

Numerical analysis of a model for Nickel-Iron alloy electrodeposition on rotating disk electrode*

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Abstract

To better understand the nickel-iron electrodeposition process, we have developed one-dimensional numerical model. This model addresses dissociation, diffusion, electromigration, convection and deposition of multiple ion species. The reaction mechanism in this model differs in that Ni^{2+} and Fe^{2+} are the electroactive species and $NiOH^+$ and $FeOH^+$ are not involved whatsoever. To take account of the anisotropic behaviour of the solution we introduce a domain decomposition numerical method. Simulations with experimental data shows that our model can predict characteristic features of the nickel-iron system.

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1 Introduction

Electrodeposition of alloys based on the iron group of metals is one of the most important recent developments in the field of alloy deposition. Films of *NiFe* alloy, in particular, have widely been adopted for electronics industry for recording, memory and storage devices [9].

Electrodeposition of *NiFe* alloys is anomalous [3]. In the anomalous codeposition, the less noble metal deposits preferentially; consequently its relative content in the alloy deposits is much higher than in the solution.

Since some properties of the film are also strongly related to the alloys content, it is important to understand the effects of various plating operating variables and to be able to control them.

In previous research, most of the proposed models [2], [12] for *NiFe* codeposition involve hydrolysis of Ni^{2+} and Fe^{2+} ions in solution. In these models, the anomalous codeposition was related to iron hydroxide that precipitated on the electrode surface and inhibited nickel reduction alone. However, it was shown that this hypothesis could not explain some of the experimental data and consequently it was supplanted by another mechanism [7], [6]. According to this newer model, $NiOH^+$ and $FeOH^+$ formed from the hydrolysis of Ni^{2+} and Fe^{2+} are reduced at the cathode. The anomalous codeposition occurs because $FeOH^+$ is present near the electrode at higher concentrations than $NiOH^+$.

Despite of the success realized by Gangasing and Talbot [4], Hessami and Tobias [7], Grande and Talbot [6], and Ramasubramanian et al. [14] in the application of this mechanism of codeposition onto a rotating disk electrode some unresolved issues still remain for many reasons [9].

A newer successful model proposed by Matlosz [11] stipulated that the reduction of each metal ion occurs via two-step mechanism with electroabsorption of a monovalent intermediate in the first step and its reduction in the second step. Anomalous codeposition arises from the preferential surface coverage of the adsorbate iron intermediate without having to assume the presence of $NiOH^+$ and $FeOH^+$.

In light of this Pritzker et al. [9], [15] proposed transport model for codeposition onto a rotating disk electrode (*RDE*) without assuming the presence of $NiOH^+$ and $FeOH^+$ as the electroactive species. As in some of the earlier model developments for *NiFe* codeposition [7], [6], they consider the system to involve one-dimensional steady-state transport of the various species to a rotating disk electrode (*RDE*).

In the present work we conduct a type of modelling similar to that done by Pritzker et al., which is the subject of the section 2. Section 3 is devoted to the numerical simulation of the system. Indeed we propose an iterative scheme and the finite element discretization for resolving the system of equations. Numerical examples are presented in section 4.

2 The model problem

We consider the species conservation equation for a species A_i as

$$\frac{\partial w_i}{\partial t} = -\text{div}(J_i) + S_i \quad (1)$$

where w_i is the concentration of species A_i , S_i denotes the production rate of A_i due to all the homogeneous reactions in which it is involved and J_i is its molar transport flux. The electrolytes used for *NiFe* codeposition always contain electroactive nickel ions as one of their major components. Consequently, migration is included along with diffusion and convection as possible modes of transport for each species. The molar flux J_i then becomes

$$J_i = -d_i \nabla w_i + v w_i - m_i w_i \nabla \Phi \quad (2)$$

where d_i is the diffusion coefficient of species A_i , v is the fluid velocity vector, Φ is the potential and m_i is the electrical mobility of species A_i (see [16]). The mobility and diffusion coefficient are related through the Einstein equation

$$m_i = \frac{d_i z_i F}{RT} \quad (3)$$

where $z_i F$ is the charge carried by a mole of species A_i , R is the universal gas constant and T is the local temperature.

We consider the system to involve one-dimensional steady-state transport of the various species to a rotating disk electrode with simultaneous homogeneous reaction. Furthermore, the homogeneous reactions are assumed to have much more rapid kinetics than the electrode reactions and to instantaneously reach thermodynamic equilibrium. Edge and double-layer effects are not included. Accordingly, the transport equation for each species becomes

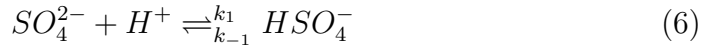
$$-d_i \Delta w_i + \text{div}(v w_i) - m_i \text{div}(w_i \nabla \Phi) = S_i \quad (4)$$

The species must also satisfy the electroneutrality condition everywhere in the system, i.e.

$$\sum_{i=1}^{NS} z_i w_i = 0 \quad (5)$$

where NS is the number of soluble species.

The solution of the governing differential equations together with the algebraic equations for homogeneous equilibrium requires first combining the transport equation for the individual species so as to eliminate the homogeneous reaction rate terms. The resulting equations which depend on the stoichiometry of the homogeneous reactions amount to mass balances on different components of the system (nickel, iron, hydrogen, etc.). In this analysis, we consider a problem of the codeposition of nickel and iron from a sulfate solution. This particular codeposition process is important because it permits the fabrication of magnetic devices from permalloy. For this nickel-iron sulfate bath $NiSO_4$, $FeSO_4$ and H_3BO_3 are dissolved in water and H_2SO_4 is used for pH adjustment. Consequently, the five dissolved species considered are Ni^{2+} , Fe^{2+} , H^+ , SO_4^{2-} and HSO_4^- . The metals do not form complexes with sulfate. The only homogeneous reaction considered is that between SO_4^{2-} and HSO_4^-



This reaction is commonly described as bimolecular in the forward direction and monomolecular in the backward direction. With k_1 and k_{-1} the reaction rate constants of the forward and backward reaction.

In this case, the homogeneous reaction term in 4 takes the form

$$\begin{aligned} S_3 &= -k_1 w_3 w_4 + k_{-1} w_5 \\ S_4 &= -k_1 w_3 w_4 + k_{-1} w_5 \\ S_5 &= k_1 w_3 w_4 - k_{-1} w_5 \end{aligned}$$

for all ions involved in reaction 6.

$K = \frac{k_{-1}}{k_1}$ denotes the equilibrium constant for homogeneous reaction and w_i ($1 \leq i \leq 5$) are respectively the concentrations of Ni^{2+} , Fe^{2+} , H^+ , HSO_4^- and SO_4^{2-} .

As mentioned previously, cathode reactions at the electrodeposition surface will involve the doubly-charged metal ions. During *NiFe* codeposition, we consider the following two electrode reactions



All the species are considered to be inert with regard to cathode reactions, with the exception of hydrogen. The formation of hydrogen is involved only in one cathode reaction from the protium cation,



The rates associated with these fundamental reactions can all be expressed in terms of local potential V , and local ion species concentrations w_i . Fluxes at the cathode surface ($y = 0$) are given by [9], [7]

$$J_k(0) = \frac{i_k}{2F} = -\beta_k w_k(0) \exp \left[-\alpha_k z_k \frac{FV}{RT} \right] \quad (10)$$

where i_k $k = 1, 2, 3$ are the current densities for reactions (7),(8), (9), V is the cathode potential on the surface hydrolysis electrode (SHE) scale after ohmic correction and β_k , α_k are respectively the rate constants and transfer coefficients. The rate relations are commonly known as Butler-Volmer equations. Values of the constants in these relations are widely publish [9], [7].

The three partial currents given in equations (10), (11), (12) are of practical importance because they are directly related to the deposition rates of nickel and iron and to the rate of hydrogen generation. The latter is important when ion fluxes are comparable to the diffusion limited ion transport rates since hydrogen that can not be diffused from the cathode surface will lead to hydrogen bubble formation. Hydrogen bubbles that do not detach from the cathode give rise to poor morphology of the deposited metal. Moreover, even high concentrations of hydrogen may lead to poor metal properties as hydrogen may become entrapped in the metal during the deposition process.

The bulk region considered is a domain Ω and δ is the hydrodynamic boundary layer thickness. As mentioned elsewhere [17], we consider the bulk region to be fully established beyond a distance 3δ from the electrode surface.

The presence of boric acid has not been explicitly included in this model. Over the normal range of operating conditions for *NiFe* codeposition, this species remains undissociated and consequently is transported by diffusion and convection, but not by migration. In addition, it is not known to participate in any homogeneous or electrochemical reaction. Thus, the transport of H_3BO_3 is completely decoupled from that of the other dissolved species. As proposed by Horkans [8], the role it plays in codeposition may be to adsorb onto the electrode surface and modify the kinetics of nickel and iron deposition. It is beyond the scope of this analysis to account for this effect in a detailed explicit way.

Boundary conditions have to be added as follows :

$$\begin{cases} -d_i w'_i(0) - m_i w_i(0) \Phi'(0) = -\beta_i w_i(0) \exp[-\alpha_i z_i FV/RT] & \text{for } 1 \leq i \leq 3 \\ w_4(0) = w_5(0) = 0 \\ \Phi(0) = V \end{cases} \quad (11)$$

$$\begin{cases} w_i(3\delta) = w_i^* & \text{for } 1 \leq i \leq 5 \\ \Phi(3\delta) = 0 \end{cases} \quad (12)$$

where $V \leq 0$, w_i^* represents the total amount of component A_i added to the bulk solution.

Let us also include electroneutrality condition (5) and the homogeneous equilibria (6), as well as the following material balance expressions

$$\begin{aligned} w_1^* &= w_1^T \\ w_2^* &= w_2^T \\ w_4^* + w_5^* &= w_5^T \\ 2w_1^* + 2w_2^* + w_3^* - 2w_4^* - w_5^* &= 0 \\ w_5^* &= Kw_3^* w_4^* \end{aligned}$$

where w_i^T represents the total amount of component i added to the bulk solution and $K = \frac{k_{-1}}{k_1}$. One can deduce easily

$$\begin{aligned} w_4^* &= w_5^T - w_5^* \\ w_3^* &= -2(w_1^T + w_2^T) + 2w_5^T - w_5^* \\ kw_5^{*2} - (1 + K(w_1^T + w_2^T) + w_5^T)w_5^* + 2Kw_5^T(w_5^T - w_1^T - w_2^T) &= 0 \end{aligned}$$

Now we are able to give the system satisfied by the concentrations of different species that are involved in our model

$$\left\{ \begin{array}{ll} -d_i w_i'' + b_i(y) w_i' - m_i(w_i \Phi')' = 0 & \text{in } \Omega \quad \text{for } i = 1, 2 \\ -d_i w_i'' + b_i(y) w_i' - m_i(w_i \Phi')' = S_i & \text{in } \Omega \quad \text{for } i = 3, 4, 5 \\ 2w_1 + 2w_2 + w_3 - w_4 - 2w_5 = 0 & \text{in } \Omega \\ w_i(3\delta) = w_i^* & \text{for } 1 \leq i \leq 5 \\ -d_i w_i'(0) - m_i w_i(0) \Phi'(0) = -\beta_i w_i(0) \exp \left[-\alpha_i z_i \frac{FV}{RT} \right] & \text{for } 1 \leq i \leq 5 \\ \Phi(0) = V; \Phi(3\delta) = 0; \end{array} \right. \quad (13)$$

where $b_i(y) = v_y$ and $\beta_4 = \beta_5 = 0$.

Finally let's examine the expression of the velocity of the electrolyte v . Cochran and Von Karman [10], [1] obtained that the fluid velocity component v_y of v can be expressed in term of power series expansion that involves a reduced variable $\gamma = y \sqrt{\frac{\omega}{\nu}}$:

$$v_y = \sqrt{\nu\omega} H(\gamma) = \sqrt{\nu\omega} \left(-a\gamma^2 + \frac{1}{3}\gamma^3 + \frac{b}{6}\gamma^4 + \dots \right)$$

where $a = 0.51023$, ω is the rotation speed of the *RDE*, and ν is the kinematic viscosity of the solution. The expansion also yields the boundary layer thickness δ ,

$$\delta = \left(\frac{3d}{a} \right)^{\frac{1}{3}} \omega^{-\frac{1}{2}} \nu^{\frac{1}{6}}$$

where d is a reference diffusion coefficient taken to correspond to the species in solution with the smallest diffusion coefficient.

3 Numerical analysis of the model

For $x \in [0, 3\delta]$, we put

$$\psi(x) = \Phi(x) - \frac{V}{3\delta}(3\delta - x) \quad (14)$$

and for $i = 1, \dots, 5$,

$$\begin{aligned} v_i(x) &= w_i(x) - w_i^* \\ m_i &= \frac{F}{RT} d_i z_i \\ \gamma_i &= \beta_i \exp(-\alpha_i \frac{m_i}{d_i}) \\ b_i &= b. \end{aligned} \quad (15)$$

System (13) is then equivalent to the two following systems :

$$\begin{cases} -d_i v_i'' + (b(y) + m_i \frac{V}{3\delta}) v_i' - m_i (v_i \psi')' = m_i w_i^* \psi'' + \tilde{S}_i & \text{in } (0, 3\delta), \\ -d_i v_i'(0) - m_i (v_i(0) + w_i^*) (\psi'(0) - \frac{V}{3\delta}) = -\gamma_i (v_i(0) + w_i^*), \\ v_i(3\delta) = 0, & \text{for } 1 \leq i \leq 5 \end{cases} \quad (16)$$

and

$$\begin{cases} -[\sum_{i=1}^5 z_i m_i (v_i + w_i^*) \psi']' = \sum_{i=1}^5 z_i d_i v_i'' - \frac{V}{3\delta} \sum_{i=1}^5 z_i m_i v_i' & \text{in } (0, 3\delta) \\ \psi(0) = \psi(3\delta) = 0; \end{cases} \quad (17)$$

with

$$\begin{aligned} \tilde{S}_1 &= \tilde{S}_2 = 0 \\ \tilde{S}_3 &:= \tilde{S}_3(v_3, v_4, v_5) = -k_1(v_3 + w_3^*)(v_4 + w_4^*) + k_{-1}(v_3 + w_3^*) \\ \tilde{S}_4 &= \tilde{S}_3 \\ \tilde{S}_5 &= -\tilde{S}_3. \end{aligned} \quad (18)$$

In order to solve the coupled system (16) and (17) we consider a fixed point method with respect to the reaction term (18). That means : at each iteration we consider $\tilde{S}_i$ given and at each step of the fixed point method we solve a coupled systems of the type :

$$\begin{cases} -d_i v_i'' + (b(y) + m_i \frac{V}{3\delta}) v_i' - m_i (v_i \Psi')' = m_i w_i^* \Psi'' + f_i & \text{in } (0, 3\delta), \\ -d_i v_i'(0) - m_i (v_i(0) + w_i^*) (\Psi'(0) - \frac{V}{3\delta}) = -\gamma_i (v_i(0) + w_i^*), \\ v_i(3\delta) = 0, & \text{for } 1 \leq i \leq 5 \end{cases} \quad (19)$$

and

$$\begin{cases} -[\sum_{i=1}^5 \varepsilon_i \psi']' = \sum_{i=1}^5 g_i & \text{in } (0, 3\delta) \\ \psi(0) = 0, \psi(3\delta) = 0; \end{cases} \quad (20)$$

with $(f_i, \varepsilon_i) \in (C^1([0, 3\delta]))^2$, $g_i \in C([0, 3\delta])$ and $\Psi \in C^2([0, 3\delta])$. The functions f_i, ε_i and g_i depends on the numerical method to solve (16) and (17)

and it change at each iteration.

To show the existence and uniqueness of the solution of system (19) we consider a variational formulation.

Let

$$H = \{\varphi \in H^1(0, 3\delta) / \varphi(3\delta) = 0\} \quad (21)$$

and we define the norm $\| \cdot \|_H$ in H by :

$$\| \varphi \|_H = \left(\int_0^{3\delta} (\varphi')^2(x) dx \right)^{\frac{1}{2}}. \quad (22)$$

Let $a_i(v_i, \varphi)$ be the following bilinear form :

$$\begin{aligned} a_i(v_i, \varphi) &= (\gamma_i + m_i \frac{V}{3\delta}) v_i(0) \varphi(0) + d_i \int_0^{3\delta} v_i'(x) \varphi'(x) dx \\ &\quad + \int_0^{3\delta} (b(x) + m_i \frac{V}{3\delta}) v_i'(x) \varphi(x) dx + m_i \int_0^{3\delta} v_i(x) \Psi'(x) \varphi'(x) dx. \end{aligned} \quad (23)$$

By multiplying the first equation of (19) by $\varphi \in H$ and integrate by part we obtain the weak formulation

$$a_i(v_i, \varphi) = -(\gamma_i + m_i \frac{V}{3\delta}) w_i^* \varphi(0) - m_i \int_0^{3\delta} w_i^* \Psi'(x) \varphi'(x) dx + \int_0^{3\delta} f_i(x) \varphi(x) dx. \quad (24)$$

Definition 1 We say that $(v_1, v_2, v_3, v_4, v_5)$ is a solution of (19) if and only if

$$\begin{cases} (v_1, v_2, v_3, v_4, v_5) \in (H)^5, \\ a_i(v_i, \varphi) = -(\gamma_i + m_i \frac{V}{3\delta}) w_i^* \varphi(0) - m_i \int_0^{3\delta} w_i^* \Psi'(x) \varphi'(x) dx \\ \quad + \int_0^{3\delta} f_i(x) \varphi(x) dx \text{ for } \varphi \in H \text{ and } 1 \leq i \leq 5. \end{cases} \quad (25)$$

Let $u = \max_{1 \leq i \leq 5} |m_i|$, $d = \min_{1 \leq i \leq 5} |d_i|$, $\eta = \max(\| \Psi' \|_\infty, \| \Psi'' \|_\infty)$ and $\varepsilon = d - a(3\delta)^2 + \frac{uV}{2} - \frac{3\delta u \eta}{2}(3\delta + 1)$.

Proposition 2 Suppose that $\varepsilon > 0$. Then problem (19) has a unique solution in $C^2([0, 3\delta])$.

Proof. First we will prove that the form a_i is bilinear continuous on $H \times H$, for $1 \leq i \leq 5$. It is clear that the form $a_i(., .)$ is bilinear. In the other hand for all $v \in H$ we have

$$v(x) = \int_{3\delta}^x v'(t) dt.$$

By the Hölder's Inequality we deduce

$$\|v\|_{L^2(0,3\delta)} \leq 3\delta \|v'\|_{L^2(0,3\delta)} \quad \forall v \in H \quad (26)$$

and

$$\|v\|_{L^\infty(0,3\delta)} \leq \sqrt{3\delta} \|v'\|_{L^2(0,3\delta)} \quad \forall v \in H, \quad (27)$$

then

$$\|v\|_{L^1(0,3\delta)} \leq (3\delta)^{3/2} \|v'\|_{L^2(0,3\delta)} \quad \forall v \in H. \quad (28)$$

Using (23), (27) and the Hölder's Inequality, we obtain

$$\begin{aligned} |a_i(v, \varphi)| &\leq 3\delta \left| \gamma_i + m_i \frac{V}{3\delta} \right| \|v'\|_{L^2(0,3\delta)} \|\varphi'\|_{L^2(0,3\delta)} \\ &\quad + d_i \|v'\|_{L^2(0,3\delta)} \|\varphi'\|_{L^2(0,3\delta)} \\ &\quad + \|b + m_i \frac{V}{3\delta}\|_{L^\infty(0,3\delta)} \|v'\|_{L^2(0,3\delta)} \|\varphi\|_{L^2(0,3\delta)} \\ &\quad + |m_i| \|\Psi'\|_{L^\infty(0,3\delta)} \|v\|_{L^2(0,3\delta)} \|\varphi'\|_{L^2(0,3\delta)}. \end{aligned} \quad (29)$$

For $x \in [0, 3\delta]$, we have $b(x) = -ax^2$ and $V \leq 0$, then

$$\|b + m_i \frac{V}{3\delta}\|_{L^\infty(0,3\delta)} \leq a(3\delta)^2 - u \frac{V}{3\delta}, \quad (30)$$

It follows from (26), (29) and (30) that

$$|a_i(v, \varphi)| \leq (a(3\delta)^3 + 3\delta\gamma_i + 3\delta u\eta - 2uV + d_i) \|v'\|_{L^2(0,3\delta)} \|\varphi'\|_{L^2(0,3\delta)},$$

then

$$|a_i(v, \varphi)| \leq (a(3\delta)^3 + 3\delta\gamma_i + 3\delta u\eta - 2uV + d_i) \|v'\|_H \|\varphi'\|_H, \quad (31)$$

which proves that the form a_i is continuous in $H \times H$.

Second we will prove that the form a_i is coercive on $H \times H$.

For all $(v, \varphi) \in H \times H$, we have

$$\begin{aligned}
a_i(v, \varphi) &= (\gamma_i + m_i \frac{V}{3\delta})v(0)\varphi(0) + d_i \int_0^{3\delta} v'(x)\varphi'(x)dx \\
&\quad + \frac{1}{2} \int_0^{3\delta} (b(x) + m_i \frac{V}{3\delta})v'(x)\varphi(x)dx \\
&\quad + \frac{1}{2} \int_0^{3\delta} (b(x) + m_i \frac{V}{3\delta})v'(x)\varphi(x)dx \\
&\quad + \frac{1}{2} m_i \int_0^{3\delta} v(x)\Psi'(x)\varphi'(x)dx \\
&\quad + \frac{1}{2} m_i \int_0^{3\delta} v(x)\Psi'(x)\varphi'(x)dx.
\end{aligned} \tag{32}$$

By integration by part we obtain

$$\begin{aligned}
a_i(v, \varphi) &= d_i \int_0^{3\delta} v'(x)\varphi'(x)dx + \frac{1}{2} \int_0^{3\delta} (b(x) + m_i \frac{V}{3\delta})v'(x)\varphi(x)dx \\
&\quad + \frac{1}{2} m_i \int_0^{3\delta} v(x)\Psi'(x)\varphi'(x)dx \\
&\quad + (\gamma_i + m_i \frac{V}{3\delta})v(0)\varphi(0) - \frac{1}{2} m_i \frac{V}{3\delta} v(0)\varphi(0) \\
&\quad - \frac{1}{2} \int_0^{3\delta} ((b(x) + m_i \frac{V}{3\delta})\varphi(x))'v(x)dx \\
&\quad - \frac{1}{2} m_i v(0)\varphi(0)\Psi'(0) - \frac{1}{2} m_i \int_0^{3\delta} \varphi(x)(\Psi'v)'(x)dx.
\end{aligned} \tag{33}$$

It follows that

$$\begin{aligned}
a_i(v, \varphi) &= \left\{ \gamma_i + \frac{m_i}{2} \left(\frac{V}{3\delta} - \Psi'(0) \right) \right\} v(0)\varphi(0) \\
&\quad + d_i \int_0^{3\delta} v'(x)\varphi'(x)dx - \frac{1}{2} \int_0^{3\delta} (b' + m_i \Psi'')(x)v(x)\varphi(x)dx \\
&\quad + \frac{1}{2} \int_0^{3\delta} [(b + m_i \frac{V}{3\delta} - m_i \Psi')(v'\varphi - v\varphi')](x)dx.
\end{aligned} \tag{34}$$

Then

$$\begin{aligned}
a_i(v, v) &= \left\{ \gamma_i + \frac{m_i}{2} \left(\frac{V}{3\delta} - \Psi'(0) \right) \right\} v^2(0) + d_i \int_0^{3\delta} v'^2(x)dx \\
&\quad - \frac{1}{2} \int_0^{3\delta} (b' + m_i \Psi'')(x)v^2(x)dx.
\end{aligned} \tag{35}$$

It follows that

$$\begin{aligned} a_i(v, v) \geq & \gamma_i v^2(0) - \left| \frac{m_i}{2} \left(\frac{V}{3\delta} - \Psi'(0) \right) \right| v^2(0) + d_i \int_0^{3\delta} v'^2(x) dx \\ & - \left| \frac{1}{2} \int_0^{3\delta} (b' + m_i \Psi'')(x) v^2(x) dx \right|. \end{aligned} \quad (36)$$

Therefore by the fact that $\gamma_i \geq 0$ and by (26), (27), we deduce

$$\begin{aligned} a_i(v, v) \geq & - \left| \frac{m_i}{2} \left(\frac{V}{3\delta} - \Psi'(0) \right) \right| 3\delta \|v'\|_{L^2(0,3\delta)}^2 + d_i \|v'\|_{L^2(0,3\delta)}^2 \\ & - \frac{1}{2} (3\delta)^2 \|b' + m_i \Psi''\|_{L^\infty(0,3\delta)} \|v'\|_{L^2(0,3\delta)}^2. \end{aligned} \quad (37)$$

Or $\|\Psi'\|_\infty < \eta$, $\|\Psi''\|_\infty < \eta$ and $\|b'\|_\infty = 6a\delta$, it follows that

$$a_i(v, v) \geq [d_i - a(3\delta)^2 + \frac{uV}{2} - \frac{3\delta u\eta}{2}(3\delta + 1)] \|v'\|_{L^2(0,3\delta)}^2.$$

Then

$$a_i(v, v) \geq \varepsilon \|v'\|_{L^2(0,3\delta)}^2. \quad (38)$$

Which means that the form a_i is coercive on $H \times H$.

Now let prove that the form F_i defined by

$$F_i(\varphi) = -(\gamma_i + m_i \frac{V}{3\delta}) w_i^* \varphi(0) - m_i \int_0^{3\delta} w_i^* \Psi'(x) \varphi'(x) dx + \int_0^{3\delta} f_i(x) \varphi(x) dx$$

for $\varphi \in H$ is continuous.

We have

$$\begin{aligned} |F_i(\varphi)| \leq & (\gamma_i + u \frac{V}{3\delta}) w_i^* \|\varphi\|_{L^\infty(0,3\delta)} + u w_i^* \|\Psi'\|_{L^\infty(0,3\delta)} \|\varphi\|_{L^1(0,3\delta)} \\ & + \|f_i\|_{L^\infty(0,3\delta)} \|\varphi\|_{L^1(0,3\delta)}. \end{aligned} \quad (39)$$

It follows from (27) and (28) that

$$|F_i(\varphi)| \leq 3\delta \left\{ (\gamma_i + u \frac{V}{3\delta}) w_i^* + u w_i^* \eta(3\delta) + (3\delta)^2 \|f_i\|_H \right\} \|\varphi\|_H, \quad (40)$$

therefore F_i is continuous on H .

Then by the Lax-Milgram Theorem we deduce that problem (25) has a solution $(v_1, v_2, v_3, v_4, v_5) \in (H)^5$. Finally let prove that $(v_1, v_2, v_3, v_4, v_5) \in (C^2([0, 3\delta]))^5$.

We note by $1_{(0,3\delta]}$ the function defined on $\mathbb{R}$ by

$$1_{(0,3\delta]}(x) = \begin{cases} 1 & \text{if } x \in (0, 3\delta] \\ 0 & \text{if not.} \end{cases} \quad (41)$$

By (24), for all $\varphi \in H^1([0, 3\delta])$, we have

$$\begin{aligned} & \int_0^{3\delta} [d_i v'_i + m_i(v_i + w_i^*)\Psi'](x) \varphi'(x) dx \\ &= \int_0^{3\delta} \left[f_i - (b + m_i \frac{V}{3\delta})v'_i - \frac{1}{3\delta}(\gamma_i + m_i \frac{V}{3\delta})(w_i^* + v_i)(1 - 1_{(0,3\delta]}) \right] (x) \varphi(x) dx. \end{aligned} \quad (42)$$

Then by the fact that

$$\left[f_i - (b + m_i \frac{V}{3\delta})v'_i - \frac{1}{3\delta}(\gamma_i + m_i \frac{V}{3\delta})(w_i^* + v_i)(1 - 1_{(0,3\delta]}) \right] \in L^2((0, 3\delta)),$$

it follows that

$$[d_i v'_i + m_i(v_i + w_i^*)\Psi'] \in H^1((0, 3\delta)).$$

Therefore $v'_i \in H^1((0, 3\delta))$, then $v'_i \in C([0, 3\delta])$, which implies that

$$v_i \in C^1([0, 3\delta]). \quad (43)$$

Or $\Psi' \in C^1([0, 3\delta])$, then $v'_i \in C^1([0, 3\delta])$, which implies that

$$v_i \in C^2([0, 3\delta]). \quad (44)$$

and proposition 2 follows. ■

With a similar method as proposition 2 we show the following result :

Proposition 3 *Suppose that there exists $k > 0$ such that for all $x \in [0, 3\delta]$, $\sum_{i=1}^5 \varepsilon_i(x) \geq k$. Then problem (20) has a unique solution in $C^2([0, 3\delta])$.*

3.1 Domain decomposition

3.1.1 Concentrations

The domain decomposition algorithm considered here has previously been used and analyzed by F. Gastaldi, L. Gastaldi and A. Quarteroni (see [5]), in the case of constant coefficients. We have generalized the Gastaldi- Quarteroni's iterative substructuring method to the case with non constant coefficients and Robin boundary conditions in $x = 0$.

System (16) is equivalent to the following system :

$$\begin{cases} -d_i v''_i + (b(y) + m_i \frac{V}{3\delta})v'_i = m_i[(v_i + w_i^*)\psi']' + \tilde{S}_i & \text{in } (0, 3\delta), \\ v_i(3\delta) = 0, \\ -d_i v'_i(0) = [m_i(\psi'(0) - \frac{V}{3\delta}) - \gamma_i](v_i(0) + w_i^*) & \text{for } 1 \leq i \leq 5 \end{cases} \quad (45)$$

For $1 \leq i \leq 5$ we put :

$$\begin{cases} B_0^i = b + m_i \frac{V}{3\delta}. \\ F_i(v_1, v_2, v_3, v_4, v_5, \psi) = m_i[(v_i + w_i^*)\psi']' + \tilde{S}_i. \\ G_i(v_i, \psi)(0) = [m_i(\psi'(0) - \frac{V}{3\delta}) - \gamma_i](v_i(0) + w_i^*). \end{cases} \quad (46)$$

Then the system (45) comes

$$\begin{cases} -d_i v_i'' + B_0^i(y) v_i' = F_i(v_1, v_2, v_3, v_4, v_5, \psi) & \text{in } (0, 3\delta), \\ v_i(3\delta) = 0, \\ -d_i v_i'(0) = G_i(v_i, \psi)(0) & \text{for } 1 \leq i \leq 5. \end{cases} \quad (47)$$

We note

$$L^i v = -d_i v_i'' + B_0^i v_i', \quad \text{for } 1 \leq i \leq 5. \quad (48)$$

For the resolution of the system (47), we will proceed in two steps :

Initialization

Let $v_{i,0}$ be the solution of the homogeneous system :

$$\begin{cases} L^i v_i = 0 & \text{in } (0, 3\delta), \\ v_i(3\delta) = 0, \\ G_i(v_i, \psi)(0) = -d_i v_i'(0), & \text{for } 1 \leq i \leq 5. \end{cases} \quad (49)$$

External loop: for $n \in \mathbb{N}$, $v_{i,n+1}$ we solve the linear system :

$$\begin{cases} L^i v_i = F_i(v_{1,n}, v_{2,n}, v_{3,n}, v_{4,n}, v_{5,n}, \psi) & \text{in } (0, 3\delta), \\ v_i(3\delta) = 0, \\ G_i(v_i, \psi)(0) = -d_i v_{i,n}'(0), & \text{for } 1 \leq i \leq 5. \end{cases} \quad (50)$$

and the potential equation(17). The system (17) is equivalent to the following system :

$$\begin{cases} -[p\psi']' = q & \text{in } (0, 3\delta) \\ \psi(0) = \psi(3\delta) = 0; \end{cases} \quad (51)$$

with

$$\begin{cases} p = \sum_{i=1}^5 z_i m_i (v_{i,n} + w_i^*) \\ q = \sum_{i=1}^5 z_i d_i v_{i,n}'' - \frac{V}{3\delta} \sum_{i=1}^5 z_i m_i v_{i,n}' \end{cases} \quad (52)$$

Internal loop: Resolution of system (50) by an iterative methods on subdomain.

Let

$$n \in \mathbb{N} \text{ and } c \in (0, 3\delta) \text{ fixed.} \quad (53)$$

Let A and B two real parameters such that $AB \leq 0$, $A \neq B$, $v_{i1}^0 = v_{i2}^0 = v_{i,n}$ and

$$\lambda_i^0 = d_i(v_{i2}^0)'(c) - \left(\frac{1}{2}B(c) + A\right)v_{i2}^0(c), \quad (54)$$

solve for $k \geq 0$

$$\begin{cases} L^i v_{i1}^{k+1} = F_i(v_{1,n}, v_{2,n}, v_{3,n}, v_{4,n}, v_{5,n}, \psi) & \text{in } (0, c) \\ d_i(v_{i1}^{k+1})'(c) - \left(\frac{1}{2}B_0(c) + A\right)v_{i1}^{k+1}(c) = \lambda_i^k, \\ G_i(v_{i1}^{k+1}, \psi)(0) = -d_i(v_{i,n})'(0). \end{cases} \quad (55)$$

then

$$\begin{cases} L^i v_{i2}^{k+1} = F_i(v_{1,n}, v_{2,n}, v_{3,n}, v_{4,n}, v_{5,n}, \psi) & \text{in } (c, 3\delta) \\ d_i(v_{i2}^{k+1})'(c) - \left(\frac{1}{2}B_0(c) + B\right)v_{i2}^{k+1}(c) = \\ d_i(v_{i1}^{k+1})'(c) - \left(\frac{1}{2}B_0(c) + B\right)v_{i1}^{k+1}(c), \\ v_{i2}^{k+1}(3\delta) = 0, \end{cases} \quad (56)$$

and finally set

$$\lambda_i^{k+1} = d_i(v_{i2}^{k+1})'(c) - \left(\frac{1}{2}B(c) + A\right)v_{i2}^{k+1}(c). \quad (57)$$

3.1.2 Resolution of the potential equation

For the resolution of the system (51), we use the same iterative subdomain method.

Let c the real given by (53), A' , B' two real parameters such that $A'B' \leq 0$ and $A' \neq B'$, Given β^0 .

Solve for $k \geq 0$

$$\begin{cases} -[p(w + v^*)(\psi_1^{k+1})']' = q(w + v^*) & \text{in } H^1(0, c), \\ \psi_1^{k+1}(0) = 0, \\ [p(w + v^*)(\psi_1^{k+1})'](c) - A'\psi_1^{k+1}(c) = \beta^k, \end{cases} \quad (58)$$

then

$$\begin{cases} -[p(w + v^*)(\psi_2^{k+1})']' = q(w + v^*) & \text{in } H^1(c, \delta), \\ \psi_2^{k+1}(\delta) = 0, \\ [p(w + v^*)(\psi_2^{k+1})'](c) - B'\psi_2^{k+1}(c) = [p(w + v^*)(\psi_1^{k+1})'](c) - A'\psi_1^{k+1}(c), \end{cases} \quad (59)$$

and finally set

$$\beta^{k+1} = [p(w + v^*)(\psi_2^{k+1})'](c) - A'\psi_2^{k+1}(c). \quad (60)$$

Existence and uniqueness of solution of problems (58) and (59) can be proved using the same argument used for the demonstration of existence and uniqueness of the solution of the concentration equations in subdomains given in the following section.

3.2 Existence and uniqueness of the solutions of the concentration equations on subdomain problems

Let $1 \leq i \leq 5$, $a_i^1(v, \varphi)$ and $a_i^2(v, \varphi)$ be the followings bilinear forms :

$$\begin{aligned} a_i^1(v, \varphi) = & d_i \int_0^c v'(x) \varphi'(x) dx + \frac{1}{2} \int_0^c (b(x) + \frac{m_i V}{3\delta}) (v(x)' \varphi(x) - \varphi'(x) v(x)) dx \\ & - \frac{1}{2} \int_0^c b'(x) v(x) \varphi(x) dx - Av(c) \varphi(c) + \gamma_i v(0) \varphi(0) \end{aligned} \quad (61)$$

and

$$\begin{aligned} a_i^2(v, \varphi) = & d_i \int_c^{3\delta} v'(x) \varphi'(x) dx + \frac{1}{2} \int_c^{3\delta} (b(x) + \frac{m_i V}{3\delta}) (v(x)' \varphi(x) - \varphi'(x) v(x)) dx \\ & - \frac{1}{2} \int_c^{3\delta} b'(x) v(x) \varphi(x) dx + Bv(c) \varphi(c) \end{aligned} \quad (62)$$

for $(v, \varphi) \in H \times H$.

By multiplying the two systems (55) and (56) by $\varphi \in H$, H is from (21), we obtain for all $n \geq 0$, $k \geq 0$:

$$\begin{aligned} a_i^2(v, \varphi) = & -m_i \int_0^c (v_{i,n}(x) + w_i^*) (\psi)'(x) \varphi(x) dx + \int_0^c \tilde{S}_3(v_{3,n}, v_{4,n}, v_{5,n})(x) \varphi(x) dx \\ & - (\gamma_i + \frac{m_i V}{3\delta}) w_i^* \varphi(0) - \frac{m_i V}{6\delta} v_{i,n}(0) \varphi(0) + (\lambda_i^k + m_i (v_{i,n}(c) + w_i^*) (\psi)'(c)) \varphi(c), \end{aligned} \quad (63)$$

$$\begin{aligned} a_i^2(v, \varphi) = & -m_i \int_c^{3\delta} (v_{i,n}(x) + w_i^*) (\psi)'(x) \varphi(x) dx + \int_c^{3\delta} \tilde{S}_3(v_{3,n}, v_{4,n}, v_{5,n})(x) \varphi(x) dx \\ & + (B - A) v_{i1}^{k+1}(c) \varphi(c) \\ & - (d_i (v_{i1}^{k+1})'(c) - (\frac{1}{2} (b(c) + \frac{m_i V}{3\delta}) + A) v_{i1}(c) + m_i (v_{i,n}(c) + w_i^*) (\psi)'(c)) \varphi(c) \end{aligned} \quad (64)$$

and

$$\lambda_i^{k+1} = d_i (v_{i2}^{k+1})'(c) - (\frac{1}{2} (b(c) + \frac{m_i V}{3\delta}) + A) v_{i2}^{k+1}(c). \quad (65)$$

Definition 4 Let $n \geq 0$, $k \geq 0$ and $(v_{i,n}, v_{i1}^k, \psi) \in (C^2([0, c]))^3$, we say that v_{i1}^{k+1} is a solution of (55) if and only if for all $\varphi \in H^1(0, c)$:

$$\begin{cases} v_{i1}^{k+1} \in H^1(0, c), \\ a_i^1(v_{i1}^{k+1}, \varphi) = -m_i \int_0^c (v_{i,n}(x) + w_i^*)(\psi)'(x) \varphi(x) dx \\ + \int_0^c \tilde{S}_3(v_{3,n}, v_{4,n}, v_{5,n})(x) \varphi(x) dx \\ - (\gamma_i + \frac{m_i V}{3\delta}) w_i^* \varphi(0) + \frac{m_i V}{6\delta} v_{i,n}(0) \varphi(0) \\ + (\lambda_i^k + m_i(v_{i1}^k(c) + w_i^*)(\psi)'(c)) \varphi(c), \end{cases} \quad (66)$$

Then we have the following result :

Proposition 5 Suppose that $A \leq 0$, then the problem (55) has a unique solution $v_{i1}^{k+1} \in C^2([0, c])$.

Proof. Since $A \leq 0$ and $\gamma_i \geq 0$, it follows that the form a_i^1 is coercive. Then we proceed by the same manner as in the proof of proposition 2 to deduce the result. ■

Definition 6 Let $n \geq 0$, $(v_{i,n}, \psi) \in C^2([c, 3\delta]) \times C^2([c, 3\delta])$ and v_{i1}^{k+1} given by (66), we say that v_{i2}^{k+1} is a solution of (56) if and only if for all $\varphi \in H^1(c, 3\delta)$:

$$\begin{cases} v_{i2}^{k+1} \in H^1(c, 3\delta), \\ v_{i2}^{k+1}(3\delta) = 0, \\ a_i^2(v_{i2}^{k+1}, \varphi) = -m_i \int_c^{3\delta} (v_{i,n}(x) + w_i^*)(\psi_2)'(x) \varphi(x) dx \\ + \int_c^{3\delta} \tilde{S}_3(v_{3,n}, v_{4,n}, v_{5,n})(x) \varphi(x) dx + (B - A) v_{i1}^k(c) \varphi(c) \\ - (d_i(v_{i1}^k)'(c) - (\frac{1}{2}(b(c) + \frac{m_i V}{3\delta}) + A) v_{i1}^k(c) + m_i(v_{i,n}(c) + w_i^*)(\psi)'(c)) \varphi(c), \end{cases} \quad (67)$$

Then we have the following result :

Proposition 7 Suppose that $B \geq 0$, then the problem (56) has a unique solution $v_{i2}^{k+1} \in C^2([c, 3\delta])$.

Proof. Since $B \geq 0$ it follows that the form a_i^2 is coercive. Then we proceed by the same manner as in the proof of proposition 2 to deduce the result. ■

3.2.1 Convergence of the subdomain decomposition algorithm

To prove the convergence of the subdomain decomposition algorithm applied to problem (50), we consider two problems :

$$\begin{cases} L^i v_{i1} = F_i(v_{1,n}, v_{2,n}, v_{3,n}, v_{4,n}, v_{5,n}, \psi) & \text{in } (0, c) \\ d_i(v_{i1})'(c) - (\frac{1}{2}B_0(c) + A)v_{i1}(c) = \\ d_i(v_{i,n})'(c) - (\frac{1}{2}B_0(c) + B)v_{i,n}(c) \\ G_i(v_{i1}, \psi)(0) = -d_i(v_{i,n})'(0). \end{cases} \quad (68)$$

then

$$\begin{cases} L^i v_{i2} = F_i(v_{1,n}, v_{2,n}, v_{3,n}, v_{4,n}, v_{5,n}, \psi) & \text{in } (c, 3\delta) \\ d_i(v_{i2})'(c) - (\frac{1}{2}B_0(c) + B)v_{i2}(c) = \\ d_i(v_{i1})'(c) - (\frac{1}{2}B_0(c) + B)v_{i1}(c), \\ v_{i2}(3\delta) = 0, \end{cases} \quad (69)$$

Proposition 8 *Suppose that c is near 0 or near 3δ , the sequence v_{i1}^k converge to v_{i1} in $C(0, c)$ and the sequence v_{i2}^k converge to v_{i2} in $C(c, 3\delta)$*

Proof. Let us define the errors $e_{ij}^k = v_{ij} - v_{ij}^k$, $1 \leq i \leq 5, j = 1, 2$, and study their behavior as k grows.

We prove the following inequality :

$$\|e_{i1}^{k+1}\|_\infty \leq \gamma \|e_{i1}^k\|_\infty \quad \text{and} \quad \|e_{i2}^{k+1}\|_\infty \leq \gamma \|e_{i2}^k\|_\infty, \quad (70)$$

where $\gamma < 1$.

By proceeding straightforwardly, the following iterative scheme is obtained for the error functions :

$$e_{ij}^0 = v_{i,n}, \quad (71)$$

$$\begin{cases} L^i e_{i1}^{k+1} = 0 & \text{in }]0, c[\\ d_i(e_{i1}^{k+1})'(c) - (\frac{1}{2}B_0(c) + A)e_{i1}^{k+1}(c) = \\ d_i(e_{i2}^k)'(c) - (\frac{1}{2}B_0(c) + B)e_{i2}^k(c) \\ e_{i1}^{k+1}(0) = 0. \end{cases} \quad (72)$$

and

$$\begin{cases} L^i e_{i2}^{k+1} = 0 & \text{in }]c, 3\delta[\\ d_i(e_{i2}^{k+1})'(c) - (\frac{1}{2}B_0(c) + B)e_{i2}^{k+1}(c) = \\ d_i(e_{i1}^{k+1})'(c) - (\frac{1}{2}B_0(c) + B)e_{i1}^{k+1}(c), \\ e_{i2}^{k+1}(3\delta) = 0. \end{cases} \quad (73)$$

Setting :

$$\begin{aligned}
c_1 &= \frac{1}{d}(\frac{1}{2}B_0^i(c) + A), \\
c_2 &= \frac{1}{d}(\frac{1}{2}B_0^i(c) + B), \\
f(x) &= \int_c^x \exp(\frac{B_0^i(t)}{d})dt, x \in [0, 3\delta], \\
G(x) &= \int_c^{3\delta} f(y)dy, x \in [c, 3\delta], \\
H(x) &= \int_0^x f(y)dy, x \in [0, c].
\end{aligned} \tag{74}$$

The corresponding solutions are :

$$e_{i1}^{k+1}(x) = \frac{\frac{(1 - c_1 G(c))}{H(c)} - c_2(1 - c_1 G(c))}{(1 - c_1 H(c))(1 - c_2 G(c))} e_{i1}^k(c) H(x) \tag{75}$$

and

$$e_{i2}^{k+1}(x) = \frac{(1 - c_1 G(c))(1 - c_2 H(c))}{(1 + c_2 G(c))(1 - c_1 H(c))} e_{i2}^k(c) G(x). \tag{76}$$

It follows that :

$$\| e_{i1}^{k+1} \|_{\infty} \leq \gamma_1 \| e_{i1}^k \|_{\infty} \quad \text{and} \quad \| e_{i2}^{k+1} \|_{\infty} \leq \gamma_2 \| e_{i2}^k \|_{\infty}, \tag{77}$$

where

$$\gamma_1 = \left| \frac{(1 - c_1 G(c)) - c_2(1 - c_1 G(c))H(c)}{(1 - c_1 H(c))(1 - c_2 G(c))} \right|$$

and

$$\gamma_2 = \left| \frac{(1 - c_1 G(c))(1 - c_2 H(c))}{(1 + c_2 G(c))(1 - c_1 H(c))} G(c) \right|.$$

By comparing $(\gamma_j)^2, j = 1, 2$ and 1 we deduce that :

$$\gamma_j < 1 \quad \text{if and only if} \quad (G(c) - F(c))\Theta(A, B) < 0, \tag{78}$$

where

$$\begin{aligned}
\Theta(A, B) &= \frac{B - A}{d} \left(2 - \frac{1}{d}(F(c) + G(c))(B_0^i(c) + A + B) \right. \\
&\quad \left. + \frac{2}{d}F(c)G(c)\left(\frac{B_0^i(c)}{2} + A\right)\left(\frac{B_0^i(c)}{2} + B\right) \right).
\end{aligned}$$

We have $c(c - 3\delta)$ is near 0, then $F(c)G(c)$ is near 0, it follows that $\Theta(A, B)$ and $\frac{B - A}{d}(2 - \frac{1}{d}(F(c) + G(c))(B_0^i(c) + A + B))$ have the same sign. Then $\Theta(A, B) > 0$, which implies that :

$$(G(c) - F(c))\Theta(A, B) < 0. \quad (79)$$

Finally we take

$$\gamma = \max(\gamma_1, \gamma_2). \quad (80)$$

■

The convergence of the subdomain decomposition algorithm applied to the potential equation solution can be proved using the same argument.

4 Numerical result

The method developed in previous sections was applied to a real experimental case.

The parameter $\delta = 1.1341 \cdot 10^{-5}$ gives the domain $(0, 3\delta)$. The diffusion constant are the following $d_1 = 6.8 \cdot 10^{-10}$; $d_2 = 7.6 \cdot 10^{-10}$; $d_3 = 9.31 \cdot 10^{-9}$; $d_4 = 1.33 \cdot 10^{-9}$; $d_5 = 1.065 \cdot 10^{-8}$.

The charges are the followings $z_1 = 2$; $z_2 = 2$; $z_3 = 1$; $z_4 = -2$; $z_5 = -1$. The electrical mobility m_i of species A_i are given: $m_1 = 5.2133 \cdot 10^{-8}$; $m_2 = 5.827 \cdot 10^{-8}$; $m_3 = 3.569 \cdot 10^{-7}$; $m_4 = -5.179 \cdot 10^{-8}$; $m_5 = -8.295 \cdot 10^{-8}$.

The fictitious boundary values of the solutions in $x = 3\delta$ are the followings $w_1(3\delta) = 500$; $w_2(3\delta) = 10$; $w_3(3\delta) = 10$; $w_4(3\delta) = 514.9$; $w_5(3\delta) = 0.05$ and $\Phi(3\delta) = 0$. In $x = 0$, $\Phi(0) = -0.85 \cdot 10^{-2}$.

In figure 1 we plot the concentration of Ni^{2+} obtained in the simulation. The concentration of Fe^{2+} is presented in figure 2.

The domain decomposition considered is in two subdomains with a fictitious boundary in $c = \delta$. The parameters of the fictitious boundary conditions in c are $A = 0$ and $B = 1.2 \cdot 10^{-4}$. Linear problem in each subdomain is solved using a finite element method.

5 Conclusion

We present in this paper a numerical method to solve a systems of reaction diffusion equations coupled to a potential equation modeling an electrodeposition process. A subdomain decomposition technique taking account of the

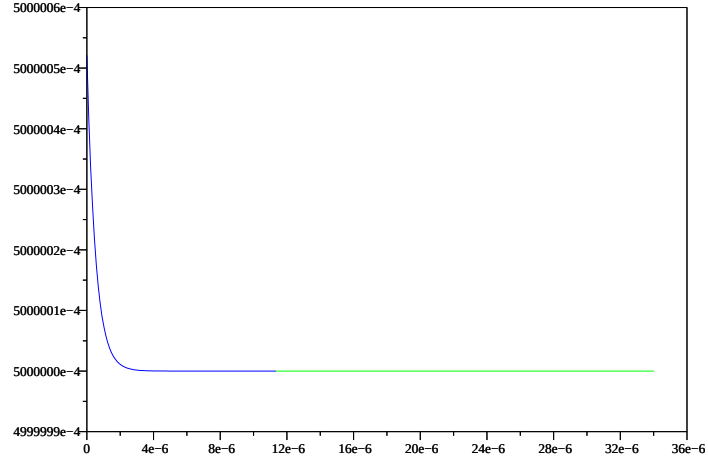


Figure 1: concentration of Ni^{2+}

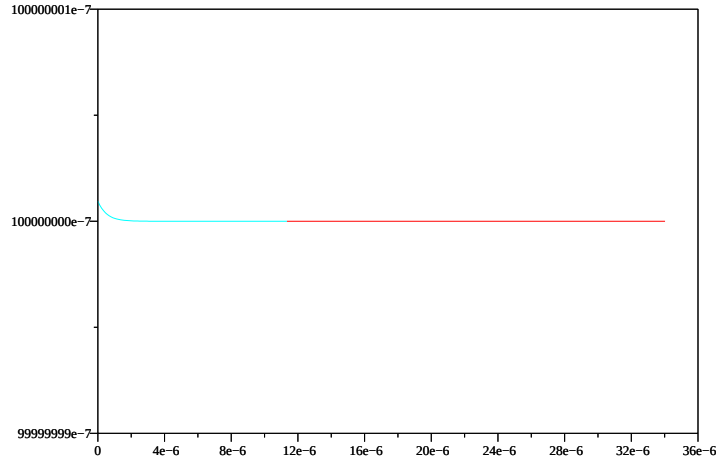


Figure 2: concentration of Fe^{2+}

anisotropic behaviour of the solution is introduced. The proof of the convergence of the domain decomposition method is given. The numerical results

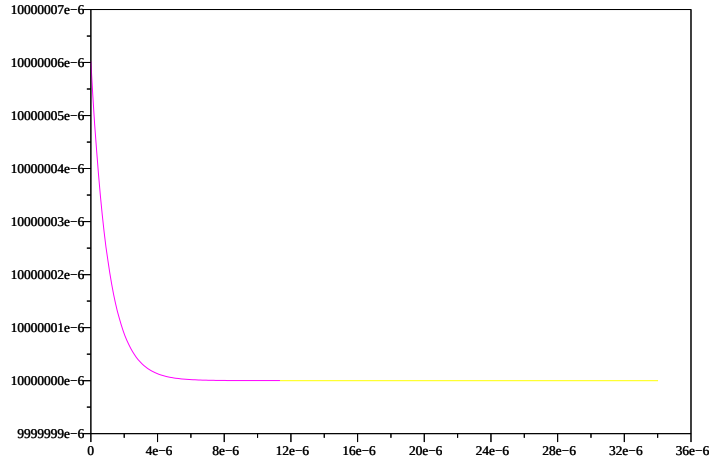


Figure 3: concentration of H^+

in a real case shows clearly that the process take place near the cathode.

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