Presented at the COMSOL Conference 2008 Boston

High-Temperature Sodium | Metal Chloride Storage Battery

Michael A. Vallance[*,1] and Ralph E. White[2]

[1]GE Global Research

[2]Department of Chemical Engineering, University of South Carolina

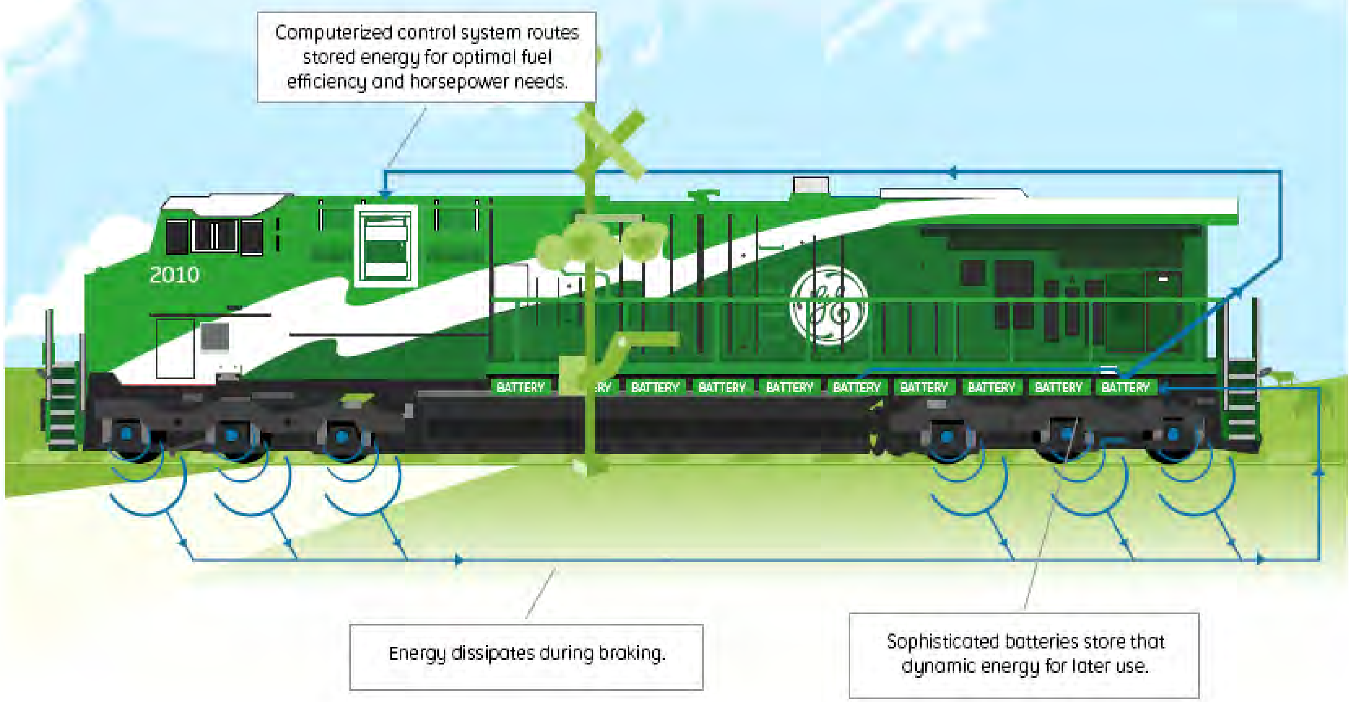
*One Research Circle
Niskayuna, NY 12309

vallance@crd.ge.com

imagination at work

UNIVERSITY OF SOUTH CAROLINA

- Up to 1.5 MW battery assist
- Up to 15% fuel savings
- $425 million potential annual savings (North America)



Electrochemical battery model required:

Mission simulation
Evaluate design options
Verify degradation modes

imagination at work

Battery Cell Description

Electrochemistry

Microstructure

Packaging

imagination at work

UNIVERSITY OF SOUTH CAROLINA

Cell Chemistry

Anode

$$Na\ (L) - e^- \xrightarrow[300°C]{\beta''\ \text{Alumina (BASE)}} Na^+$$

Cathode

$$FeCl_2\ (S) + 2\ e^- \xrightarrow[300°C]{NaAlCl_4\ \text{(STCA)}} Fe\ (S) + 2\ Cl^-$$

Net Cell

$$FeCl_2\ (S) + 2\ Na\ (L) \xrightarrow[300°C]{} Fe\ (S) + 2\ Na^+ + 2\ Cl^-$$

$$E^0 = 2.33\ V$$

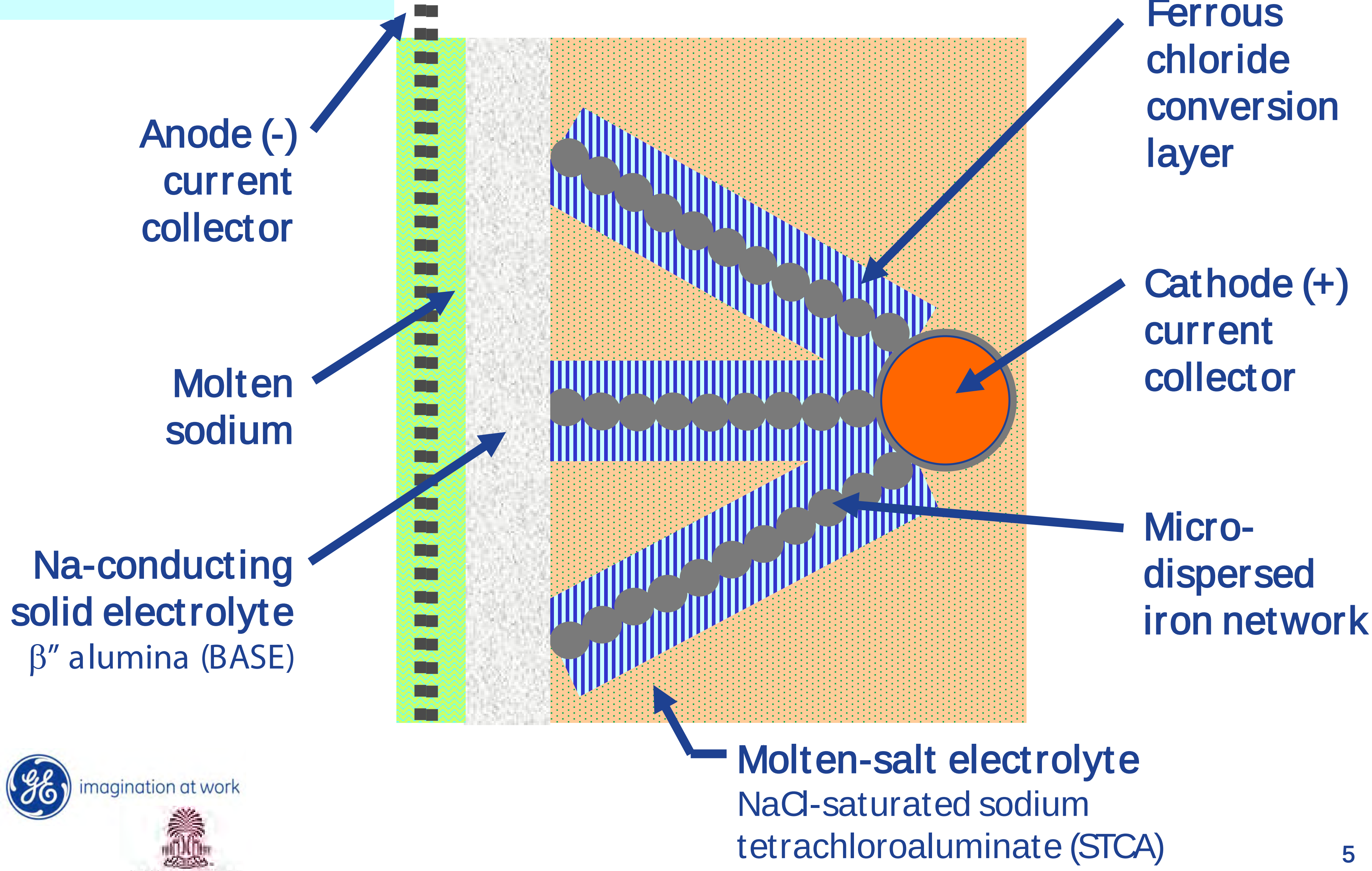
Sodium – Ferrous Chloride (Discharge Reaction)

imagination at work

UNIVERSITY OF SOUTH CAROLINA

Cell Structure

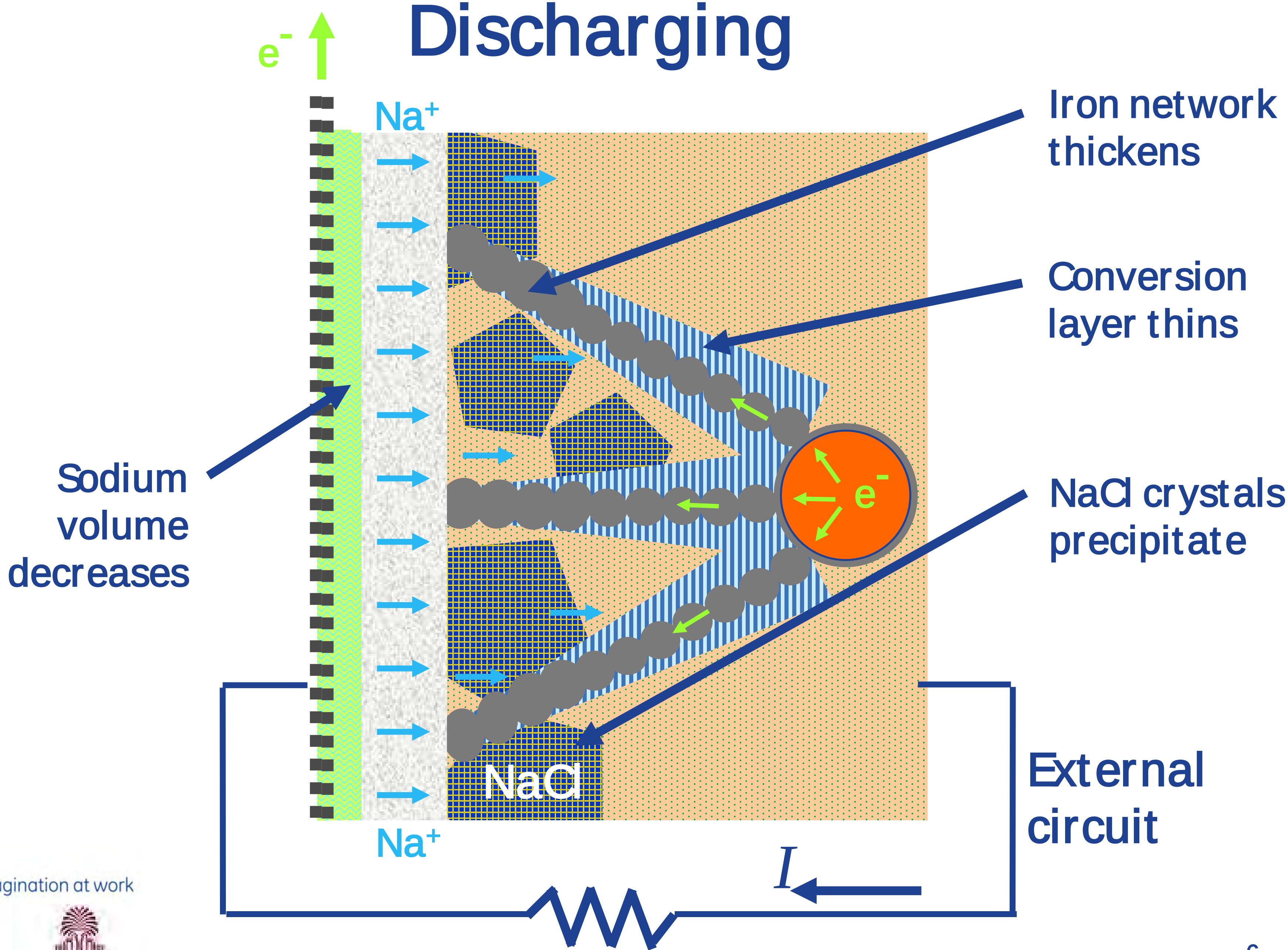
Fully Charged



imagination at work

UNIVERSITY OF SOUTH CAROLINA

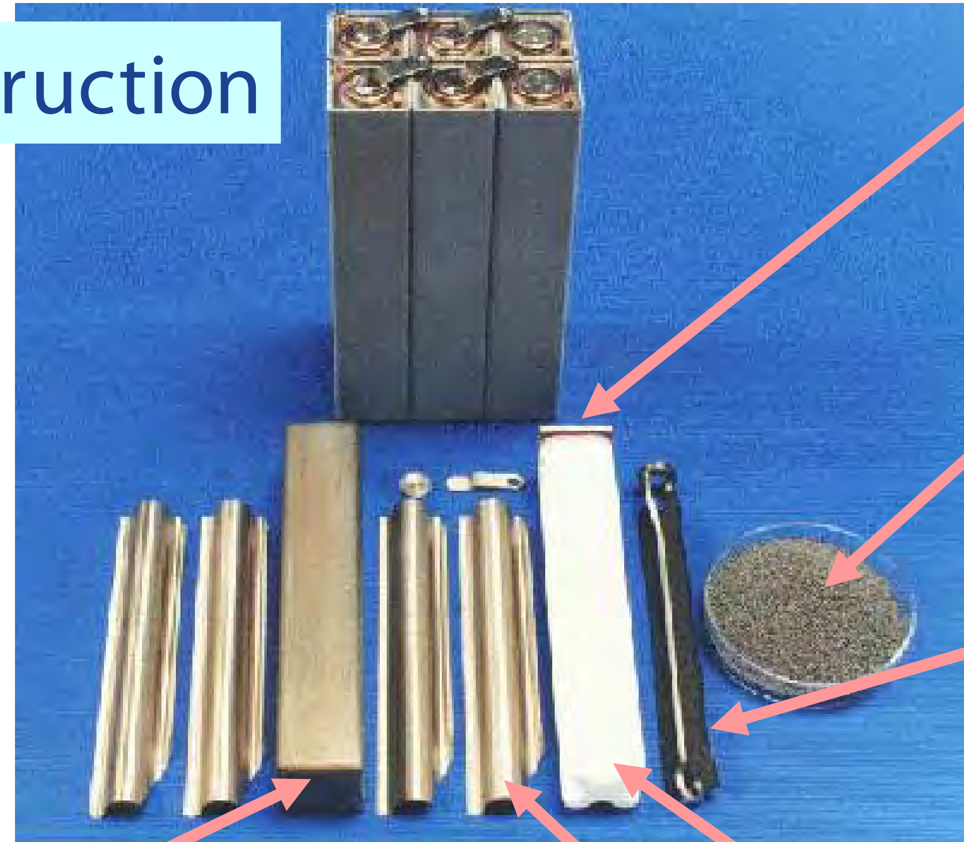
Discharging



imagination at work

UNIVERSITY OF SOUTH CAROLINA

Cell Construction



Top of case. Hermetically sealed to tube and case

Cathode: powdered iron + NaCl

Cathode current collector + electrolyte reservoir

Steel cell case. Doubles as anode current collector

Spring clips (4) to center tube in case

β” alumina fluted tube (Na^+ conducting solid electrolyte separator)

imagination at work

UNIVERSITY OF SOUTH CAROLINA

Cathode inside of solid electrolyte tube
Anode outside of tube

FEM Model

Geometry

Model Formulation

- 2-D model of 0.21 m cylindrical cell
- 300°C isothermal operation
- Constant current discharge @ -8.13 A
- Initially fully charged @ 50 A-h

imagination at work

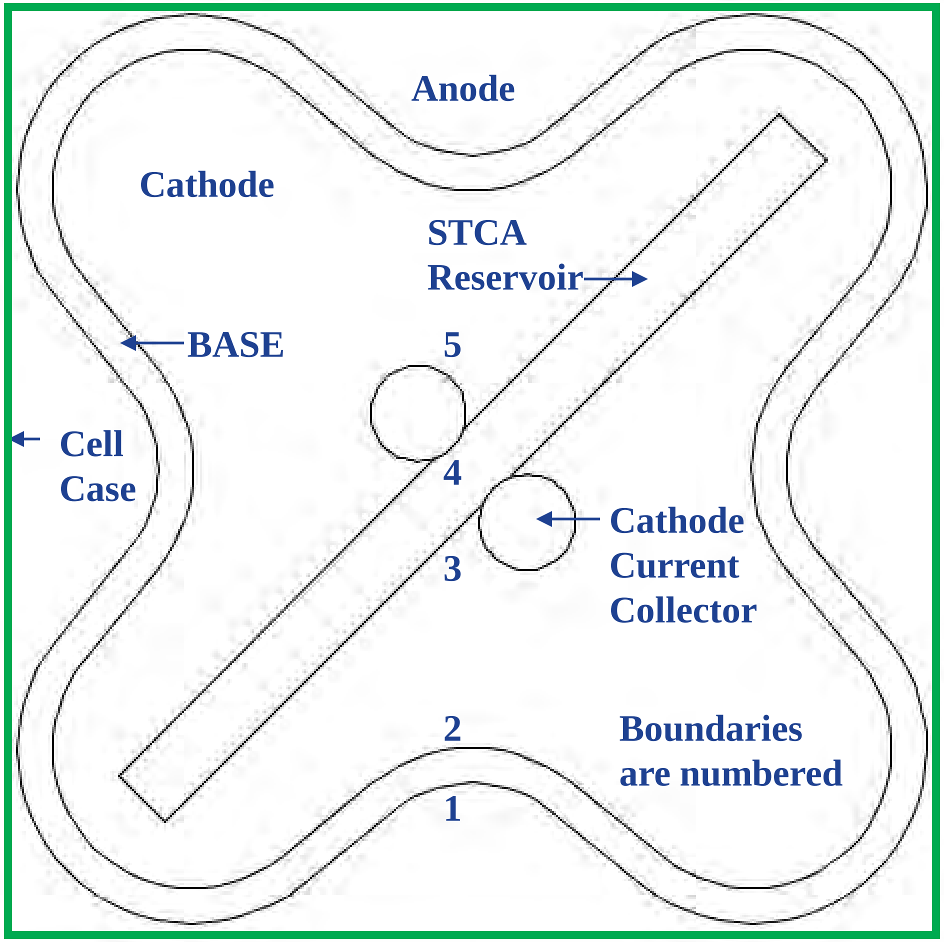
UNIVERSITY OF SOUTH CAROLINA

Model Geometry

3 subdomains:

1. Cathode
2. STCA reservoir
3. BASE

5 interfaces
indicated by 1 - 5

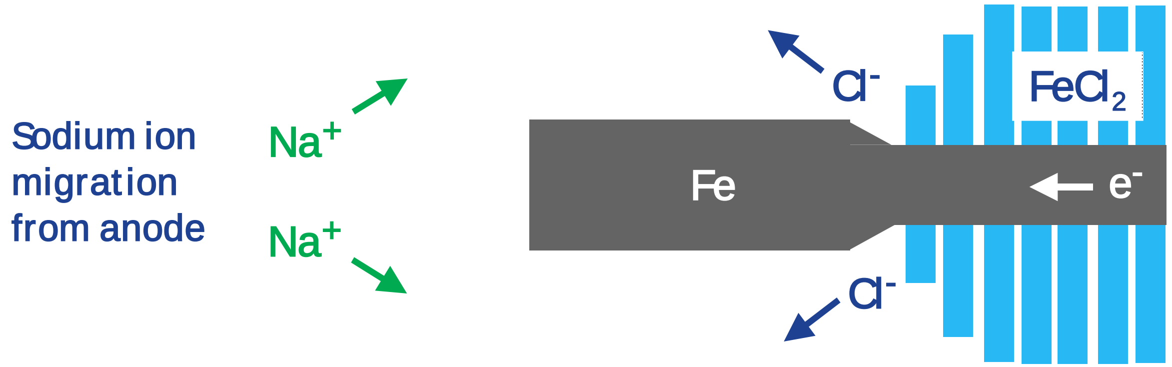


Model Formulation

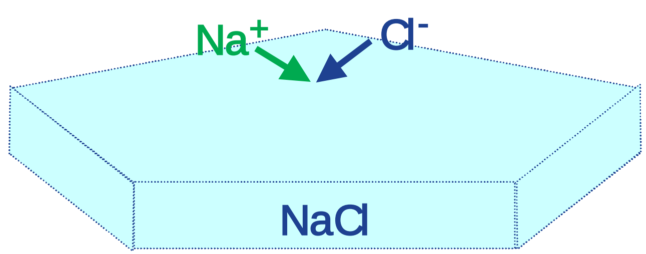
Subdomain / Transport Equation	Cathode	STCA Reservoir[1]	BASE	Dependent Variable	Initial Condition
electronic charge continuity	X (Fe phase)	X		field potential	
ionic charge continuity	X (STCA phase)		X	field potential	
mass continuity	X			superficial mole-avg velocity[2]	
NaCl (s) mass balance	X			NaCl volume fraction[3]	0.010
$FeCl_2$ (s) mass balance	X			$FeCl_2$ volume fraction[4]	0.264
Fe (s) mass balance	X			Fe volume fraction	0.184
$NaAlCl_4$ (sol'n) mass balance	X			$NaAlCl_4$ mole fraction[5]	0.897

1) STCA distribution assumed discontinuous -- no molten-phase transport
2) Binary molten-electrolyte solution assumed (NaCl + $NaAlCl_4$).
3) Initial NaCl volume fraction associated with seed area.
4) Initial $FeCl_2$ volume fraction represents 1.25×10^9 coulomb/m^3.
5) Initial mole fraction represents NaCl-saturated STCA at 300^oC.

Pore-Wall Flux Reactions



Mass-transfer-limited Butler-Volmer electrode kinetics for electrode over-potential



NaCl crystallization from solution: 1st order in [Na^+] and [Cl^-]

Results

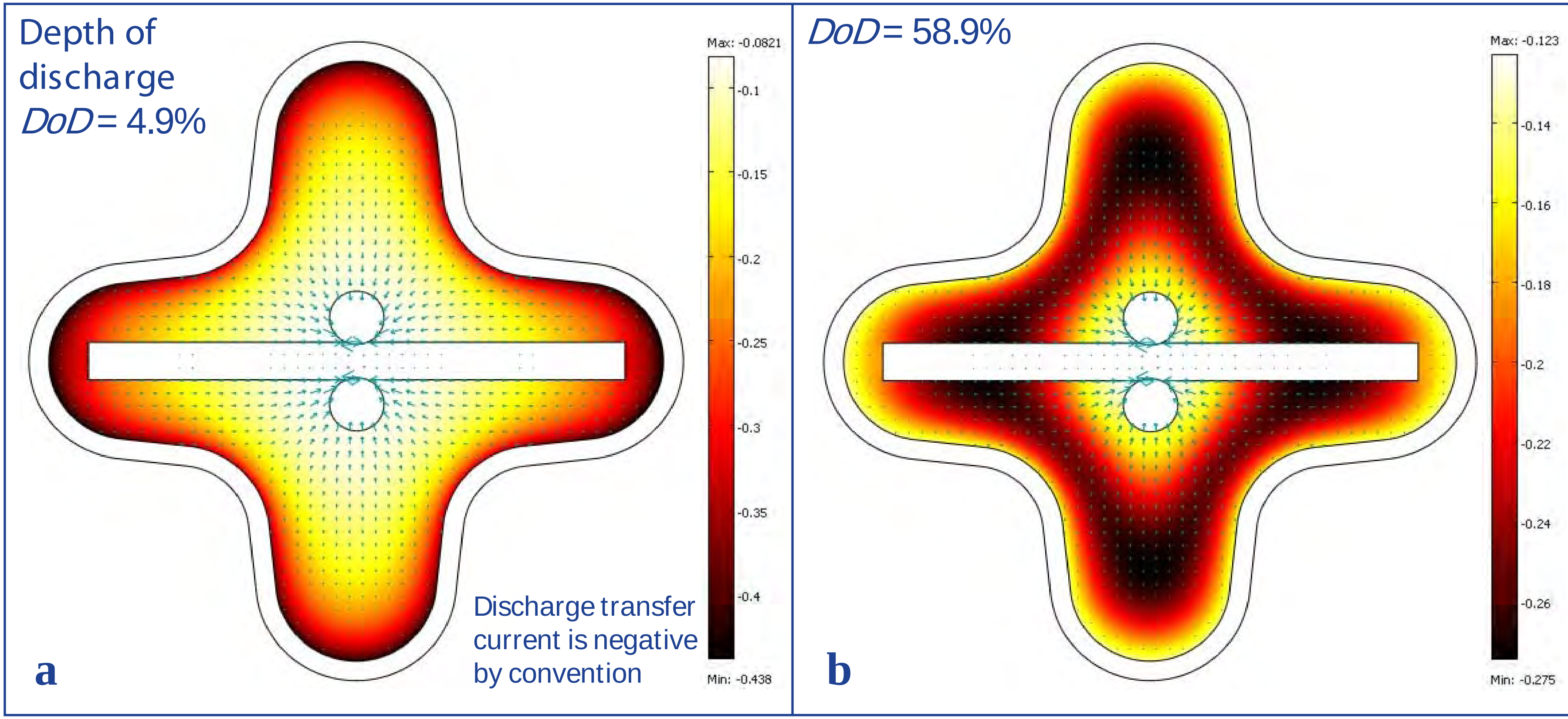
Transfer Current Density

NaCl Concentration in Electrolyte

$FeCl_2$ Volume Fraction

imagination at work

UNIVERSITY OF SOUTH CAROLINA



Color map: transfer (Faraday) current density (A/m^2)

Arrow map: electronic current density (Fe & C phases)

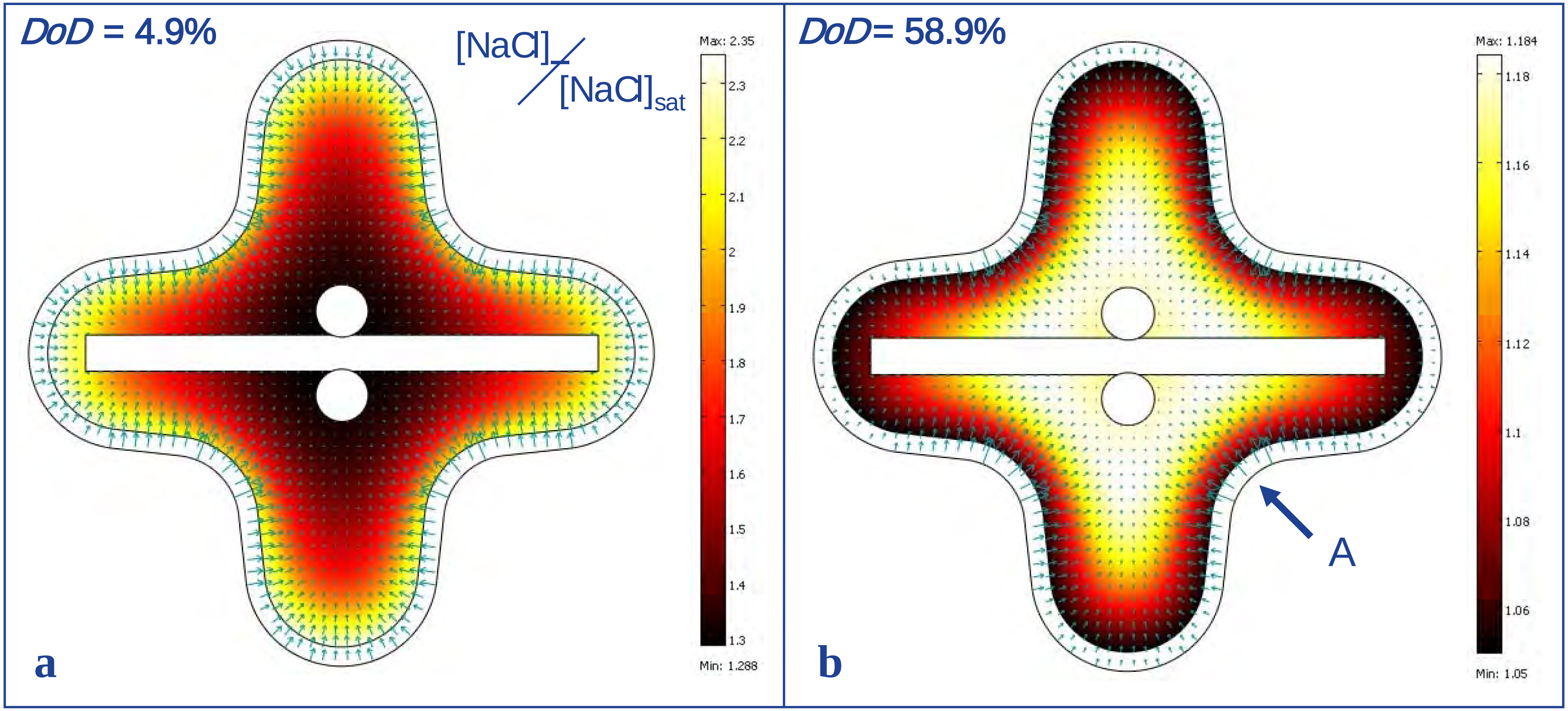
Transfer current density wave *v DoD*

broadens with lower density

translates away from separator

imagination at work

UNIVERSITY OF SOUTH CAROLINA



Color map: concentration ratio [NaCl] / $[NaCl]_{sat}$

Arrow map: ionic current density (molten electrolyte)

[NaCl] *v DoD*

initial super-saturation >100%

opportunity for model refinement

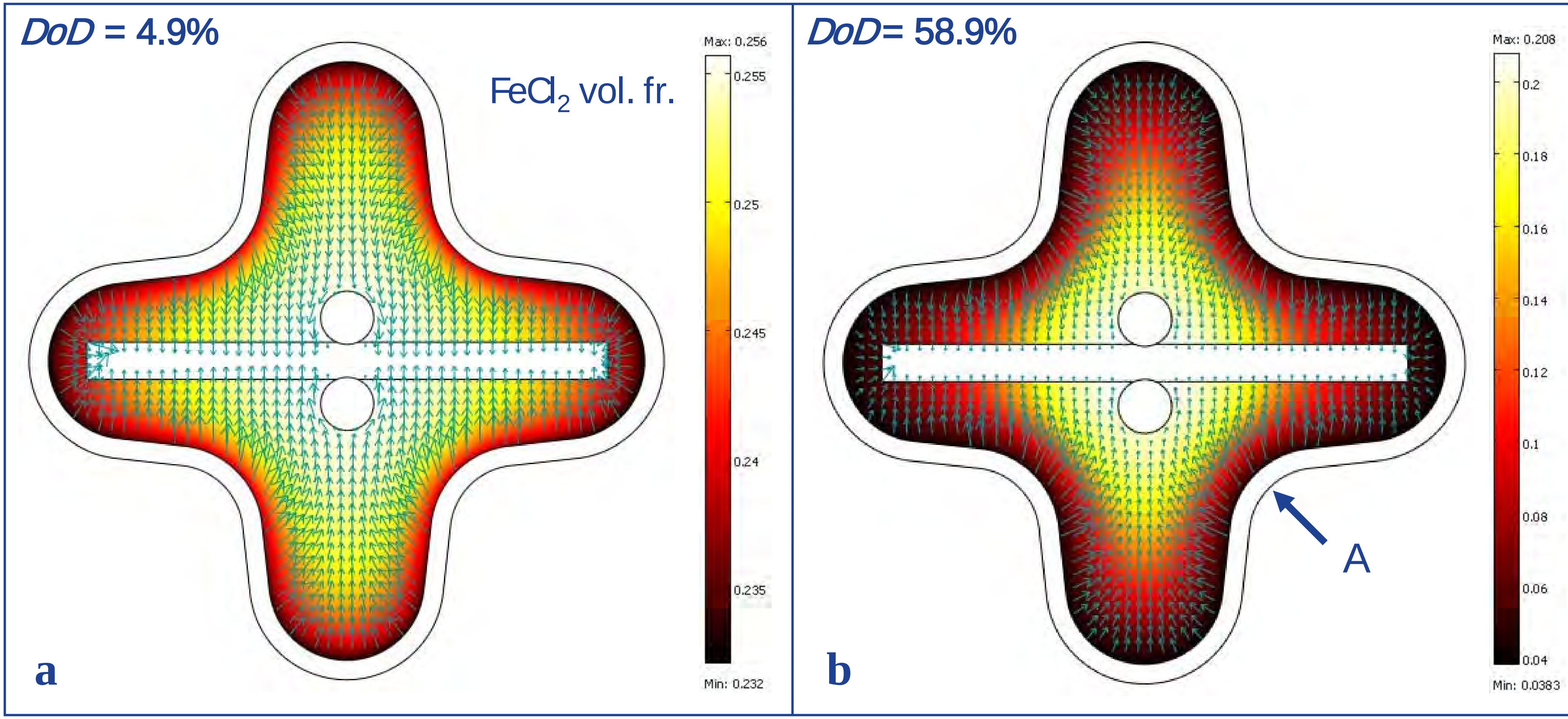
Ionic current density

concentrated between lobes (A) at high *DoD*

imagination at work

UNIVERSITY OF SOUTH CAROLINA

Vallance/White | Comsol 2008



Color map: $FeCl_2$ solid-phase volume fraction

Arrow map: superficial mole-avg. convection velocity

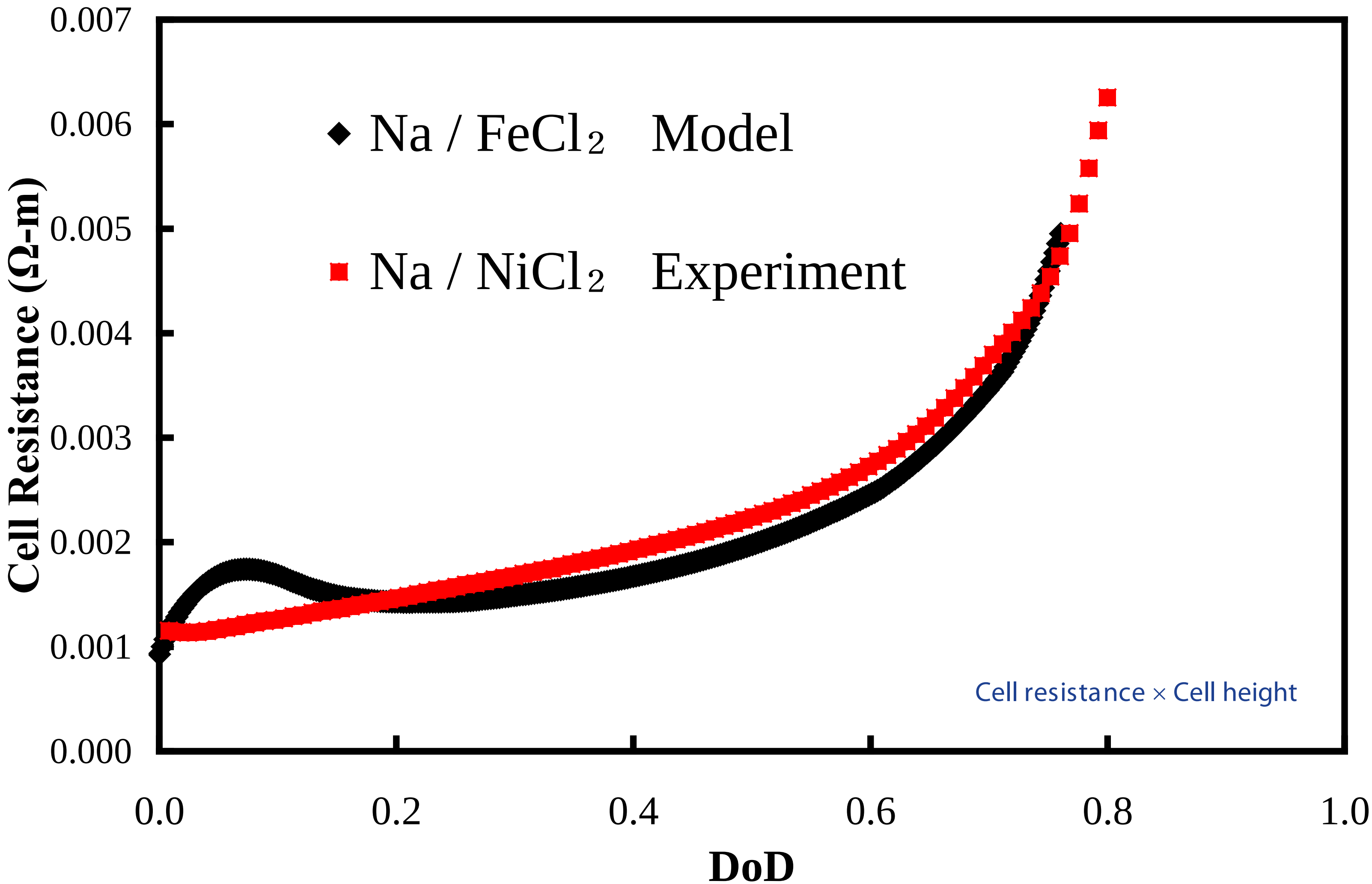
$FeCl_2$ distribution *v DoD*

- $FeCl_2$ depleted in wake of transfer current wave

Electrolyte squeezed out of cathode into reservoir

- Sodium flux across BASE
- Reduced pore vol. fr. due to NaCl precipitation

Comparison With Experiment



D.C. resistance -- model *v* experiment

- Good agreement
- Dominated by ionic IR drop
- Initial divergence ⇒ over-estimate of [NaCl]

imagination at work

University of South Carolina

Summary

- Nernst-Planck model of Na | $FeCl_2$ cell
- Visualization provides valuable insights
- Good agreement with experiment
- Opp’ty for improved mass transfer kinetics

This work is supported by
Jeff Immelt, CEO & Chairman, GE

imagination at work

UNIVERSITY OF SOUTH CAROLINA