

A GEOMETRICAL CONFIGURATION AND ITS EFFECT ON THE PERFORMANCE OF AN ELECTROCHEMICAL CELL UNDER FREE CONVECTION

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Abstract

The effect of positioning or location of the cathode electrode with respect to the surface margin of the electrodeposition electrolyte solution under free convection was numerically studied. The importance of such study arises from the fact that there is no study, according to the author's knowledge regarding the effect of electrode positioning (depth effect) and its effect on the current distribution and on the free convection (absence of forced convection) hence, its effect on mass transfer, that highly appears in the industrial application. It was shown that positioning of cathode near the surface of the solution gave bad results of deposits distribution while moving it downward has comparable results to that when the electrodes are in the middle of the electrolyte. Accordingly, the best configuration was achieved when the cathode location approximately is in the middle of the electrolyte with applied currents-as in this study of about 4.6 mA/cm^2 -. According to this study, it was found that there was no effect of free convection on the mass transfer or on the flux of Cu^{+2} ions and the main contributed mechanism is the diffusion one.

Keywords: Comsol, Concentration distribution, Current distribution, Electrodeposition, Electrode positioning, Natural convection.

1. Introduction

Electrochemical process is affected by the hydrodynamics of the system through variation of the mass transfer of the process. An electrochemical process works either without forced convection or with. The external stirring is obtained when the work is allowed to move while the electrolyte or the solution is still as in the rotating cylinders or discs stirring, pumping or vice versa, etc. [1, 2].

According to Donahue [1], in the absence of forced convection, an enhancement of the rate of transport is possible by some sort of convective flow. Volgin and Davidov [2], during electrolysis at an electrode, the density and viscosity in the vicinity of the electrode can change substantially from those in the bulk of the solution. For example, during dissolution of a metal at high rates, the solution in the vicinity of the anode will be enriched with metallic ions with a resultant increase of the density of the fluid near the anode.

In the presence of a gravitational field, the solution at a vertical anode will tend to fall due to this increased density. As the solution falls, it will move parallel to the electrode face and cause of flow of solution with a finite velocity. This flow tends to enhance the rate of material transport when compared to molecular diffusion. While a node process is of considerable interest in electrochemical engineering, many properties of the system such as degree of supersaturation of the anolyte, etc., make a quantitative description virtually impossible. Some of the related relations with deep analysis can be found elsewhere [3, 4].

Wagner [5] reported the importance of free convection effect on the hydrodynamic and since then numerous papers were issued regarding such importance [6-9]. There are many theoretical and numerical studies on the current distribution were reported in various electrochemical systems such as the rotating electrode disk [10, 11] and other configurations [12-14]. Current distribution is very important, especially in the electrodeposition process where it gives how the uniformity of deposits will be [15-18]. As stated by Deconinck [18] and Lowenheim [19], this uniformity of distribution depends on the geometry of the works, the type of electrolyte, hydrodynamic and kinetic factors.

In industrial process, high mass transfer rates are required for quick process and profitable outputs and in many electrodepositions process the free convection is the sole means. The parts or work (cathode) here is submerged inside the electrolyte or solution to some depth surrounded by the anode electrodes and the shape of the work depends on engineering demands. According to our knowledge, the effect of the position of the cathode electrode with respect to the surface margin (depth of electrode) of the electrolyte - on the deposition process in the absence of forced convection was not reported. In this study, such task will be handled from a theoretical basis. As stated by Lowenheim [19], the electrolyte is considered to be 0.75 M CuSO_4 +0.76 M H_2SO_4 assuming it is composed of binary components; Cu^{+2} and SO_4^{-2} where the H^+ has a minor effect at pH of 4. Two anodes with dimensions of 0.5 cm \times 0.5 cm made of inert material such as graphite and one cathode (work) with 0.7 cm \times 0.5 cm of copper. The shape of the cell is shown in Fig. 1.

The parameter used in this study is the location of the electrodes with respect to the height of the cell y , which it is extended from $y = -1$ to $y = 2$ as in Fig. 1 while the effect of the applied current and the Cu^{+2} concentration will be postponed to a future study. The studied parameter will be checked through its effects on the

distribution of current, concentration of Cu^{+2} and through their effects on the evolved velocity.

2. Formulation of Numerical Simulation

The following physics [2, 20-22] were used throughout this study; the Navier-Stokes and continuity equations are used to solve the velocity u .

The first physic is the Nernst-Planck, which describes the flux of species i N_i to be composed of three mechanisms of transfer; by diffusion, migration and convection as follows:

$$N_i = -D_i \nabla C_i - Z_i u_{mi} F C_i \nabla V + C_i u \quad (1)$$

and the material balance is expressed,

$$\frac{\partial C_i}{\partial t} + \nabla N_i = 0 \quad (2)$$

where D_i is the diffusivity, u_{mi} is the mobility and V is the electrolyte potential. Electroneutrality is applicable;

$$\sum C_i Z_i = 0 \quad (3)$$

Equation (1) in the absence of concentration gradients and convection is reduced to the Laplace equation of potential;

$$\nabla^2 V = 0 \quad (4)$$

Steady state, laminar, incompressible flow has been considered and hence,

$$\nabla u = 0 \quad (5)$$

$$\rho \frac{\partial u}{\partial t} + \rho u \cdot \nabla u = -\nabla P + \nabla \cdot \left(\mu (\nabla u + (\nabla u)^T) - \frac{2}{3} \mu (\nabla u) I \right) + F \quad (6)$$

where ρ is the density, P is the pressure, F is the volume force vector and I is the identity matrix.

Depending on the boundary conditions Eq. (4) is solved to give the appropriate type of current distribution. The secondary current distribution takes the Tafel equation form;

$$\eta = bc \ln\left(\frac{i}{i_0}\right) \quad (7)$$

where i_0 is the exchange current density, bc is the Tafel slope and η is the overpotential.

When the concentration has a substantial effect on the current distribution, the tertiary current distribution is applicable and it has the following formula:

$$i = -i_0 \exp\left(-\frac{\eta}{bc}\right) C/Cb \quad (8)$$

where C and Cb are the surface and bulk concentrations respectively. When the concentration deviation has an important role especially in the vicinity of the electrode, the following equation is applicable;

$$\nabla^2 C = 0 \quad (9)$$

To model the process with appropriate boundary and initial conditions, Comsol Multiphysics 4.4 was used in the simulation process other features as it will be shown. As reported by Kawai et al. [14], it is assumed that the potential of the solution is zero at the auxiliary electrode while an average current density of 4.6 mA/cm^2 is applied on the cathode. It is assumed that the diffusion, migration and convection are the contributing mechanism of transfer. The values of kinetic and transport parameters used in the numerical simulation are shown in Table 1.

Table 1. Properties and values of the model.

Property	Value
Concentration of species 1, C_1 (mol/m ³)[19]	750
Concentration of species 2, C_2 (mol/m ³)[19]	750
Valence of species 1, Z_1	2
Valence of species 2, Z_2	-2
$D_{\text{Cu}^{+2}}$ (m ² /s)[3]	0.72×10^{-9}
$D_{\text{SO}_4^{2-}}$ (m ² /s)[3]	1.06×10^{-9}
Tafel slope, [23]	0.13
Time of electrolysis (s)	1600

3. Results and Discussion

Figure 1 shows the electrochemical cell where there are two insoluble anodes surrounding the cathode and all these electrodes are submerged inside the electrolyte. The reason for using two anodes is to give a uniform distribution of deposits on the cathode electrode. In the industry, it could be used more than two electrodes surrounded the cathode from all directions. The time of the process was divided into values from 0-1600 s as shown in the legends of the figures. The following configurations of the electrodes will be handled and discussed.

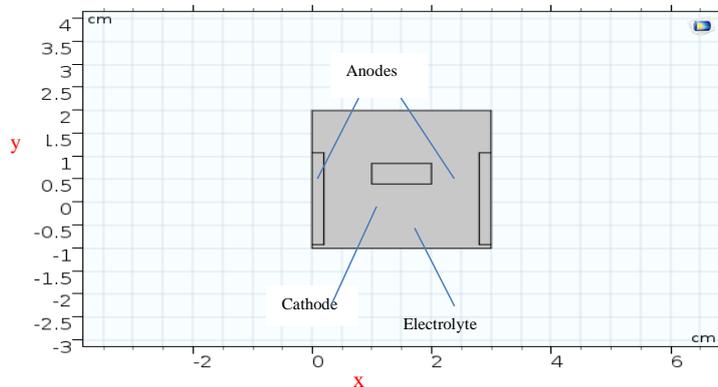


Fig. 1. Electrochemical cell used in simulation.

3.1. Electrode position at $y = 0.4$

For this configuration the local current density distribution on the upper surface of the cathode and on its lower surface (starting from left direction) are shown through Figs. 2 and 3 respectively.

From Figs. 2 and 3, the local current is approximately distributed uniformly on both surfaces with slight deviations, therefore, only attention will be focused on the

upper face of the cathode in the forthcoming discussion. In general, the top surface is slightly received less current than the bottom surface. The local current, hence, the deposits thickness, are slightly decreased as the time increases that is due to a reduction in the surface concentration of Cu^{+2} as shown in Fig. 4.

From Fig. 4, it is obvious that as the time increases a non-uniform concentration of Cu^{+2} along the electrode is established due to depletion of Cu^{+2} according to the electrodeposition process:

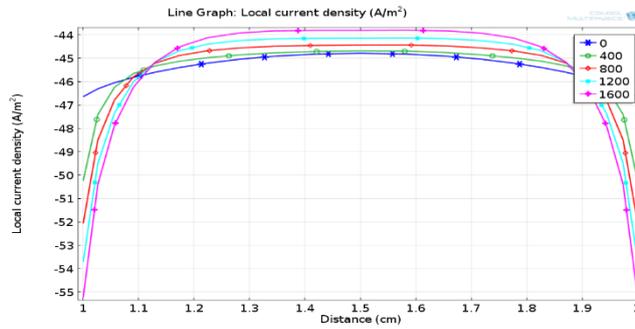
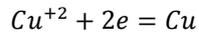


Fig. 2. Local current distribution along the upper surface of the cathode at different time intervals.

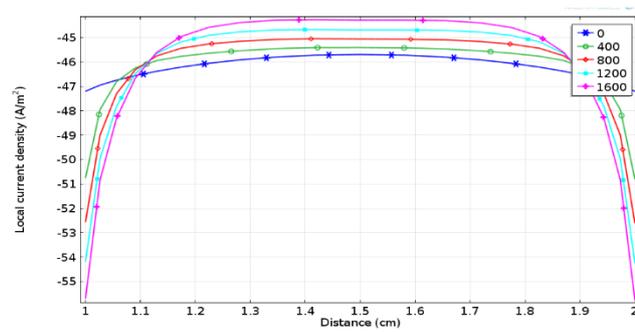


Fig. 3. Local current distribution along bottom of cathode.

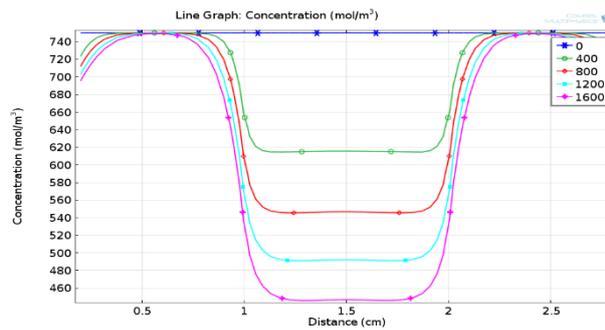
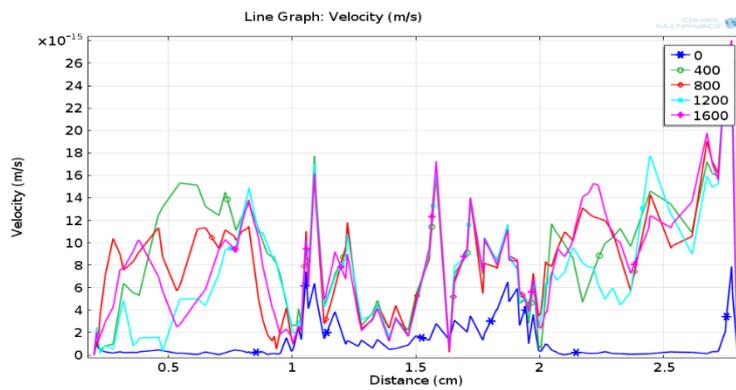
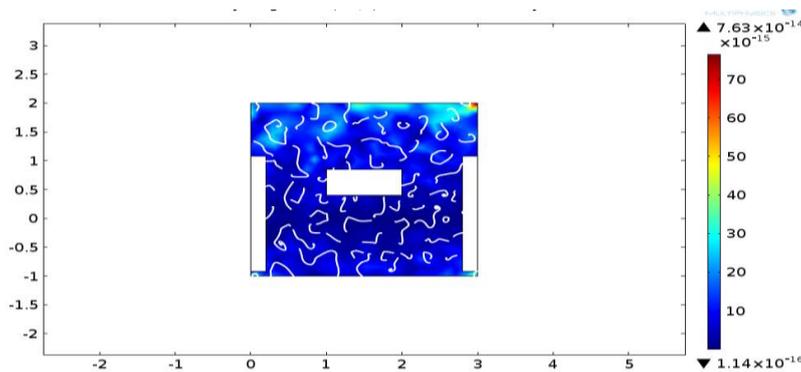


Fig. 4. Cu^{+2} concentration distribution along upper face of the electrode at several time intervals.

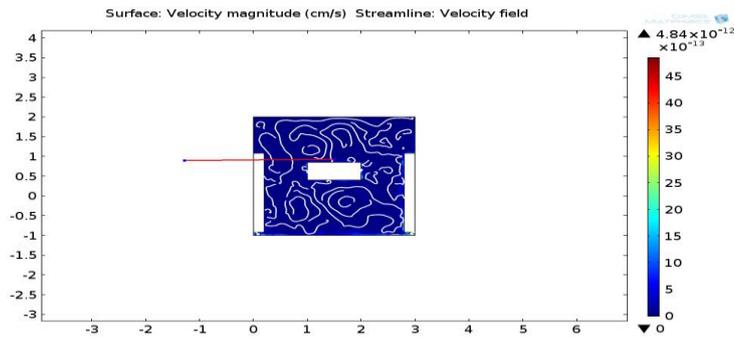
Since there is a deviation of concentration along the electrode for the same time as well as its deviation with time variation from that of bulk, therefore, it is expected that the velocity arises due to these variations. It is interesting to note that there will be a reference line (cut line) from the left edge of the cell until the right one passing just above the upper surfaces of the electrodes. This line will be used to give the values of the free velocity (although it has a very low value) in that region. Figure 5(a) shows the variation of the fluid velocity along that line for different times. At time zero where there is no electrolysis, Fig. 5(b), the free velocity is about zero, as the time proceeds a rising value of the velocity is initiated that differs in value with the progressing of the electrolysis time where the concentration variation is detected clearly and due to the evolution of eddies at some time steps. It is very important to see that the velocity has higher values around the region, which separates the anodes from cathode where the concentration difference has a pronounced effect as the time progresses. Figures 5(b) to (e) show the selected values of the velocity field at some time intervals 0, 100, 800 and 1600 seconds respectively. As can be shown, that while time proceeds the distribution and values of the velocity are grown as stated before due to disturbances in concentration of copper ions. It is shown that at all times the velocity gains its minimum value around the upper cathode surface and it gains maximum fluctuations near anodes edges.



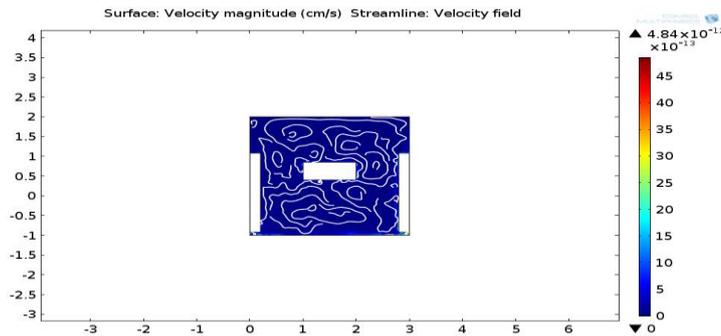
(a) Variation of the free velocity values along cut line at upper electrodes surface at different time values.



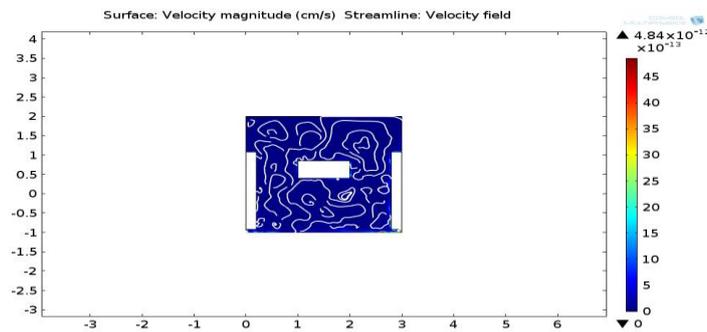
(b) Velocity field values at 0 s.



(c) Velocity field values at 100 s.



(d) Velocity field values at 800 s.



(e) Velocity field at 1600 s.

Fig. 5. Velocity field along the upper electrode surface and within the solution at different time intervals.

3.2. Electrode position at $y = 0.92$

The current distribution at the top surface of cathode is shown in Fig. 6. From Fig. 6 and comparing with Fig. 2, it can be shown that the deposition rate is slightly less and the uniformity is less.

Although in this position the concentration difference of Cu^{+2} (bulk concentration-surface concentration) at each time interval is greater than that in

Fig. 4 (see Fig. 7) accordingly the velocity fluctuation is greater than that in Fig. 5(a) as can be seen in Fig. 8 and from Cottrel equation; $\text{flux} = \Delta C / (\sqrt{\pi Dt})$, where the flux or the current is proportional to the concentration and inversely proportional to the time, which must be increased. However, due to disturbances around electrodes, the current is decreased.

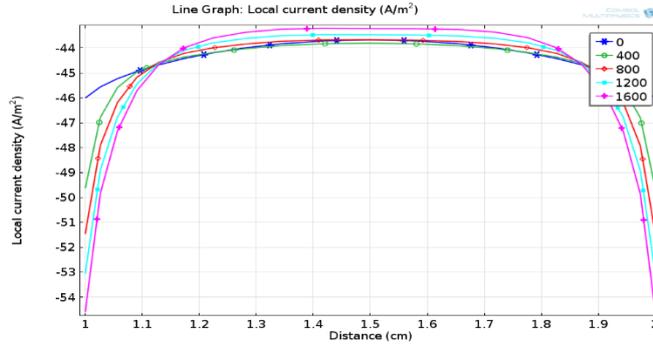


Fig. 6. Local current distribution along cut line at upper electrodes surface.

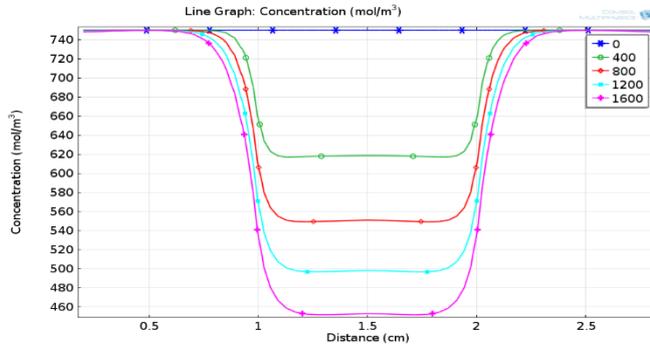


Fig. 7. Cu^{+2} concentration distribution along cut line at upper electrode surface.

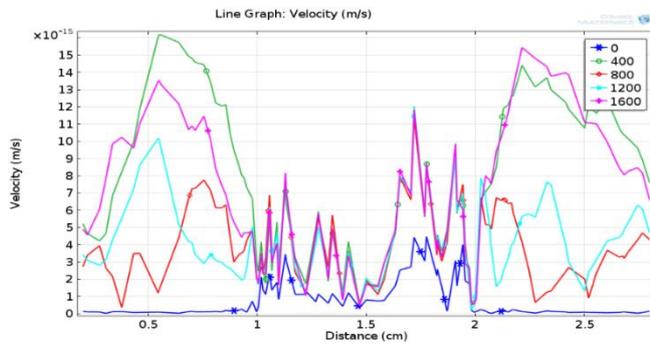


Fig. 8. Variation of the free velocity values along cut line at upper electrode surface.

3.3. Electrode position at $y = -0.91$

The current distribution has a less uniformity at this position (see Fig. 9) and it is less than that at position 0.4, Fig. 2.

The concentration at the cathode, Fig. 10 has a smaller value compared to that in Fig. 4, which leads to greater concentration difference, hence, more velocity values as expected, (see Fig. 11), nevertheless, it is interesting to see that the velocity values approximately are evenly distributed along the electrodes with comparable values to that in Fig. 4 (see Fig. 11), therefore, it is expected that other variable must play a negative role, it is either the height of the solution or the pressure that counterbalances the concentration effects.

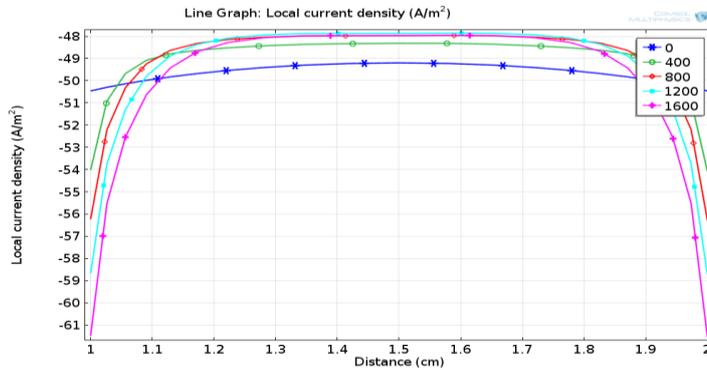


Fig. 9. Local current distribution along cut line at upper electrodes surface.

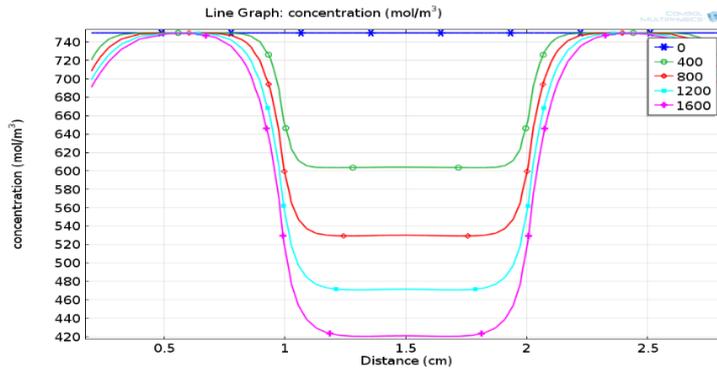


Fig. 10. Cu²⁺ concentration distribution along cut line at upper electrode surface.

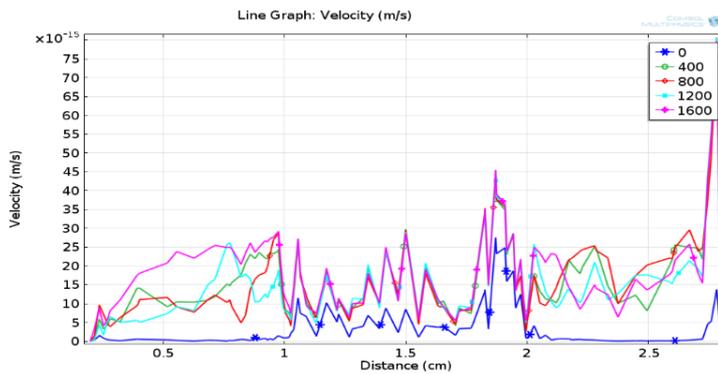


Fig. 11. Variation of the free velocity values along cut line at upper electrodes surface.

From what mention in the above sectors, it is noticed that the local current density is reduced as the time proceeds, which it is an expected result, according to Cottrel's equation; $\text{flux} = \Delta C / (\sqrt{\pi Dt})$, which implies that the flux is inversely proportional to the diffusion layer thickness $\delta = (\sqrt{\pi Dt})$. However, since the concentration is also reduced with time, therefore, there are two effects on the flux. For example, at 400 seconds for $y = -0.91$ (from Table 2.) the flux = $190 / 0.000951 = i / n f D$ where the value $0.000951 = (3.14 \times 0.72 \times 10^{-9} \times 400)^{0.5}$ and for $n = 2, f = 96500$ and $D_{Cu+2} = 0.72 \times 10^{-9} \text{ m}^2/\text{s}$, this will give the value of $i = 27 \text{ A/m}^2$. By comparing this value with that in Fig. 9 where the value of current i is about 48 A/m^2 it can be seen that there is a pronounced difference. This difference in current value could be due to uncertainty in constant values in literature that was used in the model or to some values of concentration difference. It is obvious that the results imply that δ has more effects than ΔC . Table 2 and Figs. 12 to 14 show the values of ΔC and δ respectively, where Table 2 is abstracted from those figures. Figures 12 to 14 were drawn by taking a cutline perpendicular on the upper surface of the cathode extending from its surface to the bulk effect and the δ is drawn as a sample on the graph at $t = 400 \text{ s}$. It must be assured that by inspection the model- the entire results are not shown- convection here has negligible effects as well as migration and the only acting mechanism is the diffusion component Fig. 15 shows the contributing mechanisms of transfer for $y = 0.4$ at 800 s as an example (all other configurations have about the same trend).

Table 2. Abstracted values of ΔC for all locations at different times.

Time, s	0	400	800	1200	1600
Concentration mol/m³ at y					
-0.91	0	190	250	310	460
0.4	0	140	225	270	240
0.92	0	180	250	300	280

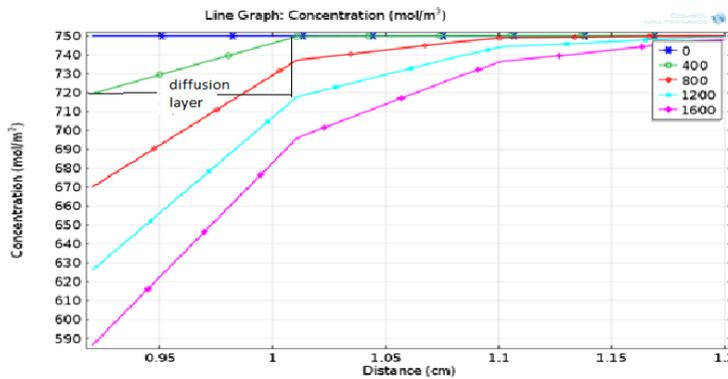


Fig. 12. Concentration difference between bulk and cathode surface concentration at $y = 0.4$.

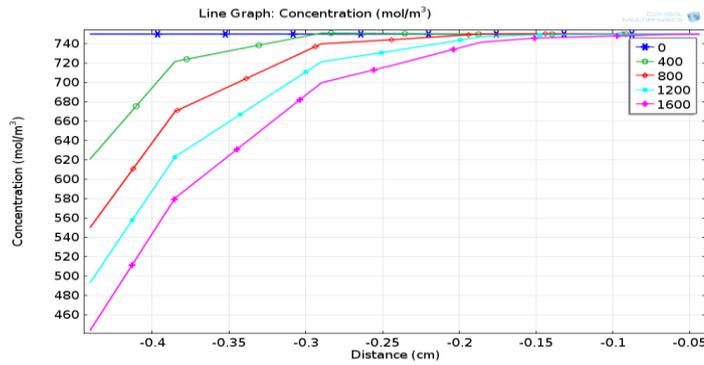


Fig. 13. Concentration difference between bulk and cathode surface concentration at $y=-0.91$.

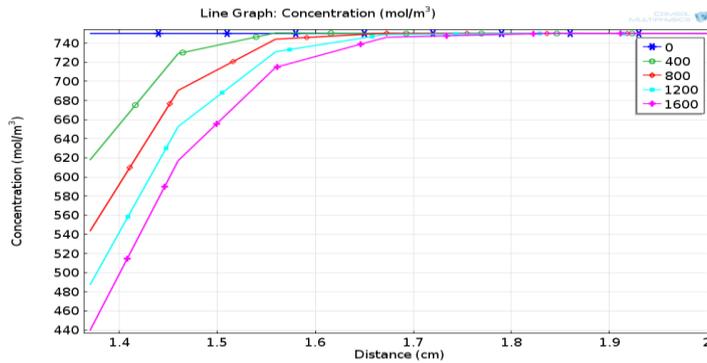


Fig. 14. Concentration difference between bulk and cathode surface concentration at $y = 0.92$.

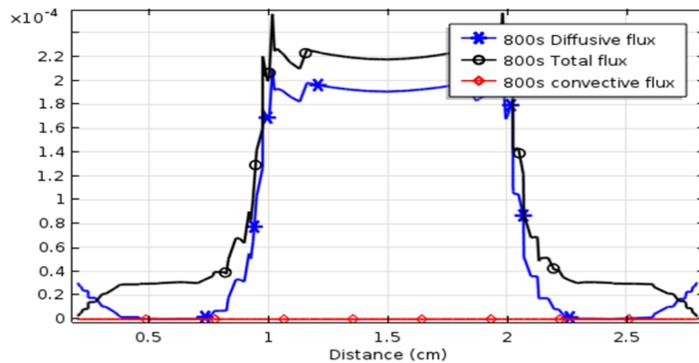


Fig. 15. Contributing mechanisms of transfer at 800 s and $y = 0.4$.

4. Conclusions

Three positions of cathode electrode with respect to surface margin of the electrolyte were treated throughout this study, i.e., when the cathode submerged in the middle of the electrolyte, near its surface and at the bottom. It was found that when the cathode was in the middle at $y = 0.4$, the current distribution was uniform and this uniformity was disturbed as the time of the process increases while when the cathode was moved upward or at $y = 0.92$ the distribution of current in general

is less uniform compared to that at $y = 0.4$ while the resultant velocity was highly disturbed at this position. As the cathode is moved downward at $y = -0.91$, the current along the cathode is comparable in its value to that at $y = 0.4$. Accordingly, the best position for cathode was when it is submerged in the middle of the electrolyte. It was found also that alteration of the cathode position has no convective contribution to the deposition process, i.e., free convection has no role in sustaining flux and the main contributed mechanism is the diffusion process.

Nomenclatures

bc	Cathodic tafel slope, V
C_b	Bulk concentration, mol/m ³
C_i	Concentration of i th species, mol/m ³
D_i	Diffusivity of i th species, m ² /s
F	Faraday constant, coulombs /mol
i	Current density, A/m ²
i_0	Exchange current density, A/m ²
m	Mass flow rate, kg/s
N_i	Molar flux of i th species, mol/m ² s
p	Pressure, kg/m ²
R	Gas constant, 8.3 J/mol, K
T	Temperature, K
u	Velocity vector, m/s
u_{mi}	Ion mobility of i th species, m ² /Vs
V	Potential or voltage, V
z_i	Charge number of i -th species

Greek Symbols

η	Overpotential, V
μ	Viscosity, kg/ms
ρ	Density, kg/m ³

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