Journal of Solid State Electrochemistry
https://doi.org/10.1007/s10008-023-05429-6

ORIGINAL PAPER

Electrochemistry for non-electrochemists: a postgraduate formative project

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Received: 12 January 2023 / Revised: 10 February 2023 / Accepted: 13 February 2023

Abstract
The essential guidelines are presented of a postgraduate course on electrochemistry for master studies at the University of Valencia (Spain). This course has been designed for students with a minimal knowledge of electrochemistry. It is based on laboratory experiments that, starting from an initial theoretical core, promotes the in-laboratory discussion of concepts, operations, functional relations, etc. The course, although focused on voltammetric techniques, covers the main concepts and experimental aspects of electrochemistry and particular attention is put to erroneous conceptions regarding fundamental physicochemical concepts and operations (misconceptions) as well as on general aspects of the scientific methodology (meta-conceptions) around this discipline.

Keywords Electrochemistry · Learning · Laboratory · Evaluation

Introduction

Since the times of Faraday, electrochemistry has played an ever-growing capital role in the development of concepts and theories in physics and chemistry [1]. Currently, electrochemistry is directly involved in important application fields, namely, energy generation and storage, electrosynthesis, corrosion, and electroanalysis [2–7]. Figure 1 summarizes one of the possible schemes of the main areas of electrochemistry divided into fundamental research and fields of application.

In spite of this significant role, electrochemistry is not everywhere presented as an individual subject in the curriculum of chemistry studies, and is mainly covered in physical chemistry and analytical chemistry programs [8, 9]. There, electrochemistry is usually taught within thermodynamics and kinetics (in physical chemistry), and within "instrumental methods" (in analytical chemistry), where it is taught together—and preferentially—with spectroscopy (atomic and molecular) and chromatographic techniques, in graduate and postgraduate (master) courses. In the context of the recent Bologna reorganization of university studies in Europe [10], postgraduate masters have been implemented as tools for effectively linking the recent graduates to the professional context in two directions: research associated to universities and R&D programs and normalized professional activities such as analytics, plant and process control in industry, etc. [9].

In this context, the University of Valencia (Spain) developed since 2010 a "master of analytical techniques in chemistry" (*Técnicas analíticas en Química*, TAC), ascribed to the departments of analytical chemistry and inorganic chemistry, to be imparted to graduates in physics, chemistry, biology, chemical engineering, and environmental sciences. The subject comprised a monographic course on "electrochemical techniques" with a scheduled time equivalent of 24 h with mixed theoretical–experimental character. The "open" character of this master implies that a part of the students have only a very basic (almost naïve) knowledge of electrochemistry so that there is a need to address the concepts for "non-electrochemists." This situation can be seen as particularly interesting [11] but in turn

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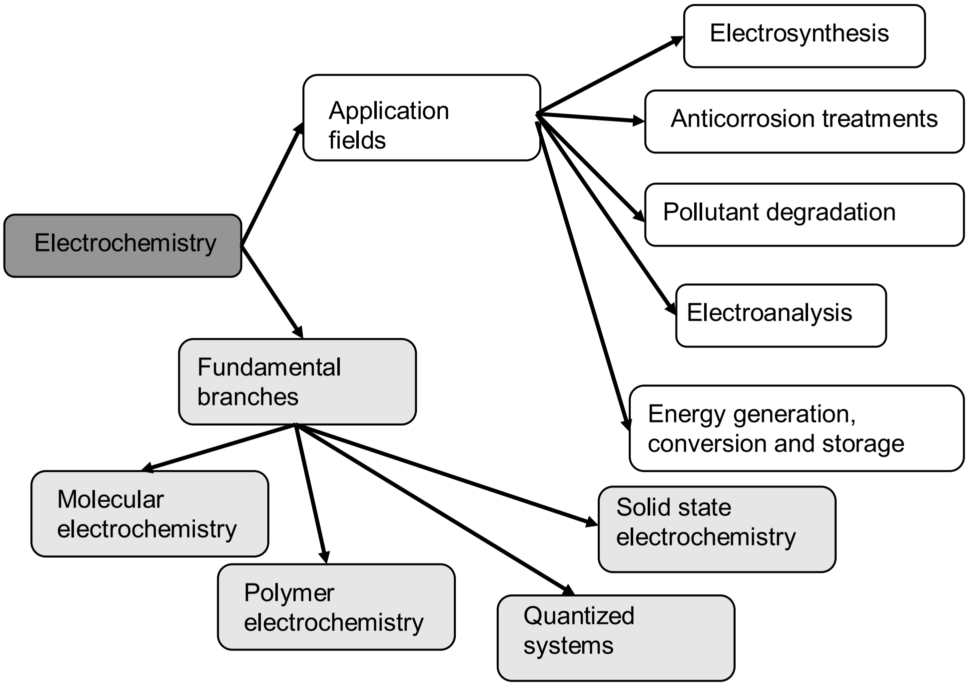


Fig. 1 Main areas of electrochemical science dealing with its fundamental research and the corresponding application fields

involves difficulties from the educational point of view. It is known that alternative conceptions are particularly influential in chemistry imparted to non-chemists, in particular with regard of electrochemistry, as recently reviewed by Tsarpalis [12]. The current report describes the aims, structure, and epistemological and educational basis of an educational project devoted to impart an electrochemistry course in the frame of the aforementioned master.

Educational approach

Challenges on teaching electrochemistry

The first challenge to be faced in the postgraduate electrochemistry course is topical: roughly, first-level electrochemistry is confined to the Nernst equation(s) and the Faraday laws of electrolysis in general chemistry courses [13], whereas a second-level electrochemistry is provided in instrumental analysis courses. The latter is focused on coulometry, potentiometry, and amperometry, frequently extended to the essential aspects of voltammetry, including stripping analysis for trace metals in solution. The access to this second-level approach to electrochemistry is exclusively given to chemistry graduates. It is not taught for biology and chemical engineering graduates.

The second problem deals with the wide variety of techniques and application fields of electrochemistry [14, 15]. These range from pH measurements, widely used by chemists, engineers, biologist, etc., to techniques used in specialized contexts, such as electrochemical impedance spectroscopy, which is important in corrosion science and polymer science. Keeping in mind that the aim of the postgraduate course is to link the instruction of graduates to a future professional context, it seems obvious that the lack of specific treatment of electrochemistry is a problem superimposed to the variety of techniques potentially accessed by the graduates in their future professional activity.

A third (group of) issue(s) deals with the intrinsic difficulties of teaching/learning electrochemistry, most of them common to all science, but several of which are specific to chemistry and electrochemistry. The persistence of misconceptions, spontaneous conceptions, or alternative conceptions, widely studied by educational research in the last decades [16, 17], is one of the essential trends in this regard. The "spontaneous conceptions" refer to those acquired by the students as a result of a variety of influences differing from the genuine scientific knowledge. These were characterized by (i) the variety of influences determining their generation ("common sense," mass media information, …) and (ii) their reluctance to be changed by means of most conventional educational approaches. The first examples were studied around the persistence of a pre-Galilean view of motion in secondary school students despite orthodox instruction [16, 17]. Subsequent research identified erroneous conceptions having the above characteristic trends in almost all branches of science, chemistry in particular [18–20]. Research in electrochemistry teaching has been focused on common misconceptions of students in understanding electrochemical cells [21, 22], electric circuits and oxidation–reduction equations [23], galvanic cells and potentials [24–28], among others [29–33]. However, these studies are largely focused on secondary school students and there are no systematic studies at the graduate/postgraduate level. Table 1 summarizes several of the described students' misconceptions in electrochemistry.

In the graduate/postgraduate context, studies on analytical chemistry education showed the existence of a "black box" view of instrumentation [34, 35], which even extends to electrochemistry. For our purposes, the relevant point to emphasize is that such misconceptions concern not only specific concepts and methods, but also meta-conceptions. The meta-conceptions involve concepts sustained by concrete definitions and also concepts "in flux," associated with operational and or relational definitions [36], analytical strategies, and operational skills [34]. The meta-conceptions can be viewed as the spontaneous ideas about of how science works, how scientific knowledge in constructed, and how science and technology are applied to solve problems. Ultimately, these meta-conceptions deal with something like a naive epistemology. Several were characterized around chemical analysis [34, 35] and also operate in the context of teaching electrochemistry (see Table 2).

Additionally, postgraduate teaching should involve the analysis of uncertainties in measurements, which are frequently misinterpreted even in the research literature, including differentiation/integration [37]. Also, the links between thermodynamics and kinetics [38, 39], the meaning of the Butler-Volmer equation and electron transfer coefficients [40–42], nucleation phenomena, etc., need careful attention [43, 44].

Methodological approaches

There is a variety of methodological options available for educational purposes. Specifically treating instrumental analysis, purely laboratory-based approaches [45], and mixed theory/laboratory [46] approaches, as well as investigative [47], technological-based [48], among others [49–53], strategies have been proposed. In the field of electrochemistry, there are plenty of experiments available for their use in education (graduate level) [54–61], all essentially focused on voltammetric measurements. However, the problem is how to integrate the experiments into a significant teaching of basic concepts of basic electrochemical basic concepts and techniques.

In this context, the transition between preconceived ideas of the studied phenomena and the "scientific," elaborated understanding of the same plays a crucial role in higher education [62], where students' unreflective studying may lead to a fragmented perception of scientific knowledge [63]. Inquiry-based approaches [64, 65] emphasize the interest of integrating the conceptual knowledge into the inquiry and discovery sequences [66, 67], ultimately aimed to construct scientific description of phenomena (either physical or physical-technological) consistently with the hypothetical-deductive nature of science [68]. In this regard, given the organization constraints (vide infra), the proposed postgraduate course is based on a series of laboratory experiments conceived as investigative, laboratory mini-projects [69] with a des-regulated configuration. The central idea is to obtain a series of empirical results immediately submitted to collective discussion through open questions complemented by exercises to be solved at home.

Aims, structure, and methodology of the postgraduate master

The postgraduate master was conceived on the basis of two main aims:

(a) To promote the understanding of the fundamental science concepts and procedures involved in electrochemistry with particular attention to common misconceptions.
(b) To promote an operational view of the concepts and methods involved in the most common electrochemical techniques.

The lessons, in total 24 h, are taught to two groups of 12 postgraduate students. The classroom/laboratory sessions are divided into one preliminary classroom session (3 h) and five laboratory sessions (20 h). Finally, a written test follows (1 h). This structure is common and necessarily adopted to all disciplines within the TAC master. According to this educational structure, the adopted methodology combines investigative [47], mixed theory/laboratory [46], and discovery [49] approaches. They follow an inquiry learning

Table 1 Some common misconceptions described in electrochemistry teaching [21–23]

Misconceptions	Source
Electrons flow through the salt bridge and electrolyte solutions to complete the circuit	[21, 23]
Plus and minus signs assigned to the electrodes represent net electronic charges	[21, 23]
Water is unreactive in the electrolysis of aqueous solutions	[21, 23]
Half-cell potentials are absolute and can be used to predict the spontaneity of individual half-cells	[22]
Electrochemical cell potentials are independent of ion concentrations	[22]
Ions move only due to the application of an electric field	[21–23]

Table 2 Summary of meta-conceptions about electrochemistry

Meta-conception	Context
Electrochemistry as “complete” scientific field	Static view of science: currently accepted theories are complete and “true”
Theories can entirely be verified by experimentation	Popper’s falsacionism and equivalent epistemological issues neglected
Experiments are “unique,” always conclusive	Non-critic view of science, ultimately, neglecting Kuhn’s view of paradigms and directly related epistemological views
Electrochemical processes are all described by the Nernst equations	Negation of complexity, reductionism in science: science is limited to several laws which apply to all situations
Superficial view of instrumentation and processes	Instruments operate as “black boxes” without need of critical data interpretation

philosophy [62–67] by presenting a series of “open,” deregulated laboratory experiments. The latter comprise data analyses involving inferences and predictions with detailed concept clarifications. Table 1 summarizes the structure and topics of the course. For reasons of time confinements, experiments are based on voltammetric measurements using conventional equipment. Due to the availability of three potentiostatic devices, the group of 12 students is divided into 3 groups, each group working with an electrochemical device in the research laboratory. The customary safety cautions were adopted.

The first “theoretical” session starts with the description of the well-known experiment of water electrolysis, presenting a basic concept of electrochemistry. Here, the emphasis is put on the idea that electrochemistry is focused on processes involving the *transfer* of electrons (more generally, charge) across the interface separating an ionic conductor (the electrolyte) and an electronic conductor (the electrode). This process is treated as a heterogeneous chemical reaction coupled to processes of charge *transport* (diffusion as a typical case) in each of the involved phases. Possible parallel chemical reactions (e.g., gas evolution, precipitation/dissolution of solids) are mentioned in order to outline how complicate the overall electrode process may be. Depending on the electron *transfer* rate and the rate of *transport* of electroactive species, the electrochemical processes can be divided into electrochemically reversible (operationally, “fast” charge *transfer* as compared to a slower *transport*) and electrochemically irreversible (similarly, “slow” charge *transfer* as compared to a faster *transport*). This distinction is essential, because only reversible processes can provide electrochemical parameters having thermodynamic significance; i.e., only for such processes, the Nernst equation applies. It is also important to remark that electrochemical measurements are an important source of thermodynamic and kinetic data. However, most electrochemical data (for instance, most standard electrode potentials) are not obtained from direct electrochemical measurements because of the irreversibility of the involved electrochemical processes. An approximation to this generalized, introductory view to electrochemistry can be seen in [70].

Each laboratory session was conducted upon launching an experiment whose performance was accompanied/followed by possible descriptions, predictions, etc., intercalating explanations and concept definitions. In the development of the laboratory lessons, attention was paid to the clarification of electrochemistry concepts, procedures, and scope. Figure 2 shows a simplified scheme representative of the implementation of misconceptions and meta-conceptions in the laboratory lessons. The experiments have been selected among well-known electrochemical processes following a flexible sequence in which the students are challenged to propose explanations and predictions and subsequently propose methods for testing predictions. Two consecutive experiments are scheduled in each laboratory session, as described in Table 3, but eventually, additional experiments are performed. The discussions are intended to clarify experimental aspects (what concrete operations/observations provide information on electrochemical features), conceptual aspects (what concepts are involved in descriptions), and integrated explanations.

Discussion

Table 4 summarizes the experiments, conceptual aspects, and implications to be discussed in the laboratory sessions L1 and L2, both structured around molecular electrochemistry. Session L1.1 starts from a brief description of the cell, electrodes, equipment, software, etc., and the performance of cyclic voltammograms using air-saturated aqueous buffer solutions (sodium acetate buffer at pH 4.75 and potassium phosphate at pH 7.00) at glassy carbon and gold working electrodes. Figure 3 depicts typical cyclic voltammograms recorded at Au electrodes in these solutions. Here, the students are challenged to describe the different voltammetric signals appearing in the voltammograms. The oxygen evolution reaction (OER), the hydrogen evolution reaction (HER), and the reduction of dissolved oxygen (oxygen reduction reaction, ORR) can easily be seen by the students at both glassy carbon and Au (or alternatively Pt) electrodes. At Au electrodes, however, additional processes appear consisting

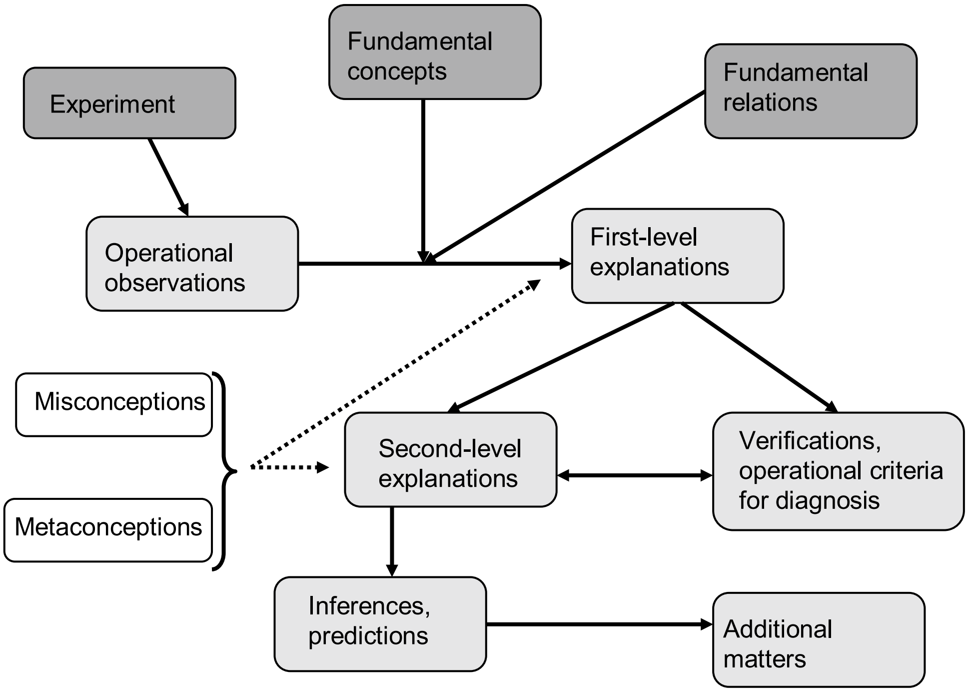


Fig. 2 Simplified scheme for the possible implementation of strategies for removal misconceptions and meta-conceptions in the laboratory lessons

of an anodic wave at ca. 1.0 V vs. Ag/AgCl followed by a sharp cathodic peak at ca. 0.5 V in the subsequent potential scan in the negative direction. The interpretation of these signals in terms of Au oxidation to a fine layer of gold oxide(s)/oxohydroxydes has motivated abundant literature [71, 72]; for the purposes of the course, the relevant point to underline is the non-inert character of the electrodes.

Several "open" questions can be proposed to the students around the application of the Nernst equations:

– Are the recorded (approximate) electrode potentials equal to those expected from the standard potentials?
– Are the potentials shifted according to the experimental pH variations?

Table 3 Structure of the postgraduate course on electrochemistry

Session (time/hours)	Type (place)	Matters
1 (3)	Classroom	Water electrolysis and electrochemical processes; general view of electrochemistry and application fields. Classification of electrochemical methods Thermodynamic and kinetic descriptions of electrochemical processes; charge transfer across interfaces and charge transport through phases; the Helmholtz double layer Electrochemical processes as heterogeneous reactions: electrochemical mechanisms: HER Impedance measurements, fundamentals of electrochemical impedance spectroscopy
2 (4)	(L1.1) (L1.2)	Cyclic voltammetry, instrumentation, types of electrodes, HER, ORR, and OER processes at glassy carbon and gold electrodes Study of an electrochemically reversible process; operational parameters; reversibility tests and diffusion control tests Deviations from reversibility and uncompensated ohmic drops
3 (4)	(L2.1) (L2.2)	Cyclic voltammetric study of apparently irreversible processes: electrochemical irreversibility vs. coupled chemical reactions; diagnostic criteria "Free" see text
4 (4)	(L3.1) (L3.2)	Electrochemistry of surface-confined species: stripping processes and trace metal analysis Electropolymerization; conducting polymers and strategies of electrode modification
5 (4)	(L4.1) (L4.2)	Solid-state electrochemistry; voltammetry of microparticles and ion intercalation processes: Prussian blue electrochemistry Solid contact potentiometric sensing
6 (4)	(L5.1) (L5.2)	Polarization curves and corrosion potentials Impedance techniques: Nyquist and Bode representations; modeling and fitting
7 (1)	Classroom	Written test

Table 4 Electrochemical experiments and aspects to be subsequently developed. Laboratory sessions L1 and L2

Experiment	Questions/concrete aspects	Subsequent implications
L1.1: CV in buffered aqueous solutions	What are the extreme processes at highly positive and highly negative potentials? Observation of differences depending on the electrode material pH dependence of the voltammetric records Observation of the response of dissolved oxygen The Ag/AgCl reference electrode as a "redox buffer"	Available range of potentials: "the solvent window" Electrode kinetics for oxygen evolution reaction and hydrogen evolution reaction The inertness of the electrodes, formation (and stripping) of Pt and Au electrodes The need/convenience of degasification The need of supporting electrolyte
L1.2: CV in a $Fe(CN)_6^{4-}$ aqueous solution	Electrochemically reversible voltammetric response, peak currents and peak potentials Variation of such parameters with the potential scan rate Reversibility criteria and diffusive control criteria Influence of resistive and capacitive effects	The problem of defining a proper base line for current measurements Separation of experimental data from the strict reversibility criteria: electrode kinetics vs. resistive and capacitive effects Testing the independence of the mid-peak potential on the potential scan rate Testing the proportionality of the peak current on the square root of potential scan rate
L2.1: CV in a dopamine aqueous solution	Apparently irreversible voltammetric response Electrochemical irreversibility vs. coupled chemical reactions Possible diagnostic criteria upon varying the potential scan rate Analysis of the voltammetric response involving different voltammetric signals in different potential regions	Exposition of the complicated voltammetric pathway for the electrochemical oxidation of dopamine Testing the possible reversibility of the electron transfer process, voltammetry at high potential scan rate Attribution of voltammetric signals for the reduction of dopamine quinone Description of different possible electrochemical pathways
L2.2: Several alternative options	Voltammetry of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ Voltammetry of air-saturated Bu_4NPF_6/DMSO Voltammetry of Cu(II) in concentrated chloride solutions Research projects	Determination of the redox state Electrochemistry in non-aqueous solvents, generation of reactive species Successive electrons transfers/stabilization of oxidation states via complexation Presentation of research projects on electrochemistry

- How to explain the differences between the response at glassy carbon and Au electrodes?
- What is the role of the Ag/AgCl reference electrode and how to explain its (essentially) constant potential?

Apart from the general aspects dealing with the available potential range, these questions are addressed to identify the electrochemical processes which frequently occur under non-thermodynamic control and need considering the kinetics of the charge *transfer* charge *transport* processes.

With regard to the electrode materials, it is important to remark on the need to deeply treat the interpretative schemes on electrochemical phenomena. For instance, the students frequently propose that "there is different hydrogen overpotential at carbon and at Pt"; the question is that this overpotential can be seen as the expression of the kinetic complications appearing in the electrochemical process. The Volmer-Heyrovsky and Volmer-Tafel mechanisms of HER can be briefly discussed here.

Several important details can be treated here, for instance, the need for supporting electrolyte and the definition from the above experiments of the "solvent window"; i.e., the interval of potentials available for studying other electrochemical processes. This "solvent window" depends on the electrode material and the pH, as can be clearly seen upon examining the voltammograms in Fig. 2b, recorded at pH 4.75 and pH 7.00. The solvent window also depends on the currents which are measured. The smaller these currents are, the narrower the window. Additional questions can be optionally treated here: mercury electrodes and non-aqueous solvents. Another important question is the cleaning/activation of solid electrodes, also accessible to available experimentation.

The session L1.2 is centered on the voltammetry of a 1–5 mM solution of $K_4Fe(CN)_6$ in 0.10 M KCl at different potential scan rates. This permits to study an essentially reversible electrochemical system with well defined and essentially symmetrical anodic and cathodic peaks [51, 52]. In this case, the electrochemical process is a single electron

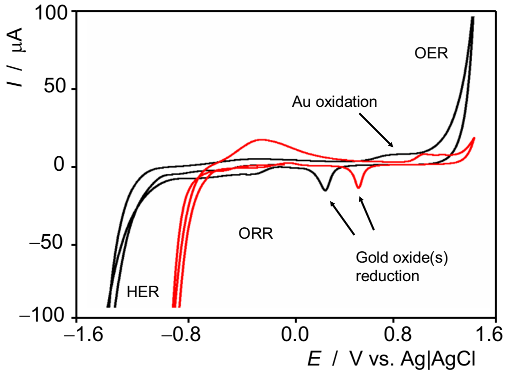


Fig. 3 Cyclic voltammograms at Au electrode (geometrical surface area 0.018 cm^2) recorded in air-saturated aqueous solutions buffered with 0.25 M HAc/NaAc (pH 4.75, red lines) and 0.10 M KH_2PO_4/K_2HPO_4 (pH 7.00, black lines). Potential scan initiated at 0.0 V vs. Ag/AgCl in the negative direction; potential scan rate 50 mV s^{-1}

transfer ($Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-$) but the interpretation of the voltammetric features is not trivial. Here the foot of the peak corresponds to a region of Nernstian control where the current growths exponentially upon varying the potential, but the justification of the appearance of a peak requires the consideration of the depletion of oxidized/reduced species in the vicinity of the electrode so that passing the peak. A more detailed discussion is made based on the general equation expressing the proportionality of the current to the gradient of concentration of the electroactive species in the vicinity of the electrode. The variation of the concentration gradients along the voltammogram, although qualitatively, can promote a rather complete view of the coupled mass transfer/electron transfer process [14, 38].

Importantly, the students should realize that the well-established theoretical diagnostic criteria [73–75] for reversibility (typically, peak potential separation of 59 mV (for a one-electron transfer) at 298 K, peak potentials independent on the potential scan rate) are generally not accomplished as a result of deviations from reversibility and the presence of uncompensated resistive and capacitive effects distorting the voltammetric response [74, 76]. In practice, the process would be considered as reversible when the half sum of the cathodic and anodic peak potentials, i.e., the mid-peak potential, remains independent of the potential scan rate. The students are challenged to verify this behavior upon performing experiments at different sweep rates. The same experimental arrangement allows us to verify the condition of diffusive control (peak current proportional to the square root of the potential scan rate). Here, the students should previously define a criterion for peak current measurement by defining a proper base line.

The session L2.1 is structured around the voltammetry of a 1–5 mM dopamine solution in phosphate or acetate buffer. Here, the response is clearly different from that recorded in potassium hexacyanoferrate solutions, the cyclic voltammograms displaying an anodic peak with no coupled cathodic counterpart. The interpretation of this voltammetry involves the consideration of two possibilities: an irreversible electron transfer process and/or coupled chemical reactions. The voltammetry of dopamine has been widely studied [77–79] and consists of an initial two-electron oxidation yielding dopamine quinone which is followed by fast cyclization reaction and other subsequent processes. Operational criteria for testing this complicated pathway can be obtained by varying the potential scan rate. The central idea is that at high sweep rates the experimental observation time is short enough to detect the initial oxidation product before it reacts significantly. Then, the students can predict that, at large sweep rates, a cathodic signal coupled to the initial oxidation peak should appear.

The session L2.2 is conceived as a flexible academic space for introducing, optionally, aspects complementing the precedent core of voltammetric issues. In several courses, the research projects under development were presented by collaborators. In several others, different alternatives were treated (see Table 4). One of them is the electrochemistry in non-aqueous solvents, based on the reversible reduction of dissolved oxygen to the superoxide anion radical in DMSO solution (important remark: the need of the disposal of suitable supporting electrolytes such as Bu_4NPF_6) [80]. This process offers the possibility of easily studying the importance of chemical reactions coupled to electron transfer, simply adding water or any proton-donating species [81]. Another alternative is to discuss how to discern the oxidation state of an electroactive species in cyclic voltammetry, a problem for which different proposals are available [82, 83]. Finally, another interesting case study is the voltammetry of Cu(II) in aqueous media containing high concentrations of chloride ions. Here, the voltammograms, as illustrated in Fig. 4, show two pairs of cathodic/anodic peaks corresponding to the stepwise reduction of Cu(II)-chloride complexes to Cu(I)-chloride complexes and Cu metal. This experiment provides an excess to discuss the stabilization of the Cu(I) oxidation state by chloride complexation, the estimate of complexation constants from voltammetric data, disproportionation equilibria, and stripping analysis.

The session L3.1 is devoted to the study of the conventional stripping analysis of trace metal ions in aqueous media. Experiments with ca. 0.1 mM $CuSO_4 \cdot 5H_2O$ solutions in acetate buffer are carried out using glassy carbon working electrodes. Testing the influence of the potential range, electrodeposition potential, and electrodeposition time is carried out, eventually using pulsed techniques (differential pulse voltammetry or square wave voltammetry) as a detection

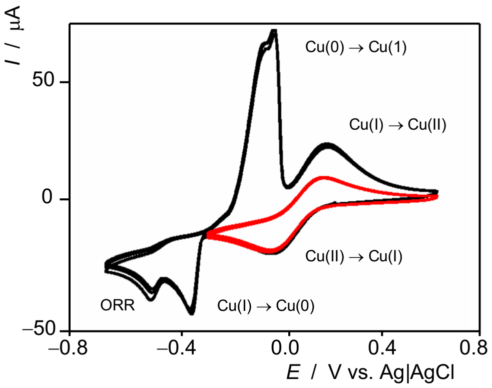


Fig. 4 Cyclic voltammograms at glassy carbon electrode (geometrical surface area 0.071 cm^2) recorded in an air-saturated 2 mM CuSO4·5H2O solution in 0.50 M NaCl. Potential scan initiated at 0.25 V vs. Ag/AgCl in the negative direction; potential scan rate 50 mV s^{-1}. Black line: extended potential range; red line: potential range restricted to the region where the Cu(II)/Cu(I) interconversion occurs

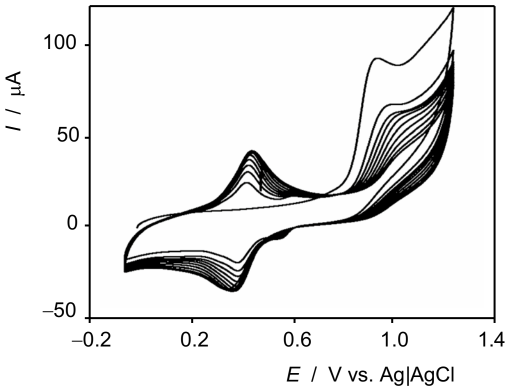


Fig. 5 Repetitive cyclic voltammetry at glassy carbon electrode (geometrical surface area 0.071 cm^2) immersed into 0.01 M solution of aniline hydrochloride in 0.10 M H_2SO_4. Potential scan initiated at 0.0 V in the positive direction; potential scan rate 50 mV s^{-1}

mode. Importantly, the well-known capabilities and limitations of this technique for multicomponent analysis are discussed [14, 84]. This discussion opens the introduction of electrode modification strategies.

In all cases, the structure of the laboratory lessons is configured around an initial core of experimental features with its concomitant series of explanatory schemes, derivations, and related aspects. Particular importance is paid to make explicit the operational aspects and functional relations to be known. This is the case of electropolymerization as illustrated in Fig. 5. Here, the formation of polyaniline layers on a glassy carbon electrode is demonstrated by the progressive decrease of the initial oxidation wave of the monomer at + 1.0 V coupled with the increase of the peak height for reversible reduction/oxidation of polyaniline forms in successive scans. Electropolymerization is seen within the frame of an important concept: electrode modification. Here, a variety of modification strategies can be applied involving a tremendous variety of materials. It is important to connect the idea of electrode modification with the basic concept of electrocatalysis and its application not only for analytical purposes but also for preparative ones and energy production [85, 86].

The sessions L4.1 and L4.2 are devoted to the introduction of ion-insertion electrochemistry, which is of crucial importance in the fields of electroanalysis and energy production and storage. The first session is devoted to the electrochemistry of Prussian blue-modified graphite electrodes in contact with 0.10 M KCl solution. The oxidation and reduction of Prussian blue have been widely studied in the context of the voltammetry of immobilized particles [87–89] literature, being the classical example [90–92] of ion insertion electrochemistry [93]. Applications in the heritage field are also presented [94–97]. Electrocatalysis is often introduced using the reduction of H_2O_2 at Prussian blue-modified graphite electrodes.

Table 5 summarizes an example of development of an educational sequence initiated by the performance of a single experiment: the voltammetry of a microparticulate deposit of Prussian blue (PB) transferred by abrasion onto the surface of a graphite lead. The relevant point to emphasize is that the electrochemical processes can be described in terms of the reduction and oxidation in the solid state mediated by the entrance/issue of K^+ ions into/from the solid lattice. This experiment provides an opportunity for removing an extended misconception: that electrochemical processes operate necessarily through dissolved species and, in particular, that only dissolved species can be analyzed by means of electrochemical methods.

The first-level description of the experimental results corresponds to the appearance of two one-electron essentially reversible couples. The solid-state nature of such processes involves the need of a second-level description, based on the coupling of electron *transfer* across the electrode|PB interface and the electron *transport* in the PB solid [87–93]. This experiment is expanded to develop a potentiometric sensor for K^+ ion determination and the concomitant treating of the concepts of sensitivity and selectivity. The session L4.2 is just devoted to the application in the analytical field through so-called solid contact potentiometric sensors. We used the sensing of chloride and perchlorate ions using microparticulate deposits of Au(I)-Cu(I) heterotrimetallic alkynyl cluster complexes containing ferrocenyl groups [98,

Table 5 Concepts, misconceptions and meta-conceptions in the laboratory session L4.1. B: basic ideas and operations; 1D: first-level description; 2D: 2nd-level description; MR: misconceptions/meta-conceptions to be removed; PD: predictions; OP: open problems

Action/observation	Discussion
Preparation of Prussian blue-modified graphite electrode	(B) strategies of electrode modification; in this case abrasive attachment of an insoluble solid to an inert electrode
Cyclic voltammetric response in contact with 0.10 M KCl aqueous solution	(1D) voltammetric features corresponding to two essentially reversible couples (MR) the analyte does not is necessarily in solution (OP) it is possible to use this strategy for analyzing solids? (2D) topotactic solid-to-solid transformation involving the ingress/issue of K^+ ions into/from the solid lattice (MR) most solids are permeable to the diffusion of ions and electrons through their lattice (PD) from the model of Scholz, the peak potentials should vary with the concentration of supporting electrolyte
Voltammetry upon varying the concentration of the supporting electrolyte	(1D) shift of peak potentials and variation of peak currents upon varying the electrolyte concentration
Deviations from linearity in the E_p vs. log[K^+] plots	(MR) redox potentials are effectively dependent on the concentration of species (MR) Application of the Nernst equation requires reversibility (2D) linear variation of peak potentials on the logarithm of the concentration of K^+ is predicted from the usual form of the Nernst equation (2D) linearity is attained estimating activities (MR) thermochemical activities rather than concentrations should be considered (OP) It is possible to prepare a potentiometric sensor for K^+ ion determination based in Prussian blue-modified electrodes? (OP) selectivity; determination of K^+ ion in the presence of interferents such as Na^+ (OP) There are other possible strategies for electrode modification?

99]. These deposits provide essentially reversible ferrocenyl-based oxidation processes mediated by anion insertion. The formal potentials become linearly dependent on the logarithm of the anion concentration in a wide range of concentrations. Here, two aspects can be discussed: (i) ideally, the response is Nernstian and slopes of 59 mV decade^{-1} should be obtained when the temperature is of 25 °C and (ii) the formal potentials deviate from linearity at high anion concentrations. By the first token, it is pertinent to remark that there is the possibility of potentiometric sensing even when non-Nernstian behavior is operative. By the second, there is an opportunity to discuss a frequently neglected theoretical aspect: thermochemical activities rather than concentrations enter, strictly, in the Nernst equation. Deviations from the above linearity derive from the fact that the numerical value of activities and concentrations diverge as larger is the concentration of the analyte.

Session L.5 is built around the study of eurocent coins (or equivalent) in contact with electrolytes having different aggressive characters: water, 0.10 M $NaClO_4$, 0.10 M NaCl. In the first part (L5.1), the potentiodynamic polarization curves are obtained. Figure 6 illustrates typical results. Here, for reasons of time economy, potential scan rates of 10 mV s^{-1}, higher than those routinely used in this type of measurements, are employed. The discussion is limited to the general information provided by this technique around the corrosion potential. Eventually, the discussion of the Tafel regions and the calculation of the corrosion resistance are made.

The second part of the session is devoted to record the EIS data on eurocent coins in contact with the above electrolytes.

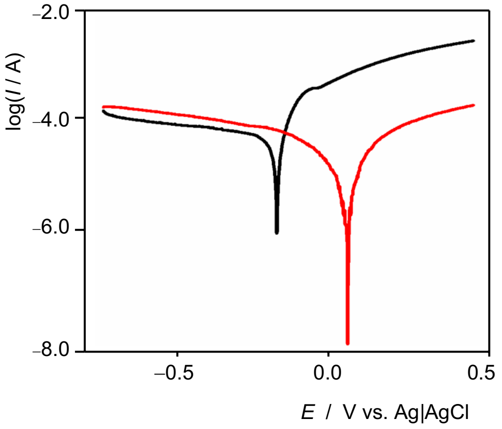


Fig. 6 Potentiodynamic polarization curves recorded for eurocent coins immersed into deionized water (red line) and 0.10 M NaCl (black line). Potential scan initiated at – 0.65 V in the positive direction; potential scan rate 10 mV s^{-1}

The impedance spectra are obtained at the open circuit potential previously approximated by a short equilibration (2–5 min) time. Optionally, the bias potential can be fixed at ca. − 0.60 V vs. Ag/AgCl in order to use the reduction of dissolved oxygen as a redox probe [100]. The impedance spectra are initially modeled using the Randles circuit introducing subsequent modifications (replacement of capacitors by constant phase elements, addition of Warburg elements). The essential educational aims are to present the three basic representations (Nyquist and Bode plots), discuss the physical meaning of the basic circuit elements, namely, solution resistance (R_s), charge transfer resistance (R_{ct}), and double-layer capacitance (C_{dl}) and fitting experimental data to the proposed equivalent circuits, establishing several operational associations; for instance, between inclined sections in Nyquist plots with Warburg elements. Figure 7 shows the Nyquist plot corresponding to the impedance spectrum recorded for a eurocent coin in contact with mineral water. This can be used to illustrate how successive equivalent circuits lead to approximate experimental data starting from the classical Randles circuit (Fig. 7a) and incorporating new elements (two parallel RC units in Fig. 7b) representative of the resistance and the capacity associated with the corrosion patina. Of course, it has to be emphasized that the modeling process is not arbitrary and that the circuit elements should necessarily have a definite physical meaning.

Implications for teaching/learning

Annotations taken during the open laboratory lessons, systematically performed since 2012, permitted us to identify several specific misconceptions and meta-conceptions in the graduate students. These are complemented by the results obtained in the writing test usually carried out several days after the end of the series of laboratory sessions. Here, we attempted to acquire information not only on specific electrochemical issues but also on general abilities. An example of the "final test" is provided as an Annex. As relevant conclusions for learning/teaching, one can mention:

(a) The students underestimate to a great extent the capabilities of electrochemistry. This is reflected, for instance, by the ignorance of the use of electrosynthesis as the main method to fabricate aluminum [7] always exhibited by ca. 90% of students (see Fig. 8a).
(b) A significant proportion of students (around 60%) was not aware of the existence of methods of data treatment (deconvolution, mathematical differentiation, etc.) applicable to electrochemical (and other instrumental) techniques (see also Fig. 8a).
(c) The electrochemical process was usually seen as reversible-like and the kinetics of the electron transfer process was frequently considered as a negligible matter.

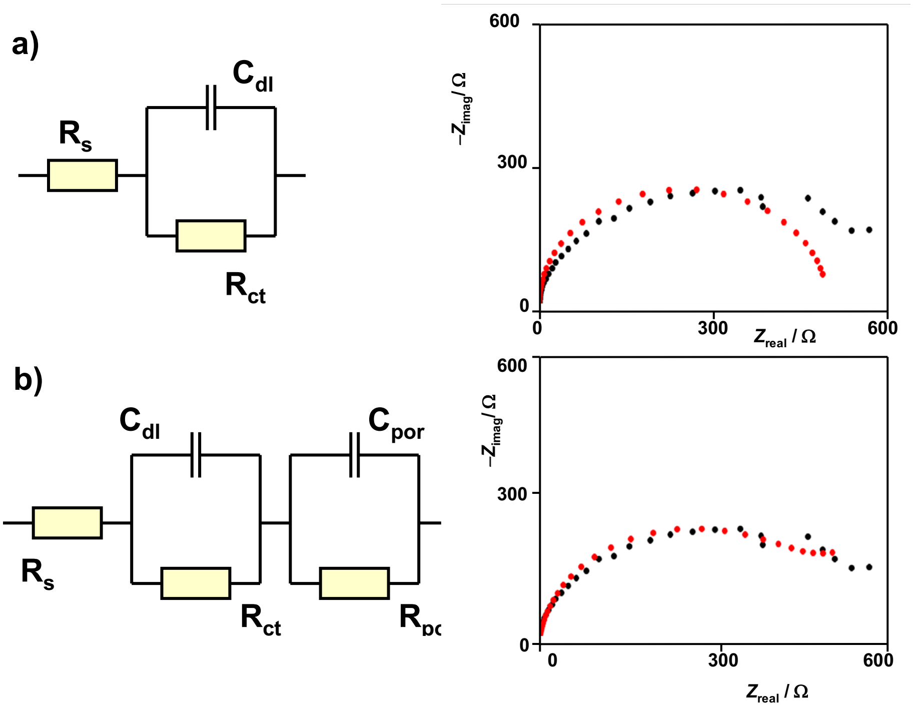
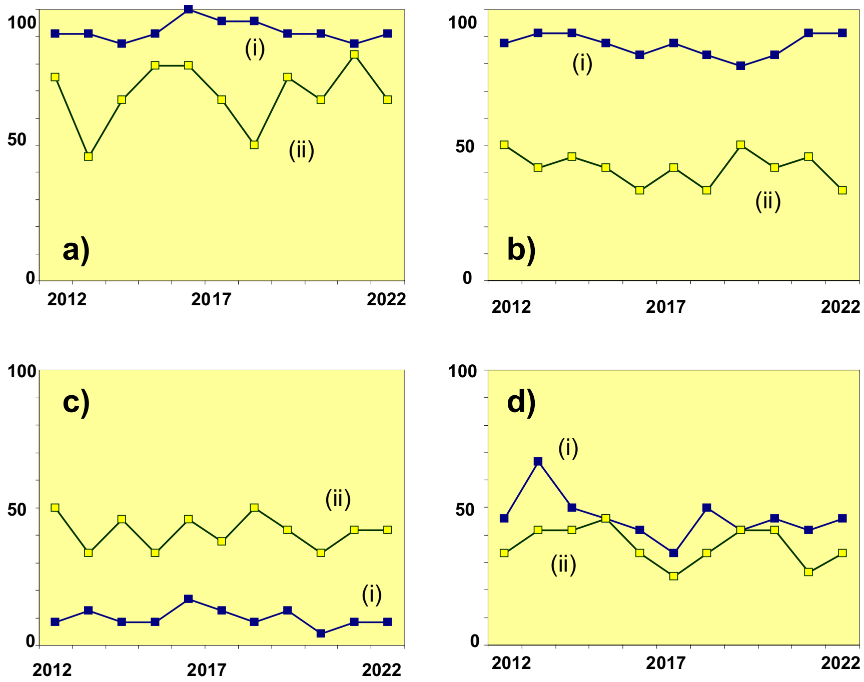


Fig. 7 Experimental impedance spectrum (black circles) recorded for a eurocent coin in contact with mineral water. "Best" simulated spectra using **a** the simplest Randles circuit and **b** more complex circuit with two parallel RC units (red circles)

Fig. 8 Year by year data concerning several general and specifically electrochemical misconceptions detected in the described postgraduate course in the 2012–2022 period. Percentages of **a** students ignoring Al electrochemical production (i) and ignoring the deconvolution method for data treatment (ii); **b** students analyzing peak current vs. square root of scan rate data without the pertinent graphical representation (i, see Annex, exercise 1A, B) and ignoring the essentials of the standard additions method of data analysis (ii, see Annex, exercise 1C); **c** incomplete identification of electrochemical processes (i, see Annex, exercise 2) and incorrect drawing of the cyclic voltammogram at a different pH (ii, see Annex exercise 2); **d** erroneous interpretation of deviations from linearity in potentiometric calibrations (i) and ignorance of organic electrochemistry (ii, see text)



Then, the overall electrochemical experiment is seen as a single, monolithic process with no kinetic constraints nor modification of the composition of the system.

(d) The electrochemical experiment was seen as depending almost exclusively on the composition of the electrolyte solution; the reference electrode, composition of the working electrode, the presence of dissolved oxygen, etc., are generally ignored.

(e) The electrode was understood as an inert component of the system at all. Electrode cleaning, activating, and modifying was frequently avoided.

(f) The students suffer from a tendency to perform an "automatic" analysis of data. In cases in which one disparate point (see Annex, Exercise 1A), or a non-linear tendency (Annex, exercise 1B) appear, these features are ignored; simply, by do not performing the pertinent graphical representation. Incorrect problem solving was of ca. 90% (Fig. 8b).

(g) In analytical applications, interference of other than the analyte electroactive compounds are regarded as absent. The same for subtle matrix effects associated with parallel reactions. In fact, the standard addition method, a general analytical method, was correctly applied (Annex, exercise 1C) by only ca. 50% of graduates (Fig. 8b, c).

(h) Electrochemical techniques were applied exclusively to analytes in solution. The possibility of solid-state electrochemistry analysis was in generally not considered avoided.

(i) Once described in the laboratory sessions, the students correctly identify electrochemical processes (see Annex, exercise 2) with errors and/or omissions around 10%. However, the percentage of erroneous responses increases up to ca. 50% when predictive issues are demanded (Fig. 8c).

(j) The routine interpretation of data resulted in omission of the activity/concentration dichotomy (Fig. 8d).

(k) The traditional focus of redox chemistry in the inorganic context motivates a lack in organic electrochemistry when, for instance, the oxidation of catechols to quinones is treated (Fig. 8d).

In summary, current data suggest that there is a need of a serious consideration of general learning problems in chemistry from a much more practical perspective not limited to electrochemistry.

Conclusions

A proposal of postgraduate course on electrochemistry corresponding to master studies in the University of Valencia (Spain) to be imparted to students with minimal previous studies on this discipline is described. As essential guidelines, the attendance of covering the main conceptual and operational aspects of electrochemistry, focused on voltammetric techniques, and the attendance to misconceptions and meta-conceptions around the same.

The proposed methodology is based on the performance of open, partially regulated laboratory experiments, giving opportunity for an in-lab discussion of concepts, relationships, and operational aspects dealing with the main electrochemistry topics. There are, however, significant problems associated with the presence of misconceptions and meta-conceptions conditioning the learning.

Annex

Writing "final test"

It consists of three questions within the general types exemplified above.

1(A).- We obtain the following data corresponding to the variation of peak current with potential scan rate for the oxidation of ferrocene at Pt electrode (data recorded for a 2.0 mM ferrocene solution in DMF using 0,10 M Bu_4NPF_6 as the supporting electrolyte):

v (mV/s)	5	10	50	100	200	500	1000
i_{pc} (μA)	23	35	71	104	199	238	327

Discuss if the process can be considered as diffusion-controlled.

1(B):- We obtain the following data corresponding to the variation of peak current with potential scan rate for the oxidation of $Fe(CN)_6^{4-}$ at glassy carbon electrode (data recorded for a 2.0 mM $K_4Fe(CN)_6$ plus 0.10 M KCl aqueous solution):

v (mV/s)	5	10	50	100	200	500	1000
i_{pc} (μA)	10	18	96	192	383	940	1780

Discuss if the process can be considered as diffusion-controlled.

1(C).- We dispose of a Cu^{2+} solution of unknown concentration. An aliquot of the same is spiked with different volumes of a standard solution of Cu^{2+} and the peak current for the stripping peak recorded in a conventional experiment are recorded. Based in the following experimental data, calculate the concentration of Cu^{2+} in the problem solution.

Conc. of added Cu^{2+} (μM)	20	30	40	50	60
Peak current (μA)	55	76	93	114	135

2.- The figure below shows two cyclic voltammograms recorded at a gold electrode (geometrical surface area 0.018 cm^2) on a 2 mM $K_4Fe(CN)_6$ plus 0.25 M HAc/NaAc aqueous solution at pH 4.75 previously degasified. Describe all the electrochemical processes and draw (approximately) the voltammogram to be recorded in the extended potential range in an equivalent solution at pH 8.75.

3.- The figure below shows three Nyquist plots corresponding to three different impedance spectra. Discuss:

(a) What spectrum would be the most appropriate to be described by a Randles circuit.
(b) What spectrum would require for its description (at least) two capacitive elements.
(c) What spectrum shows significant diffusive effects.

Acknowledgements The authors wish to thank Prof. Fritz Scholz by his constructive comments and suggestions during the preparation of the manuscript. Financial support from Project PID2020-113022GB-I00 supported by MCIN/AEI/10/13039/501100011033, Fondo Europeo de Desarrollo Regional (ERDF), and Agencia Estatal de Investigación (AEI), is gratefully acknowledged.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature.

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