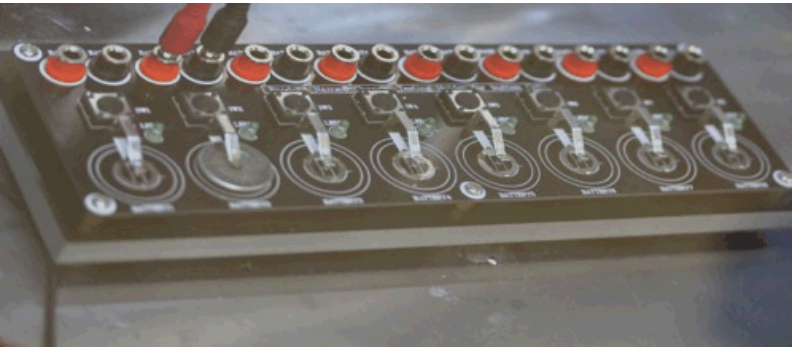
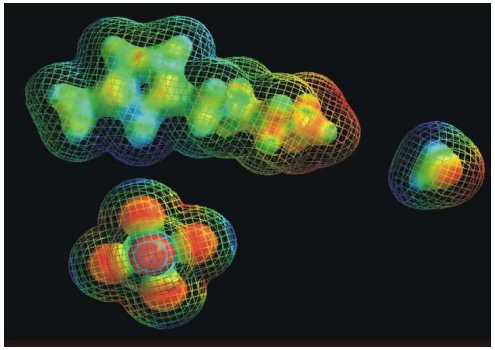
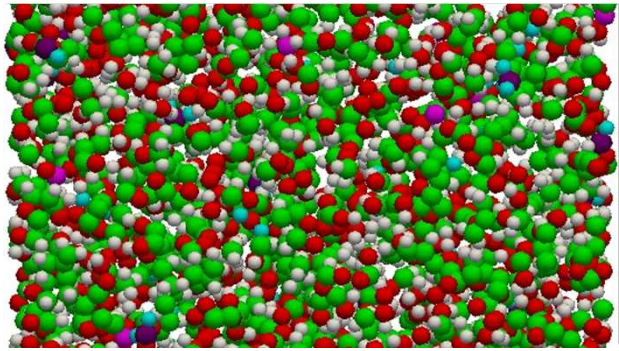
SAND2016-3581C

Exceptional service in the national interest

Sandia National Laboratories







Modeling Species Diffusion and Electrolyte Interaction in Li-Air Batteries

Forrest Gittleson, Reese Jones, Donald Ward,
Michael Foster, Jeremy Templeton, Mitch Anstey

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

The promise of Li-air batteries

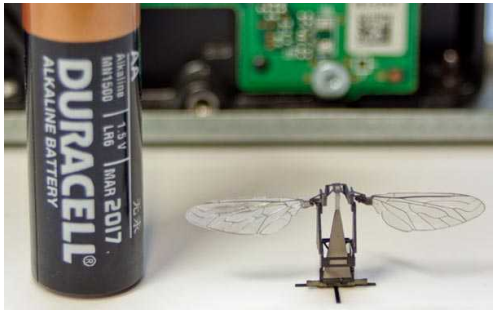
Sandia National Laboratories

Lighter, Smaller

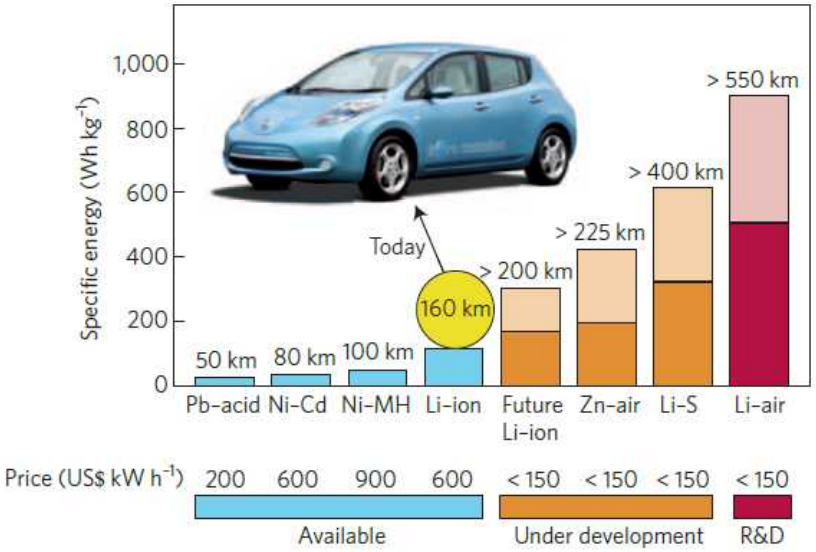
Grid Scale

Transportation

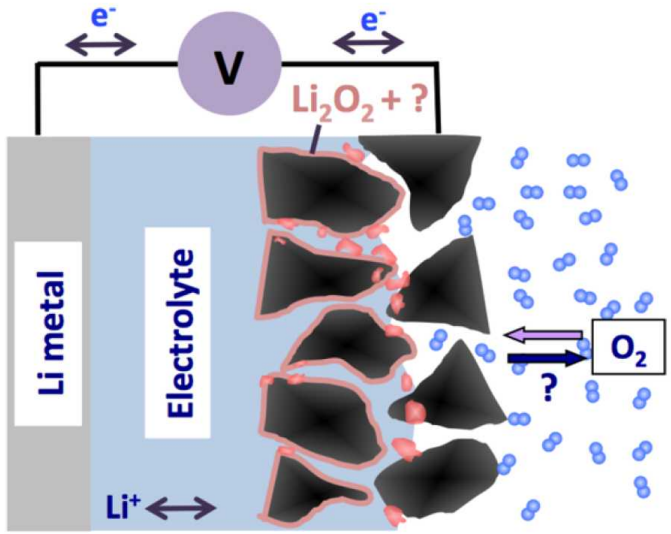
Portable Electronics



Microelectronics



Bruce et al. *Nat. Mater.*, 2011, **11**, 172–172.



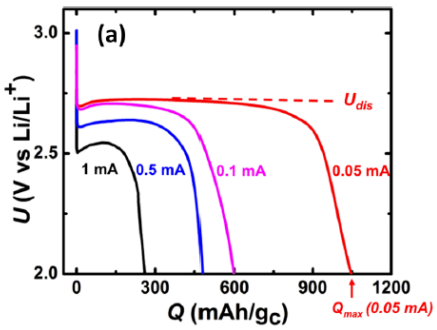
Luntz and McCloskey, *Chem. Rev.*, 2014, **114**, 11721–11750.

Focus on electrolyte

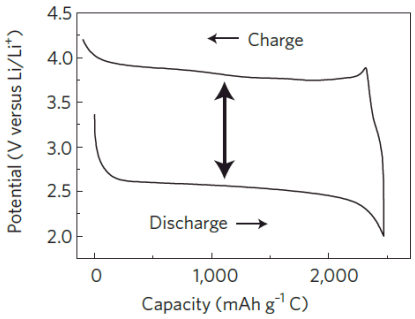
- Battery performance
  - Power density → mass transfer, kinetics
  - Energy density → mass transfer, kinetics, electrode surface area
- Material instability
  - Solvents/salts react with Li metal anode
  - Reaction intermediates and products react with electrolyte
- Reversibility of reactions

- **Electrolyte materials**
  - **Space is large and unexplored**
  - **Greatest impact on cell function**

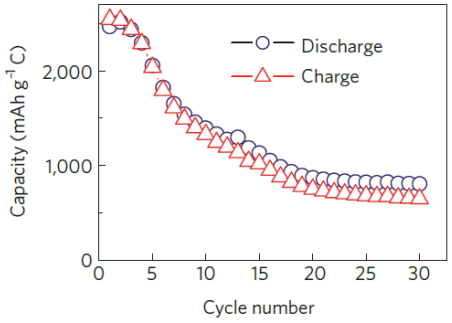
Power density



Energy density

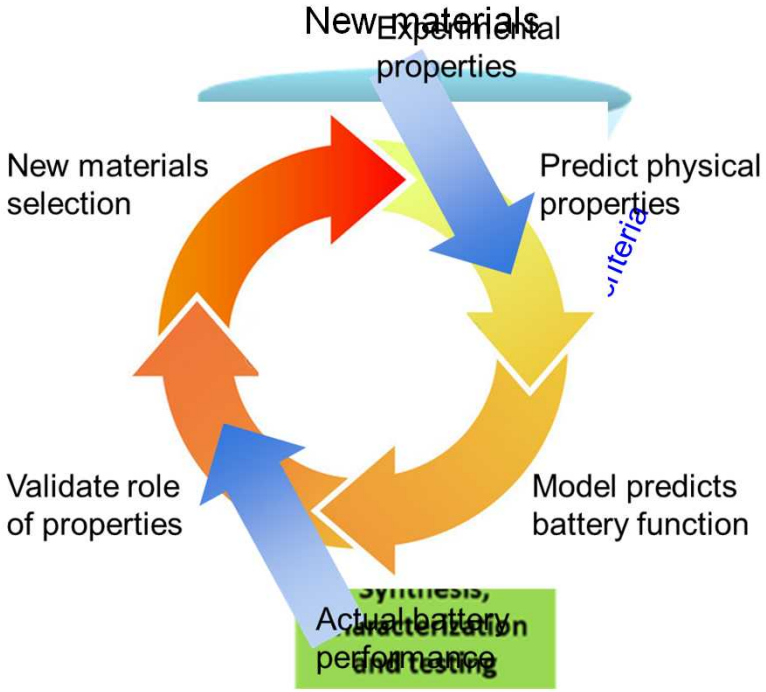


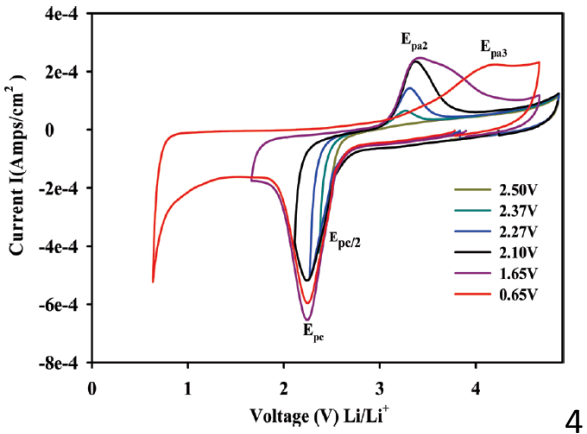
Reversibility



Modeling and experimental feedback

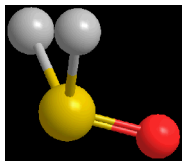
- Predict actual battery function
  - Self-consistency between experimental inputs and validation
- Tool for validation → **voltammetry**
- Get out:
  - Diffusion coefficients of mobile species
  - O_2 concentration
  - Role of electrode geometry
  - Influence of electrolyte composition
    - Solvent, anion, salt concentration etc.



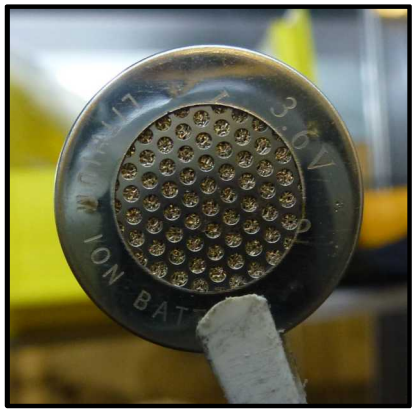


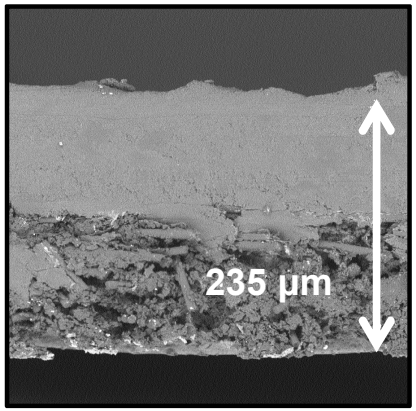
Reliable experimental methods

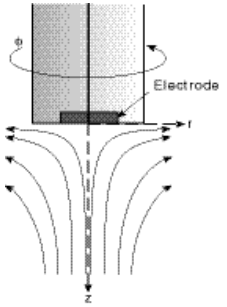
- 2032 standard coin cell with open mesh
  - Operating under dry air conditions (<6 ppm H_2O)
- Consistent cathode with known porosity
  - Sigracet 25BC gas diffusion layer (used in fuel cells)
  - Measured electrochemical (capacitive) surface area
- Electrolyte
  - Dimethyl sulfoxide (DMSO) solvent
  - Strongly dissociating $LiBF_4$ (low molarity)
- Focus on **discharge (reduction) reaction** only
- Independent **flat electrode** experiments to compare diffusion coefficient (D_O) and charge transfer coefficient (α)



DMSO



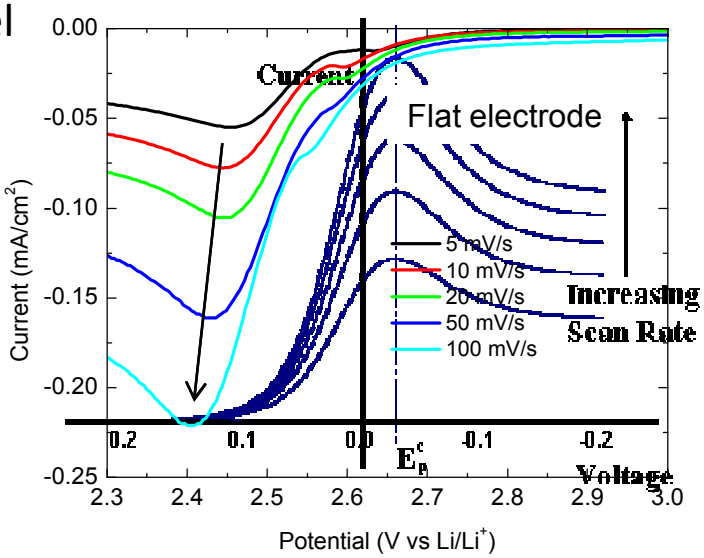


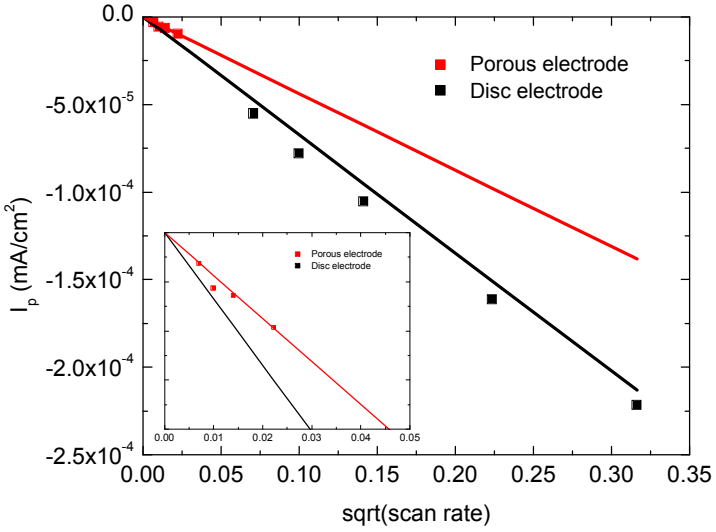


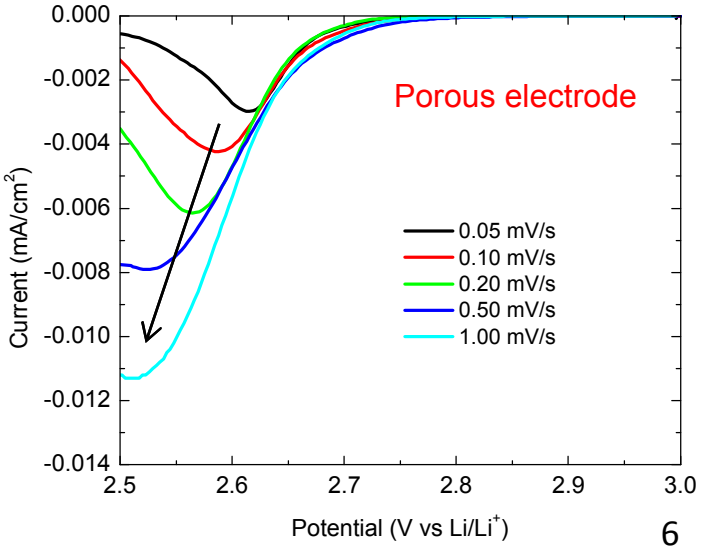
Classic model does not explain real behavior

- Reaction kinetics + diffusion → voltammetric model
- Classical correlation:
  - Peak current (i_p) to sqrt(scan rate) ($\sqrt{v}$)
  - Nernstian reaction kinetics
  - **Stagnant electrolyte, saturated with reactant**
  - **Flat electrode**
  - Reversible (Randles-Sevcik) or semi-irreversible (Nicholson)
- Li-air cells demand:
  - **Stagnant electrolyte, saturated with reactant**
  - **Porous electrode**

$$\frac{i_p}{A} \propto C_O {D_O}^{1/2} v^{1/2}$$







Basics of the model

- Assumptions
  - Irreversible electron transfer
    - Secondary reactions are fast
  - Flooded porous electrode
  - Metallic-like electrode conduction
  - No cross-species diffusion
  - Average concentration/diffusion of O_2 is one dimensional
- Fundamental foundation
  - Butler-Volmer kinetics
  - Reaction-diffusion equation

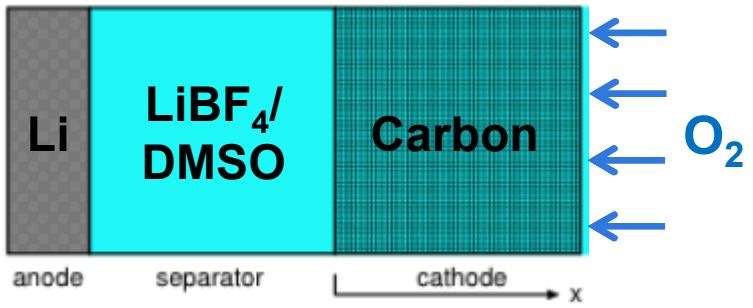
Oxygen Reduction (Discharge)

(1) $O_2 + e^- \rightarrow O_2^-$ (rate limiting)

(2) $O_2^- + Li^+ \rightarrow LiO_2$

(3a) $2LiO_2 \rightarrow Li_2O_2 + O_2$

(3b) $LiO_2 + Li^+ + e^- \rightarrow Li_2O_2$



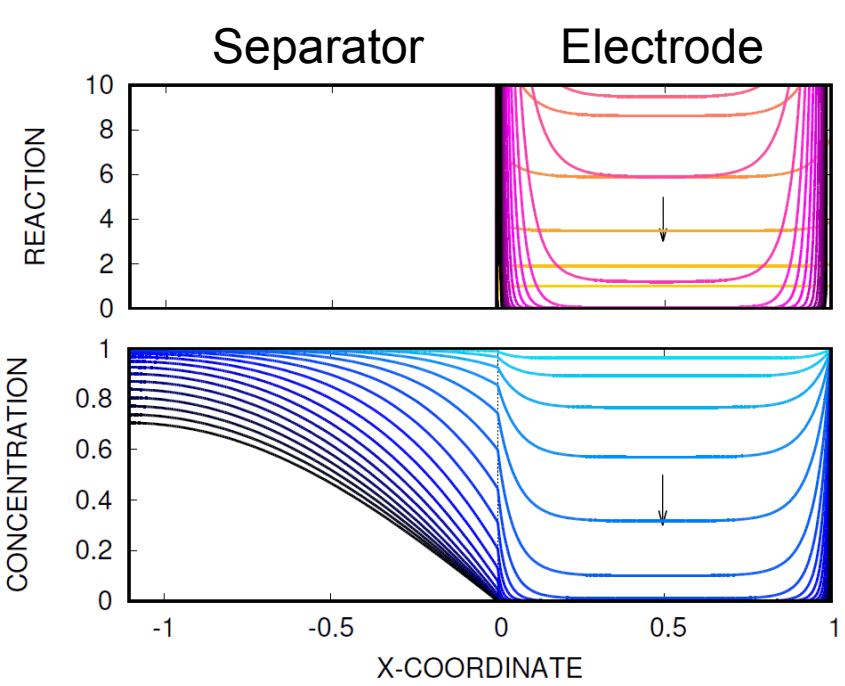
$$i = FAk[C_O(0,t)e^{-\alpha\frac{e\varphi}{k_BT}} - C_R(0,t)e^{(1-\alpha)\frac{e\varphi}{k_BT}}]$$

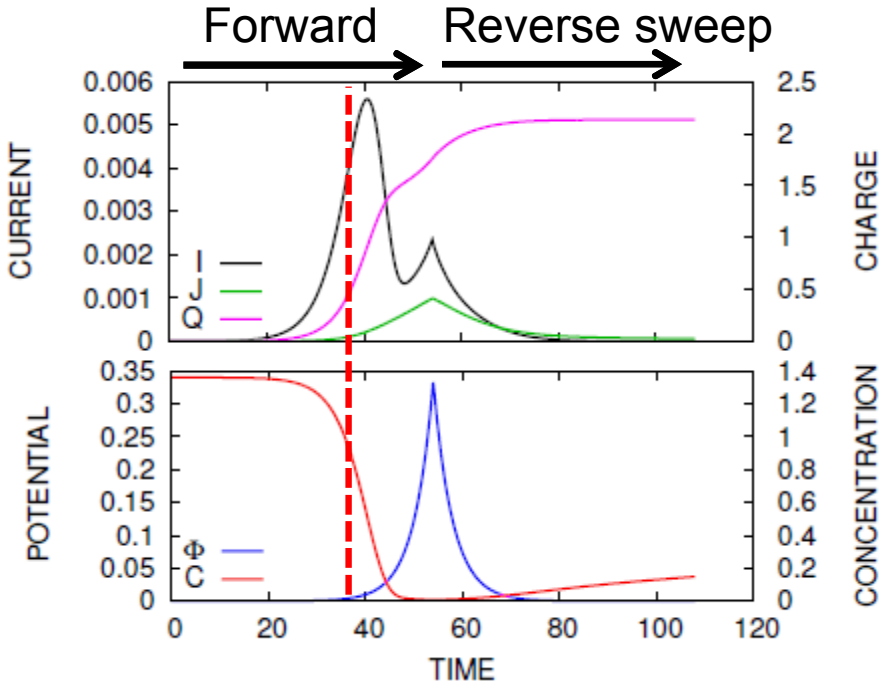
$$r = \sigma k c \exp\left(\alpha\frac{e\varphi}{k_BT}\right)$$

$$\dot{c} = Dc_{,xx} + r$$

$$I = FA\int_0^L r\,\mathrm{d}x = \underbrace{F\,V\,\sigma k c_\infty}_{I_0}\underbrace{\int_0^1 \tilde{c}\,\mathrm{d}s}_{\bar{c}(t)}\underbrace{\exp(\alpha\tilde{\varphi})}_{\Phi(t)}$$

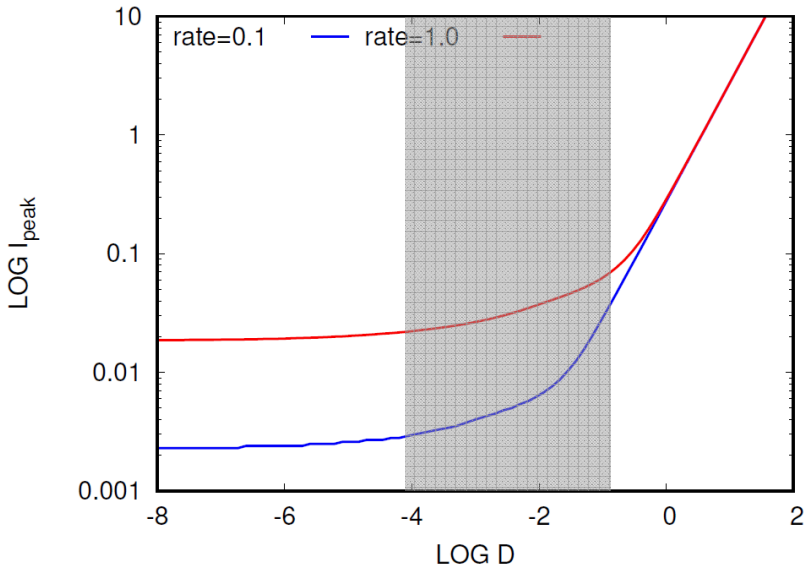
Diffusion and reaction dynamics

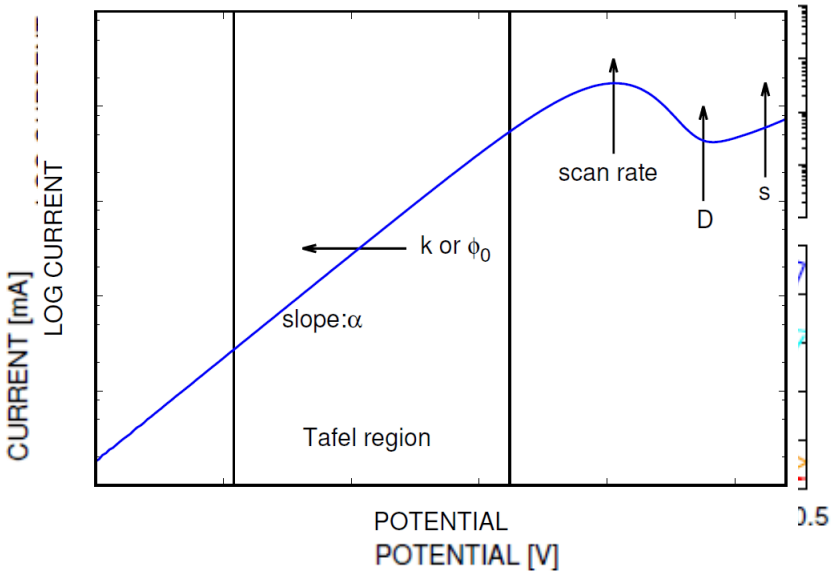




- Oxygen is depleted, replaced by diffusion from separator and air interface
  - Reaction profile peaks at ends of electrode
- I varies with average of concentration across electrode
- Oxygen depletion → voltammetric peak current
- Bulk oxygen diffusion → secondary peak/tail
  - At long times, diffusion rate dominates

Physical properties affect cell behavior





- Diffusion coefficient → peak current
  - At high diffusion coefficient, I_p is independent of scan rate
  - Practical electrolytes have dimensionless D ≈ 10^{-1}-10^{-4}

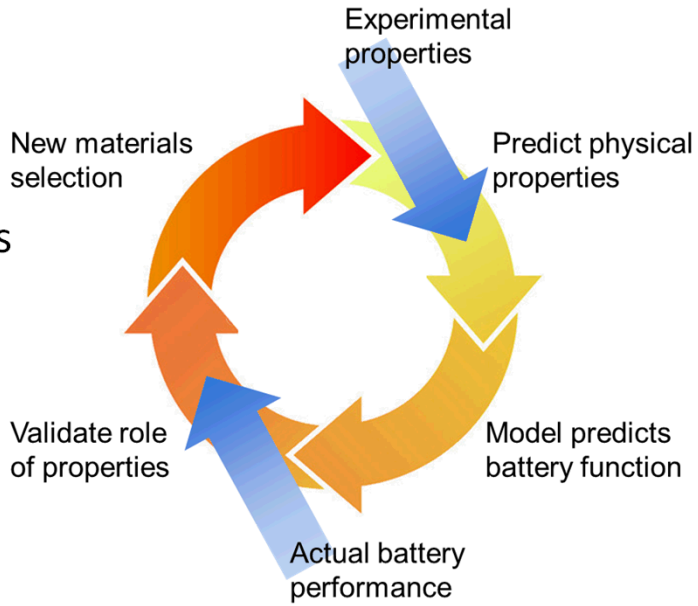
M $LiBF_4$/DMSO	D_O (cm^2/s)	Effective D_O (cm^2/s)	Dimensionless D	α
0.1	6.56E-06	8.20E-07	1.49E-03	0.64
0.5	4.41E-06	5.51E-07	9.97E-04	0.56
1	3.56E-06	4.45E-07	8.06E-04	0.62

  - α → charge transfer efficiency/rate
  - k, ϕ_0 → shift in "onset" (aka kinetics)
  - D → current "tail" (discharge at long times)

Applying the model

- Simplest possible model that represents the data
  - Predicts behavior that deviates from classical (Nicholson) model
  - C_O and D_O influence voltammetric profile
  - α and *k* derive from electrode-electrolyte interaction
    - Requires experimental input

- Next steps
  - Robust model validation with varied electrolytes
  - Adding complexity
    - Local variation in electrode potential (resistance)
    - Varied pore size and gradients of porosity
    - Changing length scales of cathode
  - Prediction of galvanostatic cycling performance
    - Role of cycle rate
    - Long-term battery function



Sandia National Laboratories

THANK YOU

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

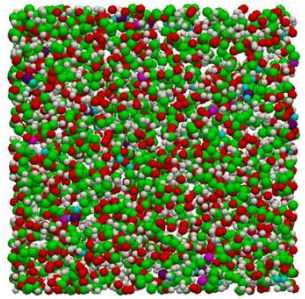
Sandia National Laboratories

SUPPLEMENTAL SLIDES

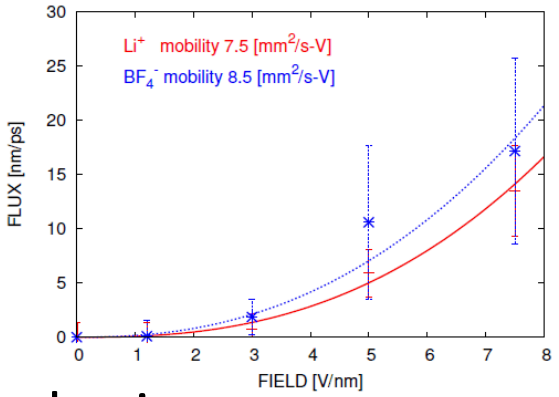
Classical experimental correlations

- Tafel slope → α (charge transfer coefficient)
  - Experimental values vary based on electrode geometry/scan rate
  - $\eta = \frac{k_B T}{e\alpha}\ln(i_0) - \frac{k_B T}{e\alpha}\ln(i)$
- Randles-Sevcik (reversible reaction)
  - $i_p = (2.69 \times 10^5) n^{2/3} A C_O {D_O}^{1/2} v^{1/2}$
- Nicholson-Shain (semi-irreversible reaction)
  - $i_p = (2.99 \times 10^5) \alpha^{2/3} n^{2/3} A C_O {D_O}^{1/2} v^{1/2}$

Molecular dynamics



- Molecule builder
  - Create systems of unexplored electrolyte solvents
  - Varying salt and salt concentration
  - Simple measure → viscosity, density
- Derive properties:
  - Cross species diffusivities (Onsager)
  - Relative flux of ions under applied electric fields



- Discover discrepancies compared to classical physics
  - i.e. Stokes-Einstein diffusivity

Solvents	Experimental		MD	
	γ (g/ cm^3)	η (cP)	γ (g/ cm^3)	η (cP)
PC	1.2047	2.43	1.27	2.85
DMSO	1.10	2.07	1.11	2.1