Modeling and Simulation of Zinc-Air Batteries with Aqueous Electrolytes

Simon Clark, Birger Horstmann, Arnulf Latz[1,2,3]

Helmholtz Institute Ulm
Electrochemical Energy Storage

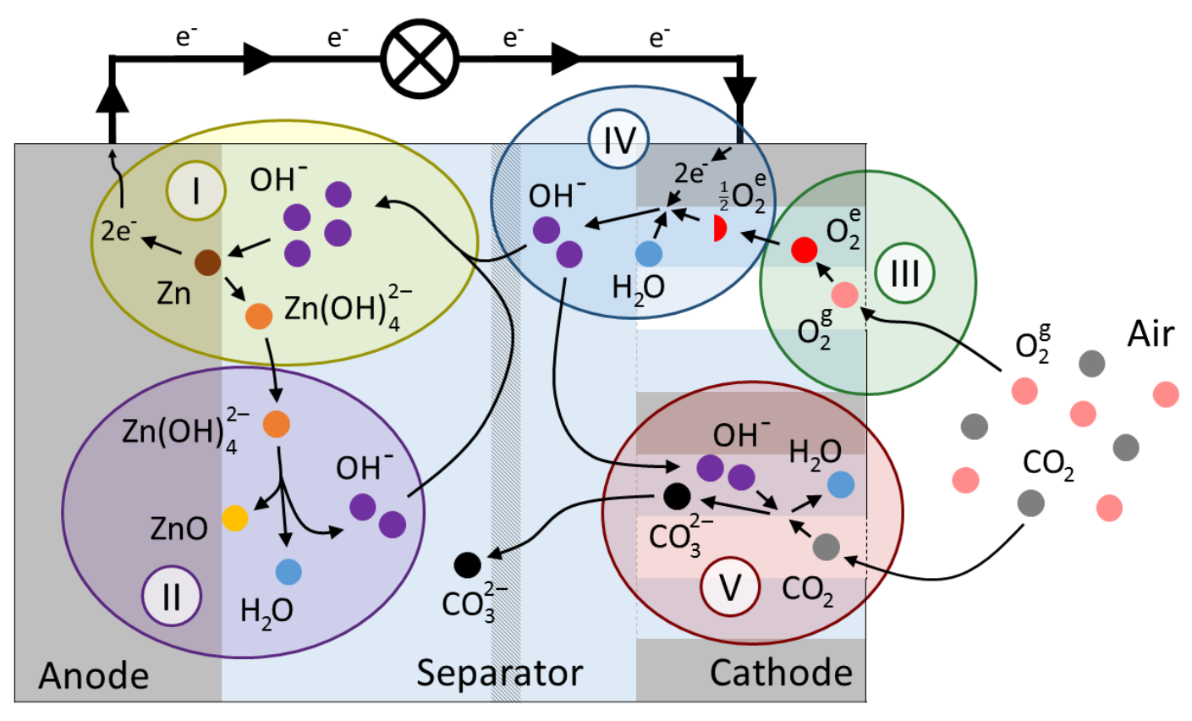
[1] German Aerospace Center, Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany.
[2] Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstraße 12, 89081 Ulm, Germany.
[3] University of Ulm, Institute of Electrochemistry, Albert-Einstein-Allee 47, 89081 Ulm, Germany.

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



I. $Zn + OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$
II. $Zn(OH)_4^{2-} \rightleftharpoons ZnO + 2OH^- + H_2O$
III. $O_2^g \rightleftharpoons O_2^e$
IV. $\frac{1}{2}O_2^e + H_2O + 2e^- \rightleftharpoons 2OH^-$

  - Consistent transport: diffusion, migration, and convection

$$\partial_t\left(\epsilon_e^\beta c_i\right) = \vec{\nabla}\cdot\left(\epsilon_e^\beta D_i \vec{\nabla} c_i\right) + \vec{\nabla}\cdot\left(\epsilon_e^\beta \frac{t_i}{z_i F}\vec{j}\right) + \vec{\nabla}\cdot\left(\epsilon_e^\beta c_i \vec{v}_e\right) + S_i$$

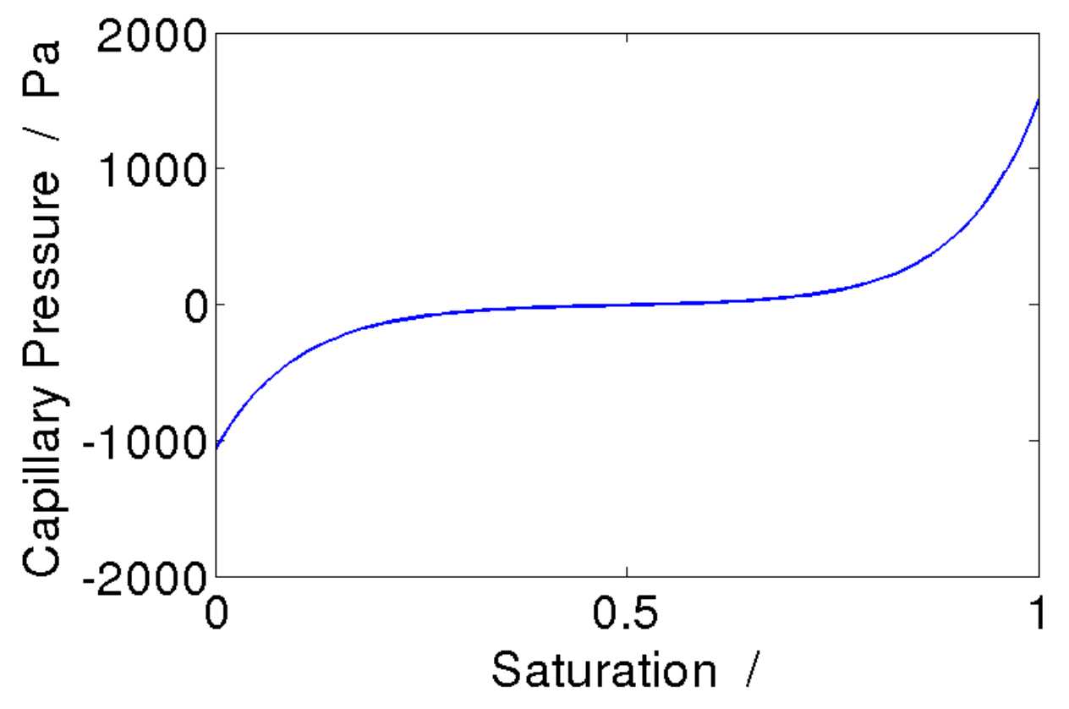
- Coexisting gas, liquid, and solid phases
  - Cathode: hydrophobic gas diffusion electrode (GDE)
  - Anode: spherical zinc particles, porous ZnO shells
  - Electrolyte: aqueous KOH solution

Gas Diffusion Electrode

- Solid, liquid, and gas phases coexist and interact in the GDE
  - Saturation of pores with electrolyte modeled via a capillary pressure approach

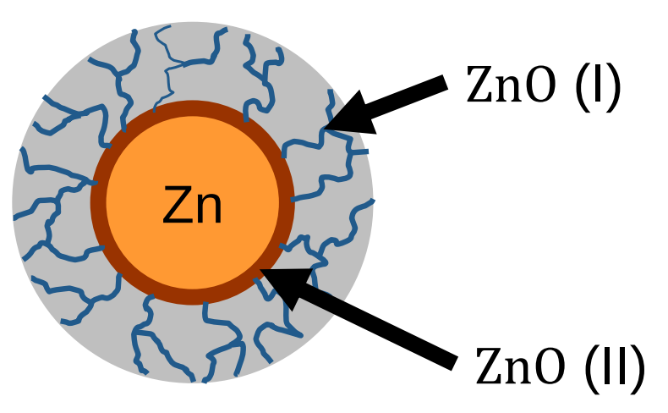
$$\tilde{s} = \frac{\varepsilon_{\text{liq}}}{\varepsilon_{\text{liq}} + \varepsilon_{\text{gas}}}$$

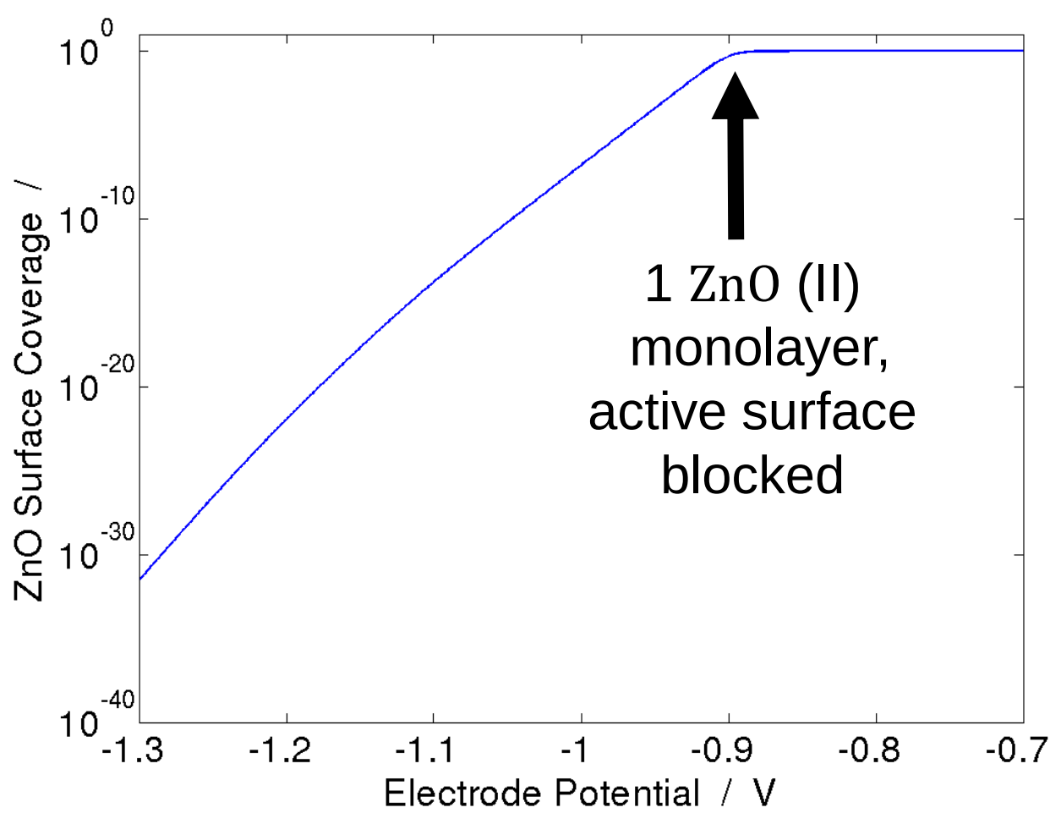
$$p_{\text{cap}} = p_{\text{liq}} - p_{\text{gas}} = \sigma J(\tilde{s})\sqrt{\frac{\varepsilon_0}{B}}$$



Zinc Anode Passivation

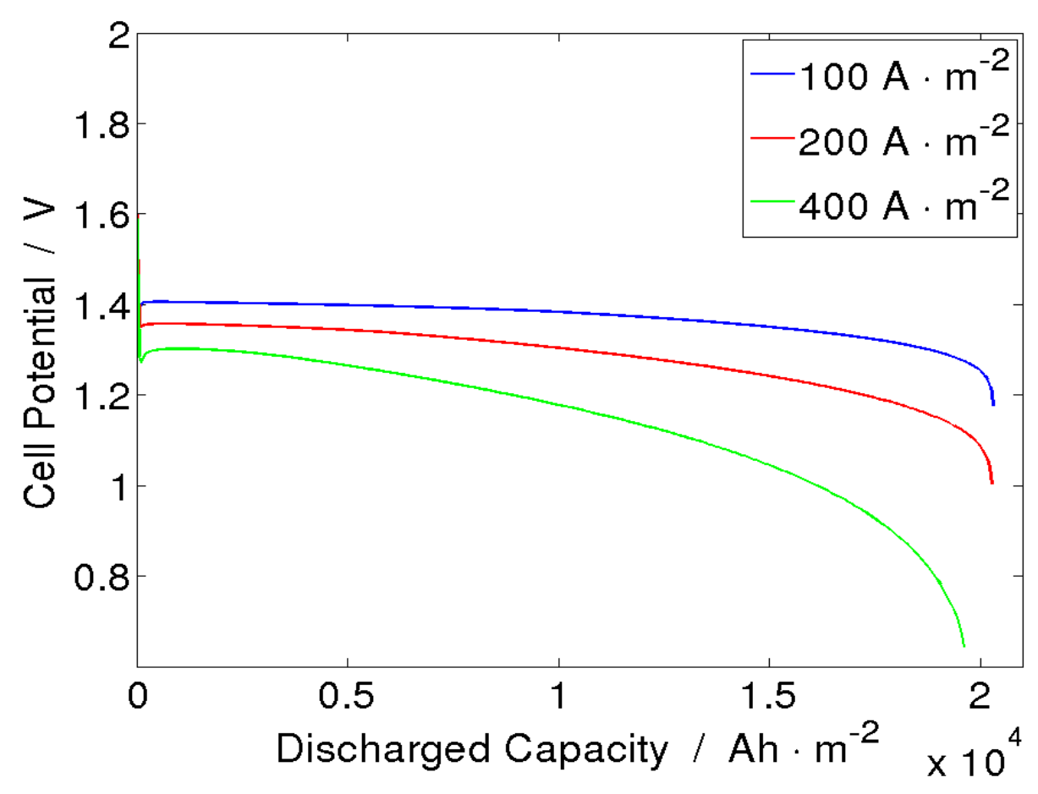
- Zinc anode passivation occurs as ZnO precipitates near the electrode surface
- ZnO may precipitate in two forms:
  - ZnO (I): porous shell
    - Barrier to reactant transport
    - Reversible precipitation
  - ZnO (II): surface absorption
    - Blocks active sites
    - Permanently shuts down electrode

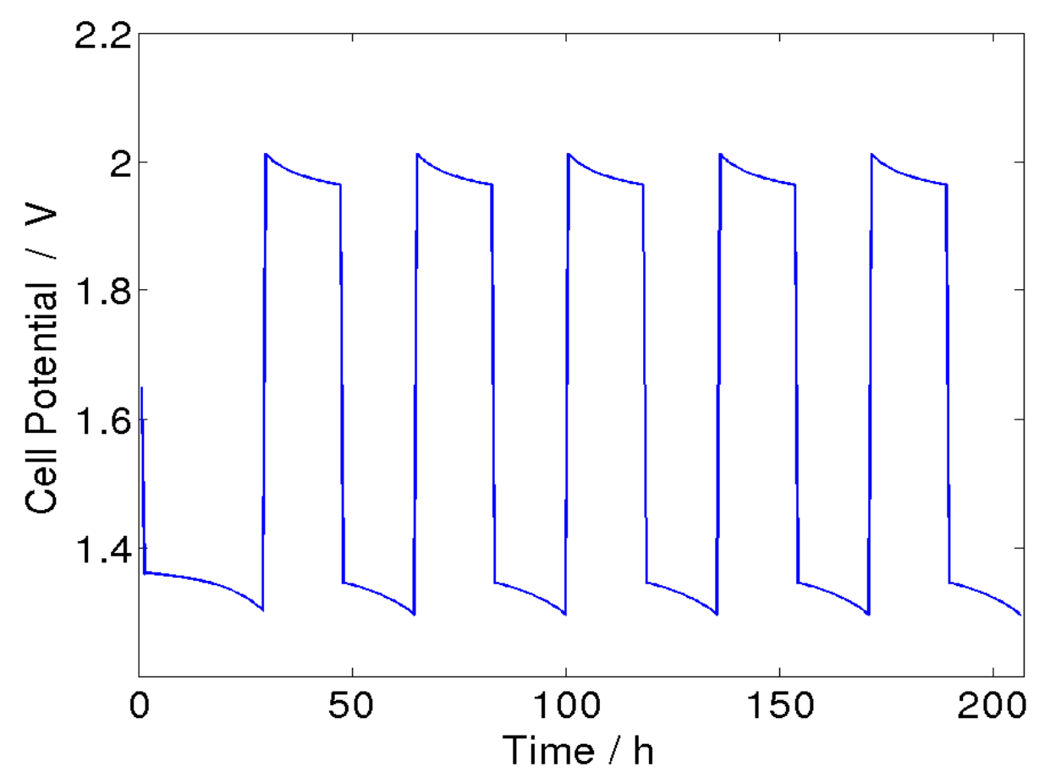




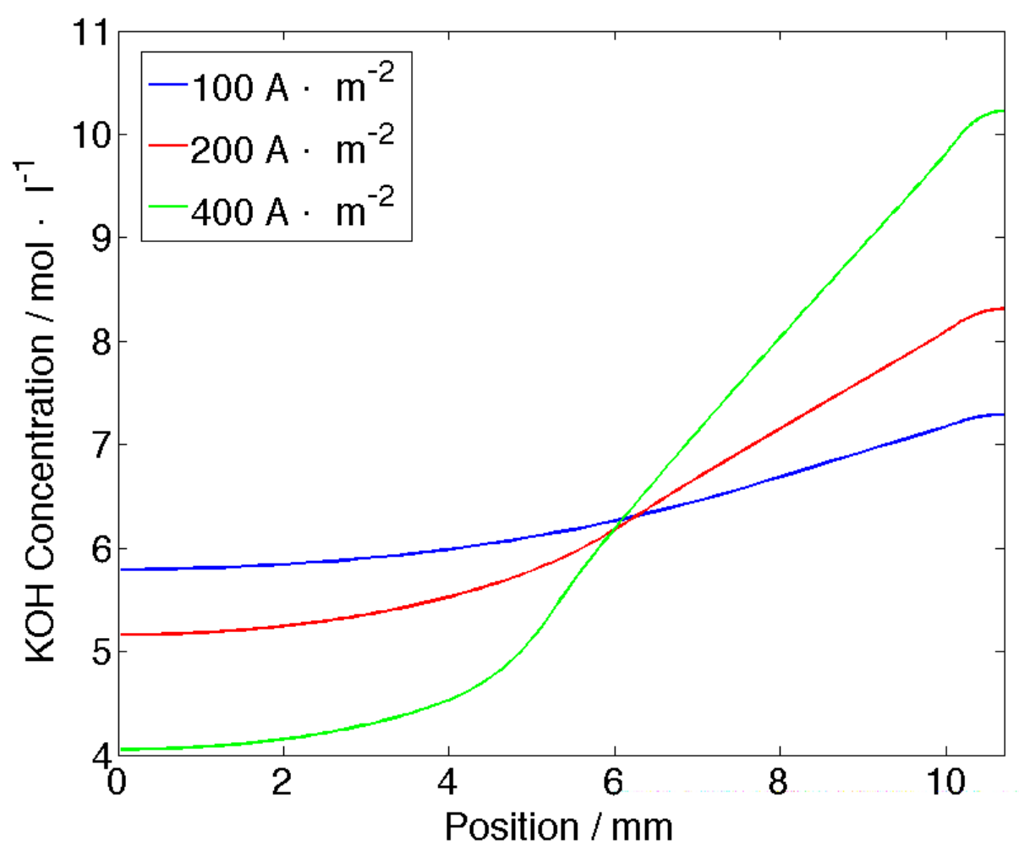
Simulations: Cell Performance

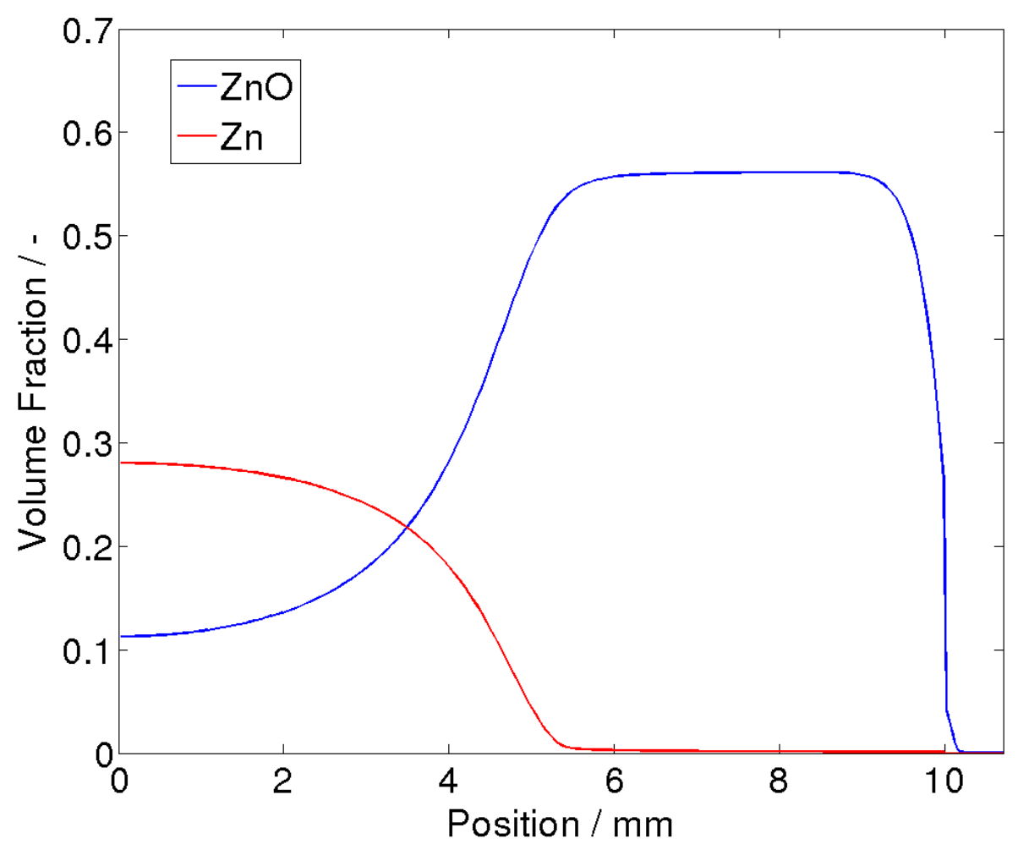
- Galvanostatic operation of prismatic zinc-air cells
  - Thick anode (10 mm), large energy capacity
  - Long reactant transport path and pore blockage with ZnO
    - Cell performance limited by mass transport





- ZnO precipitates first at the separator
  - Non-reactive zone creates barrier for KOH transport
  - Becomes performance-limiting at high current densities



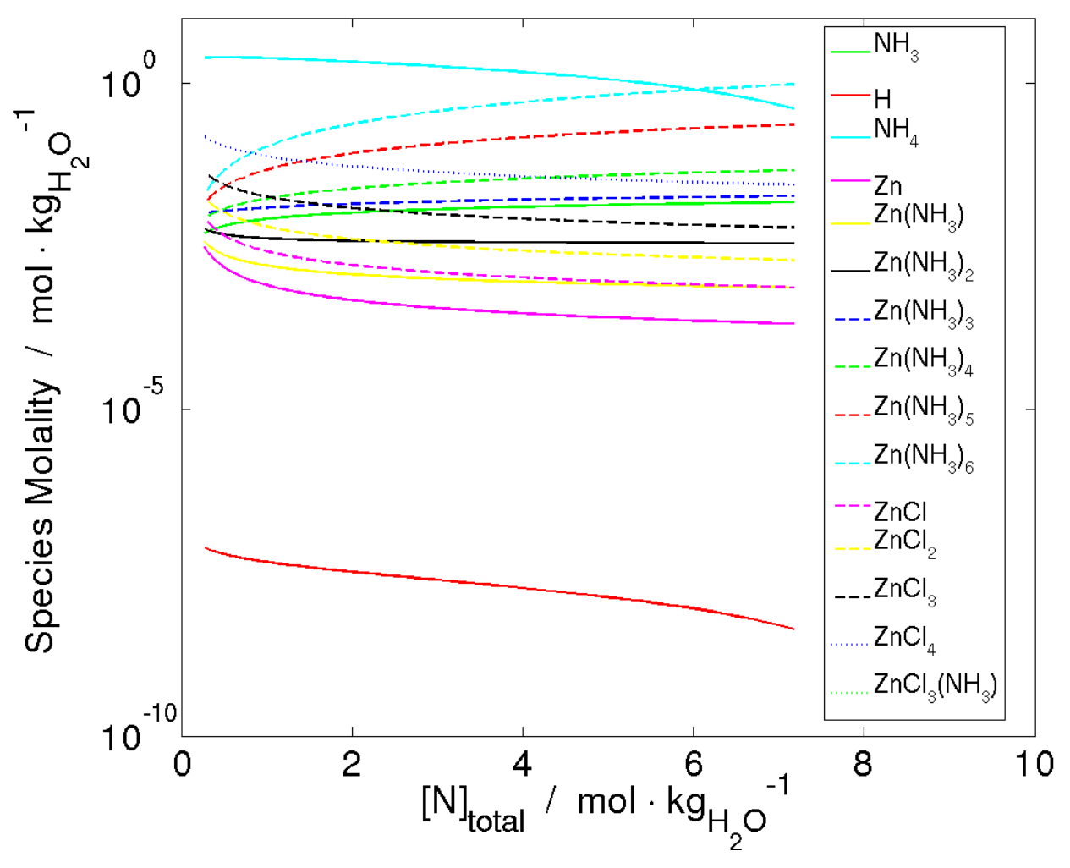


Outlook: Near-Neutral Electrolyte

- $NH_4Cl + ZnCl_2$ electrolyte eliminates carbonation effects and improves cycling stability
  - Chemical reactions

I. $Zn + 6NH_3 \rightleftharpoons [Zn(NH_3)_6]^{2+} + 2e^-$
II. $[Zn(NH_3)_6]^{2+} + H_2O \rightleftharpoons ZnO + 6NH_3 + 2H^+$
III. $O_2^g \rightleftharpoons O_2^e$
IV. $\frac{1}{2}O_2^e + 2H^+ + 2e^- \rightleftharpoons H_2O$
V. $NH_4^+ \rightleftharpoons NH_3 + H^+$
VI. $H^+ + OH^- \rightleftharpoons H_2O$

- Electrolyte composition in thermodynamic equilibrium
  - Ammonium buffer solution stabilizes pH
  - Variations in pH affect reaction kinetics
  - $Zn(NH_3)_6^{2+}$ is the dominant zinc-ammine complex



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
  - Near-neutral chloride aqueous electrolyte
  - Cell architecture optimization

Federal Ministry of Education and Research

simon.clark@dlr.de

KIT
ulm university universität uulm
ZSW
DLR Deutsches Zentrum für Luft- und Raumfahrt
German Aerospace Center