FROM RESEARCH TO INDUSTRY
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COMSOL CONFERENCE 2015 GRENOBLE

ÉCOLE DOCTORALE
I-MEP2

Na-MCl$_2$ CELL MULTIPHYSICS MODELING: STATUS AND CHALLENGES

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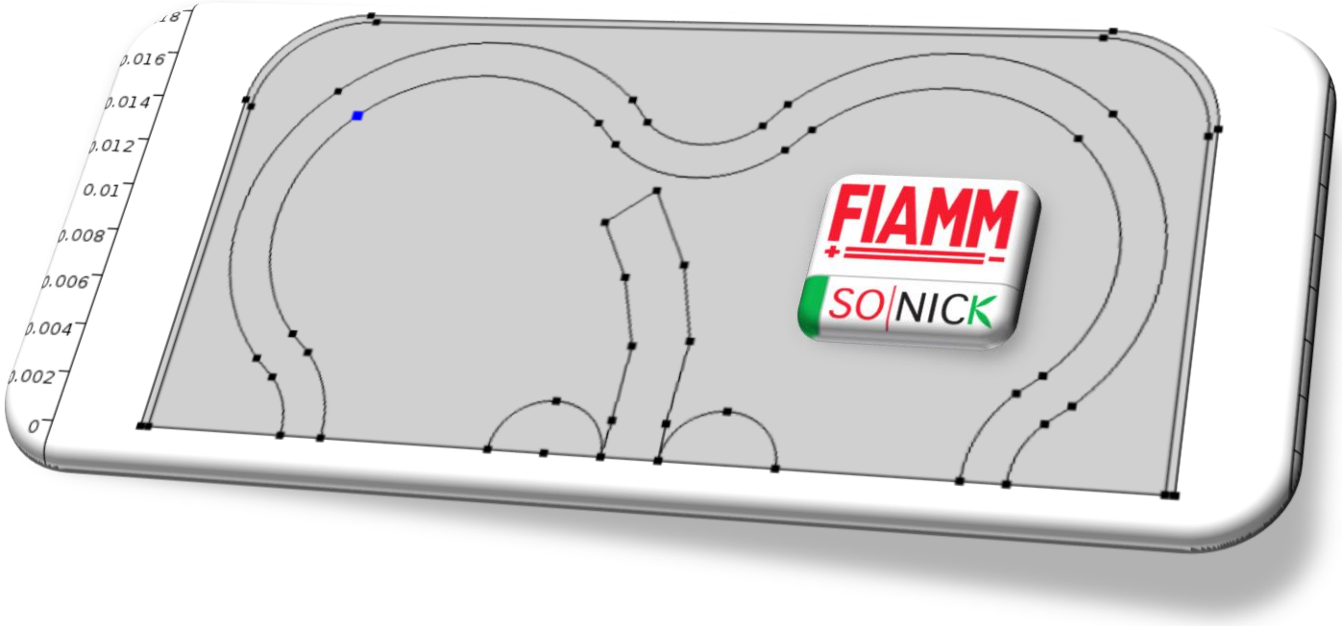

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Conventions

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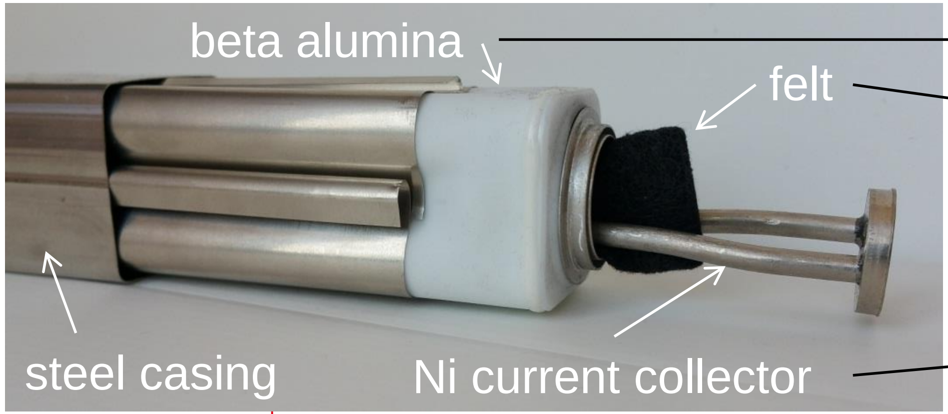
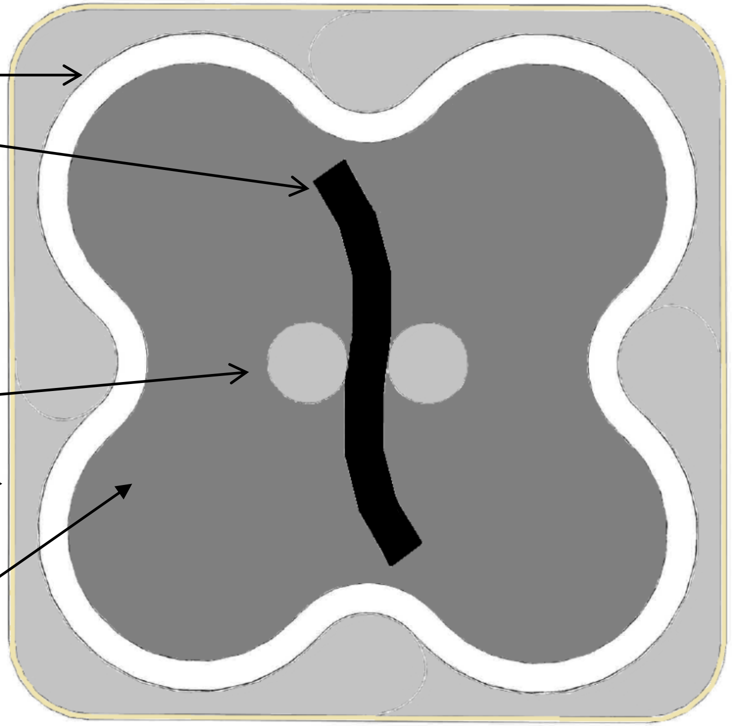
Na-MCl_2 TECHNOLOGY (300 °C)

- **Design and active materials**
  - Clover-shaped beta alumina

23.5 cm

Imp 154 C - INES





3.5 cm x 3.5 cm

FIAMM SO|NICK

Mixed Ni/Fe cell

NaCl solid (100% of SOC)
Ni solid (80% of SOC + 70% excess)
Fe solid (20% of SOC)
Additives
Secondary liquid electrolyte **$NaAlCl_4$**

$Na\text{-}MCl_2$ TECHNOLOGY (300 °C)

- **Design and active materials**
  - Clover-shaped beta alumina

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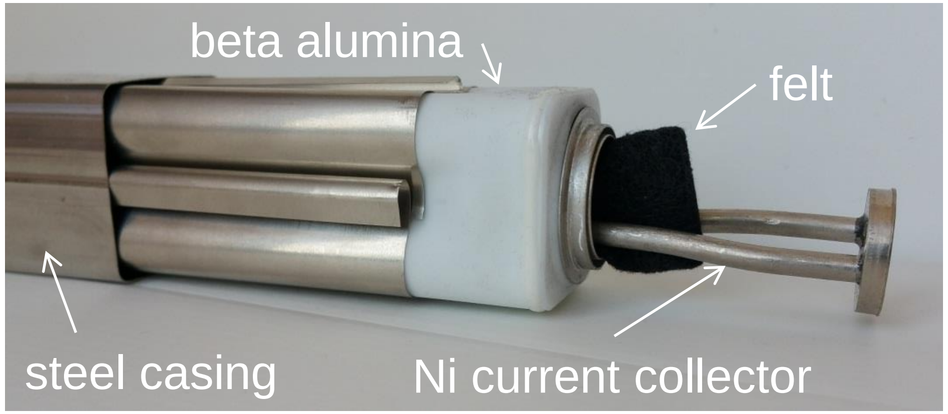

FIAMM SO|NICK

Mixed Ni/Fe cell

NaCl solid (100% of SOC)
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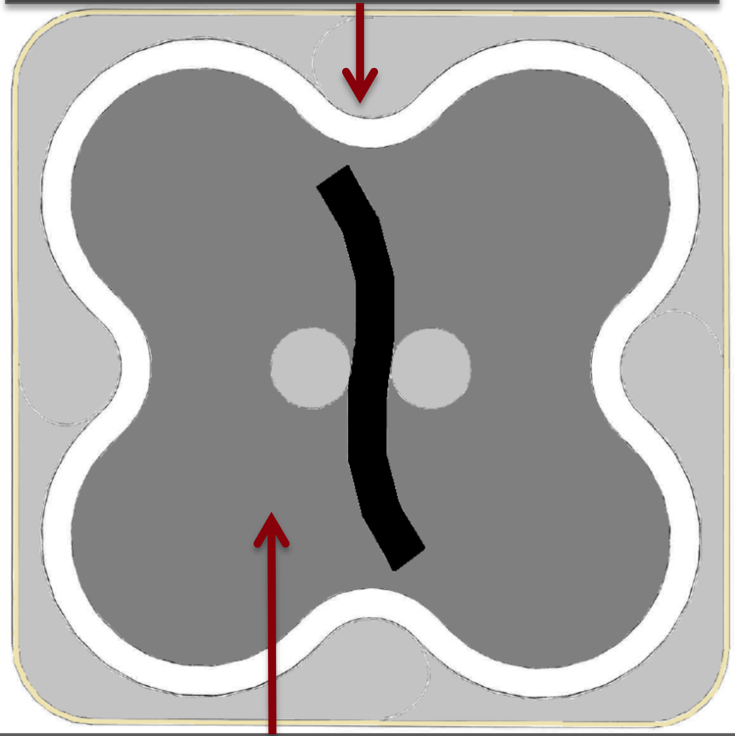
Additives
Secondary liquid electrolyte **$NaAlCl_4$**

Discharge scheme

negative: $2Na \rightarrow 2Na^+ + 2e^-$



3.5 cm x 3.5 cm

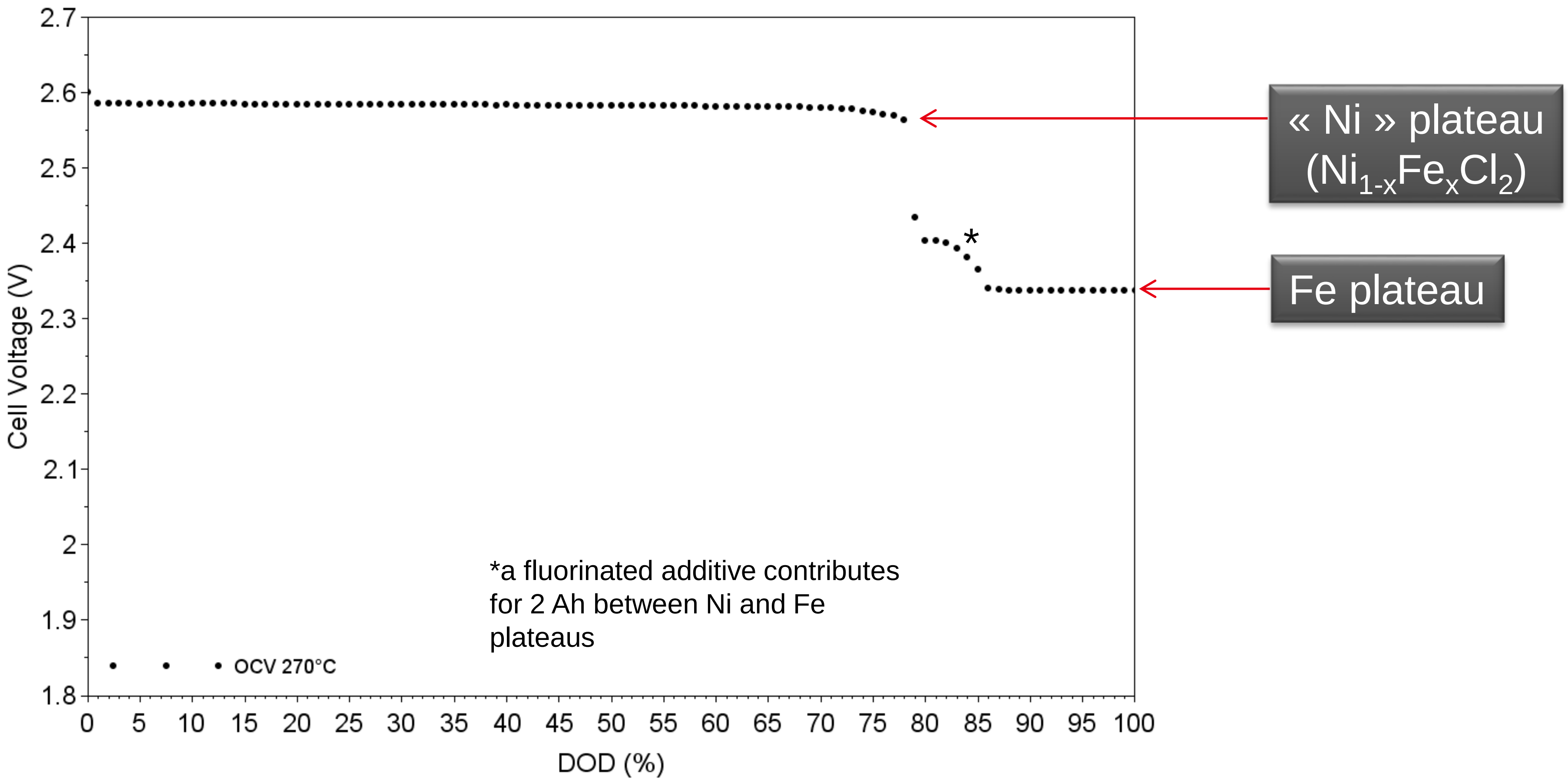
positive: $MCl_2 + 2Na^+ + 2e^- \rightarrow M + 2NaCl$

$$\mathbf{MCl_{2(s)} + 2Na_{(l)} \rightarrow M_{(s)} + 2NaCl_{(s)}}$$

M = Ni then Fe

FIAMM MIXED 40 Ah CELL

- **Experimenal 40 Ah discharges from 270 °C for validation**
  - Oven settings: temperature changes emanate only from the cell (increases during discharge)



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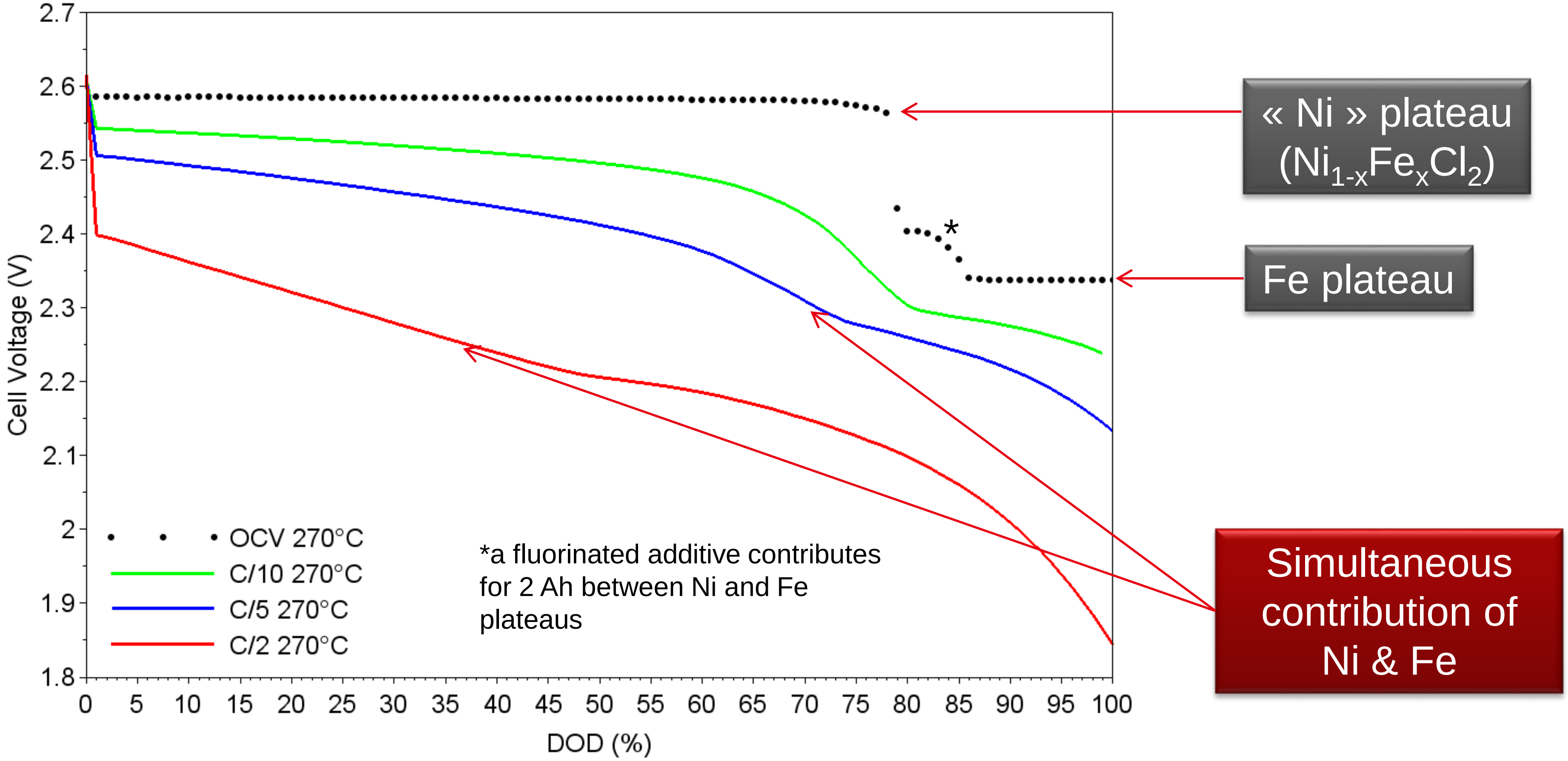


2D MODEL IMPLEMENTATION

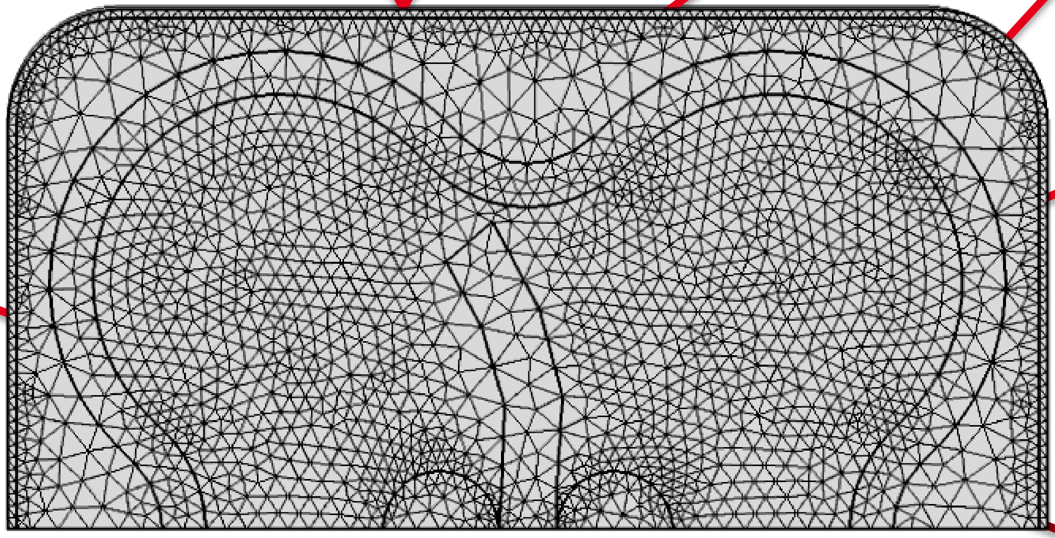
- **Geometry, Meshing and Governing Equations (from seminal paper)**

Anodic domain
- Ohm's law in metal ($\mathbf{\Phi_1}$)
- Linearized Butler-Volmer on beta alumina external surface (i_N)

Casing domain
- Ohm's law in metal ($\mathbf{\Phi_1}$)
- Origin of potential (Φ_1 = 0V)

Solid electrolyte domain
- Ohm's law in electrolyte ($\mathbf{\Phi_2}$)

Current collector
- Ohm's law in metal ($\mathbf{\Phi_1}$)
- Applied current (I_{exp}) on collector surface



Cathodic region and felt
- Ohm's law in $NaAlCl_4$ ($\mathbf{\Phi_2}$)
- Ohm's law in metal backbone and carbon ($\mathbf{\Phi_1}$)
- Electrochemical reactions (j_i)

Porosity, volume fractions, exchange current densities
- $\epsilon = 1 - \sum \epsilon_{\mathrm{M}} - \sum \epsilon_{\mathrm{MCl2}} - \epsilon_{\mathrm{NaCl}}$
- $\frac{\partial \epsilon_{\mathrm{M/MCl2}}}{\partial t} \propto j_{\mathrm{M}}$ and $\frac{\partial \epsilon_{\mathrm{NaCl}}}{\partial t} \propto j$
- ➔ $j = j_{\mathrm{Ni}} + j_{\mathrm{Fe}}$

THERMAL IMPLEMENTATION

- From Li-ion cells studies[1,2], distributed heat sources flux can be expressed as:

$$Q_{\mathrm{irrev}} = j_{\mathrm{i}}\eta_i + \sigma(\nabla\phi_1)^2 + \kappa(\nabla\phi_2)^2$$

overpotentials in positive electrode

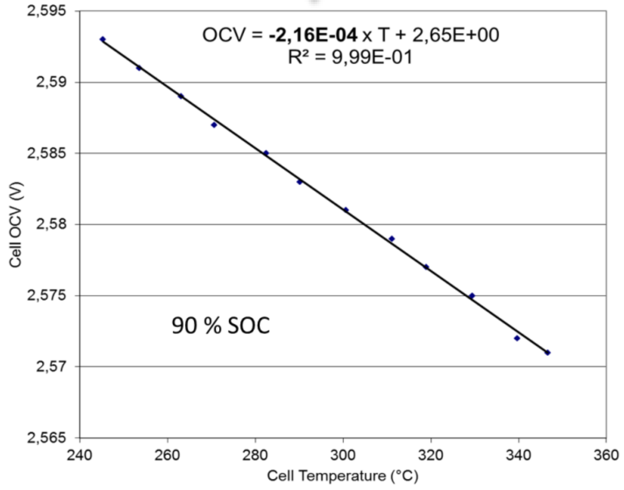
electronic ohmic losses in all cell

ionic ohmic losses in BASE and positive electrode

i = Ni or Fe

$$Q_{rev} = j_{\mathrm{i}}\mathrm{T}\frac{\partial OCV_{\mathrm{cell,i}}}{\partial T}$$

entropic term from experimental Measurements



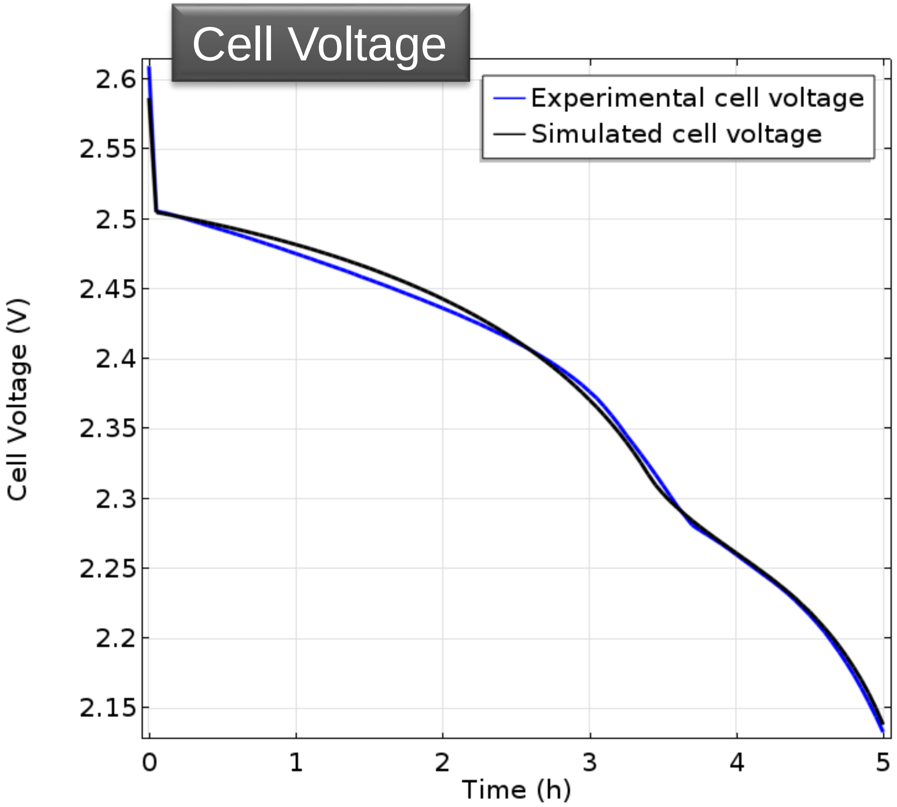
Q = f(variables of the electrochemical model), Variables of the electrochemical model = f(*T*)

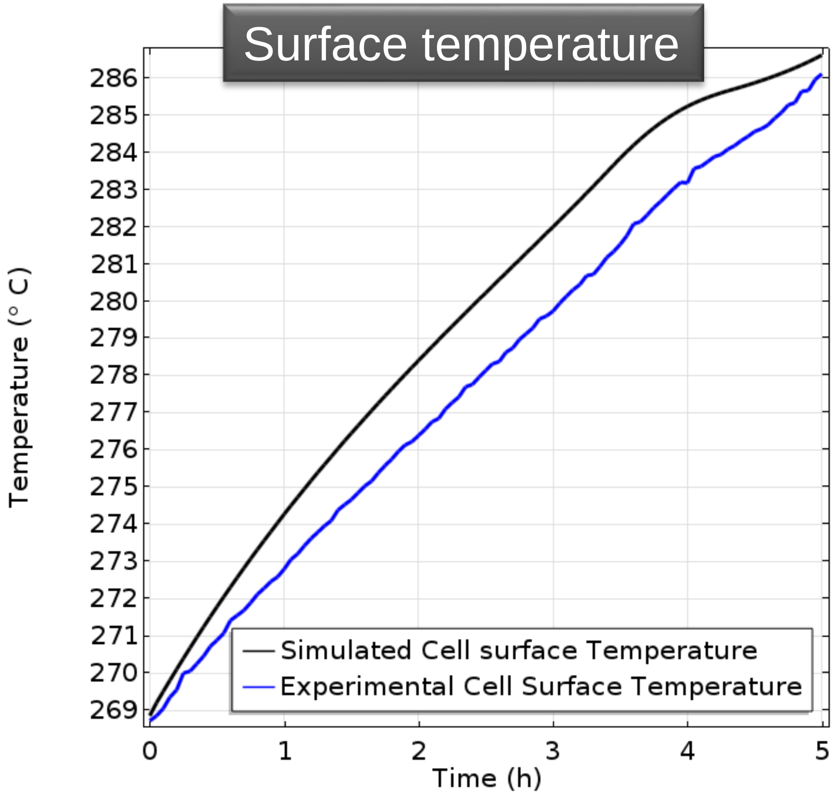
➔ fully coupled model

1 Srinivasan V, Wang CY, J Electrochem Soc 150, 2003.
2 Somasundaram K, Birgersson E, Mujumdar AS, J Power Sources 203, 2012

BASELINE SIMULATION

- 40 Ah discharge at C/5, $T_{initial}$ = 270 °C

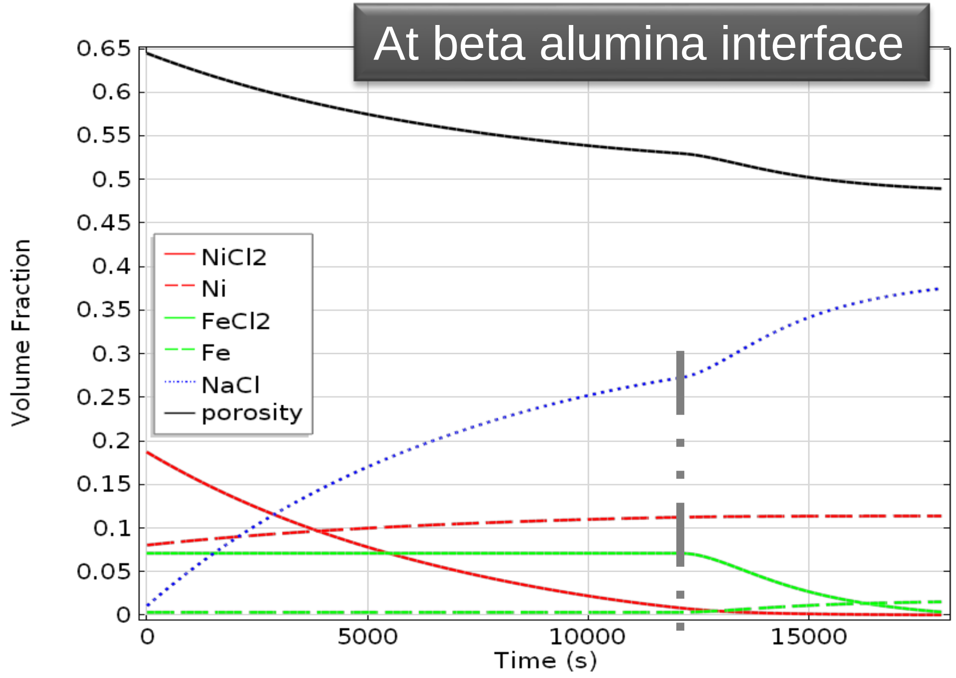


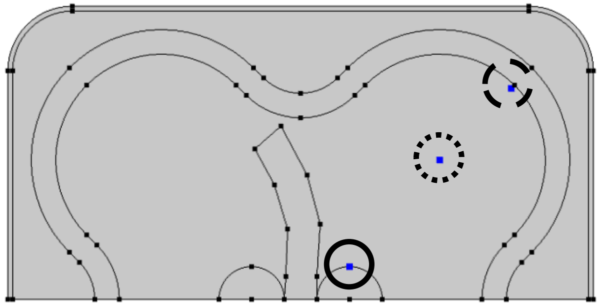


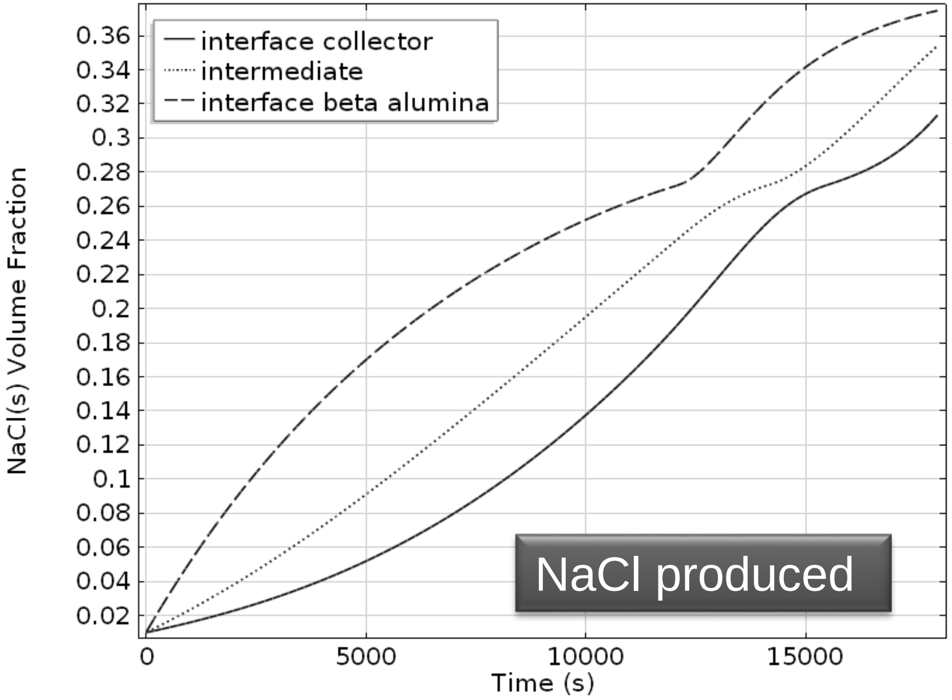
➔ The model is validated for this cell voltage and cell surface temperature simulation (relative error < 2 %

BASELINE SIMULATION

- **40 Ah discharge at C/5, $T_{initial}$ = 270 °C**
  - Volume fractions of active materials with time







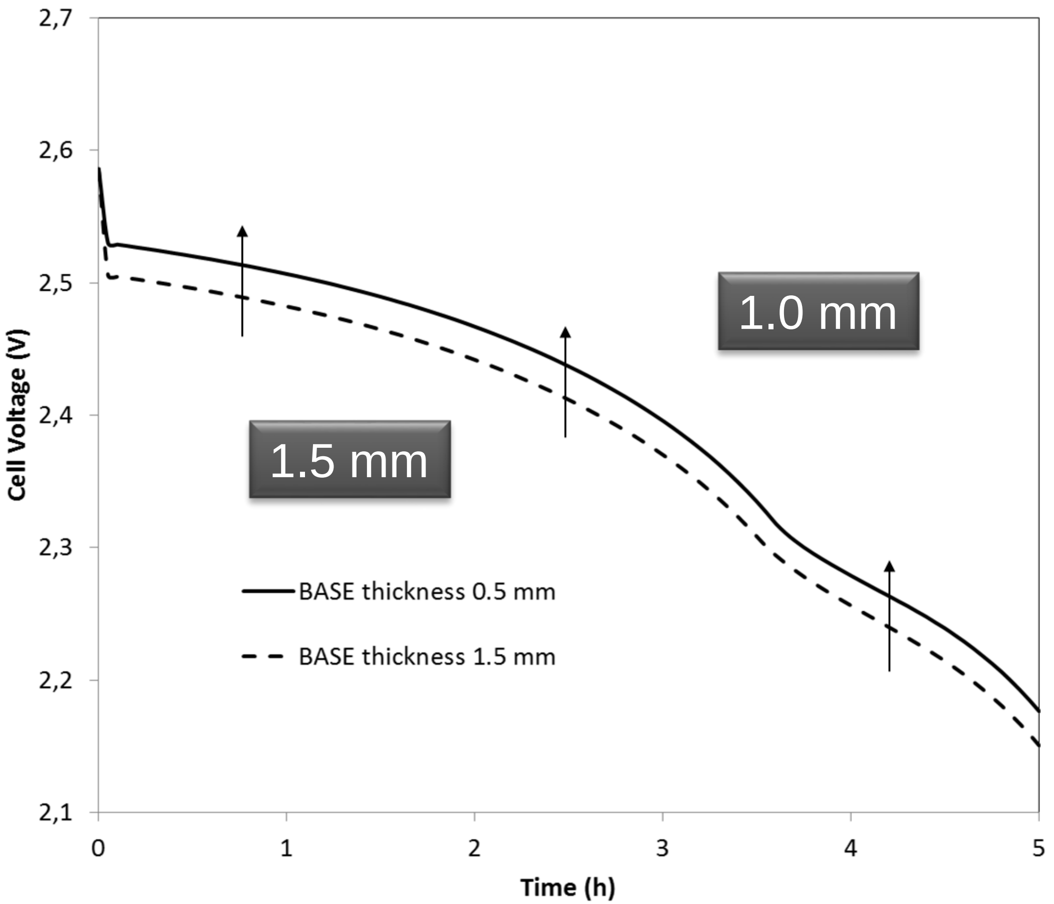
Fe contributes only if $U_{cell} < OCV_{Fe}\ (T)$

Results at end of discharge are very closed to expected values from initial weights

➔ a <u>diffuse</u> reaction front moves from the beta alumina towards the central collector

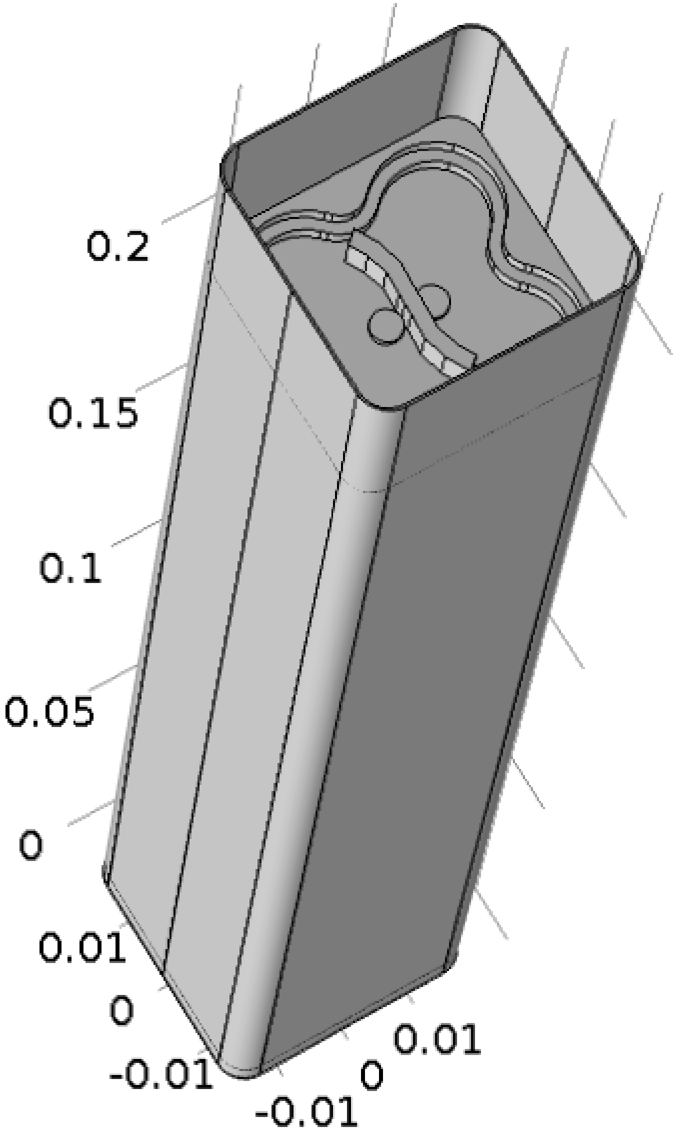
INFLUENCE OF THE THICKNESS OF THE SOLID ELECTROLYTE

- **40 Ah discharge at C/5, $T_{initial}$ = 270 °C**
  - Cell Voltage



Only the thickness of the beta alumina has been changed between simulations

➔ As expected, the model predicts less overall polarization with a thinner solid electrolyte



THANK YOU FOR YOUR ATTENTION

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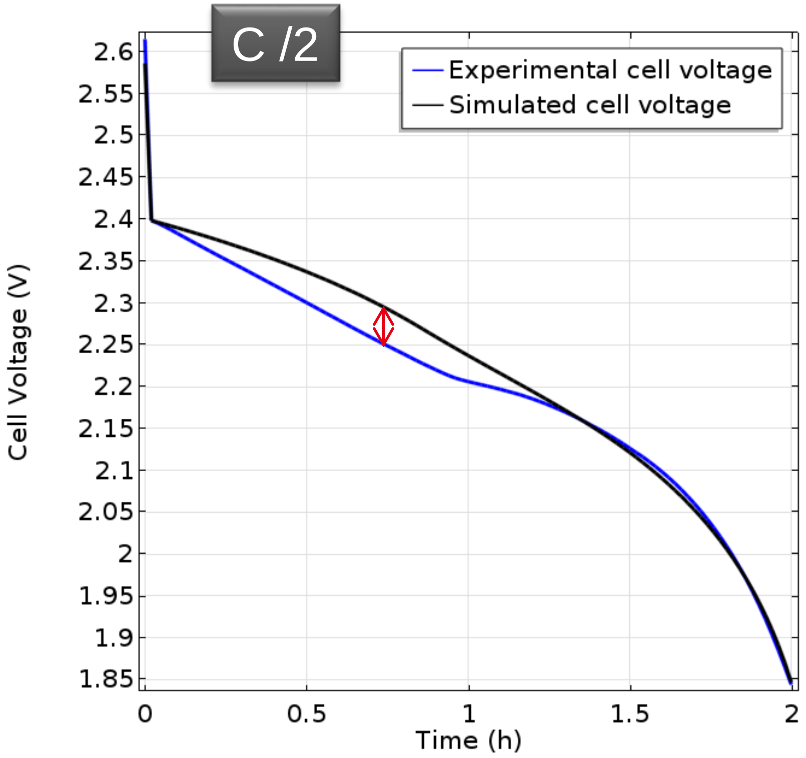
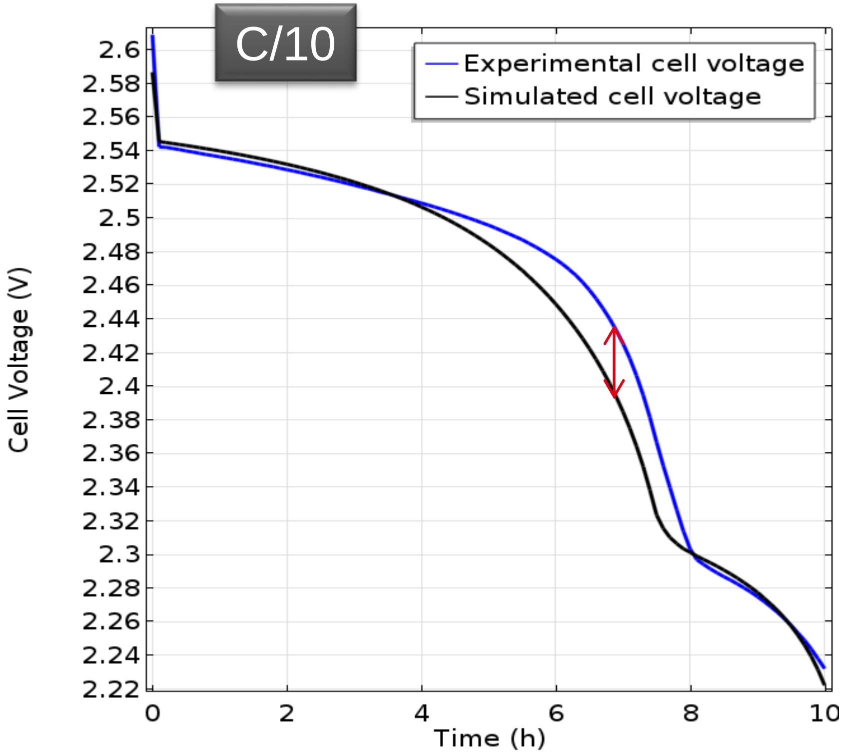
Technological Research Division
Solar Technologies Department
Laboratory LSE

INFLUENCE OF THE RATE

- **40 Ah discharge at C/2 and C/10 from 270 °C**
  - Cell Voltage

Only the I_{exp} parameter has been changed from the reference simulation

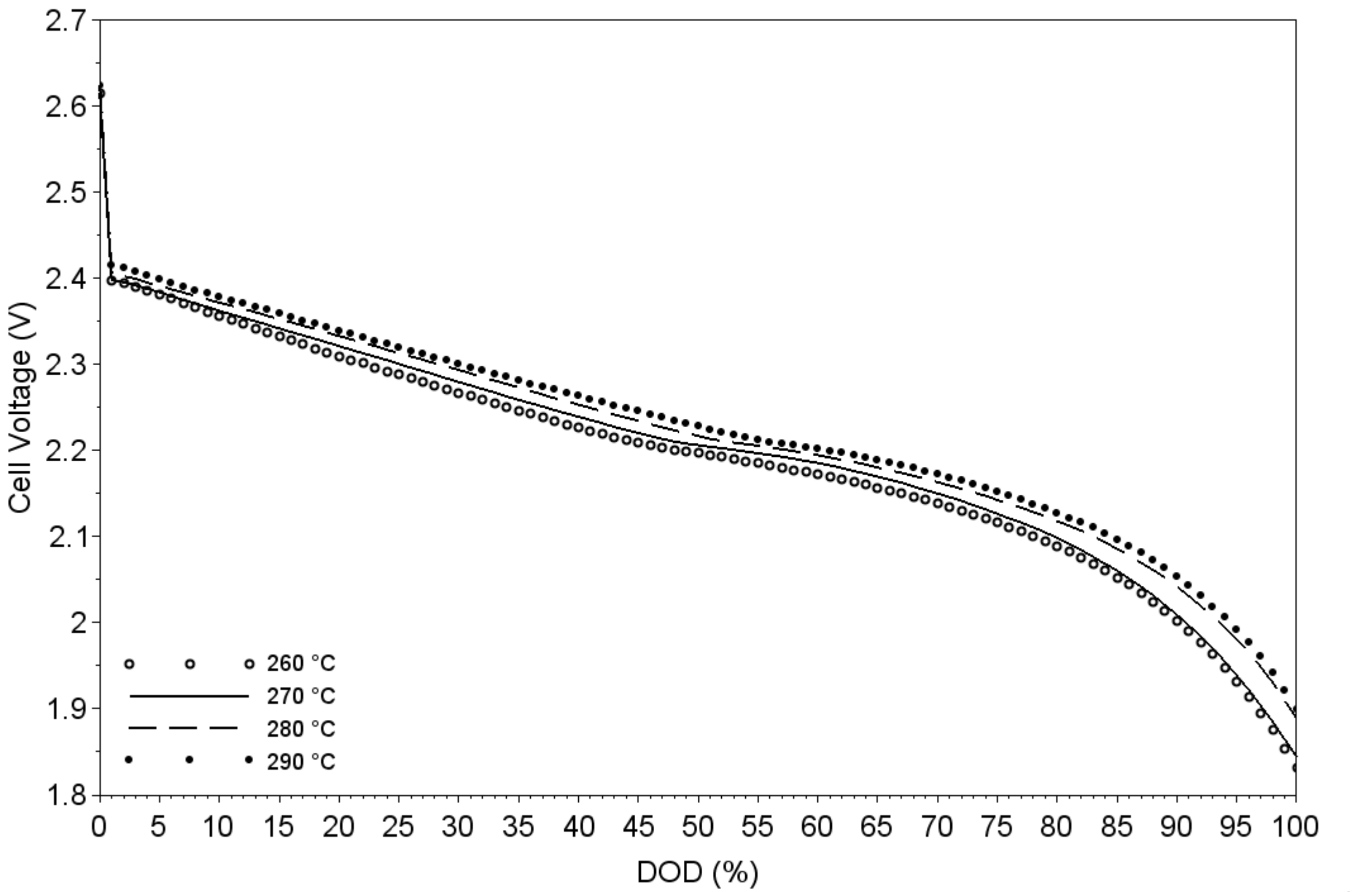




➔ The model is validated from C/10 to C/2 (error < 2%)

FIAMM ML3X GENERIC 40 Ah CELL

- **C/2 40 Ah discharges from different initial temperatures**
  - For experimental data, furnace is supplied by constant power, hence temperature changes emanate from the cell (increase during discharge)



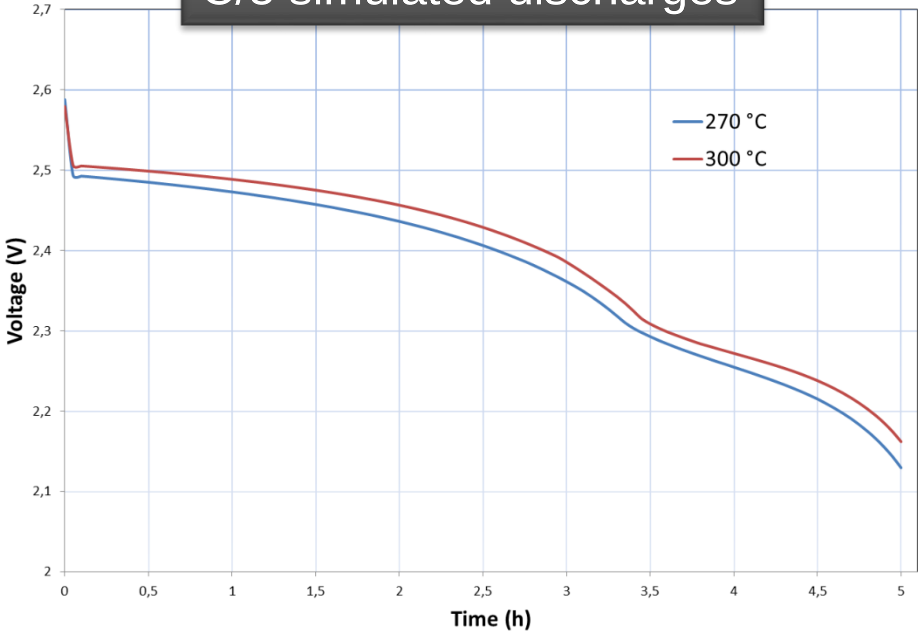
polarization ↘
if temperature ↗

INFLUENCE OF THE INITIAL TEMPERATURE

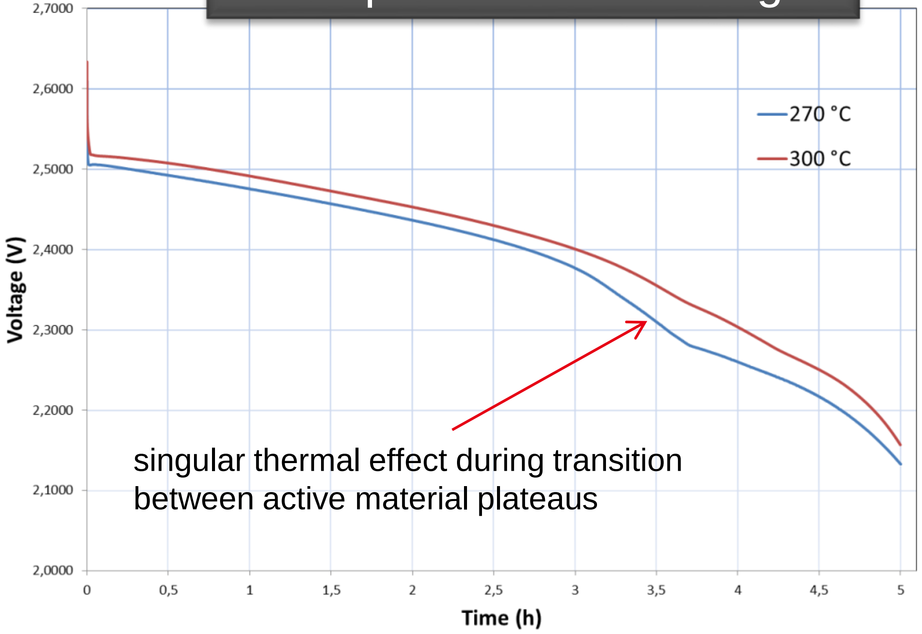
- **40 Ah discharges at different temperatures**
  - Cell Voltage

Only the *T* parameter has been changed from the related simulation

C/5 simulated discharges



C/5 experimental discharges



➔ The model is validated in terms of operational temperature. Temperature does not have a significant effect on the voltage curves

PREVIOUS WORKS

- **Eroglu & West* (small modifications, isothermal)**

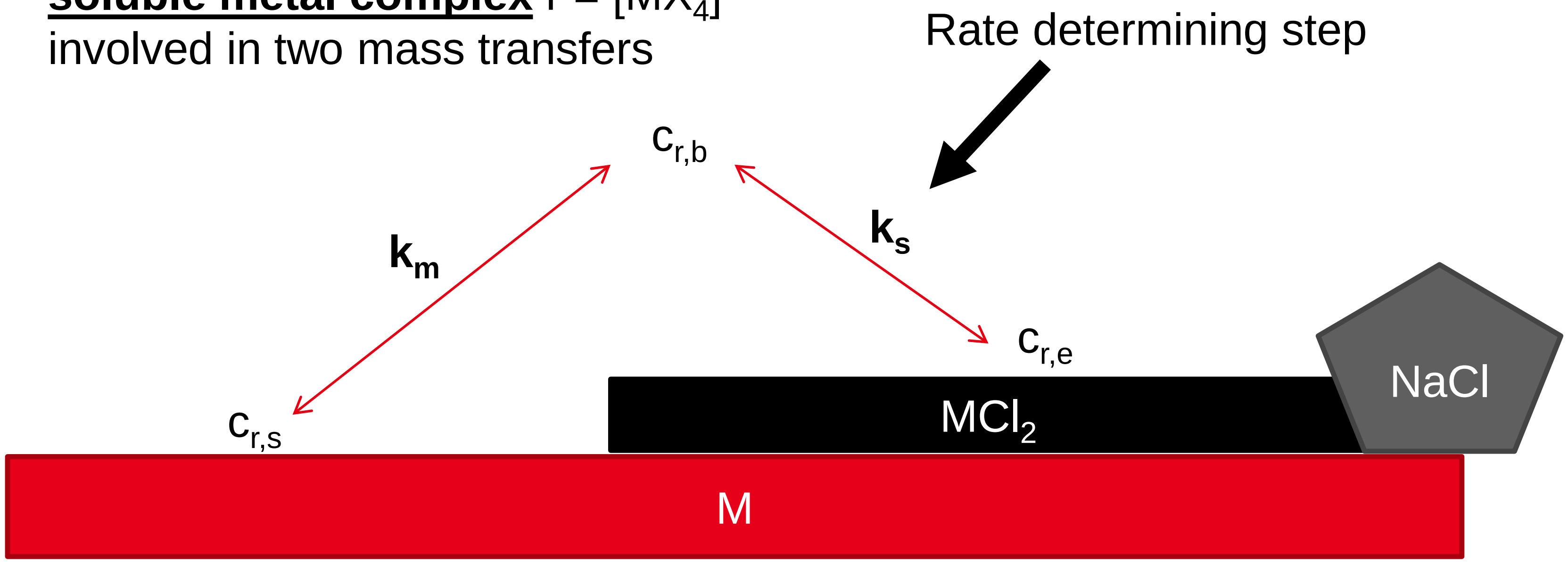
$$j = \frac{exp\left(\alpha_a \frac{F}{RT}\eta\right) - \frac{c_{r,b}}{c_{r,e}} exp\left(-\alpha_c \frac{F}{RT}\eta\right)}{\frac{1}{i_0 a_m} + \frac{1}{nF c_{r,e}}\left(\frac{1}{k_m a_m}\right) exp\left(-\alpha_c \frac{F}{RT}\eta\right)}$$

Bulk: $X = Cl^- \; or \; AlCl_4^-$

$$c_{[MX4]^{2-}} = c_{r,e} = \propto K_{sp,MCl2}$$

Discharge $MCl_2 + 2e^- \rightarrow M + 2Cl^-$

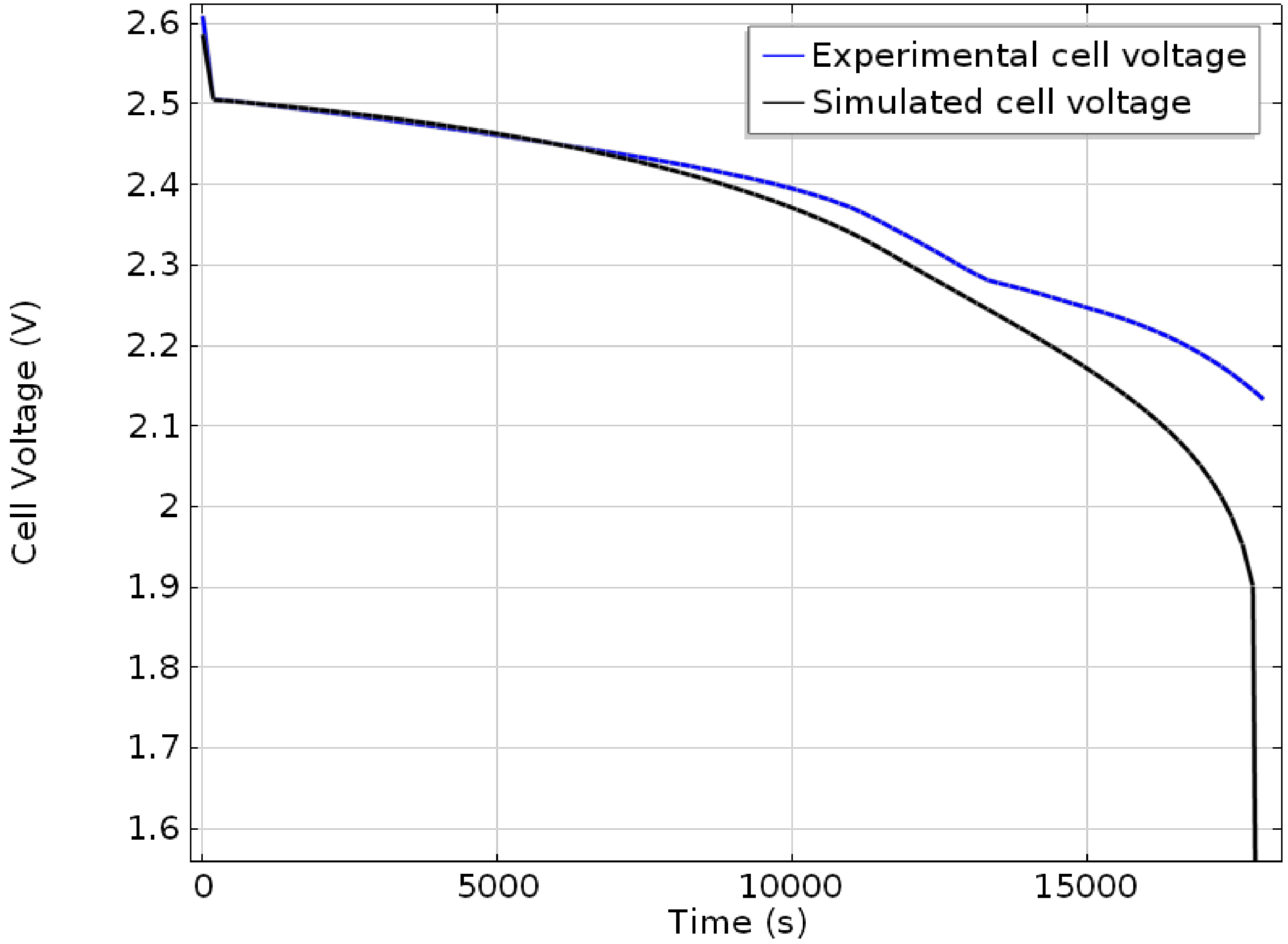
Electrochemical process involving a **soluble metal complex** r = $[MX_4]^{2-}$ involved in two mass transfers



*D. Eroglu and A. C. West, *Journal of Power Sources*, vol. 203, pp. 211–221, Apr. 2012

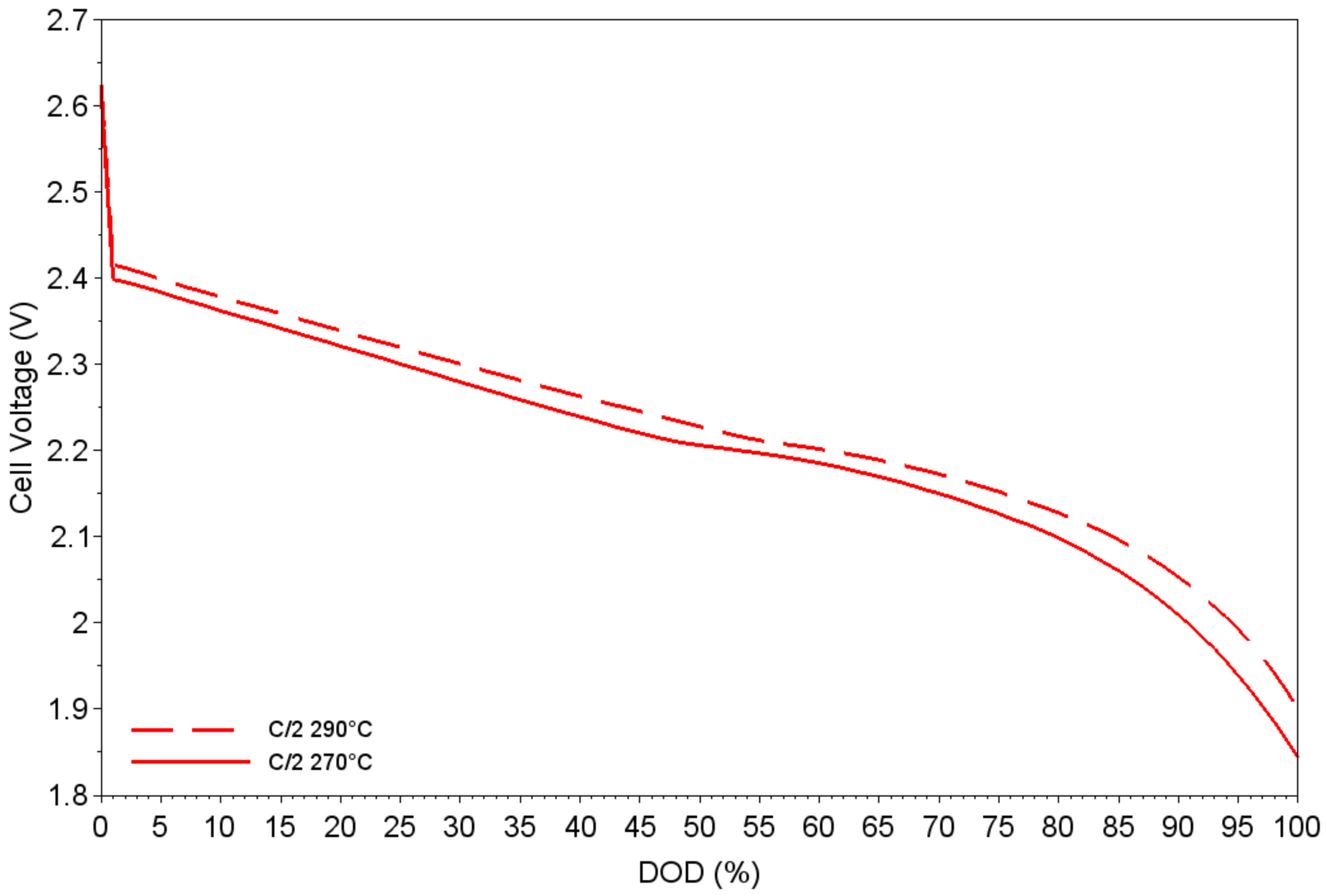
PREVIOUS WORKS

- **Orchard and Weaving implementation results**



FIAMM MIXED 40 Ah CELL

- **40 Ah discharges from 270 °C**
  - For experimental data, furnace is supplied by constant power, hence temperature changes emanate from the cell (increase during discharge)



polarization ↘
if temperature ↗

PREVIOUS WORKS

- **Orchard & Weaving* (important model simplifications)**

$$j = j_0\left[e^{\left(\alpha_a \frac{F}{RT}\eta\right)} - e^{\left(-\alpha_c \frac{F}{RT}\eta\right)}\right]$$

$$j_0 = j_{0,ref}(1 - \mathrm{DOD})^p$$

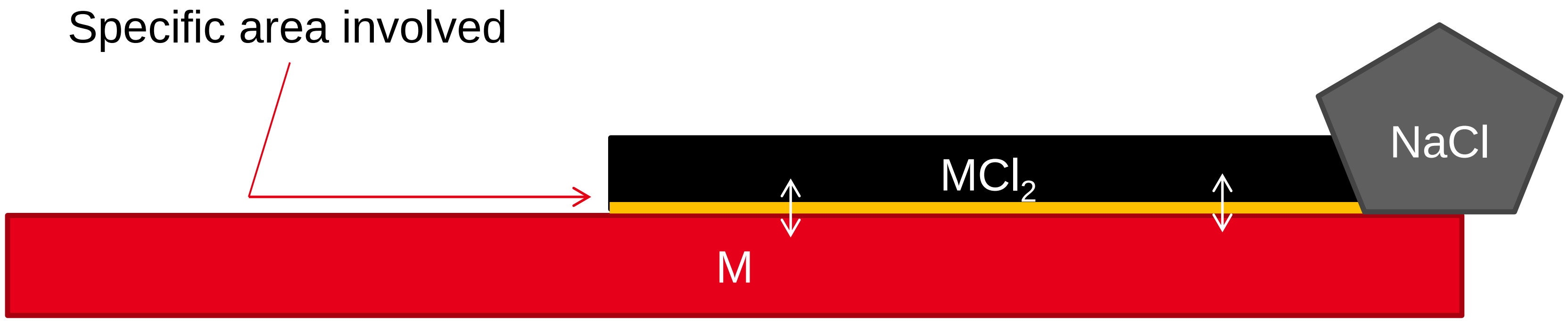
p: exponential term (= 2/3 assuming regular shaped particles, cubical or spherical)

Discharge

$$MCl_{2(s)} + 2e^- + 2Na^+ \rightarrow M_{(s)} + 2NaCl_{(s)}$$

<u>Solid state process</u>, eventual solubilities not taken into account (no mass transfer limitations)

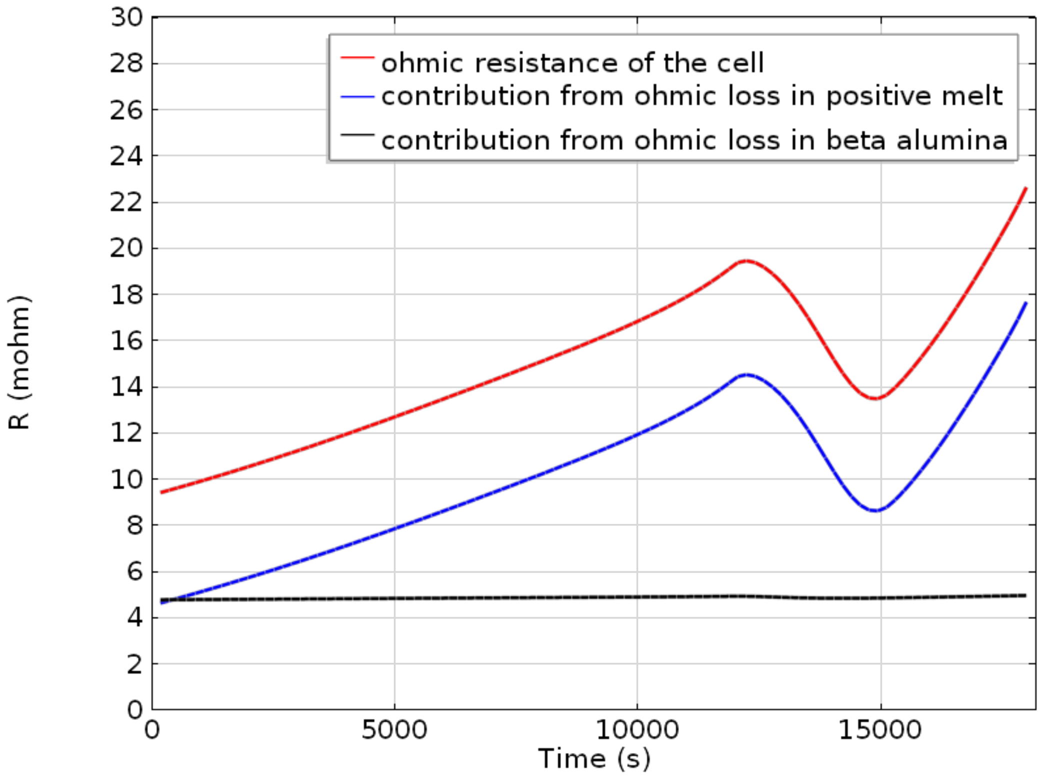
➔ constant bulk composition (x_A cst)



*S. W. Orchard and J. S. Weaving, *J Appl Electrochem*, vol. 23, no. 12, pp. 1214–1222, Dec. 1993

REFERENCE SIMULATION CONSTANT OPERATIONAL TEMPERATURE

- **40 Ah discharge C/5, 270 °C**
  - Simulated ohmic resistance of the cell

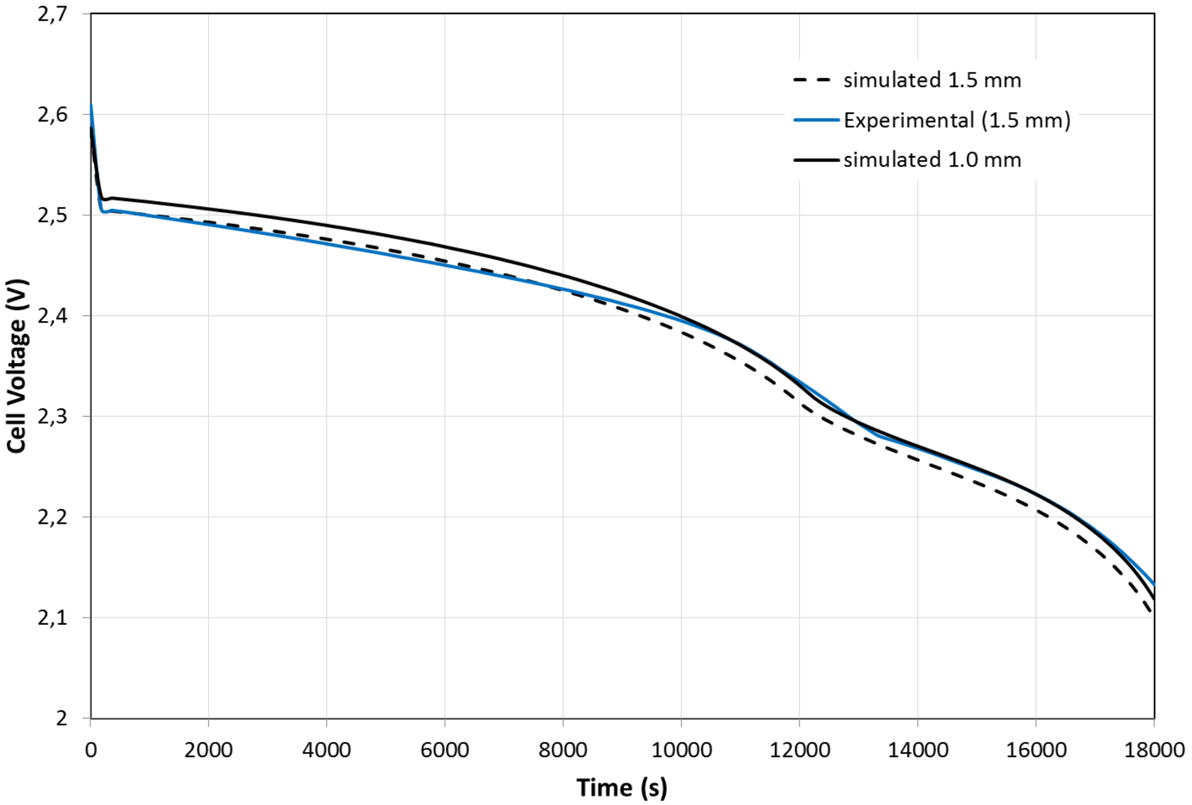


➔ In accordance with the literature: at the beginning of the iron chloride active material reaction, a new reaction front appears at the interface of the beta alumina where the ohmic loss in the melt is minimum (nickel backbone)

INFLUENCE OF THE THICKNESS OF THE SOLID ELECTROLYTE

- **40 Ah discharge at C/5 @ 270 °C**
  - Cell Voltage

Only the thickness of the beta alumina has been changed between simulations



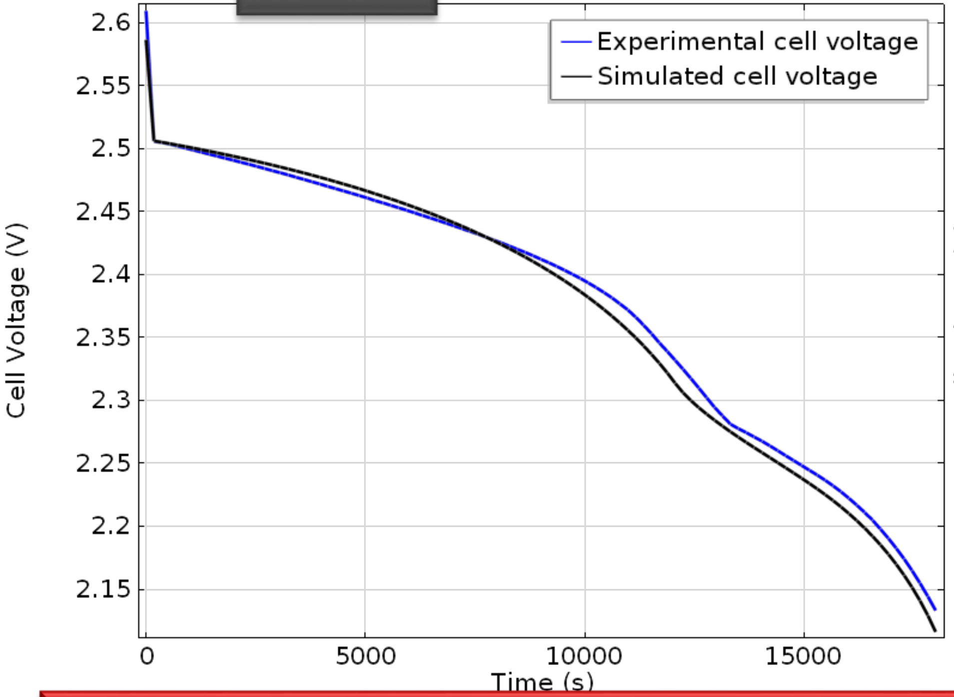
➔ As expected, the model predicts less overall polarization with a thinner electrolyte

INFLUENCE OF THE THICKNESS OF THE SOLID ELECTROLYTE

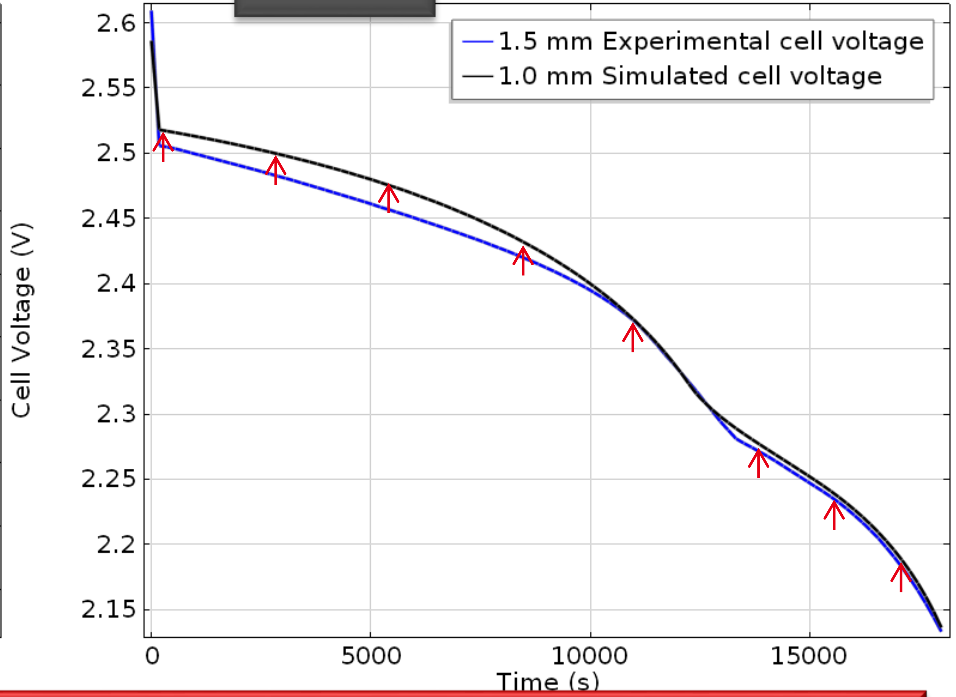
- **40 Ah discharge at C/5 @ 270 °C**
  - Cell Voltage

Only the thickness of the beta alumina has been changed between simulations

1.5 mm



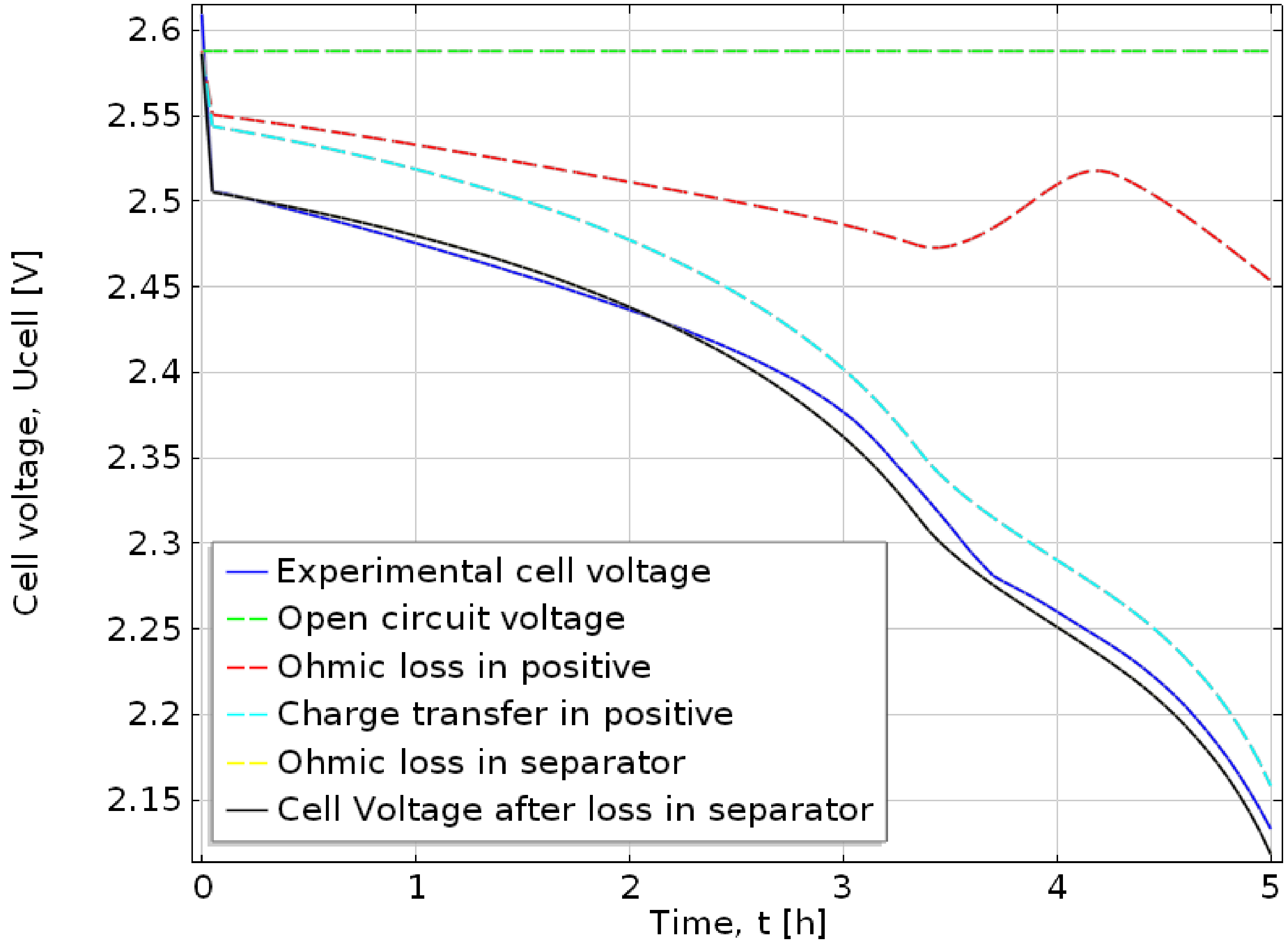
1.0 mm



➔ As expected, the model predicts less overall polarization with a thinner solid electrolyte

REFERENCE SIMULATION CONSTANT OPERATIONAL TEMPERATURE

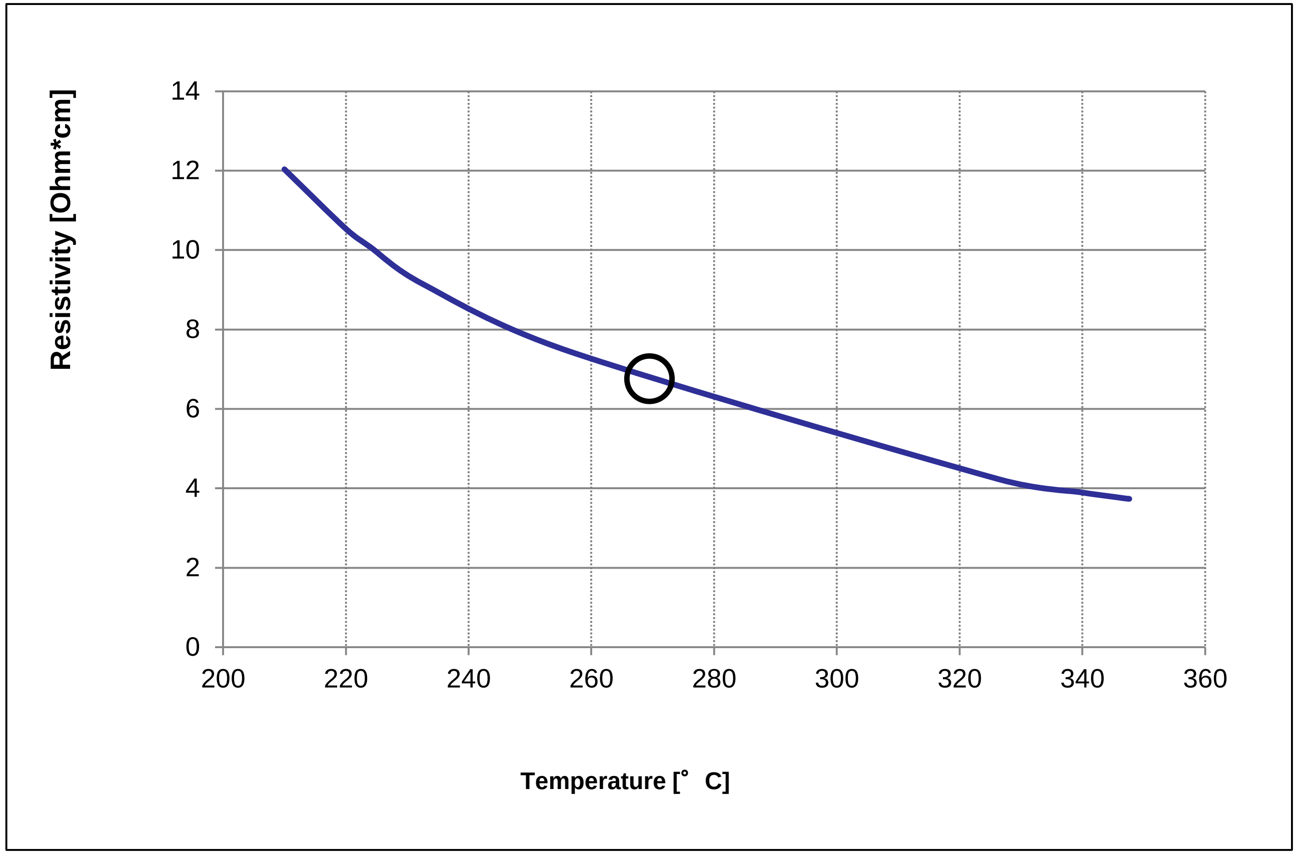
- **40 Ah discharge C/5, 270 °C**
  - Cell Voltage



Ohmic loss in negative and charge transfer in negative contributions are surimposed on the cell voltage

From $U_{cell} = E°_{Fe}$, displaying all the contributions is tricky because we don't know the mixed potential related to C/5, and charge transfer in positive is spatially inhomogeneous

FIAMM BETA ALUMINA RESISTIVITY



Relation implemented in the model (FIAMM data)

2D MODEL IMPLEMENTATION

- **Solid-state mechanism and constant melt composition**

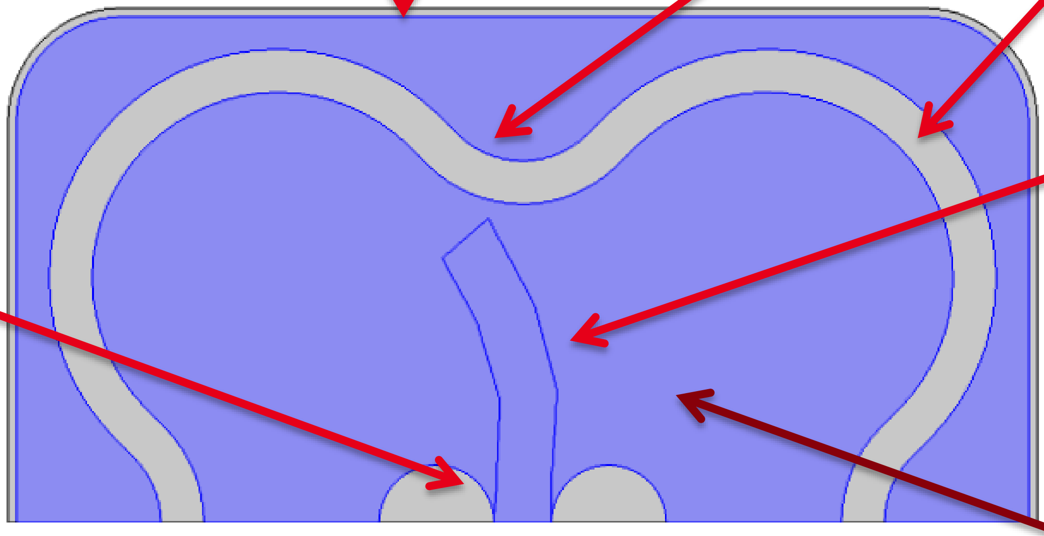
Casing domain
- Ohm's law in metal ($\mathbf{\Phi_1}$)
- Origin of potential (Φ_1 = 0V)

Anodic domain
- Ohm's law in metal ($\mathbf{\Phi_1}$)
- Linearized Butler-Volmer on beta alumina external surface (i_N)

Solid electrolyte domain
- Ohm's law in electrolyte ($\mathbf{\Phi_2}$)

Cathodic region and felt
- Ohm's law in $NaAlCl_4$ ($\mathbf{\Phi_2}$)
- Ohm's law in metal backbone and carbon ($\mathbf{\Phi_1}$)
- ~~Material balance (x_A)~~
- Electrochemical reactions (j_i)
- Chemical reaction (ϵ_{NaCl})

Current collector
- Ohm's law in metal ($\mathbf{\Phi_1}$)
- Applied current (I_{exp}) on collector surface



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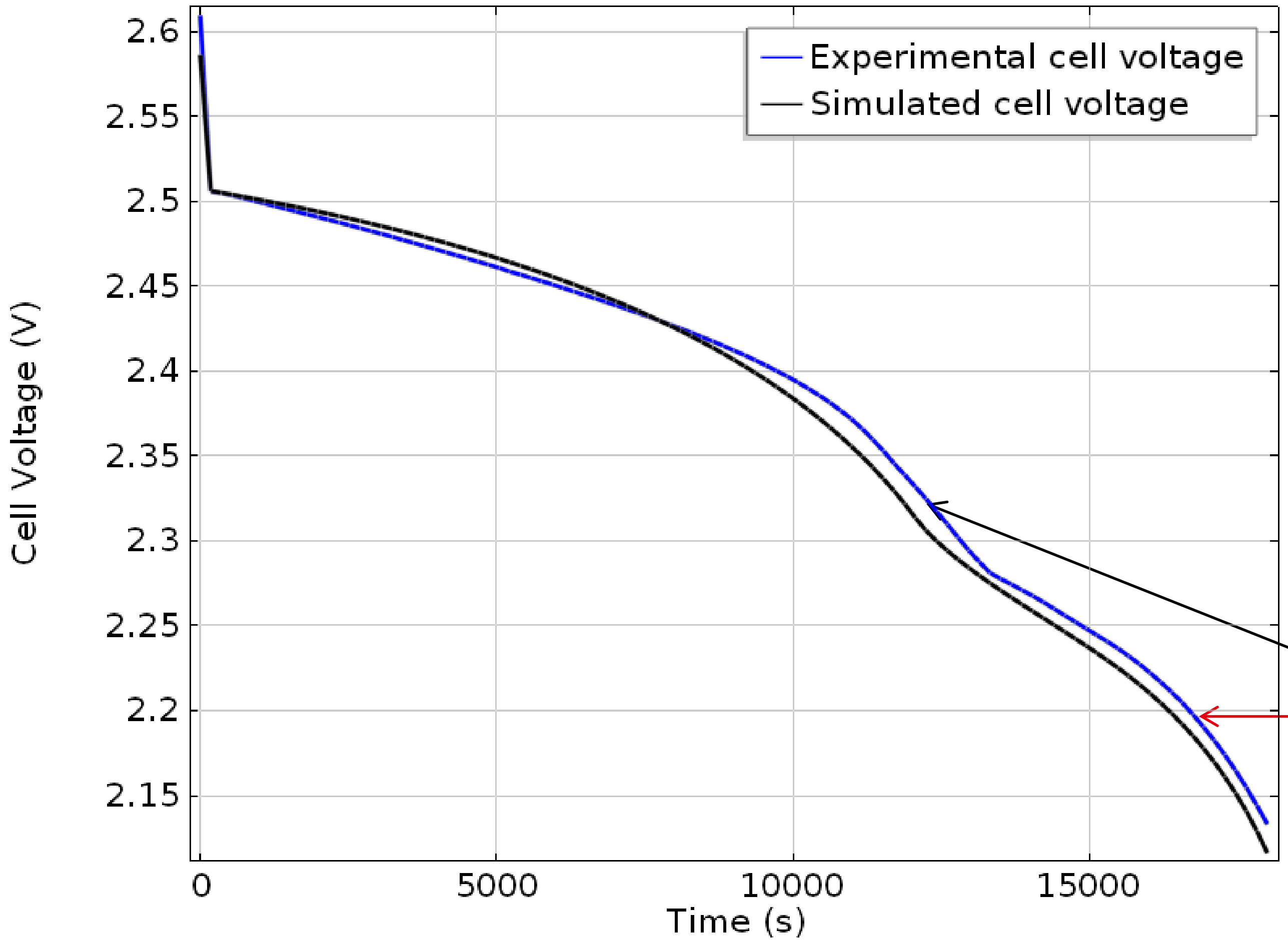
Porosity, volume fractions, exchange current densities
- $\epsilon = 1 - \sum \epsilon_{\mathrm{M}} - \sum \epsilon_{\mathrm{MCl2}} - \epsilon_{\mathrm{NaCl}}$
- $\frac{\partial \epsilon_{\mathrm{M/MCl2}}}{\partial t} \propto j_{\mathrm{M}}$ and $\frac{\partial \epsilon_{\mathrm{NaCl}}}{\partial t} \propto \cancel{k_p}\, j$
- $\boldsymbol{j = j_{\mathrm{Ni}} + j_{\mathrm{Fe}}}$

SIMULATION ISOTHERMAL MODE

- **40 Ah discharge C/5, 270 °C**
  - Cell Voltage



$n_{MCl2,init}$ from cyclic voltammetry measurements (apparent Ah contributions)
$S_{\text{collector}} = 48\ \text{cm}^2$
$i_{0,\text{ref,Ni}} = 3 \cdot 10^{-5}\ \text{A/cm}^2$
$i_{0,\text{ref,Fe}} = 5 \cdot 10^{-5}\ \text{A/cm}^2$
Active material form: $p = 1.3$

Simulation does not managed temperature rise and fluorinated additive contribution

Na-MCl_2 TECHNOLOGY

- **General Principles**

Beta alumina with conductivity similar to common aqueous electrolytes (260 - 350 ºC)

secondary electrolyte melt Na^+ conductor $NaAlCl_4$

Na	β"- Al_2O_3	MCl_2
Negative active material	Solid electrolyte **and** separator	Positive active material

FIAMM SO|NICK

23.5 cm x 3.5 cm

Fe based solution Na-$FeCl_2$
OCV_{Fe} = 2.33 V @ 300 ºC

Ni based commercial solution Na-$NiCl_2$
OCV_{Ni} = 2.58 V @ 300 ºC