Current Density Distribution for a Full Scale Industrial Alluminization Process

Giaccherini, A.[1],Martinuzzi, S.[2], De Luca, A.[1], Lavacchi, A.[3], Caporali, S.[2] and Innocenti, M.[1]
[1] Chemistry Department, University of Firenze, Firenze, Italy
[2] Consorzio INSTM, Firenze, Italy
[3] Institute of Chemistry of Organometallic Compounds, CNR, Firenze, Italy

Introduction: A complete computational model, taking into consideration tertiary current distribution, chemical equilibria and turbulence models, such as k-ε, to assess the electrodeposited layer thickness even on sharp edges. Finally, the computational model has been applied to the classical Rotating Hull Cylinder (RHC) apparatus obtaining reasonable results.

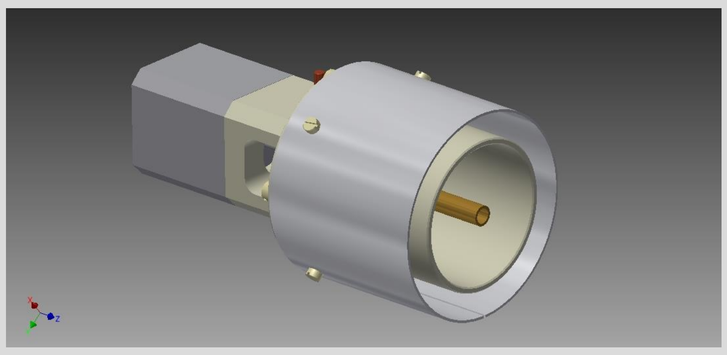

Figure 1. 3D sketch of a RHC

Computational Methods: For the case in study, we used a tertiary current distribution with the Butler-Volmer boundary condition. A concurrent chemical equilibrium has been considered.

$$\boldsymbol{N_i} = -D_i \boldsymbol{\nabla} c_i - z_i u_{m,i} F\, c_i \boldsymbol{\nabla} \phi_l + \boldsymbol{u} c_i$$

$$K_{eq} = \frac{C(AlCl_4^-)C(AlCl_3)}{C(Al_2Cl_7)}$$

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

Regarding the convection field, boundary conditions for the Navier-Stokes equations had been considered, modelling a swirl flow imposing cathode rotation speed of 300 rpm. At the top vertex of the RHC 1 bar pressure condition has been imposed.

The axialsimmetric model used to simulate RHC, is depicted in figure 2.

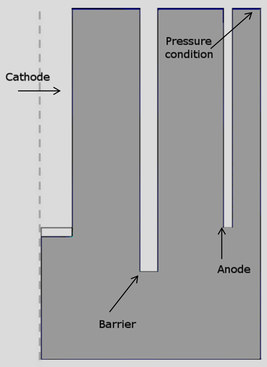

Figure 2. Scheme of the axial symmetric model

D(BMIm)	**2.8 10^{-11} $m^2 s^{-1}$ [1]**
D($AlCl_4$)	6.1 10^{-11} $m^2 s^{-1}$ [1]
D(Al_2Cl_7)	1.7 10^{-11} $m^2 s^{-1}$ [1]
c(BMIm)	3416 mol m^{-3} [2]
c($AlCl_4$)	1708 mol m^{-3} [2]
c(Al_2Cl_7)	1708 mol m^{-3} [2]
i_0	1 10^{-3} A m^2 [3]
K_{eq}	2.410^4 mol m^{-3} [4]
η (viscosity)	15 mPa s [5]

Table 1. Proprieties of the ionic liquid BMIm/$AlCl_3$ (1:1.5)

Results: Figure 3 shows the compared results, in terms of deposited charge density after 120 minutes of potentiostatic electrodeposition (potential between the two electrodes -1.1V). The Butler-Volmer condition, results in Figure 3a, constitutes our reference since conditions, we considered 3 of its approximation, such as concentration independent (3b), linear (3c), and linear concentration dependent(3d). The results suggest that condition the "concentration independent" boundary condition, leads to an overestimation of the charge deposited by a 2%.

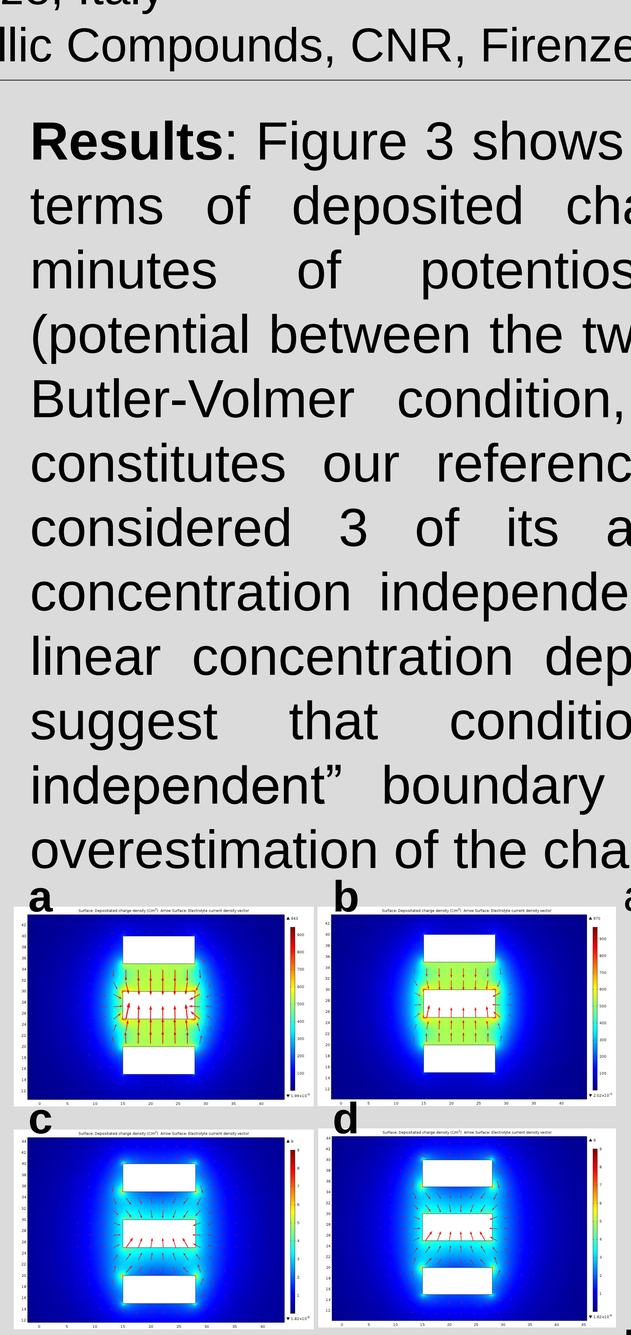

Figure 3. Effect of boundary condition approximations on the charge density deposited.

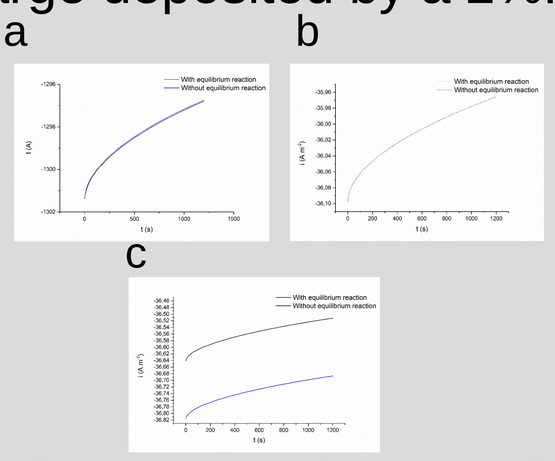

Figure 4. Effect of the chemical equilibrium on total current **(a)**, current density on the center **(b)** and on the edge **(c).**

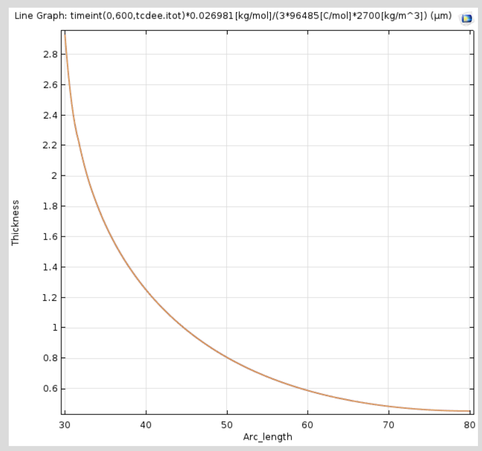

Figure 5. Thickness distribution (RHC)

This study focused on the Rotating Hull Cylinder at 300rpm. This trend has been confirmed by means of experimental investigations of the deposit, obtained in the same condition.

Conclusions: The equilibrium reaction can be used to refine the results since it make just a 1% difference on the current density at the edges. Further studies will be necessary to validate the results at different rotating speed and extend the model to more complex geometry.

References:
1. Stijn Schaltin, Murugan Ganapathi, Koen Binnemans and Jan Fransaer, *J. Electrochem. Soc.*, **158** (10), D634-D639, (2011)
2. S. Caporali, PhD thesis, Università Studi di Firenze, XVIII (2006) *in italian*
3. D. Pradhan, R.G. Reddy and A. Lahiri, *Metallurgical and materials transactions B*, **40B**, 114-122, (2009)
4. L. G. Joel and E. Gary *Journal of American Chemical Society*, **103**, 7147-7151, (1981)
5. Y. Zheng, K. Dong, Q. Wang, J. Zhang and X. Lu, *J. Chem. Eng. Data* **58**, 1, 32-42, (2013)

Excerpt from the Proceedings of the 2015 COMSOL Conference in Grenoble