



Numerical simulation of electro-deposition process influenced by force convection and migration of ions



M. Zahraei *, M.S. Saidi, M. Sani

Micro electro kinetic Laboratory, Department of Mechanical Engineering, Sharif University of Technology, Tehran, Iran

ARTICLE INFO

Article history:

Received 22 July 2015

Received in revised form 5 October 2016

Accepted 7 October 2016

Available online 12 October 2016

Keywords:

Diffusion

Effective diffusion layer

Migration

Force convection

Transient current density

ABSTRACT

Electro-deposition process is one of the main steps in the LIGA procedure to fabricate microstructures. In this paper, one-dimensional modeling of Nickel electro-deposition process is implemented on Rayan and developed for simulation of time-dependence diffusion and migration of charge species with reduction reactions on the cathode surface. This model is proposed by considering governing equations on electro-kinetic phenomena consist of Nernst-Planck equation and Poisson's equation of electric potential. Transport of ions toward the cathode is considered based on the effect of convection, reaction rate, diffusion and migration. The numerical results cover two series of data consisting of effective diffusion layer thickness δ_{eff} and the transient current density. The effect of force convection and diffusion terms on effective diffusion layer δ_{eff} is validated by Ribeiro analytical model. The transient current densities for different applied voltage.

s are in well agreement with Hyde and Compton's experimental model. Effect of every term on effective diffusion layer δ_{eff} is shown and we found that for velocity lower than $v_c = -0.0005 \text{ cm s}^{-1}$, convection term does not have any influences on effective diffusion layer δ_{eff} . Moreover, the relationship between the applied voltages, current density, effective diffusion layer δ_{eff} and hydrodynamic velocity is proposed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Electro-deposition is a well-known coating technique which has the potential to fabricate high aspect ratio structures with uniform deposition regardless of the surface size and shape [1–4]. The techniques, which are based on controlled current or controlled potential electrochemical deposition on the cathode electrode from a solution containing the appropriate compounds [5,6]. Large number of metals can be deposited from aqueous electrolytes (Ni, Cu, Au and Fe to name a few). Nickel electro-deposition is more useful to form mechanical and magnetic elements [7].

The first modeling of diffusion term in electro-deposition process has taken place in the paper of Scharifker and Hills [8]. A review of current response to the potential step perturbation, the influence of diffusion in nuclei growth for unique geometry can be found in references [9,10]. In these models the only factor which influences on ion movement is diffusion term. All of these modeling used a Cottrellian diffusion term to describe the total flux to the electrode surface, since these models are inapplicable under hydrodynamic condition.

In Hyde, Klymenko and Compton's work [11] the diffusion term at the same way with Scharifker's paper [8] under forced convection condition has theoretically been explored. Furthermore, the current density

response to this model has experimentally been derived and compared with theoretical results. In Hyde and Compton's paper [12] application of Hyde model in lead deposition growth under two different hydrodynamic conditions has also been computed.

In Ajello's paper [13] an expression for the transient current density verified during the electro-deposition of metals has derived as a function of concentration, reaction rate and time, i.e., $I = I(c, k, t)$. In Ajello and Schervenski's paper [14] the general form for the transient current density $I = I(c, V, T, t)$ has also been considered. In this models [13,14] the diffusion and reaction terms take part in transport of ions.

One-dimensional model formulated by Ribeiro's paper [15] based on the concentration equation to describe transport of ion species toward cathode with considering diffusion and force convection has theoretically been solved via separation of variables. In fact in Ribeiro's work [15] the transient current density is a function of concentration, time, hydrodynamics velocity and reaction rate, $I = I(c, k, v, t)$. Constant velocity is also assumed to demonstrate the effects of forced convection on the current density-potential profiles and transient current density.

One of the main steps in cathodic deposition of alloy or single metals is ionic migration, meaning that the hydrated ions in the electrolyte migrate toward the cathode under the influences of the applied voltage as well as diffusion and convection. In all previous models, the effect of migration term on concentration distribution and current density were not mentioned.

In this model we consider all three mechanism of electro-migration, diffusion, and convection into the concentration equation; indeed we

* Corresponding author.

E-mail address: zahrae.mohsen@gmail.com (M. Zahraei).

Nomenclature

D	Diffusion coefficient of species [cm^2s^{-1}]
v_c	Convection velocity [cm s^{-1}]
T	Temperature [K]
T_r	A reference temperature [K]
e	Electric charge [C]
F	Faraday constant [$96485.5 \text{ C mol}^{-1}$]
Z	Charge number of the ionic species
V_1	Start deposition potential [V]
V_k	Start deposition potential in the sigmoidal [V]
V_{app}	Applied voltage [V]
K	Reaction rate of ions on the electrode surface [s^{-1}]
I_{sta}	Stationary current density [mA cm^{-2}]
I	Current density [mA cm^{-2}]
R	Universal gas constant [$\text{J mol}^{-1}\text{K}^{-1}$]
C	Concentration of the species [M]
B	Constant that regulate the sigmoidal inclination [V^{-1}]
c_s	Limit concentration of the species on the electrode surface [M]
c_b	Bulk concentration of the species [M]
E	Electric potential [V]
E_0	Constant applied voltage on the cathode surface [V]
t	Time [s]
I_D	Diffusion term of cathode current density [M s^{-1}]
I_c	Convection term of cathode current density [M s^{-1}]
I_m	Migration term of cathode current density [M s^{-1}]
$I_{\text{sta}}^R(t)$	Stationary current density developed by Ribeiro's model [mA cm^{-2}]
$I^R(t)$	Current density developed by Ribeiro model [mA cm^{-2}]
$I_{\text{sta}}^{\text{HK}}(t)$	Stationary current density developed by Hyde and Klymenko's model [mA cm^{-2}]
$I^{\text{HK}}(t)$	Current density developed by Hyde and Klymenko's model [mA cm^{-2}]

used Nernst–Planck equations to describe the transport and distribution of ion in distance between cathode ($x=0$) and diffusion layer thickness ($x=\delta$). The transient current density $I=I(c, k, v, E, t)$ is also obtained by considering all parameters. Since the migration term in concentration equation makes it impossible to solve this equation in theoretical method, we used numerical solution of electro-deposition process generated by Rayan¹ software. To validate results of first solution without migration effect, we compared the concentration profiles with theoretical model of Ribeiro [15]. By considering migration term of charge species the effect of hydrodynamic velocity and applied voltage on the effective diffusion layer δ_{eff} and current density are recognized. Since in Hyde and Compton model [12] the current density profiles force convection effect have experimentally been exploited, we used experimental results of Ribeiro's paper [15] and Hyde and Compton's work [12] to validate transient current density at the beginning of the electro-deposition process for different voltages on the cathode surface.

Greek letters

ε	Dielectric constant permittivity [F cm^{-1}]
δ	Diffusion layer thickness [cm]
δ_{eff}	Effective diffusion layer [cm]
σ_f	Free charge density [cm^{-2}]

2. Mathematical model

Scalar equation of movement of the ions between electrodes is governed by the Nernst-Planck equation. This equation includes diffusion, convection and migration of ions and for each ionic species in one dimension can be written as [16]:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - v_x \cdot \frac{\partial c_i}{\partial x} + \frac{FD_i z_i}{RT} \frac{\partial}{\partial x} \cdot \left(c_i \frac{\partial E}{\partial x} \right) \quad (1)$$

where v_x is the hydrodynamic velocity of the electrolyte and E is the electric potential. x is the position in the direction normal to the electrode surface, which is located at $x=0$. D_i , c_i and z_i represent ion species valency, diffusion coefficient and ionic concentration for species i , respectively [16]. The electric potential distribution in the electrolyte solution is related to the volumetric free charge density by Poisson's equation [17]:

$$\frac{\partial^2 E}{\partial x^2} = - \frac{\sigma_f}{\varepsilon} \quad (2)$$

where ε is the dielectric constant permittivity and σ_f is the free charge density is expressed as follow:

$$\sigma_f = \sum_i z_i e c_i \quad (3)$$

To solve the Poisson equation local electro-neutrality constraint is enforced. In this case, the electric field becomes an unknown constant to be determined as part of the overall solution and the electric potential equation becomes a Laplace equation [17]. In this work, we considered a Nickel sulfate solution consisting of Ni^{+2} and SO_4^{-2} ions. The Nickel reduction reaction takes place on the cathode surface according to:



Furthermore, homogeneous reactions occur in the electrolyte solution, such as reaction (5), which potentially could affect the Nickel ion concentration.



Since in this modeling the bath pH was assumed to be maintained below $\text{PH} = 4$, the concentration of $\text{Ni}(\text{OH})^+$ and the corresponding concentration change of Ni^{+2} due to its production is negligible and is not considered in the analysis [17,18]. Whereas we considered two ions with equal and opposite valences and electro-neutrality condition for electrolyte, we have the same concentration in any point for each of these ions. Diffusion coefficient, temperature and electrode kinetic parameters are constant during this modeling. To produce convection term a constant hydrodynamic velocity v_c in ($-x$) direction is considered. By considering these conditions, governing equations are simplified as follows:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v_c \frac{\partial c}{\partial x} + \frac{FDz}{RT} \frac{\partial}{\partial x} \cdot \left(c \frac{\partial E}{\partial x} \right) \quad (6a)$$

$$\frac{\partial^2 E}{\partial x^2} = 0 \quad (6b)$$

To solve both Eqs. (6a) and (6b) we adopted the following initial and boundary conditions:

$$C(x, 0) = c_b \quad E(x, 0) = 0 \quad \forall x > 0, \quad (7a)$$

$$C(\delta, t) = c_b \quad E(\delta, t) = 0 \quad \forall t, \quad (7b)$$

¹ A polyhedral grid co-located incompressible finite volume solver.

Download English Version:

<https://daneshyari.com/en/article/4908243>

Download Persian Version:

<https://daneshyari.com/article/4908243>

[Daneshyari.com](https://daneshyari.com)