSI solutions were made and soaked separator paper and LSV was conducted cells, as shown in figure 3a. In figure 3a, the y-

axis is current over electrode area, or current density; however, in figure 3b, the y-axis is in units $\left[\frac{\text{mA}}{\text{S cm}}\right]$, which is the current density normalized over each sample's respective ionic conductivity.

The system was normalized this way because, in order to compare the current for such dramatically different concentrations of ions and mediums, the currents had to be normalized over each systems' propensity to transport ions across a potential difference. The conductivity [S/m] of an ionic solution is defined by:

$$(1) \quad \sigma_{ion} = \frac{Nq^2D}{k_B T}$$

where N is the number of ions, q is the charge, k_B is the Boltzmann constant, T is temperature, and D is diffusivity [29]. And a simplified variation of the Butler-Volmer equation is described by:

$$(2) \quad i_{lim} = \frac{zFD}{\delta} c$$

Where i_{lim} is the limiting current density, z is the number of electrons with an ion, F is Faraday's constant, D is the diffusivity, c is the ion concentration in a solution, and δ is the diffusive boundary layer thickness [30].

The conductivity is highly dependent on the diffusivity, which in turn, is dependent on the viscosity of the fluid. Similarly, the Nernst-Planck equation, which describes diffusive flux within an electrolyte, is also directly dependent on diffusivity as well as concentration [29]. Furthermore, the limiting current is defined as the current at which the rate of reduction and oxidation at electrode interfaces becomes constant. This is related

to the electrochemical stability of the cell and gives a value that describes how the electrolyte and its properties limit charge transfer and to what extent.

Ideally, we would normalize the current density over the limiting current density itself to accurately normalize over changes in electrolyte properties. However, since it is not straightforward to measure it, we must find an alternative. Naturally, conductivity becomes an attractive option. Since the current measured in all battery tests is limited by the properties of the electrolyte itself, and the speed by which ions can react at electrodes, the ionic conductivity becomes the clear variable that describes this best.

The systems in question are very different from one another when it comes to how effectively they can transport ions, so naturally, normalizing over conductivity is an effective way of minimizing differences in diffusivity, viscosity, and ion speed affecting the results.

Each membrane, as well as each electrolyte, has its own conductivity, which both affect the current response measured during linear sweep. Measuring them together exactly how they appear in the system allows us to understand their respective behavior as ionic conductors and therefore normalizing the current eliminates this as a subject of contention. For example, the conductivity of a membrane-containing cell was measured together in the same type of coin cell set up as mentioned previously.

Because conductivity is a measure of a rate of charge as a function of voltage, the normalization turns out to be $\left[\frac{\text{mA}}{\text{S cm}}\right]$, or a unit of order $\left[\frac{\text{V}}{\text{m}}\right]$. This unit is equivalent to electric field strength. Curiously, with an increase of conductivity, the normalized y-axis tends to decrease in magnitude. This is an indication that the easier ions are able to flow in the

system, the less far-reaching the field is, and the lower the electrical force on each electrode will be. This turns out to be positive because a lower and more controlled rate of flow to electrodes produces an essentially more stable battery by damping fast reactions.

A 3-electrode system for 1m LiTFSI was conducted to adequately find the bounds at which reduction and oxidation occur. In a 2-electrode set-up, there is no reference electrode, so the voltage axis has no real meaning as there is no known reference value as to interpret it by. However, the voltage stability window itself remains the same as the with the 3-electrode system. The 3-electrode system, on the other hand, allows the reduction and oxidation potential values to be meaningful and compared with systems of other electrodes. Within three-electrode systems tested, the reference electrode chosen was 1M KCl with Ag/AgCl electrodes. The 3-electrode 1m LiTFSI data was used to extrapolate the equivalent voltage in terms of Li/Li⁺ with reference to steel-steel electrodes (denoted St/St here). Zero voltage with reference to St/St turns out to be approximately equal to 2.796V in reference to Li/Li⁺. The equation that was extrapolated for conversion to the Li/Li⁺ axis is described by:

$$(3) \quad E_{\text{Li}/\text{Li}^+} = E_{\text{St}/\text{St}} + (2.796\text{V} \pm 0.26\text{V})$$

In comparison to data from this work and similar data, the approximation stands accurate [14].

Finally, floating point tests were conducted. Floating point tests differ from linear sweep tests such that instead of very quick scan rates of 0.01mv/S, the scan rate is incredibly slow, held at one voltage for three hours. Floating point tests also require working electrodes rather than just steel. The purpose of floating point tests is to allow the electrolyte to fully react under a realistic system where long-term constant voltage is applied. Figure 3 depicts an example of a floating point test that was performed in this study.

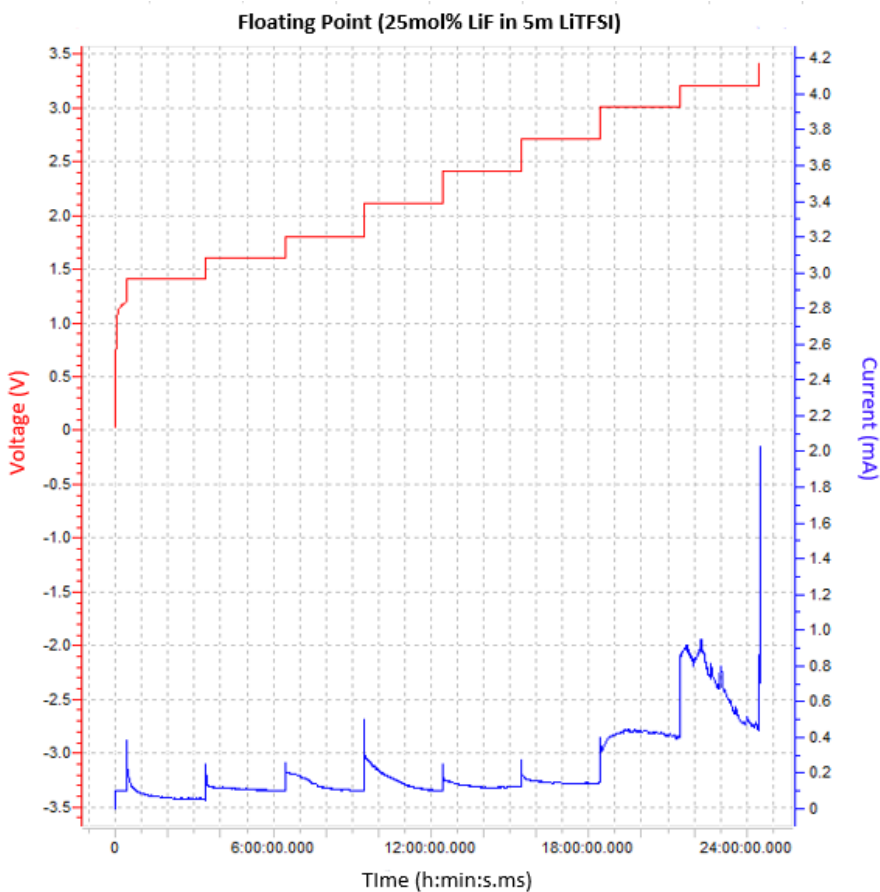


Fig. 2 Depicts a floating point test result of the cell containing 25mol% LiF in 5m LiTFSI with no membrane. The

Based off of previous studies, the electrode capacity of all electrodes used in this work remains constant with a change in capacity [31,32]. This allows us to assume that the potential of the battery does not change significantly during the experiment and we

are therefore able to convert the voltage measurement into a different reference (Li/Li⁺). This is true namely for namely, (Lithium titanate) LTO, (Lithium iron phosphate) LFP, (Lithium nickel manganese oxide) LNMO, and carbon cloth. In figure 3, the oxidation point corresponds to around 1.8V to 2.1V which occurs at about 6 hours. The electrodes used in this cell were LTO as the anode and LFP as the cathode. When converted to a reference of Li/Li⁺, the oxidation is about 3.8V to 4.1V which is consistent with the floating point measurements shown in The extrapolated oxidative stabilities are generally in agreement with the linear sweep results in all cases.

Results & Discussion

Observing the replicated results from the original paper in figure 3a, it is apparent that, in general, the results generated from LSV are in agreement with the original. In figure 3, the only point of contention is that the 21m case turned out to be 2.85V on average, whereas 3.0V was captured in the original paper [14]. However, 3.0V is well within the bounds of error in the data in this work. Overall, we can conclude that the conditions for creating a water-in-salt cell are reproducible. When observing figure 3b, the stark difference between the salt-in-water electrolytes (1m, 5m) and the water-in-salt electrolytes (10m, 21m). The conductivities of the water-in-salt electrolytes is lower than that of salt-in-water (see Table 2)³. This is likely due to the viscosity induced by a high concentration of ions impairing flow by overcrowding the free space in the system. As

³ See Appendix for full list of conductivity values.

discussed before, viscosity impaired diffusivity, which in turn, reduces the conductivity, so this behavior is expected.

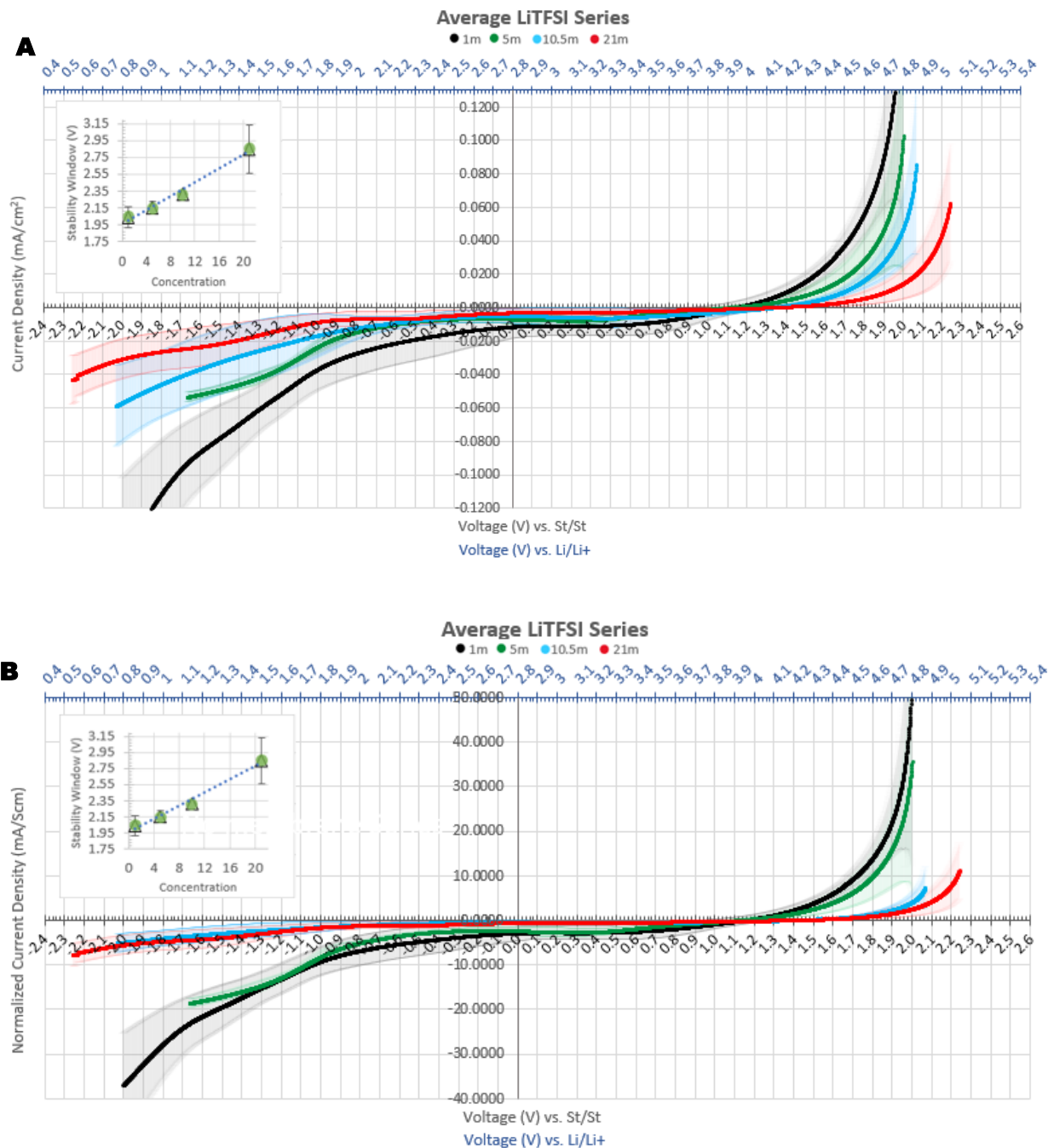


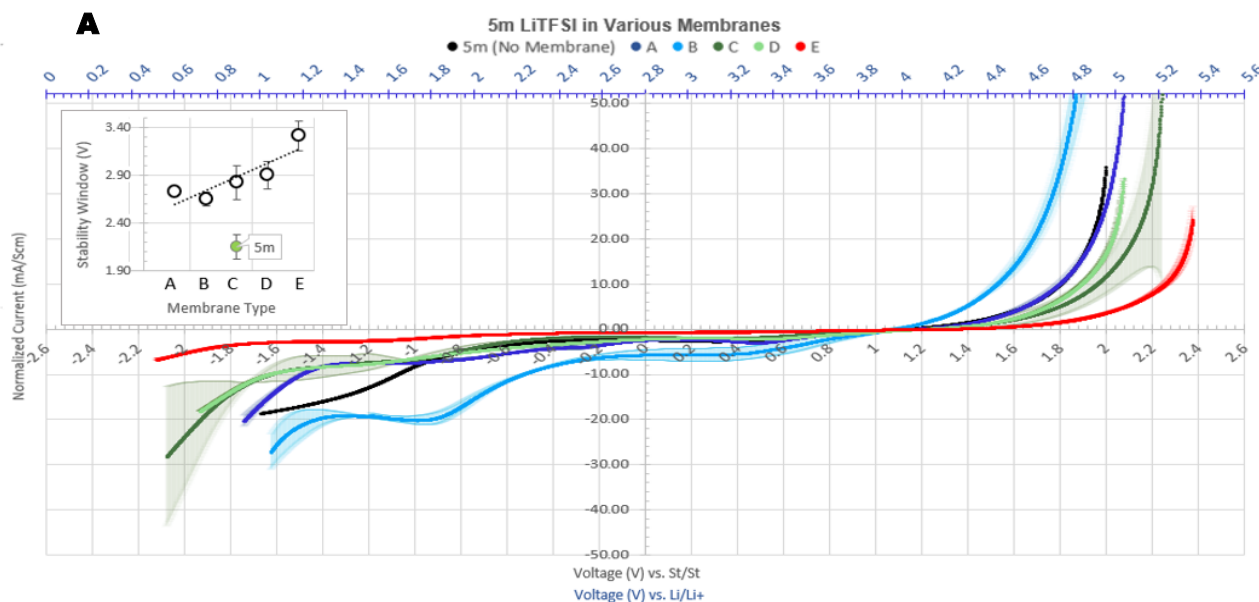
Fig. 3 (a) Average LiTFSI series normalized over respective conductivity. (b) Average LiTFSI series without normalization. The shaded area represents the error bars of the averaged series.

Next, we compare membrane-containing cells with one another on the basis of swelling ratio, denoted the constant concentration series. This is depicted in figure 4a, where 5m LiTFSI was chosen as the constant electrolyte and all five membranes were measured. We hypothesized that because 21m LiTFSI performed well electrochemically due to its high solubility parameter, similarly, a polymer with an ability to attract water to a high amount would also increase electrochemical stability. We can see that this is the case. The membranes with lower swelling ratios performed well electrochemically using the linear-fit method, however, they clearly deviate from the stability window more severely than polymer E, and even 5m LiTFSI itself. This may be due to the structural weakness of these specimen, as discussed before, that may damage the cell upon sealing. Even so, in comparison to 5m LiTFSI with a paper separator, the electrochemical stability is increased from 2.2V to 2.7V with polymer A, which has the lowest swelling ability of all five polymers. Polymer E, on the other hand, is able to drastically increase the 2.2V up to 3.4V. This is apparent in the graph when observing that polymer E (red) reduces and oxidizes later and less severely than the other polymers.

The constant membrane series in figure 4b represents the electrochemical plot of polymer D being soaked in all four of respective electrolytes. Similar to the constant concentration case, the most concentrated electrolyte in polymer D yields a similar stability window on average with that of 5m LiTFSI in polymer E. 1m LiTFSI is able to be brought to a stability of 2.7V on average from 2.0V. Comparing both figure 4a and 4b, we can see that the membrane has an effect on the stability.

The membranes increase the electrochemical stability in part due to their ability to carry more fluid in the same amount of space, thereby increasing the

concentration of ions in the system. However, when swelling ratio is compared with the amount of fluid absorbed into the polymer, the most stable cells did not always have the most fluid. The membranes increased stability more likely because their complex capillary systems made it difficult for water to escape the membrane within a closed cell. Without air flow or any other place to diffuse to, the water in the system has less thermodynamic drive to escape the membrane, even under a potential difference.



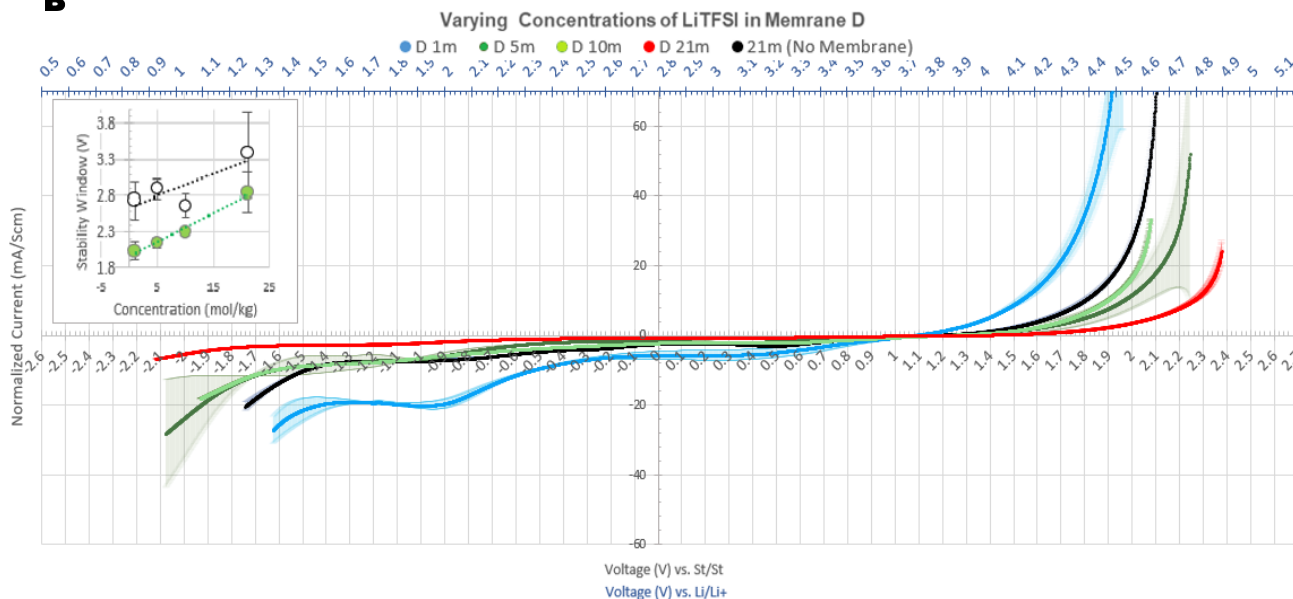
B

Fig. 4 (a) Constant electrolyte case, 5m LiTFSI soaked in all five membranes (A, B, C, D, & E). (b) Constant membrane case, Polymer D soaked in all four electrolyte concentrations (1m, 5m, 10, and 21m LiTFSI) and their respective electrochemical curves. The green circles represent the no-membrane LiTFSI series, whereas the white circles represent the windows depicted in each respective graph.

A concurrent experiment to study the effect of lithium halides on stability was conducted as well. Alkali metal halides are known to be highly ionic due to their high electronegativities. Lithium halides (LiX) have been used as additives in lithium metal batteries in the past. They have been shown to stabilize electrodeposition and suppress dendrite formation [25,26,27]. Lithium halides have a lower diffusion barrier than common SEI's such as LiOH and Li_2CO_3 in nonaqueous PC/LiTFSI systems [25]. They form SEI's with lithium metal at the interface near the anode, and for this reason For this reason, as an SEI in lithium metal batteries, lithium halides would allow faster diffusion of lithium ions through the barrier [26]. Since the main reason explored in other works as to why LiTFSI works so well to increase the stability of aqueous electrolytes is because LiF is produced,

a secondary question presents itself: what effect do LiX have on aqueous Li-ion systems [14]. The salts examined here will be lithium halides, particularly LiF, LiCl, and LiBr.

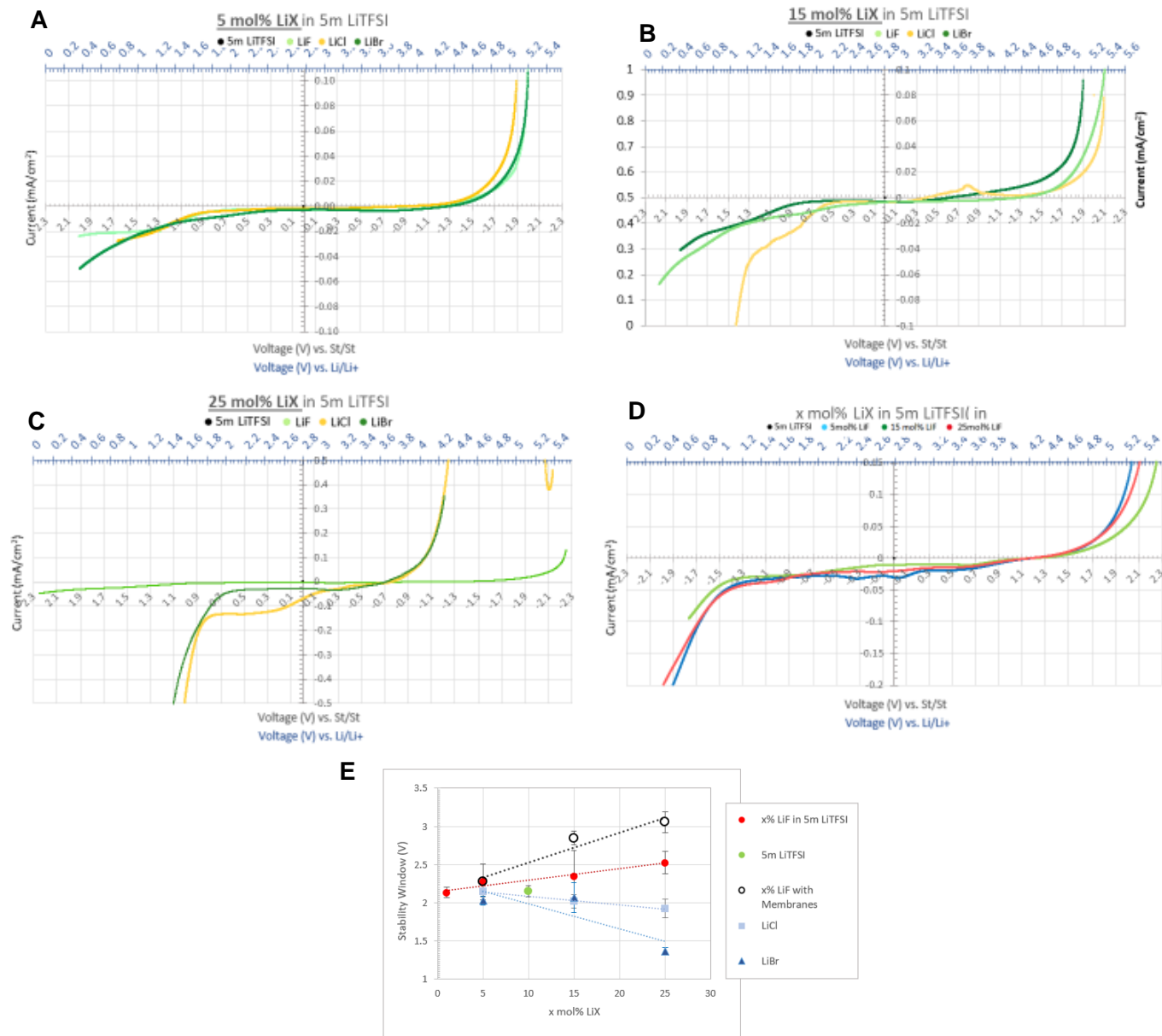


Fig. 4 (a) 5 mol% of LiF, LiCl, and LiBr respectively. (b) 15 mol% of LiF, LiCl, and LiBr. (c) 25 mol% of LiF, LiCl, and LiBr. (d) LiF, the best performing halide, soaked in membrane D. (e) A comparison of lithium halide performance.

Unlike previous work where a mole fraction of LiX was replaced in a preexisting electrolyte mixture to have a total fraction of 1, in this work, a mole percentage of LiX was simply added to a known quantity of electrolyte, particularly 5m LiTFSI.

In figure 5, LiBr is somewhat stable for both 5 mol% and 15 mol%, however, there is not a significant difference between these two percentages in terms of stability. There is a slight increase in stability with respect to 5m LiTFSI, however. Furthermore, at 25 mol% addition of LiBr, the stability drops suddenly and severely. Other studies have found that LiBr as an additive increases stability in dilute LiTFSI in propylene carbonate, so it is possible that it LiBr interacts with water differently than it does so with ether-based solvents [26, 27]. LiCl does not change the stability of 5m LiTFSI for the better and steadily decreases its stability with each consecutive addition. LiF additions, however, do exhibit a notable improvement in stability from 5m LiTFSI on its own. The addition of 25 mol% LiF is able to increase the 2.2V window of 5m LiTFSI up by about 0.3V on average. This is a small change, however, it is an indication that what is done in a water-in-salt case with LiTFSI, can be accomplished with a lower concentration of electrolyte. The primary difference between these halides are their solubilities, as LiCl and LiBr both readily dissolve in water, but LiF does not. In fact, it forms a cloudy solution when added to the electrolyte rather than a clear one like LiCl and LiBr do. This is significant because it specifies that it may be the insolubility of LiF that makes it especially useful as an additive here, physically preventing water from degrading at electrode interphases.

Finally, we apply LiF additive electrolytes to membrane D. We are able to see a tremendous increase in stability as shown in figure 5e. At the highest addition of LiF, there is an increase of stability of 5m LiTFSI by about 0.7V on average, making its stability on

par with the original water-in-salt 21m case. This is significant because it yields another way to increase the stability of a relatively low performing electrolyte cost effectively.

Conclusion

Super absorbent membranes swollen in a lower concentration of aqueous LiTFSI radically increase the electrochemical stability window of water. Membranes with a high swelling ratio significantly increase the stability window of 5m LiTFSI so much so that it performs better than 21m LiTFSI by 0.4V on average. Furthermore, the addition of a small amount of LiF in 5m LiTFSI increases the stability window without the need for a highly concentrated LiTFSI solution. increase Further studies on the subject using lower molecular weight membranes and higher concentrations of LiF should be conducted to learn more about how swelling ratio affects electrochemical stability. To conclude, these developments provide an exciting prospect for the future of water-based Li-ion batteries, such that they may be used to make water a commercially viable solvent.

References

1. Volta, A. (1832). On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds. Abstracts of the Papers Printed in the Philosophical Transactions of the Royal Society of London, 1.
a. doi: <https://doi.org/10.1098/rspl.1800.0016>
2. Scrosati B. (2011). History of Lithium Batteries, *Journal of Solid State Chemistry*, 15(7-8), doi: 10.1007/s10008-011-1386-8
3. Peercy P. (2004). The drive to miniaturization, *Nature*, 406(6799),
a. doi: 10.1038/35023223
4. Aoshima K, Horiguchi H. *Cadmium Toxicity*, 1st Ed, Springer, 2019.
5. Barsova N. (2019) Current state and dynamics of heavy metal soil pollution in Russian Federation—A review, *Environmental Pollution*,
doi: 10.1016/j.envpol.2019.03.020.
6. Sun H, (2010). *Transactions of Nonferrous Metals Society of China*, 20(2),
doi: [https://doi.org/10.1016/S1003-6326\(09\)60139-4](https://doi.org/10.1016/S1003-6326(09)60139-4)
7. Goodenough et al. (2010). *Chemistry of Materials*, 22(3),
doi: 10.1021/cm901452z
8. Reichardt C, Welton T, *Solvents and Solvent Effects in Organic Chemistry*, 5th Ed, 2011
9. Daniels I et al, *Journal of Physical Chemistry*, 2017.
10. Huggins R, *Advanced Batteries: Materials Science Aspects*, 1st Ed., Springer, 2009
11. Van den Bossche P. (2006). *Journal of Power Sources*, 162(2),
doi: <https://doi.org/10.1016/j.jpowsour.2005.07.039>
12. Lisbona D. (2011). *Process of Safety and Environmental Protection*, 89(6),
doi: <https://doi.org/10.1016/j.psep.2011.06.022>
13. Serway A, Jewett J, *Physics for Scientists & Engineers with Modern Physics*, 9th Ed., Cengage Learning, 2013.
14. Suo et al (2015), *Science*, 350(6263), doi: 10.1126/science.aab1595
15. Liu J, *Green Energy & Environment*, 2018

16. Gong J. (2015). *Soft Matter*, 6, doi: 10.1039/B924290B
17. Haque A. (2012). *Polymer*, 53(9), doi:
<https://doi.org/10.1016/j.polymer.2012.03.013>
18. Hibbs M, *Biofouling*, 2015
19. Kao CW, *RSC Advances*, 2017
20. Wu J, *Acta Biomaterialia*, 2018
21. Mousavi M. (2015). *Journal of the Electrochemical Society*, 162(12), doi :
10.1149/2.0271512jes]
22. Chen CH. (2001). *Journal of Power*,
doi: [https://doi.org/10.1016/S0378-7753\(00\)00666-2](https://doi.org/10.1016/S0378-7753(00)00666-2)
23. Griffiths, *Introduction to Electrodynamics*, 4th Ed
24. Marcinek et al. (2015). *Solid State Ionics*, 276,
doi: <https://doi.org/10.1016/j.ssi.2015.10.002>
25. Lu Y (2015). Stable lithium electrodeposition in salt-reinforced electrolytes.
Journal of Power Sources, doi: <https://doi.org/10.1016/j.jpowsour.2015.01.030>
26. Lu Y. (2014). *Nature*, 13, doi : <https://doi.org/10.1038/nmat4041>
27. Li L, *Chemical Communications*, 2018
28. Jian G et all., *Chinese Physics B*, 2016
29. Schaschke C. *Dictionary of Chemical Engineering*. 1st ed., Oxford University Press, 2014.
30. Gamburg YD, Zangari G, *Theory and Practice of Metal Electrodeposition*, Springer, 2011.
31. Liu GQ. (2010). *Journal of Solid State Electrochemistry*, 14(12),
doi : 10.1007/s10008-010-1061-5
32. Sun X. (2015). *Journal of Chemistry*, 39(1), doi : 10.1039/C4NJ01390

Appendix

Polymer Blend Name	Polymer Ratio (by wt%)
A	1:0:0
B	$1:\frac{1}{10}:0$
C	$1:\frac{1}{10}:\frac{3}{40}$
D	$1:\frac{1}{10}:\frac{3}{40} + 10\text{wt\% DMAPS (with respect to total polymer mass)}$
E	1:0:0

Table 1 The ratio of certain polymers in each polymer blend. It is important to note that the PAMPS additive was purchased from Sigma Aldrich as a 15wt% PAMPS solution in water, of M_w 1,000,000 and the ratio listed here is by actual weight of PAMPS. The ratio of the solution itself was 1/2. Polymer E is PEGDMA purchased from Polysciences of M_w 8000.

The ratios are as follows: (PEGDMA-3400K):(PEGDMA-10K):(PAMPS), with the exception of polymer blend E, which is simply just Polysciences 8K PEGDMA.

Membrane	Electrolyte	Conductivity (S/cm)	Standard Deviation
Paper Separator	<i>1m</i>	0.00328	0.00193
	<i>5m</i>	0.00288	0.00191
	<i>10m</i>	0.00182	0.00013
	<i>21m</i>	0.00118	0.00006
Poly A	<i>1m</i>	0.00486	0.00309
	<i>5m</i>	0.00624	0.00000
	<i>10m</i>	0.00685	0.00430
	<i>21m</i>	0.02452	0.02514
Poly B	<i>1m</i>	0.02464	0.00073
	<i>5m</i>	0.00272	0.00031
	<i>10m</i>	0.01066	0.01246
	<i>21m</i>	0.00647	0.00475
Poly C	<i>1m</i>	0.00966	0.00718
	<i>5m</i>	0.01000	0.00573
	<i>10m</i>	0.06354	0.02545
	<i>21m</i>	0.02463	0.01816
Poly D	<i>1m</i>	0.00447	0.00254
	<i>5m</i>	0.01305	0.00212
	<i>10m</i>	0.00861	0.01065
	<i>21m</i>	0.03666	0.04814
Poly E	<i>5m</i>	0.02352	0.00016

Additive	X mol%	Conductivity (S/cm)	Standard Deviation
LiF (Paper)	<i>5 mol%</i>	0.00391	0.00049
	<i>15 mol%</i>	0.00164	0.00020
	<i>25 mol%</i>	0.00239	0.00076
LiF (Poly D)	<i>5 mol%</i>	0.01662	0.00223
	<i>15 mol%</i>	0.19769	0.04764
	<i>25 mol%</i>	0.19925	0.08591

Table 2 All measured conductivity values. (Left) Values for the main polymer series in electrolyte, including the paper separator or no-membrane case, and (Right) the values for LiF as an additive in 5m LiTFSI in both a no-membrane case and in polymer D.