Designing High Lithium-Ion Transference Number and High Stable Electrolytes for Lithium Batteries

Bryan D. McCloskey, Principal Investigator
Lawrence Berkeley National Laboratory
June 21-25, 2021
Project ID: bat419

Overview

Timeline

- Start Date: Oct. 1, 2019
- End Date: Sept. 30, 2022
- Percent complete: 50%

Budget

- Total budget (3 years): $825K
- FY21 funding: $250K

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** at **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
- Accurately and precisely measuring the complete set of transport coefficients Li-ion electrolytes is notoriously challenging, but essentially for predicting cell-level battery performance.

Objectives for FY21

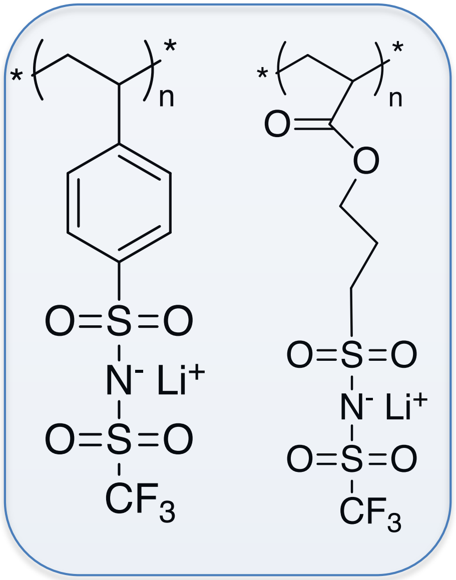
- Understand, using simulations and experiments, correlated ion motion and how electrolyte composition influences ion dynamics/pairing.
- Understand the poor reproducibility of transport measurement determination from reported experimental methods.
- Develop continuum scale modelling to help understand shortcomings in electrochemical transport analysis.

Milestones

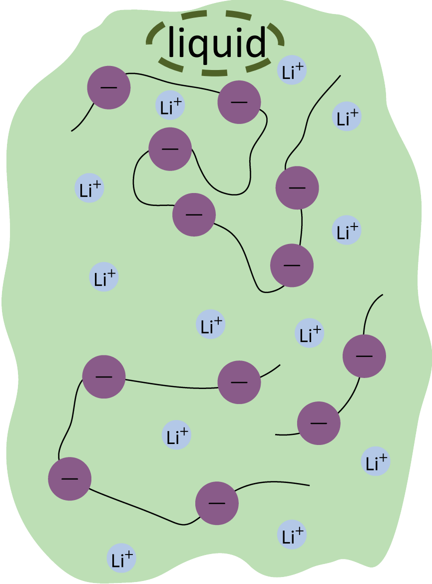
Date	Milestones	Status
December 2020	Establish a simple method to measure activity coefficients and thermodynamic factors for a model electrolyte.	Completed
March 2021	Synthesize very low molecular weight oligomer triflimide-based polyions (pTFSI).	Completed
June 2021	Measure conductivity, self diffusion, and potentials in concentration cells for model triflimide-based polyion (pTFSI) solutions.	On track
September 2021	Establish electrophoretic NMR techniques for measuring the true Li^+ transference number of pTFSI solutions.	On track

Approach

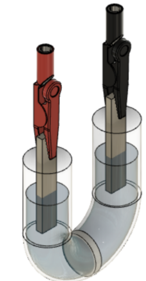
- Focus this year: Characterize transport properties using a combination of AC impedance, Li-Li symmetric cell polarization, concentration cells, restricted diffusion measurements.
- Focus this year: Use molecular dynamics to understand molecular underpinnings of ion transport trends.
- Synthesize single ion-conducting polymers.
- Prepare polyelectrolyte solutions to study influence of solvent composition and polymer molecular weight.



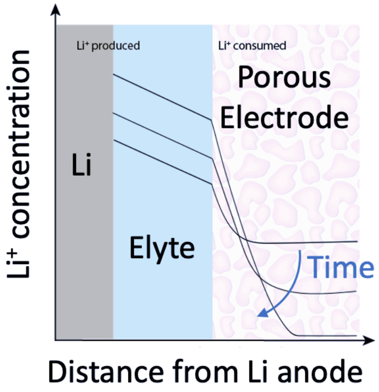
Synthesis



Preparation

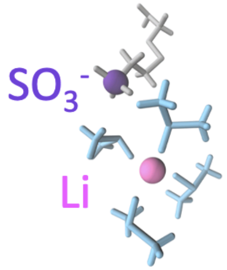


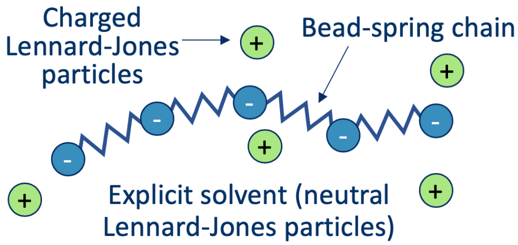
Concentration cell



Characterization

Solvent-Separated Ion Pair (SSIP)

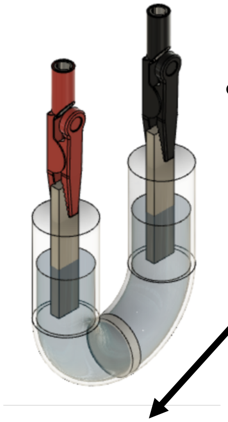




Modeling
(w/ K. Persson)

Approach (II): Characterization of electrolyte transport

- For a binary salt electrolyte, **3 transport coefficients** (salt diffusion coefficient, conductivity, transference number) and the **thermodynamic factor** (activity coefficient) need to be determined as a function of concentration.



experiments

- Li metal cells with well-studied system of $LiPF_6$ in 3:7 EC:EMC to study validity of theory & measurements
    - complex & highly non-ideal

theory

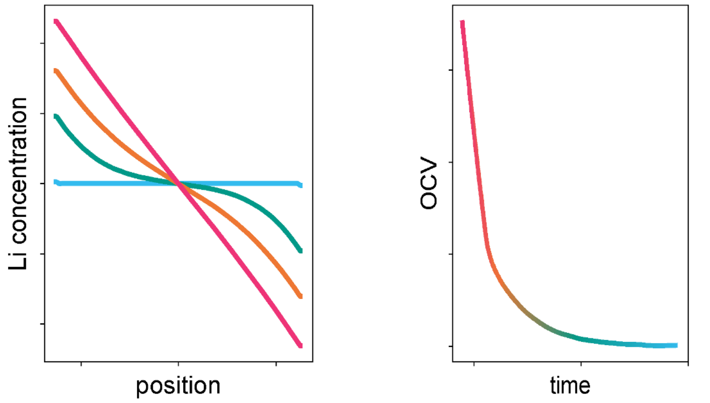
- understand ion transport theory
    - neglects other phenomena within the cell (e.g. corrosion, SEI, double layer)

$$t_i = \frac{\sum_j L^{ij} z_i z_j}{\sum_k \sum_l L^{kl} z_k z_l} = \frac{F z_i c_i u_i}{\kappa}$$

simulations

- 1-D finite element model of entire cell with physics from theory
    - allows evaluation of resistance contributions
    - $LiPF_6$ in 3:7 EC:EMC

Li-Li- symmetric cell



Concentration profiles during polarization

Open circuit voltage after polarization

ECSarXiv (2021) doi:10.1149/osf.io/b3yjm

Accomplishment: Provide guidance on restricted diffusion fitting window

Problem: Many fitted time windows have been used in restricted diffusion measurements, with different time windows yielding different results on the same relaxation data

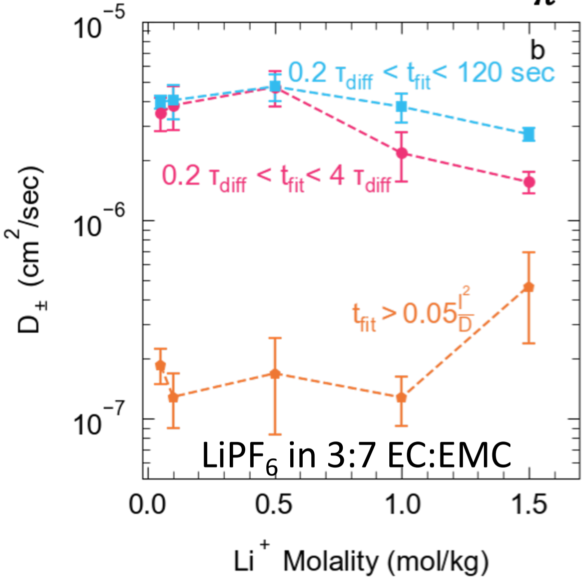
Goal: Identify appropriate time window to implement to accurately quantify salt diffusion in restricted diffusion measurements

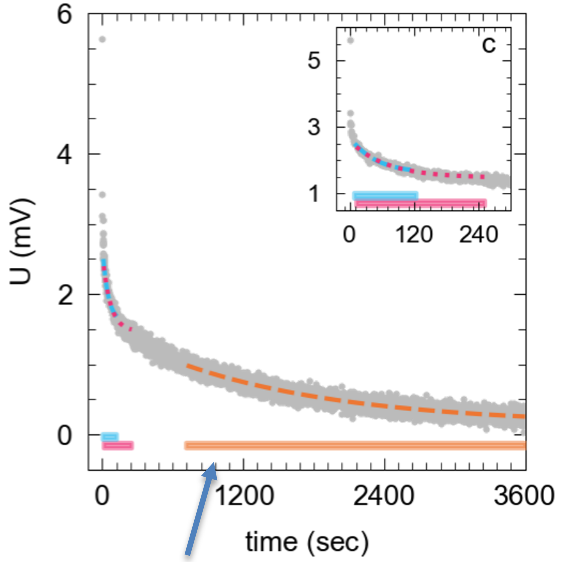
$$\tau_{\text{diff}} = \frac{1}{\pi^2}\frac{l^2}{D} \sim 60\ \text{sec}$$ for our cell

Experiment (Li|EC:EMC:1M LiPF$_6$|Li cell):

- Polarize cell constant voltage (15 mV) until steady state current is reached
- Stop current and monitor OCV relaxation
- Relate OCV to concentration relaxation to extract salt diffusion coefficient:

$$U(t) \approx \alpha \exp\left(\frac{-\pi^2 D_{\pm}(C_0)}{l^2}t\right)$$

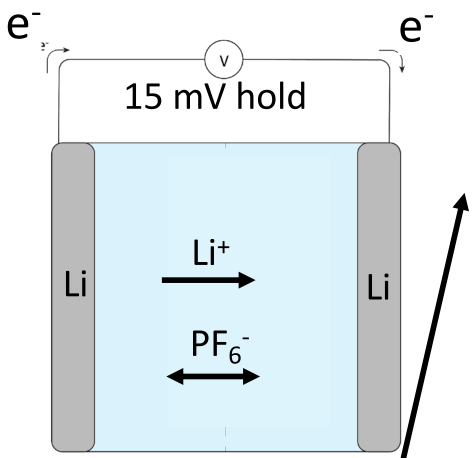


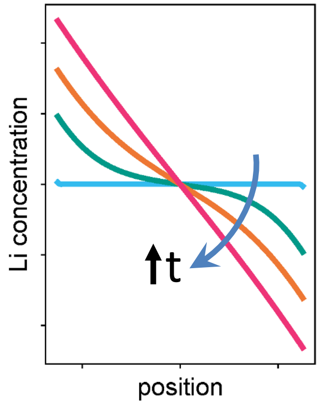


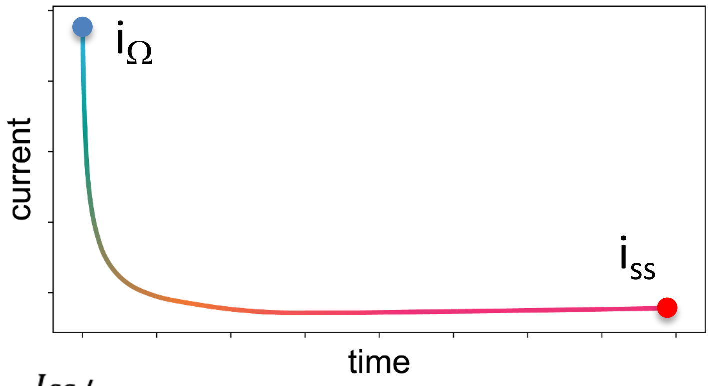
Captures relaxation response from SEI,
Perhaps SEI relaxation also partly captured
In shorter time window fits?

From analysis of many cells, we recommend restricting fit window to $0.2\tau_{\text{diff}} < t_{\text{fit}} < 4\tau_{\text{diff}}$ for any restricted diffusion measurement

Accomplishment: Identifying the outweighed influence of interfacial resistances on potentiostatic polarization measurements





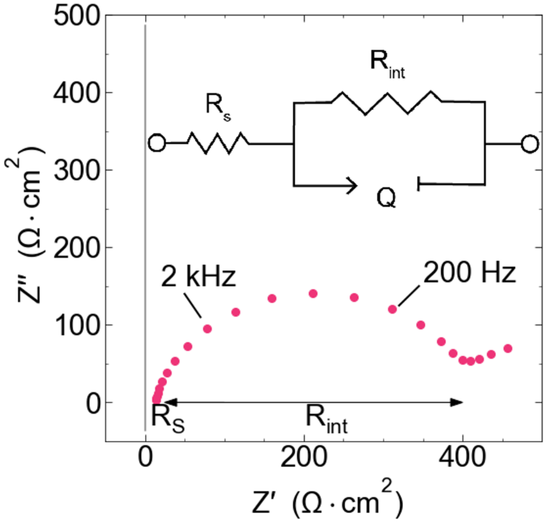


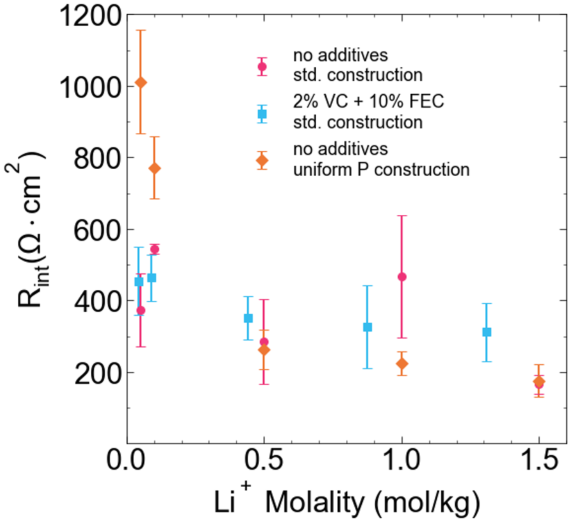
$$\frac{I_{ss}/\Delta\phi_{ss}}{I_\Omega/\Delta\phi_0} = \frac{I_{ss}(\Delta V - I_\Omega R_0)}{I_\Omega(\Delta V - I_{ss}R_{ss})} = t_+^{id} = \rho_+$$

R_0 and R_{ss} are total cell resistances at beginning and end of polarization

ρ_+ is necessary to calculate true Li$^+$ transference number

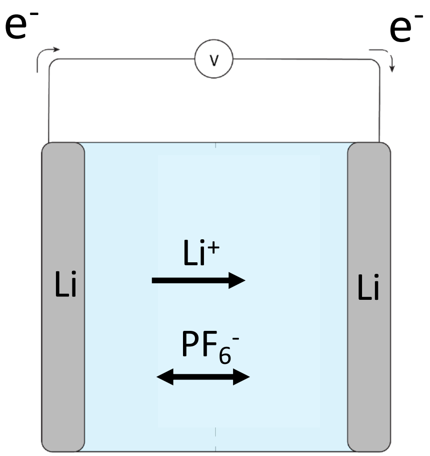
Li interfacial resistance (R_{int}) and its error are both substantially larger than bulk electrolyte resistance (R_s)

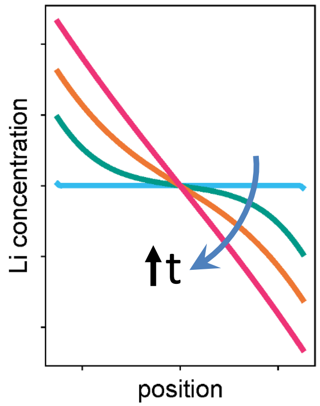


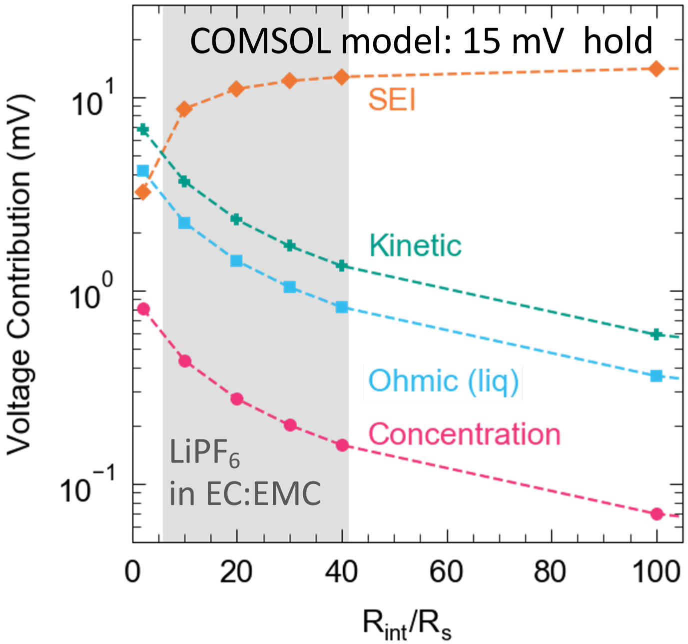


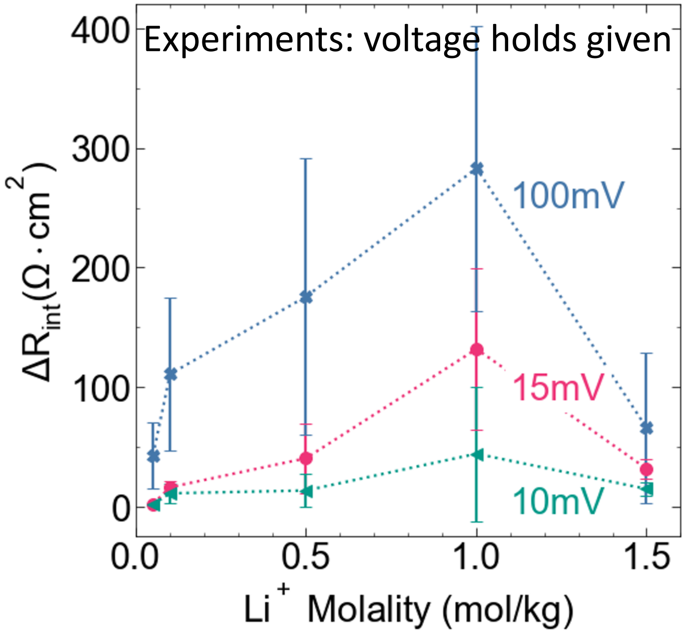
Accomplishment: Voltage loss breakdowns across a polarized Li-Li symmetric cell

- COMSOL model constructed to include potential drops due to interfacial kinetics, ohmic drop, Nernstian (concentration) drops, and SEI resistance.
  - SEI resistance used was that of a typical 1 m $LiPF_6$ in EC:EMC solution (~190 Ω cm^2)





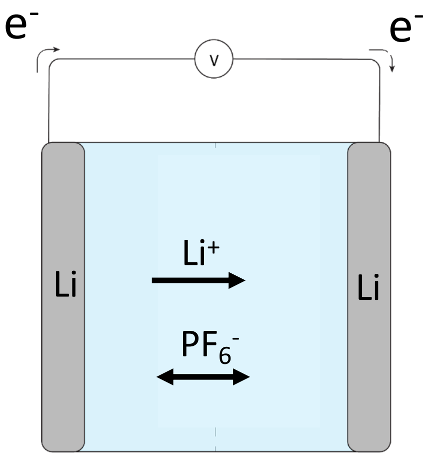


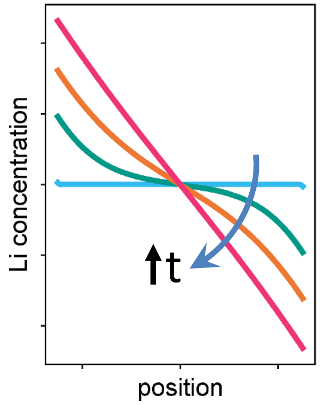


Ohmic contribution is desired quantity for ρ_+ calc.

For a 15 mV hold, Ohmic contribution only accounts for ~1 mV, SEI dominates. For larger holds, interface becomes unstable, results in large resistance deviations during polarization

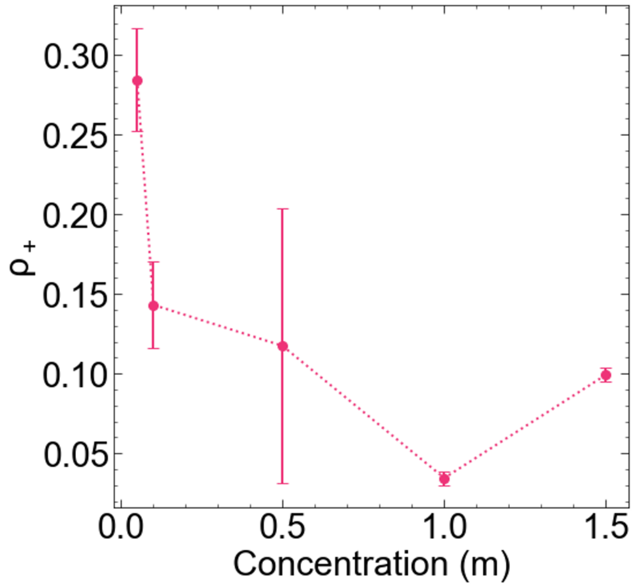
Accomplishment: ρ_+ is found to be a function of both SEI and electrolyte resistance (should only be a function of electrolyte resistance)



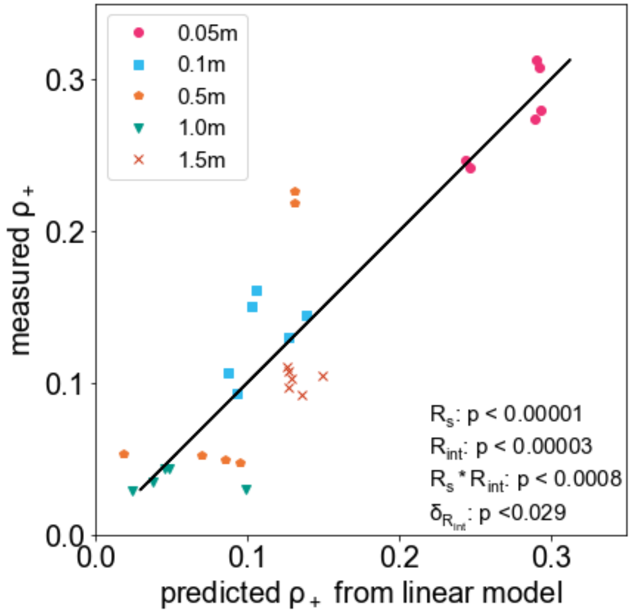


- Measured current ratio (ρ_+) can be predicted from a linear statistical effects screening model using interfacial resistance (Rint), its standard deviation (δ_{Rint}), and electrolyte Ohmic resistance (R_s)
- ρ_+ should only depend on i_{ss} and R_s

$$\rho_+^{\text{expt}} = aR_s + bR_{\text{int}} + c\delta_{R_{\text{int}}} + dR_sR_{\text{int}}$$



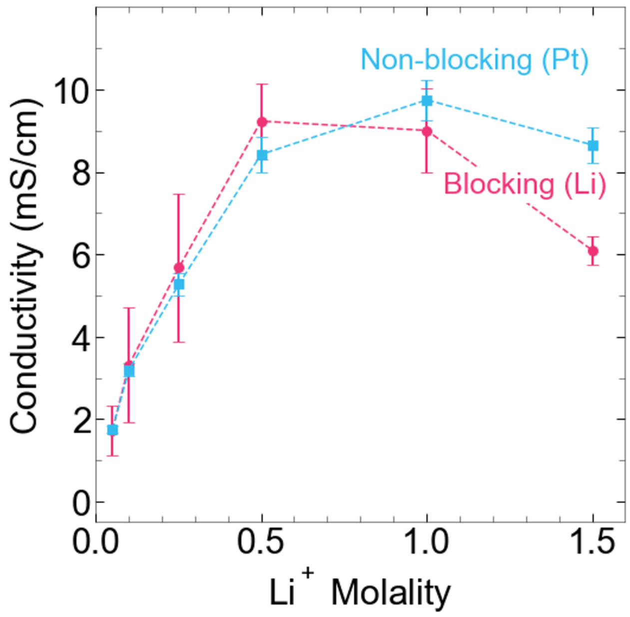
ρ_+ much lower than expected

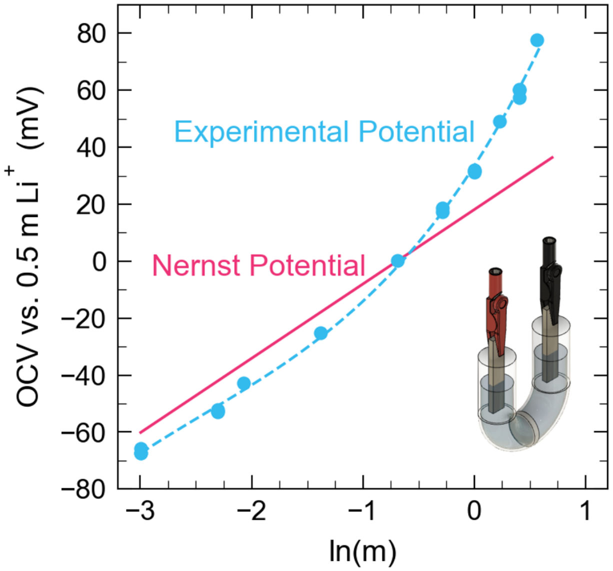


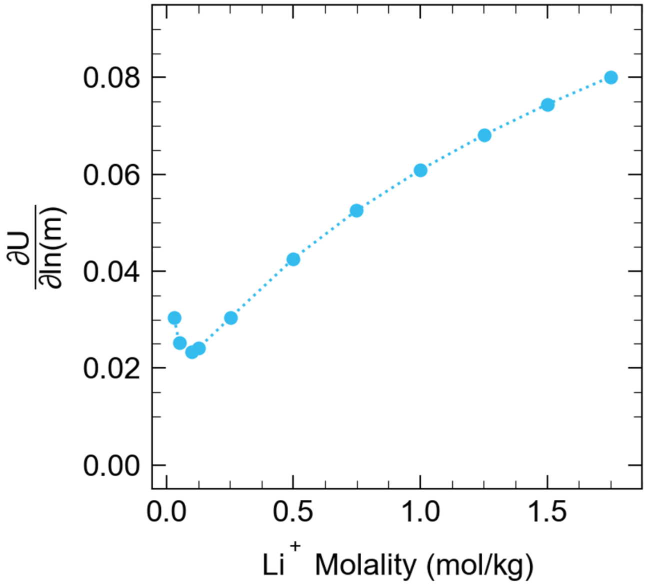
Polarization measurements involving high interfacial impedance, low electrolyte resistance result in experimental artefacts that make deconvolution of both difficult

Accomplishment: Conductivity and concentration cell data can be measured with high reproducibility

- Conductivity measured in either a Li-Li or Pt-Pt symmetric cell and AC impedance.
- Concentration cell data important for calculation of thermodynamic factor to capture non-idealities





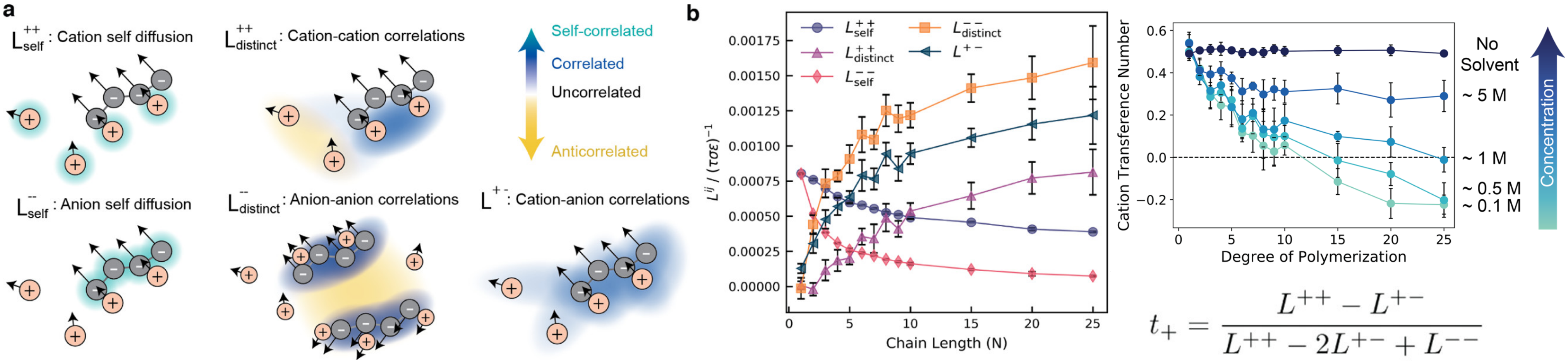


Measurements not involving polarization are reproducible and accurate

Accomplishment: Completion of molecular dynamics simulations of polyelectrolyte solutions

Macromol. (2020) 53(21), 9503-9512; ***Macromol.*** (2021) 54, 6: 2575-2591;
AIChE Journal (2020) 66(12), e17091

- Coarse grained model combined with Onsager transport theory to understand ion correlations and ion dynamics



$$t_+ = \frac{L^{++} - L^{+-}}{L^{++} - 2L^{+-} + L^{--}}$$

Increasing concentration and creating highly entangled solutions could provide a pathway to high transference number and conductivity

Onsager transport coefficients:

Collab. w/ K. Persson (LBNL)

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

Accomplishment: Publications and presentations (FY20-21)

Publications

1. Fong, KD, Bergstrom, HK, McCloskey, BD, Mandadapu, KK. Transport phenomena in electrolyte solutions: Nonequilibrium thermodynamics and statistical mechanics. ***AIChE Journal*** (2020) 66(12), e17091.
2. Fong, K. D.; Self, J.; McCloskey, B. D.; Persson, K. A. "Onsager Transport Coefficients and Transference Numbers in Polyelectrolyte Solutions and Polymerized Ionic Liquids." ***Macromolecules*** (2020) 53(21), 9503-9512.
3. Fong, K.D.; Self, J.; McCloskey, B. D.; Persson, K. A. "Ion Correlations and Their Impact on Transport in Polymer-Based Electrolytes." ***Macromolecules*** (2021) 54, 6: 2575-2591.
4. H. K. Bergstrom, K. D. Fong, B. D. McCloskey. "Interfaicial Effects on Transport Coefficient Measurements in Li-ion Battery Electrolytes." ECSarXiv (2021) doi:10.1149/osf.io/b3yjm
5. Grundy, L. S.; Shah, D. B.; Nguyen, H. Q.; Diederichsen, K. M.; Celik, H.; DeSimone, J. M.; McCloskey, B. D.; Balsara, N. P. "Impact of frictional interactions on conductivity, diffusion, and transference number in ether- and perfluoroether-based electrolytes." ***Journal of the Electrochemical Society*** (2020) 167(12), 120540.

Presentations

1. ***American Institute of Chemical Engineering Annual Conference 2020*** (virtual, November 16-20): "Molecular Dynamics Characterization of Onsager Transport Coefficients and Transference Number in Polyelectrolyte Solutions"; Oral, presented by Kara Fong
2. ***American Institute of Chemical Engineering Annual Conference 2020*** (virtual, November 16-20): "Theory of Irreversible Thermodynamics and Non-Equilibrium Statistical Mechanics for Transport Phenomena in Electrolyte Solutions"; Oral, presented by Kara Fong
3. ***American Institute of Chemical Engineering Annual Conference 2020*** (virtual, November 16-20): "The Effect of Interfacial Phenomena on Ion Transport Characterization in Electrolyte Solutions for Li Metal and Li-Ion Batteries"; Oral, presented Helen Bergstrom
4. ***Women Excelling in Computational Modeling Engineering Seminar Series*** (virtual, Apr. 15, 2021). "Ion Correlations in Li-Ion Battery Electrolytes"; Oral, presented by Kara Fong
5. ***The Electrochemical Society (ECS) PRiME 2020*** (virtual, Oct. 4-9, 2020): "Characterizing Ion Transport in Non-Aqueous Electrolyte Solutions for Li-Ion and Li- Metal Batteries"; Oral, presented by Helen Bergstrom
6. ***Battery Modeling Webinar Series*** (virtual, Oct. 6, 2020): "Transport Phenomena in Electrolyte Solutions: Non-Equilibrium Thermodynamics and Statistical Mechanics"; Oral, presented by Kara Fong

Response to previous year's reviewer's comments

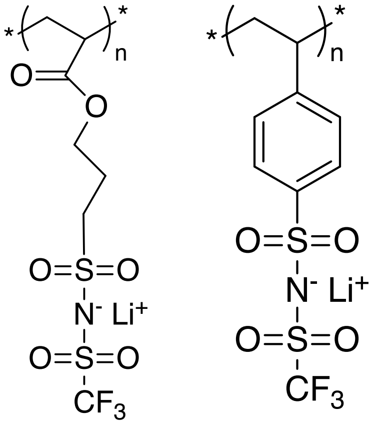
- This is the first year that the project has been reviewed

Summary

- 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.
- A new protocol for fitting restricted diffusion data was developed.
- Restricted diffusion measurements in Li-Li-symmetric cells could capture SEI relaxation process on top of electrolyte concentration relaxation
  - Will develop a Raman microfluidic device to more reliably analyze $D_{\pm}$
- For high conductivity liquid electrolytes that form high impedance Li metal interfaces, polarization techniques measure artefacts associated with the high impedance interface
  - Results in current ratios (ρ_+) that are correlated to the interfacial resistance, making ρ_+ not solely related to electrolyte transport.
  - Develop a small volume Hittorf-type cell to quantify the transference number directly [see Hou, T., Monroe, C. Electrochim. Acta (2020)]
- Necessary experiments that do not rely on polarization (concentration cells and AC impedance conductivity) are reproducible and accurate.
- Developed Onsager transport theory and applied it to a coarse-grained molecular dynamics simulation model to guide polyelectrolyte design.

Future work

- Develop a Raman microfluidic device to more reliably analyze $D_{\pm}$
- Develop a small volume Hittorf–type cell to quantify the transference number directly [see Hou, T., Monroe, C. Electrochim. Acta (2020)]
- Characterize transport properties of polyelectrolyte solutions as a function of solvent, binary salt incorporation, molecular weight, concentration
  - Polymers to be studied are shown at right (already synthesized)
- Characterize Li metal stability in the presence of polyelectrolyte solutions using outgassing and titration techniques



PA-TFSI PS-TFSI

Any future work is subject to change based on funding levels

Remaining challenges and barriers

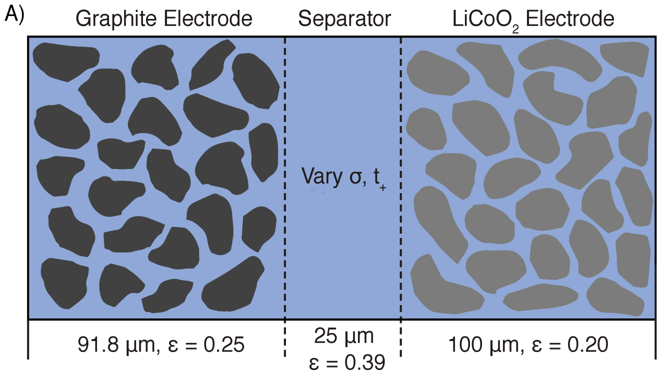
- Li metal interfacial impedance. Can we identify other planar electrodes with lower impedance?
- Transport characterization is nuanced for high conductivity electrolytes. In concentrated solution framework, sensitivity of each measured parameter on calculated properties (e.g., transference number) can make propagated error rather large. Methods need to be precise, accurate, and data spacing over a concentration range needs to be narrow.
  - Will develop new techniques (Raman microfluidic device for diffusion coefficient, Hittorf cell for transference number) that don't rely on a polarization experiment.
- 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

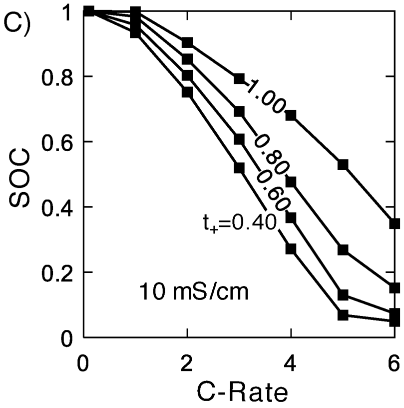
- Past attempts at designing high transference numbers have not succeeded due to poor conductivity of resultant single-ion conductors and a poor understanding of the underlying molecular mechanisms for ion transport.
  - We aim to understand the influence of polymer/solution properties on ion transport 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.

Motivation to study polyelectrolyte solutions

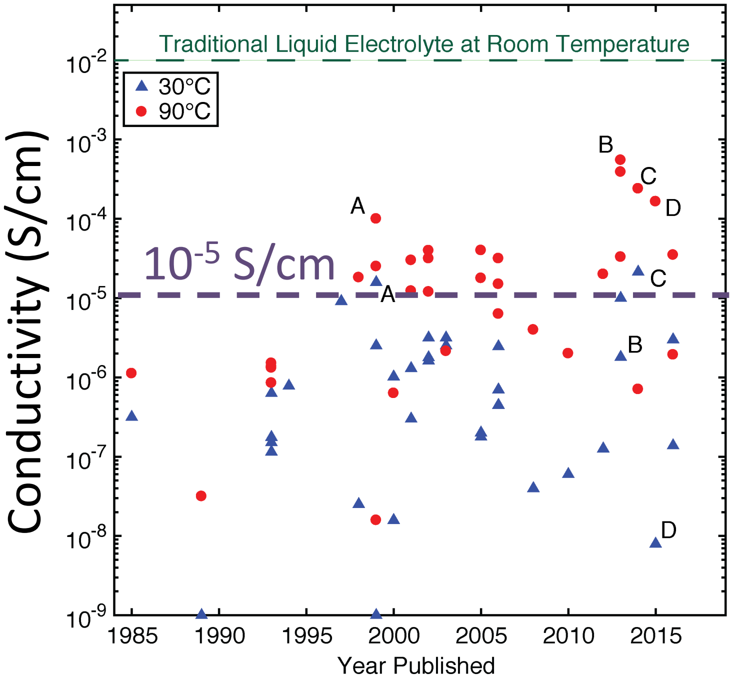
- Newman-type modeling predicts high transference number electrolytes would enable higher C-rates in Li-ion batteries

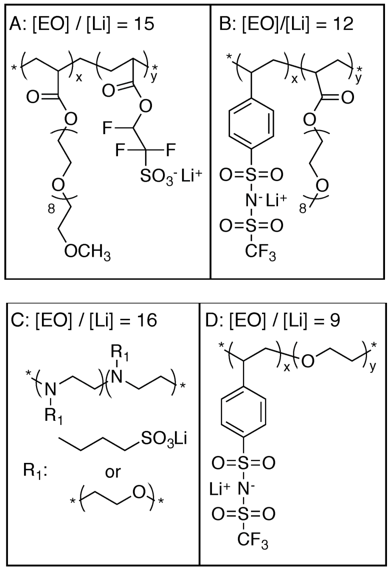


$$t_+ = \frac{D_+}{D_+ + D_-}$$



- 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.