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Current density distribution for a full scale industrial alluminization process

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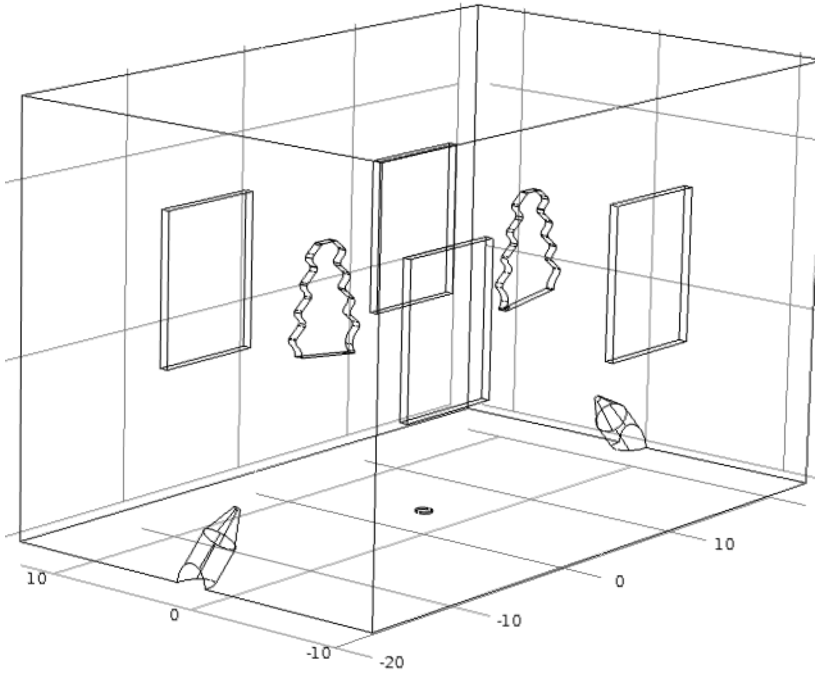
The term «Ionic Liquid (IL)» describes salts characterized by a melting temperature below 100 °C, thus we can refer to these substances as «Room Temperature Molten Salts». (RTMS)

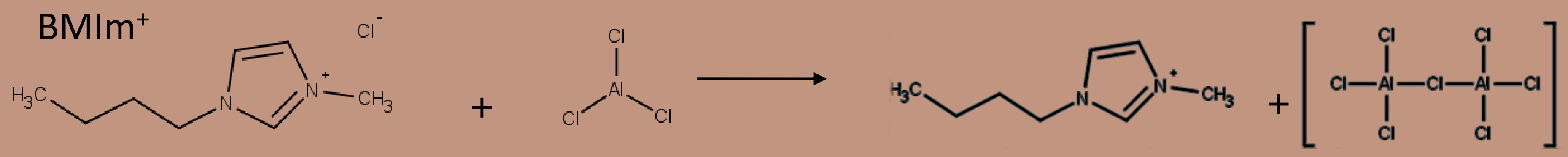
Their main features are:

- Low vapour pressure
- Low flammability
- Long shelf life under suitable condition
- Wide electrochemical window

A turbine blade usually coated with alluminium from vacuum techniques. Bumper trim usually coated with nichel-chromium.



Ideal galvanic cell at an industrial scale for the Al electrodeposition on complex shaped cathodes.



Acid chloroalluminated ILs are a common choice as electrolytes for electrodeposition process of alluminium. BMImCl/$AlCl_3$ (Butyl Methyl Imidazole), is one of the most promising in terms of reliability in the perspective of an industrial scale up.

- Very high concentration of electroactive species
- Low vapour pression ensure safer use

Different formulation of the BMImCl/$AlCl_3$ has been considered, the most affordable is characterized by a molar ratio 1:1.5 BMImCl/$AlCl_3$.

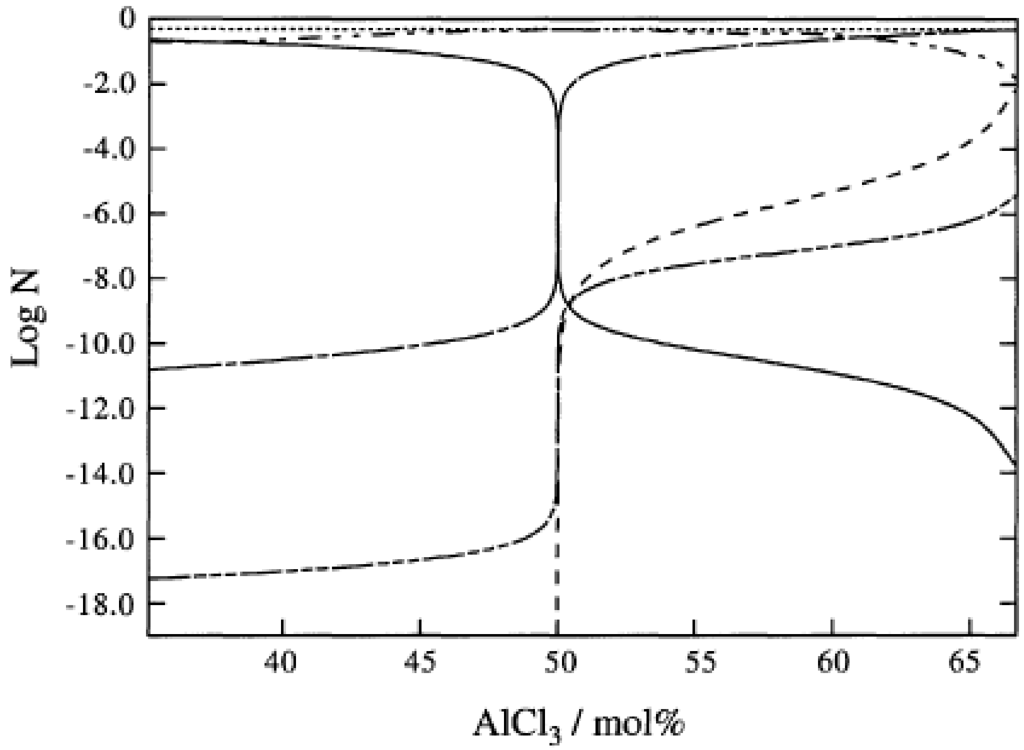
- Less moisture sensitive than 1:2 (BMImCl/$AlCl_3$)
- Lower viscosity than 1:2 (BMImCl/$AlCl_3$)
- Higher performance than 1:1 (BMImCl/$AlCl_3$)

$4Al_2Cl_7^- + 3e^- \longrightarrow 7AlCl_4^- + Al$ Electrodeposition reaction

$Al_2Cl_7^- + 6H_2O \longrightarrow 6HCl\uparrow + 2Al(OH)_3\downarrow + Cl^-$ Reaction with water

The estimated composition of the main chemical species in the IL is:

- $Al_2Cl_7^-$ = 1.708 mol dm^{-3}
- $AlCl_4^-$ = 1.708 mol dm^{-3}
- $AlCl_3$ = 2.161 10^{-7}mol dm^{-3}



S. Caporali, PhD thesis, Università Studi di Firenze, XVIII (2006) *in italian*

Distribution of chloroalluminated species to percentage of molar fraction: $AlCl_3$ a 60°C[3]

- __ : Cl^-
- _ . _ : $Al_2Cl_7^-$
- _ . . _ $AlCl_4^-$
- _ _ _ : Al_2Cl_6
- _ . . . _ : $AlCl_3$.

Build of a reliable model of the electrochemical system using COMSOL Multiphysics ®

This task aim to obtain a reliable model for the simulation of the electrodeposition process of alluminium from ionic liquids, by means of the finite elements analysis (FEA).

The simulations will allow to optimize the geometry of the electrochemical cells for different electrodeposition process.

Modelling details for the BMImCl/$AlCl_3$ (1:1.5)

Λ	0.8242 S cm^{-1}
D($AlCl_4$)	6.1 10^{-11} m^2s^{-1} [1]
D(Al_2Cl_7)	1.7 10^{-11} m^2s^{-1} [1]
D(BMIm)	2.8 10^{-11} m^2s^{-1} (Appello model)
c(BMIm)	3416 mol m^{-3}
c($AlCl_4$)	1708 mol m^{-3}
c(Al_2Cl_7)	1708 mol m^{-3}
i_0	1 10^{-3} A m^2 [2]
α_a	0.6 (a_c=1-a_a)
K_{eq}	2.4 10^4 mol m^{-3} [3]

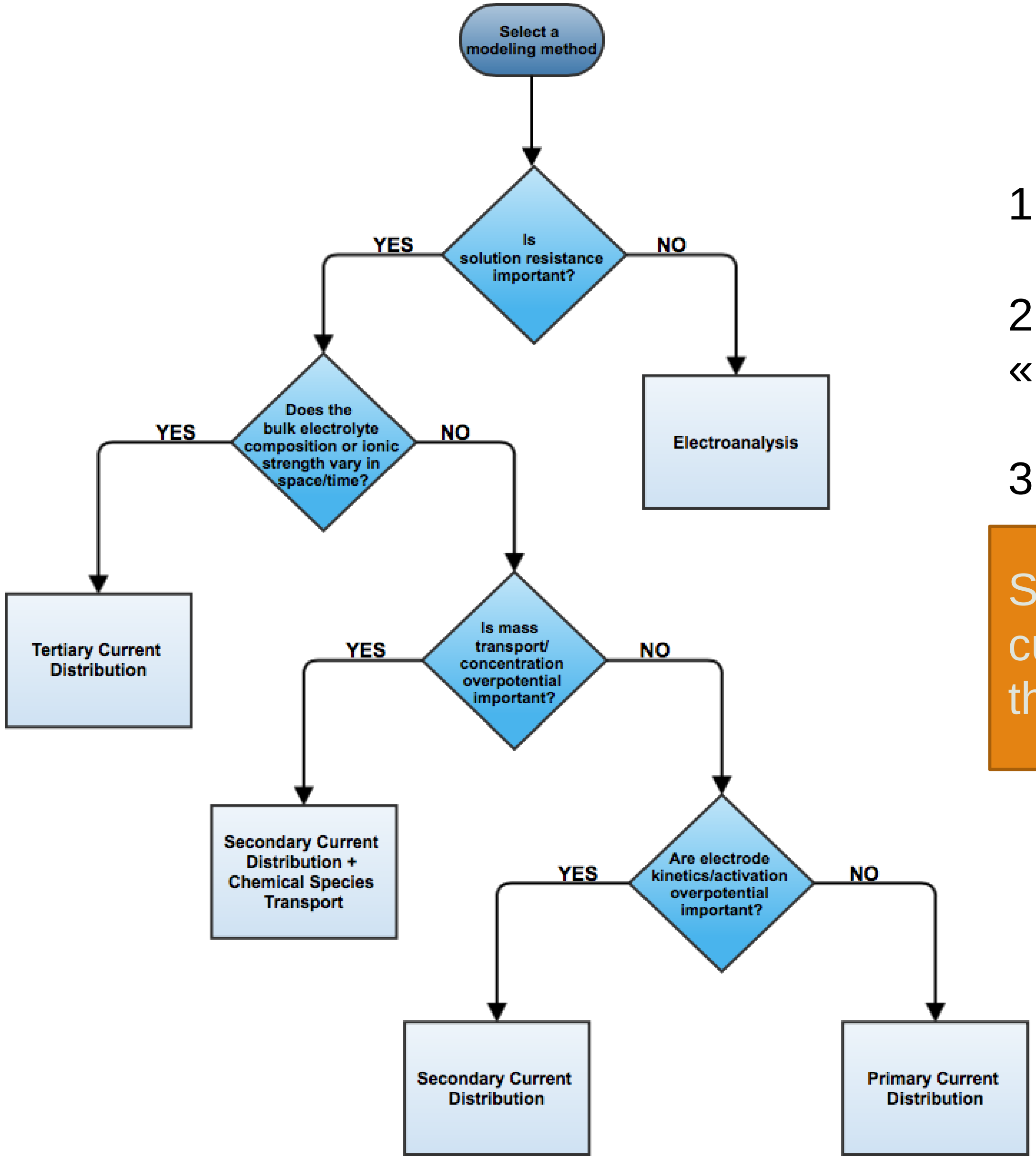
$$AlCl_3 + AlCl_4^- \rightleftharpoons Al_2Cl_7^-$$

K_{eq} extrapolated from a similar system

1. *Modeling of Aluminium Deposition from Chloroaluminate Ionic Liquids* - Journal of The Electrochemical Society, **158 (10), D634-D639 (2011)**

2. *Low-Temperature Production of Ti-Al Alloys Using Ionic Liquid Electrolytes: Effect of Process Variables on Current Density, Current Efficiency, and Deposit Morphology* – Metallurgical and materials transactions B, **40B, 114-122 (2009)**

3.*Alluminium-27 Nuclear Magnetic Resonance Study of th Room-Temperature Melt AlCl3/n-Butylpyridinium Chloride* – J**ournal of American Chemical Society**, **103, 7147-7151 (1981)**



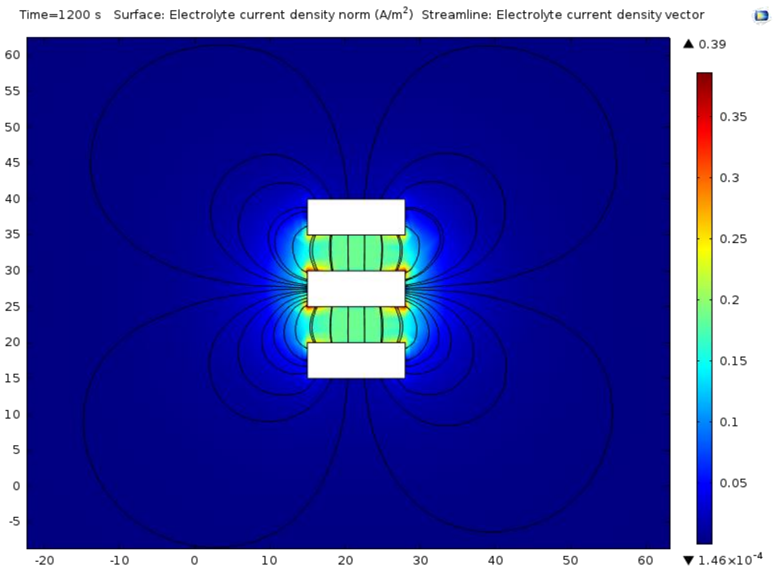
1. BMImCl/$AlCl_3$ conductivity is 0.8242 mS cm^{-1}

2. The concentrations gradients are expected to be «large» (low diffusion coefficients)

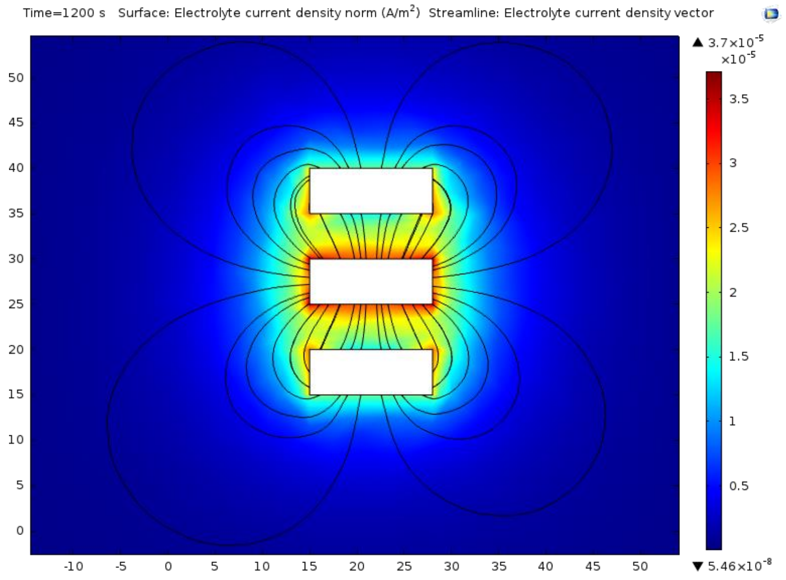
3. Likely: Tertiary current distribution

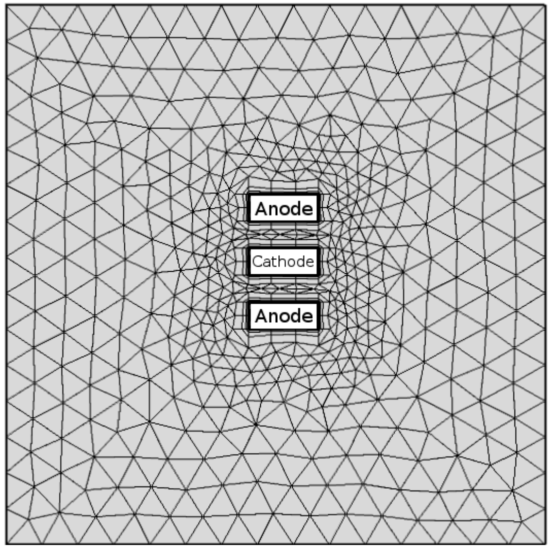
Secondary current distribution does not fit the current density on the edges (Rif. Proceedings of the comsol conference, Caporali et al 2009)

Primary current distribution

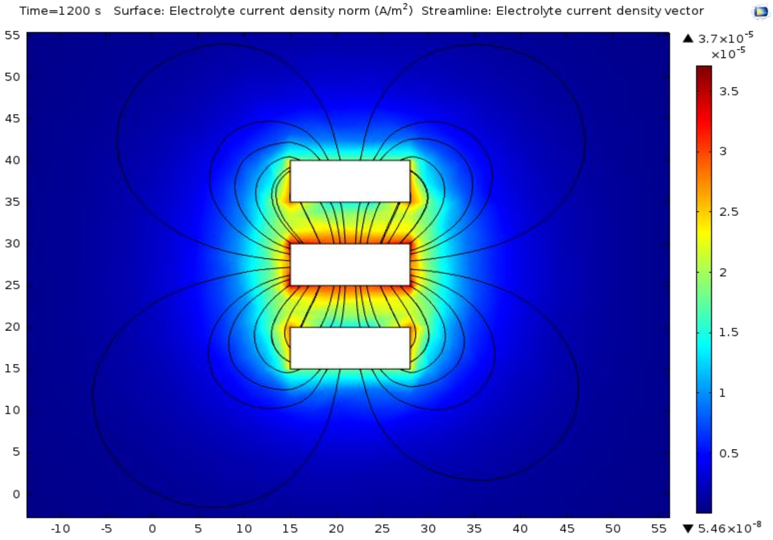


Secondary current distribution

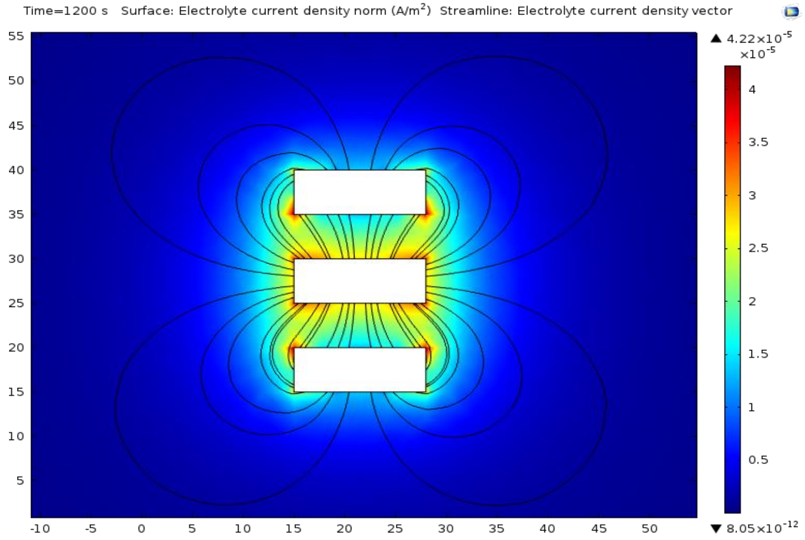




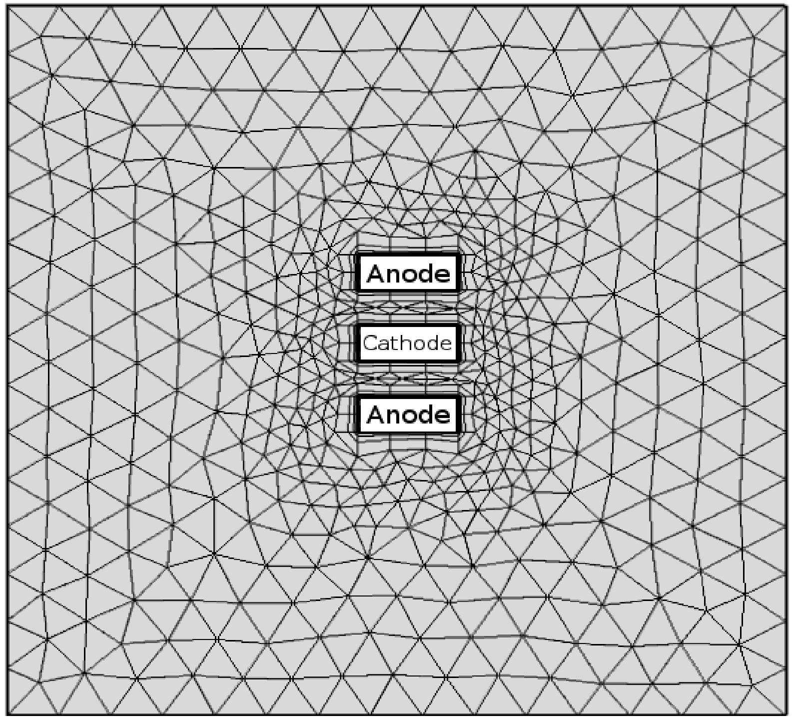
Sec+transport current distribution



Tertiary current distribution



Analysis of the boundary condition on the WE



1. $i_{loc} = i_0 \left(\frac{C_R}{C_R^0} e^{\frac{\alpha_a F\eta}{RT}} - \frac{C_O}{C_O^0} e^{\frac{-\alpha_c F\eta}{RT}} \right)$

2. $i_{loc} = i_0 \left(e^{\frac{\alpha_a F\eta}{RT}} - e^{\frac{-\alpha_c F\eta}{RT}} \right)$

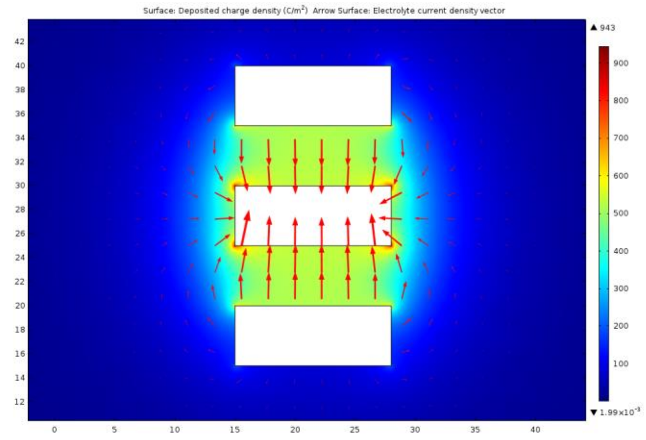
3. $i_{loc} = i_0 \left(\frac{C_R}{C_R^0} \frac{\alpha_a F\eta}{RT} + \frac{C_O}{C_O^0} \frac{\alpha_c F\eta}{RT} \right)$

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

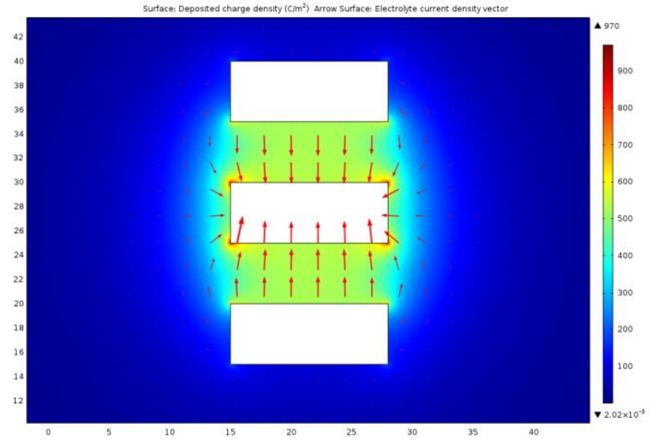
- 3,4 are expected to be suitable B.C. for η<5mV
- 2 is expected to be suitable B.C. for small concentration changes in the interphase

Charge density deposited (120 min, -1.1V)

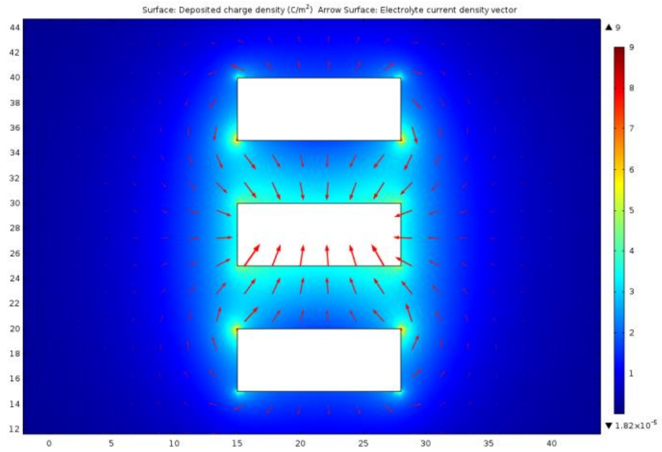
1. Butler - volmer



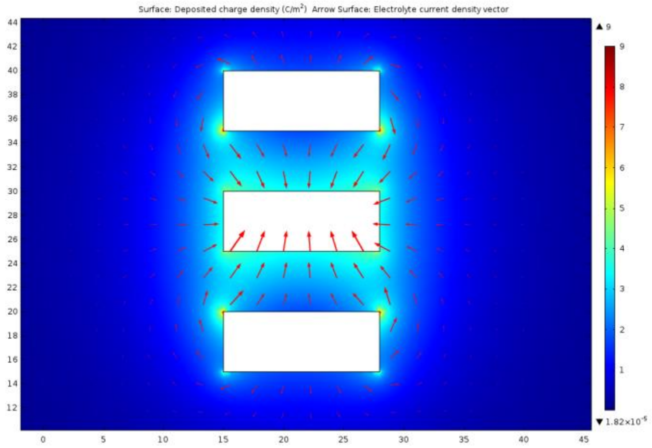
2. Butler – Volmer without conc.



3. Linearized Butler - Volmer



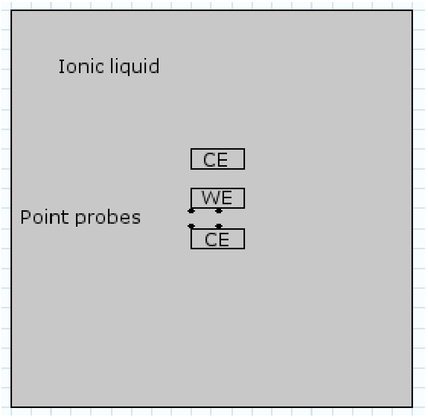
4. Linearized Butler – Volmer without conc



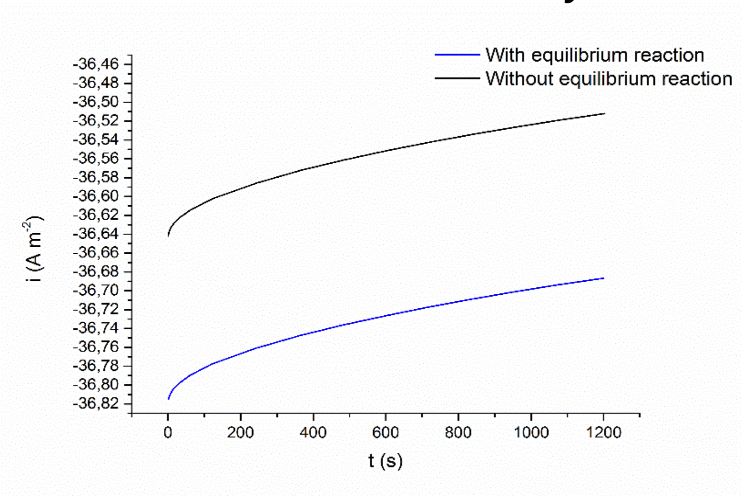
The higher level of theory (1st B.C.) is necessary for a better assesment of the charge depositated on the interface.

Effect of homogeneous reaction: $AlCl_3 + AlCl_4^- \rightleftarrows Al_2Cl_7^-$

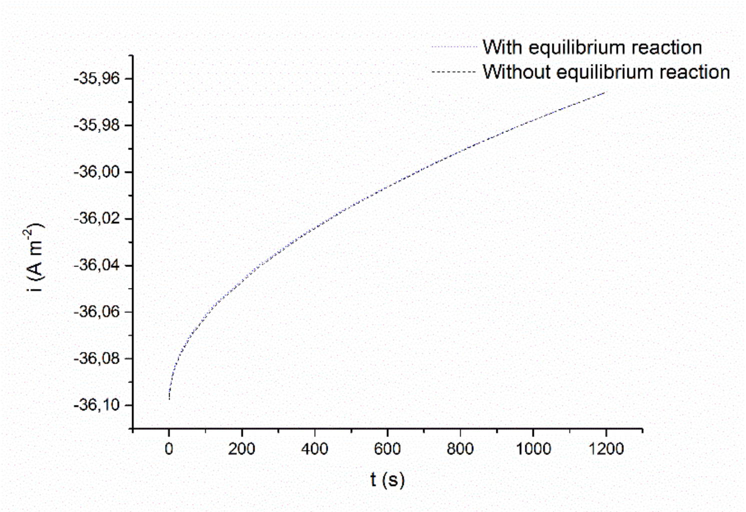
Analysis of the effects on the WE



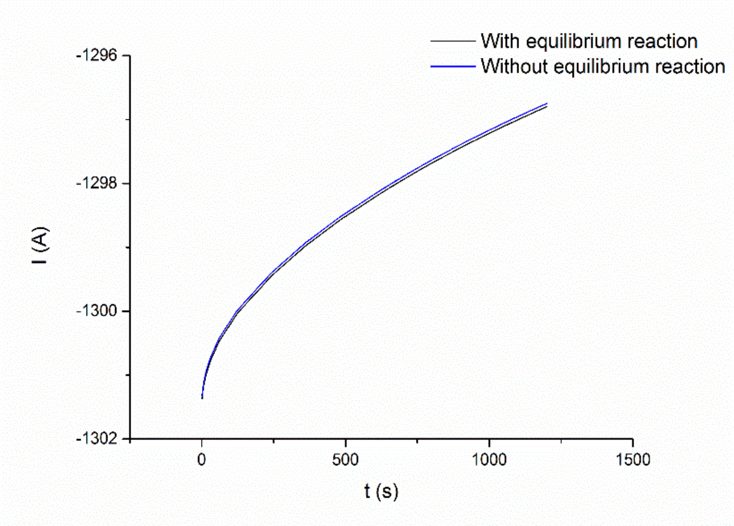
Normal current density on the edge



Normal current density on the center

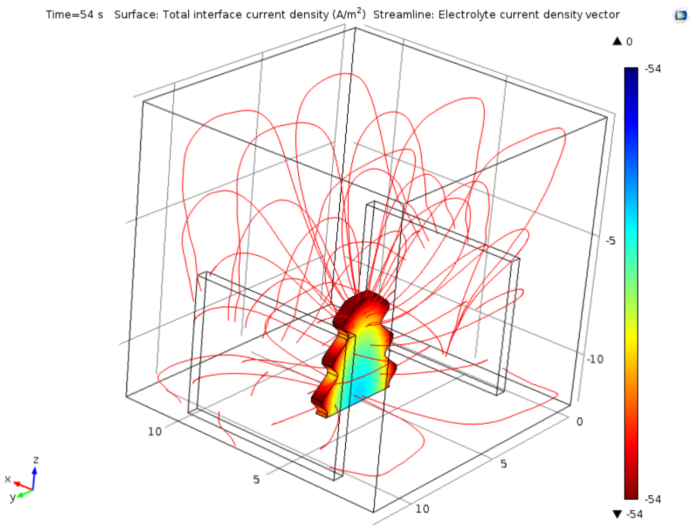


Total current on the cathode

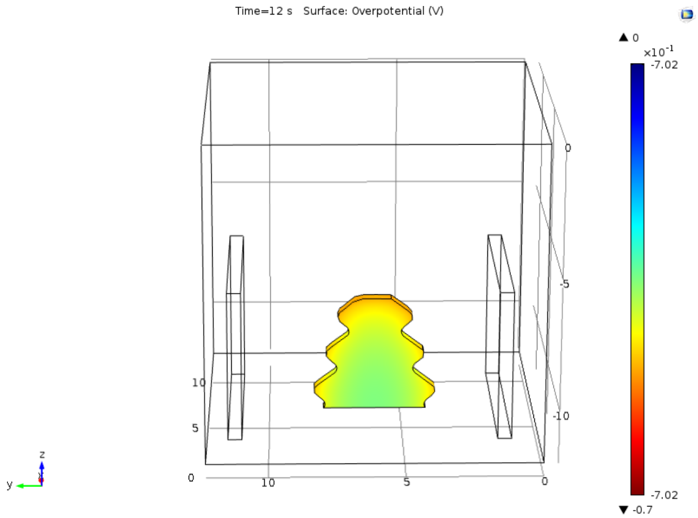


Example: Section of a turbine blade

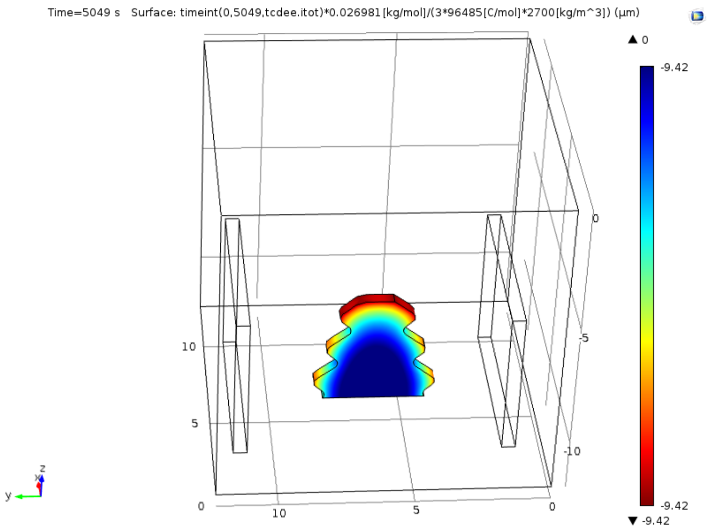
Current density



Overpotential



Thickness



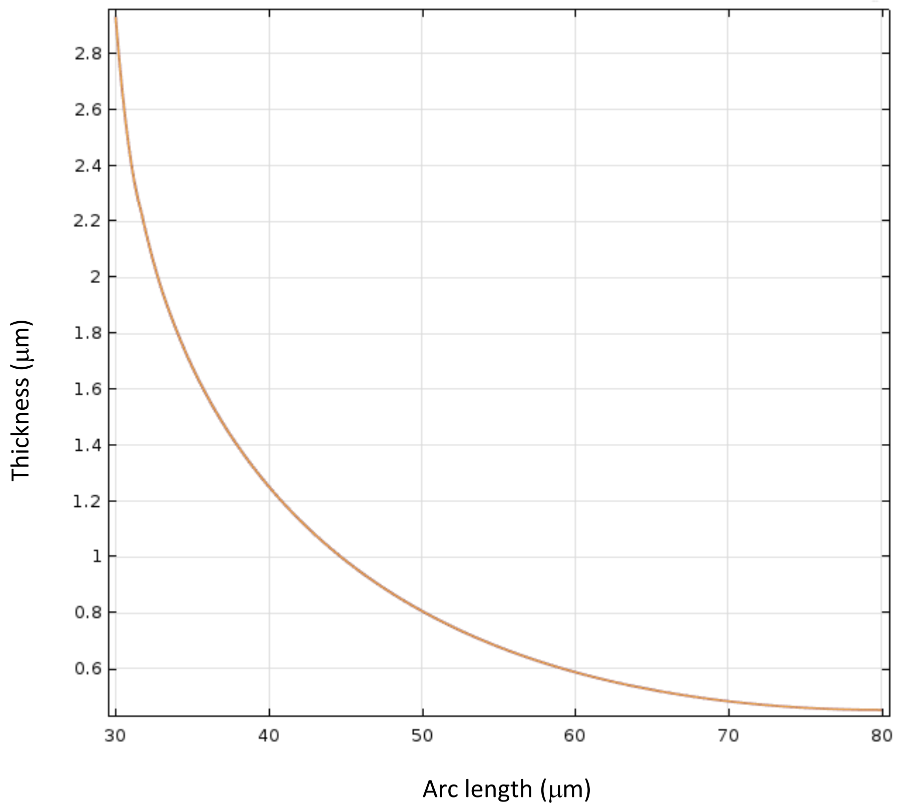
Simulation parameters:

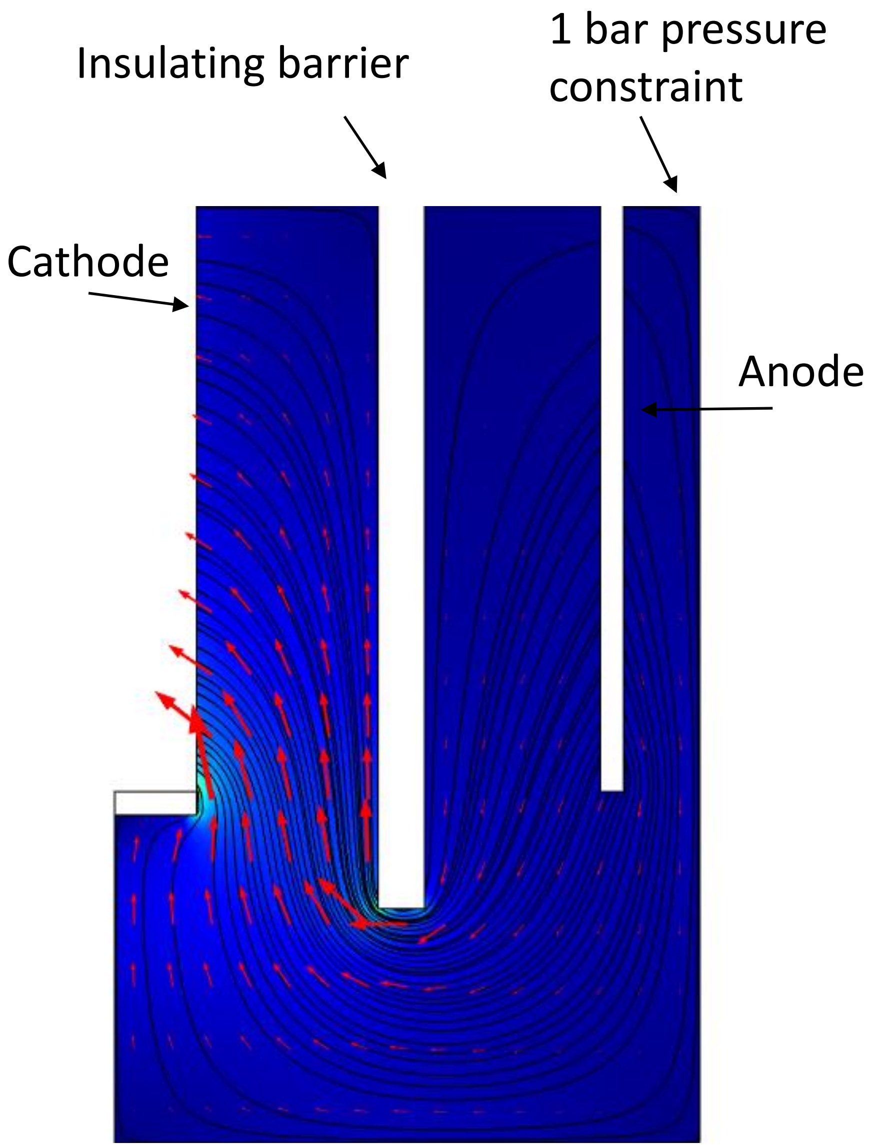
- Potentiostatic: -1.1 V
- Total time: 5051 s
- Total charge: ~900 C deposited, good agreement with the experiments (less than 2%)

Coupled model, electrodeposition-convection

A case study: Rotating Hull Cylinder (RHC)

- Total time: 600s
- Direction of advection field: Swirl flow
- Turbolence model k-ε (300 rpm)





Conclusions

1. Tertiary current distribution
2. BV as a boundary condition
3. Electrochemical process coupled with chemical equilibrium
4. Electrodeposion coupled with convenction field

Further perspectives

1. Saving computational time by using higher grades of the Taylor series for the BV

2. Study of the advection in a typical galvanic cell at a pilot plant scale.

3. Evaluation of the free-energy associated with the homogeneous reaction by QC methods.

4. Validation of the model on both laboratory and pilot plant scale.

THANK YOU VERY MUCH

SCAIL-UP

SCALING-UP OF THE ALUMINIUM PLATING PROCESS FROM IONIC LIQUIDS

Acknowledgements
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