

Mathematical Modelling and Computer Simulation of Particle Size Growth in Electrochemical Reactor

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Abstract:- A mathematical model to describe the effect of increase in bed volume of a three-dimensional fluidized bed electrode operating under the condition of mass transfer is presented. The process of electrodeposition within electrochemical reactor results in the increase of particle sizes. This phenomenon increases the volume of the bed. The model incorporates the pseudo-stationary behaviour in the reactor since the bed increases in volume due to the particle size growth. The developed differential equations are resolved using finite difference method. The overpotential distribution and the reaction rate within the reactor are calculated. The principal results are the effects of the limiting current operation on the superficial displacement with time. The mathematical modelling shows that the bed expansion is independent of the reactor width, the porosity and the current densities.

Keywords:- Fluidized bed electrodes, electrochemical reactors, perpendicular configuration, mathematical modelling and limiting current.

I. INTRODUCTION

Fluidized bed electrodes have been widely used in the removal processes of toxic and pollutant materials and recovery of heavy metals from industrial effluents. This technique offers direct use of electrochemical reactors designed to carry out such industrial waste cleaning. Fluidized bed electrodes, consisting of electrically conducting particles in an electrolyte, behave as three-dimensional electrodes which are suitable for the design of many electrochemical reactors. Such electrodes provides high rate of mass transfer and large area per unit volume for electrochemical reactions to occur even in very dilute solutions that need low current densities. Consequently, fluidized bed electrodes have found their numerous industrial applications, such as organic electrosynthesis, industrial effluents purification and electrowinning of metals from very dilute solutions. Generally, the rate of reaction is controlled either by mass transport of chemical species from the bulk of the solution to the surface of the electrodes or by electrode transfer on the electrode surface. The control is termed mist if none of these mechanisms is explicit in the system [1, 2]. Generally, in terms of configuration, fluidized bed electrodes are classified as perpendicular when the electrolyte flow is in the axial direction and the current flow in the lateral direction and parallel when they are in the same direction. A perpendicular configuration is preferred being that it offers a better potential distribution (more uniform potential) and high conversion factor.

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Mathematical modelling of electrochemical reactors is utilized for detailed analysis of the systems. One of the advantages is usually to improve productivity or save costs in investment and operation. Phenomenological understanding of the system behaviour and performance is usually necessary to carry out such mathematical simulations. Sometimes such calculations may introduce certain innovations of technical importance for engineering design and scale up. For the engineering and scale up applications of the fluidized bed electrode, potential distribution and reaction rate distribution within the system must be investigated and properly analysed. Some authors have elaborated on models which describe the behaviour of electrochemical reactors with perpendicular configuration [3-5]. A parallel configuration has been reported by several authors [6-9]. These authors obtained results which were in agreement with theoretical predictions. The basic information on how to treat the kinetics involved in the electrochemical engineering systems can be found in refs [9-10]. A reformulation of the Butler-Volmer equation, introducing limiting current showed to be important for the optimization of porous electrode systems with carbon particles because such electrodes possess high superficial area [10]. It will be interesting to note that for a fluidized bed electrochemical reactor, the transfer of charge in the dispersed phase takes place by intermittent particle contact and the quality of transferred charge from one particle to another is proportional to the potential difference between them at moment of contact [9]. In terms of current efficiency and productivity, fixed beds offer better results, however, with time, the particles grow, closing the pores and thereby retarding the continuous functioning of the bed.

Fluidized bed electrodes offer an adequate alternative to resolve this difficulty and from the engineering point of view, easy construction, apart from the possibility of on line removal of particle [7]. Some other distinct advantages that electrochemical techniques offer relative to other conventional technologies include: energy efficiency, versatility, environmental compatibility, safety, amenability to automation and selectivity.

The process of electrode position or electrowinning occurring within electrochemical reactor results in the increase of particle sizes and consequently increases the volume of the bed. This paper aims at developing a mathematical model capable of predicting the behaviour of a three dimensional fluidized bed electrode (electrochemical reactor) with perpendicular configuration and in expansion. In addition, this investigation has an added advantage of assisting in engineering project and scale-up.

The reactor in consideration is fluidized bed electrochemical reactor, with rectangular geometry and perpendicular configuration operating under *limiting current* condition. The reactor was modelled with emphasis on the reaction mechanisms occurring in the system. The analysis done in this investigation is based on numerical solution (finite difference) of differential balances of mass and electrical charges in the reactor, thereby permitting a prediction of the over potential distribution in the reactor.

II. MATHEMATICAL MODEL OF THE FLUIDIZED BED

The modelled system shown in figure 1 is a fluidized bed electrochemical reactor with a rectangular geometry and perpendicular configuration whose thickness, width, and height are marked X,Y and Z respectively. The bed is composed of very highly conductive non porous particles whose specific surface area is a_m , a uniform porosity ε and a thickness X. If the electric current direction is the same as that of the movement of the positive charges, the current feeder is then located at surface $x = L$ and the reception or the counter current on the surface $x = 0$. A superficial velocity of the electrolyte solution u entering the reactor is uniform along the transversal area. The electrical conductivities of the solid and liquid phases are denominated respectively by σ_m and σ_s .

The formulation of the model is based on the transport equations proposed by Gubulin [1, 2]. These equations were applied to a two-phase solid-liquid system resulting in the following charge and mass balances:

i. Solid phase mass balance

$$\frac{\partial}{\partial t}[(1 - \varepsilon)C_{k,m}] + \text{div}[(1 - \varepsilon)C_{k,m}\vec{V}_{k,m}] = (1 - \varepsilon)R_{k,m} \quad (1)$$

ii. Solid phase charge balance

$$\text{div}[(1 - \varepsilon)\vec{i}_m] = (1 - \varepsilon)F \sum_k \frac{z_k}{M_k} R_{k,m} \quad (2)$$

The respective constitutive equations are:

$$C_{k,m}v_{k,m} = C_{k,m}\vec{v}_m$$

$$\vec{i}_m = -\sigma_m \text{grad}\phi_m$$

iii. Liquid phase mass balance

$$\frac{\partial}{\partial t}[\varepsilon C_{k,s}] + \text{div}[\varepsilon C_{k,s}\vec{v}_{k,s}] = \varepsilon R_{k,s} \quad (3)$$

iv. Liquid phase charge balance

$$\text{div}[\varepsilon\vec{i}_s] = \varepsilon F \sum_k \frac{z_k}{M_k} R_{k,s} \quad (4)$$

The constitutive equations for the liquid phase are:

$$C_{k,s}\vec{v}_{k,s} = -D_{k,s}^{ef} \text{grad}C_{k,s} + C_{k,s}\vec{v}_s - z_k F C_{k,s} \mu_{k,s} \text{grad}\phi_s$$

$$i_s = - \sum_k F \frac{z_k}{M_k} D_{k,s}^{ef} \text{grad}C_{k,s} - \sigma_s \text{grad}\phi_s$$

Where by conservation of mass and charge,

$$(1 - \varepsilon) \sum_{k=1}^m R_{k,m} = -\varepsilon \sum_{k=1}^m R_{k,s} \quad (5)$$

$$(1 - \varepsilon) \sum_{k=1}^m \frac{z_k}{M_k} R_{k,m} = -\varepsilon \sum_{k=1}^m \frac{z_k}{M_k} R_{k,s} \quad (6)$$

The equation for the rate of reaction of the chemical specie k, in the electrolyte is generally written as:

$$R_{k,s} = a_m \frac{(1-\varepsilon) i_{k,s}^*}{\varepsilon F \frac{z_k}{M_k}} \quad (7)$$

where

$$i_{k,s}^* = i_{k,s}^*(\phi_s, \phi_m, C_{1,s}, C_{1,s}^*, \dots)$$

$R_{k,s}$ and $i_{k,s}^*$ are, respectively, the rate of reaction of the chemical specie k, per unit volume of the liquid phase and the rate of reaction for the chemical specie k, in terms of charge transferred per unit area of the liquid phase; z_k is the charge transferred, M_k is the molecular mass of the chemical specie, and F is the Faraday constant

whose value is approximately 96500C/mol. The three-dimensional fluidized bed electrode used for this work is schematized in Fig. 1.

For the purpose of simplifying the transport equations, we make the following restrictions:

- i. Only component $k = 1$ reacts in the system;
- ii. There is no accumulation of the chemical species $k > 1$, in the liquid phase;
- iii. Hydrodynamic and electrochemical operating conditions are kept constant;
- iv. In the bulk of the solution, outside the diffusion layer, the effects of diffusion and dispersion are negligible compared to that of convection, which implies that This implies that $\vec{v}_{k,s} = \vec{v}_s$
- v. The solid phase does not leave the system, or the average velocity of the solid phase is zero which implies that $\mathbf{v}_m = \mathbf{0}$; Then

$$\frac{\partial}{\partial t}[(1 - \varepsilon)C_{k,m}] + \text{div}[(1 - \varepsilon)C_{k,m}\vec{V}_m] = -\varepsilon R_{k,s} \quad (8)$$

$$\frac{\partial}{\partial t}[\varepsilon C_{k,s}] + \text{div}[\varepsilon C_{k,s}\vec{V}_s] = \varepsilon R_{k,s} \quad (9)$$

$$\text{div}[\varepsilon C_{k,s}\vec{V}_s] = 0, \quad k = 3,4,\dots,m \quad (10)$$

$$\text{div}[(1 - \varepsilon)\vec{i}_m] = -\varepsilon F \frac{z_k}{M_k} R_{k,s} \quad (11)$$

$$\text{div}[\varepsilon\vec{i}_s] = \varepsilon F \frac{z_k}{M_k} R_{k,s} \quad (12)$$

$$\vec{i}_s = -\sigma_s \text{grad}\phi_s \quad (13)$$

$$\vec{i}_m = -\sigma_m \text{grad}\phi_m \quad (14)$$

Potential Distribution Equations in the Reactor

These equations are simplified and applied to a system of rectangular geometry and perpendicular configuration as shown in Fig. 1. The suppositions made for the simplification of the above equations are:

1. The potential and the current density are only functions of the variable x ,
2. The superficial velocity of the electrolytic solution is sufficiently high to ensure that concentration change through the through the bed height is insignificant,
3. The porosity and the specific area are kept uniform and do not vary with time during the operation.
4. The operation is isothermal.

With these conditions equations 10 through 16 reduce to

Potential in the solid phase

$$\frac{d^2\phi_m}{dx^2} = \frac{1}{\sigma_m} \frac{\varepsilon}{(1-\varepsilon)} F \frac{z_k}{M_k} R_{k,s} \quad (15)$$

Potential in the liquid phase

$$\frac{d^2\phi_s}{dx^2} = -\frac{1}{\sigma_s} F \frac{z_k}{M_k} R_{k,s} \quad (16)$$

Boundary Conditions

The boundary conditions in the system in terms of the charge transfer are:

1. At the feeder, practically, all the current is carried by the liquid phase and at the receptor all the current is by the metallic phase. Therefore,

$$\mathbf{x} = \mathbf{0}; \frac{d\phi_s}{dx} = \mathbf{0} \quad \text{and} \quad \mathbf{x} = \mathbf{X}, \frac{d\phi_m}{dx} = \mathbf{0} \quad (17)$$

2. If the system operates under constant current, then

$$\mathbf{x} = \mathbf{0}; \frac{d\phi_m}{dx} = -\frac{I}{(1-\varepsilon)\sigma_m A} \quad (18)$$

$$\mathbf{x} = \mathbf{X}, \frac{d\phi_s}{dx} = -\frac{I}{\varepsilon A \sigma_s} \quad (19)$$

where I is the total current applied and $A = A_L = Y.L(t)$ is the lateral area of the bed.

Kinetics of the System

If, in the neighbourhood of the solid phase, exists a boundary layer of width δ , the rate of reaction of the chemical specie k , in the liquid phase in terms of electron transfer is:

$$i_{k,s}^* = -F \frac{z_k D_k}{M_k \delta} (C_{k,s} - C_{k,s}^*) \quad (20)$$

A combination of this equation with equation 7 results:

$$R_{k,s} = -a_m \frac{(1-\varepsilon) D_k}{\varepsilon \delta} (C_{k,s} - C_{k,s}^*) \quad (21)$$

At the solid-liquid interface, an intrinsic kinetic will always exists and can be represented by the Butler-Volmer equation given as:

$$i_{k,s}^* = i_0 \left\{ \exp \left[-\frac{\alpha n F}{RT} \eta \right] - \exp \left[\frac{(1-\alpha) n F}{RT} \eta \right] \right\} \quad (22)$$

Where

$$i_0 = n F k_0 C_{k,s}^* \quad (23)$$

A combination with equation 7 results:

$$R_{k,s} = -a_m \frac{(1-\varepsilon) M_k}{\varepsilon F z_k} i_0 \left\{ \exp \left[-\frac{\alpha n F}{RT} \eta \right] - \exp \left[\frac{(1-\alpha) n F}{RT} \eta \right] \right\} \quad (24)$$

In these equations, D_k is the diffusion coefficient of the chemical specie k participating in the reaction, n is the number of electrons involved in the reaction, i_0 is the exchange current density, $C_{k,s}$ and $C_{k,s}^*$ are the bulk and superficial concentrations, respectively, δ is the width of the boundary layer, α is the charge transfer coefficient, and η is the surtension in the reactor defined by the relation:

$$\eta = \phi_m - \phi_s - \left[E_{eq} + \frac{RT}{nF} \ln(C_{k,s}^*) \right] \quad (25)$$

The process control of the reaction, generally, depends on both the mass and intrinsic kinetic. Eliminating $C_{k,s}^*$, between equations 18 and 21 results:

$$R_{k,s} = -a_m \frac{(1-\varepsilon)}{\varepsilon} C_{k,s} \frac{\Theta}{\left[1 + \frac{\delta}{D_k} \Theta \right]}; \quad (26)$$

$$\Theta = \frac{M_k}{z_k} n k_0 \left\{ \exp \left[-\frac{\alpha n F}{RT} \eta \right] - \exp \left[\frac{(1-\alpha) n F}{RT} \eta \right] \right\}$$

A close look at equation 26 shows two limiting cases:

- i. If $\delta \rightarrow 0$, then $\left[1 + \frac{\delta}{D_k} \Theta \right] \rightarrow 1$, then equation 26 reduces to

$$R_{k,s} = -a_m \frac{(1-\varepsilon)}{\varepsilon} \Theta C_{k,s} \quad (27)$$

- ii. If $\delta \gg 0$ then $\left[1 + \frac{\delta}{D_k} \Theta \right] \rightarrow \frac{\delta}{D_k} \Theta$ and equation 26 becomes

$$R_{k,s} = -a_m \frac{(1-\varepsilon) D_k}{\varepsilon \delta} C_{k,s} \quad (28)$$

If the system is controlled by intrinsic reaction, equation 27 is used and if controlled by mass transfer, equation 28 is used. On the other hand, if none of these is the controlling factor, equation 26 should be used. In this work we are considering that the system is being controlled by mass transfer. This means that the system is operating under limiting current condition.

Over potential in the Reactor:

If equation 16 is subtracted from equation 15, the model for the distribution of the surtension in the reactor is obtained after substituting equation 21:

$$\frac{d^2 \eta}{dx^2} = -a_m \left[\frac{1}{\sigma_m} + \frac{(1-\varepsilon)}{\varepsilon \sigma_s} \right] \frac{D_k F z_k}{\delta M_k} (C_{k,s}) \quad (29)$$

The respective boundary conditions are

$$\left(\frac{d\eta}{dx} \right)_{x=0} = -\frac{I}{(1-\varepsilon)\sigma_m A} \quad (30)$$

$$\left(\frac{d\eta}{dx} \right)_{x=L} = \frac{I}{\varepsilon \sigma_s A} \quad (31)$$

The Model for the Displacement of the Bed Surface

If the electrochemical phenomena are more rapid than the fluid dynamic phenomena of the increase in volume of the reactor, the process can be considered pseudo-stationary. The equation that predicts the interfacial displacement, $L(t)$ is given as:

$$\frac{dV}{dt} = A_b \frac{dL}{dt} \quad (32)$$

But

$$V = \frac{M_k}{\rho_m (1-\varepsilon)} \quad (33)$$

Therefore,

$$\frac{dM_k}{dt} = \rho_m (1-\varepsilon) A_b \frac{dL}{dt} \quad (34)$$

On the other hand, if the reactor operation approximates a steady state operation of an ideal discontinuous reactor, then

$$\frac{dM_k}{dt} \approx -\varepsilon A_L \int_0^{x=X} R_{k,s}(x) dx \quad (35)$$

Based on Fig. 1, $A_L/A_b = L/X$ and equation 31 equal to equation 32, therefore:

$$\frac{dL}{dt} = -\frac{\varepsilon}{\rho_m(1-\varepsilon)} \frac{L}{X} \int_0^{x=X} R_{k,s}(x) dx \quad (36)$$

Since the bed is subject to an expansion with time due to the particles growth, the specific surface area a_m and the lateral area A_L of the bed automatically become time dependent variables. Consequently, if the initial height of the bed and the initial particle radius are respectively, L_0 and r_0 , then, in any given time, we get:

$$r = r_0 \sqrt[3]{\frac{L}{L_0}} \quad (37)$$

Consequently, for equilateral cylindrical particles used in this investigation, the specific surface area can be written as:

$$a_m = \frac{A_p}{V_p} = \frac{3}{r_0 \sqrt[3]{\frac{L}{L_0}}} \quad (38)$$

Substituting equation 38 in equation 33 results:

$$\frac{dL}{dt} = \frac{3}{\rho_m} \frac{L}{r_0 \sqrt[3]{\frac{L}{L_0}}} \int_0^{x=X} R_{k,s}(x) dx \quad (39)$$

Equations 29, 30, 31 and 39 represent mathematical model for a reactor in expansion. The method of finite difference is implemented on equation 39 after substitution of equation 28 and resolved with the boundary conditions, 30 and 31. The position of the interface in a given time can be calculated by equation 39, with $L = L_0$ for $t = 0$. The model is applied to the system where copper is being deposited.

The conductivities σ_m and σ_s used in these simulations are respectively, $250.0\Omega^{-1}\text{m}^{-1}$ and $50.0\Omega^{-1}\text{m}^{-1}$. The simulations were based on a laboratory reactor having initial height of 0.0880252m, and thickness of 0.019m, 0.024m and 0.029m. Copper ion concentration in the electrolytic solution was 508.368g/m^3 . The simulation parameters were the current density, bed porosity, concentration, and position of the superficial interface of the bed.

III. RESULTS AND DISCUSSION

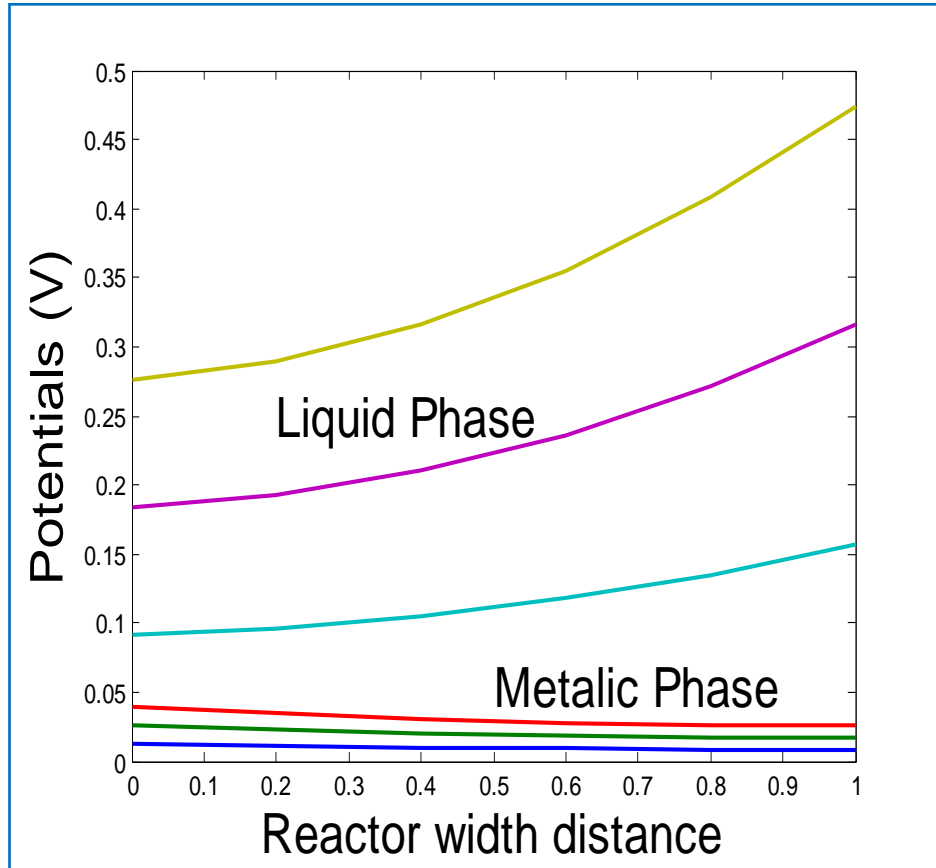


Fig. 2 Potential distribution of metallic liquid phases for fixed bed reactor ($\varepsilon = 0.36$)

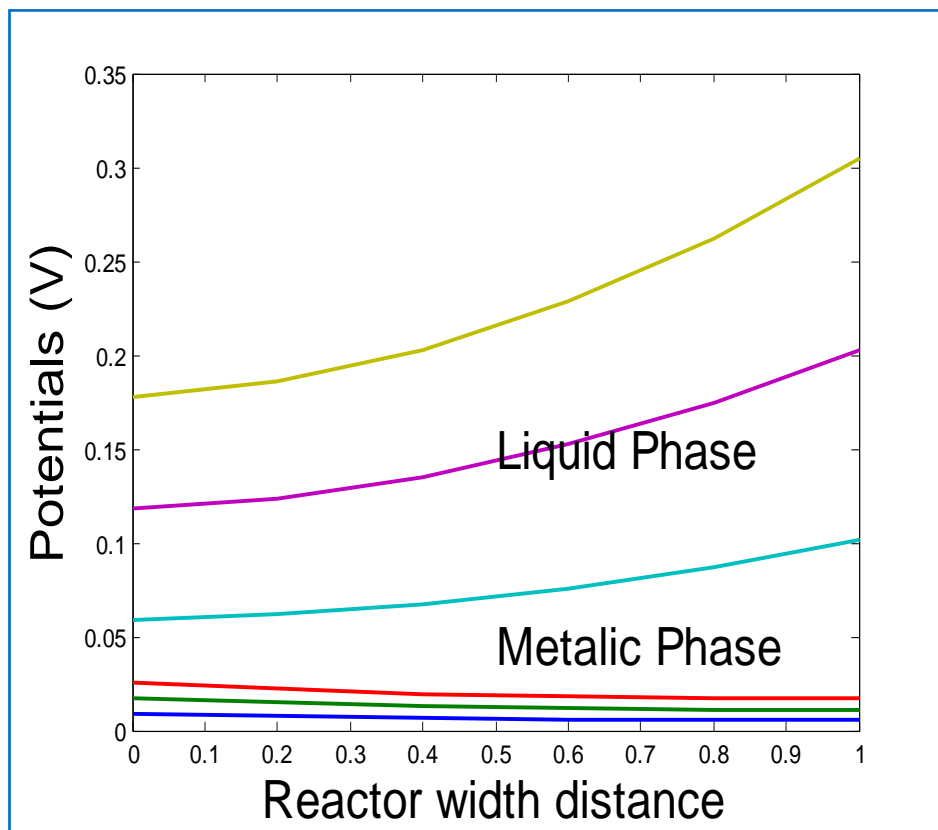


Fig. 3 Potential distribution of metallic and liquid phases for fluidized bed reactor ($\epsilon = 0.5$)

Figures 2 and 3 show typical potential distributions of metallic and liquid phases in the reactor with bed porosities of 0.36 and 0.50, respectively, for different values of applied currents. The potentials of the metallic phase are practically uniform in relation to the liquid phase, probably due to the effect of the higher values of the electrical conductivities of the metallic phase used in relation to that of the liquid phase.

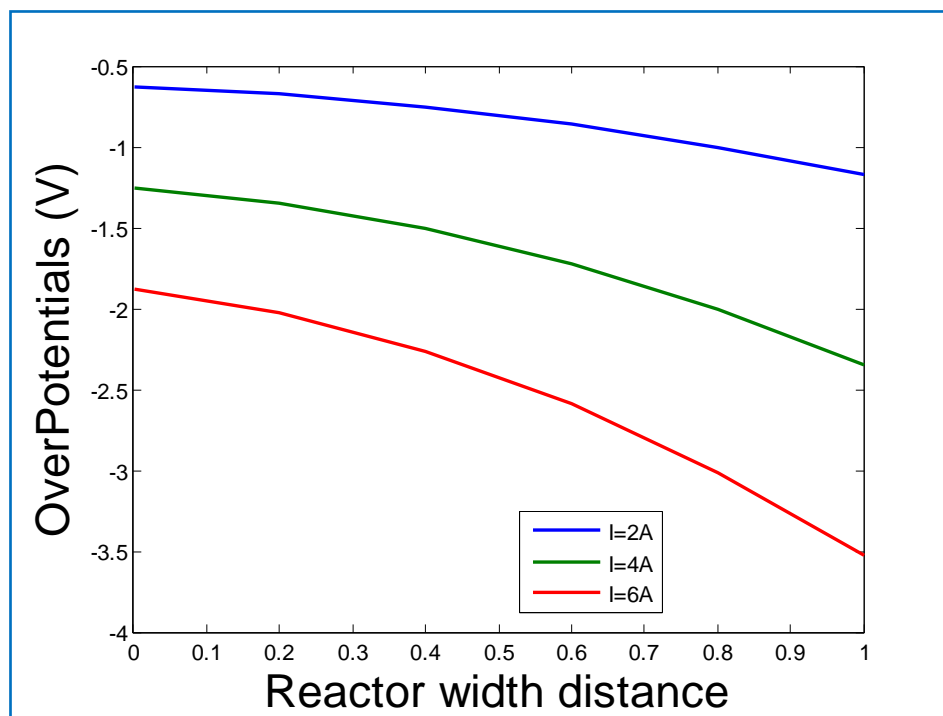


Fig. 4 Distribution of the over potentials in fixed bed reactor ($\epsilon = 0.36$) for different values of the applied current.

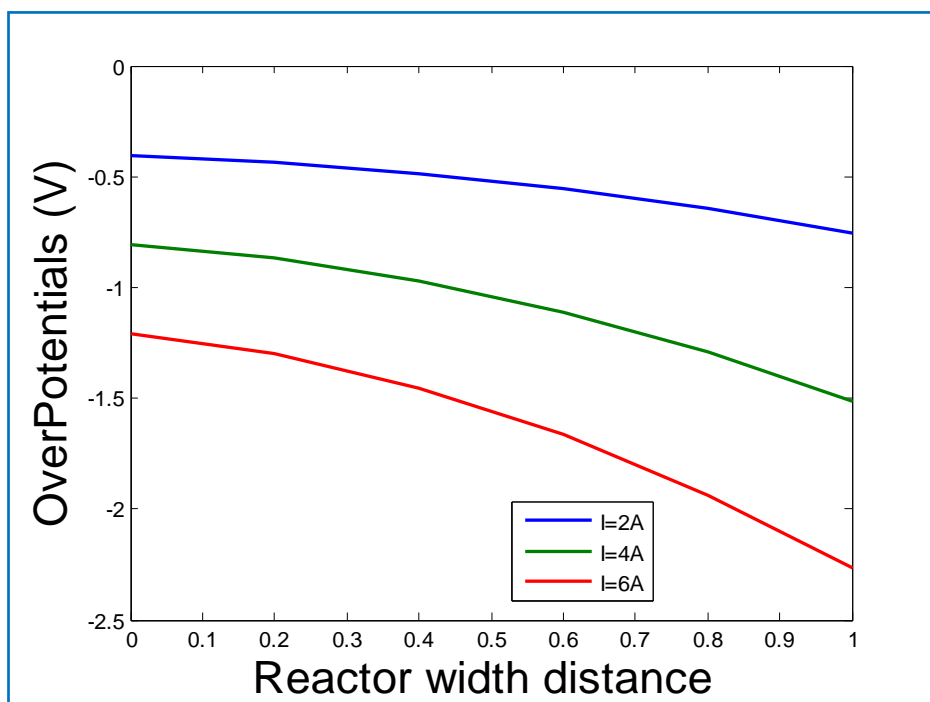


Fig. 5 Distribution of the over potentials in fluidized bed reactor ($\epsilon = 0.5$) for Different values of the applied current.

Figures 4 and 5 illustrate the overpotential distributions in the reactor for different values of applied current. The distributions show a negative increase of overpotential for high applied currents. This behaviour signifies that high current density produces a high reaction rate. Increase in the density of current means increase in the number of electrons available to react with copper ions present in the solution. It can also be observed that electrochemical activities are confined to the region close to the receptor or membrane. This behaviour has been observed in the electrosynthesis of organic products by German and Goodridge [8]. A comparison of these figures shows that low overpotential values are associated with high bed porosity. Consequently, fixed-bed reactors are associated with high electrochemical reaction rates in contrast to fluidized ones.

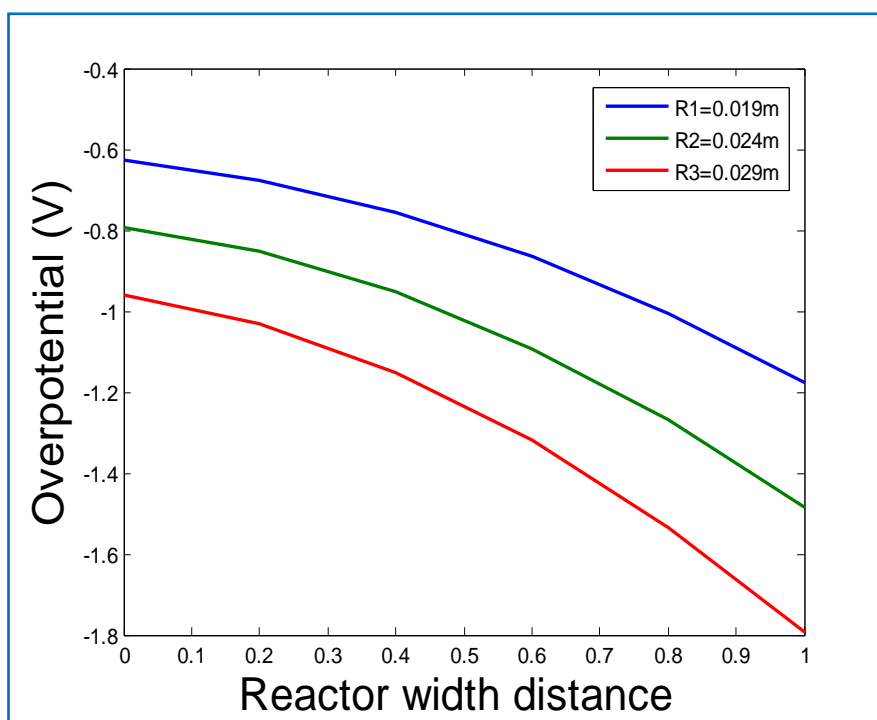


Fig. 6 Distribution of over potentials for fixed bed reactor ($\epsilon = 0.36$) for different reactor widths.

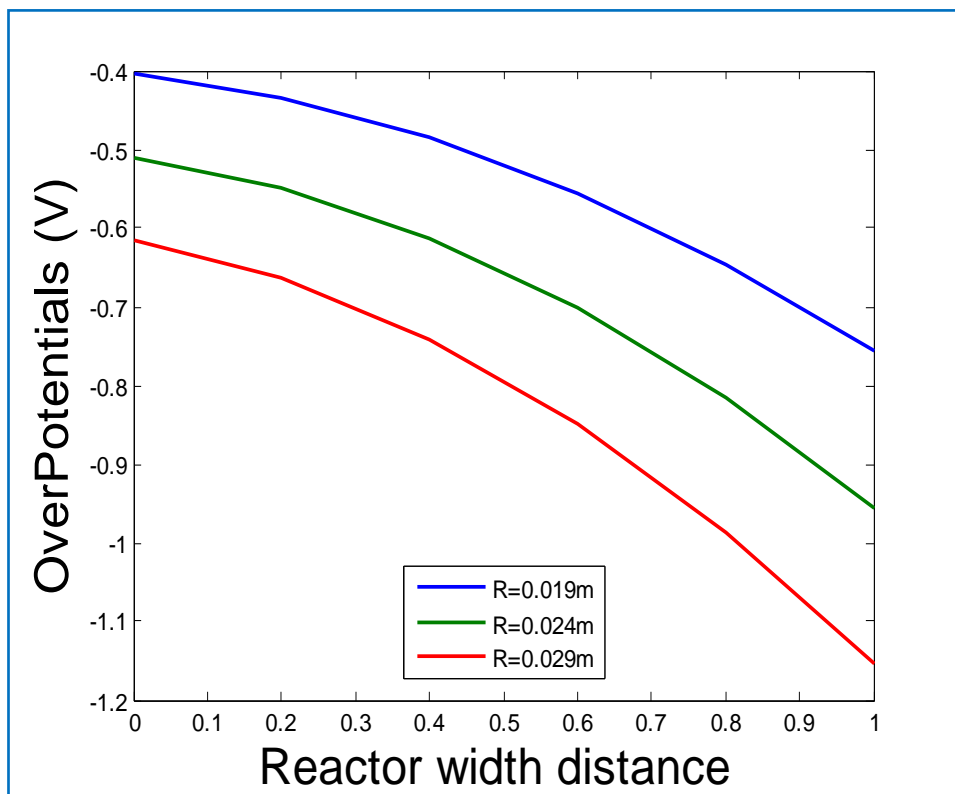


Fig. 7 Distribution of over potentials for fluidized bed reactor ($\epsilon = 0.5$) for different reactor widths

Figures 6 and 7 show the distributions of over potentials for fixed and fluidized beds respectively, for different reactor widths. Close observation of these figures shows that the higher the porosity, the higher the values of the overpotentials in both cathodic and anodic regions. These figures also show that the higher the reactor width, the more cathodic are the overpotentials. These figures demonstrate that the major alterations of the overpotentials, occur at vicinity of the current feeder or the micro porous diaphragm.

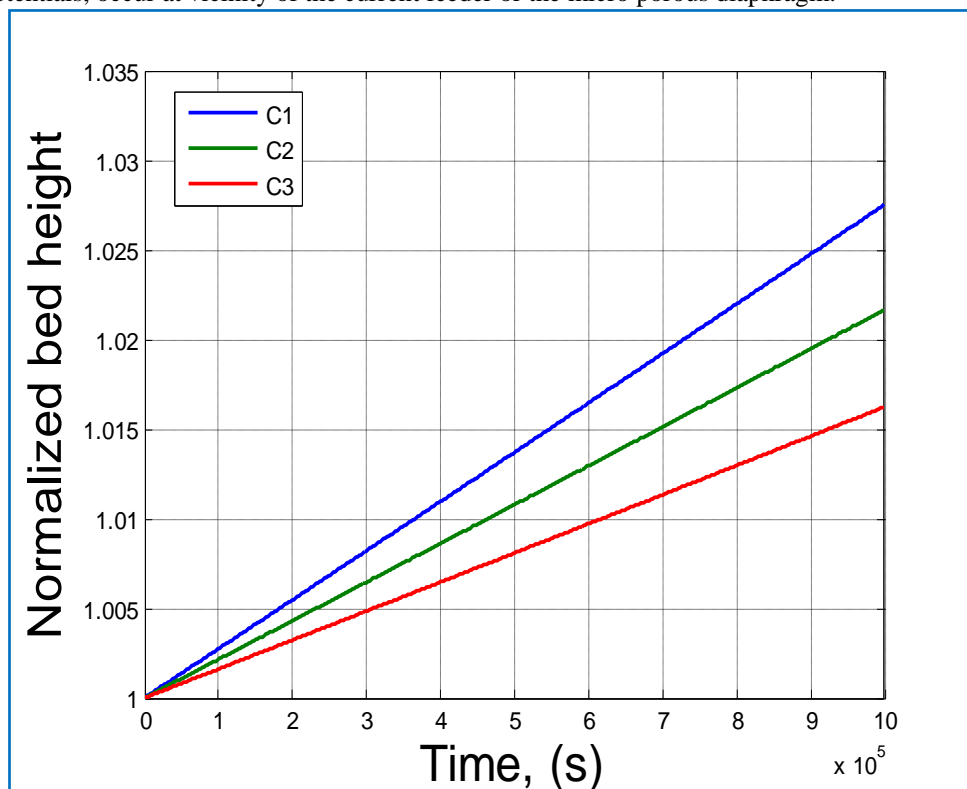


Fig. 8 Distribution of bed expansion over time for various concentrations

The displacement or the increase in the bed height with time is illustrated in figures 8 for different concentrations of $C_1 = 508.36$, $C_2 = 408.36$ and $C_3 = 308.36$, respectively. A notable feature of these distributions is that the bed growth is proportional to the concentrations. That is, the reactor with a least concentration experienced least expansion. This result is true since the rate of electrodeposition is proportional to the local mass density.

IV. CONCLUSIONS

This investigation has theoretically demonstrated the behaviour of a three-dimensional fluidized bed electrode operating under current limit and pseudo-static conditions as seen in the literatures [3,6,11]. The electrochemical active regions are situated close to the receptor and about ten percentage of this region is electrochemically active. The model is capable of predicting the behaviour of a fluidized bed in expansion. It is important to note that the expansion model is independent of the local porosity, width of the reactor, and the applied current density. In these simulations, only the reaction of copper was analysed, consequently, the current efficiency will be 100%. However, experimental investigations have shown that, despite the fact that the increase in the applied current caused an increased reaction rate, its effect, as far as the efficiencies of current and energy are concerned, there was no benefit, because, there is always a decrease in both the current and energy efficiencies as we increase the current density.

Nomenclature

a_m	Specific surface of the solid[m ⁻¹]
A_L	Lateral area of the bed[m ²]
A_p	Particulate phase area[m ²]
A_b	Base area of the bed[m ²]
$C_{k,s}$	Concentration of the chemical specie k in the liquid phase [g/m ³]
$C_{k,s}^*$	Concentration of the chemical specie k in the liquid phase on the electrode surface[g/m ³]
D_k	Diffusion coefficient of the chemical specie k [m ² /s]
E_{eq}	Equilibrium potential[V]
F	Faraday constant[96500C/m]
I	Current density [A/m ²]
i_s	Liquid phase current density [A/m ²]
i_m	Solid phase current density [A/m ²]
I	Total applied current [A]
$i_{k,s}^*$	Reaction rate of the chemical specie k in term s of charge per area [A/m ²]
i_0	Exchange current density [A/m ²]
L_0	Initial bed thickness [m]
L	Bed height at a particular instant [m]
M_k	Mass of the copper particles[g]
N	Number of electrons
$R_{k,s}$	Mass rate of reaction of chemical specie k per unit volume of the liquid[g/m ³ s]
R	Universal gas constant [8.314Jmol ⁻¹ K ⁻¹]
r_0	Initial particle radius[m]
R	Particle radius at a particular instant, t [m]
T	Time [s]
T	Temperature [K]
U	Superficial velocity of the electrolyte [m/s]
$v_{k,s}$	Local velocity of the chemical specie k in the solution bulk [m/s]
v_s	Average velocity of the solution phase [m/s]
V	Bed volume [m ³]
V_p	Particle phase volume [m ³]
X	Space coordinator[m]
z_k	Number of transferred charges [-]

Greek Symbols

A	Kinetic constant [-]
η	Overpotential[V]
δ	Thickness of diffusion layer[m]
ϵ	Porosity [-]
σ_m	Metal conductivity [$\Omega^{-1}m^{-1}$]
ϕ_m	Metal phase potential [V]
ϕ_s	Liquid phase potential [V]
σ_s	Solution conductivity [$\Omega^{-1}m^{-1}$]

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