



Benefits of electrochemistry studies for the majority of students who will not become electrochemists

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Abstract

In teaching electrochemistry, it is of primary importance to make students always aware of the relations between electrochemistry and all the non-electrochemical topics, which are taught. The vast majority of students will not specialise in electrochemistry, but they all can very much benefit from the basics and concepts of electrochemistry. This paper is aimed to give suggestions how the teaching of electrochemistry can easily be interrelated to topics of inorganic, organic, analytical, environmental chemistry, biochemistry and biotechnology.

Keywords Electrochemistry · Education · Basic concepts · Thermodynamics · Kinetics · Interfaces · Electroanalysis · Measuring techniques

The general situation of electrochemistry in education

It is very appropriate that the *Journal of Solid State Electrochemistry* devotes a special issue to all aspects of education in electrochemistry (EC). The eminent importance of education [1, 2] for the advancement of science is beyond any doubt. It always has to be anchored in high-quality research activities of the teaching people. In order to foster education in chemistry, I have started a new journal in 2014: *ChemTexts – The Textbook Journal of Chemistry* [3]. It is aimed to disseminate lecture-type papers to supplement the current, and often outdated, textbook literature. Several references in this paper are taken from ChemTexts.

Considering the needs of teaching electrochemistry, a detailed analysis is needed. This analysis has to be specific for the various branches of electrochemistry and the various routes of education, degree programs, specific courses and so on. Recently, Uwe Schröder [4] has pleaded for more electrochemistry in the teaching of non-electrochemical courses e.g., in inorganic, organic, industrial chemistry, biochemistry and geochemistry! This is indeed most desirable, as otherwise electrochemists may be put in the position of

callers in the wilderness, and their message may be easily stay unvalued.

In this feature article, I will not dwell on the importance of mathematical modelling (esp. with respect to experiment–theory testing), mathematical data treatment and generally computer applications in courses of electrochemistry. These aspects are very well covered by other authors in this issue. The same holds true for laboratory work, which I will not mention in this paper.

It is rather clear what topics need to be taught to an audience of future electrochemists [5, 6]. Most electrochemists give such lectures to small groups of students in the framework of specialisation. However, it is much more challenging to teach electrochemistry (here I always mean equally electroanalysis) to the wide audience of students, who will choose inorganic, organic, physical, industrial, or environmental chemistry, or biochemistry and biotechnology. The audience of engineering students poses other problems [7], which will not be discussed here. Most of these students have the following (mis)understandings of electrochemistry (provided that they had at all some lectures on electrochemistry): (i) It is a very special branch of chemistry, almost unrelated to all other chemistry. (ii) It is very difficult to understand because it is based on terms like ‘potential’ (all sorts, from Galvani and Volta potential to electrochemical potential), ‘current’, ‘charge’, ‘impedance’, etc., which have not been clearly defined before. (iii) It is useless for the own specialisation. (iv) It is boring as nothing modern

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is presented (may be with the exception of lithium batteries and fuel cells). Who is responsible for this situation? I think we have to blame ourselves. The smallest number of our students will major in electrochemistry. Most of them will go to biochemistry, biotechnology, organic synthesis, material science, environmental science, etc., and we have to find connections between their interests and electrochemistry. We do not have to find these connections to cosy up to students, but to help students gaining a wider view on science, and finally to better prepare them to solve their own scientific tasks, later in life. I had such rare moment of satisfaction, when a postdoc has sent me an e-mail from a US University, writing “Once, in second year, you have explained us formal potentials, and I think this is what I need to consider now in my biochemical research...” It followed a nice exchange of e-mails and explanations from both sides. This brings me to the point that I rate the understanding of concepts to be much more important than celebrating math derivations, although the latter are very important; however, usually at a later time, when the concepts have been at least roughly understood.

Electrochemistry is mostly taught as an appendix of physical chemistry. Depending on the interests of the lecturing person, it is either overemphasized or rather ignored. Doubtless, it would be most desirable that electrochemical considerations are an integral part of lectures on inorganic (e.g., aluminium production [8]), organic (e.g., organic electrosynthesis [9]), industrial and analytical chemistry, biochemistry and biotechnology, but this is not always the case.

The present boost of electric vehicles and energy storage and conversion has drawn electrochemistry in to the awareness of a wide public. However, this also lead to an unjustified narrowing of the importance of electrochemistry. Further, I have seen that future biochemists/biotechnologist are usually not very enthusiastic about batteries and fuel cells, unless they are introduced to microbial fuel cells. The links between batteries and fuel cells and the biochemistry of energy metabolism in living organisms, can be another motivation.

Here, I like to contemplate on electrochemical concepts, which can help future chemists of whatever specialisation to improve their understanding of their own chemical systems. It is unavoidable that this paper has some national flavour, and also a personal flavour, as the curricula differ across the countries, and the personal interests of the teaching persons are also not uniform.

Before electrochemistry can be taught, the used terms have to be explained. Since physics and physical chemistry are normally taught long before electrochemistry and electroanalysis, students have to be reminded again to the meaning of terms like: energy, potential energy, electrical potential, electrical field, electrical field strength, work, Coulomb work, current, current density, resistance, impedance, admittance, electrochemical potential, Gibbs energy, entropy, etc. These are by far not all necessary terms, but

they need to come first. Later, in electrochemical kinetics, more specific terms, like overpotential and charge-transfer resistance, etc. need to be introduced.

When students listen to electrochemistry lectures, textbooks need to be suggested. A highly recommendable textbook, which starts with the very basics and also presents the higher levels of electrochemistry in an understandable way, is “Electrochemical science and technology” [10].¹ To be quickly informed about the many specific terms of electrochemistry, students may use the “Electrochemical dictionary” [11].

Let me know list the concepts, which I rate to be important for lectures on electrochemistry and electroanalysis. (I think it is impossible to give lectures on electroanalysis without lecturing first on general electrochemistry). Here, I will not dwell on experimental laboratory work, as this is the topic of many other contributions to this special issue.

Interfaces

It is necessary to discuss the omnipresence of interfaces in nature and the thermodynamic prerequisite of their existence i.e. a positive interfacial free energy. This should be followed by a presentation of the electrical double layer [12, 13] at interfaces. The Helmholtz, Gouy-Chapman and Stern models suffice for the general public of chemistry students. More elaborate models can be kept for students specialising in electrochemistry. The structure of the electrochemical double layer at electrified metallsolution interfaces should be related to the Debye-Hückel treatment of ions in solution [14]. Here is the place to introduce the terms *outer potential*, *Volta potential difference*, *surface potential* and *Galvani potential difference*. The concept of Debye length needs a serious discussion and explanation, as it is of eminent value to understand the nature of ions and particles in solutions. Thus it is also the basis for understanding the Derjagin-Lifschitz-Vervev-Overbeek (DLVO) theory of colloids. The stability of colloidal dispersions of clays in water at different salt concentrations can be easily demonstrated in lecture hall experiments. Here is also the place to discuss environmental issues, e.g. the precipitation of clays in estuaries, e.g. where the Amazonas waters mix with the saltwater of the Atlantic. Looking at biochemistry, another related topic is the stability of proteins as colloidal solutions. In comparing the double layer at electrified interfaces with the structure of solvated ions, it is also straightforward to mention the term Gouy length [15], introduced by K. Oldham in analogy to the Debye length of ions and non-conducting particles and surfaces. In the explanations it should be mentioned that ions and non-conducting particles have a *fixed* charge, whereas the charge density of a metal or semi-conductor interface can

¹ Most of the cited references have a clear educational character and lend themselves for being suggested to students.

be tuned when the interface is part of an electrical cell. This is a good place to mention and explain electrophoretic painting (e.g., varnishing automobile parts) and also wastewater cleaning.

The topic *interfaces* is also a good place to treat the terms hydrophobicity and lipophilicity. The structure of water on hydrophobic and hydrophilic surfaces needs to be presented and compared with the water structure around hydrophilic and hydrophobic molecules and ions. Here, the so-called hydrophobic effect [16] is central. It is very worth to explain students how that is responsible for the immiscibility of water with hydrophobic solvents, for the structure of monolayers of amphiphiles [17], cell membranes, micells, vesicles (e.g. liposomes) etc., and what role it plays for the structure of proteins. It is worth to tell students that electrochemical studies of vesicles are very useful to understand their properties [18] A related topic from industrial chemistry is froth flotation [19].

Electrochemical thermodynamics

Thermodynamics is the favoured topic of only very few chemistry students, since it is complex and needs a lot of mathematics. Even great men of science had their struggles with it and did not easily grasp the meaning of entropy [20]. Usually, chemical thermodynamics precedes lectures on electrochemistry. Unfortunately, for the majority of students this does not mean that they will have the basics of chemical thermodynamics at their disposal. Unfortunately, in the European Union, the restructuring of University studies along the Bologna path lead to a kind of short-term learning strategy of students. The Bologna Process [21] has attractive goals, like making the educational systems more coherent and more permeable on national and international scale. However, this also produces new problems: The intended higher mobility of students brings students with very different prerequisites together in the same courses. In the past, it was rather clear, what qualifications students have when listening to lectures. Now this is not anymore the case. This means in teaching electrochemistry (and also in all other subjects) it is necessary to repeat a lot of basics, if one likes that all students can follow. For electrochemistry it is of special importance that students have an understanding of enthalpy, entropy, free energy and chemical potential and generally of chemical equilibrium [22]. Only then, an introduction of the electrochemical potential and the Nernst equation is possible. Even when this already was part of the lectures on physical chemistry during Bachelor studies, only the best students will remember it. Another more or less repetitive part concerns the thermodynamics of reference electrodes [23], esp. of the hydrogen and the silver/silver chloride electrode, the electrochemical series (electromotive series), the understanding of standard and

formal potentials and the definition of biochemical standard potentials. A thorough discussion of formal potentials is of utmost importance, as in physical chemistry they are often taught only to include activity coefficients, forgetting that the coupled chemical equilibria have by far larger effects [24]. I have witnessed seemingly full-blooded electrochemists at conferences, who were not aware of this! This part may also include a presentation of Pourbaix diagrams, giving special attention to their limits, which are set by the used models and data of chemical and electrochemical equilibria. Of course, lectures on electrochemical thermodynamics need to include batteries and fuel cells [25, 26]. Especially interesting for biochemically oriented students are microbial fuel cells [27–29].

Because of the eminent role of secondary batteries, especially lithium batteries, it is necessary to present the essentials of insertion electrochemistry (see e.g. [30]) and also discuss electrochromism of such systems [31]. The thermodynamics of insertion electrochemical systems [32] give a good chance to mention and explain that the electron and the ion transfer are in fact two simultaneously proceeding electrode reactions, which can even be measured by voltammetric techniques. Here is plenty of room for considering inorganic chemistry of insertion reactions.

Further, a topic with which one can easily attract the attention of students is the electrochemical transfer of ions across the interface of immiscible solutions. Usually students are surprised to see that not only electrons can be transferred between a metal electrode and dissolved species in a solution, but also ions between two immiscible electrolyte solutions [33, 34], a story that goes back to Walther Nernst and Ernst Riesenfeld [35]. The free partition of ions between immiscible solvents and between an ionic crystal and its solution [36] can be included here. Further, phase transfer catalysis [37, 38], normally discussed in courses on organic chemistry, is perfect to be related to ion transfer, ion solvation and thermodynamics.

A detailed discussion of the thermodynamics of interfaces and its mathematical background (see for example the paper of Láng [39]) must be reserved for specialised courses on electrochemistry. The thermodynamics and kinetics of nucleation and growth, especially that observed in electrochemical deposition, is also a topic better suited for specialised courses [40, 41]. However, a phenomenological discussion of nucleation and growth can be well used to expand the student's understanding of many natural phenomena, like cloud and rime formation, fogging of windows, etc.

Electrochemical kinetics

Talking about electrochemical kinetics first needs to make clear that electrode reactions are heterogeneous reactions.

Normally, students are used to handle homogeneous kinetics and know much less about heterogeneous reactions. It is important to make students aware of the great advantage of electrode reactions that the reaction rate can be directly assessed by current measurements, and explain that the concept of heterogeneous reactions leads to other units of the reactions rate. What has to follow is the introduction to the Butler-Volmer (or Erdey-Grúz–Volmer) equation [42]. The essential point here is the application of the concept of Linear Free Energy Relationships (LFERs). This gives a nice opportunity to remind students to LFERs in organic chemistry, which are well treated in Hammett's book on physical organic chemistry [43]. Students may have heard earlier about the Brønsted relation and the Hammett equation and they will find it interesting to see that LFERs are also pivotal in electrochemical kinetics [44]. Clearly, electrochemical kinetics needs also a discussion of mass transport to and from the electrode surface by diffusion, convection and migration. What follows then, is in my opinion one of the most important topics: the discussion of electrochemical reversibility/irreversibility. This concept is essential to understand electrochemical energy conversion (batteries and fuel cells), electrochemical synthesis, the interpretation of electrochemical signals in electroanalysis, biosensors and bioelectrochemistry. Especially the biosensors, which are mostly based on electrocatalytic systems, can only be understood, when the interplay between thermodynamics, reaction kinetics and mass transport is clear to students. At this place attention can be given to ferrocene [45], its unique chemistry and its role as electron shuttle in many sensors. Bioelectrochemistry [46, 47] is a topic, which is ideally suited to discuss the interplay of thermodynamics, kinetics and biochemistry. Electrocatalysis is a very wide topic and lectures on the theoretical basis of electrocatalysis have to include references to fuel cells [48] and organic electrosynthesis [49].

For a wider audience of students, corrosion and corrosion protection are also issues needing an understanding of electrochemical kinetics [50, 51].

Electroanalysis

As mentioned before, electroanalysis can be taught only following basics of electrochemistry. Electroanalysis comprises a very large number of different techniques. They can be structured as follows: methods based on transport properties (what Bockris called ionics), as e.g. conductivity measurements and electrophoresis (migration in an electrical field), and methods based on (mostly) faradaic electrode reactions, i.e. based on interfacial electrochemistry and called by Bockris electrocatalysis: e.g. amperometry, coulometry, all kinds of voltammetry, chronoamperometry, chronocoulometry, chronopotentiometry, to name just a few. Whereas conductometry, amperometry and potentiometry are usually discussed in

analytical chemistry (indication of titrations) and electrophoresis, as a separation technique, is taught together with chromatography, the other techniques need special discussion in separate lectures on electroanalysis. The guiding concept that I followed in my lectures on (interfacial) electroanalysis is the discrimination of capacitive currents and the relative or absolute enhancement of faradaic currents in order to achieve the highest possible sensitivity. This concept can be discussed as the leading motive for the development of the many electroanalytical techniques. Here, the three main approaches are (i) electrode construction (e.g. the static mercury drop electrode having a constant electrode surface area and thus decreasing the capacitive current), (ii) electronics (e.g. current sampling, pulse techniques, alternating current techniques and measurement of higher harmonics [52]) and (iii) chemical means (e.g. catalytic currents and stripping techniques). The development and strategies of stripping voltammetry are most easily understandable to chemistry students [53], as one can refer here to simple chemical reactions and procedures of enrichment. It is good to compare the ways of signal processing with similar problems in spectroscopy, where, as an example, the background absorption has to be discriminated, and very small signals to be amplified. Students should understand that the general problems are very similar in all analytical techniques. Another concept that is omnipresent in analytical techniques, better to say in all measurements, is that of time constants. According to my experience, students never heard before about time constants, and they are also not aware of the fact that the math behind time constants is the same as that in case of the Bouguer–Lambert–Beer law in spectroscopy, chemical reaction kinetics, radioactive decay, relaxation in nuclear magnetic resonance and the RC constants of an electrode [54].

In teaching electroanalysis we have to say 'bye-bye' to classical polarography, and should mention it only in the context of an historical survey [55, 56]. However, I always recommend students specialising in electroanalysis, to consult the book of Heyrovský/Kůta [57] as it helps to understand what is now known as voltammetry. Just to give an example: the shifting of half-wave potentials in dc-polarography upon complex formation of metal ions is so well presented by Heyrovský/Kůta that it will be easy for students to apply this knowledge to measured formal potentials with the help of modern techniques. It goes without saying that students have now also to study modern texts, like [58–62]. Generally, we should beware of any glorification of electroanalysis and very critical tell students in what cases it is really better than other instrumental techniques of analysis. Such examples are the determination of ultratraces of platinum, uranium and some other transition metal ions, and speciation studies. Almost no spectroscopic technique is able to perform speciation analysis at concentrations below the $\mu\text{mol/l}$ level. It may help future chemists also to know that there are plenty of possibilities to

study and analyse solid materials directly i.e. without a previous dissolution [63, 64]. A very modern application of solid state electroanalysis is the determination of the age of metal objects [65]. Here, and also in applications to analyse objects of cultural heritage [66], concepts of electroanalysis enter archaeometry, which adds to its attraction in teaching. Electroanalysis would be incomplete without presenting surface modified electrodes, especially conducting polymers [67]. Again, this is a topic lending itself to discuss jointly thermodynamics, kinetics, organic and inorganic chemistry. Electrochemical imaging is another topic worth to be discussed [68, 69]. If time suffices, it is also worth to mention the possibility of using adsorption phenomena for analysis (tensammetry [70, 71]), which can be looked at from the point of view of thermodynamics, kinetics and analysis. A very general aspect is the signal processing in electrochemistry and electroanalysis. A very suitable introductory text [72] treats both analog and digital signals and demonstrates the similarity of electrochemical and non-electrochemical measurements.

The elucidation of the kinetics and mechanisms of electrochemical and purely chemical reactions is another topic, worth to be included in electrochemistry lectures, especially when dealing with the so-called ‘electroanalytical techniques’. Whereas the mathematical simulation of electrochemical measurements, e.g. of cyclic voltammograms, is better suited for specialised courses, some basic understanding of voltammetric techniques is desirable, since, especially cyclic voltammetry, entered many inorganic and organic chemistry labs.

Hyphenated techniques, like EC-AFM, EC-STM, EC-VIS spectrometry, EC-NMR, EC-ESR, EC-X-ray diffraction, etc., are also excellently suited to demonstrate students the versatility of electrochemical and electroanalytical techniques, and they provide ample examples, which students will find interesting and even exciting. Thorough lectures on hyphenated techniques have to be reserved for specialised course.

Conclusions

For reasons of limited time, it is probably impossible to include all the topics, which I listed in this paper, in lectures on electrochemistry. Of course, the specific circumstances have always to be taken into account. Therefore, I also resigned to suggest how many hours should be scheduled for teaching the mentioned topics. The paper has rather been written to stimulate some ideas.

I think that we have to teach electrochemistry in such way that students understand it as an integral part of chemistry. For this, it is essential that they learn about the importance of electrochemistry for other fields of chemistry, and that

they understand that certain concepts are useful and important in various branches of chemistry. I also believe that we should integrate historical aspects in our lectures. They are well suited to brighten our lectures and widen the view of students. History of science facilitates to discover the innate laws and the role of chance and luck in the development of science [73]. If we present electrochemistry along concepts of wider significance, electrochemistry will lose its outsider position, which it still has in the minds of students. This paper is also a plea to and hopefully also stimulation of our non-electrochemist colleagues, to include more electrochemistry in their teaching.

There is another aspect of teaching to students, who will go to other branches of science: Our teaching will reach out to much wider circles of the society. If we will expand our teaching even to laymen, as Michael Faraday did so successfully, we will make an important contribution to improve the acceptance of science in our societies.

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