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Solutions industrielles en ingénieries avancées

Electrochemical Modelling of Processes in Batteries

Empirical and Mechanistic Approches

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Key data on battery market

Key data on battery market

- ~ 100 Billions USD / y*
- High growth : 8 % / y*

Global Information, Inc.

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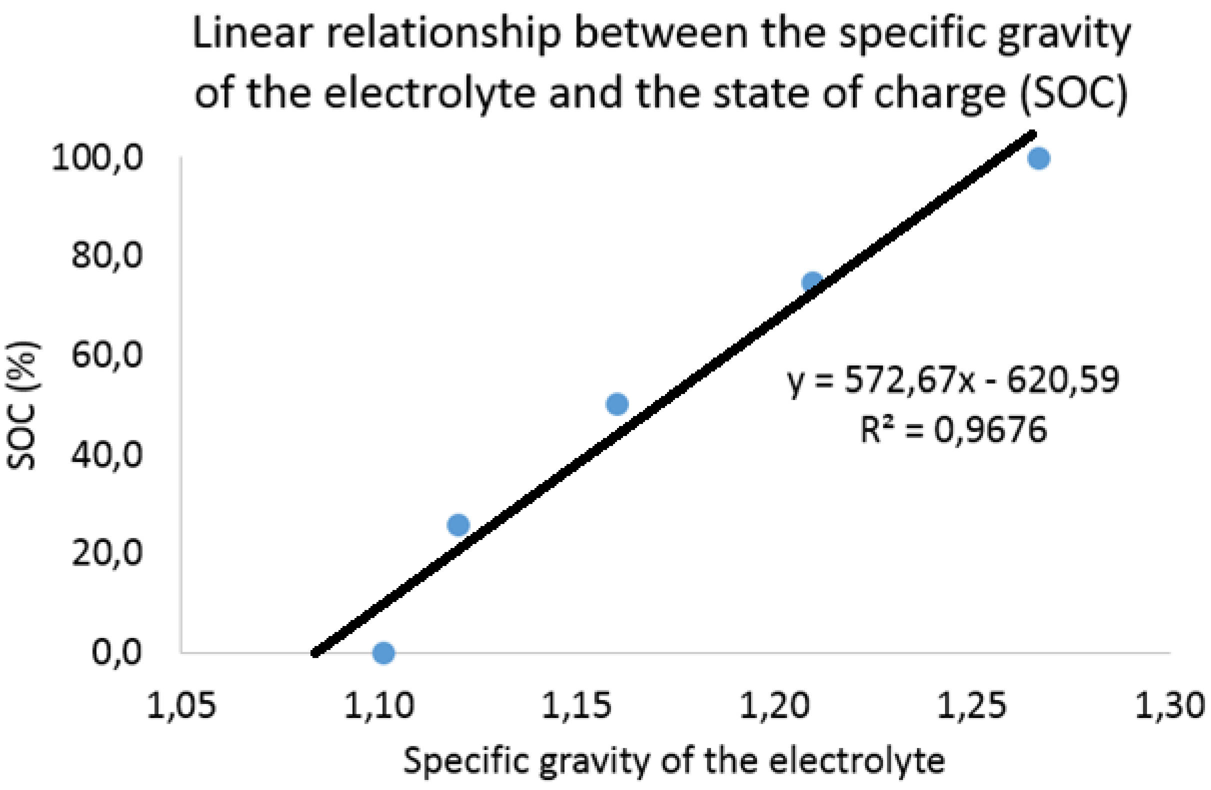
Aim of modelling

- Improvement of experimental set-up design
- Improvement of battery design
- Performance optimization (Voltage, current, power,….).
- Cost reduction
- Improvement of safety (fire, explosion).
- Robust model → Gain of time and money in the developpement stage

Empirical approach

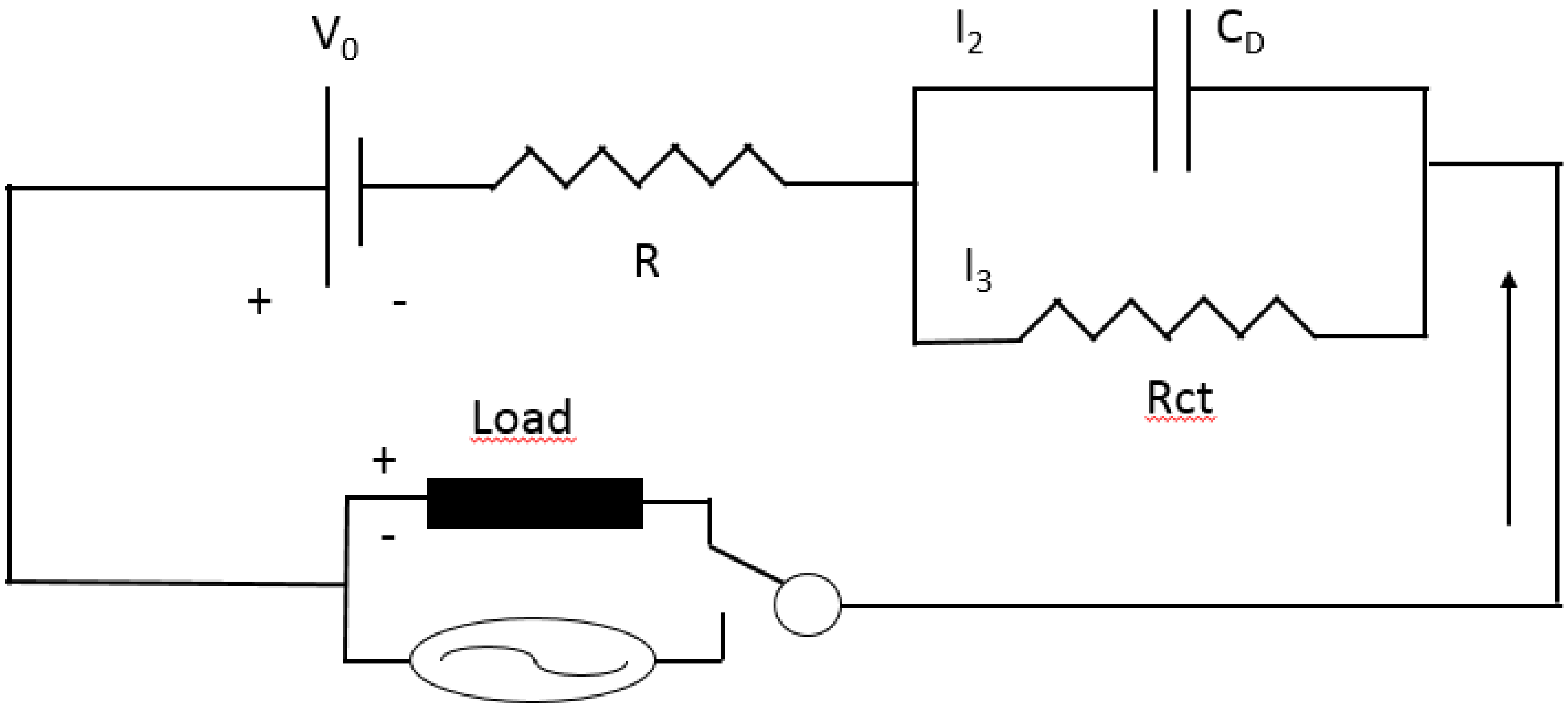
Battery Modelling : Empirical approach*

- An empirical model often assumes the form of an expression that relates operating conditions (rate of charge/discharge, load) with the measured quantities (voltage, temperature,…).
- A basic understanding of the limitations within the cell serves as guideline.
- Example : Electrolyte conductivity as a function of the SOC



Battery Modelling : Empirical approach*

- NiMH Battery



* Linden's handbook of batteries, 4th edition.

Battery Modelling : Empirical approach*

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$$V = \frac{Q_0}{C_D} e^{\left(-\frac{t}{R_{ct} C_D}\right)} + V_0 + I\,R + I\,R_{ct}\,\left(1 - e^{\left(-\frac{t}{R_{ct} C_D}\right)}\right)$$

Q_0 : total capacity of the battery (A.s)

C_D : capacitance (F)

R_{ct} : Resistance (Ohm)

V_0 : Open circuit voltage (Volt)

I : Current (A)

R : Resistance (Ohm)

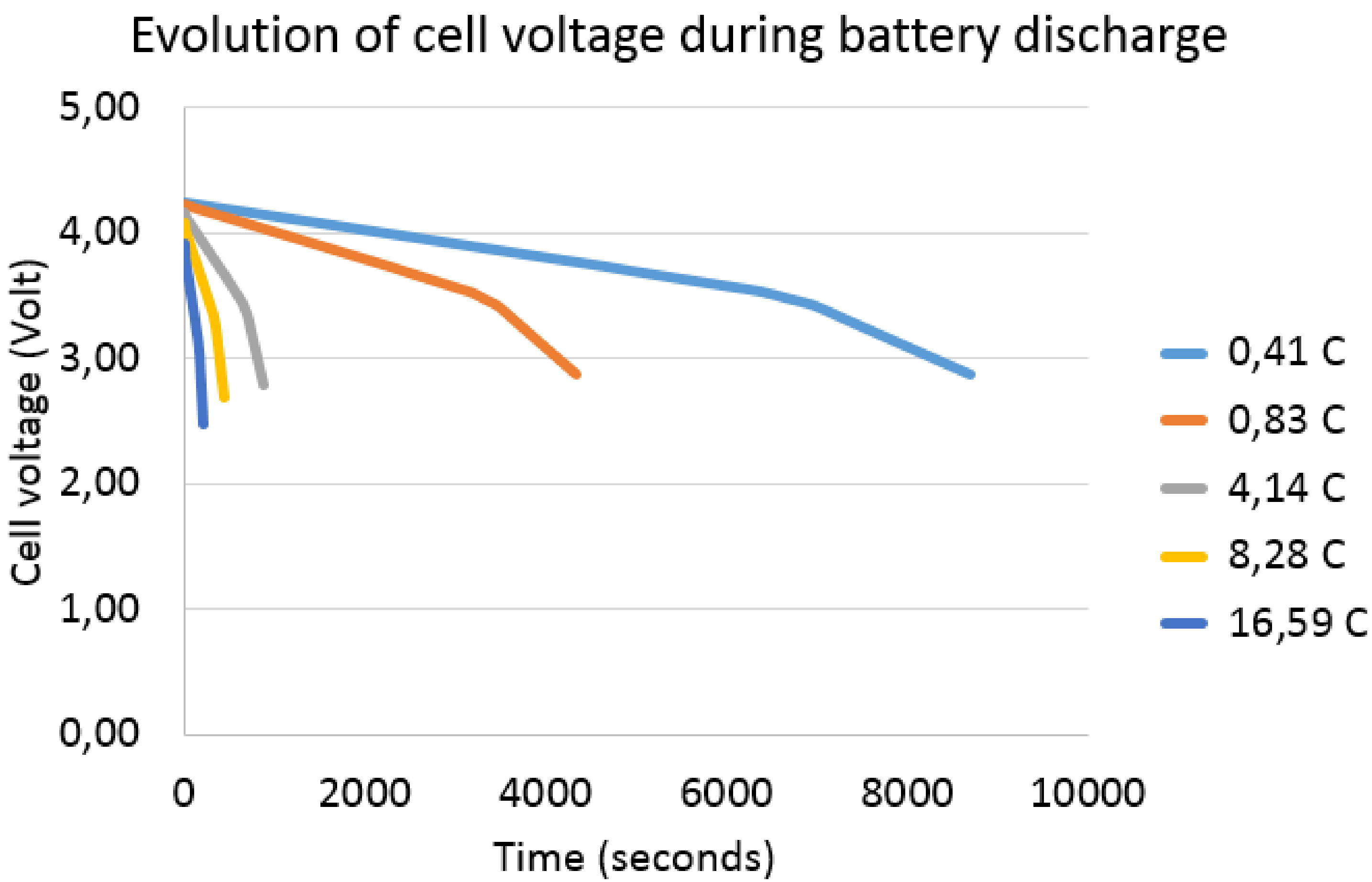
Battery Modelling : Empirical approach*

Parameters used in the equivalent circuit model to predict the response of a Lithium – Ion cell

Parameter	Discharge	Charge
$\tau = 1/(R_{CT}\, C_D)$ (s)	5	5
C_D (F)	12 500	16 667
R, mΩ	1,637	1,637
R_{ct}, mΩ	0,4	0,3

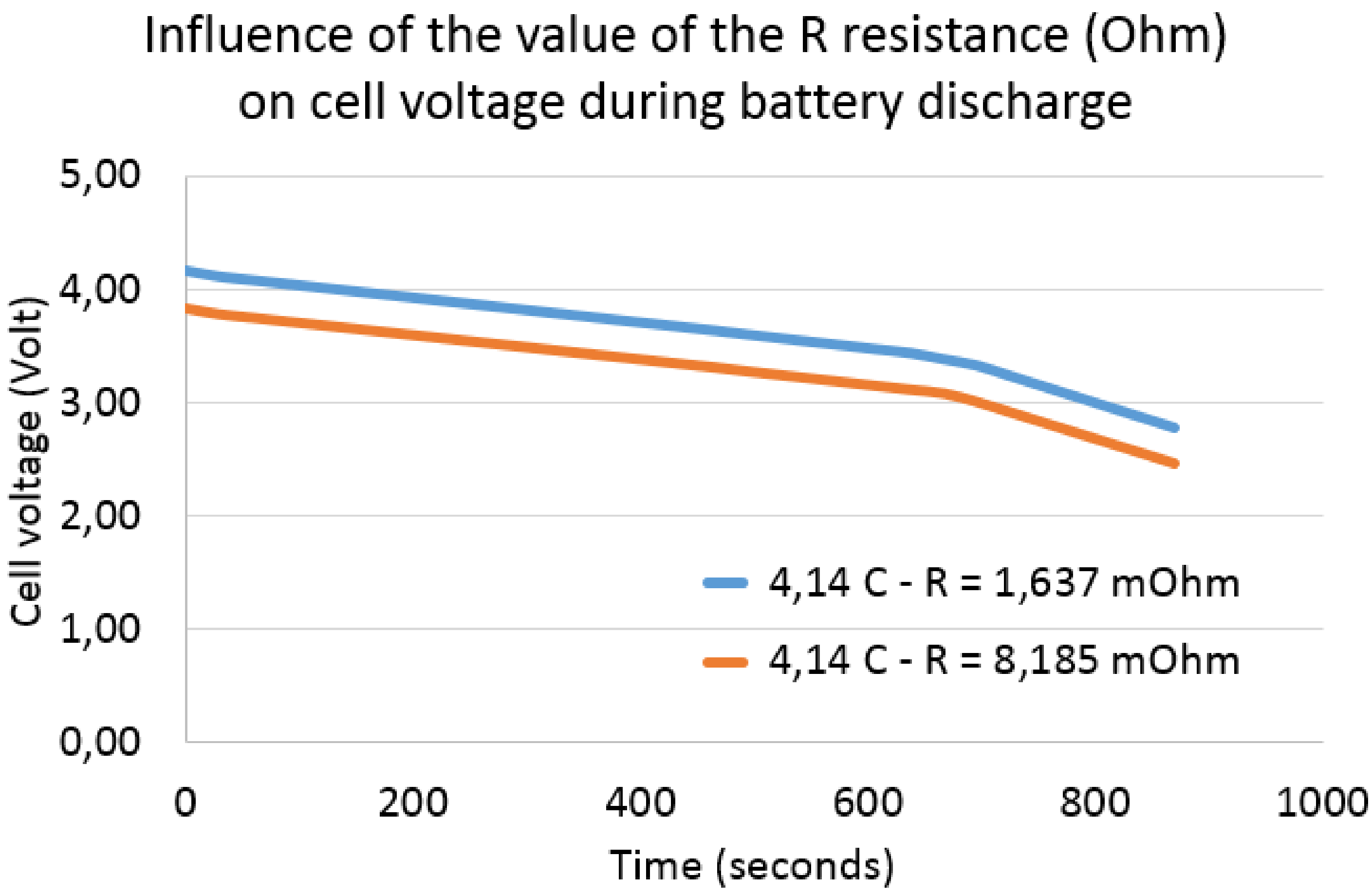
Battery Modelling : Empirical approach*

Calculation of cell voltage as a function of time for various discharge rates (at constant power)



Battery Modelling : Empirical approach*

Parameters changing : Value of the R resistance (Ohmic drop)



Mechanistic approach

Mechanistic models relate the battery characteristics to physical properties of the constituent materials.

Such properties can me measured in independent experiments

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TYPE OF CURRENT DISTRIBUTIONS

Primary current distribution :

Accounts for : - Losses du to solution resistance only

Secondary current distribution :

Accounts for :
- Losses due to solution resistance
- Electrode kinetics

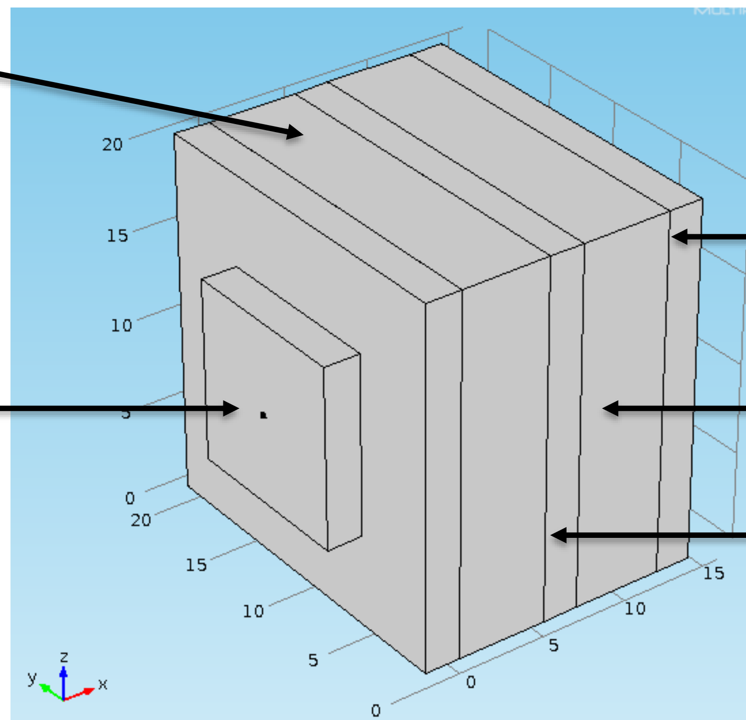
Tertiary current distribution :

Accounts for :
- Losses due to solution resistance
- Electrode kinetics
- Impact of concentration evolution on conductivities and kinetics

MECHANISTIC MODELLING

Software used for modelling : Comsol Multiphysics®

Size of the cell : 20 mm x 20 mm x 20 mm



Description of physical and electrochemical phenomenon occuring in the battery : Secondary current distribution

Current collectors

$$\nabla \cdot \mathbf{i}_s = Q_s, \quad \mathbf{i}_s = -\sigma_s \nabla \phi_s$$

Anode current collector

Material : copper

$\sigma s = 6{,}00 \times 10^{7}$ S.m^{-1}

Cathode current collector

Material : titanium

$\sigma s = 7{,}4 \times 10^{5}$ S.m^{-1}

Description of physical and electrochemical phenomena occuring in the battery

Anode

$$i_{loc} = i_0\left(\frac{(\alpha_a + \alpha_c)F}{RT}\right)\eta$$

Eeq = + 1,0 Volt
α_a = 0,5
α_c = 0,5
i_0 = 1,0 $A.m^{-2}$
S/V = 3 000 m^{-1}

Cathode

$$i_{loc} = i_0\left(\frac{(\alpha_a + \alpha_c)F}{RT}\right)\eta$$

Eeq = - 1,0 Volt
α_a = 0,5
α_c = 0,5
i_0 = 1,0 $A.m^{-2}$
S/V = 3 000 m^{-1}

Description of physical and electrochemical phenomena occuring in the battery

Electrolyte

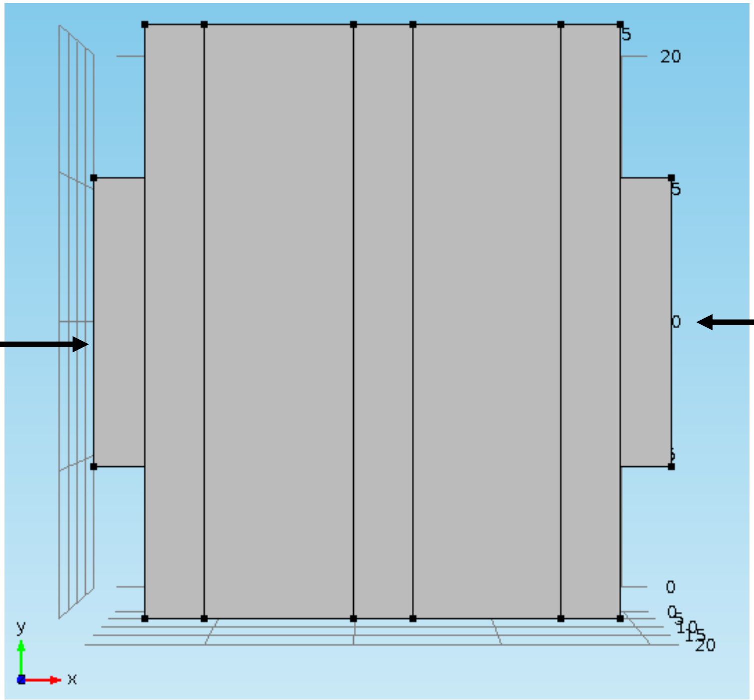
$$\nabla \cdot \mathbf{i}_l = Q_l, \quad \mathbf{i}_l = -\sigma_l \nabla \phi_l$$

$\sigma_l = 0{,}1\ S.m^{-1}$

Boundary conditions :

Anode Current Collector :

$\phi s = 0$



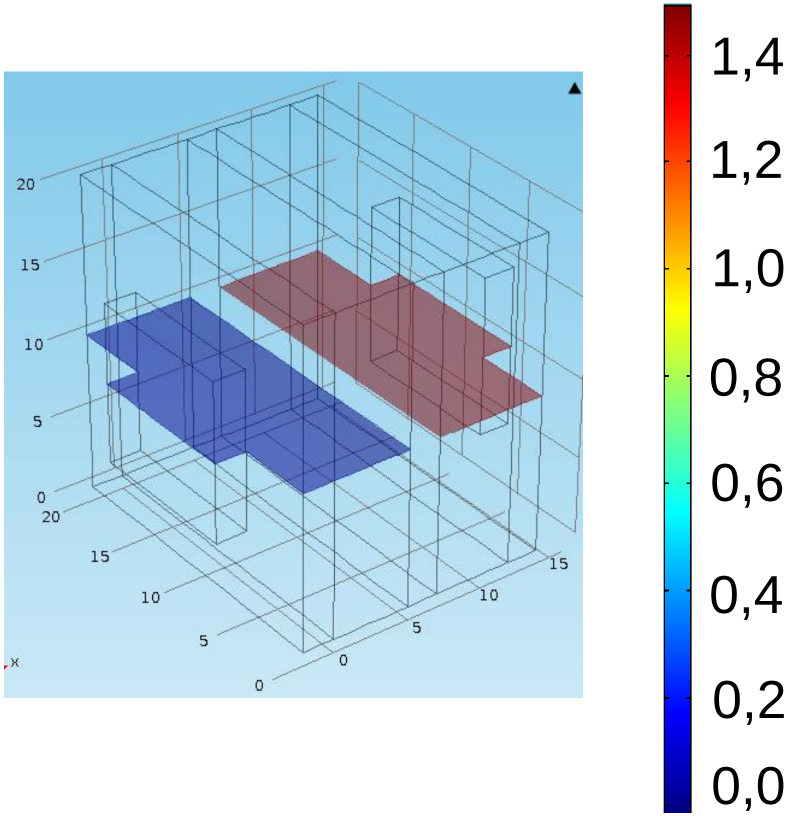
Cathode Current Collector :

$j = 10\ A.m^{-2}$

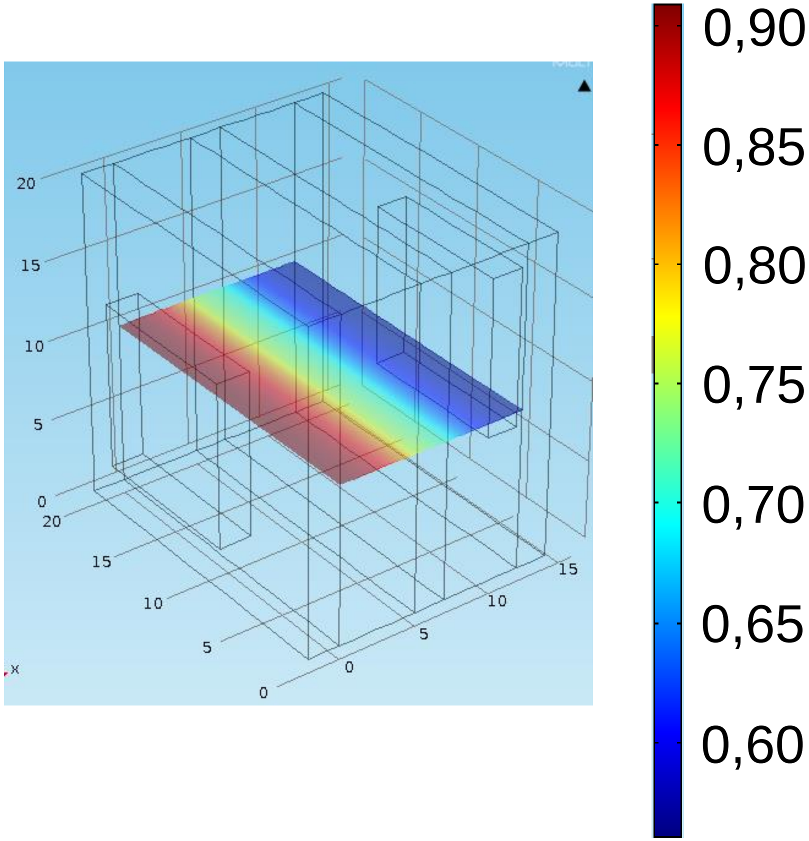
RESULTAS

With « Standard conditions » :

Solid phase potential (Volt)



Liquid phase potential (Volt)

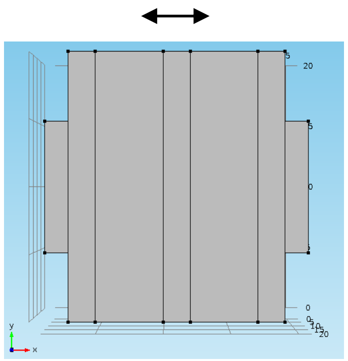


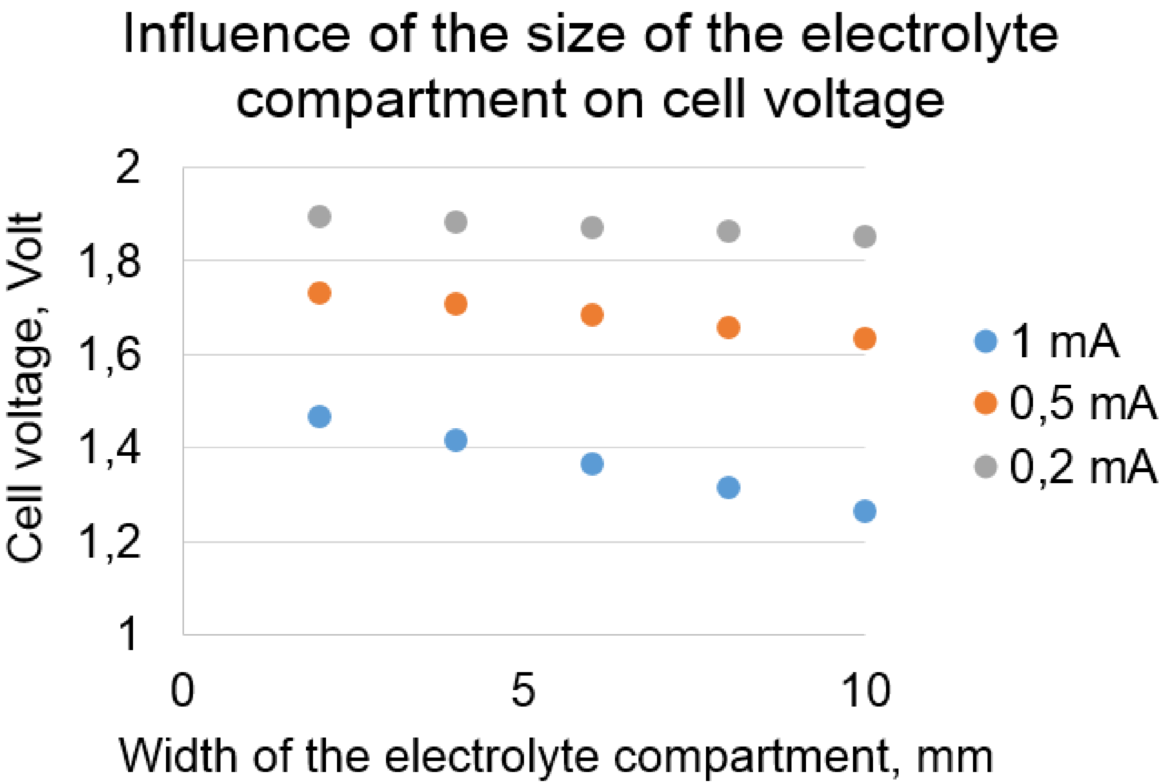
PARAMETRIC STUDY

Battery discharge with a total current of 5,0 mA, 2,5 mA and 1,0 mA

Study 1 :Width of the electrolyte compartment (2 - 10 mm)

Electrolyte compartment



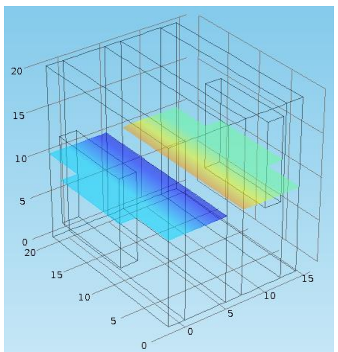


PARAMETRIC STUDY

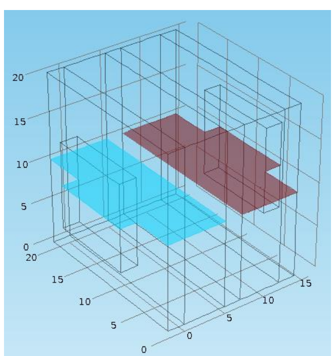
Battery discharge with a total current of 4,0 mA, 2 mA and 0,1 mA

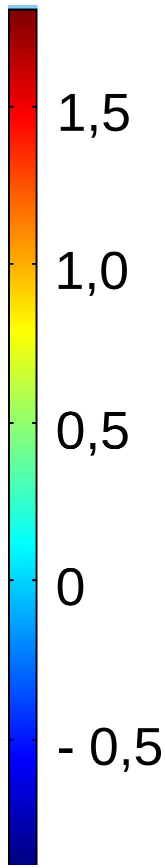
Study 2 : Anode and cathode conductivities (0,1 – 1000 $S.m^{-1}$)

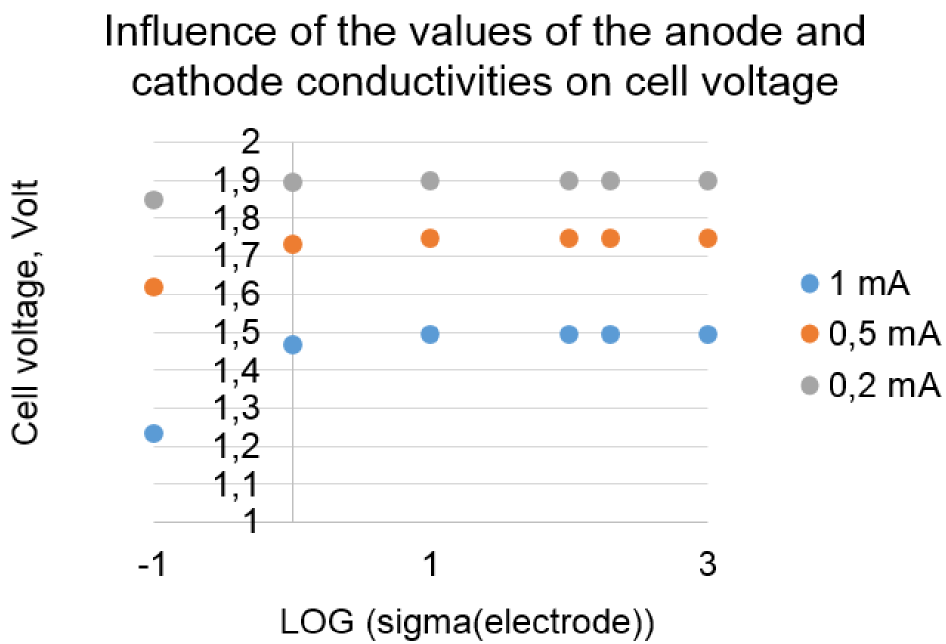
σs =
0.1 $S.m^{-1}$



σs =
1000 $S.m_{-1}$





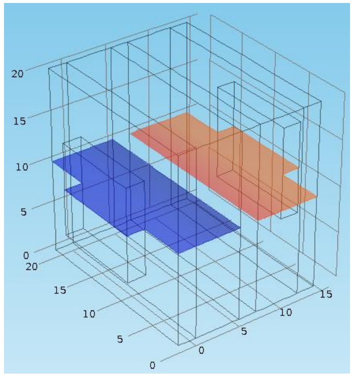


PARAMETRIC STUDY

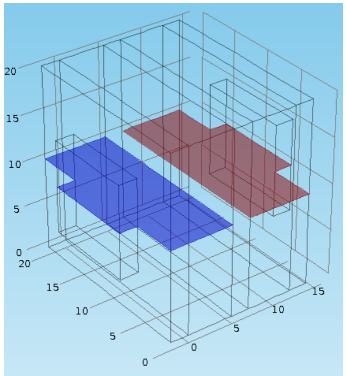
Battery discharge with a total current of 4,0 mA, 2 mA and 0,1 mA

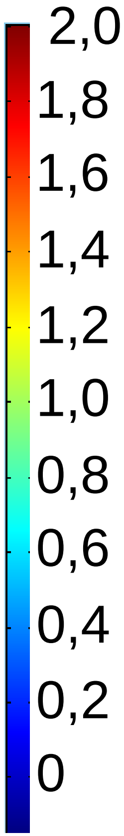
Study 3 : Electrolyte conductivity (0,1 – 10 $S.m^{-1}$)

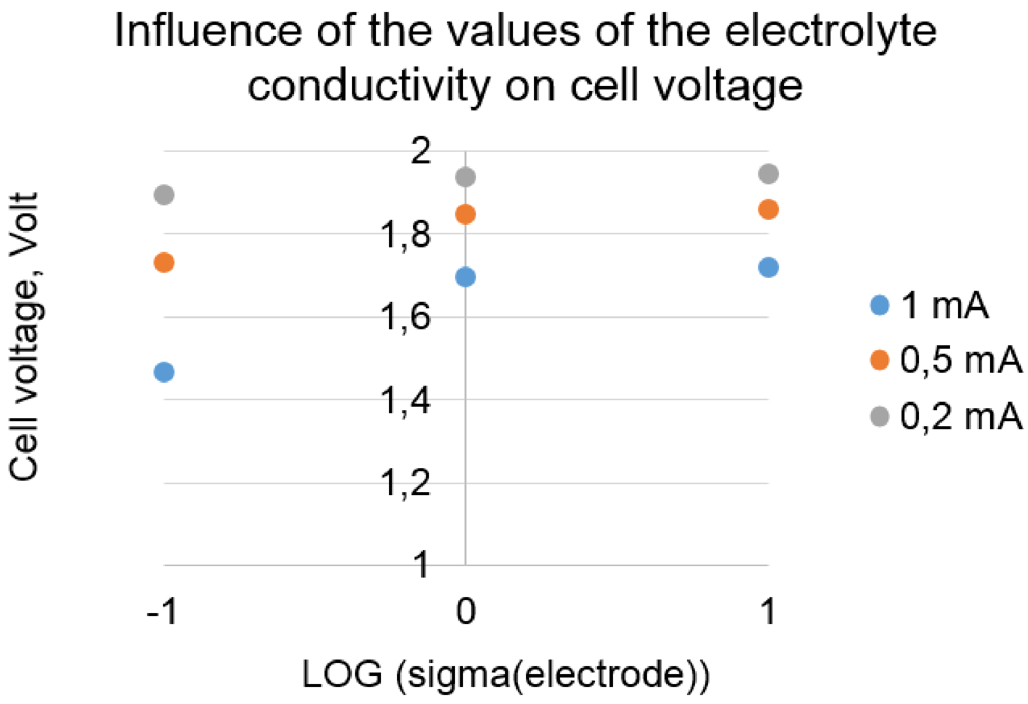
σl = 0.1 $S.m^{-1}$



σl = 10 $S.m^{-1}$







TERTIARY CURRENT DISTRIBUTION

- Takes into account to impact of concentration evolution on conductivities and kinetics

Example : Additionnal terms and modifications compared to the secondary current distribution presented previously :

Kinetics expression type:

Linearized Butler-Volmer

Exchange current density:

i_0 i_cathode*c/c0 A/m^2

Anodic transfer coefficient:

α_a 0.5 1

Cathodic transfer coefficient:

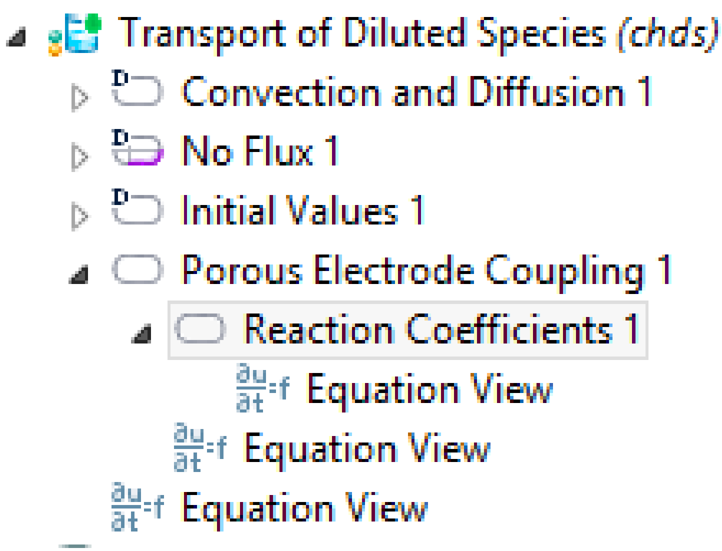
α_c 0.5 1

$$i_{loc} = i_0\left(\frac{(\alpha_a + \alpha_c)F}{RT}\right)\eta$$

Local cathodic current depends on overpotential (Volt) AND concentration of the c counpound (mol.m^{-3})

TERTIARY CURRENT DISTRIBUTION

→ Transport of diluted species module (Comsol ®)



Porous electrode coupling

Initial concentration : 1 000 mol.m^{-3}

→ Reactant consumption proportionnal to the local current

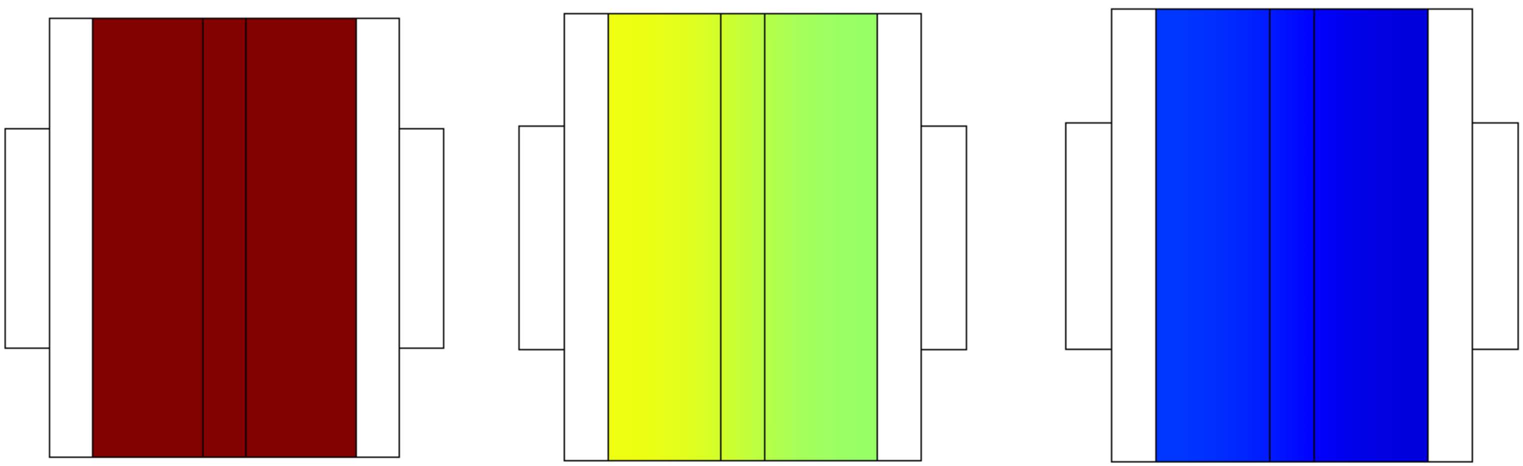
$D = 10^{-9}\ m^2.s^{-1}$

MECHANISTIC MODELLING

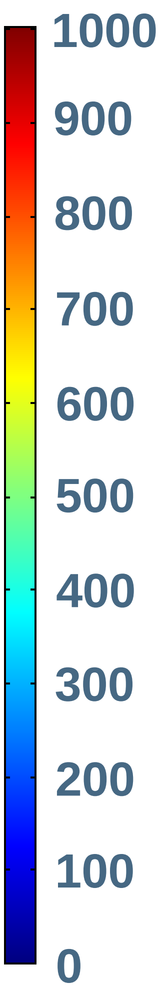
Transient modelling

t = 0 to 4.10^5 seconds

Concentration of the ionic species c in the electrolyte



t = 0 s | t = 2.10^5 s | t = 4.10^5 s



Average concentration in the cell :

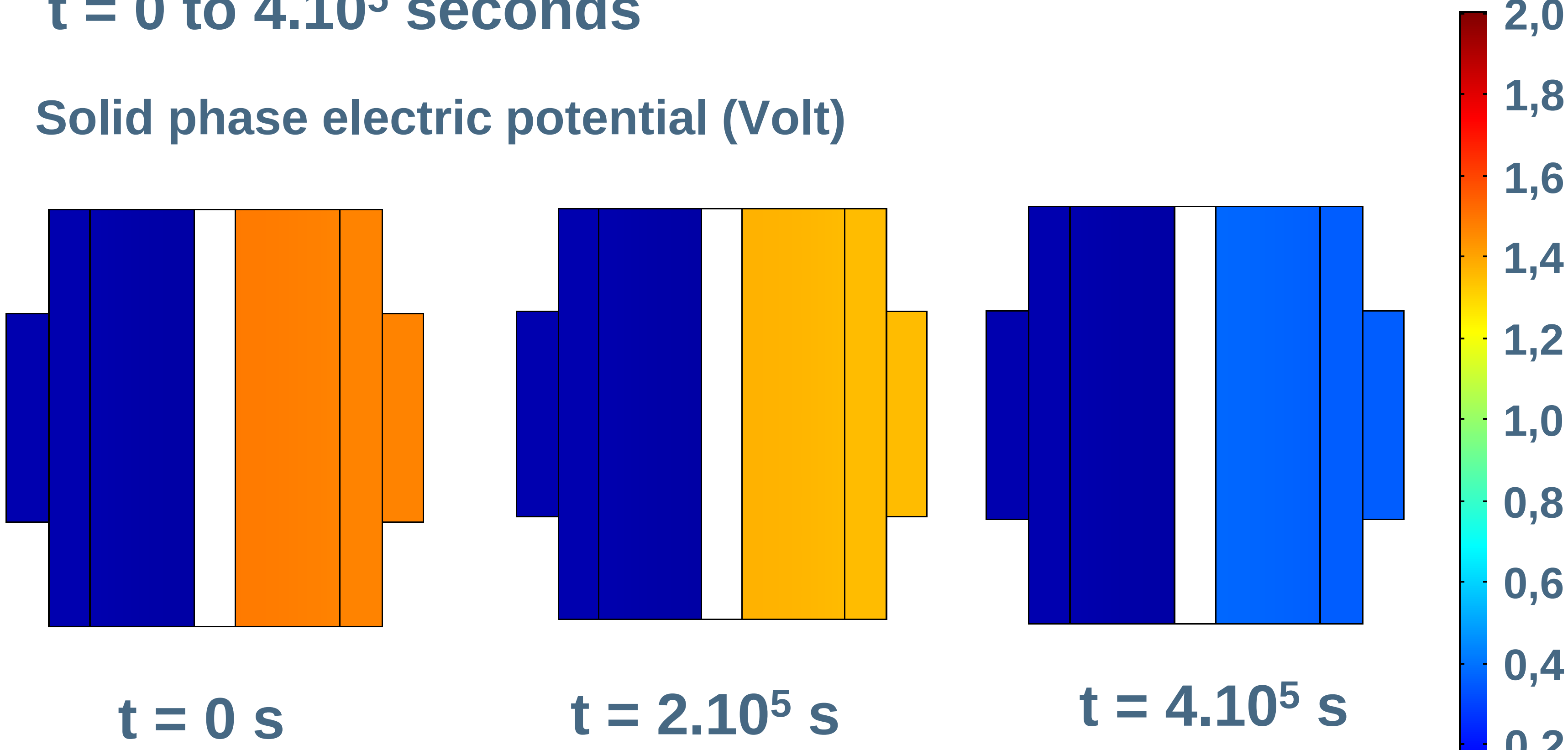
1000 mol.m-3 | 568 mol.m-3 | 136 mol.m-3

MECHANISTIC MODELLING

Transient modelling

t = 0 to 4.10^5 seconds

Solid phase electric potential (Volt)



Average concentration in the cell :

1000 mol.m-3 | 568 mol.m-3 | 136 mol.m-3

CONCLUSIONS

Modelling is useful for better understanding of performance limitations and battery optimization.

Empirical modelling is usefull to model the performance of an existing system.

Mechanistic modelling is usefull to study the influence of various parameters (conductivities, electrode material, current collector materials,…).