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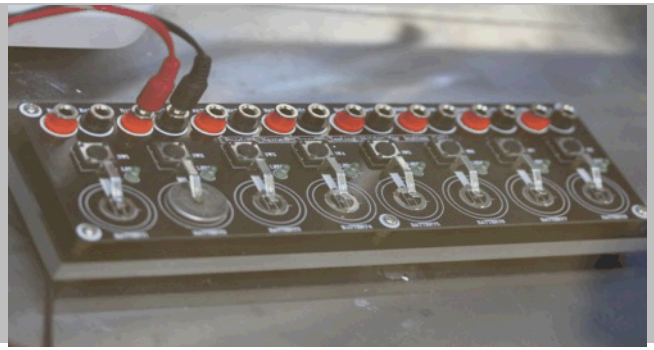

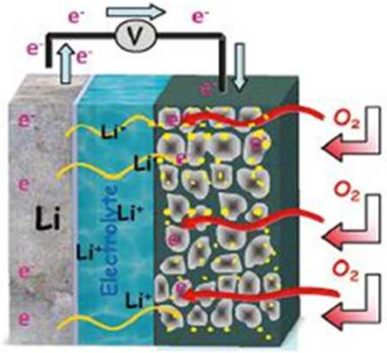

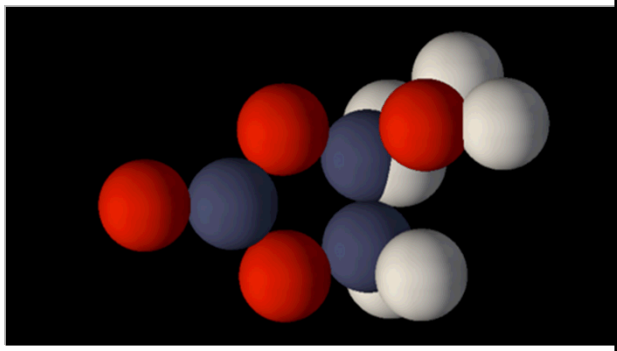

Improving Li-Air batteries by accurately predicting lithium diffusion coefficients

M. Kane, D. Ward, J. Templeton, R. Jones, K. Erickson and K. Reyes

U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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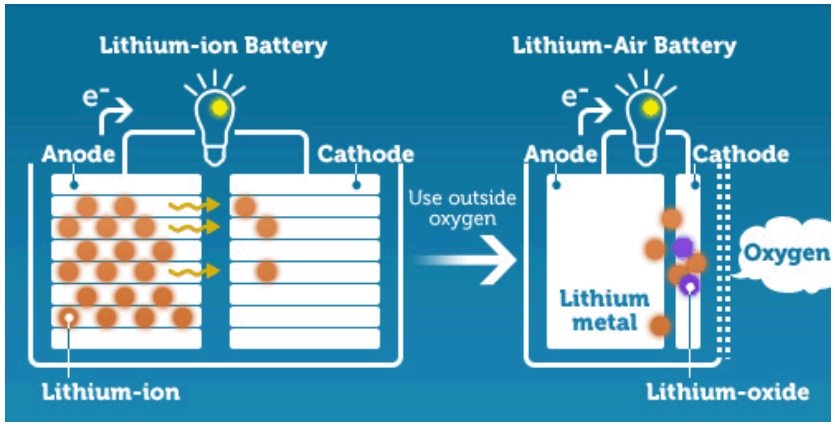
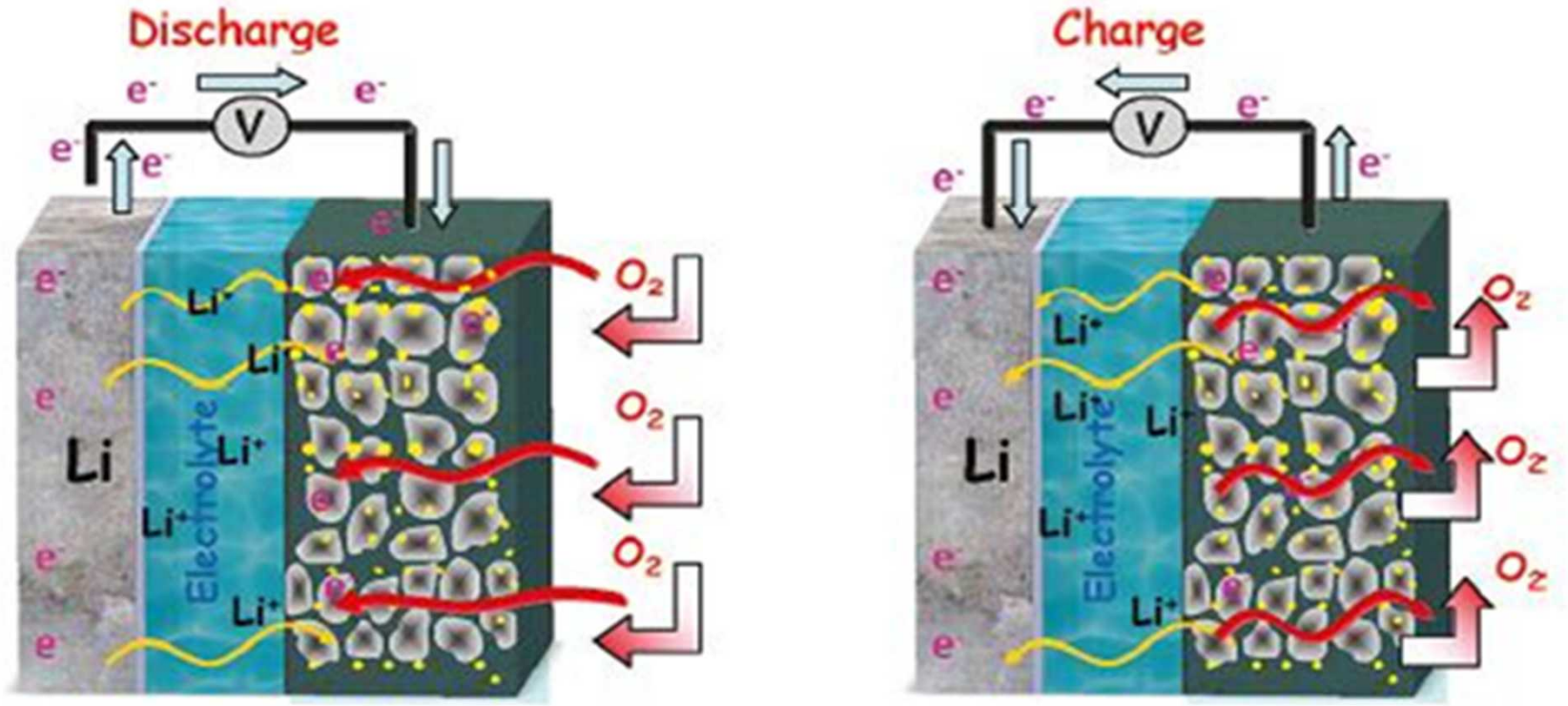
Motivation

- Li-O_2 batteries →
  - Highest possible theoretical energy density of any known battery chemistry
  - Cathode eliminated, uses oxygen (air) at nearly half the volume and weight of other Li batteries
  - No thermal runaway issues
  - Many applications: vehicles, portable power, defense
  - There are many challenges that need to be overcome



Background – Li-air batteries



Possible reaction products formed at the cathode:

$$Li^+ + O_2 \rightarrow LiO_2$$

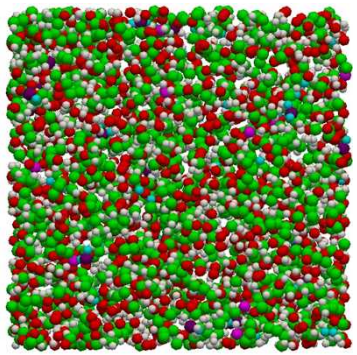
$$4Li^+ + O_2 \rightarrow 2Li_2O$$

$$Li^+ + LiO_2 \rightarrow Li_2O_2$$

*Note: figure not to scale

Significance of our work

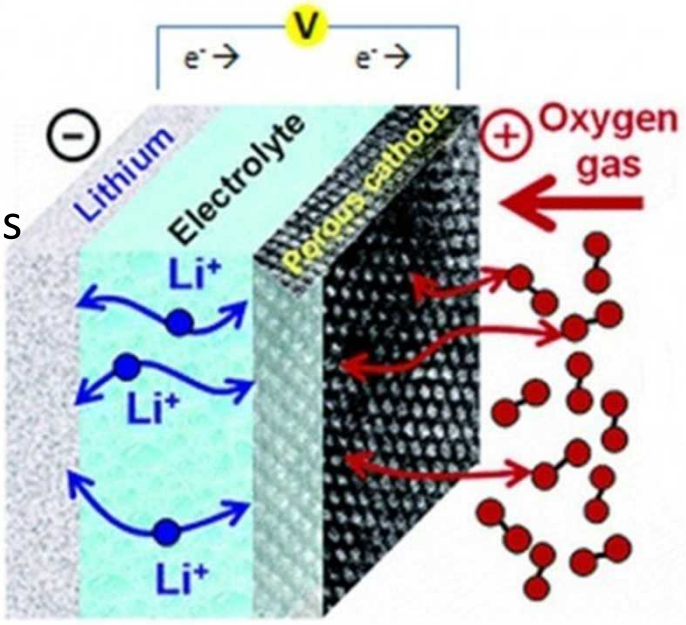
- **To our knowledge, this is the first attempt to quantitatively compare modeled values of battery electrolyte transport properties will those obtained from real Li-air batteries.**
- Why is this important?
  - Quickly screen new materials
  - Predict battery performance and kinetics
  - Evaluate the differences between model and reality



?

Project Overview

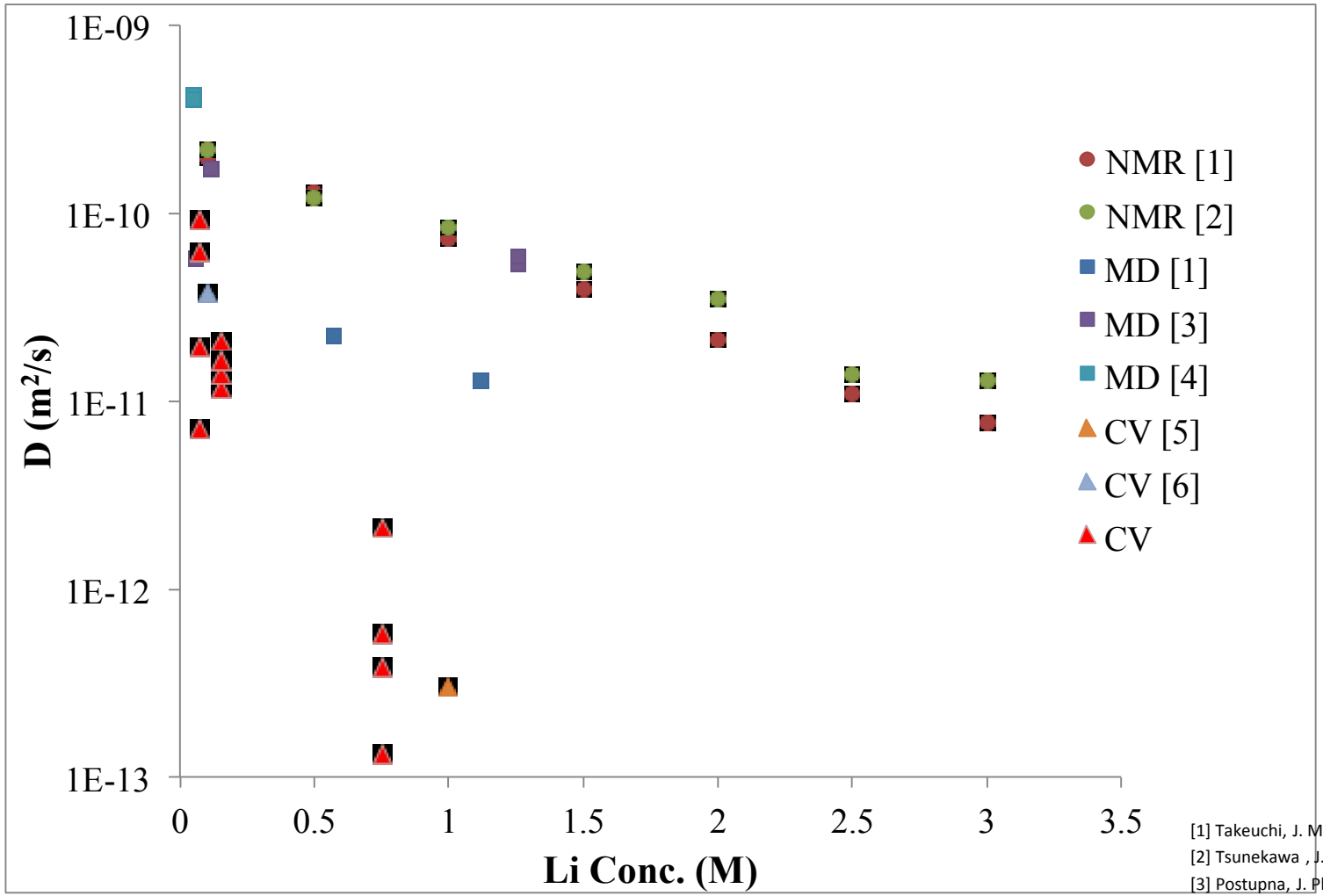
- **Overall goal:**
  - Develop/validate a predictive model as an electrolyte screening tool for Li-air batteries using Li+ diffusion as the **figure of merit**
- **Modeling:**
  - Evaluate literature potentials for accuracy for a model electrolyte
  - Determine validity of literature approach and calculation methods
- **Experiment:**
  - Perform electrochemical experiments on validation electrolytes
  - Calculate Li+ diffusion coefficients
  - Make corrections for physical differences in battery cell



Diffusion coefficient

- Mass transfer across given surface area
- What are you talking about?
  - Chemical diffusion
  - Self diffusion
  - Effective diffusion – diffusion through pores in porous media
  - Fickian diffusion

Modeling vs. Experiment - Diffusion



Most modelers compare their data to NMR for validation
Experimentalists usually just report their data

[1] Takeuchi, J. Molec. Liqu. 148 (2009) 99
[2] Tsunekawa , J. Phys. Chem. B 107 (2003) 10962
[3] Postupna, J. Phys. Chem B 115 (2011) 14563
[4] Soetens, J. Phys. Chem A 102 (1998) 1055
[5] Jung, N. Chem. 4 (2012) 579
[6] Laoire, J. Phys. Chem. C, 113 (2009) 20127

Differences between model and experiment

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MODEL

- Ideal conditions
- No physical barriers to ion diffusion
- No competing chemistry
- Diffusion calculation – Fickian vs. others

EXPERIMENT

- Non-ideal conditions
- Physical barriers to diffusion – separator, cathode
- Side reactions, electrolyte stability
- Diffusion calculated based on certain assumptions

How to compare?

- **Carefully constructed experiments to avoid non-ideal conditions**
- **Correct experimental results for diffusion barriers**

Updated Approach to Modeling Mass Transfer Properties for Batteries

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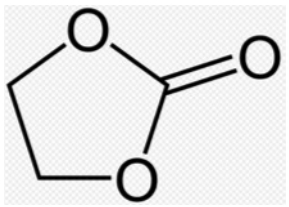
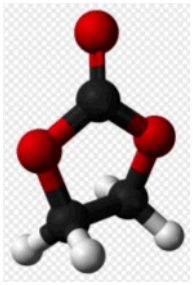
Model Details

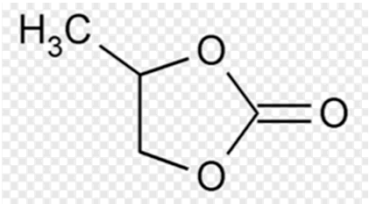
- Molecular Dynamics model using LAMMPS software (SANDIA)
- Atom interactions (energies and forces) described using CHARMM potential
  - Intermolecular forces:
    - Lennard-Jones potential
    - Coloumbic long-rang interactions
  - Intramolecular forces:
    - Combination of harmonic functions defining bonds and preferred orientations
    - Bonds can not be broken or formed on the fly

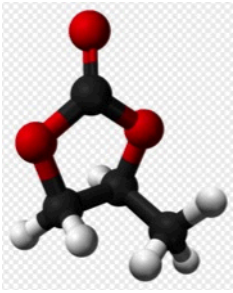
Ethylene Carbonate (EC)



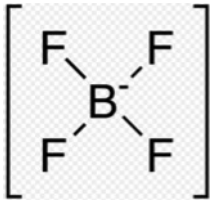


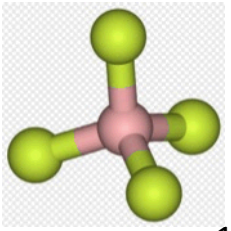
Propylene Carbonate (PC)



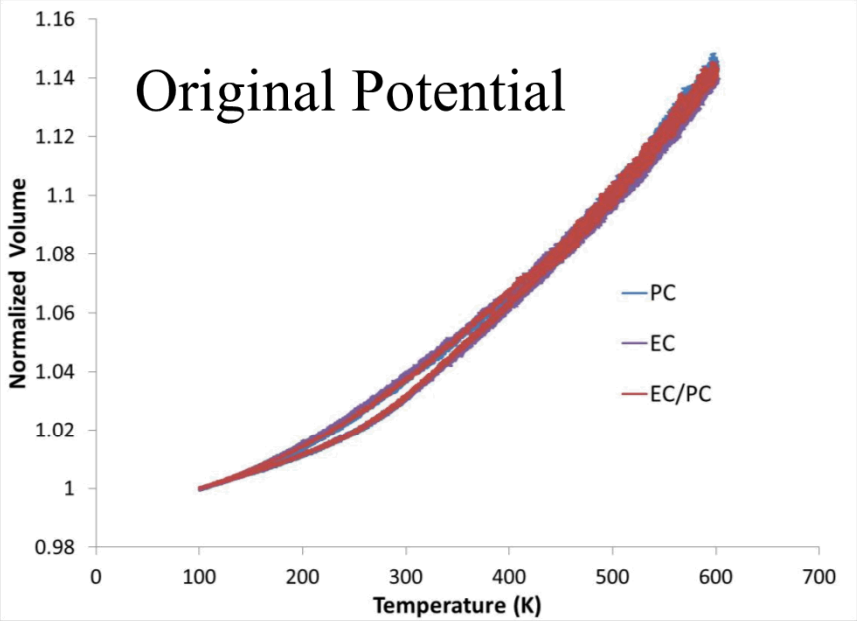


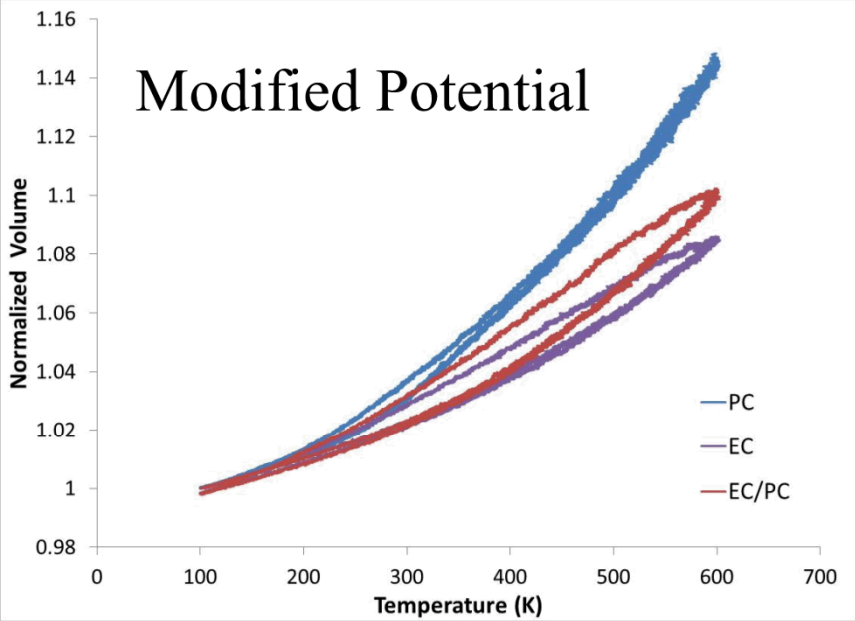
Tetrafluoraborate (BF_4)





Model validation

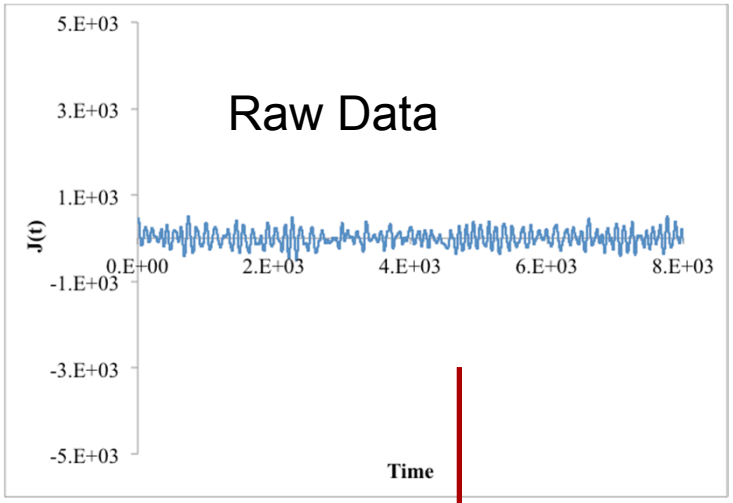




- **New potential now distinguishes between EC and PC**
- **PC no longer solid at room temperature**

	Rigid	Flex	Flex (np)	Exp.
EC Density (g/cm^3)	1.36	1.28	1.23	1.32
T_g (K)	321	323	371	310
PC Density (g/cm^3)	1.27	1.22	1.15	1.20
T_g (K)	332	324	352	225

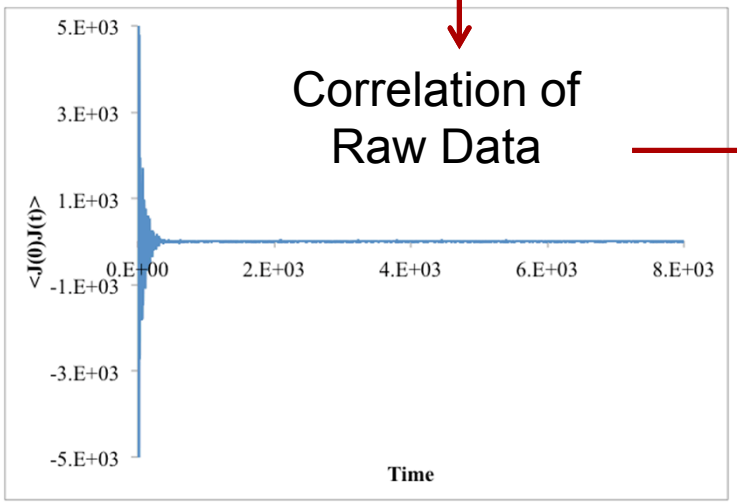
Green-Kubo for diffusion

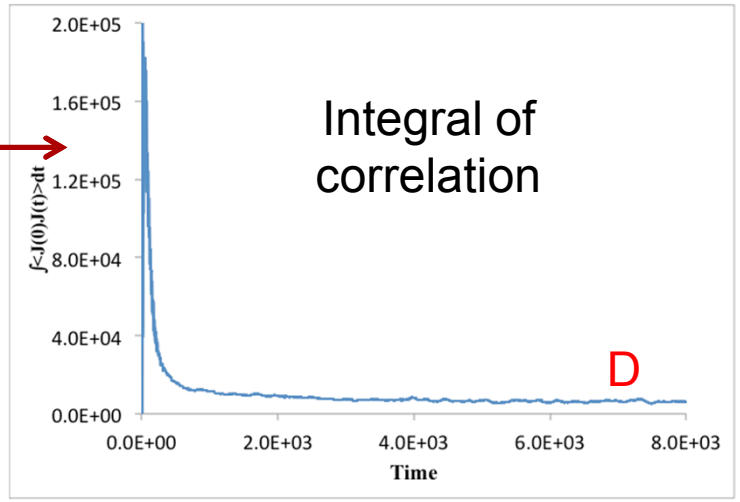


- Uses Green Kubo techniques to get D

$$D = \frac{1}{3}\int_0^\infty \langle J(0)J(t)\rangle dt$$

- The integral converges to D





What makes these models different from Literature

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- Potentials modified to reflect correct material properties

Experimental Battery Data

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Experimental Techniques

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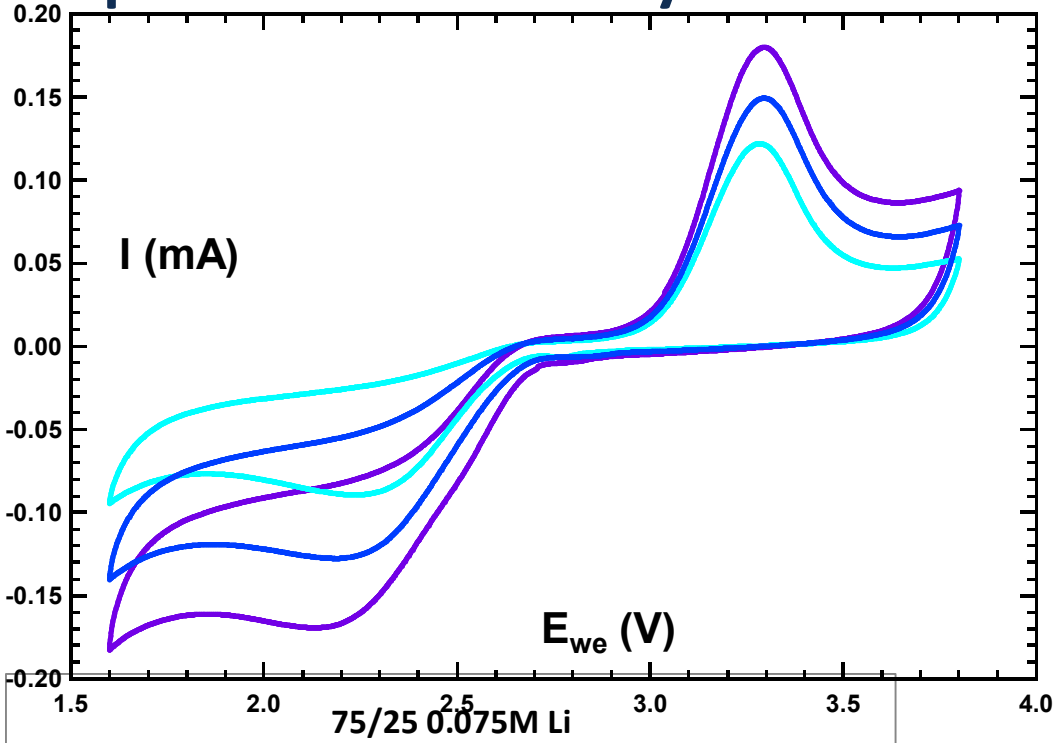
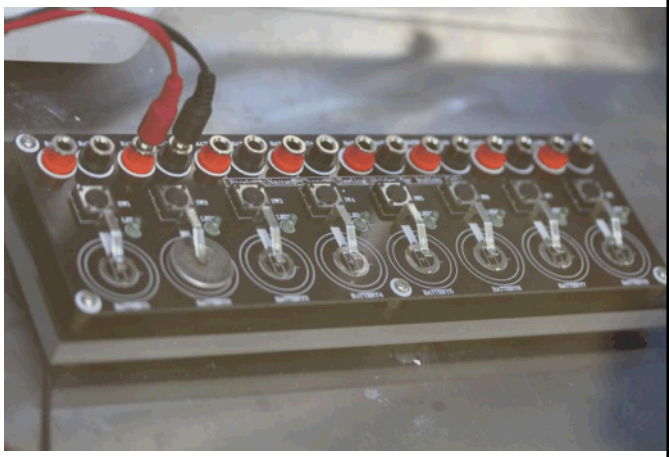
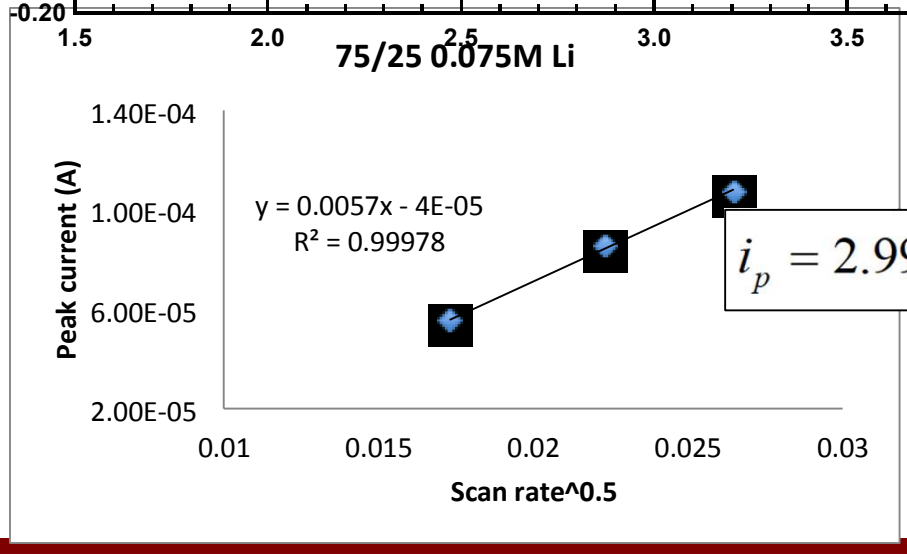
- Cyclic voltammetry
  - Direct calculation of diffusion coefficient
  - Long experiments (1 data point = 3 days)
  - Effects of ion diffusion and charge transfer are combined (slow/complicated kinetics covers up diffusion)
- Electrochemical impedance spectroscopy
  - More convoluted methods required for diffusion coefficient calculation
  - Short experiment times (~1hr)
  - Separation of diffusion and charge transfer effects

→ Both techniques are needed to fully understand the reaction kinetics, but CV was used for diffusion coefficient calculation

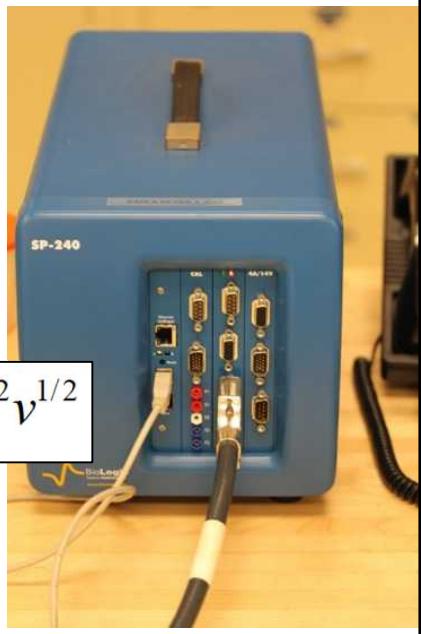
Experiment – cyclic voltammetry





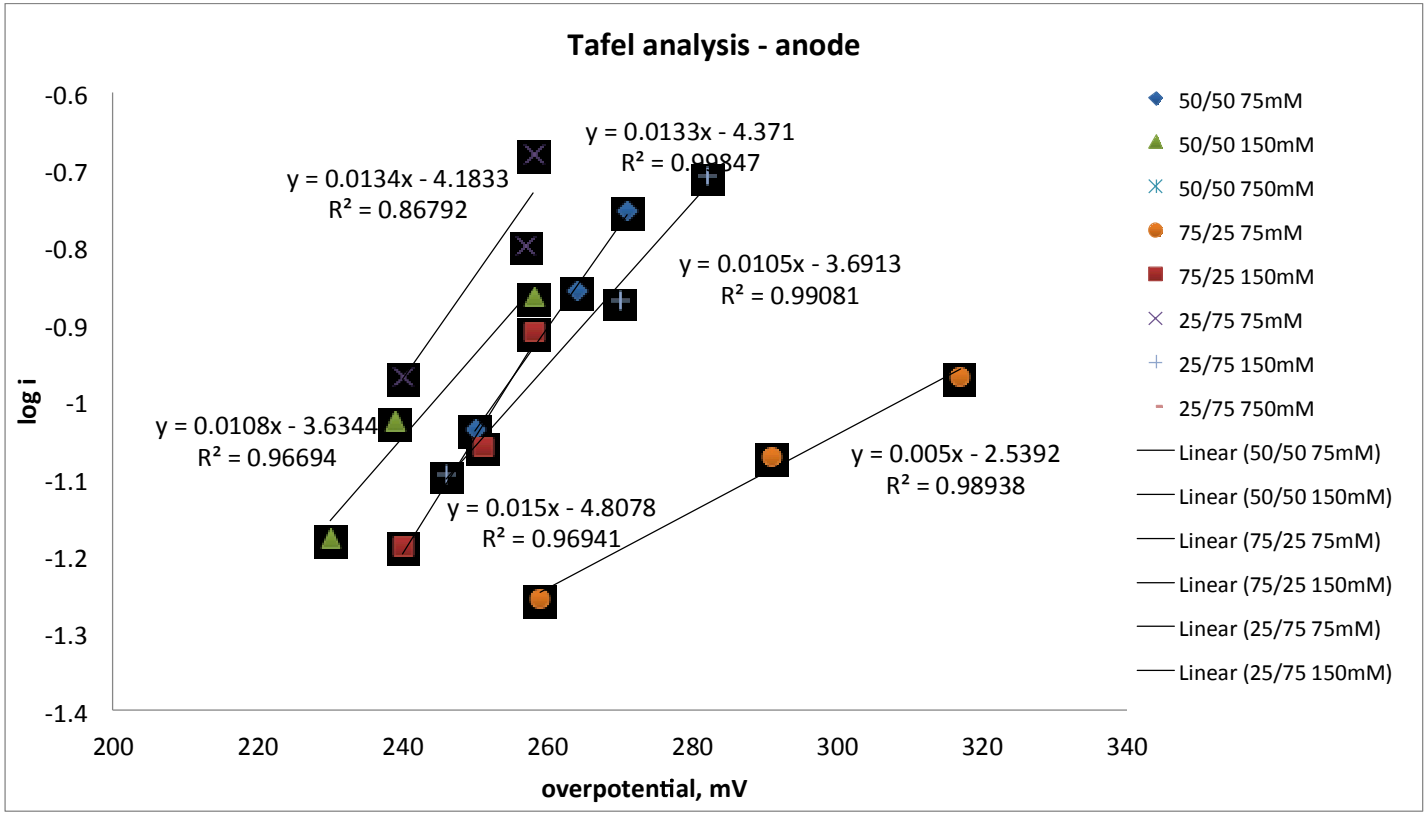


$$i_p = 2.99 \times 10^5 n\left[\alpha n_\alpha\right]^{1/2} ACD^{1/2} v^{1/2}$$



Calculation of diffusion coefficient

- Nicholson-Shain relation $i_p = 2.99 \times 10^5 n\left[\alpha n_\alpha\right]^{1/2} ACD^{1/2} v^{1/2}$
- Tafel equation for α (transfer coefficient) $slope = \frac{(1-\alpha n_a)F}{2.3RT}$

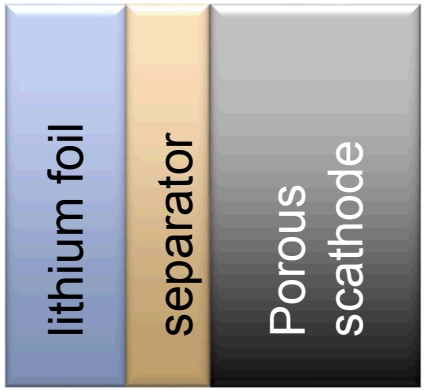


Experimental Corrections

How do we account for the physical difference between modeling and experimental results?

Physical corrections:

- tortuosity of separator
- porosity of separator
- tortuosity of scathode
- porosity of scathode



$$D_{eff} = D_{meas}\left(\left(\frac{L\tau}{L_{total}\varepsilon}\right)_{separator} + \left(\frac{L\tau}{2L_{total}\varepsilon}\right)_{cathode}\right)$$

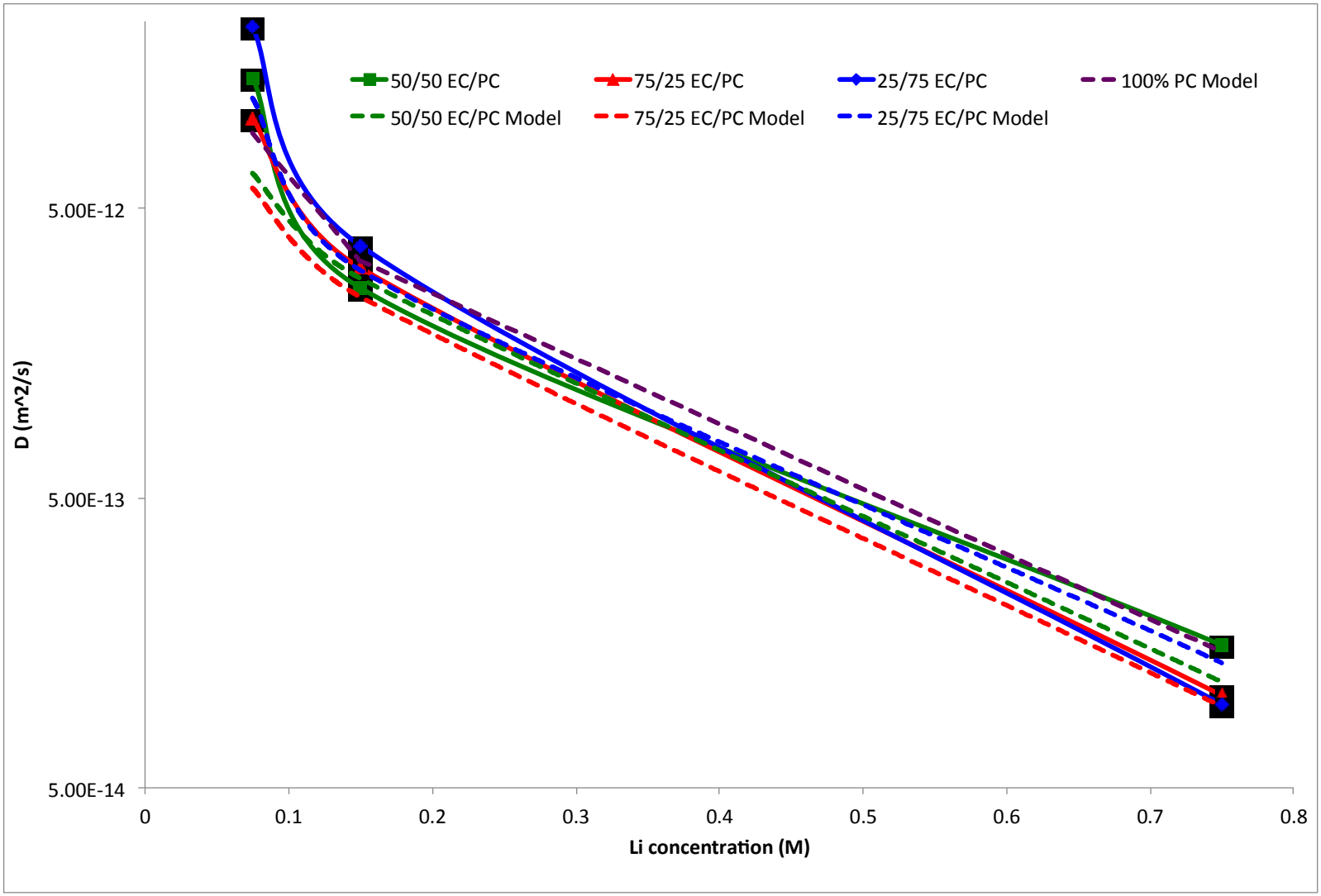
What we model

What we measure

*where $\tau = 1.8\varepsilon^{-0.53}$

*Thorat, et al. *J. Power Sources* 188 (2009) 592-600

Results


50/50 EC/PC
75/25 EC/PC
25/75 EC/PC
100% PC Model
50/50 EC/PC Model
75/25 EC/PC Model
25/75 EC/PC Model
5.00E-12
5.00E-13
5.00E-14
D (m^2/s)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Li concentration (M)

Lessons learned

- Carbonate system was probably not the best “model” system choice – Li-carbonate interactions are an issue
- Know how the modeled data and experimental data compare and what is physically being measured/modeled
- Know what type of diffusion coefficient you are reporting and comparing to other data

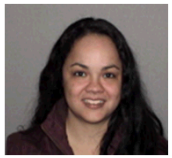
Summary

- For the first time, there is a quantitative validation of the MD model of transfer properties from real experimental data.
- This new model provides a predictive/screening tool for new Li-air electrolyte materials
- We have validated our models by looking at the physical differences between model and “real battery”.

- **Questions?**

The Battery Team-

- M. Kane - PI



- K. Reyes - electrochemistry

- D. Ward – MD simulation

- R. Jones – First priciples/DFT calculations

- J. Templeton – MD simulation

- K. Erickson – electrochemistry post-doc