Continuum-Scale Battery Modeling for Space Applications

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1. Batteries for Aviation

Courtesy NASA

2. Batteries for Space

Courtesy NASA/JPL-Caltech

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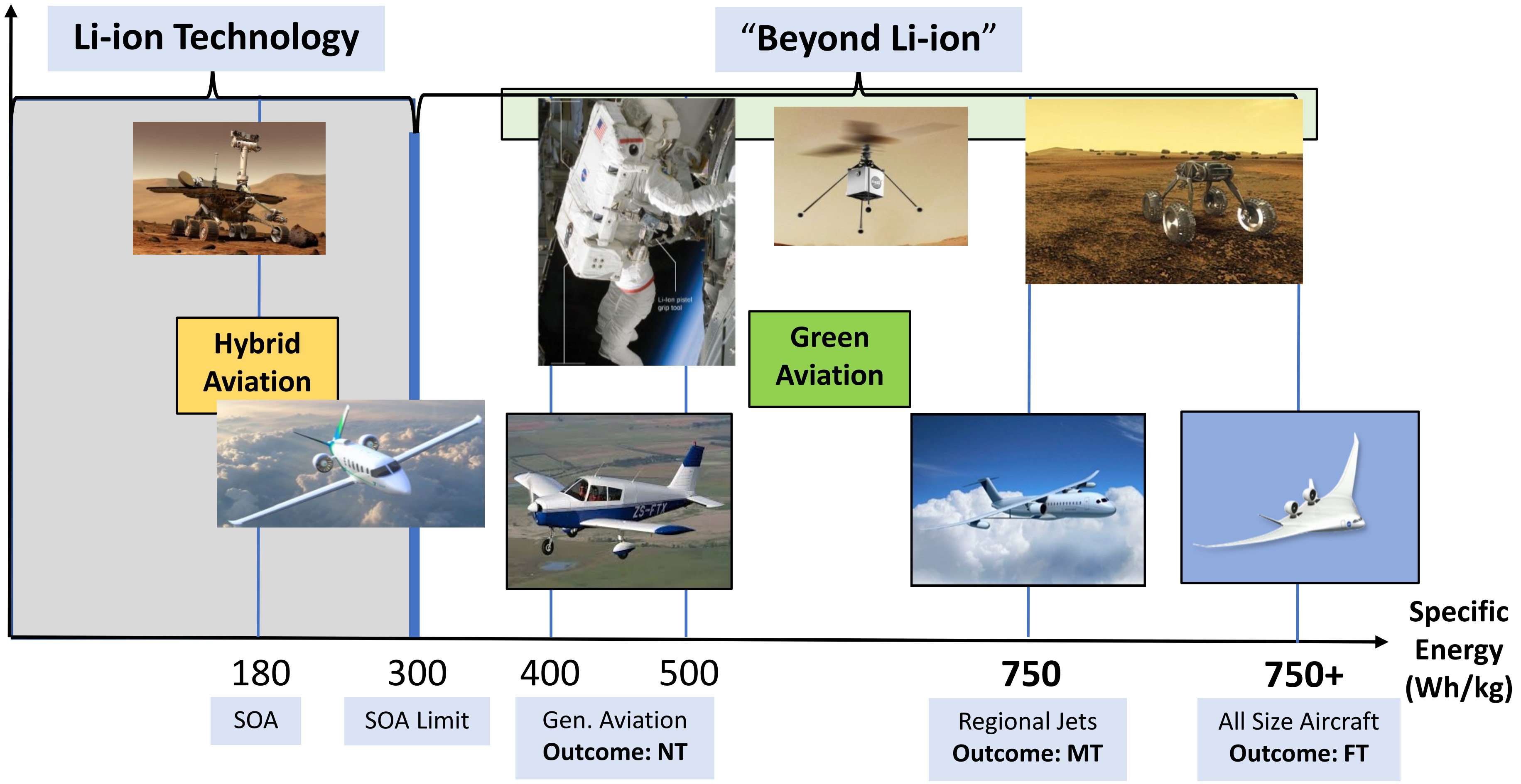
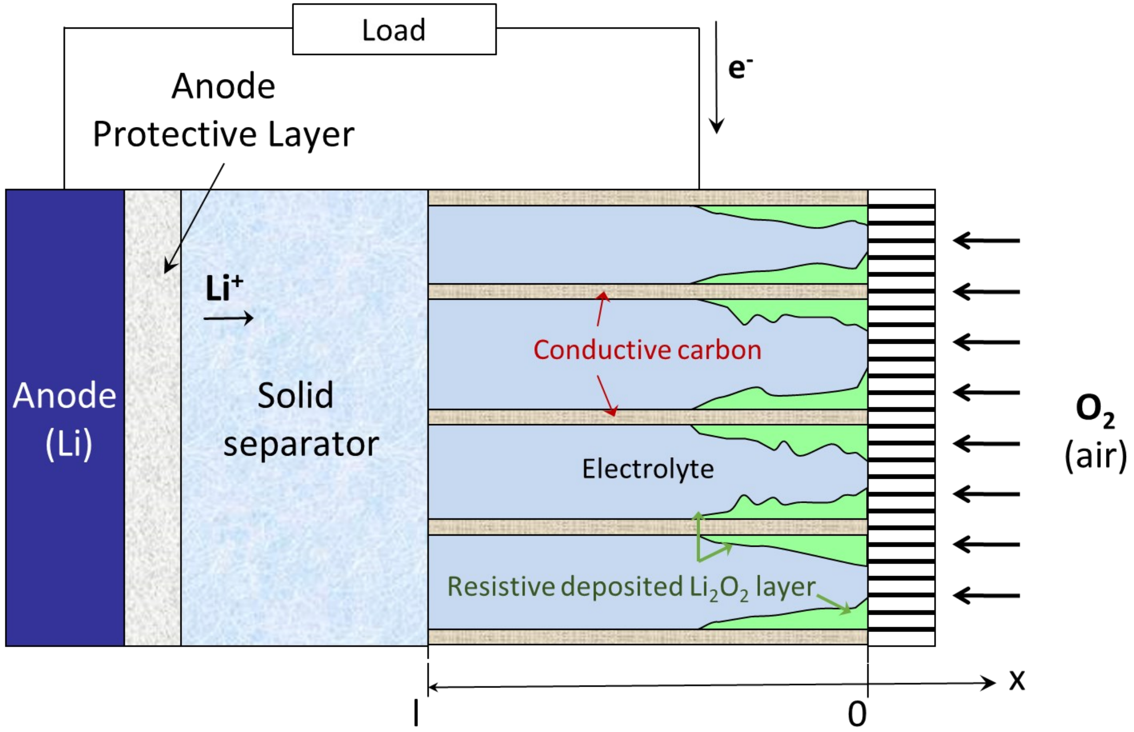
Why Li-O2?

Major requirement is: High Energy Density

Other requirements are **rechargeable**, **safety**, power, recharge time, cost, etc.



Continuum Battery Modeling



Discharge:	$Li \rightarrow Li^+ + e^-$	$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_{2(s)} \downarrow$
Charge:	$Li^+ + e^- \rightarrow Li \downarrow$	$Li_2O_{2(s)} \rightarrow 2Li^+ + 2e^- + O_2 \uparrow$

Mehta, M. & Andrei, P., 2014. *ECS Transactions*, 61(15), pp.39–55

Continuum Battery Modeling

Over-voltage, thermodynamic

$$\underbrace{\overbrace{\eta}^{\text{Over-voltage}} = \phi_{\mathrm{Li}}}_{\text{electrolyte}} - \underbrace{\phi}_{\text{electrode}} - \overbrace{E^0}^{\text{thermodynamic}} - \underbrace{V_{\mathrm{discharge}}}_{Li_2O_2}$$

electrolyte, electrode, Li_2O_2

-*I* (electron current)

$$\nabla \cdot \left(\sigma_{\mathrm{eff}} \nabla \phi\right) + R_C = a C_d \frac{\partial\left(\phi - \phi_{\mathrm{Li}}\right)}{\partial t}$$

-*I*$_{\mathrm{Li}}$ (electrolyte current)

$$\nabla \cdot \left(\kappa_{\mathrm{eff}} \nabla \phi_{\mathrm{Li}} + \kappa_{\mathrm{D}} \nabla \ln c_{\mathrm{Li}}\right) - R_C = a C_d \frac{\partial\left(\phi - \phi_{\mathrm{Li}}\right)}{\partial t}$$

$$V_{\mathrm{discharge}} = j_{\mathrm{dis}} \delta_{Li_2O_2} \rho_{\mathrm{Li_2O_2}} \exp\left(\alpha_{j_{dis}} \frac{-\delta_{Li_2O_2}}{10\mathrm{nm}}\right)$$

-*I*$_{\mathrm{O2}}$ (O_2 diffusion flux)

$$\frac{\partial\left(\epsilon c_{\mathrm{O_2}}\right)}{\partial t} = \nabla \cdot \left(D_{\mathrm{O_2,eff}} \nabla c_{\mathrm{O_2}}\right) - \frac{R_C}{nF}$$

ϵ (porosity change -from Li_2O_2 deposition)

$$\frac{\partial \epsilon}{\partial t} = -R_C \frac{M_{\mathrm{discharge}}}{nF\rho_{\mathrm{m,discharge}}}$$

-*I*$_{\mathrm{Li}}$ (electrolyte diffusion flux)

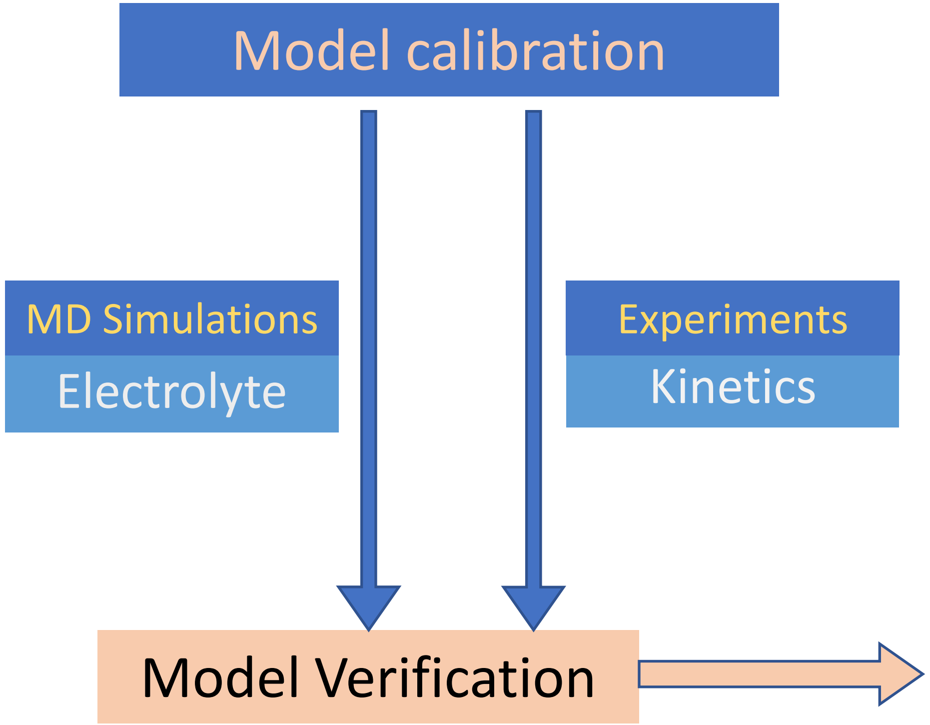
$$\frac{\partial\left(\epsilon c_{\mathrm{Li}}\right)}{\partial t} = \nabla \cdot \left(D_{\mathrm{Li,eff}} \nabla c_{\mathrm{Li}}\right) - \frac{1 - t^+}{F} R_C - \frac{\boldsymbol{I}_{\mathrm{Li}} \cdot \nabla t^+}{F}$$

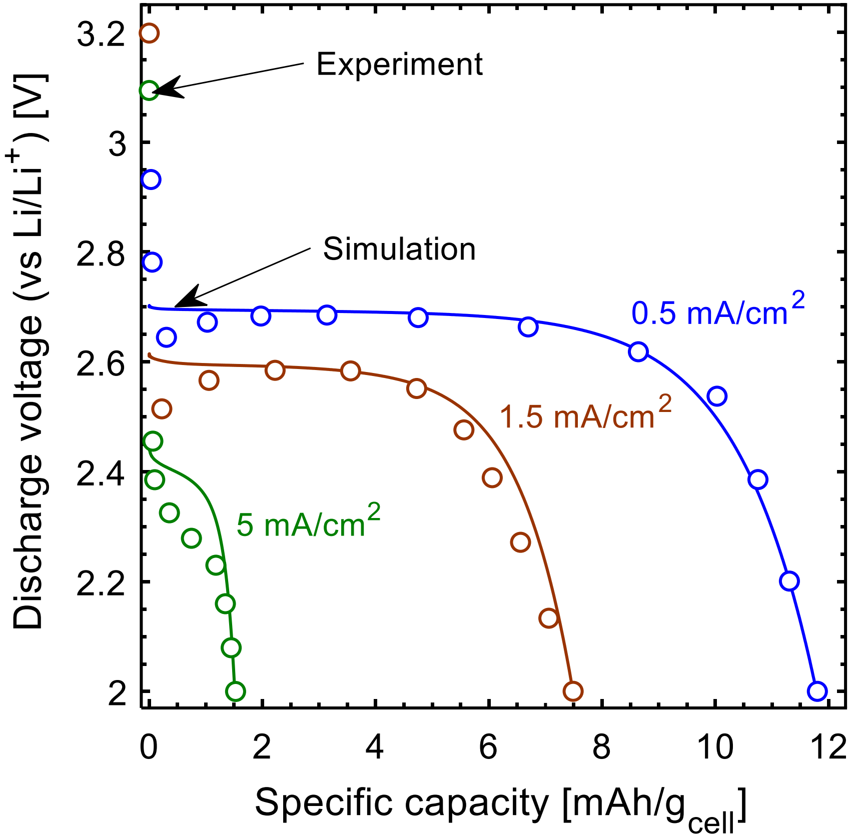
Reaction rate

$$R_C = nF c_{\mathrm{O_2}} k_0 a \left(e^{\frac{(1-\beta)n}{V_T}\eta} - e^{\frac{-n\beta}{V_T}\eta}\right)$$

Oxygen dissolvation $\quad c_{O_2}(L_c) = N_{O2} = k_f\left[p_{O2} - k_H c_{O2}(0)\right]$

Model Calibration and Simulation





Simulating cells for high power cell needs accurate electrolyte properties and current dependent kinetics

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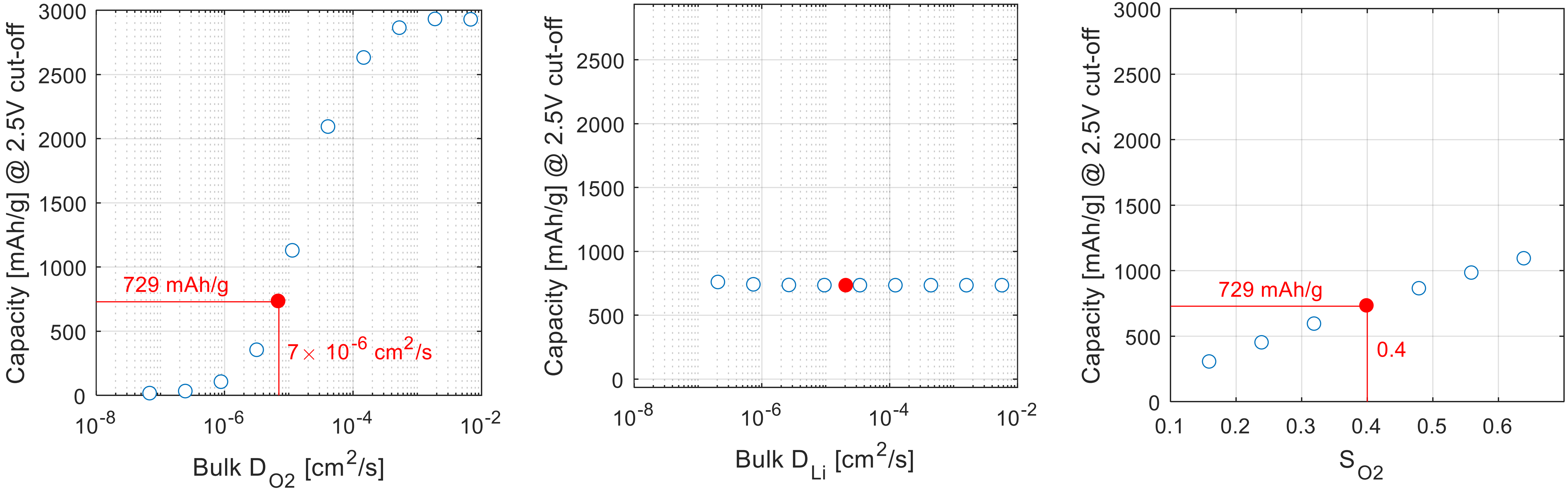
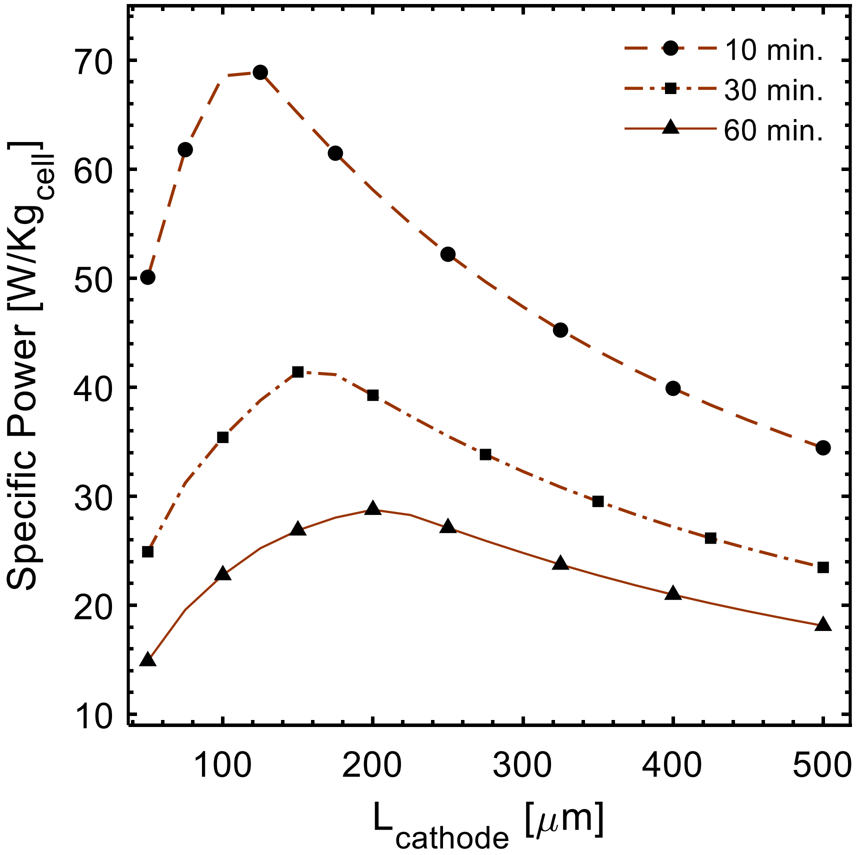
Sensitivity Studies

Identifying the salient electrolyte properties for high specific capacity



Mass transport of oxygen is the
most influential parameter

Influence of Cell Geometry



Oxygen diffusion length determines the optimal cathode thickness

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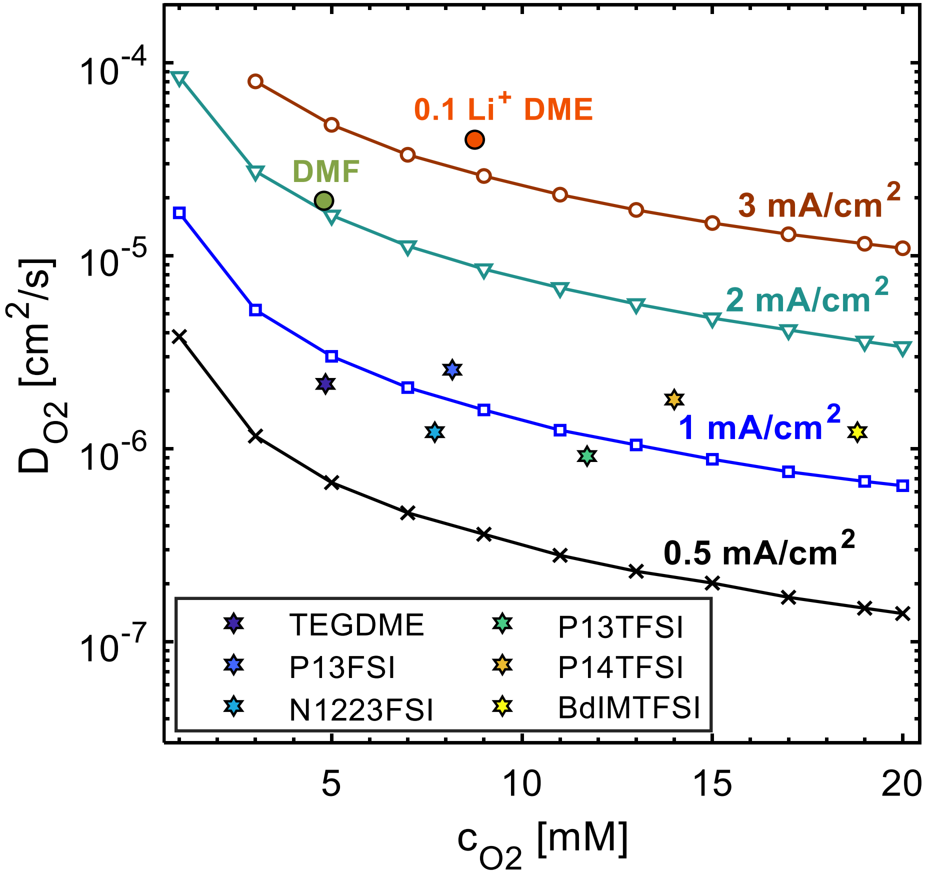
Influence of Cell Materials



Simulations can aid in selection of optimized electrolytes based on mission requirements

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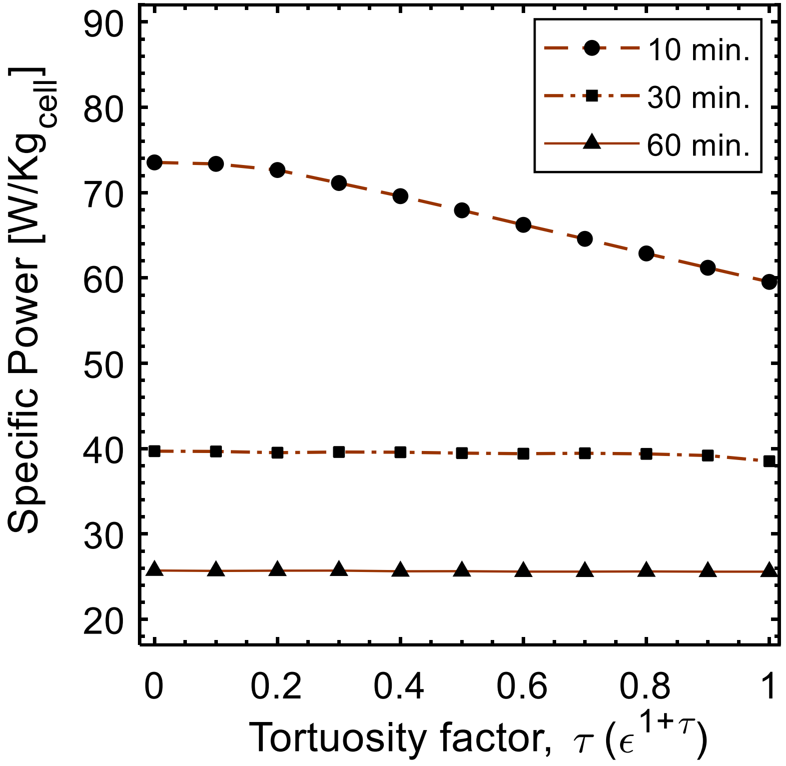
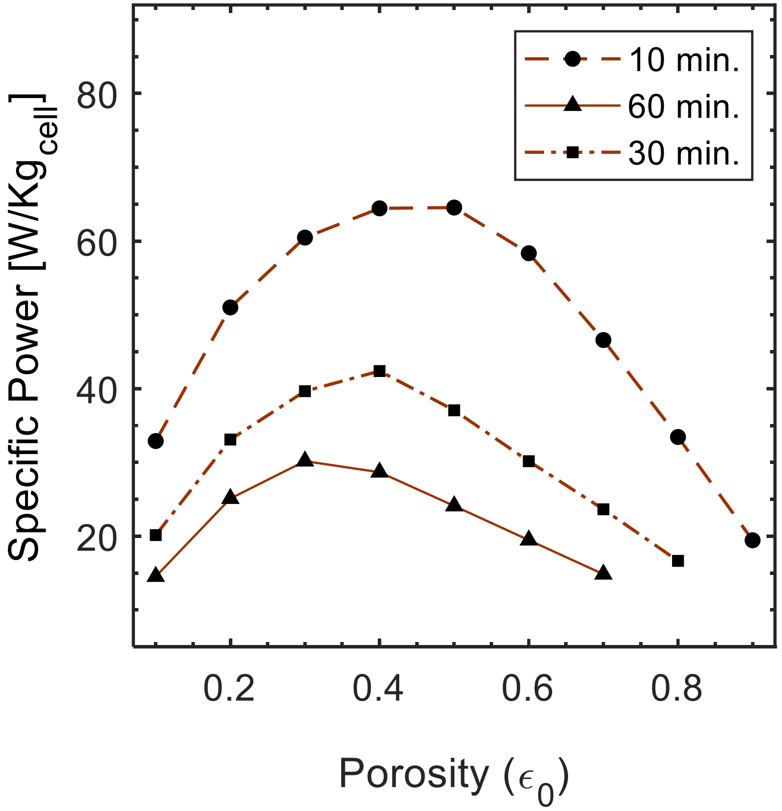
Influence of Cell Microstructure





Microstructure can be tuned to improve mass transport or to increase cell impedance

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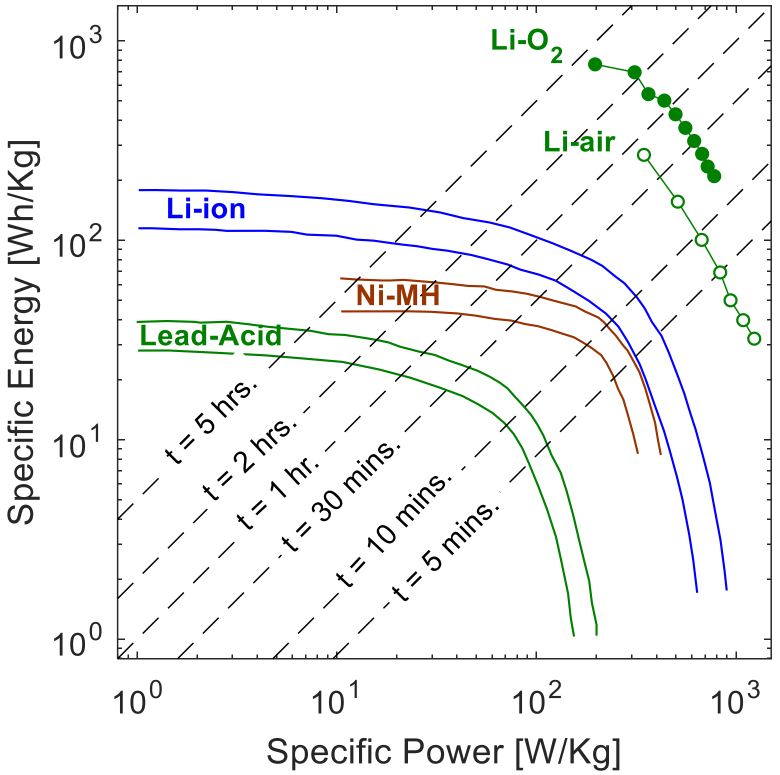
Multivariate Optimization



Multivariable optimization can suggest path to improvement for a given chemistry

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Thermal Modeling

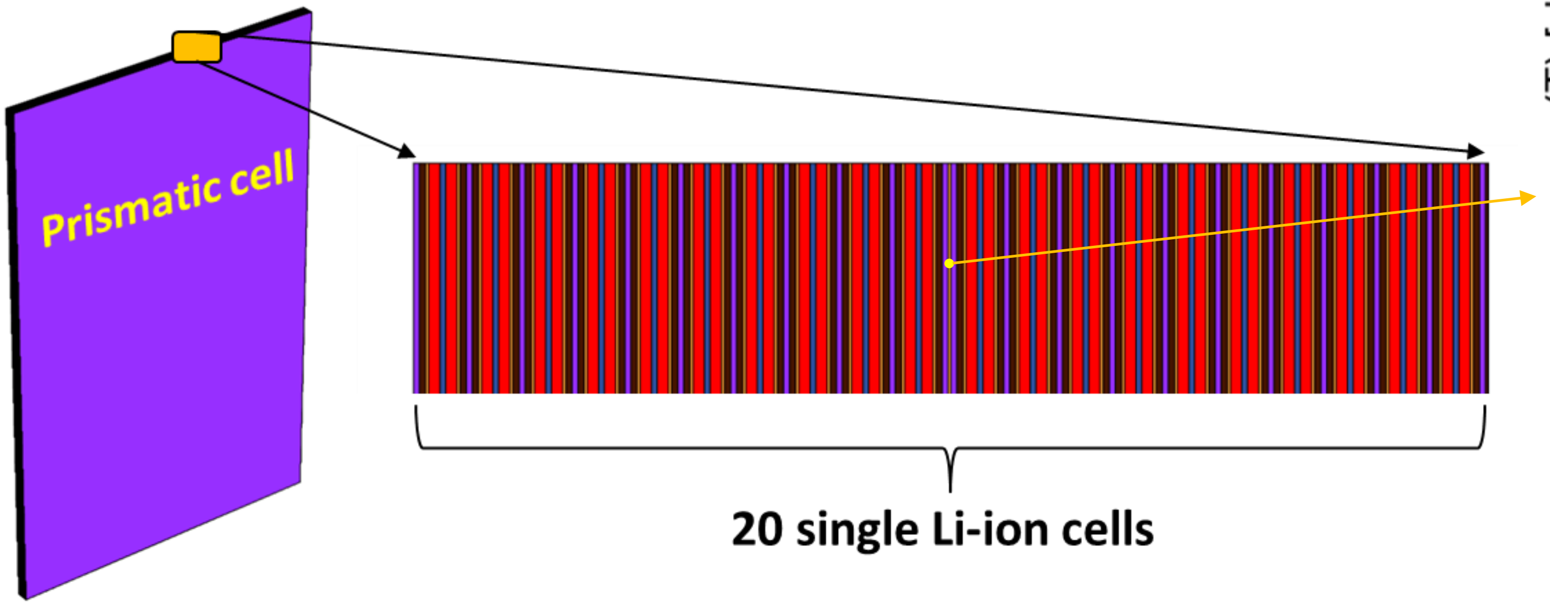
Chemical decomposition

Electrochemical

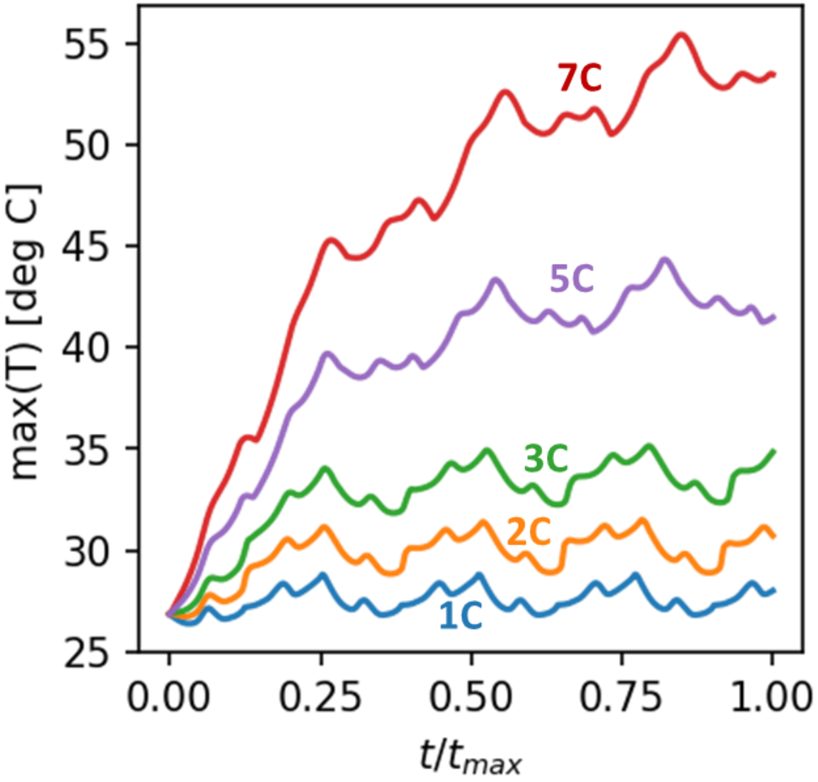
$$\rho C_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T + q_{rev} + q_{irr} + q_{ohm} + q_{chem}$$

Thermodynamic

Ohmic and short-circuit



Thermal profile without q_{chem}



Optimal microstructural designs can improve thermal performance

Reducing Model Complexity

Total cell voltage:

$$\boldsymbol{V_{\text{cell}}(t) = E_{eq} - \eta_a - \eta_c(t) - \eta_{\text{Li}_2\text{O}_2}(t) - \eta_{\text{other}}}$$

$$\eta_{\text{other}} = 0$$

Anodic overpotential:

$$\eta_a = 2V_T \sinh^{-1}\left(\frac{j_{dis}}{2j_{a0}}\right)$$

Cathodic overpotential:

$$\eta_c(t) = 2V_T \sinh^{-1}\left(\frac{\epsilon(t)}{a(t)}\frac{D_{O2}}{2\lambda(t)^2 k_c}\right) \quad \Bigg\| \quad \tanh\left(\frac{L_c}{\lambda}\right) = \frac{\lambda j_{dis}}{nFc_{O_2}\,\epsilon(t)D_{O2}}$$

Potential drop across Li_2O_2:

$$\eta_{\text{Li}_2\text{O}_2}(t) = R_{\text{Li}_2\text{O}_2}(t) j_{dis} \epsilon_{\text{Li}_2\text{O}_2}(t)$$

$$R_{\text{Li}_2\text{O}_2}(t) = \rho_{\text{Li}_2\text{O}_2} r_{p,0}\left[\left(\frac{\epsilon_{\text{Li}_2\text{O}_2}(\tau) + 1}{1 - \frac{2}{3}\epsilon_{\text{Li}_2\text{O}_2}(\tau)}\right)^{\frac{1}{3}} - 1\right]$$

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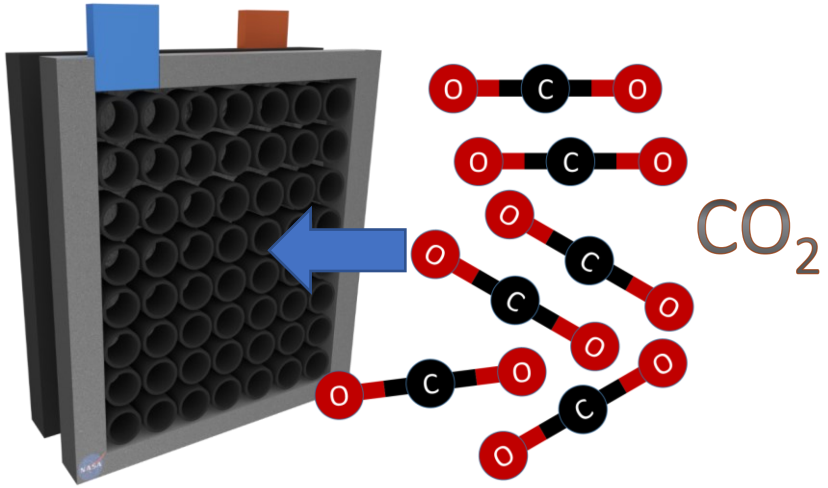
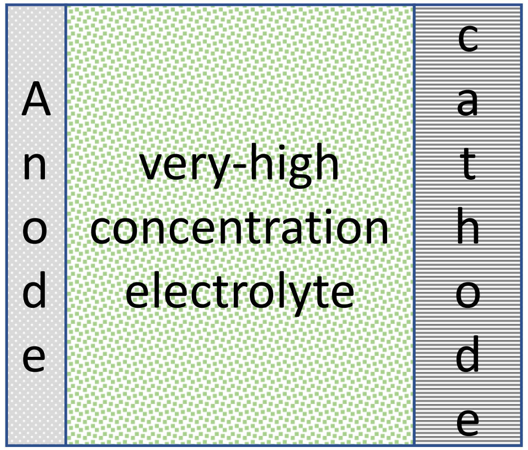
Developing Batteries for Space

Emerging Battery Technologies for Space

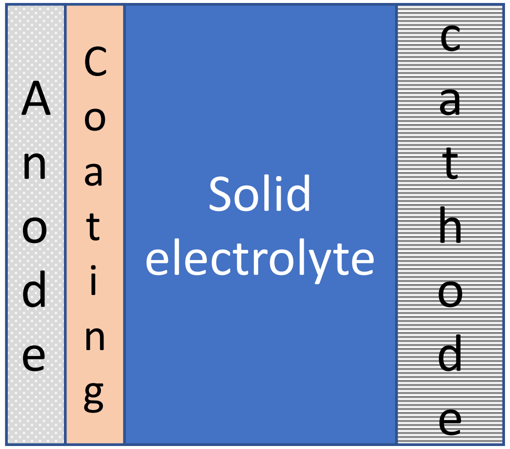
Li-CO_2 Battery:



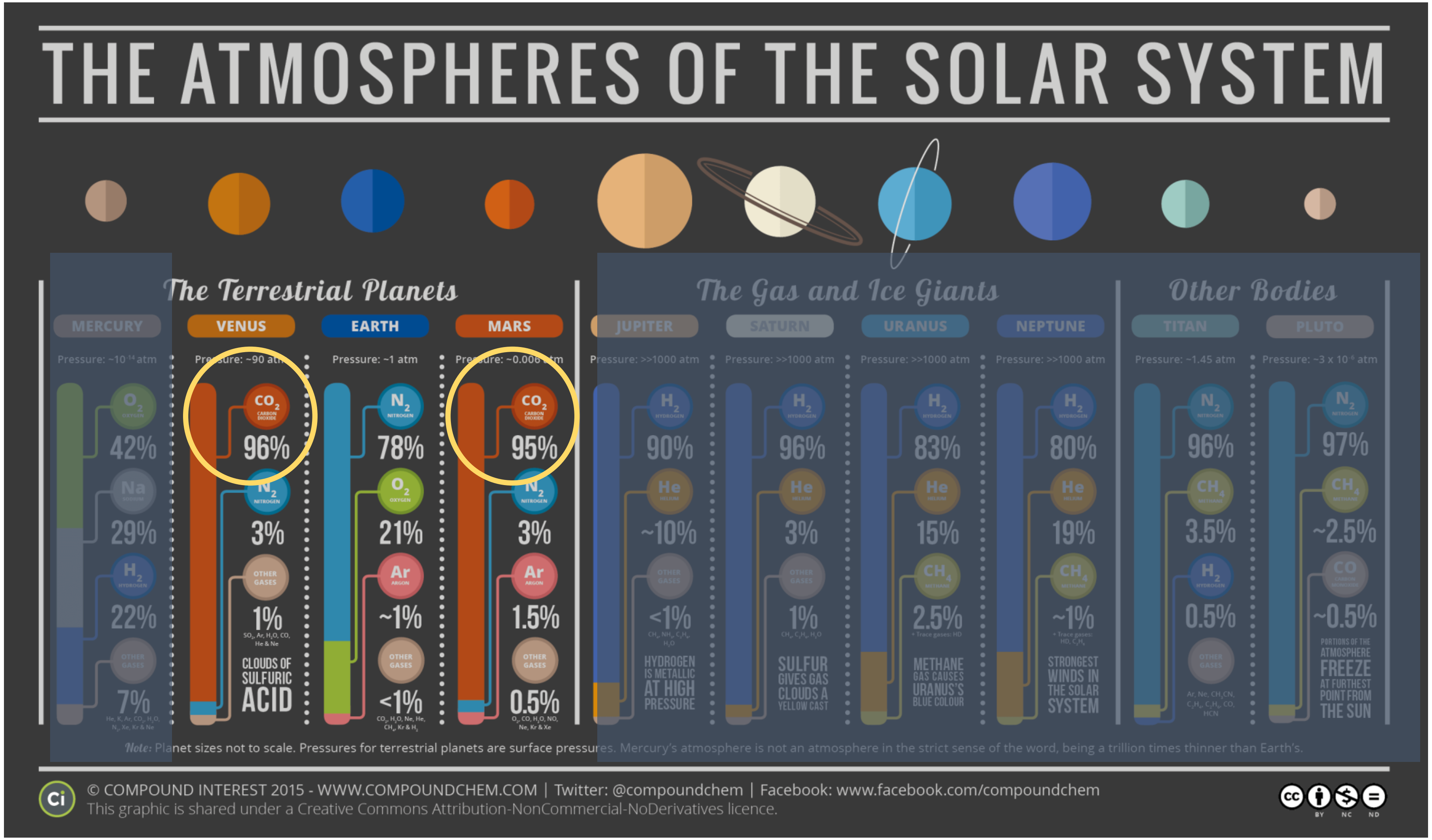


Solvent-in-Salt Battery

Solid-State Battery:



Batteries for Space (Motivation)



Utilizing Venus and Mars atmosphere

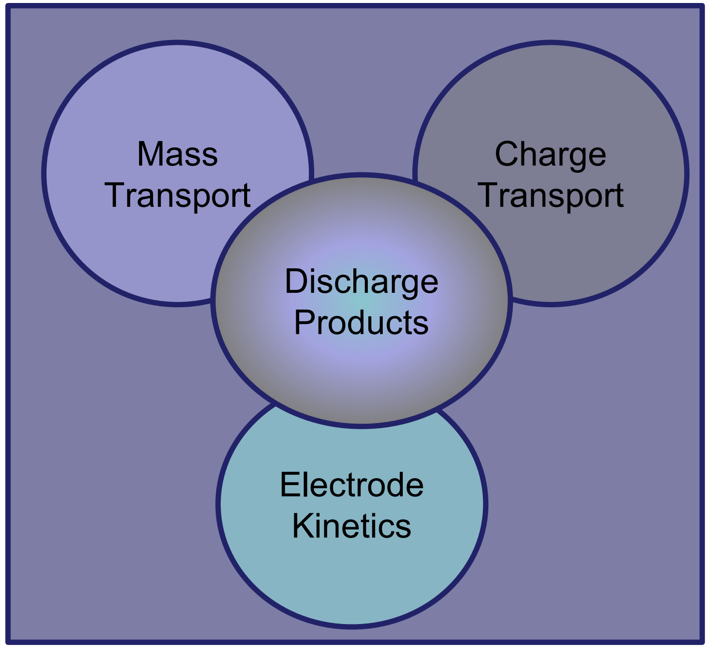
Li-CO_2 Battery:

$$4Li^+ + 3CO_2 + 4e^- \rightarrow 2Li_2CO_3 + C \; (E^0 = 2.8V)$$

$$4Li^+ + 2CO_2 + 4e^- \rightarrow 2Li_2O + C \; (E^0 = 1.89V)$$

$$2Li_2CO_3 \rightarrow 4Li^+ + 2CO_2 + O_2 + 4e^- \; (E^0 = 3.82V)$$

Modeling Framework identical to Li-O_2



- OCV similar to Li-O_2 chemistry
- The reaction pathway changes below 1.89V
- Lithium carbonate is more insulating than Li_2O_2
- The kinetics are facile than Li-O_2

Summary

1. Batteries for Aviation

- Physics-based models can guide cell and pack designs for aviation batteries
- Optimal cell design changes based on discharge time, discharge current density, and operating conditions
- UQ provides insights into the evolution in probability distributions (Bayesian framework)

2. Batteries for Space

- Physics-based models for emerging chemistries need to be developed
- Models on Li-O_2 can be ported to simulate Li-CO_2 batteries for Mars and Venus
- Highly resistive microstructure or molten salt batteries can improve performance at low temperatures