ELECTROCHEMISTRY: FUNDAMENTAL ASPECTS

G.V.Zhutaeva and **V.S.Bagotsky**

A.N.Frumkin Institute of Electrochemistry, Russian Academy of Sciences, Moscow 117071, Russia

Keywords

Iionic conductors, electrolyte, electrode, electrode reaction, ion solvation, electrolytic dissociation, Faraday's laws, electrode polarization, electric double layer, electrochemistry, electronic conductors, ionic conductors, electrolytic dissociation, conductivity, redox electrode, rotating electrode, microelectrode, ultramicroelectrode, electrode potential, standard electrode potential, zero charge potential, electrochemical kinetics, electrochemical reaction, electrocatalysis, bioelectrocatalysis, batteries, electrolysis, electroplating

Content

1. Introduction
2. Ionic conductors and their conductivity
3. Electrodes and electrode reactions
4. Electrode Potentials
5. The structure of the electrode/electrolyte interface
6. The Volta problem in Electrochemistry
7. Electrochemical kinetics
8. Outlook
Glossary
Bibliography
Biographical Sketches

Summary

Electrochemistry is a branch of science that is devoted to systems containing ion conductors (solutions, melts, and solid electrolytes) and also to processes proceeding at the interface of ionic and electronic conductors (and/or semiconductors). Phenomena in these systems and their properties are examined under equilibrium conditions in absence of electric currents, as well as under nonequilibrium conditions when an electric current is passing through the system. Historically the development of theoretical electrochemistry is closely linked with efforts in the field of applied electrochemistry (industrial electrolysis, batteries, etc).

One of the important tasks of electrochemistry is to investigate the properties and the structure of ionic conductors: aqueous and nonaqueous electrolyte solutions, salt melts, and different kinds of solid electrolytes.

Electrodes, i.e. electronic conductors contacting with ionic conductors can be classified according to different criterions. A current flow through this interface is connected with electrochemical reactions, which either generates or consume electrons in the metal and

ions in the electrolyte. An important feature of the electrode/electrolyte interface is the existence of a potential difference between the contacting conductors, due to charge exchanges at the interface and the formation of electric double layers. The structure of this interface and of the adjacent zones in both phases determines many electrochemical phenomena and influences the rate of electrochemical reactions.

Prospective new directions in electrochemistry are electrocatalysis and bioelectrochemistry.

1. Introduction

Electrochemistry is a branch of science that is devoted to systems containing ion conductors (solutions, melts, and solid electrolytes) and also to processes proceeding at the interface of ionic and electronic conductors (and/or semiconductors). Phenomena in these systems and their properties are examined under equilibrium conditions in absence of electric currents, as well as under non equilibrium conditions when an electric current is passing through the system. According to another definition, electrochemistry deals with processes of mutual transformation of electric and chemical energy.

The appearance of electrochemistry can be dated at 1779 when Alessandro Volta after the historical experiments of Luigi Aloysius. Galvani announced the creation of the first electrochemical power source the "Volta's pile" or "galvanic cell". Such cells gave the possibility to realize the hitherto unknown phenomenon of continuous flow of electrical charges or an "electric current". Soon afterwards many properties of this current were discovered and studied including the action of current on ionic solutions – the phenomenon of "electrolysis". During the last two centuries the development of fundamental aspects in electrochemistry was closely linked with the development of different electrochemical processes and devices.

In 1843 M.Faraday discovered the fundamental laws of electrolysis which are now known as Faraday' laws. In the second half of the 19th century the thermodynamic aspects of electrode potentials and the emf of galvanic cells were the topics of basic works by Josiah Willard Gibbs, Wilhelm Ostwald and others. In 1883-1887 the Swede Svante Arrhenius developed his theory of electrolytic dissociation which led the foundation for an understanding of the behavior of the most important group of ionic conductors, *viz*. electrolyte solutions. Studies in the field of electrochemical kinetics during the first half of the 20th century were intimately related to the advance of various electrochemical industries. At about this time fundamental researches on the structure of the electrode/electrolyte interface and its influence on electrodes were initiated (Alexander N.Frumkin). The desire to further speed up the processes occurring in electrolyzers and fuel cells was responsible for the emergence of a new area of theoretical electrochemistry after 1950, viz. electrocatalysis.

2. Ionic Conductors and their Conductivity

Among ionic conductors (or electrolytes) different groups can be distinguished the largest being liquids – aqueous and nonaqueous solutions of salts, acids, and bases as well as salt melts. Solid ionic conductors – oxides and high-molecular polyelectrolytes attract more

and more attention recently. The term "electrolyte" is often used not only in the sense of an ionic conductor, but also in speaking of substances which ordinarily are not conducting but produce ionic conduction after being dissolved in water or other solvents. Aqueous solutions of acids, bases and salts ("electrolytes" in the second meaning of this term) are the ionic conductors most widely used and most thoroughly studied. Their significance goes far beyond electrochemistry as such. They are of exceptional importance in the form of intra-cellular fluids in biological and physiological processes in all living beings. They are of equally great importance as natural waters in oceans, rivers, and underground morphological processes.

The properties of aqueous solutions are related to properties of water itself and to the structure of water molecules. The conductivity of water depends on the extent of its purification. The theoretical value of this parameter at the temperature 20-25 $^{\circ}$C is 3.8×10^{-6} S m^{-1}. The conductivity of usual distilled water is significantly higher – about $(80-100) \times 10^{-6}$ S m^{-1} because of absorption CO_2 from the atmosphere and the formation of ions H^+ and HCO_3^- (the so-called equilibrium water). Water molecules have an effective radius of 0.138 nm and are dipolar the negative charge being closer to the oxygen atom and the positive charge closer to the hydrogen atoms. The dipole moment of a water molecule μ_{H2O} is 6.2×10^{-30} CÌm. The relative permittivity (dielectric constant) of water at 25 $^{\circ}$C is 78.5.

Electrolytic dissociation of "electrolytes" in solutions which leads to their ionic conductivity is due to an interaction of the solute with the solvent giving rise to solvation (in aqueous solutions also called hydration) of the ions and weakening of their electrostatic interaction. The energy necessary for dissociation is provided by the solvation energy. According to the degree of dissociation α (the ratio of dissociated molecules to the overall amount of dissolved molecules) one can distinguish between weak ($\alpha \ll 1$) and strong electrolytes ($\alpha \cong 1$) which are practically completely dissociated. Among strong electrolytes are many inorganic salts, certain acids and bases in aqueous solutions and also in solvents with a high dissociating ability (*e.g.* alcohols, amides). Molecules of weak electrolytes are only partially dissociated and their ions are in a dynamic equilibrium with nondissociated molecules. Numerous organic acids and bases in aqueous and nonaqueous solutions behave as weak electrolytes. However the degree of dissociation depends not only upon the nature of the solute and the solvent, but also on the concentration of the solute, the temperature, etc.

The process of solvation gives rise to changes in the properties of species in solution and also affects physico-chemical processes in solutions. Solvation results in the surrounding of ions with a solvation shell consisting of solvent molecules and the formation of constant or temporary solvates, i.e. molecular compositions. The lifetime of individual solvates is small because of a continuous exchange of particles in the solvation shell. In accordance with the type of intermolecular interaction, it is possible to distinguish nonspecific (due to van der Waals's interaction) and specific solvation (caused by electrostatic interaction or by formation of coordination and hydrogen bonds). The structure of solvated ions is complex. The nearest to the ion solvent molecules form the so-called primary solvation shell. The interaction in this shell is great because of small distances between the central ion and the dipolar solvent molecules; therefore this shell is relatively stable and is not disturbed by thermal motions of its components. In the

secondary and more remote shells there is an orientation of the dipolar solvent molecules, but the interaction forces are weaker. With an increasing distance between the central ion and the solvent molecules the influence of the former on the solvent diminishes. Thus solvation of ions results in a considerable reorganization (reorientation) of the solvent in vicinity of the ions. The solvation ability of a solvent is determined by some parameters, *e.g.*, its permittivity. The solvation state of ions can be characterized in two ways: by their energetic parameters (heat, energy, and entropy of solvation) and by their physical parameters: the solvation number η (that is the number of solvent molecules associated with an ion) and the radius of the solvated ion. These parameters are referred to the primary shell. The values of η for various ions vary from 0 to 15. As a rule, the smaller is the ion's crystallographic radius, the larger is the solvation number. That is why the effective size of various hydrated ions is fairly close. This fact explains similar values of mobilities and diffusion coefficients of different ions in solutions. For cations (which are usually relatively small) the solvation numbers are as a rule larger than those for anions. At the same time, the solvation number for large cations *e.g.* of the type $(C_4H_9)_4N^+$ is close to zero.

The behavior of protons in aqueous solutions differs substantially from that of other ions. The hydration energy of protons (about 1100 kJ Mol^{-1}) and their mobility in aqueous solutions exceed by 2-4 times the values for other ions. These peculiarities can be explained by the fact that the interaction of protons with one water molecule is not only of an electrostatic nature but involves also covalent forces and leads to the formation of a new chemical particle, *viz.* the hydronium ion H_3O^+. The existence of such ions in the gas phase was shown by mass-spectrometry and in solid phase by X-ray analysis and by NMR. The H^+–H_2O bond energy is 712 kJ Mol^{-1}, *i.e.* nearly two-third of the total hydration energy of protons. The particle H_3O^+ is further hydrated in the described manner. In the primary shell there are three molecules of water associated with the ion by electrostatic force and partially by hydrogen bonds. Thus the composition of a proton with its primary shell is $H_9O_4^+$. Two mechanisms of transfer take place in solutions of hydronium ions: transfer of hydrated ions of hydronium (analogously to the transfer of other kind of ions) and transfer of nonhydrated protons along a comparatively immobile skeleton of oriented water molecules. As the result of the mutual action of these two mechanisms, the mobility of protons in aqueous solutions is higher than that of other ions. In the same manner one can explain the increased mobility of hydroxyl ions.

Thus, electrolyte solutions are complex systems consisting of ions surrounded by solvent molecules, of nondissociated molecules of the solute, and of ion pairs and larger-sized aggregates.

The modern theory of electrolytic dissociation was developed in 1887 by Svante Arrhenius (who for this theory was awarded in 1903 with the Nobel Prize). In developing this theory S.Arrhenius used a suggestion of J.Van't Hoff (Nobel prize, 1894) to describe the osmotic pressure in solutions by the laws for ideal gases. Somewhat later the Arrhenius's theory was combined with W.Ostwald's dilution law. The creation of the theory of ED resulted in the appearance of a new classification of compounds into ionophors and ionogens. The first ones combine ionic crystals the lattice of which are destroyed upon dissolution in water (or another solvent) with the ions becoming mobile. The latter ones consist of molecules with covalent bond. In this case the ions are formed

only during dissolution as the result of the action of the solvent. The author of the chemical theory of solutions D.Mendeleev (1889) first pointed to the importance of the formation of hydrates upon interaction of the solutes with the solvent, and I.Kablukov (1891) pointed to the role of ion hydration on dissociation of electrolytes.

The character of ion-ion and ion-molecule interactions determines the properties of solutions. In dependence of the electrolyte concentration, one can distinguish diluted and concentrated solutions. Highly diluted solutions of weak electrolytes in which ion-ion interactions are very weak behave like ideal solutions and are well described by the classical theory of electrolytic dissociation. The properties of diluted solutions of strong electrolytes substantially deviate from the properties of ideal solutions which is due to strong electrostatic interionic interactions. The behavior of these solutions fits in the framework of the P.Debye-E.Hückel (1923) theory of strong electrolytes. In this theory the interionic interactions are described by a model according to which each ion ("central ion") is surrounded by an ionic atmosphere of ions with opposite sign. This theory describes adequately the concentration dependences of thermodynamic parameters (ion activity coefficients, osmotic factors) and nonequilibrium properties of electrolytes (viscosity, diffusion, conductance). Upon increasing the concentration of strong electrolytes it is also necessary to take into account effects of the ion's size and of solvation on the character of interionic interaction. In the transition concentration region substantial changes in the solvent structure arise. Upon a further concentration increase almost all the solvent molecules are connected with ion solvation structures and a lack of free solvent molecules manifests itself. The structure of highly concentrated solutions approaches that of ionic melts or sold crystal solvates.

The conductivity of electrolyte solutions, *i.e.* is their ability to conduct electric current upon application of an electric voltage is connected with the transfer of positively and negatively charged ions, cations and anions, moving in the electric field in opposite directions. Thus the conductivity of electrolytes, unlike electronic conductivity in metals, is accompanied by the transfer of matter to and from the electrodes and the formation of new chemical compounds on them. The total conductivity is composed from those of the cations and anions. The fraction τ_j of the total charge which is transferred by individual ions j is called the transport number τ_j of this ions. The sum of these numbers for all kinds of ions participating in the transport is equal to 1. The transport number represents not an individual property of the ion but describes its role in the migration of charges in definite electrolyte solutions. The most important properties of individual ions, namely, ionic conductivity and mobility, can be calculated from experimental data on molar conductivity on the basis of their transport numbers in binary electrolytes. There exist several techniques for a comparatively precise determination of transport numbers in solutions. For example, the W.Hittorf (1859) method based on the measurement of concentration changes in the solution near the electrode; the method of moving boundary between two electrolytes (the working electrolyte and the indicator one) (O.Lodge, 1886; L.Longsworth, 1923).

For a quantitative characterization of the conductivity of solutions the parameter molar conductivity of the solution Λ, is used, *i.e.* the conducting ability of all ions formed by dissolution of 1 mol of electrolyte. The quantity Λ is connected to the specific conductivity κ by the relation $\Lambda = 1000 \, \kappa/c_k$, where c_k is the electrolyte concentration.

The molar conductivity of the electrolyte can be presented as the sum of the molar conductivities λ_j of the cations and the anions $\Lambda = \tau_+ \lambda_+ + \tau_- \lambda_-$. These parameters depend on the nature of the solute and the solvent and also on concentration, temperature, etc. The limiting values of these parameters Λ^o and λ_j^o correspond to the value in extremely diluted solutions in which all the molecules are dissociated into ions. The molar conductivity of an individual ion is proportional to the rate of its movement in solution and characterizes the ion's mobility in solution.

In solutions of strong electrolytes, the concentration dependence of the ion's molar conductivities is influenced by interionic interactions. In the electric field the central ion and its ionic atmosphere are moving in opposite directions. This creates the so-called electrophoretic effect. A change of configuration of the ionic atmosphere upon moving in an electric field is responsible for the so-called relaxation effect. L.Onsager (1927) proposed an equation accounting for the influence exerted by both effects.

Besides electrolyte solutions with pure ionic conductivity a class of substances exists which shows simultaneously electronic and ionic conductivity. As an example solutions of alkaline and alkaline-earth metals in polar solvents (ammonia, amines, ethers) and also in saline melts can be quoted. In these systems with increasing metal concentration a phase transition into a metallic state takes place accompanied with an abrupt (by several orders of magnitude) increase of conductivity. In the electrolytic state (at lower metal concentrations) solvated electrons, *i.e.* the lightest possible anions are formed imparting to the solution a specific blue color.

-

-

Biographical Sketches

G.V.Zhutaeva was born 28 August 1939 in Moscow Russia. Education: graduated from the Chemical department of the V.V.Lomonosov Moscow State University (Moscow, Russia). Degree of PhD in 1968 (candidate of chemical sciences) Jobs: from 1962 up to now scientific worker at the F.N.Frumkin Institute of Electrochemistry of the Russian Academy of Sciences, Moscow, Russia. Publications: about 70 scientific papers in the Russian Journal of Electrchemistry, Russian Journal of Analytical Chemistry, Electrochimica Acta, Synthetic Metals a.o., chapters in the monograph "Standard Potentials in Aqueous Solutions" (Eds.A.J.Bard, R.Parsons, J.Jordan. New York. Marcel Dekker. 1985), and in the "Encyclopedia of Electrochemistry of the Elements" (Ed. A.J.Bard. New York. Marcel Dekker. 1978). Main scientific interests: electrochemical behavior of ion- and electroconductive polymers, nonmetallic electrocatalysts, bioelectrocatalysis, electrochemical sensors and biosensors.

V.S.Bagotzky was born 22 January 1920 in Bern (Switzerland). Education: graduated 944 from the M.V.Lomonosov Moscow State University (Moscow, Russia). Ph.D. in 1947. In 1958 was awarded the degree of Doctor of technical Sciences. Jobs: 1950-1966 head of department at the Moscow Power Sources Institute; 1966-1999 subsequently: head of department, principal scientist and consulting professor at the A.N.Frumkin Institute of Electrochemistry of the Russian Academy of Scienes (Moscow, Russia). After retirement in 1999 is living in the USA. Publications: over 400 scientific papers in different Journals. Five monographs on Electrochemistry and electrochemical power sources. More than ten years as member of the editorial boards of the Russian Journal of Electrochemistry and of the Journal of Power Sources.