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Short Communication

CFD Approach to Wagner Number Estimation for a Current Distribution Uniformity in a Rotating Cylinder Hull Cell

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In an electrochemical metal refining process, the deposit quality and purity are dependent on the current distribution over the surface of the working electrode within an electrochemical cell. A uniform current distribution leads to an increased refining performance. A comprehensive approach was applied to the copper electrodeposition model in a rotating cylinder Hull (RCH) cell configuration. The secondary current distribution in the RCH cell is investigated using a numerical calculation. Dimensionless Wagner numbers were three-dimesionally simulated in a CFD-based model and compared with an analytical equation from the Tafel kinetics approximation as a guide to a uniform deposition for a practical scale-up design.

Keywords: Electrodeposition, Electrorefining, Current distribution, Wagner number, CFD, Rotating cylinder Hull cell

1. INTRODUCTION

The electrochemical metallurgy industry is essentially based on the use of an electrochemical system for the refined metal deposition. More sophisticated designs are a desirable task to provide a good refining performance in an electrochemical cell [1-5].

In electrometallurgy, the current distribution is a key parameter characterizing the operation of the electrochemical cell. The electrochemical cell design of metal refining is essential for achieving a uniform current density over the electrode surface. The current distribution on an electrode is very important in the technical metal refining process [6-7]. In the electrorefining of metal, a non-homogenous current distribution can cause a short circuit with the counter electrode, and the corner weakness effect in electroforming. The current distribution determines the local variations in the impurity of the electrodeposition. Thus a uniform current distribution over the working electrode is required for the quality deposit, and has been promoted for improved current density conditions.

In an electrochemical reactor design, a scale-up criterion is required for the electrical similarity in dimensional consistency. The dimensionless Wagner number (*Wa*) has been used as a quantity that characterizes the equalizing influence of an overpotential on the current distribution. This Wagner number can be used as a guide to a uniform current distribution in a scale-up design [6-11].

The prediction of the current distribution using a numerical method is an essential step in an engineering analysis and scale-up of the electrochemical reactors. In recent years, Computational Fluid Dynamics (CFD) has been shown to be an effective tool to study a scale-up of the electrochemical processes for attaining the optimal conditions at the industrial scale [12, 13]. This modeling approach could lead to the need for an expected electrochemical performance in designing practical cell geometries together with information on the operational guidance for the product quality.

In this study, secondary current distributions along the working electrode in the rotating cylinder Hull (RCH) cell [13-19] are spatially modeled to quantify the Wagner numbers at different applied current densities during the copper electrodeposition as a test system. The apparent uniformity of the current distribution was also characterized using a Tafel kinetics based approximation in this cell configuration.

2. CELL DESCRIPTION AND MODELING

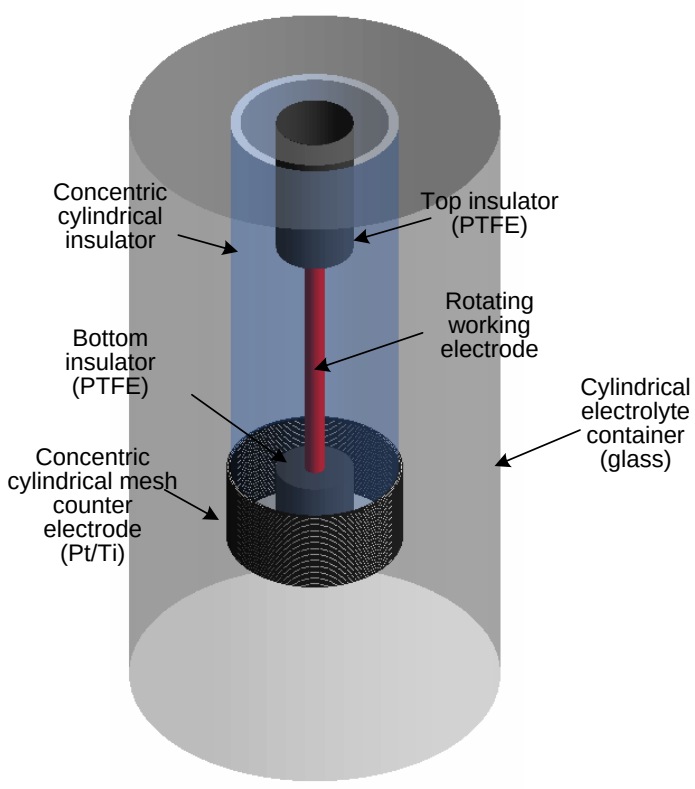

Figure 1. Schematics of the rotating cylinder Hull (RCH) cell, RotaHull®[20], The working electrode is a rotating cylindrical electrode (316 stainless steel, 0.006 m diameter, 0.08 m length); the counter electrode is a concentric cylindrical electrode (Pt/Ti, 0.001 m thickness, 0.052 m inside diameter, 0.025 m height).

Modern commercially developed RCH cells are available and have provided an important experimental tool for quantitative electrodeposition studies. This sophisticated cell geometry enables the investigation of a wide range of current density in an electrodeposition experiment. In addition, the RCH model has been experimentally proven for a well-controlled and characterized current distribution. Modern commercially developed RCH cells are available and provide the important guidelines for electroplating conditions [20]. A schematic of the RCH cell configuration used as a benchmark simulation in this study is shown in Figure 1. Its cell configuration and detailed dimensions are schematically described in a related paper [17].

A secondary current distribution model is based on the charge transfer and potential drop between the electrodes in a unit cell. The uniformity of the secondary current distribution is often described in terms of dimensionless Wagner numbers (*W*a) of the following form:

$$Wa = \frac{\kappa}{L}\left(\frac{\partial \eta_a}{\partial i}\right) \quad \text{(l)}$$

where κ is the conductivity of the electrolyte solution, $\frac{\partial \eta_a}{\partial i}$ is the slope of the cathodic activation overpotential(η_a)-current(i) dependence under the secondary conditions, and L is a characteristic length of an electrode system, which in our case is equal to the cathode length (L=0.08 m). It has been well established that the current distribution can be characterized by a single dimensionless group. This equation has a concept of presenting the ratio of the polarization resistance to the electrolyte resistance in an electrochemical cell. The partial derivative, $\frac{\partial \eta_a}{\partial i}$, can be locally evaluated at a position of the electrode in three-dimensional CFD software. This local gradient normal to the electrode wall (w) is determined by

$$\left.\frac{\partial \eta_a}{\partial i}\right|_w = \left.\frac{\partial \eta_a}{\partial n}\right|_w \Big/ \left.\frac{\partial i}{\partial n}\right|_w \quad (2)$$

where, n represents the coordinate normal to the electrode surface in direction of the interior of the electrolyte. Local gradients ($\frac{\partial \eta_a}{\partial n}$ and $\frac{\partial i}{\partial n}$) in a scalar quantity can be computed using the definition of the derivatives which are normal to an electrode wall.

When the system is in galvanostatic control at the cathode, the average (or applied) current density (i_{ave}) can be expressed by the integral constraint of the local current over the electrode surface area:

$$i_{ave} = \frac{\int_A i ds}{A} \quad (3)$$

where A is the electrode surface area, and s is the surface element for a numerical integration. This expression is explained as the area-weighted average on the electrode surface.

For the Tafel kinetics approximation, the equation related to the Wagner number evaluated in the high cathodic polarization region can be given as [17]:

$$Wa_T = \frac{\kappa}{L}\frac{\beta_c}{i_{ave}} \quad (4)$$

where β_c is the cathodic Tafel slope.

It is known that a CFD technique allows coupling with electrochemical reactions in a geometrical domain divided into small volumes, commonly known as a mesh. In this platform, a complete three-dimensional simulation can be carried out for the electrochemical phenomena arising in a given cell configuration.

3. RESULTS AND DISCUSSION

A benchmark system for a simulation of the current distribution is copper electrodeposition from an acid sulphate electrolyte containing 50 mM $CuSO_4$ and 0.5M Na_2SO_4 at 20ºC in the RCH cell as described in detail in literature [17]. The relevant governing equations and parameters used for the numerical simulation were referred to the literature [17]. Computations of the secondary current distributions were performed using a constant applied current density for the working electrode. Under this condition, the electrochemical reaction is solely dependent on the charge transfer.

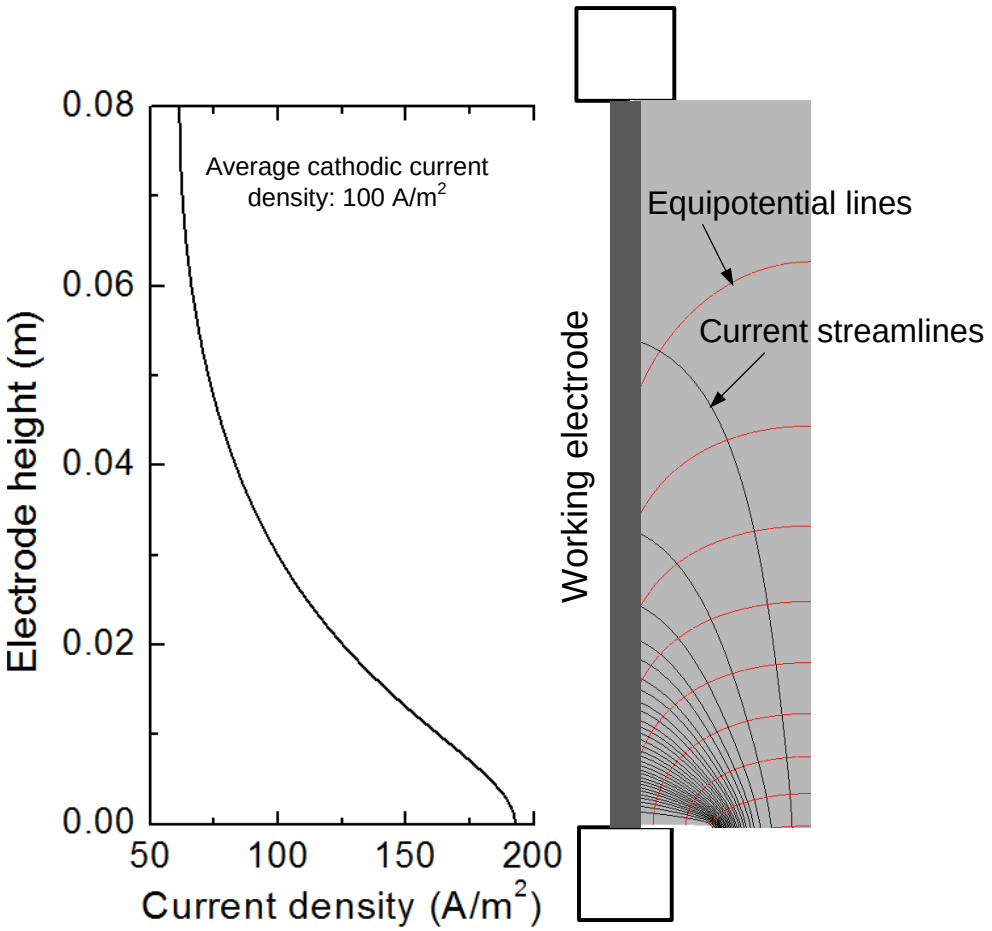

Figure 2. Simulation for the secondary current density distributions, and 2-dimensional equipotential and current streamlines for average cathodic current density:100 A/m^2.

In this simulation, the focus is on the current distributions on the working electrode surface, and the anodic reaction rate is assumed to be reversible with a constant current distribution over the counter electrode. This assumption is an ideal case of no secondary overpotential at the counter electrode.

For the case of a two-dimensional electric field, the current streamlines (electric field lines) are drawn around the electrode surface to confirm the current density distribution along the working electrode, as shown in Figure 2. The red lines show the equipotential profile contours, which are lines

of constant potential in two-dimension as well. A current line is related to the electric field which is the gradient of the electric potential in an electrolyte region. The electric field contours are a set of surfaces that are everywhere normal to the equipotential lines. On the other hand, equipotential lines are perpendicular to the insulator surfaces because the current cannot flow into the insulator. Current lines do not terminate at the insulating surfaces except for the electrodes. The electrodeposition occurring at the electrode interfaces results in a discontinuity in the potential field. Thus, there is a relationship, usually non-linear, between the potential drop across the metal-electrolyte interface and the crossing current.

In connection with the above pattern density of the current streamlines, Figure 2 also shows the simulated secondary current distributions along the cathode at an applied average current density of 100 A/m^2. The position of x=0 m is nearest to the counter electrode and x=0.08 m is the farthest from the counter electrode. The distributions show that the local current density decreased monotonically with the distance away from the anode. In this figure, the electrode position at which the current streamlines are denser (close packing of lines) shows a higher current density region, whereas a sparser region represents the lower values. The local current density is inversely proportional to the length of the streamlines. These current streamlines are formed in the direction of the charge-flow from the anode (positively charged) to the cathode (negatively charged). It was found that little current flows to the working electrode surface, which faces away from the counter electrode.

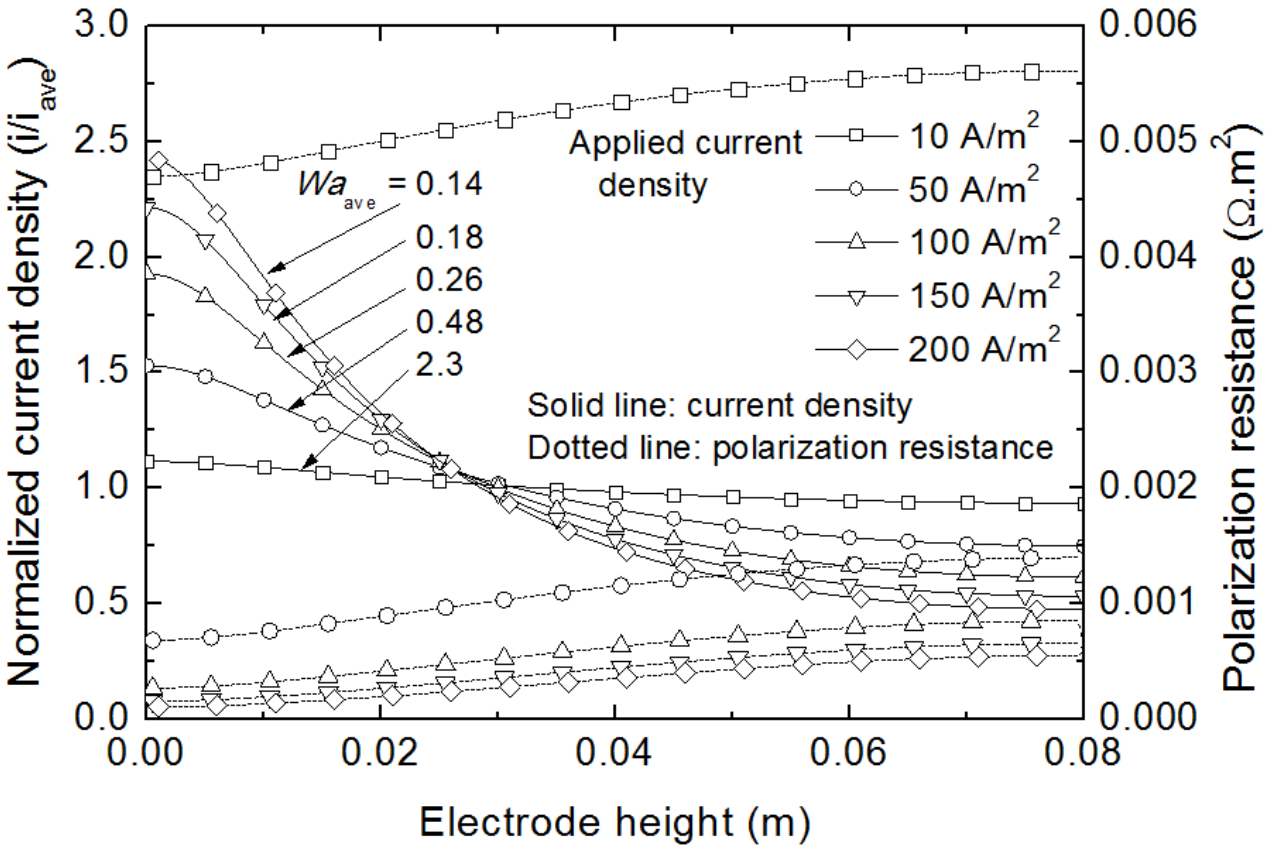

Figure 3. Simulation for the secondary current (solid) and local polarization resistance (dashed) distributions along the cathode height, and corresponding their average Wagner numbers for different values of applied current density.

The polarization resistances can be locally taken from the partial derivatives ($\frac{\partial \eta_a}{\partial i}$) with the units of $\Omega \cdot cm^2$) at any position on the electrode surface in which a negative current flux is imposed in the CFD platform. Figure 3 shows the simulated secondary current (scaled) distributions along the cathode for different applied average current densities. The polarization resistance distribution is also shown in Figure 3. The dependence of uniformity of the secondary current distribution on the applied current density is clearly shown along the cathode height. As can be seen in the figure, increased values of polarization resistance look good in terms of uniformity for each corresponding current distribution. A higher applied current density gives less uniform current distribution on the cathode. To estimate a single dimensionless parameter, the average values of the polarization resistances were used to express the Wagner numbers along the cathode surface. The simulated Wagner numbers have decreased values with increasing applied current density as investigated in experimental study [14].

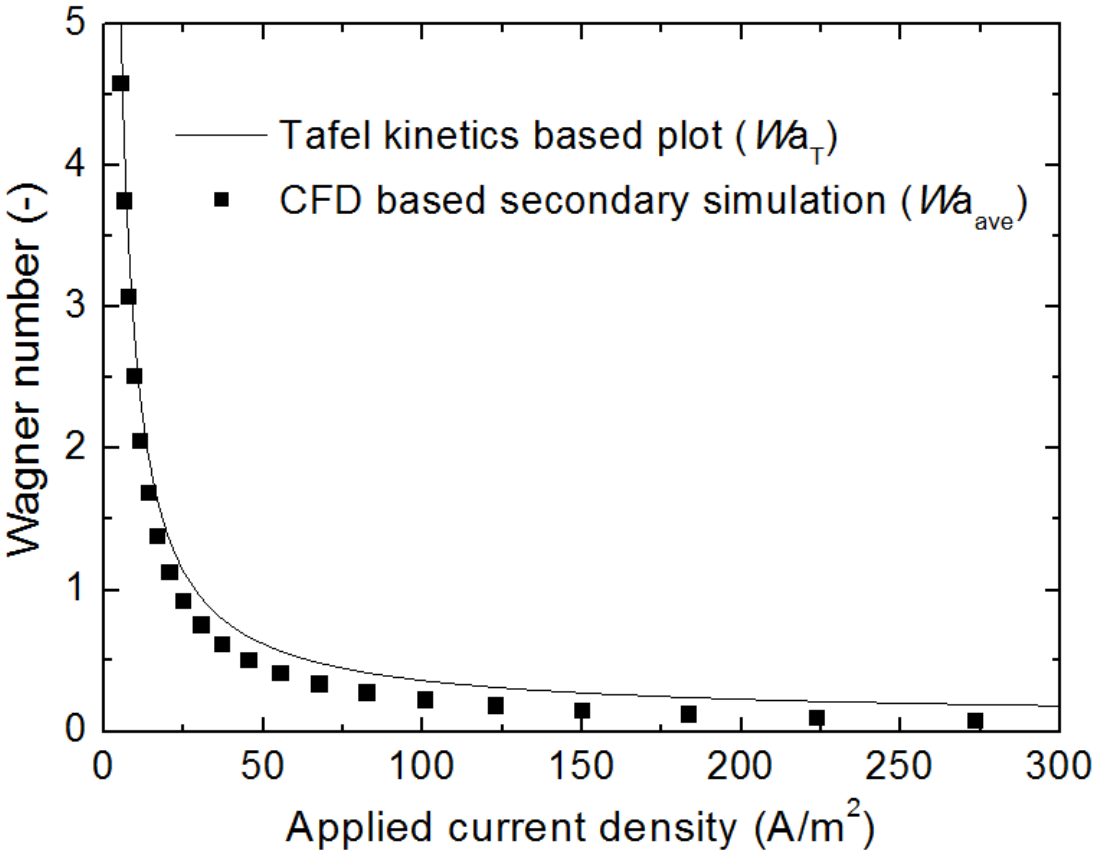

Figure 4. Average simulated and Tafel kinetics based Wagner number as a function of applied current density.

The Wagner numbers evaluated from a Tafel kinetics approximation were also evaluated. The applied average current density on the cathode surface was used for the estimation of a single dimensionless parameter at the Tafel limit [21]. Both Wagner numbers obtained from the Tafel kinetics approximation and numerical simulation for secondary current distribution are compared at different applied current densities. They were found to have good agreement with each other for a range of high cathodic polarization, as shown in Figure 4. As the Wagner numbers decrease with the

increased applied current conditions, the current distributions become less uniform along the cathode surface. The Tafel kinetics based Wagner number (Wa_T) seems to be a reasonable approach to quantify the current density uniformity at any pertinent values of the applied current density in a rotating cylinder Hull cell system. For a region of high cathodic polarization, an approximation using the Tafel kinetics approach was also shown to give an efficient measure of the current distribution uniformity in a cell of simple geometry.

For many practical applications to a quantification of the current distribution uniformity, the above mentioned simulation technique is sufficiently useful for a scale-up design of the electrochemical reactors. This approach allows us to estimate the deposition qualities on an electrode for any cell configuration of the electrochemical reactors.

4. CONCLUSION

The design and scale-up of an electrochemical reactor play an important role in the development of practical scale process for an actual application. Among the controlling factors, the current distributions are the most significant parameter characterizing the operation of the electrochemical cell for the desired process quality. The geometric configuration of the rotating cylinder Hull cell, as a well-defined electrochemical system, was used to investigate a benchmark simulation for quantifying the secondary current distributions along the cathode surface. A single dimensionless parameter, the Wagner number, was numerically simulated and quantified in connection with the uniformity of current distributions over a wide range of applied current on the cathode. The Wagner numbers based on the Tafel kinetics approximation were shown to be in a good agreement with the simulated values for a range of high cathodic polarization in the RCH cell.

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References

1. J. O'M. Bockris, B. E. Conway, E. Yeager, and R. E. White (Eds.*), Comprehensive Treatise of Electrochemistry*, Plenum Press, (1981) New York.
2. D. R. Sadoway, *Mater. Sci. Forum*, 73-75 (1991) 555.
3. D. Pletcher and F. C. Walsh, *Industrial Electrochemistry*, 2nd Ed., Chapman and Hall Ltd., (1990) New York.
4. N. T. Beukes and J. Badenhorst, *Copper Electrowinning: Theoretical and Practical Design, Hydrometallurgy Conference, The Southern African Institute of Mining and Metallurgy*, 2009, 213.
5. V. Stankovic, *J. Electrochem. Sci. Eng*., 2 (2012) 53.
6. V. Linkov and J. Kleperis (Eds.), *Electrolysis*, InTechOpen Limited, (2012) London. United Kingdom
7. R. C. Alkire, H. Gerischer, D. M.Kolb and C. W. Tobias (Eds.), Advanced in Electrochemical Science and Engineering, Vol.5, Wiley-VCH, (1997) Weinheim, Germany.
8. Wagner R. G. Kelly, J. R. Scully, D. W. Shoesmith and R. G. Buchheit, *Electrochemical Techniques in Corrosion Science and Engineering*, Marcel Dekker, Inc., (2003) New York.

9. J. O. Dukovic, *IBM J. Res., Develop*., 34(2) (1990) 693.
10. J. O'M. Bockris and D. M. Drazic*, Electrochemical Science*, Taylor and Francis Ltd., (1972) London.
11. A. D. McNaught and A. Wilkinson, *IUPAC Compendium of Chemical Terminology*, 2nd Ed., International Union of Pure and Applied Chemistry, (1997) NC, USA.
12. K. R. Kim, S. Y. Choi, S. Paek, J. Y. Park, I. S. Hwang and Y. Jung, *Int. J. Electrochem. Sci*., 8 (2013) 12333.
13. F. J. Almazan-Ruiz, F. V. Caballero, M. R. Cruz-Diaz, E. P. Rivero and I. Gonzalez, *Electrochim. Acta*, 77 (2012) 262.
14. C. Madore, M. Matlosz and D. Landolt, *J. Appl. Elctrochem*., 22 (1992) 1155
15. C. Madore, A. C. West, M. Matlosz and D. Landolt, *Elctrochim. Acta*, 37 (1992) 69.
16. C. Madore, D. Landolt, C. Habenpflug and J. A. Hermann, *Plat. Surf. Finish*, 82 (1995) 36.
17. C. T. J. Low, E. P. L. Roberts, F. C. Walsh, *Electrochim. Acta*, 52 (2007) 3831.
18. C. T. J. Low, F. C. Walsh, *Surf. Coat. Tech*., 202 (2008) 1339.
19. R. Enciso, L.A. Padilla, C. Ojeda, J. A. Delgadillo, and I. Rodriguez, *Int. J. Electrochem. Sci*., 7 (2012) 12181.
20. Metrohm, Determination of Copper Impurities in a Bright Nickel Bath using the Autolab HT RotaHull, *Autolab Application Note 7*, http://metrohm-autolab.com/.
21. S. Palli and S. R. Dey, *Int, J. Electrochem*., 2016 (2016) 1.