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Power and Energy Tradeoffs in Li-Air Batteries: The Importance of Electrolyte Dynamics

Dr. Forrest Gittleson

BMW Technology Office USA

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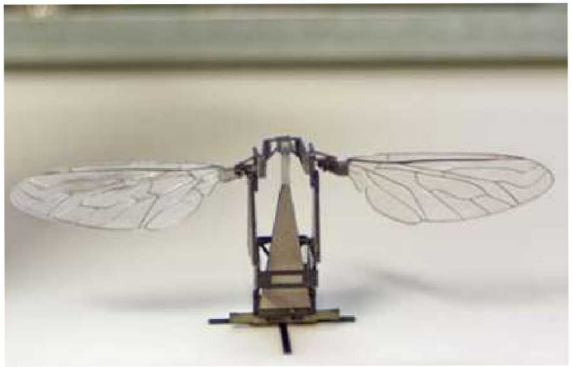
The promise of Li-air batteries

Grid Scale

Transportation

Portable Electronics



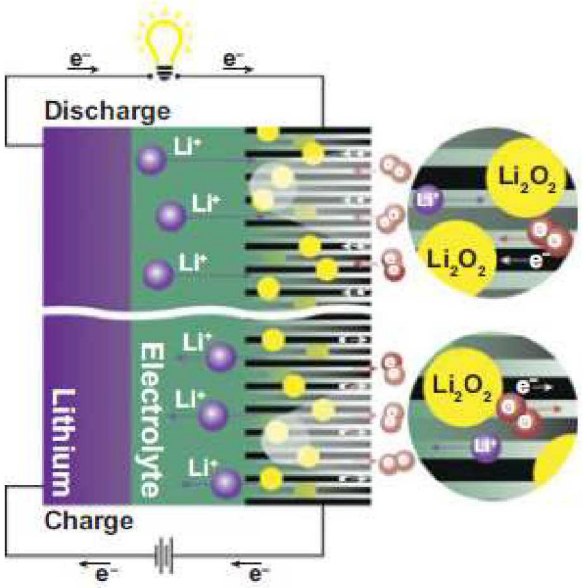
Microelectronics/sensors

Lighter, smaller batteries

Why Li-air/Li-oxygen?

- Conversion chemistry
- Energy density 2-3X state-of-the-art
- Low self discharge

Reversible Chemistries	Voltage	Energy Density (Wh/kg)	Energy Density (Wh/L)	Self Discharge (per month)
Pb-acid	2	30-50	70	4-6%
Ni-Cd	1.2	45-80	100	15-20%
Ni-MH	1.2	60-120	250	0.3%
Li-ion	~3.7	120-300	400	2-3%
Zn-air	1.4-1.6	300-400	1500	severe
Li-S	1.7-2.5	500-600	350	?
Li-air	**2.5-3.0**	**~1000**	**?**	**?**



Kwabi, D. G. *et al. MRS Bull.* **39,** 443–452 (2014).

Oxygen Reduction (Discharge)

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

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

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

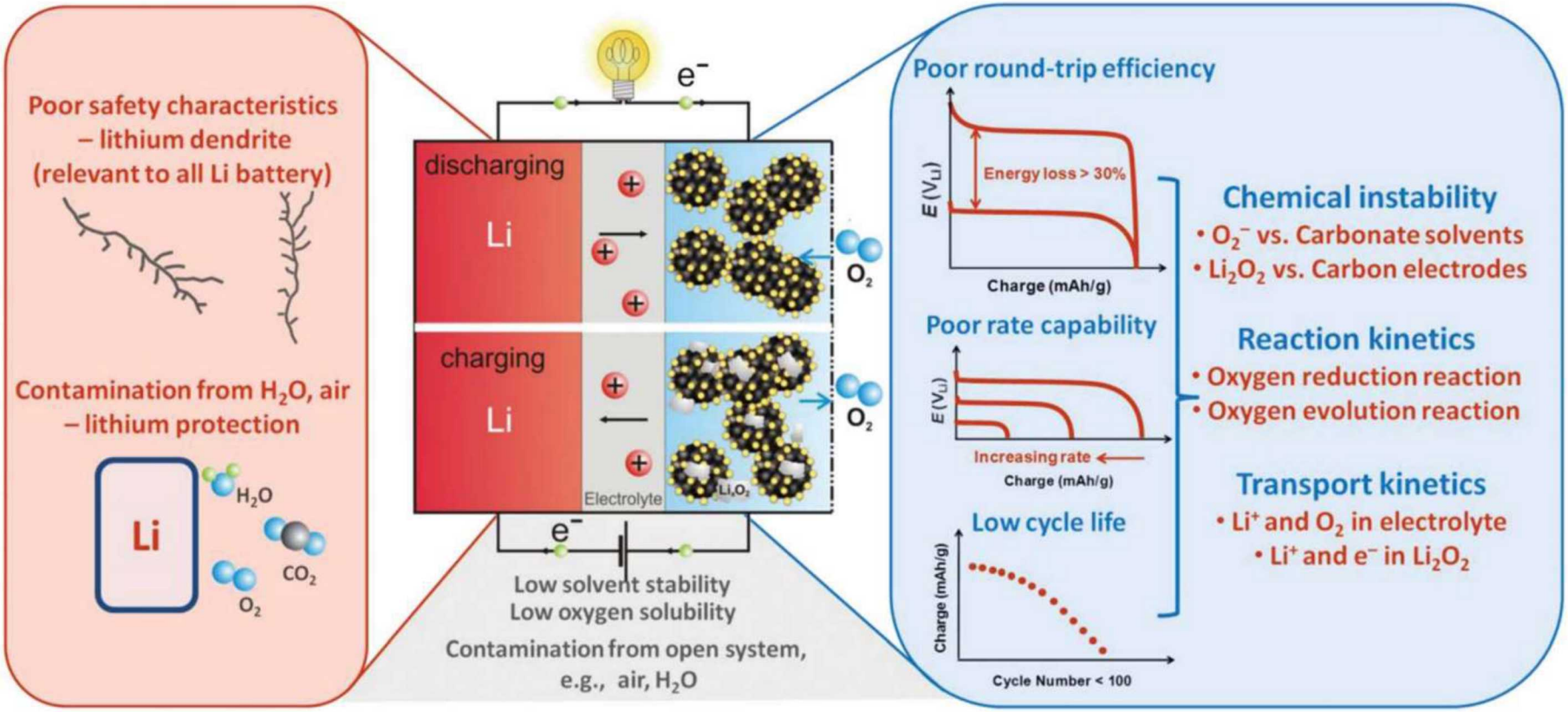
(3b) $LiO_2 + Li^+ + e^- \rightarrow Li_2O_2$

Oxygen Evolution (Charge)

(4) $LiO_2 \rightarrow Li^+ + O_2 + e^-$

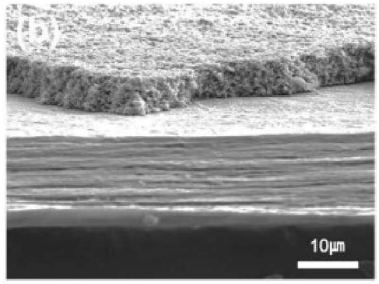
(5) $Li_2O_2 \rightarrow 2Li^+ + O_2 + 2e^-$

Why *not* Li-air?



Y-C. Lu, et al. *Energy & Environmental Science.*, 2013, **6**, 750-768.

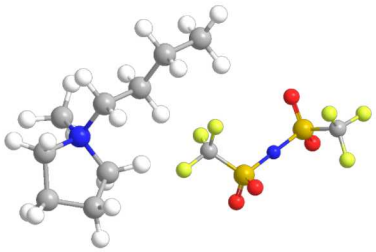
The ideal Li-air system



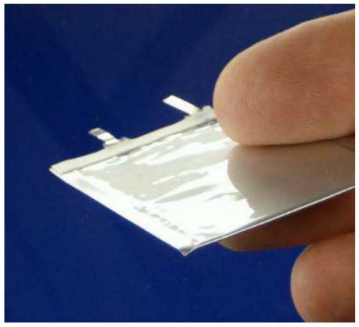
Ceramic-coated Li electrode

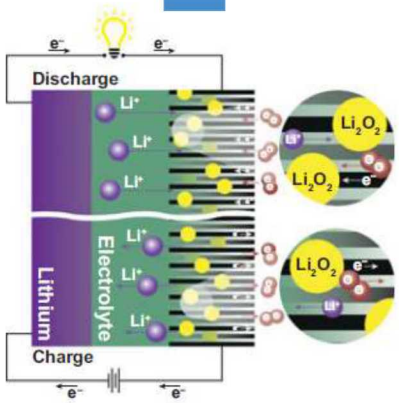
Lithium Anode
Stable interface → long shelf life
Non-reactive with electrolyte

- Low volatility
- Low flash point
- Protect Li anode



Packaging
Lightweight, small and flexible/conformal





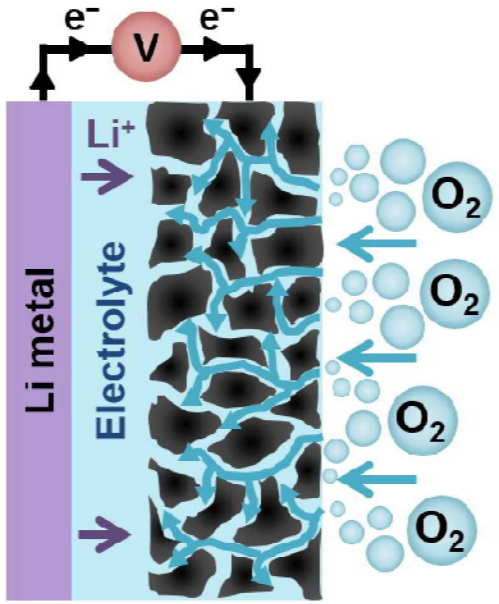
Cathode
High surface area
Good conductivity
Non-reactive

Carbon paper electrode

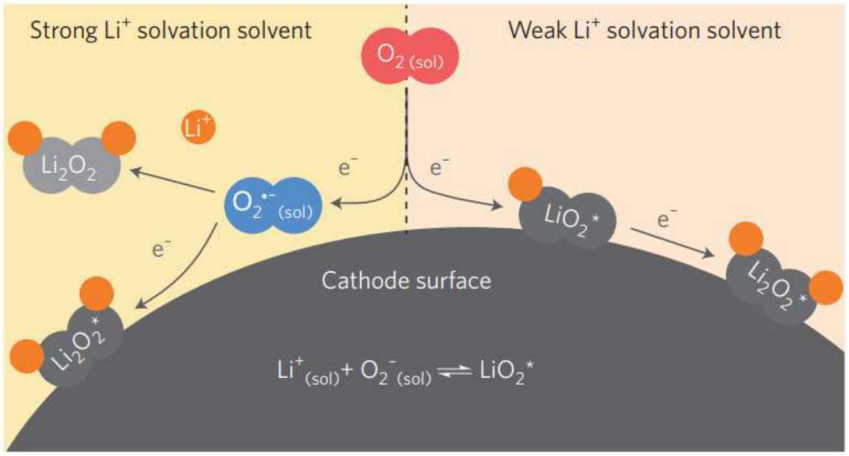
Electrolyte
Ionically conductive
Stable to electrochemistry
Minimal evaporation
Solubility of O_2 and Li^+
Good safety profile

Finding an optimal electrolyte

- Non-aqueous electrolyte
  - Selection of solvent, anion and Li^+ concentration
  - Major physicochemical parameters:
    - Electrochemical stability
    - Volatility
    - Viscosity or diffusivity
    - Solvation; Li^+, anion, O_2^- interactions
- Critical questions
  - How does reactant **diffusion** relate to power and energy density?
  - How important is **solubility**?
  - How does **solvation** change kinetics?
- Large experimental screening
- Computational simulation

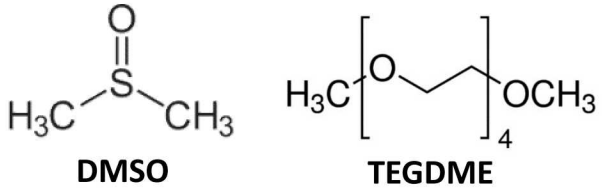


Gittleson, F. S. et al. *Energy Environ. Sci.* **2017**, *10* (5), 1167–1179.

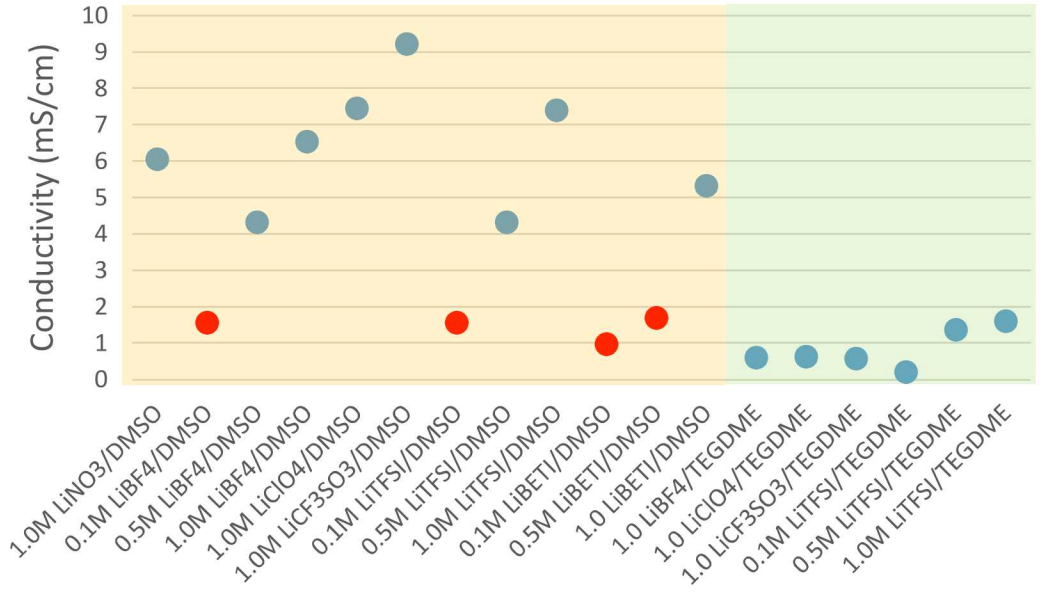


Aurbach, D., et al. *Nat. Energy*, 2016, **9**, 16128.

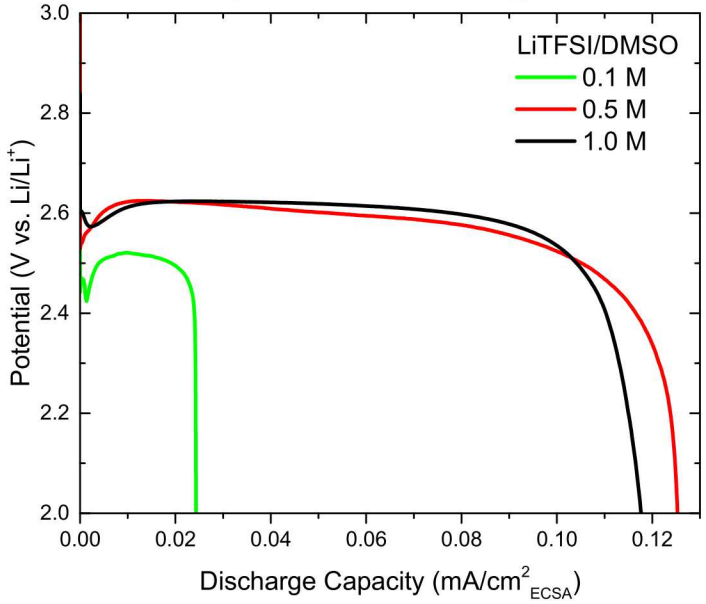
Electrolyte transport: Li^+



Conductivity/diffusivity of Li^+ dictated by concentration and solvent interactions



Capacity affected by conductivity-power relationship



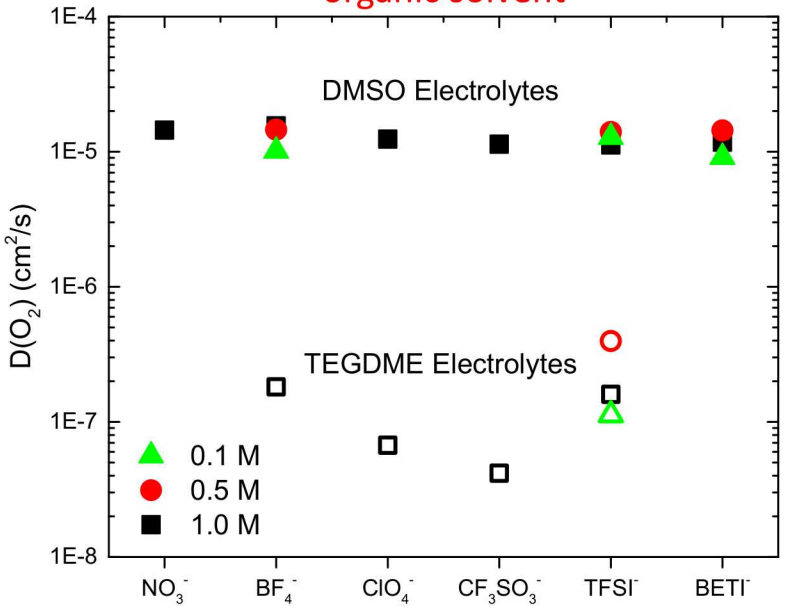
Gittleson, F. S. et al. *Energy Environ. Sci.* **2017**, *10* (5), 1167–1179.

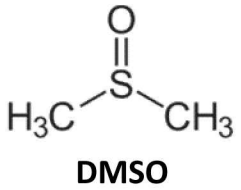
Li^+ transport is rate limiting at low Li concentrations in solvents with high O_2 diffusivity

Electrolyte transport: O_2

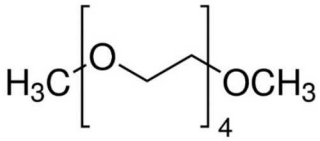
- O_2 diffusivity and solubility (from air) measured with electrochemical methods
  - Two groups of solvent
  - Different anions
  - Different Li^+ concentrations

O_2 diffusion is largely dependent on organic solvent





DMSO



TEGDME

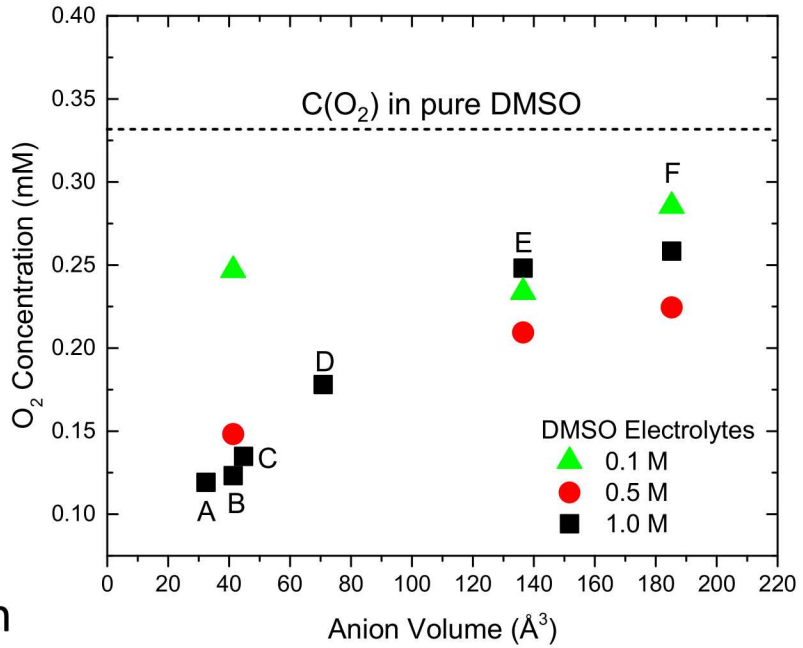
Gittleson, F. S. et al. *Energy Environ. Sci.* **2017**, *10* (5), 1167–1179.

O_2 transport is rate limiting when using ambient pressure air
Anions affect O_2 diffusion in less coordinating solvents

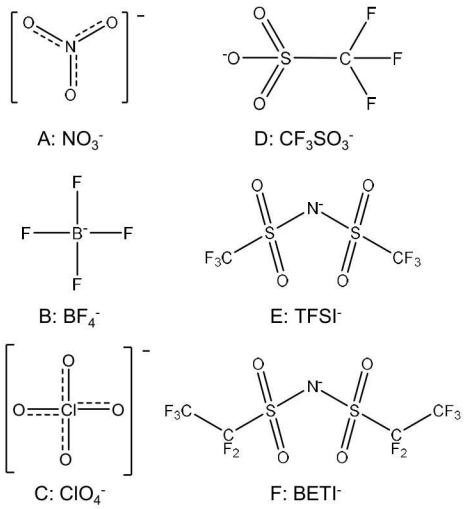
O_2 solubility

- Oxygen solubility varies significantly with electrolyte chemistry
- Electrostatics and molecular packing influence O_2 concentration
  - Salting-in/salting-out
  - Confirmed by simulation

O_2 solubility directly related to ion size in addition to solvent



Anion species



Gittleson, F. S. et al. *Energy Environ. Sci.* **2017**, *10* (5), 1167–1179.

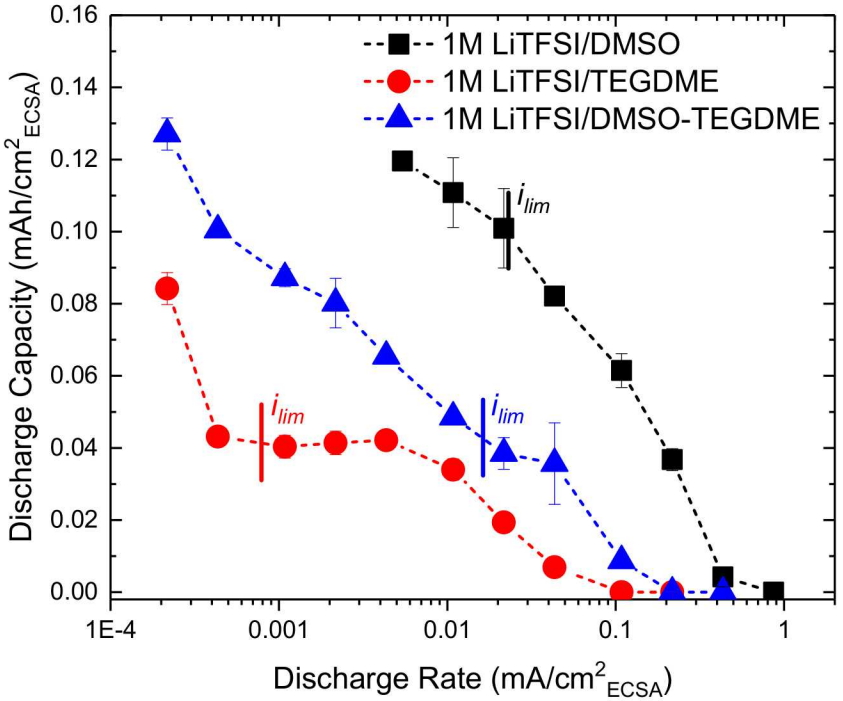
Larger (less polar) anions yield higher O_2 solubility by disrupting electrolyte structure

Power/energy dictated by O_2 transport

Limiting current: maximum current to avoid transport limitations

$$i_{\text{lim}} = \frac{nFADC}{\delta_O}$$

n – electrons
F – Faraday's number
A – surface area
D – diffusion coefficient of O_2
C – concentration of O_2
δ_O – stagnant electrolyte layer thickness

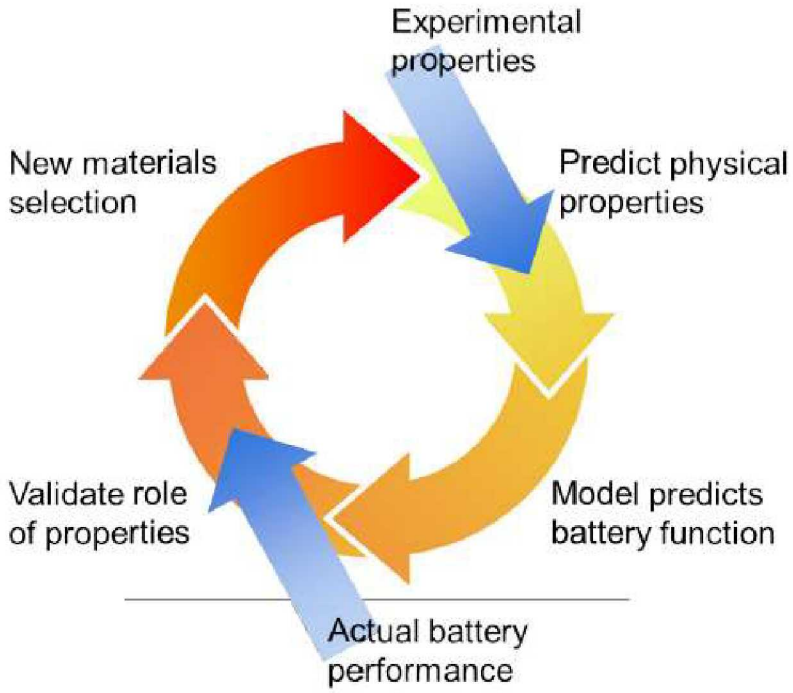


Gittleson, F. S. et al. *Energy Environ. Sci.* **2017**, *10* (5), 1167–1179.

A combination of O_2 diffusivity and solubility can be used to screen and rank electrolytes in rate capability

Experiment to simulation

1. **Target** large set of solvent+salt combinations
2. **Build** molecular structures
3. **Equilibrate** mixtures
4. **Validate** with existing data
5. **Evaluate** properties
6. **Rank**, downselect and test



feedback cycle augmented by injections of reality (experimental data)

Structure: high-throughput molecule/electrolyte builder

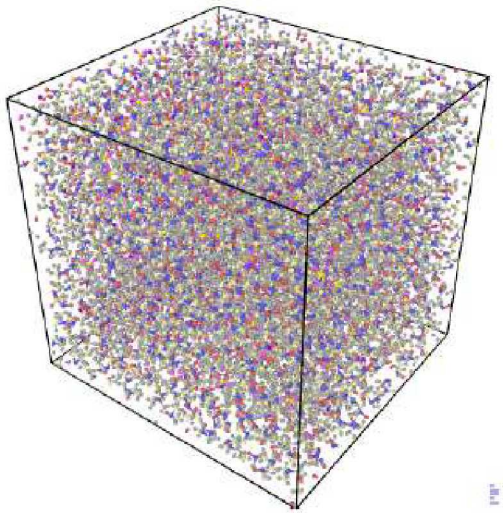
- **Structures:** typically known via spectroscopy & crystallography
- **Interactions:** general purpose potential (CHARMM, AMBER, OPLS).
  - Short-range Lennard-Jones with cross terms from mixing rules.
  - Long-range Coulomb with partial charges from DFT.
  - Harmonic terms to enforce covalent bonds/molecule structure based on molecule topology.
- **Equilibration:** long relaxation due to electrostatics & large molecules near glass transition

+

$$\phi = \sum_{\alpha\beta} 4\epsilon \left(\left(\frac{\sigma}{r_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma}{r_{\alpha\beta}} \right)^{6} \right)$$

$$+ \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{\varepsilon r}$$

=



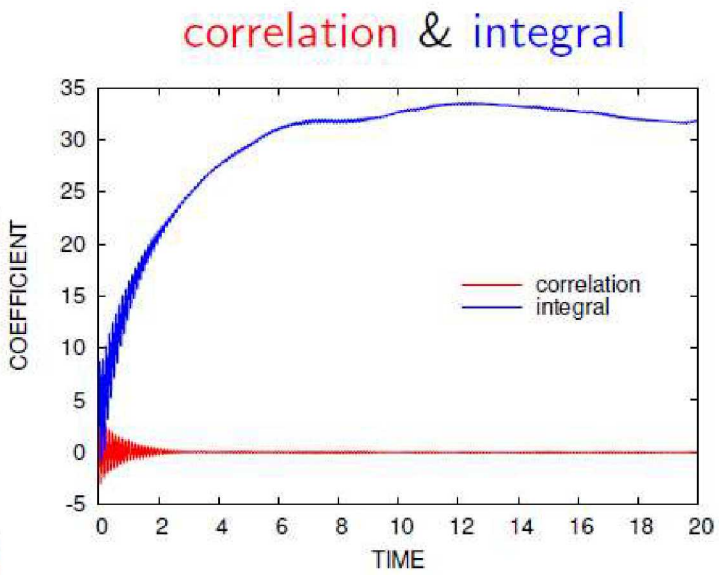
Transport: Green-Kubo methods

Generically, the transport coefficient L for flux $\mathbf{J} = -L\boldsymbol{\nabla}\mu$ can be determined from the temporal correlation (*Onsager regression hypothesis*):

$$\mathbf{D} = \frac{1}{k_B T} \int_0^\infty \langle \mathbf{J}(0) \otimes \mathbf{J}(t) \rangle \, \mathrm{d}t$$

Many advantages of just observing not *perturbing* dynamics:

- equilibrium – no large gradients
- minimal size dependence – small cells & multiple replicas (error estimates)
- full coefficient **D** tensor at once
- multiple properties at once (viscosity, dielectric, diffusion)



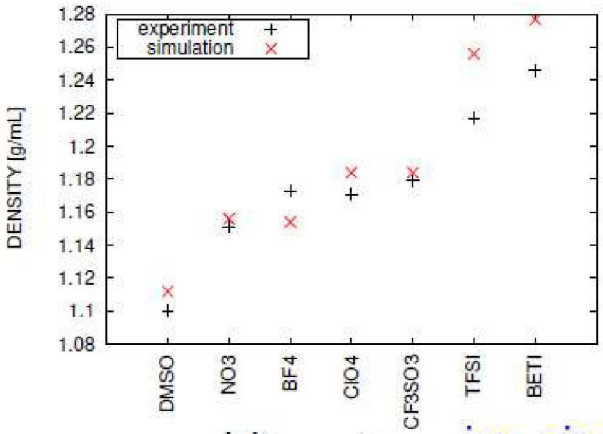
Validation: LiX in DMSO

Validation with properties that are: (a) **easy to measure** experimentally & (b) possibly **correlated** with the prediction properties, e.g. viscosity & diffusion via Stokes-Einstein

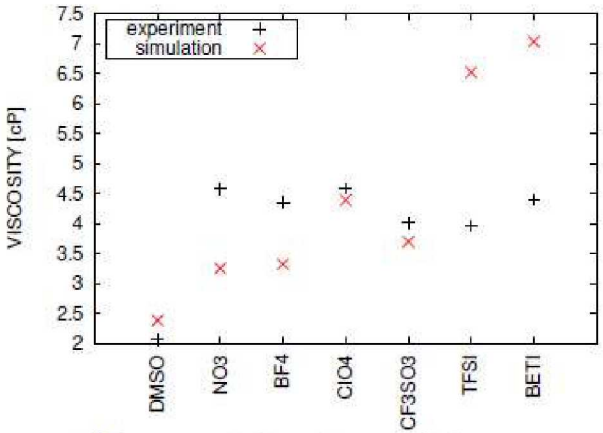
Static
- density
- dielectric

Dynamic
- viscosity
- ionic conductivity

Density



Viscosity ion size $\longrightarrow$

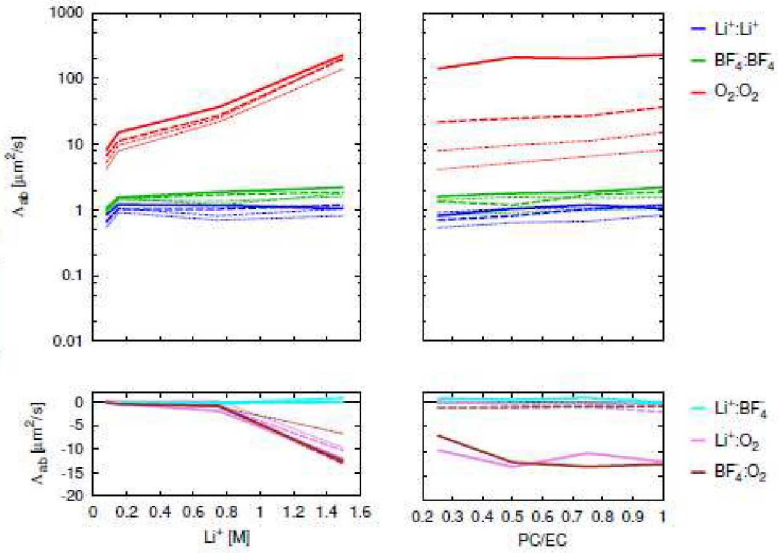


From a *unified* potential we expect a self-consistent ranking, possibly with a systematic bias.

Transport: diffusion $LiBF_4$ in PC/EC

Diffusion: *Onsager* coefficients for flux driven by a chemical potential gradient result from correlations of *average species velocities*

$$
\begin{aligned}
\mathsf{L}_{ab} &= \frac{V}{3k_B T}\int_0^\infty \mathrm{d}t\ \langle \mathsf{J}_a(0)\cdot \mathsf{J}_b(t)\rangle \\
&= \frac{V}{k_B T}\left[\frac{1}{3}\int_0^\infty \mathrm{d}t\ \langle c_a\bar{\mathsf{v}}_a(0)\cdot c_b\bar{\mathsf{v}}_b(t)\rangle\right] \\
&= \frac{c}{k_B T}\left[\frac{N_a N_b}{3N}\int_0^\infty \mathrm{d}t\ \langle \bar{\mathsf{v}}_a(0)\cdot \bar{\mathsf{v}}_b(t)\rangle\right] \\
&= \frac{c}{k_B T}\boldsymbol{\Lambda}_{ab}
\end{aligned}
$$



All except O_2 relative constant

Components of diffusion matrix L for $LiBF_4$ in PC/EC: diagonal (upper), off-diagonal (lower), as a function of Li concentration (left) and PC/EC ratio (right)

Transport: Onsager to Fick coefficients

Batteries are typically designed with concentration driven diffusion coefficients (Fick) vs chemical potential driven fluxes (Onsager)

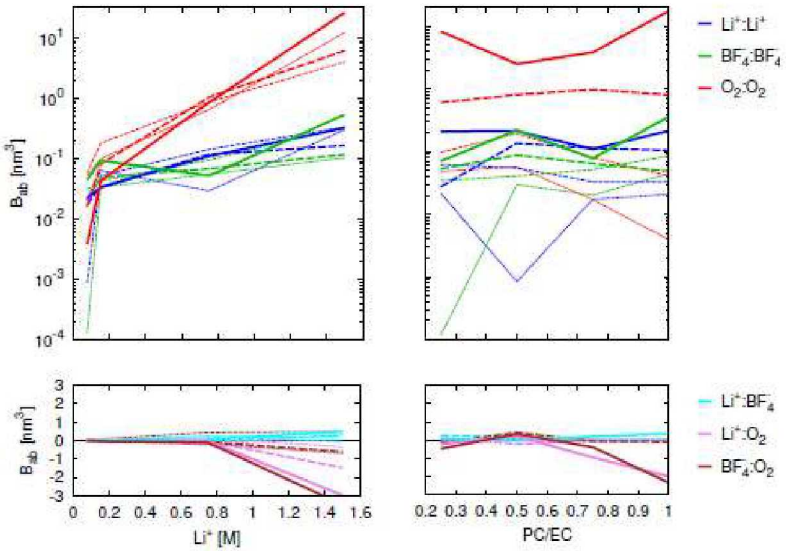
There are a number of methods to calculate the thermodynamic factor matrix $\mathbf{\Gamma} = \frac{\partial \boldsymbol{\mu}}{\partial \mathbf{c}}$

- Monte Carlo based: Widom energy change with particle insertion
- Box-in-box based on Kirkwood-Buff theory

$$\frac{1}{k_B T V} \mathbf{\Gamma}_{ab}^{-T} = \langle c_a c_b \rangle - \langle c_a \rangle \langle c_a \rangle$$

- Direct differentiation from thermodynamic integration

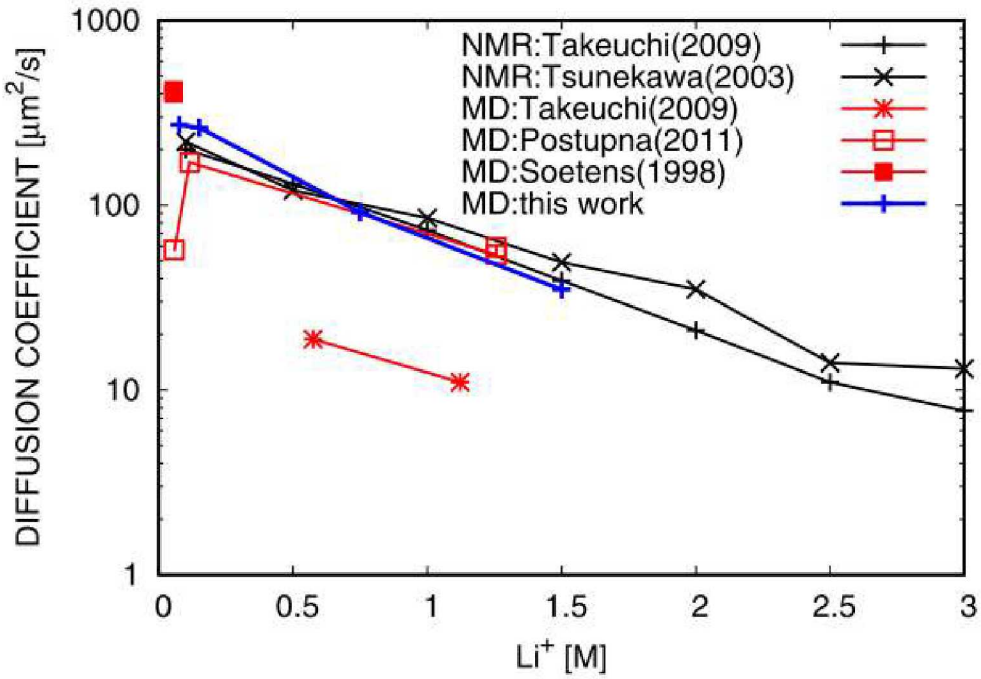
$$\frac{\partial \mu}{\partial c} = \frac{1}{V} \frac{\partial^2 G}{\partial c^2} \sim G_1^2 - G_0^1$$



strongest trends with Li

Experimental validation

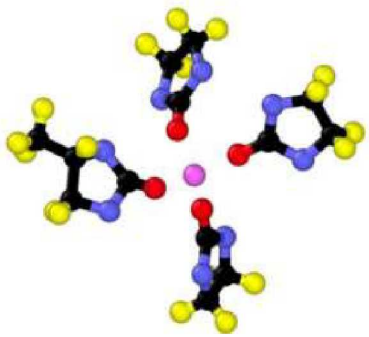
- Diffusivity decreases as Li^+ concentration increases
- Consistent with NMR self-diffusion analysis
- Error introduced in calculating Fickian diffusion coefficients



Jones, R. E., Ward, D. K., Gittleson, F. S. & Foster, M. E. *J. Electrochem. Soc.* **2017**, *164*, A1258–A1267.

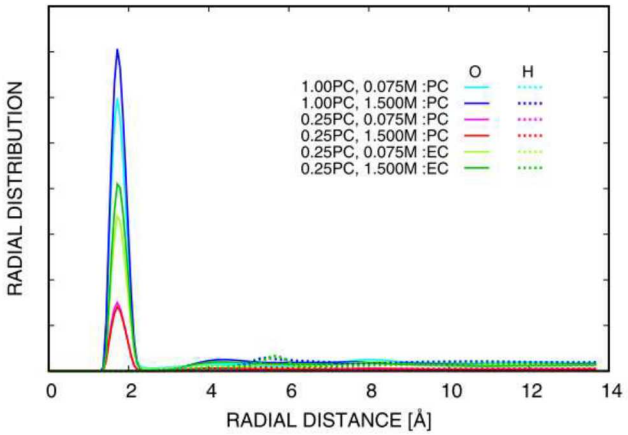
Diffusion estimates are accurate with EC:PC model electrolyte

Evaluating electrolyte solvation structures

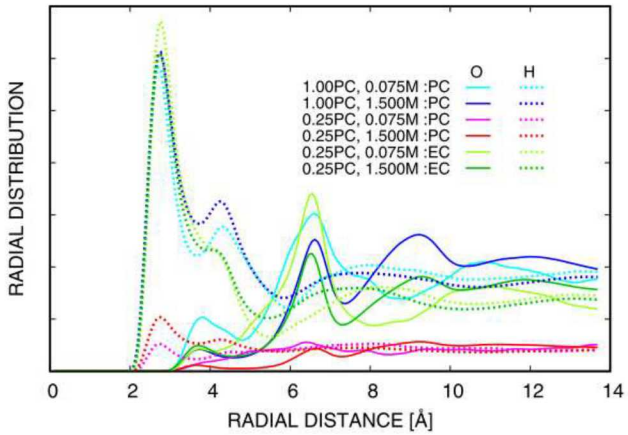


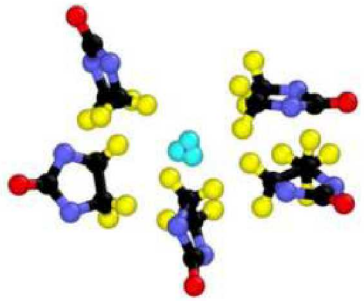
$Li^+[EC_3PC]$

Li^+ coordination



BF_4^- coordination





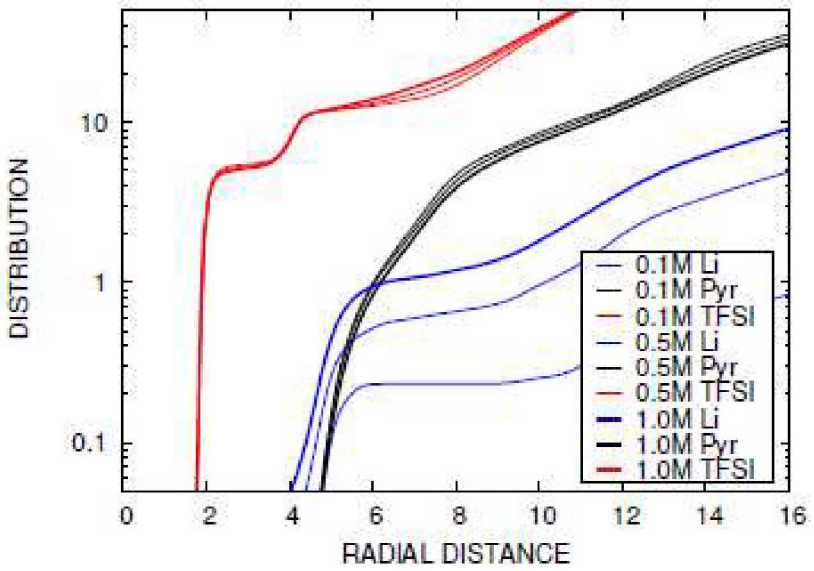
$BF_4^-[EC_4PC]$

Jones, R. E., Ward, D. K., Gittleson, F. S. & Foster, M. E. *J. Electrochem. Soc.* **2017**, *164*, A1258–A1267.

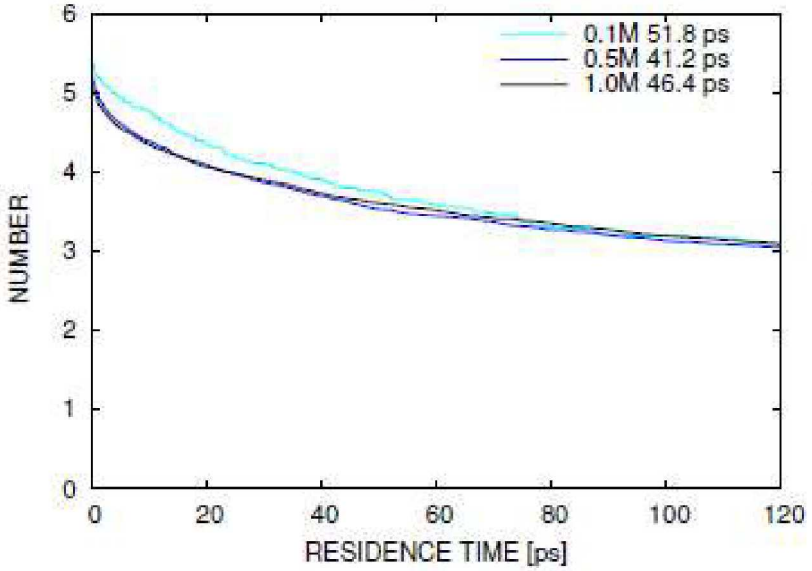
Radial density functions capture electrolyte interactions and connect electrolyte structure to dynamics

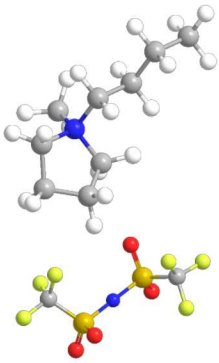
Electrolyte structure in novel ionic liquids

Li^+ coordinates with $TFSI^-$, small effect on Pyr_{14}^+ with increasing concentration



Co-transport of Li and TFSI in solvation shell means Li has high barrier to transport





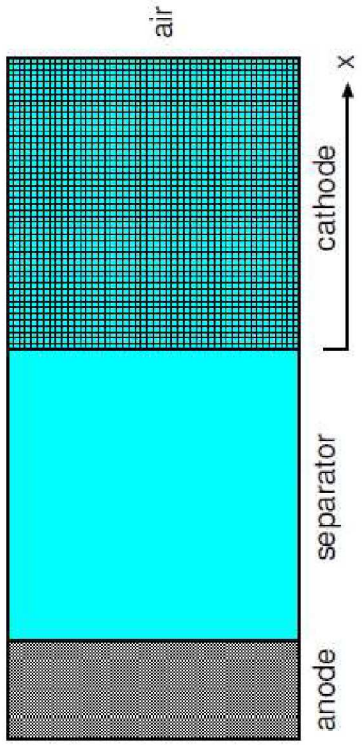
$Pyr_{14}TFSI$

Strong Li-anion coordination yields slow Li^+ transport in ILs

Full battery modeling

Battery components:

- **Electrodes** - electro-chemistry, structure
  - Flat Li anode: ultimately determines capacity. SEI/passivation formation
  - Porous cathode: typically carbon. Surface area, clogging.
- **Electrolyte** - transport, chemical stability *large* combinatorial problem with greatest impact on cell function
  - counter ions: BF4, BETI, TFSI,... and concentration
  - solvent: dimethyl sulfoxide (DMSO), ionic liquids, alkyl carbonates, crown ethers, glymes (TEGME), esters, nitriles, amides (DMA), sulfones, ... pure, in blends, segregated

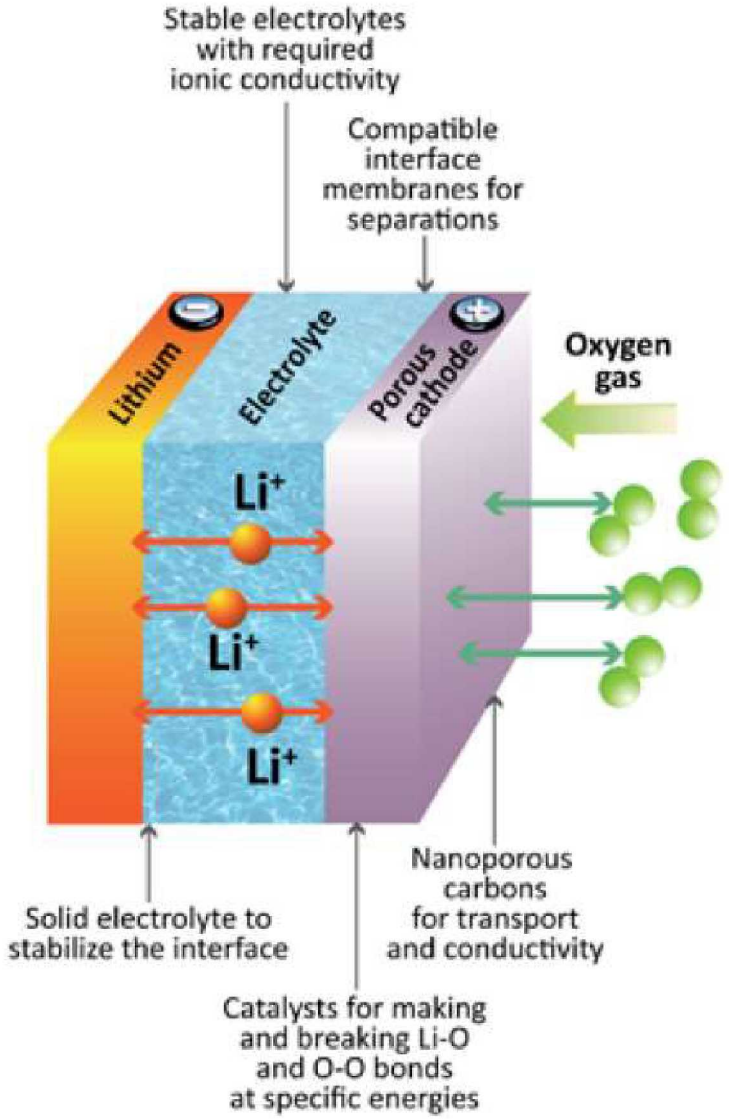


Battery model: parameters

- **D diffusion matrix**
- **m mobility**
- c_∞ **oxygen solubility**

- s surface diffusion
- k reaction coefficient

- σ surface area density
- ϵ porosity
- τ tortuosity
- L_c cathode thickness
- L_s separator thickness



Battery model: simplest

Primary reaction (irreversible) $\boxed{O_2 + e^- \rightarrow O_2^-}$

O_2 is reduced in the cathode & is the mobile species of interest

Butler-Volmer reaction model, dependent on: the potential φ & concentration c:

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

Nerst-Planck expression for drift & diffusion species flux J:

$$\mathrm{J} = -\mathrm{L}\boldsymbol{\nabla}\boldsymbol{\mu} - \mathrm{m}\boldsymbol{\nabla}\phi = -\mathrm{D}\boldsymbol{\nabla}\mathrm{c} - \mathrm{m}\boldsymbol{\nabla}\phi \ ,$$

Governing reaction-diffusion equation:

$$\varepsilon \dot{c} = \frac{1}{\tau}\boldsymbol{\nabla} \cdot \mathrm{J} + r$$

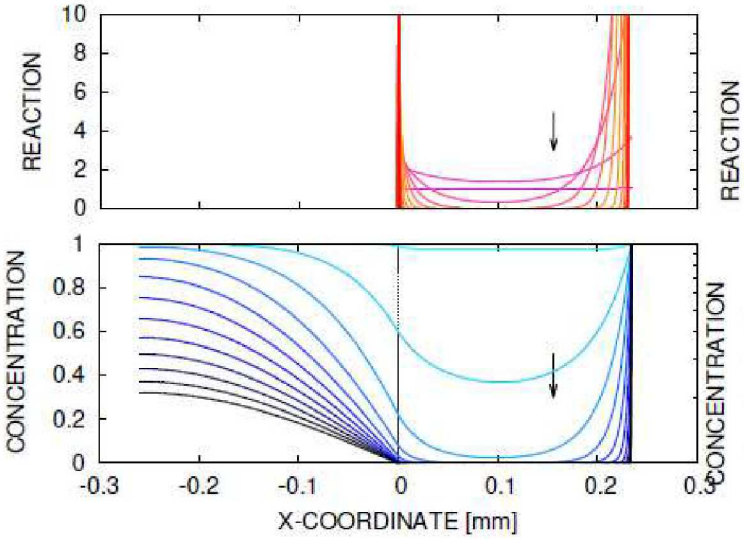
where σ: surface density, ε: porosity & τ: tortuosity

Boundary conditions, e.g. $c = c_{\text{equilibrium}}$ for O_2 at the air boundary

Battery model: phenomenology

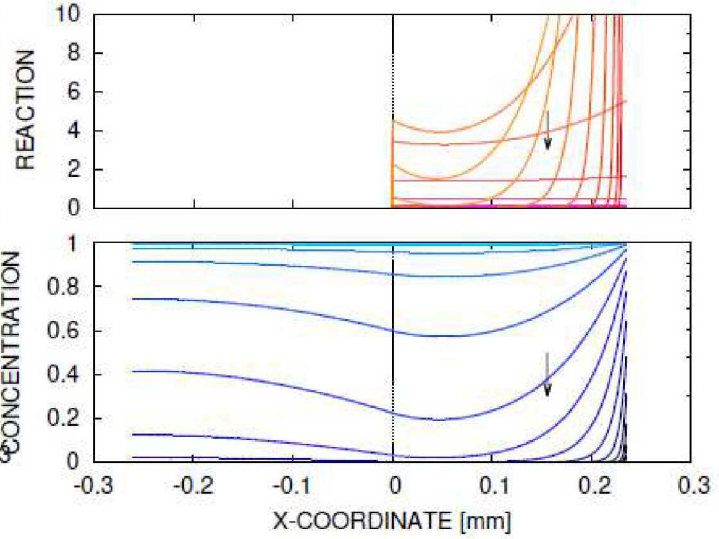
In addition to providing insight to overall performance, we obtain *spatial* data from simulation not accessible by experiment

Discharge



Dirichlet open boundary condition (common)

singularities at cathode boundaries



Robin/limited surface diffusion boundary condition

Summary

- Electrolyte selection and design
  - Reactant transport (particularly O_2) impacts power/energy in Li-air systems
  - Simulation helps to understand the role of molecular interactions
  - Screening and prediction of properties is possible with experimental validation
- Suite of simulation tools to screen electrolytes
  - Diffusivity – large scale molecular dynamics
  - Solubility – free energy of solvation
  - Electrolyte interactions – radial density functions
  - Macro-distributions - finite element model
- Techniques applicable to Li-ion and other beyond Li-ion chemistries

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