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

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:

$$4H^+ + 4e^- \rightarrow 2H_2 \tag{1}$$

(ii) Anode or oxygen electrode reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{2}$$

B. Alkaline Medium

(i) Cathode reaction:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \tag{3}$$

(ii) Anode reaction:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \tag{4}$$

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:

$$E_{rev} = \frac{-\Delta G^\circ}{nF} \tag{5}$$

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:

$$E = E_{rev} + \Sigma\eta + IR \tag{6}$$

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 form[1]:

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

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.:

$$i_0 = \frac{nF}{\nu} k_0 \tag{8}$$

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:

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

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 (~1.0 Ω cm and ~3.0 Ω 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_{memb}, m	IR drop, V	Electrolyte thickness, l_{elect}, 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 ~ 1.0 $(\text{ohm cm})^{-1}$ and asbestos membrane ~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:

$$\varepsilon = \frac{\Delta H}{\Delta G + \text{losses}} \tag{10}$$

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

For water electrolysis, the value of ΔH is 68.3 kcal mole^{-1} and ΔG is 56.69 kcal mole^{-1}. Hence, under ideal conditions, $\varepsilon = 1.20$. 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:

$$E_{tn} = \frac{\Delta H}{nF} \tag{12}$$

where E_{tn} 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:

$$\varepsilon = \frac{68{,}300 \times 4.18}{2.08 \times 2 \times 96{,}484} = 0.71 \tag{13}$$

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 × 0.39 = 28%.

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

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

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 loss[8] (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 moment[9] 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