

Modeling and Simulation of Zinc-Air Batteries with Aqueous Electrolytes

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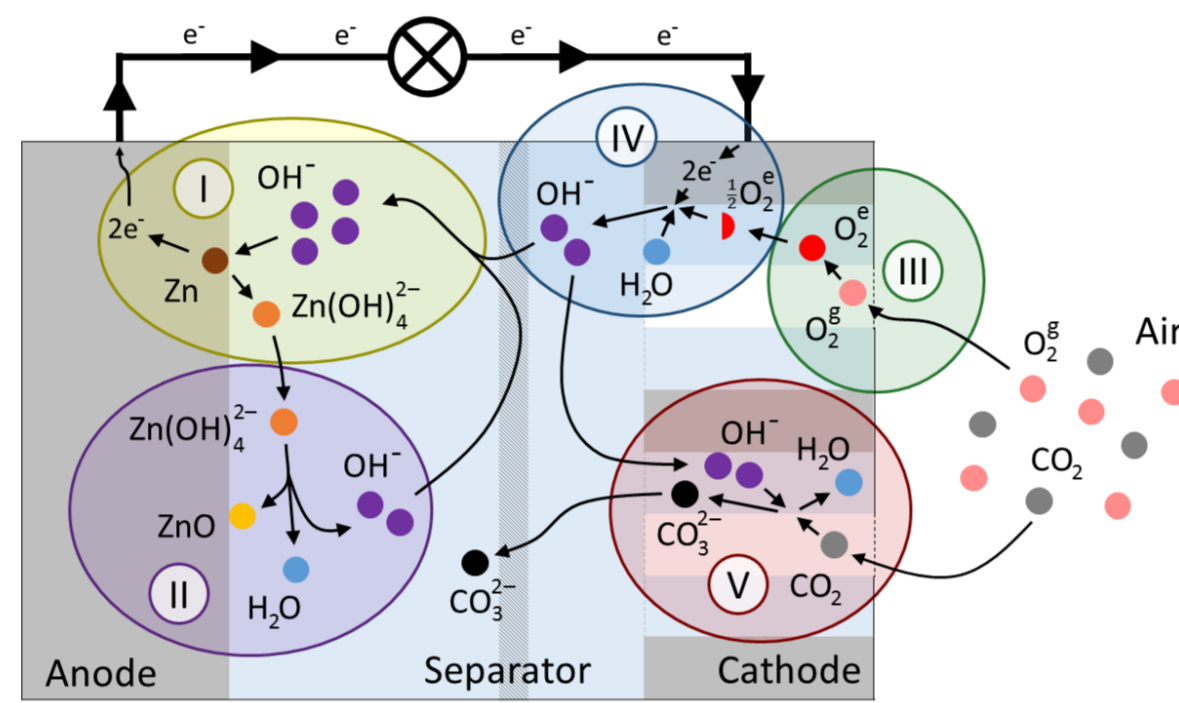
Motivation

- 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

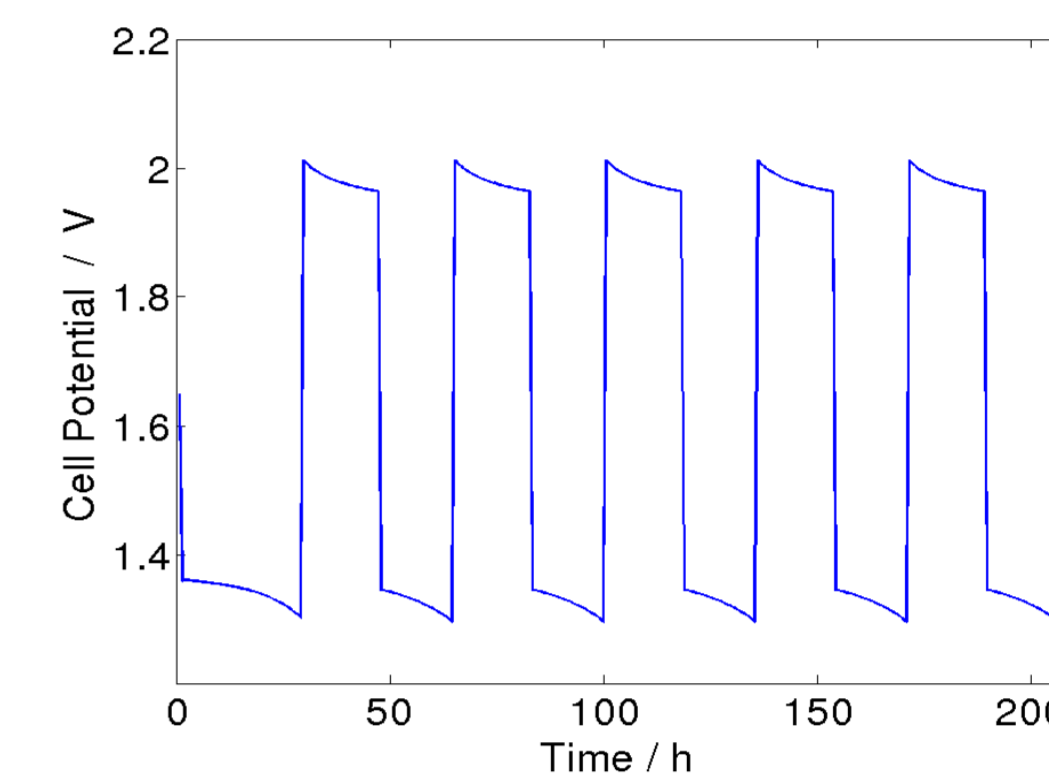
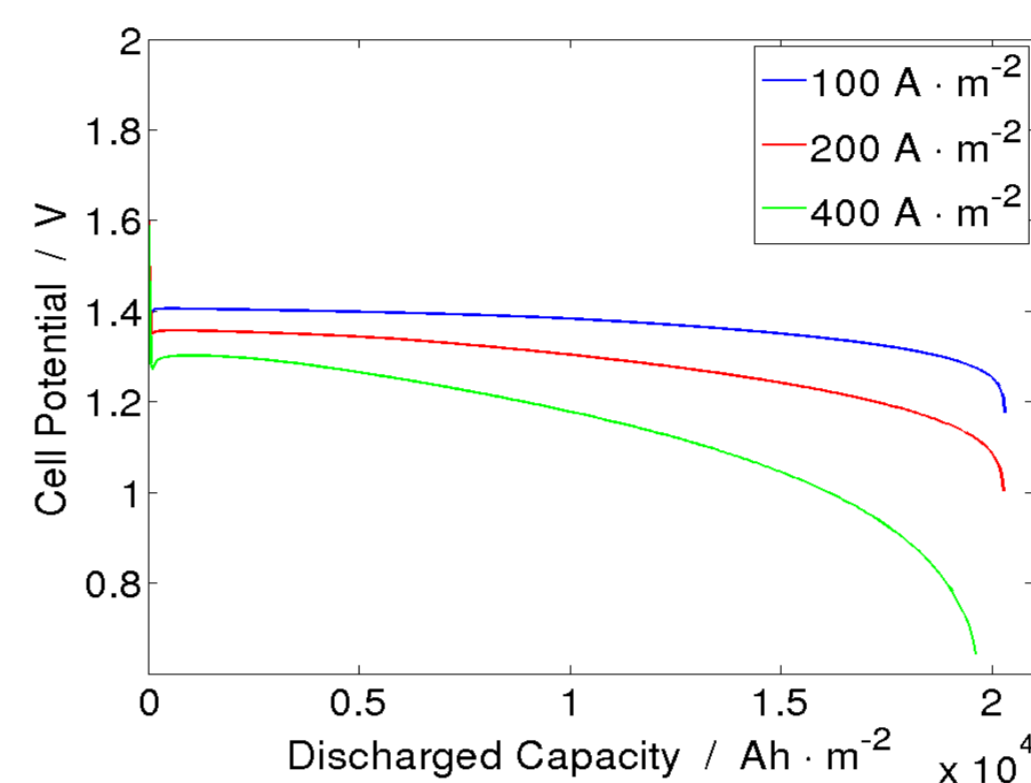
- 1D continuum model of alkaline zinc-air battery
 - Chemical reactions
 - $\text{Zn} + \text{OH}^- \rightleftharpoons \text{Zn}(\text{OH})_4^{2-} + 2e^-$
 - $\text{Zn}(\text{OH})_4^{2-} \rightleftharpoons \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O}$
 - $\text{O}_2 \rightleftharpoons \text{O}_2^{\cdot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

$$\partial_t (\epsilon_e^\beta c_i) = \vec{\nabla} \cdot (\epsilon_e^\beta D_i \vec{\nabla} c_i) + \vec{\nabla} \cdot \left(\epsilon_e^\beta \frac{t_i}{z_i F} \vec{j} \right) + \vec{\nabla} \cdot (\epsilon_e^\beta c_i \vec{v}_e) + S_i$$
 - Coexisting gas, liquid, and solid phases
 - Cathode: hydrophobic gas diffusion electrode (GDE)
 - Anode: spherical zinc particles, porous ZnO shells
 - Electrolyte: aqueous KOH solution

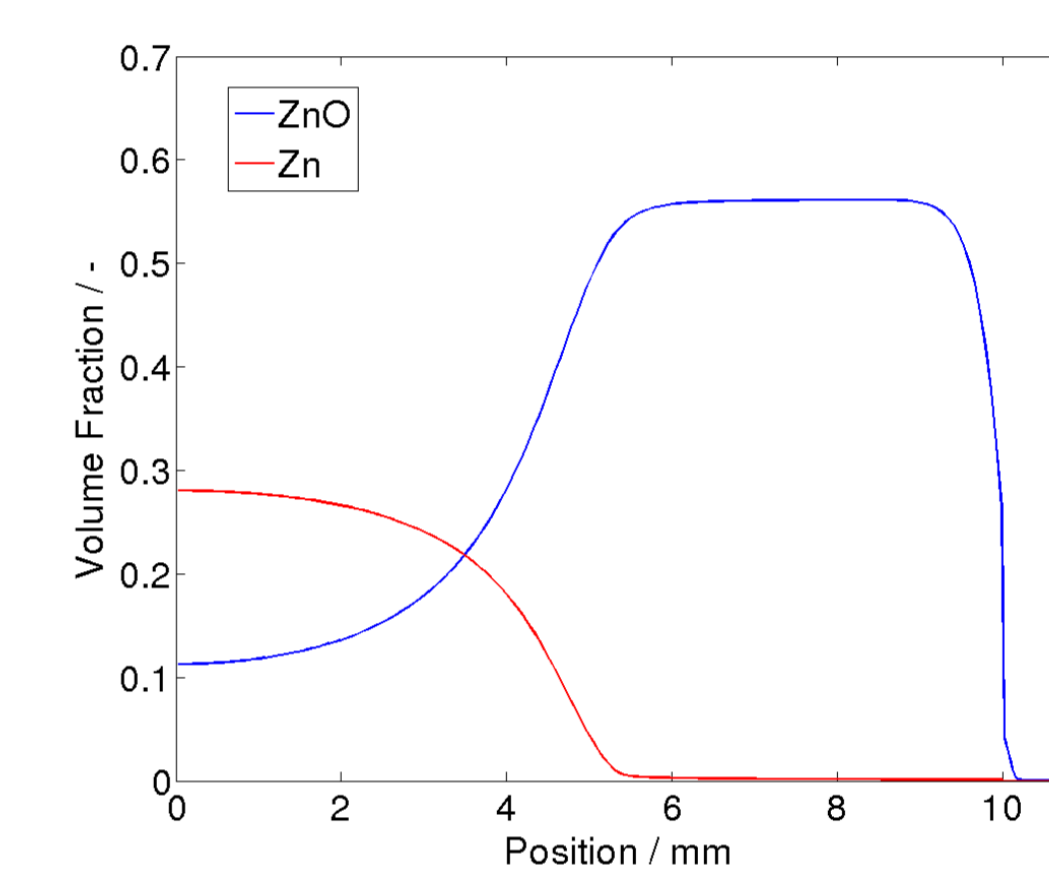
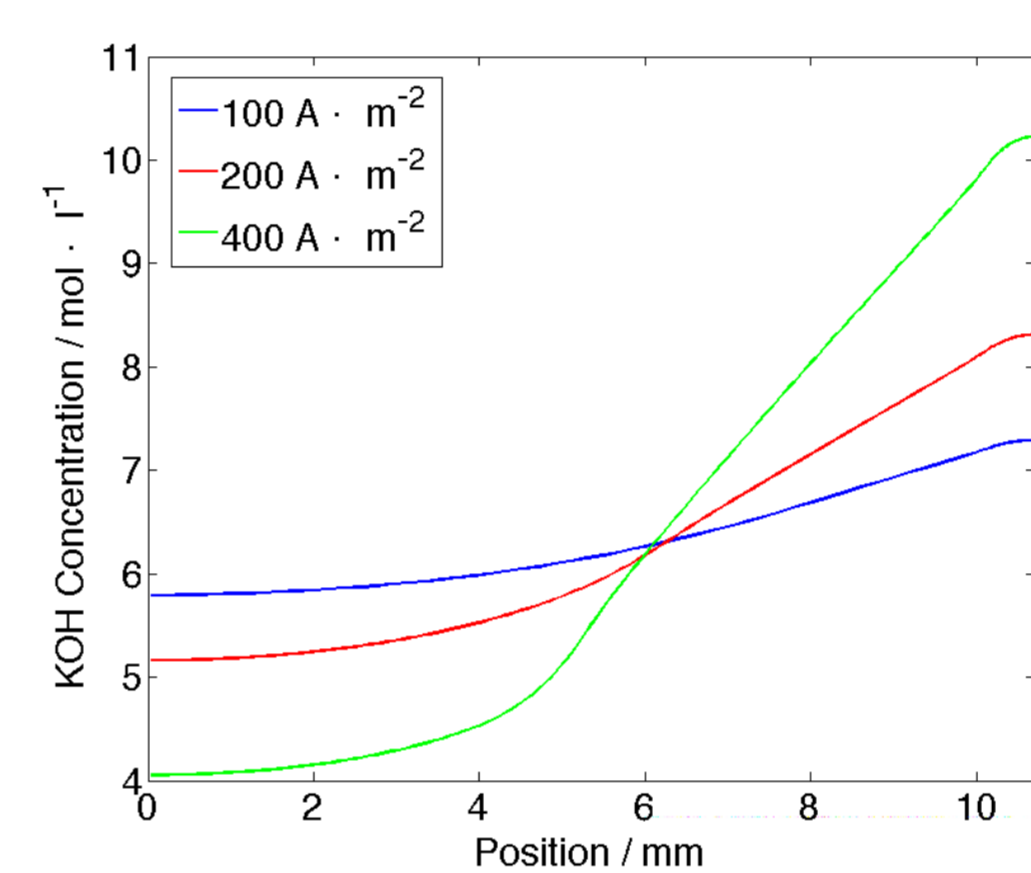


Simulations: Cell Performance

- 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

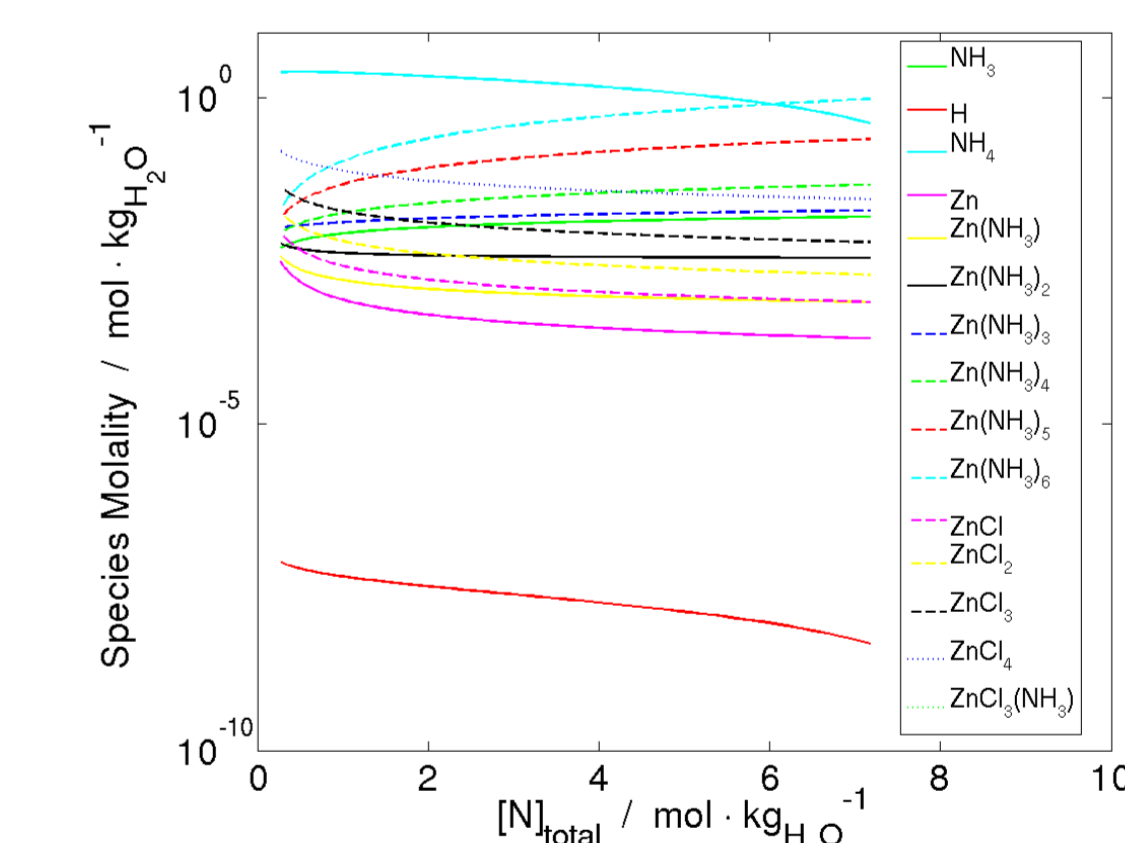


- ZnO precipitates first at the separator
 - Non-reactive zone creates barrier for KOH transport
 - Becomes performance-limiting at high current densities



Outlook: Near-Neutral Electrolyte

- $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ electrolyte eliminates carbonation effects and improves cycling stability
 - Chemical reactions
 - $\text{Zn} + 6\text{NH}_3 \rightleftharpoons [\text{Zn}(\text{NH}_3)_6]^{2+} + 2e^-$
 - $[\text{Zn}(\text{NH}_3)_6]^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{ZnO} + 6\text{NH}_3 + 2\text{H}^+$
 - $\text{O}_2 \rightleftharpoons \text{O}_2^{\cdot -}$
 - $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}$
 - $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$
 - $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$
 - Electrolyte composition in thermodynamic equilibrium
 - Ammonium buffer solution stabilizes pH
 - Variations in pH affect reaction kinetics
 - $[\text{Zn}(\text{NH}_3)_6]^{2+}$ is the dominant zinc-ammine complex

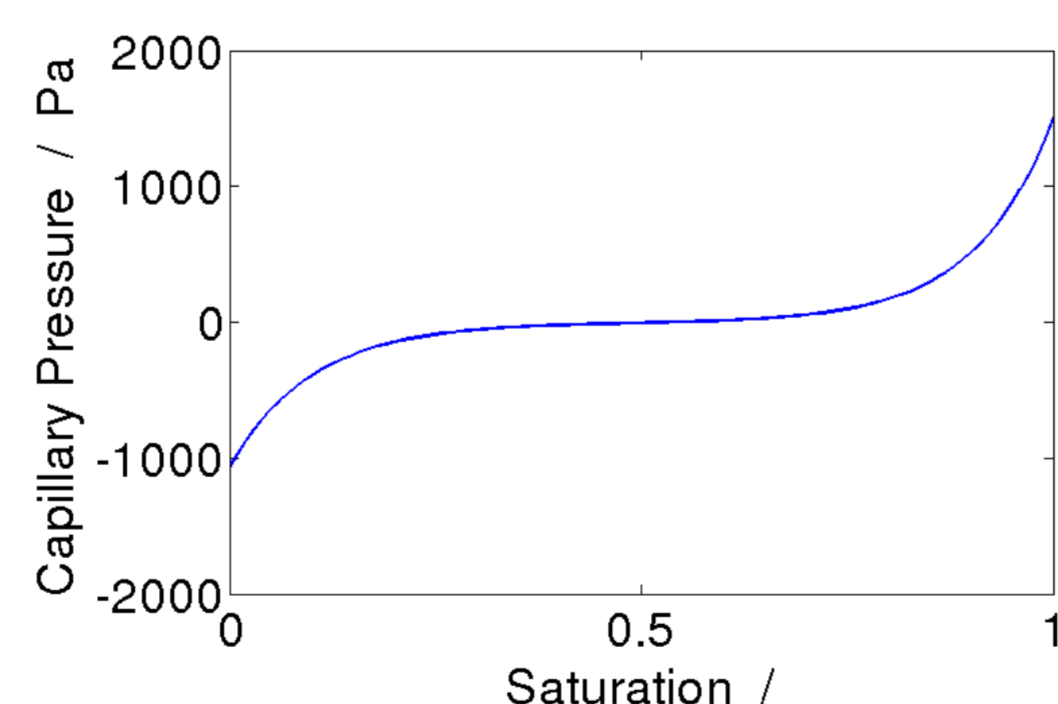


Gas Diffusion Electrode

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

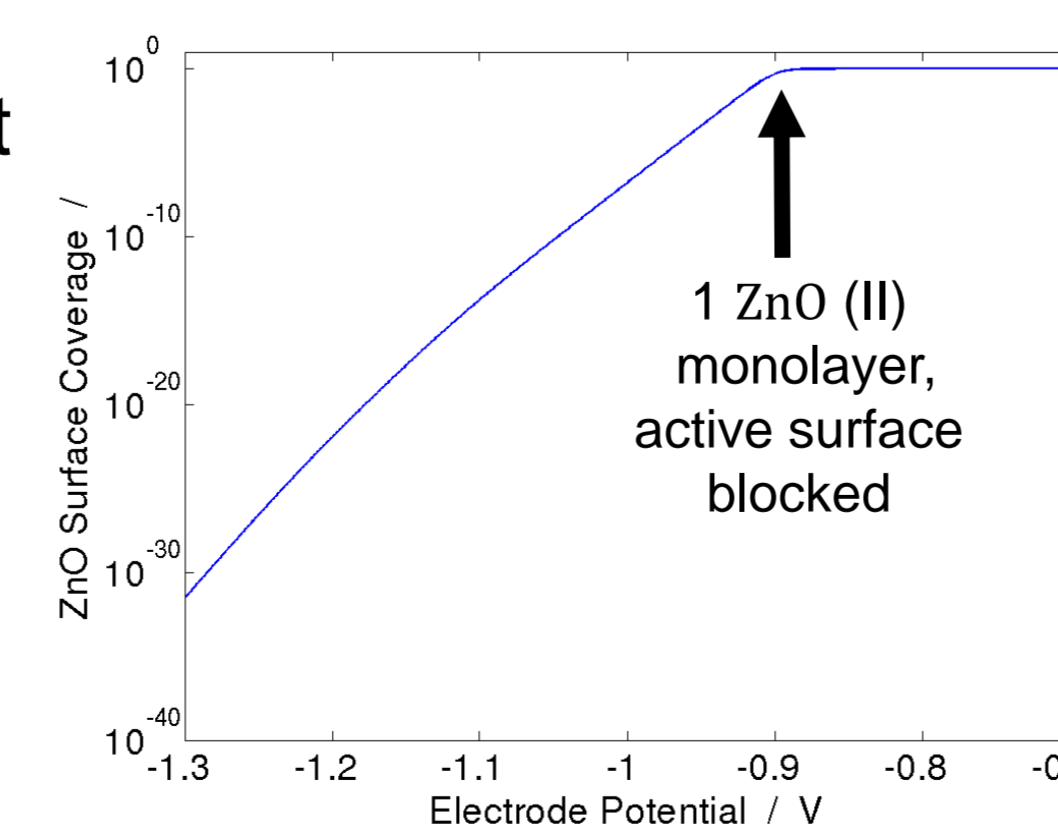
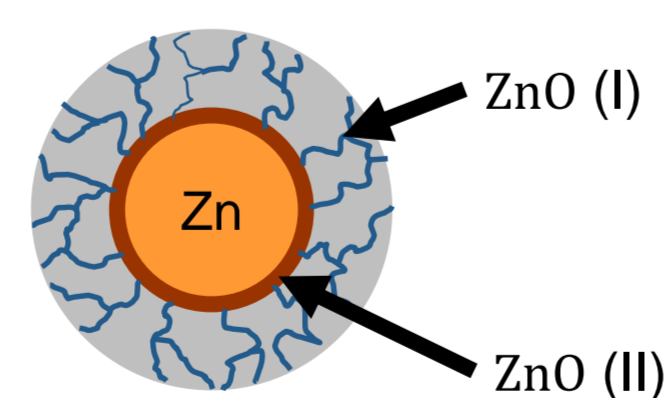
$$\tilde{s} = \frac{\epsilon_{\text{liq}}}{\epsilon_{\text{liq}} + \epsilon_{\text{gas}}}$$

$$p_{\text{cap}} = p_{\text{liq}} - p_{\text{gas}} = \sigma J(\tilde{s}) \sqrt{\frac{\epsilon_0}{B}}$$



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



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