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*Feature article*

# Electrochemical Engineering - its appearance, evolution and present status. Approaching an anniversary.

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> *The goal of electrochemical engineering is to achieve*
> *in a quantitative way an optimal cell design*
> **N. Ibl**

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***Abstract***

*Through this story an attempt has been made to present a chronology of electrochemical engineering - from its appearance as an individual science, via its growth throughout the five decades of its existence as an individual science, until today. The collaboration and linkage of electrochemical engineering with other disciplines has also been discussed in this essay. The role and duties of electrochemical engineering in the 21<sup>st</sup> century have been touched upon to the extent that it was possible.*

**Keywords**

Electrochemical engineering, Electrochemical reactors, Cell productivity, Education in electrochemical engineering

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## 1. Circumstances of the emergence of electrochemical engineering as a new scientific discipline

The term “electrochemical engineering“ first appeared in the literature as a novel title of the fourth edition of C.L. Mantel’s book Industrial Electrochemistry [1], published in 1960 (the first edition was published in 1931 and later editions in 1940 and 1950). Just looking through its contents, one can easily realize that this book mainly describes the electrochemical technologies for production of some particular electrochemical products. Although there was an attempt to group and systematise the exposed technologies in separate chapters, such as: basic electrochemical relationships and laws; molten salt electrochemistry, metal electrowinning and electrorefining; gases production; corrosion and electroplating, a big gap still remained between the title and the contents. This book, along with others relating to industrial electrochemistry from around that time, demonstrated that, at the end of the '50s, the number of electrochemistry technologies had expanded to the extent that it was not possible even to describe each of them in a textbook without a lot of repetition in describing each technology. This made books more and more voluminous, making it troublesome for students, who had to learn each technology for the production of every particular electrochemical product. This was one of the reasons, maybe not the most important but still a very serious one, for starting to consider establishing a new discipline in a similar manner to what had been done when chemical engineering appeared at the end of the 19th and the very beginning of the 20th century - firstly through unit operations and afterwards through transport phenomena and reaction engineering. Hence, at the end of the '50s and in the early '60s, chemical engineering had already developed its capabilities to treat unit operations and processes in a way that interconnects physical and physico-chemical phenomena with chemical processes to chemical technology.

At that time (the end of the '50s), it became evident that similar transformations to those that had occurred in chemical technology had to be implemented in industrial electrochemistry to get more engineering and a more scientific approach to improving the existing technologies and establishing new ones. By then, almost all that had been achieved in improvements to any electrochemical technology was due to the art of engineering rather than to an applied science.

## 2. Interconnection between chemical engineering and electrochemistry - pioneering works linking the two sciences

During the '50s a close interconnection between electrochemistry and chemical engineering was established, on a theoretical level, through the penetration of electrochemistry into chemical engineering and *vice versa*. During that period, firstly C.S. Lin with his co-workers [2], and shortly afterwards Tobias, Eisenberg and Wilke [3] considered, both experimentally and theoretically, the mass transfer phenomenon of ions coming from the bulk electrolyte to the electrode surface by molecular diffusion, migration and convection. Their considerations resulted in the well-known equation connecting limiting current density with the other variables affecting it:

$$i_\mathrm{L} = k_\mathrm{L} z F c_\mathrm{b} \tag{1}$$

Where: $i_\mathrm{L}$ - is limiting current density; $k_\mathrm{L}$ - mass transfer coefficient; $z$ - number of exchanged electrons in electrochemical reaction; $F$ – Faraday's constant; $c_\mathrm{b}$ – bulk concentration of reacting ions, all given in arbitrary units.

The published papers in which an electrochemical method of limiting current measurement was used to evaluate the mass transfer coefficient at convective mass transport forged a strong connection between electrochemistry and chemical engineering. The few early works [2,3] relating to local limiting current measurements had opened new opportunities – employing electrochemical methods for evaluation either local or overall, as well as instantaneous or time-averaged transport characteristics of flowing liquid systems, *e.g.* to quantify mass, heat and momentum transfer features. In this way, methods of adsorption, dissolution, or sublimation used till then for evaluation of the mass transfer coefficient, were replaced by a much faster and more reliable electrochemical method of the limiting current measurement and computation of a mass transfer coefficient from experimentally recorded polarization curves, using Eq. (1). This method was widely exploited during the '60s and particularly the '70s, until today, for studying the mass transport rate in different electrochemical model-systems. The electrochemical method of limiting current measurement, in its early or advanced form, contributed greatly towards providing evidence about the hydrodynamic image of flowing systems. Thanks to the Chilton-Colburn analogy widely used at that time in transport phenomena, data obtained for local or overall mass transfer coefficients were then employed to estimate heat transfer as well as momentum transfer in similar flowing systems. Indeed, these works confirmed the great influence of flowing conditions in electrochemical reaction rate *via* mass transport in electrochemical reactors, opening up a new research area for creating new, or improving the existing electrochemical cells.

In that period (the middle of the ‘60s), the method of conductivity measurement was also introduced in chemical engineering for local or overall porosity measurement in liquid fixed or fluidised beds and later for a gas hold-up quantification in gas-liquid systems, regardless of whether gas is dispersed in a liquid phase, or generated therein due to a chemical or electrochemical reaction.

This close collaboration between electrochemistry and chemical engineering also had a reverse direction – bringing benefits for electrochemistry. The marker pulse technique, a method widely used in chemical engineering for axial and radial dispersion measurement of a tracer in a reaction chamber, was adopted and modified at the end of the ‘60s, to be used for investigation of ionic species distribution, generated in a flowing electrolyte in electrochemical reaction systems. At that time, terms like “plug flow reactor” or “perfectly mixed reactor” were reserved for chemical and/or catalytic reactors, but not yet used for electrochemical cells.

Mass transfer in a cell when changing the hydrodynamic conditions was investigated at that time as a method for mass transfer enhancement when a diffusion-controlled electrochemical reaction takes place. The use of dimensional analysis and similarity theory adapted for and applied in chemical engineering, was at that time introduced in electrochemical studies in order to minimize the possible combinations of operating variables that have to be tested in the research and development of new electrochemical processes, new electrochemical reactors, or new technologies. This was very important in the scaling of laboratory results to the pilot-plant and then from pilot data to the industrial scale. The experimental data obtained were then expressed in the form of dimensionless relationships, either as:

$$\mathrm{Sh} = f(\mathrm{Re}, \mathrm{Gr}, \mathrm{Sc}, \mathrm{Fo}, \Gamma_1, \dots \Gamma_\mathrm{n}) \tag{2}$$

or, based on the Chilton-Colburn analogy, as:

$$f_\mathrm{fr}/2 = j_\mathrm{h} = j_\mathrm{D} = f(\mathrm{Re}), \tag{3}$$

describing mass, heat and momentum transfer. Equations like these had been introduced as a tool in the consideration of diffusion-controlled electrochemical reaction systems and published at that time in the literature. In equations (2) and (3) Sh is Sherwood number; Re – Reynolds number; Gr – Grashof number; Sc – Schmidt number; Fo – Fourier number; $\Gamma_\mathrm{i}$ – dimensionless groups dictated by geometric similarity; $f_\mathrm{fr}$ – Fanning friction factor; $j_\mathrm{D}$, $j_\mathrm{h}$ – mass and heat transfer factor, respectively.

Moreover, new similarity criteria, like the Wagner number (Wa), relating particularly to the nature of electrochemical reaction systems, were derived and introduced in dimensionless expressions similar to equations (2) and (3).

Obviously, both sciences – electrochemistry and chemical engineering - profited from their mutual collaboration during the ‘50s and ‘60s.

The main benefit from this interrelation between electrochemistry and chemical engineering was the appearance of a new discipline – named electrochemical engineering.

## 3. Establishing electrochemical engineering on the scientific scene

In the early '60s, as a result of the interrelation between chemical engineering and electrochemistry, numerous qualitatively new papers appeared in the relevant literature (mainly in chemical engineering rather than in electrochemical journals), founding the conditions for the appearance of a new multi-disciplinary science – electrochemical engineering.

C. Wagner, V.G. Levich, N. Ibl, C. Tobias, P. Le Goff, and J. Newman with their collaborators, as well as some others not mentioned here due to limited space, contributed a lot to the establishment and early development of the new discipline. These scientists may be considered as the founders of electrochemical engineering - a separate scientific discipline born from the mutual influence of chemical engineering and electrochemistry. Wagner first introduced the name to this discipline, publishing a paper in the second volume of Advances in Electrochemistry and Electrochemical Engineering in 1962, entitled *"The Scope of Electrochemical Engineering"* [4]. In that article, Wagner makes a clear distinction between electrochemical engineering science and electrochemical engineering technology.

In the middle of the 20th century there were not so many electrochemical technologies. From this time-distance, we might suppose that improvements of these technologies, starting from their appearance, occurred little by little through decades, more by intuition or by trial and error than by a scientific approach to basic phenomena affecting features of these processes. The contribution of electrochemical engineering, in its early stage (at the beginning of the '60s), to the design of industrial electrochemical cells and processes was very modest - almost negligible. Mass transfer considerations in electrochemical reactors had an academic rather than an engineering approach. This was mainly because there was no mass transfer limitation when the process operated with electrolytes having high concentrations of reacting ions, as was mostly the case with industrial electrochemical processes from that period. Current density distribution was not of major importance in those cases and for the side by side electrode configuration that was mainly used in electrochemical cells from that time. The operating current density was not limited by diffusion of reacting ions, but more by the cell voltage and consequently the specific energy consumption than by mass transport limitations or irregular current distribution.

At that time, electrochemical reaction engineering was a term of no significance for industrial practice. It was enough to find empirically the cell volume and inter-electrode distance needed to estimate the highest degree of conversion and the highest current efficiency at the lowest cell voltage. Not much attention was paid to enhancing the cell productivity by changing either the hydrodynamics conditions in a cell or the cell voltage in order to get optimal operating energy conditions.

A great step towards new cell design and its optimisation was made when the pioneering work of Jottrand and Grunhard [5] appeared in 1962, concerning the mass transfer enhancement in a tubular cell with a fluidised bed of inert particles in the inter-electrode space. Very soon after, numerous articles on the same subject but with different aims were published in the literature, providing evidence on how many times various inert turbulence promoters (ITP), placed in inter-electrode space in a cell, enhance the limiting current density due to an increase in the mass transfer coefficient. Besides higher cell productivity, a smoother electrode surface was obtained in the case of either metal deposition or dissolution, so that these types of cells were further developed with the aim of employing them in electroplating, electro-polishing, electroforming and other similar processes of electrochemical surface treatment, but also for metal removal from various sources. Several years after this series of articles, a new type of cell with expanded mesh electrodes, in which mass transport is facilitated by a fluidised bed of glass beads, was developed, and later marketed by BEWT engineers, UK, as a “Chemelec cell” for the recovery of metals from wastewaters and industrial effluents.

At that period (the second half of the ‘60s), a new electrochemical reactor also appeared, named the three-dimensional electrode cell (TDE-cell). The first articles on this subject were published at the end of the ‘60s and early ‘70s by English scientists from Newcastle and Southampton Universities and shortly afterwards by French scientists from the University of Nancy, as well as by German scientists from DECHEMA Institute.

Two revolutionary things, with a strong influence on further electrochemical engineering development and electrochemistry technology, also happened in the field of materials engineering during the ‘60s:

- dimensionally stable anodes (DSA®) were introduced in 1968 in industrial practice, providing many advantages over the existing electrodes at that time, first of all a lower cell voltage, thus making a great contribution in energy saving, and better anti-corrosive features, thus having a longer lifetime;
- a co-polymer, having ionic features (ionomer) was synthesised and patented in 1966, called NAFION and, due to its ability to conduct protons, it was considered and applied first as a proton exchange membrane (PEM) in fuel cells and later in many other electrochemical technology areas (chlor-alkali electrolysis, water electrolysis, metal electrowinning, electroplating, electrodialysis, sensors and battery fabrication, ...), mainly for dividing the anode from the cathode chamber in various electrochemical reactors. These two discoveries had a great influence on the philosophy of thinking of scientists and engineers, opening up new frontiers in the design and development of electrochemical cells and processes.

## 4. Growth (expansion) of electrochemical engineering as a science and art from the ‘70s till the end of the ‘90s

Through these three decades of electrochemical engineering growth, several directions were profiled and developed, mainly simultaneously. These directions are:

- Electrochemical reactors – development, modelling and optimisation;
- Electrochemical processes – improvements of the existing ones, and research and development of new ones;
- Interconnection of electrochemical engineering with other sciences, in some cases forming new scientific sub-disciplines;
- Publishing affairs – education of new generations in the electrochemical engineering community.

### *4.1. Electrochemical reactors research and development*

During the ‘70s and ‘80s electrochemical engineering had a very fruitful and progressive period contributing to electrochemical reactor engineering development, which resulted in new electrochemical reactors, as well as new electrochemical processes that appeared and found their place in electrochemical technology. One can say that the ‘70s and ‘80s were the peak of the electrochemical reactor research and development, when a lot of new cells appeared. Some of them were developed on an industrial scale and marketed in that period, as:

- “Chemelec” cells (already mentioned) for metal removal from rinse and wastewaters;

- Filter press cells for multipurpose use, either in mono- or bipolar mode (applied in water electrolysis, in electrowinning, in electro-organic synthesis, known as ICI Cell, or SU Cell);
- Swiss-roll cells employed in the electro-organic synthesis of vitamin C in the period when anodic oxidation had still to play a role;
- Pump cells;
- Capillary-gap mono- or bipolar cells, also for multipurpose usage;
- Rotating cylinder and rotating drum cells, both used for silver removal from spent photo-chemicals;
- TDE cells either as a fixed bed cell, such as an en-Viro cell, or as a fluidised bed cell for heavy metal ions removal from various industrial effluents;
- Cylindrical cells with coaxial electrodes configuration and TDE anodes used in the NALCO process;
- Bipolar trickle bed cells for electro-organic synthesis, as well as some others that can be found in the relevant literature that have found their use for all the aforementioned purposes [6].

Particular attention in that period was paid to the TDE cells with fluidised bed cathode and en-Viro cells, considered as a new very promising and very powerful electrochemical reactor. Very quickly after the first papers were published on the subject of TDE cells, a pilot-plant for the fluidised bed cell was constructed by CJB Developments UK in 1972, and afterwards the first industrial plant was built in 1978 in Germany by AKZO Zout Chemie Netherlands, only to be closed a few years later, having exhibited certain disadvantages [7]. Later, during the ‘90s, thanks to the appearance of advanced conductive materials with a very developed surface area and high porosity, a new generation of TDE cells, including the Poro-cell, Reno-cell, and Retech-cell, was developed and marketed. Although these cells were originally investigated and developed mainly for metal recuperation from various industrial waste solutions containing a low level of metal ions, sometimes a few p.p.m. only, they were later modified and used for electro-generation of different oxidants used for oxidation of different organic or inorganic compounds.

The theoretical knowledge and laboratory experience in electrochemical reactor engineering accumulated in that period contributed significantly to producing an optimal version of some of these cells on an industrial scale.

In fact, scientists working in electrochemical reactor engineering were faced with the problem of how to explore in the best way a simple relationship connecting the cell productivity with other variables affecting it. Cell productivity per unit of installed volume and unit of time (termed also as space-time yield [8]) is defined by the basic, well-known equation:

$$\frac{1}{V}\frac{\mathrm{d}m}{\mathrm{d}t} = \eta_{\mathrm{e}} \alpha k_{\mathrm{L}} a M c_{\mathrm{b}}(t) \tag{4}$$

where: $\eta_e$ is the current efficiency; $\alpha = i/i_L$ – ratio between operating and limiting current density; $a = A/V$ – specific surface area (working electrode surface per unit of cell volume); $k_L$ - mass transfer coefficient; $M$ – molar mass; $c_b(t)$ – concentration of metal ions in the bulk.

It follows from Eq. (4) that, for a given and constant bulk concentration $c_b(t)$, as is usually the case in effluent and wastewater treatments, there are three possibilities for an increase in the limiting current density as a measure of the maximum cell productivity:

A. to increase the mass transfer coefficient;
B. to increase the specific surface area of the working electrode; or
C. to increase both the mass transfer and specific electrode surface area in the same cell.

**A:** Mass transfer around an electrode can be enhanced by making and keeping forced convection in a cell. This can be carried out by:

1. changing the electrolyte flow conditions around working electrodes by either pumping or stirring, or using an ultrasound source; rotating, shaking or vibrating a working electrode, or in some other way;
2. introducing different ITPs in the inter-electrode space that will locally change electrolyte flow close to the electrode surface;
3. bubbling gas around the electrodes.

All three methods of mass transfer enhancement were extensively investigated and the contribution of each of them was quantified by scientists through the ’60s and particularly the ‘70s.

**B:** Specific electrode surface (*a*) area can be increased by:

1. decreasing the inter-electrode distance;
2. using either dispersive or porous conductive material connected with a current feeder as a working electrode (TDE).

**C:** A cell with a TDE fulfils both requirements – it has a high specific surface area and, at the same time, it has good mass transport properties independently, whether electrolyte flows by, or through, the TDE. This aspect of enhancing the productivity of a TDE cell particularly occupied the attention of scientists at that time, resulting in many papers relating to this issue.

Table 1 presents an approximate specific surface area and corresponding maximum space-time yield (productivity) for different cells as an illustration supporting the statements made in the previous text, but also to demonstrate an appreciable progression in designing a cell of high performances.

***Table 1*** *Specific surface area and maximum productivity of some particular cells compared under similar operating conditions [7]*

| **Type of cell** | **Specific surface area, $m^{-1}$** | **Productivity at $\alpha$ =1, mol $m^{-3}$ $h^{-1}$** |
|---|---|---|
| Conventional cell | 7.5 | 0.14 |
| Filter press cell | 30 – 170 | 0.56 – 3.17 |
| Capillary gap cell | 100 – 500 | 1.9 – 9.33 |
| Fixed bed cell | 1000 – 10 000 | 18.65 – 186.5 |
| Fluidized bed cell | 1000 – 10 000 | 37.3 – 186.5 |
| Rotating drum cell | 50 – 5000 | 9.32 – 93.3 |

It is important to emphasise that, when the bulk concentration in Eq. (4) is time-dependent (metal removal, for example), the current efficiency - $\eta_e$ is also a complex and time-dependent variable, depending, among other things, on the galvanostatic or potentiostatic mode of operation. Numerous papers on the modelling and optimization of electrochemical reactors were published at that time and later, in order to achieve the best working conditions, *i.e.*, the highest cell productivity at optimum energy consumption for not only the cells considered in Table 1 but also for others. These papers made a great contribution to the development of electrochemical reactor theory and engineering practice.

### *4.2. Establishing new and improving the existing electrochemical processes*

Thanks to the achievements in developing the new electrochemical reactors that are the core of every electrochemical process, great success was attained in developing new processes and technologies and in improving the existing ones.

i. A particularly significant contribution was made in electro-organic synthesis, where various organic compounds were produced electrochemically on an industrial scale, such as: tetraethyl lead, sorbitol/mannitol, glyoxylic acid, methoxy-benzylalcohol, adiponitrile, methoxy-benzaldehyde, methylethylketone, propiolic acid, anthraquinone, naphthoquinone and others. Many other organic products are under research and development on a pilot plant scale and many more are still on a bench scale and will be commercialized soon.

ii. In electrochemical metal surface treatment, comprising electro-coating, electro-polishing, electro-sinking and grinding, many new electrochemical tools and new electrolytes were developed and commercialised. Great success was achieved in electroforming, where numerous micro-products appeared, and various micro-fabrication methods were developed and marketed. Micro-reactor technology was one of the more propulsive areas, and very promising for the electrochemical production of some special chemicals in very small amounts. In that period – the early ‘70s – the so-called LIGA process had already been developed and employed, spreading its role into many areas of present day techniques and technologies: in micro-mechanics, micro-acoustics, micro-optics, in information technologies, in biotechnologies, biomedicine, and many other areas.

iii. The principle of the fuel cell (FC) was first described by W. R. Grove in 1839. Since then, many efforts have been made and many types of FCs have been considered for producing energy at low or high temperatures using mainly hydrogen as a fuel but also natural gas and coal gas, in a mixture with hydrogen or alone. The greatest improvements in development of proton exchange membrane (PEM) FCs capacity was achieved during the ‘90s. An almost 25-fold increase in output power was achieved in that period, starting from 70 kW $m^{-3}$ in 1989 and reaching 1.8 MW $m^{-3}$ in 1997. This leap was a consequence of the increased interest of the automotive industry, backed with adequate financial support, and was due also to new catalytic materials and cells development.

iv. In parallel with FC developments, electrochemical engineering contributed a lot to developing new and improving the existing water electrolysis and hydrogen production technologies. The improvements of alkaline water electrolysis technology consist mainly in improving the electrolytic cells to have an increased specific surface area; using advanced materials as separators has led to a reduced inter-electrode gap, thus reducing specific cell resistance. This, coupled with an increased operating temperature, as well as the introduction of new catalytic materials, makes the whole process more energy/economy viable. Besides these improvements, new technologies were developed in that period, based on Nafion membranes offering qualitatively new approach to hydrogen/oxygen production as well as water steam splitting on oxide ceramic.

v. Several substantial improvements were made at that time in chlor-alkaline electrolysis in that period (from the ‘70s till the end of the ’90). The most important was substitution of graphite with DSA, thus prolonging the anode life-time many times and preserving lower chlorine evolution overpotential. The other improvements were similar to those applied in water electrolysis, and relate to decreasing the inter-electrode space of electrolysers; monoor bi-polar mode of operation; and substitution of amalgam process by diaphragm and membrane processes, thus making the whole technology more environmentally sustainable.

### *4.3. Electrochemical engineering and other disciplines*

The period between the ‘70s and the end of the past century was also characterized by the penetration of electrochemical engineering into or interconnection with other disciplines. Here we will discuss only those that I consider to be the most important. The others will only be touched upon.

#### *Extractive metallurgy*

Electrochemical engineering has particularly contributed a great deal to the development of hydrometallurgy, which also made its own very substantial progress during the ‘60s and on, of the past century. Now, electrowinning is usually the last link in the technology chain for production of various metals from ores by leaching followed by solvent extraction/ion exchange and an electrowinning pathway. As a response to a significant growth in the theoretical knowledge and its experimental confirmation, many attempts were also made in that period to improve the existing or establish new purely electrochemical or metallurgical processes, as well as processes linked with other adjoining disciplines. We will mention here only those processes and technologies relating mainly to metallurgical engineering and environmental processes - the fields I am more familiar with:

- Copper electrowinning from pregnant leach solutions, namely, the leaching-solvent extraction-electrowinning (L-SX-EW) process of copper production, as a qualitatively new technology was introduced on an industrial scale at the end of the ‘60s. As the major cost component of this technology is the electrowinning step, which requires 8 to 10 times more power than electrorefining, shortly afterwards many attempts were made with the aim of making electrowinning less expensive and more efficient. One approach was an attempt to replace the anodic reaction of $O_2$ evolution by $SO_2$ oxidation at copper or zinc electrowinning, which would be a great step in making the process more economically acceptable than it is now. So far, it is still at a development level. Another interesting attempt was to carry out the electrowinning from an electrolyte containing cuprous instead of cupric ions, thus cutting significantly the energy costs. Another interesting process is electrolytic production of metals from corresponding sulphide mattes cast and served as anodes in electrorefining plants. So far, only in nickel metallurgy has such an approach been successfully implemented.
- The improvements made in extractive metallurgy of basic heavy metals were implemented in some other technologies, in which electrowinning is the final step;
- Replacing the cementation processes by direct electrowinning in zinc electrolyte purification from other metal ions using advanced cells based on TDE, prior to the zinc electrowinning;
- Recuperation of metals from spent electroplating baths, from spent solutions in electronics, from spent pickling solutions in the metal working industry, from mother solutions in salt production and from some other similar effluents that are produced in metallurgy or the inorganic chemical industry;
- Electrolytic metal powder production is nowadays an important segment, providing starting materials for sinter metallurgy, as well as in electronics, in metallic pastes production and for many other products;

- Applying different electrochemical coating and surface finishing methods leads to minimising the corrosion effects in wastage of materials, to which electrochemical engineering contributed greatly in the past and still currently does.
- Organic chemistry and organic chemical technology (electrochemical reactor design for massive production; micro-reactors design and implementation for production of very hazardous chemicals).

*Environmental protection*

In that period (‘70s to ‘90s), particular attention was given to environmental pollution and environmental protection, due to an increasing demand for environmentally sustainable chemical processes. As an answer to this demand, electrochemical engineering opened a new direction in the treatment of different industrial effluents. Coming into this important and broad area, electrochemical engineering started to play a key role in different aspects of pollution abatement, in both aqueous and gaseous phase. Electrochemical methods and devices were developed and employed for wastewater purification, either for removal of hazardous heavy metal ions from them or for cyanide or chromate destruction; for direct anodic destruction of organic species that must be destroyed prior to releasing such wastewaters into the recipient; for “in situ” water disinfection for human usage or for special purposes.

Nowadays, also thanks to the development of advanced materials, boron-doped diamond (BDD) anode is an industrial reality in drinking and wastewater treatment processes, and particularly useful for anodic destruction of those organic pollutants from wastewaters that can only be decomposed into less hazardous or even inert compounds at higher overpotentials with no water electrolysis [9].

Electrochemical engineering has found its place also in off-gas cleaning technologies for either direct electrochemical or indirect (using a proper electrochemically generated red/ox mediator) conversion of harmful gaseous off-gas stream constituents such as: $SO_2$, $H_2S$, $NO_x$, ammonia, $Cl_2$, amines, hydrocarbons and other organic constituents, previously absorbed by a proper absorbing solution, from off-gas streams. So, for example, different variants were considered and developed for $SO_2$ removal from flue gases and its oxidation by an electro-generated oxidant (Ispra-Mark 13), using a proper redox pair. A similar concept was also considered for $NO_x$ and $SO_2$ removal from gaseous mixture *via* absorption and oxidation of absorbed species by $Ce^{4+}$ ions electrochemically generated in a separate electrochemical reactor. An interesting and promising approach to direct gas purification from organic and nitrogen compounds is the electrochemical catalyst promotion, known also as NEMCA. By polarising a catalyst layer deposited onto solid electrolyte, its catalytic activity increases 10 to 100 times. So far this method is still at the laboratory and bench scale.

Soil remediation is another area where electrochemical engineering has found itself contributing significantly to resolving the problem of the purification of soil polluted by previous industrial activities.

*Recycling technologies*

Following the concept of “zero discharge effluent technology”, electrochemical engineering found its place in different recycling technologies, as an ultimate stage, for reclaiming and recovery of useful or harmful metals from different waste devices such as: spent batteries, printed boards and other electronic scrap –the amount of which grows ever greater; for metals removal from spent electroplating baths, as already discussed; from spent pickling solutions; from mother liquors; from spent photo-chemicals, different rinsing waters and other similar liquid sources.

Significant results were achieved in the recycling of acids and alkalis by splitting corresponding salts from large volume solutions produced in chemical industry or in metallurgy by means of electrodialysis or a combination of membrane and ion-exchange resin techniques assisted by electrochemical regeneration of loaded resin.

Wastewater purification and recycling in a process is in many cases more economically viable than to treat it to a purity level tolerable to be discharged into a recipient. Besides removing metal ions or destroying organic molecules, new electrochemically assisted techniques were developed and included in technologies for removal of fine suspended particles from rinse waters such as: electro-coagulation and electro-flotation, both efficiently employed on an industrial scale.

Some of the above-mentioned processes or technological innovations were developed and marketed, while others remained only as an attempt on a laboratory or pilot-plant scale waiting for further research, or were completely abandoned.

*Other areas*

Electrochemical engineering also penetrated the medical sciences, contributing to developing new medical tools, new devices, new indicators, new drugs, new compatible materials for orthopaedic purposes, for example, and many others.

In biochemistry, thanks to close collaboration with electrochemistry and electrochemical engineering, a new sub-discipline has appeared recently, named bio-electrochemistry, where a lot of new projects have been driven in developing new alternative sources for green energy production, such as bio-fuel cells; for promoting or inhibiting bacterial activity and its proliferation; for bioelectrocatalysis and for similar purposes using small currents to manage the bacterial life and features.

Obviously the three decades of the past century we have considered were very productive for electrochemical engineering science, as well as for electrochemical engineering technology.

### *4.5. Education of new generations of electrochemical engineers*

Due to a significant increase of papers relating to electrochemical engineering subjects, a strong need appeared, at the end of the ‘60s, to establish a new, specialized journal for publishing such articles. So, the first issue of the Journal of Applied Electrochemistry was published in 1970 [10].

In 1974, based on many theoretical and experimental contributions in electrochemical engineering, **Electrochemical Reactor Design**, written by D.J. Picket, was published as the first book on this subject. Later, several books with the keyword ***electrochemical engineering*** in their titles appeared, with the aim of spreading the basic principles of the new science among younger scientists and students studying chemical and metallurgical engineering. Some of the writers of these textbooks, who significantly contributed to the development of electrochemical engineering, are listed here chronologically as their books appeared: F. Coeuret and A. Stork (1984), I. Roushar (1986), E. Heitz and G. Kreysa (1987), T. Fahidy (1988), K. Scott (1991), F. C. Walsh (1993), H. Wendt and G. Kreysa (1999).

At that time (the early ‘80s) the first scientific symposium entitled Electrochemical Engineering was held at Loughborough University UK, as a response to the increased interest in presenting the research results amongst a specialised group of scientists. After this first attempt, the next symposia were held every three years, always at Loughborough. These events were a good indicator for identifying major areas of research interest and key directions which electrochemical engineering had moved towards, in the period between two events.

In the meantime, the EEWP (Electrochemical Engineering Working Party) was constituted as a branch of the EFCE (European Federation of Chemical Engineers).

Following a successful tradition of organizing electrochemical engineering symposia, the EEWP took over this duty from Loughborough University, and the 1st European Symposium on Electrochemical Engineering was organized soon after in Bad-Soden, Germany, in 1990. The 9th was held in 2011 in Patras, Greece. Besides this symposium, held every three years and having a European character, similar symposia are organized in the frame of world meetings such as ISE Annual meetings and CHISA congresses, allowing the gathering of scientists from other parts of the world to present their results.

Also, taking care of the young scientific population interested in coming into electrochemical engineering science, the European Summer School on Electrochemical Engineering was held for the first time in Toulouse, France in summer 1995 and thereafter in Ferrara, Italy; Patras, Greece; then in Palić, Serbia and most recently in Almagro, Spain, in 2009.

## 5. Electrochemical engineering at the end of the first decade of 21st century

Electrochemical engineering has extended far beyond the limits which were drawn by the early works in the ‘60s when the main theme was the mass transport of ions to or from an electrode. One can still occasionally find in the literature papers concerning this subject, but this is rather a reflection on the works done during the ‘60s to ‘80s. Such papers are mainly directed towards the corrosion process induced by mono- or two-phase flows. The published relationships at that time on mass transfer in electrochemical systems can today cover any particular technical problem. Also, current density distribution is something that can be routinely solved employing modern computational techniques and reliable numerical methods. With these tools, modelling of any electrochemical reaction system with mono- or two-phase flow of electrolyte and a dispersed gas- or solid phase in a cell with or without separator is now possible and something that can be successfully used in everyday practice. In these circumstances, what does electrochemical engineering at the end of the first decade of the new century mean? What is the role of the electrochemical engineer in following the established principles and in finding challenging new subjects and directions for further upgrading electrochemical engineering science? It may sound too declarative, but the following text could be an answer to the above questions:

> *“It is the responsibility of the electrochemical engineer in industry to simultaneously manage electrical consumption and chemical production. He or she must apply relevant scientific and engineering principles to design, construct, and operate a process in an economical, safe, and environmentally conscious manner. Improved understanding of scientific principles and the application of new materials can lead to more efficient cell designs and processes. The constant evolution of technology provides challenging and rewarding careers to engineers and scientists in a range of disciplines. Among the considerations that influence cell efficiency and lower consumption are temperature, spacing between electrodes, electrode material, electrolyte consumption, cell size, source of raw material, and production rate. Clearly, engineering skill is required for understanding these effects and for achieving optimum production conditions”.*

From “Industrial electrolysis and electrochemical engineering”
by M. Grotheer, R. Alkire and R. Varian [10].

## 6. New challenges and frontiers in electrochemical engineering [11]

According to the last sentence from the cited text, there will be a great period for further development of electrochemical engineering.

Indeed, one should expect the further influence of electrochemical engineering on improvements of existing electrochemical technologies, and development and establishment of new ones that are still on the laboratory scale. Some of them have already been mentioned in the previous sections.

In the past, electrochemical engineering faced much more towards electrochemistry and less towards chemical engineering. Closer collaboration with the second science has to be established in the future, particularly in solving problems arising in cell scaling and optimisation, and particularly those with three-dimensional electrodes (their implementation in different separation/purification processes is not as expected), as well as those with membrane processes. Knowledge about transport processes across membranes, for example, is not complete yet, in spite of the fact that many industrial membrane processes exist.

How to design and construct more efficient cells and large processes for electrowinning of copper to work at lower specific energy consumption? Few new hydrometallurgical processes are at present under development. The question is when they will be marketed. Each of them has metal electrowinning as the last stage in the whole technology chain. The contribution of electrochemical engineering to research and development of these processes could be extremely valuable.

How to design cells and the process for electrorefining of metals to improve their purity? In this view, fundamental principles of thermodynamics, kinetics, hydrodynamics, mass transport and potential and current distribution have to be transformed into engineering concepts in order to achieve economical operation and high quality products, lessening impurities into deposit as much as is permitted.

The contribution of electrochemical engineering to the research and development of these processes could be very valuable.

How to make fuel cells less expensive for wider applications? This is mainly connected with the kind and amount of materials to be built in, but also with fuel cells design and their scaling, with fuel production and storage and with many other things, which electrochemical engineering may contribute towards. How to make fuel cells capable of operating and surviving in extreme conditions?

What has electrochemical engineering still to do in the pollution abatement area? How to achieve a zero discharge of pollutants in both gaseous and liquid exit streams? Beside improvement of the existing technologies, a problem with the existing relationships, describing kinetics and thermodynamics, and with their validity at concentrations approaching zero, needs to be reconsidered. This is a great challenge on the theoretical level. Many opportunities exist in areas a few of which are listed below:

- Wider application of BDD electrode in wastewater treatment can be expected, which will allow a successful anodic destruction of hazardous organics from wastes.
- Electrokinetic soil remediation is an emerging technology that has attracted increased interest among scientists and officials because of its great potential.
- It can be expected that electrochemical promotion of catalyst (NEMCA effect) should emerge from the laboratory scale, turning a new page in exhaust gas purification.

- The appearance of room temperature ionic liquids (RTIL) opens new opportunities where electrochemical engineering has to find its place and role in establishing new processes based on a new approach.

How can electrochemical engineering contribute in materials recovery, waste minimisation and recycling? This problem is an area where electrochemical engineering is already involved, but it is also an area where there are a lot of still unsolved problems. In particular, this relates to the recycling of electronic devices and scrap and the recovery of valuable materials.

What could bioelectrochemistry and bioelectrochemical engineering, as sub-disciplines undergoing very fast development, do to establish new electrochemical processes, products and cells for different purposes?

What more can electrochemical engineering do in and for nano-technologies?

What should be next? Where then is the limit? I do not know. Do you?

In the end, what does electrochemical engineering mean nowadays compared to the definition given below the title, provided almost half a century ago? Do we have to redefine it according to the current state?

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