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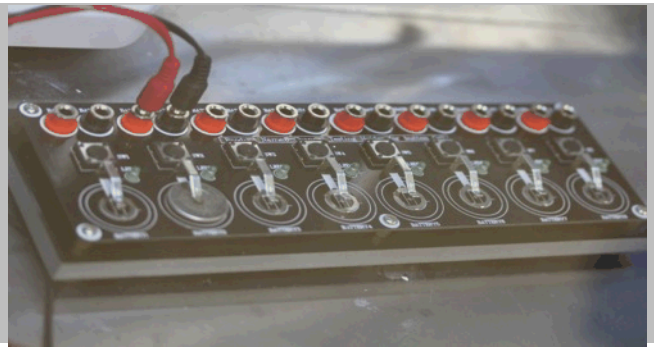

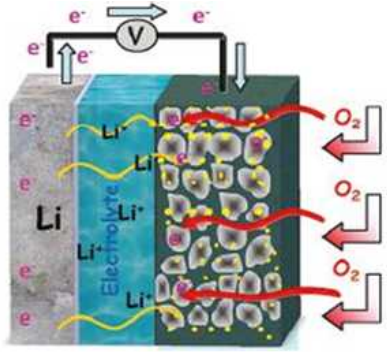


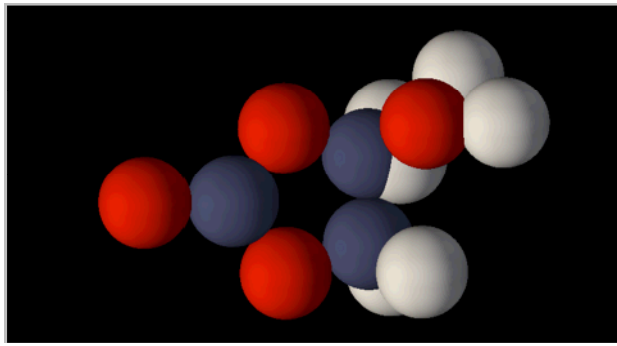

# Li-Air Batteries for Advanced NW Power Sources

PI: Marie Kane

U.S. DEPARTMENT OF ENERGY | NNSA

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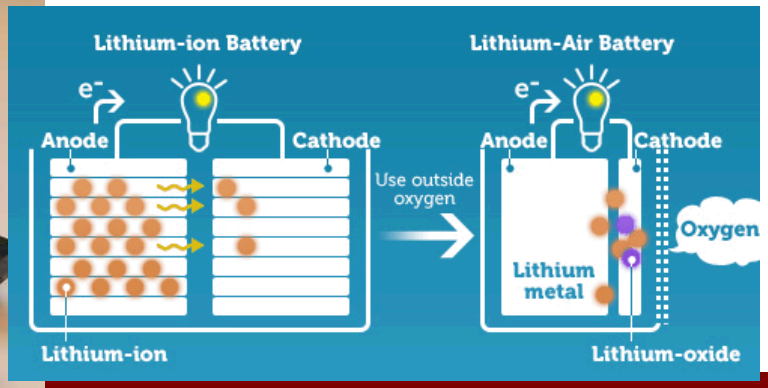
# Project Motivation

- NW power sources demand:
  - Safety! – during operation, storage and retrieval
  - Low weight, small volume
  - High energy density
- Li-$O_2$ batteries can provide solutions...
  - No thermal runaway issues, low volatility electrolyte, non-toxic
  - Cathode eliminated, uses oxygen (air) at nearly half the volume and weight of other Li batteries
  - Li-air provides highest possible theoretical energy density of any known battery chemistry



# Why Li-Air?


ies using a
f lithium and
otential to increase the
nit of mass) of recharg
tor of up to 10.
15900 g
2200 g
300 g
Lead/Acid Battery (Today)
Energy: 480 Watt-hours
Weight: 15900 Grams
48 Lithium-Ion Cells (Today)
Energy: 48 x 10 = 480 Watt-hours
Weight: 2200 Grams
10 Lithium/Air Cells (Future)
Energy: 10 x 50 = 500 Watt-hours
Weight: 300 Grams
Comparison of Three

# Why should Sandia research Li-Air?

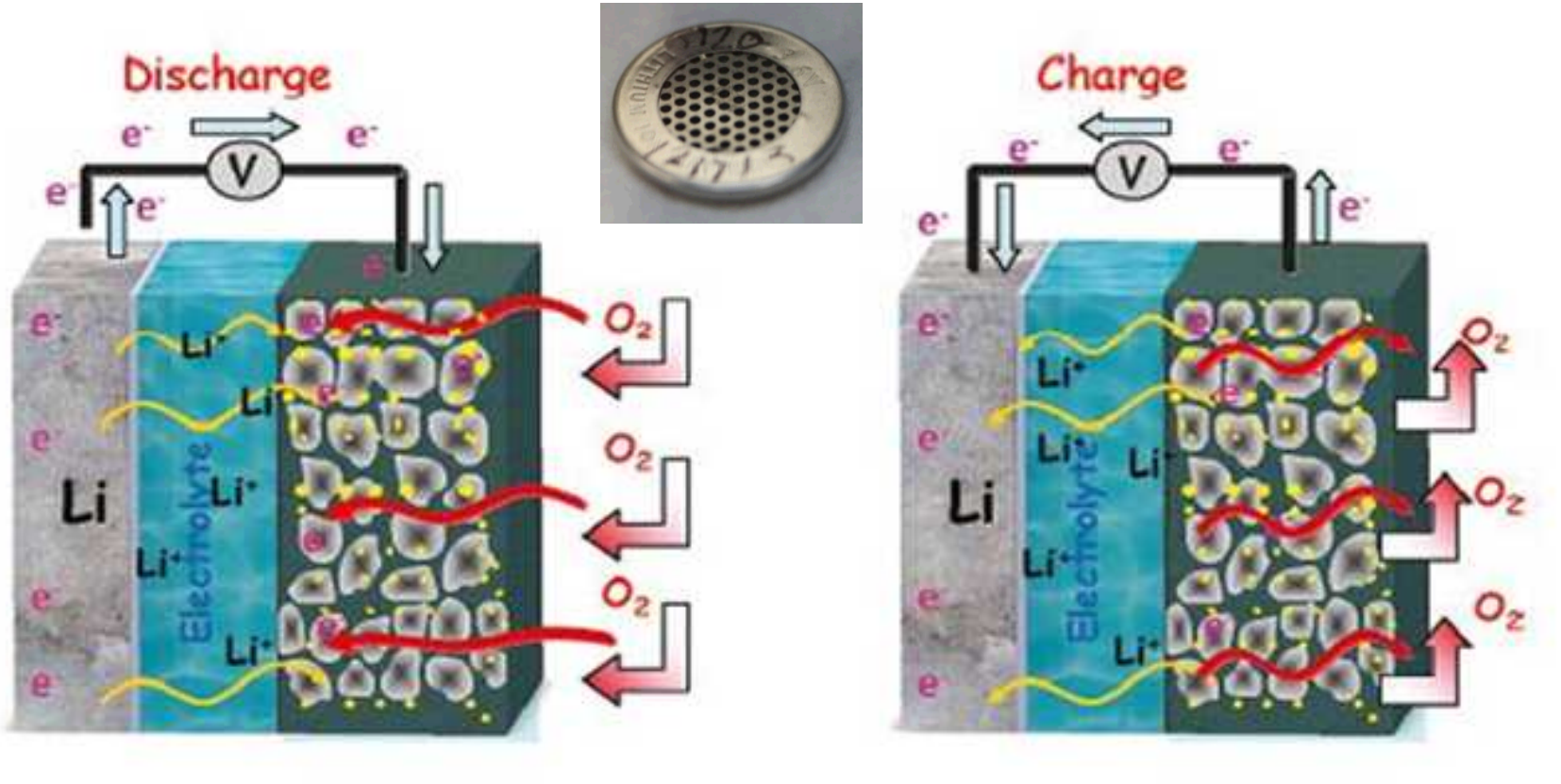
- Li-Air batteries are a current “hot topic” in the literature, what makes our efforts different?


≠

- **Industry/academic efforts DO NOT meet our NW needs**
  - Power requirements
  - Charging cycles required (if any)
  - Environment*
  - Packaging*
  - Storage*… etc.

*These battery properties are also of commercial interest

# Background – Li-air batteries




Reaction products formed at the cathode:

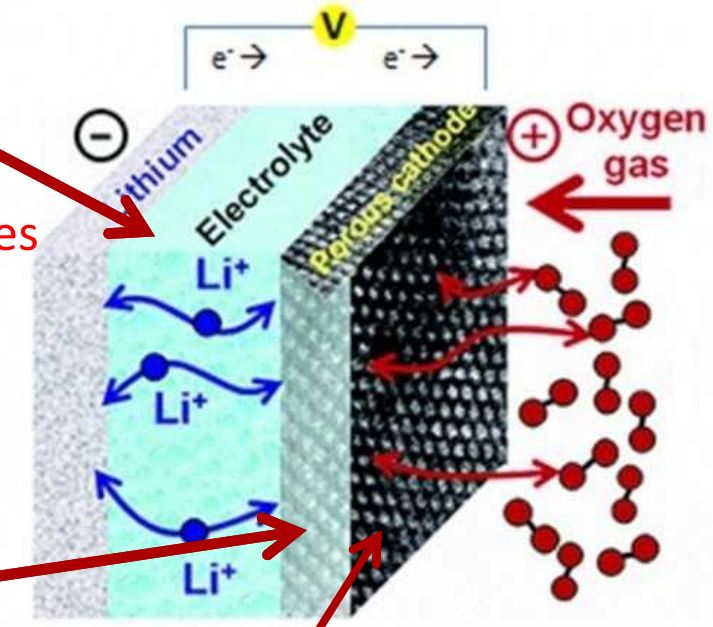
$Li^+ + e^- + O_2 + \rightarrow LiO_2$

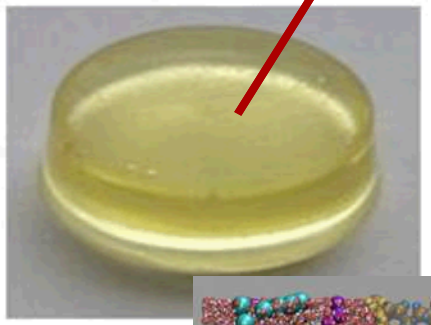
$Li^+ + e^- + LiO_2 \rightarrow Li_2O_2$

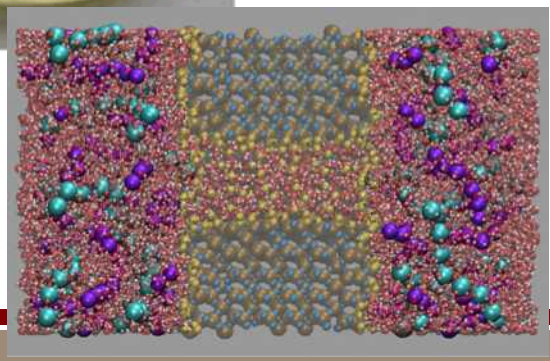
*Note: figure not to scale

# Project Plan

- **Develop an air-stable non-toxic electrolyte**
  - Material selection of ionic liquid candidates
  - Model potential ionic liquids
  - Electrochemically test ionic liquids
- **Develop a novel "Cathode" (Scaffold)**
  - Develop novel porous aerogel scaffold
  - Model optimal pore size
  - Model the species concentrations
- **Full Battery**
  - Build a working prototype power source
  - Develop overall predictive models
  - In-situ investigation of battery through AFM



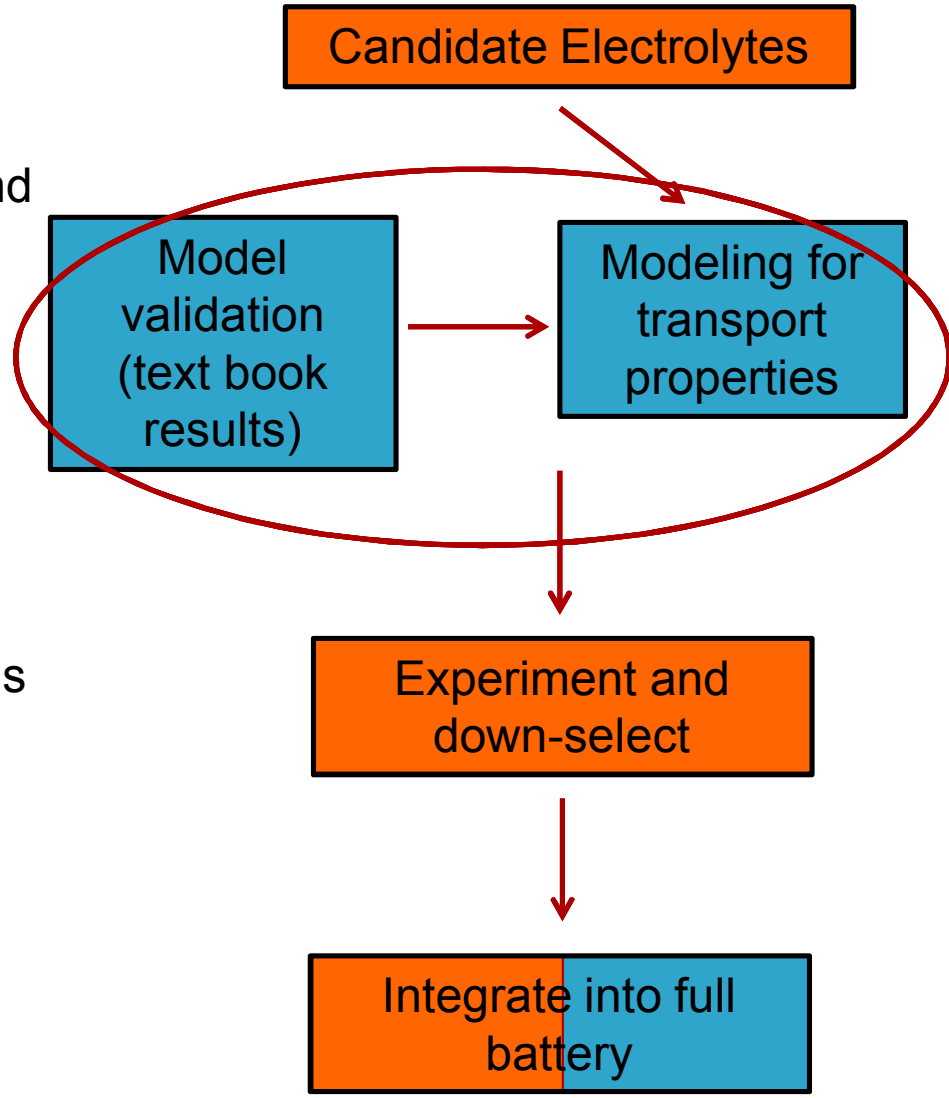





# R&D - Electrolyte

- **What makes a good electrolyte?**
  - **Ion diffusion** through the scaffold and electrolyte (FOM)
  - **Stability, compatibility and aging**

- **How do we select a good electrolyte?**
  - Modeling to screen potential materials
  - Electrochemical tests
  - Safety and reliability testing



# Model validation

- Begin with a system well represented in the literature.
  - $LiBF_4$ and EC/PC
- Use a potential from the literature (CHARMM).
- Compare properties of EC/PC combinations to literature

$$V = E_b + E_a + E_d + E_i + E_{nb}$$

$$E_b = \sum_{bonds} k_b (b - b_0)^2$$

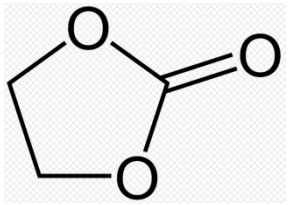
$$E_a = \sum_{angles} k_\theta (\theta - \theta_0)^2$$

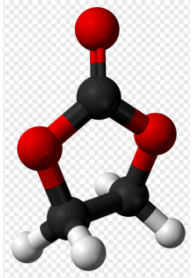
$$E_d = \sum_{dihedrals} k_\varphi [1 + \cos(n\varphi - \delta)]$$

$$E_i = \sum_{impropers} k_\omega (\omega - \omega_0)^2$$

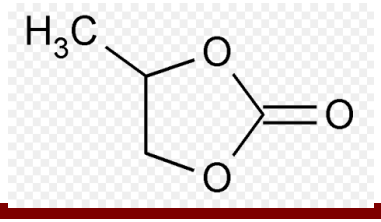
$$E_{nb} = \sum_{nonbonded} \varepsilon_1 \left[ \left( \frac{R_{\min ij}}{r_{ij}} \right)^{12} - \left( \frac{R_{\min ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{\varepsilon_2 r_{ij}}$$

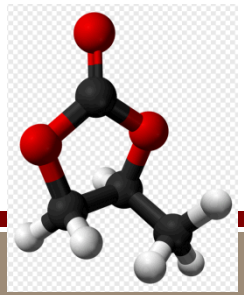
**Ethylene Carbonate (EC)**



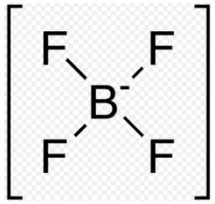


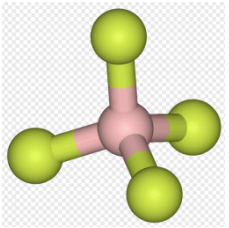
**Propylene Carbonate (PC)**



**Tetrafluoraborate ($BF_4$)**



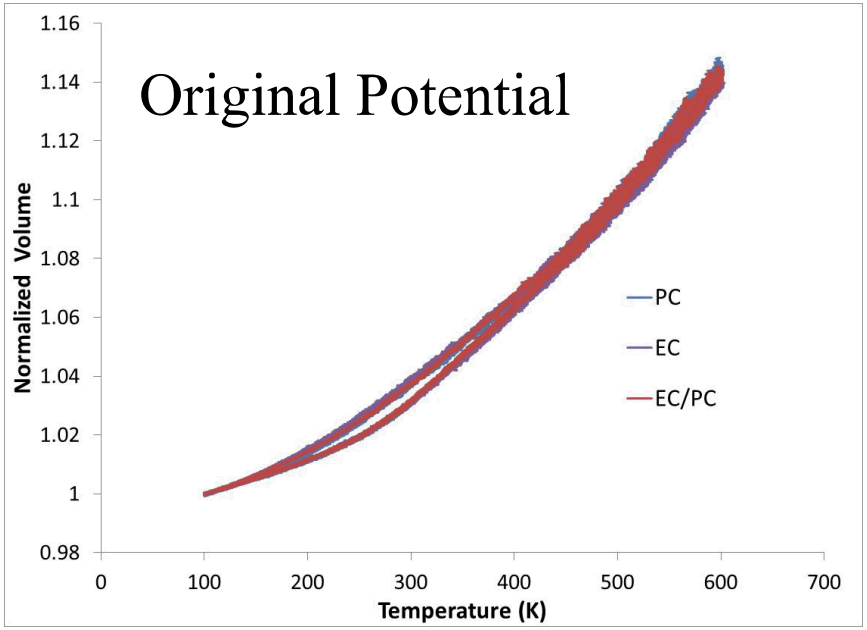



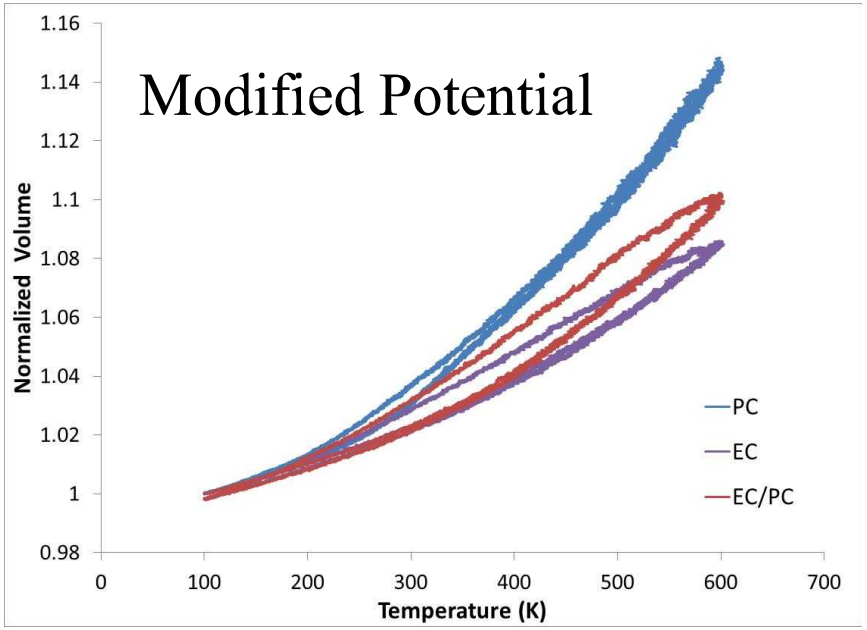
2 cases

a) Flexible carbonates

b) Rigid carbonates

# Model validation



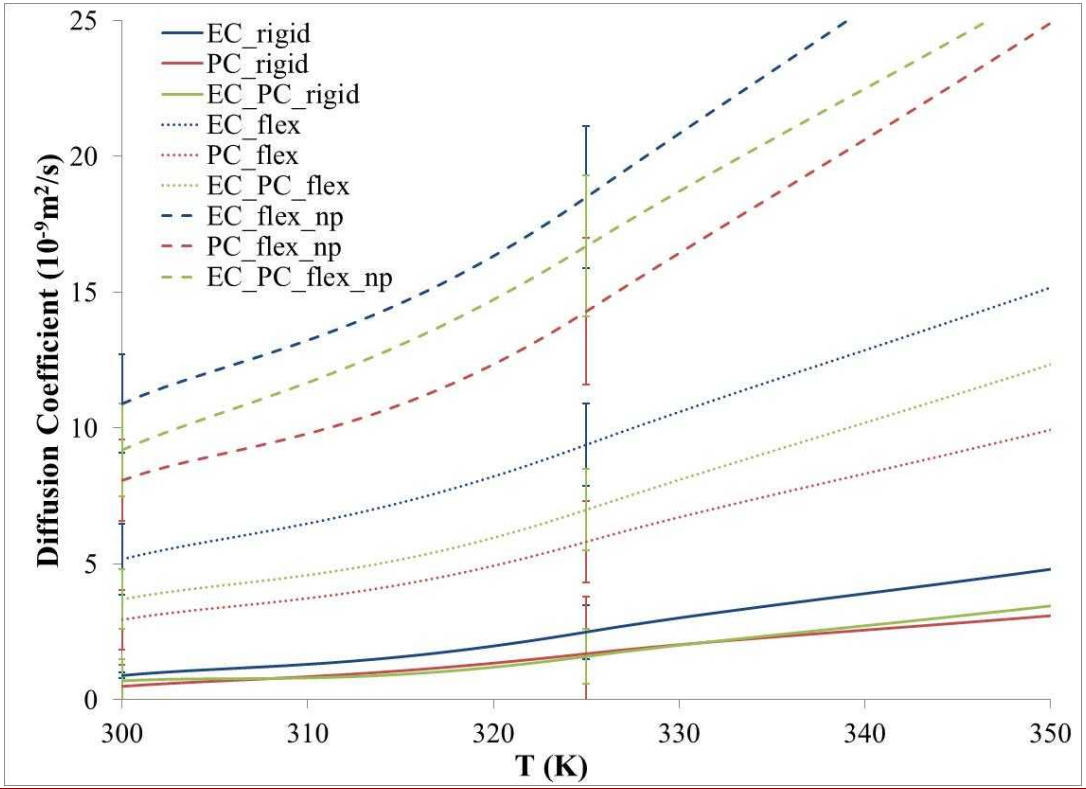




- **New potential now distinguishes between EC and PC**
- **PC no longer solid at room temperature**

| | 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 |

# Model validation

- Calculate diffusion constants of $Li^+$ using Green-Kubo techniques in Molecular dynamics (MD).
  - Electrolyte composition
  - Temperature
  - $Li^+$ concentration




**Viscosity**

$$\eta = \frac{1}{Vk_BT}\int_0^\infty dt\left\langle \sigma_{xy}(t)\sigma_{xy}(0)\right\rangle$$

**Thermal Conductivity**

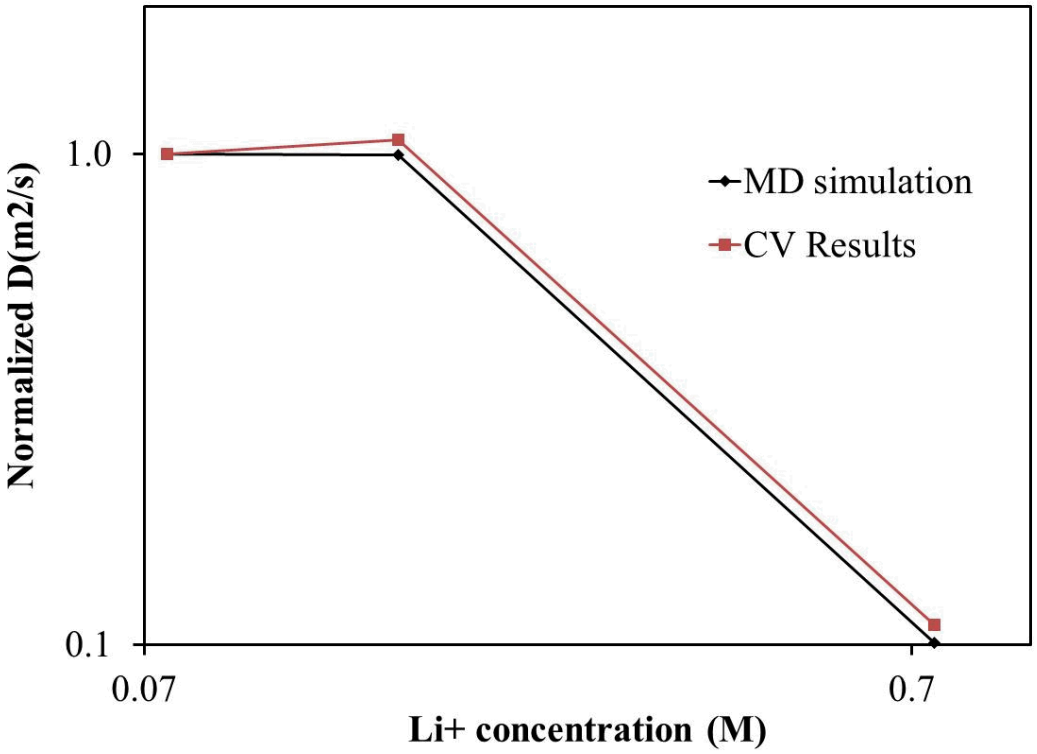
$$\lambda_T = \frac{1}{Vk_BT}\int_0^\infty dt\left\langle j_z^e(t)j_z^e(0)\right\rangle$$

**Electrical Conductivity**

$$\sigma_e = \frac{1}{Vk_BT}\int_0^\infty dt\left\langle j_x^{el}(t)j_x^{el}(0)\right\rangle$$

# Model validation

- These results match the trends of the electrochemical experiments for different $Li^+$ concentrations for EC/PC system
- This model can now be extrapolated to other systems



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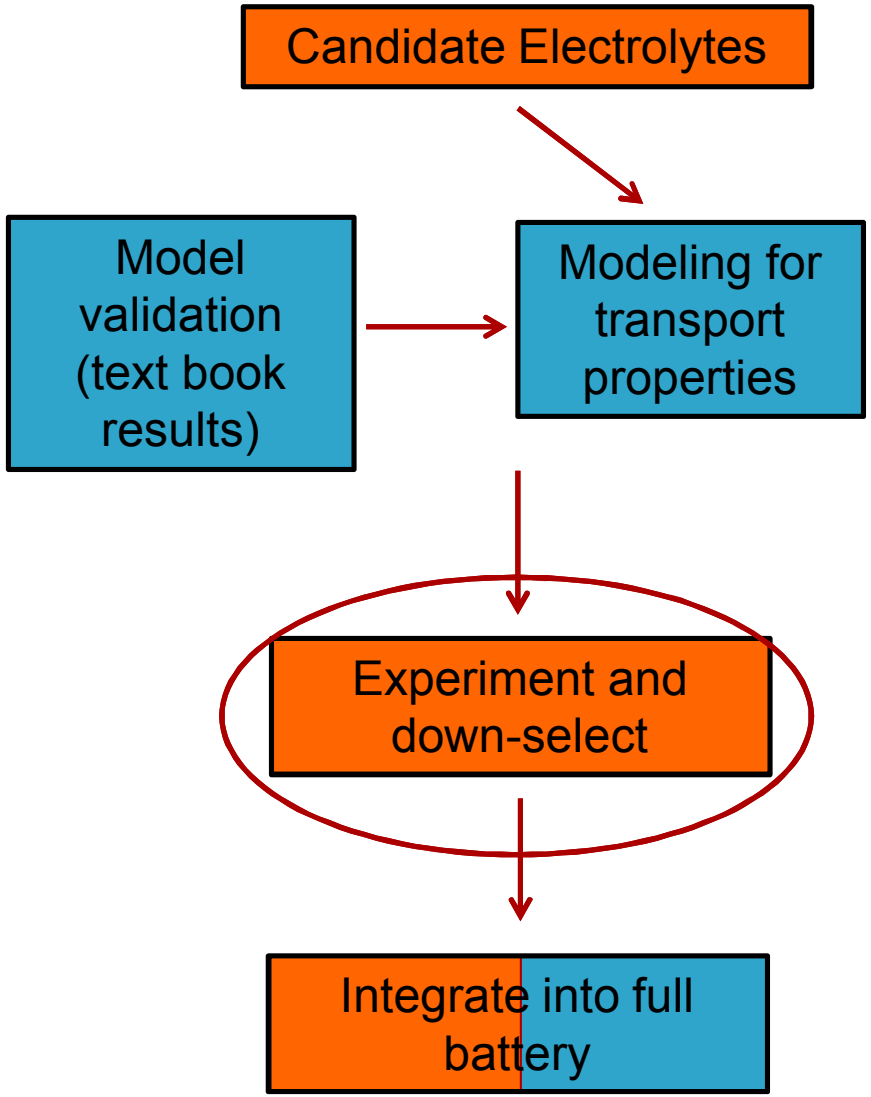
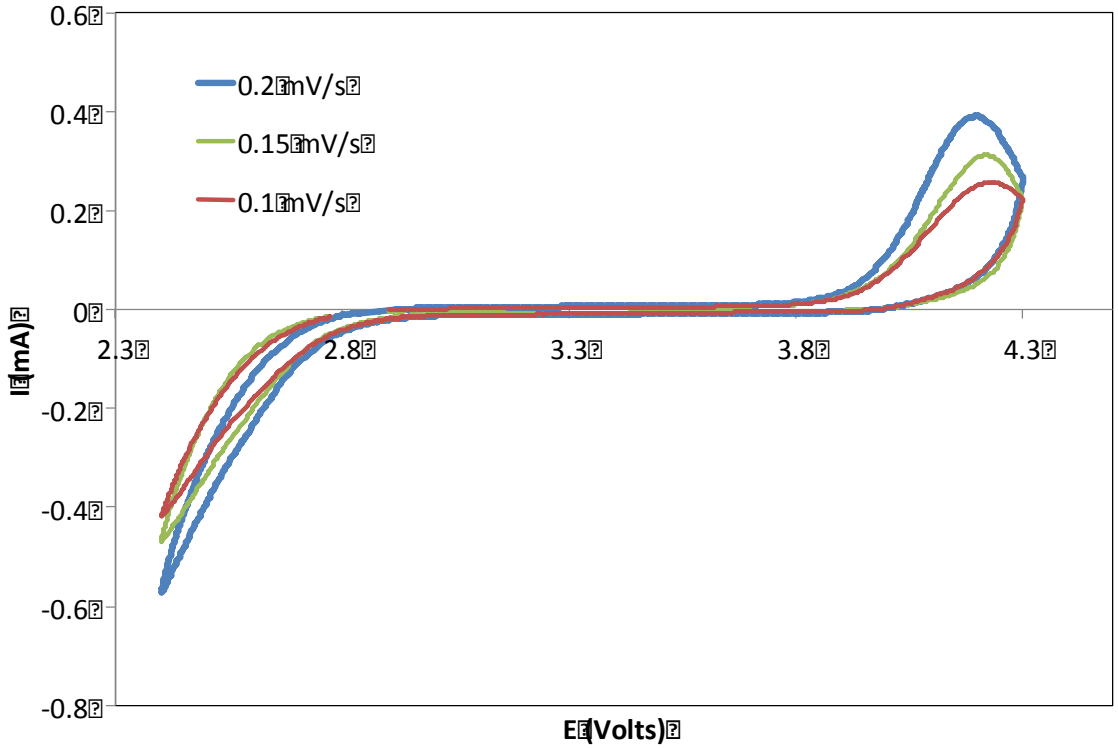
  - Electrochemical tests (Cyclic voltammetry and EIS)
  - Safety and reliability testing

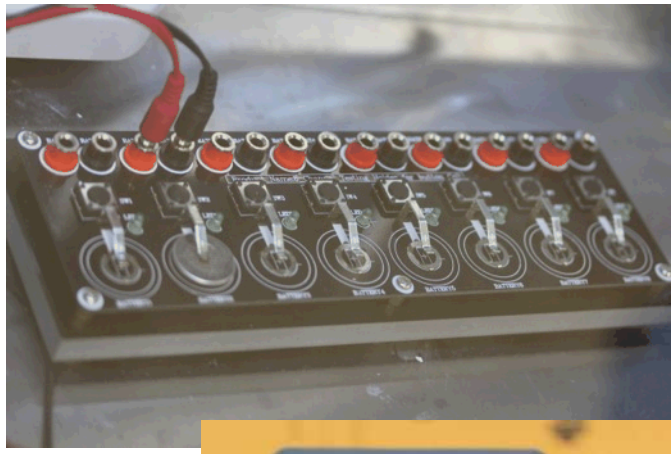


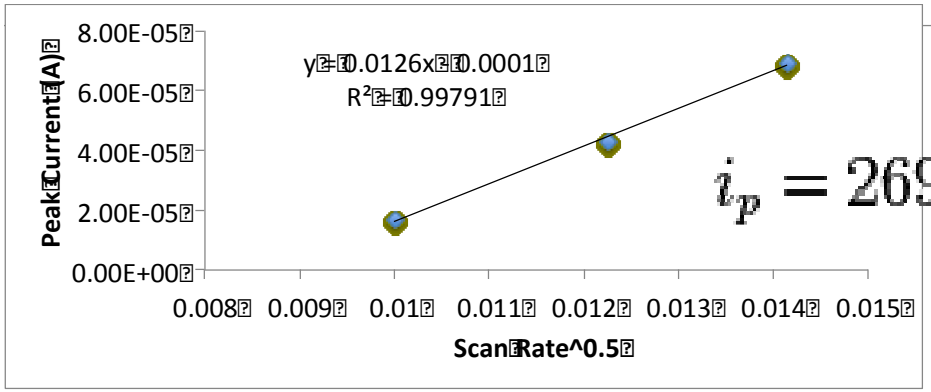
# Experimental Techniques

- Cyclic voltammetry
  - Direct calculation of diffusion coefficient
  - Long experiments (1 data point = 1 week)
  - 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

# Experiment – cyclic voltammetry



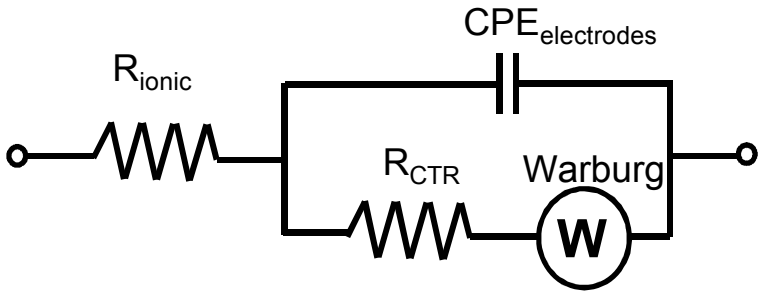




$$i_p = 269{,}000\, n^{\frac{3}{2}} A D^{\frac{1}{2}} C v^{\frac{1}{2}}$$

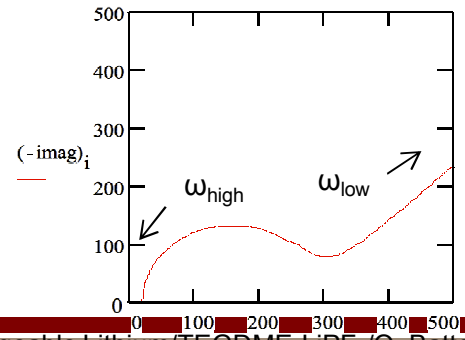
# Experiment - EIS

- **Electrochemical impedance spectroscopy** – response of an electrochemical reaction to slight frequency variations above and below potentials (V) of interest
- Battery is modeled as a combination of circuit elements and fit to the data
- For a simple, single electrode battery, the circuit could be[1]:

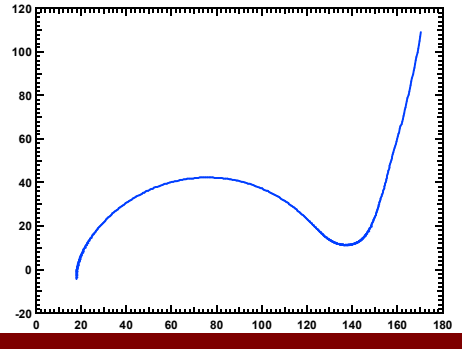



- $R_{ionic}$ is the electrolyte ionic resistance, $R_{CTR}$ is the charge transfer resistance at the electrodes, and the $CPE_{electrodes}$ is a capacitive element from the electrodes but experimentally acts as a constant phase element

The Nyquist plot for this simple battery would look like[2]




An Example Nyquist plot from our EIS Data

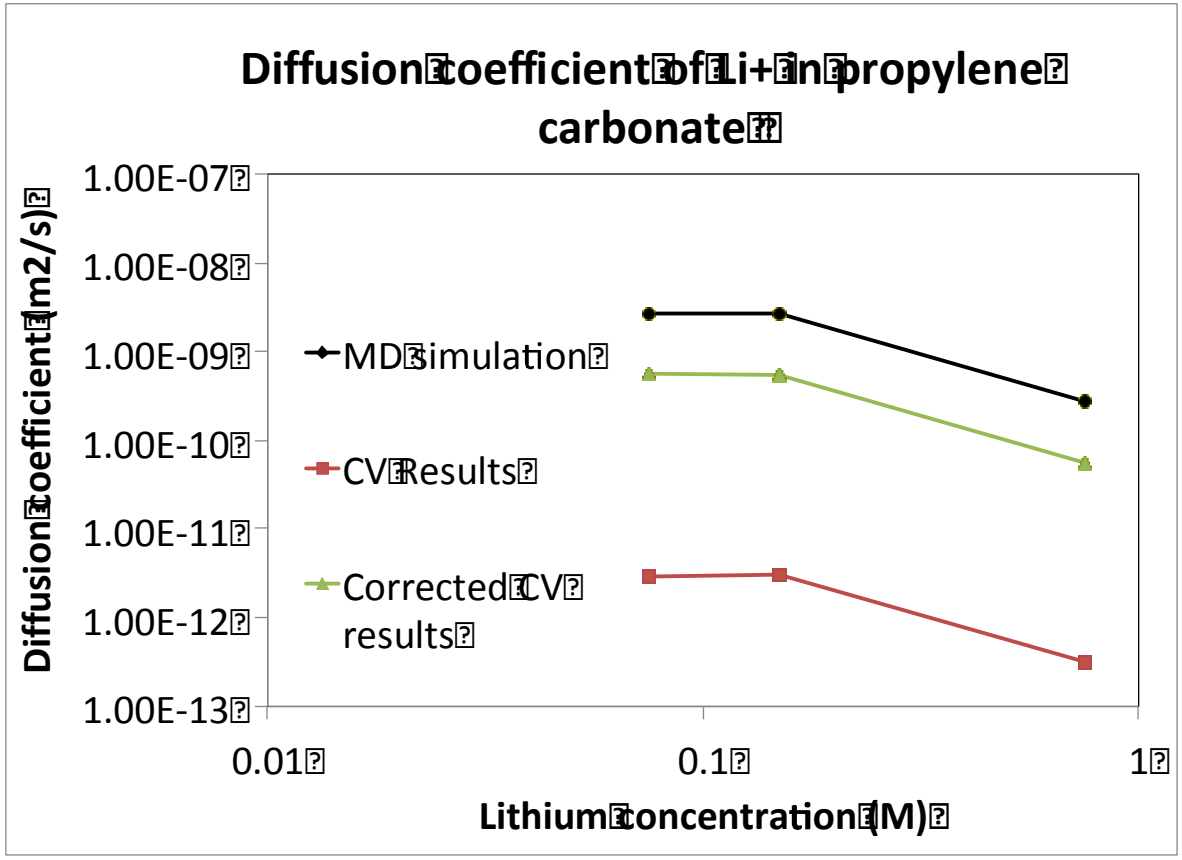





1. Rechargeable Lithium/TEGDME-LiPF$_6$/O$_2$ Battery *J. Electro. Soc.* **2011**, 158, *3*, A302
2. <www.gamry.com/application-notes/basics-of-electrochemical-impedance-spectroscopy/>

# R&D - Electrolyte

**What is the physical difference between modeling results and experimental coin cell results?**



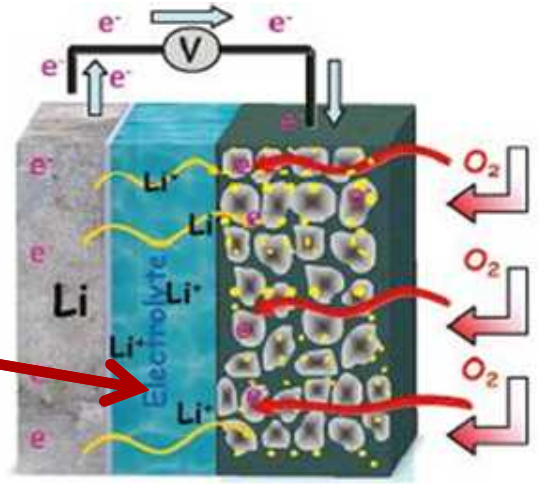

**Physical corrections:**

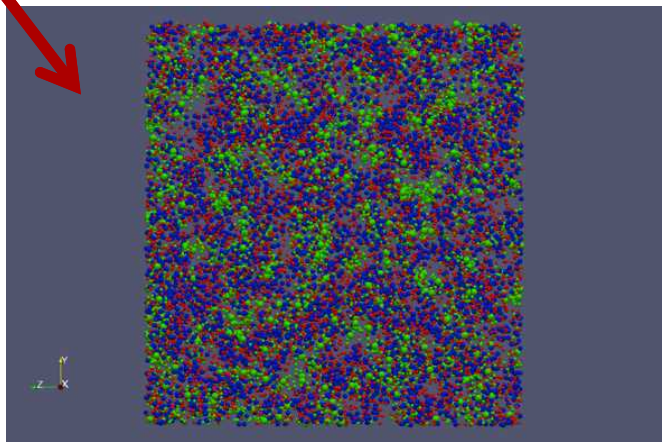
- tortuosity of cathode
- tortuosity of separator
- which Li ions are "counted" in each case?
- Resistance to diffusion from reaction products

**This discrepancy is consistent throughout the literature!**
**Physical corrections can get us much closer, but which ones are most important?**

# Electrolyte – Ionic Liquids

- Material candidates:
  - Stable, low toxicity ionic liquids (IL's) with Li salts
    - 1-ethyl-3-methyl-imidazolium (EMITFSI)
    - 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide
    - 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)amide
    - 1-butyl-3-methylimidazolium nonafluorobutyl sulfonate
    - **1-butyl-3-methylimidazolium hexafluorophosphate**
- New algorithms have been developed to build IL structures as input for MD simulations.
- Simulations are being performed to verify the IL interatomic potentials are under way
  - Densities
  - Transition temperatures



# Summary

- Nuclear weapons power sources **demand safety as a top priority**, but also have stringent operational requirements that are **not the same a commercial applications**
- Li-Air batteries are low volume/weight and high energy density with **no thermal runaway issues**
- In process of validating our models by looking at the physical **differences between model and "real battery"**.
- Modeling of ionic liquids will provide insight into Li+ diffusion and aid in down-select
- A **novel cathode material** is proposed and will be explored in FY15.

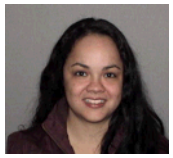
# Publications/Collaborations

- Publications
  - Spatial resolution of the conductivity of ionic fluids using a Green-Kubo method, *J. Physical Chemistry* (submitted)
  - Li+ transport in carbonate solutions: a molecular dynamic study, Phyical Review E (in process)

- Collaborations
  - Prof. Mark Orazem (University of Florida)
    - collaborated on electrochemical techniques (specifically EIS)
  - Cleantech Institute at NASA Ames Research Center
    - Li-O2 Industries

# The Battery Team-

- M. Kane – PI, scaffold synthesis, catalyst development/design, electrochemical testing



- K. Reyes – electrochemical testing, battery cell integration

- D. Ward – Green-Kubo Li+ transport modeling

- R. Jones – Direct modeling of pore flow, full battery model

- J. Templeton – Diffusion and system level models

- K. Erickson – post doc, electrochemical testing