Coupled Modeling of Transport and Electrochemistry in Zinc-air Batteries
Model: Mean-Field Theory

- Mean-field theory of surface species
- Nearest-neighbor interactions:
  \[ \mu = \mu^0 + 2 \cdot 3 \cdot E_{NN} \sum_j \frac{\theta_j}{\sigma_j} \]
- Parameters from DFT-calculations
  - Acid water (pH = 0)
  - Surface Pt(111)
  - Temperature \( T = 298.15K \)
  - Thermodynamics and activation energies
  - 3 reaction mechanisms

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

\[ i_0 = 2.8 \times 10^{-12} \text{ A/m}^2 \]
\[ \alpha = 0.39 \text{ (38 mV/decade)} \]

\[ i_0 = 2.4 \times 10^{-3} \text{ A/m}^2 \]
\[ \alpha = 0.11 \text{ (131 mV/decade)} \]
Motivation: Aqueous Zinc-Air Batteries

- Primary zinc-air battery commercially available
  - High specific energy (1086 Wh·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. \[ \text{Zn} + 4\text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} + 2\text{e}^- \]
  II. \[ \text{Zn(OH)}_4^{2-} \rightleftharpoons \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} \]
  III. \[ \text{O}_2^g \rightleftharpoons \text{O}_2^e \]
  IV. \[ \frac{1}{2} \text{O}_2^e + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{OH}^- \]
  V. \[ \text{CO}_2 + 2\text{OH}^- \rightleftharpoons \text{CO}_3^{2-} \]

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

Model: Multi-Species-Transport

- Consistent transport: diffusion, migration, and convection

- Ionic species continuity

  Mass continuity
  \[ \frac{\partial c_i \varepsilon}{\partial t} = -\text{div} \overrightarrow{N}_{i,D,M} - \text{div} c_i \vec{v} + \dot{s}_i \]

  Flux densities
  \[ \overrightarrow{N}_{i,D,M} = -D_i \varepsilon \beta \text{grad} c_i + \frac{t_i}{z_i F} \vec{j} \]

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

- Electric current density

  \[ \vec{j} = -\kappa \varepsilon \beta \text{grad} \phi - \frac{\kappa \varepsilon \beta t_2}{-F} \frac{\partial \mu_2}{\partial c_2} \text{grad} c_2 - \frac{\kappa \varepsilon \beta t_3}{-2F} \frac{\partial \mu_3}{\partial c_3} \text{grad} c_3 \]

  \[ 2 \equiv \text{OH}^-, 3 \equiv \text{Zn(OH)}_{4}^{2-} \]
Model: Multi-Species-Transport

• Local electroneutrality

Charge conservation: \[ 0 = \frac{\partial q}{\partial t} = -\nabla \vec{j} + \dot{s}_q \]
\[ \dot{s}_q \equiv \text{Charge reaction source} \]

• Incompressible electrolyte

Convection of center-of-mass: \[ \frac{\partial \rho \varepsilon}{\partial t} = -\nabla (\rho \vec{v}) + \dot{s}_T \]
\[ \text{div} \vec{v} = - \sum_i \nu_i \vec{N}_i \]
\[ \nu_i \equiv \text{Partial molar volume} \]
\[ \dot{s}_T \equiv \text{Mass reaction source} \]
Coin Cell: Galvanostatic Discharge

1. Dip: nucleation of ZnO
2. Plateau: conversion reaction
3. Step: inhomogeneous nucleation
4. Drop: OH\(^-\) diffusion through ZnO
Coin Cell: Volume Fractions during Discharge

Aqueous Zinc-Air Batteries

Gas
Electrolyte
Zinc oxide
Zinc
Coin Cell: Lifetime Analysis

- Absorption of atmospheric CO₂, 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

Graphs showing cell potential versus discharged capacity and time.
Prismatic Cell: Galvanostatic Discharge

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

Model: Neutral Electrolyte

- NH₄Cl + ZnCl₂ electrolyte
  - Ammonium as pH buffer
  - Elimination of Carbonation

- Equilibrium electrolyte composition
  - Zn(NH₃)₂⁺ is the dominant zinc species
Model: Neutral Electrolyte

- Chemical reactions

I. \[ \text{Zn} + 6\text{NH}_3 \rightleftharpoons [\text{Zn(NH}_3)_6]^{2+} + 2\text{e}^- \]

II. \[ [\text{Zn(NH}_3)_6]^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{ZnO} + 6\text{NH}_3 + 2\text{H}^+ \]

III. \[ \text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+ \]

IV. \[ \text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O} \]

V. \[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \]
Thank you for your attention

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