Modeling Secondary Zinc-Air Batteries with Advanced Aqueous Electrolytes

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Motivation
- Primary zinc-air battery commercially available
- High specific energy, low cost, high operational safety
- Hearing aid battery, e.g., VARTA PowerOne PR44
- Development of rechargeable zinc-air battery
- Zinc dendrites, electrolyte carbonation, oxygen redox chemistry, anode passivation
- Stationary energy storage
- Electrolytes: aqueous alkaline, aqueous near-neutral

Model: Alkaline Electrolyte
- 1D continuum model of alkaline zinc-air battery
- Chemical reactions:
  - \( \text{Zn} + 4\text{OH}^- = \text{Zn(OH)}_4^{2-} + 2\text{e}^- \)
  - \( 2\text{Zn(OH)}_2^{2-} = \text{Zn(OH)}_4^{2-} + \text{H}_2\text{O} \)
  - \( \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- = 2\text{OH}^- \)
- Consistent transport: diffusion, migration, and convection

Simulations: Alkaline Electrolyte
- Galvanostatic operation of prismatic zinc-air cell
- Thick anode (10 mm), large energy capacity
- Long reactant transport path and pore blockage with ZnO
- Cell performance limited by mass transport
- ZnO precipitates first at the separator
- Non-reactive zone creates barrier for KOH transport
- Zinc electrode shape change during cycling

Model: Neutral Electrolyte
- \( \text{NH}_4\text{Cl} + \text{ZnCl}_2 \) electrolyte
- No carbonation effects, improved cycling stability
- Zinc forms complexes with chlorine, ammonia, and hydroxide
- Dominant aqueous species shifts with pH and composition
- System modelled with quasi-particles of conserved quantities:

Simulations: Neutral Electrolyte
- Galvanostatic discharge at 5 mA \cdot cm\textsuperscript{-2}
- Initial potential drop due to reduction of \( \text{MnO}_2 \) catalyst
- Thick separator (30 mm)
- Long transport path causes gradient in pH
- Dominant aqueous species shifts across the cell

Conclusions
- Zinc-air: promising technology with long history
- Challenges:
  - Carbonation of alkaline electrolyte
  - Efficient and reversible oxygen reaction
  - Stable and reversible zinc deposition
  - Efficient electrolyte transport
- Development:
  - Neutral chloride aqueous electrolyte
  - Cell architecture optimization

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