

One to two-phase electrolysis processes behavior under spatial conditions

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Abstract

Homogeneous accelerations, like gravity or inertia, leads to a buoyant force and a natural electro-induced flow, due to density gradients (one phase) or due to evolving bubbles (two phases) which occurs during some electrolysis processes such as the water electrolysis. There are interesting effects when the acceleration value is modified. Only few knowledge on the impact of the acceleration forces upon the deposit properties at continuous and mesoscopic scales, for both one and two-phase electrolysis processes, is available.

In the present work, predictive calculations result of the deposition rate and the deposit structure with uniform buoyant forces are presented. Numerical simulations for 0, 1 and 10 times the earth acceleration have been performed and are explored in detail. Continuous scale calculations have been done using the finite volume method. The mesoscopic properties in term of structure are obtained using random walker calculations. The link between the inputs of this algorithm and the outputs of the continuous scale calculations is discussed. Finally, qualitative and quantitative evolution of the structure with acceleration is proposed and discussed regarding experimental results. The consequence of a two-phase character upon the electro-induced flow at a vertical bubble evolving electrode is finally presented in terms of primary current density distribution evolution with the imposed electrical potential.

1. Introduction

Many electrolysis processes aim to produce tailored materials for different applications. Most of them are called one-phase processes leading to one species deposition of copper, silver or chromium for example (electrodeposition), or binary to multinary materials, like semi-conductor materials such as zinc oxide (ZnO), copper selenide (CuSe₂) or copper indium selenide (CuInSe), with applications in sustainable energy production such as photovoltaic- or fuel cells. Other processes have a strong two-phase character such as the Hall-Heroult process for aluminium production, the water electrolysis or semiconductors anodization. Many investigations have been already published on this topic (references [1-6]) but many experimental results have been obtained before a sufficient and accurate understanding of such processes. In both, one and two phase processes, an electro-induced flow, due to buoyant forces, takes place in the electrolysis reactor due to the change in density in the working electrode vicinity [7-12]. In one-phase processes, the density variation is linked to the chemical composition evolution in electro-active species. This is as well the case in two-phase processes where the density distribution is moreover affected by the bubbles presence.

The engineering of tailored materials deals with the great complexity to integrate multi physico-chemical phenomena and multi scale information: deposition rate due to transport from the single molecular species or complex to the micrometric aggregates, and convective transport induced from the insulated bubble to the group of bubbles. The continuous modeling which descriptions hypothesis and interest are from the micrometric scale to the laboratory or industrial macroscopic scales, gives local and, eventually, unsteady properties process properties in term of deposition rate and chemical composition. For example, for the deposition process, each layer of the final deposit is formed at different time and eventually, properties also depend on location. It is then interesting to be able to access to local unsteady thermodynamical (species speciation composition) and kinetics conditions (transport fluxes, reactivity terms...) such as species concentration, convective and diffusive transport, local reactivity, deposit shear stress... This interesting information must be linked to mesoscopic modeling inputs. The family of processes description, using discrete mathematics and random walker calculations with transport and reactivity probabilities and statistics, leads to interesting practical information upon the deposit structure from nano to micro scale (porosity and

roughness).

These tailored materials at all scales synthesis are possible with the use of experimental factors such as the usual main ones, the bath chemical composition and temperature, but also cell design, injection geometry or hydrodynamic agitation. There are also other less explored factors such as magnetic fields or applied gravity level. It is easier to simulate zero gravity experiments with numerical calculations than to actually perform experiments with the use of drop towers, parabolic flights from the International Space Station (ISS). The gravity factor is then what focuses our interests in the present paper.

2. Continuous modeling from the actual to the virtual experiment

The copper electrodeposition process is considered as an illustrating example. The chemical bath is done in an acidic medium solution of CuSO_4 0.567 M and H_2SO_4 1.63 M at $T = 45^\circ\text{C}$. The working electrode is a rotating cylinder (see **Fig. 1**) performing at a rotation rate of $\omega = 10$ rpm.

This actual electrochemical cell defines a virtual one which is the mesh of the calculation domain (see figure 2). The used mesh contains 26711 cells with thinner cells which are $10\ \mu\text{m}$ near the working electrode in order to be able to calculate the physico-chemical boundary layers.

The mathematical modeling associated with the continuous scale is:

Continuity equation: $\text{div}(\rho V) = 0$ (1)

where ρ (kg m^{-3}) is the local density and V (m s^{-1}) is the vector local velocity with $V=(V_z, V_r, V_\theta)$.

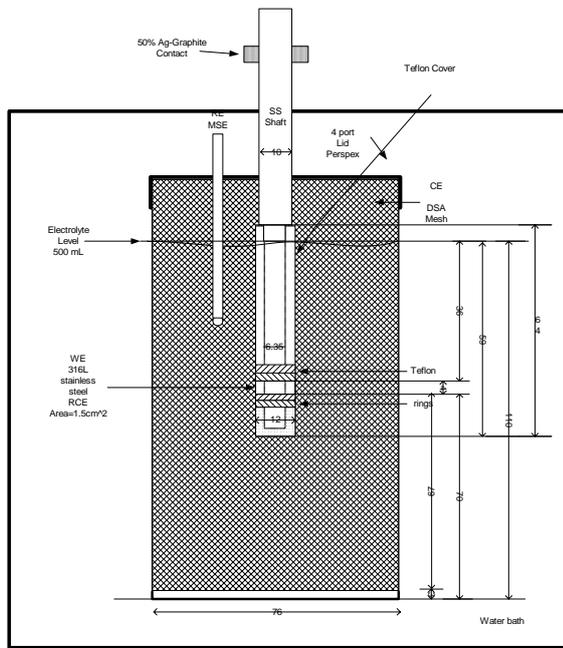


Fig.1 Rotating cylinder electrode (RCE) experimental set-up (units in mm)

Navier-Stokes equation:

$$\rho V \text{grad } V = \text{div } \tau - \text{grad } P + \rho g$$
 (2)

where τ (Pa) is the local hydrodynamic shear stress, P (Pa) is the local gauge pressure and g (m s^{-2}) is the gravity acceleration. The flow properties calculation is done with finite volume method and SIMPLEC algorithm of Fluent® (see reference [7]).

Copper mass balance equation:

$$\rho V \text{grad } C = \text{div}(\rho D \text{grad } C)$$
 (3)

where C (mol m^{-3}) is the local copper concentration, and D ($\text{m}^2 \text{s}^{-1}$) is the Fick diffusion coefficient.

The density variation with local composition is supposed to follow the compressibility law [10-11]:

$$\rho = \rho_0(T) - M_{\text{CuSO}_4} \times (C_{\text{Cu,bulk}} - C_{\text{Cu}})$$
 (4)

This last thermodynamic modelling is needed to allow the existence of one-phase buoyant flows.

Figure 3 shows the hydrodynamic profiles in the z direction normal to the electrode (in black in **Fig. 2**). The higher the gravity, the larger is the tangential (to the working electrode) flow. Then the electrode shear stress increases with the gravity and it is commonly accepted that it has a important impact upon structural deposit properties such as porosity and roughness. This shows how the numerical calculation are interesting to build information usable with experimental measurements. In the present case we are able to quantitatively follow the non-linear increase of the electrode shear stress with the gravity level.

Fig. 4 shows that the species fluxes or composition gradient at electrode are strongly related with the electrode shear stress shown in **Fig. 3**. If the wall shear stress is really important to describe feeding or erosion of the deposit at the micrometric to macroscopic scales,

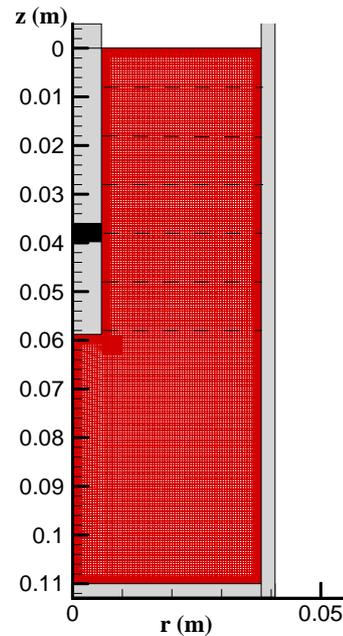


Fig.2 Rotating cylinder electrode (RCE) mesh (units in m)

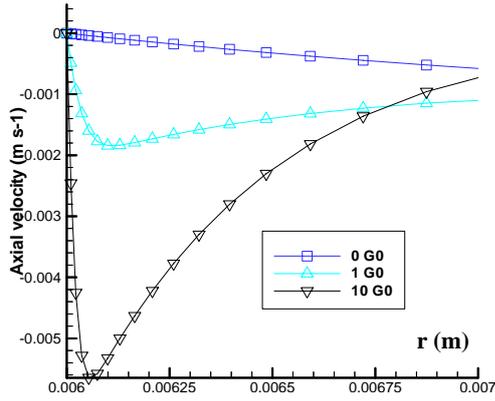


Fig.3 Axial velocity V_z profiles at the working electrode centre: evolution with acceleration (Fluent®)

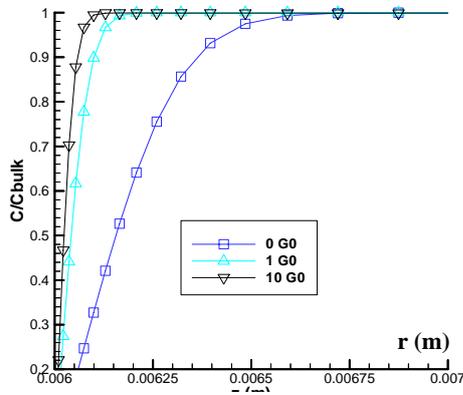


Fig.4 Chemical species boundary layers for different level of acceleration (Fluent®)

the knowledge of the transport and reactivity kinetic properties are, for the same goal, important at the molecular to sub-micrometric scales. The calculation of electro-active species profiles in the electrode vicinity is done with boundary conditions associated with the equation (3).

For a general electrochemical reaction at the working electrode like (R1):



n is the electron number transferred.

The boundary conditions can be written :

For the bulk:

$$\begin{aligned} C_{\text{ox}}(t=0, x) &= C_{\text{ox}}(\text{bulk } t) = C_{\text{ox}}^0 \\ C_{\text{red}}(t=0, x) &= C_{\text{red}}(\text{bulk } t) = C_{\text{red}}^0 \end{aligned} \quad (5)$$

At the working electrode in case of a reduction like for the copper deposition process:

$$\begin{aligned} J_{\text{ox}}|_{x=0} &= -D_{\text{ox}} \frac{\partial C_{\text{ox}}}{\partial x} = -k_{\text{red}} C_{\text{ox,el}} + k_{\text{ox}} C_{\text{red,el}} = j / (nF) \\ J_{\text{red}}|_{x=0} &= -D_{\text{red}} \frac{\partial C_{\text{red}}}{\partial x} = k_{\text{red}} C_{\text{ox,el}} - k_{\text{ox}} C_{\text{red,el}} \end{aligned} \quad (6)$$

With: $J_{\text{ox}} = -D_{\text{ox}} \mathbf{grad} C_{\text{ox}}$ and $J_{\text{red}} = -D_{\text{red}} \mathbf{grad} C_{\text{red}}$
Where the Faraday constant is $F=96500 \text{ C mol}^{-1}$, j (A m^{-2}) is the local unsteady electrical current density and the electrochemical constants k_{red} and k_{ox} are given according with the Boltzman and Buttler-Volmer law:

$$k_{\text{red}} = k_{\text{red}}^0 \exp[-\alpha_{\text{red}} \cdot n \cdot F \cdot (E - E^0) / (R_g \cdot T)]$$

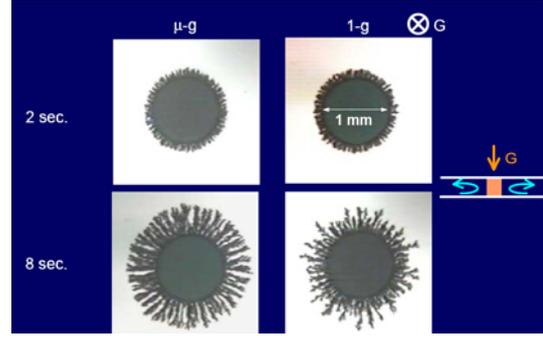


Fig.5 Microscopic images of copper dendrites for $j=2.5 \text{ A cm}^{-2}$ (after prof. Fukunaka)

$$k_{\text{ox}} = k_{\text{ox}}^0 \exp[\alpha_{\text{ox}} \cdot n \cdot F \cdot (E - E^0) / (R_g \cdot T)] \quad (7)$$

with E^0 (V), k_{red}^0 and k_{ox}^0 (m s^{-1}) the standard electrochemical properties, respectively thermodynamical and kinetic for a given imposed potential E (V) at the working electrode; α_{red} and α_{ox} are the Taffel electrochemical dimensionless coefficients, $R_g = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the perfect gas constant and T (K) is the temperature.

As it can be seen with electrode equations (6), electro active species transport and electrochemical reaction rate are coupled and the relation at the deposit layer formation links both the species compositions and gradients with the wall shears stress. The figure 4 shows the composition profile under the diffusion limited hypothesis. Once again the quantitative evolution of the limiting current density with the gravity factor is predicted with the use of numerical simulations. Then the maximum deposition rate is smaller under zero gravity than under normal earth gravity as it has been experimentally shown by the professor Fukunaka team (references [8-9]).

3. Mesoscopic modelling: from the actual deposit to the simulated deposit according to continuous information

The experiments of interest in this paper are those performed by professor Fukunaka's team (references [8-9] and **Fig. 5**). The first experiments we focus on, are the one phase copper electrodeposition. In the experimental set-up, a disc shape working electrode inside a circular Petri box has been used (see Fig. 5) in order to obtain a two-dimensional geometrical configuration. Then, in this configuration, the macroscopic impact of the electro-induced flow (presented in the previous part, see Fig. 3 for example), is negligible and the interest can focus upon the deposit structural properties.

As it can be seen on these two images, the uniformity in height of copper dendrites is more important for micro gravity experiments than at normal earth gravity. A mesoscopic modelling was developed in order to describe the deposited microstructures. Modelling uses random walkers introduced randomly in a calculation box (see **Figs. 5, 6** and **7**).

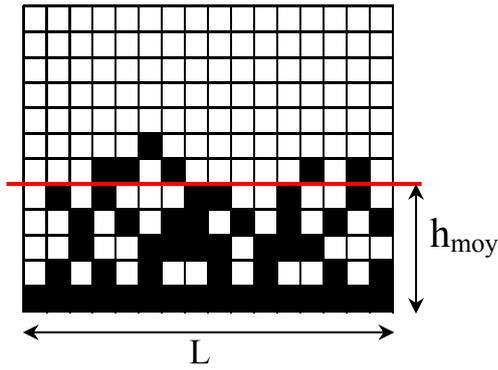


Fig.6 Monte Carlo calculation box with definition of the average deposit height

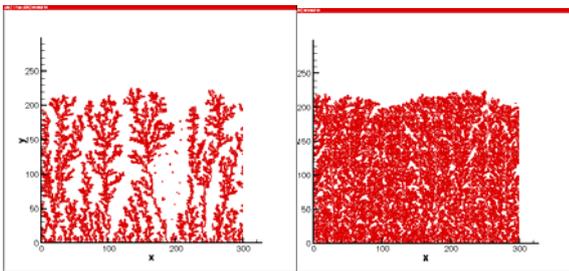


Fig.7 Monte Carlo deposits for Pecllet number $V_r=1$ (left) and $V_r=10$ (right)

The displacement probabilities of the random walkers are expressed in term of tangential V_r and normal V_x electrode Pecllet numbers:

- to the right: $P(r+) = (1 + V_r) / (4 + V_x + V_r)$
- to the left: $P(r-) = 1 / (4 + V_x + V_r)$
- to the top: $P(x+) = 1 / (4 + V_x + V_r)$ (8)
- to the bottom: $P(x-) = (1 + V_x) / (4 + V_x + V_r)$

The results for increasing the normal Pecllet number V_r are given in Fig. 7.

These results are not able to describe the large change in height measured experimentally as seen in Fig. 5. This is due to the necessity to take into account micro-free-convection which appears between dendrites. When gravity level is zero, these micro-convective structures disappear resulting in higher uniformity between dendrites.

4. Two-phase electrolysis processes

The two-phase electrolysis processes with evolving gas or bubbles at electrodes are illustrated with the alkaline (KOH) water electrolysis. **Fig. 8** shows the evolution of the bubbles electrode coverage with gravity level. As it can be seen, for both hydrogen (left side) and oxygen (right side), the bubble accumulation is larger at 0 G (bottom) than at 1G. (top).

During two-phase electrolysis process, bubbles are shadowing the working electrode: This is the screening effect which has two components. The first effect is interfacial and the actual active area of the working electrode is modified due to the bubbles presence. The

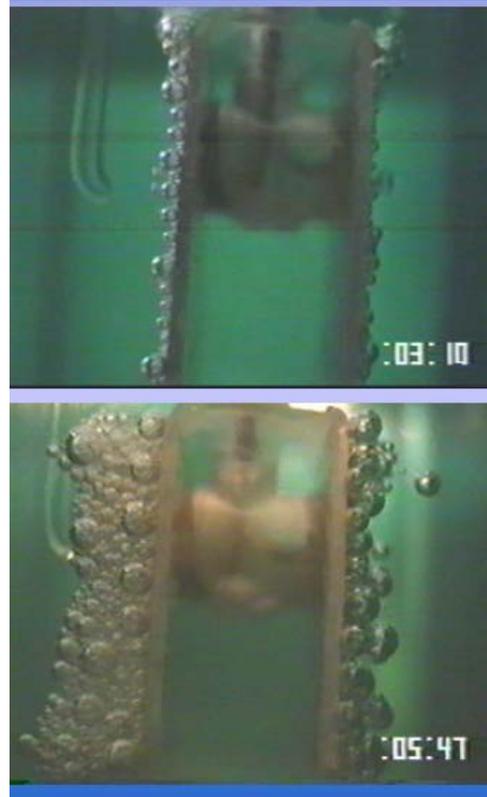


Fig.8 Water electrolysis 1G (top) and 0G (bottom) (after prof. Fukunaka)

local current density is modified and therefore the electrochemical kinetics [12]. The second bubble screening effect is homogeneous: Bubbles modify all the thermo-physical properties and particularly the density which is the main property concerning the sensitivity with gravity level. One other important property is the local electrical conductivity κ related to the local void fraction α . The Brugeman law is generally used: $\kappa = \kappa_0 (1 - \alpha)^{3/2}$

In the present work the primary current density distribution for a vertical evolving electrode has been calculated and is presented in **Fig 9**. The behaviour of these primary current distributions are coherent and in good agreement with obtained previous results [12].

These primary current distributions show the decrease of the local current density with height due to bubble accumulation at the top of the electrode when gravity level is 1G. When the gravity level is 0G, the current density distribution is uniform.

5. Conclusion

It has been shown that the gravity level has an effect upon electrolysis, and one or two-phase processes, due to the buoyant motion source. The effect is upon the macroscopic to the mesoscopic scale. These numerical results show the interest of the calculation, particularly concerning zero gravity experiments, due to the simplification in absence of the free-convective flow.

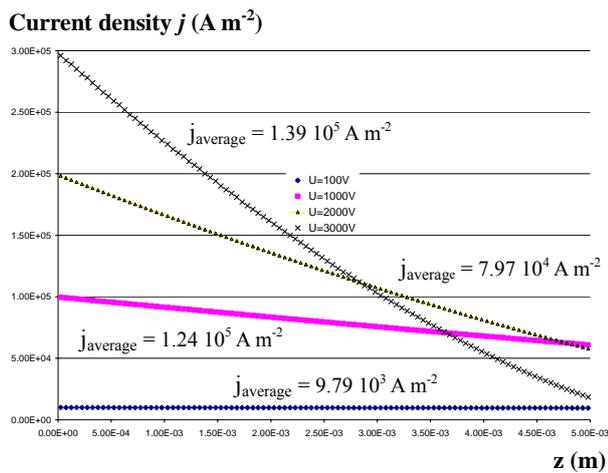


Fig.9 Primary current distribution evolution with imposed potential

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