ELECTROCHEMICAL REACTORS

F. Lapicque
Laboratoire des Sciences du Génie Chimique, CNRS - ENSIC, Nancy, France

Keywords: Electrochemistry, electrode, reactions, electrochemical cells, mass transport, momentum transport, current density, potentials, electrochemical processes, modeling

Contents

1. Introduction
2. Background of electrochemistry
   2.1. Electrode Interface and Double Layer
   2.2. Potentials and Currents
   2.3. Faraday’s Law
   2.4. Electrodes and Cells at Equilibrium
   2.5. Electrode Overpotential
   2.6. Cell Voltage and Yields
3. Transport and transfer phenomena in electrochemical processes
   3.1. Mass Transport Rates and Current Density
   3.2. Mass Transfer to Electrode Surfaces
      3.2.1. Transfer Phenomena
      3.2.2. The Nernst’s Film Model
      3.2.3. Mass Transfer Coefficient and Existing Correlations
4. Technology of electrochemical reactors
   4.1. A typical Cell: the Filter-press Cell
      4.1.1. General Aspects
      4.1.2. Electrical Connection
      4.1.3. Hydraulic Connection
   4.2. Other Cell Configurations in Liquid Media
      4.2.1. “Pool” or Tank Cells
      4.2.2. Use of Turbulence Promoters
      4.2.3. Three-dimensional Electrodes
      4.2.4. Bipolar Electrode Cells
   4.3. Cells for Gas Generation
      4.3.1. Water Electrolysis
      4.3.2. Chlorine-alkali Electrolysers
5. Current distribution in electrochemical cells
6. Design of electrochemical cells: an introduction
   6.1. General Features
   6.2. An Example: The Continuous Filter-press Operated at Limiting Current
7. Current trends in electrochemical engineering.
Bibliography
Biographical Sketch

Summary

After reminding shortly backgrounds of electrochemistry, the chapter deals with the main features of electrochemical engineering. In comparison to what happens in chemical reactors, formation of the double layer together with the existence of ohmic drop and charge transfer phenomena, rule the behavior of electrochemical cells. Transport and transfer phenomena are significant elements in the design of electrochemical cells since the electrochemical reaction occurs at the solid/liquid interface. Technology of electrochemical reactors is shortly introduced with emphasis of specific aspects e.g. ohmic drop, electrode activity and transport phenomena, and with references to representative processes of industrial significance. Current and potential distributions represent an important feature of electrochemical cells, with concern to the local production rate and selectivity. Finally, modeling and design of cells can be derived from the techniques developed in chemical reaction engineering, taking into account the specific features of electrochemical reactions, as shown in examples. The chapter has to be considered as an extended introduction to the scope, and readers can refer in more specialized papers and in the textbooks cited.

1. Introduction

Electrochemical processes have been used for decades in various industrial branches e.g. synthesis of fine chemicals, production of particular metals e.g. aluminum and sodium, production of gaseous elements such as hydrogen, chlorine or fluorine, deposition of metals or alloys, and pollution treatment.

In addition to these industrial applications, electrochemical techniques represent powerful tools for investigation of physical phenomena e.g. mass transfer or hydrodynamics in the vicinity of solid surfaces in contact with a liquid. The large panel offered by electrochemical techniques results from two main features of electrochemical systems:

- Electrochemical reactions are heterogeneous processes, therefore exhibiting numerous similarities with catalytic processes. The electrochemical conversion consists of the sequence of chemical steps e.g. adsorption, electrode reactions, together with possible chemical reactions, and physical steps such as transport and transfer processes.

- Electrical charges obey specific laws such as Ohm’s law their transports, or Faraday’s law for the conversion of matter.

Electrochemical processes consist of cells, i.e. anode-cathode assemblies, separated by the electrolyte medium containing reactants and products, as shown in Figure 1.

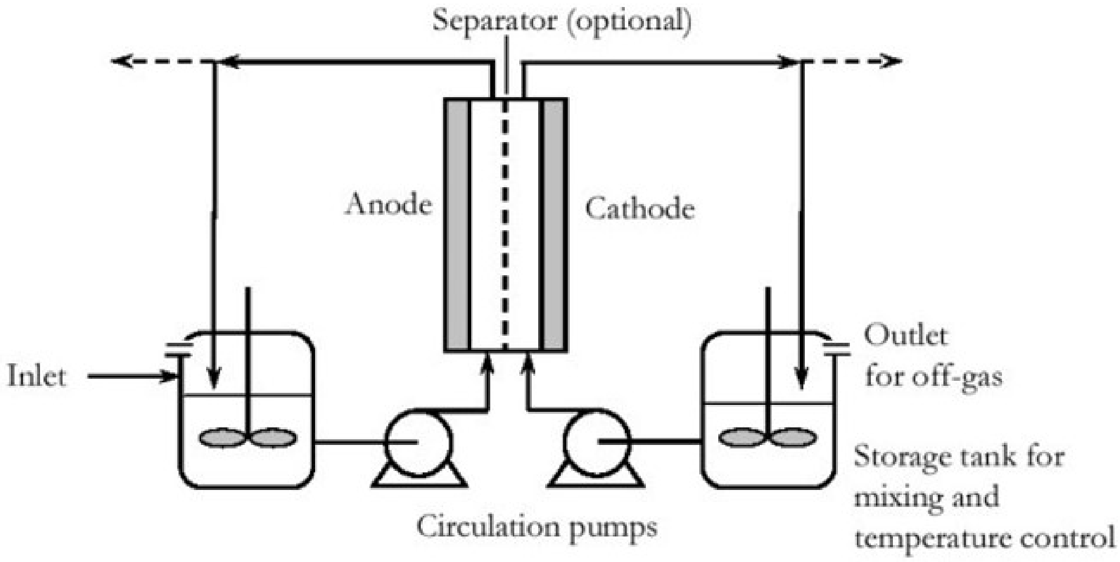

Figure 1: Schematic of an electrochemical process with flow recirculation

Membranes or separators can be necessary when the species produced at one electrode can be consumed at the counter-electrode, or to avoid the simultaneous presence of two species forming a hazardous mixture – as for hydrogen and oxygen in a water electrolysis cell. Electrochemical cells have to be designed in a way to respect the two above constraints, and the above comments can be made:

- Motion, circulation of the electrolytic media has to favor mass transfer to the electrode. For some cases, the electrode motion induces mass transfer to the electrode.
- The electrolytic media is of finite electrical conductivity and the occurrence of resistive – ohmic- phenomena represent additional constraints in the design of the process, to avoid too large heat production. The electrode gap is therefore generally reduced to a few millimeters, whereas the electrode length can attain one meter or more.
- The surface of the electrodes has to be controlled to ensure both high activity – i.e. high production rates - and high selectivity of the key-reaction. The range of electrode potential/current density will be chosen for this purpose.
- The residence time in electrochemical cells is usually low, to allow high mass transfer rates at the electrodes. However, the conversion in single-pass configuration is usually low, and recirculation of the solution is necessary in most cases, for both continuous and discontinuous processes.

Although some electrochemical processes are operated with various electrode configurations as in electrodialysis cells, or with bipolar electrodes, the two sides of which have different polarity, the presentation only concerns simple cells having only one anode and one cathode. After a brief description of electrochemistry backgrounds, the chapter presents successively specific aspects of electrochemical reactors, transport and transfer phenomena in cells, elements of their technology, and an introduction to modeling and design. The reader interested by more detailed presentation of the topic may read reference textbooks such as for instance those written by Newman (1972, 1991), Rousar et al. (1986), Coeuret and Storck (1993), Goodridge and Scott (1995).

2. Backgrounds of Electrochemistry

Only basic things required for understanding of the behavior and operation of electrochemical cells are given here. More extensive description can be found in Albery (1975), Newman (1991), Hamann et al. (1995), or Girault (2001) for instance.

2.1. Electrode Interface and Double Layer

The electrode interface is a transition region for charge transport: in electrolytic media, being conducting liquids or molten salts, charges are mainly transported by ions under the action of the electrical field. In the metal phase, namely the electrodes, the current leads and the wires, the current is transported by electrons. Charge transfer occurs then at the electrode interface.

The metal surface is generally charged, i.e. covered by a monolayer of ions, with a sub-layer of solvent molecules – water for instance, due its appreciable dipolar moment. In most cases, anions are preferentially adsorbed on the metal surface. Outside this layer and contrary to the solvent molecules, very few counter ions (cations) are adsorbed. The ion layer is stable on the interface plane and represents the so-called rigid part of the double layer (Helmoltz layer), according to the Gouy-Chapman theory. The potential exhibits a steep variation in the rigid part of the double layer, and the intense electric field of the order of 10^8 V/m or more, corresponds to the charge of the ions forming the first layer. Further from the electrode surface, the solvent molecules, anions and cations are present in the solution: at the local scale, more anions are present close to the interface, and electroneutrality equation does not hold there. This region is also called the diffuse (Stern) part of the double layer, and appears as a transition zone to the bulk of the electrolytic medium. Its thickness is of the order of 1-10 nm, depending on the electrolyte concentration.

The electrical current, I , can be used in two processes:

- formation or modification of the double layer structure: this contribution being the capacitive current is only significant in electrical transient regimes,
- chemical conversion of matter, corresponding to the faradaic current as presented below.

2.2. Potentials and Currents

The potential of a phase at one point in a phase is linked to the energy required to carry one electron from infinite to the location considered. Volta potential of an electrode surface is related to the energy required to reach a point a few 10^{-9} m distant from the interface. Getting closer to the electrode surface through the double layer, results in a sharp potential variation, and Galvani potential is defined as the potential difference from infinite to the metal phase. The electrode potential is defined as the difference between Galvani and Volta potential. Though defined by a potential difference, the electrode potential cannot be measured, and a reference is required. Various reference potentials can be used on the basis of a redox reaction: NHE, normal hydrogen electrode, based on the H^+/H_2 couple, silver chloride electrode, based on the Ag/AgCl couple etc…

The potential in the electrode structure can often be considered constant, for sufficient conductivity of the metal, κ_M, taking into account the generalized form of Ohm's law:

$$\vec{i} = -\kappa_\mathrm{M}\overrightarrow{\mathrm{grad}}\Phi_\mathrm{M} \tag{1}$$

Ohm's relation is also written in the liquid phase, with variables κ and Φ_s :

$$\vec{i} = -\kappa\overrightarrow{\mathrm{grad}}\Phi_\mathrm{s} \tag{2}$$

The current density, in A m^{-2}, can be defined at the electrode surface as well as in any location of the electrolytic phase, as explained in Section 2.1.

2.3. Faraday's Law

Faraday's law establishes the relationship between the current passing through the metal-liquid interface, I , and the conversion rate of the reactant of interest A. For the example of reduction of species A involving n_e electrons:

$$A + n_\mathrm{e}\, e^- \rightarrow B$$
$$I = n_\mathrm{e}F\dot{n}_\mathrm{A} \tag{3}$$

where F is the Faraday constant, equal to 96487 Coulombs, i.e. the electrical charge of one mole electrons, and $\dot{n}_\mathrm{A}$ the conversion rate of A (mol s^{-1}). The above relation can be expressed in terms of current density, in A m^{-2}, and specific conversion rate (or specific molar flux), in mol m^{-2} s^{-1}, as follows:

$$i = \frac{I}{S} = \frac{n_\mathrm{e}F\dot{n}_\mathrm{A}}{S} = n_\mathrm{e}FN_\mathrm{A} \tag{4}$$

Should two electrode reactions or more occur at the electrode surface, faradaic yield Φ_e - or current yield - is defined as the likelihood of one electron to be transferred for the completion of the considered reaction. For the case of the reduction of species A:

$$i = \frac{n_\mathrm{e}FN_\mathrm{A}}{\Phi_\mathrm{e}} \tag{5}$$

Fraction $(1-\Phi_\mathrm{e})$ of the current is to be consumed in other reactions such as solvent electrolysis.

2.4. Electrodes and Cells at Equilibrium

Consider the electrode reaction A + n_e → B. The standard electrode potential is proportional to the difference of the Gibbs formation enthalpies, as follows:

$$\Delta G_{\mathrm{B}}^{\mathrm{f}} - \Delta G_{\mathrm{A}}^{\mathrm{f}} = -n_{\mathrm{e}} F . E_0^0 \tag{6}$$

From IUPAC conventions, positive standard potentials correspond to negative enthalpy differences, i.e. for exothermal reactions such as oxidations. For temperature and pressures different from the standard conditions i.e. 298.K and 1Atm, the enthalpy difference involves the activity of species A and B, and the reversible electrode potential, E_0, is then given the Nernst's law:

$$E_0 = E_0^0 + \frac{RT}{n_{\mathrm{e}} F} \ln \frac{a_{\mathrm{A}}}{a_{\mathrm{B}}} \tag{7}$$

The cell voltage is defined as the potential difference between anode and cathode:

$$U_{\mathrm{c}} = E_{\mathrm{a}} - E_{\mathrm{c}} \tag{8}$$

When the net current circulating in the cell and through the electrodes is zero, the cell voltage is at its lowest value, U_0, and is equal to the difference ($E_{0,\mathrm{a}}$ - $E_{0,\mathrm{c}}$), where each potential is given by the above Nernst's law. When a current is applied, the cell voltage, U_{c}, exceeds voltage U_0 by (i) the ohmic drop between the two electrodes, which can be calculated by using rel. (1), and (ii) the overpotential of the two electrodes, as explained below.

2.5. Electrode Overpotential

Electrochemical reactions are catalytic processes for which monitoring the electrode potential allows the corresponding available current density. Charge transfer phenomena can be of a finite rate, and various models have been developed to predict the additional potential contribution – overpotential - required for the considered current density to pass through the electrode. For anode processes, overpotential η is positive, and is equal to (E_{a} - $E_{0,\mathrm{a}}$). For cathodic processes, $\eta < 0$ and is equal to (E_{c} - E_{c0}).

The most well-known model for description of charge transfer kinetics was proposed decades ago by Butler-Volmer. The electrochemical reaction is assumed to be reversible and to involve one electron:

A + e $\leftrightarrow$ B

Assuming in addition that the charge transfer at the electrode is rate-controlling process in the overall conversion, leads to the expression of the current density – proportional to N_A - with overpotential η:

$$i = i_0 \left\{ \exp\left(\frac{\alpha n_{\mathrm{e}} F}{RT} \eta \right) - \exp\left(-\frac{(1-\alpha) n_{\mathrm{e}} F}{RT} \eta \right) \right\} \tag{9}$$

where η can be positive or negative, α is the charge transfer coefficient, and i_0 is the exchange current density, i.e. the specific flux of electrons crossing the interface at equilibrium: although the net current is zero at equilibrium, this flux differing from zero, depends on the rate constants of both cathodic and anodic processes (Vetter, 1967). For sufficient polarization, i.e. for $|\eta|$> 50-100 mV, one of the two exponential vanishes, and the above relation can be approximated by the empirical Tafel law:

$$i \approx i_0 \exp\left(\frac{\alpha n_\mathrm{e} F}{RT}\eta_\mathrm{a}\right) \text{ for an anodic process, i.e. } \eta_\mathrm{a} = a + b\log(i) \qquad (10)$$

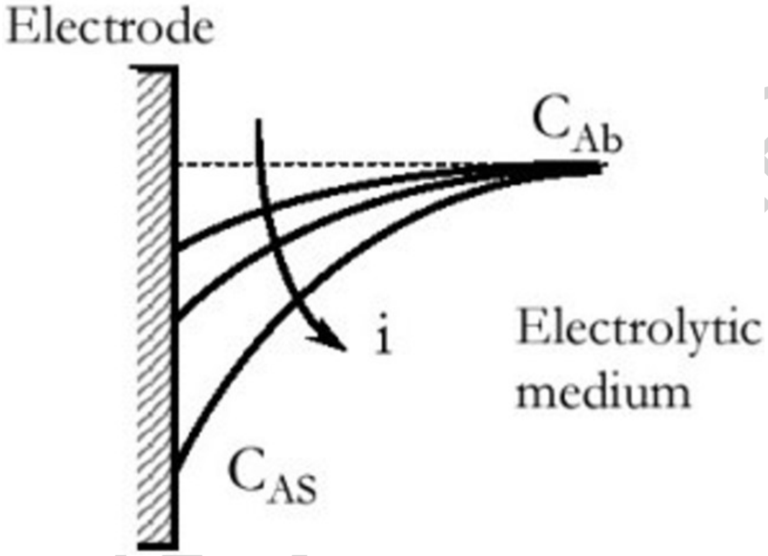

Figure 2: Concentration profile of electroactive species A in the vicinity of the electrode surface

Similar law can be derived for cathodic processes. Contrary to Butler-Volmer’s law, Tafel’s law expresses the reaction rates of irreversible processes. For sufficient current densities, mass transport to the electrode can be controlling, as for catalytic processes: as soon as transferred to the electrode surface by diffusion and migration, reactant A is converted to B, and a concentration profile is formed near the electrode surface, as shown in Figure 2 (This point will be detailed in Section 2).

This profile is the source of additional overpotential η_d expressed by the relation:

$$\eta_\mathrm{d} = \frac{RT}{(1-\alpha)n_\mathrm{e}F}\ln\left(\frac{C_\mathrm{Ab}}{C_\mathrm{As}}\right) \text{ for the reduction of A into B} \qquad (11)$$

where C_Ab and C_As denote the concentrations of A in the bulk and at the electrode surface, respectively. η_d is called the concentration overpotential and can be defined at both electrodes. For partial control by mass transfer rates, a more general for expression for Butler Volmer’s law taking into account both mass and charge transfer kinetics, can be used. Typical current – overpotential curves with both charge and mass transfer controls are given in Figure 3.

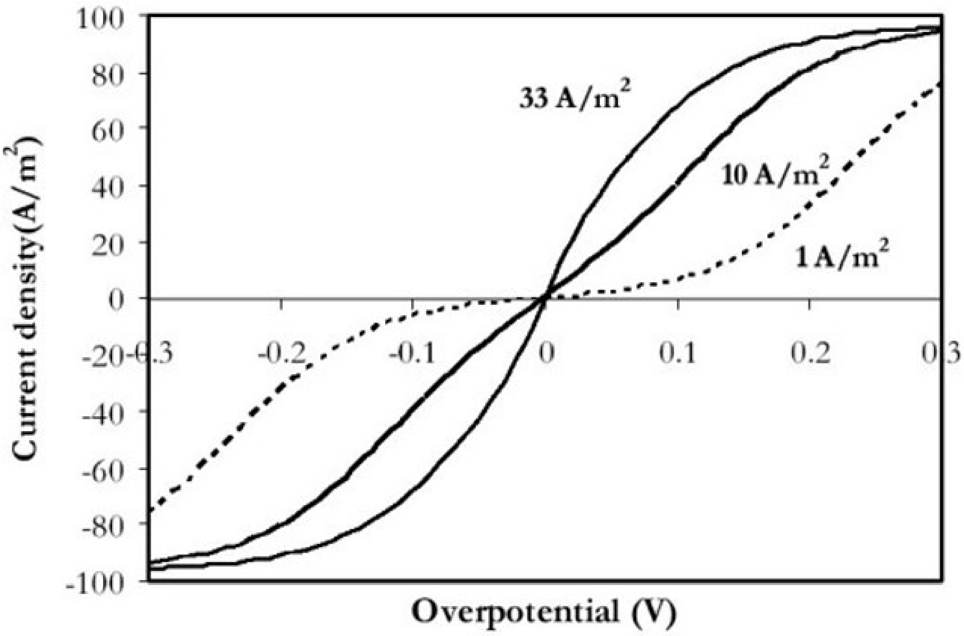

Figure 3: Voltammetric curves. Fictitious example: limiting current density (see Section 2.1): 96.5 A m^{-2}, α =0.5, and various values of the exchange current density, i_0

-
-
-

Bibliography

Albery J. (1975) *Electrode kinetics*, Clarendon Press, Oxford, England.

Bard A.J. and Faulkner L.R. (1980) *Electrochemical methods. Fundamentals and applications*, Wiley, New York, USA.

Bello B. and Junker M. (2005) *Large-scale water electrolysers*, (in French), Survey B4.1.1.6/BBe/01-05, Alphea, Forbach, France.

Carlsson L., Holmberg H., Johansson B., Nilsson A. (1982). *Design of a multipurpose, modularized electrochemical cell*, Chap. III in Technique of Electroorganic Synthesis, Scale-up and Engineering Aspects, Editors Weinberg N.L., Tilak B.V., Wiley & Sons, New York, 179-194.

Coeuret F. and Storck A. (1993). *Elements of electrochemical engineering* (in French), Lavoisier, Paris.

Cussler E.L. (1976) *Multicomponent Diffusion*, Chemical Engineering Monographs 3, Elsevier, Amsterdam, the Netherlands.

Delaunay G., Storck, A., Laurent A. et Charpentier J.C. (1980), Electrochemical study of liquid-solid mass transfer in packed beds with upward cocurrent gas-liquid flow, *I.E.C. Process Des. Dev.*, **19**, 514-521

Girault H.H. (2001) *Physical und analytical electrochemistry* (in French), Presses Polytechniques et Universitaires Romandes, Lausanne, Switzerland.

Goodridge F. and Scott K. (1995) *Electrochemical Reaction Engineering*, Plenum Press, New York, USA.

Hamann C.H., Hamnet A. and Vielstich W. (1995) *Electrochemistry*, Wiley-VCH, Weinheim, Germany.

Hine F. (1985) *Electrode processes and electrochemical engineering*, Plenum Press, New York, USA.

Lacoste G. (1990) *Procédé et installation d'électrolyse par percolation à travers une ou des électrodes volumiques poreuses*, French Patent N° 259758 (26 Oct. 1990), extension to Europe N° 0302891.

Lamoureux C., Moinet C., Tallec A. (1986) Cellule d'électrolyse à circulation. Montages particuliers et applications à des réactions électrochgimiques consécutives et opposées, *Electrochim. Acta*, **31**, 1- 12

Lapicque F. (2004) Electrochemical Engineering. An overview of its contributions and promising features, *Chem. Eng. Res. Design*, **82**(A12) 1571-1574.

Larminie J. and Dicks A. (2000) *Fuel cell systems explained*, John Wiley and Sons Ltd, London.

Levenspiel O. (1962) *Chemical Reaction Engineering*, Wiley & Sons, New York.

Letord-Quemere M.M., Cœuret F. and Legrand J. (1988) Mass transfer at the wall of a thin channel containing an expanded turbulence promoting structure, *Journal of Electrochemical Society*, **135**, 3063-3067.

Lévèque, in Schlichting H., (1979), Boundary layer theory, Mc Graw Hill, New-York

Midoux N. et Storck A. (1989) *Fluid Transports in Electrochemical Reactor Systems* in "Electrochemical reactors, their science and Technology, Part A", Ed. M.I. Ismaïl, Elsevier, Amsterdam.

Newman J. (1973) Electrochemical Systems, Prentice Hall, Englewood Cliffs, NJ, USA.

Newman J. (1991) *Electrochemical Systems*, 2nd Edition, Prentice Hall Inc., Englewood Cliffs, NJ, USA.

Picket D.J. and Ong K.L. (1974) Influence of hydrodynamic and mass transfer entrance effects on the operation of a parallel plate electrolytic cell *Electrochimica Acta*, **7**, 875-882.

Pickett D.J. (1979) *Electrochemical Reactor Design*, Elsevier, Amsterdam, the Netherlands.

Reiss L.P. and Hanratty T.J. (1963) An experimental study of the unsteady nature of the viscous sublayer, *AIChE Journal*, **9**, 154-159.

Rousar I., Micka K., Kimla A. (1986) Electrochemical Engineering, Academia Praha and Elsevier, Amsterdam, The Netherlands.

Savall A., Quesado J., Rignon M., Malafosse J. (1991) Amino-alcohol electrosynthesis. Modelling of a set-up for producing amino-2-méthyl-2-propanediol-1.3. *J. Appl. Electrochem.*, **21**, 805-815.

Wall K. (1986) *Modern chlor-alkali technology*, Vol. 3, Ellis Horwood Publishers, Chichester, UK.

Westerterp K.R., van Swaaij W.P.M. ans Beenackers A.A.C.M. (1984) *Chemical Reactors Design and Operation*, Wiley & Sons, New York.

Biographical Sketch

Francois Lapicque, was born on Jan. 26, 1957 at Epinal, France. He is married and has two children Chemical Engineer in 1979 in the National Polytechnic Institute of Lorraine, Nancy, he prepared his engineer doctor PhD on high temperature solar systems with application to water splitting for hydrogen production (1983) under the guidance of Prof. J. Villermaux. He obtained then a CNRS Scientist position in the Laboratory for Chemical Engineering Sciences (LSGC) at the same university, in the area of electrochemical engineering: PhD on two-phase electroorganic synthesis (1987) with Prof. A. Storck. Since then, he has worked on various aspects of electrochemical engineering: electroorganic sysnthesis in protic and aprotic solvents, metal and alloy deposition, pollution control by treatments of flue gases through gas-liquid absorption and electrolytic treatment of the liquid phase, treatments of liquids by electrochemical technique (electrocoagulation, ion-exchange electrodialysis, electrolixiviation…), and more recently on fuel cell technology. In addition to electrochemical systems, he has been partly active in gas-liquid systems, in particular in the area of regenerative absorption of sulphur dioxide, VOC, and CO_2. He has supervised more than twenty PhD students and is the authors of circa 85 papers in scientific journals.

He has been the head of the “Multiphase Systems” group of the lab since 2002, member of the International Society of Electrochemistry, and is the current Chairman of the Working Party on Electrochemical Engineering of the European Federation of Chemical Engineering.

Interest in novel writing, jogging, music, foreign languages and working out.