Electrochemical Reactions and Mechanisms in Organic Chemistry

ELECTROCHEMICAL REACTIONS AND MECHANISMS IN ORGANIC CHEMISTRY

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This book is dedicated to my wife Jadwiga
and to our children, Amelia and Edwin

PREFACE

This book is concerned with reactions carried out at an electrode on a preparative scale. The impact of organic electrochemistry on synthetic organic chemistry has a long history beginning with the Kolbe reaction, which is still in the repertoire in first year teaching. In the early 1900's electrochemical methods for the oxidative or reductive transformation of functional groups were actively pursued.. They offer the advantage of having no spent oxidant or reductant for disposal. However electrochemical processes fell out of favour in the face of conventional chemical reactions because the outcome from electrochemistry was often far from predictable. Now that the mechanisms of these processes are generally well understood, many of the former pitfalls can be avoided.

Electrochemical processes use the electron as a reagent and so avoid a chemical oxidant or reductant. The environmental impact of electrochemistry needs to be assessed by looking at the global cell reaction. In the electrochemical cell, every oxidation step at the anode must be accompanied by a reduction at the cathode. During an oxidation, whatever is evolved at the cathode is in effect a spent reagent. The cathode reaction can be controlled to give a desirable product, even hydrogen for use as a fuel. During a reduction process this spent reagent is produced at the anode. It can be oxygen, which is vented to the atmosphere. Control of the reaction at the counter electrode gives to electrochemical processes the advantage of being non-polluting, relative to corresponding steps using a chemical reagent.

The discovery of the Baizer hydrodimerization process for preparation of adiponitrile from acrylonitrile led to a resurgence of interest in organic electrochemistry. This process synthesises adiponitrile at the cathode and the spent reagent is oxygen evolved at the anode. Its immense technical success prompted extensive investigations into reaction mechanisms in organic electrochemistry with a view to improving the old functional group interchange reactions. At the same time new reactions of potential use in organic synthesis have been discovered. In parallel with these investigations, significant improvements have been made in the design of electrochemical cells both for laboratory and for industrial scale use.

Electrons are transferred at an electrode singly, not in pairs. The primary reactive species to be generated is either a delocalised radical-ion or a radical formed by cleavage of a σ-bond, together with an ion. The first formed radicals can be further converted to ions by electron transfer. Thus organic electrochemistry involves a study of the reactions of both radical and ionic intermediates. Electron transfer at the electrode is a surface reaction while intermediates undergo chemical reactions in the bulk solution. An appreciation of the existence of these two types of often competing processes is required to understand the outcome of organic electrochemical reactions.

Recent work has developed reactions for carbon-carbon bond formation or cleavage and has introduced new routes for the introduction of functional groups, all of which are attractive to those planning synthesis on both laboratory and industrial scales. The mechanisms of these processes are now generally well understood.

This book aims to be more than just an introduction to such current areas of research. It is intended also to show how the subject of Organic Electrochemistry is integrated across the spectrum of oxidation and reduction by a general set of mechanisms. The discussion centres around reactions on a preparative scale and on the mechanisms governing the outcome of such processes. The book will be of interest to inquisitive final year undergraduates, research students and research directors both in academia and in the fine chemicals industry. An understanding of general organic chemistry is assumed. Physical chemistry has to be introduced into a discussion on electrode kinetics and this area is kept to a minimum. Discussions on the preparation and properties of radical-ions are also necessary since these are the first reactive species produced at an electrode.

The redox properties of an electrode are determined by its potential measured relative to some reference electrode. Many different reference electrodes are used in the literature. In order to make cross comparisons easily, most of the electrode potential quoted for reactions have been converted to the scale based on the saturated calomel electrode as reference. Electrode materials and electrolyte solutions used by the original workers are quoted. In many cases, the electrodes could be fabricated from more modern materials without affecting the outcome of the reactions. In the not too distant past perchlorate salts were frequently used as electrolytes. This practise must be discouraged for preparative scale reactions because of the danger of an explosion when perchlorates and organic compounds are mixed. Alternative electrolytes are now readily available.

I acknowledge many discussions over the years with research students and with the international research community on problems in organic electrochemistry. The assistance given to me by Sheila Landy and her staff of the Science Library in Queen's University is gratefully acknowledged. Finally, I thank my wife for her help and her patience in dealing with all the disruptions to normal life which writing this book has caused.

James Grimshaw,
Belfast, July 2000

CONTENTS

CHAPTER 1

ELECTROCHEMICAL OXIDATION AND REDUCTION OF ORGANIC COMPOUNDS

General Technique

During an electrochemical reaction, electrons are transferred between a molecule of the substrate and the electrode. Electrons are always transferred singly and the substrate first is converted to an intermediate with an unpaired electron. Transformation of this reactive intermediate to the final product involves a sequence of bond forming or bond cleaving reactions and frequently further single electron transfer steps. The complete electrochemical reaction vessel requires both an anode and a cathode. Only one of these electrodes, the working electrode, is involved with the chemical reaction of interest, oxidation at the anode or reduction at the cathode. The second electrode is the counter electrode and usually some simple inorganic reaction occurs here, such as hydrogen evolution if this is a cathode or oxygen evolution if this is an anode. The space between the anode and cathode is filled with an ionised salt solution and charge passes through the solution between the electrodes by migration of ions.

The simplest design of electrochemical cell has two electrodes dipping into the solution containing the substrate and the supporting electrolyte. A cell of this type is suitable for the Kolbe oxidation of carboxylate ions (see p. 316) where the anode reaction is given by Equation 1.1 and the cathode reaction is the evolution of hydrogen (Equation 1.2). Both the substrate and the hydrocarbon product are inert

$$2\ C_6H_{13}CO_2\ -\ 2e \longrightarrow C_6H_{13}{-}C_6H_{13}\ +\ 2\ CO_2 \qquad \text{Eq. 1.1}$$

$$2\ H^+\ +\ 2e \longrightarrow H_2 \qquad \text{Eq. 1.2}$$

towards reduction at the cathode.

For many processes, however, it is necessary to employ a divided cell in which the anode and cathode compartments are separated by a barrier, allowing the diffusion of ions but hindering transfer of reactants and products between compartments. This prevents undesirable side reactions. Good examples of the need for a divided cell are seen in the reduction of nitrobenzenes to phenylhydroxylamines (p. 379) or to anilines (p. 376). In these cases the reduction products are susceptible to oxidation and must be prevented from approaching the anode. The cell compartments can be divided with a porous separator constructed from sintered glass, porous porcelain or a sintered inert polymer such as polypropene or polytetrafluoroethene. Another type of separator uses woven polytetrafluoroethene cloth which has been exposed to a soluble silicate and dilute sulphuric acid so that silicic acid precipitates into the pores [1]. On a laboratory scale porous porcelain and sintered glass are the most commonly used materials.

On an industrial scale, ion-exchange membranes are most frequently used for the separator material [2]. Cationic and anionic types are both available and a sulphonated polytetrafluoroethene cation exchange resin, which can withstand aggressive conditions, is frequently used. Arrangements for sealing this type of separator into a laboratory scale glass cell are also available.

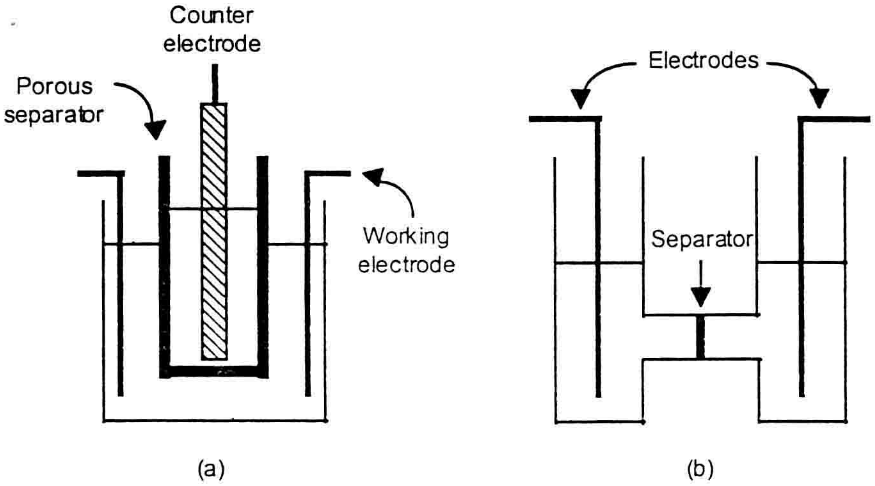

Figure 1.1. Cells used for laboratory scale electrochemical preparations: (a) a beaker-type cell; (b) an H-type cell.

General purpose laboratory scale glass cells are either of the beaker-type (Figure 1.1a) or the H-type (Figure 1.1b). The early pioneers of organic electrochemistry used beaker-type cells, with cylindrical symmetry, and the separator was either a porous porcelain pot or a sintered glass disc [3]. Designs for beaker-type cells in more modern materials have been described [4]. The H-type cell can be designed to use either one or two sintered glass separators [5]. Oxygen must be excluded from the cathode compartment during electrochemical reduction otherwise current is consumed by the reduction of oxygen to water and the highly reactive superoxide anion is generated as an intermediate. A flow of inert gas is maintained in the cathode compartment. It is not essential to exclude oxygen during electrochemical oxidation but usually a flow of inert gas is maintained in the anode compartment so as to dilute any oxygen, which is evolved. A stirring device is necessary to decrease the thickness of the diffusion layer around the working electrode.

The voltage drop across a working electrochemical cell is not uniformly distributed. This is shown schematically in Figure 1.2. A large proportion is due to the electrical resistance of the electrolyte and the separator. This, of course, can be decreased by a suitable cell design. The voltage drop across the working electrode solution interface determines the rate constant for the electrochemical reaction. It is often advantageous to maintain a constant potential drop across this interface to control the rate of unwanted side reactions. The working potential is measured relative to a reference electrode and probe, placed close to the working electrode surface. An aqueous saturated calomel electrode is the most frequently used reference. The relative potentials of other reference half-cells are given in Table 1.1. The reference electrode dips into a salt bridge containing the electrolyte used in the main electrochemical cell. The salt bridge can be terminated either by a thin Luggin-Harber capillary [6] placed close to the working electrode or by a plug of porous Vycor glass [7] or an inert fibre [8]. For non-aqueous electrochemistry IUPAC recommends the ferrocene-ferricinium couple as an internal reference standard of potential [9]. It is suitable for use in linear sweep and cyclic voltammetry but not for preparative scale experiments. The couple has potentials of +0.69 and +0.72 V *vs*. nhe in acetonitrile and dimethylformamide respectively [10].

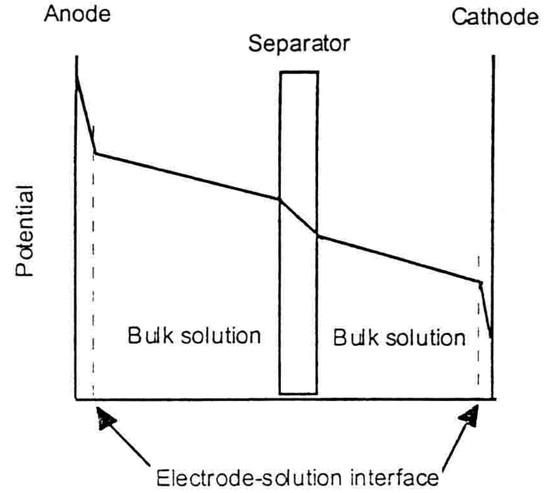

Figure 1.2. Distribution of potential across a working electrochemical cell. The potential drop across the working electrode-solution interface drives the cell reaction.

There is a potential drop V across the solution between the layer around the working electrode and the tip of the reference probe. This is related to the separation distance d by Equation 1.3 where *i* is the current flowing through the cell and κ is the specific conductivity of the electrolyte. The reference electrode probe is placed as close as possible to the working electrode in order to minimise this voltage drop. The voltage drop is termed the iR-drop and in preparative electrochemistry using currents of 10^{-1} A, or more, it is not negligible [11].

$$V = \frac{i}{\kappa} d \qquad \text{Eq.1.3}$$

TABLE 1.1

Potentials of some reference electrodes relative to either the standard hydrogen electrode or the saturated calomel electrode. Further data in ref. [17].

Electrochemical cell	Potential / V	Ref.
$(Pt)/H_2, H_3O^+$ (a = 1) $\parallel$ KCl (satd.) / AgCl (satd.) /Ag	0.199	[12]
$(Pt)/H_2, H_3O^+$ (a = 1) $\parallel$ KCl (1.0 M) / Hg_2Cl_2 (satd.) / Hg	0.283	[12]
$(Pt)/H_2, H_3O^+$ (a = 1) $\parallel$ KCl (satd.) / Hg_2Cl_2 (satd.) / Hg	0.244	[12]
Aqueous sce $\parallel$ 0.1 M $NaClO_4$ in CH_3CN $\parallel$ 0.01 M $AgNO_3$ in CH_3CN / Ag	0.253	[13]
Aqueous sce $\parallel$ 0.1 M Et_4NClO_4 $\parallel$ Me_2CHO NaCl(satd.), $CdCl_2$ (satd) / Cd, Hg	-0.737	[14]
Aqueous sce $\parallel$ 0.1 M Bu_4I in 0.1 M Bu_4NI in Me_2NCHO / AgI (sat.) / Ag	-0.32	[15]
Aqueous sce $\parallel$ 0.1 M Et_4NI in Me_2CHO / AgI (satd.) / Ag	-0.638	[16]

The overall rate of an electrochemical reaction is measured by the current flow through the cell. In order to make valid comparisons between different electrode systems, this current is expressed as current density, *j*, the current per unit area of electrode surface. The current density that can be achieved in an electrochemical cell is dependent on many factors. The rate constant of the initial electron transfer step depends on the working electrode potential. The concentration of the substrate maintained at the electrode surface depends on the diffusion coefficient, which is temperature dependent, and the thickness of the diffusion layer, which depends on the stirring rate. Under experimental conditions, current density is dependent on substrate concentration, stirring rate, temperature and electrode potential.

Conditions of constant potential are frequently employed in laboratory scale experiments. In these experiments, the current through the cell falls with time due to depletion of the substrate. Under conditions of constant diffusion layer thickness, the current i_t at time t is given by Equation 1.4 [17] where D is the diffusion coefficient of the active species, A is the electrode area, V is the solution volume and δ is the diffusion layer thickness. Controlled potential bulk electrolysis resembles a first-order reaction in that the current decays exponentially with time, eventually reaching a background level.

$$i_t = i_0 \exp\left(-\frac{DA}{V\delta} t\right) \qquad \text{Eq.1.4}$$

Chemical yields from an electrochemical reaction are expressed in the usual way based on the starting material consumed. Current efficiency is determined from the ratio of Coulombs consumed in forming the product to the total number of Coulombs passed through the cell. Side reactions, particularly oxygen or hydrogen evolution, decrease the current efficiency.

On a large scale, it is more difficult to maintain constant electrode potential and conditions of constant current are employed. Under these conditions, as the concentration of the substrate falls, the voltage across the cell rises in order to maintain the imposed reaction rate at the electrode surface. This causes a drop in current efficiency towards the end of the reaction, since as the working electrode potential rises, either oxygen or hydrogen evolution becomes significant.

Electrochemical reactions require a solvent and electrolyte system giving as small a resistance as possible between the anode and cathode. Protic solvents used include alcohol-water and dioxan-water mixtures and the electrolyte may be any soluble salt, an acid or a base. During reaction, protons are consumed at the cathode and generated at the anode so that a buffer will be required to maintain a constant pH. Aprotic solvents are employed for many reactions [18], the most commonly used being acetonitrile for oxidations and dimethylformamide or acetonitrile for reductions. In aprotic solvents, the supporting electrolyte is generally a tetra-alkylammonium fluoroborate or perchlorate [19]. The use of perchlorate salts is discouraged because of the possibility that traces of perchlorate in the final product may cause an explosion.

The designs of some early electrochemical cells for industrial use were based on the beaker-type laboratory cell. One improvement to mass transport conditions was to rotate the working electrode, which decreases the thickness of the diffusion layer [20]. As small a gap as is practical between the working electrode and the counter

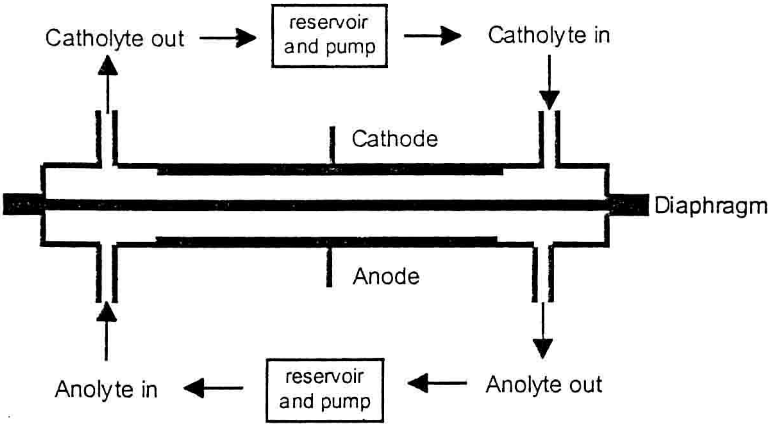

Figure 1.3. The narrow gap electrochemical cell. For large-scale work, several cells are connected in parallel from the same reservoirs.

electrode is necessary to decrease the voltage drop across the whole cell and reduce heating of the electrolyte due to passage of current. Cells with the basic design shown schematically in Figure 1.3 are available commercially. Each compartment contains only a small volume of electrolyte so both the anode and cathode compartments are connected to larger volumes of solutions, which are pumped continuously around the cell. Electrolyte flow also decreases the thickness of the diffusion layer. Cells can be connected in parallel to give a large overall electrode area. Starting from this basic design concept, many cells have been constructed to improve current efficiency in a particular reaction and some of these are described later.

Anode and Cathode Materials

Working electrode materials are selected to provide good electron transfer properties towards the substrate while showing high activation energy for electron transfer in the principal competing reaction. The most significant competing reactions in the presence of water are evolution of oxygen at the anode and hydrogen at the cathode. Accessible electrode potential ranges for some working electrode, solvent combinations are given in Table 1.2. The oxygen and hydrogen evolution reactions occur in several steps involving both bond cleavage and bond formation processes. At many electrode surfaces each reaction requires a potential substantially removed from the equilibrium reaction potential to drive the process at a significant rate. This difference between a working potential and the equilibrium potential is called the overpotential.

TABLE 1.2
Useable electrode potential range for some electrode-solution combinations

Electrode material	Solvent	Electrolyte $LiClO_4$		Electrolyte Et_4NClO_4	
		Cathodic V *vs.* sce	Anodic V *vs.* sce	Cathodic V *vs.* sce	Anodic V *vs.* sce
Pt	H_2O	-1.1	+1.8	-1.1	+1.8
Pt	CH_3CN	-3.2	+2.7	-3.0	+2.7
Pt	Me_2CHO	-3.3	+1.5	-2.7	+1.8
Hg	H_2O	-2.3	+0.4	-2.7	+0.4
Hg	CH_3CN	-1.8	+0.8	-2.8	+0.8
Hg	Me_2CHO	-1.8	+0.4	-2.8	+0.2
C	H_2O	-1.0	+1.0	-2.8	

Smooth platinum, lead dioxide and graphite are anode materials commonly used in electrooxidation processes. All show large overpotentials for oxygen evolution in aqueous solution. Platinum coated titanium is available as an alternative to sheet platinum metal. Stable surfaces of lead dioxide are prepared by electrolytic oxidation of sheet lead in dilute sulphuric acid and can be used in the presence of sulphuric acid as electrolyte. Lead dioxide may also be electroplated onto titanium anodes from lead(II) nitrate solution to form a non-porous layer which can then be used in other electrolyte solutions [21].

Mercury, lead, cadmium and graphite are commonly used cathode materials showing large overpotentials for hydrogen evolution in aqueous solution. Liquid mercury exhibits a clean surface and is very convenient for small-scale laboratory use. Sheet lead has to be degreased and the surface can be activated in an electrochemical oxidation, reduction cycle [3, 22]. Cadmium surfaces are conveniently prepared by plating from aqueous cadmium(II) solutions on a steel cathode.

Synthetic graphite is available in many forms for use as electrode material. A polycrystalline pyrolytic graphite is prepared by thermal decomposition of hydrocarbon vapours on a hot surface. It has the carbon ring planes oriented to a high degree parallel with the original surface for deposition. Less well oriented graphites with the crystalline phase embedded in a non-porous but amorphous carbon are prepared by the pyrolysis of carbonaceous materials. This type of material includes carbon-fibre, which is woven into a carbon felt, and a non-porous glassy carbon. Glassy carbon can be fabricated into plate form or as a solidified foam, termed reticulated carbon, with a large surface area and allowing free flow of electrolyte. Reticulated carbon and carbon felt allow electrochemical transformation at low current density to be completed on a shorter time scale because of their large surface area. This is important when further chemical reactions of the product can occur during the electrochemical process [23].

Surfaces of synthetic diamond, doped with boron, are electrically conducting and show promise as very inert electrode materials [24]. Boron carbide (B_4C) has been used as an anode material but this cannot be conveniently prepared with a large surface area [25].

Platinum and carbon are frequently used as counter electrode materials for both anode and cathode. Platinum is resistant to corrosion while carbon is cheap and can be discarded after use. Nickel is a suitable counter cathode material in aqueous solution because of the low overpotential for hydrogen evolution. Titanium coated with platinum and then over coated with ruthenium dioxide is a stable counter anode material with a low overpotential for oxygen evolution.

The separator is often the weakest component in any electrochemical cell. There are also difficulties in employing ion-exchange diaphragms in aprotic media. Particularly with large industrial cells, it is advantageous to devise reaction conditions that allow the use of an undivided cell. One solution to these problems for an electrochemical reduction process employs a sacrificial anode of magnesium, aluminium or zinc in a single compartment cell when the most favoured anode reaction becomes oxidation of the metal to an anion [26, 27]. Zinc and magnesium ions formed in this way are beneficial to cathodic reactions which involve alkyl and aryl halides (p. 134) [28, 29]. On a laboratory scale, the sacrificial anode is a rod of metal concentric with a cylindrical working cathode. Tetraethylammonium fluoride can be added to the electrolyte to precipitate magnesium ions as the fluoride [30]. A V-shaped narrow gap cell (Figure 1.4) has been devised for use on an industrial scale using a magnesium sacrificial anode which fits into a stainless steel working cathode [31]. The combination of a working magnesium cathode and a sacrificial magnesium anode is used for the reduction of functional groups such as carboxylic

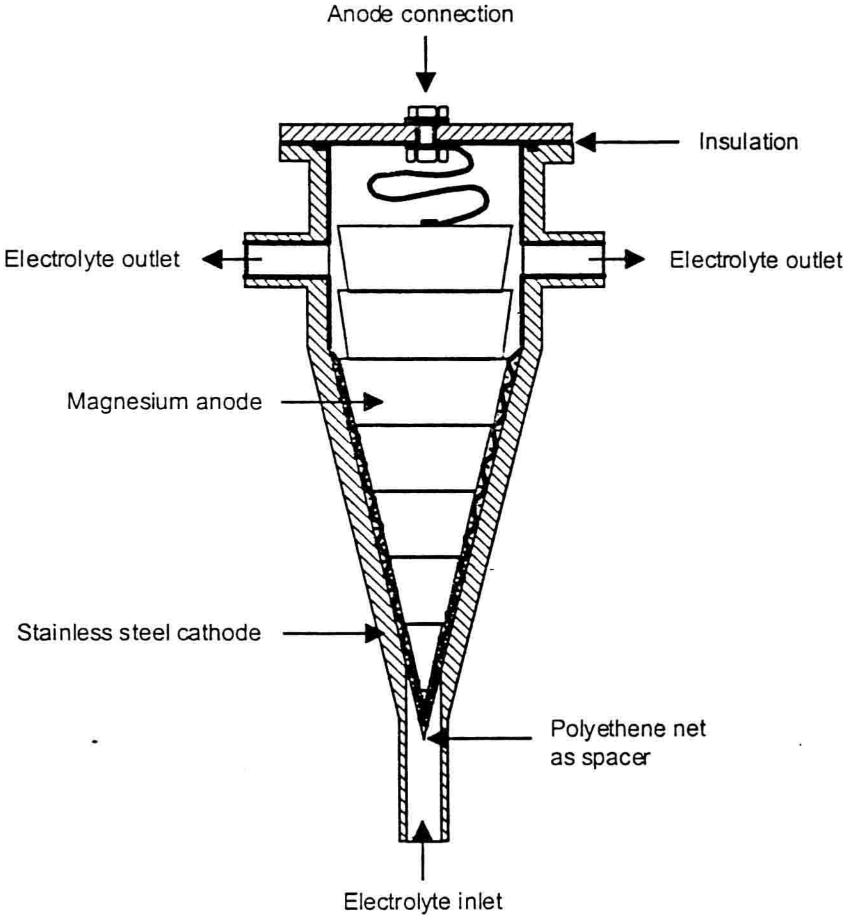

Figure 1.4. An undivided electrochemical cell fitted with a sacrificial magnesium anode. Diagram adapted from Ref. [31].