Lawrence Berkeley National Laboratory

Recent Work

Title

Electrochemical Processing (Introduction)

Permalink

<https://escholarship.org/uc/item/87g1j263>

Journal

Kirk-Othmer Encyclopedia of Chemical Technology, 9

Authors

Fuller, T.F.
Newman, J.

Publication Date

1993

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials Sciences Division

To be published as a chapter in *Kirk-Othmer Encyclopedia of Chemical Technology*, Mary Howe-Grant, Ed., Fourth Edition, Vol. 8, John Wiley & Sons, Inc., New York, NY, 1993

Electrochemical Processing (Introduction)

T.F. Fuller and J. Newman

February 1993

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Electrochemical Processing (Introduction)

Thomas F. Fuller and John Newman

Department of Chemical Engineering
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

February 1993

This work was supported in part by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

Printed on recycled paper

Electrochemical Processing (Introduction)

Electrochemical systems convert chemical and electrical energy through charge-transfer reactions. These reactions occur at the interface between two phases. Consequently, an electrochemical cell contains multiple phases, and surface phenomena are important. Electrochemical processes are sometimes divided into two categories: electrolytic, where energy is supplied to the system (e.g., the electrolysis of water and the production of aluminum); and galvanic, where electrical energy is obtained from the system (e.g., batteries and fuel cells).

The industrial economy depends heavily on electrochemical processes. Electrochemical systems have inherent advantages such as ambient temperature operation, easily controlled reaction rates, and minimal environmental impact. Electrosynthesis is currently used in a number of commercial processes; these will be discussed in the two subsequent sections. Batteries and fuel cells, used for the interconversion and storage of energy, are not limited by the Carnot efficiency of thermal devices. Corrosion, another electrochemical process, is estimated to cost hundreds of millions of dollars annually in the United States alone.

Electrochemical systems can be described with the fundamental principles of thermodynamics, kinetics, and transport phenomena. We shall illustrate these principles with the electrochemical cell used in the production of chlorine and caustic soda. The details of the industrial process will be discussed in the next section.

Thermodynamics of Electrochemical Cells

Consider the cell shown below.

for which the electrode reactions are

and

The electrode where oxidation occurs is the anode, and the electrode where reduction occurs is called the cathode. Electrons released at the anode travel through an external circuit and react at the cathode. The vertical lines denote phase separation, and the squiggly ones separate a junction region. Although adjacent phases are in equilibrium, not all species are present in every phase. Here the membrane provides an ionic path for sodium ions (which are transported from the anode to the cathode) but also separates the chlorine and hydrogen gases. Within the junction region (the membrane), transport processes occur.

Determining the cell potential requires knowledge of the thermodynamic and transport properties of the system. The analysis of the thermodynamics of electrochemical systems is analogous to that of neutral systems. With ionic species, however, the electrochemical poten-

tial replaces the chemical potential. This concept was first introduced by Guggenheim.

$$\mu_i = RT \ln \lambda_i = RT \ln \left(c_i f_i a_i^\theta \right) . \quad (3)$$

The electrochemical potential, μ_i , of a species is a function of the electrical state as well as temperature, pressure, and composition. λ_i is the absolute activity, which can be broken down into three parts (as shown). Consider an electrolyte, A, which dissociates into ν_+ cations and ν_- anions. We can express the chemical potential of the electrolyte by

$$\mu_A = \nu_+ \mu_+ + \nu_- \mu_- = \nu RT \ln (c f_{\pm} a_{\pm}^\theta), \quad (4)$$

where the subscript $\pm$ indicates a mean coefficient. For instance,

$$f_{\pm}^\nu = f_+^{\nu_+} f_-^{\nu_-} . \quad (5)$$

At open-circuit, the current in the cell is zero, and species in adjoining phases are in equilibrium. For example, the electrochemical potential of electrons in phases α and β are identical. Furthermore, the two electrochemical reactions are equilibrated. Thus,

$$2\mu_{\text{Cl}^-}^\epsilon = \mu_{\text{Cl}_2}^{\beta'} + 2\mu_{\text{e}^-}^{\alpha'} , \quad (6)$$

and

$$2\mu_{\text{H}_2\text{O}}^{\delta} + 2\mu_{\text{e}^-}^{\alpha} = \mu_{\text{H}_2}^{\beta} + 2\mu_{\text{OH}^-}^{\delta} \quad (7)$$

The cell potential U is

$$FU = -F(\Phi^{\alpha} - \Phi^{\alpha'}) = \mu_{\text{e}^-}^{\alpha} - \mu_{\text{e}^-}^{\alpha'} \quad (8)$$

By convention, U denotes the potential of the right electrode relative to the left. Substituting equations 6 and 7 gives,

$$FU = \frac{1}{2}\mu_{\text{H}_2}^{\beta} - \mu_{\text{H}_2\text{O}}^{\delta} + \frac{1}{2}\mu_{\text{Cl}_2}^{\beta'} + (\mu_{\text{OH}^-}^{\delta} - \mu_{\text{Cl}^-}^{\epsilon}) \quad (9)$$

Since only differences in chemical potential can be measured, the chemical or electrochemical potential of each species is broken down as in equation 3. An arbitrary secondary reference state is defined for each compound. For instance, the chemical potential of chlorine gas is expressed as

$$\mu_{\text{Cl}_2} = \mu_{\text{Cl}_2}^* + RT \ln p_{\text{Cl}_2} \quad (10)$$

The superscript $*$ refers to the ideal-gas secondary reference state, and p is the fugacity. Equation 4 is used for the ionic species. Hence,

$$FU = FU^{\theta} + RT \ln \left[\frac{p_{\text{H}_2}^{\frac{1}{2}} p_{\text{Cl}_2}^{\frac{1}{2}} c_{\text{OH}^-}^{\delta}}{a_{\text{H}_2\text{O}}^{\delta} c_{\text{Cl}^-}^{\epsilon}} \right] + 2RT \ln \left[\frac{f_{\text{NaOH}}^{\delta}}{f_{\text{NaCl}}^{\epsilon}} \right] + (\Phi^{\epsilon} - \Phi^{\delta}), \quad (11)$$

where the electric potential Φ of the solution has been defined by

$$\mu_{\text{Na}^+} = RT \ln c_{\text{Na}^+} + F\Phi. \quad (12)$$

The standard cell potential U^θ is given by

$$FU^\theta = \frac{1}{2}\mu_{\text{H}_2}^* - \mu_{\text{H}_2\text{O}}^0 + \frac{1}{2}\mu_{\text{Cl}_2}^* + (\mu_{\text{OH}^-}^\theta - \mu_{\text{Cl}^-}^\theta). \quad (13)$$

In equation 11 the superscripts denoting the phases have been omitted where the meaning is clear, that is, for the fugacity of hydrogen and chlorine. U^θ is the composition independent part of the cell potential, and its value can be obtained by looking up the values of the secondary-reference-state quantities in a table of chemical thermodynamic properties. This yields a value of 2.1875 V for U^θ . It is convenient to consider the reaction as the sum of two half-cell reactions. The standard cell potentials are tabulated¹ (typically at 25°C) as half-cell reactions referenced to the hydrogen electrode, whose potential is arbitrarily set to zero. This yields 1.3595 V for the chlorine electrode and -0.828 V for the hydrogen electrode in basic media; the difference being 2.1875 V. The second term on the right side of equation 11 accounts for the principal variation of the cell potential with composition of the reactants.

The third term is the corresponding ratio of the mean molar activity coefficients. The last term on the right side results from transport processes in the junction region and cannot be determined from thermodynamics. This term is often small and will not be treated here. Neglecting this junction region and activity corrections leads to

$$U \approx U^\theta + \frac{RT}{2F} \ln \frac{P_{H_2} P_{Cl_2} c_{OH^-}^2}{a_{H_2O}^2 c_{Cl^-}^2} \quad (14)$$

Equation 14 is a form of the Nernst equation. The overall chemical reaction (for the passage of 2 faradays of charge in the external circuit from right to left) is

Each reactant and product appears in the Nernst equation raised to its stoichiometric power. Pourbaix² has compiled thermodynamic data for cell potentials as a function of pH. These data are valuable for the study of corrosion, electrodeposition, and other phenomena in aqueous solutions.

From the above thermodynamic analysis, the cell potential can be related to the Gibbs energy change;

$$\Delta G = -nFU. \quad (16)$$

Thus we can conclude that since the standard cell potential for reaction 15 is positive, the reaction will proceed spontaneously as written. Consequently, to produce chlorine and hydrogen gas a potential must be applied to the cell that is greater than the open-circuit value. This is an example of an electrolytic process.

As we have seen, predicting the cell potential requires knowledge of thermodynamic properties and transport processes in the cell. Conversely, the measurement of cell potentials can be used to determine

both thermodynamic and transport properties.³

Kinetics and Interfacial Phenomena

The rate of an electrochemical process can be limited by kinetics and mass transfer, and these limitations are often of interest. Before we consider the electrode kinetics, however, we shall examine the nature of the interface between the electrode and the electrolyte, where electron-transfer reactions occur.

Since some substances may preferentially adsorb onto the surface of the electrode, the composition near the interface differs from the bulk solution. If the cell current is zero, there is no potential drop from ohmic resistance in the electrolyte or the electrodes. Yet we have seen from the thermodynamic analysis that there is a measurable cell potential. Where, then, does this potential arise? At the interface between phases, there is a region, called the electrical double layer, where the potential variation occurs.

Figure 1 shows this region. The metal may have a net charge near the surface. The layer closest to the electrode consists of specifically adsorbed molecules, called the *inner Helmholtz plane* (IHP). Ions that are hydrated can approach the metal surface only to a finite distance, the *outer Helmholtz plane* (OHP). The electrode and electrolyte are overall electrically neutral. The nonspecifically adsorbed molecules are distributed by thermal agitation; this region is called the *diffuse double layer* and lies just outside the OHP.

In most electrochemical systems, the double layer is very thin (1 to 10 nm). The thickness is characterized by the Debye length,

Figure 1. The structure of the electrical double-layer. The inner Helmholtz plane (IHP) represents the center of specifically adsorbed molecules. The outer Helmholtz plane (OHP) is the closest point of approach for solvated molecules. The corresponding electric potential, Φ , is shown below the figure.

$$\lambda = \sqrt{\frac{\epsilon RT}{2z^2 F^2 c_{\infty}}} \quad (17)$$

In addition, one can vary the potential of the electrode and change the structure of the interface. If no current is passed when the potential of the electrode changes, the electrode is called an *ideally polarizable* electrode and can be described with thermodynamics.

Even in the absence of faradaic current, i.e. an ideally polarizable electrode, changing the potential of the electrode causes a transient current to flow to charge the double layer. The metal may have an excess charge near its surface to balance the charge of the specifically adsorbed molecules. These two planes of charge separated by a small distance are analogous to a capacitor. Thus, the electrode is analogous to a double-layer capacitance in parallel with a kinetic resistance.

Electrode kinetics seeks a relationship between the current density and the composition of the electrolyte, surface overpotential (see below), and the electrode material. Whereas the double layer provides a microscopic description, generally electrode kinetics regards the double layer as part of the interface, and kinetics gives a macroscopic relation. It should be clear, nevertheless, that the structure and chemistry of the double layer affects the electrode kinetics.

Consider the general reaction

The cathodic and anodic reaction rates can be written as

$$r_a = k_a c_R \exp \left[(1-\beta) \frac{nF}{RT} V \right], \quad (19)$$

and

$$r_c = k_c c_O \exp \left[-\beta \frac{nF}{RT} V \right]. \quad (20)$$

β is a symmetry factor equal to the fraction of the potential that promotes the cathodic reaction. The reaction rate and current are related through Faraday's law,

$$\frac{i}{nF} = r_a - r_c. \quad (21)$$

These two reactions may be generalized to the Butler-Volmer equation,

$$i = i_o \left\{ \exp \left(\frac{\alpha_a F \eta_s}{RT} \right) - \exp \left(-\frac{\alpha_c F \eta_s}{RT} \right) \right\}. \quad (22)$$

The exchange current density, i_o , depends on temperature, the composition of the electrolyte adjacent to the electrode, and the electrode material. The exchange current density is a measure of the kinetic resistance. High values of i_o correspond to *fast* or *reversible* kinetics. The three parameters, α_a , α_c , i_o , are determined experimentally. The surface overpotential, η_s , is the difference in potential of the metal and the potential of an electrode of the same kind in the electrolyte adjacent to the electrode (just outside the double layer) but passing no current. The surface overpotential appears in the exponential terms for both the anodic and cathodic reactions and can be considered the driving force for the electrochemical reaction.

The relationship between the surface overpotential and the current is shown in figure 2. Two simplifications of the Butler-Volmer expression are often encountered. First, at low surface overpotentials equation 22 can be written as

$$i = (\alpha_a + \alpha_c) i_o \frac{F}{RT} \eta_s \quad (23)$$

This limit is called linear kinetics. On the other hand, if the surface overpotential is large, one of the exponential terms is negligible. This limit is called Tafel kinetics in honor of Tafel, who found this relationship empirically. In the anodic Tafel region,

$$\eta_s = \frac{RT}{F\alpha_a} \left(\ln i - \ln i_o \right) \quad (24)$$

While the Butler-Volmer equation can be applied to many systems, not all follow this expression. Moreover, many of the systems that don't follow the Butler-Volmer model are of great practical importance, e.g., in the corrosion of passivating metals (see Corrosion).

Because of the unique nature of the electron-transfer reactions, they have been of great theoretical interest. More recently research has centered on a microscopic picture of the electron-transfer reactions and predicting reaction rate constants.^{4,5}

Transport Processes

In addition to electrode kinetics, the rate of an electrochemical reaction can be limited by the rate of mass transfer of reactants to and from the electrode surface. In dilute solutions, four principal

Figure 2. Tafel plot. α_a and α_c are both chosen to be 0.5, and the temperature is 298.15 K.

equations are used. The flux of species i is

$$N_i = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i + c_i \mathbf{v}. \quad (25)$$

The three terms represent contributions to the flux from migration, diffusion, and convection. The bulk fluid velocity is determined from the equations of motion. Equation 25, with the convection term neglected, is frequently referred to as the Nernst-Planck equation. In systems containing charged species, ions experience a force due the electric field. This effect is called migration. z_i is the charge number of the ion, F is Faraday's constant, u_i is the ionic mobility, and Φ is the electric potential. The ionic mobility and the diffusion coefficient are related:

$$D_i = RTu_i. \quad (26)$$

This relation, which was discovered by Nernst and Einstein, applies in the limit of infinite dilution.

A material balance on an element of the fluid gives,

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i, \quad (27)$$

where R_i is the homogeneous reaction rate. Except near the diffuse double layer, to a good approximation the solution is electrically neutral,

$$\sum_i z_i c_i = 0. \quad (28)$$

The current density is given by,

$$i = F \sum_i z_i N_i. \quad (29)$$

These four equations, with the appropriate boundary conditions, can be solved to give current and potential distributions and concentration profiles. Electrode kinetics would enter as part of the boundary conditions. The solution of these equations is not easy and often involves detailed numerical work.

Electroneutrality (equation 28) is not strictly correct — more properly it should be replaced with Poisson's equation:

$$\nabla^2 \Phi = -\frac{F}{\epsilon} \sum_i z_i c_i. \quad (30)$$

It is important to stress that although the assumption of electroneutrality is appropriate for many systems, electroneutrality does not imply that Laplace's equation holds for the potential. Further details are given by Newman.⁶

When concentration gradients in the solution can be ignored, equations 25 through 29 show that the electric potential is governed by Laplace's equation;

$$\nabla^2 \Phi = 0. \quad (31)$$

Laplace's equation is applicable to many electrochemical systems, and solutions are widely available in the literature.⁷ The current distribution is obtained from Ohm's law,

$$i = -\kappa \nabla \Phi, \quad (32)$$

where κ is the conductivity of the solution. For dilute solutions the conductivity is given by

$$\kappa = F^2 \sum_i z_i^2 u_i c_i \quad (33)$$

Both the anions and cations can contribute to the current. In the absence of concentration gradients, the *transference number* relates the fraction of current carried by each species,

$$t_j = \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i} \quad (34)$$

The distribution of current (local rate of reaction) on an electrode surface is important in many applications. When surface overpotentials can also be neglected, the resulting current distribution is called *primary*. Primary current distributions depend on geometry only and are often highly nonuniform. If electrode kinetics is also considered, Laplace's equation still applies but is subject to different boundary conditions. The resulting current distribution is called a *secondary current distribution*. Here, for linear kinetics the current distribution is characterized by the Wagner number.

$$Wa = \frac{\kappa RT}{i_o (\alpha_a + \alpha_c) FL} \quad (35)$$

This is a dimensionless ratio of kinetic to ohmic resistance. For large Wa , the current distribution is uniform. For example, when electroplating (see Electroplating) an object, usually one desires a uniform depo-

sit. Equation 35 suggests that a larger piece (low W_a) would be more difficult to plate uniformly than a small one.

One other limit is also of interest here. As the rate of an electrochemical reaction increases, the concentration of reactants at the surface of the electrode will decrease. When the concentration reaches zero, further changes in the overpotential will not increase the rate of reaction. The reaction is mass-transfer limited; this condition is called *limiting current*. Under these conditions, the system can be analyzed with the traditional convective-diffusion equations. Selman and Tobias⁸ provide a number of mass-transfer correlations for systems relevant to electrochemistry.

As the Nernst equation suggests, concentration variations in the electrolyte lead to potential differences between electrodes of the same kind. These potential differences are concentration polarizations or concentration overpotentials. Concentration polarizations can also affect the current distribution. Predicting these is considerably more difficult. If concentration gradients exist, equations 25 and 27 through 29 must generally be solved simultaneously.

Applications

Electrochemical systems are found in a number of industrial processes. These are discussed in detail elsewhere, for example: see batteries, fuel cells, electroplating, corrosion, and the two subsequent sections on electrosynthesis. We have provided the fundamentals necessary to analyze most electrochemical systems. More details of the fundamentals of electrochemistry are contained in the general references.

Electrochemical techniques are also used to measure transport and kinetic properties of systems (see electroanalytical techniques).

Nomenclature

a	activity
c_i	concentration of species i , mol/m^3
D_i	diffusion coefficient, m^2/s
f_i	molar activity coefficient of species i ,
F	Faraday's constant, 96,487 C/eq
G	Gibbs energy, J/mol
i	current density, A/m^2
i_o	exchange current density, A/m^2
k	reaction rate constant
L	characteristic length, m
N_i	molar flux of species i , $\text{mol/m}^2 \cdot \text{s}$
n	number of electrons transferred in reaction
p	fugacity or pressure, bar
r	heterogeneous reaction rate, $\text{mol/m}^2 \cdot \text{s}$
R_i	homogeneous reaction rate for species i , $\text{mol/m}^3 \cdot \text{s}$
R	universal gas constant, 8.3143 J/mol·K
t	time, s
T	temperature, K
U	open-circuit potential, V
u_i	mobility of species i , $\text{m}^2 \cdot \text{mol/J} \cdot \text{s}$

v	velocity, m/s
V	cell potential, V
W_a	Wagner number, dimensionless
z_i	charge number of species i
α	transfer coefficient
β	symmetry coefficient
ϵ	permittivity, F/m
η_s	surface overpotential, V
κ	electrical conductivity, S/m
λ	Debye length, m
λ_i	absolute activity of species i
μ_i	electrochemical potential of species i , J/mol
ν	total number of moles an electrolyte dissociates into
ν_+, ν_-	number of moles of cations and ions a mole of electrolyte dissociates into
Φ	electrical potential, V

Subscripts

∞	far from the electrode surface
O	oxidized species
R	reduced species
a	anodic
c	cathodic
$+$	cation
$-$	anion

Superscripts

- * ideal gas
- θ secondary reference state at infinite dilution

Bibliography

- [1] *Standard Potentials in Aqueous Solution*, edited by A. J. Bard, R. Parsons, and J. Jordan, IUPAC, Marcel Dekker, Inc., New York (1985).
- [2] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE, Houston, Texas (1974).
- [3] W. H. Smyrl and J. Newman, "Potentials of Cells with Liquid Junctions," *J. Phys. Chem.*, 72, 4660-4671 (1968).
- [4] R. A. Marcus, "Chemical and Electrochemical Electron-transfer Theory," *Ann. Rev. Phys. Chem.*, 15, 155 (1964).
- [5] *Comprehensive Chemical Kinetics*, Vol. 27, Elsevier, Amsterdam (1987).
- [6] John Newman, *Electrochemical Systems*, pp. 256-259, Prentice-Hall, Englewood Cliffs, N. J., (1991).
- [7] A. C. West and J. Newman, "Determining Current Distributions Governed by Laplace's Equation," B. E. Conway, J. O'M. Bockris, and R. E. White, eds., *Modern Aspects of Electrochemistry*, 23, 101-147 (1992).
- [8] J. R. Selman and C. W. Tobias, "Mass-transfer Measurements by the Limiting-Current Technique," *Adv. Chem. Eng.*, 10, 211 (1978).

General References

John Newman, *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, N. J., 1991.

A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, New York, 1980.

G. Prentice, *Electrochemical Engineering Principles*, Prentice-Hall, Englewood Cliffs, N. J., 1991.

K. J. Vetter, *Electrochemical Kinetics*, Academic Press, New York, 1967.

Advances in Electrochemical Science and Engineering, edited by C. W. Tobias and H. Gerischer, VCH, from 1990.

Advances in Electrochemistry and Electrochemical Engineering, edited by C. W. Tobias and P. Delahay, John Wiley & Sons, New York, 1961-1984.

Modern Aspects of Electrochemistry, edited by B. E. Conway, J. O'M. Bockris, and R. E. White, Plenum Press, New York, from 1954.

Comprehensive Treatise on Electrochemistry, edited by J. O'M. Bockris, B. E. Conway, E. Yeager, R. E. White, Plenum Press, New York, from 1980.

Electroanalytical Chemistry, edited by A. J. Bard, Marcel Dekker, Inc., New York, from 1966.

A. T. Kuhn, *Industrial Electrochemical Processes*, Elsevier Publishing Co., Amsterdam, 1971.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720