

The use of basic concepts of electrochemistry in industry

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Summary

An outline of a document with a basic vocabulary used in electrochemical industries is indicated following an historical development with references to sources where it would be properly explained. The objective would be to avoid having to include "definitions" on elementary concepts in CEN and ISO standards. The inadequacy of those definitions in standards is indicated and the present approach is justified.

Key words: corrosion, coatings, electrochemical industry, electrochemical vocabulary.

1 - Introduction

In a CEN meeting in London [1] where standard prEN 12508 on vocabulary was being discussed, I defended that terms on basic science should not be defined on those standards, namely in cases where teaching the concepts involves a long story, often with references to its historical development.

One example is the "definition" of "oxidation" that, in the proposed CEN standard, was as follows:

"Oxidation: A reaction in which electrons are removed from a reactant. Sometimes, more specifically, the combination of a reactant with oxygen".

The above definition is quite inadequate. Obviously, oxidation comes from oxygen, itself meaning "generator of oxides" because it easily reacts with most elements. But if the expert doesn't know basic chemistry to understand oxidation, he will not profit from the indicated definition. Suppose a user reads in some standard about the oxidation of a sugar by potassium permanganate, eventually showing the appropriate equations. A reader that understands the concept of oxidation will immediately see that the oxidation number of carbon went from 0 to +4, whereas that of manganese came down from +7 to +2 and therefore he will say that the sugar was oxidized. But a reader who does not understand the concept of "oxidation" will not get any better with the above definition. He will ask: but how are "electrons [being] removed from [the] reactant ? I cannot see here any combination of a reactant with oxygen !" The same applies to many other "definitions" of basic concepts presented in CEN and ISO standards.

I proposed the elimination of the above definition (as well as similar ones) from the standard. I also proposed that a document written not as a standard but as a kind of review article could be published by CEN and/or ISO where all the words and concepts of basic electrochemistry would appear with references to well known text books, scientific encyclopaedias, etc., where an appropriate explanation of the concept could be found. A comprehensive list of *technical* vocabulary would be given with references to the relevant standards. Such a document could be an appendix of terminology standards or indicated in the appropriate section.

An attempt to fulfil that idea is presented here as a mere outline. The author greatly appreciates comments and suggestions from electrochemists, including those that in industry deal with processes involving electrochemistry. If this idea is accepted as useful, then a comprehensive document written along these lines could be prepared.

2 - Basic vocabulary used in electrochemical industries

The well known experiments of the Italian Professor of anatomy Luiggi Galvani (1737-1798) in the 1790's may be considered, for the nomenclature purposes of the present work, the starting point of electrochemistry. Because of his pioneering work, words derived from "galvani" are abundant in the scientific and technical fields connected with electrochemistry^(*): **galvanic cell**, **galvanic corrosion**, **galvanization**, etc. Though not diminishing Galvani's importance, I have defended in international meetings the gradual replacement of those words by others better suited to the purpose. Thus, "**galvanic cell**" should be replaced by "**electrochemical cell**". Because of its large use in industry, it is acceptable that the term **galvanization** be retained.

Being professor of anatomy, Galvani's interests and interpretations were around the concepts of the "vital forces" (the forces responsible for the movements of animals). Shortly after Galvani's experiments, his colleague, but professor of physics, Alessandro Volta (1745-1827), in the nearby University of Pavia looked at those findings in a more rigorous physical manner. He soon found out that the frog's legs were merely the electric conducting medium (the electrolytic solution as we would now say) and that the root of the matter lay on the metals and respective metallic oxides involved. Thus he built a "pile" of many discs of metals like silver and zinc in contact with humid disks of material like paper. This way he could produce measurable electric currents, generated by chemical reactions, that is, he was actually founding "**electrochemistry**". We should remember that up to Volta's experiments, electricity concerned basically what we would now call electrostatics, and therefore Volta's experiments were the first uses of significant electric currents. Volta's work justifies the use of his name in science, the most notable case being the unit of electric potential: the **volt**. Again, as with Galvani, we must not misuse his name, otherwise most electrochemistry concepts would have a word from Volta, which would be confusing. Therefore we should avoid saying **voltaic cell**, etc.

The fact that Volta piled up the electrochemical units or layed them side by side, gave rise, in European languages, to words connected with pile or battery. This still gives unfortunate confusions [2].

Scientists all over the world were soon using Volta's electrochemical cells to study interactions of electrical current and matter: Among them, Sir Humphry Davy

(*) Words in **bold** are terms defined in ISO, CEN or NP standards.

(1778-1829) and his disciple Michael Faraday (1791-1867), at the London's Royal Institution. With the help of an expert on Greek and Latin, Faraday coined now well known words: **ion**, **anion**, **cation**, **electrode**, **electrolysis**, [3], etc. Naturally, the industrially extremely important field of **electroplating** was then born. Gradually, a vast vocabulary on the field grew up. New electrochemical cells were eventually developed. According to Uhlig [4] "Sir Humphry Davy reported in 1824 that copper could be successfully protected against corrosion by coupling it to iron or zinc. He recommended cathodic protection of copper-sheathed ships, employing sacrificial blocks of iron attached to the hull in the ratio of iron to copper surface of about 1 : 100." And so came a vast amount of vocabulary on **corrosion**: **anaerobic**, **anodic area**, **blistering**, **coating defect**, **coupon**, etc., etc.

The discovery of the telegraph and governments interest in rapid communications also greatly accelerated the development of **batteries** (**electrochemical cells**). They were the only means of producing electric current. But the development of the dynamo around the 1880's caused a revolution. There was now a much better way of producing electric current and consequently the acceleration of the electrochemical industries (**electrodeposits**, **electromachining**, **electromoulding**, etc.). Also, there were now practical means of recharging secondary elements, e.g. the **lead acid battery**. Of previous little use (it had to be recharged "consuming" other cells), its use was then in great expansion. Thus the appropriate vocabulary.

Along the first half of the XIX century the structural concepts of atoms and molecules were being clarified. **Formulae**, that is, abbreviated ways to represent molecules, were slowly being developed, though meeting with some opposition [5]. The concepts and vocabulary originated from the atomic theory of matter, also important in electrochemical industries, are well presented in books of "General Chemistry": **atomic weight**, **molecular weight**, **isotopic mass** (called by the physicists atomic mass [6]).

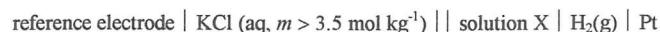
In the second half of the XIX century scientists like Ostwald (1853-1932), Arrhenius (1859-1927), Nernst (1864-1941) gave important contributions to electrochemistry as a science. For example, though meeting tough opposition up to the point of nearly failing in his Ph.D. examination, Arrhenius eventually convinced the scientific community that a salt like sodium chloride spontaneously dissociates, in a polar solvent like water, in sodium and chloride ions. Thus, the concepts of **electrolyte** [7], **electrolytic solution**, **complexation**, **complexing agent**, **chelant**, **electrode potential**, etc.

A better understanding of the chemical bonding, the evolution from Arrhenius to Lewis and to Bronstead on the concept of **acids** and **bases**, and other factors allowed a better concept of **oxidation** (and **reduction**) based on the rather artificial (but very useful) concept of **oxidation number** itself based in the so called **Lewis formulae** (or diagrams). It is far better to understand **oxidation** based on this historical development than on a "definition" as given in the introduction.

In 1909 Sorensen introduced the formula $\text{pH} = -\log [\text{H}^+]$ merely as an easier way of presenting (and printing) a large number of calculated hydrogen ion concentrations in a number of aqueous solutions of weak acids. Instead of having to type, e.g. " $[\text{H}^+] = 1.81 \times 10^{-5}$ " which at the time of manually movable printed characters involved a lot of labour, the printers would typeset merely $\text{pH} = 4.75$, obviously far less costly if dozens of cases had to be printed. Also for typographical

reasons, it was decided that the H should be on the same line as the p (standing for "power", in German, French and English). It was soon found out that the hydrogen ion concentration, that is, Sorensen's **pH**, was an important parameter of aqueous solutions, because the equilibrium position of many reactions (precipitations, complex formations, redox reactions, etc.) depends strongly on hydrogenion concentration. Thus the popularity of Sorensen's idea. It was also soon found out that the pH of some solutions could vary tremendously by the addition of small quantities of acids or bases. For example, the pH of a carefully prepared dilute solution of sodium chloride can vary widely [8] from less than 5 to above 9 (10 000 times less H^+) merely because of the amounts of CO_2 , NH_3 , H_2S , etc., absorbed from the atmosphere on the process of preparation. However, if one adds to the solution a reasonable quantity of a **conjugated acid-base pair** such as acetic acid + sodium acetate so as to have the solution 0.1 M in CH_3COOH and 0.1 M in $NaCH_3COO$, the pH will be very close to 4.75 and it will not alter significantly when the additions of small quantities of acids or bases (as above said for CO_2 , NH_3 , H_2S , etc.) somehow are added (or substrated from) to the solution. Thus came the concept of a **buffer** and **buffered solution**. The application of the recently developed concepts of chemical thermodynamics soon showed that what is important is not so much the hydrogen ion concentration but the **hydrogen ion activity**. However, we cannot measure the activity of a single ion and eventually the 1909 Sorensen's definition of pH gave rise to the present operational IUPAC definition [9], unfortunately not widely known:

For a solution X the emf $E(X)$ of the galvanic cell



is measured, and likewise the emf $E(S)$ of the cell that differs only by the replacement of the solution X of unknown $pH(X)$ by the solution S of standard $pH(S)$. The unknown pH is then given by

$$pH(X) = pH(S) + (E_s - E_x)F / (RT \ln 10)$$

Thus defined, pH is dimensionless. The reference value pH standard is an aqueous solution of potassium hydrogen phthalate at a molality of exactly 0.05 mol kg^{-1} : at 25°C (298.15 K) this has a pH of 4.005.

In practice a glass electrode is almost always used in place of the $\text{Pt} \mid \text{H}_2$ electrode. The cell might then take the form



The solution to the right of the glass electrode is usually a buffer solution of KH_2PO_4 and Na_2HPO_4 , with 0.1 mol dm^{-3} of $NaCl$. The reference electrode is usually a calomel electrode, silver/silver chloride electrode, or a thallium amalgam/thalious chloride electrode. The emf of this cell depends on $a(H^+)$ in the solution X in the same way as that of the cell with the $\text{Pt} \mid \text{H}_2$ electrode, and thus the same procedure is followed.

Most of the scientific principles of modern electrochemical industries were developed by the time of the 1914-18 war. However, technological achievements allowed and continue to allow the development and expansion of many electrochemical industries and consequently new vocabulary: **electrophoretic painting**, etc.

It is this last type of technical vocabulary that I think should be in ISO and CEN standards of terminology. It is far easier to define than concepts like **oxidation**. Being specific of certain industrial processes, it is highly advisable to have it included in standards on terminology. However, a document properly written along the lines here suggested could serve as a useful introduction to any standard on terminology.

References

- [1] CEN is the European Commission for Standardization (Commission Européene de Standardization) which includes the national standard bodies of Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom, that is, all European Union Countries plus Iceland, Switzerland and Norway. ISO, the International Organization for Standardization, is a world-wide federation of national standard bodies (ISO member bodies).
- [2] For example, in Portuguese, the words **pilha** (pile) and **bateria** (battery) have been used with distinct meanings: "pilha", a Leclanché type of electrochemical cell for electronic devices, flash lights, etc.; "bateria" used virtually only for the lead acid battery. Consequently "pilha" became associated with a primary (non-rechargeable) element (though not piled up because it is only one) and battery with secondary (rechargeable) electrochemical elements. But now the Cd-Ni elements are secondary and still called "pilhas" by physical analogy. Similar confusions exist in other European languages and industrial technicians must be aware of them, and understand the basic electrochemistry concepts to avoid confusions.
- [3] Virtually any text book on "General Chemistry" teaches elementary electrochemistry and therefore has these words. In the suggested ISO or CEN document, a list of the most appropriate books in chemistry and electrochemical industries would be given.
- [4] H.H. Uhlig and R.W. Revie (*Corrosion and Corrosion Control - An Introduction to Corrosion Science and Engineering*), 3rd edition, John Wiley and Sons, New York (1985).
- [5] M. Teresa Lobo and V.M.M. Lobo (*Problems with chemical formulae: XX century school pupils and XIX century scientists*). Port. Electrochim. Acta 15, 61 (1997).
- [6] There has been some confusion in textbooks about this nomenclature. Some textbooks use **atomic mass** (and consequently **molecular mass**) for what IUPAC says, and quite rightly, should be (as has been since last century) **atomic weight** and consequently **molecular weight**. In fact, this wrong use of **atomic mass** causes confusion with the physicists use of **atomic mass** for what the chemists say **isotopic mass**.

- [7] V.M.M. Lobo (*The definition of electrolyte*), Port. Electrochim. Acta 14, 27 (1996).
- [8] V.M.M. Lobo, A. Valente and M. Araujo (*The question of the pH "adjustment" in aqueous electrolyte solutions*), Russ. J. Electrochem. 31, 496 (1995).
- [9] I. Mills et al. (*Quantities, Units and Symbols in Physical Chemistry*), IUPAC, Blackwell Scientific Publications, Oxford (1993).

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