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Coupled Modeling of Transport and Electrochemistry in Zinc-air Batteries

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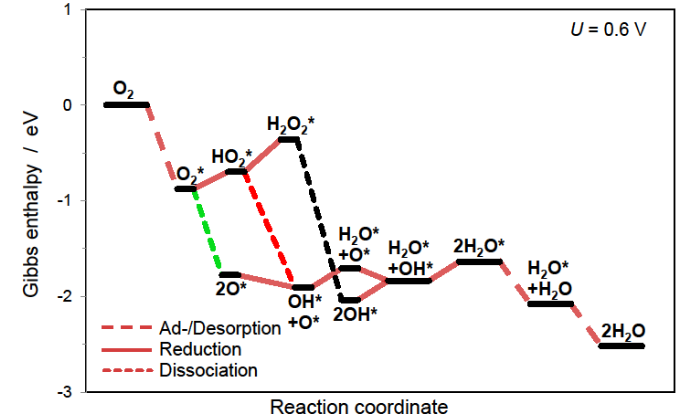
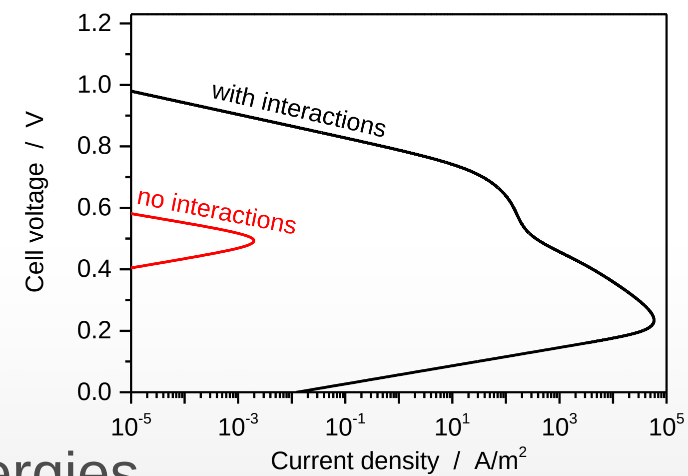
Model: Mean-Field Theory

- **Mean-field** theory of surface species
- Nearest-neighbor interactions:

$$\mu = \mu^0 + 2 \cdot 3 \cdot E_{\mathrm{NN}} \sum_j \frac{\theta_j}{\sigma_j}$$

- Parameters from DFT-calculations
  - Acid water ($\mathrm{pH} = 0$)
  - Surface Pt(111)
  - Temperature $T = 298.15\mathrm{K}$
  - Thermodynamics and activation energies
  - 3 reaction mechanisms

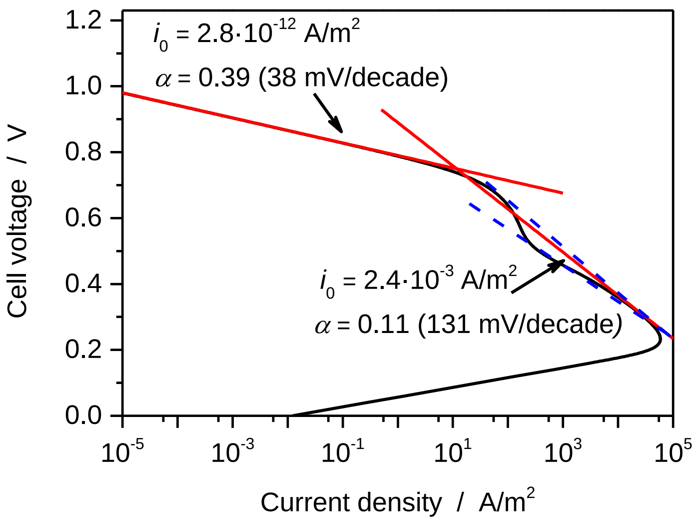


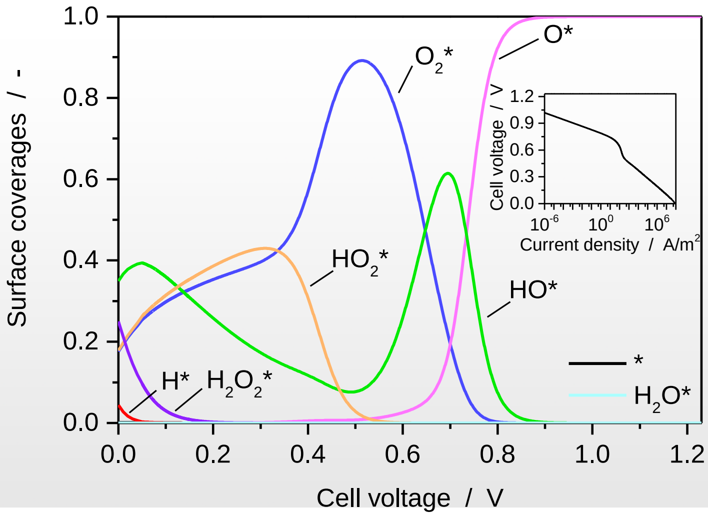


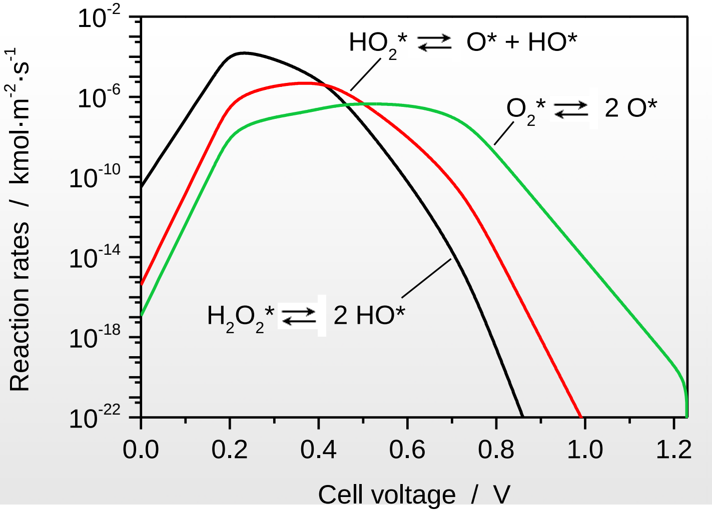
D. Eberle and B. Horstmann, "Oxygen Reduction on Pt(111) in Aqueous Electrolyte: Elementary Kinetic Modeling," *Electrochim. Acta* **137**, 714–720 (2014).

Simulations: Reaction Mechanisms

- Polarization curve
  - 3 reaction mechanisms
  - dissociation rates (O_2, OOH, HOOH)
- Working range
  - U > 0.8 V: O* blocks surface
  - U < 0 V: H* blocks surface

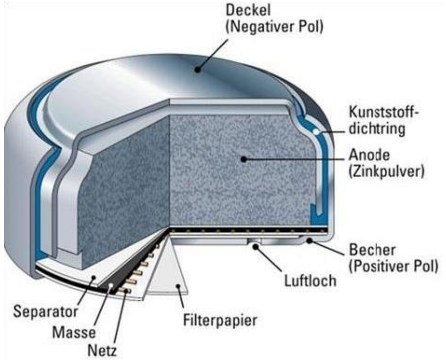






Motivation: Aqueous Zinc-Air Batteries

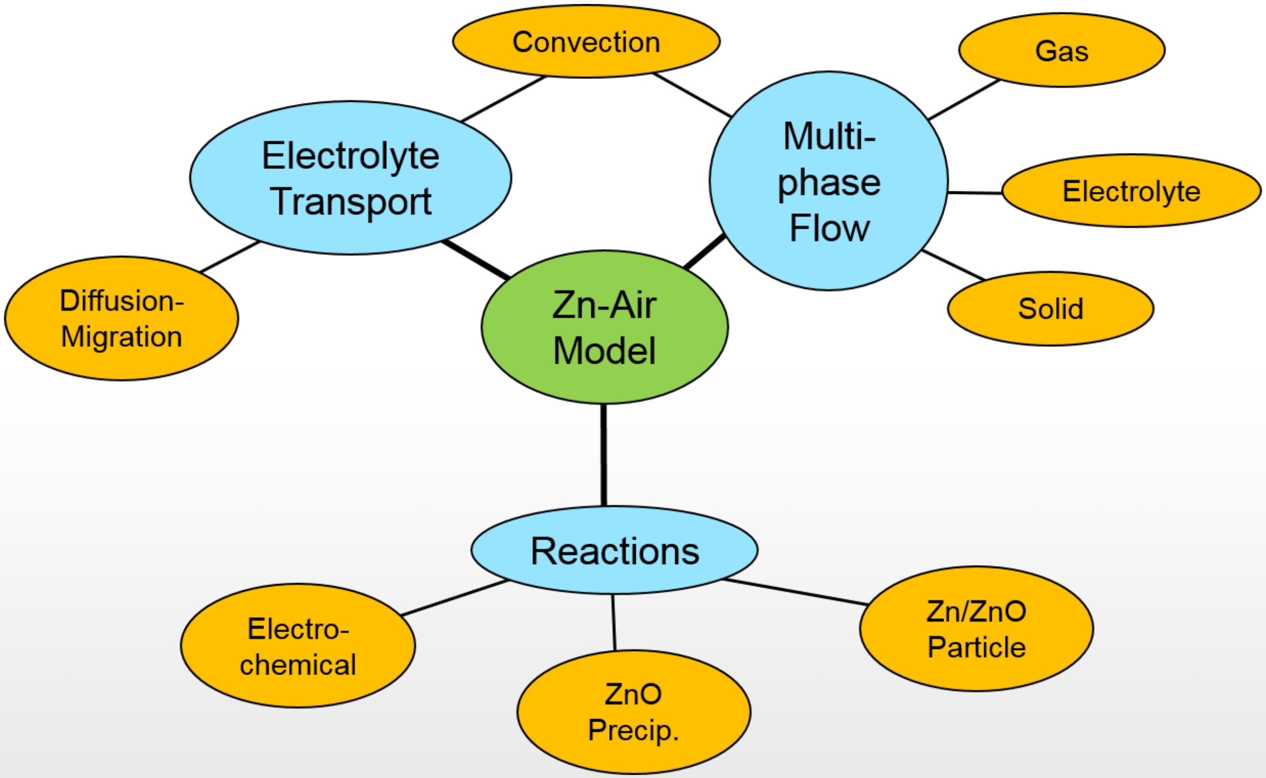
- Primary zinc-air battery commercially available
  - High specific energy (1086 $Wh \cdot kg^{-1}$), low cost, high operational safety
  - Hearing aid battery, e.g., VARTA PowerOne PR44



- Development of rechargeable zinc-air battery
  - Zinc dendrites, electrolyte carbonation, oxygen redox chemistry, anode passivation
  - Stationary energy storage
- Electrolytes: aqueous alkaline, aqueous neutral, ionic liquids

Model: Alkaline Electrolyte

- 1D continuum model of alkaline zinc-air battery



Model: Alkaline Electrolyte

- **Chemical reactions**

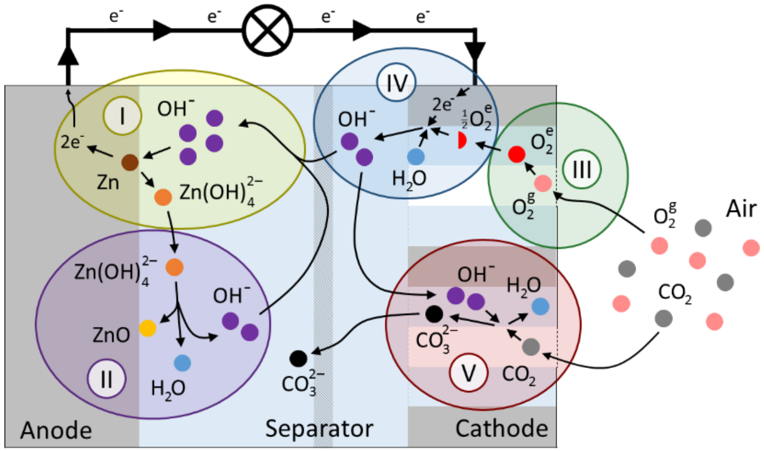
I. $Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^-$

II. $Zn(OH)_4^{2-} \rightleftharpoons ZnO + 2OH^- + H_2O$

III. $O_2^g \rightleftharpoons O_2^e$

IV. $\frac{1}{2}O_2^e + H_2O + 2e^- \rightleftharpoons 2OH^-$

V. $CO_2 + 2\,OH^- \rightleftharpoons CO_3^{2-}$

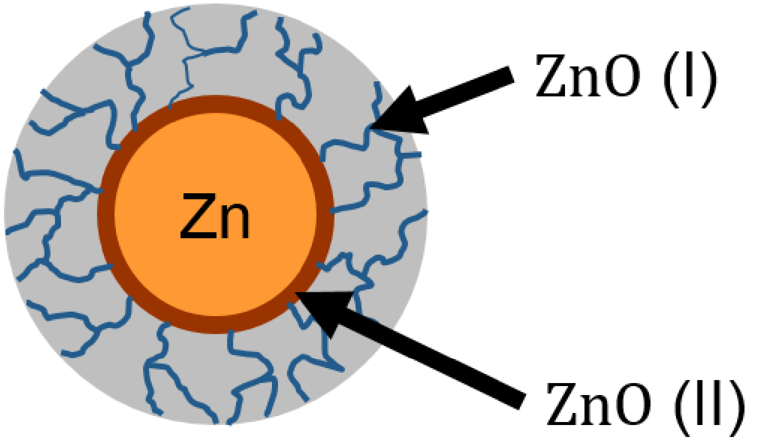


- **Reaction rates**
  - Electrochemical reactions: Butler-Volmer equation
  - ZnO precipitation: diffusion-limited process
  - Oxygen dissolution: Hertz-Knudsen rate
  - Carbon dioxide absorption: quasi-stationary diffusion zone

Horstmann, B. et al. *Energy Environ. Sci.* **2013**, *6* (4), 1299.
Danner, T. et al. *J. Power Sources* **2014**, *264*, 320–332.

Model: ZnO precipitation

- **Anode passivation** due to ZnO
- Type I ZnO
  - Reversible precipitation process
  - Porous diffusion barrier
- Type II ZnO
  - Non-reversible electrochemical process
  - **Blocks** active sites at low voltages
- Model:
  - Spherical Zn particles with porous ZnO shell



G. Prentice. A Model for the Passivation of the Zinc Electrode in Alkaline Electrolyte. Journal of The Electrochemical Society, 138 (4), 1991.

Model: Multi-Species-Transport

- **Consistent transport: diffusion, migration, and convection**

- **Ionic species continuity**

Mass continuity $$\frac{\partial c_i \varepsilon}{\partial t} = -\mathrm{div}\vec{N}_i^{\mathrm{D,M}} - \mathrm{div} c_i \vec{v} + \dot{s}_i$$

Flux densities $$\vec{N}_i^{\mathrm{D,M}} = -D_i \varepsilon^{\beta} \mathrm{grad} c_i + \frac{t_i}{z_i F} \vec{j}$$

Reaction source $$\dot{s}_i = \sum_j n_{i,j} k_j A_{sp,j}$$

- **Electric current density**

$$\vec{j} = -\kappa \varepsilon^{\beta} \mathrm{grad}\phi - \frac{\kappa \varepsilon^{\beta} t_2}{-F} \frac{\partial \mu_2}{\partial c_2} \mathrm{grad} c_2 - \frac{\kappa \varepsilon^{\beta} t_3}{-2F} \frac{\partial \mu_3}{\partial c_3} \mathrm{grad} c_3$$

$$2 \equiv \mathrm{OH}^-, 3 \equiv \mathrm{Zn(OH)}_4^{2-}$$

Horstmann, B. et al. *Energy Environ. Sci.* **2013**, *6* (4), 1299.
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Model: Multi-Species-Transport

- Local electroneutrality

  Charge conservation: $0 = \frac{\partial q}{\partial t} = -\vec{\nabla}\vec{j} + \dot{s}_q$

  $\dot{s}_q$ ≡ Charge reaction source

- Incompressible electrolyte

  Convection of center-of-mass: $\frac{\partial \rho\varepsilon}{\partial t} = -\vec{\nabla}(\rho\vec{v}) + \dot{s}_T$

  $\mathrm{div} v = -\sum_i \nu_i \vec{N}_i$

  ν_i ≡ Partial molar volume

  $\dot{s}_T$ ≡ Mass reaction source

Horstmann, B. et al. *Energy Environ. Sci.* **2013**, *6* (4), 1299.
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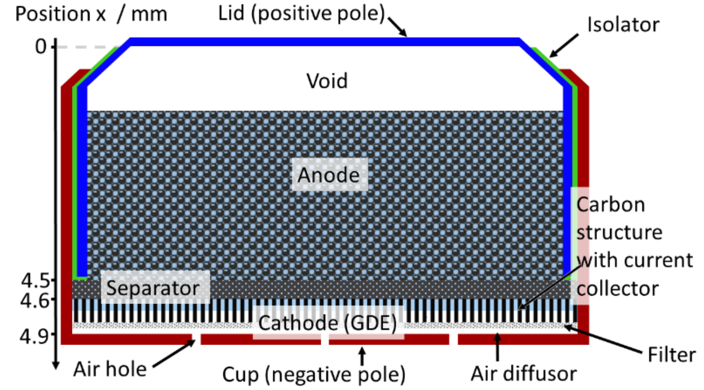
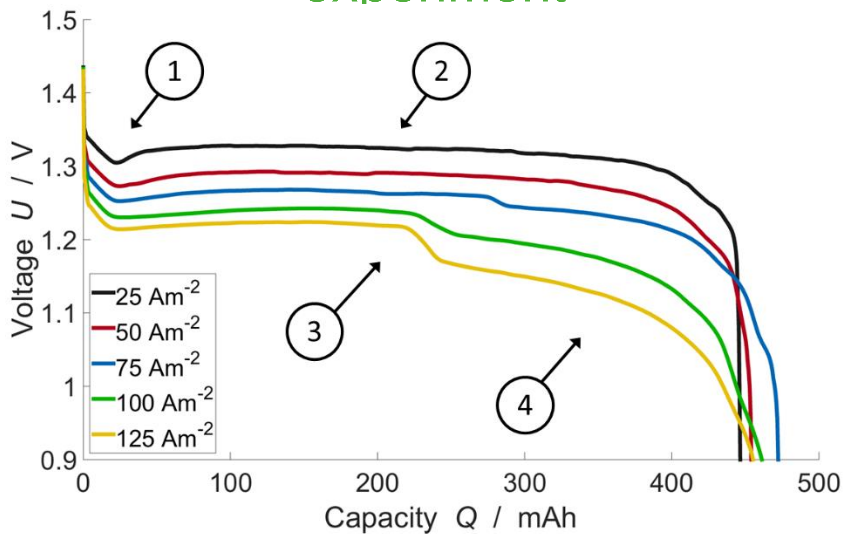
Coin Cell: Galvanostatic Discharge

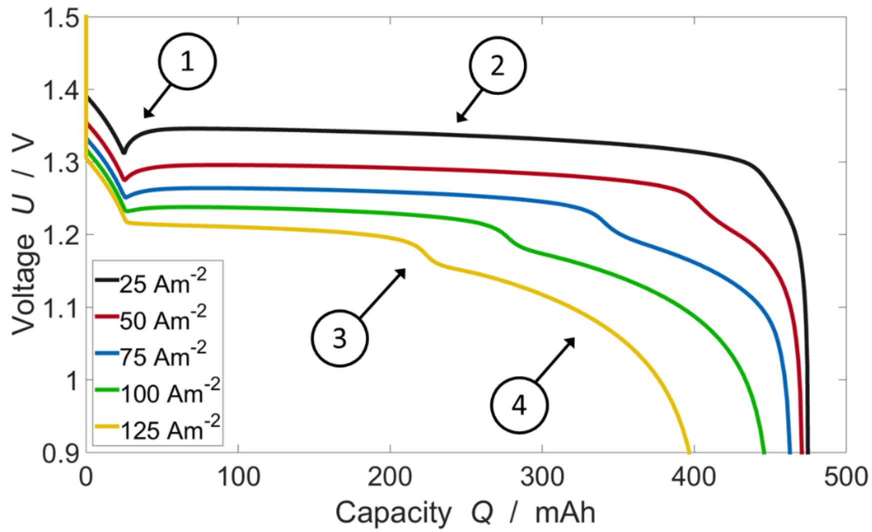
1. Dip: nucleation of ZnO
2. Plateau: conversion reaction
3. Step: inhomogeneous nucleation
4. Drop: OH^- diffusion through ZnO



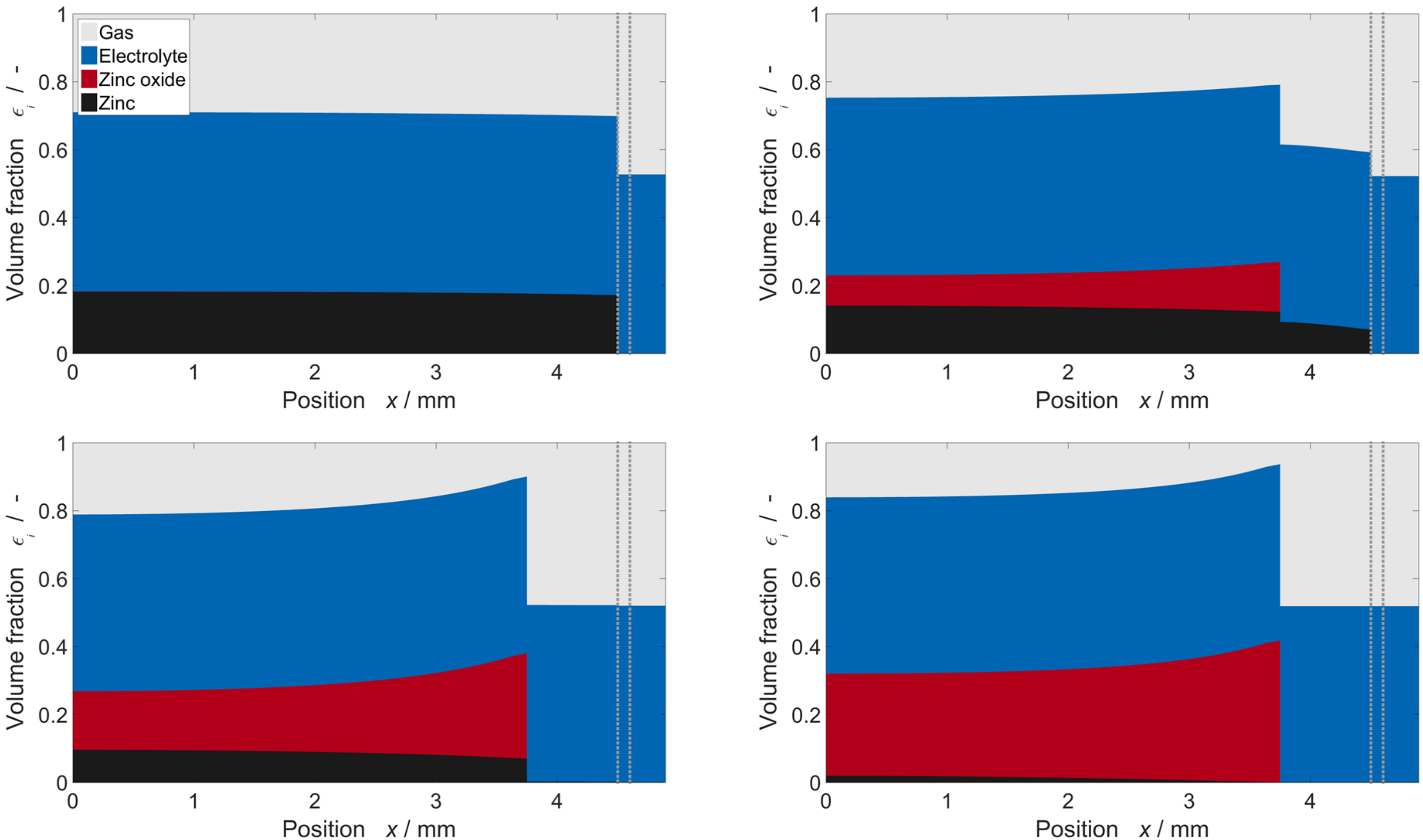
experiment



simulation

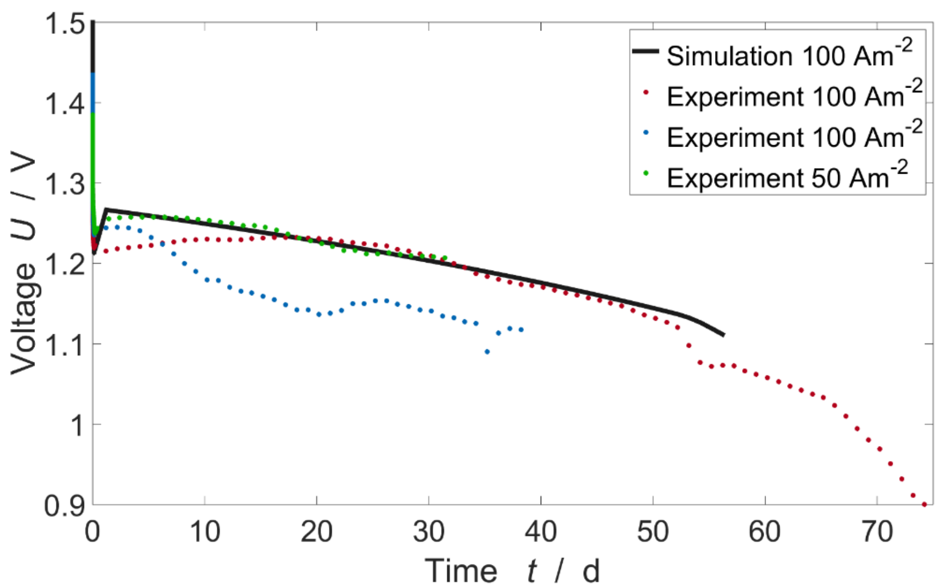


Coin Cell: Volume Fractions during Discharge



Coin Cell: Lifetime Analysis

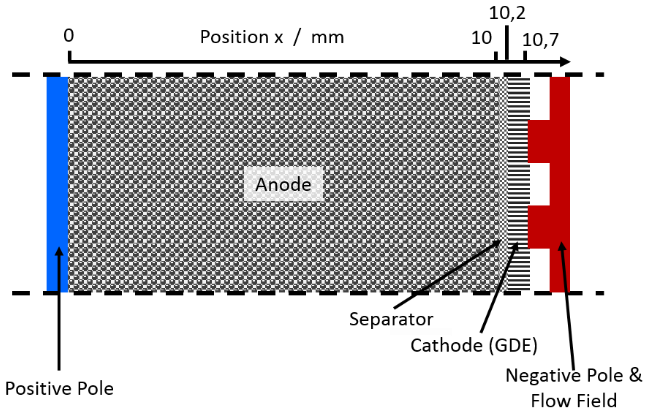
- Absorption of atmospheric CO_2, consumption of OH^-
- Linear decay in cell voltage
  - Daily measurement of cell voltage
  - Initial galvanostatic discharge to reach voltage plateau

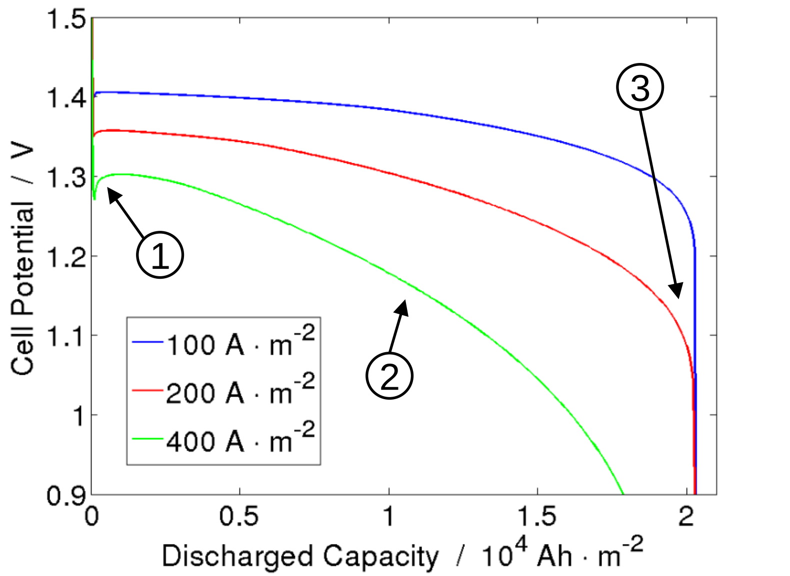


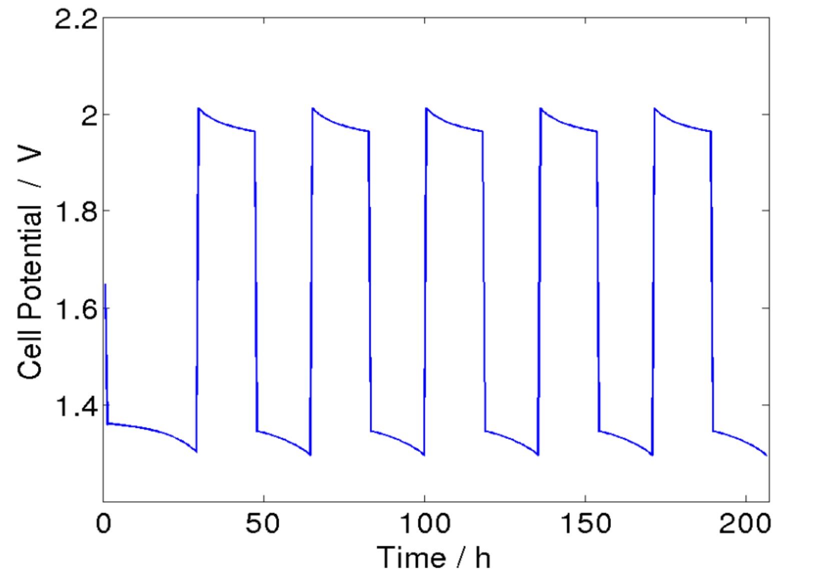
Prismatic Cell: Galvanostatic Discharge

Large anode for high capacity

1. Dip: nucleation of ZnO
2. Drop: OH^- diffusion through ZnO
3. Drop: Zn depletion

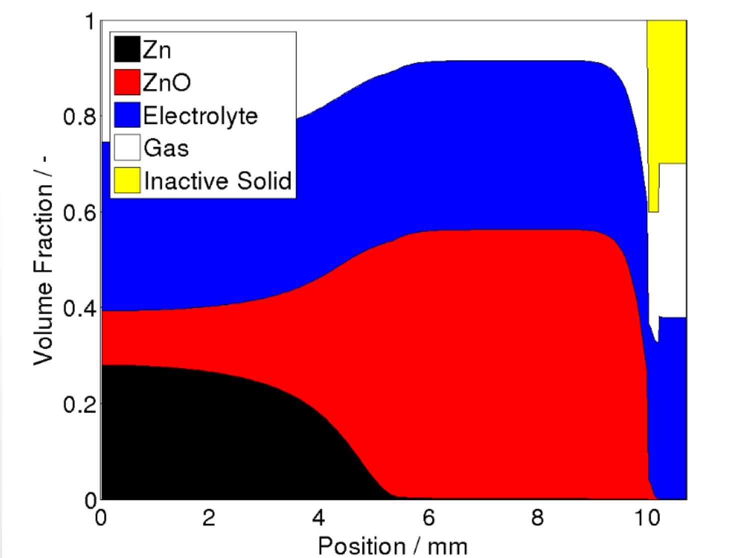


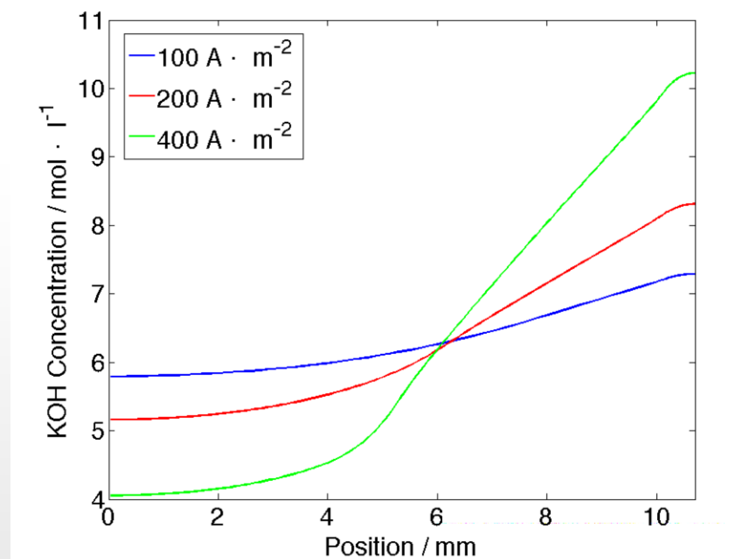




Prismatic Cell: Galvanostatic Discharge

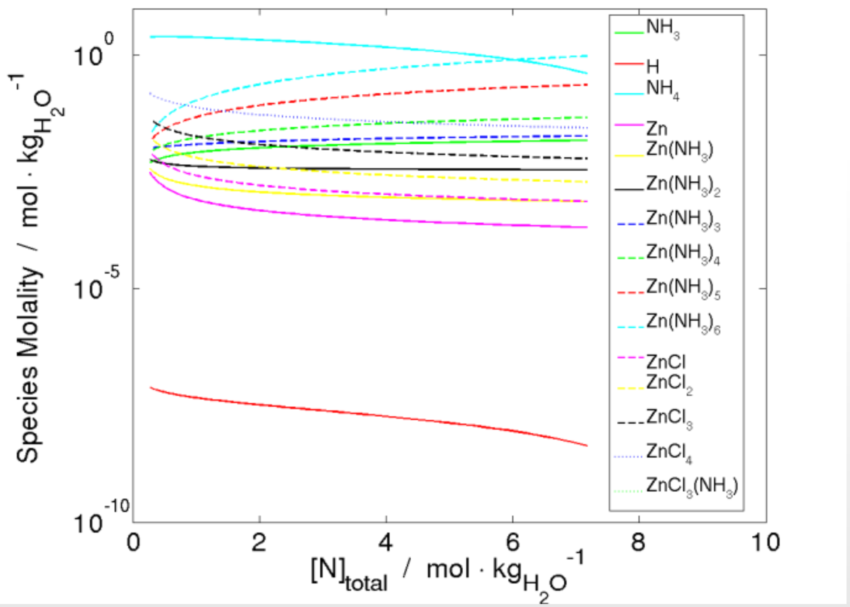
- ZnO first precipitates at the separator
- Non-reactive zone barrier for mass transport
- Performance limiting at high current densities





Model: Neutral Electrolyte

- $NH_4Cl + ZnCl_2$ electrolyte
  - Ammonium as pH buffer
  - Elimination of Carbonation
- Equilibrium electrolyte composition
  - $Zn(NH_3)_6^{2+}$ is the dominant zinc species



Model: Neutral Electrolyte

- Chemical reactions

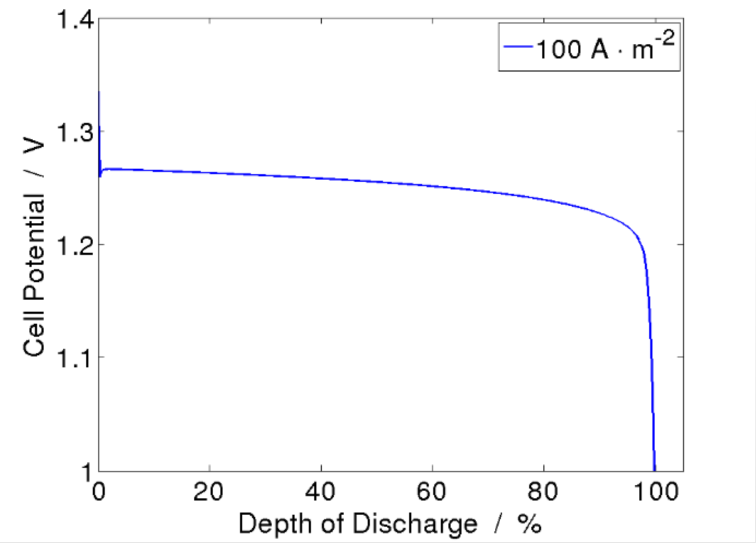
I. $Zn + 6NH_3 \rightleftharpoons [Zn(NH_3)_6]^{2+} + 2e^-$

II. $[Zn(NH_3)_6]^{2+} + H_2O \rightleftharpoons ZnO + 6NH_3 + 2H^+$

III. $NH_4^+ \rightleftharpoons NH_3 + H^+$

IV. $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

V. $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$



Thank you for your attention

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