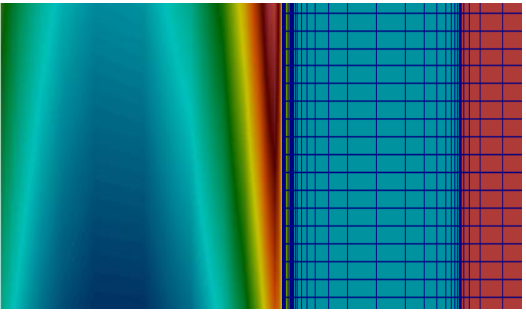

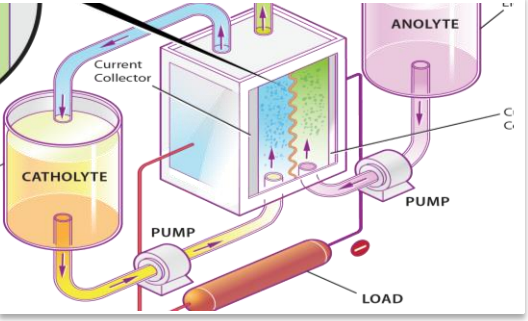

Flow Battery Modeling

Energy Storage Systems Peer Review

September 26-28, 2012

MJ Martinez (PI), J Clausen, SM Davison, HK Moffat

Sandia National Laboratories

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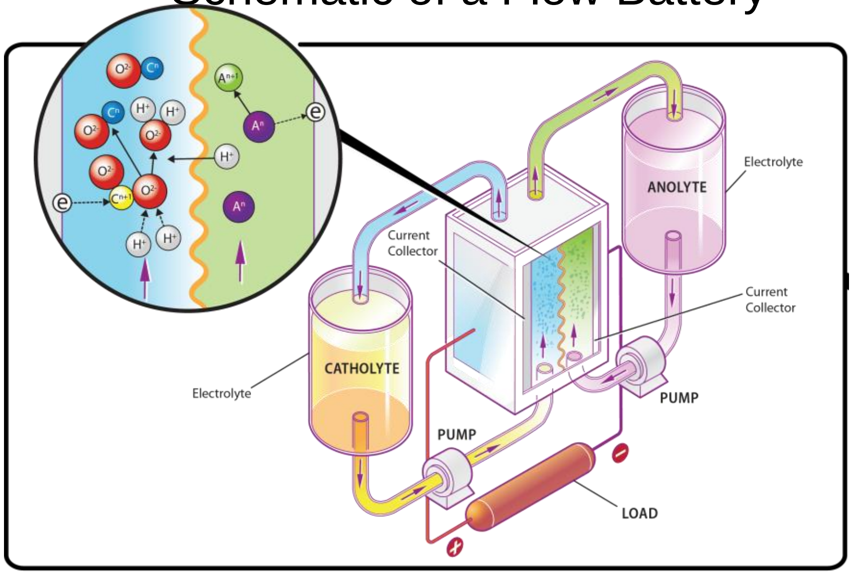
Flow Battery Modeling

Sandia National Laboratories

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.

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

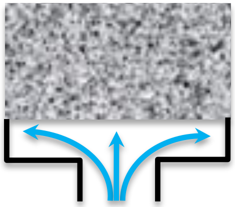
IMPACT: Models provide a virtual laboratory for design and optimization, enabling:

- Improved performance and safety
- Lower cost of battery development
- Development of new designs using new materials and configurations

How models can improve battery development

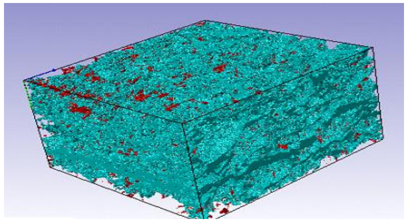
- Engineer improvements in existing designs
- Explore new designs on a computer, rather than in the lab.
- Explore the performance of new materials (e.g. ionic liquids) and advanced physics (gas generation)

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

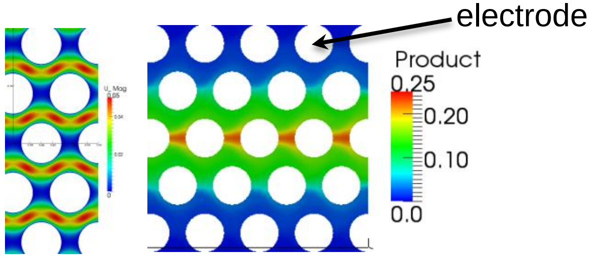


Chemistry:
• general aqueous chemistries
• ionic liquids
• side reactions

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



Pore-scale electrode models



Flow speed Species concentration

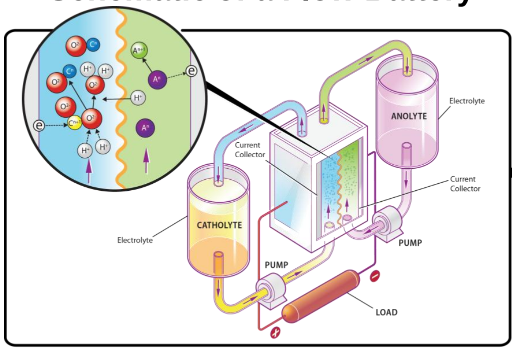
Key Accomplishments

- ***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*

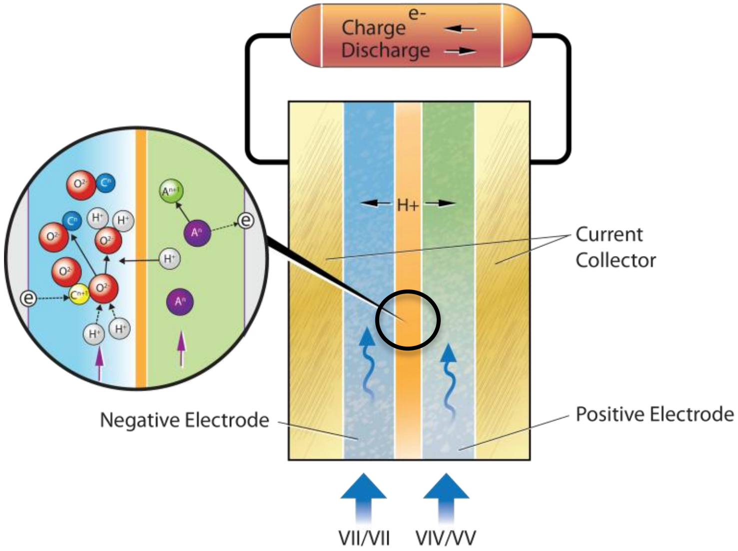
Our model development approach combines SNL simulator development and Comsol applications

- 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

Schematic of a Flow Battery



Cell-Level Flow Battery Model
(Porous Electrode Type)

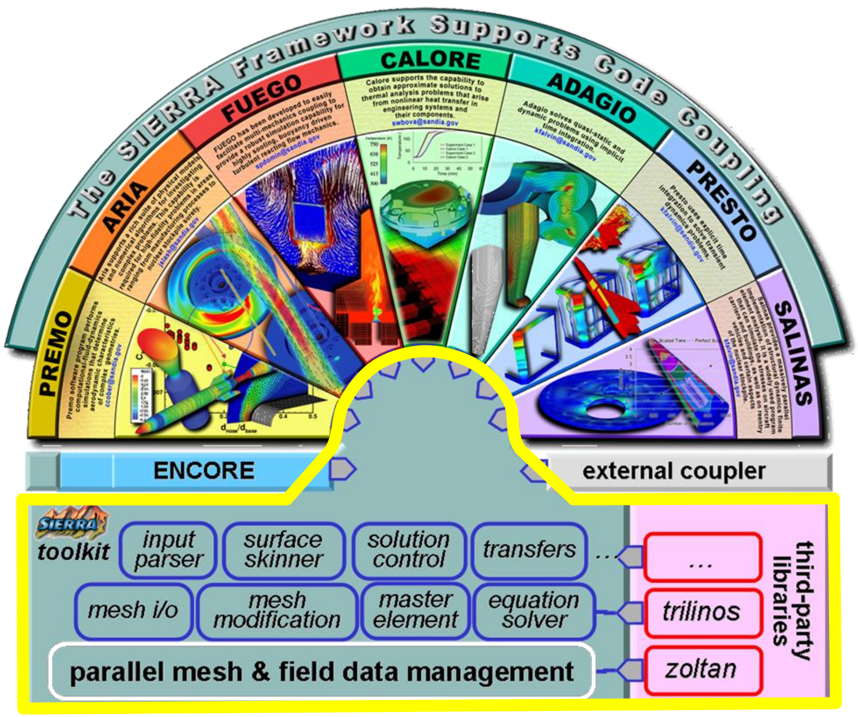


<u>Sierra Redox Flow Battery Development</u>:

- 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)

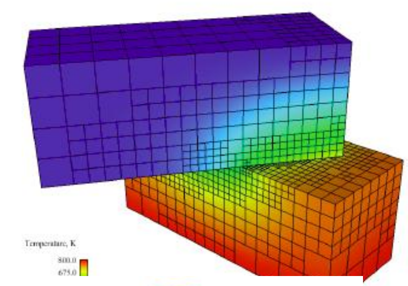
SIERRA provides enabling capability for multiphysics modeling

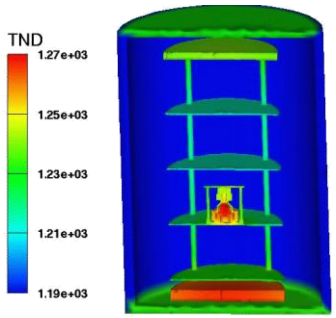
SIERRA
FE application Framework and code services

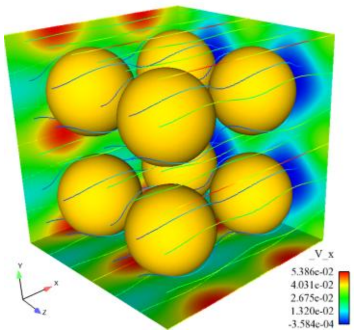


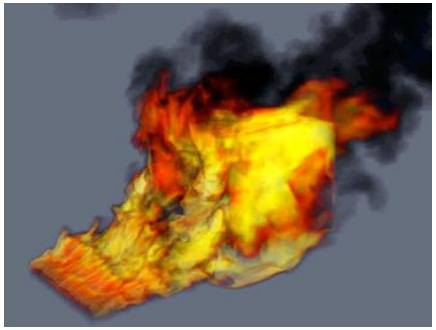
Services provided to mechanics applications:

- 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.)

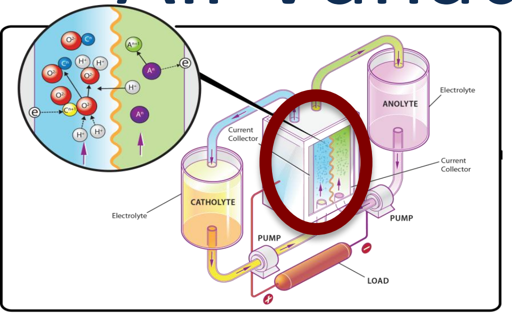








All-Vanadium Flow Battery Model



electrode

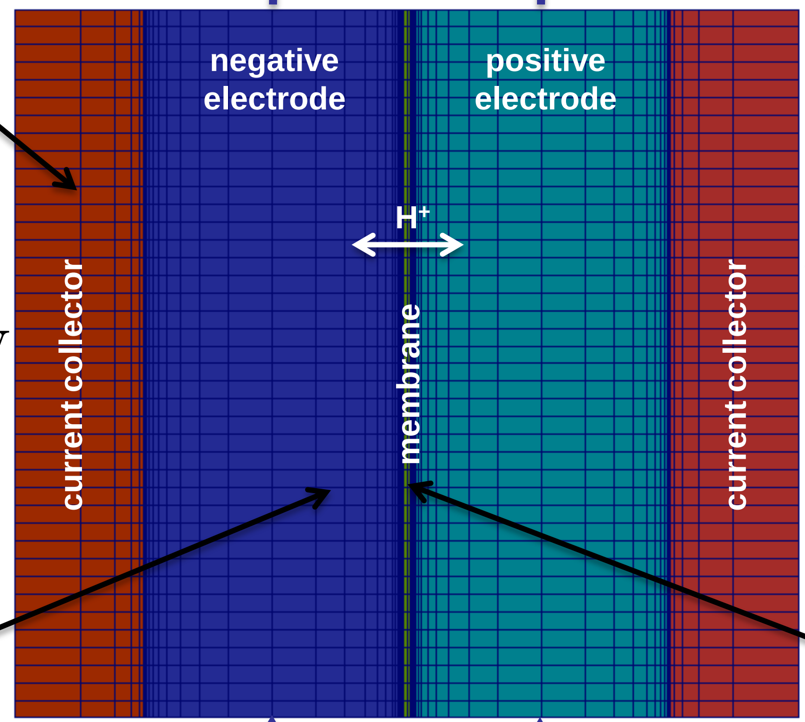
10 cm x 4 mm

membrane

180 microns

pressure specified
open species flux

• current transport



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

$\phi = 0 \text{ V}$

$i = 1000 \text{ A/m}^2$

• current transport (ohmic and ionic)
• porous flow
• ion migration
• electroneutrality
• current transfer

•ion transport

VII/VII

VIV/VV

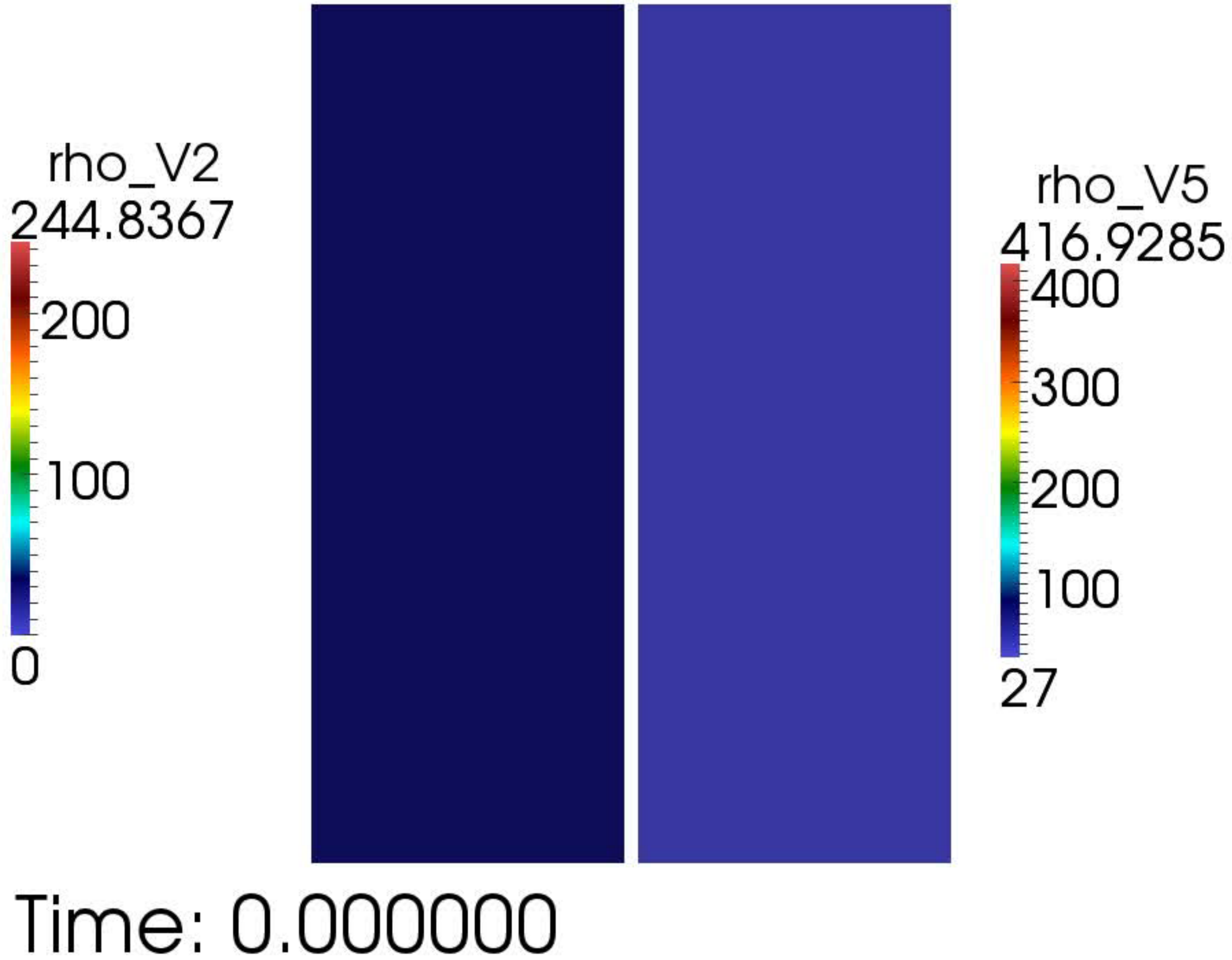
species
bulk flow rate

Ref: Shah, Watt-Smith, and Walsh (2008)

All-Vanadium Porous Flow Battery System

Start-up of charge cycle

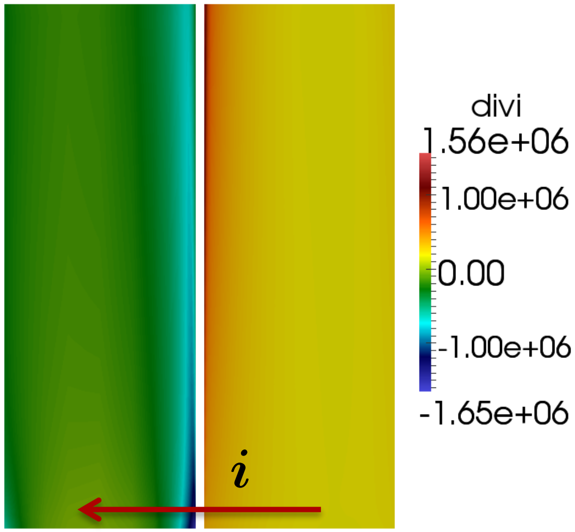
inlet conditions (mol/m^3)	
VII	27
VIII	1053
VIV	1053
VV	27

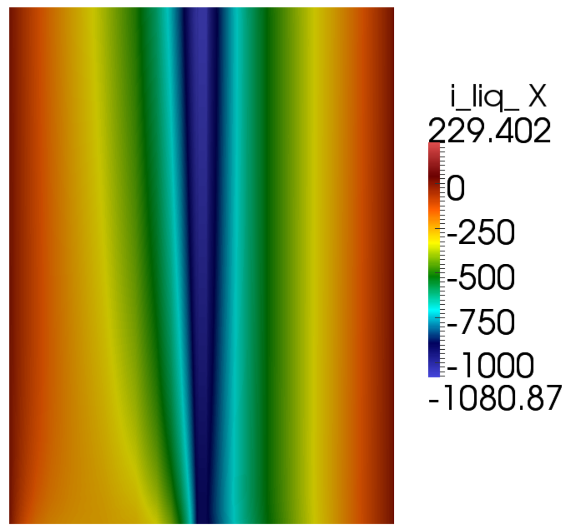


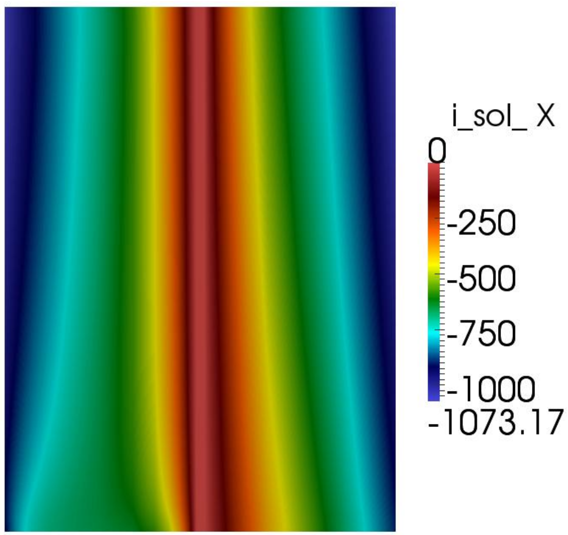
$$V(III) + e^- \rightleftharpoons V(II)$$

$$\overbrace{VO^{2+}}^{V4} + 2H_2O \rightleftharpoons \overbrace{VO_2^+}^{V5} + 2H^+ + e^-$$

Spatial distribution of current and species





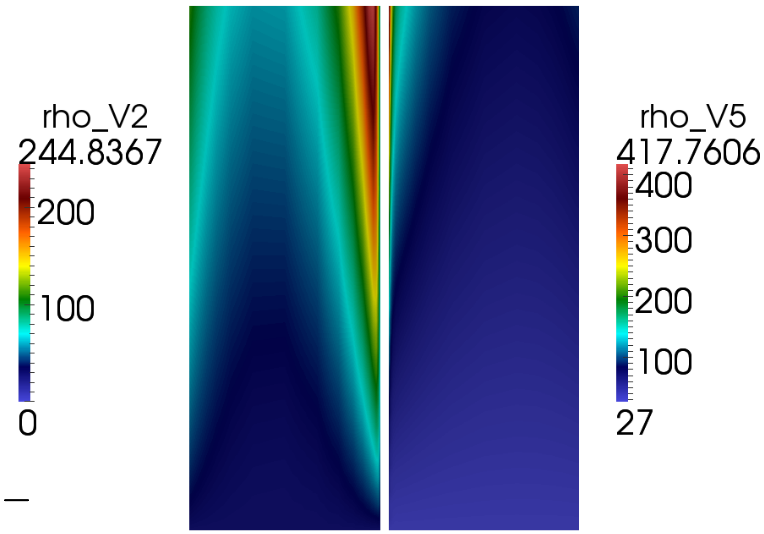


$$\nabla \cdot \boldsymbol{i}$$

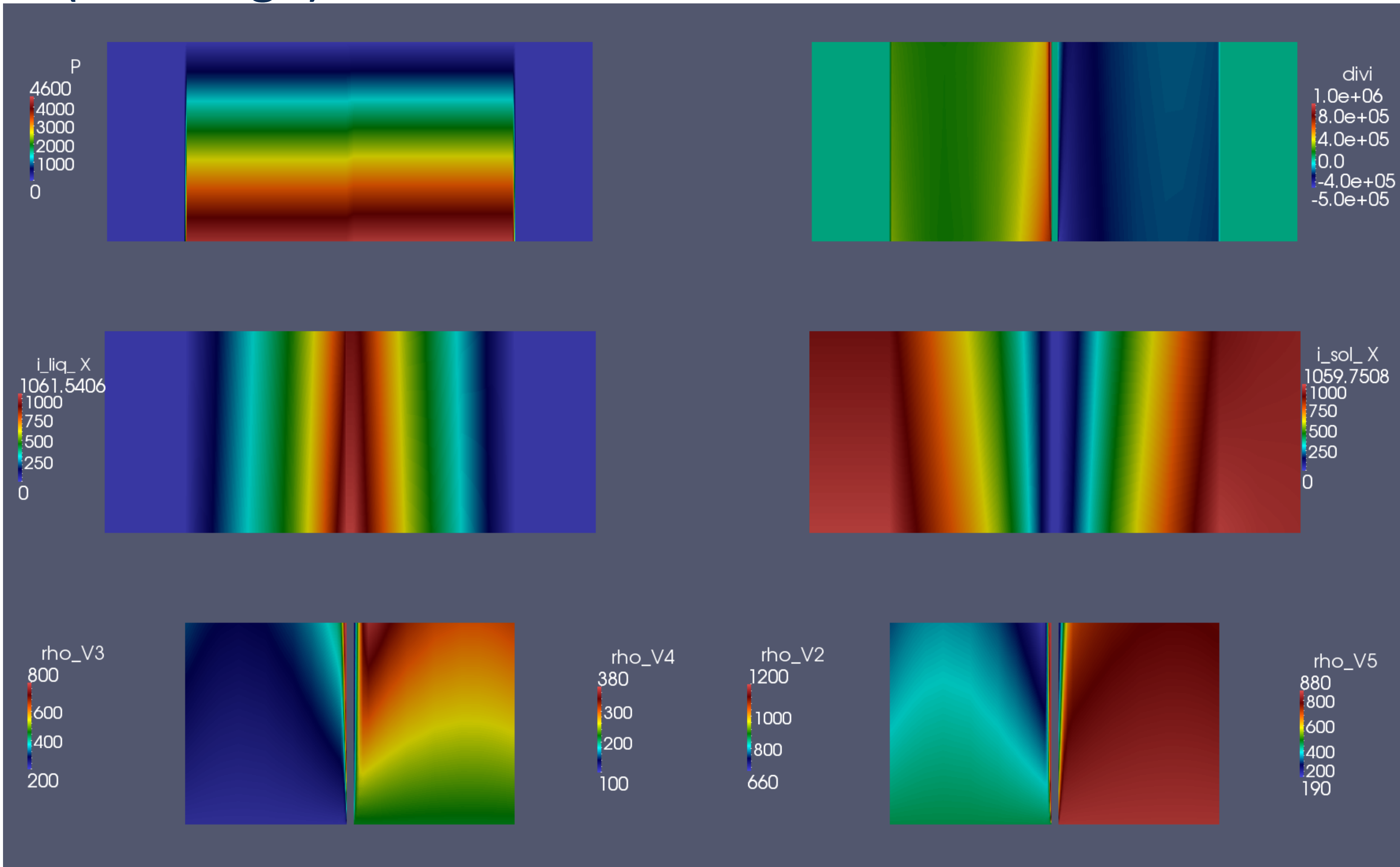
transfer from solid to electrolyte

$$V(III) + e^- \rightleftharpoons V(II)$$

$$\underbrace{VO^{2+}}_{V4} + 2H_2O \rightleftharpoons \underbrace{VO_2^+}_{V5} + 2H^+ + e^-$$



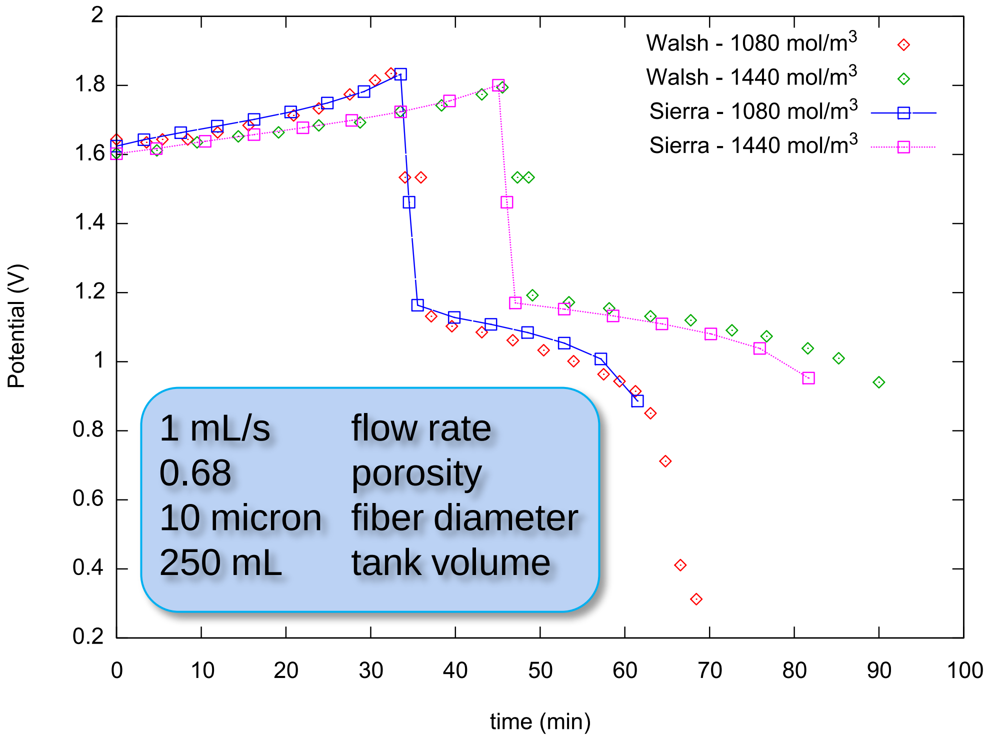
Spatial distribution of current and species (discharge)



Modeled Battery Characteristics

Model Validation: Comparison to Walsh data

Charge – Discharge Cycle All-Vanadium RFB



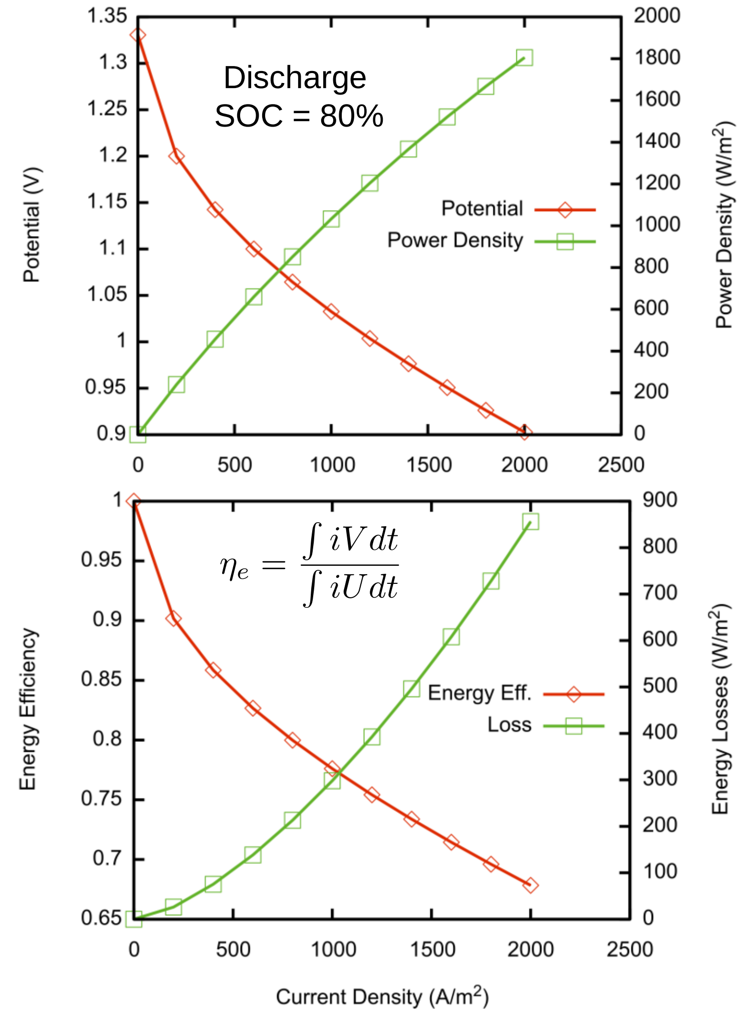
Model can be used to:

- predict round-trip efficiency
- energy efficiency
- heat losses, ….

as a function of concentration, discharge rates, …

Figures of Merit

Efficiency & Losses

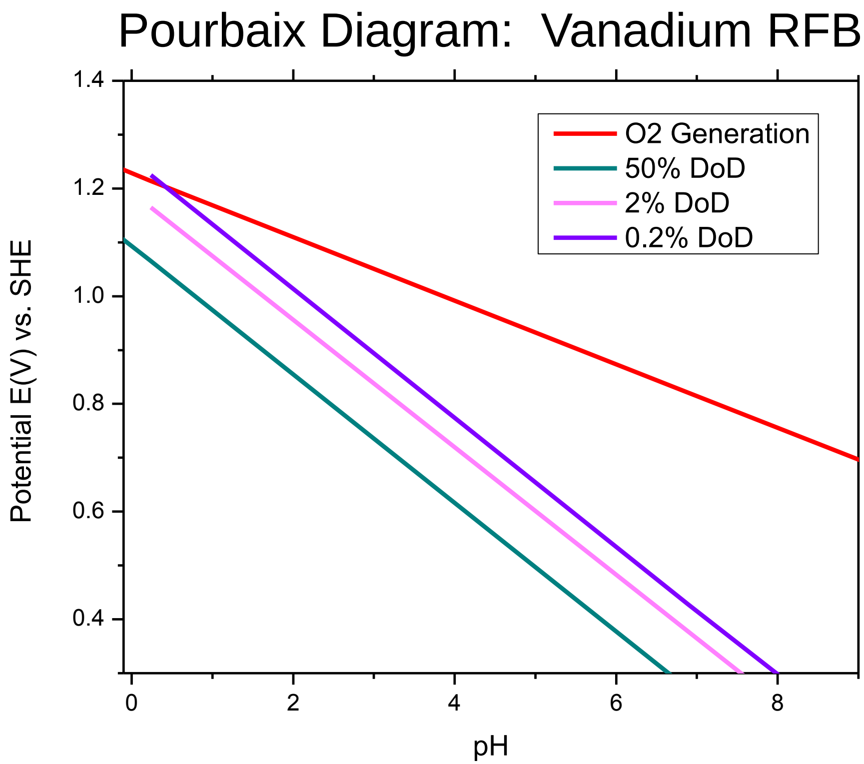


O_2(g) Generation at Positive Electrode of Vanadium RFB

During recharge, 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 V^{4+} to V^{5+} reaction with O_2(g) production.

Finite overpotentials (over-charging) can drive O_2(g) production at the end of the recharge stage.



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

$$\tfrac{1}{2}O_{2(g)} + 2H^{+} + 2e^{-} \rightleftharpoons H_2O$$

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

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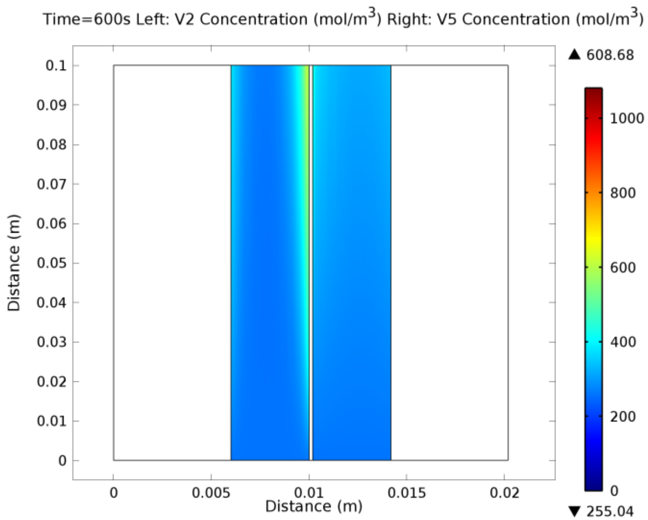

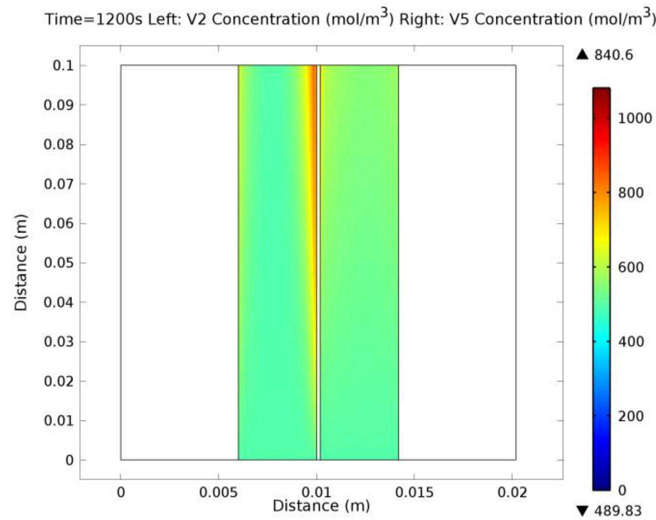

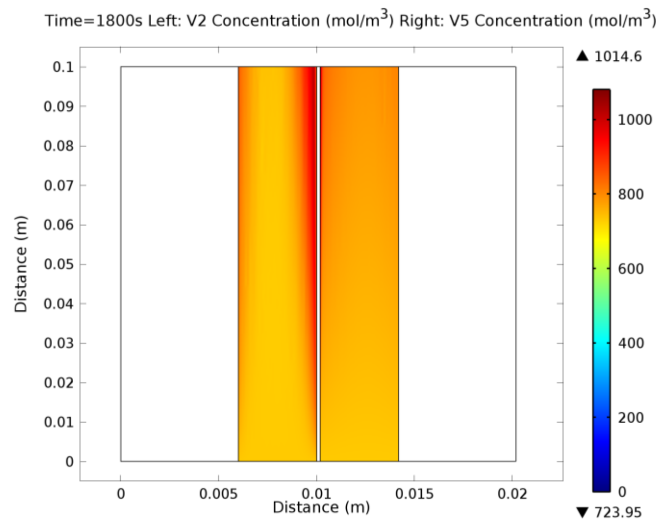

concentration shown every 10 min

**membrane flux uniform*

$$V(III) + e^- \rightleftharpoons V(II)$$

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