Modelization of a Bipolar Electrochemical Reactor

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Abstract. We explain the principles of a software able to compute electrical potentials and currents in electrochemical plane systems, composed of electrodes, electrolytes, and insulators. At interfaces electrodes-electrolytes, the relationship between the potential jump and the crossing current is modeled by any nondecreasing function (called generalized Butler-Volmer function, Eqn. 1.2). This takes in account the thermodynamical barriers, oxydations, reductions, and diffusion limitations. The conductivity of the different environments can be constant or variable. We give three formulations of the problem to solve (Eqns. 2 and 3), then (Eqn. 4), we show the finite element discretization. This yields to a nonlinear equations system that we discuss. Furthermore, we describe an original method to determine floating potentials of electrodes (Eqn. 8). Examples are chosen to show the possibilities of softwares and methods. These examples are relatively simple, but we are able to compute more complex configurations.

1. Introduction, General Points

A bipolar electrochemical reactor is a system composed of electrodes (metal, good electrical conductor), electrolyte (liquid, middle conductor) in which electrodes and insulators are immersed. We put two electrodes to different potentials. We want to compute the potential and the electrical current distribution in all the system.

1.1. Geometry

\(\Omega^e\) is the bounded domain of \(\mathbb{R}^2\) or \(\mathbb{R}^3\) occupied by the system. Suppose that we have only one electrolyte \(\Omega^e\). \(\Omega^m_i\) is the domain occupied by the electrolyte. The domains \(\Omega^e\) and \(\Omega^m_i\) (\(i = 1, 2, 3, \ldots, nm\)) are related. (Fig. 1).

Let \(\Omega^e\), \(\Omega^m_1\), \(\Omega^m_2\), \(\Omega^m_3\), \(\ldots\), \(\Omega^m_{nm}\) the domains occupied by the \(nm\) electrodes. The domains \(\Omega^m_i\) and \(\Omega^m_j\) (\(i \neq j\)) are related. (Fig. 1).

\[\Omega^e = \Omega^e \cup \Omega^m_1 \cup \ldots \cup \Omega^m_{nm}\]

The frontier \(\partial \Omega^m_i\) of each electrode \(\Omega^m_i\) are of the following three types:

\(\Gamma^m_{in}\): part of \(\partial \Omega^m_i\) in contact with an insulator.

\(\Gamma^m_{id}(V_i)\): part of \(\partial \Omega^m_i\) at a fixed potential \(V_i\).

\(\Gamma_{iBv}\): part of \(\partial \Omega^m_i\) in contact with the electrolyte.

With \(\partial \Omega^m_i = \Gamma^m_{in} \cup \Gamma^m_{id}(V_i) \cup \Gamma_{iBv}\)

The frontier \(\partial \Omega^e\) of the electrolyte \(\Omega^e\) are of the following two types:

\(\Gamma^e_{N}\): part of \(\partial \Omega^e\) in contact with an insulator.

\(\Gamma_{iBv}\): part of \(\partial \Omega^e\) in contact with the electrode \(\Omega^m_i\)

All the considered frontiers are either empty, either of non-null length.

1.2. Physics

Suppose that all phenomena are stationary. All time-derivatives variables are null \((\partial t = 0)\). Ohm's law gives the relationship between the electrical current density \(i\) and the electrical field \(E\); \(i = \sigma E\), where \(\sigma\) is the electrical conductivity of the environment \((\sigma\) may be variable).
Knowing that the electrical field derives from the potential \( \Phi, E = -\text{grad} \Phi \), we obtain: \( i = -\sigma \text{grad} \Phi \).

Then the conservation law of the electrical current, here, \( \text{div}(i) = 0 \) gives:

\[
\text{div}(\sigma \text{grad} \Phi) = 0
\] (1.1)

Suppose that equation gives the potential distribution in the electrodes and electrolyte. Dirichlet boundary condition gives no particular problem. To describe the others boundary conditions or interfaces electrodes-electrolyte conditions, we adopt the following conditions:

a) Electrolyte-Insulator or Metal-Insulator frontiers (Fig. 2)

\( \gamma \): normal to the frontier pointed to the insulator; \( \| \gamma \| = 1 \).

The current does not cross the frontier is expressed by:

\[
\frac{d \Phi}{d \gamma} = \left. \Phi \right|_{\gamma} = 0
\] (1.2)

b) Electrolyte-Metal Frontier (Fig. 3)

\( \gamma \): normal to the frontier pointed to the metal; \( \| \gamma \| = 1 \).

\( i = \left. \sigma \text{grad} \Phi \right|_{\gamma} \): current flow density crossing the interface at \( P \).

Generalized Butler-Volmer's law indicates that current flow density is in relationship with the potential jump at the interface.

\[
i = \varphi (\Phi_m - \Phi_r)
\] (1.3)

where \( \varphi : \mathbb{R} \to \mathbb{R} \) is a nondecreasing, continuous function with \( \varphi(0) = 0 \). It is built with tables and data provided from ALYSER\textsuperscript{a} company, and we use it for the numerical examples (Fig. 4).

Then (Eqn. 1.3) gives

\[
\sigma^m < \text{grad} \Phi^m \left| \gamma \right. + \varphi (\Phi_m - \Phi_r) = 0
\] in the electrolyte or

\[
\sigma^m < \text{grad} \Phi^m \left| \gamma \right. + \varphi (\Phi_m - \Phi_r) = 0
\] in the electrolyte (metal)

(1.4)

There is current conservation crossing the interface.

1.3. Remark

The generalized Butler-Volmer relation is a characteristic of the couple electrolyte-metal. And for each couple, we have a different relation. Suppose that all electrodes are from the same metal, thus there is only one generalized Butler-Volmer relation.

2. Differential Formulation of the Problem

In each electrode \( \Omega^m_i \) the electrical potential \( \Phi^m_i \) is solution of the problem:

\[
\begin{align*}
\text{div}(\sigma^m_i \text{grad} \Phi^m_i) &= 0 & \text{in } \Omega^m_i \\
\frac{d \Phi^m_i}{d \nu} &= 0 & \text{on } \Gamma^m_{iN} \\
\Phi^m_i &= V_i & \text{on } \Gamma^m_{iB}(V_i) \\
\sigma^m_i < \text{grad} \Phi^m_i \left| \gamma \right. + \varphi (\Phi^m_i - \Phi^e) &= 0 & \text{on } \Gamma_{iBV}
\end{align*}
\] (2.1)

(\( i = 1, 2, \ldots, nm \))

\( \sigma^e \): electrical conductivity of the electrolyte, it is a continuous, differentiable function defined on \( \Omega^e \).

\( \Gamma^e_N \) is the part of the border of the electrode that the current do not cross.
To determine the potential distribution in the electrochemical system $\Omega$, we have to solve all the Eqs. 2.1 and 2.2. These equations are linked with generalized Butler-Volmer conditions at interfaces electrodes-electrolyte. This system is not linear due to the non-linearity of the generalized Butler-Volmer relations.

Eqs. 2.1 and 2.2 defined the differential or classical formulation.

The problem 1 is:

Find functions $\Phi^\sigma$ and $\Phi^\tau$ verifying Eqs. 2.1 and 2.2.

3. Adapted Formulations to the Finite Element Method (FEM)

Consider first some spaces of functions adapted to the problem. Let $\Omega$ a bounded domain of $\mathbb{R}^2$ (or $\mathbb{R}^3$), $\partial \Omega$ is the frontier of $\Omega$. ($\partial \Omega$ is a closed curve if $\Omega \subset \mathbb{R}^2$ and a closed surface if $\Omega \subset \mathbb{R}^3$.) Let $\Gamma$ a non-null length part of $\partial \Omega$. $\mathcal{H}^1(\Omega)$ is the set of all the functions defined on $\Omega$ and, if $f$ is a such function, the integral:

$$\int_{\Omega} f^2 + \| \text{grad} f \|^2 \, d\tau$$

exists and is bounded.

d is the surface element if $\Omega \subset \mathbb{R}^2$ and the volume element if $\Omega \subset \mathbb{R}^3$. The functions of $\mathcal{H}^1(\Omega)$ have no constraints on $\partial \Omega$, the frontier of $\Omega$. We introduce constraints on $\Gamma$, then we select some functions of $\mathcal{H}^1(\Omega)$. We choose the functions taking the fixed value $V$ on $\Gamma$. This set of functions is:

$$\mathcal{H}^1(\Omega, \Gamma(V)) = \{ f \in \mathcal{H}^1(\Omega); f|_\Gamma = V \}$$

Then, the problem 2, called weak formulation of the problem 1, becomes:

Find $\Phi^\sigma \in \mathcal{H}^1(\Omega(V))$; $i = 1, 2, \ldots, nm$

and $\Phi^\tau \in \mathcal{H}^1(\Omega)$ such that:

$$\sum_{i=1}^{nm} \left( \int_{\Omega} \sigma^\sigma < \text{grad} \Phi^\sigma \cdot \text{grad} u^\tau \, d\tau \right) + \int_{\Gamma} \sigma^\sigma < \text{grad} \Phi^\tau \cdot \text{grad} u^\tau \, d\tau +$$

$$\int_{\Gamma_{\text{by}}} \phi (\Phi^\tau_{i} - \Phi^\sigma_{i}) (u^\tau_{i} - u^\sigma) \, ds = 0$$

for any $u^\tau \in \mathcal{H}^1(\Omega)$ and for any $u^\sigma \in \mathcal{H}^1(\Omega(V))$; $i = 1, 2, \ldots, nm$

where $ds$ is the length element, if $\Gamma_{\text{by}}$ is a curve, and $d\tau$ is the surface element, if $\Gamma_{\text{by}}$ is a surface.

Introduce a primitive of $\phi$.

3.1. Theorem 1: The Problem 2 Has a Unique Solution

1. The demonstration of this theorem is in an internal report [5]. The important hypothesis is that the generalized Butler-Volmer function $\phi$ is nondecreasing. This theorem is important for the practical aspects, proving the mathematical modeling consistency.

2. The demonstration of this theorem is constructive: it uses a method allowing the numerical solving of the problem. This method is quite complicated to employ, and we have preferred (without excluding), more simple methods. There will be developed in Eqn. 4.

3. We show also that the problem 3 is equivalent to the problem 2.

4. If the solution of problem 2 is enough normally regular, it is solution of the problem 1.

5. Thus, whatever the conductivities of the environments (strictly positive, continuous functions in each environment), whatever the potentials $V_i$ given, whatever the generalized Butler-Volmer functions $\phi_i$, the problem 2 has a unique solution which gives the potential distribution in all the system. From there, we obtain the current distribution.
We built the triangulation shown on Fig. 8. Then, the contribution to the integral (3.2) relative to the node \( P \) is:

\[
\varphi \left( \Phi_i^m(P) - \Phi_e(P) \right) (u_i^m - (u_e^*)) \left[ |PC| + |PD| \right]
\]

and this integral (3.2) is approached by:

\[
<\mathcal{B}_i(\Phi_i^m, \Phi_e) \left( u_i^m - u_e^* \right)>
\]

where \( \mathcal{B}_i(\Phi_i^m, \Phi_e) \) is a vector depending on the interface \( \Gamma_{ibv} \). Pratically, we introduce only one vector \( \Phi \) of the node values triangulation, and we give two numbers to each node of an interface electrolyte-electrode. Then, the approached problem of the problem 2 becomes:

Find \( \Phi \) satisfying Dirichlet boundary conditions, solution of the system:

\[
A \Phi + \mathcal{B}(\Phi) = 0 \quad (4.2)
\]

(4.2) is a nonlinear equations system, composed of a linear part \( A \Phi \), coming from electrolytes and electrodes (non-constant potential) and a nonlinear part, \( \mathcal{B}(\Phi) \), coming from interfaces where a generalized Butler-Volmer condition is fixed.

4.3. Physical Interpretation

A physical interpretation of the components of the vector \( \mathcal{B}(\Phi) \) can be given. Let \( P \) a interface node (Fig. 8). This node has two numbers \( I_1 \) and \( I_3 \). Let \( \Phi \) the solution of the system (4.2). The component \( I_1 \) of \( \Phi \) is the potential in the electrolyte \( P \) and the component \( I_2 \) is the potential in the electrode.

Let \( \Phi_1 \) and \( \Phi_2 \) are these two components. \( \mathcal{B}_{i1}(\Phi) \) : \( I_1 \) component of the vector \( \mathcal{B}(\Phi) \).

\( \mathcal{B}_{i2}(\Phi) \) : \( I_2 \) component of the vector \( \mathcal{B}(\Phi) \).

Then, \( \mathcal{B}_{i1}(\Phi) \) is the current crossing \( CD \).

If \( \mathcal{B}(\Phi) > 0 \), the current is entering into the metal.

If \( \mathcal{B}(\Phi) < 0 \), the current is entering into the electrolyte.

And \( \mathcal{B}_{i1}(\Phi) = -\mathcal{B}_{i2}(\Phi) \).

If the situation is like in Fig. 9, It is only the length of \( PC \) which is taken instead of \( PC + PD \).

4.4. Remark

The vectorial equation Eqn. 4.2 says, in a certain way, that there is full current conservation.

\[
\int_{\Gamma_{ibv}} \varphi \left( \Phi_i^m - \Phi_e \right) (u_i^m - u_e^*) ds
\]

(4.1)
4.5. Theorem 2: The Approached Problem has a Unique Solution

This unique solution is the vector \( \Phi \)
and its components are the electrical potential values in each node of the mesh. Solving the set down approached problem, we obtain the potential in the electrolyte, in the electrodes and the potential jumps at the interfaces electrodes-electrolytes. Finally, from potentials, we get easily the currents.

5. The Potentials in the Electrodes Are Given

The conductivities of the electrodes is largely superior to the conductivity of the electrolyte \((\sigma_e/\sigma = 10^5)\). This yields the near constancy of the potential of each electrode. \(V_i\) is the constant potential of the electrode \(\Theta^e_i\), \(i = 1, 2, \ldots, nm\). Then the only unknown potential distribution is in the electrolyte.

If \(\Phi^e\) is this distribution, it is a solution of a similar problem to (2.2).

For the finite element approximation of (5.2), we discretize only the electrolytic domain. The problem of potential jumps at the interfaces electrode-electrolyte is solved, because the potential of the electrodes is supposed to be known, and only the potential in the electrolyte is unknown. Then, in Egn. 4, we obtain for the vector \(\Phi^e\) of the potential values at the nodes, the Egn. 5.3

\[
A \Phi^e + B(\Phi^e) = 0
\]  

with the same meaning of terms as the Egn. 4.2.

6. Examples Showing the Difference between the Two Systems of Eqns. 4.2 and 5.3

6.1. The Electrodes Potential is Unknown

The situation is described line Fig. 10. We give the elements and the node numbers. One node of the interface receive two numbers, one for what is happening in the electrode and the following number for what is happening in the electrolyte. (This order is conventionally choosen.)
The potential in the electrodes are unknown, they are meshed.

\[ x_i \] is the \( i_{th} \) component of \( \Phi \), i.e., the unknown value, of the potential at the node number 1.

\[ x_1 \] : potential at the node number 1.

\[ x_3 \] : potential at the node number 3, at the interface, in the electrode.

\[ x_4 \] : potential at the node number 4, at the interface, in the electrolyte.

Then, the equation number 2 of (4.2) has the following form:

\[
\begin{align*}
\alpha_2.1x_1 + \alpha_2.2x_2 + \alpha_2.3x_3 + \alpha_2.4x_4 + \\
\alpha_2.9x_9 + \alpha_2.10x_{10} + \alpha_2.12x_{12} &= 0 \quad (6.1)
\end{align*}
\]

This is the equation relative to the node 2. All the equations relative to nodes which are not on an interface are similar: they are linear.

The coefficients \( \alpha_{2,1} \), \( \alpha_{2,2} \), \( \alpha_{2,4} \), \( \alpha_{2,7} \), \( \alpha_{2,9} \), \( \alpha_{2,10} \), \( \alpha_{2,12} \) are the non-null elements of the matrix \( A \).

Taking the two equations relative to a same node interface:

\[
\begin{align*}
\alpha_{3,1}x_1 + \alpha_{3,3}x_3 + \alpha_{3,5}x_5 + \alpha_{3,9}x_9 + \alpha_{3,11}x_{11} + \\
\mu \Phi (x_3-x_4) &= 0 \quad (6.2)
\end{align*}
\]

\[
\begin{align*}
\alpha_{4,2}x_2 + \alpha_{4,4}x_4 + \alpha_{4,8}x_8 + \alpha_{4,12}x_{12} - \\
\mu \Phi (x_5-x_4) &= 0 \quad (6.3)
\end{align*}
\]

where \( \mu \) is the half-length of the segments 4–9 and 4–12. Here, the term \( \Phi (x_3-x_4) \) is the third line of the vector \( B \Phi \) and \( \mu \Phi (x_5-x_4) \) is the fourth.

6.2. Remark

The two Eqs. 6.2 and 6.3 are in relationship only, because there is the non-linear term. This observation is very important for the numerical solving of the system (4.2).

6.3. The Electrodes Potential is Known

The situation is described Fig. 11. The nodes at the interfaces receive only one number. The second line of the system of Eqn. 5.3 is, in this case:

\[
\begin{align*}
\alpha_{1,1}x_1 + \alpha_{1,3}x_3 + \alpha_{1,5}x_5 + \alpha_{1,9}x_9 + \\
\alpha_{1,11}x_{11} + \alpha_{1,13}x_{13} + \mu \Phi (V-x_4) &= 0 \quad (6.4)
\end{align*}
\]

This is an equation relative to a node in the electrolyte. For a node on the interface, we have, for the equation relative to the node 3:

\[
\begin{align*}
\alpha_{3,1}x_1 + \alpha_{3,3}x_3 + \alpha_{3,5}x_5 + \\
\alpha_{3,9}x_9 - \mu \Phi (V-x_4) &= 0 \quad (6.5)
\end{align*}
\]
7. Numerical Solving of the Nonlinear Equations System

To solve a system of \( N \) \( \text{Eqns.} \) with \( N \) unknown values (\( N \) can be huge), which possesses a unique solution, it is necessary to choose a method taking into account all the information known about this system. This yields to a reduction of the computation time.

The system has the following form:

\[
A \Phi + B(\Phi) = 0
\]

where \( A \) is a \( N \times N \) sparse matrix and \( B(\Phi) \) a vector of \( N \) components which many are null.

Computerize an alternating direction method due to Kellogg \[3\], let a parameter \( A > 0 \), and from an initial vector \( \Phi_0 \), we build two sequences \( \Phi_n \) and \( \Phi_{n+1/2} \) of vectors with the following relations:

\[
\begin{align*}
\lambda [\Phi_{n+1/2} - \Phi_n] + A [\Phi_{n+1/2} + B(\Phi_n)] &= 0 \quad (7.1) \\
\lambda [\Phi_{n+1/2} - \Phi_{n+1/2}] + A [\Phi_{n+1/2} + B(\Phi_{n+2})] &= 0 \quad (7.2)
\end{align*}
\]

The Eqn. 7.1 can be written:

\[
(\lambda I + A) \Phi_{n+1/2} = \lambda \Phi_n - B(\Phi_n) \quad (7.1)
\]

\( (I: \text{unit } N \times N \text{ matrix}) \) and now \( \Phi_{n+1/2} \) is determined knowing \( \Phi_n \), solving the linear system (7.1).

The Eqn. 7.2 can be written:

\[
\lambda \Phi_{n+1} + B(\Phi_n) = (\lambda I - A) \Phi_{n+1/2} \quad (7.2)
\]

This is a nonlinear system for \( \Phi_{n+1} \), the vector \( \Phi_{n+1/2} \) is known from (7.1).

\( \Phi_0 \) and \( \lambda \) chosen, we solve consecutively both systems, obtaining iteratively a series of vectors \( \{\Phi_n\} \). This sequence should converge to the unique solution of the initial system.

7.1. Theorem 3: When the Potential of Each Electrode Is Known (6.2), the Sequence Converges to the Solution, for All \( \lambda > 0 \) and \( \Phi_0 \)

In this case (6.2), we programmed the Kellogg's algorithm and proved numerically the truth of this theorem. The exact demonstration has of course been done \[5\].

Examine how the equation relative to the node 3 - Eqn. 6.5 is expressed in the form of (7.2).

Let \( u \) unknown, the value \( x_u \) at the step \( n+1 \), solve the following equation:

\[
\lambda u - \mu \Phi (V - u) = b \quad (7.3)
\]
where $b$ is known. The Eqn. 7.3 due to the discretization that we made, has only one unknown. Thus, all the equations of the system (7.2) are decoupled. We have built a powerful and fast method to solve (7.3).

Figs. 12 and 13 show computation results when the electrodes potential is known.

In the case (6.1), where the electrodes potential are unknown, it is not possible to prove a similar theorem to the theorem 3, although the system (4.2) has a unique solution. We even programmed the Kellogg's method ((7.1) and (7.2)) in this case, and we remarked that this algorithm can converge or not, depending on the geometry, the value of the parameter $\lambda$ and the values of the physical constants.

Figs. 14–16 show computation results when the electrodes potential is not given.

8. Determination of the Electrodes Potential: Floating Potentials

The computation method in the electrolyte, knowing the electrodes potential, is very powerful. We preferred to find the floating potentials in the electrodes instead of developing a new solving method of the nonlinear system (4.2). To determine the floating potentials, we have two different methods:

8.1. The System Possesses Some Symmetries

This case is frequent in practice. On the horizontal symmetry axis, the electric current follows this axis. (see Fig. 17). Then, the computation becomes unidimensional and allows the determination of potentials.

8.2. General Case

Let $\Omega_i^v$, $i = 1, 2, \ldots, nm$, the electrodes. $\Gamma_{iBV}$ is the interface of the electrode $i$ and the electrolyte. Suppose that the potentials $\Omega_1^v$ and $\Omega_{nm}^v$ are known and equal, respectively, to $V_1$ and $V_{nm}$. The potentials $V_2, V_3, \ldots, V_{nm-1}$ are unknown.

We show that the observable physical potentials are the potentials minimizing the total power needed to establish a current crossing the interfaces.

This total power is:

$$P(V_2, V_3, \ldots, V_{nm-1}) = \sum_{i=1}^{nm} \int_{\Gamma_{iBV}} \varphi(V_i - \Phi^e) (V_i - \Phi^e) \, ds$$  \hfill (8.1)

where:

$$\varphi(V_i - \Phi^e) \, ds$$

is the current and

$$V_i - \Phi^e$$

is the potential jump.

The minimization can be done by computing values of $P$ varying floating potentials values.

Each computation of $P$ needs the computation of the electrolyte potential knowing the electrodes potentials. (System (5.3)).

Figs. 18–21 show computation results in a bipolar cell with one floating electrode.

Figs. 22 and 23 show computation results in a bipolar cell with three floating electrodes.

9. Conclusion

This software built from finite element analysis, is a flexible tool of simulation of diverse electrochemical systems including nonlinear interfaces conditions. This software gives us the potential distribution, then the current distribution at interfaces and by-pass are easily reachable.

This software has been successfully employed for the thesis of G. Bonvin 1992 [6]. The author shows that simulation results are near to measurements.

Numerical simulation can replace a large number of experiences and has the
advantage to avoid to build costly equipment. Scale-up variables can be fastly evaluated.

The delicate problem of analysis of the geometry which consisted to translate mathematical objects to objects readable by the mesh generation software was done via [4] and the software SIMAIL®. These tools help us to build meshes related to experiences.

At the moment, our software is used in collaboration with G. Bonvin [7] to determine a dimensionless number Gb of the relation: \( \Psi = Gb(Bn + 1) \) where \( \Psi \) is the global by-pass.

The software must be modified to take in account the evolution of gas along the electrodes. This can be done by modifying the apparent conductivity in the electrolyte in the channels between the electrodes.

Received: October 20, 1994

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The Industrial Electrolytic Regeneration of Mn$_2$(SO$_4$)$_3$ for the Oxidation of Substituted Toluene to the Corresponding Benzaldehyde

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Abstract. A new industrial process for the electrolytic regeneration of Mn$_2$(SO$_4$)$_3$ is presented in which:
- a slurry of MnSO$_4$/Mn$_2$(SO$_4$)$_3$ in 55% H$_2$SO$_4$ is used as a carrier,
- the electrolyte is purified with an optimum mode before electrogeneration, and
- a new industrial electrochemical reactor is developed for an economical electrogeneration of Mn$_2$(SO$_4$)$_3$.

1. Introduction

Benzaldehyde and its derivatives are important organic intermediates in the production of dyes, pharmaceuticals, perfumeries, and pesticides.

There are currently three commercial routes for the production of substituted benzaldehyde [1]:
- i) vapor phase oxidation of substituted toluene by air over a catalyst (V$_2$O$_5$) at high temperature (500°C); ii) side-chain halogenation of substituted toluene followed by hydrolysis; iii) liquid-phase oxidation of substituted toluene with pyrolusite (natural MnO$_2$).

For a chlorine-free product (required for the production of pharmaceuticals and fragrance ingredients) liquid-phase oxidation with pyrolusite by the batch process is suitable. The main problem in this process is the formation of large amounts of wastewater containing H$_2$SO$_4$, MnSO$_4$, organics, and other impurities (initially present in the pyrolusite) which must be treated before disposal.

The electrolytic oxidation of substituted toluene to the corresponding benzaldehyde is one alternative that should be considered. Since direct electrooxidation of substituted toluene is not capable of giving the aldehyde with good productivity, the indirect two-stage electrochemical process (‘ex-cell’ process) becomes the method of choice [2-4]. In the ‘ex-cell’ process, a carrier (M$^{4+}$) is oxidized in the electrochemical reactor [M$^{4+}$] and then

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