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Electrochemistry

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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 alone. A truly interdisciplinary field, electrochemistry 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 -Al₂O₃-Na₂O); and (v) fused salts (e.g., molten NaCl).

When an electric field is applied to 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 charac-

teristic number of solvent molecules. Point defects in solid electrolytes deform the lattice around them. 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 \mathbf{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.

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 gas 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 charge 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. Electrode reactions are thus examples of oxidation–reduction or “redox” reactions. 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 applies only under open-circuit conditions for a cell in thermal 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,

$$i = i_0 [\exp\{(1 - \alpha)nF\eta/RT\} - \exp\{-\alpha nF\eta/RT\}],$$

in which 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 potential from its equilibrium value; n is the number of electrons transferred; and α is the “transfer coefficient,” determined by the shape of the potential barrier which must be overcome in the charge transfer process.

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. A perfectly polarizable, or blocking, electrode is one in which no ion current flows regardless of the overpotential. A perfectly nonpolarizable, or reversible, electrode is 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. In this case the double layer consists of the metal surface, which usually bears a net charge, an adjoining plane of chemisorbed water molecules (and, in some cases, 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, while the region of space charge beyond the ohp is the diffuse double layer.

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 layers 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. A dramatic

recent development has been the demonstration that the probability of blood clot formation on an implanted electrode is a function of its potential. Such information may prove essential to the design of useful artificial organs.

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

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Electrodynamics, Classical

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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., ELECTROSTATICS, ELECTROMAGNETIC RADIATION, 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 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 presently accepted experimental value is $c = 299\,792\,458 \pm 1.2$ m/s.

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 charge inside. It can be shown that this is a consequence of (a) the inverse-square law of force between point charges, (b) the central nature of that force, and (c) linear superposition. These, plus isotropy of the field of a point charge, are the elements of Coulomb's laws of electrostatics. The corresponding integral of Eq. (1d) has zero on the right-hand side—there are (as far as we presently know) no magnetic charges.

Ampère's (and Maxwell's) law has the integral form

$$\oint_C \mathbf{B} \cdot d\boldsymbol{\ell} = \int_{S_0} \left(\frac{4\pi}{c} \mathbf{J} + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} \right) \cdot \mathbf{n} \, da \quad (5)$$

where $d\boldsymbol{\ell}$ is an element of length tangent to the curve C . The sense of the normal \mathbf{n} to the surface S_0 is determined by the right-hand rule with respect to $d\boldsymbol{\ell}$. For static fields the second term on the right is absent. Then Eq. (5) is equivalent to Ampère's laws of forces between current loops. The second term on the right shows that time-varying electric fields produce magnetic fields just as do currents. This term is sometimes called Maxwell's displacement current. It is an essential modification of Ampère's laws for rapidly varying fields.

The analogous integral statement of Eq. (1c), *Faraday's law*, is

$$\oint_C \mathbf{E} \cdot d\boldsymbol{\ell} = - \frac{1}{c} \frac{d}{dt} \int_{S_0} \mathbf{B} \cdot \mathbf{n} \, da. \quad (6)$$