

# Changing face of electrochemistry

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**Abstract** Over 200 years of development of modern electrochemistry was divided into five periods. Period I from the beginning up to the end of nineteenth century, Period II from 1901 to 1945, Period III from 1946 to 1965, Period IV from 1966 to 1990, and the last Period V from 1991 till the present. This division is based on (1) use of different research methods in these periods, as well as (2) different intensity and organization of research work. In each period, the main research interests were briefly characterized, followed by short discussion of the main achievements. The expected trends of future development of electrochemistry were also briefly discussed.

**Keywords** Electrodes · Electrochemical methods · Electrochemistry progress

In course of development of each science in different periods, dynamic changes in trends and research programs are observed. Problems important in one period become less important in the other, while new trends, resulting either from new discoveries or from the cooperation of researchers of a given science with people working in the other fields, appear.

Such changes were observed also in the development of modern electrochemistry.

Since the definition of electrochemistry has also changed over the years, it is desired to briefly describe this field. Electrochemistry is a part of chemistry which deals with the transformation of simple and complex compounds at the interface of electrode with different ion-conducting media. Such transformations occur with interconversion of chemical and electrical energy. Use of electrical energy brings about chemical changes; on the other side, from transformation of substances on electrodes in a cell, we can obtain electrical energy. Electrochemistry has also many applications in the industry—for instance, in production of aluminum, chlorine, and sodium hydroxide or in electrorefining.

Such description of electrochemistry, however, differs from the traditional understanding of that science. Namely, electrochemistry has developed in two main streams—electrodics and ionics. Only electrodics is connected with the interconversion of electrical and chemical energy. Discoveries in ionics, however, were very important in the development of electrochemistry, especially in the second half of nineteenth century [1]. Nowadays, in my opinion, ionics separates from electrochemistry and moves slowly towards solution chemistry.

In order to discuss briefly and systematically the changing face of electrochemistry over the years, I divided the time when the modern electrochemistry was developed into five periods.

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Period I, from the beginning up to the end of nineteenth century

Period II, from 1901 to 1945

Period III, from 1946 to 1965

Period IV, from 1966 to 1990

Period V, from 1991 till present

The time limits of each period are, to some extent, chosen arbitrarily. They are mostly based on the fact that electrochemistry in these periods has developed in different fashion. Especially different were methods used for solving research problems. Also, the intensity of work in these periods, measured, for instance, by the number of people involved in research work or the number of published papers, was different.

I will try to highlight these differences, characterizing briefly each period.

### **Period I. Development of electrochemistry till the end of nineteenth century. The time of great discoveries and formation of basis for modern electrochemistry**

One may assume that modern electrochemistry has begun with the works of Luigi Galvani in 1791. Galvani studied the influence of the electrical energy from an electrostatic generator on the dissected frogs. Choice of the object of that study makes it also the beginning of bioelectrochemistry.

Later in 1800, Alessandro Volta formed a pile composed of silver and zinc plates separated by paper saturated with an aqueous solution of brine. This prototype of an electrical cell—a fascinating discovery—was the basis of further important achievements.

Soon after the invention of the galvanic cell, electrolysis in molten salts was used by Humphry Davy (1806) to isolate potassium, sodium, and calcium. Davy was first who used the term “electrochemical”. These experiments not only led to the development of electrochemistry but also pointed at its importance among the chemical sciences.

The work on the electrowinning of metals and in general on electrolysis has led later Faraday (1833–1834) to formulate his famous laws of electrolysis which became the quantitative basis of all electrode reactions. The Faraday constant introduced then appears in all derived later electrochemical dependences which relate current or potential of the electrode from one side and concentration of the electroactive species from the other.

In that period, electrolysis has also found important industrial applications. Electrolytic winning of magnesium and aluminum on an industrial scale initiated in the early 1870s, after introduction of the electric dynamo, is, with improvements, used till now. In that time also, the term “electrometallurgy” was introduced to describe industrial

production of metals by means of electrolysis. Also, several new galvanic cells and charge storage devices were invented in Period I [1]. A number of them has been improved over the years and is still in use. From among these, the Leclanché cell (1867), consisting of zinc anode and manganese dioxide cathode with  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$  in water as an electrolyte and the lead-acid cell introduced in 1859 by Gaston Planté are worth mentioning. The latter cell, with porous lead as a negative electrode and  $\text{PbO}_2$  as a positive electrode in solution of sulfuric acid is still the most common vehicle battery type. Finally, one should mention also the work of Helmholtz on the double-layer structure. The most important achievements in electrochemistry of the nineteenth century in the fundamental concepts and technical applications are listed in Table 1.

Though the accomplishments in electrochemistry in the nineteenth century were quite impressive, very fundamental achievements were also recorded in ionics, especially in the second half of that century. Some of these achievements are also reported in Table 1. It was the time when fundamental concepts of ionics were developed. The works on the dissociation and theory of electrolytes, on the theory of weak and strong acid and bases, and on the conduction of electrolytes and independent migration of ions were listed.

All these achievements clearly show that electrochemistry in nineteenth century was a very important science and played important role in the development of natural sciences and also of industry. This conclusion is supported by the fact that several researchers who worked in ionics in that time were distinguished by the Nobel Prize in the first years of twentieth century soon after this prize was founded. The list of such persons is given in Table 2. This list also features Nernst who received the Nobel Prize for his work in thermochemistry; however, his earlier works in the field of electrochemistry contributed largely to his scientific reputation. Nonetheless, looking at Table 2, we see that three Nobel Prizes in the period of 9 years were granted to scientists working at least partly in ionics.

At the turn of nineteenth century, electrochemistry constituted an important part of physical chemistry. Sometimes, even titles and descriptions, like “physical chemistry and electrochemistry” were used which point to the significant position of electrochemistry.

It should be added that, already, in the early years of nineteenth century, separate books devoted to electrochemistry [1] were published—such as “Elemente der Elektrizität und Elektrochemie” by G.J. Singer published in 1824 or “Grundriss der Elektrochemie” by W.T. Lampadius, published in 1817.

Also, electrometallurgy was presented in quite early works such as “Die Galvanoplastik” by M.H. Jacobi (1840) and “A Manual of Electro-metallurgy” by J. Napier (1851).

**Table 1** The most important achievements in electrochemistry in the nineteenth century

Inventor	Achievement	Year of invention
Volta	Electrochemical potential series of metals	1793
Volta	A prototype of battery	1800
Davy	Obtaining of sodium and potassium by electrolysis	1806
Faraday	Electrolysis laws	1833
Bunsen	Production of Mg from molten salts	1852
Helmholtz	Double-layer model	1853
Saint-Claire Deville and Bunsen	Production of Al from molten salts	1854
Planté	Lead-acid battery	1859
Leclanché	Battery	1867
Kohlrausch	Law of independent migration	1876
Arrhenius	Theory of electrolytic dissociation	1886
van't Hoff	Theory of solutions	1887
Nernst	Nernst equation	1889
Ostwald	Dilution law	1889
Lippmann	Lippmann equation	1895
Caspari and Nernst	Concept of overvoltage	1898

In the early years of nineteenth century, elaborations on galvanic cells were also published.

At the end of nineteenth century, electrochemists had their own journals where they could present their discoveries and achievements. One may mention such journals as *Zeitschrift für Elektrotechnik und Elektrochemie* (1894), *Elektrochemische Zeitschrift* (1894), *L'electrochimie* (1895), or *L'industrie electrochimique* (1897).

Concluding, all these achievements point to a very important role of electrochemistry at the end of nineteenth century, not only in the development of natural sciences but also in the development of chemical industry.

## Period II. Development of electrochemistry in years 1901–1945. Studies of electrochemical reactions.

### Background of electrochemical kinetics

In Period II, which can be dated from the beginning of twentieth century till its late 1940s, the development of electrochemistry was continued in a fashion similar to that observed in the second half of nineteenth century. However, in this period, the development of electrochemistry was relatively faster in relation to ionics.

At the beginning of twentieth century, fundamentals of potentiostatic and galvanostatic methods were presented. Also, the concept of the diffusion layer in its general form was formulated by Nernst for moving electrolytes or rotating electrodes. In 1905, Tafel presented his well-known equation (for details, see [2]). However, these basic equations and theoretical concepts, without corresponding instruments and electrodes, were not sufficient to stimulate further more dynamic progress of electrochemistry.

Evidently, the greatest stimulus for its progress was given by invention of polarography by Heyrovsky in 1922. Significance of this method in the progress of electrochemistry was recognized later. In 1959, Heyrovsky received the Nobel Prize. Two factors combined with polarography were important: first, the use of the dropping mercury electrode (DME) and second, automatic, though at the beginning very simple, way of recording of the observed current–potential dependences. The use of DME was important because this electrode with periodically (dependent on drop time) renewed clean surface led to reproducible results. Solid electrodes, which were used earlier, were very often not sufficiently pure which frequently led to erroneous results.

By adding surfactants to studied solutions while using DME, one could demonstrate their influence on the kinetics of electrode reactions. Such studies have shown the fundamental role of the purity of the electrode surface and stimulated further works on the proper preparation of clean gold, platinum, and other electrodes.

Also, the automatic recording of polarograms has shown the importance of such approach for better analysis of obtained results and proper documentation of experiments.

**Table 2** List of the Nobel Prize winners from early period of development of electrochemistry

Name	Contribution to	Year
van't Hoff	Osmotic pressure	1901
Arrhenius	Theory of electrolytic dissociation	1903
Ostwald	Chemical equilibria and rates of reaction	1909
Nernst	Thermochemistry	1920

In the field of electrode reactions in that period, also very important were studies which finally led to the well-known Butler–Volmer equation (1930). The work of Gurney (1931) on the first quantum-chemical theory of electrode reactions should be also mentioned.

Along with the progress in the study of electrode reactions, the significant works were noted on the double-layer structure and theory. Gouy (1910) and Chapman (1913) improved the earlier model of Helmholtz. Later, an even more advanced model was presented by Stern (1924).

Also, the work of Frumkin was important in that field because he presented the thermodynamics of the double layer and also introduced the concept of the zero charge potential (1928).

Very important progress in the understanding of the structures and behavior of molecules held at the surface of solids and liquids was made by Langmuir. His works, though not inherently connected with electrochemistry, have influenced significantly the further development of this branch of science, especially at the end of twentieth century.

I have mentioned the achievements in electrodictics to a larger extent than those of ionics because, in my opinion, electrodictics is the heart of electrochemistry. However, the first half of twentieth century also brought us a significant development in ionics. In 1907, Lewis introduced the concept of the thermodynamic activity and activity coefficient. Later, Debye and Hückel presented the theory of electrolyte. Also, the theory of acids and bases was worked out by Brønsted.

The pH scale proposed by Sørensen (1909) and the glass electrode developed by Haber and Klemensiewicz (1909), so widely used during last hundred years, are also worth mentioning.

The most important research achievements of that period, both in electrodictics and ionics, are presented in Table 3.

Table 4 lists a number of most important electrochemical methods and electrodes introduced and developed in that time. The progress of electrochemistry during Period II was important; however, the discoveries were not as fundamental as those noted in the nineteenth century. Other natural sciences like physics (nuclear, quantum mechanics) noted more spectacular achievements in the first half of twentieth century.

The intensity of research work in electrochemistry in the Period II was similar to that in the second half of nineteenth century. The number of researchers working in that field was not large, and the number of published electrochemical papers was rather limited. However, this remark is probably also valid in relation to other chemical disciplines.

### Period III. From 1946 to 1965. Development of electrochemical methods. Theory of electrode reactions

In the 1950s, one could already observe the increase of intensity of electrochemical works. Not only new methods but also new working electrodes were invented, and their properties were investigated. Evidently due to large amounts of money offered in that time to research in natural sciences, a large increase of the number of people working in research laboratories was noted.

In Europe, three new electrochemical journals appeared at that time—namely *Electrochimica Acta* (from 1959), *Journal of Electroanalytical Chemistry and Interfacial Chemistry* (from 1959), and the Russian *Elektrokhimiya* (from 1965) which has, in recent years, also been published in English as *Russian Journal of Electrochemistry*. For several years (starting from 1963), bimonthly *Electroanalytical Abstracts*, an international journal dealing with the documentation of all

**Table 3** Main achievements of electrochemistry in the first half of twentieth century

Inventor	Achievement	Year
Tafel	Tafel equation	1905
Lewis	Thermodynamic activity and activity coefficient	1907
Sørensen	pH scale	1909
Gouy, Chapman, and Stern	Theory of electrode–electrolyte double layer	1913 and 1924
Debye and Hückel	Theory of strong electrolytes	1923
Butler, Audubert Erdey-Gruz, and Volmer	Concepts of slow electrode reactions Butler–Volmer equation	1924–1930
Onsager	Works on conductivity, Onsager equation	1926
Frumkin	Thermodynamic theory of surface phenomena on the phase boundaries and adsorption of organic compounds	1928
Brønsted	Theory of acids and bases	1929
Frumkin	Influence of the double layer on the rate of electrode reaction	1932
Gurney	Quantum mechanics applied to electrode reaction	1932

**Table 4** Methods and more important electrodes introduced in the first half of twentieth century

Inventor	Achievement	Year
Sand	Chronopotentiometry–sand equation	1901
Cottrell	Potentiostatic method–Cottrell equation	1902
Nernst	Hydrodynamic voltammetry	1904
Haber and Klemensiewicz	Glass electrode	1909
Heyrovsky	Polarography–dropping mercury electrode	1922
Beckman	pH meter	1935
Hickling	Potentiostat	1942
Davis and Brink	Microelectrodes	1942
Heyrovsky and Forejt	Streaming mercury electrode	1943
Randles, Ershler	Measurement of electrochemical impedance	1947
Randles, Ševčík	Linear potential scan voltammetry	1948

aspects of electroanalytical chemistry including fundamental electrochemistry, was also published.

Also in that time, other—earlier founded electrochemical or partly devoted to electrochemistry—journals, such as *Journal of Electrochemical Society*, *Zeitschrift für Elektrochemie und Angewandte Physikalische Chemie*, and *Transactions of the Faraday Society*, were published. The foundation of several new electrochemical journals resulted from a large number of new research results produced by very active electrochemists in growing number of electrochemical laboratories. The existence of these journals had a positive influence on further intensification of development of electrochemistry, the more so, that these journals kept good standards, accepting, as a rule, only good papers for publication. One should add that the chief editors of these journals were well-recognized electrochemists—Roger Parsons (*J. Electroanal. Chem.*) and Alexander Frumkin (*Elektrokhimiya*).

A significant positive impact on the development of electrochemistry was also the formation of the international society which grouped many electrochemists. In 1949, the organization called “Comité International de la Thermodynamique et Cinétique Electrochimique” (CITCE) was formed in Brussels, which, in 1970, was transformed into “International Society of Electrochemistry” (ISE).

Among the scientific achievements of Period III, the theory of the simple charge transfer processes occurring at electrodes and homogeneous between redox reactants was worked out by Marcus and by Levich and Dogonadze. Though the theory was limited only to simple charge transfer reactions, these works were very fundamental to the further development of the study of electrode reactions in various media. The importance of these works was recognized by the Nobel Prize Committee which honored R.A. Marcus by giving him a Nobel Prize in 1992.

It is characteristic that, in Period III, numerous papers devoted to the development of new methods and to

theoretical description of various types of different processes (EE, EC, ECE, CE, and others) in the frame of newly invented and also introduced earlier methods were published. For instance, chronopotentiometry, introduced at the beginning of twentieth century, until around 1950, had no theoretical descriptions of various mechanisms. Also, polarography, invented in the early 1920s, up to 1953, had only theoretical description of limiting currents (the Ilkovič equation) [2].

The methods used in electrochemical studies may be divided into two groups: (1) simple, or traditional, strictly electrochemical methods and (2) non-traditional, complex methods, like, for instance, spectroelectrochemistry, where measurement of electrochemical parameter is accompanied by simultaneous measurement of other non-electrochemical property.

This division and classification is schematically shown in Table 5. I should add that distinction between periods III and IV is mostly based on the use of only traditional (Period III) and both traditional and non-traditional methods (Period IV). The time of introduction of complex methods begins in Period IV. Among methods shown in Table 5, the linear scan voltammetry, especially in its cyclic version, is very important. Though this method was introduced earlier, the basic equation which describes the peak currents was given in 1948 by Randles and Ševčík. The fast development and wide use of this method in a cyclic version occurred in the 1960s when the hanging mercury drop electrode was introduced by Kemula and Kublik (1958). Later, different sorts of solid electrodes were applied in such studies.

Cyclic voltammetry is, at present, probably the most widely used electrochemical method. Other cyclic methods are also known (see Table 5), however, rather occasionally used in practice. Probably, simple equipment and clear representation of cyclic current–potential curves explain the so frequent use of this method. The theory for different types of processes in linear scan voltammetry

**Table 5** Research methods introduced in different periods

Period	Methods
I–III Traditional methods	Chronoamperometry one and double step
	Chronocoulometry one and double step
	Chronopotentiometry one step and cyclic
	Linear scan cyclic voltammetry
	Rotating disk voltammetry also with ring electrode and other hydrodynamic voltammetries
	Electrochemical impedance
	Staircase voltammetry
	Square-wave voltammetries
	AC voltammetry, tensammetry
	Stripping voltammetries
	Pulse voltammetries
	Chromatopolarography
	IV Non-traditional methods
Ellipsometry	
Infrared reflectance–absorption spectroscopy	
Surface-enhanced Raman spectroscopy	
Radiotracer methods	
X-ray absorption spectroscopy	
Electroreflectance spectroscopy	
X-ray diffraction methods	
Second harmonic generation	
Quartz crystal microbalance	
Electrochemistry–electron paramagnetic resonance (EC-EPR)	
Electrochemistry–nuclear magnetic resonance (EC-NMR)	
V Imaging methods	Scanning tunneling microscopy (STM)
	Atomic force microscopy (AFM)
	Scanning electrochemical microscopy (ECSM)

was given in 1964 by Nicholson and Shain (see, for instance, [2]). In order to minimize the influence of capacity currents on the recorded cyclic voltammetric curves, the staircase voltammetry was introduced but

found no wider acceptance. Also, cyclic chronopotentiometry is rarely used in ordinary studies; mostly, people who study rechargeable cells and batteries use this method in their investigations.

In the more extensive studies of the mechanisms of electrode reactions, two methods were preferentially used—rotating disk and rotating ring-disk electrodes and measurements of the electrochemical impedance—both developed in the Period III.

Several new working electrodes were also introduced and developed in Period III. The list of such electrodes is given in Table 6. The new electrodes were introduced (1) in order to improve analytical determinations, especially at very low concentration of analytical impurities, (2) to study electrode reactions in a wide range of potentials, and (3) to enhance the rate of selected reactions.

Double layer at interfaces of different electrodes with various electrolytes was studied in that period using mostly electrochemical methods. The use of other non-traditional techniques started and became frequent in the next period.

Concluding, Period III was very successful for the development of electrochemistry. Introduction of new methods and elaboration of theoretical basis for electrochemical methods for various types of electrode reactions gave good basis for fast progress of this science. Different electrode reactions were experimentally studied and analyzed. Many works and published papers were devoted also to the description of the double-layer structure at different electrodes in different media. The influence of the double-layer structure on the kinetics of electrode reactions was also quite intensively studied in that time. Very important progress was observed in the development of electrochemical methods of analysis. Stripping voltammetry, especially, invented and developed in this Period, appeared to be very useful. On the other side, the papers dealing with ionics appeared less frequently in electrochemical journals. They were located in other types of journals, for instance, those dealing with solution chemistry.

**Table 6** Electrodes introduced in electrochemistry in the second half of twentieth century

Authors	Electrode	Year of introduction
Kemula and Kublik	Hanging mercury drop electrode	1956
Adams	Carbon paste electrode	1958
Frumkin and Nekrasov	Rotating ring-disk electrode	1958
Zittel and Miller	Glassy carbon electrode	1965
Pungor	Ion-selective membrane electrode	1967
Florence	Mercury film electrode	1970
Lane and Hubbard	Various chemically modified electrodes	1973
Adams	Microelectrodes	1976
Peterson	Static mercury electrode	1979

#### **Period IV. From 1966 to 1990. Introduction of non-traditional methods and computers to electrochemical experiment. New modified and ion-selective membrane electrodes**

It is not easy to determine a strict border between Periods III and IV. However, both non-traditional methods (with exclusion of imaging methods, see Table 5) and computers started to be introduced to the electrochemical practice in late 1960s and then Period IV began.

Now, in the study of surface reactions or adsorption, mostly non-traditional methods like, for instance, infrared reflection spectroscopy or quartz crystal microbalance were developed and used. Some of these methods were invented earlier, for instance, electrochemistry with the use of radiotracers or ellipsometry; however, their intense use and development occurred in the Period IV.

Other methods, like infrared spectroscopy; electroreflectance spectroscopy; second harmonic generation and sum frequency generation spectroscopies; surface-enhanced Raman spectroscopy; synchrotron-based X-ray diffraction and X-ray absorption techniques; and others were later introduced (Table 5).

The use of spectroscopic methods for the study of processes occurring on electrodes could not rather be carried out with mercury electrodes. Therefore, this development was combined with efforts aimed at preparation of high-quality solid electrodes. In that time, the electrodes made from monocrystals (mainly Au) became frequently used in the surface electrochemical studies.

In Period IV, processes of reactants adsorbed on electrodes were studied quite extensively. Though such processes were investigated earlier, in this Period, they were studied more profoundly using non-traditional methods and supplied new information about the state, structure, and interactions of adsorbed molecules. The results of such studies were useful not only by allowing a deeper understanding of electrode reactions of adsorbed reactants, but, to some extent, also of reactants deposited on the support electrodes in order to modify their surface.

The non-traditional methods were widely used especially in the study of adsorption and identification of the initial, intermediates, and final products adsorbed on the electrode surface. Certain model compounds, like, for instance, pyridine, were also studied in order to determine the orientation of that compound on the electrode surface or its eventual reorientation with the change of the potential of the electrode.

In that time, the theory of electrochemical processes of adsorbed compounds in the frame of different methods was also developed (see [3]).

Numerous studies were carried out on the adsorption and electrode reactions of compounds such as methanol which

may serve as a fuel in some fuel cells. The other reaction which, as a rule, occurs in the fuel cells—the electroreduction of oxygen—was also intensely studied in that period. Different electrodes and conditions were explored to make this electroreduction faster. For construction of convenient electrodes, different materials were used, and their electrocatalytic properties were explored. These works were oriented onto substitution of expensive platinum with cheaper materials or composites with good electrocatalytic properties. Many interesting new materials were discovered or synthesized and used for construction of modified electrodes. In 1977, Heeger and MacDiarmid have shown [4, 5] that doping polyacetylene with iodine led to the polymer which exhibited the metallic properties with conductivity higher for many orders of magnitude than that of the original material.

In the following years, many other such conducting polymers were synthesized. Almost all these compounds could be prepared by electrochemical oxidation of corresponding monomers. Electrochemistry used in electro-synthesis of such polymer species has an advantage, since the polymers produced are in the doped state.

The work on new conducting polymers in 1980s was quite intense as shown already in 1990 by Heinze [6] who, in his review, listed 26 of the most important conducting polymers known at that time. Such fast progress resulted from the potential applications of these species in different fields, such as rechargeable batteries, materials for micro-electronics (diodes, transistors), photovoltaic and electrochromic devices, and many others.

The other class of compounds which were known for a long time but not used for modification of electrodes is hexacyanoferrates of various metals. These ill-soluble compounds were deposited on support electrodes and electrochemically studied in various solutions. Such studies initiated in late 1970s were later intensely continued by many researchers in various laboratories. Also, in this case, the fast development was stimulated by expectation that electrodes modified with hexacyanoferrates may be used for construction of batteries, sensors in electrocatalysis, and in other fields.

Many other substances were used for modification of electrodes such as metallic oxides, e.g., iridium and titanium oxides, heteropolyacids, and other substances which may exhibit electrocatalytic properties.

In earlier periods and in Period IV, voltammetric studies of different systems were carried out in aqueous, mixed, and non-aqueous media. In the mid-1970s, Ralph Adams moved experiments to another media by introducing *in vivo* voltammetry [7]. It was shown that animals such as rats may serve as an object of voltammetric studies with electrodes implanted permanently in their brains. Stamford and Justice Jr. wrote [8] in their review that “Ralph Adams

was crazy enough to put an electrode in the brain in the first place, but smart enough to recognize its potential”.

Though first *in vivo* experiments were not quite satisfactory, later, the experimental methodology was improved by Adams and his group and also by other researchers. These experiments not only led to the development of *in vivo* voltammetry but also served to develop ultramicroelectrodes, since only very small electrodes could be used in such *in vivo* experiments.

Small electrodes such as dropping or hanging mercury electrode were used earlier, but these electrodes had the diameter of the order of millimeter. Now, new ultramicroelectrodes to be used *in vivo* had diameter of the order of micrometers or less. Such electrodes, properly located in the brain, could be used for the detection and determination of neurotransmitters secreted from a single cell, to measure rate of transport of important substances introduced to the body and for other purposes.

Ultramicroelectrodes appeared also to be very useful in other applications. Very small electrodes (with the radius of several micrometers or less) can be applied in measurements of the rate of very fast electrode reactions. Since the linear scan voltammetry with such electrodes may be carried out even with the scan rate of the order of  $10^6 \text{ V s}^{-1}$ , the mass transport rate,  $v$ , calculated from the equation  $v = [D/(3t)]^{1/2}$  will be equal to about  $10 \text{ cm s}^{-1}$  (assuming diffusion coefficient of a reactant,  $D$ , equal to  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ). It is possible to obtain a similar value of  $v$  with low scan rate and radius of the electrode ( $r$ ) around  $10^{-6} \text{ cm}$ , using a simple equation  $v = D/r$ . This simple estimation shows that, under such conditions, practically all known electrode reactions should appear to be at least quasi-reversible and their kinetics could be measured.

In Period IV, ion-selective membrane electrodes were also intensely studied and used for analytical purposes (Pungor, 1967).

Electrochemical experiments in this Period were carried out with the increasing role of computers. While at the beginning of Period IV computers were only very rarely used in electrochemistry, at its end around 1990, they were used very frequently and in several ways. They enabled digital simulation of various types of electrode processes, for which analytical solution was not possible to derive.

Computers also changed the electrochemical experiments. They could be programmed, obtained results stored in the memory and analyzed in a short time, since simple programs for basic analyses are often available with purchased equipment. Experiments can be performed much faster and more precisely.

Concluding, in Period IV, due to the developed theory and new advanced methods, a more profound understanding of the nature of the electrode reactions was found. Also, new electrode materials oriented onto

different applications were introduced, studied, and applied in various studies.

#### Period V. From 1991 till present. Time of nanoelectrochemistry

In the last period, which begins around 1991, a wide use of imaging methods in the study of surface reactions and adsorption of various ions and molecules on well-defined surfaces of electrodes was observed. Instead of limited information obtained by traditional or non-traditional methods, new techniques are used—the scanning tunneling microscopy (STM) and the atomic force microscopy (AFM)—which give the real image of the interface. Also, the scanning electrochemical microscopy should be mentioned. Such studies, characteristic for that period, open a new era in the surface electrochemistry [9].

Now, the real surface of the electrode may be observed with its kinks and steps and some possible imperfections of the surface. On such well-defined surfaces, the adsorption of various ions and compounds was investigated. Not only the extent of adsorption but also the structure of adsorbate on different electrodes and surfaces was studied, with the atomic scale resolution. Instead of assumptions based on results obtained by earlier methods, now, without any assumptions, one obtains an image of the studied interface.

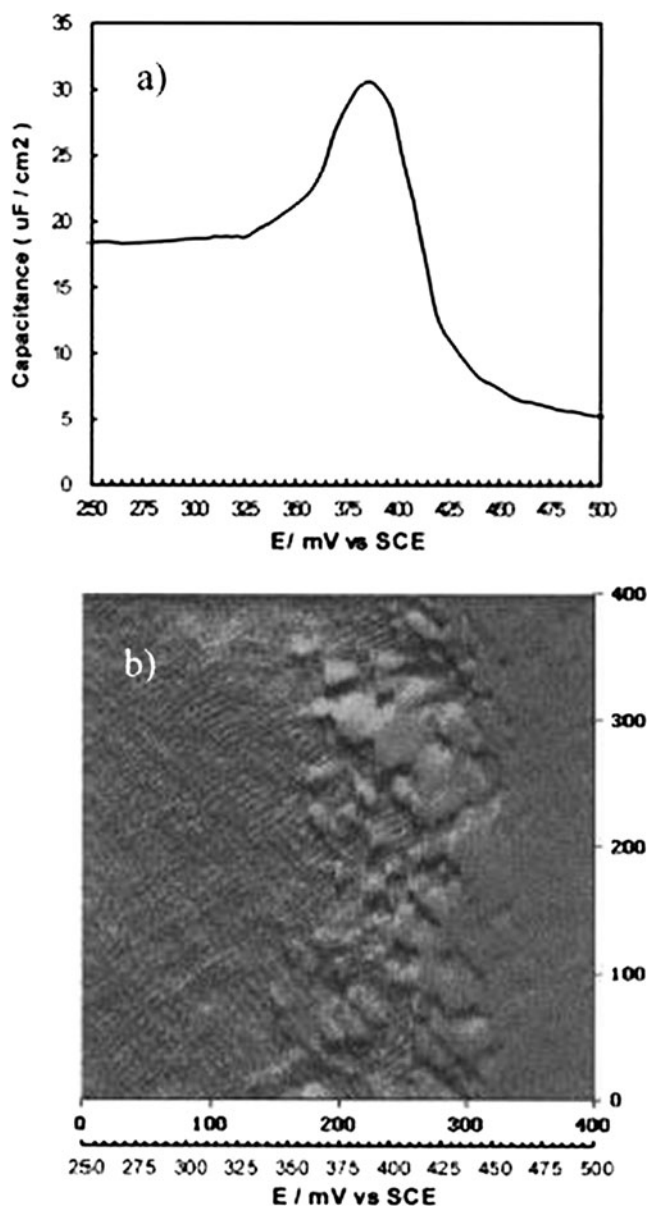
I do not show any image of such interfaces with atomic resolution because they are published in numerous papers; instead, I give an image of the molecular reorganization which occurs in the adlayer under the influence of the change of potential [10] (Fig. 1).

These new techniques also enabled the study of the behavior of individual molecules, especially of important biomolecules.

It has been shown that a conducting probe AFM and also STM may be used to measure conductance of single molecules and the change of this parameter with the potential. There are several approaches, which make such measurements possible. They are briefly described in a review entitled “Charge Transfer and Interfacial Bioelectrochemistry at the Nanoscale and Single-Molecule Levels” [11]. These approaches are based on the use of STM with thiols as reactants. Sulfur from thiol ensures the chemical and electrical contact with the surface and tip.

Related to that problem, molecular electronic junctions and single-molecule electronics were also studied and developed. McCreery [12] has shown that there is a shift from donor–bridge–acceptor system to molecular junction by attachment of a bridge to two electrodes. In Fig. 2, we show, following Lindsay [13], a family of current–potential curves taken for few-molecule nanojunctions and two models to account for the observed quantization.





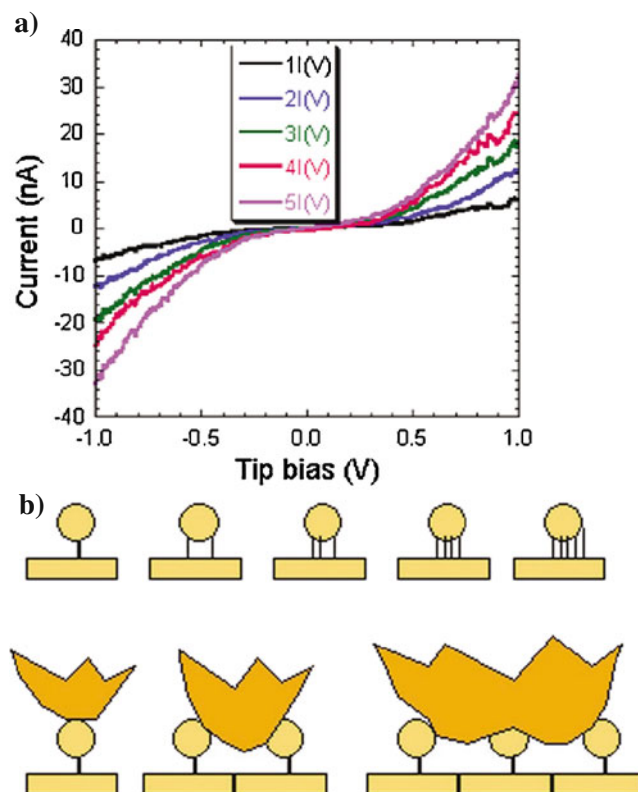
**Fig. 1** Au (111) electrode in 16 mM solution of SDS. **a** The dependence of the differential capacity on potential scanned with  $v=5$  mV/s; **b**  $400 \times 400$  nm AFM deflection image recorded at a scan rate of 10.2 Hz. The potential of the working electrode was also scanned at  $v=5$  mV/s. Taken from [10], where additional details are given

Molecular junctions, also carbon-based, made by a single molecule or a collection of parallel-oriented molecules, may exhibit rectification, negative differential resistance conductance switching, and bistable memory behavior [13]. However, there are technical obstacles which should be overcome before useful electronic junctions may be prepared. Nevertheless, the results obtained so far seem to be promising.

Single molecule devices may exhibit a theoretical data density  $10^4$  to  $10^6$  times higher than that possible today [12].

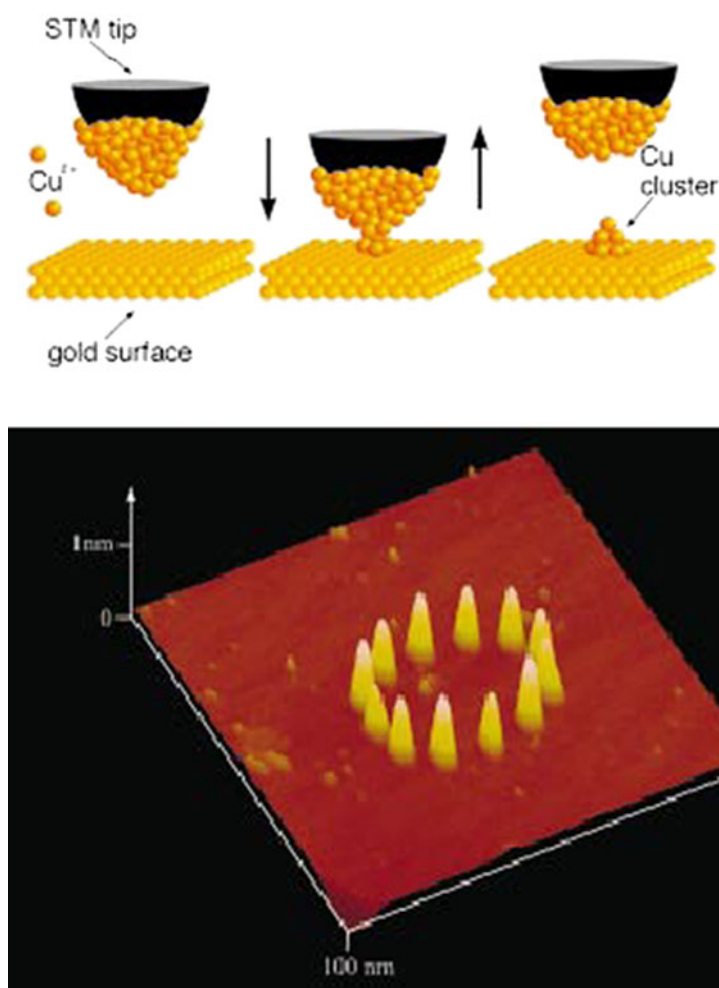
Using STM, one may also locate atoms or molecules on the surfaces in a desired order with high precision constructing different nanostructures. As an example, copper clusters deposited on the Au(111) electrode (see Fig. 3) are shown [14]. Such and similar methodologies were developed and led to a new discipline electrochemical nanotechnology [15].

Other works in the area of bioelectrochemistry are also worth mentioning. Electron transfer reactions in different biological systems were the subject of these studies. It is obvious that these reactions, together with the transport of ions, play a fundamental role in the processes occurring in biological cells. It was shown that the electron exchange reaction of metal redox systems, not very fast in typical solutions, may be very fast when these systems are located in protein interiors. For instance, the reorganization energy for electron self-exchange in  $\text{Cu}(\text{phen})_2^{2+/+}$  placed in solution is about 2.4 eV, while the value for  $\text{Cu}^{2+/+}$  placed in *Pseudomonas aeruginosa* azurin is much lower, being equal only to 0.7 eV. Such large decrease of the reorganization energy may be explained by the stabilization of the transition state by the azurin fold. In general, the



**Fig. 2** **a** Several current–voltage curves taken for few-molecule nanojunctions. The curve with lowest current corresponds probably to a single molecule in the junction. Further curves with increasing currents correspond to increase of a number of molecules in a junction as it is modeled in part **b** of that figure. Taken from [13], where additional details are given

**Fig. 3** Twelve Cu clusters formed on Au (111) surface with the use of STM tip (*top part*). Taken from [14], where details are given



protein fold plays the main role in the decrease of the reorganization energy in biological electron transfer reactions. One should also remember that moving a redox center from aqueous solutions to a medium with a low dielectric permittivity causes, at least theoretically, a considerable decrease of the outer-sphere reorganization energy [16].

The interest in bioelectrochemical studies results not only from the aspiration to learn how biological systems function but also from the desire to apply this knowledge in practical applications. For instance, the results of such studies may be useful in construction of new electrocatalytic systems for four-electron reduction of oxygen, which is used in fuel cells, since this reaction occurs in the mitochondrial electron transport chain. The problems of bioenergetics and biological electron transport were reviewed recently by Bartlett [17].

The processes of electron transfer and also ion transfer are fundamental for activity of biological membranes. The understanding of the functioning of such membranes and of

all processes (including catalytic) in which these structures are involved is essential for different aspects of our life [18].

Typical for that period of the development of electrochemistry is also the use of nanomaterials such as carbon nanotubes, for example, for modification of the properties of electrodes. These materials exhibit several very interesting properties such as large chemical surface activity, chemical stability, good electrical conductivity, and unusually high mechanical strength. They were used as a support for the deposition of metal and semiconductor particles and other modifiers as, for instance, hexacyanoferrates of heavy metals. The electrodes covered by such electroactive nanomaterials may be successfully used in electrocatalytic processes or applied for instance for the formation of supercapacitors.

In Period V and also in Period IV, many other problems and questions, in addition to those which I briefly discussed, were worked on. Major topics from that time are listed in Table 7.

**Table 7** Electrochemical topics developed in Periods IV and V

Topics
Double layer
• Studies of self-assembled monolayers
• Interface between two immiscible liquids
• Adsorption phenomena
• Reactions of the surface attached reactants
• Surface spectroscopic methods
• Non-traditional methods and progress in surface electrochemistry
• Studies of the interface with the use of imaging methods
Applications
• Electrolytic production of metals
• Electrochemical nanotechnology
• Bioelectrosynthesis
• Environmental electrochemistry
• Electrochemical protection against corrosion
• Electrochemistry in medicine—sensors, electrotherapy of cancer
• Fuel cells, biofuel cells
• Simple and rechargeable batteries
• Solar energy conversion
• Supercapacitors
• Toxic waste disposal
Various topics
• Voltammetry with monocrystal electrodes
• Electrodes modified with various chemicals
• Impedance and noise analysis methods
• Medium and solvent influence on potentials of electrodes and electrode kinetics
• Electrocatalysis
• Electrochemistry of redox enzymes
• Charge transport in biological systems
• In vivo voltammetry
• Theory of charge transfer reactions
• Underpotential deposition
• Photoelectrochemistry
• Electrochemistry of semiconductors and insulators
• Use of computers in instrumentation, digital simulation of complex electrochemical processes
Electroanalysis
• Ion-selective electrodes
• Stripping analysis
• Electroanalytical methods in trace analysis
• Electroanalysis in flow streams
• Ultramicroelectrodes in various applications
• Sensors, biosensors, and molecular recognition devices

It should be mentioned that, in Period V, computerized instruments are in common use. Computers changed dramatically the performance of electrochemical experi-

ment and also very significantly shortened the calculation of different parameters which can be obtained from the electrochemical experiment.

Writing about Period III, to show that already in that period fast progress of electrochemistry started, I mentioned the establishment of new electrochemical journals. The same argument may be used also now because, in the last 40 years, several new additional journals were established. I do not present a full list of these journals but mention only the most well-known with wide international circulation (year of foundation in brackets): *Journal of Applied Electrochemistry* (1971), *Journal of Power Sources* (1976), *Langmuir* (1987), *Electroanalysis* (1989), *Journal of the Solid State Electrochemistry* (1997), *Electrochemical and Solid State Letters* (1998), *Electrochemistry Communications* (1999), *Electrocatalysis* (2010). So, many new electrochemical journals show that the electrochemical community was and is very active and that laboratories are busy with numerous research studies which brought results worth publishing.

In Periods IV and V, numerous technical electrochemical works were also carried out. They often led to published papers, but perhaps more frequently, to different important technical discoveries and improvements. Especially, one should mention various types of rechargeable batteries with improved stability, safe and easy to use. If we suddenly removed batteries which are used in different instruments and equipment (portable computers, mobile phones, cameras, pacemakers, and others), it would appear that our life would be difficult, if at all possible.

Also, in industrial electrolysis and electrochemical engineering, great changes have occurred in the recent past [19]. These changes and reoptimizations of different processes were inspired by saving of energy and pollution constraints.

New materials, better understanding of electrochemical processes, and progress in electrochemical engineering led to improvement of old and elaboration of new electrochemical technologies.

## Perspectives

Before considering the future developments of electrochemistry, one should discuss the limits of this discipline, since such limits for different sciences were discussed in the not-so-distant past [20, 21].

### The limits of electrochemistry

The limits predicted for some specific science result frequently from our limited knowledge and limitation of

the human mind. Considering limits, we may distinguish three groups of sciences.

1. In this group, we may locate such sciences as astronomy or physics, where the limits are not expected. For instance, astronomers with more sophisticated equipment may more efficiently penetrate the universe. Also, physicists may make new discoveries, for example, in the world of elementary particles.
2. The second group may be comprised of sciences where the progress is limited by their subject. Following Stent [20], one may locate in this group such sciences of limited research field as for instance anatomy of a man or geography.
3. In the third group, one may place sciences where limits of knowledge are not evident. We may argue that chemistry belongs to this group.

I should recall, however, that Stent [20], in his book, sees the limits of this science. He writes that, though the number of possible chemical reactions is extremely large, the understanding of the rules which govern the interaction of different atoms and molecules is quite limited.

Also, Horgan, in his “The End of Science” [21], has similar views about chemistry, when, following Pauling, writes that all chemical reactions may be explained with the use of quantum mechanics.

Speaking about limits of chemistry, one should remember that new discoveries and methods bring further discoveries and new questions and expand the fields of research, making the limitations rather problematic. Such philosophy relates also to electrochemistry. However, the use of electrochemical methods in the study of different systems is limited to some

materials and to defined ranges of several factors such as material and surface of the working electrode, potential of this electrode, time of individual experiment, solvents, temperature, and pressure. These ranges and limits were discussed earlier by Bard [22].

There are limitations in the potentials applied to working electrodes. For the cathodic reactions, the limit is probably near to  $-4.4$  V vs. NHE, determined by the electron in vacuum  $e_{\text{vac}}^-$ . Solvated electrons generated in liquid ammonia and liquid amines differ from electron in vacuum,  $e_{\text{vac}}^-$ , by the free energy of solvation.

In anodic reactions, limits in positive potential applied to the electrode are imposed by the stability of electrode material, solvent, and oxidation of ions of the background electrolyte used. Nevertheless, the use of ultramicroelectrodes enabled carrying out electrooxidation near to  $+6.0$  V vs. SCE. Perhaps, new solvents and electrolytes may shift this limit to even more positive values.

The limits in the shortest time of electrochemical experiments were discussed earlier (in Period IV).

The electrochemical studies at different temperatures were carried out for long time, starting from the beginning of nineteenth century. There are a lot of experiments carried out at high temperatures with molten salts, and there are industrial processes conducted in such media (for instance, production of aluminum). On the other side, the studies at low temperatures are not so numerous. There is a lack of good solvents which would be liquid under such conditions and would exhibit sufficient conductivity (with certain electrolyte). If we had a solvent liquid at very low temperature, it would be interesting to study the behavior of electrodes made of superconductors [22]. Electrochem-

**Table 8** Electrochemistry-friendly science

→	Electrochemistry + Physics	→	Physical Electrochemistry
→	Electrochemistry + Biology	→	Bioelectrochemistry
→	Electrochemistry + Analytical Chemistry	→	Electroanalysis
→	Electrochemistry + Technology, Metalurgy	→	Electrochemical Technology Electrometalurgy Electrochemical Engineering
→	Electrochemistry + Computer Science	→	Computational Electrochemistry
→	Electrochemistry + Medicine	→	Medicinal Electrochemistry
→	Electrochemistry + Environmental Sciences	→	Environmental Electrochemistry
→	Electrochemistry + Electronics	→	Electrochemical Physics
→	Electrochemistry + Material Science	→	Material Electrochemistry
→	Electrochemistry + Chromatography	→	Electrochromatography
→	Electrochemistry + Quantum Chemistry	→	Quantum Electrochemistry

ical studies at high pressures are rather rare, though they could be useful in the elucidation of mechanisms of some complex reactions. Perhaps, the use of semiconducting and poorly conducting materials as electrodes in such studies would be also interesting.

Though electrochemical experiments have to be carried out under some limitations, the fast progress in electrochemistry, which we observe in recent years, does not point to any limits. This progress, indicated by the establishment in recent years of new electrochemical journals and, in consequence, by increasing number of electrochemical papers, was discussed earlier. It results, to a large extent, from the cooperation of electrochemists with people of other disciplines. Their cooperation was strengthened by different meetings and specialized symposia which were frequently organized in recent years; it seems, however that, in the time of easy communication by Internet, the number of meetings is perhaps too large. Cooperation of electrochemistry with other disciplines was sometimes so intensive and fruitful that it resulted in the creation of new subdisciplines with their own specific names. For example, cooperation of electrochemists and biologists led to bioelectrochemistry.

In Table 8, I have listed such subdisciplines which have the word “electrochemistry” or a shorter “electro” (as in: “electroanalysis”) in their names.

Electrochemistry is probably a unique science in this respect. Such broad cooperation of electrochemists exerts a positive influence on progress of cooperating sciences and also extends the field of interest of electrochemistry bringing new problems and questions.

The number of papers, which resulted from the cooperation of electrochemists with researchers from other branches of science, has been increasing in recent years. At the same time, the number of papers which deal only with purely electrochemical problems decreases.

It is expected that the process of cooperation of electrochemists with people of other disciplines may become even more intense in the future.

#### Future trends

It is not easy to predict the ways of development of electrochemistry in the coming years. Prior experience shows that simple extrapolation from earlier behavior not always leads to satisfactory results.

Nevertheless, I find the courage to expect that, in the near future, electrochemistry will develop principally in four main fields: (1) bioelectrochemistry, (2) studies of nanoobjects, (3) modified electrodes oriented on different applications, mainly electrocatalysis, and (4) energy con-

**Table 9** Expected future electrochemical topics

Topics
Bioelectrochemistry
• Charge transport across various phase boundaries
• Membrane processes
• Biomimetic research
• In vivo electrochemistry
• Bioelectrocatalysis
• Electrochemistry of redox enzymes
• Bioelectrosynthesis
• Biosensors
• Applications in medicine
Surface phenomena and nanoobjects
• Single molecule studies
• Molecular electronic systems and devices
• Molecular junctions
• New nanomaterials, their modifications and applications
• Further development and use of electrochemical scanning microscopy
• Further development and applications of STM and AFM
• Selectivity in electrode reactions
• Dynamics of the components of the interface
Modified electrodes and their applications
• Modified electrodes with catalytic properties
• Composite electrodes
• Self-assembled multimolecular films
• New sensors
• New ion-selective membrane electrodes
• New sensitive and selective methods of electroanalysis
Energy conversion, energy storage, and applications
• New and improved batteries
• Fuel cells for transportation
• Fuel cells for power systems
• Solar energy conversion, photoelectrochemistry
• Photovoltaic devices
• Organic semiconductors
• Solid and semiconducting materials
• Biofuel cells
• Analogs of photosynthetic systems leading to N <sub>2</sub> fixation and CO <sub>2</sub> transformation
• Electrocatalysis oriented on the improvement of fuel cells performance
• Clean electrochemical technologies
• New methods of toxic waste disposal
• Corrosion and its inhibition

version devices and energy storage devices. More detailed problems which perhaps will be explored and studied in future are listed in Table 9.

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