



Anion Effects on Solid Polymer Electrolytes Containing Sulfur Based Ionic Liquid for Lithium Batteries

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Solid polymer electrolytes for lithium batteries possess increased safety over traditional carbonate electrolytes, but have not been shown effective at temperatures close to ambient. The inclusion of triethyl sulfonium based ionic liquids (IL) into poly(ethylene oxide) (PEO) homopolymers has demonstrated the ability to reach the necessary figures of merit for use in a lithium battery below physiological temperature. The effect of the anion for the IL and the lithium salt was measured for bis(perfluoroethylsulfonyl) imide, bis(oxalato) borate, perchlorate, hexafluorophosphate (PF₆) and bis(trifluorosulfonyl) imide (TFSI), and all showed ionic conductivity on the order of 1 mS/cm at physiological temperature. T_{Li^+} ranged from 0.19–0.31 for the systems and some anions demonstrated stability exceeding 5 V vs. Li/Li⁺. The ability to reversibly plate and strip lithium was also measured and was largely influenced by the resistance of the electrolyte-electrode interface. This research demonstrated that TFSI is the best choice of anions for the solid polymer electrolyte system, while PF₆ is the worst. The other anions demonstrated a range of properties that depending on the needed properties could potentially be favored relative to TFSI.

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Lithium is the premier chemistry for high energy and power density batteries. However, its widespread deployment in batteries has been limited due to safety. Complete cells have had a propensity to overheat and combust. The development of a new generation of electrolytes that replaces organic carbonate based electrolytes would ultimately lead to the goal of safer batteries.¹ The progress in developing polymer electrolytes, which possess superior voltage, temperature and mechanical stability, has been stalled due to low conductivity.^{1–3} The commercial focus of polymer electrolytes has been largely relegated to polymer gel electrolytes, which does not avoid the combustible carbonate solutions.⁴ Although, it is possible to elevate the conductivity of a solid polymer electrolyte while still avoiding the use of combustible components.

Ionic liquids (ILs) have been used successfully to overcome the limited conductivity of polymer matrices because they possess ideal electrochemical properties; namely high conductivity, electrochemical stability, and no volatility. When incorporated into poly(ethylene oxide) (PEO) based polymer matrices they have been shown to elevate the ionic conductivity of the electrolyte several orders of magnitude.^{5–7} Of the most commonly used IL architectures for electrochemical purposes, the imidazolium architecture⁸ has the highest conductivity and thus makes it an ideal starting point for the development of an electrolyte. However, this same scaffold has encountered problems with its stability at low voltages and its intercalation into the graphite anode has resulted in exfoliation and rapid capacity fade.^{9,10} In recognition of this Shin et al.⁵ have shown that adding 1-butyl-1-methyl pyrrolidinium bis(trifluoromethane sulfonyl) imide (TFSI) to PEO leads to a marked increase in ionic conductivity of 2 orders of magnitude for the highest tested concentrations (molar ratio of 20 PEO: 1 LiTFSI: 3.24 IL). However, the large ratio of ionic liquid to polymer in Shin's optimized electrolyte has adverse effects upon the transference number, inherently limiting the capacity that can be delivered by lithium with each cycle.^{11,12}

The success of IL additives spurred interest in novel IL scaffolds that would overcome such observed limitations while mimicking the preferred method of Li⁺ conduction through the polymer chains.^{13,14} Prior research into sulfur based IL systems has demonstrated superior electrochemical stability and conductivity values relative to nitrogen based architectures.^{15,16} Motivated by this, our previous work centered on the development of triethyl sulfonium TFSI.¹⁷ A flexible and mechanically stable electrolyte was characterized. The PEO based solid

polymer electrolyte was able to demonstrate ionic conductivity of 1.20 mS/cm at room temperature and ~7.0 mS/cm at 40°C (molar ratio of 20 PEO:1 LiTFSI: 1 IL). This elevated conductivity of the electrolyte was accompanied by reversible stability against both lithium and at voltages exceeding 4.5 V vs. Li/Li⁺.

Lingering concerns about the reactivity of TFSI with aluminum motivated our research to investigate different anions which possess similar electrochemical properties without reactivity to aluminum.¹ Among all possible anions, those for lithium batteries are chosen for their ability to dissociate completely from the lithium ions allowing for single ion movement. There are several salts that meet this basic criterion, although the prevailing commercial choice has been LiPF₆ due to its combination of stability and conductivity. Relative to a TFSI based system, the PF₆ anion has both benefits such as its high conductivity and price, but also drawbacks such as its moisture and temperature stability.^{1,18} Numerous other anions exist that exhibit good lithium conductivity in solid polymer electrolytes including bis(perfluoroethyl sulfonyl) imide (BETI) and bis(oxalato) borate (BOB) and ClO₄.¹⁹

Since no single anion possesses all the ideal characteristics related to conductivity and stability, we replaced all of the anions in the system with both experimental and commercial anions using the triethyl sulfonium cation as our starting point. This fundamental change in the chemistry of the electrolyte was investigated with the intention of demonstrating an improvement over our previous sulfur based IL polymer electrolyte system, while also adding stability to aluminum current collectors. Herein, we report on the electrochemical characterization of the different formulations of our solid polymer electrolyte systems.

Experimental

Materials.— LiTFSI (LiN(SO₂CF₃)₂), lithium foil, AgNO₃, HClO₄ (70%) HPF₆ (65%), LiTFSI, LiClO₄, and LiPF₆ were used as received from Aldrich. Poly(ethylene oxide) (Mw 300k), triethyl sulfonium iodide (97%) (S₂I), boric acid (99%), and oxalic acid (10% aqueous solution) were used as received from Alfa-Aesar. LiBOB was used as received from Chemetall. An aqueous solution of LiBETI was prepared with HBETI (Synquest Laboratories) and LiOH.

RTIL preparation.— S₂OH.—Procedure adapted from Golding et al.²⁰ Equimolar amounts of AgNO₃ (2010 mg, 1.83 mmol) and NaOH (473.1 mg, 11.83 mmol) were mixed in 10 mL of water to form AgOH. The resulting solution was sonicated and vacuum filtered to

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obtain AgOH as a brown solid. Quantitative yield was assumed and the silver hydroxide was combined with S₂I (2000 mg, 7.89 mmol) in 10 mL of water and allowed to stir for 1 h. The solution was then vacuum filtered and dried to produce an orange-brown liquid.

S₂BOB.—Procedure adapted from Vijayaraghavan and MacFarlane²¹ A flask was charged with one equivalent each of S₂OH (7.89 mmol, 1074 mg) and of boric acid (487.8 mg, 7.89 mmol) and two equivalents of oxalic acid (1420 mg, 15.78 mmol) and allowed to stir under vacuum for 2 h until dry. 80.9% of a white solid was yielded. ¹H: 3.317 (q, *J* = 7.4 Hz, 6H), 1.444 (t, *J* = 7.4 Hz, 9H). ¹³C: 33.80, 9.02. ESI⁺: 119.0999, ESI⁻: 186.9554.

S₂PF₆.—S₂OH (1074 mg, 7.89 mmol) was added to aqueous solution of HPF₆ (1346 mg, 9.22 mmol, 15% stoichiometric excess) and stirred under vacuum for 2 h. The product was then filtered and washed with acetone. A clear liquid was isolated after drying under vacuum for 2 h at 20.2% yield. ¹H: 3.337 (q, *J* = 7.4 Hz, 6H), 1.467 (t, *J* = 7.4 Hz, 9H). ¹³C: 33.75, 9.06. ESI⁺: 119.0910, ESI⁻: 144.9635.

S₂ClO₄.—S₂OH (1074 mg, 7.89 mmol) was added to an equimolar aqueous solution of HClO₄ (1132 mg, 7.89 mmol) and stirred under vacuum for 2 h. The mixture was allowed to stir for 24 h while drying under high vacuum. 82.8% S₂ClO₄ was yielded as a copper colored solid. ¹H: 3.35 (q, *J* = 8 Hz, 6H), 1.47 (t, *J* = 8 Hz, 9H), ¹³C: 33.80, 9.09. ESI⁺: 119.0897, ESI⁻: 98.9519, 100.94890 (large splitting due to ³⁵Cl and ³⁷Cl isotopes).

S₂BETI and S₂TFSI.—Prepared as per our previous publication¹⁷ 86.5% was yielded for S₂BETI and 54.0% was yielded for S₂TFSI, both as yellow liquids. S₂BETI: ¹H: 3.43 (q, *J* = 8 Hz, 6H), 1.56 (t, *J* = 8 Hz, 9H), ¹³C: 33.77, 9.03, ESI⁺: 91.0637, 119.0990 ESI⁻: 379.91528. S₂TFSI: ¹H: 3.372 (q, *J* = 7.6 Hz, 6H), 1.516 (t, *J* = 7.4 Hz, 9H), ¹³C: 33.78, 9.06, ESI⁺: 119.0975, ESI⁻: 279.9238.

Electrolyte preparation.— All electrolytes were assembled in the molar ratio of 20 PEO : 1 LiX: 1: S₂X, where X is the anion of interest. Low molar ratios are ideal for synthesis of solid thin-film electrolytes; greater concentrations of IL result in poor film properties. The weight percent of IL ranges from 18% to 28% depending on the anion. The electrolyte films of different composition were solution cast from tetrahydrofuran (TFSI, BETI, BOB), dimethylformamide (PF₆) or acetonitrile (ClO₄) onto Bytac molds in an MBRAUN Labmaster 100 argon glove box. The resultant films were dried for several days at 60°C, before being placed into CR2032 coin cell enclosures for electrolyte testing.

Electrolyte characterization.— Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q100 differential scanning calorimeter. Samples were hermetically sealed in Al pans under Ar prior to measurements, which were run using a heat/cool/heat method to erase thermal history at a heating rate of 10°C/min and a cooling rate of 5°C/min from -50°C to 120°C.

Conductivity measurements for electrolytes were performed in a SS/electrolyte/SS coin cell set up on a Solartron 1287A/1255B platform over the frequency range 1 MHz to 1 Hz. Testing parameters were controlled by the associated CorrWare and ZPlot software, while data analysis was performed using CorrView, ZView and Origins 8. All temperature testing was done in a RevSci IncuFridge with ±0.5°C temperature accuracy allowing 45 mins to equilibrate at each temperature. Prior to testing constructed cells were annealed for 3 hrs at 50°C.

Transference measurements were performed in a Li/electrolyte/Li coin cell set on the Solartron setup. A potential of 10 mV was applied across each cell until steady state current reached. All tests were run at 40°C except for ClO₄, which was run at 50°C after allowing for 1 hour of temperature equilibration. Impedance spectroscopy was conducted before and after steady state to determine resistance of the electrolyte.

Linear sweep voltammetry was performed on Li/electrolyte/SS cells. Cells were stepped at 1 mV/sec from 2.5 V vs. Li/Li⁺ reference to 6.5 V vs. Li/Li⁺ reference, and breakdown was determined by the first change in derivative.

Overvoltage experiments were performed on the Solartron set-up to determine the interfacial stability and reversibility of the electrolyte material. The electrolyte was sandwiched between two lithium electrodes. A current density of 0.1 mA/cm² was applied to the film and was reversed every hour. 25 cycles, each consisting of 1 hr positive current and 1 hr negative, were applied to the cell at 55°C. All cells were annealed for 1 hour at 55°C prior to testing. Impedance spectroscopy was periodically conducted to monitor development of resistances at the interface during the galvanostatic cycling.

Results and Discussion

The effect of the anion on the electrochemical properties of polymer electrolytes has been a source of ongoing research. With this in mind, it was of tantamount importance to characterize the effect of the anion on the observed electrolyte properties. As a comparison to previous work TFSI was used as the baseline to compare ClO₄, BOB, BETI and PF₆. Given the novel nature of some of the triethyl sulfonium based ILs, DSC was first performed to characterize the thermal properties. Elevated temperatures are crucial for promoting conductivity to threshold values in solid polymer electrolytes. Additionally, the physical state of the IL is important as not all of the anions are liquids at room temperature. The DSC thermograms are also seen to closely mirror the ionic conductivity values determined from AC impedance in the full electrolyte system.

The studied pure ILs underwent numerous transitions (tabulated in the Supplementary Information²²). The largest peak was taken to be either the melting or freezing point of the neat IL. All other transitions tabulated by whether they occurred during the heating or cooling cycle because of the large hysteresis. S₂TFSI and S₂BETI had the lowest transition temperatures and are both liquids at room temperature. TFSI and BETI are both imide based architectures, which have been promising anions for ionic liquid development. S₂BOB was a low melting point solid; at the slightly elevated temperatures of interest, it is a liquid. It was also the only ionic liquid to undergo a 2nd order phase change. The absence of its freezing point is believed to be the result of the slow kinetics of crystallization. S₂ClO₄ is a solid up to ~100°C, barely allowing it to be considered an ionic liquid. This ability of S₂ClO₄ to crystallize is strongly believed to be the source of its low ionic conductivity in the solid polymer electrolyte. S₂PF₆ was also isolated as a solid, but with a significantly lower melting point. All of the pure ILs tested had observable hysteresis between the observed transition in the heating and cooling cycle.

The ionic conductivity of the solid polymer electrolytes during cooling can be seen in Figure 1. Each anion demonstrates varying ionic conductivity over the measured temperature range. The lower limit of conductivity is approximately physiological temperature for all anions except for ClO₄ which drops from 0.17 mS/cm at 45°C to 0.012 mS/cm at 35°C. At 45°C all five of the solid polymer electrolyte have sufficient conductivity to be functional in a lithium battery system. At 45°C the ionic conductivity of BOB is 2.29 mS/cm, BETI 4.15 mS/cm, PF₆ 2.10 mS/cm, ClO₄ 0.17 mS/cm, TFSI 8.28 mS/cm. At this slightly elevated temperature all of the anion systems, except ClO₄, show ionic conductivity >1 mS/cm, which is necessary for higher current applications. When values drop below this threshold, the polymer electrolytes have been shown ineffective at conducting lithium ions.

The conductivity is intimately related to the transition temperature observed during DSC (Table I). The freezing and melting points are tabulated separately because of the large thermal hysteresis observed in the polymer electrolytes. The transition from semicrystalline to amorphous, allows for the PEO chains to move past each other without the inhibition of long range ordering. This ultimately allows PEO to reversibly coordinate to ions, permitting their conduction down electrical and concentration gradients. This phase transition in the electrolyte manifests itself as an endothermic peak. Comparing the relative transition temperatures of all the anions shows a strong correlation with the relative ordering of each anion's conductivity of the polymer electrolyte. TFSI had the lowest transition at 13.53°C, and over the studied temperature range maintained the highest

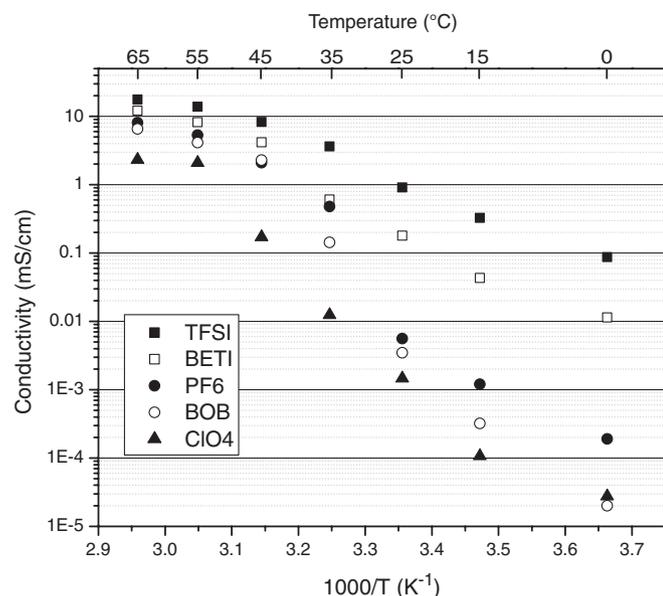


Figure 1. Ionic conductivity of the solid polymer electrolytes determined by AC impedance spectroscopy upon cooling of the SS/electrolyte/SS cells from 65°C.

conductivity values. BETI had a similar transition temperature of 15.98°C, and possessed the second highest ionic conductivity values. The DSC values of the other three anions, suggest that BOB should be third, followed by ClO₄, with PF₆ lowest. The conductivity values did not follow this trend as ClO₄ generally demonstrated the lowest conductivity. Between BOB and PF₆, the latter generally maintained a higher conductivity despite having a higher transition temperature. This disagreement with the relationship between DSC and conductivity is hypothesized to be the result of the unfavorable movement of ions in the IL itself. Elevated melting points limit ionic mobility because of the association of microscopic crystalline domains, which ultimately lowers the observed ionic conductivity values. It is also of note that ionic conductivity values are measured not the lithium conductivity. The difference between these numbers could falsely indicate movement of the anion and not the lithium cation.

All of the trend lines for ionic conductivity show a discontinuity on either side of the transition temperature observed by DSC. At high temperature the gain from increased temperature is minimal. At low temperatures the gain in conductivity over temperature is significant. This region of steeper slopes however, has not shown enough conductivity to be a functional lithium electrolyte. Ordinal ranking of the ionic conductivities of the anions shows that TFSI and BETI have the best ionic conductivity over the observed temperature range, while ClO₄ possessed the worst ionic conductivity.

The other important element of conductivity is the determination of which ionic species are the charge carriers. To accomplish this we followed the procedure outlined by Evans et al.,²³ whereby a small voltage is applied until steady state current is attained. Equation 1 is used to calculate the lithium transference number (T_{Li^+}), with the resistances in the equation measured by impedance spectroscopy. This

Table I. DSC peaks of the electrolyte.

Anion	Freezing	Melting
BOB	24.66	44.18
ClO ₄	30.63	42.9
PF ₆	35.28	48.01
BETI	15.98	39.97
TFSI	13.53	41.87

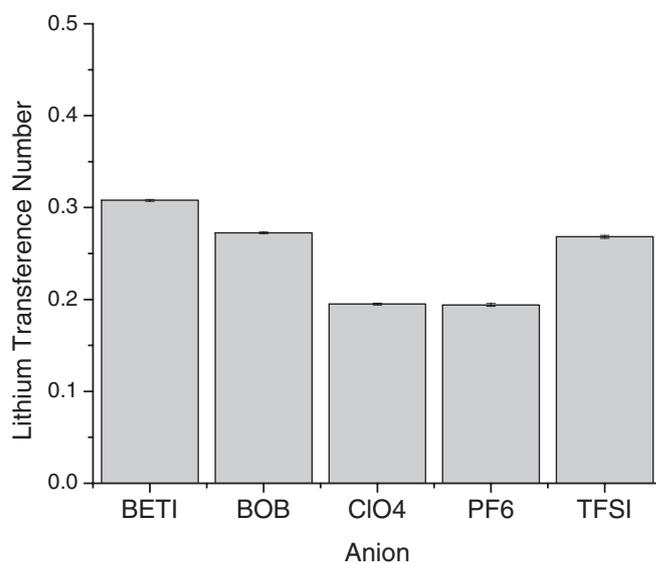


Figure 2. Lithium transference number of the solid polymer electrolytes. T_{Li^+} was determined using the potentiostatic measurement conducted at 40°C for all anions except ClO₄, which was run at 50°C.

value between 0 and 1 is a measure of what fraction of the total current is due to the movement of a given species. T_{Li^+} vary widely depending on the electrolyte as well as the testing method but are typically below 0.5.²⁴ Polymer systems range from ~0.1 to 0.5 while ionic liquid systems with a larger number of charged species typically range from ~0.1 to 0.3.^{11,25} The T_{Li^+} values for the different anions can be seen in Figure 2.

$$T_{Li^+} = \frac{I_c (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_c R_c)} \quad [1]$$

The T_{Li^+} values for the studied solid polymer electrolytes range from ~0.2 to 0.3. These numbers are on the high end of the range for IL based electrolyte systems. And although the transference numbers are below average for polymer systems with only lithium salts, the researched polymer/IL/Li salt hybrid electrolytes demonstrate significantly higher conductivity. BETI demonstrates the highest T_{Li^+} at 0.31. The lowest values are for ClO₄ and PF₆, which are 0.20 and 0.19, respectively. Ranging between these two values were the measured T_{Li^+} of BOB and BETI which are both 0.27. It is of note with ClO₄ that due to low ionic conductivity its transference measurements were conducted at 50°C, while all other anions were run at 40°C. This can be easily explained from Figure 1 where the conductivity of ClO₄ based systems lags significantly behind other anion systems at a given temperature.

Given the interest in having electrolytes which are single Li⁺ conductor, it was of great interest to understand the differences between the anions. Table II, which contains the molar volumes of the anions, shows that a trend is readily apparent.²⁶ Larger volumes correspond to larger T_{Li^+} . Categorically separating the volumes into small (~60–70 Å³) medium (~145 Å³) and large (~200 Å³) anions matches the

Table II. Volume of anion as determined by molinspiration program.²⁶

Anion	Volume Å ³
BOB	143.665
ClO ₄	56.546
PF ₆	72.615
BETI	200.377
TFSI	147.645

observed T_{Li^+} . This relationship between size and ion mobility can be explained in a straight forward manner by the ability of small ions to move with greater ease through the dense polymer matrix. Large molar volumes require more concerted movements of the polymer chains to allow movement of the ions. While this thinking suggests it would be possible to generate a single lithium ion conductor by increasing the size of the counterion, it obfuscates the duality of conductivity in polymer systems. By increasing the volume of the counterion, ultimately the local environment around Li^+ is significantly altered, such that all ion movement is limited, resulting in a carefully balanced tradeoff between T_{Li^+} and conductivity.²⁷

The stability of the electrolyte to the cathode, herein referred to as cathodic stability, is critical for the development of high voltage cells. Some olivine and spinel type cathode systems have voltage plateaus well above 4 V vs. Li/Li^+ , which leads to premature decay with carbonate based electrolyte systems. Solid polymer electrolytes with ILs generally are able to meet these higher stability windows with cathodic stabilities exceeding 5 V vs. Li/Li^+ .⁵ The incorporation of ILs is expected to have little impact upon this value, as sulfur based ILs have demonstrated wide ESWs.

To determine the limit for cathodic stability linear sweep voltammetry was undertaken from a voltage well within operational range (2.5 V vs. Li/Li^+) to one exceeding operational stability (6.5 V vs. Li/Li^+). Upon the first large change in derivative of current, breakdown of the electrolyte was assumed such that the electrolyte would no longer be able to electrochemically function as a lithium conductor. While other counter electrodes besides stainless steel were investigated they have been unable to yield satisfactory results. However half cell assemblies with $LiFePO_4$ and $LiCoO_2$ have shown stability over cycling. Thus it is believed that the results are reflective of the breakdown of the electrolyte under operating conditions. Figure 3, shows the measured breakdown voltage for each electrolyte formulation. All the solid polymer electrolytes displayed sufficient stability to be useful in the currently commercialized cathodes, $LiFePO_4$ and $LiCoO_2$. With all cathodes it is necessary to provide a buffer region above the fully charged potential ensuring that all energy is stored reversibly in the electrode. The next generation of high voltage cathodes ranges up to 5 V vs. Li/Li^+ , and thus requires cathodic stability of the electrolyte to exceed this value. The ClO_4 based system demonstrated stability up to 5.37 V, which is promising for future work on high power batteries. The imide based chemistries, BETI and TFSI, demonstrated stabilities of 5.00 and 4.97 V respectively. This figure

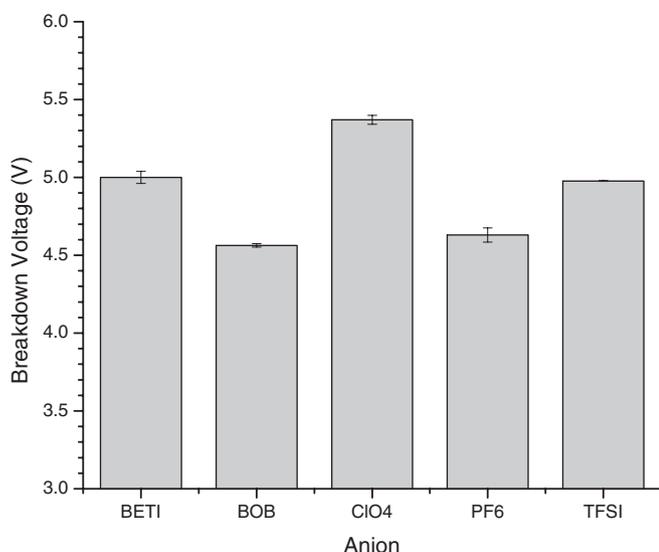


Figure 3. Cathodic stability of the solid polymer electrolytes. Breakdown was determined by first change in the derivative of the potential upon sweeping a SS/electrolyte/Li cell from 2.5 to 6.5 V vs. Li/Li^+ . Cells were run at 25°C.

of merit is promising for most experimental cathode systems, but is tempered by concern for stability to aluminum which is used as the cathode's current collector. BOB and PF_6 , which have cathodic stabilities of 4.56 and 4.63 respectively, only offer promise for electrodes that have been already commercialized and other lower voltage experimental cathodes. While $LiPF_6$ is investigated in high voltage systems, the observed failure is believed to be the result of testing at elevated temperature, which are necessary for lithium conduction. Given the high stability of several of these anion polymer electrolyte systems there are a number of possibilities to develop high voltage lithium battery systems.

Overvoltage studies measure a cell's stability to lithium and the energy required to move a lithium ion from the bulk electrolyte onto the surface of an electrode. Over extended cycling the energy expended in moving lithium ions should be minimal and constant. To confirm this aggressive cycling was undertaken to characterize the effect of the different anions on the electrolyte. Testing was conducted at 55°C to allow for comparison between all of the anions; several were more conductive at lower temperatures.

In Figure 4a, the end voltage over 25 cycles can be seen for each anion. The most salient observation is the low end voltage and its constant nature for the TFSI anion relative to the other anions. Low

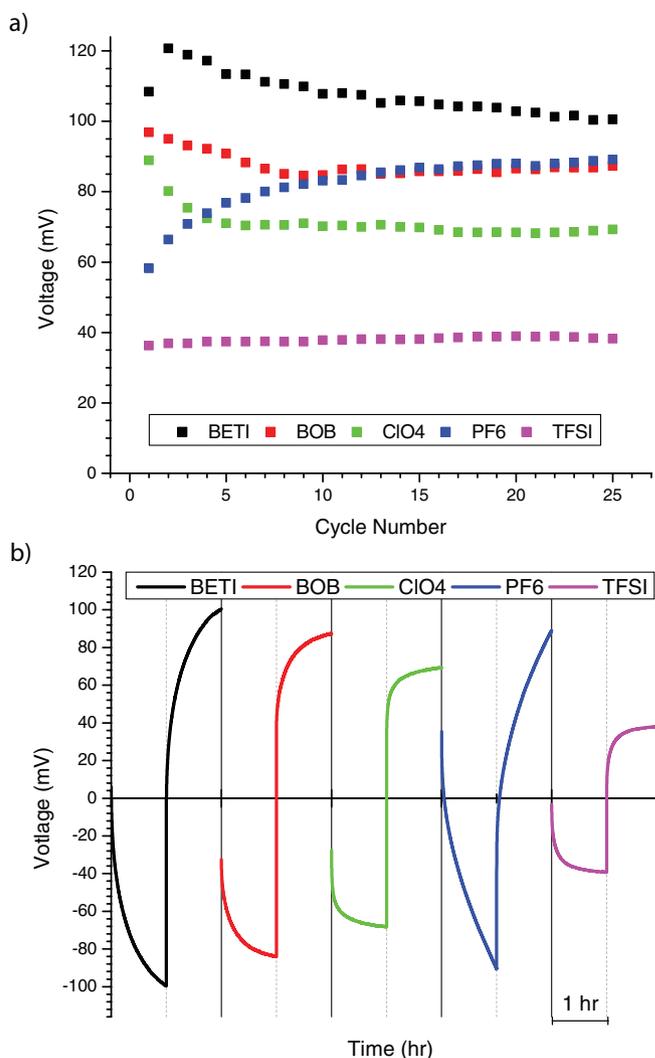


Figure 4. (a) Value of overpotential at the end of each 2 h cycle for symmetrical Li /electrolyte/ Li cells. b. Overpotential as a function of time during the 25th cycle for the indicated ionic liquid. Each cycle was 1 h negative current followed by 1 h positive current both at 0.1 mA/cm^2 . Testing was conducted at 55°C.

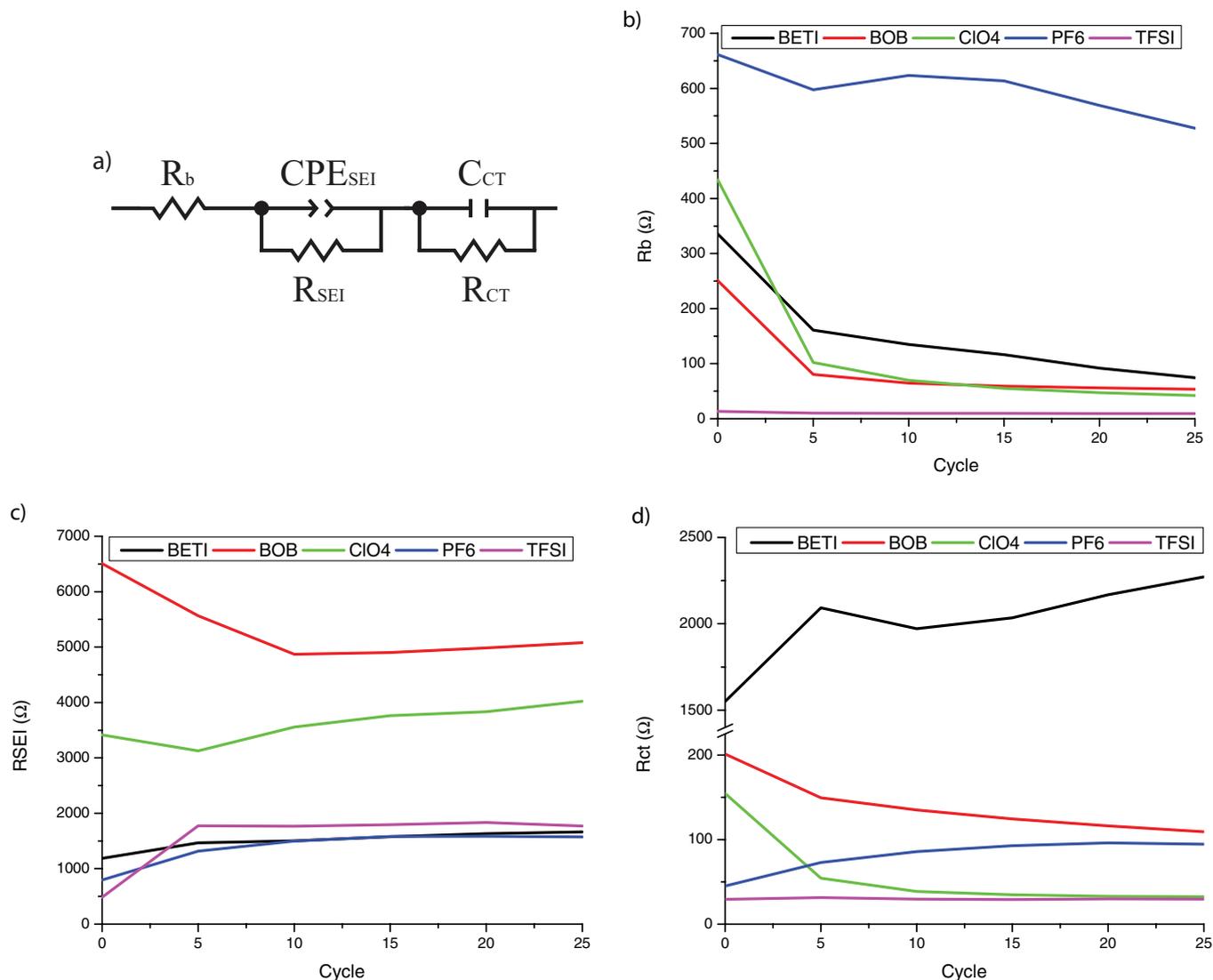


Figure 5. (a) Equivalent circuit used to model the electrolyte during overvoltage cycling (b) bulk resistance of each anion formulation during the overvoltage cycling (c) the resistance of the SEI film (d) the resistance due to charge transfer. To highlight the low resistance of the charge transfer there is a gap in the y-axis values. The electrolyte tested had a thickness of 0.0254 cm and a cross sectional area of 0.217 cm².

absolute overvoltages are critical for the electrolyte as it is a measure of the energy lost in the cell at the interface, which ultimately detracts from the voltage a single cell is able to deliver. This indicates the ideal ability of the TFSI based electrolyte to transport lithium ions effectively through the bulk and across a stable interface. BETI, BOB and ClO₄ all demonstrated decreasing end voltage values over the cycling. This is believed to be the result of the slow kinetics of the solid polymer electrolyte in chain rearrangement to permit bulk conductivity. After the initial decline BOB and ClO₄ reach a plateau, which lasts for the duration of the test. Lastly, with PF₆ a sizable increase in the end voltage values can be seen. Given the elevated temperature at which this cycling is conducted it is believed that the PF₆ anion is decaying. Evaluating the end voltages over 25 cycles for the anions and their long term stability, a ranking can be established which indicates that TFSI is the best anion tested, while PF₆ or BETI is the worst.

In evaluating the overvoltage it is important that the data for a given cycle demonstrate a plateau, which indicates that no additional resistance is accumulating in the interface as lithium is plated after formation of the concentration gradient. The voltage profile for the 25th cycle of each electrolyte tested at 55°C is shown in Figure 4b. To measure the stability of the plateau region over each hour segment the

time at which the voltage reached 90% of the end overpotential was recorded. From the overvoltage test it appears that some electrolytes more accurately fit the desired results. BETI and PF₆, which do not demonstrate a stable plateau region, reached the 90% threshold at 64.7% and 85.4% of full time respectively. Conversely, ClO₄ which demonstrated the most stable plateau among tested anions reached the 90% threshold at 21.7% of full time. TFSI which demonstrated the lowest absolute potential reached the 90% threshold at 30.3% of full time. BOB the 3rd most stable reached the 90% threshold at 39.3% of full time. Taken in conjunction with the change in voltage over time, TFSI demonstrates the most ideal overvoltage properties of all tested anions in the solid polymer electrolyte.

Interspersed every 5 cycles during the overvoltage cycling, impedance spectroscopy was conducted to monitor the resistance of each electrolyte composition. To model the electrolyte and the corresponding interface with the lithium electrode a model circuit consisting of three elements was used. The three components: the bulk electrolyte (R_b), the solid-electrolyte interphase (R_{SEI} and CPE_{SEI}), and the charge transfer (R_{CT} and C_{CT}) can be seen in Figure 5a. The model circuit, while a simplification of the complex electrochemical movement occurring in the electrolyte, fits closely to the Nyquist plots.

The change in resistance over the cycling is plotted in Figures 5b–5d (b-electrolyte resistance, c- resistance of the SEI, d-charge transfer resistance). The bulk resistance of the electrolyte is generally the lowest value for a given anion. Over the duration of the testing all anion chemistries showed a decrease in R_b . With the systems this initial decrease is believed to be related to the relaxation of the polymer chains, which facilitates ion movement. Only for the PF₆ system did this decrease appear to extend beyond the 1st time point. If as proposed at higher temperatures PF₆ is degrading, there would in fact be additional charge carriers. If correct, this would indicate that a decreasing portion of the ionic conductivity for PF₆ is Li⁺.

The resistance of the SEI develops quickly during the first few cycles and then remains constant for BETI, PF₆ and TFSI. ClO₄ shows a constant increase in resistance over the cycling, which is not exhibited by the end voltages which remain constant over the cycling. The constant increase in the SEI against lithium electrodes points to instability in the interface; this however must be related to a non-essential component to lithium transport. BOB which has the most resistive SEI demonstrates an initial drop in the interface followed by a gradual increase over cycling. Given that BOB is known to form resistive interfaces,¹ its relative position is unsurprising. For the constant resistances the formation of a stable SEI bodes well for their usage in lithium battery systems.

The R_{ct} of the electrolyte systems are generally fairly small relative to the R_{SEI} . For all anion systems except BETI the values are <250 Ω and remain largely constant over the testing. BETI however, had markedly high R_{ct} , which is increasing over the cycling. As no other negative charge carriers are present such a large difference between BETI and the other anions can be easily attributed to the difficulty in arranging such a bulky anion at the interface. This difference is especially clear when comparing the two imide based anions; the R_{SEI} appears similar between the two systems, while the R_{ct} are more than an order of magnitude apart. On the whole the TFSI-based solid electrolyte system demonstrated the lowest resistances for any system. All except for BETI were dominated by the R_{SEI} , which points towards needing further work developing and characterizing the interface.

Conclusions

The development of solid polymer electrolytes has been hindered by their ability to demonstrate conductivity at close to ambient temperatures without compromising the main benefits of a polymer-based system. Our previous work demonstrated the real possibility of using triethyl sulfonium TFSI as an additive to accomplish this goal. Concern over the stability of TFSI led to the pursuit of alternative electrolyte formulations that replaced the TFSI anion. In substituting the TFSI anions there was a sizable decrease in ionic conductivity, which became less significant at higher temperatures. The systems cross the threshold value of 0.1 mS/cm below 45°C in the ascending order TFSI, BETI, PF₆, BOB, and ClO₄ from lowest to highest temperature. Lithium transference for these solid polymer systems ranged from 0.19 to 0.31, and is directly correlated to the size of the anion. The largest anion BETI demonstrated the highest T_{Li^+} while the smallest anions of ClO₄ and PF₆ demonstrated the lowest T_{Li^+} . Solid polymer electrolyte systems generally demonstrate wide electrochemical stability windows, which would ultimately be useful for the next generation of high voltage cathode materials. The tested anion formulations all demonstrated cathodic stability sufficient to

meet the commercial cathodes LiCoO₂ and LiFePO₄. BETI, TFSI and ClO₄ demonstrated sufficient stability to be useful in 5 V cathode systems, which would allow for more power and voltage from each lithium battery cell. Anodic stability and low lithium plating voltages was confirmed for the varied anion system. BOB, ClO₄ and TFSI have demonstrated reasonable voltages that are stable over cycling. The voltage that is observed for lithium plating is strongly dependent upon the formation of the SEI of the electrolyte. Herein a series of hybrid solid polymer electrolytes containing sulfur based ILs that demonstrate potential for high power biomedical applications.

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