

S. TORII

ELECTRO-  
ORGANIC  
SYNTHESES

Methods and Applications

Part I: Oxidations

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**KODANSHA**

**VCH**



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## Preface

The advance of "electroorganic synthesis" in recent years has provided organic chemists with a versatile synthetic device of great promise. Despite the long history of electroorganic chemistry, most electroorganic reactions which provide product-selectivity have been developed only within the last decade, and research on various applications has spread gradually to cover many areas of fundamental and industrial organic chemistry. There is an increasing awareness of the versatility and uniqueness of electrolysis procedures in organic synthesis, and recent progress of methodology, including basic concepts for the design of electrolysis conditions and apparatus, should now be of quite general interest to organic chemists.

This book is a translation, with revisions and additions, of the volume entitled "Electroorganic Syntheses—Methods of Electrooxidation and Their Application", previously published by Kodansha Ltd. in the Japanese version (1981). It provides a survey of synthetically interesting references on electrooxidation reactions of organic compounds in terms of electrolysis conditions and product-selectivity, and aims to present the results in a form useful for synthetic application. Although over 800 references are cited, I have not attempted to provide an exhaustive review, and articles which appeared before 1970 have generally not been included. The results presented here can be readily understood on the basis of organic chemical considerations, and a detailed discussion of electrode reactions and reaction mechanisms is not included, since the major aim of this book is to aid electrosynthetic studies. Appendix 1.1 in Chapter 1, which indicates the relation between partial structures before and after electrolysis together with typical electrolysis conditions, should especially assist readers to gain easy access to appropriate electrolysis conditions for a desired functionalization.

I am particularly indebted to my colleagues Dr. Kenji Uneyama, Dr. Hideo Tanaka, and Dr. Tsutomu Inokuchi for their invaluable assistance in checking references, discussing the contents, and commenting on the manuscript. Dr. Seiki Saitoh of our faculty read the whole of the manuscript, and I thank him for his useful advice. I am also grateful to Professor Makoto Okawara (Tokyo Institute of Technology) and Professor Manfred Schlosser (Université de Lausanne) for their enthusiastic support. I would also like to express my deep appreciation to Professor Akira Takeda (Okayama University, Department of Synthetic Chemistry), who first gave me the opportunity to work on electroorganic synthesis. I acknowledge the careful secretarial work of Mrs. Noriko Banno, Miss Shoko Nakayasu, and Mrs. Junko Ohmori, who arranged the data concisely and typed the manuscript. Dr. Hans F. Ebel of Verlag Chemie and Mr. Ippei Ohta of Kodansha were always helpful and cooperative, and I am grateful to Mr. Andrew Smith and Mr. Richard Steele for their assistance in finalizing the the English manuscripts. Finally, I am especially grateful to my wife, Hiroko, for her consistent support and encouragement.

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June, 1984

S. Torii

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# 1. Electrooxidation and Product-selectivity

## 1.1. Introduction

The history of "electroorganic chemistry" as a tool for organic synthesis may be traced back to the traditional Kolbe reaction, which involves the electrolysis of carboxylate ions resulting in decarboxylation and combination of the generated radicals [1]. However, at that time, electroorganic reactions were not available as a means for the synthesis of complex molecules. Although considerable data had been accumulated by 1940, as documented by Fichter in his excellent monograph [2], it is only in the last few decades that electroorganic chemistry has assumed a character distinct from usual electrochemistry, which occupies a well-defined position in inorganic chemistry. During 1955–65, great efforts were made to introduce electrochemical concepts into synthetic organic chemistry. This led not only to the establishment of a large-scale manufacturing plant by Monsanto (U.S.A.) for the production of adiponitrile by means of electroreductive coupling of acrylonitrile [3] but also to the successful commercial production of tetraethyl lead by Nalco (U.S.A.) [4]. These achievements stimulated researchers to recognize the wider potential of electroorganic chemistry. In the 1960's, significant advances in the theory of electroorganic reactions coupled with improvements in equipment and sophisticated systems for the analysis of electron-transfer processes led to developments in the measurement of the electrochemical constants of organic compounds and elucidation of the electroorganic reaction mechanisms [5]. The excellent results obtained in this decade have been summarized in several monographs [6]. By the end of the decade, a wide range of electroorganic reactions had been developed. However, the majority of organic chemists were still unaware of its real potentiality. Only a few pioneering synthetic chemists took full advantage of the novel and versatile methods of electrochemistry.

In the early 1970's, increased social awareness of environmental damage caused by chemicals and chemical processes stimulated a reappraisal of the basis of industrial technology [7]. Since then, every industrial community has been obliged to install facilities for cleaning industrial wastes or for rendering them as harmless as possible. Moreover, the so-called oil shock as well as the energy and resources crisis prompted a reevaluation of previously used chemosynthetic methods. It became widely recognized that future chemical technologies must meet the new requirements imposed on industry for environmentally acceptable and lower-energy routes, utilizing readily available and less expensive materials. In these circumstances, electrosynthetic reactions began to attract much attention among synthetic chemists due to their high energy efficiency and cleanness, and the application of such reactions began to spread into all fields of organic chemistry [8]. Partly because of the profound impact of the abrupt change in technological requirements, many highly imaginative investigations were initiated, with the previous strong emphasis on the elucidation of product compositions being replaced to some extent by greater investment in designing more acceptable electrolysis systems and optimizing the electrolysis conditions to obtain high yields of the desired products. Indeed, the aim of investigations in electrosynthesis shifted from assessing rather arbitrary electrolysis conditions to identifying those which would provide the most efficient route to the desired molecules. In this sense, electroorganic synthesis in the 1970's was able to emerge from its infancy and be more fully assimilated into routine synthetic organic chemistry.

The formation and cleavage of chemical bonds in traditional organic reactions can be equated loosely with the two typical successive electrolytic processes of electron transfer (E process) and chemical reaction (C process). In particular, electrosynthesis emphasizes the reactivity control of reactive intermediates generated *via* the E process. Indeed, many product-selective electrosynthetic processes have been discovered by designing appropriate solvent-electrolyte-electrode systems. This is the basis on which modern electrosynthesis stands. Synthetic chemists who utilize modern electrosynthetic methods can eliminate many of the annoying problems which used to be encountered in the practical application of electrolysis. Without using a potentiostat and a divided cell, electrosynthesis can be conducted by means of electrodes, a beaker, and a conventional electricity supply. The choice of solvent, electrolyte-electrode system can be easily made, as in the choice of suitable reagents and solvents in organic synthesis (chemosynthesis).

Apart from the advances in the field of electrosynthesis made in the 1970's, various other novel concepts and methodologies for organic synthesis were developed during this period. These include the concept of "dipole inversion" proposed by Corey and Seebach, which is of vital importance and has been widely accepted [9]. For example, it is possible to generate a cationic species in a basic medium and/or anionic species in an acidic medium and to obtain nucleophilic attack at the  $\alpha$ -position of a carbonyl group. In such ways, the potentiality of electrosynthesis can be expected to have a profound impact on research in organic chemistry in the 1980's. Many chemosynthetic reactions which employ chemicals stoichiometrically may possibly be abandoned in favor of direct and indirect electrosynthetic procedures [10], of which the latter employ only catalytic amounts of chemicals as electron carriers (mediators). The progress of electrolysis technology has also been striking in recent years [21]. The developments include the filter press flat plate cell [21g], capillary gap cell [21d,e,f,i], pumped slurry cell [21c,d], packed bed cell [21c,d,m], fluidized bed cell [21c,d], cross-sectional cell [21h], undivided foam cell [21k], tubular flow cell [51], three compartment cell [21m], Swiss-Roll cell [21n], etc. matching respective purpose. In addition, newly developed technological options such as the paired-reaction [11], emulsion method [12], two phase electrolysis [13], etc., may have a role as basic approaches to complex transformations [14].

In order to assist the organic chemist to carry out electrochemical experiments in practice, details will be given below of the manipulation of the electrolysis apparatus as well as of the choice of electrolysis media such as solvent, electrolyte, additive, and electrode. In addition, the correlation between the electrolysis conditions and product-selectivity will be briefly discussed. At the end of this chapter, an electrolytic reaction index of the modes of reaction and electrolysis conditions (Appendix 1.1) is presented with the aim of providing easy access to suitable solvent-electrolyte-(electrode) systems for directed electrosynthesis. However, it should be noted that the listed electrolysis conditions have not necessarily been optimized.

## 1.2. Principal Concepts and Design of Electrosynthetic Reactions

It is only rather recently that organic chemists have developed the idea of utilizing electrochemically generated reactive species for selective synthetic reactions. In contrast with traditional methods, electrochemical procedures involve neither bond-forming nor bond breaking steps as an initial process, but electron transfer from substrates to the anode. The active species are expected to be the radical  $[S]^\cdot$ , cation  $[S]^+$  [16], cation radical  $[S]^{\cdot+}$  [15], and dication  $[S]^{2+}$ .

Table 1.1. Expected Reactive Species Formed by Electron Transfer on the Anode

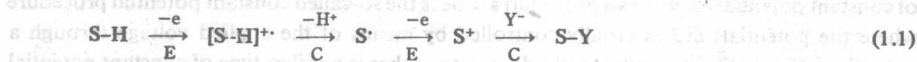
Electron transfer process	Reactive species
$S \longrightarrow S^+ + e$	Radical cation
$S^{+\cdot} \longrightarrow S^{2+} + e$	Dication
$S^- \longrightarrow S^{\cdot-} + e$	Radical
$S^{\cdot-} \longrightarrow S^+ + e$	Cation

as shown in Table 1.1. The activated intermediates  $[S]^{\cdot-}$  and  $[S]^+$  are generally derived from carboxylates, alcoholates, phenolates, thiolates, halides, etc., by one- or two-electron discharge around the anode, while  $[S]^{+\cdot}$  and  $[S]^{2+}$  species may arise from aromatic, unsaturated, and hetero atom-containing compounds by one- or two-electron loss. From the synthetic viewpoint, one major concern is how to discriminate specifically one of these reactive intermediates under electrolysis conditions. Before discussing such problems, however, let us consider first the basic electrosynthetic reaction process.

### 1.2.1. Electron Transfer (E Process) and Chemical Reaction (C Process)

Most electrooxidations of organic compounds proceed strictly in a stepwise fashion through the loss of electrons by electrolysis (E process) and subsequent chemical reaction (C process). In the E process, it is essential to produce the desired reactive species selectively and in the C process, to control the reactivity and the reaction course of the intermediates so generated by designing a situation (reaction site) in which such reactive species can be directed in the desired ways. Therefore, product-selective electrosynthesis cannot be attained only by controlling the proper oxidation potential in the electrolysis media, although this must be one of the requirements.

At the outset, we must consider the E process which can be specified by a controlled potential electrolysis as discussed in section 1.2.2. The importance of the C process becomes clear when we realize that even starting from the same reactive intermediate, it is possible to obtain widely disparate results by changing the constituents of the electrolysis media. Apparently, the fate of the reactive intermediates is always affected by the solvents, electrolytes, additives, and electrodes. It is thus essential to decide precisely which electrolysis system should be adopted, in relation to the desired fate of the reactive intermediates. An outline of elemental electrosynthetic reactions through well controlled E and C processes is given in Fig. 1.1. In contrast to the electrochemical reaction of metal redox systems in aqueous media, most electrochemical reactions involving organic compounds do not terminate in the E process, but the reactive intermediates further undergo chemical reactions leading eventually to stable products after substitution, elimination, addition, degradation, recombination, fission, or rearrangement reactions. Such a reaction sequence for the substrate S-H proceeding by an ECEC mechanism is shown in Eq. (1.1).



Most efforts in electroorganic chemistry have so far been made to investigate the mechanisms of the electrode process, i.e. the E process. The electrode reactions involve phenomena on the

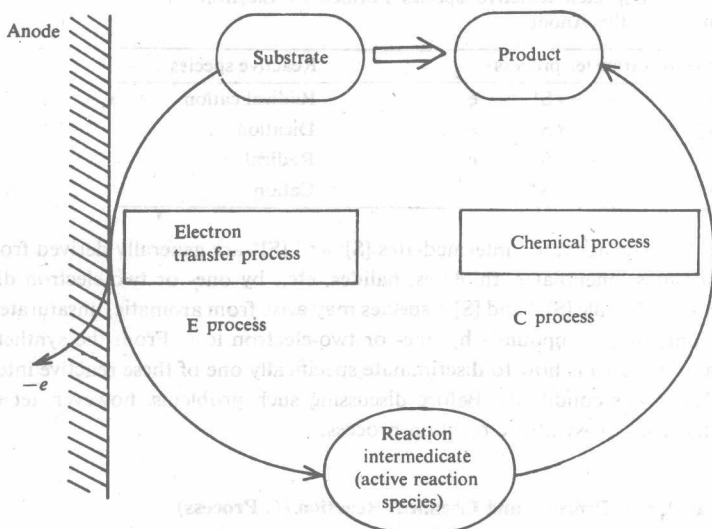


Fig. 1.1. Electroorganic reaction by a combination of electron-transfer and chemical processes.

electrode surface in which electron transfer from substrate to anode occurs [17]. Nevertheless, such efforts have unfortunately not yet succeeded in upgrading electroorganic chemistry to a synthetic tool with high efficiency in pursuing chemical transformations leading to target molecules, although the basic importance of the techniques must not be underestimated. Thus, today's concept of electroorganic synthesis is necessarily an extension of that of classical electrode reactions, and embraces all chemical and physical phenomena involved in the electrolysis system. The E process in electroorganic synthesis, for example, comprises all the possible electron transfer processes which may exist not only around the electrode surface but also in the diffusion layer, or even in the bulk solution.

Strictly speaking also, modern electroorganic synthesis lays stress on the product-selectivity, which is influenced by the C process rather than the E process. The difference from the traditional reagent-based organic reaction is that the solvent-electrolyte-electrode system and also the electrolysis conditions such as the current density, potential, pH, etc., play an important role in deciding the outcome of the C process. Accordingly, a suitable choice of electrolysis system and conditions can provide an excellent product-selectivity.

### 1.2.2. Control of the E Process

The experimental methods for controlling the E process can be divided into two different types of constant potential electrolysis procedures: one is the so-called constant potential procedure where the potentials are externally controlled by means of the applied voltage through a potentiostat (donating potential method), and the other is another type of constant potential electrolysis in which the current density is kept at a constant value throughout the electrolysis and, thereby, the potential of the electrolysis system is necessarily controlled (self-controlled potential method). Such self-controlled potential methods tend to be widely used because of

the simplicity of both the apparatus and operation when the electrolysis conditions are definitely optimized. In addition, it must be emphasized that the oxidation potential of the substrates is influenced by the electrolysis conditions such as the solvent, electrolyte, additive, pH, electrode, etc. This means that such factors are of sufficient importance that the E process can be controlled by them, while they are of course, at the same time, the factors which delicately and sometimes critically govern the C process.

### 1.2.3. Control of the C Process

Particular attention should be given to the reaction site, which may be designated as the microscopic circumstances under which electrogenerated active species come in contact with the solvents, electrolytes, additives, etc. and undergo subsequent chemical reactions. Apparently, the chemical fate of the substrates is determined by two factors: one is the *a priori* chemical nature of the substrate (the kinds of functional groups and their arrangement, and also the stereochemical features) and the other is a *posteriori* factor which comes into play when the active intermediate enters the "reaction site" and which, thereafter, dominate the chemical reaction it undergoes. Ultimately, the control of the C process depends on optimizing many functions including the solvents, electrolytes, additives, electrode materials, current density (oxidation potential), pH, and temperature.

## 1.3. Electrolysis Procedures

### 1.3.1. Electrooxidation and Electrolysis Apparatus

Details of the experimental techniques for electroorganic synthesis are well documented in the literature [21]. A schematic diagram of a cell and the principle of electrosynthesis are illustrated in Fig. 1.2. Since organic solvents possess very poor conductivity, it is necessary for a conductive electrolyte, *e.g.*,  $\text{LiClO}_4$  etc., to be dissolved in the solvent in order to obtain a workable electrolysis solution which can transmit electricity. There are two types of electroorganic processes which can be described as direct or indirect electrooxidation. In direct electrooxidation, a substrate  $[\text{S}]$  gives up electrons to the anode, affording a reactive intermediate,  $[\text{S}]^{+\cdot}$ . On the other hand, the indirect electrooxidation process involves electron transfer between  $[\text{S}]$  and a carrier (a mediator) which, initially, discharges at the anode, generating a reactive oxidizing carrier capable of accepting electrons from the substrate molecules in the medium. If the reactive intermediate such as  $[\text{S}]^{+\cdot}$  produced around the anode or products formed by a follow-up reaction can undergo a reverse reaction at the opposite electrode, a two-compartment cell divided by appropriate microporous separators such as fritted glass or porous ceramics, or ion-exchange membranes, should be used. However, since many electrooxidation reactions have been performed successfully in an undivided cell, a first attempt at oxidative electrosynthesis may be done in a simple beaker-type electrolysis apparatus as shown in Fig. 1.3. Actually, numerous electroorganic reactions have been carried out in undivided cells equipped with two electrodes, a thermometer, a gas outlet, and a magnetic stirring bar as depicted in Fig. 1.3. A short, wide-bore test tube with a side arm is adequate for ordinary purposes and a double-bored rubber stopper carry-



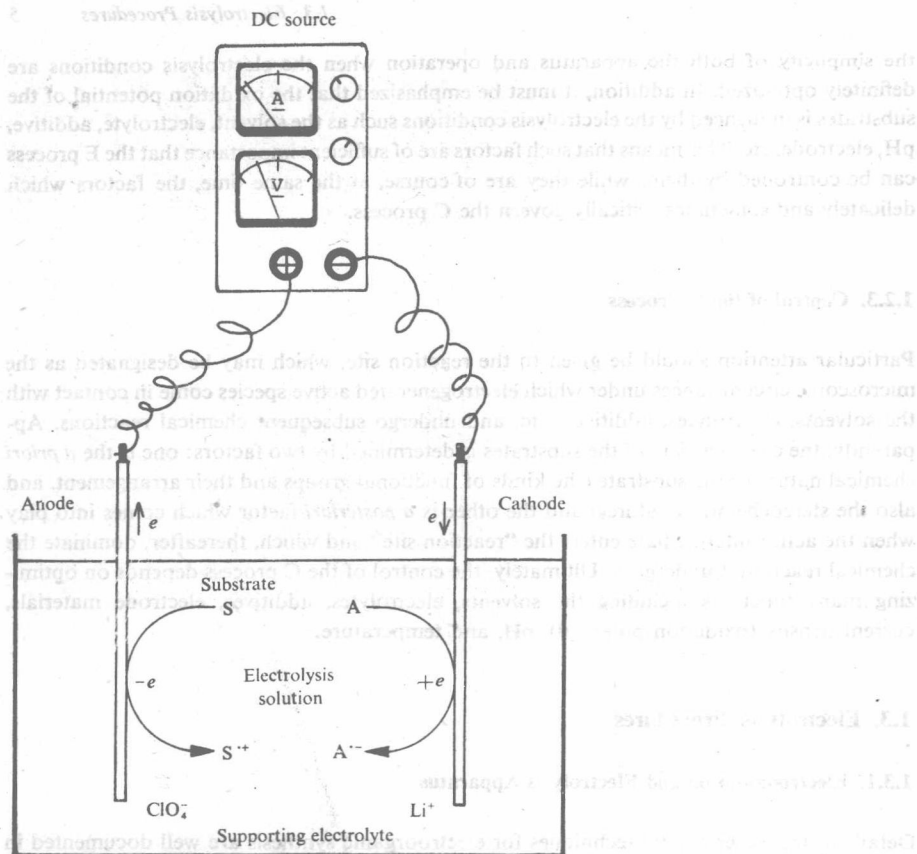
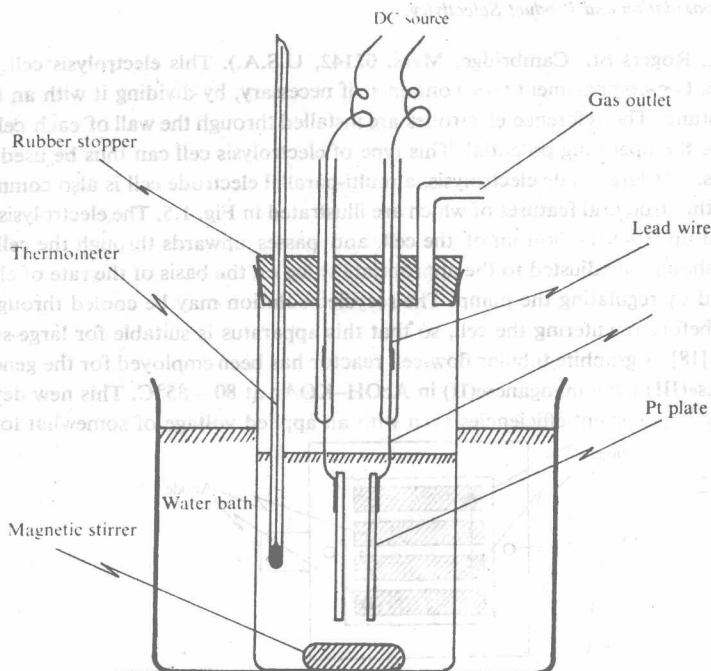


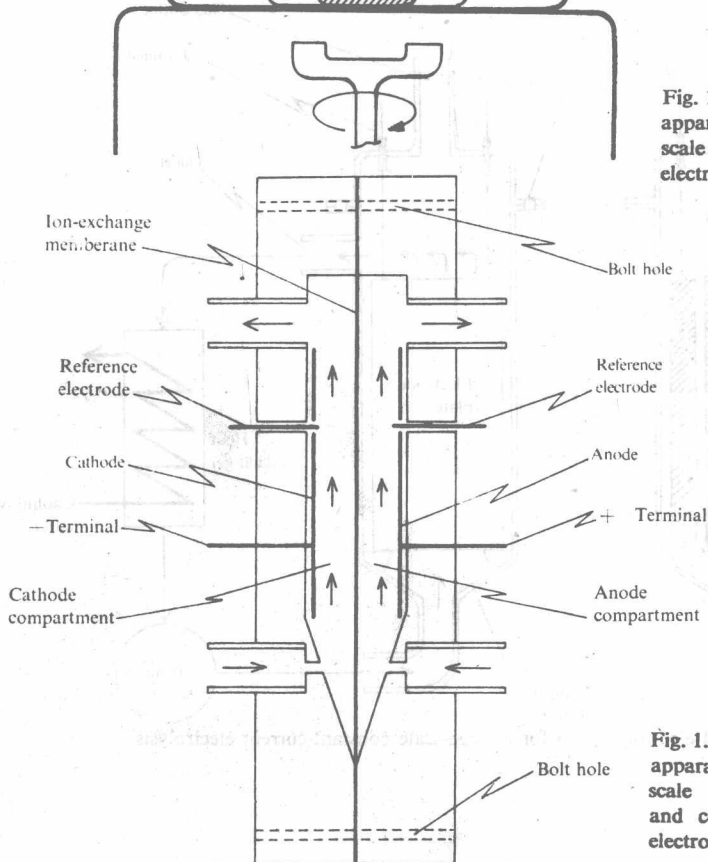
Fig. 1.2. Schematic outline of electrolysis.

ing two electrodes can be mounted onto it, if no thermometer is needed. For small scale experiments in the laboratory run with 1–10 g of substrate, compact DC suppliers are commercially available which can be operated at a standard output of 0.5–2.5 A/0–35 V. These are fitted with current and voltage meters as shown in Fig. 1.2. Usually, a carbon or platinum electrode is used as the anode material. In some cases, lead oxide ( $\beta$ -PbO<sub>2</sub>) is also beneficial and other specific electrodes with a particular finish can be recommended for those who are experienced. The interelectrode gap should ideally be adjusted according to the amount of applied current which is required in the experiment. In general, the distance is kept within the range of 1–5 mm in order to maintain a current-density of within 10–100 mA/cm<sup>2</sup>. The following summarizes the actual steps of an electrolysis experiment. After setting up the electrolysis cell in the above simplified manner, the electrolysis solvent, electrolyte, and substrate are charged (see Fig. 1.3) and then the two electrodes are connected to the DC supply (see Fig. 1.2). In laboratory-scale electrolysis, a magnetic stirring system is convenient and is used in almost all cases (Fig. 1.3). The temperature of the electrolysis solution can be controlled conventionally by cooling the cell with tap water (Fig. 1.3). A small-scale cell for preparative experiments (Fig. 1.4) is commercially available from an American company





**Fig. 1.3. Electrolysis apparatus for a small-scale constant-current electrolysis.**



**Fig. 1.4. Electrolysis apparatus for a small-scale constant-current and constant-potential electrolysis.**

(ECO Co., 56th, Rogers St., Cambridge, Mass. 02142, U.S.A.). This electrolysis cell can also be used as a two-compartment type container, if necessary, by dividing it with an ion-exchange membrane. The reference electrodes are installed through the wall of each cell in order to monitor the operating potential. This type of electrolysis cell can thus be used for various purposes. For large-scale electrolysis, a multi-parallel electrode cell is also commercially available, the structural features of which are illustrated in Fig. 1.5. The electrolysis solution is pumped up from the bottom of the cell, and passes upwards through the cell. Its linear flow rate should be adjusted to the appropriate value on the basis of the rate of electrolysis concerned by regulating the pump. The recycled solution may be cooled through a heat exchanger before re-entering the cell, so that this apparatus is suitable for large-scale electro-synthesis [18]. A graphite tubular flow-cell reactor has been employed for the generation of manganese(III) from manganese(II) in  $\text{AcOH-KOAc}$  at  $80 - 85^\circ\text{C}$ . This new device can provide very high current efficiencies even with an applied voltage of somewhat lower

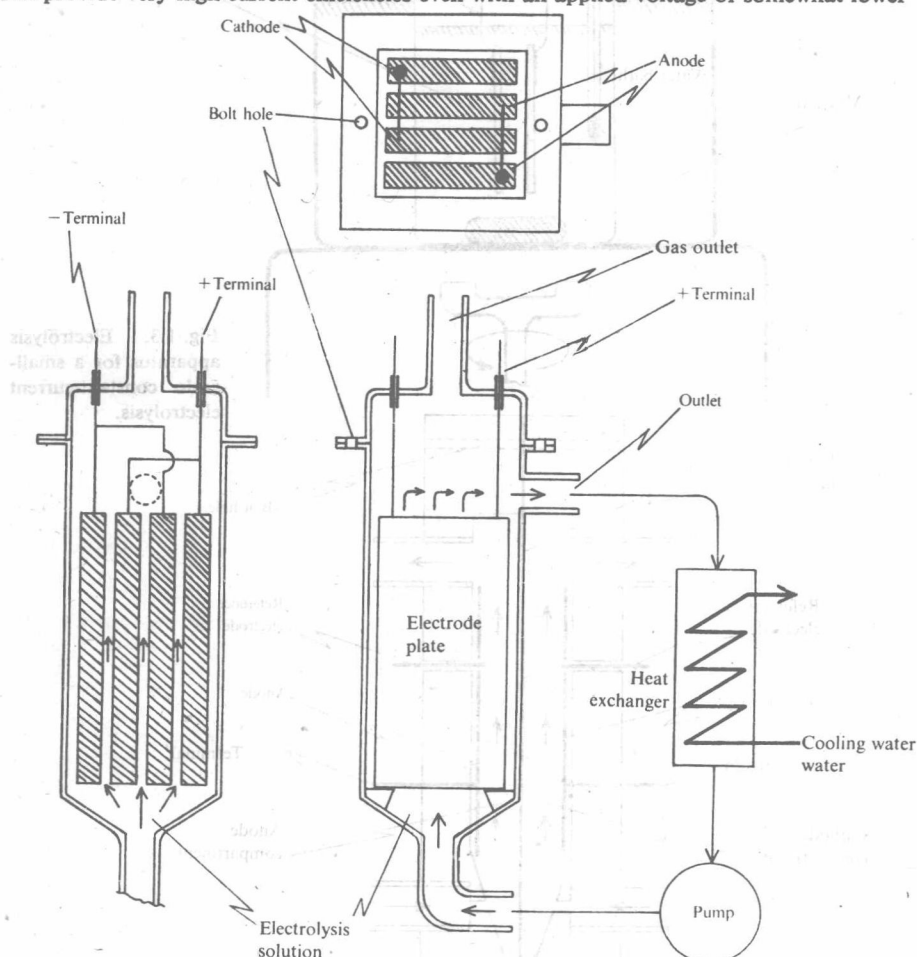


Fig. 1.5. Undivided electrolysis cell for a large-scale constant-current electrolysis.