Exceptional service in the national interest
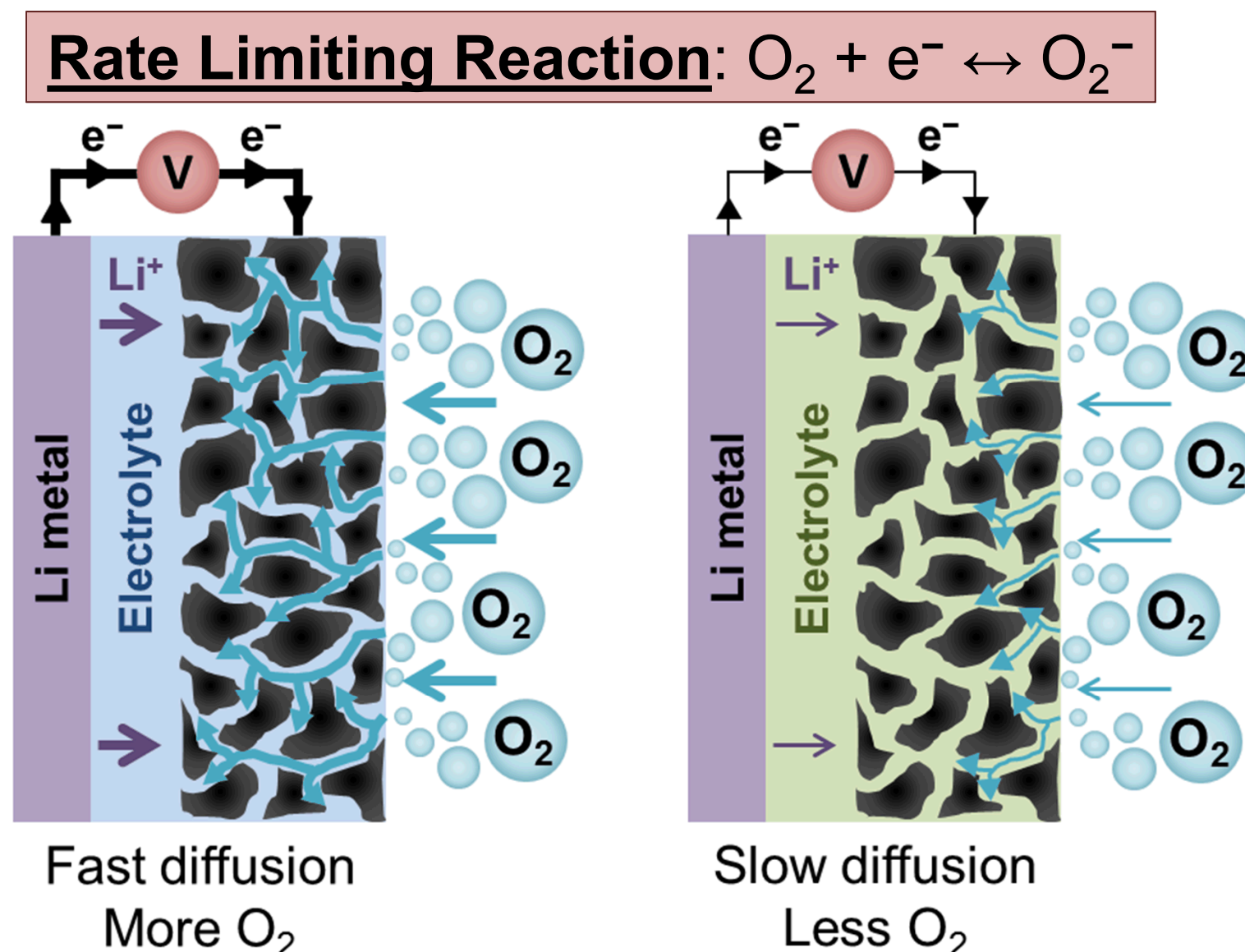
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Electrolyte Composition Influence on Oxygen Reduction in Li-Air Cells

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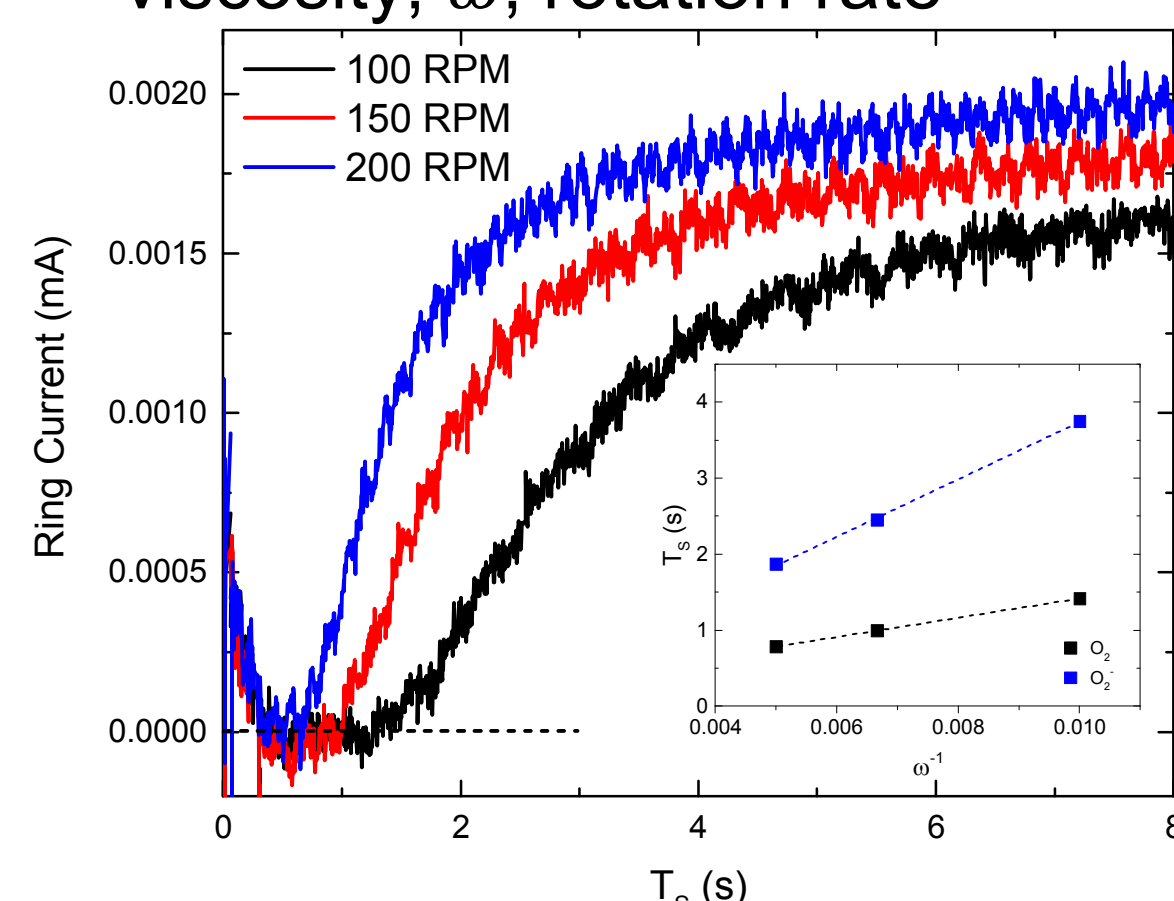Sandia National Laboratories, Livermore, CA, USA

Background and Motivation

- Li-air and Li-O$_2$ batteries can achieve energy densities **10X** greater than Li-ion
- These systems require a constant influx of O$_2$, but slow diffusion through a stagnant liquid electrolyte impedes the O$_2$ supply
- Delivering O$_2$ rapidly to the electrode surface is essential for high power and high energy operation
- To design a better battery, we must understand the influence of electrolyte on O$_2$ diffusion and solubility

Rate Limiting Reaction: O$_2$ + e$^-$ ↔ O$_2^-$

Fast diffusion
More O$_2$

Slow diffusion
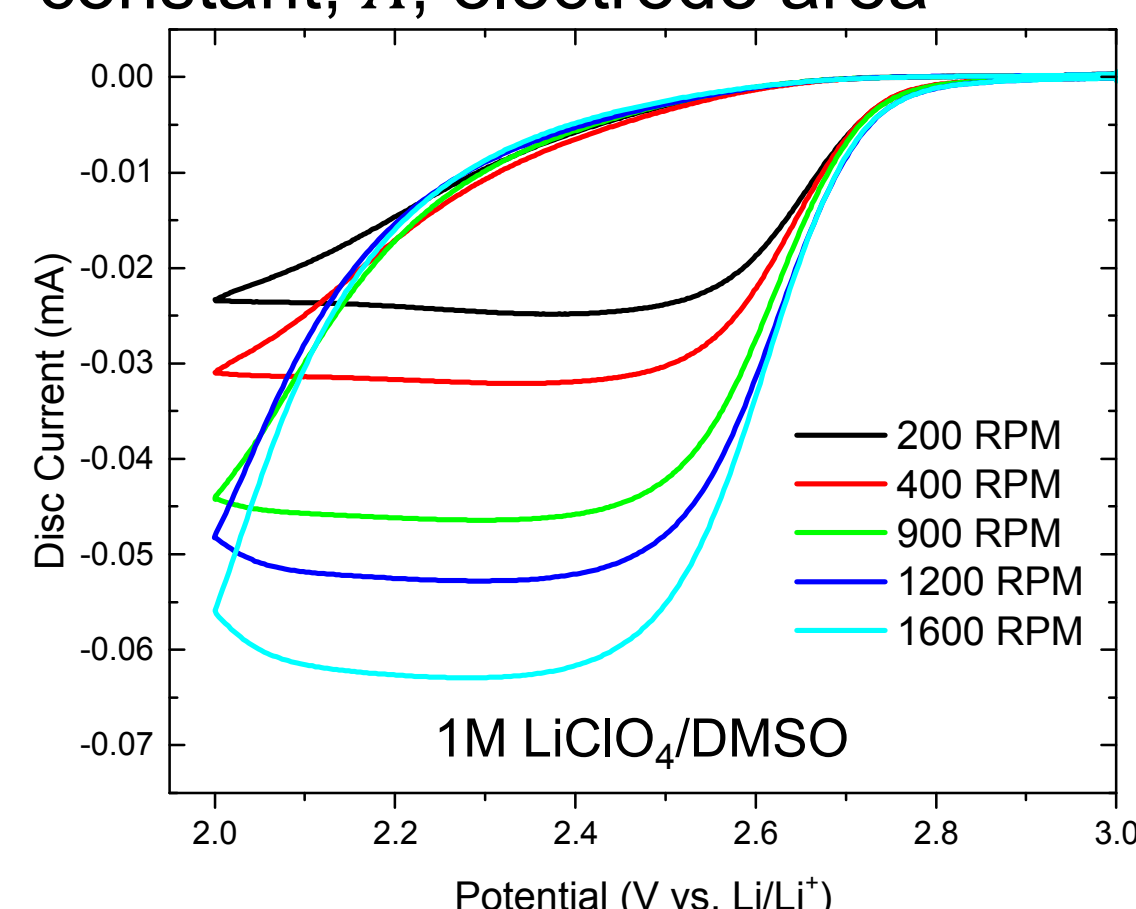Less O$_2$

Experimental

Diffusion Coefficients

- The transit time method using a rotating ring disc electrode (RRDE) measures D(O$_2$) and D(O$_2^-$)
- $T_s = K \left(\frac{\nu}{D(O_2)} \right)^{\frac{1}{3}} \omega^{-1}$
- K, geometric constant; ν, kinematic viscosity; ω, rotation rate
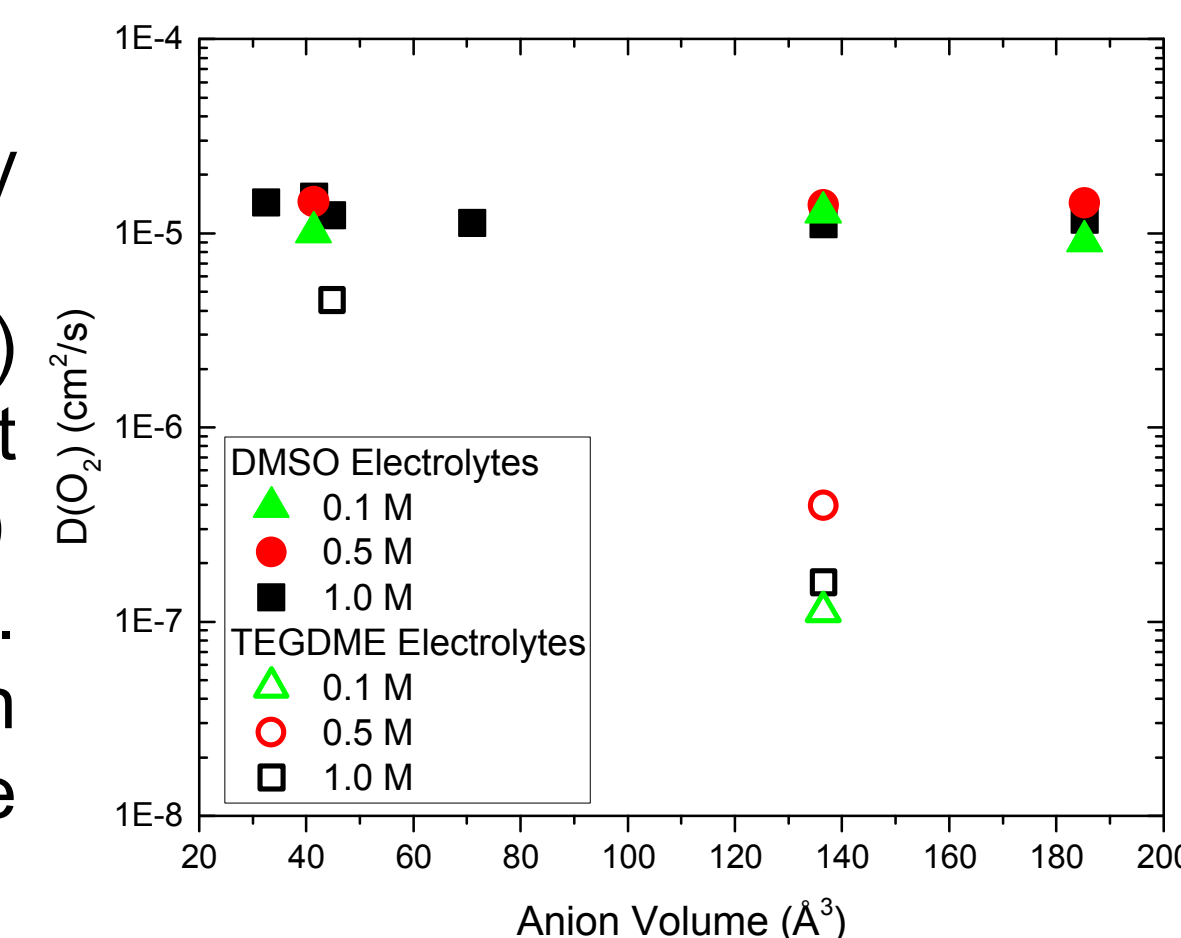

Oxygen Concentration

- Cyclic voltammetry using a rotating disc electrode (RDE) measures C(O$_2$) by the Levich equation
- $i_{lim} = 0.62nFAC(O_2)D(O_2)^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}$
- n, number of electrons; F, Faraday's constant; A, electrode area
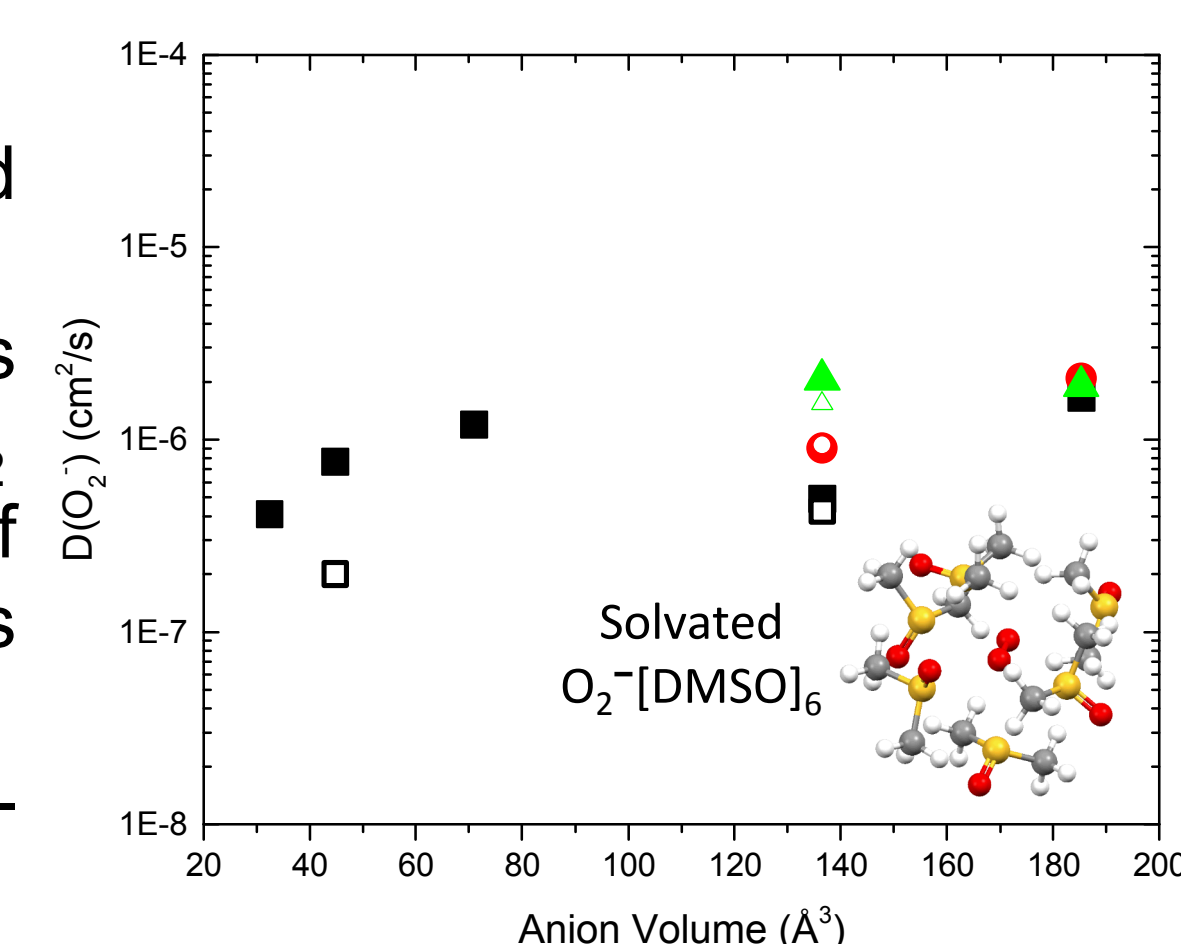

1M LiClO$_4$/DMSO

Diffusion

O$_2$ Diffusivity

- Traditionally related to solution viscosity (i.e. Stokes-Einstein relation)
- No strong correlation found between D(O$_2$) and electrolyte viscosity (i.e. high salt concentration in dimethyl sulfoxide, DMSO)
- For low donor number solvent (i.e. tetraglyme, TEGDME), salt concentration and anion type do, however, influence D(O$_2$) (through O$_2$-anion coordination)

O$_2^-$ Diffusivity

- Influenced by the solvation of O$_2^-$ and solution viscosity
- The solvated structure of O$_2^-$ in DMSO is ~29X larger (in volume) than unsolvated O$_2$
- Stokes' correlation predicts an order of magnitude lower O$_2^-$ diffusivity with this larger size – confirmed by the data
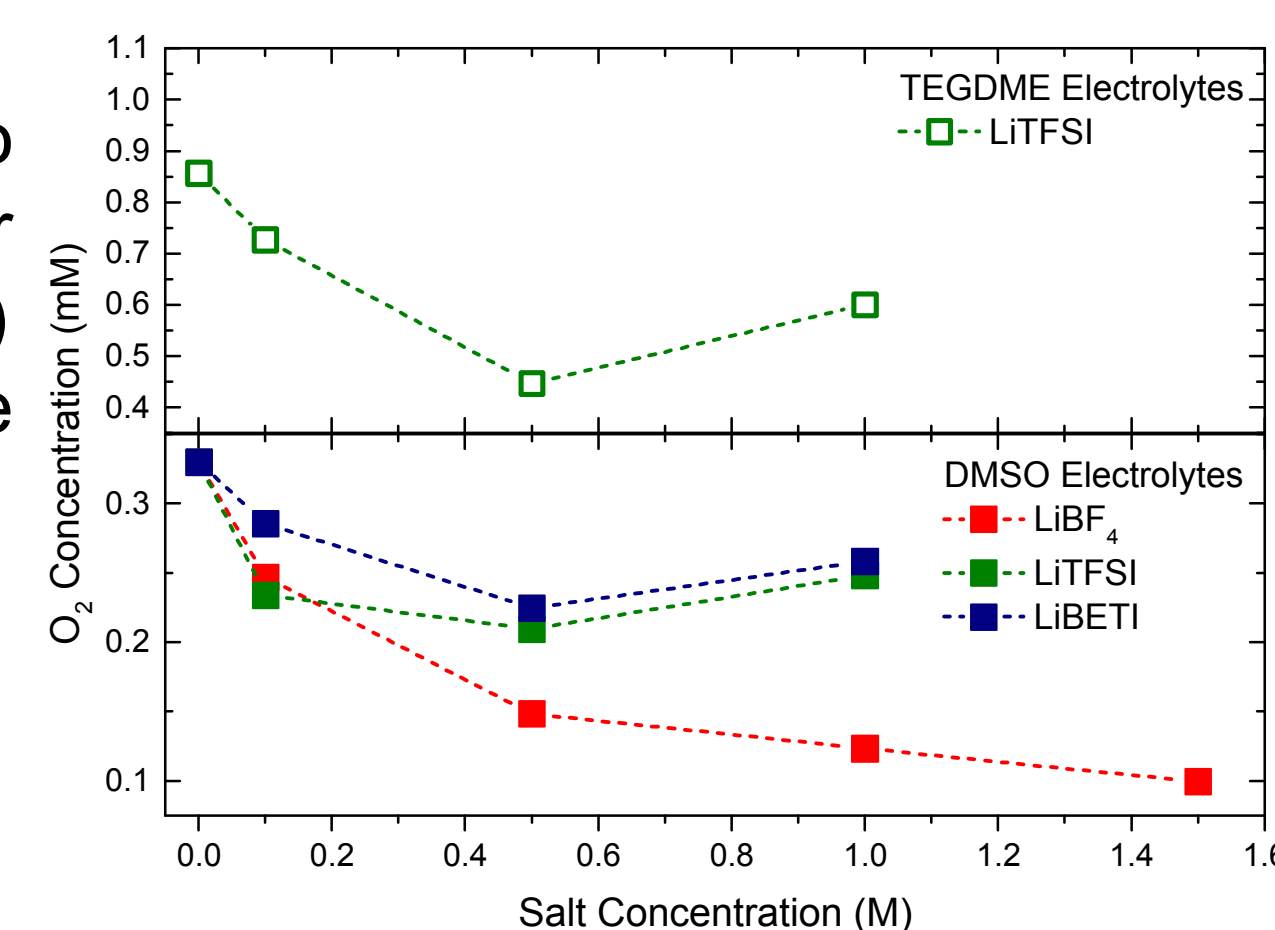- Data also shows an influence from O$_2^-$-anion coordination (a change in solvation)

Solvated O$_2^-$[DMSO]$_6$

Oxygen Concentration

O$_2$ Solubility *(from 1 atm dry air)*

- Solubility of a gas in a liquid is related to the free-volume of intermolecular cavities (i.e. between solvent molecules)
- However, the presence of electrolyte species affects solubility in two ways:

Salting-out: electrostatic ion-solute interactions reduce solubility
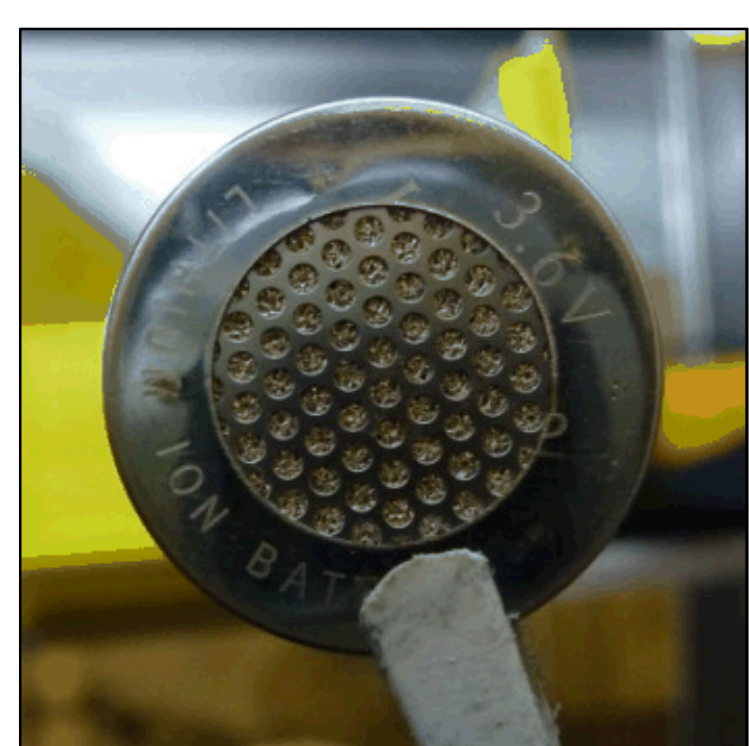**Salting-in:** dispersion forces make room for additional solute

- Data shows that C(O$_2$) is reduced with the addition of Li$^+$ salt
- An analysis of 6 anions illustrates that larger anions can reduce the impact of salting-out from high Li$^+$ concentrations
- Large TFSI$^-$ and BETI$^-$ salt anions also exhibit good D(O$_2$) in DMSO, suggesting a better O$_2$ supply
- Concentration of salt is important to show the affect of anion size on C(O$_2$)

A: NO$_3^-$
B: BF$_4^-$
C: ClO$_4^-$
D: CF$_3$SO$_3^-$
E: TFSI$^-$
F: BETI$^-$
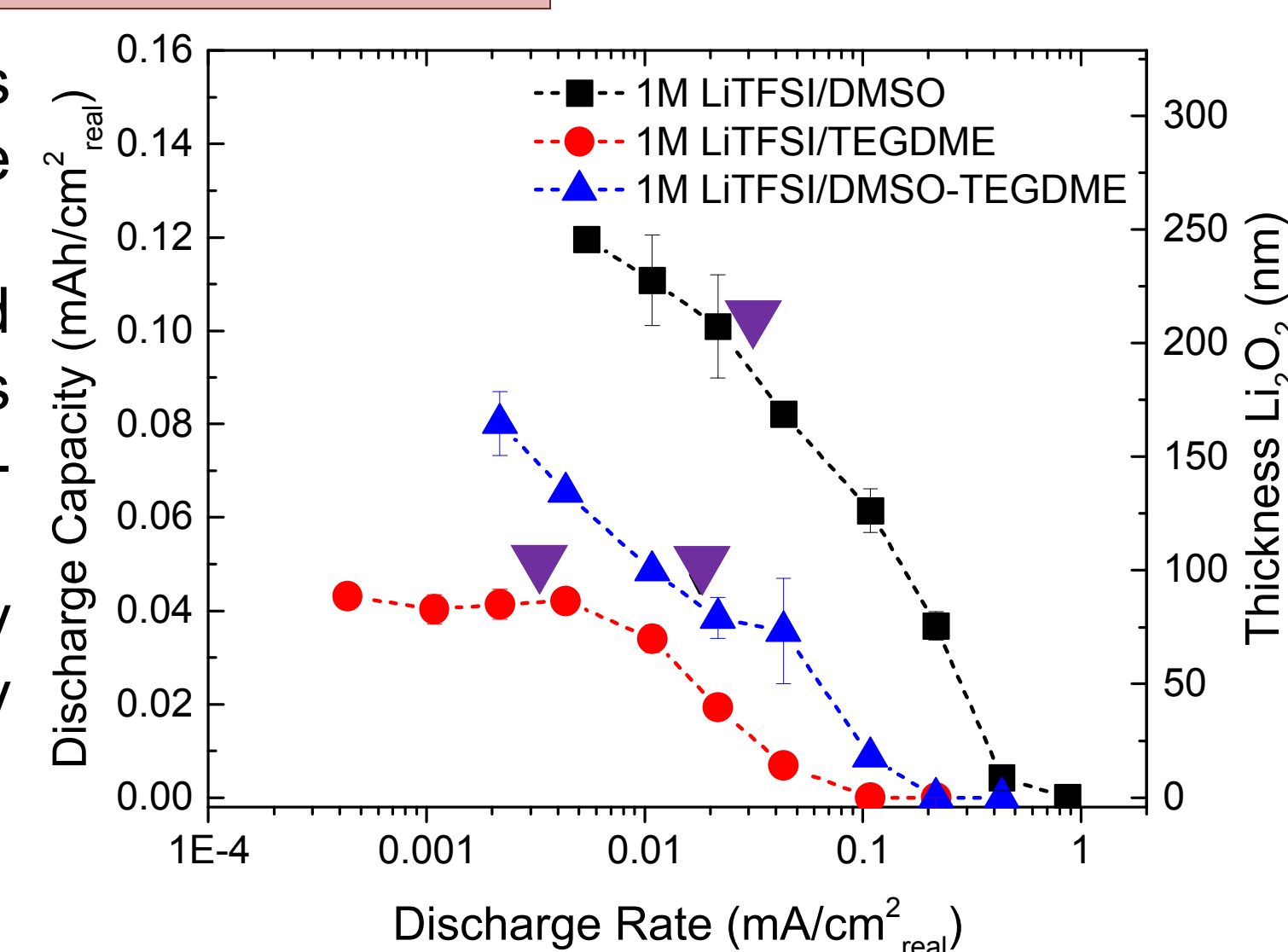
Li-Air Cell Performance

- To validate the impact of mass transport on cell performance, Li-air coin cells were constructed and discharged under dry air at various rates
- Theory indicates that the product of D(O$_2$) and C(O$_2$) divided by a characteristic length (δ_0) is a good metric to determine the mass transfer-limited discharge rate:

$$i_{lim} = \frac{nFAD_O C_O}{\delta_O}$$

δ_O: thickness of the stagnant electrolyte diffusion layer

- Discharge capacity and current is compared for different electrolyte solvents of varying D(O$_2$), C(O$_2$)
- Calculated i_{lim} values correspond well to transition between mass transport-limited and kinetically-limited behavior
- Passivation of the electrode by products also affects cell capacity at longer time scales

▼ indicate calculated i_{lim} values

Conclusion

Selection of Li-air and Li-O$_2$ electrolytes must account for oxygen solubility and diffusivity in addition to stability and reaction kinetics. Mass transport in these cells affects both the cycle rate and the capacity of cells. The influence of electrolyte concentration, anion size and solute-ion interactions cannot be neglected. Salt and solvent species must be selected synergistically to promote these properties. Here, we highlight several electrolyte design parameters to tune and improve battery performance.

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