Modeling Secondary Zinc-Air Batteries with Advanced Aqueous Electrolytes

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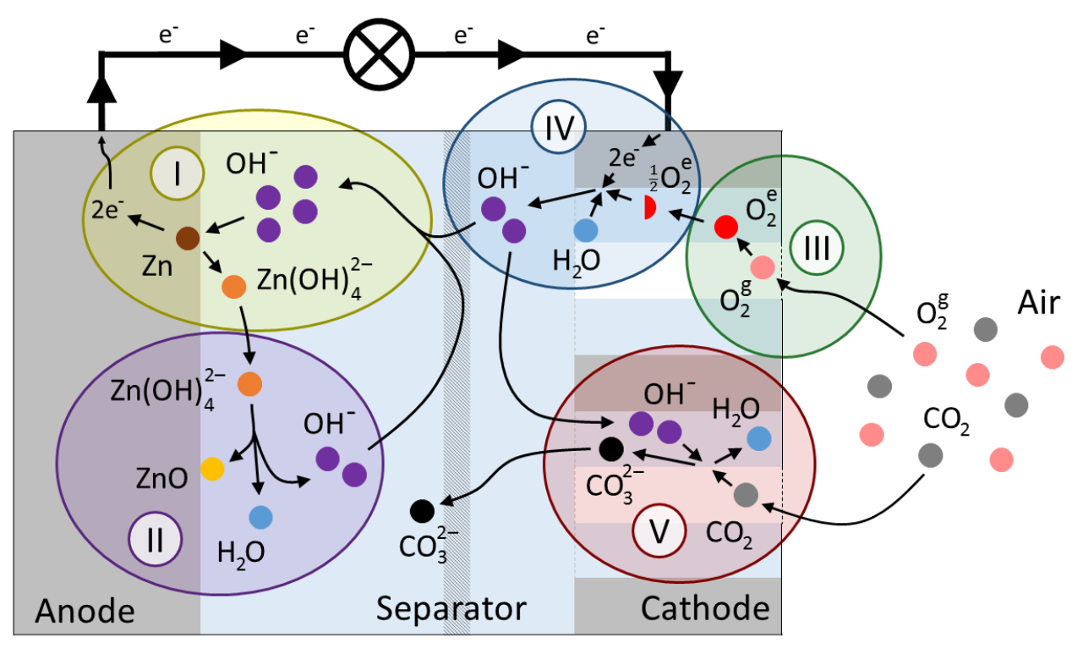
Motivation

- 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:



I. $Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$
II. $Zn(OH)_4^{2-} \rightleftharpoons ZnO + 2OH^- + H_2O$
III. $O_2^g \rightleftharpoons O_2^e$
IV. $\frac{1}{2}O_2^e + H_2O + 2e^- \rightleftharpoons 2OH^-$

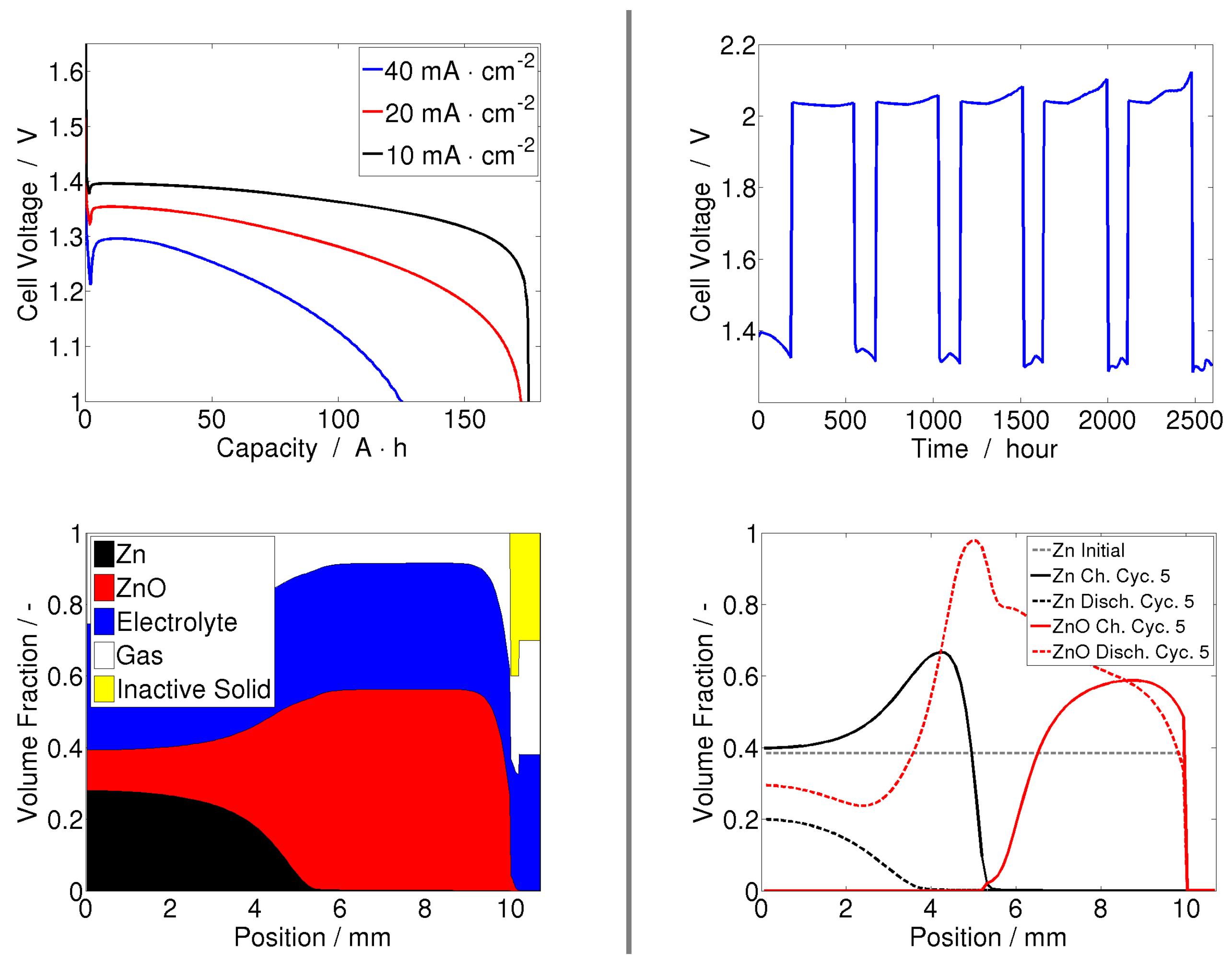
- Consistent transport: diffusion, migration, and convection

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

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

Simulations: Alkaline Electrolyte

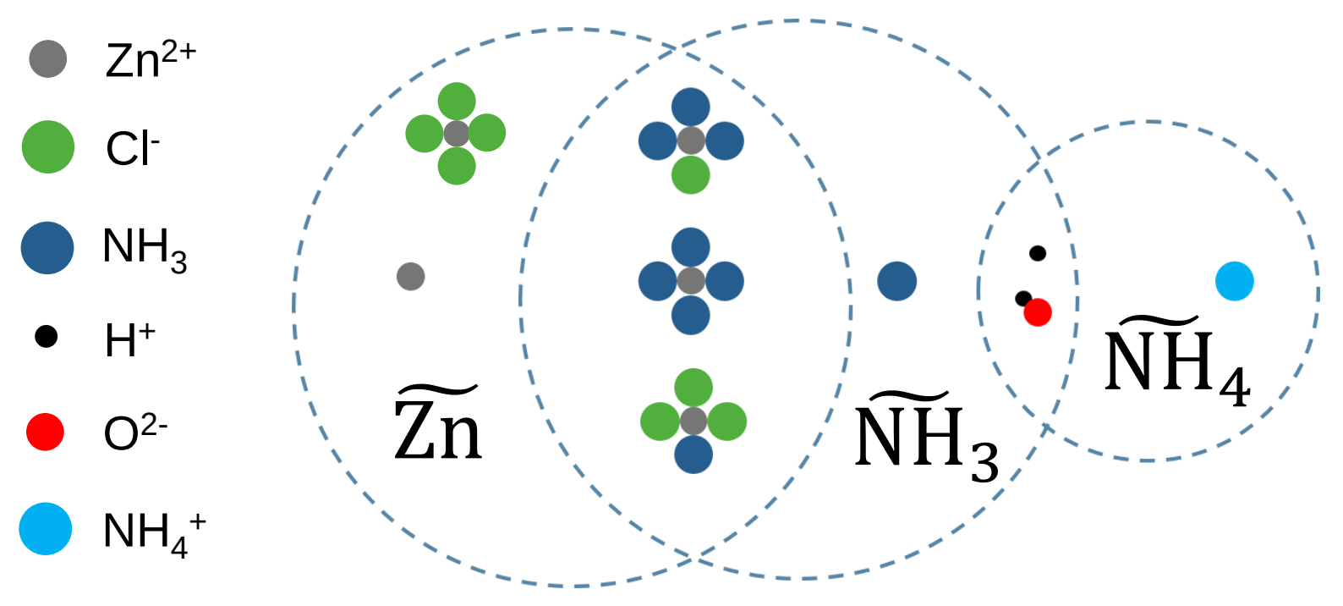
- Galvanostatic operation of prismatic zinc-air cell
    - Thick anode (10 mm), large energy capacity
    - Long reactant transport path and pore blockage with ZnO
        - Cell performance limited by mass transport

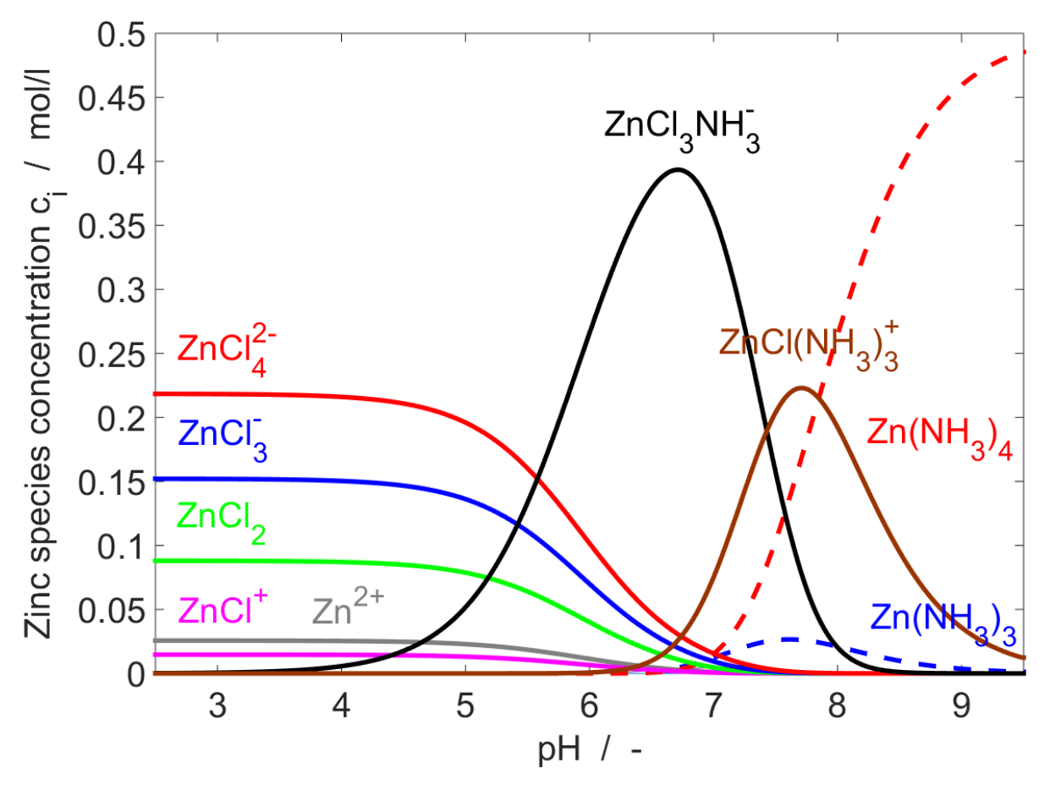


- ZnO precipitates first at the separator
    - Non-reactive zone creates barrier for KOH transport
    - Zinc electrode shape change during cycling

Model: Neutral Electrolyte

- $NH_4Cl + ZnCl_2$ 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:

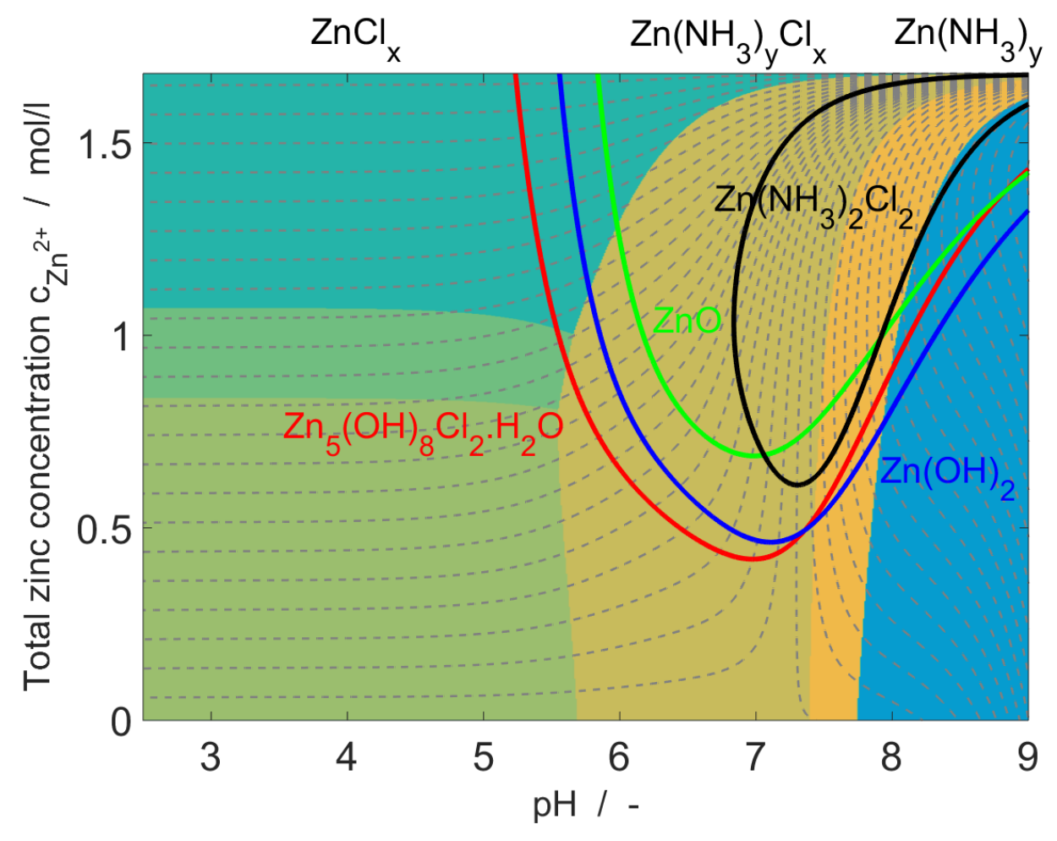


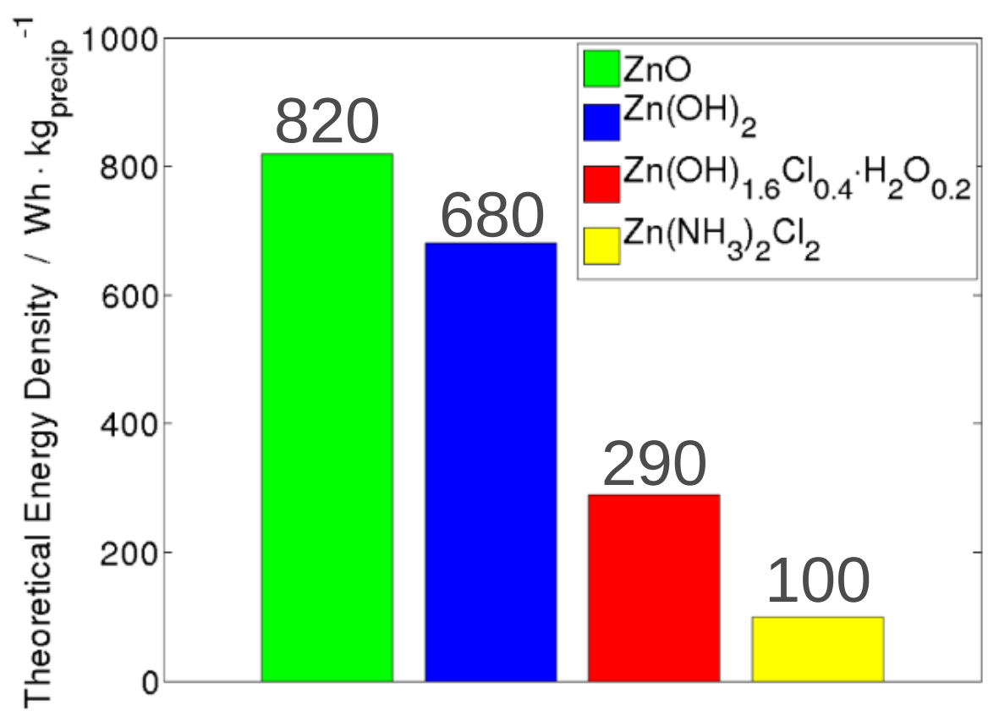


- Chemical reactions:

I. $Zn \rightleftharpoons \widetilde{Zn}^{2+} + 2e^-$
II. $5\widetilde{Zn}^{2+} + 8\widetilde{NH}_3 + 2\widetilde{Cl}^- + H_2O \rightleftharpoons Zn_5(OH)_8Cl_2 \cdot H_2O + 8\widetilde{NH}_4^+$
III. $O_2^g \rightleftharpoons O_2^e$
IV. $\frac{1}{2}O_2^e + 2\widetilde{NH}_4^+ + 2e^- \rightleftharpoons H_2O + 2\widetilde{NH}_3$

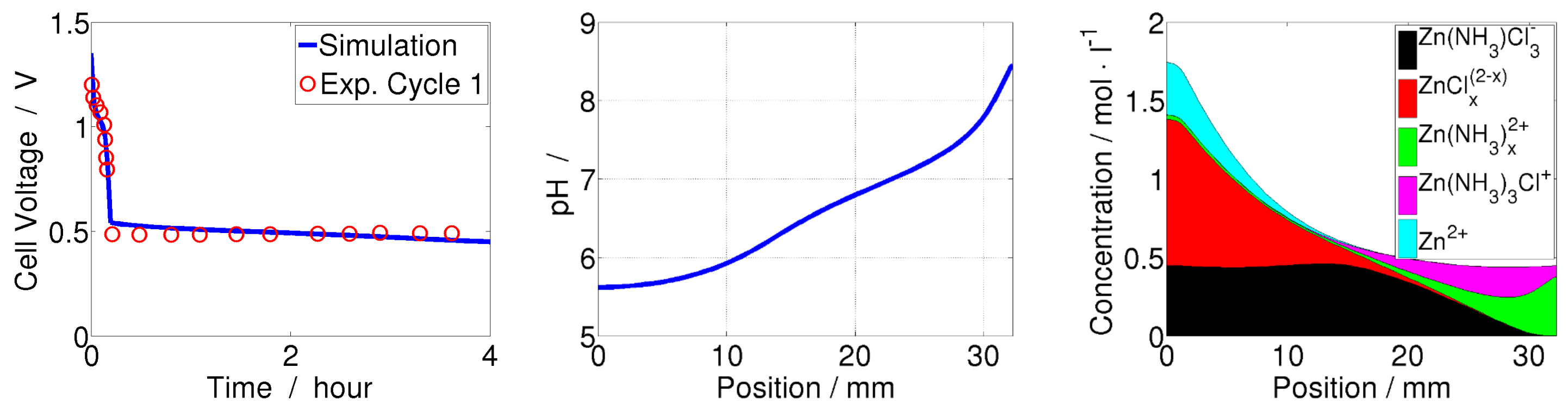
- Final discharge product determined by electrolyte composition and pH:





Simulations: Neutral Electrolyte

- Galvanostatic discharge at 5 mA · cm⁻²
- Initial potential drop due to reduction of 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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Limpo, J. L., et al. *Hydrometallurgy* **32**, 247–260 (1993).
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