Fluid Flow, Potential and Concentration Distributions in Electrochemical Processes

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In this paper a software tool called ELSY$^+$ (Electrochemical Systems + fluid flow) to calculate the fluid flow, current densities and mass transport effects in arbitrary shaped electrochemical reactors is presented.

In a first step the fluid flow in a given reactor is obtained numerically. In a second phase the mass transport due to diffusion, convection and migration due to electrical forces (the dilute solution model), together with complex electrode reaction is calculated. The main advantage of this dilute solution model is the ability to study local mass transport effects.

After a brief mathematical description of the model, practical examples are presented. They highlight clearly the interactions of the fluid flow on the concentration, potential and current density distributions in a reactor.

Furthermore, the analysis capabilities of the external electrical network module in ELSY are demonstrated by examining the current density distribution in a cascade of continuous strip plating reactors.

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Introduction

Although advanced numerical methods exist and have been applied with great success in a broad range of engineering domains (hydrodynamics, aerodynamics, structural mechanics, heat transfer, …), the use of these methods for electrochemical applications remains very limited. One of the main reasons for this might be the complexity of the processes that govern electrochemical reactors. These processes are:

- electrochemical kinetics at electrodes,
- hydrodynamics of the electrolytic solution,
- mass transport of ions and uncharged species due to convection, diffusion and migration,

and eventually also

- homogeneous reactions,
- gas evolution,
- heat generation in the bulk and at the electrode-electrolyte interfaces.

Ideally, a numerical software system should treat (almost) all the effects described above to simulate an electrochemical process.

In what follows a brief mathematical description of the equations governing electrochemical processes is given. Then, some examples calculated by the software ELSY$^+$ are presented. They take already important aspects into account. In a second part of the paper the potentialities of combining electrical networks with electrochemical reactor simulations are presented. To that purpose a simpler reactor model is used.

Simulations of mass and charge transfer

Introduction

An electrochemical system essentially consists of ionic solutions bounded by electrodes, membranes and insulators. At the electrodes, electrochemical reactions take place. The flow of electrons in the outer electrical circuit is converted into a flow of ions in the electrolyte. At the same time, there will be a transfer of material and charge in the solution. The mass transfer of the ions from the solution to the surface of the electrodes requires a description of each mobile ionic species, based on fluid mechanics, material balances, and electroneutrality.

Fluid dynamics equations

The conservation of mass of an electrolyte solution is given by :

$$\frac{\partial r}{\partial t} = -\vec{\nabla}.\left(r\vec{v}\right), \qquad (2a)$$

with the density of the electrolyte and $\vec{v}$ the velocity vector. If the electrolyte density can be assumed constant, equation (2a) reduces to:

$$\vec{\nabla}.\vec{v} = 0. \qquad (2b)$$

The Navier-Stokes equation describes the fluid flow in an electrochemical reactor. It is the expression for the conservation of momentum for viscous fluids. For a Newtonian incompressible with a dynamic viscosity , the momentum equation is:

$$r\left(\frac{\partial \vec{v}}{\partial t} + \left(\vec{v}.\vec{\nabla}\right).\vec{v}\right) = m\vec{\nabla}^2\vec{v} - \vec{\nabla}p + r\vec{g}\,, \quad (3)$$

with:

$m\vec{\nabla}^2\vec{v}$ the viscous forces,

$\vec{\nabla}p$ the gradient of the hydrostatic pressure,

$r\vec{g}$ the force of gravity,

and all terms expressed in $\frac{kg}{m^2 s^2}$. The solution of equations (2b) and (3) yields the velocity field $\vec{v}$ and pressure p in each point of the reactor.

Transport equations in dilute solutions

In many practical situations, the solution contains a large amount of solvent (water) which does not contribute to the reactions. It is then assumed that the motion of the charged species does not influence the fluid flow. Thus the general equations describing the "dilute solution model" are obtained [1]. It is considered that in a given fluid flow field the motion of each species is due to the combined effect of *migration* (the electrical field acting upon charged species), *diffusion* (concentration differences) and *convection* (the flow field). In that case, the local molar flux of each dissolved species k is given by:

$$\vec{N}_k = -z_k u_k F C_k \vec{\nabla} U - D_k \vec{\nabla} C_k + \vec{v} C_k \qquad (4)$$

with C_k the molar concentration in mol/m^3, z_k the charge, u_k the mechanical mobility in m^{2}mol/Js, U the potential in V, D the diffusion coefficient in m^2/s, $\vec{v}$ the velocity of the solvent in m/s and F Faraday's constant (96487 C/mol).

Migration is specific to electrochemical systems and is caused by the movement of charged species due to external electrical forces. It is described by the mechanical mobility, the electric charge, the concentration of the ionic species and the electric field.

Diffusion is caused by the concentration difference of an ion from point to point in the solution. The ions will move to places with lower concentration until a uniform distribution of this species in the solution is achieved. This movement is well described by Fick's law, which indicates that the diffusion is proportional to the minus gradient of the concentration. The proportionality is described by the coefficient D_k, which in dilute solutions can be considered constant at constant temperature and pressure.

Convection is caused by the motion of a particle together with the whole fluid. In the case of a dilute solution, the fluid's motion is not affected by the presence of the ions. Therefore the flux due to convection is only determined by the velocity of the fluid $\vec{v}$ and the concentration C_k of the ion.

For each species k one can state that at each point in the solution, the change of concentration is equal to the net input plus the local production (or reduction) due to chemical reactions. In differential form this is described as follows:

$$\frac{\partial C_k}{\partial t} = -\vec{\nabla}.N_k + R_k \,, \qquad (5)$$

with:

$\vec{\nabla}.\vec{N}_k$: the divergence of the flux vector,

R_k : the production rate of an ion.

The production per unit volume R_k (in mol/m^{3}s) involves homogeneous chemical reactions in the bulk of the solution, but no electrode reactions. In electrochemical systems, reactions are frequently restricted to electrode surfaces, in which case R_k is equal to zero.

Furthermore, the electroneutrality of the solution needs to be imposed. For an electrolyte containing I ions, this is expressed by:

$$\sum_{k=1}^{I} z_k C_k = 0 \qquad (6)$$

The combined solution of equation (5) and (6) will yield the concentration and potential in each point of the electrochemical reactor. From this, the current density in the bulk and along the electrodes, and the total current through the electrodes can be calculated.

Heat transport equation

The equation describing the temperature distribution in the electrolyte is:

$$c_p \rho \left(\frac{\partial T}{\partial t} + \vec{v}.\vec{\nabla}T \right) = \vec{\nabla}.\left(\lambda \vec{\nabla} T\right) + Q_s \qquad (7)$$

with c_p the heat capacity, T the temperature, $\vec{v}$ the velocity field, the heat conduction and Q_s the local heat dissipation. This equation will allow to calculate the temperature distribution in the electrochemical system. The heat dissipation in the fluid, due to ohmic losses is in many cases negligible. On the other hand, the heat dissipation due to electrode processes may be considerable (e.g. anodising processes).

In reality the material properties like the diffusion constant, the viscosity and the density vary with the temperature. This means that when the temperature can no longer be assumed constant, all the equations mentioned above become temperature dependent through their material properties. In that case, the simultaneous treatment of equations (2a),(3),(5),(6) and (7) is required.

Boundary conditions

The boundary conditions in an electrochemical system will be different for flow inlets and outlets, insulating walls and electrodes (cathodes and anodes).

On an inlet, the velocity, the values of the bulk concentration of each species and the temperate of the fluid must be imposed. On outlets, only the reference pressure needs to be imposed.

On non-moving insulating walls, the velocity vectors zero, and there is no current going through them, so the concentration and potential gradients are also zero.

The electrode boundary conditions for the electrochemical equation are much more complex, depending on the reaction mechanism of the electrode reactions [2]. For a wide variety of plating applications, the potential difference between two electrodes forces metal ions to be deposited at the more negative electrode (cathode), and eventually metal is also dissolved at the other electrode (anode). Both metal deposition and dissolution involve also a driving force, the overvoltage, the difference between the potential of the electrode (V) and the potential of the electrolyte next to electrode (U). This overpotential depends only on the local current density j. In general one can write

$$h = V - U = f(\mathrm{j}) \,. \qquad (8)$$

Particular mathematical expressions of the overpotential relation will be shown in the examples section.

Examples

Submerged jet – Copper plating

A submerged jet cell is used to demonstrate the different possibilities of the ELSY$^+$ software system. A schematic drawing of the geometry of this axi-symmetrical cell is shown in figure 1. Remark the small inlet channel with a radius of 1 mm on the left and the working electrode (cathode) with a radius of 20 mm (Electrode 1) on the bottom of the cell. The axis of symmetry is on the left hand side of the drawing.

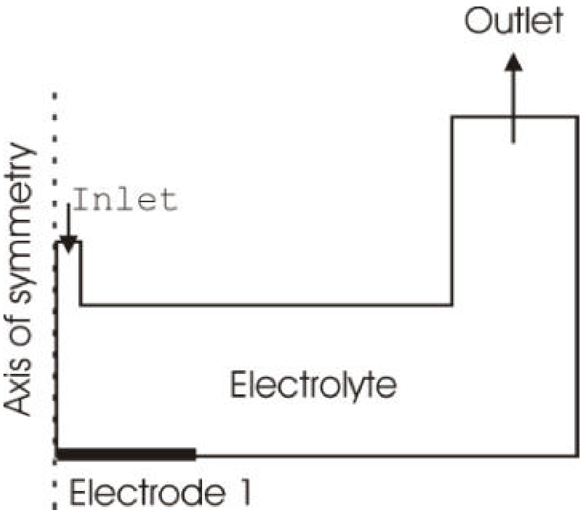

Figure 1 : The geometry of the jet cell.

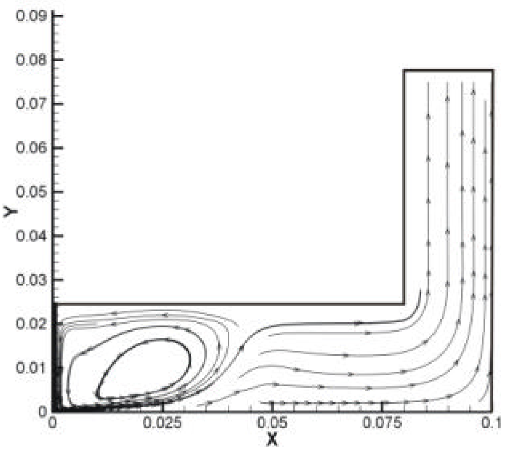

Figure 2 : The flow field in the jet cell. Dimensions in m.

The fluid flow as shown in figure 2 was calculated for a Reynolds number of 330. Close to the axis of symmetry, the flow has to change direction, but at some distance from the wall the parallel flow regime is reached. Figure 7 also shows a detail of the flow field close to the cathode.

In a next step, the concentration, potential and current density distributions were calculated. This was done for an electrolyte consisting of 3 ions with the following properties:

	Z	C (mole/m^3)	D (m^2/s)
Cu^{2+}	+2	300	4.2E-10
HSO_4^-	-1	2300	8.1E-10
H^+	+1	1700	5.7E-9

The overpotential relation describing the cathode reaction (deposition of cupper) is

$$J = J_0 \left(\frac{C}{C_n} \right)^g \left(e^{a \frac{zF}{RT} h} - e^{-b \frac{zF}{RT} h} \right) \qquad (9)$$

with J_0= 5 Am^{-2}, α = 0.25, β = 0.25, T = 300 K and Z = 2. C is the concentration of the reacting ion, C_n the bulk concentration of the reacting ion (300 mole/m^3) and γ is chosen to be equal to 1. The applied potential difference between cathode and anode, here placed on top of the cell, is -0.9 V, with a reference potential of zero at the anode. The corresponding potential distribution is shown in figure 3. The concentration distribution of the reacting ion is given in figure 4, with a zoom near the cathode extremity given in figure 5.

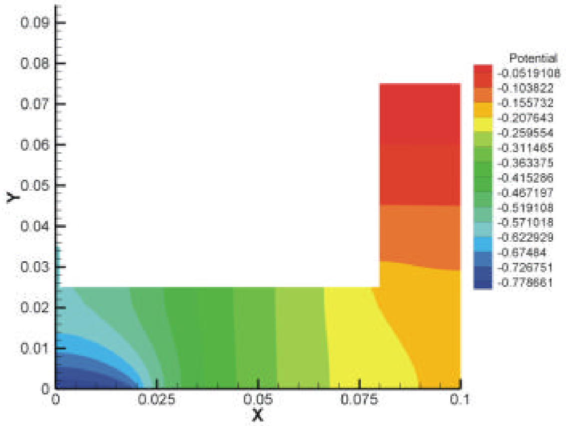

Figure 3 : Potential distribution in the jet cell. Dimensions in m.

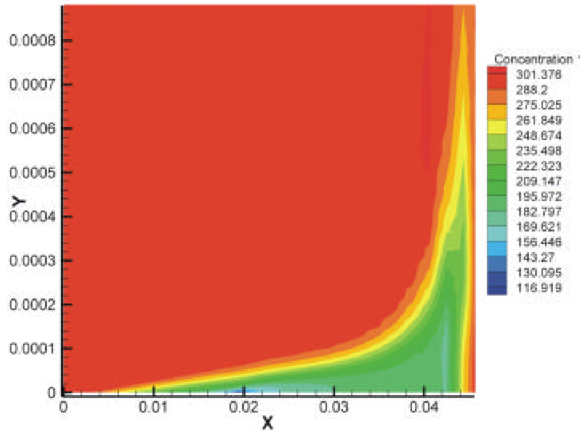

Figure 4 : The concentration distribution. Dimensions in m.

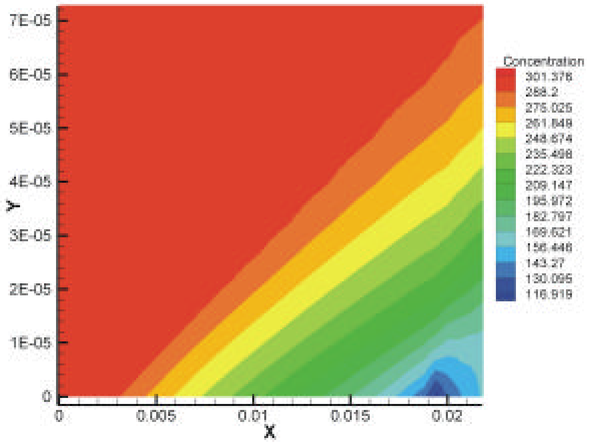

Figure 5 : Concentration boundary layer next to the cathode extremity. Dimensions in m.

Remark that the concentration boundary layer is very small (about 50 m) and that the fluid flow has a much smaller effect on the potential distribution then on the concentration.

Figure 6 is a plot of the current density along the cathode. It is can be noticed that the current density (and thus the deposit thickness) varies considerably over the cathode. This is due to mass transport effects but also to the fact that the inner part of the cathode is less accessible to the potential.

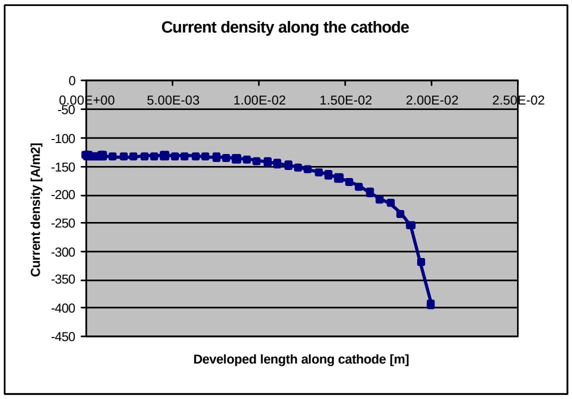

Figure 6 : Current density along the cathode.

Submerged jet – Anodising

The temperature distribution was calculated in the submerged jet cell of figure 1 in which electrode 1 is now the anode. It is well known that the anodising reaction generates a considerable amount of heat equal to J, in this example equal to 8500 W/m2. The resulting temperature field near the cathode is shown in Figure 7. Also the streamlines of the flow near the cathode are shown. The temperature at the inlet is 298 K. As can be seen from figure 7, a temperature difference of 14 K is reached over the length of the cathode. Although not considered in this example, the characteristics of the anodising reaction are highly depending on the local temperature. This will in turn influence the oxide layer thickness.

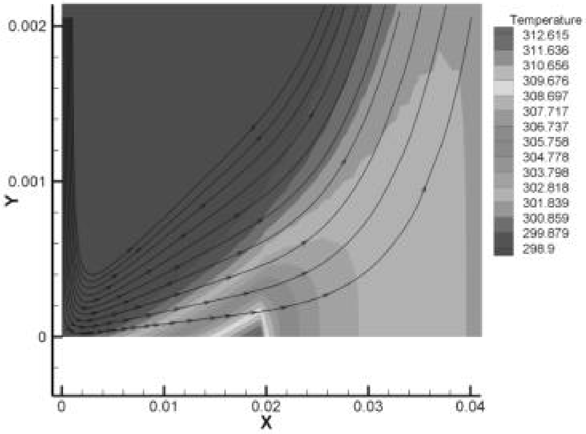

Figure 7 : temperature distribution near the cathode during anodising. Dimensions in m.

Simulations of electrical circuits connecting electrodes

Introduction

In practice, all electrodes of an electrochemical cell are connected to a rectifier. These connections have small but non negligible resistances that can considerably influence the current balance between the electrodes. In quite some other applications, such as in continuous steel strip or wire plating lines, several electrochemical cells are put in series. This means that the behaviour of one cell influences all the others.

In order to enable such simulations, a new module has been added to the ElSy software [3]. The theoretical aspects of this module can be found in [4].

In what follows an example is given.

Feeding two reactors

In figure 8 part of a steel plating line is presented. In this example a steel strip, being the cathode and passing simultaneously through all cells, realizes a first electrical connection between the cells. On the other hand also the current source(s) and earth contacts make that cells are coupled. One current source of 8000 A feeds two identical cells. All connections as well as the strip are resistive. Due to the voltage drop in the steel strip the current distribution can be influenced and a circulation current via the earth can occur.

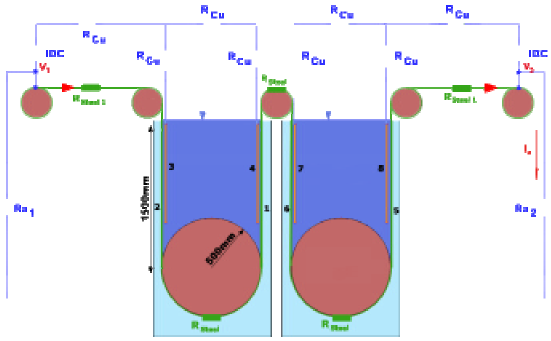

Figure 8 : Two-dimensional cross section of a steel Zinc plating line.

Remark that, due to the anode configuration[1] and the two-dimensional cross section, only the part between the bottom roll and the strip forms the cell geometry is to be modeled. The electrodes with numbers 2, 1, 6 and 5 are to be galvanized (cathodes). The electrodes 3, 4, 7 and 8 are the anodes. The numerical data used in this example are:

- Dimension of the steel strip: 1000x3 mm,
- Dimension of the cell: 1500x1000 mm with semi-circular bottom,
- Conductivity of the solution: 20 $^{-1}$m^{-1},
- Dimension of the four anodes: 1000x20 mm,
- Anodic reaction: J=5000. ,
- Cathodic reaction: Butler-Volmer:

$$J = J_0\left(e^{a\frac{nF}{RT}h} - e^{-b\frac{nF}{RT}h}\right) \qquad (10)$$

with J_0=300A/m², α=0,7, β=0,3 *and* n=2,

- $R_{Cu} = 1.10^{-5}$, $R_{Steel1} = 2,5.10^{-3}$, $R_{Steel} = 4.10^{-5}$, R_{e1}=2 en R_{e2}=5 .

With these data, the current density distributions shown in figure 9 are obtained.

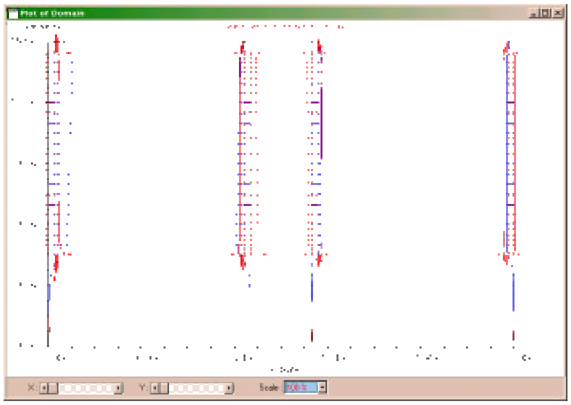

Figure 9 : Current density distributions along the electrodes.

The mean current densities of the four cathodes (from entrance to outlet with numbers 2, 1, 6 and 5) are respectively 2268 A/m^2, 1322 A/m^2, 983 A/m^2 and 752 A/m^2. In other words, the efficiency of the second cell is about 50 % lower than the first one. The voltage drop in the steel strip between the entrance of the first cell and the outlet of the second cell is 24,5 V. With a total earth resistance of 7 the circulation current is 3,5 A.

Starting from this initial situation the designer can improve the performances of the global system by changing the resistances, the cell geometries, the number of sources, the way of connecting the reactors, etc. .

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[1] Only the upper side of the strip is galvanized.

Conclusions

It is believed that the use of numerical models can considerably improve the understanding of many electrochemical processes. As the examples show, simulation software can be a powerful tool to comprehend and optimise a wide variety of electrochemical systems. Therefore the authors believe simulation is an essential step on the way to more performing electrochemical reactors.

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