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Flow Battery Modeling

ECIS Energy Storage Project

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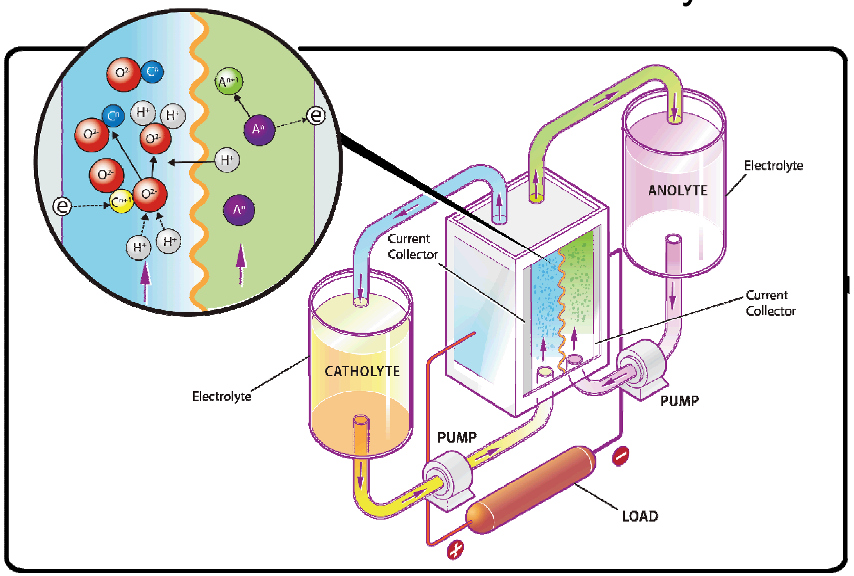
Schematic of a Flow Battery



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.

How Models Can Improve Flow 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 configurations (porous electrodes vs. activated plates)

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

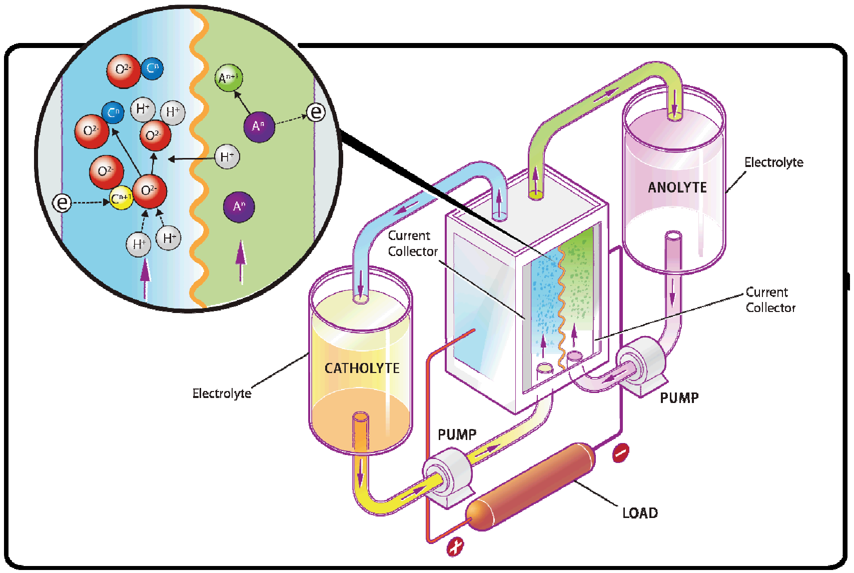
- Improved performance and safety
- Lower cost of battery development
- Development of new designs using new materials and configurations

Core Program New Start

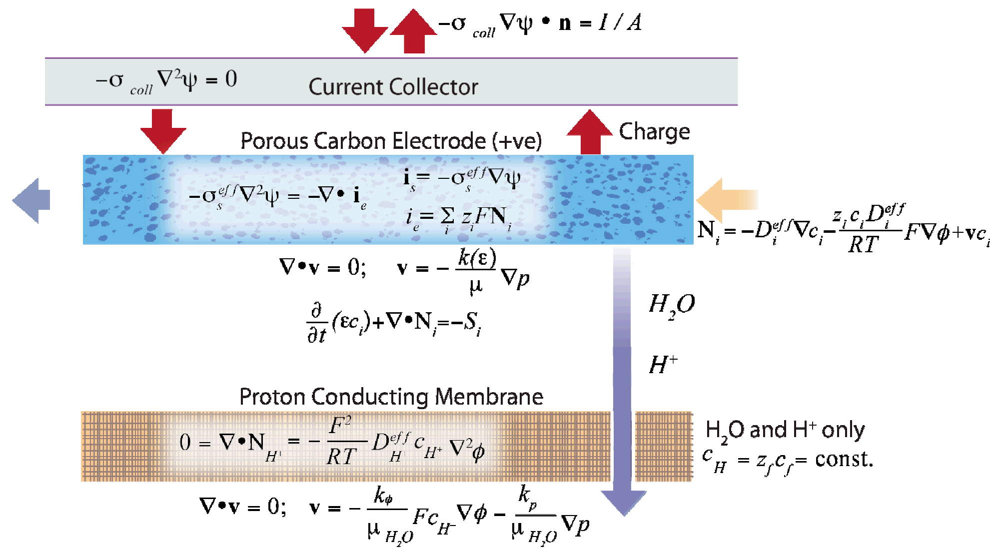
Sandia National Laboratories

Flow Battery Model

Schematic of a Flow Battery



Flow Battery Components Implemented in SNL Sierra Code



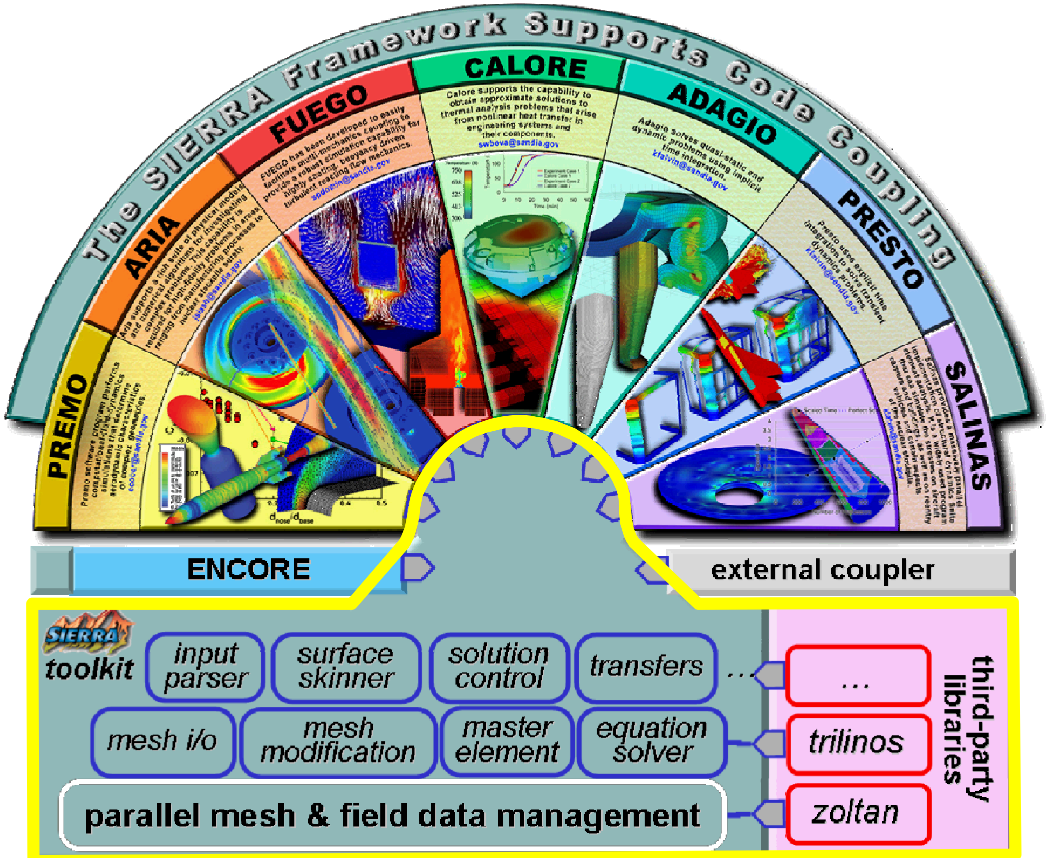
Our modeling approach combines SNL code development and commercial code applications

- Comsol provides quick access to electrochemistry/flow
- Sierra provides access to advanced multiphysics and numerics

SIERRA Mechanics represents enabling capability for suspension/slurry modeling

SIERRA_toolkit

FE application code services

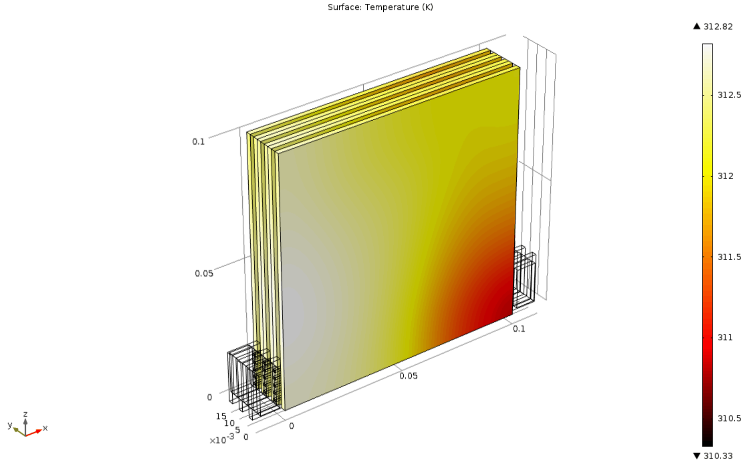


Services provided to mechanics applications:

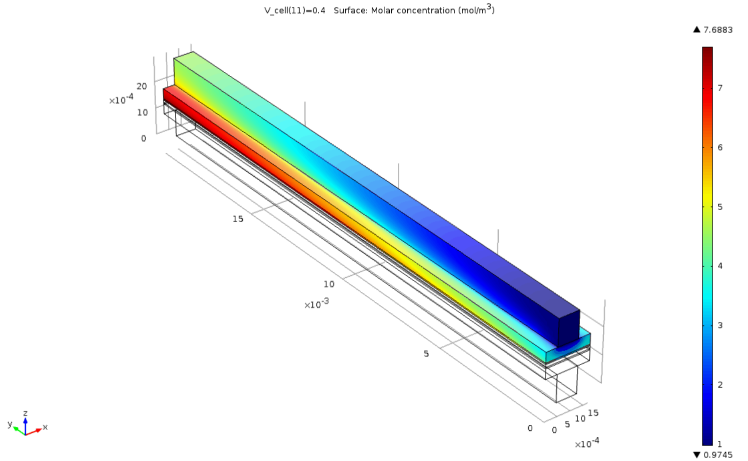
- Mesh & field data management (parallel, distributed)
- Transfer operators for mapping field variables from one mechanics to another
- Solution controller for code coupling: Arpeggio
- Includes third party libraries (e.g. solver libraries, MPI communications package)
- Accommodates heterogeneity

Comsol is a commercial finite element software package specializing in multiphysics couplings

- **Comsol includes predefined physics couplings for some batteries and fuel cells**
- **Comsol 4.2a was used to create a simplified model of the Vanadium flow battery**
- **Current distribution; species diffusion, migration, and convection; and porous fluid flow currently included**



Li-ion battery stack



PEM fuel cell

Initial Modeling Steps - Sierra

- **Nernst–Planck migration**

$$N_i = -\frac{F}{RT} z_i D_i c_i \nabla \phi - D_i \nabla c_i$$

- **current in electrolyte**

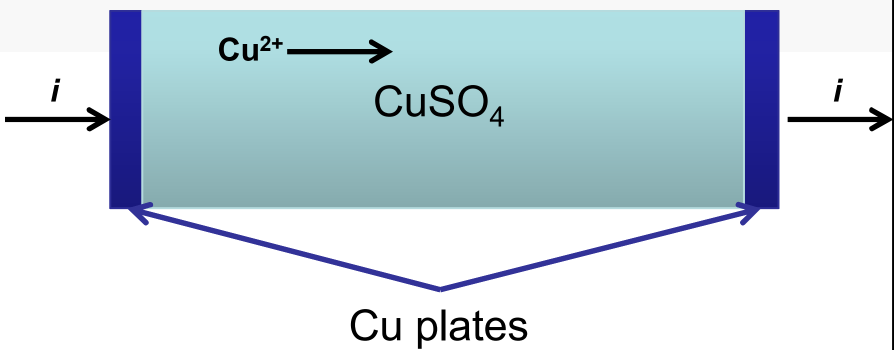
$$i = F \sum z_i N_i$$

- **condition of electroneutrality**

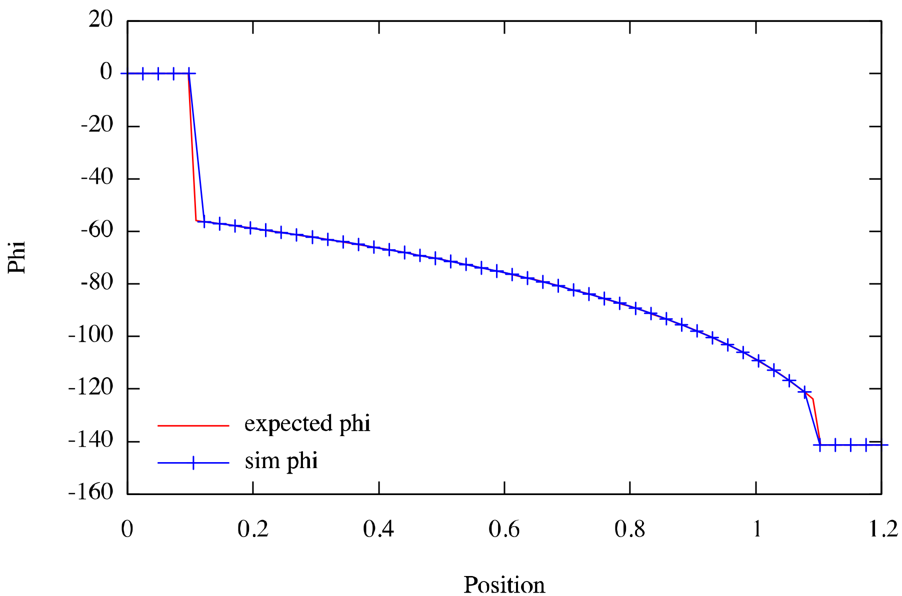
$$\sum z_i c_i = 0$$

- **above tested in non-porous binary electrolyte system**
- **Butler–Volmer kinetics at metal–electrolyte interface causing discontinuity in potential (voltage)**

test system

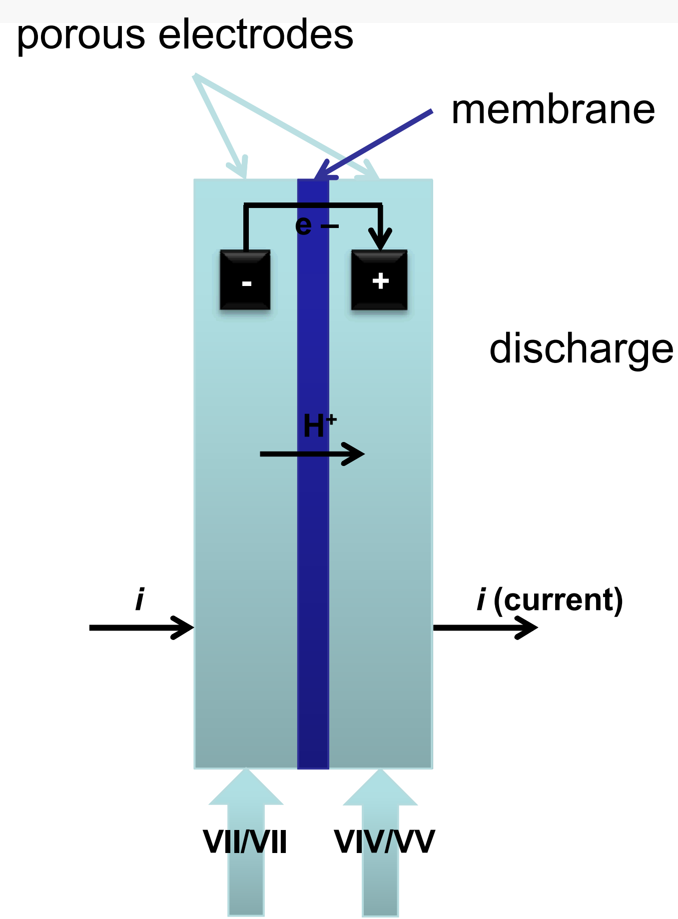


compared with analytical solution (nonphysical material properties)



Porous Flow Battery System
All-Vanadium

Ref. Shah, Watt-Smith & Walsh, 2008



Use reference solution from Shah et al. 2008 to:

- Learn how to model aqueous flow battery with Comsol
- Develop and implement flow battery model in Sierra/Aria multiphysics FE code

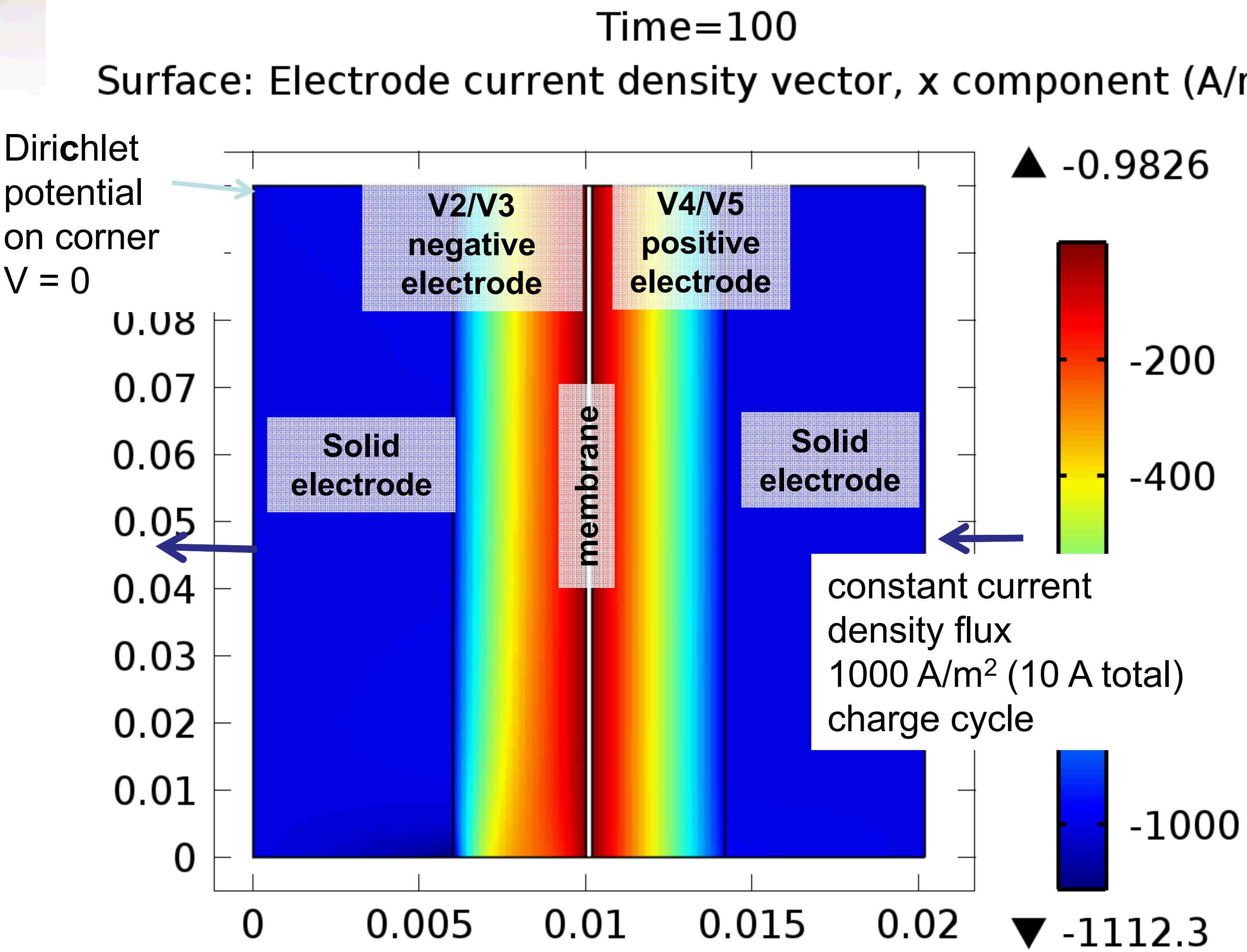
Some features:

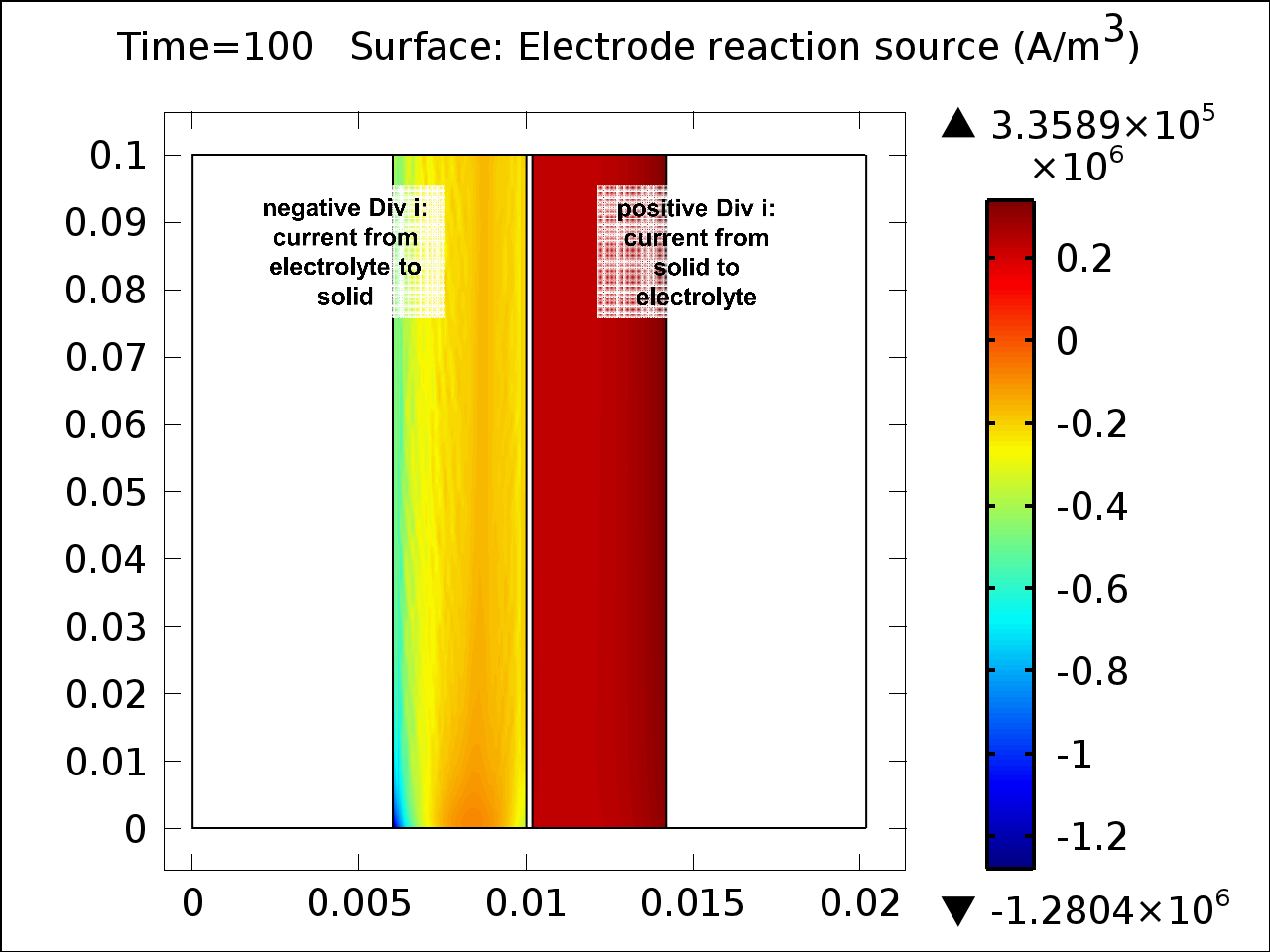
- Single-phase porous flow (multi species)
- Nernst–Planck species migration
- current flow through carbon electrode and electrolyte
- Butler–Volmer reaction kinetics to transport current from electrode to electrolyte

Simulation and Comparison Notes

- Problem solved with constant inflow concentrations (infinite sized tanks of electrolyte)
- Surface reactions not included
- Comsol models include the solid electrodes
- Comsol images follow; Aria and Comsol results compare well

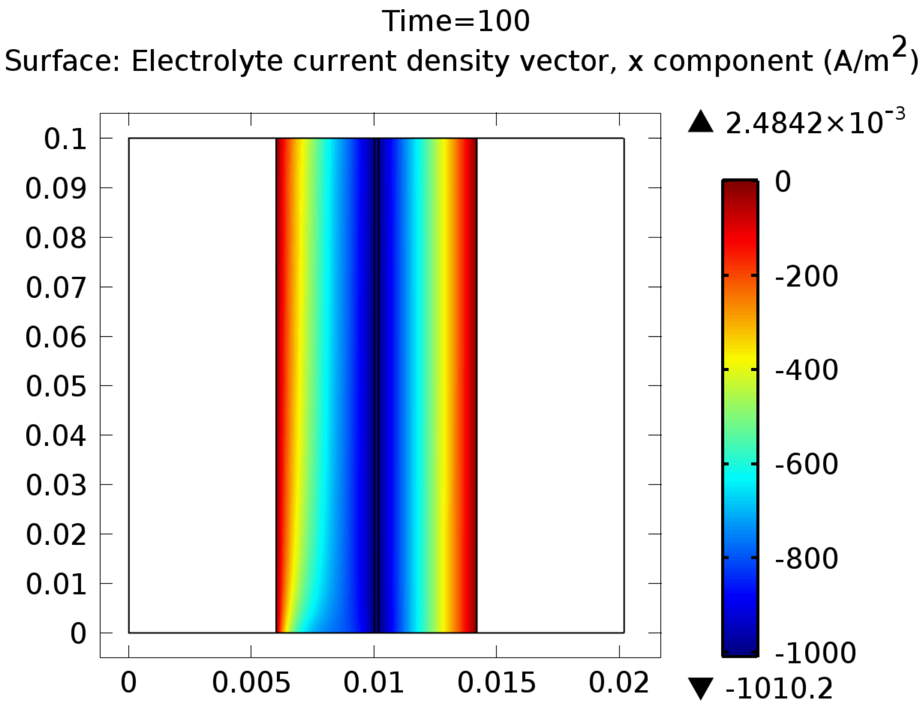
Comsol Results



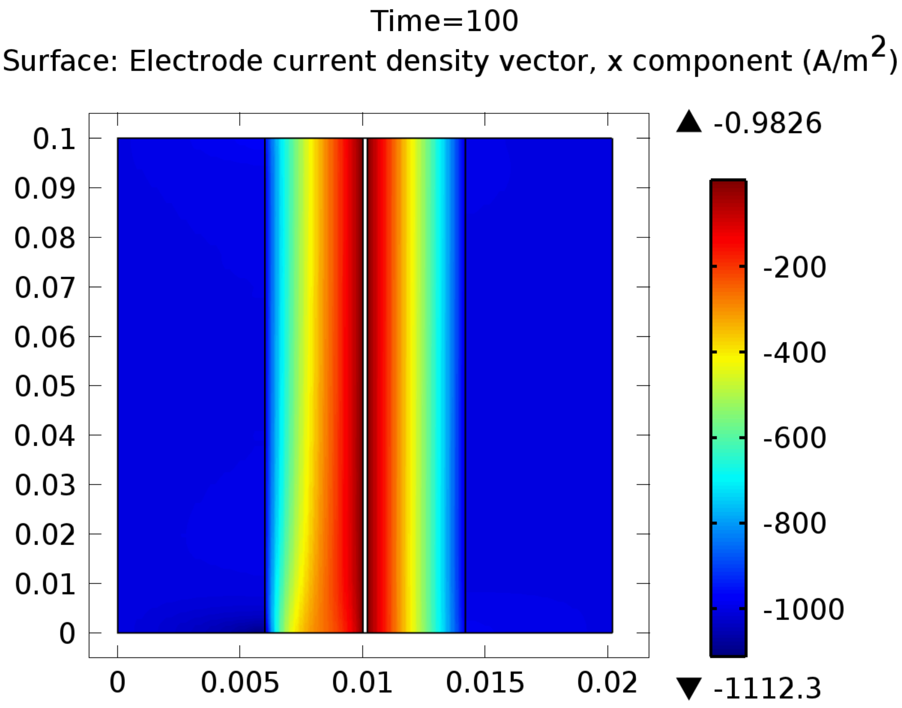

Time=100 Surface: Electrode reaction source (A/m3)
▲ 3.3589×10^5
×10^6
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
▼ -1.2804×10^6
negative Div i: current from electrolyte to solid
positive Div i: current from solid to electrolyte
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.005
0.01
0.015
0.02

Current Density

i_liquid_x



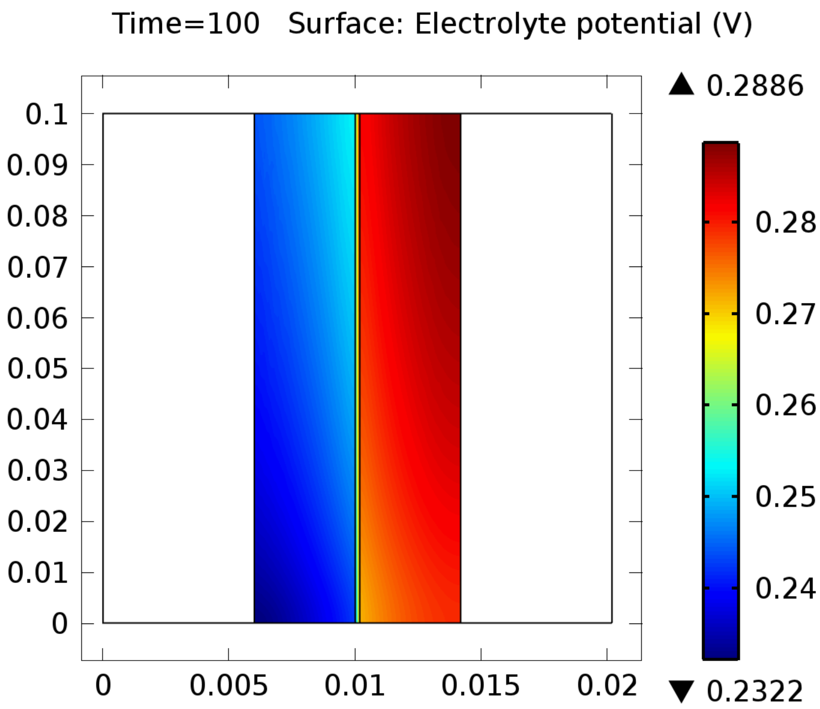
i_solid_x



Note the transfer of current between electrolyte and porous electrode

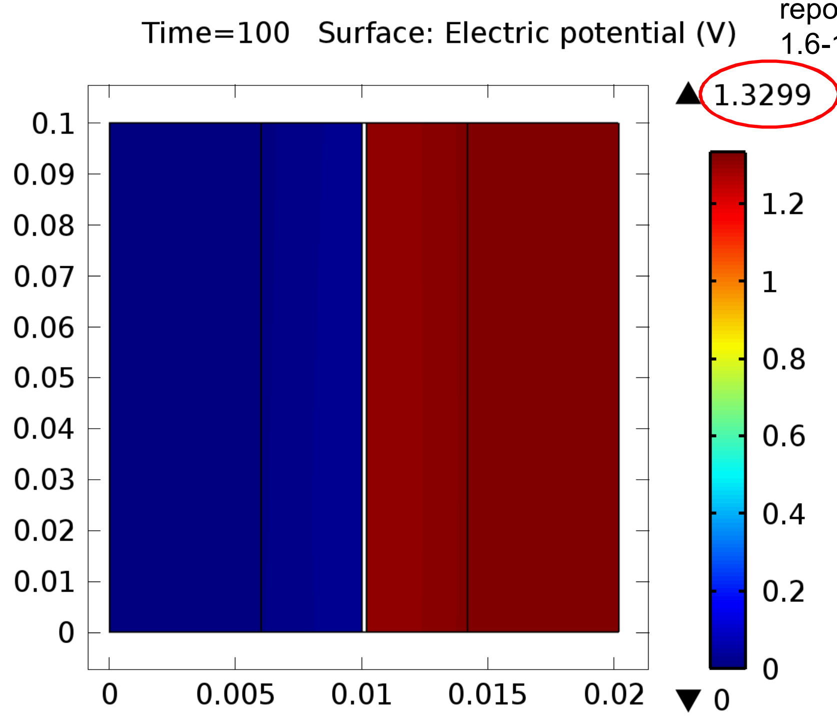
Electric Potentials

ϕ_{liquid}



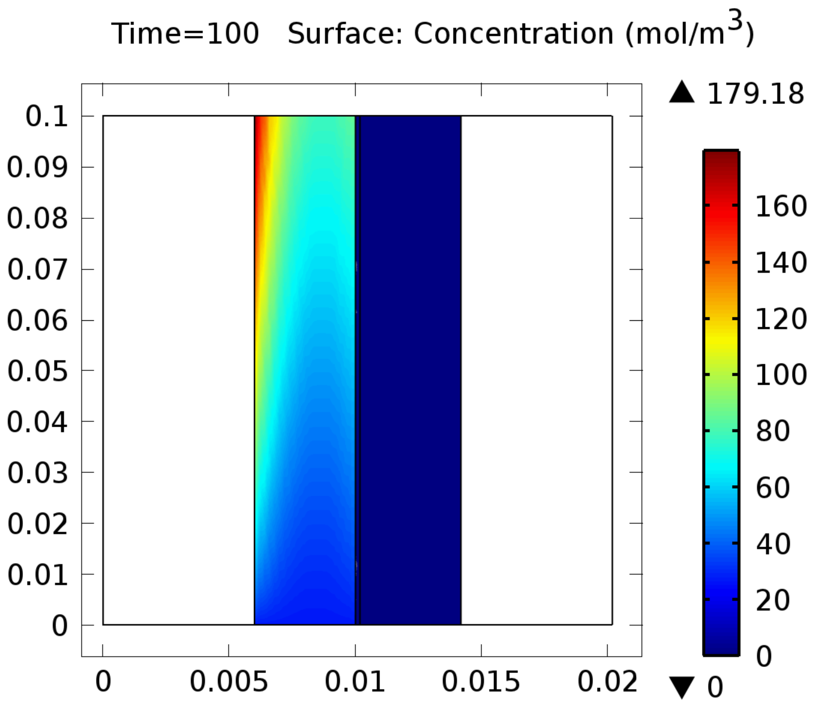
ϕ_{solid}

Shah et al report 1.6-1.8 V

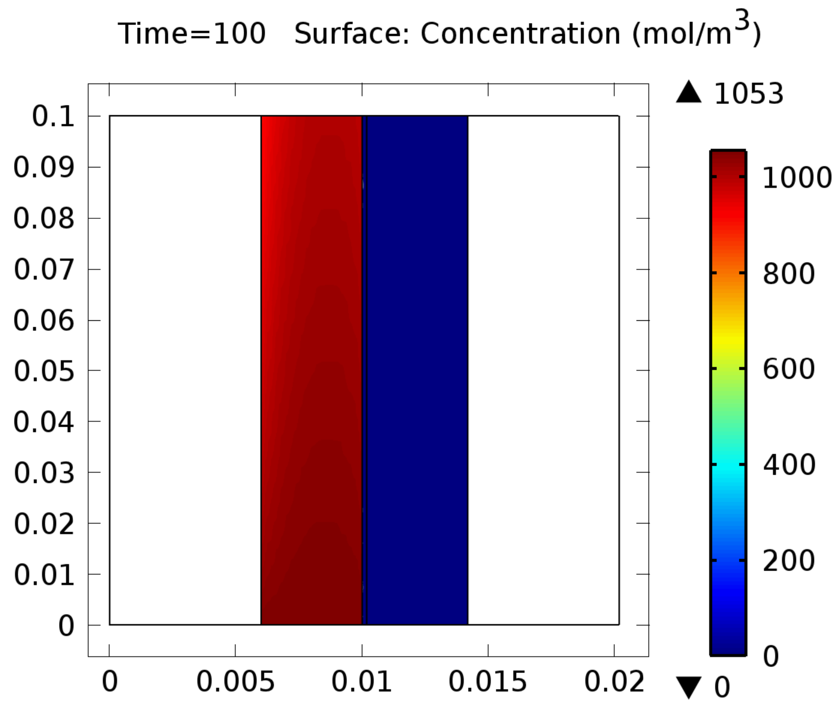


Concentration Distribution

C_{V2}

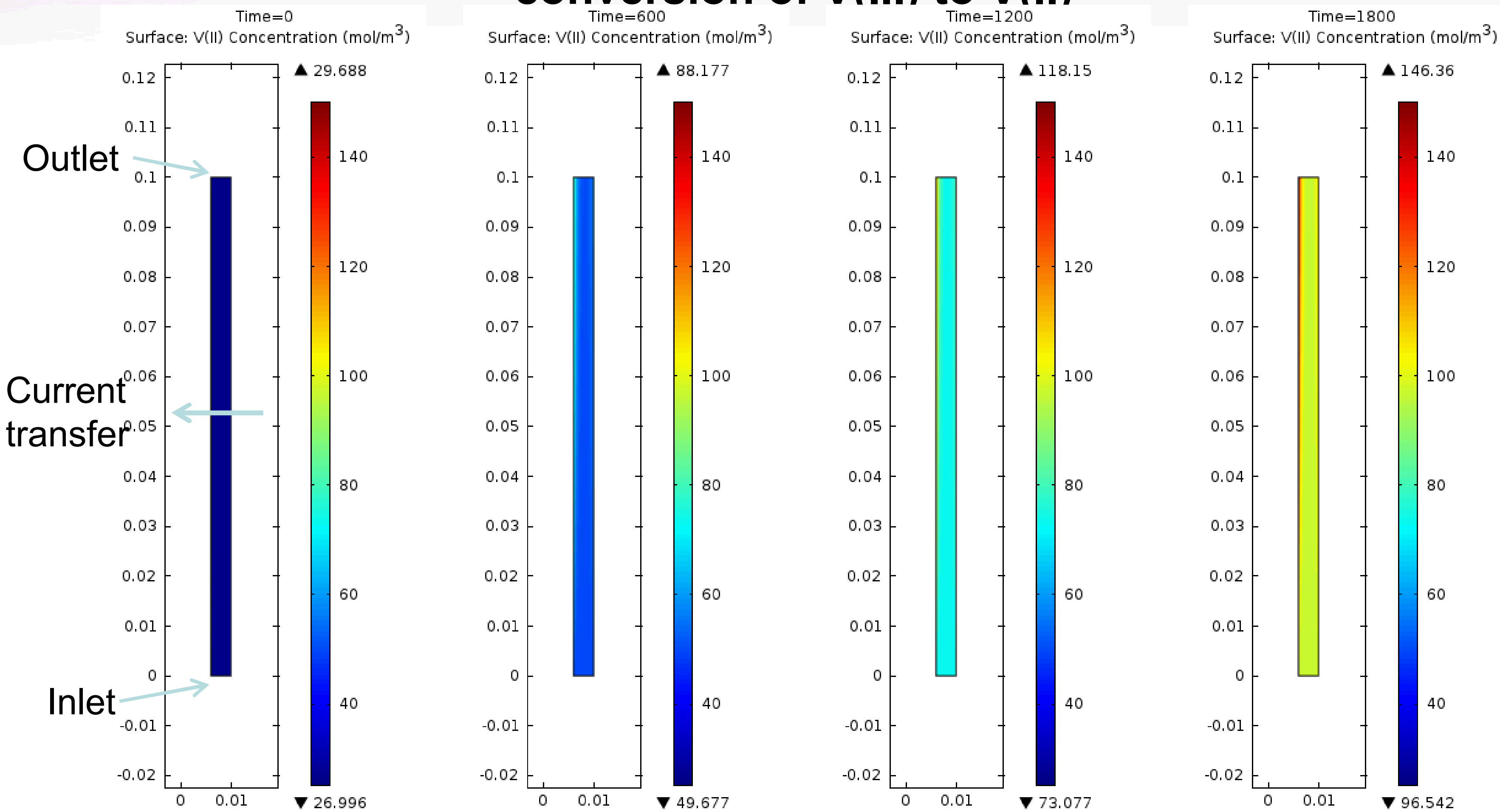


C_{V3}



COMSOL model of negative electrode:

Charge cycle (30 min) of the negative electrode showing the conversion of V(III) to V(II)



V(II) concentration shown every 10 minutes

Reaction during charge: V(III) + e → V(II)

Summary

Key Accomplishments:

•Comsol

•Vanadium flow battery model in verification stage (including tank model)

• Preliminary work with soluble lead-acid battery

•Sierra

• Electrochemistry implemented

• Verification: Cu – sulfate electrolytic cell , half-cell VFB

• all-Vanadium in verification stage

• Vanadium side reactions

•IL flow battery support initiated

Next:

• Apply model to build understanding and for design improvement of aqueous flow battery

• Analysis/modeling support of SNL ionic liquid flow battery (Travis Anderson).

Potential collaborations:

• Savinell (Case Western) – Iron based FB

• PNNL – advanced Vanadium FB

•Rick Winter (primus) – gas generation, two-phase flow

• General Atomics – soluble lead acid

• Steve Hickey (redflow) -- stack models, shunt current losses

• Andy Gewirth (Battery HUB) - SNL capabilities for slurries