Reaction and Transport in Gas Diffusion Electrodes of Li-O\textsubscript{2} batteries: Experiments and Modeling

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Content

I. Motivation and background

II. Continuum model of an aqueous Li-O₂ system

III. Model parameterization

IV. Model validation

V. Electrode and cell design

VI. Summary
I. Motivation and background

- Proposed designs
  - **Aprotic** Li-O₂ batteries \((U = 3 \text{ V})\)
    \[
    \text{O}_2 + 2 \text{Li}^+ + 4 \text{e}^- \rightleftharpoons \text{Li}_2\text{O}_2^{(s)}
    \]
    - Stable electrolyte?
    - Solubility and diffusivity of \(\text{O}_2\)?
    - Insulating discharge products
  
  - **Aqueous** Li-O₂ batteries \((U = 3.45 \text{ V})\)
    \[
    \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightleftharpoons 4 \text{OH}^-
    \]
    - Stable anode protection?
    - Precipitation of \(\text{LiOH}\cdot\text{H}_2\text{O}\)
    - Advantage: GDEs
    - …

\[\Rightarrow\text{Very high theoretical energy densities}\]

I. Motivation and background

- Porous Gas Diffusion Electrode
  \[ \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightleftharpoons 4 \text{OH}^- \]
  - High surface area
  - Fast transport of O\(_2\)
    \(\Rightarrow\) High current densities

- Lithium metal anode
  \[ \text{Li} \rightleftharpoons \text{Li}^+ + \text{e}^- \]
  - Stable anode protection

- Separator
  - Precipitation of LiOH·H\(_2\)O (\(c_s = 5.3 \text{ mol} l^{-1}\))
    \[ \text{Li}^+ + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons \text{LiOH} \cdot \text{H}_2\text{O}^{(s)} \]
  - Clogging of transport pathways
II. Continuum modeling

- 1D spatially resolved continuum model
- Transport in liquid electrolyte
  - Concentrated solution theory
  - Electro-neutrality condition
  - Darcy flow \( \mathbf{\vec{v}} = -B/\mu \cdot \text{grad } p_{\text{liq}} \)
    
    \[
    \frac{\partial (\varepsilon_{\text{liquid}}c)}{\partial t} = -\text{div}(\mathbf{\vec{v}}\varepsilon_{\text{liq}}c) - \text{div}\mathbf{j} + A_{\text{spez}}\dot{s}
    \]
  - Global kinetics (Butler-Volmer type)
    \( \Rightarrow \) ORR/OER
  - Single set of parameters
    \( \Rightarrow \) Literature or own experiments

\( \Rightarrow \) Simulation software DENIS

II. Continuum modeling - Transport in porous media

- Effective transport properties

- Bruggeman equation:

\[ D_j^{\text{eff}} = D_j^0 \cdot \varepsilon_{\text{liq}}^\beta = D_j^0 \cdot (\varepsilon^0 s)^\beta \]

- Capillary pressure in porous electrodes

\[ p_c = p_{\text{gas}} - p_{\text{liq}} = -\sigma_t \sqrt{\varepsilon^0 / k} \ J(s) \]

- Constant Total Volume \( \sum_k \varepsilon_k(p_k) = 1 \)

- Liquid equation of state: \( \sum_s \frac{\partial V_{\text{liquid}}}{\partial N_s} c_s = 1 \)

- Gas equation of state: \( p_{\text{gas}} V_{\text{gas}} = N_{\text{gas}} RT \)

III. Model parameterization

- Thermodynamic parameters
  - LiOH\(\cdot\)H\(_2\)O precipitation
  - 'Salting-out' of oxygen

- Kinetic parameters
  - ORR/OER

- Structural parameters
  - Porosity, tortuosity, etc

- Transport parameters
  - Leverett function
  - Effective transport

Literature

LiOH solubility
III. Model parameterization – Electrochemical characterization

- Three-electrode setup
  - Alkaline LiOH solution (0.1-2M)
  - Pure oxygen (1 atm)
- Ag-GDE (commercial)
  - Defined structure
- Measurements
  - CV, EIS

→ Broad parameter range for parameterization and validation

### III. Model parameterization – Structural characterization

**FIB-SEM** → **Binarization** → **Reconstruction**

- **Good agreement to experimental results**

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Measurements</th>
<th>FIB-SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (vol%)</td>
<td>0.479</td>
<td>0.495</td>
</tr>
<tr>
<td>$d_{50}$ (µm)</td>
<td>0.51</td>
<td>0.82</td>
</tr>
<tr>
<td>Specific surface area (m$^{-1}$)</td>
<td>$3.3 \times 10^6$</td>
<td>$1.1 \times 10^6$</td>
</tr>
</tbody>
</table>

**Collaboration with S.K. Eswara Moorthy, Central Facility of Electron Microscopy, University of Ulm**
III. Model parameterization – Transport parameters

Collaboration with Prof. Arnulf Latz

- Lattice-Boltzmann modeling
  - 2D and 3D simulations
  - SRT-BGK model
  - Multiphase simulations (Rothmann-Keller type)
  - Heterogeneous structures

- Simulation of $p_c$-S curves

- Effective transport properties

Initial code provided by Prof. Volker Schulz (DHBW Mannheim)

III. Model parameterization

- Thermodynamic parameters
  - LiOH·H₂O precipitation
  - ’Salting-out‘ of oxygen

- Kinetic parameters
  - ORR/OER

- Structural parameters
  - Porosity, tortuosity, etc

- Transport parameters
  - Leverett function
  - Effective transport

→ Single set of parameters
IV. Model validation

- IV curves and impedance spectra
  - Good qualitative agreement
- Deviation at high temperature, overpotential
  - Change in reaction mechanism?
  - Additional transport limitations?

Nyquist plot - 1 M - 25 °C

Nyquist plot - 2 M - 75 °C
V. Electrode and cell design - Gas Diffusion Electrodes

- Sensitivity of current density
  
  \[ S_j = \frac{(i^0 - i^+)}{i^0} / \frac{(\zeta^0 - \zeta^+)}{\zeta^0} \]

- No influence of
  - Anode (three electrode setup)
  - \( \text{O}_2 \) pore-space transport (no liquid film modeled)

- High sensitivity of
  - Cathode kinetics \((k^0, \beta)\)
    ➔ Development of new catalysts
  - Structural parameters \((\epsilon, \tau, A^V)\)
    ➔ Optimization of GDE structure

➔ Validated 1D model as design tool
V. Electrode and cell design – Precipitation in aqueous Li-O₂ batteries


- Classical theory of nucleation and growth
  \[ \text{Li}^+ + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons \text{LiOH} \cdot \text{H}_2\text{O}^{(s)} \]

(a) Nucleation on *surfaces*
  ➔ Porous separator

(b) Nucleation on *dust* particles
  ➔ Bulk separator

 ➔ Precipitation mainly on anode side

III. Modeling and simulation – Precipitation in aqueous Li-O₂ batteries

- Evaluation of battery design
  - **Flooded** electrodes best at low rates
  - **Gas Diffusion Electrodes** best at high rates
  - **Bulk separator** superior at very high rates

→ Precipitation as engineering task

→ Design depends on operating conditions
IV. Summary

- Model experiments on Ag GDEs
  - Parameterization and validation

- FIB-SEM for electrode reconstruction
  - Structure determination

- Lattice-Boltzmann simulations
  - Multiphase flow

- Detailed model of precipitation in aqueous Li-O₂ batteries
  ➔ Operating conditions determine battery design

- Validation of transport model
  ➔ Good qualitative agreement

Thank you for your attention!