TECHNIQUES OF ELECTROCHEMISTRY

Volume 3

ERNEST YEAGER ALVIN J. SALKIND

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PREFACE

Electrochemistry and electrochemical techniques are generally regarded as a specialty, rather than a basic discipline. Most of the researchers and practitioners using electrochemical techniques were trained in some other field, usually chemistry, biology, physics, electrical engineering, or chemical engineering. As a result, there has existed for some time a need for a compilation of the various standard techniques.

The chapters in this book, and in other volumes in the series, are all written by authors recognized for their work with electrochemical techniques. The material is directed to the nonelectrochemist as well as to the electrochemist who wishes to gain insight into techniques with which he is not very familiar. The background knowledge required of the reader is that ordinarily obtained in undergraduate courses in physical chemistry and instrument analysis. The emphasis here differs substartially from that in the Advances in the Electrochemistry and Electrochemical Engineering series, now edited by Charles Tobias and Heinz Gerischere. We refer the reader to this excellent series for reviews of a rather sophisticated nature, principally directed to the advanced technical student and the experienced electrochemist.

This volume is devoted mainly to industrial and applied techniques. In Volume 1, techniques relating to electrode processes are discussed. Volume 2 was devoted mainly to techniques relating to studies of electrolytes.

We thank the contributors to this volume, and this series, who gave generously of their time in helping to make this third document of the techniques of electrochemistry. We hope that our colleagues will bring to our attention any errors of omission or comission that have occurred.

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January 1976

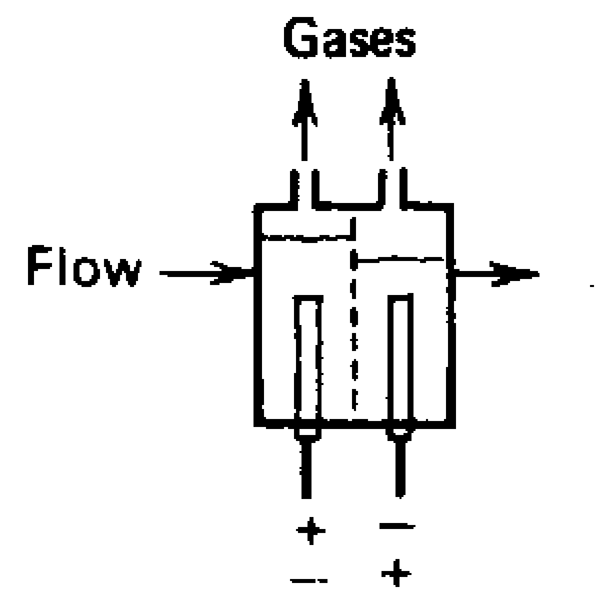
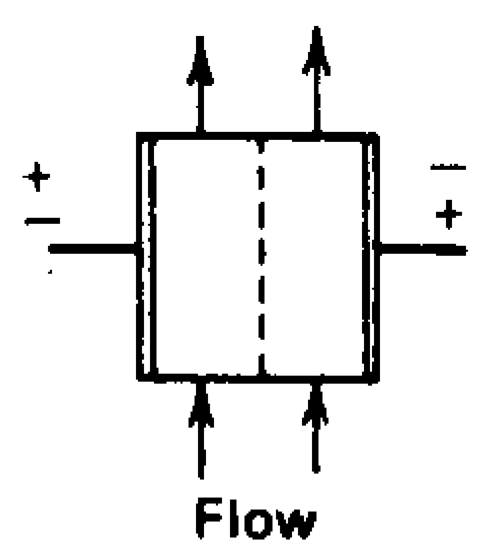
Type	Applications	Advantages	Disadvantages or limitations
B. Closed–diaphragm cell Convection parallel to current 	Chlorine–caustic–hydrogen Hydrogen–oxygen	Same as A Separate collection of gasses	
C. Membrane cell Convection perpendicular to current 	Oxidation and reduction Acid–base generator Electrodialysis Electrodimerization for adiponitrile	Electrolytes may be different and have only one common ion transported by membrane; complete separation of neutral reactants on products	

TABLE 1 (Continued)

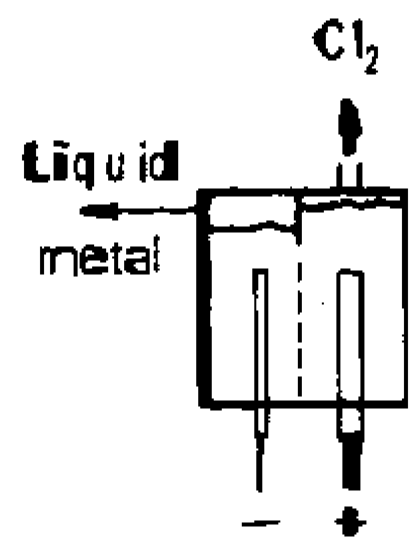
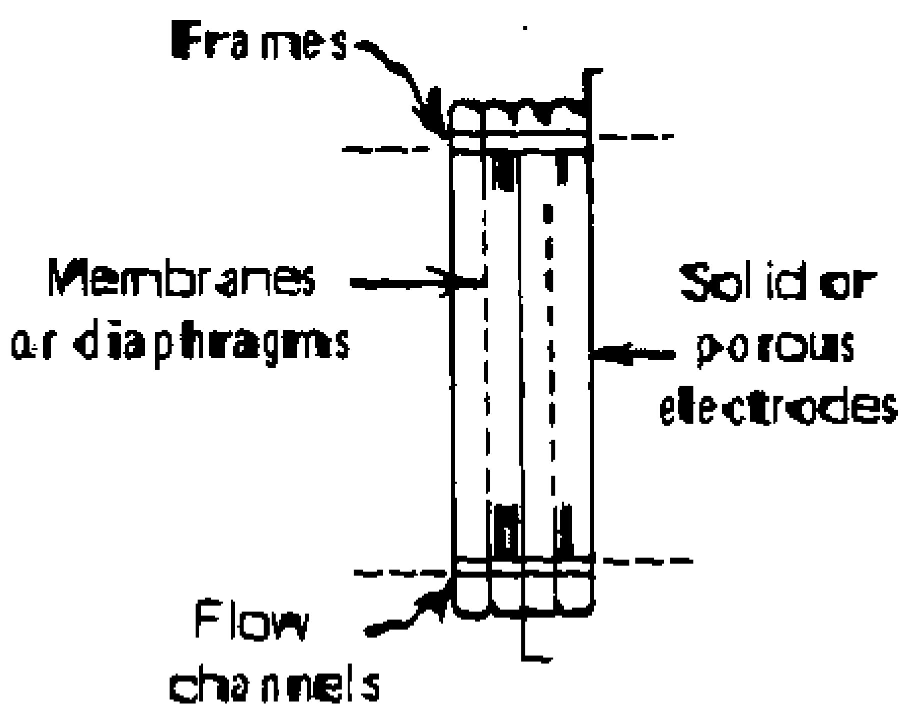
Type	Applications	Advantages	Disadvantages or limitations
D. Cells for producing liquid metals—convection not desired 	Magnesium Sodium Potassium Lithium	Separation of metal and chlorine products	High voltage drop Fouling of separators
II. Multicompartment Filter–press construction A. 	Hydrogen—oxygen generation Hydrogen—oxygen fuel cell Other fuel cell systems Electrodialysis Adiponitrile HCl electrolysis	Compactness Precision assembly Can operate under pressure Flow channels can be built in Adaptable to a wide variety of configurations with solid and porous electrodes, membranes, diaphragms and flow channels	Limited to inert or long–lived electrodes Long–time operation between disassembly required

TABLE 2

Type	Example
I. Planar	
A. Inert	Graphite anode in chlor–alkali cell Platinized titanium or ruthanium–oxide coated titanium anodes Platinum anodes in perchlorate cell Iron cathodes in chlorate and perchlorate cells
B. Active consumable	Carbon anode in Hall–Heroult cell Copper anodes in refining cell
C. Base for deposition	Mercury cathode in chlor–alkali cell Aluminum cathode in Hall–Heroult cell Stainless steel cathodes in manganese metal cell Copper cathodes in refining cell Electroplated objects Carbon base for deposition of MnO_2
D. Phase change on surface	Anodizing aluminum Thin–film battery Solid–state coulometer
II. Mesh or screen	Steel cathode in diaphragm type Chlor–alkali cell Metal anodes in chlor–alkali cells
III. Porous	Hydrogen–oxygen fuel cell Hydrogen–oxygen generator Electrochemical fluorination
1. Gaseous reactants or products	

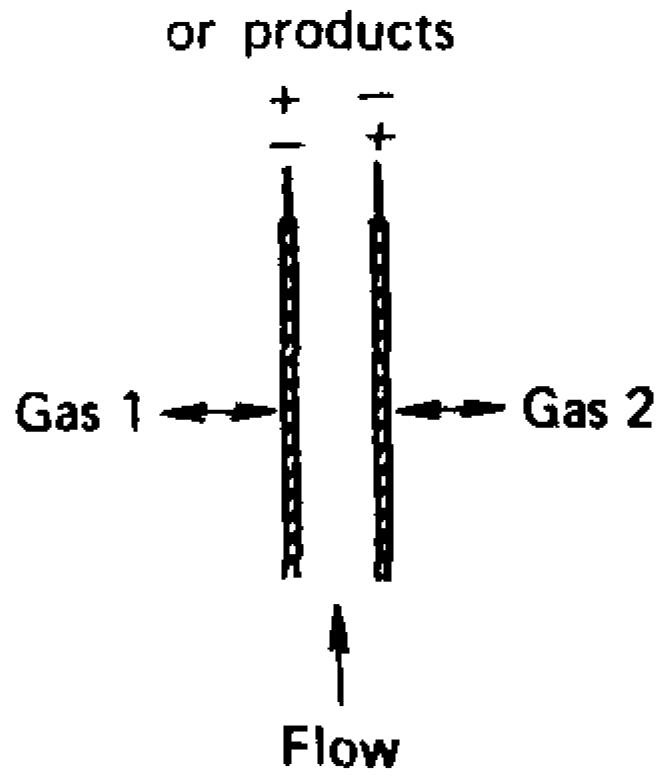
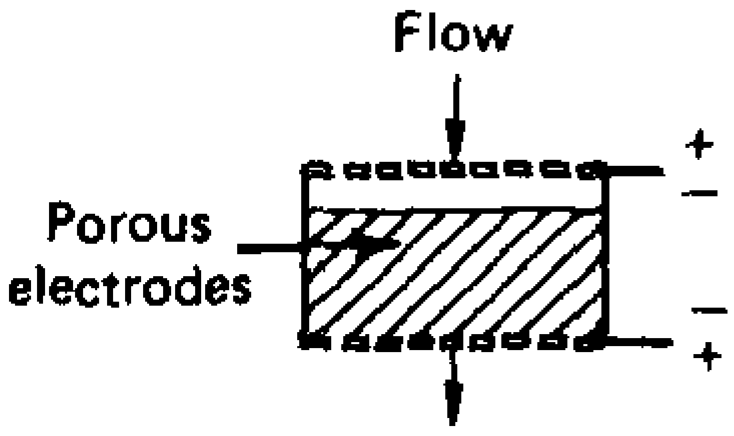
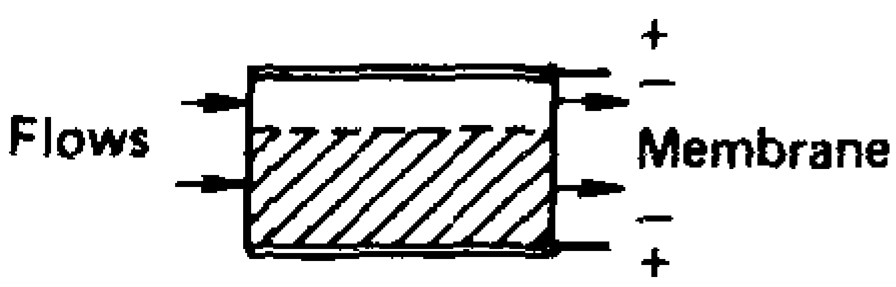
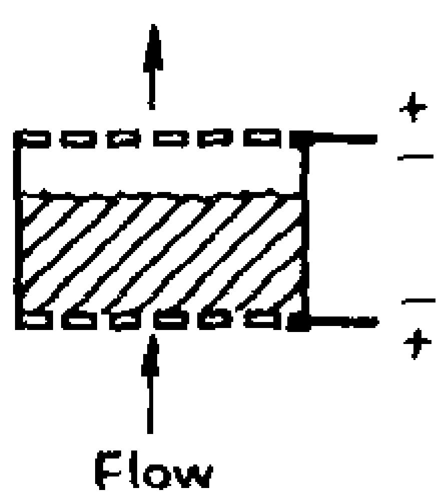
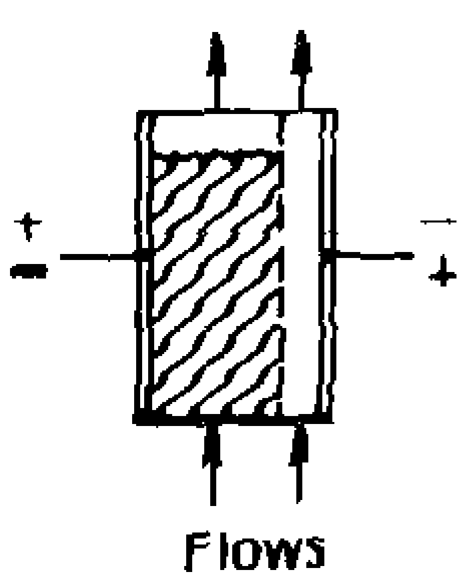


TABLE 2 (Continued)

Type	Examples
2. Flow–through electrode	
(a) current and flow parallel 	Hydrazine or methanol fuel cell Oxidation or reduction of dilute constituents Concentration of dilute metal ions
(b) current and flow perpendicular 	Mfg. of tetraalkyllead
B. Active phase change	Lead–acid battery plates, $Pb/PbSO_4$ and Pb/PbO_2 Other battery systems
IV. Fluidized bed	
(A) current and flow parallel 	
(B) current and flow perpendicular 	

CONTENTS

I. INDUSTRIAL ELECTROCHEMICAL PROCESSES

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1. Introduction

Industrial electrochemistry provides a variety of products used by modern society; aluminum, magnesium, sodium, chlorine, sodium hydroxide, chlorates, perchlorates, adiponitrile, tetraalkyllead, and electrorefined metals to mention a few. Increasing use of electrochemical processes is expected as electrochemical tehcniques become better and more widely understood and as the economics of electrochemical processing improve through use of larger and more efficient cells. Continuation of the decrease in cost of electrical energy over the long term relative to other forms of energy or to chemical oxidizing and reducing agents would add further impetus to use electrochemical processes.

Many types of electrochemical techniques are used in the electrolytic industries:

- Laboratory and pilot plant studies
  - Exploratory
  - Directed
  - Scale down (reverse of scale up)
- Cell and process design
  - Empirical techniques
  - Mathematical modeling from first principles
  - Optimization
- Process operation
- Process measurement and control

We may consider these techniques to be part of electrochemical and chemical engineering. An attempt will be made to discuss certain techniques and to give a general industrial perspective.

A. Objectives

The objectives of this chapter are to identify the features that distinguish industrial electrochemistry and its techniques from other branches of electrochemistry; categorize and illustrate the various types of electrode, electrolyte, separator, and cell systems now used; illustrate the economic basis that rules all actions and selects the techniques used; and discuss the relation of electrochemical engineering to the design and operation of industrial cells.

While the orientation of the chapter is toward industrial electrochemical processing, features common to the electrodeposition field and battery and fuel cell technology will be mentioned as they arise. There is much to be learned by crossing technological boundaries. The electrochemical technologies are all based on the same fundamental electrochemical engineering principles: thermodynamics, kinetics, mass, heat and momentum transport, current distribution, and scaling laws. Likewise, the technologies use the same applied aspects of electrochemical engineering: cell design techniques, materials selection, and economic optimization. Advances in one technology may be applied to others; for example, throwing power and current distribution calculations developed for plating are equally applicable to process cells.

B. Audience

This chapter is directed in particular toward the young electrochemist or electrochemical engineer. Industry can be quite bewildering to the fresh product of academe because the objectives of the two institutions are rather different. The university is entrusted by society to search for, transmit, and preserve knowledge. Industry, on the other hand, is intended to provide products and services at a fair return on its investment. The different goals and the separation of the two institutions has resulted in some cases in a lack of mutual understanding.

Economic forces are very powerful and all pervasive in industry. A plant or laboratory, generally treated as an economic unit, must earn a satisfactory return on investment if it is to survive. These economic forces establish procedures and shortcuts in design and operation that may appear to lack the rigor of technical analysis instilled by academe, although they have their own logic. The young scientist or engineer must develop an overall perspective if he is to make an adjustment to industry. A goal of this chapter is to outline an electrochemical engineering and economic perspective of electrochemical processing.

C. Specific Tasks

Two specific tasks were chosen for this chapter: to classify and summarize the various cell and electrode configurations used in industrial electrochemical processes, and to provide a brief perspective on the application of electrochemical engineering techniques to industrial processes with emphasis on the role of economic optimization.

Three important aspects set the techniques used in electrochemical processes apart from the laboratory techniques described in the first two volumes (1) of this series. The first aspect is that the processes considered here are many orders of magnitude larger than those involved in laboratory techniques. Instead of micrograms or grams of material in laboratory, the industrial plant may have an output of hundreds of tons per day. Instead of microamperes or amperes, the plant deals with 10^4 to nearly 10^6 A per cell.

The second aspect is that industrial processes are enormously complex compared to laboratory experiments. An objective in scientific research is to eliminate all but a few essential variables. In industrial electrochemical processes one is forced to simultaneously juggle many variables, including those of thermodynamics, kinetics, transport processes, current distribution, materials, materials handling, process control, labor relations, economics, finance, law, and so on.

The third and overriding consideration is that the process must earn a satisfactory and identifiable profit and return on investment. If a process cannot meet this criterion, a plant is not built. A plant must continue to meet this criterion by improvements or it is scrapped. The return from basic research on the other hand is more difficult to identify but in the long run it may be greater than from an existing industrial process. Society, for example, is still receiving dividends from the work of Michael Faraday.

D. Exclusions

Techniques used in the electrochemical process industries cover such a broad range that an encyclopedia would be required to describe them adequately. Therefore, it is appropriate to note areas of exclusion from this chapter.

This chapter does not give a detailed description of industrial electrochemical process. Other books (2 - 5) are addressed to this topic.

This chapter is not a course of electrochemical plant or cell design. A need exists for a definitive book on this subject. MacMullin has made an excellent start with two pioneering papers (6, 7) relating to cell design and scaleup. Many books on chemical plant design (8-13) cover process areas other than cells in an electrochemical plant.

This chapter is not a text on electrochemical engineering, and no attempt was made to review, comprehensively the electrochemical engineering literature. Newman (14) has developed an excellent and rigorous work that covers the interrelations of thermodynamics, kinetics, mass transport, current distribution, etc., in electrochemical systems. Levich (15) has formulated a treatise, dealing in large part with electrochemical mass transport, that is invaluable to the electrochemical engineer. Periodic reviews of particular aspects of electrochemical engineering appear in a series edited by Delahay and Tobias (16). Several electrochemical texts have sections relating to industrial processes (17-20). A need remains for a quantitative book including the applied aspects of electrochemical engineering.

This chapter is not a definitive exposition on economics of electrochemical plants. Rather, it is intended to serve only as a general introduction because there are so few papers concerning industrial cells (21-29) and fuel cells (30-32) in the literature. Several works are available on chemical processes economics (33-39).

This chapter does not discuss measurement techniques in electrochemical plants. Many parameters are measured including current, potential, potential drops, concentrations, pH, temperature, pressure, pressure drops, flow rates, current efficiency, anode-cathode spacing, and so on. These measurements include standard, well-known, laboratory techniques that need no elaboration. Instruments and techniques related specifically to the electrochemical industries might also deserve documentation.

II. CELL DESIGNS

Industrial electrochemical cells deal with a wide variety of liquid and gaseous reactants and products at temperatures from below ambient to 1000°C or above. Electrolytes may be aqueous, organic, molten or solid salt, or ion-exchange membranes. The electrolyte may be very corrosive in combination with the reactants, products, or intermediates. The state of technology and materials available changes with time. It is therefore not surprising to see a large variety of shapes and sizes of electrochemical cells. MacMullin (42) has given a detailed classification of industrial cells by various functions, including type of anode and cathode, type of electolyte, and type of divider.

Many other considerations are involved in the detailed design of industrial electrochemical cells. In general, although the cells may be essential, they are only part of a total plant process that is optimized as whole. This puts certain constraints on the design and operation of cells. In turn, the plant exists in a particular, technical, economic, and political climate, which reflects back on cell design. Source and cost of raw materials and construction materials, location and size of markets, freight costs, cost and availability of electrical energy, labor cost, land cost and zoning, environmental factors, taxes, and the like also may exert an influence.

Table 1 categorizes industrial cell designs into major types. The classification was intended primarily to include cells for making industrial products; but designs used also in batteries, fuel cells, electrowinning, and electroplating are indicated. Cell design and operating techniques have grown in parallel in different industries without much cross communication. In the present discussion, attention is focused on the common features of cells used in different industries.

A classification of electrode types is given in Table 2 and of separators in Table 3.