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Strongly coupled model for the prediction of the performances of an electrochemical reactor

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Abstract

A mathematical model is developed to investigate and predict the performances of electrochemical reactors. It is implemented with a finite volume method, and solved by means of the open source package OpenFOAM. The new solver, named ECpisoFOAM, deals with an intricate set of equations and boundary conditions which describe an electrochemical copper deposition system. The code uses the PISO algorithm for the transient incompressible flow field. A second predictor-corrector sequence combines mass fraction, electric potential and current density. It considers the convection, migration and diffusion mechanisms under the assumption of a dilute solution, mass conservation, and local electro-neutrality. The conservation of charges provides the electrical field which in turn allows the reconstruction of the tertiary current density distribution. At the electrodes, the presence of a charged double layer affects the behavior of the neighbor electrolyte. The effect of this interaction is modeled through the Butler-Volmer equation or its two commonly used simplifications: linear and logarithmic. Furthermore the fluid dynamic and the electrochemical modeling are coupled with the geometric changes of the active plates due to either material deposition or consumption of the electrodes. A dynamic mesh method has been integrated, increasing yet the level of coupling between electrical, chemical and fluid dynamic fields. Results are here presented and analyzed.

Keywords: Electrochemical reactor, Copper depletion, Butler-Volmer, Tertiary current density
1. Introduction

Electrochemical reactors and in general electrochemical systems nowadays, have a leading role in a wide range of applications: from batteries to fuel cells, from electroplating to water treatments. The main physical characteristic of an electrochemical system, as viewed through the eyes of engineers and scientists, is indeed the simultaneous treatment of many complex and interacting phenomena [1, 2]. To overcome the issue, several simplifications are commonly used with the intent to decrease the level of coupling. They provide satisfactory estimation of the solution, but cut down the generality of the problem and restrict the solution’s domain to very specific cases. Alternatively, commercial software use specific packages for electrochemical reactors, presenting “black-box” solutions that allow little insight into the mathematical and numerical difficulties of the model. Therefore, it is of interest for research engineers the need to operate with a tool having a penetrable architecture such as OpenFOAM (OF). This is a free, open source software package, specialized in Computational Fluid Dynamics (CFD) with a large user base across most areas of engineering and science, offering complete freedom to customize and extend its existing functionality. In this work the flexibility of OF is exploited to allow a more direct control over the performances of an electrochemical cell in terms of:

- uniform current density distribution
- uniform electrode potential distribution
- high mass transfer rates [3]

An example of a typical electrochemical cell is the FM01-LC reactor. It is a scaled-down version of the FM21-SP cell (2.1 m²) which is employed in the chloralkali production [4]. Its design produces a controlled flow by means of a parallel plate cells, often in a modular, expandable, filter-press configuration [5]. Despite the fact that this technology is well-spread, fluid mechanics, turbulence and electro chemistry remain strongly coupled, hence the modeling of these systems is still today a very challenging task. For this reason the present work aims to set up, implement and develop a numerical model that can investigate and predict the productivity of an electrochemical reactor system.
2. Geometry and mesh

The above mentioned FM01-LC belongs to the family of the Parallel Plate Electrochemical Reactors (PPER). A PPER, is a vessel which facilitates chemical reactions through the introduction of electrical energy, where an anode and a cathode are assembled on parallel slabs [6]. The electrodes are physically separated by an electrolyte medium containing reactants and products. The electrolyte is injected in the reactor with a certain known velocity, and it reacts with the active electrodes. Inside the cell two half-sides are identified. Species are oxidized in one half-cell (anode), while in the other half-cell (cathode) species are reduced.

In this work the parallel plate configuration is used as a test-case. The full cell is represented by a rectangular geometry. Table 1 provides its dimensions and the number of grid elements for both the active plates (read anode and cathode), and the not actives. It can be noticed that the flow is 2D (1 grid element in the y-direction), and it is discretized with a total number of 22 750 elements for the entire reactor. Figure 1 shows a simplified sketch of it.

<table>
<thead>
<tr>
<th>Plates</th>
<th>Dimensions [cm]</th>
<th>Number of elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-direction</td>
<td>70</td>
<td>140</td>
</tr>
<tr>
<td>y-direction</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>z-direction</td>
<td>1</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 1: Geometry and mesh characteristics

Figure 1: Sketch of the geometry
3. Mathematical and numerical formulation

This work simulates a copper depletion system. The electrolyte is modeled as a plug flow, and it is composed of [0.002 M] $CuSO_4 + [0.1 M] H_2SO_4$. Once the electrolysis starts, the anode releases cupric ions while the cathode captures and transforms them into solid copper. The same reaction (1) occurs at both the electrodes, reducing cupric ions at the cathodic side (left to right), and oxidizing them at the anode (right to left). No secondary reactions are taken into account.

$$Cu^{2+} + 2e^- \leftrightarrow Cu(s)$$ (1)

Previous works [7–10] have investigated a similar electrochemical process in a rotating disk electrode configuration, implying a multi-ion deposition model and partial dissociation of $HSO_4^-$. In this study the low dissociation of the acidic bath was not included into the model as suggested in [11], since the diffusivity of $HSO_4^-$ and $SO_4^{2-}$ in dilute media is almost identical. Therefore the electrolyte is made of $Cu^{2+}$, $SO_4^{2-}$, and $H^+$, and spatial variations of its properties are considered. For further details Table 2 presents the composition of the electrolytic solution, and Table 3 provides the required input parameters to start the simulation and regulate the electrode kinetics. The electrolyte is injected in the cell always with the same composition.

<table>
<thead>
<tr>
<th>Species</th>
<th>$Y_{Cu^{2+}}$</th>
<th>$Y_{SO_4^{2-}}$</th>
<th>$Y_{H^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial $Y_i$</td>
<td>0.013</td>
<td>0.33</td>
<td>0.657</td>
</tr>
<tr>
<td>Diffusivity $10^{-9} m^2 s^{-1}$</td>
<td>0.610</td>
<td>1.065</td>
<td>9.312</td>
</tr>
</tbody>
</table>

Table 2: Electrolytic solution properties

In this work, the author has also implemented the changes in the geometry due to the amount of deposited copper at the cathode and the consumption of the anode.
The equations are implemented with finite volume method in OpenFOAM. The solver is named ECpisoFOAM, it has a tree-structure where each branch is responsible for the modeling of a field so that everything is interconnected through the central trunk, but still independently accessible.

3.1. Pressure and velocity fields

The solver ECpisoFOAM starts by solving the pressure \( p \) and velocity \( \mathbf{U} \) fields. It considers the continuity Eq.2 and the Navier-Stokes Eq.3:

\[
\nabla \cdot (\mathbf{U}) = 0 \tag{2}
\]

\[
\frac{\partial \mathbf{U}}{\partial t} + \mathbf{U} \cdot \nabla \mathbf{U} = -\frac{\nabla P}{\rho} + \nu \nabla^2 \mathbf{U} \tag{3}
\]

In a preliminary phase turbulence was considered, but no relevant effects were found in the investigated range of velocities. The two equations are solved together inside a PISO algorithm (Pressure Implicit with Splitting of Operators [13–17]), which helps the handling of the non linearity in Eq.3. It basically splits the operators into an implicit predictor and multiple explicit corrector steps. The predictor uses the pressure values from the previous time step to discretize the equation of motion and estimate a first guess velocity which is non-divergence free. At this point the coefficient matrix of the system is decomposed into two matrices: the first containing just the diagonal terms, and the second all the off-diagonals. Next, with Eq.2 a predicted value of pressure is estimated, and it is used in an explicit scheme to correct the velocity, which this time results to be divergence-free. The number of pressure updates and velocity corrections can vary depending on the desired
accuracy. The advantage of using this algorithm lies on the splitting operators. Thanks to it in the corrector loops the solution is provided by inverting a diagonal matrix instead of a full one. Therefore store and access matrices is faster, and the CPU time required decreases. In short the PISO-loop:

- imposes an initial \( p \)
- predicts \( U \) (Eq.3)
- evaluates \( p \) (Eq.2)
- corrects \( U \) (Eq.3)

3.2. Mass transport

The mass transport equation (Eq.4) models the transport of ions within the cell:

\[
\frac{\partial Y_i}{\partial t} = - \nabla \cdot \left[ - D_i \nabla Y_i - \left( \frac{F}{RT} z_i D_i Y_i \right) \nabla \Phi + U Y_i \right] + S \quad (4)
\]

In Eq.4 \( Y_i = C_i / C_{TOT} \) is the mass fraction, and the subscript \( i \) identifies the species. Each species has its own diffusion coefficient \( D_i \), and its own charge number \( z_i \) indicating the sign and the number of charges carried by each species, \( z < 0 \) for anions and \( z > 0 \) for cations. The Faraday’s constant is \( F \), while \( R \) is the constant of perfect gas, and \( T \) the flow average temperature. The equation presents a transient term on the left hand side. On the right side within the squared brackets there is the flux of ions (see Eq.8), which consists of three contributions. The first is the diffusion, which is driven by the concentration gradients (\( \nabla Y_i \)) and points towards small concentrations. The second is the migration and it is led by the gradient of the electric potential (\( \nabla \Phi \)) pushing positive ions to the negative electrode and vice versa. Finally the third share is the convection mechanism, and moves ions with the flow velocity (\( U \)). The last term outside the brackets (\( S \)) represents the rate of homogeneous chemical reaction in the solution that produces or consumes the species under investigation. It might be seen as a source or sink term according to which side reaction occurs. In this work, as previously mentioned, no side reactions are considered, hence this term is null. To ensure mass conservation, Eq.5 is added to the system.

\[
\sum_i Y_i = 1 \quad (5)
\]

Further details on the strength of the coupling are given in Section 3.3.
3.3. Electro-Chemistry (EC)

Inside the electrolyte Eq. 6 makes sure that the total current density is maintained divergence-free.

\[ \nabla \cdot i = 0 \quad (6) \]

where \( i \) is the sum of the single current densities carried by each species as shown in (Eq. 7)

\[ i = F \sum_i z_i N_i \quad (7) \]

\( N_i \) is the flux of the \( i \)-th ion transported by diffusion, migration, and convection (Eq. 8).

\[ N_i = -D_i \nabla Y_i - \left( \frac{F}{RT} z_i D_i Y_i \right) \nabla \Phi + U Y_i \quad (8) \]

Now Eq. 7 and Eq. 8 can be combined together transforming Eq. 6 into an equivalent equation (Eq. 9) where the tertiary current density distribution seems to disappear in favor of the electric potential \( \Phi \). This manipulation permits a straightforward coupling with the mass transport Eq. 4 without passing through the total current density.

\[ \nabla^2 \left( \frac{F^2}{RT} \sum_i z_i^2 D_i Y_i \cdot \Phi \right) + \nabla^2 \left( F \sum_i z_i D_i Y_i \right) = 0 \quad (9) \]

It can be noticed that in Eq. 9 there are only two contributions, the first coming from the migration transport and the second from the diffusive mechanism. The missing term is related to the convection. Its absence is caused by the electroneutrality Eq. 10, which states that it cannot exist any significant unbalance of positive and negative ions in the solution.

\[ \sum_i z_i Y_i = 0 \quad (10) \]

Due to the strong coupling between the mass fractions and the electric potential, the two cannot be split and solved independently. Therefore, the strategy of solution is to use another predictor-corrector loop counting 4 unknowns \( (Y_{Cu^{2+}}, Y_{SO_4^{2-}}, Y_{H^+}, \Phi) \), and 4 equations (Eq. 4, Eq. 5, Eq. 9, Eq. 10). Eq. 4 models the distribution of cupric ions, using the electric potential at the previous time iteration. Subsequently the other two mass fractions of \( SO_4^{2-} \) and \( H^+ \) are estimated by means of Eq. 5 and Eq. 10. Finally, the electric potential field is corrected and updated through Eq. 9. The loop is repeated until the desired accuracy of the solution is reached.
3.4. Boundary conditions

In an electrochemical cell, the interface between the bulk solution and the solid metal plate presents a Double Layer (DL). It plays an important role linking simultaneously electric potential, surface tension, composition of the bulk solution, and surface concentrations of various species [1]. The complexity of this physical-chemical system, does not allow an easy solution for the closure of the PDEs system. Nevertheless, a set of boundary conditions have to be defined (Eqs.11). Boundaries are named after Figure 1.

\[
\begin{align*}
\text{Inlet} & : & \begin{cases}
U &= U_{in} \\
\nabla p &= 0 \\
Y_i &= Y_{b_i} \\
\partial n \Phi &= 0
\end{cases} & \quad \text{Inactive walls} & : & \begin{cases}
U \cdot n &= 0 \\
\nabla p &= 0 \\
\partial n Y_i &= 0 \\
\partial n \Phi &= 0
\end{cases} & \quad \text{Outlet} & : & \begin{cases}
\nabla \cdot U &= 0 \\
p &= p_{atm} \\
\nabla \cdot Y_i &= 0 \\
\nabla \cdot \Phi &= 0
\end{cases}
\end{align*}
\]

(11)

Assuming that the electrodes’ metal surface are impenetrable, the boundary conditions on the velocity and pressure are the same for all the active and inactive walls. This is not the case for the mass factions (Eq.12). At the electrodes depending on the species reactivity the conditions become:

\[
\begin{align*}
\text{Active walls} & : \begin{cases}
N_i \cdot n &= \pm \sum_i s_{ik} i_k \cdot n \\
N_i \cdot n &= 0
\end{cases} & \quad i &= Y_{Cu^{2+}} \\
& & \quad i &= Y_{SO_2^-}, Y_{H^+} (12)
\end{align*}
\]

where \( s_{ik} \) is the stoichiometric coefficient of the \( i \)-th species in the \( k \)-th reaction, and \( n \) is the number of electrons exchanged in the specific reaction. This work only considers the reaction in Eq.1, so the subscription \( k \) can be omitted. The sign \( \pm \) depends whether the reaction is occurring at the anode or at the cathode. The modeling of the product \( i \cdot n = i_n \), hides the exponential bounding of the current density with the the surface overpotential as expressed in Eq.13.

\[
i_n = i_{0,el} \left[ \frac{Y_{red}^s}{Y_{red}^b} \exp \left\{ \alpha \frac{nF}{RT} \eta_{el} \right\} - \frac{Y_{ox}^s}{Y_{ox}^b} \exp \left\{ -(1 - \alpha) \frac{nF}{RT} \eta_{el} \right\} \right] (13)
\]

Here \( i_{0,el} \) is the exchange current density associated to the null potential, \( \alpha \) is the symmetry factor also known as the charge transfer coefficient, the subscripts \( ox \) and \( red \) stand respectively for oxidant and reductant components,
while the superscripts $s$ and $b$ indicate whether the mass fractions are respectively at the surface or in the bulk. The surface electrode over-potential $\eta_{el}$ is a function of the measured electrode potential $V_{el}$, the calculated equilibrium potential $E^{\infty}$, and the solution potential close to the surface $\Phi^s$ as shown in Eq.14, [18].

$$\eta_{el} = V_{el} - \Phi^s - E^{\infty}$$

(14)

where the equilibrium potential is expressed as in Eq.15 (see Nomenclature)

$$E^{\infty} = E^0 - E_{RE}^0 - \frac{RT}{nF} \ln \left\{ \Pi_i \left( \frac{Y_i^b}{\rho} \right)^{s_{ik}} \right\} + \frac{RT}{nF} \ln \left\{ \Pi_i \left( \frac{Y_i,RE}{\rho} \right)^{s_{ik,RE}} \right\}$$

(15)

The non-linear Eq.13 can degenerate into one of the 3 following formulations:

- **No mass transfer effects.**
  If the solution is well mixed, or currents are low such that concentrations at the surfaces and at the bulk are indistinguishable, Eq.13 turns into the well known Butler-Volmer (BV) formulation Eq.16

$$i_n = i_0 \left[ \exp \left\{ \frac{\alpha nF}{RT} \eta_{el} \right\} - \exp \left\{ -(1 - \alpha) \frac{nF}{RT} \eta_{el} \right\} \right]$$

(16)

- **Small $|\eta_{el}|$**
  For small value of $\eta_{el}$ the current is linearly related to the overpotential, where the charge transfer resistance $R_{ct}$ is introduced

$$i_n = \frac{\eta_{el}}{R_{ct}}, \quad R_{ct} = \frac{RT}{i_0 F}$$

(17)

- **High $|\eta_{el}|$**
  For high values of the overpotential, one of the exponential terms becomes negligible with respect to the other, leading to a much easier formulation of the BV equation also known as Tafel equation

$$i_n = \begin{cases} 
  i_0 \left[ \exp \left\{ \frac{\alpha nF}{RT} \eta_{el} \right\} \right] & \eta_{el} >> 0 \\
  i_0 \left[ \exp \left\{ -(1 - \alpha) \frac{nF}{RT} \eta_{el} \right\} \right] & \eta_{el} << 0 
\end{cases}$$

(18)
To complete the Eqs.11 it is still necessary to impose a constraint on $\Phi$ affected by the presence of the DL as well. This is done by making explicit $\Phi_{el}$ from Eq.14:

$$\text{Active walls}$$

$$\left\{ \begin{array}{l}
\Phi_{el} = V_{el} - \eta_{el} - E^\infty
\end{array} \right.$$  \hspace{1cm} (19)

The overpotential $\eta_{el}$ is provided by the inversion of Eq.16 or 17, or 18. While the manipulation of the latter two can be easily done, the BV equation requires a particular attention. First the current density is estimated at the boundaries, then the overpotential and in turns the $\Phi_{el}$ are calculated by using the Ridders’ method [19]. It is a false position method for exponential functions, which requires two initial values lying on different sides of the root being sought. The function to be inverted $f(x)$ is then evaluated at those initial values, and it is transformed into a straight line $g(x)$ thanks to the linearisation in Eq.20

$$g(x) = f(x) e^{(x-x_1)Q}$$  \hspace{1cm} (20)

This method can be seen as a non-linear regula-falsi method, and a sequence of evaluations of $g(x)$ are performed until the roots ($\eta_{el}$) are found.

In short the $EC$-loop:

- imposes an initial $\Phi$ and $\eta_{el}$
- predicts $Y_{Cu^{2+}}$ (Eq.4)
- predicts $Y_{SO_4^{2-}}$ (Eq.5)
- predicts $Y_{H^+}$ (Eq.10)
- evaluates the $\Phi$ (Eq.9)
- reconstructs $i$ (Eq.7)
- inverts $i_n$ to get $\eta_{el}$ (Eq.16, 17 or 18)
- updates boundary conditions (Eqs.12 and 19)

and iterates until reaching the desired tolerance.
3.5. Geometry changes

The electrochemical reactions occurring inside the cell, cause small changes in the geometry of the active plates. At the cathode the deposition of pure solid copper confines the flow in a smaller channel volume. On the contrary at the anode a corrosive mechanism takes place releasing cupric ions and increasing the original electrolyte channel volume, as shown in Figure 2.

Figure 2: Sketch of the geometry changes

In this study a dynamic mesh is used to reproduce the stretching and squeezing of the original grid. The reactor shape is preserved, and no topological changes arise. The mesh manipulation model solves the grid motion equation (Eq.21) written in terms of the laplacian of the displacement:

\[ \nabla(\gamma \nabla d) = 0 \]  \hspace{1cm} (21)

The displacement \( d \) represents a point vector field, while \( \gamma \) is the diffusion coefficient propagating the grid motion information all over the geometry. In this study it is modeled with an inverse distance method in its quadratic form (Eq.22)

\[ \gamma \sim \frac{1}{l^2} \]  \hspace{1cm} (22)

At each time iteration a routine updates the mesh grid by:

- identifying the electrodes
- finding the link between the local and global reference systems
- getting the point vector field of the selected electrode
- interpolating the quantities from the grid-faces to the points
• shifting the grid-points an imposed time-dependent displacement $d_{imp}$
• updating the mesh

The vector $d_{imp}$ previously mentioned, imposes the desired displacement to the surfaces where the impingement is occurring (Eq.23). It is proportional to the flux of cupric ions which approaches the electroactive plates, and it varies linearly with time $t$. Only its $z$-component is tracked since it is the largest and consequently the limiting one.

$$d_{imp} = (N_{Cu^{2+}} \cdot n)t$$ (23)

The mesh manipulation routine is the very last part of the solver because it requires the most updated values of the copper mass fraction. The way the active plates are changing their geometry gives a feedback on how unevenly the electrodes are consuming, providing information about the system lifetime.

4. Results and discussions

Numerical results are presented and discussed in this section. All the graphs below report steady-state solutions along a simulation time of 1000s. Before presenting the full set of results, it is necessary to spend few words about the numerical schemes used. The time derivative, although it does not represent a crucial point for this work, is implemented with a first order implicit Euler scheme. The gradient and the laplacian are discretized by a Gauss linear integration with central difference. Orthogonal corrections are required when the deformations of the active plates occur. A limited linear scheme is involved in the discretization of the divergence. It is a second order scheme bounded by a Sweby limiter [15].

Furthermore Table 4 shows the relaxation factors on pressure, velocity, and overpotential imposed to improve the stability and speed up the convergence of the solution. The mass fractions make use of a relaxation factor of 1 to reinforce and guarantee their matrix diagonal dominance.
4.1. Mesh dependency study

A spatial grid convergence analysis is carried out. The discretization error is quantified by performing the simulation on three different grid sizes with a minimum grid refinement ratio of $r \geq 1.1$, [20]. The functional $f$ is the mass fraction of copper integrated over the electrode length. Table 5 provides the information about each mesh.

<table>
<thead>
<tr>
<th>Grid ID</th>
<th>Tot cells</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>91,000</td>
<td>0.0161</td>
</tr>
<tr>
<td>2</td>
<td>22750</td>
<td>0.0160</td>
</tr>
<tr>
<td>3</td>
<td>5700</td>
<td>0.0158</td>
</tr>
</tbody>
</table>

Table 5: Grids specifics

The order of convergence of the solution is estimated as in Eq.24, where $f_i$ is the functional related to the $i$-th grid ID:

$$m = \ln \left( \frac{f_3 - f_2}{f_2 - f_1} \right) \frac{1}{\ln(r)}$$

To estimate the “real” solution, Richardson extrapolation [21] predicts what is the value of the functional if a zero grid spacing would be applied (Eq.25):

$$f_0 = f_1 + \frac{(f_1 - f_2)}{r^m - 1}$$

The generalized theory of Richardson extrapolation makes use of the two finest grid resolutions and requires the calculation of a Grid Convergence
Index (GCI) as expressed in Eq.26. It gives an indication on how much the solution would change with further refinement of the grid.

\[ GCI_{ij} = \frac{F_s}{r^m - 1} \left| \frac{(f_i - f_j)}{f_i} \right| \times 100\% \]  

(26)

where \( F_s \) is a security factor set to 1.25 [22]. Besides, an asymptotic range of convergence (Eq.27) of 1 is desired to assure that the solution is within the estimated error band [22].

\[ \text{asyR} = \frac{GCI_{23}}{r^m GCI_{12}} \sim 1 \]  

(27)

Table 6 shows the final details of this analysis, and indicates that the grid with ID 2 has the best trade-off between accuracy and computational time.

<table>
<thead>
<tr>
<th>( r )</th>
<th>( m )</th>
<th>( GCI_{12} )</th>
<th>( GCI_{23} )</th>
<th>( \text{asyR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.66</td>
<td>0.0164%</td>
<td>0.2081%</td>
<td>1.0013</td>
</tr>
</tbody>
</table>

Table 6: Mesh dependency study - Results

4.2. \textit{ECpisoFOAM}

In this subsection the numerical performances of the new developed solver \textit{ECpisoFOAM} are examined. The cell geometry is configured according to Table 1 (see Section 2), and the mesh in use has the ID 2 in Table 5. Figure 3a presents the evolution of copper mass fraction along the anode. Cupric ions are released from the anode and pushed through the electrolyte. At the entrance of the electrode it is observed that the production is lower than at its end. This is because the effect of the convective mechanism is stronger at the entrance of the electrode and it is decreasing with the electrode length where the migration effect is becoming more important. To verify what just said, an additional test has been carried out. It reproduces the same scenario with the only difference being an extremely reduced velocity of the electrolyte (almost stagnant). In this way the convective mechanism is negligible, and the entire active surface reacts simultaneously driven just by the migration and the diffusive contributions. In order to control the contribution of the
diffusive transport, the cupric mass fraction along the $z$-axis is shown in Figure 3b at different Peclet numbers. By observing the graph, at high Peclet the convective contribution promotes a constant $Y_{Cu^{2+}}$ along the bulk of the electrolyte ($0.1 < z/H < 0.9$). For $Pe = 1$, the sum of the migrative and diffusive mechanism becomes comparable to the convective share, and the range of uniformity in the bulk is reduced to $0.2 < z/H < 0.7$. Besides, it is remarkable that for both cases the concentration of copper at the top of the cell is higher than at the bottom. The reason is because at the cathode ($z/H = 0$) the reacting cupric ions produce solid copper, therefore they leave the cell and are not any more accounted in the modeling.

![Figure 3: Mass fraction of cupric ions](image)

(a) Along the anode  
(b) Along a vertical cut

To better investigate this behavior close to the electrodes, the time evolution of the punctual mass fraction of copper is plotted. Figure 4a shows the decrease of $Y_{Cu^{2+}}$ close to the electrode ($z/H = 0.02$). The variation is of the order of $10^{-3}$, as it was already anticipated in Figure 3b. It indicates that the limiting current density is reached, and that the electrode process is mass transfer controlled. On the contrary close to the anode ($z/H = 0.98$) the cupric mass fraction increases by time and is released into the electrolytic solution.
Figure 4: Time evolution of the $Y_{Cu^{2+}}$ extrapolated from two different points.

(a) Point close to the cathode

(b) Point close to the anode

Figure 5 plots the electric potential along a vertical cut. It is a straight line with an angular coefficient of 0.4. The initial potential drop of the cell is set to $-0.1$ [V], and for simplicity purposes the anode is set to zero, so that the $\Delta V_{cell}$ coincides with the initial cathode potential ($z/H = 0$). The vertical cut is extrapolated from Figure 6 (black line) where just the region including the active plates is reported.

Figure 5: Electric potential along a vertical cut
Figure 6: 3D contour of the electric potential $\Phi$ [V]

The curvatures of the equipotential $\Phi$ at the extremities of the electrodes (Figure 7a and 7b) are reflected in the current density field where they result to be more pronounced. Figure 8a presents the effects at the entrance of the active plates, and Figure 8b at the exit.

Figure 7: 3D contours at the extremities of the electrodes of the electric potential [V]

Figure 8: 3D contours at the extremities of the electrodes of the current density magnitude [(A m)/kg-mol]
It is now interesting to see what happens alongside the surface of the electrodes in terms of overpotential. Figure 9a displays the maximum value at the entrance of the anode, and then its value rapidly decrease with an exponential behavior until the minimum is reached at the end of the electrode. On the contrary at the cathode the conduct of the $\eta_{\text{cathode}}$ is reversed (Figure 9b). The minimum peak is gained as soon as the electrode starts, and its value raises up to the maximum asymptotic value right at the end of the active plate. The two overpotential solutions are the result of the inversion of Eq.16 through the Ridders’ method [19].

![Graphs showing Anodic and Cathodic Overpotential](image_url)

(a) Anodic overpotential
(b) Cathodic overpotential

Figure 9: Overpotential along the anode (a), and along the cathode (b)

Due to the very high non-linearity of Eq.16, when the Ridders’ method is applied [19] to reverse the double exponential function, a relaxation factor (see Table 4), is considered at both electrodes to improve the stability of the problem. Furthermore, to avoid any unwanted divergent solutions it is strongly suggested to bound the overpotential to any finite values. A similar exponential behavior is found in Figure 10. It shows the tendency of the normalized current density along the electrode. Two different test cases are plotted to point out the relevant dependency to the electrolyte velocity. The dashed curve is produced with an almost negligible velocity. Here, with the exception of the two lateral peaks, there is no appreciable variation of the current density, and the case is limited by ohmic drop. On the contrary in the red curve, the velocity becomes important and the limiting mechanisms turn out to be the convection.
These behaviors result to be consistent with the theory expressed in [1]. The limiting current density distribution is used to estimate the efficiency of the system in terms of mass transport through the Sherwood number (Eq.28):

\[
Sh = \frac{i_{lim} L_c}{n F C^b_{Cu^{2+}} D_{Cu^{2+}}} \quad \text{or} \quad Sh = \frac{k_m L_c}{D_{Cu^{2+}}}
\] (28)

Equalizing the two definitions of \( Sh \), it is possible to calculate the mass transfer coefficient \( k_m \) as in Eq.29. The result is plotted in Figure 11 and obviously it turns to be linearly proportional to the current density distribution but inversely dependent to the cupric ions concentration in the bulk solution. The mass transfer rate is infinite at the upstream edge of the electrode where fresh solution is brought in contact with the electrode. The current decreases with increasing \( x \), since the solution in the diffusion layer has already been depleted by the electrode reaction further upstream [1].

\[
k_m = \frac{i_{lim}}{n F C^b_{Cu^{2+}}}
\] (29)
The last part of this section analyzes the stretching and squeezing of the mesh to reproduce the changes in the shapes of the active plates due to the electrochemical reactions. Figure 12 shows the solid copper deposited at the cathode after 1000 s of simulation. It acts like a solid block, obstructing the contact between the fresh electrolyte, rich of $Y_{Cu^{2+}}$, and the metallic plate. Firstly only the left part of the cathode is affected, but later on the whole surface diminishes its production rate. The efficiency of the cell is strongly corrupted and it is necessary to remove the solid copper. The process at the anode is reversed. The solid copper is turned into ions dissolving in the electrolytic solution. Nevertheless, the release of $Y_{Cu^{2+}}$ ions causes the corrosion of the anode plate itself. The degradation of the anode takes place following the flow direction (from left to right). The replacement of the active plates is suggested when the efficiency of the system is reduced by approximately 50% of its initial value.
4.3. Validation

The predictions of the new solver ECpisoFOAM are compared to analytic and numerical solutions, as well as the experimental data of Gerth L. [12], in terms of current density at the electrode. The electrolyte properties, and the input parameters are the same as those shown in Table 2 and 3. The analytic solution of Leveque [1] is used for limiting current density conditions. As expressed in Eq.30, the limiting current density is proportional to the copper ions concentration, and to the cubic root of the ratio $U/x$.

$$i_{lim} = 0.9783 \frac{nFD}{s} \frac{C_{Cu^{2+}}}{C_{Cu^{2+}}} \left( \frac{\langle U \rangle}{HDx} \right)^{1/3}$$

(30)

In this frame, two additional data sets are used to prove the validity of the ECpisoFOAM solution. The first simulates the same test case with the commercial software Comsol, and the latter is the result of a numerical work performed by Georgiadou M. [11]. Figure 13 presents all the data of the normalized current density evolution along the cathode’s length.
The trend is the same for all the five sets of data. The peaks at the electrode entrance exponentially decrease until the end of the plate, where the asymptotic value of approximately 0.7 is reached. Starting by analyzing Leveque’s solution, it underestimates the normalized current density because of the limiting assumptions of its theory [1], for instance it does not account for the migration transport mechanism. Besides, the solution implemented in Comsol (dashed line) has a sharper transition from the peak to the asymptotic value, while at the exit of the electrode it overestimates the local current density with a small curl. These issues might be related to the discretization method used by the software, but no further investigations have been carried out about this small discrepancy. The curve of ECpisoFOAM presents a slightly higher peak at the entrance of the electrode, nevertheless its trend follows the other solutions alongside with the numerical result provided by Georgiadou [11]. Finally, the last set of data presents some deviations from the other trends, specially at the center of the active plate. It could be possible that those gaps are due to some experimental errors not better identified by the author, like the placement of the sensors, or the uncertainty of the instruments used. The entrance peak and the final asymptotic value are catch anyhow. By assuming an error band of 20% on the experimental measures the same graph is plotted in Figure 14 comparing exclusively the experimental results and the ECpisoFOAM solution.
Figure 14: Comparison between ECpisoFOAM and the experimental data assuming an error band of 20%.

The maximum relative error (Eq. 31) is estimated to be 3.74. Before and after the middle of the electrode, the measures fall within the 20% range with two exceptions around 0.4 \( x/L \), and other two around 0.1 \( x/L \).

\[
Err_{rel} = \frac{|i_{ECpisoFOAM} - i_{Experiments}|}{i_{Experiments}} \tag{31}
\]

5. Conclusions

A numerical model has been implemented in OpenFOAM-2.3.1 to predict and investigate the performances of a generic electrochemical reactor. A copper depletion system in a rectangular geometry has been selected as the test case. The new solver ECpisoFOAM makes use of the finite volume method to solve the highly coupled set of equations. ECpisoFOAM is realized in fact with a tree architecture where each branch is easily accessible from the main body. The solver contains two predictor-corrector loops. The first takes care of the fluid-dynamics, solving pressure and velocity fields. The second predictor-corrector solves the electric potential field coupled together with the mass transport equations. Ohmic drops and gradient concentrations in the electrolytic solution contributes to the \( \Phi \) distribution, while
diffusion, convection and migration are responsible of the transport of ions in the electrolyte. The current density distribution is accurately predicted and validated through experimental, analytic, and numerical data from the literature.

This study allows the investigation of the performances of a wider range of electrochemical systems without any strong limiting simplifications. The strength of ECpisoFOAM is the use of the Butler-Volmer equation in its original and integral form. Few precautions though, have to be accounted for, such as the use of relaxation factors, and the bounding of the overpotential to avoid any undesired divergent solutions. For those systems where the absolute value of the electrode overpotential is relevantly high or extremely low, the solver offers also the possibility to switch respectively to the logarithmic or linear form of the BV-equation saving computational time without losing accuracy. ECpisoFOAM is equipped with a moving mesh to reproduce the geometric deformations caused by deposition or corrosion at the active plates. This tool becomes important in the estimation of the system life-time, and can be used to evaluate the efficiency of the system and to predict the replacement time of the electrodes. In fact, improvements in the geometry have shown to have a deep impact on the efficiency of the active plates. A new design might be also including turbulence promoters, to have a more performing mixing level of the electrolytic solution. Results can be used to optimize the performances of electrochemical reactors on industrial scales.

6. Acknowledgments

The authors are very grateful to Dr. Ing. Gaetan Lantagne for his stimulating discussions and his precious comments. At the time this project started he was the director of the Institut de Recherche d’Hydro-Québec (IREQ). A special thanks to the Canadian company Hydro-Québec, and to the NSERC which financially supported this study. The authors thank also the Université de Sherbrooke for its fellowship.
7. Bibliography


## Appendix A. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$as\bar{y}R$</td>
<td>–</td>
<td>asymptotic range of convergence</td>
</tr>
<tr>
<td>$C_i$</td>
<td>$kg\cdot mol\cdot m^{-3}$</td>
<td>concentration of the $i$-th species</td>
</tr>
<tr>
<td>$C_{TOT}$</td>
<td>$kg\cdot mol\cdot m^{-3}$</td>
<td>total electrolytic concentration</td>
</tr>
<tr>
<td>$d$</td>
<td>$m$</td>
<td>point displacement vector field</td>
</tr>
<tr>
<td>$d_{imp}$</td>
<td>$m$</td>
<td>imposed point displacement</td>
</tr>
<tr>
<td>$D_i$</td>
<td>$m^2\cdot s^{-1}$</td>
<td>diffusivity of the $i$-th species</td>
</tr>
<tr>
<td>$E^0$</td>
<td>$V$</td>
<td>standard electric potential</td>
</tr>
<tr>
<td>$E^0_{RE}$</td>
<td>$V$</td>
<td>standard electric potential of the reference electrode</td>
</tr>
<tr>
<td>$E^\infty$</td>
<td>$V$</td>
<td>equilibrium potential</td>
</tr>
<tr>
<td>$F$</td>
<td>$As\cdot (kg\cdot mol)^{-1}$</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>$F_s$</td>
<td>–</td>
<td>security factor</td>
</tr>
<tr>
<td>$f$</td>
<td>$m$</td>
<td>functional</td>
</tr>
<tr>
<td>$H$</td>
<td>$m$</td>
<td>electrode’s height</td>
</tr>
<tr>
<td>$i$</td>
<td>$Am\cdot (kg\cdot mol)^{-1}$</td>
<td>current density per units of $C_{TOT}$</td>
</tr>
<tr>
<td>$i_0$</td>
<td>$Am\cdot (kg\cdot mol)^{-1}$</td>
<td>exchange current density associated to the null potential</td>
</tr>
<tr>
<td>$i_k$</td>
<td>$Am\cdot (kg\cdot mol)^{-1}$</td>
<td>current density of the $k$-th reaction per units of $C_{TOT}$</td>
</tr>
<tr>
<td>$i_{lim}$</td>
<td>$Am\cdot (kg\cdot mol)^{-1}$</td>
<td>limiting current density</td>
</tr>
<tr>
<td>$k_m$</td>
<td>$m\cdot s^{-1}$</td>
<td>mass transfer coefficient</td>
</tr>
<tr>
<td>$L$</td>
<td>$m$</td>
<td>electrode’s length</td>
</tr>
<tr>
<td>$L_c$</td>
<td>$m$</td>
<td>characteristic length</td>
</tr>
<tr>
<td>$l^2$</td>
<td>$m^2$</td>
<td>distance from the moving node</td>
</tr>
<tr>
<td>$m$</td>
<td>–</td>
<td>order of convergence of the solution</td>
</tr>
<tr>
<td>$N_i$</td>
<td>$m\cdot s^{-1}$</td>
<td>flux of the $i$-th species per units of $C_{TOT}$</td>
</tr>
<tr>
<td>$n$</td>
<td>–</td>
<td>number of electrons exchanged</td>
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Table A.7
<table>
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<th>Symbol</th>
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<tr>
<td>$Pe$</td>
<td>–</td>
<td>Peclet number</td>
</tr>
<tr>
<td>$p$</td>
<td>Pa</td>
<td>pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>$J (kg\cdot mol K)^{-1}$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>$\Omega \ kg\cdot mol$</td>
<td>charge transfer resistance</td>
</tr>
<tr>
<td>$r$</td>
<td>–</td>
<td>grid refinement ratio</td>
</tr>
<tr>
<td>$S$</td>
<td>$s^{-1}$</td>
<td>rate of homogeneous chemical reaction</td>
</tr>
<tr>
<td>$Sh$</td>
<td>–</td>
<td>Sherwood number</td>
</tr>
<tr>
<td>$s_{ik}$</td>
<td>–</td>
<td>stoichiometric coefficient of the i-th species</td>
</tr>
<tr>
<td>$T$</td>
<td>$K$</td>
<td>bulk temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>s</td>
<td>time</td>
</tr>
<tr>
<td>$U$</td>
<td>$m \ s^{-1}$</td>
<td>velocity</td>
</tr>
<tr>
<td>$U_{in}$</td>
<td>$m \ s^{-1}$</td>
<td>inlet velocity</td>
</tr>
<tr>
<td>$V_{el}$</td>
<td>$V$</td>
<td>measured electrode potential</td>
</tr>
<tr>
<td>$\Delta V_{cell}$</td>
<td>$V$</td>
<td>imposed cell voltage</td>
</tr>
<tr>
<td>$y_{i}^{b}$</td>
<td>–</td>
<td>bulk mass fraction of the i-th species</td>
</tr>
<tr>
<td>$y_{i}$</td>
<td>–</td>
<td>mass fraction of the i-th species</td>
</tr>
<tr>
<td>$y_{i,RE}$</td>
<td>–</td>
<td>mass fraction of the i-th species at the reference electrode</td>
</tr>
<tr>
<td>$y_{ox}^{b}$</td>
<td>–</td>
<td>bulk mass fraction of the oxidant component</td>
</tr>
<tr>
<td>$y_{ox}^{s}$</td>
<td>–</td>
<td>mass fraction of the oxidant component at the plate</td>
</tr>
<tr>
<td>$y_{red}^{b}$</td>
<td>–</td>
<td>bulk mass fraction of the reductant component</td>
</tr>
<tr>
<td>$y_{red}^{s}$</td>
<td>–</td>
<td>mass fraction of the reductant component at the plate</td>
</tr>
<tr>
<td>$z_{i}$</td>
<td>–</td>
<td>charge number of the i-th species</td>
</tr>
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**Greek letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>–</td>
<td>symmetry factor</td>
</tr>
<tr>
<td>$\eta_{el}$</td>
<td>$V$</td>
<td>electrode overpotential</td>
</tr>
<tr>
<td>$\nu$</td>
<td>$m^2 \ s^{-1}$</td>
<td>kinematic viscosity</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>$V$</td>
<td>electric potential</td>
</tr>
<tr>
<td>$\Phi^{s}$</td>
<td>$V$</td>
<td>surface electric potential</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$kg \ m^3$</td>
<td>solvent density</td>
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Table A.8
Strongly coupled model for the prediction of the performances of an electrochemical reactor

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- Through this model, a wider range of electrochemical systems can be investigated without any strong simplifications
- Butler-Volmer equation is used in its original form with the possibility to switch to its linear or logarithm form accordingly to the overpotential
- Current density distribution is correctly predicted along the active plates
- Deformations of the electrodes due to material deposition and corrosion are modelled
- Results could be used to optimize the performances of electrolytic cells on industrial scales