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Application of Orthogonal Collocation Method to Fluidised Bed Electrochemical Reactor Models

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ABSTRACT: *A mathematical model is presented to describe the behaviour of a three-dimensional fluidized bed electrode operating under the condition of electron 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 behaviour. The developed model is adequate to describe the behaviour of these types of electrochemical reactors and the results obtained are in agreement with existing measured values [1].*
KEYWORDS: *Mathematical Modelling, Orthogonal Collocation, Overpotential, Fluidized bed Electrode*

I. INTRODUCTION

Particulate electrode in general and fluidized ones in particular stimulates considerable interest in the field 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 electrolytic solution, behave as three-dimensional electrodes which are use 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 none of these mechanisms is explicit in the system [2,3](Gubulin 1995, 1997). 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 (uniform potential) and a high conversion factor. Some authors have elaborated on models which describe the behaviour of electrochemical reactors with perpendicular configuration (Kreysa and Bisang, 1993)[4]. A parallel configuration has been studied experimentally and theoretically by Olive and Lacost (1979)[5]. These authors obtained results which were in agreement with theoretical previsions. Scott et al. (1995)[6], studied theoretically and experimentally the behaviour 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 and limiting current). A reformulation of the Buttler-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)[7]. 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 charged from one particle to another is proportional to the potential difference between them at moment of contact (Goodridge et al. 1971)[8].

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 functional 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 possibility of on line particles renovation, is attractive (Fleischmann and Oldfield 1971)[9]. Various numerical methods have been employed in the resolution of these

models (Saback and Evans 1979; Sun, Xu and Scott 1995)[10,11]. 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 behaviour 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 behaviour 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 modelled with emphasis to the reaction mechanisms occurring in the system. The analysis done 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 and the overpotential in the reactor.

II. MATHEMATICAL MODEL OF THE FLUIDIZED BED.

The formulation of the model is based on the transport equations proposed by Gubulin (1995, 1997)[2,3]. These equations can be applied to the two-phase system resulting in the following charge and mass balances:

Solid Phase

- Mass and Charge Balances

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)C_{k,m}\right] + \nabla \cdot \left[(1-\varepsilon)C_{k,m}\vec{v}_{k,m}\right] = (1-\varepsilon)R_{k,m} \tag{1}$$

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

$$\nabla \cdot \left[(1-\varepsilon)\vec{i}_m\right] = (1-\varepsilon)F\sum_k \frac{z_k}{M_k}R_{k,m} \tag{2}$$

$$\vec{i}_m = -\sigma_m \nabla \emptyset_m$$

Liquid Phase

- Mass and Charge Balances

$$\frac{\partial}{\partial t}\left[\varepsilon C_{k,s}\right] + \nabla \cdot \left[\varepsilon C_{k,s}\vec{v}_{k,s}\right] = \varepsilon R_{k,s} \tag{3}$$

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

$$\nabla \cdot \left[\varepsilon \vec{i}_s\right] = \varepsilon F \sum_k \frac{z_k}{M_k}R_{k,s} \tag{4}$$

$$\vec{i}_s = -\sum_k F \frac{z_k}{M_k}D_{k,s}^{ef}\nabla C_{k,s} - \sigma_m \nabla \emptyset_s$$

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:

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

$$i_{k,s}^* = i_{k,s}^*\left(\emptyset_s, \emptyset_m, C_{1,s}, C_{1,s}^*, \cdots, \right) \tag{7}$$

In these equations, $\mathbf{R_{k,s}}$ is the rate of reaction of the chemical specie, per unit volume of the liquid phase, $\mathbf{i_{k,s}^*}$ 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 liquid phase, z_k is the number of the charge transferred, **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.
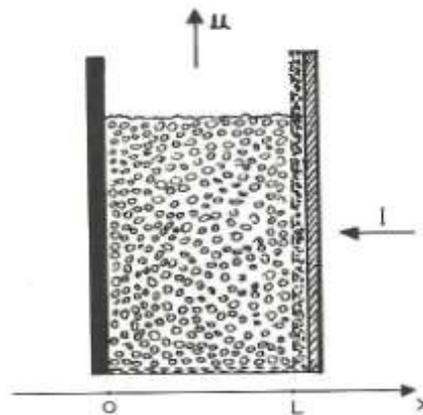
Fig.1: Representation of the electrode for the application of the mathematical model.

The bed is constituted of highly conductive porous particles whose specific surface area is a_m. It has a width of L and a uniform porosity of ε. If the electric current is the movement of the positive charges, the current feed is done on the surface x = L and the reception on the surface x = 0. A superficial velocity of the electrolyte solution u entering the reactor is uniform along the transversal area . The electrical conductivites of the solid and liquid phases are denominated respectively by σ_m and σ_s.

For the purpose of simplifying the transport equations presented here, the following assumption were made:
1. Only the compunent k =1 reacts in the system;
2. There is no accumlation of the chemical species k > 1, in the liquid phase
3. Hydrodynamic and electrochemical operating conditions kept constsnt
4. In the bulk of the solution, outside the diffusion layer, the effects of diffusion and dispersion are neglegible compared to that of convection, which implies that $\vec{v}_{k,s} = \vec{v}_s$.
5. The solid phase does not leave the system or in other words the average velocity of the velocity of the solid phase is zero which implies that $\vec{v}_m = 0$, then

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

$$\frac{\partial}{\partial t}\left[\varepsilon C_{k,s}\right] + \nabla \cdot \left[\varepsilon C_{k,s}\vec{v_s}\right] = \varepsilon R_{k,s} \tag{9}$$

$$\nabla \cdot \left[\varepsilon C_{k,s}\vec{v_s}\right] = 0 \quad k=2,3,...,m \tag{10}$$

$$\nabla \cdot \left[(1-\varepsilon)\vec{i_m}\right] = -\varepsilon F \frac{z_k}{M_k} R_{k,s} \tag{11}$$

$$\nabla . \left[\varepsilon \vec{i_s}\right] = \varepsilon F \frac{z_k}{M_k} R_{k,s} \tag{12}$$

$$\vec{i}_s = -\sigma_s \operatorname{grad}\emptyset_s \tag{13}$$

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

2.1. 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 sufficient high to ensure that concentration change through the bed height is insignificant
3. The porosity and specific area are kept uniform and do not vary with time during operation.
4. The operation is isothermal
With these conditions the relations 8 to14 reduce to:
- **Potential in the solid phase**

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

- **Potential in the liquid phase**

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

2.2. The Kinetic
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:

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

A combination of this equation with equation 7 results:

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

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

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

Where

$$i_0 = nFk_0 C_{k,s}^* \tag{20}$$

A combination with equation 7 results:

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

In these equations, D_k is the diffusion coefficient of the 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 overpotential in the reactor defined by the relation:

$$\eta = \emptyset_m - \emptyset_s - \left[E_{eq} + \frac{RT}{nF} ln\left(C_{k,s}^* \right) \right] \tag{22}$$

2.3. 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,

x = 0; $\frac{d\emptyset_s}{dx} = 0$ and x = L, $\frac{d\emptyset_m}{dx} = 0$ $\tag{23}$

2. If the system operates under constant current, then

x = 0; $\frac{d\emptyset_m}{dx} = -\frac{I}{(1-\varepsilon)\sigma_m A}$ $\tag{24}$

x = L, $\frac{d\emptyset_s}{dx} = -\frac{I}{\varepsilon A \sigma_s}$ $\tag{25}$

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

It is considered that the reaction is controlled by intrinsic reaction given by equation 19.

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 orthogonal collocation method coupled to a Newton-Rapson multivariable algorithm.

2.4. 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 substituting from equations 21 and 22:

$$\frac{d^2\eta}{dx^2} = \left[\frac{1}{\sigma_m} + \frac{(1-\varepsilon)}{\varepsilon\sigma_s} \right] \cdot i_0 \left\{ exp\left[\frac{\alpha nF}{RT} \eta \right] - exp\left[-\frac{(1-\alpha)nF}{RT} \eta \right] \right\} \tag{26}$$

The respective boundary conditions are

$$\left(\frac{d\eta}{dx} \right)_{x=0} = -\frac{I}{(1-\varepsilon)\sigma_m A} \tag{27}$$

$$\left(\frac{d\eta}{dx} \right)_{x=X} = \frac{I}{\varepsilon\sigma_s A} \tag{28}$$

III. NUMERICAL METHOD FOR THE RESOLUTION OF THE MODEL EQUATIONS: ORTHOGONAL COLLOCATION.

The set of ordinary differential none linear equations, ODEs, 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 and second order derivatives can be evaluated in terms of the 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)[12]. The system of equations obtained after application of N internal points of orthogonal collocation on equations 15 and 16 are:

$$\sum_{j=1}^{N} B_{ij} \phi_{mj} = C_{mi} f_i(\eta_i) \qquad i = 1, 2, ..., N \tag{29}$$

$$\sum_{j=1}^{N} B_{ij} \phi_{sj} = C_{si} f_i(\eta_i) \qquad i = 1, 2, ..., N \tag{30}$$

where

$$C_m = -\frac{a_m}{\sigma_m} \tag{31}$$

$$C_s = \frac{a_m}{\sigma_s \frac{(1-\varepsilon)}{\varepsilon}} \tag{32}$$

For the boundary conditions, we have:

At x = 0

$$\sum_{j=1}^{N+1} A_{1j} \phi_{mj} = C_{cmi} \tag{33}$$

$$\sum_{j=1}^{N} A_{1j} \phi_{sj} = 0 \tag{34}$$

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

$$\emptyset_{m1} = \frac{C_{cmi} - \sum_{j=2}^{N+1} A_{1j} \emptyset_{mj}}{A_{11}} \tag{35}$$

$$\emptyset_{s1} = \frac{- \sum_{j=2}^{N+1} A_{1j} \emptyset_{sj}}{A_{11}} \tag{36}$$

At x = L

$$\sum_{j=1}^{N+1} A_{N+1j} \phi_{mj} = 0 \tag{37}$$

$$\sum_{j=1}^{N+1} A_{N+1j} \phi_{sj} = C_{csi} \tag{38}$$

The respective values of the boundary condition at x = L is:

$$\emptyset_{mN+1} = \frac{- \sum_{j=1}^{N} A_{N+1j} \emptyset_{mj}}{A_{N+1N+1}} \tag{39}$$

$$\emptyset_{sN+1} = \frac{C_{csi} - \sum_{j=2}^{N} A_{N+1j} \emptyset_{sj}}{A_{N+1N+11}} \tag{40}$$

Where

$$C_{cm} = - \frac{I}{\sigma_m (1-\varepsilon) A_L} \tag{41}$$

$$C_{cs} = - \frac{I}{\sigma_s \varepsilon A_L} \tag{42}$$

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)[13], 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 known, x will be considered the only independent variables in the ODEs.

3.1 Simulations

The total number of equations is (N+2)*2, since there are two dependent variables ϕ_m and ϕ_s. In the program, the guessed values of $\phi_m(i)$ and $\phi_s(i)$, are the first given and then the collocation points and collocation matrices are calculated by Villadsen's subroutine. For solving these model equations, typically six internal collocation points were used. The convergence criterion was 1.0 x 10^{-5}.

In these simulations, the conductivities σ_m and σ_s were taken from the work of German and Goodridge (1975)[8] whose values are, respectively, 600.0 ohm^{-1}m^{-1} and 60 ohm^{-1}m^{-1}. The values of the charge transfer α, and the exchange current density, i_0 were obtained from Newmann (1973)[14] and their respective values are, 0.9 and 10.2 A/m^2. The simulations were based on a laboratory scale reactor having lateral area (current feeder) 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 of copper ions.
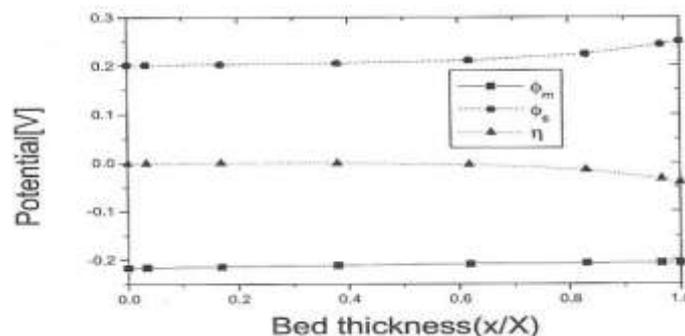
IV.   RESULTS AND DISCUSSION

Fig. 2. Potential distributions in the reactor having the total applied current as a parameter, I = 2A, bed width = 0.19m and porosity = 0.36
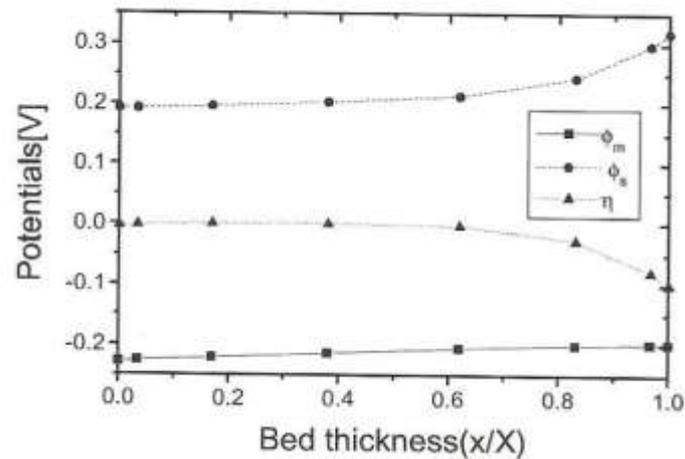
Fig. 3. Potential distribution in the reactor for a total applied current I = 4A, bed width = 0.019m and porosity = 0.36

The distributions of the metal and the liquid phase potentials and the overpotential in the reactor 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.

Figure 4 shows the effect of increasing bed width from 0.019m to 0.029m. A comparison 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 and in the appearance of anodic reactions (oxidation of metallic copper) in the system and consequently the current efficiency of the process will decrease.
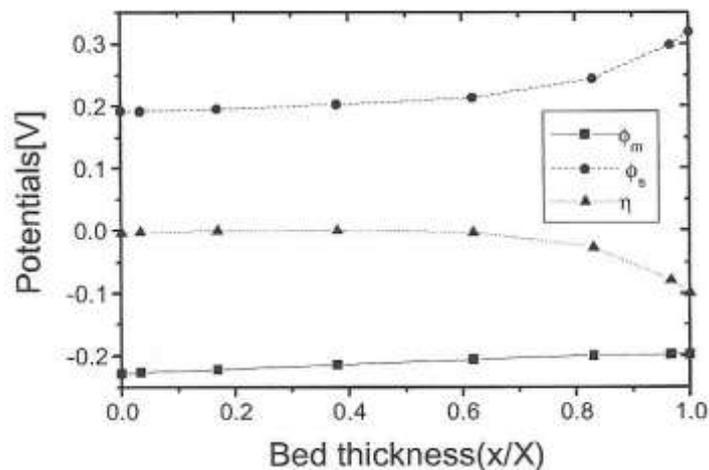

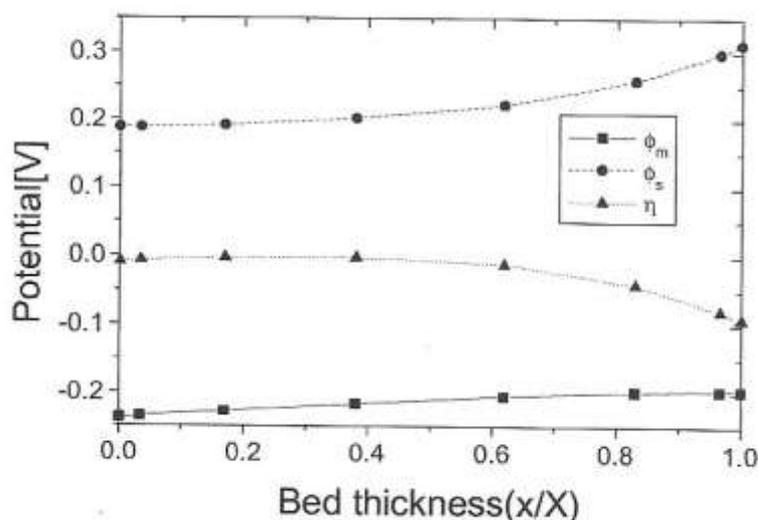**Fig. 4.** Potential distribution for I = 4A, bed width = 0.029m and porosity = 0.36

Fig. 5. Potential distributions in the reactor for a porosity of 0.6, I = 4A and bed with = 0.029m

The effect of bed porosity is shown in figure 5. This figure shows that the bed porosity has a significant effect on the behaviour of the system. It can be verified that the bed porosity caused a negative increase of the overpotentials in both regions of the electrode. It can also be observed that very close to the anode, there 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 increases towards the cathode or very close to the current feeder. This means that electrochemical reactions occur with more intensity at the region close to the membrane. A close observation shows that about 30% of the reactor is electrochemical active.

V. CONCLUSION

The electrochemical active region is situated close to the current feeder, and only about 30% of the whole bed is electrochemically active. The developed model though simplified, is capable of describing and predicting qualitatively and quantitatively, the behaviour of electrochemical reactors, offering in this way, important information for engineering projects and plant scale up. The method of orthogonal collocation proved to be efficient numerical method for solving resultant differential equations from this type of system.

VI. 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 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]
CE   Current Efficiency [%]
F   Faraday Constant [96500C/mol]
i   Current Density [A/m_2]
$i_{k,s}^*$ Reaction rate of chemical specie k in terms of charge per unit area [A/m^2]
i_s Current density in the liquid [A/m_2]
i_m Current density in the solid phase [A/m^2]
i_0 Exchange current density [A/m^2]
L   Bed width [m]
m   Particle mass [g]
n   Number of electrons
$R_{k,s}$ Rate of reaction in terms of mass of chemical specie k per unit volume of the liquid phase [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 electrode [m/s]
$\vec{v}_{k,s}$ Local velocity of the chemical specie k in the bulk of the electrolyte [m/s]
$\vec{v}_s$ Average velocity of the liquid phase [m/s]
$\vec{v}_{k,m}$ Local velocity of the chemical specie in the solid phase [m/s]
$\vec{v}_m$ Average velocity of the solid phase [m/s]
x   spatial coordinate [m]
z_k Number of transferred charges

Greek symbols
α   Kinetic constant [-]
η   Overpotential [V]
ϕ_m Solid phase potential
ϕ_s Liquid phase potential
σ_s Conductivity of the liquid phase [$\Omega^{-1}m^{-1}$]
σ_m Conductivity of the matrix [$\Omega^{-1}m^{-1}$]
ε   Bed porosity [-]
δ   Boundary layer width [m]

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