Physics-Based Modeling and Simulation of Emerging Battery Technologies for Aerospace

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Presentation date: 08/21/2019

1. Batteries for Aviation
2. Batteries for Space

Courtesy NASA/JPL-Caltech
Introduction to modeling and simulation


Aerospace Battery Requirements

Major requirement is: High Energy Density

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

- **Li Ion Technology**
- **“Beyond Li Ion”**

- **Hybrid Aviation**
- **Green Aviation**

Energy Density (Wh/kg):
- Li Ion Technology: 180 - 300
  - SOA Limit
  - Outcome: NT
- “Beyond Li Ion”:
  - Gen. Aviation: 400 - 500
    - Outcome: MT
  - Regional Jets: 750
    - Outcome: FT
  - All Size Aircraft: 750+

Green Aviation

Beyond Li Ion

Aerospace Battery Requirements

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Batteries for Aviation (exploring Li-O₂)

Discharge:
Li → Li⁺ + e⁻

Li⁺ + e⁻ → Li

2Li⁺ + O₂ + 2e⁻ → Li₂O₂(s) ↓

Charge:
Li₂O₂(s) → 2Li⁺ + 2e⁻ + O₂ ↑
Modeling a lithium-oxygen battery

$$V_{\text{discharge}} = j_{\text{dis}} \delta_{\text{Li}_2\text{O}_2} \rho_{\text{Li}_2\text{O}_2} \exp \left( \alpha_{j_{\text{dis}}} \frac{-\delta_{\text{Li}_2\text{O}_2}}{10\text{nm}} \right)$$

Reaction rate

$$R_C = n F c_{\text{O}_2} k_0 a \left( e^{\frac{(1-\phi)\eta}{V_T}} - e^{-\frac{\eta g}{V_T}} \right)$$

Oxygen dissolution

$$c_{\text{O}_2}(L_c) = N_0 \text{O}_2 = k_f [p_{\text{O}_2} - k_H c_{\text{O}_2}(0)]$$

Over-voltage thermodynamic

$$\eta = \phi_{\text{Li}} - \phi - E^0 - V_{\text{discharge}}$$

-\(I\) (electron current)

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

-\(I_{\text{Li}}\) (electrolyte current)

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

-\(I_{\text{Li}}\) (electrolyte diffusion flux)

$$\frac{\partial (\epsilon c_{\text{Li}})}{\partial t} = \nabla \cdot (D_{\text{Li},\text{eff}} \nabla c_{\text{Li}}) - \frac{1 - t^+}{F} R_C - \frac{I_{\text{Li}} \cdot \nabla t^+}{F}$$

-\(I_{\text{O}_2}\) (\text{O}_2 diffusion flux)

$$\frac{\partial (\epsilon c_{\text{O}_2})}{\partial t} = \nabla \cdot (D_{\text{O}_2,\text{eff}} \nabla c_{\text{O}_2}) - \frac{R_C}{n F}$$

\(\epsilon\) (porosity change - from \text{Li}_2\text{O}_2 deposition)

$$\frac{\partial \epsilon}{\partial t} = -R_C \frac{M_{\text{discharge}}}{n F \rho_{\text{m, discharge}}}$$
Model calibration for simulating high current

Model calibration

MD Simulations
Electrolyte

Experiments
Kinetics

Model Verification

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

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Electrochemical mass distribution

Cell mass distribution

- Cathode: 36%
- Separator: 11%
- Anode: 53%

Mass distribution separated into solid and liquid phases

- Carbon: 1.8%
- Steel Mesh: 23.3%
- Binder: 11.2%
- 1M LiTFSI in DME: 50.6%
- Glass fiber: 3.6%
- Li Foil: 9.6%

All three components of Li-O₂ cell can be optimized to achieve high specific power

Mehta et al. in preparation, 2019
Polarization test: The effect on power

Operating at “high” current densities can lead to 25% power loss during 1hr discharge

Mehta et. al. in preparation, 2019
Polarization test: Oxygen Partial Pressure

Increasing oxygen partial pressure improves power as well as non-electrochemical mass.

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Influence of separator on performance

Separator does not contribute to battery performance at high current densities

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Effect of cathode thickness on performance

Optimal cathode thickness depends on operation conditions

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Influence of microstructure on performance

Optimal values for porosity, particle size, and tortuosity depend on discharge current density and discharge time

$\varepsilon_{\text{eff}} = \varepsilon^{1+\tau}$

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Influence of electrolyte properties

Diffusion requirements can be relaxed based by changing operating partial pressure and choosing lower salt concentration
Simulation-based optimization (30 min.)

- 1. 0.3M LiTFSI P$_{13}$FSI
- 2. 0.3M LiTFSI P$_{13}$TFSI
- 3. 0.1M LiTFSI TEGDME
- 4. 0.3M LiTFSI P$_{14}$TFSI
- 5. 1M LiTFSI DME
- 6. 0.1 TEAP DMF

The oxygen diffusion length (under steady-state) determines cathode thickness and cathode mass.

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Thin and optimized cathodes, and better oxygen transport electrolytes can provide Li-O$_2$ for high-specific power cells
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Mehta *et. al.* in preparation, 2019
Pack level simulation (better optimization)

Active cathode design shows performance improvement but at a power cost of 5-30% for running external systems

Mehta et. al. in preparation, 2019
Pack level simulation (better optimization)

- Unoptimized cathode
- Unused cathode

Usable cathode

Usable area improves

Better cathode utilization improves discharge time at high current 30x

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Batteries for Space (Motivation)

MARS FACTS / ATMOSPHERE

78% NITROGEN
21% OXYGEN
1% OTHER

96% CARBON DIOXIDE
<2% ARGON
<2% NITROGEN
<1% OTHER

mars.nasa.gov

#JOURNEYTOMARS

Courtesy NASA/JPL-Caltech
Requirements for “Space” Batteries

Operating Temperature: -170°C – 200°C

Specific Energy (Reversible): > 500 Wh/Kg

Extremely Low Self-discharge (0-volt)

Battery System needs to be low mass and volume

Current systems need temperature regulation for optimal performance

Batteries need to be Safe and Reliable
Emerging Battery Technologies for Space

Li-CO₂ Battery:

Solvent-in-Salt Battery

Solid-State Battery:

Anode

Cathode

very-high concentration electrolyte

Solid coating electrolyte
Utilizing **Venus** and **Mars** atmosphere

**Li-CO₂ Battery:**

\[ 4 \text{Li}^+ + 3 \text{CO}_2 + 4 \text{e}^- \rightarrow 2 \text{Li}_2\text{CO}_3 + \text{C} \quad (E^\circ = 2.8 \text{ V}) \]
\[ 4 \text{Li}^+ + \text{CO}_2 + 4 \text{e}^- \rightarrow 2 \text{Li}_2\text{O} + \text{C} \quad (E^\circ = 1.89 \text{ V}) \]

Modeling Framework identical to Li-O₂

- OCV similar to Li-O₂ chemistry
- The reaction pathway changes below 1.89V
- Lithium Carbonate is more insulating than Li₂O₂
- The kinetics are facile than Li-O₂
Modeling similarities with Li-O$_2$ chemistry

Morphology of Discharge product

Particle deposition

Film deposition

Polymer Electrolytes (CO$_2$)

Liquid Electrolytes (CO$_2$)

Low current density (O$_2$)

High current density (O$_2$)


Electrolyte Transport

Different Solubility: 125mM (CO$_2$) > 2mM (O$_2$)

Similar Diffusivity: $10^{-5}$ cm$^2$/s (CO$_2$) $\approx 2 \times 10^{-5}$ cm$^2$/s

Summary

1. **Batteries for Aviation**
   - Physics-based models can guide cell and pack designs for aviation batteries
   - Both current density and cell mass needs to be optimized for high specific power
   - Optimal cell design changes based on discharge time, discharge current density, and operating conditions

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
Acknowledgements

**NASA Glenn Research Center**
William Bennett
Donald Dornbusch
James Wu
Vadim Lvovich
Rocco Viggiano

**NASA Ames Research Center**
Justin Haskins
Balachandran Gadaguntla Radhakrishnan
Charles Bauschlicher
John Lawson
Lauren Abbott

**UC Berkeley**
Kristian Knudsen
Pedro Arrechea
Brian McCloskey

"We’ll continue work to make flight even safer … to make it quieter … and through a healthy investment in aeronautics, we’ll reach new heights in pursuit of making it cleaner and greener."
- NASA Administrator Charles Bolden

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**Funding**

NASA Aeronautics Research Mission Directorate (ARMD) Convergent Aeronautics Solutions (CAS) Project, LiON (Lithium-Oxygen batteries for NASA) sub-project.