

ELECTROCHEMICAL ENGINEERING PRINCIPLES



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Preface

Electrochemical processes and devices have become widespread over the last century. Development of electrochemical technology paralleled understanding of basic phenomena during a period of rapid development in the 19th century. Batteries, fuel cells, plating, and the electrolytic production of aluminum and chlorine all evolved in the late 1800s. Today, products based on electrochemical phenomena account for tens of billions of dollars in the US.

Although electrochemical technology constitutes an important segment of the economy, a larger segment is dominated by the presence of abundant and relatively low-cost hydrocarbon sources. Over three-quarters of the energy in the US is derived from hydrocarbons, and hydrocarbon-based polymeric materials are ubiquitous in modern society. Because of these economic and industrial realities, academic curricula treating chemical process industries emphasize organic over inorganic chemical processes, and standard textbooks in thermodynamics, phase equilibria, kinetics, and mass transport reflect an organic chemistry emphasis.

When I developed the first course in electrochemical engineering here at Hopkins in the early 1980s, I relied on notes that I developed and several texts. Because the texts were directed toward different audiences, I found difficulty in reconciling the differences in conventions, nomenclature, and level of material. This book is an outgrowth of the notes developed for the electrochemical engineering course. In this book I emphasize the principles of electrochemical engineering at a level suitable for seniors and graduate students in chemical engineering.

In the past, one learned a modicum of electrochemistry in physical chemistry courses, which usually spanned the entire junior year. In modern chemical engineering curricula, physical chemistry is often reduced to one or fewer semesters, and electrochemistry is treated in one or two weeks. Because of this reduced emphasis on electrochemical processes, I review the basic principles of electrochemistry in Chapter 2. Simultaneously, I introduce a series of conventions and calculation

procedures, that are used in the remaining chapters.

Thermodynamics, phase equilibria, kinetics, and mass transport are all topics familiar to the undergraduate chemical engineer. Because of the emphasis on organic chemistry noted above, practicing chemical engineers commonly deal with processes such as distillation, catalytic cracking, and reactions of hydrocarbon feedstocks. The most popular textbooks addressing chemical engineering fundamentals mirror the dominance of hydrocarbon processes and avoid the topics of cell thermodynamics, ionic phase equilibria, electrode kinetics or ionic mass transport. I include this subject matter in Chapters 3 to 6.

Chapter 7 represents a synthesis of fundamental concepts. Techniques for modeling an electrochemical system are presented along with mathematical methods for determining potential and current distributions for several important classes of problems. Emphasis is on a preliminary analysis of a cell to separate essential phenomena from second order effects.

A number of texts have been written on experimental techniques in electrochemistry. Rather than survey the literature, I discuss several common methods of use to the engineer. The rotating disk electrode is a popular tool in the electrochemical laboratory, and I discuss its utility in some detail. Because the characterization of mass transfer rates is often important, other experimental techniques having well-characterized hydrodynamics and mass transfer rates are also discussed.

The final chapter is an eclectic collection of current electrochemical systems and those under development. In the examples, I attempt to illustrate the application of principles to system design. There have been several notable advances that have dramatically improved the performance of existing processes, e.g., the chlor-alkali process. In other cases, e.g., fuel cells and electric vehicles, widespread adoption awaits advances in materials, design, or catalysis. I have chosen a few examples of systems under development to highlight areas needing additional research effort.

Most of the material in this text represents a logical extension and elaboration of areas in chemical engineering curricula. Readers with backgrounds in materials science, biomedical engineering, environmental engineering, and chemistry should also be familiar with the

basic material. The mathematical treatment of ionic mass transport and current distribution requires a knowledge of ordinary differential equations. Although partial differential equations are introduced, a working knowledge of solution techniques is not required.

The material in this book can usually be covered in a one semester course. Several subjects can be eliminated with little loss of continuity. Some of these dispensable subjects include the sections on Debye-Hückel theory, mechanistic studies, and numerical methods.

Most realistic simulations of electrochemical cells require computer techniques. Several of the problems in Chapters 6 to 9 are best solved with the aid of a computer; however, the sections requiring a knowledge of computer skills can be omitted with no loss of continuity. I have included two Fortran programs, illustrating the computation of potential distributions in one- and two-dimensional cells.

A number of topics that I chose to include or exclude largely reflect personal taste. Probably, the most conspicuous inclusion is a treatment of the thermodynamics and kinetics of corrosion. I have several reasons for considering these topics. Corrosion is, in economic terms, the most important electrochemical process. It is a \$150 billion growth industry and should not be ignored by the practicing engineer. The principles pertaining to corrosion are rather general and apply to related fields. For example, the Pourbaix diagram is used by corrosion engineers as well as by environmental engineers and geochemists.

In addition, I chose to review several theories that are of more pedagogic than practical value. The Debye-Hückel theory and Stokes theory of ion conduction fall into this category. I included them because they provide a simple, yet quantitative, view of the essential phenomena. A number of topics that are arguably important were not included, among them ion transport in membranes, fluidized bed reactors, solid electrolytes, concentrated solution theory, molten salt electrolytes, semiconductor electrodes, and electrochemical impedance spectroscopy. I also chose not to include topics that are important in system design but are covered in a typical chemical engineering curriculum. Here, I have in mind areas such as heat transfer and process control.

I would like to thank colleagues and advisers who were influential in the development of the ideas in this book. At Berkeley, Charles

Tobias provided a rich and varied intellectual environment in which I conducted my doctoral work. His guidance and insight—scientific, economic, culinary, religious, and philosophical—have been invaluable. His comments and criticisms of portions of early drafts of the book were extremely useful in guiding revisions. The careful reading of the manuscript by Dan Gibbons, a teaching assistant in Charles Tobias's course, also contributed a fresh perspective. John Newman was influential as a teacher. He introduced us to the aesthetics and delights of rigor; he dazzled graduate student and colleague alike with his analytical brilliance. Rolf Muller, as co-chairman of our research seminars, introduced us to a fascinating array of experimental techniques. A number of the problems and examples in this book are based on courses, seminars, and research results from Berkeley. Former co-workers Paul Sides and Karrie Hanson helped, through extended discussions, in the clarification of many concepts in this book.

The editors at Prentice Hall were most helpful in guiding me through the various phases of production. The executive editor Michael Hays encouraged me during the initial stages of production. Barbara Marttine, the senior editor, did a fine job of massaging the prose and attending to the details through the final copy.

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Nomenclature

<i>a</i>	activity
<i>A</i>	Helmholtz free energy (J)
<i>B</i>	Tafel slope (mV/decade)
<i>c</i>	concentration (mol/cm ³)
<i>C</i>	capacitance (μF/cm ²)
<i>d</i>	diameter (cm)
<i>D</i>	diffusivity (cm ² /s)
<i>D</i>	dielectric constant
<i>e</i>	unit charge, 1.6×10^{-19} C/chg
<i>E</i>	potential (V)
<i>E_f</i>	electric field (V/cm)
<i>f</i>	fugacity (atm)
<i>F</i>	Faraday's constant, 96,500 C/equiv
<i>g</i>	acceleration of gravity, 980 cm/s
<i>G</i>	Gibbs free energy (J)
<i>Gr</i>	Grashof number, $g(\rho_{\infty} - \rho_0)L^3/\rho_{\infty}\nu^2$
<i>H</i>	enthalpy (J)
<i>i</i>	current density (A/cm ²)
<i>i₀</i>	exchange current density (A/cm ²)
<i>I</i>	current (A)
<i>I</i>	ionic strength (mol/kg)
<i>k</i>	kinetic constant (cm/s)(cm ³ /mol) ^{<i>p</i>-1}
<i>k_m</i>	mass transfer coefficient (cm/s)
<i>L</i>	characteristic length (cm)
<i>K</i>	Equilibrium constant
<i>m</i>	molality (mol/kg)
<i>m</i>	mass (g)
<i>M</i>	molarity (mol/L)
<i>M</i>	molecular weight (g/mol)
<i>M</i>	symbol for chemical formula

n	number of electrons involved in a reaction
n	number of moles (only in partial derivatives)
N	flux (mol/s-cm^2)
N	number of moles
p	reaction order
P	pressure (atm)
q	charge density (C/cm^2)
q	heat transferred (J)
Q	charge (C)
r	reaction rate (mol/s-cm^2)
r	radius (cm)
R	universal gas constant, 8.31 J/mol-K
R	homogeneous reaction rate ($\text{mol/cm}^3\text{-s}$)
R	resistance (ohm)
Re	Reynolds number, $dv\rho/\mu$
s	stoichiometric coefficient
S	entropy (J/K)
Sc	Schmidt number, ν/D
Sh	Sherwood number, $i_l L/nFDc_\infty$
t	transference number
t	time (s)
T	temperature (K)
u	ionic mobility ($\text{cm}^2\text{-mol/J-s}$)
U	internal energy (J)
v	velocity (cm/s)
V	volume (cm^3)
V	cell potential (V)
w	work (J)
z	charge number

Greek Symbols

α	transfer coefficient
α	Debye-Hückel constant (kg/mol) ^{1/2}
β	symmetry factor
β	coefficient of linear kinetic expression (mV)
γ	molal activity coefficient
δ	Nernst diffusion layer thickness (cm)
ϵ	permittivity (C ² /N-m ²)
ϵ_0	permittivity of free space, 8.85×10^{-12} C ² /N-m ²
ϵ	efficiency
η	overpotential (V)
κ	conductivity (ohm ⁻¹ -cm ⁻¹)
λ	Debye length (Å)
λ	ionic equivalent conductance (cm ² /ohm-equiv)
Λ	equivalent conductance (cm ² /ohm-equiv)
μ	electrochemical potential (J/mol)
μ	viscosity (g/cm-s)
ν	number of ions into which a species dissociates
ν	kinematic viscosity (cm ² /s)
ρ	density (g/cm ³)
ϕ	electric potential (V)
ω	rotation rate (rad/s)

Superscripts

†	activation
*	dimensionless
—	partial molar
.	rate
0	standard state
<i>chem</i>	chemical
<i>el</i>	electric
<i>ec</i>	electrochemical

Subscripts

\pm	mean
-	anion
∞	bulk
+	cation
<i>a</i>	anodic
<i>avg</i>	average
<i>c</i>	cathodic
<i>cn</i>	concentration
<i>corr</i>	corrosion
<i>f</i>	formation
<i>i</i>	species type
<i>j</i>	species type
<i>l</i>	liquid junction
<i>l</i>	limiting
<i>o</i>	surface
<i>O</i>	oxidized species
<i>r</i>	reference
<i>r</i>	reduced
<i>R</i>	reduced species
<i>rev</i>	reversible
<i>s</i>	surface
<i>w</i>	working
<i>z</i>	oxidized

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Chapter 1

Introduction

Electrochemical processes have been employed for over a century in industrial electrolysis, energy conversion, and metal deposition. An electrochemical route is usually chosen for one or more of its inherent advantages: energy efficiency, low temperature operation, ease of control, and low pollutant production.

1.1 Major Applications

Aluminum reduction and chlorine production are examples of processes that were initially carried out by ordinary chemical routes but were subsequently supplanted by more efficient electrochemical processes. In economic terms, these two processes are the most important, with a product market value of about \$10 billion in the US; together they consume over 6% of the total domestic electrical output. Reduction of other metals from ores, electroorganic syntheses, and electroplating are also carried out on a large scale.

The economic values of major electrochemical processes and products, estimated in a National Research Council study [1], are summarized in Table 1.1. Developments in electrochemical processing and device fabrication are expected to lead to new markets in microelectronic devices, fuel cells, sensors, and corrosion control.

The beauty of electrochemical devices is that the energy of chemical bonding is converted directly to electrical energy. Because electrochemical energy conversion is not based on the transfer of heat