

Industrial electrochemical: a new teaching approach

Fernando B. Mainier, Luciane P. C. Monteiro, Antonio Carlos M. Rocha,
Renata J. Mainier

*Programa de Pós-Graduação em Engenharia Civil, Escola de Engenharia, Universidade Federal Fluminense,
Niterói, RJ, Brazil.*

Abstract: - The electrochemistry is a science with great range and applications in most industries. These applications include sensors, controllers, systems analysis, corrosion and anti-corrosion protection, surface technology, power generation, metal electrolytic production, materials and chemicals, recycling and wastewater treatment. The present work consists in an attempt to link and integrate two sciences, the industrial electrochemical and education, to develop a new technical and scientific approach that come admire the ideas generated and the experience gained in teaching and research of the electrochemical industrial processes. The aim of the creation of a discipline, the Industrial Electrochemical, vector learning based on historical formation of electrochemical principles, in breadth and in the application of various products of electrochemical industry and in laboratory experiments. In addition, the process of construction of knowledge in industrial electrochemistry converges in the formation of the critical technical conscience in electrochemistry, in the development of clean technologies and consequently on environmental preservation. Finally, it is concluded that the electrochemistry is the technique of the next millennium in both the production of metals, inorganic and organic products as in the treatment of industrial effluents.

Keywords: - *Industrial electrochemical, education, laboratory, environment.*

I. HISTORY

If it was possible to return to the past, in the late 18th century and early 19th century, to interview the precursors of electrochemistry, and, if possible, shoot their experiments and its laboratories, would probably be clarified and in situ evaluation of how the knowledge of this technique has spread.

Historical surveys and the biographies of the men of science of that era reveal that was a very fertile period, mainly in Europe, to the development of sciences and techniques. Names of scientists as Ampere, Biot, Fresnel, Oersted, Laplace, Lavoisier, among others, attest and strengthen that were intense research, covering mathematics, optics (light), electricity, magnetism and the fundamentals of chemistry [1].

At the end of the 18th century, in 1786, Luigi Galvani conducted a series of experiments and observations on the seizures occurred in legs dissected frogs, suspended by a brass hook on an iron plate and subjected to a discharge of an electrostatic machine. At the time, concluded that the observed phenomenon was sourced from a new form of electricity, called "animal electricity" [2, 3].

In 1793, Alessandro Volta, Professor of Natural Philosophy at Pavia, Italy, disputes this theory and shows that this no longer happens when two metal hooks, brass and iron, was removed from the frog's leg. Although, still, I believed that muscles and nerves of the frog worked as a high sensitivity electroscope can detect a weak electric current.

In 1800, Volta proposals a electrochemical cell consists series of discs of zinc and silver separated by moist cardboard and arranged alternately to form a pile as shown in Figure 1

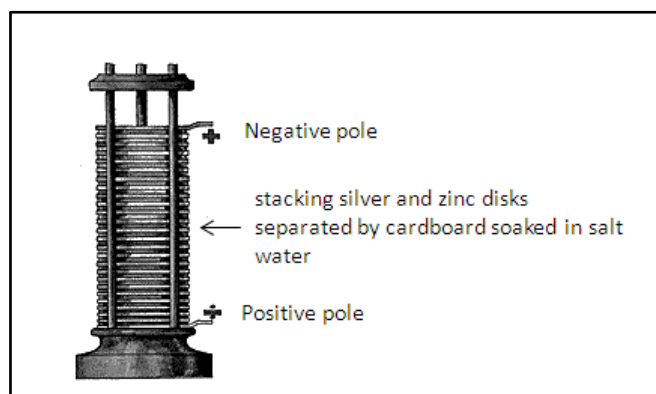


Figure 1-Cell batteries design developed by Alessandro Volta in 1800.

This historical fact has caused a great scientific twist at the time, marking the beginning of the knowledge of the "batteries", which, today, are already part of everyday life of man, is on the flashlight, portable radio, wristwatch or pacemaker, next to his heart.

A very interesting statement, dated December 1899, is the scientist Augusto Righi, who, speaking about the battery back, at the opening of the first National Congress of Italy's Electricity, said: this fact did not happen by chance, was the result of a long series of researches, insight, ingenious and intelligent experiments, inspired and based on successive logical deductions. Thanks to the pile (battery), the electricity had access, almost exclusively due to the object of this research, becoming a powerful energy source, fruitful and universal. Through this knowledge science offers a multiform energy, able to or intended to produce profound changes in human civilization, and may be compared to the power that the man obtained from fire in prehistoric eras [4].

All the evidence surveyed in the ancient literature come only confirm the importance of the discovery made by Alessandro Volta, because, without your direct participation, as experimenter, the company probably would not have enjoyed the scientific and technological development that has occurred and is still occurring in the modern world. If this does not happen, maybe the industrial development of Electrochemistry to take another direction or be waiting for 10 years! 20 years! or 100 years!

Quickly, this knowledge soon spread in the current science, because two months later, in May 1800, Nicholson and Carlisle were already the decomposition of water into oxygen and hydrogen, by means of electric current, using ideas based on the Volta. Even during the 19Th centuries, it is worth mentioning the important contributions that happened with the research and development of electrochemical techniques carried out by Humphry Davy [5, 6] and Michael Faraday [7, 8, 9].

The laboratory work performed by Humphry Davy, through the use of several batteries, allowed the discovery and elements such as sodium, potassium, magnesium, barium, strontium, calcium and chlorine. A critical appraisal of original publications of Davy shows, primarily through the diagrams and drawings of laboratory equipment, a certain amount of creativity, ingenuity and scientific criteria in the preparation of experiments, which in no way should the experiments of our century.

In 1813, Michael Faraday to 22 years went to work as an Assistant in the laboratory of the Royal Society and, from 1825, was Director of the Royal Society, replacing Humphry Davy, President. His contribution to electrochemistry was instrumental, because quantitatively defined the relationship between the mass of an element and the electric charge, passed through an electrolyte, through two fundamental laws, known as Faraday's Laws. In the field of magnetism, made two important discoveries; one was to determine the existence of diamagnetism and the other, the identification of the influence of magnetism on the optical rotation of the polarized light, plans on the basis of certain types of glasses.

In 1832, Faraday published that, through laboratory experiments, had managed to convert the magnetism into electricity. The experiment was to pass a current through a coil of wire, that generating a magnetic field, which was very recollected an electric current in the second coil.

Shortly thereafter, in 1834, Faraday published quantitative studies concerning the relationship between the amount of electricity that passes in a conductive solution and the amount of substance transformed into each of the drivers used. Their experiences were to pass an electric current by the given time in an electrolytic tank. Observed in this experiment that there was production of certain amount of substance, proportional to the amount of electricity. From these observations, began developing concepts for the establishment of the fundamental laws governing the electrochemistry.

It is important to note that the laws developed by Faraday on the electrochemistry preceded the discovery of electrons (1897), and therefore, the atomistic theory of Bohr. However, he, as a scientist, "felt" that

there was a stream, still unknown at that time (the electrons), that turning the anode to the cathode, producing the reactions in electrolytic cell.

Another fact that deserves mention is the familiar lead-acid accumulators, used in motor vehicles invented by Planté, 1859. This energy accumulator consisted of two plates of lead, as electrodes, immersed in sulphuric acid solution to 28% by weight and density equal to 1.2. The great advantage of these cells is the reversibility, meaning they could be regenerated by passing an electric current [3, 10].

According to Rieger [11] only in 1868 was created to Georges Leclanché the first dry cell, similar to current batteries, called at the period, Leclanché cell. It was composed of a zinc electrode and electrode graphite, enveloped by manganese dioxide (MnO_2) and placed in a porous medium, along with a 20% solution of ammonium chloride (NH_4Cl). Zinc is the negative pole and the graphite is positive pole providing thus a potential difference of 1.3 to 1.5 volts [3, 11]. The cell Leclanché scheme is presented in Figure 2.

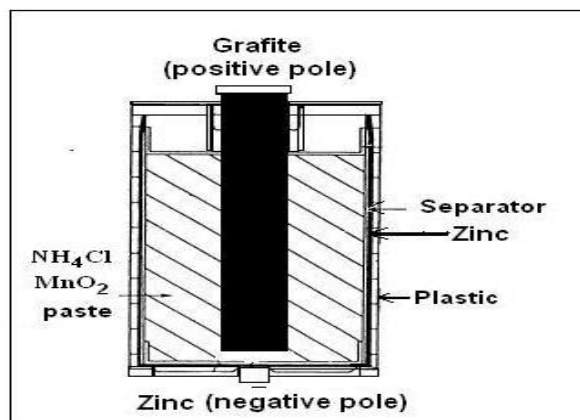


Figure 2 - The cell Leclanché scheme

The current theory about the electrode potential equating any previous knowledge of relations of electrochemistry was formulated by Nernst in 1889, to assume that every element is capable of forming an active electrode, partially dissolving when it is introduced in an electrolytic solution or pure water [12, 13, 14]. This means that in the solution, the free energy of the metal, metallic state is higher than the free energy of the metal in the ionic state. In this case, there is a tendency to pass thermodynamics of metal ions to the solution. This transfer of ions causes the metal plate to acquire negative charge due to the presence of electrons in it, and the solution get positive charge, due to new ions present in the solution [12, 13, 14].

This double layer on metal-solution interface, produces an electric field perpendicular to the interface, making the passage of more positive ions to the solution, causing the electrical current is reduced to zero, thus reaching the equilibrium State. This potential difference is called electrode potential. The value of this potential depends on the material that constitutes the electrode and electrolyte conditions (concentration, temperature, pressure).

Over the years, developed by electrochemistry Alessandro Volta, since 1800, has been solidified in more accurate theories and is currently classified as a segment of the physical chemistry and thus increasingly penetrates in other sciences that make interfaces with chemistry, finding applications in biochemistry, medicine and engineering, as show the technological segments presented below.

II. TECHNOLOGICAL SEGMENTS

The great progress of electrochemistry, directed to technology and called Industrial Electrochemistry, has provided a series of developments, reaching various segments and industrial applications, such as batteries, fuel cells, metal coatings, electrolytic refining of new metals, electrochemical synthesis of organic products, sensors, monitoring, controllers, analysers, anti-corrosion protection techniques, power generation, effluent treatment and recycling, etc [15, 16].

Electrochemistry, as science creates knowledge and applied technology develops and produces a product which, for the most part, brings benefits to society, but, on the other hand, these means of production and the final product thrown end up creating environmental impacts. But also, as a science, has the power to create knowledge in the area of cleaning up, through the development of efficient processes of contaminant removal in industrial effluents.

In this way, these applications can be classified into direct and indirect. The direct application assumes a process that uses, specifically, the electrochemical principles, whether spontaneous or non-spontaneous. The

indirect applications refer to processes that occur without a specific enforcement of the electrochemical potential, although there are grey areas difficult to be classified.

Currently, the Industrial Electrochemical no more restricted to aluminium, electrolytic copper or zinc, or the manufacture of chlorine and caustic soda and not to the production of hydrogen and oxygen by electrolysis of water; It has been designed in line with the clean technologies acting in the synthesis of new organic products, recycling and treatment of industrial effluents [15, 16, 17].

The processes and products generated through electrochemical technology represent, today, in the United States, a large share of the American market, with about 35 billion dollars.

III. ELECTROCHEMICAL INDUSTRIAL DISCIPLINE IN ENGINEERING COURSES: A CRITICAL VIEW

On the basis of the early 19th century to the present day, it turns out that a striking prints Electrochemistry in the various sectors of society, whether through the dissemination of batteries simple and rechargeable batteries sophisticated, is in obtaining metals, such as aluminium, or, in modern industrial dumps treatments aimed at the preservation of the environment. The technology demonstrates the great power of diffusion that this technology has left, through its brands and roots in various parts of the world and even in space conquest.

However, as knowledge diffusion, discipline is still tentatively presented or is jettisoned and virtually ignored in the teaching-learning process engineering education course.

To give you an insight into the importance and the relationship of electrochemistry in the context of knowledge, based on the daily life, seeking, without need of insights and interviews, the behaviour and the comments of a character of society, with social status set against electrochemistry, which, directly or indirectly, is part of your day-by-day on the way home-work-home.

Upon waking, hear the shrill sound of the alarm clock or radio music, noting that both are powered by batteries, but in his innocence is not able to assume that disposable battery, also called the "dry cell", was developed by Georges Leclanché, in 1880. In addition, does not have the dimension of that, currently, the production of disposable batteries in the world is about 13 billion per year.

At breakfast, the aluminized paper, involving the cream cracker or chocolate cake and the window with aluminium frames reflect, in this century, the presence of Electrochemistry in the great production of this metal. However, this only occurred due to the industrial electrochemical process, which transformed the cost of 1,500 dollars per kilogram aluminium in 1846 to a dollar in 2013.

To start the car, the common man never would remember of physicist Gaston Planté, man of science that developed in 1859, and lead-acid batteries in automobiles. The greatness of this invention can only be evaluated by determining the number of vehicles circulating on this planet in 100 years.

In the office, around the common man he sees the chrome coating of the chair, the cadmium coating of the door lock and the cell phone lithium battery, however, completely unaware that the computer in front of you has numerous electrochemical coated parts by metals and alloys, which provide state-of-the-art properties. The corrosive process that takes place in the city is also related to electrochemistry, electrochemical corrosion.

To get home, this citizen equal to others in society, while reflecting and questioning those times, is very clear your ignorance of the electrochemical action in number of inventions that has provided the welfare in your life. Leading him to think that without the diffusion of knowledge of electrochemistry in society, it is difficult to the understanding of these actions.

On the other hand, the birth of the critical conscience begins to take shape on the need to evaluate critically how the electrochemical technology, to be questioned about the advantages and disadvantages that this technique brings to man and the environment.

In raids made in University, technological centres, fundamentally it was noted that the scenario described for the common man is not very different from that found in the students and some teachers, especially in questions directed to technology and the environment.

There was widespread ignorance from the most important historical facts to manufacturing processes and products from these processes. Based on the assumptions of the reason of scientific and technological knowledge, it is unacceptable that is allowed to technologists and technology manager's lack of techniques and waste that such processes may cause environmental system. One of the examples of contamination can be quoted cadmium contamination both jackets as the nickel-cadmium [18].

In the same way that the Industrial Electrochemical can be used to decontaminate certain environmental contamination, she, like technology, has spawned and continues generating waste or products which, indirectly, cause environmental problems, as is the case of mercury cells for production of chlorine-soda, aluminium production, the production of electrolytic zinc and cadmium, among others. On the other hand, the power of industrial society moves precipitously and imposes its guidelines on commercial and industrial

transactions, forcing the development of processes that are often contrary to the well-being of society [18].

Today's technicians or engineers can no longer be adrift of the current technological revolution; it is increasingly important that this professional is formed in the critical view of industrial processes and have creativity, ability to work in group, multidisciplinary and a critical positioning of industrial processes that cause impacts on the environment.

It is difficult to make predictions, however, it is essential to the establishment of the responsibility of the future, mainly about the issue of contaminants and waste generation, although such liability is intrinsically linked to the permanent surveillance of environmental agencies, non-governmental organizations, to environmental and public health impact, making mandatory the knowledge of routes and the establishment of industrial standards and critical parameters.

IV. PROPOSED IMPLEMENTATION OF INDUSTRIAL ELECTROCHEMICAL DISCIPLINE COURSES IN CHEMICAL ENGINEERING AND INDUSTRIAL CHEMISTRY

Based on the requirements above is made, the following is a proposal for implementation of the teaching of Industrial courses Industrial Electrochemical discipline of Chemical Engineering and Industrial Chemistry consisting of the following parts:

IV.1 - OBJECTIVES

The discipline must achieve the following objectives:

- to demonstrate the importance of knowledge of electrochemistry since the 18th century;
- identify, interpret, and analyse the principles, laws and the mechanisms involved in the industrial electrochemical processes;
- critically evaluate the advantages and disadvantages of electrochemical processes and their products;
- analyse environmental problems, on the basis of electrochemical processes;
- expand the ability of the student to observe, reflect, analyse and develop the sense of searching and questioning, based on electrochemical experiments.

IV.2 – CONTENTS

The history of electrochemistry. Review the concepts of: oxidation-reduction reactions, electrode potential, electrochemical cells, electrolysis. Electrolytic and electrochemical corrosion. Cathodic protection. Electrochemical and electrolytic coatings. Anodizing. Electro analyses. Electrochemical synthesis: metals, inorganic and organic compounds. Electrolytic processes in industrial effluents.

IV.3 – PROGRAMME

Unit	Description
I	A vision of Electrochemistry in the timeline; technological areas of electrochemistry.
II	Review the concepts of: oxidation-reduction reactions; oxidation States; oxidation-reduction reactions balance; Ionic equations of reduction and oxidation; electrode potential; table of potential; spontaneous and non-spontaneous processes; electrochemical cells; battery types (different metal electrodes, concentration, temperature); Nernst equation; Leclanché cell; lead-sulphuric acid, nickel-cadmium and nickel-iron; fuel cells; solar cells; electrolysis; Faraday's laws.
III	Corrosion and anti-corrosion protection; electrochemical corrosion: mechanisms and types; Galvanic corrosion, dezincification, graphitic corrosion; electrolytic corrosion: mechanisms.
IV	Fundamentals of cathodic protection: criteria, galvanic anode, inert anode.
V	Electroplating; electrochemical coatings; electrodeposition of metals and alloys; metal deposition without the aid of electric current; anodizing; application of paint for electrophoresis; evaluation of zinc-based paint.
VI	Electrolytic processes of production of metals: alkali and alkaline earth metals, copper, zinc, cadmium, aluminium, silver and gold; electrolytic refining.
VII	Electrolytic processes of production of chemicals: sodium hydroxide, chlorine, hydrogen, oxygen, fluorine, hydrogen peroxide.
VIII	Electro analysis, pH meters, oxidation-reduction, selective electrodes conductivity for ions; polarography; biosensors.
IX	A vision of contaminants into the environment; clean technologies and electrolytic processes; electrolytic processes of industrial waste treatment: chromate, sulphide, cyanide; recovery of hydrogen and chlorine from residual hydrochloric acid; chlorine generators for treatment of seawater; Elimination of heavy metals (Cu, Ni, Cd, Pb).

IV.4 – PROPOSED EXPERIMENTS

Unit	Description
Fundamentals of electrochemical	Electrical conductivity of various liquids; electrochemical tensions qualitative determinations, galvanic cell; concentration cell; Leclanché cell; determination of the Faraday constant.
Electro synthesis of inorganic products	Obtaining sodium hydroxide, chlorine and hydrogen with mercury cell and diaphragm cell.
Electro synthesis of metals	Production of copper, from the acidic leaching of oxidized copper ore concentrates; electrolytic refining of copper from copper grosses (scrap); zinc production from zinc ore.
Battery	Sulphuric acid-lead battery.
Electrochemical monitoring	Determination of copper in brass; determination of resistivity of soils.
Treatment of metals and alloys	Anodizing; electroplating; metal deposition without the aid of electric current.
Corrosion and corrosion protection	Electrochemical corrosion; construction of cell Cu/CuSO_4 and potential measures; cathodic protection with galvanic anodes in seawater.
Treatment of industrial effluents	Removal of Cu^{2+} , Ni^{2+} , Pb^{2+} , chromate (CrO_4^{2-}) in industrial effluents.

As an example, then, a laboratory experiment is presented to demonstrate the concepts of carbon steel corrosion in seawater.

- **Description of Experiment: Corrosion of a steel plate without uncoated carbon steel compared to a steel sheet with two coats of epoxy paint risk penetrating.**

Two carbon steel plates (20 cm × 10 cm), one coated with two coats of epoxy paint with a total thickness of 250 μm , are fixed in the holder and immersed in a transparent acrylic container with a capacity of 50 L holding a solution containing 3.5% (by weight) sodium chloride, representing seawater, as shown in Figure 3. The plates should be immersed for 15 days to evaluate the performance of the corrosion process.

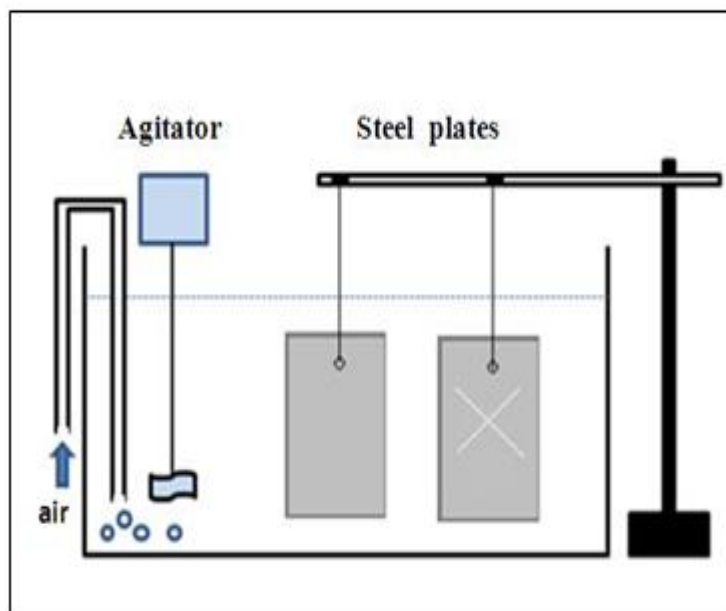


Figure 3 - Assay steel plates immersed in seawater

Figure 4 A illustrates the progress of the corrosion process in the laboratory experiment on steel plates with and without epoxy coating. The progress of the corrosion process is evidenced in steel plates photographed after three days of immersion in salt water, as shown in Figure 4 B. Note that the steel sheet is coated with epoxy which lines the corrosion area.



Figure 4– Development of the corrosion process (three days).

V. CONCLUSIONS

The experiments, the questions and the associated research made by students of the course of Chemical Engineering and Industrial Chemistry aim to:

- facilitate and broaden the understanding of electrochemistry and environment in the timeline;
- awaken in the student the need of development and clarification of physic-chemical mechanisms involved in each process;
- guide students towards research and questioning, giving them basic experience in the kind of physical and chemical measurements, leading to qualitative and quantitative results to relations with the environment;
- stimulate the relentless pursuit of technological innovation, through special projects, and if necessary to break through the direction of traditional experiments; form the critical technical and environmental consciousness.

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