Insights on the operation of Me-S batteries: a modeling perspective

Timo Danner¹,², Raphael Richter¹,², Joachim Häcker¹, Brigitta Sievert¹, Norbert Wagner¹, K. Andreas Friedrich¹, Arnulf Latz¹,²,³

¹ Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany; ²Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU) and ³Institute of Electrochemistry, University of Ulm, Ulm, Germany

**Motivation**

Development, understanding & rational design of Metal-Sulfur batteries

**Mg-Sulfur batteries:**
- High volumetric energy density
- Low rate performance
- Cheap & abundant materials
- Short cycle life

→ Transfer of knowledge & methodologies from Li-Sulfur

**Cell model** [1]

**Electrolyte**

Mass conservation:
\[ \frac{\partial \varepsilon_{\text{elode}}}{\partial t} = -P_{\text{elode}} + \sum_{m} a_{m}^{n} v_{m,\text{elode}} r_{m} \]

Charge conservation:
\[ \sum_{m} a_{m}^{n} v_{m,\text{elode}} r_{m} = 0 \]

Species flux by Nernst-Planck equation (Diffusion + Migration):
\[ N_{i} = -D_{i} F C_{i} \frac{\partial C_{i}}{\partial x} + \frac{F}{RT} D_{i} C_{i} F \text{volta} \]

**Solids** (charge conservation)

\[ 0 = -\varepsilon_{\text{elode}} F \text{volta} - \sum_{m} a_{m}^{n} v_{m,\text{elode}} r_{m} \]

Reaction rate (Butler-Volmer-Type):
\[ \gamma_{m} = k_{\text{cat}}^{\text{eff}} \text{volta}^{\sigma} \exp \left( -\frac{E_{\text{a}}}{RT} \right) \]

**Particle model** [2]

→ The whole cell model in a spherical particle

→ Coupling to cell model

- Electrolyte: Mass & charge conservation:
  \[ \frac{\partial n_{m}}{\partial t} = -D_{m} \frac{\partial^{2} n_{m}}{\partial r^{2}} + \frac{F}{RT} D_{m} C_{m} F \text{volta} \]
  \[ \frac{\partial C_{m}}{\partial t} = \frac{F}{RT} \frac{\partial n_{m}}{\partial x} \]

- Carbon matrix: Same potential

**Nucleation & growth**

- Previous work [2]: Phenomenological treatment
  \[ \frac{\partial N_{b}(r)}{\partial t} = \frac{\partial}{\partial r} \left( \frac{\partial N_{b}(r)}{\partial r} \right) \]

- Surface passivation: \( a_{m}^{n} = a_{m}^{n,\text{eff}} \) (Butler Volmer)

- Pore clogging: \( \varepsilon_{\text{elode}} = 1 - \sum_{k} \varepsilon_{k} \)

- Now: Classical theory of nucleation & growth

Particle size distribution

\[ \frac{\partial N_{b}(r)}{\partial t} = \frac{\partial}{\partial r} \left( \frac{\partial}{\partial r} \right) \]

**Li-S cell simulation**

- Discharge & charge simulations
  - Initially homogeneous Sₙ particle size distribution & no Li-S
  - Dissolution of Sₙ
  - Growth of LiS
  - Reverse processes during charge
  - No degradation: Reversible cycling

**Mg-S cell simulation**

- S/C composite cathode preparation
  - Milled vs. Melt infiltration
  - Cell model vs. Cell+particle model
  - Mg foil anode

- Electrolyte: Mg(HMDS)₂ / TEG:DEG [4]

- Capacity: Possible end product MgS₂

- Discharge mechanism?
  - Capacity: Possible end product MgS₂
  - Sloping potential in 2nd plateau
  - Surface passivation? (→ nucleation)
  - Viscosity effects? (no nucleation)
  - Experimental evidence needed!

- Infiltrated particles: Polysulfide 'bleeding' & shuttle

- Polysulfides 'escape' from particles
  - Surface loss: particles decreases
  - Polysulfide migration towards anode
  - MgS₂ film on particles increases
  - Formation of MgS₄ on anode surface

- Capacity loss

**References**