Current Density Distribution for a Full Scale Industrial Alluminization Process

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Abstract: The use of ionic liquids as electrolyte constitutes a challenging quest for galvanic industry. Their physical properties, i.e. viscosity, conductivity etc… strongly differ from aqueous solutions. Some aspects, such as high viscosity, negatively affect the electrochemical process, but some others such as the very wide electrochemical window, constitute unexpected and stimulating opportunities.
The main objective of this work is to formalize a complete computational model suitable for the description of the electrodeposition process takeing into consideration a time-dependant model of the continuous domains and variables playing active roles in the electrochemical process. A common approach is constituted by the Finite Elements Analysis (FEA) [1-3], which is a strategy to solve the governing partial differential equations by means of a suitable discretization.
Respect to the previous approaches, in this communication the electrochemical and chemical kinetics as well as the transport phenomena, were modelled at very high level of theory, taking into account all the parameters affecting the galvanic process, including turbulent convection fields. In particular, we considered 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.

Keywords: Electrodeposition, ionic-liquids, turbulence models, coupled problem.

1. Introduction

The electroplating technology from aqueous solutions has some limitations. In particular the little electrochemical window of water (1,23 V, limited respectively by hydrogen and oxygen discharge) impairs the electrodeposition of very electropositive elements [4,5]. In order to overcome this issue the use of non-protic solvents has been recently proposed. In particular, Ionic Liquids (ILs) have been applied to the electrochemical deposition of technical (several micron thick) coatings especially for anticorrosion purposes [6,7]. We refer to ionic liquids speaking of "Room temperature molten salts", which have been in their infancy more than 15 years ago, and are now assessed as viable alternative to the traditional electrochemical media. These liquids are able to join the low melting temperature (room temperature or below) typical of organic solvents with the high ionic conductivity of molten salts [8]. This paper presents the results of a Finite Elements Analysis (FEA) study aiming to determine the current distribution, which constitutes the driving force for the electrodeposition process from chloroaluminate-based ILs. In the field of FEA simulations, a typical aim is to obtain reliable models in order to "a priori" optimize the process setups [9]. We believe that this approach can be extended to electroplating industrial processes in order to determine the most favorable cell geometry [10], to achieve smooth and homogeneous aluminium coatings. The main focus of this paper is the analysis of the current density distribution at the electrodes boundaries. The calculation has been performed by means of the simulation program COMSOL Multiphysics® with the electrodeposition and the CFD (Computational Fluidynamics) modules.

2. Models

Previous studies approached this modelling problem taking into account the primary or secondary current distribution alone [11]. That allowed the design of a model able to account for the time-dependent evolution of the current density distribution, which can be related to the

change of the concentration distribution in the system. However, in the case of ILs, it fails to reproduce the current density distribution on sharp edges. In the present study we improve the reliability of the model takeing into account the tertiary current distribution and the effect of convection and homogenous chemical reactions. A simple 2D geometry, constituted by one cathode located between two anodes (Fig. 1a), has been used to investigate the electrodeposition under diffusion controlled condition; while the effect of a coupled convection field was evaluated by means RHC (Rotating Hull Cylinder) whose scheme is depicted in Figure 1b. That is constituted by an axialsymmetric 2D model, with the section of the cylindrical cathode, an insulant barrier and the anode. The symmetry axis coincides with the cathode axis.

The electrochemical media is constituted by a mixture of $AlCl_3$/$BMIm$(1:1.5), considering 1:1.5 as the molar ratio, characterized by chemical and physical proprieties reported in Table 1.
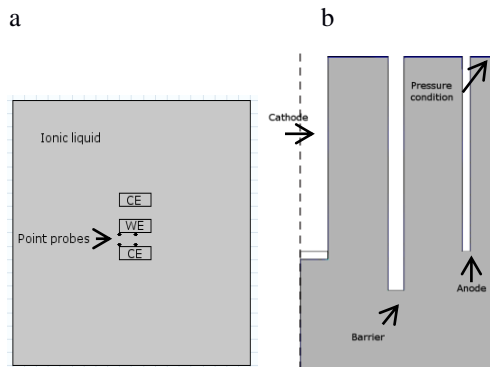
a   b

Figure 1. Scheme showing the cell geometry considered for (a) quiet and (b) fluidynamics conditions (rotating Hull cylinder).

2.1 Governing equations

Ohm's law, equation (1) takes into account for the electrical behavior of an electrochemical system [11-15].

$$\nabla^2 \phi_l = -\frac{Q_l}{\sigma_l} \qquad (1)$$

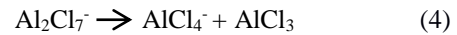ϕ_l is the electric potential in the electrolyte; σ_l is the conductivity of the electrolyte and Q_l is the electric charge. The Nernst-Plank equation describes the flux of the chemical species due to general transport phenomena including convection, diffusion and migration (2).

$$\underline{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_l + \underline{u} c_i \qquad (2)$$

Where c_i, D_i, u_i, and z_i are the concentration, the diffusion coefficient, the mobility and the charge of the of the i_{th} species, respectively; F the Faraday's constant; $\underline{u}$ the velocity field; R_i the reaction term for A and B. In order to calculate the change in composition of the electrolyte near the electrodes due to electron transfer, it's well established the validity of the following Faraday equation (3):

$$R_{i,m} = \frac{-v_{i,m} i_{loc,m}}{n_m F} \qquad (3)$$

$i_{loc,m}$ is the faradaic current density for the m_{th} process, n_m is the number of electrons exchanged Finally, there are relation between electrochemical species, that can be depicted in the following equilibrium reaction:

$$Al_2Cl_7^- \rightarrow AlCl_4^- + AlCl_3 \qquad (4)$$

Controlled by equation (5):

$$K_{eq} = \frac{C(AlCl_4^-)C(AlCl_3)}{C(Al_2Cl_7^-)} \qquad (5)$$

On the other side electroneutrality, holds for the bulk electrolyte (6).

$$\sum_i z_i c_i = 0 \qquad (6)$$

Turbulent advection has been coupled with the electrochemistry of the model, in order to take in to account for the mixing condition typical of the industrial galvanic baths. In a typical «Rotating Hull Cylinder» (RHC), the high rotation speed implies, in most cases, the turbulent swirl flow around the rotating cathode. We choose a typical k-ε model, due to its good convergence rate and relatively low memory requirements, though it does not very accurately compute flow fields that

exhibit strong curvature. However, the diameter of the Hull Cylinder can be considered to be large enough to make reliable his approximation.

2.2 Boundary conditions

Boundary conditions for the Nernst-Plank (2) can be defined as follow (7-9):

$$\underline{i}_l \cdot \underline{n} = i_{total} \tag{7}$$

$$i_{total} = \sum_i i_{loc,m} + i_{dl} \tag{8}$$

$$i_{loc} = i_0 \left(\frac{C_R}{C_R^0} e^{\frac{\alpha_a F \eta}{RT}} - \frac{C_O}{C_O^0} e^{\frac{-\alpha_c F \eta}{RT}} \right) \tag{9}$$

where, $\underline{i}_l$ is the current distribution vector; i_{dl} is the capacitive current density; $i_{loc,m}$ is the faradaic current density for the m_{th} process; i_0 is the exchange current; C_R/C_R^0 is the ratio of the concentration to the bulk concentration; α_a is the electron transfer coefficient; R is the perfect gasses constant; T is the temperature and η is the electrode overpotential defined by equation (10).

$$\eta = \phi_l + \phi_s - E_{eq} \tag{10}$$

Here, $\phi_l + \phi_s$ is the electrical potential drop across the electrode interface.

Recently, COMSOL Multiphysics® has implemented different mathematical approaches to model electrochemical systems. In particular, the electrodeposition module allows the use of different approximations of the Butler-Volmer boundary condition [16-20]. In the case of a negligible transport in the bulk electrolyte respect to the electron transfer process the ratio $C_O/C_O^0 = 1$, so that the local current can be described by equation (11).

$$i_{loc} = i_0 \left(e^{\frac{\alpha_a F \eta}{RT}} - e^{\frac{-\alpha_c F \eta}{RT}} \right) \tag{11}$$

When $\eta \approx 0$ the exponential term in the Butler-Volmer can be linearized as described in equation 12:

$$i_{loc} = i_0 \left(\frac{C_R}{C_R^0} \frac{\alpha_a F \eta}{RT} + \frac{C_O}{C_O^0} \frac{\alpha_c F \eta}{RT} \right) \tag{12}$$

In the case of a negligible transport in the bulk electrolyte respect to the electron transfer process the ratio $C_O/C_O^0 = 1$, so that the equation (12) becomes (13):

$$i_{loc} = i_0 \left(\frac{\alpha_a F \eta}{RT} + \frac{\alpha_c F \eta}{RT} \right) \tag{13}$$

For the case in study, we used a tertiary current distribution with boundary conditions (9,11-13). Regarding the RHC, boundary conditions for the Navier-Stokes equations had been considered, that the swirl flow imposing cathode rotation speed of 300 rpm. At the top vertex of the RHC 1 bar pressure condition has been imposed (Figure 1b).

2.3 Mesh

The two different problems have been 1investigated using a fine triangular mesh, in order to define the effect of the boundary conditions and of the homogenous chemical reaction (5).

2.4 Chemical and physical proprieties of the electrolyte

D(BMIm)	$2.8 \; 10^{-11} m^2 s^{-1}$ [22]
D(AlCl$_4$)	$6.1 \; 10^{-11} m^2 s^{-1}$ [22]
D(Al$_2$Cl$_7$)	$1.7 \; 10^{-11} m^2 s^{-1}$ [22]
c(BMIm)	$3416 \; mol \; m^{-3}$ [23]
c(AlCl$_4$)	$1708 \; mol \; m^{-3}$ [23]
c(Al$_2$Cl$_7$)	$1708 \; mol \; m^{-3}$ [23]
i$_0$	$1 \; 10^{-3} A \; m^2$ [24]
K$_{eq}$	$2.4 10^4 \; mol \; m^{-3}$ [25]
η	15 mPa s [26]

Table 1: Physical and chemical constant for the modelling of the AlCl$_3$/BMIm(1:1.5).

3. Results

3.1 Electrodeposition under diffusion control

That is the simplest electrochemical system (quiet solution), we approached this case study simulating the electrochemical cell as depicted in figure 1a. In principle, tertiary current distribution takes in to account the effect of the compositional variations of the electrolyte, and constitutes a reliable choice for the simulation of such systems [11]. The model has been solved for the four different boundary conditions (9,11-13). Figure 2 shows the compared results, in terms of deposited charge density after 120 minutes of potentiostatic electrodeposition (potential between the two electrodes 1.1V). Condition (9) constitutes our reference since conditions (11-13) are approximations. The solutions for the condition 9 compared with the results of condition (11) are depicted in figure 2a and 2b respectively. It suggests that condition (11) leads to an overestimation of the charge deposited by a 2%. Boundary conditions (12-13) give a tremendous drop of the charge deposited by a factor of 10^2 (Figure 2c,d). In principle for condition (11) and (13) it is possible to results in negative concentration for the depleted species at an electrode, that is physically impossible impairing the use of this conditions. Unfortunately condition (9) returns an unstable model that, in some cases, does not converge. To overcome this problem, for short time dependent simulation condition (11) can be used considering an error of 2%.
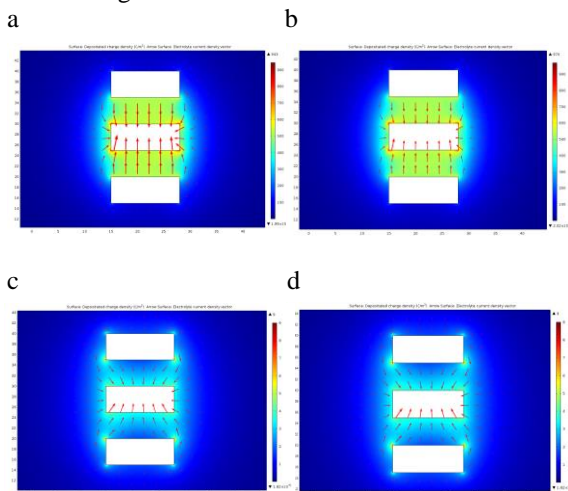
a   b

c   d

Figure 2. Effect of boundary condition approximations on charge density deposited.

In the light of these considerations the effect of homogeneous chemical equilibrium (5) has been applied only to the most reliable model: i.e. the one applying boundary condition (9). The results of this modeling are shown in figure 3. On the cathode the total current (figure 3a), and the current density on a point in the center (figure 3b) have been compared. The total current is not affected, as well as the current density in the central point. However, sensible differences has been observed in the edges (figure 3c).
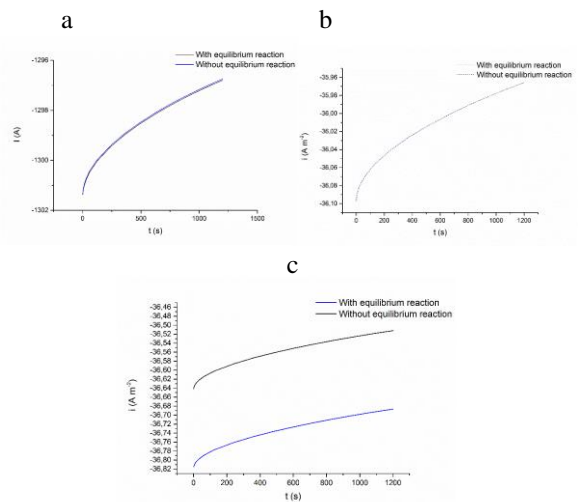
a   b

c

Figure 3. a) Total current on the cathode, b) normal current density on the center of the cathode and c) on the edge.

3.2 Electrodeposition under convection

The results of section 3.1 have been used to determine the current density on the cathode of the RHC. The electrolyte current density is shown in figure 4, confirming the effect of the barrier under the turbulent advection-diffusion condition.
The thickness of alluminium coating along the cathode, has been calculated and depicted in figure 5. After 600s of simulated potentiostatic electrodeposition (-1.1V between cathode and anode boundaries) the maximum thickness (2.8μm) have been observed in the terminal portion of the cylinder. As showed in figure 5 the

thickness decrease down to a minimum of 0.6μm in the uppermost portionof the chatode.
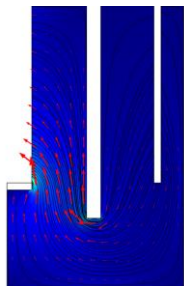

Figure 4. Streamline and modulus of the electrolyte current density for the RHC.

This trend has been confirmed by means of experimental investigations of the deposits, obtained in the same condition.
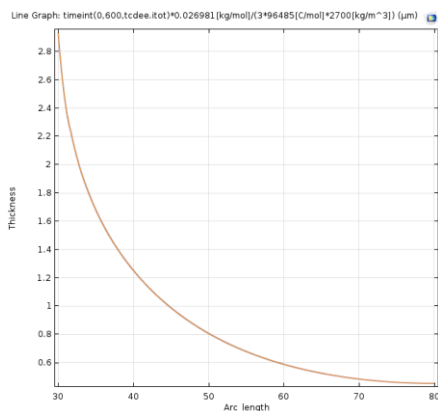

Figure 5. Thickness calculated along the cathode of the RHC.

4. Conclusions

The electrodeposition of Alluminum from AlCl$_3$/BMIm(1:1.5), under diffusion condition has been simulated with the electrodeposition module of COMSOL Multiphysics® applying different kind of approximations, resulting that the two acceptable boundaries condition for the electrode are the Butler-Volmer equation (9) and the closely related condition (11) which gives an overestimation of the deposited charge in the range of the 2%. The solution of the model with boundary condition (9), in some cases showed convergence problems that can be overcome by using condition (11) for short simulated time, in order to avoid negative concentration for the depleted species at the electrode. The equilibrium reaction can be used to refine the results since it make just a 1% difference on the current density at the edges. Finally the model has been coupled with turbulent advection field, by means of the investigation of the Rotating Hull Cylinder at 300rpm. The results show plausible values for the coating thickness distribution. Further studies will be necessary to validate the results at different rotating speed and extend the model to more complex geometry.

5. References

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