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Electrochemistry

Donald R. Franceschetti and J. Ross Macdonald

Modern electrochemistry is the study of ionic conductors, materials in which ions participate in the flow of electric current, and of interfaces between ionic conductors and materials which conduct current by electron flow, at least in part. It is a truly interdisciplinary field which draws heavily upon many branches of physics and chemistry. Electrochemical phenomena often have analogs in vacuum-tube and semiconductor electronics. Electrochemistry finds numerous applications throughout the natural sciences, the engineering disciplines, and the health-related fields.

IONICS

The study of ionic conductors in themselves has been termed ionics. Ionic conductors are also known as electrolytes. The ionic conductors of interest to electrochemists include (i) liquid solutions of ionic solids (e.g., NaCl in water); (ii) certain covalently bound substances dissolved in polar media, in which ions are formed on solution (e.g., HCl, which is completely dissociated in water, or acetic acid, which is only partially dissociated); (iii) ionic solids containing point defects (e.g., solid AgCl at high temperatures); (iv) ionic solids whose lattice structure allows rapid movement of one subset of ions (e.g., β - Al_2O_3 - Na_2O); (v) fused salts (e.g., molten NaCl); and (vi) ionically conducting polymer-salt complexes (e.g., polyethylene oxide-LiClO₄).

When an electric field is established in an electrolyte, the migration of positive ions (cations) and negative ions (anions) is observed as a flow of electric current. In defect solid electrolytes, case (iii), the charge carriers are cation and anion interstitials or vacancies (anion vacancies are regarded as positively charged, cation vacancies as negatively charged). Some solid electrolytes are also electronic semiconductors so that the current may also include important contributions from conduction-band electrons and valence-band holes.

The mobility of charge carriers is determined by their interactions with each other and with their environment. Ions in solution often form long-lived aggregates with a characteristic number of solvent molecules. Point defects in solid electrolytes deform the lattice around them. Similarly, the mobility of ions in polymer electrolytes is closely coupled to fluctuations in polymer conformation. A charge carrier is, on the average, surrounded by an "atmosphere" of carriers bearing a net opposite charge. The Debye-Hückel model of

dilute electrolytes yields $z_i e_0 \exp(-r/L_D)/\epsilon r$ as the average electrostatic potential at a distance r from a carrier of charge $z_i e_0$ (e_0 is the proton charge) in a medium of dielectric constant ϵ . The screening or Debye length, L_D , is determined by the concentrations and charges of the carriers.

The flow of current is the result of both carrier drift, in response to the electric field E , and diffusion, which acts to reduce concentration gradients. The current density resulting from charge carriers of species i is given by

$$\mathbf{J}_i = z_i e_0 (\mu_i \mathbf{E} - D_i \nabla) c_i,$$

where c_i is the concentration of carriers and μ_i is the carrier mobility, related in dilute electrolytes to the diffusion coefficient D_i by the Einstein relationship, $\mu_i = D_i z_i e_0 / kT$. Charge carriers may form pairs, bound by electrostatic or chemical forces, whose members do not readily separate. The equation of continuity for charge carriers of species i ,

$$\frac{\partial c_i}{\partial t} = G_i - R_i - (z_i e_0)^{-1} \nabla \cdot \mathbf{J}_i,$$

includes terms for the generation (G_i) and recombination (R_i) of carriers corresponding to the dissociation and formation of bound pairs.

ELECTRODICS

The study of interfaces between ionic conductors and electronic conductors constitutes electrodics, the second major subdivision of electrochemistry. Differences in electrical potential may be determined unambiguously only between electronic conductors; thus electrochemical measurements are usually made on cells with two electrodes. Such cells may be divided into two half-cells, each containing a single electrode, either metal or semiconductor, in contact with an ionic conductor. The half-cell, involving a single interface, is the basic unit studied in electrodics.

The most thoroughly studied electrode material is liquid mercury, for which a clean and atomically smooth interface with electrolyte solutions is readily obtained. Solid metal and semiconductor electrodes are also widely employed, but have not been as extensively characterized. Recently polymer electrodes, which can be formed electrochemically on metal substrates, have become a subject of appreciable interest.

Because the potential difference between the electronic and ionic phases of a half-cell is not measurable, a standard half-cell has been chosen and arbitrarily assigned an electrode potential of zero. This cell, called the standard hydrogen electrode, consists of a platinum electrode in contact with hydrogen ions at 1 atm pressure and an aqueous solution containing hydrogen ions at unit mean activity (see below). The electrode potential of other half-cells is defined as the open-circuit potential of the cell which would be formed with the standard hydrogen electrode.

Electrode potentials provide information about the electrochemical reactions by which charge is transferred between electrode and electrolyte. Simple electrode reactions include (i) ionization of the electrode metal (e.g., $\text{Ag} \rightleftharpoons \text{Ag}^+ + e^-$), (ii) change in the state of an ion (e.g., $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$

+ e^-), and (iii) ionization of a gas (e.g., $\frac{1}{2}\text{H}_2 \rightleftharpoons \text{H}^+ + e^-$, in the presence of a nonreactive metal). When electrons are removed from a species, the species is said to be oxidized; when electrons are added, the species is said to be reduced. In a half-cell in equilibrium, oxidation and reduction occur at equal rates. Away from equilibrium, the electrode is termed an anode if oxidation predominates over reduction, and a cathode in the opposite case. Most electrode reactions consist of a sequence of chemical and charge transfer steps, some of which may involve short-lived ionic species not present in the bulk electrolyte.

An example of a simple electrochemical cell is the Daniell cell, which consists of zinc and copper electrodes immersed, respectively, in aqueous solutions of ZnSO_4 and CuSO_4 , the two solutions being separated by a membrane which allows the passage of charge but prevents rapid mixing of the two solutions. When electrons are allowed to flow between the electrodes, the zinc electrode dissolves to form Zn^{2+} ions while Cu^{2+} ions are deposited on the copper electrode, in accord with the overall reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$. The open-circuit cell potential E is the energy released by the reaction per unit charge transfer between the electrodes and is related to the Gibbs free energy ΔG of the cell reaction by $\Delta G = 2FE$, where F is Faraday's constant, $96,485 \text{ C mol}^{-1}$, and two electrons are transferred for each atom of Cu deposited. E is related to the thermodynamic ion activities $a(\text{Cu}^{2+})$ and $a(\text{Zn}^{2+})$ by Nernst's equation, which in this case becomes

$$E = E^0 - \frac{RT}{2F} \ln \left\{ \frac{a(\text{Zn}^{2+})}{a(\text{Cu}^{2+})} \right\},$$

where E^0 is the cell potential at unit activity and R is the gas constant, $8,314 \text{ J mol}^{-1} \text{ K}^{-1}$. Activities are quantities related to the ion concentrations (identical at infinite dilution), which take into account ion-ion interactions in the electrolyte.

Nernst's equation is strictly applicable only to systems in thermodynamic equilibrium. In general, the potential of each half-cell is a function of the cell current, which is determined by the slowest step in the electrode reaction sequence. For many half-cells the current is approximately given by the Butler-Volmer equation, which can be cast in the form

$$i = i_0[\exp(\alpha_{\text{an}}\eta F/RT) - \exp(-\alpha_{\text{c}}\eta F/RT)]$$

with

$$\alpha_{\text{c}} + \alpha_{\text{an}} = n/\nu.$$

Here i_0 is the exchange current, determined by the rate of the electrode reaction at equilibrium; η is the electrode overpotential, the deviation of the half-cell from its equilibrium value; and n is the number of electrons transferred. The parameters α_{an} and α_{c} are transfer coefficients for the anodic (oxidation) and cathodic (reduction) processes and ν is the stoichiometric coefficient, the number of times the rate-determining step occurs in the overall half-cell reaction.

Electrodes, or more properly half-cells, are classified as polarizable or nonpolarizable depending on the amount of overpotential required for a fixed ion current flow. Limiting

cases, which can be closely approximated in practice, include the perfectly polarizable, or blocking, electrode, one in which no ion current flows regardless of the overpotential, and the perfectly nonpolarizable, or reversible, electrode, one in which the electrode potential retains its equilibrium value regardless of the amount of current flow.

By variation of the potential drop across an electrochemical cell, the rates of the electrode reactions may be altered, and one may even reverse the direction of the net cell reaction. If zinc metal is immersed in CuSO_4 solution, copper metal and ZnSO_4 are produced spontaneously. By connecting the electrodes of a Daniell cell to a load, useful work may be obtained from the energy of this spontaneous reaction. Cells operated in an energy-producing manner are termed galvanic cells. By rendering the copper electrode sufficiently positive with respect to the zinc, one may effect dissolution of copper and deposition of zinc. The operation of a cell for the production of substances not obtainable spontaneously from the cell materials is termed electrolysis and the cell so operated, an electrolytic cell.

A fundamental theoretical problem in electrochemistry is the nature of the electrical "double layer," the region of charge separation formed when an electrode is in contact with an ionic conductor. The double layer formed at a metal electrode in an aqueous electrolyte has received particularly intensive study. The traditional Gouy-Chapman-Stern model involves a (usually charged) idealized metal surface, an adjoining plane of chemisorbed water molecules and (often) ions, and a region of increased concentration of cations or anions, depending on the charge on the electrode. The plane of centers of chemisorbed molecules and ions defines the inner Helmholtz plane (ihp), while the plane of closest approach of solvated ions is the outer Helmholtz plane (ohp). The region from the metal surface to the ohp is termed the compact double layer, characterized by an effective dielectric constant which describes the loss in orientational freedom of the adsorbed molecules. The region of space charge beyond the ohp is the diffuse double layer.

More recent studies of the double layer employ a jellium (electron plasma) model for electrons in the metal and a hard-sphere model for both solvent molecules and ions, without making special assumptions about the compact layer. Understanding of double-layer behavior is bound to improve over the next few years as techniques such as scanning tunneling electron microscopy provide a detailed picture of adsorbed layer structure.

APPLICATIONS

Electrochemical methods are employed widely in quantitative and qualitative chemical analysis. Electrolytic methods are the primary industrial means of purifying many metals, of extracting several metals from their ores or salts, and of producing many nonmetallic substances. Electrolytic separation methods make possible the reclamation of valuable materials from industrial waste and reduction in the quantity of pollutants released into the environment. Much industrial research is directed at retarding the corrosion of metals, a phenomenon involving electrochemical reactions at the surface of the metal. The electroplating of metals with thin lay-

ers of inert but costly materials is one of a number of electrochemical remedies to this problem.

Electrochemical cells offer an efficient and often portable source of energy. In fuel cells, the energy of a combustion reaction, such as the combination of hydrogen and oxygen to form water, is converted directly to electrical energy, circumventing the thermodynamic restriction on the efficiency of heat engines. The use of solid electrolytes, particularly those whose crystal structure permits rapid ion movements, is a topic of high current interest and offers new possibilities for high-temperature fuel cells and for high-energy-density storage batteries. The properties of semiconductor electrodes are also of interest in their application to photogalvanic energy conversion.

Electrochemical phenomena are also of considerable importance in biology and medicine. The conduction of nerve impulses depends on the current-voltage relationship for sodium-ion transport across the cell membrane. Much of living matter is colloidal, consisting of small ($10\text{--}10^4 \text{ \AA}$) particles suspended in an aqueous solution. Through adsorption of ions, colloid particles acquire a double-layer structure which determines the stability of the suspension. Important recent medical developments include electrochemical control of drug administration across intact human skin and electrically stimulated healing of problem bone fractures.

See also CONDUCTION; CRYSTAL DEFECTS; DIFFUSION; ELECTROCHEMICAL CONVERSION AND STORAGE.

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Electrodynamics, Classical

J. D. Jackson

Electrodynamics, a word used by Ampère in his pioneering researches 150 years ago, may properly be used to encompass all electromagnetic phenomena. There is also a more restricted meaning: electromagnetic fields, charged particles, and their mutual interaction at a microscopic level, excluding in practice, if not in principle, phenomena associated with macroscopic aggregates of matter. *Classical* electrodynamics then consists of the regime where (relativistic) classical mechanics applies for the motion of particles, and the photon nature of electromagnetic fields can be ignored. Its quantum generalization, called quantum electrodynamics, is necessarily employed for phenomena without classical basis (e.g., pair production), as well as where quantum effects are significant.

Separate articles exist on many aspects of macroscopic electromagnetism (e.g., ELECTROMAGNETIC RADIATION, ELECTROSTATICS, MAGNETS AND MAGNETOSTATICS, MICROWAVES AND MICROWAVE CIRCUITRY). The emphasis here is on basic principles and selected results of classical electrodynamics in the restricted sense. The Gaussian system of units and dimensions is used. See the Appendix of Ref. 1 for the connection to the SI or mksa units of practical electricity and magnetism.

MAXWELL EQUATIONS IN VACUUM

The differential equations of electromagnetism in vacuum are the *Maxwell equations*:

$$\nabla \cdot \mathbf{E} = 4\pi\rho, \quad (1a)$$

$$\nabla \times \mathbf{B} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} = \frac{4\pi}{c} \mathbf{J}, \quad (1b)$$

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = 0, \quad (1c)$$

$$\nabla \cdot \mathbf{B} = 0. \quad (1d)$$

The quantities ρ and \mathbf{J} are the source densities of charge and current, related because of conservation of charge by the differential continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0. \quad (2)$$

The electromagnetic field quantities \mathbf{E} and \mathbf{B} , called respectively the electric field and the magnetic induction, are related to the mechanical force per unit charge according to the *Lorentz force equation*

$$\mathbf{F} = q \left(\mathbf{E} + \frac{\mathbf{v}}{c} \times \mathbf{B} \right) \quad (3)$$

where \mathbf{F} is the force exerted on a point charge q moving with velocity \mathbf{v} in the presence of external fields \mathbf{E} and \mathbf{B} . The parameter c that enters the Maxwell equations and the force equation has the dimensions of a speed (length/time). Solution of the Maxwell equations in free space shows the existence of transverse waves propagating with the speed c . It is thus the speed of light and other electromagnetic radiation. The speed of light is now defined to be 299 792 458 m/s (see METROLOGY).

The four Maxwell equations (1a)–(1d) (actually eight scalar equations) are expressions of the experimental laws of Coulomb, Ampère and Maxwell, Faraday, and the absence of magnetic charges, respectively. This can be seen more clearly in integral form—by integration over a finite volume V , bounded by a closed surface S , and use of Gauss's law, for Eqs. (1a) and (1d); by integration over an open surface S_0 , bounded by a closed curve C , and use of Stokes's theorem, for Eqs. (1b) and (1c). *Coulomb's law* then reads

$$\oint_S \mathbf{E} \cdot \mathbf{n} \, da = 4\pi \int_V \rho \, d^3r \quad (4)$$

where da is an element of area on S and \mathbf{n} is a unit, outwardly directed normal at da . Equation (4) states that the total electric flux out of the volume V is equal to 4π times the total