

MODERN ASPECTS OF
ELECTROCHEMISTRY

No. 15

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Preface

This volume contains five chapters covering four topics of current research interest: splitting of water, lithium batteries, intercalation, and fundamental aspects of electrode processes.

Two chapters are devoted to splitting of water. The first chapter, by Gutmann and Murphy, presents a comprehensive review of the classical methods of splitting water by electrolysis and also presents some novel techniques for splitting water. Chapter 2, by Grätzel, surveys the current research being done on water splitting using visible light.

Two chapters are included that deal with the timely topics of lithium batteries and intercalation. The first, Chapter 3 by Marincic, presents a practical guide to the recent development of lithium batteries, while the second, Chapter 4 by McKinnon and Haering, presents and discusses various theoretical approaches to intercalation.

The last chapter in the book, Chapter 5 by Khan, presents a survey of many of the fundamental concepts and misconceptions of electrode kinetics as applied to semiconductors in particular.

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Contents

Chapter 1

THE ELECTROCHEMICAL SPLITTING OF WATER

F. Gutmann and Oliver J. Murphy

I. Introduction	1
II. Units	1
III. Electrochemistry	2
IV. Improvements Achieved in Water Electrolysis	6
1. Oxygen Evolution Electrocatalysts	6
2. Hydrogen Evolution Reaction	20
3. Cell Membrane Developments	22
V. Novel Ways to Reduce Activation Overvoltage	25
1. Photoelectrochemical Decomposition	25
2. Electrolysis at Elevated Temperatures (150- 300°C)	26
3. Improving the Mass Transport	28
4. Pulse Electrolysis	29
5. Ultrasonics	29
6. Alternative Anodic Reactions in Water Splitting ..	30
VI. Magneto-Electrolysis	35
VII. Steam Electrolysis	38
VIII. Series or Parallel Electrolyzers	40
IX. Economical Electrolyzers	41
X. Advanced Electrolyzers	43

XI. Super Electrolyzers	43
XII. State-of-the-Art Electrolyzers	48
1. Brown-Boveri and Cie Electrolyzers	48
2. DeNora SPA Electrolyzers	49
3. Lurgi GmbH Electrolyzers	49
4. Norsk Hydro-Electrolyzers	51
5. Electrolyzer Corporation Electrolyzers	51
6. Teledyne Energy System's Electrolyzers	52
7. General Electric's Solid Polymer Electrolyte Electrolyzer	52
XIII. Applications of Electrolytic Hydrogen Generator Technology	53
1. Markets for Oxygen Gas	54
2. Chlorine Production	55
3. Other Applications	55
XIV. Cost of Hydrogen Production	57
1. Cost Comparison of Hydrogen Derived from Various Sources and between Hydrogen and Other Fuels	60
XV. Hydroelectric Resources	61
XVI. Hydrogen Storage	62
1. Bulk Hydrogen Storage	62
2. Cryogenic Hydrogen Storage	63
3. Metal Hydrides	64
4. Microcavity Storage System	67
5. Hydrogen Encapsulation in Zeolites	68
6. Liquid Organic Hydrides	70
7. Metal-Aromatics and Transition Metal Complexes as Hydrogen Storers	70
8. Storage by Conversion to Ammonia and Methanol	71
References	72

Chapter 2

**INTERFACIAL CHARGE TRANSFER REACTIONS
IN COLLOIDAL DISPERSIONS AND
THEIR APPLICATION TO WATER CLEAVAGE
BY VISIBLE LIGHT****Michael Grätzel**

I. Introduction	83
II. Dynamics of Photoinduced Electron-Transfer Reactions in Simple Micellar Assemblies	85
1. General Kinetic Features of Light-Induced Redox Reactions	85
2. Specific Features of Light-Induced Redox Reactions in Micellar Assemblies	90
3. Functional Micelles, Electron and Hole Storage Devices	98
III. Interfacial Electron- and Hole-Transfer Reactions in Colloidal Semiconductor Dispersions	108
1. Colloidal TiO ₂ Particles	109
2. Interfacial Charge Transfer in Colloidal CdS Solutions	118
IV. The Principles of Redox Catalysis	121
V. Light-Induced Water Cleavage in Microheterogeneous Solution	125
1. Choice of Light-Harvesting Unit	125
2. Selection of Highly Active Redox Catalysts	129
3. Visible Light-Induced Water Cleavage in Systems Containing Sensitizer, Relay, and Redox Catalyst ..	143
4. Water Cleavage through Sensitization of Colloidal Semiconductors with a Large Band Gap	145
5. Water Splitting through Direct Band-Gap Excitation of Colloidal Semiconductor Dispersions	146
VI. Splitting of Hydrogen Sulfide and Reduction of Carbon-Dioxide as Alternative Light-Energy-Storing Reactions	155

1. Visible Light-Induced Cleavage of H_2S	155
2. Light-Induced Reduction of Carbon Dioxide	158
VII. Conclusions	159
References	159

Chapter 3

LITHIUM BATTERIES WITH LIQUID DEPOLARIZERS

Nikola Marincic

I. Introduction	167
II. Discharge Reaction Mechanism	170
1. Cathodic Reduction of SO_2 and SO_3	170
2. Cathodic Reduction of Oxyhalides	175
3. Anodic Oxidation of Lithium	177
4. Lithium Passivation	180
III. Battery Design Procedures	183
1. Concentric Electrode Structure	185
2. Wound Electrode Structure	189
3. Parallel Plate Structure	202
IV. Materials of Construction	203
1. Cell Hardware	203
2. Current Collectors	204
3. Catalytic Cathode Materials	206
4. Separators and Insulators	207
5. Electrolyte Materials	208
6. Lithium	210
V. Processing and Assembling	210
1. Environmental Requirements	210
2. Anode Subassemblies	211
3. Cathode Subassemblies	212
4. Electrolytes	214
5. Process Control	215
6. Typical Flow Charts	217
7. Prospects for Automation	217

VI. Testing and Evaluation	219
1. Capacity vs. Discharge Rate	219
2. Internal Impedance	220
3. Self-Discharge	222
4. Voltage Delay	222
VII. Applications	223
1. Long-Term Applications	223
2. Maximized Power Requirements	224
3. Intermittent and Pulse Applications	225
4. Applications at Extreme Temperatures	226
5. Resistance to Abuse	227
6. Hazard Analysis	228
VIII. Deactivation, Disposal, and Reclamation	229
1. Destructive Deactivation and Disposal	229
2. Reprocessing and Reclamation	230
References	231

Chapter 4

**PHYSICAL MECHANISMS
OF INTERCALATION**

W. R. McKinnon and R. R. Haering

I. Introduction	235
1. Intercalation Batteries	236
II. Review of Intercalation Systems	237
1. Layered Transition Metal Dichalcogenides	238
2. Metal Dioxides with Rutile-Related Structures ...	243
3. Intercalation of Graphite	247
4. Hydrogen in Metals	248
III. Thermodynamics of Intercalation and Lattice Gas Models	250
1. Lattice Gas Models Applied to Intercalation Systems	251
2. Lattice Gas Models with Interactions	255
3. Mean-Field Solution of the Problem of Ordering ..	257
4. Other Techniques for Solving Lattice Gas Problems	263

5. Breaking the $x = \frac{1}{2}$ Symmetry	266
6. Large Changes in the Host	269
IV. Interactions between Intercalated Atoms	271
1. Electronic Interactions	271
2. Elastic Interactions	274
V. Kinetics of Intercalation Cells	280
1. Motion of the Intercalate in the Host	281
2. Behavior of $D(x)$	283
3. Diffusion Overvoltages for Constant D	284
4. Diffusion Overvoltages for Phase-Boundary Motion	289
VI. One-Dimensional Lattice Gas	293
1. Exact and Mean-Field Solutions	293
2. Model Calculations of Diffusion	294
VII. Conclusions	297
References	301

Chapter 5

SOME FUNDAMENTAL ASPECTS OF ELECTRODE PROCESSES

Shahed U. M. Khan

I. Introduction	305
II. The Meaning of Absolute Scale Potential in Electrode Kinetics	306
III. The Effect of Applied Potential on the Fermi Level in Metal and Semiconductors	309
IV. Fermi Energies in Solution	318
V. Distribution of Electron States in Ions in Solution	320
VI. The Calculation of Electronic Energy States of Ions in Solution	323
VII. Applications of the Born-Landau Equation	326
1. Neglect of Electrostatic Interaction with the First Layer in the Solvent Shell	326
2. Absence of Correlation between Experimental and Bornian Theoretical Values of the Free Energy of Activation	327

3. Volume of Activation	328
4. Solvent Effects	328
5. Measurements in D ₂ O Solution	329
6. The Tafel Linearity	329
7. Are Outer-Shell-Dominated Reactions Rare? ...	331
VIII. Nonadiabaticity	331
1. Theoretical Work	331
2. Experimental Work	333
IX. The Mechanism of Proton Transfer at Interfaces ...	334
1. Activation of the H ₂ O—H ⁺ Bond	335
2. Equal ΔF^\ddagger for CH ₃ CNH ⁺ and H ₃ O ⁺ Ions	336
3. Isotope Effect in Proton-Transfer Reactions	337
4. The Dependence of Reaction Rates on M—H Bond Strength	338
5. Harmonic Oscillator Model to Proton-Transfer Reactions	339
X. The Semiconductor/Solution Interface	341
XI. Auger Neutralization	343
Notation	345
References	347
<i>Index</i>	351

The Electrochemical Splitting of Water

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I. INTRODUCTION

The electrochemical production of hydrogen as an energy medium is becoming economically feasible. The technology is established; it is clean and requires no extra separation or purification of products; it generates suitable pressures for storage and can be used in a modular mode.

The present market for hydrogen is limited to ammonia, fats, oils, metallurgical processes, and chemicals. However, the future holds two markets that may dwarf the present one. Hydrogen is necessary as: (i) an additive in the liquefaction of coal, or (ii) a medium of energy from gravitational, atomic, and solar sources.

II. UNITS

1 British thermal unit (Btu) = 1054 joules (J) = 0.293 watt-hours (Whr)

1 kilogram-meter (kgm) = 9.3×10^{-3} Btu = 2.34 calories (cal) = 9.8 J

1 mega joule (MJ) = 10^6 J = 948 Btu

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1 erg (erg) = 9.48×10^{-11} Btu = 10^{-7} J = 6.24×10^{11} electron volts (eV)

1 kilowatt-hour (kWhr) = 3.6×10^6 J

1 ampere per square meter ($A\ m^{-2}$) = 0.093 ampere per square foot (ASF)

1 cubic foot per day (ft^3/day) = 2.83×10^4 cubic centimeters per day (cm^3/day) = 2.83×10^{-2} cubic meters per day (m^3/day)

1 liter (l) = 3.5×10^{-2} cubic feet (ft^3)

1 newton (N) = 10^5 dynes (dyne) = 0.225 pounds (lbs)

1 bar = 0.987 atmospheres (At) = 1.02 kilograms per square centimeter ($kg\ cm^{-2}$) = 14.5 pounds per square inch ($lbs\ inch^{-2}$; PSI) = 750 millimeters of mercury at zero degrees centigrade (mmHg)

1 micron (μm) = 10^{-6} meters (m) = 10^{-4} centimeters (cm) = 10,000 angstroms (Å)

1 tesla (T) = 10 kilogauss (KG) = 1 newton per ampere per meter ($N\ A^{-1}\ m^{-1}$) = 1 weber per meter squared (Weber m^{-2})

1 degree absolute (K) = 1 degree centigrade ($^{\circ}C$)

σ = conductivity = $1/\rho$ in siemens (S): $1S = 1(\Omega\ cm)^{-1}$

III. ELECTROCHEMISTRY

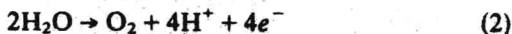
The reactions that take place at the electrodes in acid and alkaline solutions are as follows:

A. Acid Medium

(i) Cathode or hydrogen electrode reaction:



(ii) Anode or oxygen electrode reaction:

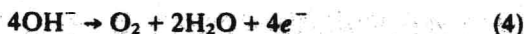


B. Alkaline Medium

(i) Cathode reaction:



(ii) Anode reaction:



There are no side reactions in water electrolysis that could yield undesired products.

The minimum necessary cell voltage, E_{rev} , is given under standard conditions by:

$$E_{rev} = \frac{-\Delta G^\circ}{nF} \quad (5)$$

where ΔG° is the change in the Gibbs free energy under standard conditions, F is the Faraday constant, and n is the number of electrons transferred.

The voltage for driving an electrolysis cell at a practical rate or current, I , is given by:

$$E = E_{rev} + \Sigma\eta + IR \quad (6)$$

where $\Sigma\eta = \eta_{cath} + \eta_{an} + \eta_{mt}$, and is a function of i , the current density. The subscripts cath, an, and mt refer respectively to the activation overvoltages at the cathode and anode, and the polarization overvoltage due to mass transport of gaseous products away from the electrode surfaces. The terms add arithmetically.

The activation overvoltages are given by expressions of the form¹:

$$\eta = \frac{RT}{\alpha F} \ln \frac{i^*}{i_0} \quad (7)$$

where i is the current density, i_0 is the exchange current density, and α is the transfer coefficient.

The activation overvoltages depend on the electrocatalytically sensitive exchange current densities, i_0 , viz.:

$$i_0 = \frac{nF}{\nu} k_0 \quad (8)$$

where k_0 is the standard rate constant of the electrode reaction and incorporates E_{rev} . ν is the stoichiometric number, a function of the rate-determining step.

Thus, the higher the i_0 , the lower will be the potential needed to get electrolysis at a certain rate.

The overvoltage arising from screening of part of the electrode surfaces from the electrolyte by gas films (gas bubble effect) is:

$$\eta_{mt} = \frac{1}{AF(z_+\mu_+c_+ + z_-\mu_-c_-)} I \quad (9)$$

where l is the interelectrode spacing, A is the electrode area, z_+ , μ_+ , and c_+ represent the charge, mobility, and concentration ($\text{mol}\cdot\text{l}^{-1}$) of the cation in the electrolyte, and z_- , μ_- , and c_- denote the charge, mobility, and concentration ($\text{mol}\cdot\text{l}^{-1}$) of the anion in the electrolyte. I is the cell current and F the Faraday constant.

R in Eq. (6) is the total ohmic series resistance in the cell and includes separator resistance and external circuit resistances, e.g., busbar contacts, as well as that of the solution. In some designs, it may include the resistance within pores and electrode resistance.

Utilizing the resistivities of 25% KOH at 75°C and asbestos, a widely used membrane material ($\sim 1.0 \Omega \text{ cm}$ and $\sim 3.0 \Omega \text{ cm}$, respectively),²⁻⁴ variation of the IR drop with membrane thickness, l_{memb} , and a fixed electrolyte path length between electrodes and membrane, l_{elect} , for various current densities is given in Table 1.

Table 1
Variation of IR Drop across Cell Membrane and Electrolyte
between Electrodes and Membrane for Various Membrane
Thicknesses at a Number of Current Densities^a

Cell current density, ^b A m^{-2}	Membrane thickness, $l_{\text{memb}}, \text{m}$	IR drop, V	Electrolyte thickness, $l_{\text{elect}}, \text{m}$	IR drop, V	Total IR drop, V
3,000	0.001	0.090	0.002	0.060	0.150
3,000	0.002	0.180	0.002	0.060	0.240
3,000	0.003	0.270	0.002	0.060	0.330
3,000	0.004	0.360	0.002	0.060	0.420
5,000	0.001	0.150	0.002	0.100	0.250
5,000	0.002	0.300	0.002	0.100	0.400
5,000	0.003	0.450	0.002	0.100	0.550
5,000	0.004	0.600	0.002	0.100	0.700
7,000	0.001	0.210	0.002	0.140	0.350
7,000	0.002	0.420	0.002	0.140	0.560
7,000	0.003	0.630	0.002	0.140	0.770
7,000	0.004	0.840	0.002	0.140	0.980
10,000	0.001	0.300	0.002	0.200	0.500
10,000	0.002	0.600	0.002	0.200	0.800
10,000	0.003	0.900	0.002	0.200	1.100
10,000	0.004	1.200	0.002	0.200	1.400

^a Conductivity of 25% KOH at 75°C $\sim 1.0 (\text{ohm cm})^{-1}$ and asbestos membrane $\sim 0.33 (\text{ohm cm})^{-1}$.

^b Electrode area taken as 0.093 m^2 .

It is apparent that considerable ohmic losses occur across the cell membrane, particularly at high-current densities. What is needed is a thinner membrane of high conductivity combined with a reduced anode-cathode gap.

The efficiency, ϵ , of an electrolysis cell is given by:

$$\epsilon = \frac{\Delta H}{\Delta G + \text{losses}} \quad (10)$$

$$= \frac{\Delta H}{nF(E_{\text{rev}} + \Sigma\eta + IR)} \quad (11)$$

For water electrolysis, the value of ΔH is $68.3 \text{ kcal mole}^{-1}$ and ΔG is $56.69 \text{ kcal mole}^{-1}$. Hence, under ideal conditions, $\epsilon = 1.20$. This means that, under ideal reversible conditions, the production of hydrogen would take place with 120% efficiency in respect to the electrical energy source. Thus, heat would have to flow into the cell from the surroundings.

When the value of the denominator in Eq. (11) is $1.48 nF$, i.e., electrolysis is performed at an overpotential of 0.25 V , a hydrogen electrolyzer would perform at 100% efficiency with respect to the electricity being used. Under these conditions, the cell neither heats nor cools.

Hence:

$$E_m = \frac{\Delta H}{nF} \quad (12)$$

where E_m is denoted as the thermoneutral potential.^{5,6}

In practice, the IR drop may itself be around 0.25 V . Typical values for older electrolyzers would be 0.25 V for the IR drop and 0.6 V for η_{cath} plus η_{an} . Then:

$$\epsilon = \frac{68,300 \times 4.18}{2.08 \times 2 \times 96,484} = 0.71 \quad (13)$$

This efficiency is with respect to the electricity, assuming that the temperature is constant. The cell gives *out* heat at potentials above 1.48 V and takes it *in* at potentials below this value.

If the manufacture of the electricity, with which the cell is being driven, occurs at, say, 39% efficiency, then the efficiency

with respect to the energy source, perhaps coal, would be $0.71 \times 0.39 = 28\%$.

It follows from the above that a simple expression for the efficiency of an electrolyzer is given by:

$$\epsilon = \frac{1.48}{\text{total cell potential at a given current density}} \quad (14)$$

IV. IMPROVEMENTS ACHIEVED IN WATER ELECTROLYSIS

As energy losses in electrolysis cells are governed by the anodic, cathodic, and ohmic overpotentials, research to make cells more efficient is devoted to improved electrocatalysis and less resistant membrane materials.⁷ Higher operating temperatures and increased real electrode surface areas, brought about by novel preparation techniques and unusual electrode geometries, are applied. Synthesis of compounds with higher lattice energies to withstand corrosion and formation of materials with mixed cation valence states, which sometimes are better electrocatalysts, is made. Apart from these factors, the following represent some trends of development in cell membranes: (i) attainment of mechanical stability to erosion, due to gas penetration and corrosive liquid flow at high temperatures; (ii) manufacture of pores of small cross section to prevent gases from mixing; (iii) achievement of high wettability; and (iv) reduction of thickness to attain a low IR drop.

1. Oxygen Evolution Electrocatalysts

The oxygen electrode that gives rise to the greatest energy loss⁸ (high overpotential, poor electrocatalysis) has received the most attention.

Many metal surfaces will, in practice, present a metal oxide surface to the electrolyte, and metal oxide (solid) catalysts will do so *a fortiori*. It is interesting to note that the adsorption of water at the oxide interface does not only result in a lowering of the dipole moment⁹ from its bulk value of 1.87 D to values as low as 0.01 to 0.1 D, but it also leads to an increase in the work function