



## MODELLING AND SIMULATION OF CURRENT DISTRIBUTION OF NICKEL ELECTRODEPOSITION FROM LOW ELECTROLYTE CONCENTRATION AT A NARROW INTERELECTRODE GAP

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### ABSTRACT

Thickness and morphology of electrodeposited coating is crucial in every application of protective finish to ensure high quality and performance is achieved. How a deposited metal is distributed across the cathode surface is greatly affected by current density distribution. To calculate current density distribution prior to the design of electrochemical system is essential in order to optimize the uniformity. The effect of cell geometry and kinetics on current density distribution in nickel electrodeposition from low electrolyte concentration and narrow interelectrode gap has been investigated. This electrochemical system was required for nickel pattern transfer using Enface technology. The modelling and simulation was carried out by solving Laplace's equation in the potential model theory considering appropriate boundary conditions using the Boundary Element Method. The simulation was accomplished by using software of Elsy (ELSYCA NV). The results show that the current density distribution using 2D and axy-symmetrical system was identical for all electrode sizes. However, current density at the electrode edge in the axy-symmetrical model was higher by around 19 % which might be due to the extra space around the electrode. Thus, 2D configuration was sufficient to represent the actual reactor geometry for the experimentation. In a parallel plane electrode configuration, the current density significantly increases at the edge of the cathode. The current density was uniform in the range of  $0.08 < x/L$  (normalized length)  $< 0.92$  which was over 80% of the surface area. Therefore, the patterns should be located at the middle of the anode for ensuring a uniform thickness of deposited nickel pattern was achieved.

**Keywords:** modelling and simulation, electrodeposition, nickel electroplating, enface technology, elsy.

### INTRODUCTION

Thickness and morphology of electrodeposited coating is crucial in every application of protective finish to ensure optimum performance is achieved [1]. How a deposited metal is distributed across the cathode surface is greatly affected by current density distribution [2,3]. The thickness and morphology of the deposit surface would be non-uniform at different points across the substrate if the current density is not well distributed [1, 2]. Therefore, it is important to calculate current density distribution prior to a design of electrochemical system in order to optimize the deposit uniformity [4,5]. This would also lead to a highly efficient and low cost process [1,2].

The current distribution is affected by [2]: (1) cell geometry, (2) conductivity of components, (3) kinetics of the electrochemical reactions at electrodes, and (4) mass transfer of reacting species. Three categories of Current distribution: primary, secondary, and tertiary depend upon inclusion of the design parameters. The primary current distribution only includes the cell geometry and the electrolyte conductivity to the calculation. An incorporation of the kinetics (activation overpotential) results in the secondary current distribution. The tertiary considers all parameters in the calculation [6].

To calculate current distribution, mathematical models for a simple electrochemical system have been developed which involves complex non-linear partial differential equations [2]. When the geometry of the reactor is more complicated and hydrodynamic parameters are taken into account, the complexity of the mathematical

equation increases [2]. A number of works to show current distribution using empirical [7] and analytical [1,3] methods have been carried out. However, more recently, numerical and computational methods are fast growing techniques to use [1-7].

In this paper, an investigation on current distribution was performed to determine electrochemical conditions that allow one to locate patterns so that uniform deposited metal would be achieved. The present study focused on the effect of cell geometry and kinetics on current density distribution. This was crucial investigation prior to nickel pattern transfer experiments using Enface technology. A numerical model for simulation of current density of nickel electrodeposition at a specifically designed electrochemical system i.e. low concentration of electrolyte and narrow electrode distance is shown here. This electrochemical system was required for laboratory experiments of nickel micropattern transfer using Enface. The numerical model and simulation were developed to obtain primary and secondary current distribution by assuming the electrochemical kinetics complies with Butler-Volmer formula. The kinetic data were experimentally determined prior to the simulation.

The modelling and simulation was carried out by solving Laplace's equation in the potential model theory considering appropriate boundary conditions using the Boundary Element Method. The simulation was accomplished by using commercially available software, Elsy (ELSYCA NV). The software provides two possible reactor geometries e.g. 2D and axy-symmetrical models to



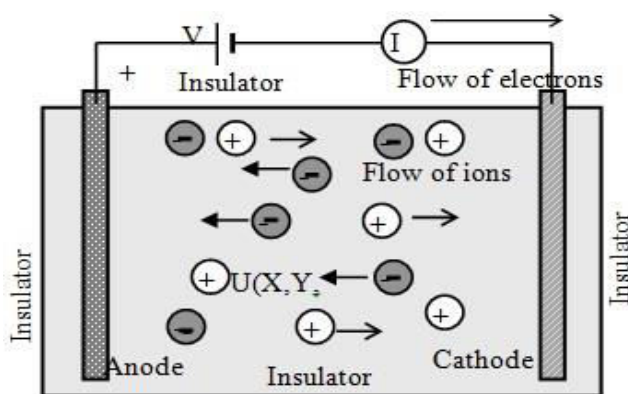
represent the electrochemical system [8-11]. A cell configuration (2D or axi-symmetrical term) was designed and defined in the software to create a geometry that closely represents the actual cell used in the experimentation. Modeling of current distribution was carried out to show the current density distribution at the cathode and the shape development of the deposit on the cathode surface.

### BASIC PRINCIPLE

Several assumptions were taken into account in the calculation of current density distribution [12,13]:

#### A. The electrochemical system

The electrochemical system is assumed to have an electrolyte bounded by electrodes and insulators (c.f. Figure-1).



**Figure-1.** Typical electrochemical cell used in simulation using Elsy with constant electrolyte conductivity and uniform ionic species gradient [12]

In this system, a transfer of charge occurs due to electron flow passing through the ionic solution and external circuit. A transfer of material also takes place driven by the potential and concentration gradient coupled with hydrodynamic. At the electrode surface, electrochemical reactions are potential to occur due to the current flow. Overall mass transfer from the bulk of the solution to the electrode surface is determined by the current flow, mass balance, ionic species mobility, and electro-neutrality. The gradient of the ion concentration is assumed to be uniform. The electrolyte and the electrodes conductivity are constant. Ions transport equation is developed from an infinitely diluted solution. All factors affecting the system are taken into consideration in solving mass and charge transfer problems.

### Multi-ion system in dilute solutions: General transport equations

#### The flux of an ionised species

At a constant temperature and pressure, the flux of an uncharged solute ( $i$ ) due to migration, diffusion, and convection in a solution of an ionised species within unionised solvent infinitely diluted can be written as [12 - 14]:

$$N_i = \underbrace{-z_i u_i F c_i \nabla \phi}_{\text{migration}} - \underbrace{D_i \nabla c_i}_{\text{diffusion}} + \underbrace{c_i v}_{\text{convection}} \quad (1)$$

Where,  $N_i$  is the flux of species  $i$  (mole/cm<sup>2</sup>s),  $z_i$  is a number of the charge,  $F$  is Faraday's constant, 96847 C/mol,  $c_i$  is the molar concentration, mole/cm<sup>3</sup>,  $\nabla \phi$  is potential gradient, Volt,  $D_i$  the diffusion coefficient, cm<sup>2</sup>/s,  $v$  is the solvent velocity, cm/s,  $u_i$  is the mechanical mobility of the species, cm<sup>2</sup>/mol/Js

#### Mass balance

The accumulation of each species  $i$  in a small volume element is given by [12-14]

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i \quad (2)$$

Where,  $R_i$  is the production rate of species  $i$ , and  $\nabla \cdot N_i$  is the flux divergence (the net flux of species  $i$  per unit volume). Since the electrochemical reactions are restricted on the electrode surface, the chemical reaction is usually ignored.

#### Electroneutrality

In the electrolyte bulk, the equation of the electroneutrality is [12 - 14]:

$$\sum_i z_i c_i = 0 \quad (3)$$

Coupled with the following equation which is derived from Poisson's equation

$$\nabla^2 \phi = -\frac{F}{\epsilon} \sum_i z_i c_i \quad (4)$$

With  $\epsilon$  is dielectric constant or the permittivity (Farad/m)

A considerably large electric field is required to separate a charge. Since the charge very quickly neutralised or flowing to the boundary due to the high solution conductivity, no free charge density is in the system. Hence, the electroneutrality term appropriately approximates this condition. [12-14].

#### The current density

The overall current density ( $j$ , mA/cm<sup>2</sup>) is defined as a sum of every component flux multiplied by its charge per mol as shown in equation 5 [12 - 14].

$$j = F \sum_i z_i N_i \quad (5)$$

#### The continuity equation

Navier-Stokes equation can be used to determine the velocity of an incompressible fluid flow in agitated electrochemical systems [12 - 14].



$$\rho \left( \frac{\partial v}{\partial t} + v \cdot \nabla v \right) = -\nabla p + \mu \nabla^2 v + \rho g \quad (6)$$

Where,  $\nabla p$  is hydrostatic pressure gradient ( $kg/m^2s^2$ ),  $\mu \nabla^2 v$  the viscous force ( $kg/m^2s^2$ ), and  $\rho g$  The gravity force ( $kg/m^2s^2$ ). The viscosity ( $\mu$ ) and the density ( $\rho$ ) of the electrolyte are assumed to be constant. In a very small element of electrolyte volume, the overall mass balance is

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho v) \quad (7)$$

If the density is constant, the above equation may be simplified to be the continuity equation

$$\nabla \cdot v = 0 \quad (8)$$

Equation (6) and (8) are used to calculate the velocity ( $v$ ) at each point [12 - 14].

### The ions transport in dilute solution

Equation (5), current density can be written as a combination of ion/electron motion due to diffusion, convection, and migration. Where, equation (1) is substituted to equation (5) [12 - 14].

$$j = -F^2 \sum_i z_i u_i c_i \nabla \phi - F \sum_i z_i D_i \nabla c_i + F v \sum_i z_i c_i \quad (9)$$

Electric conductivity ( $\kappa$ , S/m) of the solution ( $1/\Omega$ ) is

$$\kappa = F^2 \sum_i z_i u_i c_i \quad (10)$$

Using equation (3) and (10), the current density formula can be shorten to

$$j = -\kappa \nabla \phi - F \sum_i z_i D_i \nabla c_i \quad (11)$$

At condition where there is no homogeneous chemical reaction in the bulk of infinitely diluted solution, the transport of material and charge can be estimated using the following equation

$$\frac{\partial c_i}{\partial t} + v \cdot \nabla c_i = z_i F \nabla \cdot (u_i c_i \nabla \phi) + \nabla \cdot (D_i \nabla c_i) \quad (12)$$

$$\sum_i^n z_i c_i = 0 \quad (13)$$

### Potential-theory model

At steady state condition, time-dependent terms might be excluded from equation (12). The flux of the electro-active species ( $i$ ) can also possibly be neglected due to an excessive supporting solution leading to the increase of conductivity. In a well stirred electrochemical system at which forced convection becomes predominant, concentration gradient can be ignored [12 - 14].

The above condition implies to the simplification of the current density equation and the material and charge transport equation to become Laplace's equation (15).

$$j = -\kappa \nabla \phi \quad (14)$$

$$\nabla^2 \phi = 0 \quad (15)$$

Based on boundary conditions described in the following sub-section, this potential model is then solved by Elsy using the Boundary Element Method (BEM).

### Boundary conditions

At the electrodes, electrochemical reactions occurs due to a charge transfer overpotential which determine the reaction rate. The overpotential is defined by [12-14]

$$\eta = V - \phi - E_e = f(c_0, j_n) \quad (16)$$

Where,  $V$  is potential of the metal (electrode, Volt),  $\phi$  is solution potential of the solution at points near the electrode surface ( $V$ ),  $E_e$  is equilibrium potential ( $V$ ), and  $c_0$  is concentration of the species at the electrode surface.

Butler-Volmer equation relates the overpotential to the current density by [13 - 14]

$$j = j_0 \left[ \exp\left(\frac{\alpha_a n F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c n F \eta}{RT}\right) \right] \quad (17)$$

The equation shows that at a small value of the overpotential, the relationship of  $j$ - $\eta$  would be linear, whereas one of the exponential would become negligible at a large value of  $\eta$ .

### Electrodeposited metal

Faraday's formula allows one to calculate the amount of electrodeposited material. The deposit thickness ( $h$ ) for a deposition time of  $\Delta t$  is then calculated using equation (18) [12-14]

$$h = -\frac{\phi M}{z F \rho} j \Delta t \quad (18)$$

Where  $M$  is atomic/molecular weight of the deposited metal (mol/g) and  $\phi$  is the cathodic current efficiency.

### Wall (insulator)

Surrounding wall including the air are considered as insulators. The current does not pass through insulating material. Therefore, at any points at the insulator, the overall current density is equal to zero [12-14].

$$j_y = j \cdot 1_y = -\kappa \nabla \phi \cdot 1_y = -\kappa \frac{\partial \phi}{\partial y} \quad (19)$$

$$\frac{\partial \phi}{\partial y} = 0 \quad (20)$$



Where,  $y$  is normal distance from the electrode surface.

## METHOD

In Elsy, geometrical points and lines are used to denote a closed system consisting two electrodes and insulators to visualise the electrochemical cell. The lines which represent the cathode and the anode were set to 60 and 30 elements respectively. Non-convergence calculation was obtained if too high number of elements was used due to too small mesh spacing. A better result of simulation might be obtained at higher number of elements, however it was insignificant as the results of cathode elements  $> 60$  only varied by less than  $< 1\%$ . so 60 elements was sufficient for the simulation.

The boundary conditions was defined according to each line category e.g. at the insulating walls, the current and the flux of ion were set to be equal to zero. For secondary current distribution, at the cathode where electrochemical reactions occur, the kinetic were set to follow Butler-Volmer model. This kinetic parameter and the conductivity of the solution were experimentally determined.

The results would be obtained if a criterion of convergence was reached. Convergence is a condition where the input and output current density in the calculation were nearly identical. The convergence was achieved when the current residual has reached a value of  $< 0.001 \text{ mA/cm}^2$ . In this work, the convergence was achieved within 7 iterations (out of 20 iterations).

## Kinetic parameters

Kinetics of the nickel electrochemical reaction was experimentally investigated using a standard three-electrode cell as described in previous publication [15]. The kinetic parameters of the system have been determined analytically and graphically [16].

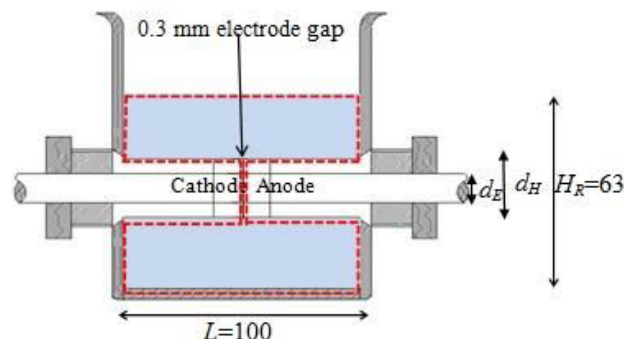
The kinetic parameters utilised in this work are those obtained by a graphical method from polarisation data of the electrolyte of  $0.19 \text{ M Ni(SO}_3\text{.NH}_2\text{)}_2$  (Table 1). The experimentally measured physicochemical properties of the electrolyte i.e. the temperature, the pH, and the conductivity are also listed.

**Table-1.** Physicochemical properties and kinetic parameters of the electrolyte.

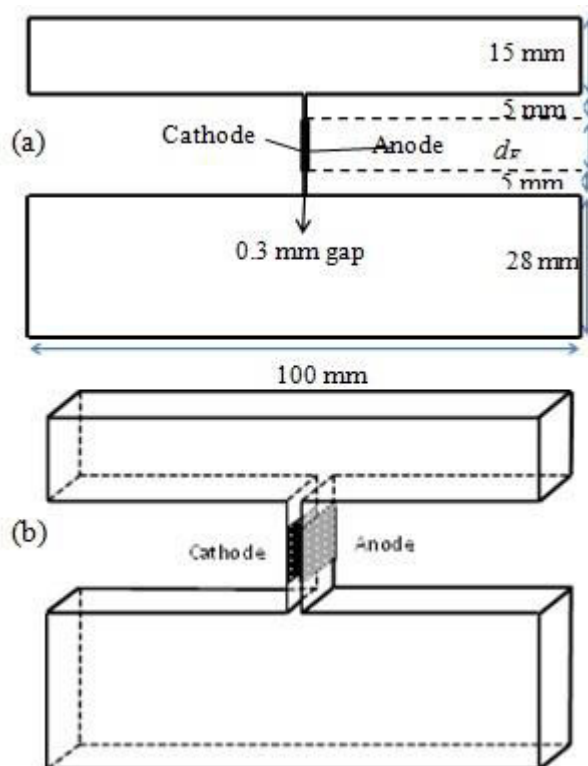
Parameter	Value
Electrolyte and Substrate	$0.19 \text{ M Ni(SO}_3\text{.NH}_2\text{)}_2$ , copper
T (°C)	$20 \pm 2$
pH	$6.70 \pm 0.22$
$\kappa$ (S/m)	$2.19 \pm 0.06$
$D_{\text{Ni}^{2+}}$ ( $\text{cm}^2/\text{s}$ )	$7.00\text{E-}06$
Tafel Slope (mV/dec)	159
$j_0$ ( $\text{mA/cm}^2$ )	$3.16\text{E-}04$
$\alpha_c$	0.37

## Configuration of electrochemical reactor

To verify the experimental results, the cell geometry defined in the simulation had to sufficiently identical to the real reactor. The actual electrochemical cell configuration used in the experiments is shown in Figure-2. The red dash-line shows the Elsy system.



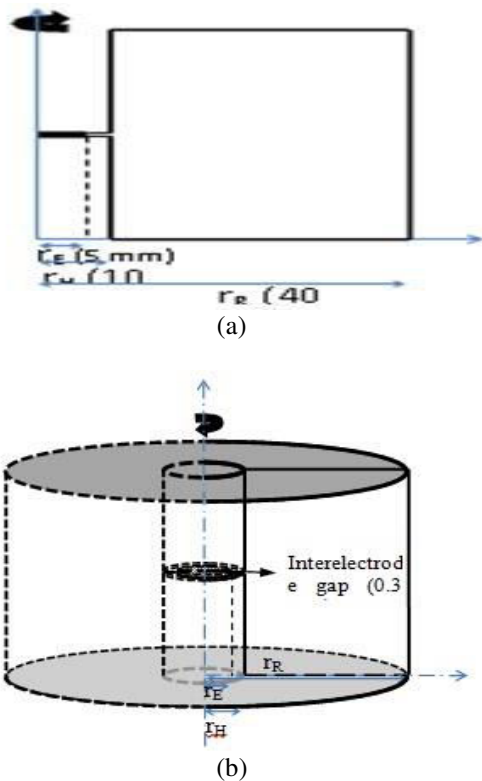
**Figure-2.** Cross-sectional view of the electrochemical reactor.



**Figure-3.** (a) 2D reactor model and (b) its actual shape.

Two possible reactor geometries are available in Elsy e.g. 2D and axy-symmetrical. The 2D reactor geometry and its shape (b) are presented in Figure-3. Figure-4 (a) and (b) show the axy-symmetrical geometry and the reactor shape. The axy-symmetrical model was obtained by rotating the original cell orientation by  $90^\circ$  clockwise.





**Figure-4.** (a) Axy-Symmetrical reactor geometry created by rotating the original cell orientation by 90° clockwise and (b) its actual shape with  $r_E$ : electrode radii,  $r_H$ : holder radii, and  $r_R$  reactor radii.

The axy-symmetrical model might be the better option to represent the shape and geometry of the actual cell. However, due to its practicality, 2D was preferable for the simulation. Therefore, a comparative study of the current density distribution in the 2D and the axy-symmetrical was carried out to see how different the current distributions along the electrode were produced. The reactor geometries were defined into the Elsy using parameters with all adjusted dimensions including the 0.3 mm electrode distance. The simulations were carried out for an electrolyte of 0.19 M nickel sulfamate with a conductivity of 2.19 S/m. The electrode kinetics was set to obtain a primary current distribution.

**Table-2.** Electrodes and holders size of electrochemical.

2D model		Axy-symmetrical model	
Electrode size (dE, mm)	Holder size (dH, mm)	electrode radius (rE, mm)	Holder radius (rH, mm)
20	20	10	10
10	20	5	10
8	20	4	10
4	20	2	10

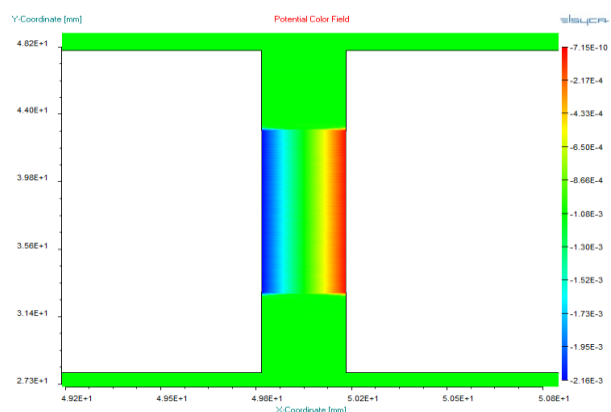
In order to thoroughly examine the current density distribution in the 2D configuration, calculations were performed with different sizes of electrode (dE) with

a constant value of electrode holder size (dH), reactor height (HR, height of filled section) and length (L). Axy-symmetrical geometry calculations were carried out on various electrode radii ( $r_E$ ) with a constant value of  $r_H$  (radius of holder) and  $r_R$  (reactor radius). A summary of the electrode sizes is presented in Table-2.

The geometry of the electrochemical reactor in Figure-3 (a) and 4 (a) were visualised in the software by geometrical points and lines. Each line was divided into a number of elements. Every line also had to be specified either as an insulator or an electrode in order to declare where Ni deposition could proceed.

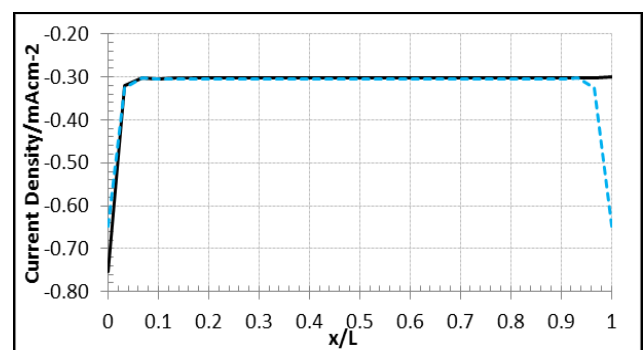
## RESULT AND DISCUSSION

When a specific value of electrical current (e.g. 0.33 mA/cm<sup>2</sup>) was imposed to the system, potential responses were calculated at any part of the cell. Figure-5 shows how the potential is distributed throughout the electrolyte and across the electrodes.



**Figure-5.** Potential colour fields showing the distribution of potential in the electrolyte and on the electrodes.

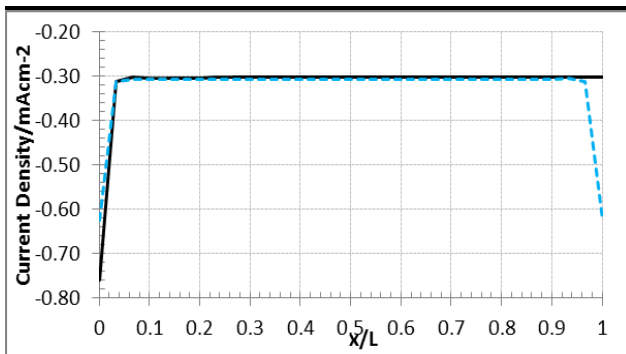
The current density distribution across the cathode for 2D model was compared to that obtained from axy-symmetrical reactor model. The current density profiles of both models at various area of electrode surface are illustrated in Figure-6 – 9.



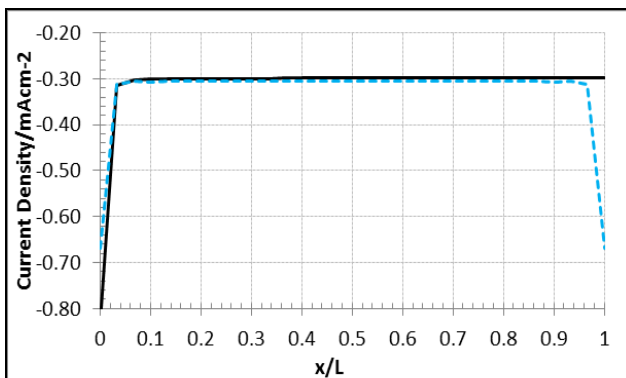
**Figure-6.** Current distributions across the cathode for 2D and axy-symmetrical configuration dE=20 and rE = 10, ( — Axy-symmetrical, - - - 2D model ).



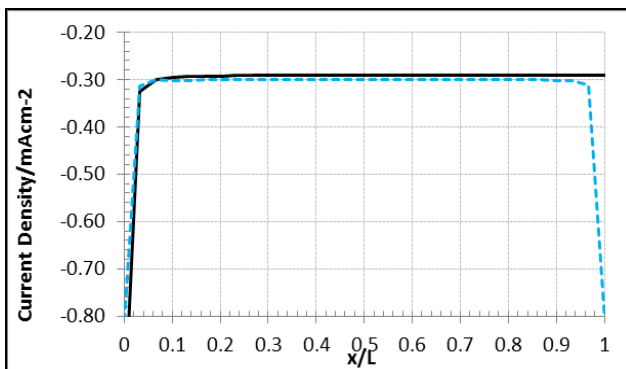
The current density is shown against normalized length  $x/L$ . As shown in the Figure, the current density is uniform between  $0.08 < x/L < 0.92$  at any electrode size. As expected in a parallel plane electrode configuration, the current density significantly increases at the edge of the cathode [14]. To achieve uniform thickness of deposited pattern, the pattern should be located on the area where uniform current density exists. This also shows that there is no significant effect of the electrode and the holder size on current density distribution.



**Figure-7.** Current distributions across the cathode for 2D and axy-symmetrical configuration  $dE=10$  and  $rE=5$ , ( — Axy-symmetrical, - - - 2D model).



**Figure-8.** Current distributions across the cathode for 2D and axy-symmetrical configuration  $dE=8$  and  $rE=4$ , ( — Axy-symmetrical, - - - 2D model ).

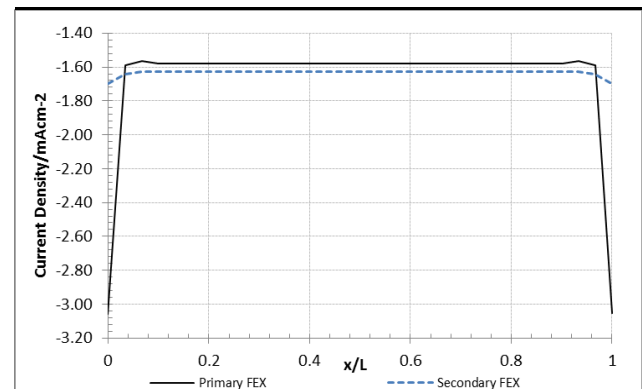


**Figure-9.** Current distributions across the cathode for 2D and axy-symmetrical configuration  $dE=4$  and  $rE=2$ , ( - - - Axy-symmetrical, — 2D model )

Figure-6 - 9 shows the location where uniform current density distribution along the electrode for the two different methodologies is obtained. The data show that the current is uniform over 80 % of the surface area. Therefore, patterns should be located at the middle of the anode for ensuring a uniform deposit thickness would be achieved.

As observed in Figure-6 - 9, the current density using 2D and axy-symmetrical system overlay each other for all electrode sizes. The only different is that current density at the edge of the electrode in the axy-symmetrical is higher by approximately 19 % than those in 2D. The difference may be due to the extra space around the electrode [14]. Based on the results, 2D configuration is sufficient for the pattern transfer simulation to represent the actual reactor geometry

The effect of kinetics was also investigated. Figure-10 shows primary and secondary current density distributions across the cathode. The kinetic of nickel electrodeposition slightly affected the current density distribution. At a uniform region, the current density is slightly greater than those in the primary model. However at the edge of the cathode, the current density is significantly lower.



**Figure-10.** Current distributions across the cathode for 2D configuration ( — primary, - - - secondary)

Figure-10 also shows that for secondary current density distribution, the current density is uniform between  $0.08 < x/L < 0.92$  across the cathode. This also supports that in pattern transfer experiment using Enface technology, patterns that would be transferred should be located at the middle of the anode for ensuring a uniform deposit thickness would be achieved.

## CONCLUSIONS

An investigation on the effect of cell geometry and kinetics on current density distribution in nickel electrodeposition from low electrolyte concentration and narrow interelectrode gap has been presented. The simulation of the process is carried out using commercial software that allows 2 (two) cell configuration. It was found that 2D configuration is sufficient for the pattern transfer simulation to represent the actual reactor geometry. To achieve uniform thickness of deposited



pattern, the pattern should be located on the area where uniform current density exists ( $0.08 < x/L < 0.92$  at any electrode size). The kinetic of nickel electrodeposition slightly affects the current density distribution. At a uniform region, the current density is slightly greater than those in the primary model. However at the edge of the cathode, the current density is significantly lower.

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