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APPLICATION OF ORTHOGONAL COLOCATION TO ELECTROCHEMICAL FLUIDIZED BED REACTOR MODEL

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Abstract. A mathematical model is presented to describe the behavior of a three-dimensional fluidized bed electrode operating under the condition of electrons transfer. The model is simulated numerically by applying orthogonal collocation method to calculate the electric potential distribution in the particulate and liquid phases, and the overpotential within the electrochemical reactor. The principal results are the effects of the constant current operation, bed width and bed porosity on the system behavior. The developed model is adequate to describe the behavior of these types of electrochemical reactors.

Keywords Mathematical Modeling , Electrochemical reactor ,Orthogonal Collocation, overpotential.

1. Introduction

Particulate electrode in general and fluidized ones in particular stimulates considerable interests in the fields of organic electrosynthesis, cleaning of industrial effluents and in metal recovery or electrodeposition of heavy metals. Fluidized bed electrodes, consisting of electrically conducting particles in an electrolyte solution, behave as three-dimensional electrodes which are used for the study of electrochemical reactors. For certain applications these electrodes, due to their large specific areas, present more advantages in relation to other treated porous electrodes in that they offer a high rate of mass transfer. Generally the rate of reaction is controlled either by mass transport of the chemical species from the bulk of the solution to the surface of the electrode or by electron transfer on the electrode surface. The control is termed mist if non of these mechanisms is explicit in the system (Gubulin 1995, 1997). Generally, in terms of configuration, fluidized bed electrodes are classified as perpendicular when the electrolyte flow 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 (uniform potential) and a high conversion factor. Some authors have elaborated on models which describe the behavior of electrochemical reactors with perpendicular configuration (Kreysa and Bisang, 1993). A parallel configuration has been studied experimentally and theoretically by Olive and Lacoste (1979). These authors obtained a results which were in agreement with theoretical previsions. Scott et al. (1995), studied theoretically and experimentally the behavior of a fixed bed electrochemical reactor with a rectangular geometry and perpendicular configuration. The bi-directional mathematical models proposed by these authors incorporated mist control (intrinsic reaction and limiting current). A reformulation of the *Butler-Volmer* equation, introducing limiting current showed to be important for the optimization of porous electrode systems with carbon particles, such electrodes possess high superficial area (Picket et al. 1996). 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 quantity of transferred charge from one particle to another is proportional to the potential difference between them at the moment of contact (Goodridge et al. 1971). In terms of current efficiency and productivity, fixed beds present better results , however, with time, the particles grow closing the pores and thereby retards the continuous functioning of the said bed. Fluidized bed electrodes offer an adequate alternative to resolve this difficulty. From the engineering point of view, easy construction, apart from the *on line* particles renovation possibility, is attractive (Fleischmann and Oldfield 1971). Various numerical methods have been employed in the resolution of these models (Saback and Evans 1979; Sun, Xu and Scott 1995). In addition to these publications mentioned in this text, several other studies have been reported on the three-dimensional fluidized bed electrode reactors with perpendicular configuration.

The purpose of this investigation is to develop a mathematical model capable of describing the behavior of a fluidized bed electrochemical reactor with a perpendicular configuration. The effects of some operating parameters such as applied current, bed width, and bed porosity on the behavior of the reactor are investigated. Apart from this, this investigation has an advantage of assisting in engineering project design and scale-up.

The reactor in consideration is a fluidized bed electrochemical reactor, with rectangular geometry and perpendicular configuration operating under constant current. The reactor was modeled with an emphasis to the reaction mechanisms occurring in the system. The analysis done in this investigation was based on the numerical solution (orthogonal collocation) of differential balances of mass and electrical charge in the reactor thereby permitting a prevision of the potential distribution in the liquid and metal phases.

2. Mathematical Model of the Fluidized Bed

The formulation of the model is based on the transport equations proposed by Gubulin (1995, 1997). These equations can be applied to a two-phase solid – liquid system resulting in the following charge and mass balances:

a) solid phase

Mass and charge balances

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)C_{k,m}\right]+ $$
$$\mathrm{div}\left[(1-\varepsilon)C_{k,m}\vec{v}_{k,m}\right]=(1-\varepsilon)R_{k,m}\ ; \tag{1}$$
$$C_{k,m}v_{k,m}=C_{k,m}\vec{v}_m$$

$$\mathrm{div}\left[(1-\varepsilon)\vec{i}_m\right]=(1-\varepsilon)F\sum_k\frac{z_k}{M_k}R_{k,m}; $$
$$i_m=-\sigma_m\mathrm{grad}\phi_m \tag{2}$$

b) Liquid phase

Mass and charge balances

$$\frac{\partial}{\partial t}\left[\varepsilon C_{k,s}\right]+\mathrm{div}\left[\varepsilon C_{k,s}\vec{v}_{k,s}\right]=\varepsilon R_{k,s} \tag{3}$$
$$C_{k,s}\vec{v}_{k,s}=-D_{k,s}^{ef}\mathrm{grad}C_{k,s}+C_{k,s}\vec{v}_s- $$
$$z_kFC_{k,s}\mu_{k,s}\mathrm{grad}\phi_s$$

$$\mathrm{div}\left[\varepsilon\vec{i}_s\right]=\varepsilon F\sum_k\frac{z_k}{M_k}R_{k,s} \tag{4}$$
$$i_s=-\sum_k F\frac{z_k}{M_k}D_{k,s}^{ef}\mathrm{grad}C_{k,s}-\sigma_s\mathrm{grad}\phi_s$$

where by conservation of mass and charge:

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

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

The rate of reaction of the chemical specie k, can be represented symbolically by:

$$R_{k,s}=-a_m\frac{(1-\varepsilon)}{\varepsilon}\frac{i_{k,s}^*}{F\frac{z_k}{M_k}}\ ; \tag{7}$$
$$i_{k,s}^*=i_{k,s}^*(\phi_s,\phi_m,C_{1,s},C_{1,s}^*,...)$$

In these equations, **$R_{k,s}$** is the rate of reaction of the chemical specie **k,** per unit volume of the liquid phase, $i_{k,s}^*$ is the rate of reaction of the chemical specie **k,** in terms of charge per unit area (being that, in this case, **k** is copper) of the liquid phase, **z_k** is the number of the transferred charge, M is the molecular mass of the chemical specie, and **F** is the Faraday constant.

The three-dimensional fluidized bed electrode studied is shown in Figure 1.
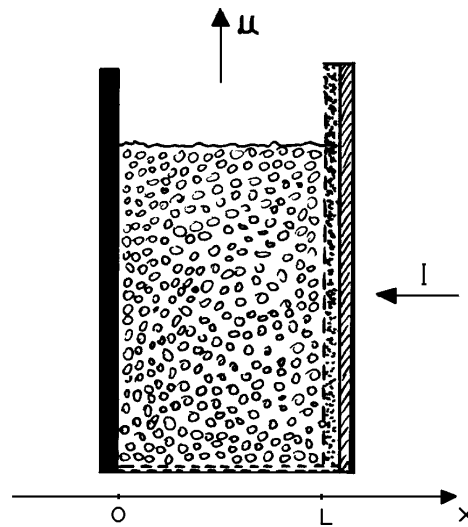

Figure 1. Representation of the electrode for the application of the mathematical model.

The bed is constituted of highly conductive porous particles whose specific surface area is $\mathbf{a_m}$. It has a width of L and a uniform porosity of $\boldsymbol{\varepsilon}$. If the electric current direction is the movement of the positive charges, the current feed is done on the surface $\mathbf{x = L}$ and the reception on the surface $\mathbf{x = 0}$. A superficial velocity of the electrolyte solution $\mathbf{u}$ entering the reactor is uniform along the transversal area. The electrical conductivities of the solid and liquid phases are denominated respectively by $\boldsymbol{\sigma_m}$ and $\boldsymbol{\sigma_s}$.

For the purpose of simplifying the transport equations presented here, the following hypothesis were made:
1. Only component k = 1 reacts in the system;
2. There is no accumulation of the chemical species k > 1, in the liquid phase;
3. Hydrodynamic and electrochemical operating conditions are kept constant;
4. 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 $\vec{v}_{k,s} = \vec{v}_s$;

The solid phase does not leave the system or in other words the average velocity of the solid phase is zero which implies that $\vec{v}_m = 0$; Then:

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)C_{k,m}\right] = -\varepsilon R_{k,s} \tag{8}$$

$$\frac{\partial}{\partial t}\left[\varepsilon C_{k,s}\right] + \mathrm{div}\left[\varepsilon C_{k,s}\vec{v}_s\right] = \varepsilon R_{k,s} \tag{9}$$

$$\mathrm{div}\left[\varepsilon C_{k,s}\vec{v}_s\right] = 0, k = 2, 3, .., m \tag{10}$$

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

$$\mathrm{div}\left[\varepsilon \vec{i}_s\right] = \varepsilon F\frac{z_k}{M_k}R_{k,s} \tag{12}$$

$$\vec{i}_s = -\sigma_s \mathrm{grad}\,\phi_s \tag{13}$$

$$\vec{i}_m = -\sigma_m \mathrm{grad}\,\phi_m \tag{14}$$

3. Potential Distribution Equations in the Reactor

Applying these equations to a system of rectangular geometry and perpendicular configuration (Figure 1), and supposing that:
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 bed height is insignificant;
3. The porosity and the specific area are kept uniform and do not vary with time during operation;
4. The operation is isothermic;

In these conditions the relations 8 a 14 reduce to :

a.) potential in the solid phase:

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

b.) potential in the liquid phase:

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

4. kinetic Consideration

If, in the neighborhood of the solid phase exists a diffusion layer of thickness δ, the rate of reaction of the chemical specie **k** in the liquid phase in terms of electrons transfer, is:

$$i_{k,s}^* = -F\frac{z_k}{M_k}\frac{D_k}{\delta}\left(C_{k,s} - C_{k,s}^*\right) \tag{17}$$

which with equation 7 results:

$$R_{k,s} = -a_m\frac{(1-\varepsilon)}{\varepsilon}\frac{D_k}{\delta}\left(C_{k,s} - C_{k,s}^*\right) \tag{18}$$

In the solid-fluid surface always exists intrinsic kinetic which can, for example, be represented by the Butler-Volmer equation,

$$i_{k,s}^* = i_0\left\{\exp\left[-\frac{\alpha nF}{RT}\eta\right] - \exp\left[\frac{(1-\alpha)nF}{RT}\eta\right]\right\} \tag{19}$$

where $i_0 = nFk_0C_{k,s}^*$ (20)

which with equation 7 result:

$$R_{k,s} = -a_m\frac{(1-\varepsilon)}{\varepsilon}\frac{M_k}{Fz_k}.$$
$$i_0\left\{\exp\left[-\frac{\alpha nF}{RT}\eta\right] - \exp\left[\frac{(1-\alpha)nF}{RT}\eta\right]\right\} \tag{21}$$

In these equations, D_k is the diffusion coefficient of the specie **k** participating in the reaction, **n** is the number of electrons involved in the reaction, **i₀** is the exchange current density, $C_{k,s}$ and $C_{k,s}^*$ are the concentrations in the bulk of the solution and on the electrode surface, respectively, δ is the thickness of the diffusion layer, α is the charge transfer coefficient and η is the overpotential in the system defined by the equation:

$$\eta = \phi_m - \phi_s - \left[E_{eq} + \frac{RT}{nF} \ln\left(C^*_{k,s} \right) \right]$$ (22)

5. Boundary Conditions

The boundary conditions in the electrochemical systems in terms of the charge transfer are:

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

$$x = 0, \ \frac{d\phi_s}{dx} = 0 \ ; \ \text{and} \ \ x = L, \ \frac{d\phi_m}{dx} = 0$$ (23)

2. If the system operates under constant potential then:

$$x = 0, \ \phi_m = \phi_{m0} \ \text{and} \ \ x = L, \ \phi_s = \phi_{s0}$$ (24)

3. If the system operates under constant current, then:

$$x = 0, \ \frac{d\phi_m}{dx} = -\frac{i_m}{\sigma_m} = -\frac{I}{(1-\varepsilon)\sigma_m A}$$ (25)

$$x = L, \ \frac{d\phi_s}{dx} = -\frac{i_s}{\sigma_s} = -\frac{I}{\varepsilon A \sigma_s}$$ (26)

where **I** is total current applied and **A** is the lateral area of the bed.

It is considered that the reaction is controlled by the intrinsic reaction given by equation 24.

When equation 21 is substituted in equations 15 and 16, the potential distribution in the solid and liquid phases can be calculated. The resultant equations are resolved numerically by applying the orthogonal collocation method coupled to a Newton Raphson multivariable algorithm.

6. Overpotential 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 the substitution of equations 21 and 22:

$$\frac{d^2\eta}{dx^2} = \left[\frac{1}{\sigma_m} + \frac{(1-\varepsilon)}{\varepsilon\sigma_s} \right] . io\left\{ \exp\left[\frac{\alpha nF}{RT}\eta \right] - \exp\left[-\frac{(1-\alpha)nF}{RT}\eta \right] \right\}$$ (27)

The respective boundary conditions are:

$$\left(\frac{d\eta}{dx} \right)_{x=0} = -\frac{I}{(1-\varepsilon)\sigma_m A}$$ (28)

and

$$\left(\frac{d\eta}{dx} \right)_{x=X} = \frac{I}{\varepsilon\sigma_s A}$$ (29)

7. Numerical Method for Solving the Model Equations: Orthogonal Collocation.

The set of ordinary differential nonlinear equations, ODEs, Equations 15 and 16 is first treated by applying the method of orthogonal collocation. According to the principle of orthogonal collocation method, the values of the first order and second order derivatives can be evaluated in terms of linear combination of values of trial functions by using the collocation matrices, A and B at the collocation point. A comprehensive description of the orthogonal collocation method is found in Richard G. Rice and Duong D. Do[1995]

The system of equations obtained after application of N internal points of orthogonal collocation on equations 15 and 16 are:

$$\sum_{j=1}^{N} B_{ij}\Phi_{mj} = C_{mi}f_i(\eta_i) \ \ i = 1, 2....., N$$ (30)

$$\sum_{j=1}^{N} B_{ij}\Phi_{sj} = C_{si}f_j(\eta_i) \quad i = 1, 2, ..., N \tag{31}$$

where

$$C_m = -a_m/\sigma_m \tag{32}$$

$$C_s = a_m/\sigma_s(1-\varepsilon)/\varepsilon \tag{33}$$

In the same way, the resultant system of equations from the boundary conditions are :
At x = 0

$$\sum_{j=1}^{N+1} A_{1j}\Phi_{mj} = C_{cmi} \tag{34}$$

$$\sum_{j=1}^{N+1} A_{1j}\Phi_{sj} = 0 \tag{35}$$

The value of ϕ_m and ϕ_s at the boundary point x = 0 are, respectively:

$$\phi_{m1} = \frac{C_{cmi} - \sum_{j=1}^{N+1} A_{1j}\phi_{mj}}{A_{11}} \tag{36}$$

$$\phi_{s1} = \frac{-\sum_{j=1}^{N+1} A_{1j}\phi_{sj}}{A_{1,1}} \tag{37}$$

At x = L

$$\sum_{j=1}^{N+1} A_{N+1j}\Phi_{mj} = 0 \tag{38}$$

$$\sum_{j=1}^{N+1} A_{N+1j}\Phi_{mj} = C_{csi} \tag{39}$$

The respective values of the boundary conditions are:

$$\phi_{mN+1} = \frac{-\sum_{j=1}^{N} A_{N+1j}\phi_{mj}}{A_{N+1,N+1}} \tag{40}$$

$$\phi_{sN+1} = \frac{C_{csi} - \sum_{j=1}^{N} A_{N+1j}\phi_{sj}}{A_{N+1,N+1}} \tag{41}$$

where

$$C_{cm} = -\frac{i_m}{\sigma_m} = -\frac{I}{\sigma_m(1-\varepsilon)A_L} \tag{42}$$

$$C_{cs} = \frac{i_s}{\sigma_s} = -\frac{I}{\sigma_s \varepsilon A_L} \tag{43}$$

From these equations i refers to the number of equations, of which there are N +2 including two boundary conditions, N is the number of inner collocation points; J is the number of the collocation points, j = 1,2,........., N+2.

Villadsen and Michelsen [1978] presents the computer programs which can be used to evaluate the zeros (as collocation points) of the orthogonal polynomial and collocation matrices, A and B. If values of A and B are know, x will be considered the only independent variables in the ODEs.

8. Simulation

The total number of equations is (N+2)*2, since there are two independent variables ϕ_m and ϕ_s. In the program, the guessed values of $\phi_m(i)$ and $\phi_s(i)$, are first given and then the collocation points and collocation matrices are calculated by villadsen's subroutine's.

For solving the model equations, typically six internal collocation points were used. The convergence criteria was 1.0×10^{-5}.

In these simulations, the conductivities σ_m and σ_s were taken from the work of German and Goodridge (1975) whose values are, respectively, 600.0 ohm^{-1}m^{-1} and 60.0 ohm^{-1}m^{-1}. The values of the charge transfer α and the exchange current density where obtained from Newman (1973) and their values are, respectively, 0.9 and 10.2A/m^2. The simulations were based on a laboratory reactor having lateral area (current feeder zone) of 0.008m^2, thickness of 0.02m, and 0.030m porosities of 0.36 and 0.6 and specific area of 6000m^{-1}. The concentration in the electrolytic solution was 14g/m^3. The simulation parameter is the current feeder whose values are 2A, 4A, and 6A. The reaction considered is the reduction reaction of the copper ions.

9. Results and Discussion

The distributions of the metal phase and the liquid phase potentials and the overpotential are shown in figures 2 and 3. These figures illustrate the effects of total applied current on the system. It can be clearly verified that, an increase in the applied current increases negatively the overpotential in the system as expected. The increase in the current density means increasing the number of electrons available to react with the copper ions in the solution. The simulations here presented, admitted only the reaction of copper in the system, consequently, the current efficiency will be 100% . However, experimental investigations show that, current efficiency curve has a maximum with the increase in the applied current. After this maximum the efficiency decreases with increase in applied current. The decrease may be as a result of the appearance of parallel reactions in the reactor.
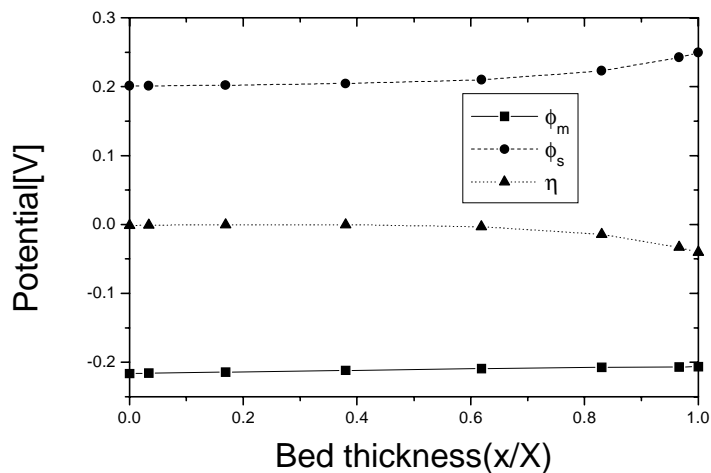

Figure 2. Potential distributions in the reactor having the total applied current as a parameter. I = 2A, bed width = 0.019m and porosity = 0.36
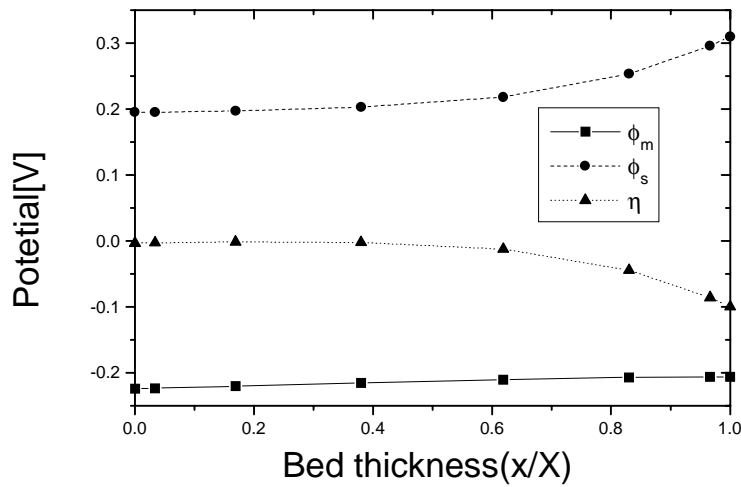
Figure 3. The potential distributions in the reactor for a total applied current I = 4 A, bed width = 0.019m and porosity=0.36

Figure 4 shows the effect of increasing the bed width from 0.019m to 0,029m. A comparation of this figure and figure 3 shows that the increase in the bed width causes a local decrease of the deposition reaction rate for the same applied current. The increase in the bed width results in the increase in the superficial surface area of the particles. This results in the appearance of anodic reactions(oxidation of metallic copper) in the system and consequently the current efficiency of the process will decrease.
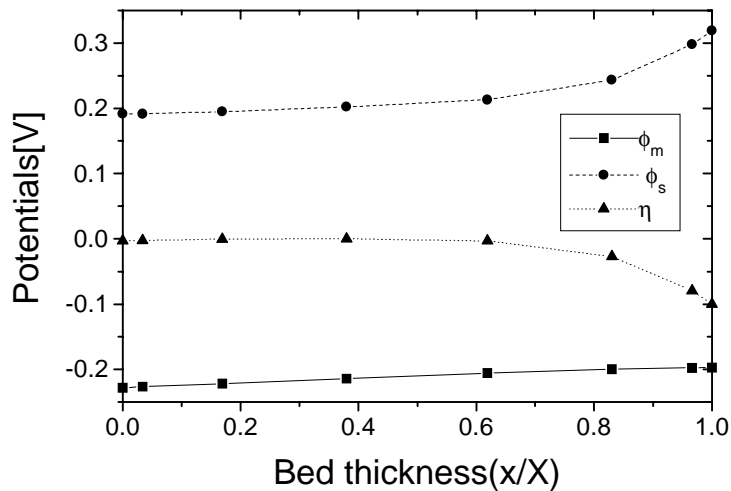

Figure 4. Potential Distributions for I = 4 A , porosity = 0.36 and bed width = 0.029m

The effects of bed porosity is shown in figure 5. This figure shows that bed porosity has a significant effect on the behavior of the system. It can be verified that the bed porosity increase causes a negative increase of the overpotentials in both regions of the electrode. It can be observed that very close to the anode, there are evidences of the overpotentials.

The distribution of the overpotential in the reactor illustrates the reduction reaction rate in the reactor. It can be verified from all these figures, that the rate of copper reduction is increases towards the cathode or very close

to the current feeder (x/X→1). This means that electrochemical reactions occur with more intensity at the regions close to the membrane.

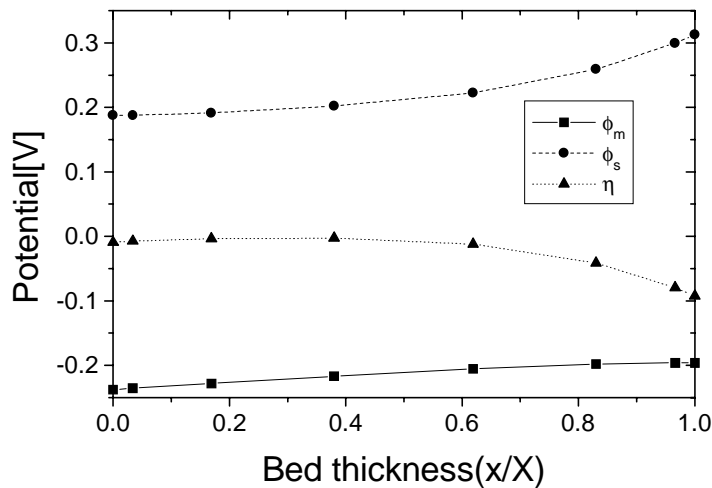A very close observation, shows that about 30% of the reactor is electrochemically active.

Figure 5. Potential Distributions in the reactor for a porosity of 0.6, I = 4 A and bed width =0,029m

10. Conclusion

The electrochemical active region is situated close to the current feeder, and only about 10% of the whole bed is electrochemically active. The developed model though well simplified, is capable of describing and predicting qualitatively and quantitatively, the behavior of electrochemical fluidized bed reactors, offering, in this way, information for engineering projects and plants scale-up. The method of orthogonal collocation proved to be an efficient numerical method for resolving resultant differential equations from this type of system.

11. Nomenclature

a_m Specific surface area of the solid[m^{-1}]

A_L Lateral 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]

CE   Energy consumption [kwh/kg]

D_k Diffusion coefficient of the chemical specie **k** [m^2/s]

E_{eq} Equilibrium Potential de [V]

Ec   Current efficiency[%]

F   Faraday constant[96500C/mol]

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 terms of charge per area[A/m]

i_o Exchange current density[A/m]

L   Bed thickness[m]

m   Mass of the particles[g]

n   Number of the electrons

$R_{k,s}$ Mass reaction rate of the chemical specie **k** per unit volume of the liquid[g/m^3s]

R   Universal gas constant [8,314 $J.mol^{-1}.K^{-1}$]

t   Time[s]

T   Temperature[K]

u   superficial velocity of the electrolyte[m/s]

$\vec{v}_{k,s}$ Local velocity of the chemical specie **k** in the solution bulk[m/s]

$\vec{v}_s$ Average velocity of the solution phase[m/s]

$\vec{v}_{k,m}$ Local velocity of the chemical specie k in the interior of the solid phase[m/s]

$\vec{v}_m$ Average velocity of the solid phase[m/s]

x space co-ordinate[m]

z_k Number of transferred charges[-]

Greek symbols

α Kinetic constant[-]

η Overpotential[V]

ϕ_m Solid phase potential [V]

ϕ_s Liquid phase potential[V]

σ_m Metal condutivity[$\Omega^{-1}m^{-1}$]

σ_s Solution condutivity[$\Omega^{-1}m^{-1}$]

ε Bed porosity[-]

δ Thickness of diffusion layer[m]

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