Flow Battery Modeling

Energy Storage Systems Peer Review
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**Flow Battery Modeling**

**Schematic of a Flow Battery**

**PURPOSE:** The flow battery modeling task seeks to improve fundamental understanding and enable high-performing, low-cost designs of flow batteries through the development of mathematical models implemented for numerical simulation of electrochemically reactive flow.

**IMPACT:** Models provide a virtual laboratory for design and optimization, enabling:
- Improved performance and safety
- Lower cost of battery development
- Development of new designs using new materials and configurations

**Key Features of a Flow Battery**
- Scalable for grid energy storage and renewable load leveling
- Independently tunable power and capacity
- Short response time
- Long cycle life
- Potential high efficiency
- Low self-discharge
How models can improve battery development

- Engineer improvements in existing designs
- Explore new designs on a computer, rather than in the lab.
- Explore the performance of new materials (e.g. ionic liquids) and advanced physics (gas generation)

**Engineer designs:**
- flow distribution
- flow rate schedule
- analysis of losses (ionic, thermal, pumping …)

**Chemistry:**
- general aqueous chemistries
- ionic liquids
- side reactions

**Performance:**
- self-discharge (cross-contam.)
- shunt current (stack model)
- new porous electrode materials

**Pore-scale electrode models**
- Flow speed
- Species concentration
Key Accomplishments

- *Developed a general cell-level flow battery finite element modeling capability including:*
  - general multi-species electrolyte flow and electrochemistry
  - Nernst-Planck species migration
  - current flow through porous carbon electrode, membrane and electrolyte
  - Butler–Volmer reaction kinetics for transfer current

- *Validated model with All-Vanadium FB data and model*

- *Applying model for design improvements of All-Vandium FB*
  - Analysis of model parameters affecting performance
  - Characterization of efficiency losses
  - Improved flow distribution
Our model development approach combines SNL simulator development and Comsol applications

- Flow battery model was developed in SNL Sierra simulator
- Sierra provides access to advanced multiphysics and numerics
  - parallel processing
  - multiphase flow
  - multiphysics coupling (e.g. thermal energy, solid mechanics)
- Comsol provides
  - quick access to electrochemistry/flow modeling capability and
  - model verification via code comparison

Cell-Level Flow Battery Model (Porous Electrode Type)

Sierra Redox Flow Battery Development:
- FE implementation
- charged ion transport & electrochemistry
  - Nernst Planck ion migration
  - Butler–Volmer reaction kinetics
- fluid flow (porous and/or single phase)
  - averaged forms of NP and BV
- current flow (ohmic & ionic)
  - DG for discontinuity in potential (plating)
SIERRA provides enabling capability for multiphysics modeling

SIERRA
FE application Framework and code services

Services provided to mechanics applications:

- Mesh & field data management (parallel, distributed)
- Transfer operators for mapping field variables between grids
- Solution control for code coupling
- Can includes third party libraries (e.g. solver libraries, etc.)
All-Vanadium Flow Battery Model

- current transport
- ohmic and ionic transport
- porous flow
- ion migration
- electroneutrality
- current transfer

\[ \phi = 0 \text{ V} \]

- species flux
- bulk flow rate

- electrode
- membrane
- tank volume
- flow rate
- porosity
- fiber diameter
- tank volume

Ref: Shah, Watt-Smith, and Walsh (2008)
All-Vanadium Porous Flow Battery System

Start-up of charge cycle

V(III) + e⁻ ⇌ V(II)

\[
\begin{align*}
V &\quad \text{V}^4 \\
V + O^{2+} + 2H_2O &\quad \text{V}^5 \\
&\quad \text{VO}^{2+} + 2H^+ + e^- \\
\end{align*}
\]

Inlet conditions (mol/m³):

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<td>VII</td>
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Time: 0.000000
Spatial distribution of current and species

\[ \nabla \cdot \mathbf{i} \]

transfer from solid to electrolyte

\[ V(III) + e^- \rightleftharpoons V(II) \]

\[ \sqrt[4]{4} \quad \sqrt[5]{5} \]

\[ VO^{2+} + 2H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^- \]
Spatial distribution of current and species (discharge)
Modeled Battery Characteristics

Model Validation: Comparison to Walsh data

Charge – Discharge Cycle All-Vanadium RFB

Discharge
SOC = 80%

Figures of Merit
Efficiency & Losses

Model can be used to:
• predict round-trip efficiency
• energy efficiency
• heat losses, ...

as a function of concentration, discharge rates, ...

1 mL/s  flow rate
0.68  porosity
10 micron  fiber diameter
250 mL  tank volume

\[ \eta_e = \frac{\int iV \, dt}{\int iU \, dt} \]
During recharge, $\text{O}_2(g)$ may be formed at high overpotential, especially at the end of a recharge stage.

Cantera thermodynamics package is used to model the competition of the $\text{V}^{4+}$ to $\text{V}^{5+}$ reaction with $\text{O}_2(g)$ production.

Finite overpotentials (over-charging) can drive $\text{O}_2(g)$ production at the end of the recharge stage.

$$\text{V}^{2+} + 2\text{H}^+ + e^- \rightleftharpoons \text{V}^{4+} + \text{H}_2\text{O}$$

$$\frac{1}{2}\text{O}_2(g) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}$$
Current and Future Tasks

- Explore improvements in existing designs and advanced physics of Vanadium RFB
  - Analysis of model parameters affecting performance
  - Characterization of efficiency losses
  - Alternate designs for improved performance

- Support of SNL ionic liquid flow battery
  - Expand the model for alternate chemical systems (e.g. ionic liquid chemistries)
  - Apply the ionic liquid FB model to help design a low cost, high performing SNL ionic flow battery

- Support of ESS flow battery development through synergistic collaborations
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COMSOL model of negative electrode:  
Charge cycle (30 min) showing production of V2 & V5  

*membrane flux uniform*  

\[ V(III) + e^- \rightleftharpoons V(II) \]

\[ VO^{2+} + 2H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^- \]