ESSAY

The third century of electrochemistry: Lowering the horizon or raising it further?

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Abstract: A survey is given of the development of electrochemistry with the author’s unmasked wish for more advanced development in the future. The survey is based on past achievements of electrochemistry, which is listed concisely herein. As far as the recent state is concerned, author’s dissatisfaction is expressed with the acceptance of electrochemistry as both a favorite profession of graduate students and a top priority field in the financing of research. For the sake of honesty, an alternative view is mentioned that takes the recent state of electrochemistry as normal and in accordance with the usual course of development, (i.e., birth, rise, achieving of maximum and then decay, fading, etc.) that is common in nature. This statement is based on the belief that today electrochemistry exists on a broader basis than before, and is mainly incorporated into other (new) branches of chemistry and science. Examples are given where recent electrochemistry failed to fulfill its promises (e.g., the production of cheap hydrogen by means of electrocatalysts with high performance for H₂ evolution, economical use of large-scale fuel cells, etc.). In summarizing the recent fields of interest that cover electrochemistry, their diversification, specialization, complexness and interdisciplinary nature must be stressed. A list of desirable highlights that could possibly help electrochemistry to improve its rating among other branches of science is composed. In addition, a list of the author’s personal preferences is given.

Keywords: electrochemistry; lost priority; recovery; desirable highlights; history; current trends; future prospects.

INTRODUCTION

If we agree that (modern) electrochemistry was born with the invention of the first ever d.c. power source (the so-called Voltaic pile, 1800), then nowadays...
this science is running the second decade of its 3rd Century**. One must admit that such a long history is not a common phenomenon in the world of science*. Therefore, if we wish electrochemistry to continue its successful story, we should follow its state, continuously evaluate its achievements and push it further up.

Recently, on the occasion of the 3rd Regional South East European Symposium on Electrochemistry, that took place in Bucharest, Romania, I presented the lecture entitled: Electrochemistry – the Central Science of Tomorrow: Reality or Fantasy?¹ My intention was to promote my wishes for electrochemistry to regain its leading position in the world of science, as it used to have for a long period in the past. I expressed my dissatisfaction with the recent low ranking of electrochemistry. In order to attract wider attention, herein some more aspects are presented that may aid electrochemistry to take in the future the place it deserves.

** Brief history

Let me start with quoting some basic and well-known facts. Electrochemistry is a science that is concerned with two phenomena: changes of the chemical nature of matter caused by the passing of an electrical current and *visa versa*, the generation of an electrical current due to certain chemical reactions. Electrochemistry is part of Physical Chemistry, together with many other branches, such as, *e.g.*, Structural Chemistry, Photochemistry, Chemical Thermodynamics and Kinetics, *etc*. Physical chemistry on its own is part of chemistry, together with parts such as, *e.g.*, General Chemistry, Inorganic Chemistry, Organic chemistry, *etc*.

It is normally to ask oneself: When there are so many branches of chemistry, “why is electrochemistry so important and why does it attract so much attention?”

The answers are simple: modern electrochemistry was founded and commenced its career long before other sciences or their branches existed. Furthermore, electrochemistry is important for a number of merits, such as, *e.g.*, demystification of some basic concepts of chemistry, structure of matter, *etc*. It should be remembered that electrochemistry commenced dealing with the electron one century before it was discovered at the dawn of the 20th Century.² Moreover, by means of electrochemistry, some ten chemical elements were in no time isolated or discovered, while the number of useful products was much higher. All this occurred in the early stages of the transition of chemistry from empirical into a modern science. In this way, electrochemistry supported the progress of other

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** “Modern” electrochemistry is the one that started with Alessandro Volta and other scientists in 18th and 19th century. This statement is just a precaution in case there is another – “ancient” electrochemistry, judging according the controversy generated with the discovery of so called “Baghdad Candle” – see further in this paper).

* Just a reminder: at the beginning of 19th century, it was hardly known that combustion is a chemical process of combining with oxygen, other sciences were in the early stage of development, and the technology had just started to exploit the fruits of the steam engine and the Industrial Revolution.
sciences. Together, they provided many benefits for people’s life and made it healthier, richer, etc.³

It is well known and widely accepted that electrochemistry started its career with the achievements of two Italian researchers at the end of the 18th century.⁴ Luigi Galvani “discovered” electricity indirectly. Bringing into contact two different metals, electricity was generated that made dead body parts (frog’s leg) contract. Yet, Alessandro Volta is credited as the founder of electrochemistry for his 18th century invention of the first d.c. power source (a column of alternatively packed silver and zinc plates) that was able to split water into hydrogen and oxygen.

Despite of this fact, there is another claim (speculation?) that the art of generating d.c. power was known 2 millenniums before Volta’s discovery. Artifacts found near Baghdad resemble very much the components of a dry cell, i.e., the clay pot could be the body, and the copper mantle and iron rod, the electrodes (see Fig. 1). The exactness of this discovery, the so-called Baghdad candle, is not yet verified.⁶

A glance over the highlights of electrochemistry in the 19th century, Table I, and the technical application resulting from them confirm the great value of this science. Important theoretical breakthroughs and advances in industrial electrochemistry were achieved and they continue to be valuable today.

The actual list of the scientist and their achievements is far richer. There are more sources (reference literature) giving a detailed survey of the electrochemical activities in the 1800s.⁸–¹⁰ The end of century was especially fruitful, with the work of S. Arrhenius on the dissociation of electrolytes and the resulting activity of ions as a function of their concentration. F. W. Ostwald continued the research in the field of electrical conductivity and catalysis. W. H. Nernst defined the dependence of electrode potential on the nature of the electrode reaction, as well as on the concentration/activity and other parameters of the ions participating in the electrode equilibrium, known as the Nernst Equation. E. Weston is

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* In previous centuries, experiments connected with electricity were a subject of interest of scientists as well. Some of them were William Gilbert, Otto von Guericke, Benjamin Franklin and Charles Coulomb.⁵

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Fig. 1. The Baghdad candle, 2200 BC: artifact parts that could be combined into a battery.
remembered for his cell with constant voltage of 1018 mV, which is used as a standard for measuring voltage. F. Haber, famous for the invention of the nitrogen-fixation process, is also credited with the invention of the glass electrode and some other work on measuring the acidity of solutions. J. Tafel, a pioneer in organic electrochemistry, with his Tafel Equation, explained how the rates of electrode reactions depend on the overpotential. The list does not end with these names only.

**TABLE I. Some of the most important discoveries of electrochemistry in the 19th century**

<table>
<thead>
<tr>
<th>Discovery</th>
<th>Author/Year</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltaic pile</td>
<td>A. Volta, 1800</td>
<td>First d.c. source</td>
</tr>
<tr>
<td>Water splitting by electrolysis</td>
<td>W. Nicholson and A. Carlisle, 1800</td>
<td>H₂ production</td>
</tr>
<tr>
<td>Extraction of base metals</td>
<td>H. Davy, 1807</td>
<td>Na, K, Ca, etc. isolated</td>
</tr>
<tr>
<td>Laws of electrolysis</td>
<td>M. Faraday, 1830</td>
<td>Quantitative aspects of electrolysis</td>
</tr>
<tr>
<td>Two-fluid battery</td>
<td>J. F. Daniell, 1836</td>
<td>Long-lasting constant d.c. source</td>
</tr>
<tr>
<td>Electroplating</td>
<td>J. Eckington, 1836</td>
<td>Electroplating of Ag</td>
</tr>
<tr>
<td>Fuel cell envisaged</td>
<td>W. R. Grove, 1839</td>
<td>Sophisticated d.c. source</td>
</tr>
<tr>
<td>Electrolysis of molten salts</td>
<td>R. W. Bunsen, 1852</td>
<td>Mg, Li isolated</td>
</tr>
<tr>
<td>Lead-acid battery</td>
<td>G. Planté, 1859</td>
<td>First portable d.c. source</td>
</tr>
<tr>
<td>Primary cell</td>
<td>G. Leclanchè, 1868</td>
<td>Forerunner of the dry cell</td>
</tr>
<tr>
<td>Refining of metals</td>
<td>J. Eckington, 1869</td>
<td>Cu refining by electrolysis</td>
</tr>
<tr>
<td>Electrowinning</td>
<td>Balbach &amp; Thum, 1871</td>
<td>Cu extraction by electrolysis</td>
</tr>
<tr>
<td>Al molten salts electrolysis</td>
<td>P. L. Heroult and C. M. Hall, 1885</td>
<td>Al extraction from molten salts by electrolysis</td>
</tr>
</tbody>
</table>

**Further strengthening, progress and diversification**

During the 20th century, electrochemistry continued to advance, to foster the theoretical basis and, consequently, to achieve more and more useful and valuable practical results.

It started with the considerations of ionic transport in solutions, defining the pH as a measure for hydrogen ion concentration, respectively, activity. Experiments in bioelectrochemistry were improved, membranes were introduced in the experiments, the charge of an electron was determined using an oil drop, etc.

Application of electrochemistry for analytical purposes started with the invention of polarography, i.e., recording and interpreting current-potential curves. The success was recognized some 30 years later by awarding the Nobel Prize to the inventor J. Heyrovsky. The properties of electrolyte solutions were interpreted in terms of their structure, etc.

The Russian Electrochemistry School, which was concerned with the fundamentals of electrode reactions, electrochemical interfaces, electron transfer, adsorption, etc., matured.
Corrosion became the subject of interest of electrochemists and its nature was explained in terms of coupled electrochemical oxidation, respectively reduction processes. This knowledge was further elaborated and applied to the understanding of corrosion and the design of corrosion protection. Passivity, local cell action, cathodic protection, Pourbaix diagrams, etc., followed. Then photochemistry was expanded to fields such as, e.g., semiconductors, solid-state ionics, and diffusion aspects of scales growth.

The energetic of electrochemical systems achieved its best in the first practical fuel cell, which was based on an alkaline electrolyte and porous gas-diffusion electrodes. It was employed in early space missions (Apollo) for providing in-flight power, heating and drinking water, Fig. 2. Later on, due to the ultimate progress in innovating cationic selective membranes sustainable under the most severe conditions, such as, e.g., in chlorine cells, membrane cells were engineered that operated at almost reversible electrode potentials.

The kinetics of electrochemical reactions dominated between the branches of theoretical electrochemistry. The achievements were the Butler–Volmer Equation, the understanding of the existence of exchange current, the order of electrochemical reactions, etc. Not only electrocatalysis, batteries and fuel cells, etc., but also the broadening of electrochemistry in new fields and the intertwining with existing ones are recent subjects of interest. Advances in materials science and perfection of characterization techniques, miniaturization down to the nano-
scopic and even atomic level, led to the benefits of obtaining knowledge of discrete surfaces.

This short summary is given here in order to stress that over a long period electrochemistry was a nest where the best bachelors were accepted after their graduation as recognition of their success. They were introduced to the secrets of scientific research, further educated and trained to become leaders not only in electrochemistry, but also in many other fields of chemistry. In other words, electrochemistry was a kind of kindergarten from where new generations of top scientists and experts were disseminated throughout traditional and new branches of chemistry.

The present status of electrochemistry

In contrast to the glorious golden ages of electrochemistry, the present state is just fading. Electrochemistry is not anymore the mainstream science or technology. The interest for electrochemistry, in education, research and industry is low. Chemistry and science in general share similar crisis.

According to the reductions in funding research and new equipment purchase, electrochemistry is not a priority for strategic research, no matter that there is disproportion between regions and countries.

The place that used to belong to electrochemistry and its different branches nowadays is occupied by some other sciences or techniques. For example, the NASA’s Mars Rover (vehicle) Curiosity is powered by a nuclear generator – not with a fuel cell. Similar substitutions occurred in some other domains that were believed to belong to electrochemistry, such as, *e.g.*, industrial hydrogen generation by thermal decomposition processes instead of electrolysis, *etc.*

The case of hydrogen generation is very illustrative. For more than 50 years, electrochemistry was promising that it is on the best way to produce cheap hydrogen by means of electrolysis and electrocatalysts with high performance for H₂ evolution, thus enabling economic use of large scale fuel cells that would supply cheap electricity for vehicles, heating/cooling and other power needs. Despite of the tremendous advances in the field of electrocatalysis, the situation so far is not that what was promised: the market share of hydrogen produced by electrolysis is rather low (5 %), so that fuel cells are still expensive and rare in application. Electricity produced by fuel cells is expensive too, and the number of electric cars on the streets is symbolic. Recent market figures show only some 5,000 electric cars are sold per annum in Europe (0.07 % of the total sale), because they are many times more expensive than classical cars.

Other exaggerations have frequently been made in presenting the performance of newly prepared electrocatalysts or fuel cells. Statements such as “our non-platinum catalysts are similar (or, in some cases, better) than those based on platinum” are frequently used in scientific papers or lectures. Or “We did prepare
a fuel cell that is very effective in the combustion of biofuel (ethanol or so); our
calculations show that with the crop harvested from a relatively small part of the
state’s agriculture land, enough electricity could be produced to satisfy all the
needs of the state (!)".

Normally, such unrealized promises do not improve the image of elec-tro-
chemistry.

As a conclusion of the recent status of electrochemistry, the following
should be stressed:
– subjects of interest of electrochemistry are numerous and diversified*;
– fields where electrochemistry is applied are highly specialized, complex
and often interdisciplinary and
– electrochemistry is no longer a top priority in many aspects**.

Actual fields of interest and electrochemistry

The quoted false expectation together with some other disappointments
caus ed contemporary electrochemistry to sink towards the bottom of the science
priority ranking. According to a list presented in the EuCheMS’ Program docu-
ment, electrochemistry is ranked 6th out of 8 areas of chemistry that are expected
to achieve significant breakthroughs, i.e.:15

Synthesis,
Analytical Science,
Catalysis,
Chemical Biology,
Computational Chemistry,
Electrochemistry,
Materials Chemistry and
Supramolecular chemistry and nanoscience.
Within electrochemistry, priority is given to the following items:
Energy,
Batteries,

* Here is an example of how rich in different subjects modern electrochemistry is. At the
RSE-SEE 3 Symposium in Bucharest, May 14th, 2012, the following fields were included:14
Biosensors & Biofuel cells (Wolfgang Schumann); Organometallic catalysis (Jutand Anny);
Proteins for biomedicine (E. Palaček); Scanning ECh microscopy (Carlos M. Sanchez-Sanchez);
CNTs for salicylic acid detection (Adriana-Ileana Remes et al); Monitoring of parameters
for the study of nephrolithiasis (Szilveszter Gáspár et al.) and an enzymatic O2
removal system for bioelectrochemical application (Nicolas Plumeré et al.).
** The author’s concern about the future of electrochemistry is only his personal opinion, not
necessarily generally accepted. It is quite possible that electrochemists working in more
advanced academic surroundings are more optimistic regarding this subject.
A recent event, “the Dissolution of a Division of Electrochemistry” realized on the EuCheMS
General Assembly in October 2013,16 further justified the author’s concern, no matter what
reasons caused the quoted decision.
Hydrogen,
Solar cells,
Sensors,
Analytical application and
Synthesis of compounds.

Reasons for giving priority to these issues are understandable. Energy supply has been the permanent concern of human societies long back in history, and will remain so in the future due to: i) further increase of the world’s population and ii) continuous increase in per capita energy consumption, especially in the developing parts of the globe. Nowadays, people are occupied with the idea of harvesting energy from renewable sources. New concepts are developing, such as, e.g., artificial photosynthesis. Batteries, the mobile sources of electricity, are part of human life. Now, the search for batteries for the next generation of electric cars is on. Clean and cheap generation of hydrogen and efficient photovoltaic cells are regular items on the energy-oriented agenda. The challenge of developing fuel cells avoiding the use of rare metal catalysts is permanent. The expectations from electrochemical sensors are wide, and they cover biological systems and healthcare, not only for analysis, but for therapy as well.

The awareness that recent catalysts are based mainly on the use of platinum and similar rare metals and that electrochemistry is not the only consumer of these metals (that approach the end of their availability) dictates the necessity for future catalysts to be based on other, more abundant metals. Even metal-free alternatives are envisaged.

Desirable highlights

It is worth the effort of forecasting highlights that could return the former glory to electrochemistry and eventually return it to mainstream science. The idea of forecasting is attractive, but risky. In such a situation, the sentence of Niels Bohr “Prediction is very difficult, especially about the future”17 seems very appropriate.

So let us compose a list of such achievements.

– Fulfillment of already promised benefits, such as hydrogen generation at a competitive price or fuel cells that will run using such hydrogen and generate a vast amount of cheap electricity.18 They were expected long time ago. They would solve the crucial global problem of energy supply and would be highly prized. In the case of a lucky event, this could happen by tomorrow, or in case of normal progress – when ongoing research gradually achieves the required level. There are some other promises as well that are on the “waiting list”.

– Less certain innovations that would address some of the recent global problems, as, e.g., cold fusion, low-energy nuclear reactions at room temperature, that involves electrolysis of heavy water on the surface of a palladium elec-
trode.\textsuperscript{19} In the 1990s, this topic\textsuperscript{20} attracted worldwide attention and raised expectations that something colossal was “knocking on the door”. Unfortunately, it had to be disclaimed due to errors in the interpretation of the experimental results. Discoveries of similar importance could put electrochemistry again among the front-runner favorites of science.

– Breakthroughs that are currently unknown could be of similar importance as the first two categories in this list. There is no warranty when and whether they will occur, but according to previous experience, continuous progress is achieved as result of advances in fundamental knowledge and performed experimental research. There are also jumps in the progress - they are desirable, but not a regular event.

As can be seen, this list is only of general nature and does not offer any specific achievement. Going into detailed descriptions of future achievements, may, on one hand, become repetition of already known items or, on the other, become a non-serious gambling with such an important subject.

Despite this precaution, I could not resist quoting some of my personal preferences, which are:

– electrochemistry must find a way of attracting more top quality young scientists. Without the best scientists, one cannot expect to be part of mainstream science.

This is the first step in the winning spiral:

“Knowledge + infrastructure + funding”

More (“knowledge + infrastructure + funding”)

High priority (“knowledge + infrastructure + funding”)

etc.

(It has to be stressed that the stage of high priority funding is of crucial importance in climbing the success hill.)

Simultaneously to officially approved research, which is often a matter of prestige for the related institution, researchers should practice some curiosity driven research. This may seem childish, but even if it fails to deliver the expected result, it will somehow refresh and cheer up the researchers (especially the younger ones).

Non-paved approaches, \textit{i.e.}, the use of non-standard ways in selecting the research subject, the method(s) or techniques used in other branches may result in surprising new achievements. Thus, from time to time, it may be amusing, if not useful, to try ones own approach in performing research.

No matter how strange, it has to be born in mind that the occurrence of a lucky event is always possible. We should do everything that is required to perform successfully our research, but we should never abandon the idea that, sometimes, unexpected success is possible. Unexpectedly, we could reach the aimed goal in one of the first trials, despite of the established practice that it takes...
tens, hundreds or more trials for such a success. There are other lucky events too, such as, e.g., when in an attempt to reach a specific goal, some quite different, but nevertheless, valuable one is attained, etc. However, in order to recognize the importance and valorize the benefits of such an unexpected gift, one should be prepared. The importance of a prepared mind was stressed in many cases. Examples of such events are given elsewhere.\textsuperscript{21}

I personally experienced what a lucky event means with a pioneer work on the discovery of supercapacitors. The goal was research of the electrochemical reactions at a Ru metal surface, in an attempt to understand the electrocatalytic phenomena already shown by TiO\textsubscript{2}–RuO\textsubscript{2} type DSA.\textsuperscript{22,23} Incidentally some voltamograms failed to serve the primary purpose but I somehow resisted to throw them. My professor, with a well-prepared mind, immediately recognized that the registered behavior was of importance, but not for the studied problem. It was tremendously valuable for another field, the field of electrochemical supercapacitors. Thus, by chance, we discovered how to prepare electrode materials with extremely developed surface areas, which later become excellent materials for supercapacitors.\textsuperscript{24}

The above examples are far from completing the list of highlights that could push electrochemistry to a higher position among other branches of science, because it is not easy to specify what merits are required for that\textsuperscript{*}.

Alternative view

One should admit that besides the above attitude, other could exist as well that take the “return to a mainstream position” as an ambitious wish.

The alternative view could be based on following reasoning. It is customary for the leading position to be taken by some new science/branch with new and promising possibilities. Electrochemistry was once in that position for a long period, due to its merits in creating exciting and useful achievements. Today, other branches share the leading position, and electrochemistry could join them only with results that offer solutions for the most important needs of humankind. It is quite uncertain when and if ever this will happen.

Such reasoning could continue in the following way:

Electrochemistry was once the most propulsive science.

So what? Does this give us the right to insist on returning to the old glory?

\textsuperscript{*} An impressive event of the newborn science that makes us be proud electrochemists occurred in 1801, as shown on the oil painting (Fig. 1) of ref. 25: Alessandro Volta demonstrates his discovery at the French National Institute. The guest of honor, Napoleon Bonaparte, highly impressed with the possibilities of electrochemistry, expresses a wish to become part of Volta’s team!

Could we imagine such an event today, e.g., some of modern electrochemists demonstrating his discovery to the UN General Assembly or at least to the Nobel Committee?
Isn’t it normal for sciences to appear, grow, flourish and at the end to decay and fade? The same way as civilizations and many other items do. So, forget the idea of leading science and similar childish ambitions.

Today electrochemistry exists on a broader basis than before, and is mainly incorporated into other (new) branches of chemistry and science. Even if electrochemistry should discover, (innovate or engineer) real colossal achievements, the recognition will probably be given not only to electrochemistry, but to some other branches, such as, e.g., material science, biochemistry, etc., as well.

Today electrochemical techniques are part of the general (universal) list of techniques. Thus, polarography, cyclic voltammetry, potentiometry, etc. are applied in a number of sciences, and their origin in electrochemistry is forgotten. This does not diminish the value of electrochemistry.

CONCLUSIONS

A brief survey is offered on the birth, progress and recent stagnation in importance ranking of electrochemistry. The main purpose of this analysis was to raise concern for the future of electrochemistry, in the expectation that it will improve its performance and return to a higher position, as it used to have for the greater part of the past two centuries. This assignment will not be easy to fulfill and requires the involvement of a number of scientist and engineers, institutions and industries.

Next to the emotive wishes and ambitions, another attitude (cold minded and probably more realistic) is given that expresses a different opinion, i.e., that electrochemistry is running the normal course of development. Contemporary electrochemistry is incorporated into many branches of chemistry and science in general, as well in technologies, etc. It is a useful tool, e.g., in biochemistry, environmental protection, mechanical engineering, etc.

Despite the differences in the evaluation of the present position of electrochemistry, a wish is expressed that electrochemistry achieve extraordinary highlights, such as, e.g., the generation of hydrogen at a competitive price, participation in low energy nuclear reactions (former: cold fusion), photovoltaic conversion of near 100 %, etc. In other words, this is repetition of some old and well-known ideals concerned with health, wealth, longevity, etc.

ИЗВОД

ТРЕЋИ ВЕК ЕЛЕКТРОХЕМИЈЕ: СУЖАВАЊЕ ВИДИКА ИЛИ ЊИХОВО ДАЉЕ ШИРЕЊЕ?

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Дат је преглед развоја електрохемије са нескривеном жељом аутора да ово подручје што више напредује. Преглед садржи кратак опис досадашњих, веома значајних, достижућа електрохемије. Садашње стање је оцењено као незадовољавајуће, како у погледу недовољне атрактивности електрохемије да привуче квалитетне студенте – младе истра-
REFERENCES