Predicting and Understanding Novel Electrode Materials from First-Principles

Principal Investigator: Kristin Persson

Julian Self, Eric Sivonxay and Jianli Cheng

Principal Investigator, Project ID BAT091

Department of Materials Science and Engineering, UC Berkeley, Berkeley, California 94720

Overview

Timeline

- October 1st 2016 - September 30st 2019.
- Percent complete: 90%

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

Budget

- Funding for FY 19: $500K

Partners

- NREL; Tony Burrell (SEista Program)
- Bryan McCloskey (LBNL)
- Brett Lucht (University of Rhode Island)

Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Tien Duong

Relevance

Impact:

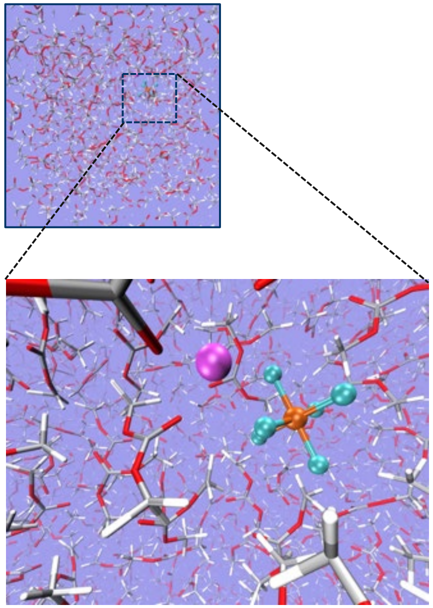
Research will aim to understand and suggest improvements for

- Li-ion conduction in non-aqueous, super-concentrated electrolytes
- Li-ion conduction in amorphous oxide coating materials
- Oxygen transport blocking in amorphous oxide coating materials
- Li-ion conduction and phase behavior in Si alloy anodes

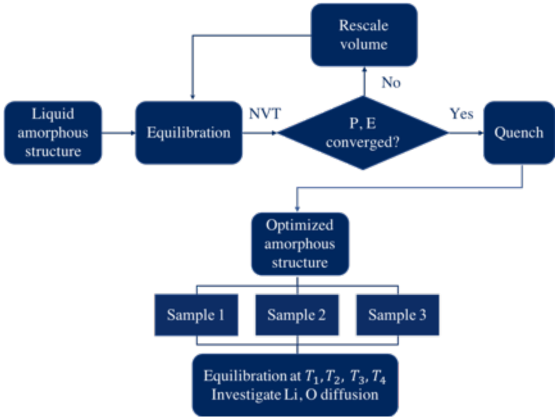
Objectives:

- Identify Li-ion and oxygen conduction mechanisms in amorphous oxide coatings to suggest optimal formulations
- Identify solvation environments, viscocity and conduction mechanisms in super-concentrated nonaqueous electrolytes, and propose changes to solvent/salt compositions to improve active ion conductivity
- Computationally screen for optimal Si alloy compositions to maximize Li-ion conductivity while promoting stable SEI formation and alloy formation.

Approach



- Larger non-reactive systems which need long equilibration time (e.g. solvation structures) are treated with semi-empirical classical molecular dynamics
- Electrochemical and chemical reactions are treated with first-principles, quantum mechanical methods (VASP, Gaussian)
- Amorphous solids are obtained through ab-initio molecular dynamics and a melt-quench process (see flow diagram: right)



Rescale volume

Liquid amorphous structure

Equilibration

NVT

P, E converged?

No

Yes

Quench

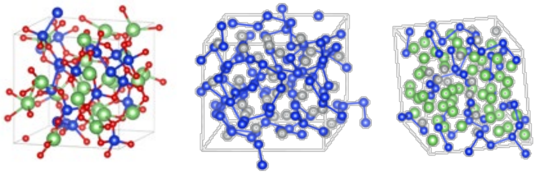
Optimized amorphous structure

Sample 1

Sample 2

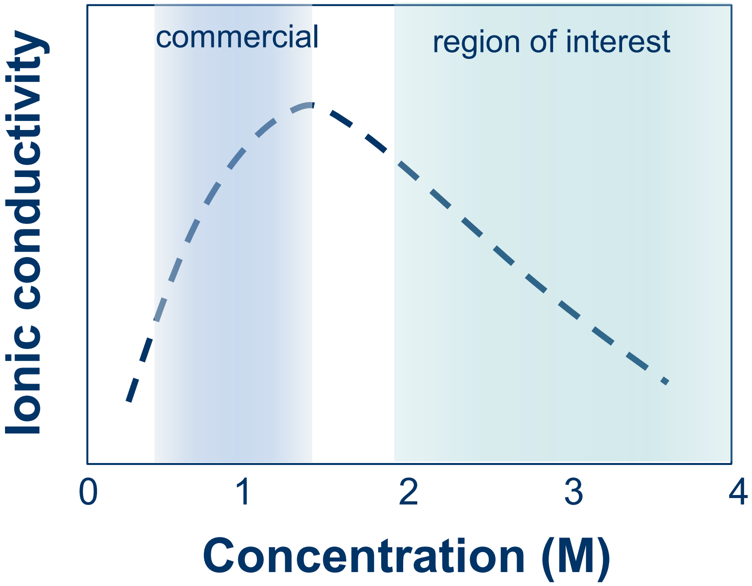
Sample 3

Equilibration at T_1, T_2, T_3, T_4
Investigate Li, O diffusion



Month / Year	Milestone	Status
December 2018	Finish benchmarking of algorithms for obtaining reliable solvation structures and ionic conductivity in highly concentrated liquid electrolytes	Completed
January 2019	Identify Li ion conduction mechanisms in Si-Sn alloy anode, using first-principles modeling.	Completed
April 2019	Evaluation of SiO_2 and SnO_2 as surface phases from the perspective of ionic conduction and reactivity with Li.	Completed
July 2019	First evaluation of amorphous oxygen-retention and Li diffusion enhancing coatings using the Materials Project infrastructure.	Ongoing

Uncertainty of transport mechanisms in superconcentrated Li electrolytes

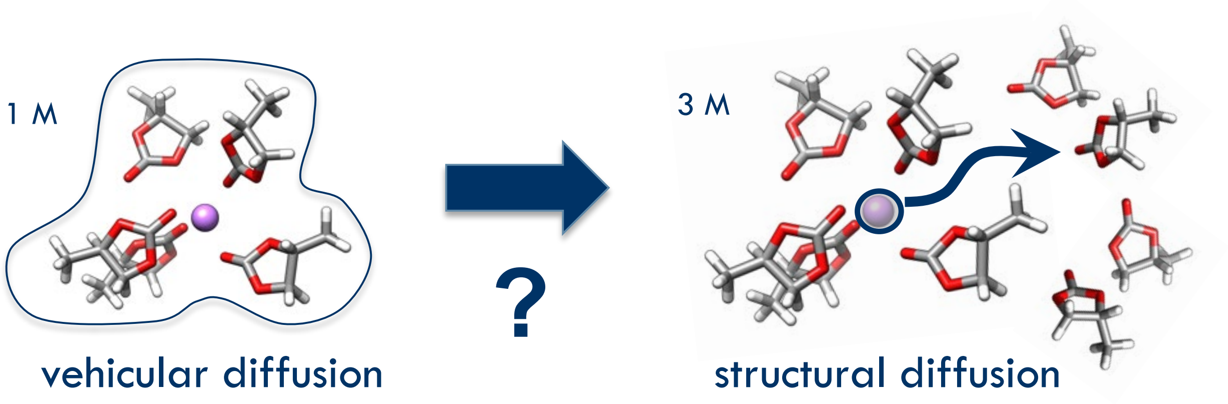


Li+ ion conduction in *dilute solutions* is generally depicted as *"vehicle-type" mechanism*, in which Li^+ conducts together with its solvation sheath as a form of $[Li(solvent)_n]^+$.

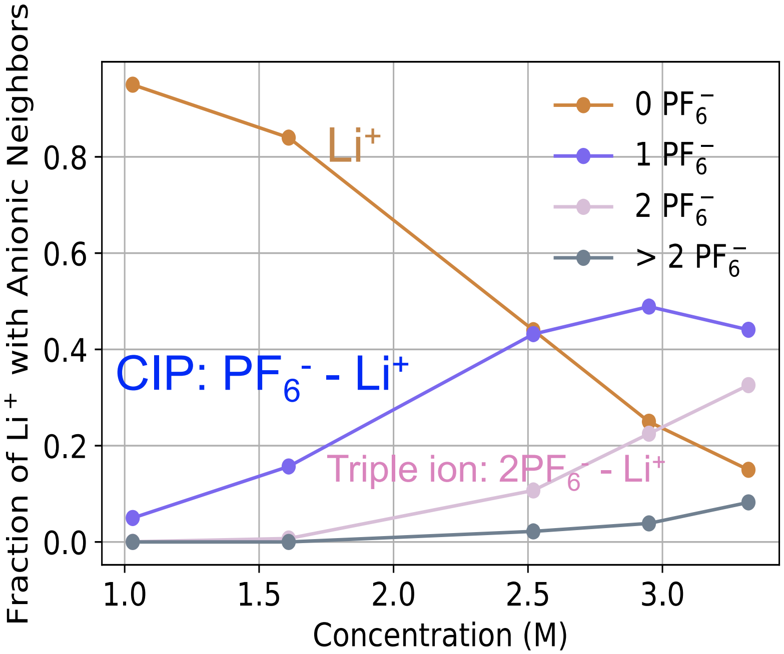
..

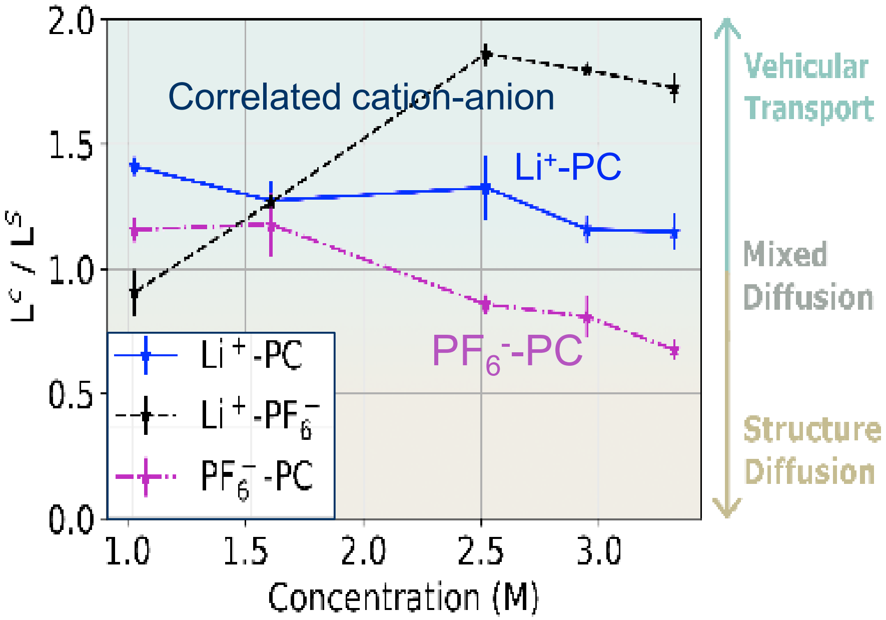
In highly concentrated solutions a *repeated ion dissociation/association process* is proposed.

Adapted from Yamada and Yamada, JECS, 162 (14) A2406-A2423 (2015)



Speciation and transport mechanisms as function of concentration

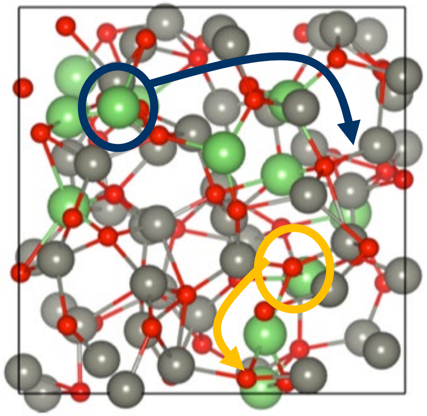




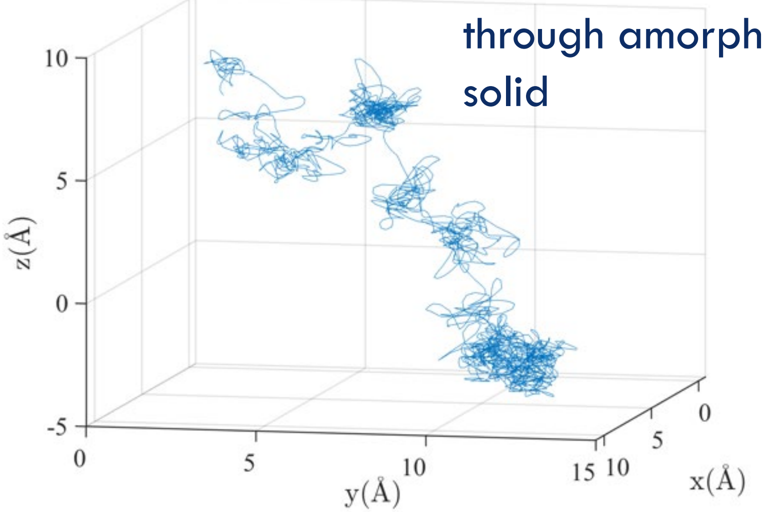
Even at 3.2 M there is still a significant fraction of solvated Li^+ clusters (e.g. free ions and/or solvent-separated ion pairs), albeit much less than at 1.0 M.

Throughout the concentration range, Li^+ diffuses with a PC solvation shell with frequent solvent exchange: **mix of structural and vehicle diffusion.** We find that **Li^+ and PF_6^- diffuse together** in a more pronounced manner at higher concentrations. Throughout the concentration range, PF_6^- with PC exhibits more **structure-type diffusion** than for Li^+.

Ionic conduction mechanisms in amorphous oxide coatings

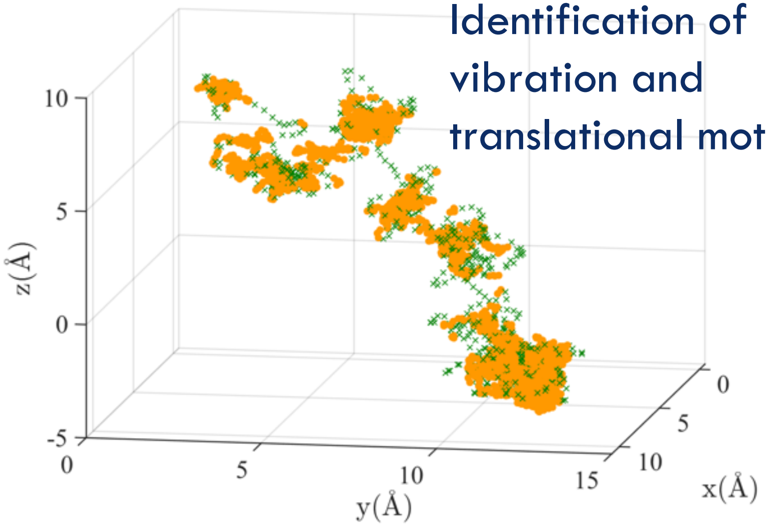


How does Li and oxygen ions move through an amorphous solid? What are the chemical coordination environments where the ions get ‘stuck’? Analyzing the trajectory and how the ions move showcases what coordination environments cause diffusion bottlenecks.



Li trajectory through amorphous solid

Density-based spatial clustering



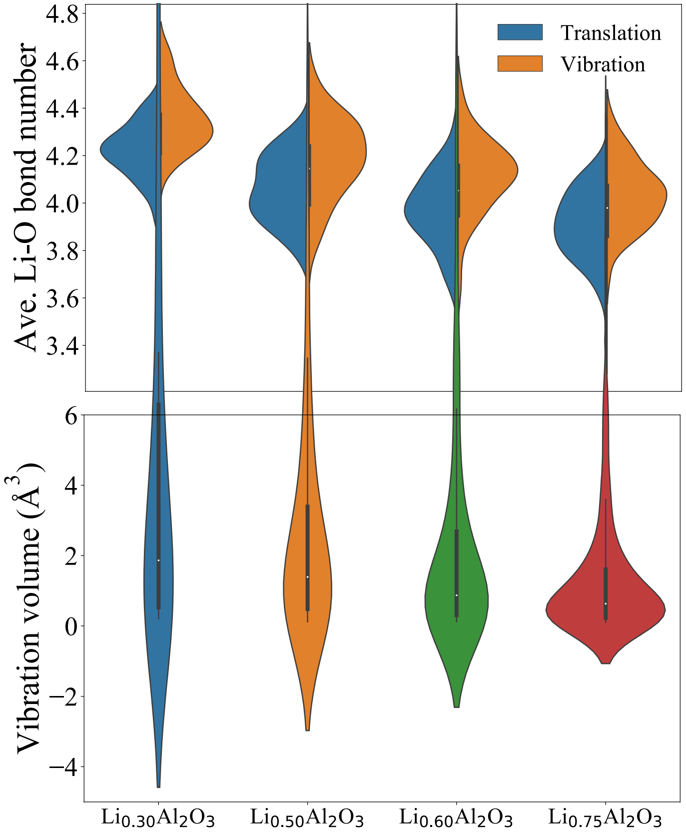
Identification of vibration and translational motion

Yellow dots: vibrational motions

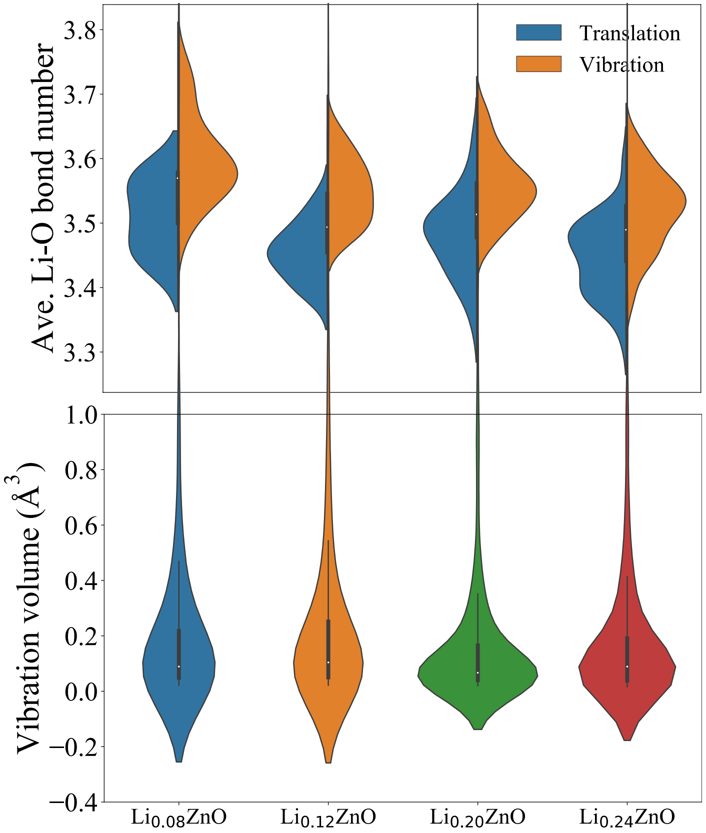
Green dots: translational motions

Li diffusion in amorphous Al_2O_3 and ZnO

amorphous $Li_xAl_2O_3$



amorphous Li_xZnO

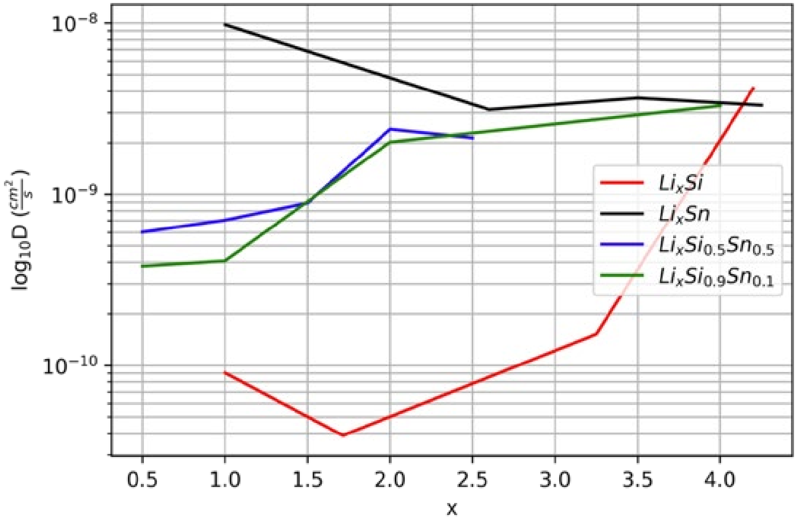


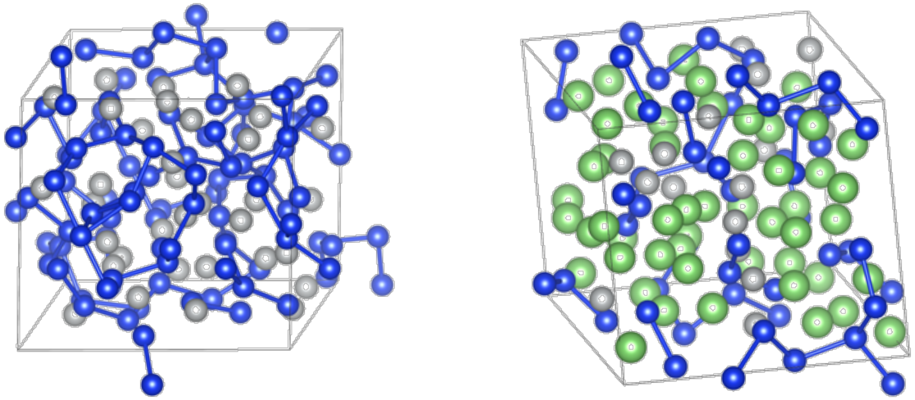
- Increased Li concentration leads to fewer Li-O bonds which causes lowering of vibrational motion and increased Li diffusion.
- Vibration environments exhibit higher Li-O bonds, and Li diffusion (translation) is accompanied by a Li-O bond disassociation/association process.
- Li^+ diffusion in Al_2O_3 is lower than in ZnO, which is conformed by higher vibrational volume, and higher number of Li-O bonds.

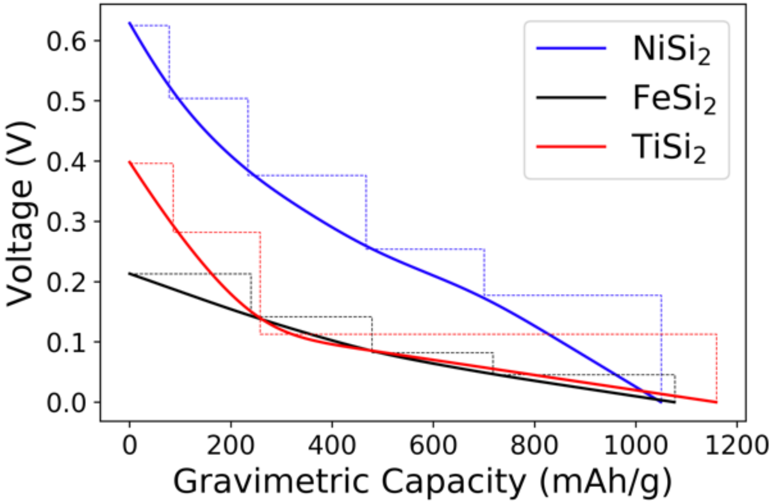
Screening Si alloys for favorable voltage and phase behavior

- Si-Sn alloys are expected to improve rate behavior as Li diffusion in Sn is significantly higher than in Si, across relevant Li concentrations.
- However, Si and Sn phase separate under lithiation, which leads to inhomogeneities.

- Screening Si-M and Si-Sn-M alloys.
- 32 out of 53 binary Si-M systems favor alloying lithiation; and 'M' will be used as candidates for to Si-Sn-M systematic explorations.







Partners and Collaborations

We are excited to discuss our electrolyte work with Bryan McCloskey at LBNL/UC Berkeley as well as working with Brett Lucht at University of Rhode Island, for measurement of bulk electrolyte properties.

The Si bulk electrode work is performed in collaboration with Brian Cunningham's SEista program, where the Si surface-interface and bulk electrolyte are modelled.

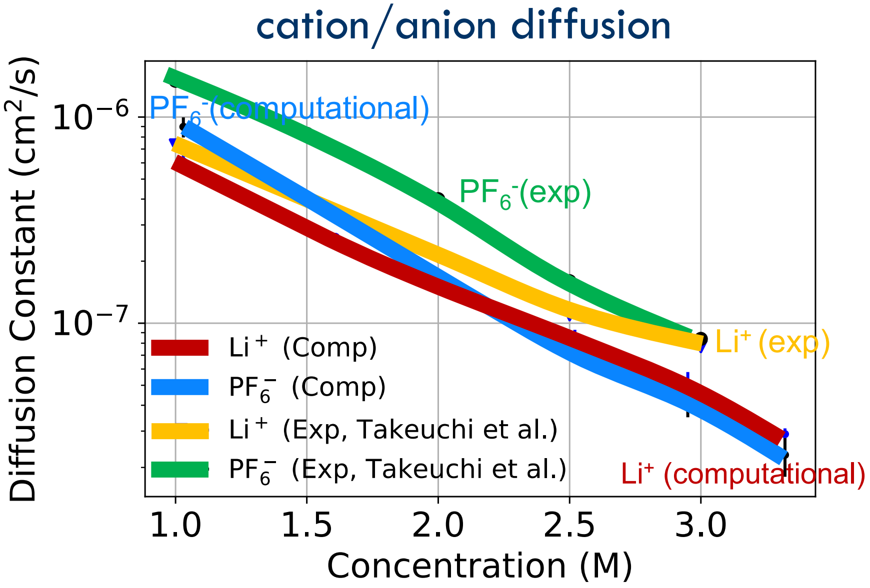
Collaborations with Robert Kostecki and Wei Tong at LBNL on synthesis and characterization of novel Si-Sn-M alloy materials.

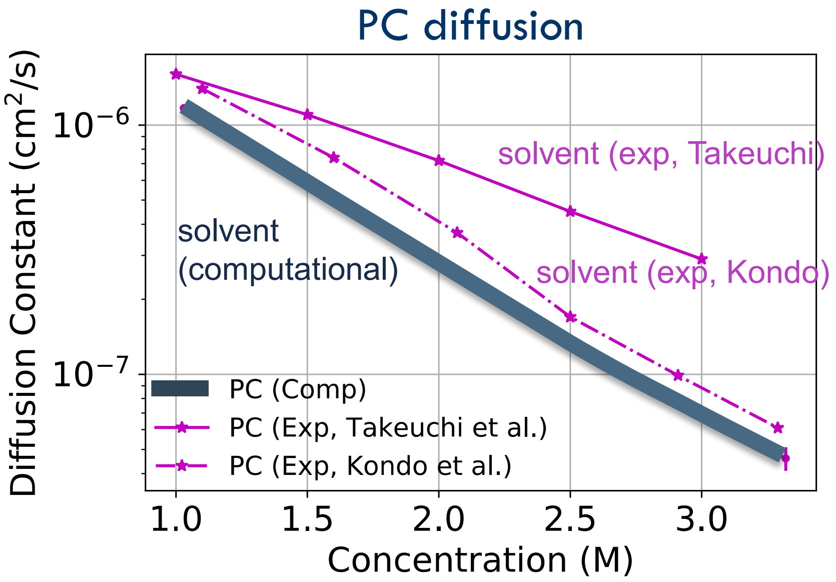
Summary and Future Work

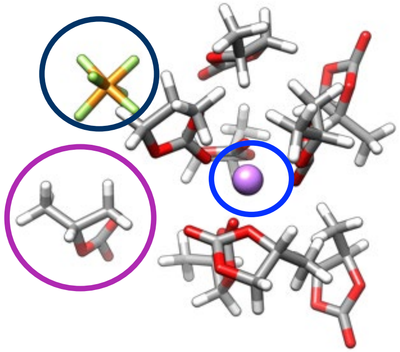
- From 1.0 M to 3.3 M $LiPF_6$ in PC, Li^+ exhibits mixed diffusion behavior. There is some structural diffusion quality to the Li^+ -transport, but more vehicular. We also find that PF_6^- follows a more structure-type diffusion than Li^+ at all concentrations: solvation shell less important. Importantly, the mode of conduction of Li^+ is not radically altered and hence we will explore different mixed solvents going forward.
- In amorphous Al_2O_3 and ZnO we have devised a methodology for quantitative measurement of ionic diffusion and identification of transport bottlenecks. We find improved Li diffusion with increasing Li concentration, where the vibrational modes are discouraged and the translational modes favored. We also find that Li^+ diffusion in Al_2O_3 is lower than in ZnO, which is confirmed by higher vibrational volume, and higher number of Li-O bonds. We will use these insights to simulate other systems, to identify materials with high Li conductivity and low O conductivity.
- Li^+ diffusivity in amorphous Li_xSn is ~100x greater than Li_xSi at low Li fraction and a small quantity of Sn can have large impact on Li-mobility. However, the Si-Sn phase separates upon lithiation which is prompting us to explore ternary Si-Sn-M systems in the future.

Technical Backup

Comparing computed diffusion constants to experiments







Dynamical analysis from classical molecular dynamics simulations showing excellent agreement with available experimental results of specific diffusion constants, indicating that the force fields accurately capture the transport of the separate species as a function of concentration.

Experimental data from Takeuchi *et al.* Journal of Molecular Liquids 2009, 148, 99. and Kondo *et al.* The Journal of Physical Chemistry B 2000, 104, 5040.