Development of polyelectrolyte solutions for Li-metal batteries

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Lawrence Berkeley National Laboratory
June 1-4, 2020
Project ID: bat419

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Overview

Timeline

- Start Date: Oct. 1, 2019
- End Date: Sept. 30, 2022

Budget

- Total budget (3 years): $825K
- FY20 funding: $275K

Barriers Addressed

- Energy Density
- Safety
- Low rate capability

Partners/Collaborators

Kristin Persson (UCB/LBNL), for molecular dynamics studies

Nitash Balsara (UCB/LBNL), for electrochemical characterization of transport properties

Relevance

- **Sluggish ion transport** through the electrolyte phase of porous electrodes **limits utilization (capacity), particularly a**t **high rates**, of thick electrodes needed for high energy density EV batteries.
- High Li-ion transference number electrolytes have been theorized to reduce these transport limitations, thereby enabling higher energy density and higher rate capabilities in Li-ion batteries
- High Li transference number electrolytes have also been theorized to **suppress dendrite growth** during lithium metal stripping and plating, which could provide a route to enable safe, stable Li electrodes

Objectives for FY20

- Overall project goal: develop polyelectrolyte solutions (charged polymers in liquid solvents) as high conductivity and transference number electrolytes for Li metal batteries.
- Understand, using simulations and experiments, how ion transport is influenced by the following polyelectrolyte solution properties: polymer molecular weight and solvent properties.
- Develop capabilities to fully characterize transport phenomena and in liquid electrolytes (conductivity, transference number, diffusion coefficients, and thermodynamic factor).
- Develop coarse grained molecular dynamics simulations to understand transport phenomena in polyelectrolyte solutions at a molecular scale, and to quickly screen solution compositions to optimize transport properties.

Milestones

Date	Milestones	Status
December 2019	Complete study of solvent influence of transport in polysulfone-based polyelectrolyte solutions.	Completed
March 2020	Complete development and validation (using known liquid electrolytes) of electrochemical transport methods.	Completed
June 2020	Complete synthesis and transport characterization of model triflimide-based polyion (pTFSI) solutions in symmetric cells with Li-metal electrodes.	Delayed (COVID); expected completion: Sept. 2020
September 2020	Complete development of coarse-grained polyelectrolyte model to study the effect of polyelectrolyte composition on transport of model polyelectrolyte systems. Progress measure: publish an article describing scaling of transport properties of polyelectrolyte solutions as a function of polymer and solvent properties.	On track

Publications and presentations (FY19-20)

Publications

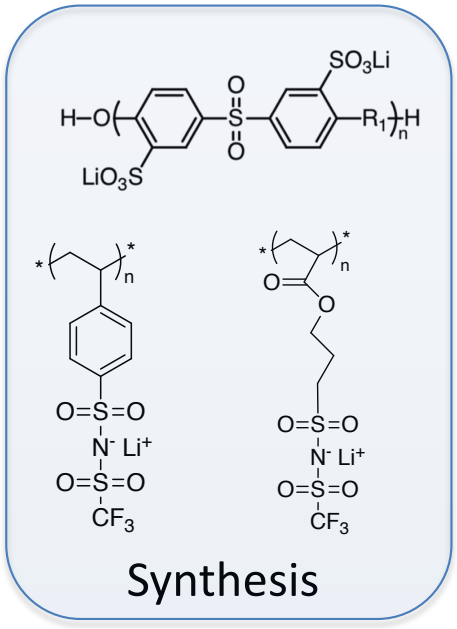
1. Diederichsen, K. M.; McCloskey, B. D. “Additive engineering to enable nonaqueous polyelectrolyte solutions for lithium ion batteries.” ***Molecular Systems Design and Engineering*** (2020), 5, 91-96.
2. Diederichsen, K. M.; Terrel, R. C.; McCloskey, B. D. “Counterion transport and transference number in aqueous and nonaqueous short chain polyelectrolyte solutions.” ***Journal of Physical Chemistry B*** (2019), 123(50), 10858-10867.
3. Abbott, L. J.; Buss, H. G.; Thelen, J. L.; McCloskey, B. D.; Lawson, J. W. “Polyanion electrolytes with well ordered ionic layers in simulations and experiment.” ***Macromolecules*** (2019) 52(15), 5518-5528.
4. McCloskey, B. D.; Xu, K. “Current trends in electrolytes.” *Editorial for special issue,* ***ECS Interface*** (2019) 28(2), 47.
5. Fong, K. D.; Self, J.; Diederichsen, K. D.; Wood, B. M.; McCloskey, B. D.; Persson, K. A. “Ion transport and the true transference number in nonaqueous polyelectrolyte solutions for lithium-ion batteries.” ***ACS Central Science*** (2019) 5(7), 1250-1260.

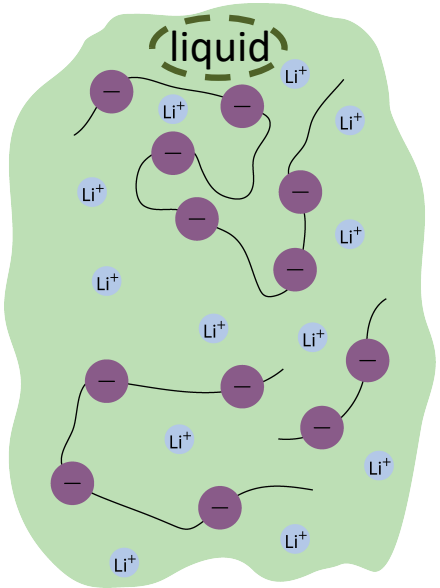
Presentations

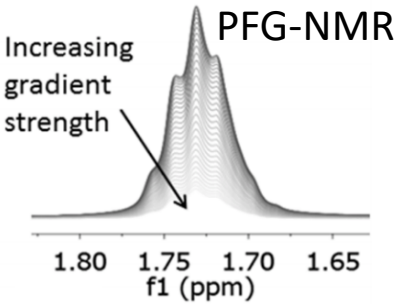
1. **Gordon Research Conference on Batteries,** Ventura, CA, Feb. 2020. “Li-Ion Transference Numbers in Nonaqueous Polyelectrolyte Solutions.” Poster, presented by Kara Fong.
2. **Berkeley Statistical Mechanics Meeting *(Invited),*** Berkeley, CA, Jan. 2020. “Transport Phenomena in Electrolyte Solutions: Non-Equilibrium Thermodynamics and Statistical Mechanics.” Oral, presented by Kara Fong.
3. **American Institute of Chemical Engineers**, Orlando, FL, Nov. 2019. “Influence of backbone solvation on polyelectrolyte solution transport properties.” Oral, presented by Kyle Diederichsen.
4. **American Institute of Chemical Engineers**, Orlando, FL, Nov. 2019. “Charge Transport in Nonaqueous Polyelectrolyte Solutions for Li-Ion Batteries: Ion-Ion Correlations and the True Transference Number from Molecular Dynamics Simulations.” Poster, presented by Kara Fong.
   - **First place in Materials Engineering and Sciences Division Poster Competition**
5. **Solid State Electrolytes Workshop, Pacific Northwest National Laboratory *(Invited),*** Oct. 2019. “Designing high Li^+ transference number and highly stable electrolytes for Li batteries.” Oral, presented by Bryan McCloskey.
6. **American Chemical Society Fall Meeting *(Invited)***, San Diego, CA, Aug. 2019. “Designing polymer-based Li^+ electrolytes with high conductivity and Li^+ transference number.” Oral, presented by Bryan McCloskey.

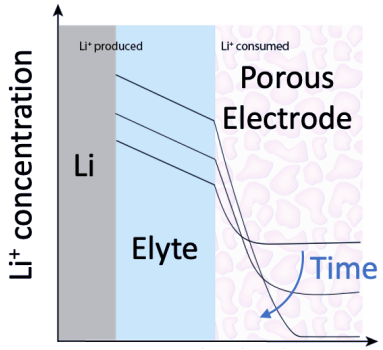
Approach

- Synthesize single ion-conducting polymers.
- Prepare polyelectrolyte solutions to study influence of solvent composition and polymer molecular weight.
- Characterize transport properties using a combination of AC impedance, pulsed field gradient NMR (self-diffusion coefficients), viscosity, electrochemical methods.
- Use molecular dynamics to understand molecular underpinnings of ion transport trends.

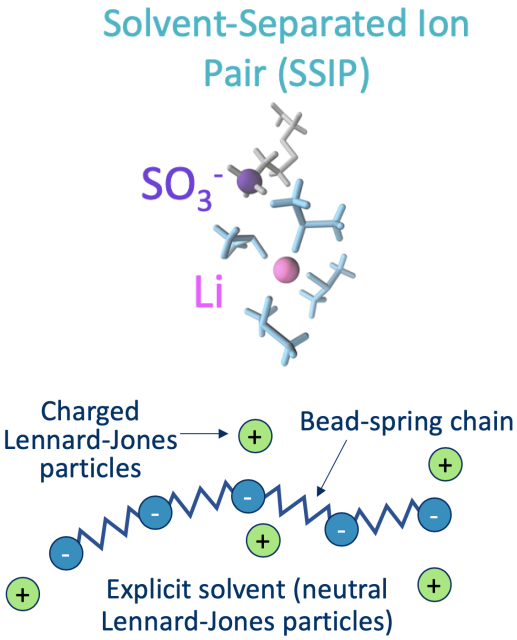








Characterization



Modeling
(w/ K. Persson)

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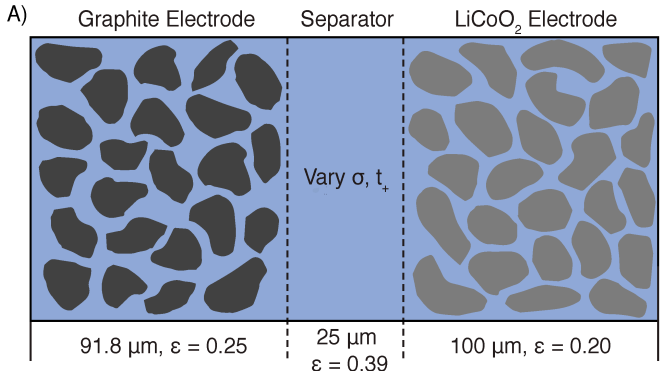
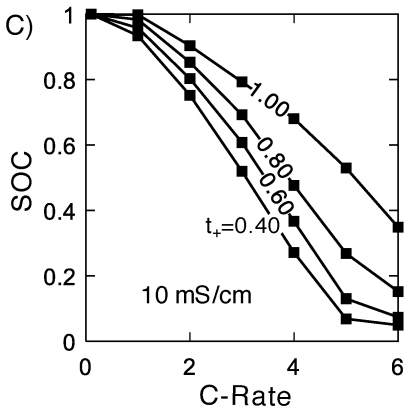
Motivation to study polyelectrolyte solutions

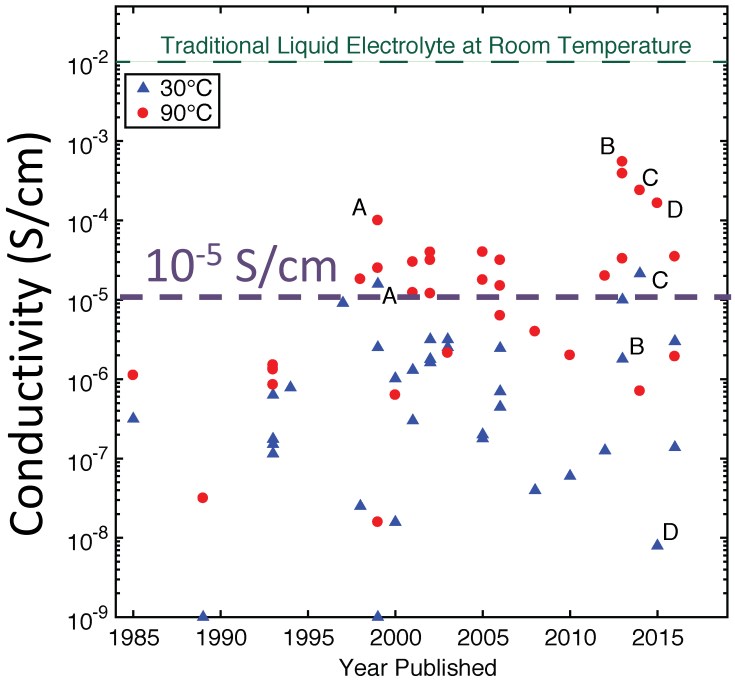
- Newman-type modeling predicts high transference number electrolytes would enable higher C-rates in Li-ion batteries

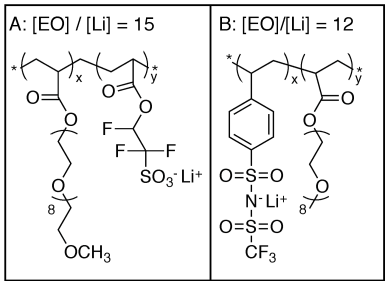


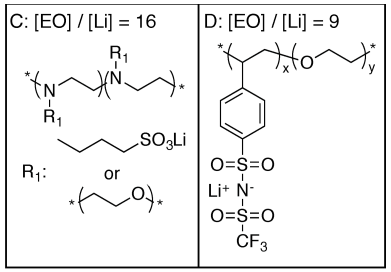
$$t_+ = \frac{D_+}{D_+ + D_-}$$



- Dry polymer electrolytes suffer from low conductivity (each point is a unique polymer)





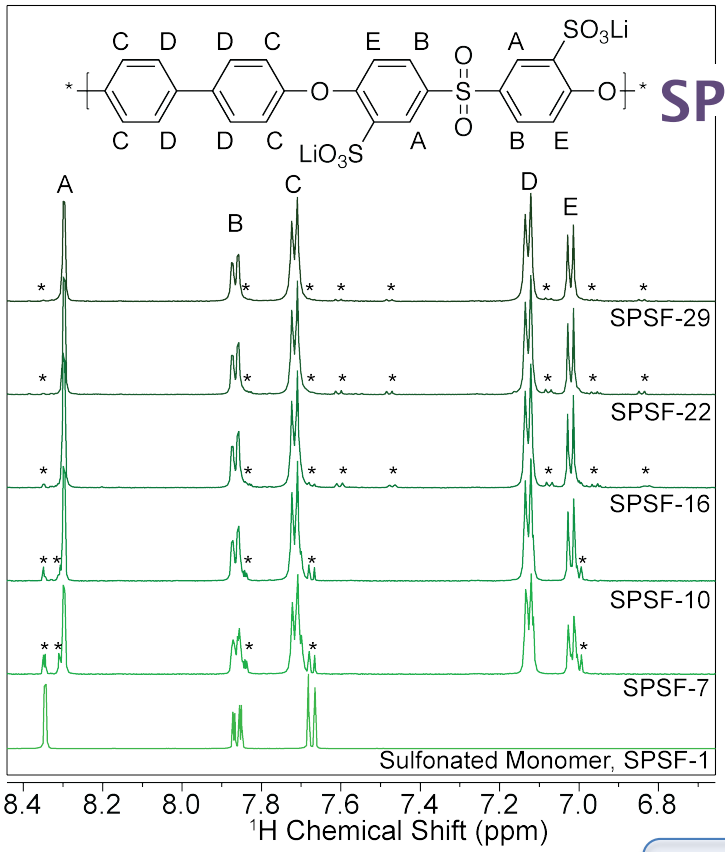


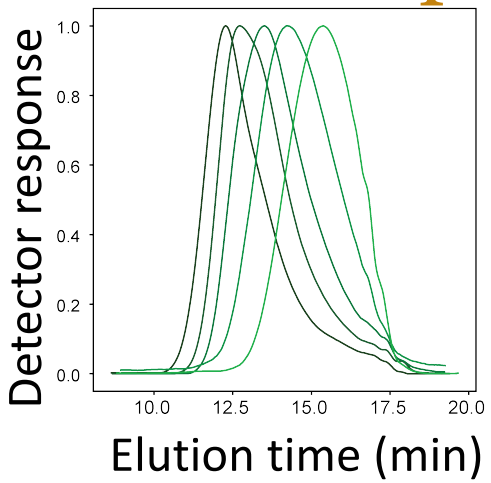
Systematically understand enhancements in transport by adding solvent

Diederichsen, McShane, McCloskey, *ACS Energy Letters* (2017), 2(11), 2563-2575.

Accomplishment: synthesis of sulfonated polysulfones

Goal: Create ionomers of same chemical composition, but varying molecular weight





Name	M_n GPC	PDI	N GPC	N NMR
SPSF-7	7,800	1.6	14	7
SPSF-10	11,300	2.0	20	10.5
SPSF-16	17,700	2.0	31	-
SPSF-22	24,500	2.2	43	-
SPSF-29	32,400	2.7	57	-

Varied molecular weight, characterized using gel permeation chromatography and ^{1}H nuclear magnetic resonance

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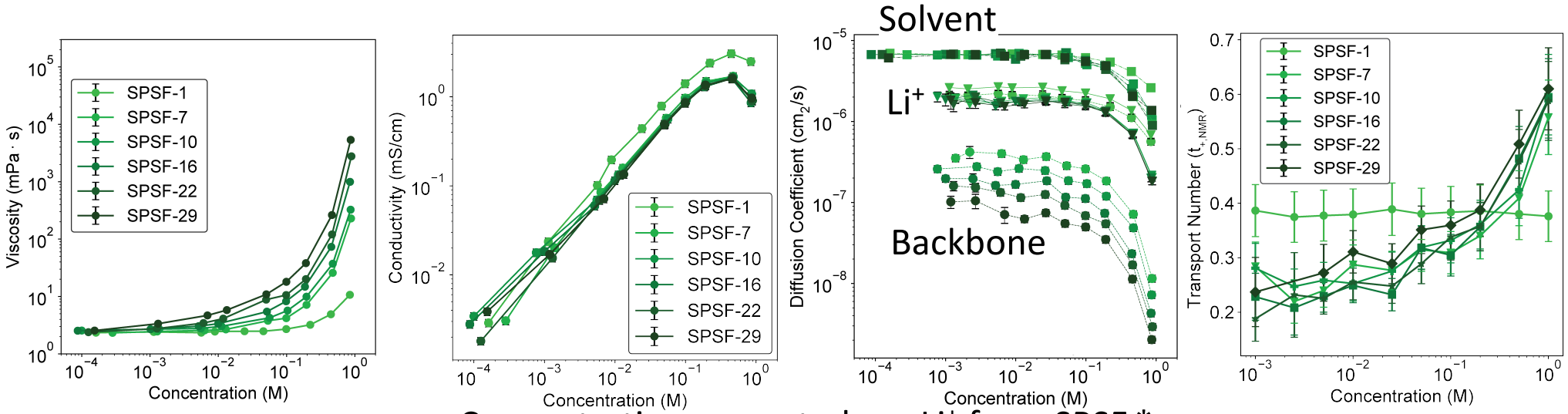
Accomplishment: transport in solutions of SPSF with varying molecular weight



Concentrations reported are Li^+ from SPSF.*

- Viscosity increases with increasing polymer/Li^+ concentration and molecular weight. Viscosity measured using a magnetic spinning ball viscometer under air/moisture-free conditions.
- Conductivity independent of molecular weight, has maximum around 1 M Li^+. Conductivity measured using a conductivity probe.
- Li^+ diffusion coefficients independent of polymer molecular weight, polymer diffusion coefficient decreases with molecular weight. Both are constant with increasing concentration up to ~0.1 M Li+, then decrease with increasing concentration. Measure using pulsed field gradient NMR.
- Li^+ transport number increases with increasing concentration, becomes greater than just the monomer itself at high concentrations.

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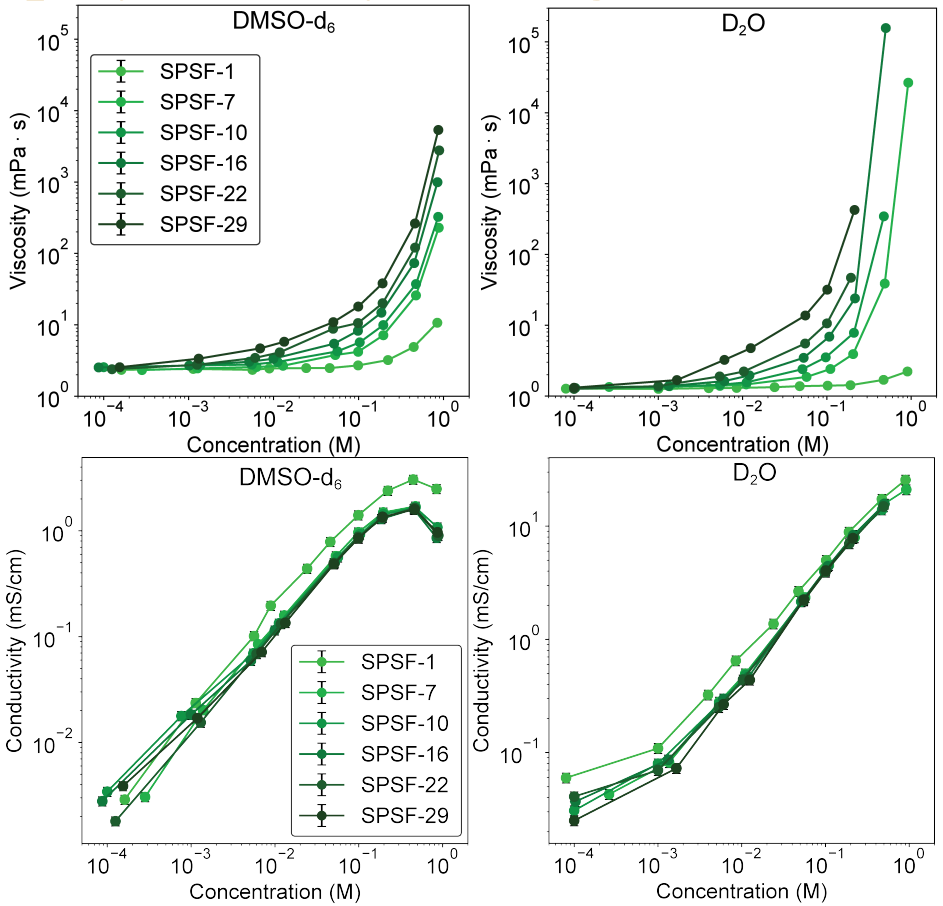
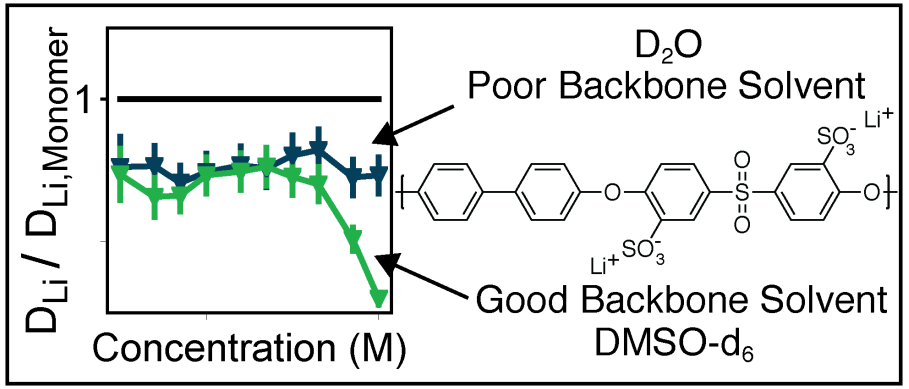
*SPSF used as salt in dimethyl sulfoxide (DMSO) solutions

$$t_{+,NMR} = \frac{D_{Li}}{D_{Li} + 2ND_{backbone}}$$

Accomplishment: Good vs. bad backbone solvent points to important polyelectrolyte design criterion



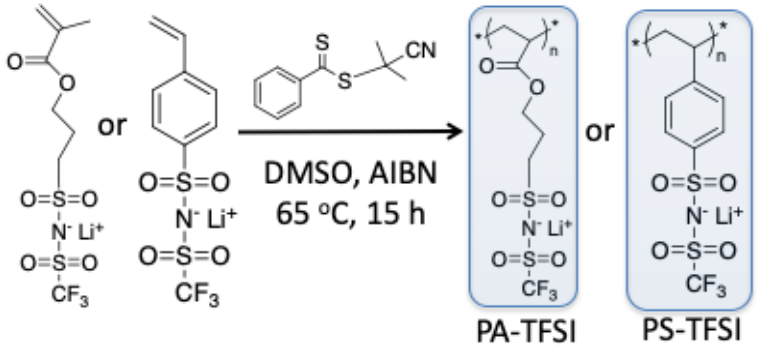
Diederichsen, Terrell, McCloskey, *J. Phys. Chem. B* (2019), 123(5), 10858.

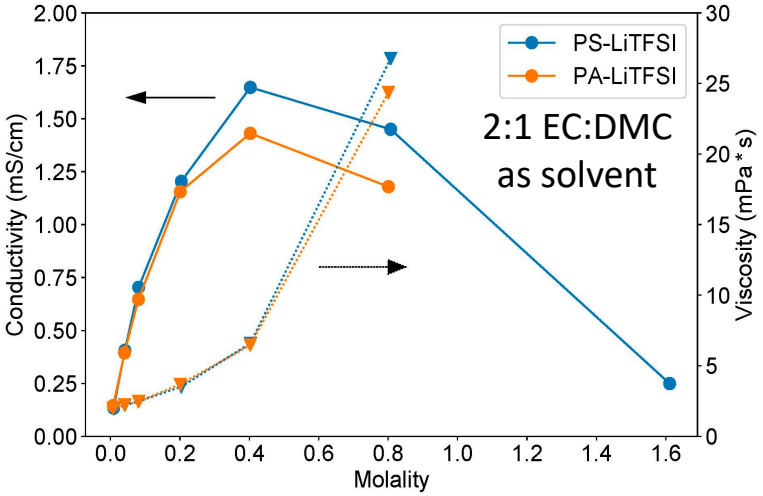


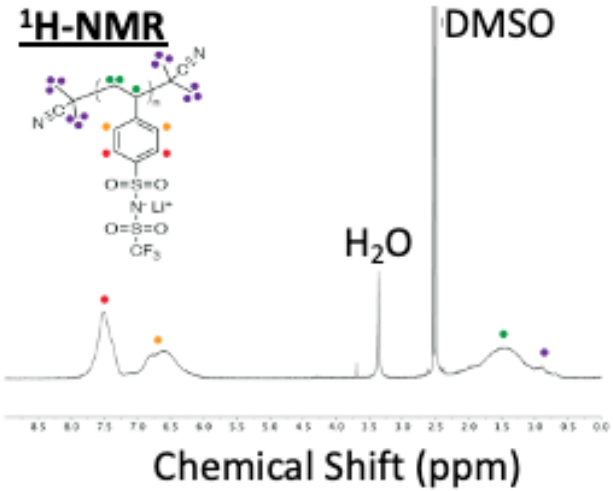
- When comparing DMSO and H_2O as solvents:
  - Viscosity at high concentrations is an order of magnitude larger in D_2O than DMSO. Becomes immeasurable at 1 M Li^+ concentration in D_2O.
  - Yet, conductivity is high in D_2O, doesn't reach maximum in concentration limits studied, similar conductivity to the monomer itself.
  - Diffusion measurements indicate that solvent and Li^+ do not interact with polymer backbone, appear to have higher mobility as a result.
  - Deuterated solvents used here for PFG-NMR diffusometry measurements.

Use ionomers whose backbones do not dissolve in carbonates/ethers, but have pendant ions that dissociate well in carbonates/ethers.

Accomplishment: Completion of initial conductivity and viscosity measurements of two carbonate-soluble polymers





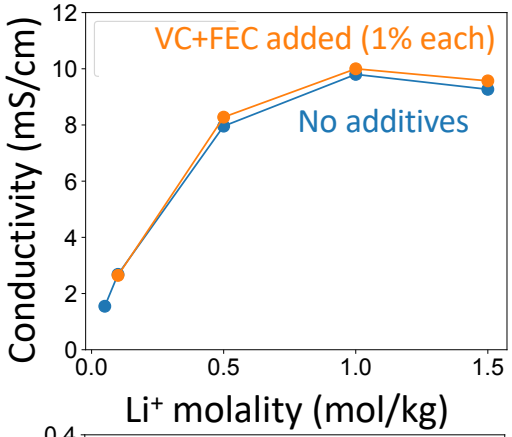


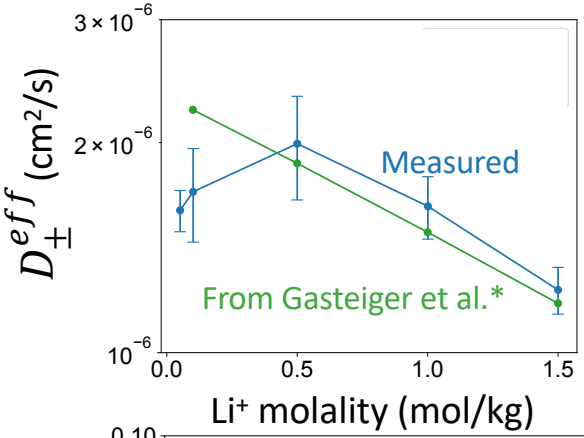
- FY19: synthesized PA-TFSI and PS-TFSI, which are soluble in liquid carbonates. Polymers were fully characterized to ensure purity and molecular weight.
- Both provide good conductivity in EC:DMC electrolytes
- Future work: Plan to explore both in carbonates and ethers for Li metal batteries.
- Future work: fully quantify electrochemical properties using Newman-Balsara electrochemical method.

PA–TFSI: poly(acrylic triflimide), PS–TFSI: poly(styrene triflimide)

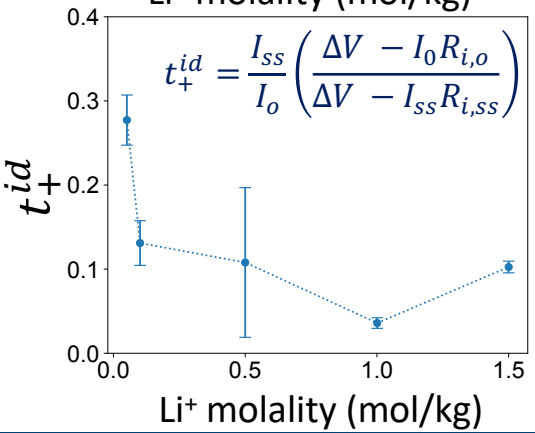
Accomplishment: Development of techniques to electrochemically characterize transport properties of liquid electrolytes

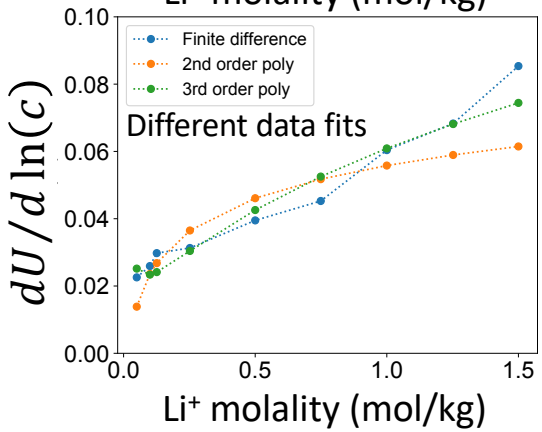
- Initially completed for 1M $LiPF_6$ in 3:7 EC:EMC



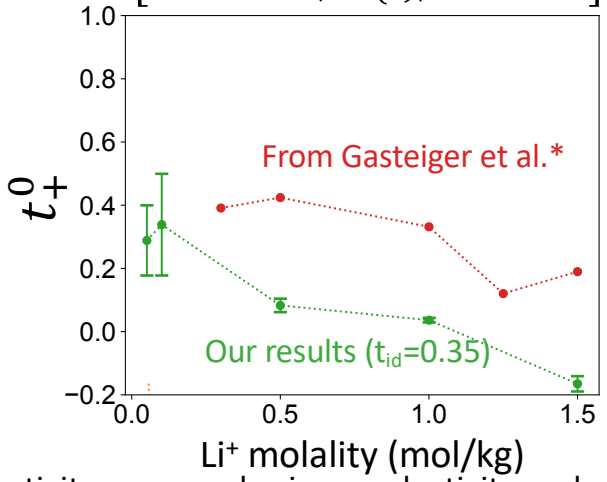


$$t_+^{id} = \frac{I_{ss}}{I_o}\left(\frac{\Delta V - I_0 R_{i,o}}{\Delta V - I_{ss} R_{i,ss}}\right)$$





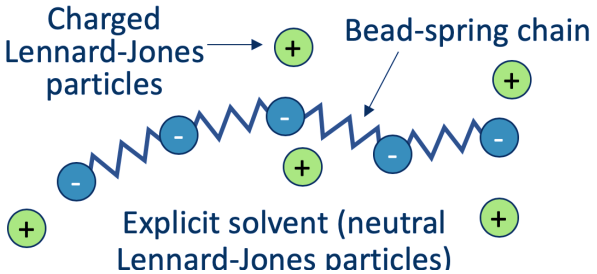
$$t_+^0 = 1 - \left[\frac{F\phi_c D_s c}{\kappa_s(\nu^+ z^+)^{\frac{1}{2}}\left(\frac{dU}{dln(c)}\right)}\left(\frac{1}{t_+^{id}} - 1\right)\right]$$



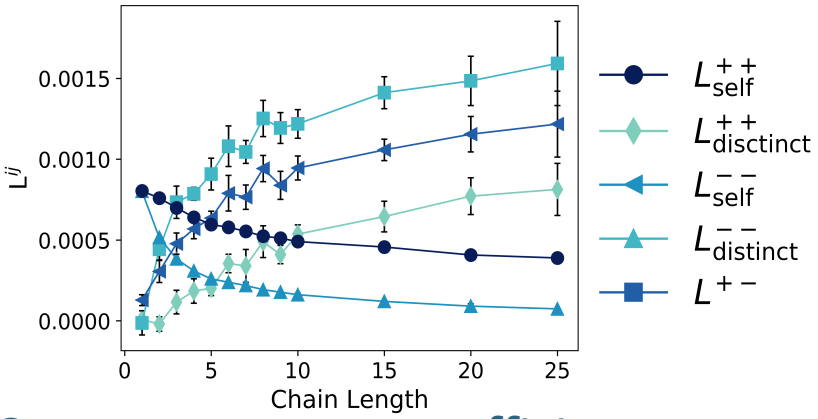
- Conductivity measured using conductivity probe
- $D_{\pm}^{eff}$ measured using restricted diffusion in Li-Li symmetric cells
- t_+^{id} (Bruce-Vincent transference number) measured using voltage holds in Li-Li cells
- dU/dln(c) (thermodynamic factor) measured using concentration cells.
- All used to calculate the concentrated solution Li+ transference number.

*Ehrl, Gasteiger et al., J. Electrochem. Soc. (2017) 164, A2716.

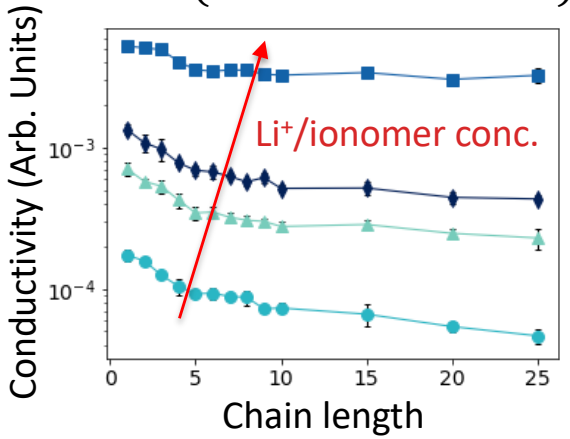
Accomplishment: Development of coarse-grained molecular dynamics to study polyelectrolyte transport (collab. with Kristin Persson, LBNL)

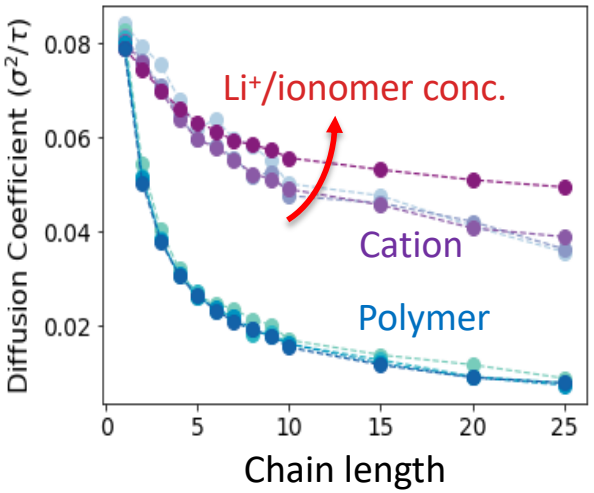


How/why does transport change:
–as we transition from a monomeric anion to a polyanion?
–with polymer/Li⁺ concentration?



$$\kappa = F^2(L^{++} + L^{--} - 2L^{+-})$$



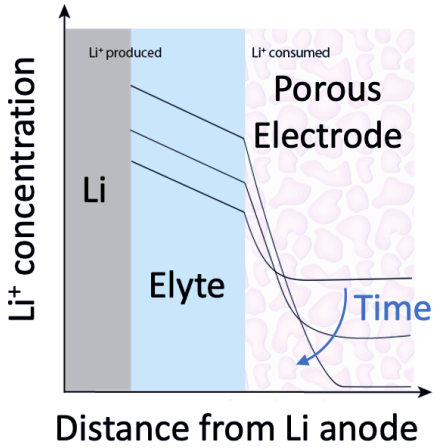


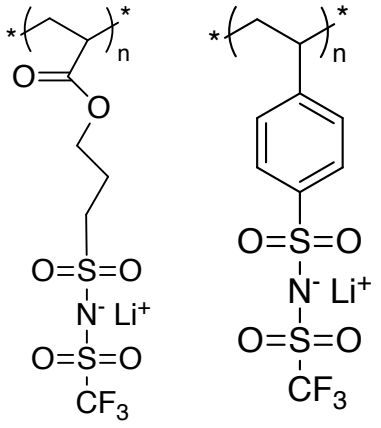
Onsager transport coefficients:

L^{+-}	• Ion pairing increases cation-anion correlations as concentration increases
$L^{--}_{distinct}$	• Cations on a given chain are highly correlated (substantial contribution)
L^{ii}_{self}	• As chain length increases, diffusion coefficient decreases
$L^{++}_{distinct}$	• Cations bound to the same polymer chain are highly correlated

Future Work (I): Experimental characterization of polyelectrolyte solutions and Li metal electrodes

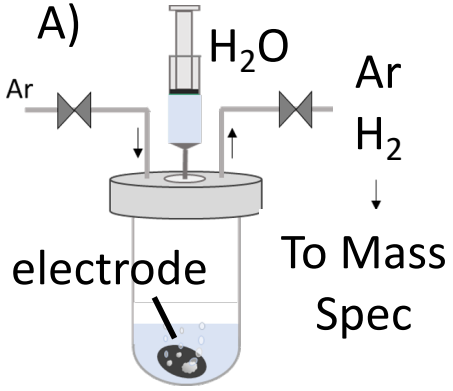
- Transport property characterization (conductivity, diffusion, transference number, thermodynamic factor) using developed electrochemical methods
  - Influence of solvent, additives, binary salt incorporation, molecular weight, charge density, concentration.



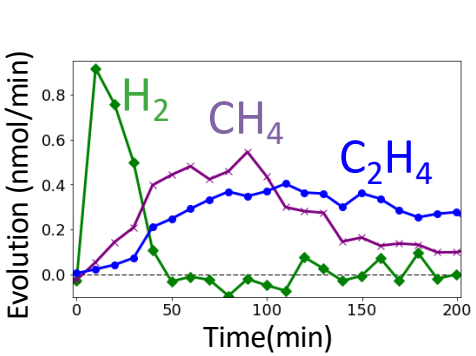


PA-TFSI PS-TFSI

- Li metal stability characterization using outgassing and titration techniques
  - Cycle electrodes, analyze dead Li using a post-mortem titration technique that quantifies dead Li by reaction with H_2O. (**Panel A**)
  - In situ gas evolution detection during Li metal plating to understand electrolyte reactivity with Li metal (**Panel B**: outgassing while plating Li metal in 1M $LiPF_6$ in 1:1 EC:DEC).



$$Li + H_2O \rightarrow LiOH + \frac{1}{2}H_2$$



In situ outgassing analysis to detect Li metal reactivity

Any proposed future work is subject to change based on funding levels

Future Work (II): Molecular dynamics simulation to probe large phase space (collab. with Kristin Persson, LBNL)

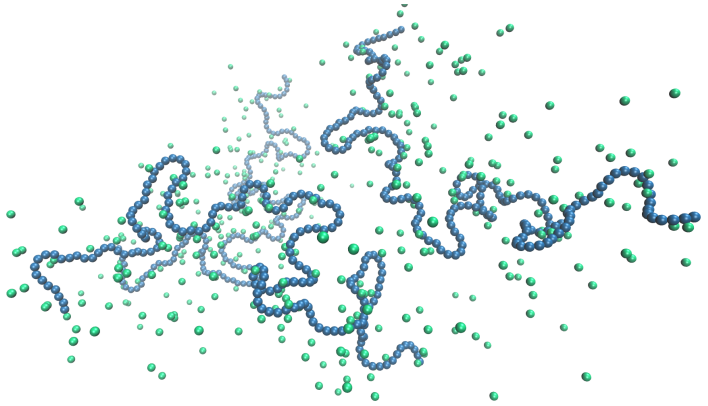
How do we design a high transference number, high conductivity polyelectrolyte solution?

Exploring larger parameter space

- Concentration
- Solvent dielectric constant
- Solvent donor number
- Polymer topology
- Presence of added salt
- Chain length
- Chain flexibility
- Polymer charge density
- Anion chemistry

Coarse-grained molecular dynamics

- Trading chemical specificity for lower computational cost
  - Higher throughput, longer timescales, bigger systems
- Key results will be verified with all-atom MD



Any proposed future work is subject to change based on funding levels

Summary

- Polyelectrolyte solutions provide a promising route towards liquid-like conductivities and single-ion conducting dry polymer transference numbers.
- We synthesized and fully characterized a sulfonated polysulfone series with varying molecular weights to understand influence of molecular weight on transport characteristics.
- We identified the influence of solvent-polymer interactions on ion transport properties and suggest that solvents that do not interact with the polymer backbone, yet still dissociate the sidechain ion pairs, will provide optimal properties.
- We developed methods to electrochemically measure the complete set of transport coefficients needed to fully define an electrolyte under the Newman-Balsara concentrated solution method.
- We have developed, and will continue to implement, a coarse-grained molecular dynamics simulation model to guide polyelectrolyte design.
- We will focus on Li metal stability and polyelectrolyte transport characterization in the near future.

Remaining challenges and barriers

- Understanding Li metal stability. Can combinations of liquids, polymers, additives provide sufficient chemical stability?
- Transport characterization is tricky for liquid electrolytes. In concentrated solution framework, sensitivity of each measured parameter on calculated properties (e.g., transference number) can make propagated error rather large. Methods need to be precise, accurate, and data spacing over a concentration range needs to be narrow.
- We need to continue to develop our understanding of how to optimize conductivity, transference number, and stability of polyelectrolyte solutions
  - Chemical analysis of Li metal stripping and plating using titrations and outgassing will help provide information on stability.
  - Coarse-grained molecular dynamics will provide molecular insight into approaches to optimize transport properties.

Critical assumptions and issues

- Past attempts at designing high transference numbers have not succeeded due to poor conductivity of resultant single-ion conductors and a poor understanding of the underlying molecular mechanisms for ion transport.
  - We aim to understand the influence of polymer/solution properties on ion transport to enable polyelectrolyte solutions with ion transport properties that are better than traditional liquid electrolytes.
  - This project is structured to develop this knowledge through a combined theory-experiment approach.
- Can we find a polymer/solution combination that is stable to Li metal?
  - We will leverage prior reported knowledge on useful additives and current collector substrates to engineer beneficial interfacial properties at Li metal electrodes.
- We assume that the 1D Newman-type model used to identify the benefits of high transference number electrolytes is not overly simplistic (e.g., it sufficiently captures the influence of solid electrolyte interface formation on electrode kinetics and transport).
  - This project will be structured to experimentally verify the importance of various electrolyte transport properties, such as the transference number, on porous electrode and Li metal battery performance.