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Electrode Materials for Electrosynthesis

A. MOTTRAM COUPER

ICI Chemicals and Polymers Ltd., P.O. Box 8, The Heath, Runcorn, Cheshire WA7 4QD, England

DEREK PLETCHER*

Department of Chemistry, The University, Southampton SO9 5NH, England

FRANK C. WALSH

Department of Chemistry, Portsmouth Polytechnic, St Michael's Building, White Swan Road, Portsmouth PO1 2DT, England

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I. Introduction

A feature of the 1980s has been the resurgence of electrolysis as a technology for the manufacture of organic and inorganic chemicals. A major factor contributing to this success has been a change in goals. In contrast to 20 years ago, when the emphasis was on the design of processes for the manufacture of very large tonnage chemicals, it is now generally agreed that the major impact of electrosynthetic processes will be in the production of fine and specialist chemicals. Hence, in most cases, the target for an electrosynthetic process is now most likely to be a product required on any scale from 1 to 10 000 tons per year.

The design of such electrosynthetic processes requires a different approach. It is an economic fact of life that small processes are very unlikely to warrant the development of cells, electrode materials, or membranes specifically for one process. Therefore, the process designer must select the cell and its components from those that are already available but probably designed and optimized for other purposes.

Hence in this review the objective is to discuss the selection of electrode materials for small-scale electrosynthetic processes. It is not the intention to discuss in detail systems such as chlor-alkali and water electrolysis; there are already many reviews[1-10] describing the development of the highly optimized materials now widely used and justified by the scale and number of commercial plants. On the other hand, some discussion of electrode materials for chlorine, hydrogen, and oxygen electrodes is inevitable since there is much experience relevant to the topic of this review. Moreover, it has to be emphasized that all cells contain two electrodes and in electrosynthesis it is essential to define counter electrode chemistry compatible with the objectives of the process. Common strategies involve "minimum damage" to the chemistry of the system or using the counter electrode to maintain a constant electrolyte pH. In this context hydrogen evolution, oxygen evolution/reduction, and chlorine evolution are important reactions. They are, however, required to occur in a broad range of conditions dictated by the chemistry of the process of interest rather than conditions selected only for the optimum performance of the hydrogen, oxygen, or chlorine electrode. On the

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A. Mottram Couper was educated at the University of Oxford, receiving his Ph.D. in 1974. Subsequently, he joined what is now ICI Chemicals and Polymers Ltd. and has since been involved in the development and evaluation of novel chlor-alkali technology, the development of electrode-coating technology, and the study of electrosynthetic processes.

Derek Pletcher attended the University of Sheffield, where he completed his Ph.D. in 1967. Then he immediately joined the Electrochemistry Goup at the University of Southampton, where he has held a number of positions; currently he is a Reader in Chemistry. His research interests include electrode kinetics, electrosynthesis, microelectrodes, electroplating, and electrode materials.

Frank C. Walsh obtained degrees from Portsmouth Polytechnic and the University of Loughborough (Ph.D., 1981). Since, he has held industrial positions and a lectureship at the University of Strathclyde; he is now a Senior Lecturer at Portsmouth Polytechnic. His research interests include cell design, mass transport characterization, corrosion, metal finishing, and the study of the electrode/electrolyte interface using synchrotron radiation. As a consultant engineer, he has also had extensive experience of scale up of electrochemical processes from the laboratory via pilot scale reactors to full, industrial-scale operation.

other hand, factors such as overpotential and selectivity may be much less important; hence different materials may be appropriate. Therefore, these reactions will be discussed, but only from the viewpoint of the designer of a small-scale electrosynthetic process.

It must also be emphasized that the choice of electrodes for laboratory experiments is often a poor guide to the engineer seeking to design a pilot plant or industrial process. Perusal of the extensive literature describing laboratory electrolyses indicates that a very wide range of materials has been used for both anodes and cathodes as well as both working and counter electrodes, although mercury, carbon, and platinum hold a predominant position. The engineer will want to achieve comparable, or better, performance with affordable but practical materials. Moreover, his choice must take account of cost, availability, stability, and performance over a long period of time, fears over toxicity, and compatibility with the electrolyzer design.

At the outset, it should be recognized that there are two limiting types of electrode reaction. In the first, the electrode acts merely as a sink or source of electrons, and the products, mechanism, and kinetics of the electrode reaction might be expected to be essentially independent of electrode material. Commonly, this type of electrode reaction will be operated under diffusion control and then there is little advantage in preparing microroughened electrode surfaces to enhance area (the current will be proportional to the geometric area). In the second type of electrode reaction, the surface acts as a catalyst and the mechanism of the electrode process involves specific interactions between the surface and solution-phase species. The products and the kinetics of the electrode reactions will be highly variable with the choice of electrode material, and even small changes in composition may be significant. Moreover, it is likely that the current will be proportional to the real surface area. Hence, there is a substantial technology in the manufacture of dispersed, "electrocatalytic" materials.

In this review the term "electrode material" will be used to include coatings as well as bulk metals/carbon. For the former, it will also be necessary to consider the influence of the substrate for the coating and the coating procedure on the performance of the overall electrode.

It should also be understood that the selectivity and other performance measures for electrosynthetic reactions depend on many experimental parameters in addition to the choice of electrode material. These will include the electrode potential (or current density), the concentration of electroactive species, solvent, electrolyte, pH, additives, temperature, mass transport, and cell design. Unfortunately, it is often difficult to separate the influence of these several parameters and, in many oft-quoted examples of the effect of electrode material (e.g., nitrobenzene reduction), the changes in products are clearly the result of variations in several parameters. In this review, we have tried hard to pick examples where electrode material is the major factor.

This review is divided into several sections that will consider (i) the properties of importance in determining the behavior of electrode materials, (ii) the ways in which the choice of electrode materials determines the performance of the electrolytic reactor, (iii) the mechanisms by which the anode/cathode determine product selectivity, (iv) available electrode materials and the choice in present processes, and (v) new ideas for the development of better electrodes. The reader is referred to a number of earlier reviews that are relevant to the above topics.[11-20]

II. Important Properties of Electrode Materials

A. General Considerations

The complexity of electrode behavior and our lack of detailed insight make it impossible to select the optimum electrode for a given process on a theoretical basis. Instead, an empirical approach must be used; the initial selection is based on process experience, and this is then tested and refined during an extensive development program. Indeed, it is very difficult to predict the success of an electrode material or to define its lifetime without extended studies under realistic process conditions. Accelerated testing is rarely satisfactory except to indicate catastrophic failure.

Nevertheless, there are some general guidelines to assist the choice of an electrode material:

(i) Physical stability: the electrode material must have adequate mechanical strength, must not be prone to erosion by the electrolyte, reactants, or products, and must be resistant to cracking.

(ii) Chemical stability: the electrode material must be resistant to corrosion, unwanted oxide or hydride formation, and the deposition of inhibiting organic films under all conditions (e.g., potential and temperature) experienced by the electrode.

(iii) Suitable physical form: it must be possible to fabricate the material into the form demanded by the reactor design, to facilitate sound electrical connections, and to permit easy installation and replacement at a variety of scales. The shape and design of the electrode may take into account the separation of products, including the disengagement of gases or solids.

(iv) Rate and product selectivity: the electrode material must support the desired reaction and, in some cases, significant electrocatalytic properties are essential. The electrode material must promote the desired chemical change (maybe at a high rate at a low overpotential) while inhibiting all competing chemical changes.

(v) Electrical conductivity: this must be reasonably high throughout the electrode system including the current feeder, electrode connections, and the entire electrode surface exposed to the electrolyte. Only in this fashion is it possible to obtain a uniform current and potential distribution as well as to avoid voltage losses leading to energy inefficiencies.

(vi) Cost/lifetime: a reasonable and reproducible performance including a lifetime probably extending over several years must be achieved for an acceptable initial investment.

It is important to note that the choice of working and counter electrodes cannot be made independently since the chemistry at each has consequences to the solution composition throughout the cell. Indeed, the selection of electrode material and its form must be an integrated decision within the prospective of the cell and process design (see section III). In some cases (e.g., the manufacture of pharmaceutical products), the electrodes and their compounds must have a low toxicity.

TABLE I. Selected Physical Properties of Metals Relevant to the Performance and Fabrication of Electrodes.[a]

	density/ g cm^{-3}	linear expansion/ 10^{-6} K^{-1}	melting point/ K	thermal expansion/ W cm^{-1} K^{-1}	electrical resistivity/ 10^{-6} ohm cm
Al	2.70	23.0	933	2.38	2.45
Cd	8.64	31.5	594	1.00	6.80
Cu	8.92	16.7	1356	1.00	1.56
Au	18.88	14.0	1337	3.10	2.04
Ir	22.42	6.5	2683	1.48	4.70
Fe	7.86	11.7	1808	0.80	8.90
Pb	11.34	28.9	601	0.38	19.00
Ni	8.90	12.8	1728	0.91	6.10
Nb	8.57	7.1	2740	0.52	15.20
Pt	21.45	8.9	2045	0.73	9.80
Ag	10.50	19.2	1235	4.18	1.50
Ta	16.60	6.5	3269	0.58	12.60
Sn	7.28	21.2	505	0.64	1.50
Ti	4.50	8.5	1933	0.20	43.10
Zn	7.14	29.7	693	1.13	5.50
Hg	13.59	180.0	234		96.0

[a] Compiled from refs 21 and 22.

B. Physical Properties

The correct combination of physical properties is essential to the successful fabrication and incorporation of the electrode into the reactor design. Some selected physical properties are shown in Table I, which largely considers pure metals. Of course, in practice, electrodes made from pure metals are uncommon; alloying is used to improve both mechanical and chemical properties while, increasingly, the electrode material will be a coating of a metal, an oxide ceramic, or mixtures on a substrate metal.

In general, the electrode and its associated current feeder should be light to aid cell construction and handling operations. Electrical resistivity is a key property since it determines the magnitude of voltage drops, which both contribute to power costs and also lead to an uneven potential distribution.[23] Indeed, in order to avoid unacceptable voltage drops, only the most conducting materials can be used as massive monopolar electrodes or current collectors (when the current path within the cell may be 1 m). Even materials such as carbon and titanium impose restrictions on cell design. Either the electrode thickness must be large, the current path must be short, or the use of a conductive backing plate, inlaid bars of more conducting material or multiple electrode connections, must be considered to avoid unacceptable voltage drops. Higher resistivity material may be used in bipolar electrodes where the current path is short and, more commonly, as coatings or cladding on a low-resistivity metal (see Figure 1). In the case of current feeders, a high thermal conductivity helps to dissipate heat to the surroundings, thereby lowering the effective resistivity (electrical resistivity generally increases with temperature).

Industrial cellhouses utilize solid aluminum busbars, perhaps copper cored, copper interelectrode connectors, and copper-cored, flexible cables. The passive film on the aluminum busbars exposed to the atmosphere helps to avoid massive corrosion but can lead to high-resistance connections if precautions are not taken. For rotating electrodes, Ag- or Cu-filled graphite brushes have largely replaced mercury contacts because of the health hazard due to Hg vapor.

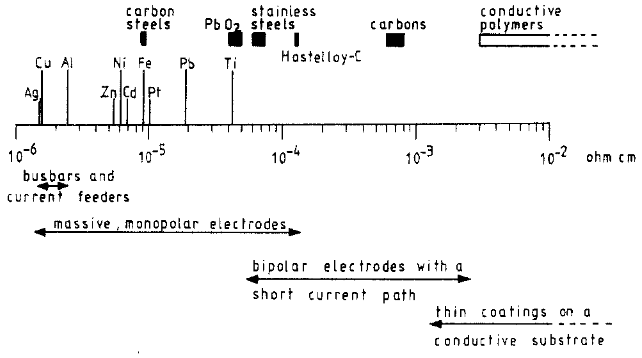


Figure 1. Typical electrical resistivity values for electrode materials, showing the approximate range of suitability for various types of electrodes.

Noble metals such as gold and the platinum metals are usually employed as thin coatings due to their inherent cost. The substrate must have a reasonable chemical resistance and be capable of fabrication in the many forms demanded by modern cell designs. Despite its rather high electrical resistivity, titanium is a common choice as substrate not only for precious metals but also for the various precious metal oxide anode coatings (e.g., RuO_2- and IrO_2-based coatings such as DSA and METCOTE); its ability to passivate strongly under most anodic conditions minimizes its corrosion if any faults appear in the coating. The use of titanium itself as an electrode material is, however, severely restricted by both these poorly conducting anodic films and its tendency to form hydrides when hydrogen is evolved. Moreover, even when used as substrate, its resistance requires the use of titanium in relatively thick sections and/or the use of copper cores.

The linear expansion may become important if dissimilar materials are joined in the production of an electrode structure (e.g., by coating, cladding, or fastening techniques). Thermal cycling is particularly likely during start up and shut down and it can lead to excessive movement and, hence, mechanical stress or sealing problems. The melting point is important during electrode fabrication. For example, it is easy to make lead alloy electrodes in a wide range of forms by casting techniques. Mechanical properties determine whether the electrodes can withstand compression (e.g., in certain filter press designs) or may be fabricated by pressing or machining from readily available forms.

Attention must also be paid to the electrode connections, which depend on the material, its form, and properties. For example, lead electrodes may be cast onto a steel backplate or dry connections may be made by soldering. With titanium, specially designed fasteners must be used, while poor welds to steel are a common source of high resistances. The low tensile strength of many carbons causes difficulties in making sound electrical contacts and hence limits the cell designs in which they may be used. In some filter press cell designs, aluminum backing plates are used to distribute the current more evenly.

C. Stability

The need for a suitable combination of mechanical, physical, and chemical stability has already been stressed. It is important to recognize that the stability must be maintained under all conditions met by the electrode material. This includes the normal operating conditions of the cell (e.g., including temperatures and current densities) but also atypical conditions. For example, the cell may be overdriven at a very high current density to achieve production demands. Also, the cell may be switched out for maintenance or to reduce production, and then the electrode will experience zero-current conditions. Depending on the nature of the synthesis and the cell design, it is possible for the electrodes to experience shorting or current reversal immediately after switch out. Start up, shut down, and dramatic changes to operating conditions may be particularly adverse to electrode performance. Clearly, such conditions must be included in the electrode testing and selection program.

The thermodynamic stability of pure metals has been widely discussed in terms of Pourbaix diagrams.[24,25] These are very useful summaries but it is important to recognize that they take no account of the kinetics of either the anode (metal dissolution) or cathode (hydrogen evolution, oxygen reduction, etc.) reactions or passivation and do not consider nonaqueous solvents, the effects of alloying elements, or complexing agents in solution. In practice, there is no substitute for a detailed study of the corrosion of the electrode materials under all conditions to be met during cell operation. On the other hand, an understanding of the principles of corrosion[4] can be very advantageous. For example, in the new Monsanto process for the conversion of acrylonitrile to adiponitrile,[26] the addition of borax (2%) and EDTA (0.5%) aims to reduce corrosion of the steel anode while encouraging slow dissolution of the cadmium cathode in order to maintain an unpoisoned cathode surface.

D. Surface Chemistry and Adsorption

The rate and selectivity of many electrode reactions depend on the adsorption of reactant, products, intermediates, or even species not directly involved in the chemical change (e.g., solvent, ions, or additives). The forces leading to adsorption and the strength of these interactions are very varied and will be discussed further in later sections. At the present time, however, it is important to note that the ability to adsorb species is central to the behavior of electrodes and hence is a strong factor determining their performance. Although adsorption depends on the detailed composition of the electrolyte solution, the properties of the electrode material are a dominant factor determining their importance.

Similarly, the surface chemistry of materials is important in determining electrode performance. In electrolyte solutions, the imposition of a potential can lead to surface oxides, hydrides, adsorbed hydrogen or hydroxyl radicals, intercalation of anions or cations, etc. All such surface chemistry can be catastrophic but can also be used to advantage in particular circumstances. Examples are given elsewhere in this review.

E. Electrocatalysis

A central theme in electrode design is the advantage to be gained from driving the desired reaction at a high rate (i.e., a high current density) with a low overpotential. In practice, however, it is equally important that the electrode material inhibits all competing reactions. For example, at a chlor-alkali anode the objective is to catalyze chlorine evolution while inhibiting oxygen evolution, the thermodynamically preferred reaction. The task of efficient electrocatalyst design is therefore the tailoring of a material to have a high exchange current density for the desired reaction and a low value for all other reactions. In general, adsorbed species play a key role in the mechanism of electrocatalysis. For example, it is universally accepted that the adsorbed hydrogen atom is the important intermediate in the catalysis of the hydrogen evolution reaction[3,4,26-28] (see below).

Usually, electrocatalysts are used in the form of a high surface area coating produced by techniques such as electrodeposition, spray coating, sputtering, thermal decomposition of sprayed solutions, etc. Since they are used as coatings, stability to corrosion and erosion is essential to achieve long lifetimes. On the other hand, relatively low conductivity materials may be considered if the substrate has an adequate electrical conductivity.

F. Economic Factors

The choice of electrode material is, of course, governed by economics. An improved electrode material or coating will only find application if the cost advantage from extended lifetime, reduced energy consumption, and/or improved selectivity outweighs the increased initial investment. Furthermore, the considerable cost of research and development associated with the development and implementation of a new electrode material will only be undertaken when a sufficient return is envisaged. This is only likely for electrodes that have outlets in several processes or for electrodes for high-tonnage processes with good future prospects.

III. The Influence of Electrode Material on Process Performance

The objective of this section is to discuss the ways in which the choice of electrode material influences the design of electrochemical reactors and process performance. For more general discussion of figures of merit[4,29] and electrolytic cell design[4,30-38] the reader is referred elsewhere. The following figures of merit generally need to be considered when electrode materials are selected:

A. Energy Consumption

The specific energy consumption (i.e., the energy consumption per unit weight of product) should be minimized in order to minimize the power costs. In general, the total power requirement has contributions for both electrolysis and movement of either the solution or the electrode. The design of electrodes and cell has an important role in reducing each of these components. Thus, a very open flow-through porous electrode will have a low pressure drop associated with it, giving rise to modest pumping costs and facilitating reactor sealing. A high surface area electrode which acts itself as a turbulence promoter (e.g., a bed electrode) will give rise to a moderately high mass transfer coefficient and active area without the need for high flow rates through the cell; the pumping cost will again be moderately low.

The direct electrolytic power is minimized by (a) obtaining a current efficiency approaching 1.0 and (b)

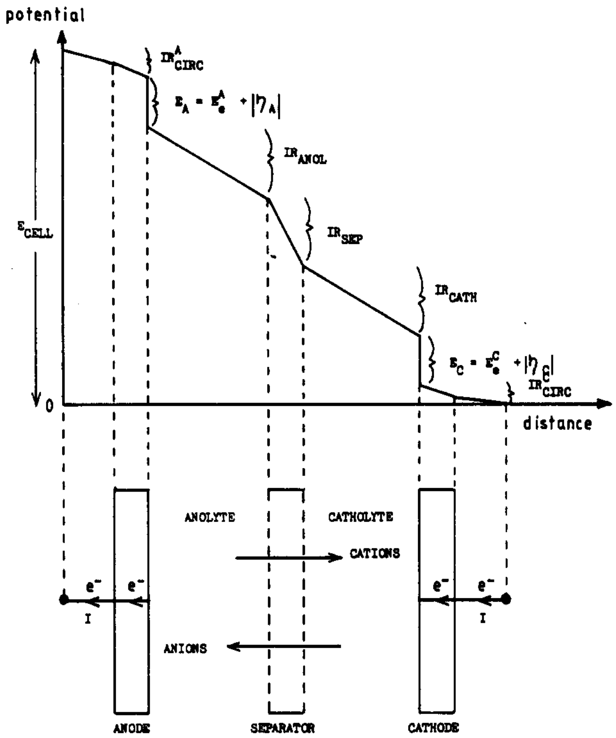


Figure 2. Schematic representation of the voltage components in a divided cell, illustrated by a plot of potential as a function of the distance in the interelectrode direction. The overall cell voltage, E_{cell}, is $E_{cell} = E_e{}^C - E_e{}^A - |\eta_C| - |\eta_A| - IR^C{}_{circ} - IR^A{}_{circ} - IR_{cath} - IR_{anol} - IR_{sep}$, where $E_e{}^C$ = equilibrium cathode potential, $E_e{}^A$ = equilibrium anode potential, η_C = cathode overpotential, η_A = anode overpotential, I = cell current, $R^C{}_{circ}$ = resistance of the current feeder and cathode, $R^A{}_{circ}$ = resistance of the current feeder and anode, R_{cath} = resistance of the catholyte, R_{anol} = resistance of the anolyte, and R_{sep} = resistance of the separator.

minimizing the cell voltage. It is therefore important to select the electrode material and operating conditions so as to maintain a high current efficiency. This also assists the operation of the process by reducing the amount of product purification that is necessary and/or byproducts that must be handled.

The cell voltage is a function of (a) the reversible cell voltage, (b) the overpotentials at the two electrodes, and (c) ohmic drops in the electrolyte, the electrodes, busbars etc., and any separator in the cell. The voltage distribution through a cell is shown schematically in Figure 2. Again, the maintenance of a low cell voltage demands attention to the design of both electrodes and cell. Where possible, the following features should be included:

(i) The counter electrode reaction should be chosen so as to minimize the reversible cell voltage. This requires the availability of a suitably stable electrode material.

(ii) The overpotentials at both electrodes should be minimized by the use of electrocatalysts.

(iii) The electrodes, current feeders, and connectors should be made from highly conducting materials to lower ohmic drops.

(iv) The electrodes should facilitate low *IR* drop in the electrolyte by, for example, allowing efficient gas disengagement and passage out of the interelectrode gap. Meshes as well as louvred and lantern blade electrodes can be used.

(v) Electrode and cell design should allow a small interelectrode or electrode–membrane gap. In the limit the electrode may touch the membrane as in zero-gap or solid polymer electrolyte cells.

(vi) A separator should be avoided by suitable selection of the counter electrode chemistry or, if essential, a thin, conductive membrane should be used.

B. Current Efficiency

Current efficiency is the fraction of the total charge passed that is used in the formation of the desired product. This can be a strong function of electrode material, e.g., because of differences in the rate of hydrogen evolution as a competing reaction. Competing reactions can also lead to the corrosion and/or erosion of the electrode material as well changes to the electrode (e.g., by formation of a hydroxide or oxide or the deposition of another metal onto the surface).

C. Material Yield

This is the fraction of the starting material that is converted into the desired product. This is also dependent on electrode material in many cases. Values less than one indicate byproducts and hence perhaps the need to introduce additional purification steps that inevitably increase the complexity of the overall process and, therefore, costs.

D. Space–Time Yield

One of the most valuable statements of reactor performance is the space–time yield or weight of product per unit time per unit volume of reactor. It is determined by the current density, the current efficiency, and the area of electrode per unit volume of cell, all dependent on the electrode material and its form. Commonly, the cell is operated in conditions where the electrode reaction is mass transport controlled (especially when a high fractional conversion is desirable or when the concentration of reactant is limited by solubility or process considerations[39,40]). Then the current density is determined by the concentration of reactant and the mass transport conditions.[4,39,40] The latter is therefore frequently enhanced by the use of high flow rates, turbulence promoters, and/or electrode movement.

The current is proportional to the active electrode area in the cell. A compact cell design requires a high area per unit cell volume. This suggests the use of a three-dimensional electrode but such electrodes make it difficult to maintain a uniform fluid flow and electrode potential, i.e., to control the reaction environment. Hence, the use of porous, flow-through electrodes often involves a trade-off between enhanced electrode area and material yield and/or current efficiency.

E. Ease of Product Isolation

Many industrial electrosyntheses benefit from clever process design to reduce the number of steps in the product isolation and purification. This can be critical to the process economics.

F. Other Factors

Of course, other factors are important in the design of electrodes and cells. These include cost, safety, ease of maintenance, and convenience to use; see section IV. It is also essential that the performance of the electrodes is maintained throughout the projected operating life of the cell, maybe several years. Examples of problems that frequently arise include (a) deposition onto cathode surfaces of hydrogen evolution catalysts due to trace transition metal ions in the electrolyte and (b) poisoning of PbO_2 anodes by organic molecules leading to enhanced corrosion as well as oxygen evolution.

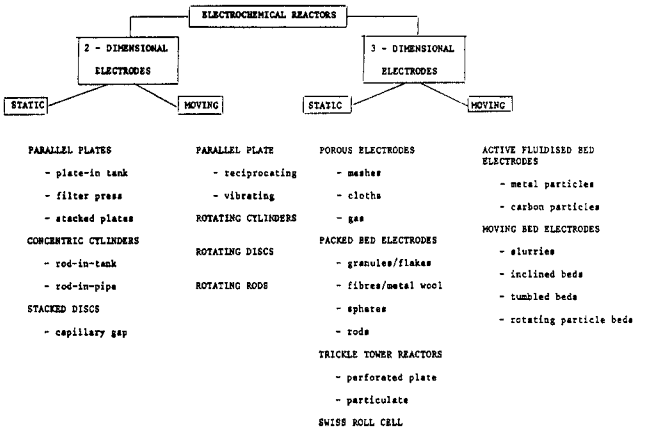


Figure 3. Classification of electrochemical reactors in terms of the electrode geometry and motion.[40]

IV. Cell Design

The design of an electrolytic reactor is predominantly determined by the form and properties of the two electrodes; this is shown by the classification of cells in Figure 3. Many interrelated factors must be considered in the design and commissioning of an electrosynthesis reactor;[4,36,40,41] the following guidelines apply: (i) moderate cost, achieved by a simple cell design that utilizes available components; (ii) convenience and reliability in operation, including ease of electrode replacement; (iii) operation at a low cell voltage; (iv) integration into the overall process and capability for scale up; (v) reasonably uniform potential, current, and flow distribution to achieve a high selectivity at an acceptable production rate; (vi) high active electrode area per unit volume of reactor and high mass transfer coefficient to provide a compact, high-performance reactor; (vii) adequate heat transfer and low pumping requirement; and (viii) simple reactor design to achieve these goals—reactor components should be minimized using an elegant engineering approach.

Inevitably, not all these goals will be achieved and the electrochemical engineer will seek the best compromise. Particularly, the balance between a simple reactor and a more complex design with enhanced performance and marketability must be struck.

For example, the advantages of porous, three-dimensional electrodes have already been mentioned. Many forms of electrode may be used in such cells; these include continuous arrays of meshes, nets, screens, woven cloths, foams, or expanded metal and particulate beds of spheroidal particles, granules, fibers, or flakes. Although such cells have largely been discussed in the context of metal recovery, the combination of good mass transfer coefficient and high active electrode area[39] makes them obvious candidates for synthesis, particularly when the synthesis requires a low current density.

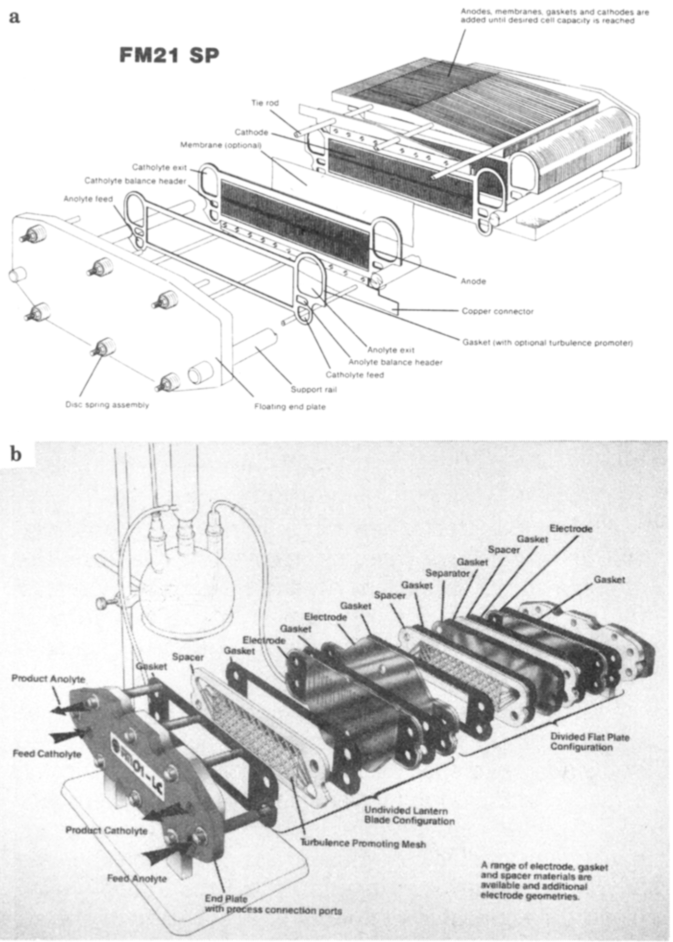


Figure 4. Examples of commercially available filterpress cells using the parallel-plate electrode geometry. (a) The FM21 SP cell is used for pilot- and full-scale electrosynthesis. It utilizes up to 60 electrode pairs; each electrode has an approximate projected area of 21 dm^2. (b) The FM01-LC cell is a general purpose cell for laboratory use; there are up to 10 electrode pairs, the projected area of each electrode being approximately 65 cm^2.

Problems with three-dimensional electrodes arise from the nonuniform potential, current, and flow distribution, plugging by solid products, gas blinding, a high pressure drop, and difficulties in maintaining good current feeder connections.

In contrast, parallel-plate cells are less expensive and easier to operate. Their properties include (i) uniform current and potential distribution, (ii) a wide variety of available electrode and cell construction materials, (iii) good control over flow with simple introduction of turbulence through plastic net turbulence promoters or profiled electrodes,[42,43] and (iv) ease of scale up using standard frames and a modular assembly.

A significant development in recent years has been the availability of cell packages from several companies. Figure 4 shows modern designs of a plate and frame cell developed by ICI,[4,44] and other suppliers include Electrocell AB,[45] Reilly Tar and Chemical,[46] and Electrocatalytic.[47] Not surprisingly, a growing trend is to seek to incorporate three-dimensional electrodes into parallel-plate cells and, hence, to gain the advantages of both strategies. One example of a three-dimensional material that fits well into parallel-plate reactors is reticulated metals,[48-50] metalized plastics,[51] and carbon.[52-54] These materials have a high-porosity, open-pore, continuous honeycomb structure and they are currently being characterized for electrochemical reactors.[48,52-55]

In cases where electrode connections prove troublesome or the ratio or electrode resistivity/electrolyte resistivity is low, it is often advantageous to operate the cell in the bipolar mode. This is possible with both filter press cells and capillary gap designs.[56-59] In bipolar cells, the construction is simplest when the anode and cathode are made from the same material. Otherwise, dissimilar materials may be formulated into a single component by a range of techniques. These include (a) electrodeposition (e.g., Cd on steel, PbO_2 on Ti or C, Pt on Ti), (b) hot dip coating (Zn or Sn on Fe), (c) lamination using fasteners, adhesive, spot welding, etc., (d) flame spraying, (e) sputtering or vacuum evaporation, and (f) chemical deposition (e.g., via thermal decomposition as for RuO_2-coated titanium), which may be followed by sintering.

V. The Influence of Electrode Material on the Mechanisms of Electrode Reactions

By the mid sixties, it was recognized that there were two limiting forms of electrode reactions: (a) those where the reactant and/or products form a bond with the electrode surface and (b) those that occur without any significant bond formation.[60,61] Now it is clear that in order to understand the role of the electrode material in electrosynthesis, it is necessary to define several more mechanisms although the same basic distinction remains valid.

A. Simple Electron Transfer

In the simplest type of electrode process, the reactant is converted to product by the transfer of an electron between the electrode and a species in solution without any significant interaction between the surface and reactant or product. In other words, our model for the electron-transfer process involves the hopping of an electron between the electrode and the electroactive species while the former is within molecular dimensions of the surface. Such a model implies that, for example, the oxidation/reduction of a neutral organic molecule will lead to a cation radical/anion radical in the electrolyte phase and hence that the final products of the electrode reaction will depend on the chemistry of the ion radicals as they are transported away from the surface into the bulk electrolyte. Hence the nature of the products and the selectivity depend only on the electrolyte medium chosen for the reaction.

Although more sophisticated theoretical descriptions of such electron-transfer reactions are available in the literature,[62-67] most experimental scientists are happy to analyze their experimental data for simple electron-transfer reactions in terms of the Butler–Volmer equation and to report kinetic data as a transfer coefficient α and either the exchange current density i_0 or the standard rate constant k_0.[67-69]

Essentially, the model for this type of electrode reaction assumes that the role of the electrode is merely to act as a source or sink of electrons. Due to their structure, metals have a large number of both filled and empty electronic levels; hence it is to be expected that the kinetics of electron transfer will be independent of the choice of electrode material provided it has a metallic structure (in contrast, at semiconductors, large variations in k_0 may be observed). In practice, the standard rate constant for electron transfer may vary to some extent even at different metal electrodes because of a number of secondary factors.

(i) The Double-Layer Effect

Electron transfer occurs because of the local potential field at the surface driving the movement of the charged species across the interface. When a potential is applied to an electrode in solution, the surface takes up a characteristic charge and electrostatics then demands an organization of ions and solvent in the solution, i.e., the formation of a double layer.[67-70] The structure of the double layer will depend on the composition of the solution (the choice of solvent, the nature and concentration of electrolytes, and the presence of any species capable of adsorbing on the surface) as well as the metal of the electrode and it will determine the potential distribution close to the surface. The structure of the double layer therefore influences the kinetics of electron transfer by determining the local driving force for electron transfer. In addition, if the electroactive species is charged, the field close to the surface will make its concentration at the site of electron transfer different from the bulk concentration. Hence, before comparing the kinetics of a couple in different conditions, the kinetic data should be corrected for the double-layer effect.[67-70]

The structure of the double layer is a function of the metal chosen for the electrode as well as the composition of the solution. In addition, the potential of zero charge (the potential where neither anions nor cations are attracted into the double layer) certainly varies with the metal of the electrode, and the magnitude of the double-layer correction to the exchange current density or standard rate constant depends significantly on the electrode material and the separation of the equilibrium potential from the potential of zero charge.

(ii) The Effect of Adsorbed Species

Although the model assumes that neither reactant nor products interact with the electrode, it is quite possible that other species in the solution, either ions or neutral molecules that may be impurities or components of the electrolyte, can absorb onto the surface. The coverage by such species will certainly depend on the electrode material. Once adsorbed, such species can lead to increases or decreases in the rate of electron-transfer reactions.

(iii) Oxidation or Reduction of the Metal Surface

As noted in section II, metal surfaces are only stable (either thermodynamically or kinetically) over a range of potentials. The formation of a surface oxide or hydride is likely to lead to substantial changes to the rate of electron transfer.

A number of groups have sought to study the kinetics of electron-transfer reactions at metal electrodes. Capon and Parsons[71] investigated the kinetics of the hydroquinone/anion radical couple at six metals (Pt, Pd, Rh, Ir, Au, and Hg) in DMF and found apparent standard rate constants in the range (3–7) × 10^{-3} cm s^{-1}. The experiments at Pt, Au, and Hg were later repeated by Rosanske and Evans;[72] they found a trend in standard rate constant (Pt < Au < Hg) but a variation only amounting to an order of magnitude. More curiously, the values of the rate constants were higher by a factor of 100 than those reported by Capon and Parsons; no reason for the difference could be found. There is insufficient experimental data for the nonaqueous solvent to make a precise double-layer correction to the rate constants, but Rosanske and Evans suggest that their observed difference between metals is consistent in trend and magnitude to be explained only by double-layer effects. Other couples to have been studied at several metals include Fe^{3+}/Fe^{2+},[60,73] $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$,[74-76] and $Ru(NH_3)_6^{3+}/Ru(NH_3)_6^{2+}$.[77,78] In general, the magnitudes of the changes in rate constant are small and the trends would indicate double-layer effects, provided no species capable of adsorption is present in solution.

Additional effects, however, can readily be observed. In the case of ferricyanide/ferrocyanide the formation of oxide on metals such as Au and Pt leads to a decrease in the standard rate constant.[75,76] Metals forming thicker or less conducting oxides would be expected to have a much larger effect.

Similarly, the influence of species capable of adsorption on the electrode surface has been investigated. Some adsorbed species influence the rate only through a change in the double-layer structure while others show specific chemical effects. Both inhibition and enhancement of electron transfer can result in each case. Moreover, all effects depend on the metal of the electrode through the free energy of adsorption of the adsorbate and/or the potential of zero charge for the metal. The influence of a double-layer effect depends on the charge on the electroactive species and whether the equilibrium potential is positive or negative to the potential of zero charge. Weaver and Anson[79] demonstrated rate enhancement of the Cr(III)/Cr(II) and Eu(III)/Eu(II) couples at mercury by addition of iodide and bromide but showed that they could be explained by changes to the double layer. On the other hand, in the presence of thiocyanate the rate of the Eu(III)/Eu(II) couple increased more than could be explained in this way;[80] they proposed that adsorbed thiocyanate could be acting as a bridging ligand during electron transfer. A much larger rate enhancement was reported for the Fe(III)/Fe(II) couple after the addition of chloride to sulfate[61] or perchlorate[73] solutions. Weber et al.[73] described a detailed investigation of the catalysis by chloride (as well as bromide and sulfate) of the couple in perchloric acid, using both Pt and Au electrodes. The rate enhancement was shown to relate to the coverage of the surface by chloride, and with dilute chloride solutions, the adsorption process was mass transport controlled; with a chloride ion concentration of 10^{-6} M, the increase in the rate constant could exceed a factor of 10^3. A ligand bridging mechanism was again proposed. Lipkowski and Galus[81] have reviewed the models by which absorbate molecules inhibit electron transfer. Qualitatively, two models are considered. In the first, the adsorbate is considered to compete with the electroactive species for sites on the electrode surface. In the second, a more complete adsorbate layer is seen to increase the distance it is necessary for the electron to hop, reducing the potential driving force for oxidation/reduction. The effectiveness of some organic molecules as corrosion inhibitors is well-known, while an example of inhibition of a redox couple is provided by the effect of triphenylbenzylphosphonium or triphenylbenzylarsonium ions on the Fe(III)/Fe(II) couple in sulfate media.[82] At a gold electrode, 10^{-3} M of either ion decreases the exchange current density by >1000.

Since impurities collect at the surface and change the kinetics of electrode process and surface films have similar effects, the history and pretreatment of solid electrodes as well as the purity of solutions are critical to experimental data. The problem of reproducing a clean surface for solid electrodes was the major factor leading to the popularity of the dropping mercury electrode for kinetic studies. More recently, techniques for obtaining reproducible results at platinum have been developed. These have, however, been well reviewed[83-86] and here it therefore seems more useful to review some of the recent work to understand the influence of experimental procedure on data obtained with carbon electrodes. In electrolysis cells, carbon is used in many forms,[1,4,87-90] and the performance (particularly the stability and product selectivity) is recognized to depend on the form. For kinetic studies, electrodes prepared from carbon paste or vitreous (glassy) carbon disks are the most popular. Taylor and Humffray[91] compared the standard rate constant for the Fe(III)/Fe(II) couple in several electrolytes at Pt, glassy carbon, carbon pastes, and wax impregnated graphite electrodes, while other papers[92,93] have looked at the effect of the carbon powder, chemical treatment, carbon loading, and pasting liquid on the kinetics of electron-transfer processes. For example, Urbaniczky and Lundstrom[93] looked at the effect of reducing the surface of the carbon powders by heating in a hydrogen atmosphere on the electrochemical properties of paste electrodes. The capacitance decreased from 290 to 29 mF m^{-2}, indicating a large decrease in surface area, but the effect on the kinetics of electron transfer depended on the couple. The standard rate constant for ferricyanide/ferrocyanide increased but that for quinone/hydroquinone decreased. More recently, several papers have examined electron transfer at vitreous carbon in greater detail. Deakin et al.[94] determined the change in standard rate constant with pH for three couples at Pt, Au, and C. They found that at Pt and Au little variation occurred while at C large changes were seen; for the couples $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and $Ru(NH_3)_6^{3+}/Ru(NH_3)_6^{2+}$ the rate constant increased with pH while for $IrCl_6^{2-}/IrCl_6^{3-}$, the opposite trend was observed. The authors suggest that the behavior is determined by the carboxylic acid functional groups on the surface and supported this conclusion by experiments where the surface was chemically reduced, heat treated, and esterified. Hu et al.[95] looked at the influence of polishing procedures on the kinetics of electron-transfer processes and used X-ray analysis to determine an O/C ratio of 0.141 on the surface of the most active electrodes. They also used pulse voltammetry to investigate electroactive surface functional groups and conclude that quinone functions are present. In another careful study, Kepley and Bard[96] used ellipsometry, X-ray analysis, and elemental analysis to monitor the thickness of "oxide film" and showed that the rate of three quinone couples all increased as the surface oxidation increased. Finally, Bowling, Packard, and McCreery[97] compared anodization with pulsed laser irradiation as methods for the activation of carbon surfaces. They found both treatments greatly accelerated electron transfer (by approximately 10^6) for both the ferricyanide/ferrocyanide and dopamine redox systems and using Raman spectroscopy of the surface were able to correlate the enhancement in rate with particular spectroscopic features. They conclude that especially the laser irradiation produces a high density of graphitic edge plane defects which are very active sites for electron transfer.

TABLE II. Current Efficiencies and Selectivities for Adiponitrile from the Monsanto Mark I and Mark II Processes[a]

	Monsanto Mark I[98]		Monsanto Mark II[26]	
cathode	current efficiency/%	selectivity/%	current efficiency/%	selectivity/%
Hg	90	90		
Pb	90	90	85	88
Cd	85		85	88
Zn	84		75	84
graphite	75		80	83
C steel	77		50	78
Ti	75		55	75
Ni	82		<5	9
Cu			<5	8

[a] References 26, 326, and 330. In the Mark I process, a membrane-divided cell is used. The catholyte is one phase (16% acrylonitrile + 16% adiponitrile + 28% water + 40% tetraethylammonium ethyl sulfate). In the Mark II process an undivided cell is used. The catholyte is an emulsion of acrylonitrile and an aqueous 15% phosphate buffer containing 0.4% quaternary ammonium salt + additives.

Overall, therefore, it must be concluded that even in the case of simple electron-transfer reactions, the kinetics can depend quite strongly on the choice of electrode material. From a synthetic viewpoint, the intermediates formed, however, and hence the selectivity of the reactions should be largely independent of the choice of electrode material. In contrast, the current efficiency for the process may vary strongly with electrode material because the solvent decomposition and maybe other reactions certainly occur via adsorbed intermediates. Hence for electrolyses in water, the current density for hydrogen or oxygen at any potential depends very strongly on the electrode material. Furthermore, there are secondary effects; for example, if a catholyte is neutral and insufficiently buffered, the hydrogen evolution reaction will cause the layer close to the cathode surface to go alkaline. This may, in turn, increase the number of side reactions for the reactant, intermediates, or product in solution (hence decreasing selectivity).

These factors are well illustrated by data for the hydrodimerization of acrylonitrile to adiponitrile. At least on the basis of the data for selectivity and current efficiency at different electrodes (Table II), this seems to be an example of a process where the electrode reaction leads to an acrylonitrile anion radical, which then reacts to give adiponitrile as it is transported through the reaction layer to the bulk solution. In the conditions of the Mark I process the current efficiencies show little variation with the cathode material and although the quantitative data are not available, the selectivity also remains high. In the quite different conditions of the phase II process, the current efficiency drops on the lower hydrogen overpotential materials; this is also true of the selectivities but the fall off is much less.

B. Reductions via Adsorbed Hydrogen

During the early part of this century, it was widely believed that most cathodic reductions occurred via "nascent hydrogen", a very active form of hydrogen present close to the cathode. This concept has been clearly disproved, and it is now certain that most electrochemical reductions occur via anion radical, carbanion, and other intermediates in solution. On the other hand, it is also clear that there is another type of reduction that occurs at cathodes whose surfaces are able to stabilize hydrogen atoms by adsorption (Pt, Pd, Ni, etc.). The chemistry observed is closely related to catalytic hydrogenation.

The electron-transfer reaction is the reduction of proton or solvent (SH), typically water, methanol, or acetic acid, to give adsorbed hydrogen atoms

$$H^+ + e^- + M \rightarrow M\text{–}H \qquad (1)$$

or

$$SH + e^- + M \rightarrow S^- + M\text{–}H \qquad (2)$$

The reduction of the organic molecule then occurs by a chemical reaction between the adsorbed hydrogen and the molecule, probably also adsorbed on the surface. Such electrocatalytic hydrogenations, of course, only take place at metals where a significant coverage by hydrogen species is possible (Ni, Pd, Pt, Rh, etc.).

Table III reports some typical electrocatalytic hydrogenations. It can be seen that the types of reaction closely resemble those familiar in catalytic hydrogenation, not surprising since it is probably only the source of hydrogen atoms that differs. Electrocatalytic hydrogenations are characterized by unusually high selectivities (commonly only one product is formed), and it is often possible to hydrogenate selectively one group in polyfunctional molecules. It is, however, common for hydrogen gas to be formed as a competing reaction, and current efficiencies are therefore variable. Moreover, real current densities are usually low and it is then essential to use a high-area cathode, usually a metal black or a Raney metal.

In recent years some very interesting synthetic chemistry has been achieved with such cathodes. As examples, we would highlight the synthesis of 1,1,4,4-tetramethoxycyclohexane,[110] the reduction of sugars,[111] the hydrogenation of steroids,[117,118] and the removal of a protecting group widely used in peptide synthesis.[119] Selective reactions require the appropriate selection of both catalyst and electrolyte medium. It is clear that many reactions are favored by particular metals but little is yet known about the design or choice of catalyst other than by trial and error. Presumably the differences in performance result from differences in the free energy of adsorption of hydrogen and, perhaps more importantly, of the organic substrate. The orientation of the organic molecule on the surface could also be significant.

C. Heterogeneous Redox Catalysis

Indirect electrolysis where the redox catalyst is dissolved in the electrolyte is now widely practiced.[127] It is also widely recognized that it would be advantageous (for example, for product isolation) if the redox catalyst were anchored to the electrode surface. Indeed many papers have now discussed various types of polymer-coated or other modified electrodes.[128] In practice, however, the only such electrodes with the necessary stability are those based on inorganic materials, particularly metal oxides.

TABLE III. Electrocatalytic Reactions of Possible Application in Synthesis

Nickel

ketones → alcohols[99-102]
aldehydes → alcohols[100,102]
acetylenes → *cis*-alkenes[100,103,104]
olefins → alkanes[99,100]
unsaturated ketones → ketones[105]
nitriles → amines[100,106]
Schiff bases → amines[100]
oximes → amines[100,107,108]
pyridine → piperidine[109]
cyclohexadiene → cyclohexane[110]
benzene → cyclohexane[111]
sugars → sugar alcohols[111]

Palladium

ketones → alcohols[112,116]
acetylenes → *cis*-alkenes[112,113]
nitriles → amines[114,115]
unsaturated ketones → ketones[105]
unsaturated steroids → steroids[117,118]
cleavage of the benzyloxycarbonyl group from peptides[119]

Platinum

ketones → alcohols[112,116,121]
ketones → alkanes[120-122]
butadienes → alkenes[123]
acetylenes → *cis*-alkenes[112,116]
nitro compounds → amines[116]
$CF_3COOH \rightarrow CF_3CH_3$[124]

Rhodium

phenols → cyclohexanols[125]

Cobalt, Iron

nitriles → amines[126]

A good example of such systems is the oxidation of organic compounds at nickel anodes in aqueous base. Many organic molecules are oxidized at nickel in base by the mechanism

$$Ni(OH)_2 + OH^- - e^- \rightarrow NiO(OH) + H_2O \qquad (3)$$

$$NiO(OH) + RCH_2X \rightarrow Ni(OH)_2 + R\dot{C}HX \qquad (4)$$

$$R\dot{C}HX \rightarrow \text{products} \qquad (5)$$

where the electron-transfer reaction leads to a higher nickel oxide (in fact the oxide/hydroxide layers are chemically much more complex than written in eq 3) and the organic substrate is oxidized in a chemical reaction with the surface.[129-132] The chief evidence for this mechanism is that the compounds all oxidize at a potential very close to that where oxidation of the nickel surface layer takes place. The limiting currents for the oxidations, however, vary strongly with the structure of the organic substrate but are generally much below that expected for a mass transport controlled process. Under conditions used for synthesis, it is accepted[129,130,132] that reaction 4 is the rate-determining step, and there is isotope effect evidence that this chemical

TABLE IV. Synthetic Reactions Employing Nickel Oxide Anodes in Basic Solution[a]

primary alcohols → carboxylic acids
benzyl alcohols → aldehydes or benzoic acids
secondary alcohols → ketones
diols → dicarboxylic acids
steroid alcohols → steroid ketones
lactones → ketocarboxylic acids
primary amines → nitriles
2-(benzylideneamino)phenols → 2-phenyloxazoles
hydrazines → dehydro dimers
diaziridines → diazirines

[a] Further information about conditions, yields, and the literature are available in ref 134.

reaction involves H abstraction from the carbon atom α to the functional group.[130] The current–potential curves for the oxidations are sometimes complicated further by reductions in the reactivity of the nickel oxide layer when it becomes overoxidized; then peaked responses are seen rather than a smooth, S-shaped response.[132]

The chemical transformations observed at nickel oxide electrodes in base strongly resemble those reported with the chemical reagent nickel peroxide.[133] Indeed, both give the chemistry expected for hydroxyl radicals complexed by the oxide surface. Hence the products are commonly quite different from those obtained with electron-transfer anodes (e.g., Pt, C). Table IV reports some typical synthetic reactions possible with nickel anodes.[134] Again, these reactions are characterized by unusually high selectivities although the current densities are uncomfortably low. This has led to various attempts to prepare high surface area nickel oxide electrodes. One method is based on electroplating a high surface area nickel deposit.[135] The more common procedures are based on modifications of a method described by Briggs et al.;[136] a thick nickel oxide layer is produced by applying a square wave or ac potential–time profile to a nickel electrode in a solution containing 0.1 M $NiSO_4$ + 0.1 M CH_3COONa + 0.005 M NaOH. Some workers also recommend the presence of a low concentration of Ni^{2+} in the anolyte to maintain activity. Such a procedure was used to produce an anode surface for a commercial process for the oxidation of the glucose derivative 2,3:4,6-di-*O*-isopropylidene-L-sorbose to L-gulonic acid, an intermediate for vitamin C.[137-139]

Very similar chemistry can be achieved at oxide-covered silver,[140-142] cobalt and copper,[130] and monel anodes in alkaline solutions. Other metals do not appear to have any advantage over nickel and indeed may be subject to a significantly faster corrosion. Cobalt/nickel spinel anodes, prepared by thermal decomposition of sprayed nitrate solutions, have, however, been found to have excellent stability and to permit the use of much higher current densities.[143]

It is also interesting to note that another surface-bound nickel(III) species (this time a fluoride) is accepted as the key intermediate in the Simons process for the perfluorination of organic molecules.[144,145] The medium is basic hydrogen fluoride.

Attempts to develop anodes that act by heterogeneous redox catalysis and are stable in acid media have met with little success. Beck and co-workers[146-148] have described anodes based on mixed titanium/chromium oxides that are suitable for synthesis in sulfuric acid solutions but their corrosion rate is high.

D. Oxygen-Transfer Anodes

There are a number of anode reactions that involve the introduction of oxygen into the electroactive species and that are almost unique to lead dioxide as an anode material. These include both inorganic (e.g., the conversion of chromium(III) to chromic acid[149,150] and of chlorate to perchlorate[151]) and organic (e.g., the oxidation of benzene rings to quinones[152-154]) reactions. Typically the current efficiency at a lead dioxide anode is 50–100% (some oxygen is also evolved) and no more than a few percent at electron-transfer electrodes such as Pt. Although it is not implied that all reactions at PbO_2 occur by such mechanisms, it is tempting to propose that it is possible for the lead dioxide surface to transfer oxygen atoms to appropriate acceptors, i.e.

$$PbO_2 + X\text{-}R \rightarrow O{=}X\text{-}R + PbO \qquad (6)$$

$$PbO + H_2O - 2e^- \rightarrow PbO_2 + 2H^+ \qquad (7)$$

More generally, the electrochemistry of lead dioxide electrodes has been reviewed.[155,156] Traditionally, lead dioxide anodes have been prepared in situ by anodizing lead, usually in a sulfuric acid medium. More recently, there has been considerable effort to develop procedures for making high-quality and long-life PbO_2 on carbon[157-159] and titanium.[160-164] Very recently, Johnson et al.[165,166] have described efforts to improve the rate of oxygen-transfer reactions at lead dioxide by including catalytic amounts of group IIIA and VA metals in the oxide coating.

E. Electrodes as Reactants

In this section only reactions where the electrode material takes part as a stoichiometric reagent will be considered. It will be shown that there are examples where the electrode material consumed is the anode or the cathode and also the working or counter electrode.

The dissolution of metals is, of course, widely used as the anode reaction in electroplating and electrowinning processes.[4] It is less commonly recognized that such reactions, even in aqueous solutions, can provide a convenient route for the synthesis of both metal salts and insoluble oxides etc. Industrially, the method is attractive when the elemental form is the least expensive source of the metal or when high product purity is important. Thus high-purity potassium stannate is manufactured[167] in a membrane cell by the anodic dissolution of tin in potassium hydroxide. To minimize the energy consumption, the conditions are chosen so that the tin dissolves as tin(II), which is then air oxidized to stannate.

$$Sn + 4OH^- - 2e^- \rightarrow SnO_2^{2-} + 2H_2O \qquad (8)$$

$$2SnO_2^{2-} + O_2 \rightarrow 2SnO_3^{2-} \qquad (9)$$

The cathode reaction is used to generate some of the required caustic potash. Another salt sold in very high purity is silver nitrate, and this is also made conveniently by anodic dissolution of silver in nitric acid, both reactants being available in very pure form. Cuprous oxide is an example of an inorganic solid made by anodic dissolution.[4] The electrolysis conditions must be carefully selected because it is essential to the applications of the cuprous oxide that the solid oxide meets specification with regard to color, particle size, chemical reactivity, and cupric oxide content. It is also necessary that the oxide when formed does not passivate the surface of the copper anode. A typical electrolyte is 2 M NaCl at 338 K and the current density may be 10–30 mA cm^{-2}.

In nonaqueous solvents the anodic dissolution of metals may be used to prepare a very wide range of compounds.[168] For example,[169] the method may be used to prepare pure samples of Fe(II), Co(II), and Ni(II) alkoxides (e.g., methoxides, ethoxides, *n*- and *tert*-butoxides, as well as phenoxides) in undivided cells with the appropriate anode and a cathode that promotes hydrogen evolution and formation of the alkoxide; the electrolyte is the alcohol or aprotic solvent containing the alcohol, and the medium can also contain a halide to promote smooth anode dissolution. Similar cells with aprotic solvent/tetraethylammonium perchlorate electrolytes have been used to prepare the pentanedione, 3-hydroxy-2-methyl-4-pyrone, and 2-acetylpyrrole complexes of Ti, Zr, Hf, V, Cr, Mn, Fe, Co, Ni, Cu, and In.[170] Eisenbach and Lehmkuhl[171,172] have applied this chemistry for the development and scale up of two processes for the electrosynthesis of ferrocene. In the first, ferrous ethoxide was made by dissolution of an iron anode in ethanol/sodium ethoxide and then reacted with cyclopentadiene. In the second, the solvent was DMF and the cell was undivided; the ferrocene was produced directly at an iron anode in the solution containing the dimer, and hydrogen was evolved at the cathode.

The anodic dissolution of metals such as Al, Mg, and Zn has also been employed as a counter electrode reaction particularly in ether media. Initially such reactions were selected because they did not interfere with the cathode chemistry of interest.[173] Later, circumstances were defined where such reactions could be used with advantage. Firstly, the metal ions were used to aid the isolation of a cathode product, oxalic acid formed by the reduction of carbon dioxide in aprotic media, by precipitation.[174,175] In addition, it was recognized that the multivalent ions resulting from the oxidation of Al and Mg might be expected to improve the selectivity of some cathodic organic syntheses by stabilizing anionic species, both intermediates and products. Indeed, it has been found that the use of Al or Mg anodes in undivided cells leads to improved yields of carboxylic acids from the reduction of alkyl halides in the presence of carbon dioxide,[176-179] keto acids from ketone reduction in the presence of carbon dioxide,[180] ketones from the reduction of alkyl halides with acid anhydrides in solution,[181] and tertiary alcohols from the coupling of alkyl halides and ketones.[182] It must be stressed that although the reactions are attractive, the metal of the anode is consumed on a mole for mole basis. Even so, a pilot plant for this chemistry has been described.[183]

Metallic electrodes are also consumed in reactions where radical intermediates are formed, and in some cases the yield of organometallic product is almost quantitative. The reduction of alkyl halides in aprotic solvents at the appropriate cathode leads to good yields of PbR_4, SnR_4, ZnR_2, CdR_2, and organomercury compounds,[168,184-190] e.g.

$$4C_2H_5Br + Pb + 4e^- \rightarrow Pb(C_2H_5)_4 + 4Br^- \quad (10)$$

while an even greater range of metal alkyls may be prepared by the oxidation of Grignard reagents or zinc or cadmium alkyls in ether solvents,[168,191-196] e.g.

$$4C_2H_5MgCl + Pb - 4e^- \rightarrow Pb(C_2H_5)_4 + 4MgCl^+ \quad (11)$$

Commonly in such syntheses, the magnesium, cadmium, or zinc alkyl is prepared in situ at the cathode in an undivided cell. In fact, such chemistry with a Grignard intermediate was the basis of the Nalco process for the large-scale production of lead alkyl gasoline additives.[192,193]

The anodic dissolution of aluminum in the presence of mono- and polyhalogenated alkanes has been used to prepare catalysts for the Friedel–Crafts reaction[197] and also Ziegler–Natta catalysts.[198] It should be emphasized, however, that although electrochemically initiated, the reaction between the metal and the alkyl halide is, generally, highly exothermic and difficult to control. Hence, the use of anodes such as Al and Mg in halogenated solvents needs to be approached with extreme caution.[199]

Organometallic products arise from a variety of other electrode reactions, for example, the reduction of acrylonitrile at tin in aqueous solution[200,201] and the reduction of aliphatic ketones at mercury.[202,203] It is interesting to note that these reactions can be extended to the electrosynthesis of sulfur compounds by using a cathode of compressed sulfur and carbon.[204,205]

F. Reactions via Organometallic Intermediates

In some electrode reactions it is clear that the organometallic species are formed during the conversion of starting material to product but are not the major reaction products. Such mechanisms are, of course, most common at electrodes of metals that most readily form metal–carbon bonds, i.e., Hg, Pb, and Cd.

In the reduction of benzyl iodide at mercury, an organomercury compound is formed prior to electron transfer[206]

$$C_6H_5CH_2I + Hg \rightarrow C_6H_5CH_2HgI \quad (12)$$

and the final product, toluene, results from the sequence

$$C_6H_5CH_2HgI + e^- \rightarrow C_6H_5CH_2Hg^\bullet + I^- \quad (13)$$

$$C_6H_5CH_2Hg^\bullet + e^- + SH \rightarrow C_6H_5CH_3 + Hg + S^- \quad (14)$$

The reduction of benzyl bromide and chloride[207,208] is thought to proceed via similar intermediates but the formation of $C_6H_5CH_2HgX$ only occurs after electron transfer and is catalyzed by radicals formed during reduction. Because of the above alternative mechanism for the reduction of benzyl iodides, their reduction occurs at much less negative potentials at mercury than other cathodes. This has been used to advantage by Lund and Lund[209] to construct a facile electrochemical reduction of benzyl alcohols and allyl alcohols to toluenes and alkenes, respectively; the choice of aqueous HI as the electrolyte allowed in situ formation of the iodide, which reduced at a Hg cathode.

Organomercury species have also been implicated in the reduction of alkyl halides. They explain the differences in both voltammetric response and products at Hg and vitreous carbon cathodes,[210,211] while Webb et al.[212,213] demonstrated that organomercury intermediates had stereochemical consequences to the electrochemical reduction of substituted cyclopropyl bromides.

Sekine, Yamura, and Sugino[214] discussed the importance of organometallic intermediates in the reduction of acetone at various cathodes in aqueous sulfuric acid. At mercury and lead, the major product was 2-propanol (organic yields of 95% and 68%, respectively) while at Cd, Zn, Al, Ni, and Cu propane was the only organic product (although the amount of competing hydrogen evolution increased along this series). With Hg and Pb, organometallic oils could be identified, and these decomposed to propane after termination of the electrolysis or could be isolated and decomposed either thermally or photochemically, again to propane.

G. Reactions with Adsorbed Intermediates

There is conclusive evidence that organic molecules can adsorb on the surface of electrodes. This has been demonstrated by studies with physical techniques such as capacitance measurement, electrocapillary curves, and in situ spectroscopy and has been used to advantage in a number of technologies, e.g., inhibition of corrosion and modification of the morphology of metal electrodeposits. Its role in organic electrosynthesis is, however, much less defined and, indeed, a matter of some controversy. Certainly, on one hand, adsorption has tended to be "a box for unexpected observations" while on the other, organic chemists have largely failed to observe the large stereochemical effects that they expect if the electroactive species or intermediates were adsorbed on the electrode surface.[215,216] Perhaps the real difficulty is that most electrode reactions of interest in synthesis are a complex sequence of events and it is seldom clear which of the species in the chain is adsorbed. Even so, the products, or at least the selectivity, of many electrode reactions vary with the choice of anode/cathode and current thinking is that adsorption is the major reason.

The term adsorption is used to cover many types and strengths of interaction between molecules and electrodes. Electrostatic interactions between the charged electrode surface and solutes can arise (depending on surface charge and thus potential) if the solute is an ion, contains a permanent dipole, or has a functional group where a dipole may be induced by the electric field close to the surface. Also, chemical bonds between certain electrode materials and substrates are possible. Many organic molecules might be expected to adsorb to some extent because they are charged, have aromatic π-electron systems, or contain double or triple bonds or functional groups (e.g., carbonyl, nitro, or nitrile groups). In understanding the extent of adsorption, two competitions need to be considered: (i) that between all species, i.e., solvent, ions, and molecules, for the limited sites on the surface and (ii) that between the surface and the solution for each species in the system. Hence the extent of adsorption depends strongly on the electrode material as well as the choice of solvent, electrolyte, and all other species in solution.

TABLE V. Major Products from the Oxidation of Acetate in Two Solvents at a Series of Anodes[a]

anode	major products CH_3OH	 CH_3COOH
Pt	C_2H_6	C_2H_6
Au	C_2H_6	C_2H_6
Pd	C_2H_6 + HCHO	C_2H_6
graphite	CH_3COOCH_3	CH_3COOCH_3
PbO_2	HCHO + $HCOOCH_3$	C_2H_6

[a] Data taken from ref 219.

A discussion of the anodic oxidation of carboxylates illustrates well the quandaries resulting from our imperfect knowledge of the role of adsorption. It is generally accepted that under some conditions products arise almost completely from radical intermediates formed in the process

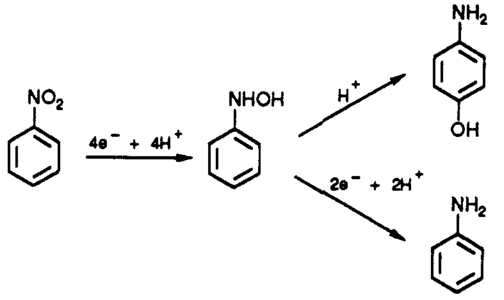
$$\mathrm{RCOO^- - e^- \rightarrow RCOO^\bullet \rightarrow R^\bullet + CO_2} \tag{15}$$

In others, the major products are those expected from carbenium ion intermediates presumably formed by the further oxidation of the radical.

$$\mathrm{R^\bullet - e^- \rightarrow R^+} \tag{16}$$

Moreover, it is clear that the type of product formed depends strongly on the electrode material. Koehl[217,218] studied the oxidation of acetate in both water and acetic acid solutions; at Pt good yields of ethane were obtained while at graphite the major product was methyl acetate. Longer chain carboxylates gave the same trend although the carbenium ions give a wider range of products (e.g., *n*-butyrate gave propylene and cyclopropane as well as isopropyl butyrate). Sato et al.[219] investigated the oxidation of acetate at five anodes in both methanol and acetic acid (see Table V). Graphite is confirmed as giving products derived from the methyl cation in both solvents while ethane is otherwise the major product. At Pd and PbO_2 the picture is complicated by oxidation of methanol. Brettle and Brennan[220] studied the oxidation of heptanoate and demonstrated that the form of carbon was also important; only at porous graphite did the carbenium ion products predominate while at vitreous carbon and baked carbon the yield of dimer approached that at Pt. At pyrolytic graphite the product depends on whether the edge or face surface is used; at edges, dimer is formed and at the face, ester and hydrocarbons. These product distributions are all compatible with the concept that the dimer is formed when the radical is stabilized by adsorption on the surface of the anode (there is other supporting evidence from the influence of solvent and added electrolytes on the product spectra[215]). Furthermore, there is much physical and chemical data to support this conclusion.[221] In sharp contrast, studies of substituted cyclohexanecarboxylates[222,223] conclude that the dimer has no preferred stereochemistry and results from random coupling of the radical intermediates. This implies that the radicals are not influenced by the surface when they react.

There are many other examples of reactions that show a strong dependence on electrode material believed to arise because of the effects of adsorption and only a few will be discussed as illustrations. The reduction of nitrobenzene to *p*-aminophenol in concentrated sulfuric acid is a process carried out on a pilot scale by a number of companies and studied by several academic groups.[224-228] The reduction occurs by the acid-catalyzed rearrangement of the 4e$^-$ product, and the major competing reaction is the further reduction of phenylhydroxylamine to aniline.



(17)

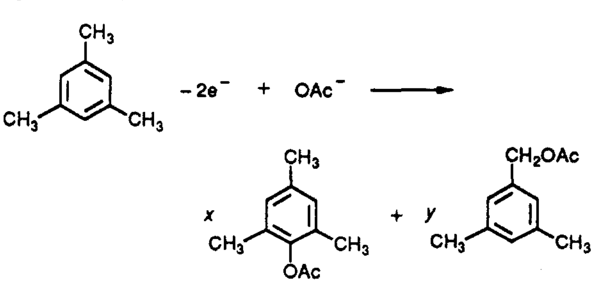
There is general agreement that the preferred electrode materials for high yields of *p*-aminophenol are Ni, Cu, or monel although one group[228] prefers Bi-plated graphite. There is some evidence that these metals catalyze the chemical rearrangement (presumably because the phenylhydroxylamine is adsorbed) but certainly electrodes such as Hg and Pb give lower selectivity despite electroanalytical evidence that at some potentials, the $4e^-$ product is formed and at higher pH, the phenylhydroxylamine can be formed in good yield. The cross coupling of acetone and acrylonitrile (eq 18) has

$$(CH_3)_2CO + CH_2{=}CHCN + 2H_2O + 2e^- \rightarrow NCCH_2CH_2C(OH)(CH_3)_2 + 2OH^- \quad (18)$$

been studied at both Hg and graphite[229] and capacitance measurements were used to show that both acetone and acrylonitrile adsorb on the cathode surface and to predict that the best yield of coupled product coincides with the maximum coverage by the activated olefin. The hydroxylation of tetrahydrofuran[230] in aqueous acid (eq 19) gives yields that vary strongly with

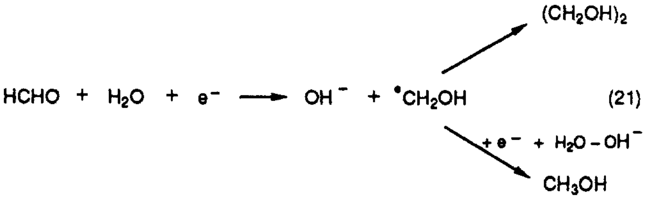
(19)

anode; on Pt, however, the selectivity is 95% and current efficiency is 70% under conditions where it may be shown that tetrahydrofuran adsorbs strongly on the platinum oxide surface. On PbO_2 the major product is butyrolactone. Eberson et al.[231] found very different ratios of nuclear to side-chain acetoxylation of mesitylene (eq 20) with electrode (from 3.6 at Au to 23 at



(20)

graphite). Finally, recent papers[232,233] report a large cathode effect in the hydrodimerization of formaldehyde to ethylene glycol. Under optimum conditions, the yield at graphite is close to 100%, while at most metals the yield is close to zero (methanol is the main product); the exception is Hg, where the yield of ethylene glycol is 30%. Organomercury intermediates are clearly involved in this case and the reason for the excellent behavior of graphite is yet to be resolved. It seems likely, however, that surface chemistry is important and one possibility is that the graphite surface is able to catalyze the dimerization of the $1e^-$ product.



$$HCHO + H_2O + e^- \longrightarrow OH^- + {}^{\bullet}CH_2OH \begin{cases} \nearrow (CH_2OH)_2 \\ \xrightarrow{+e^- + H_2O - OH^-} CH_3OH \end{cases} \quad (21)$$

Above it was noted that electrochemists have been largely unsuccessful in controlling stereochemistry[216] and especially in designing asymmetric syntheses;[234] optical yields below 10% have been the norm. On the other hand, some electrode reactions do give stereospecificity. For example, the ratio of the cis/trans alcohols from the reduction of 2-methylcyclohexanone varies with the cathode. At Hg and Pb the trans isomer predominates while at Cu the cis isomer is the main product.[235] Such systems are, however, sensitive to other factors, e.g., medium, and the least stable isomer is most readily formed with media that will favor adsorption.[236]

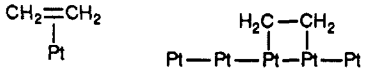
H. Fuel Cell Type Mechanisms

In fuel cell electrode reactions, clean surfaces are responsible for the catalysis of specific chemistry that commonly leads to complete oxidation to CO_2. For example, in the oxidation of formic acid or methanol the first step is the cleavage of a C–H bond[237,238] with the formation of two adsorbed fragments, i.e., at Pt

$$HCOOH + 2Pt \rightarrow Pt\text{-}H + Pt\text{-}COOH \quad (22)$$

$$CH_3OH + 2Pt \rightarrow Pt\text{-}H + Pt\text{-}CH_2OH \quad (23)$$

Usually the adsorbed hydrogen is rapidly oxidized at the applied potential while the organic fragment is either oxidized or dissociates further in similar reactions. The oxidation may occur by direct electron transfer or the formation of metal oxide species at the adjacent site followed by chemical oxidation. Both mechanisms may take place, with the relative importance depending on the potential. Olefins may interact with the surface first through the unsaturated electrons or multisite interaction may occur, e.g.



(24)

Once again, these first steps may be followed by oxidation, either with electrons passing to the surface or chemically via metal oxide/hydroxide species at adjacent sites, or dissociation into fragments stabilized by the surface may occur. Clearly, all such chemistry will depend critically on the choice of anode metal and will be subject to poisoning as in all branches of heterogeneous catalysis.

Obviously, reactions that lead to CO_2 are only of minor interest to the subject of this review although an efficient electrocatalyst for complete oxidation of methanol might be attractive for a counter electrode. There is, however, evidence that some metals permit partial oxidation, and such systems might be of interest in electrosynthesis if they gave high selectivities and were found to be reproducible (the fear is that, in common with other "fuel cell" reactions, the rate and selectivity will depend on the history of the surface). The possibilities can be illustrated by reviewing the literature on aqueous ethylene oxidation. Bockris and co-workers[239,240] studied the oxidation of ethylene in 1 M H_2SO_4 at 353 K at five metals and some alloys. At Pt, Ir, and Rh, only complete oxidation to CO_2 was observed, but at Pd and Au, they found acetaldehyde, propionaldehyde, and acetone in the electrolyte. Similar conclusions for Au were reported by Hartley and Price,[241] while in a study of palladium by Blake et al.,[242] the major products were found to be acetaldehyde, acetic acid, and butenes. Moreover, they observed substantial anode corrosion and believed that the first step in the reaction was dissolution of the metal as a Pd(II)–ethylene complex. There are a number of patents that also report ethylene glycol and ethylene oxide as products, while a porous carbon anode gave a 95% yield of acetaldehyde.[243]

Dissociative adsorption is also a key step in both oxygen reduction and hydrogen oxidation if the reactions are to occur at low overpotentials. Pt is a satisfactory catalyst for hydrogen oxidation even in aprotic solvents[244,245] but the search for a stable, low-overpotential catalyst for oxygen continues. The best materials remain highly dispersed Pt and certain forms of carbon. Both reactions are attractive as counter electrode reactions in synthesis cells.

VI. The Selection of Electrode Materials for Electrosynthetic Processes

In this section, the purpose is to review the electrode materials that are presently available and to discuss the choices that have been made in the development of pilot plant and industrial processes for electrosynthesis. Clearly, much more care is necessary in the selection of the electrode materials for pilot and commercial plants than for laboratory experiments, and the choice will be backed up by an extensive test program. Key factors influencing the selection of electrode materials are availability, cost, long-term chemical stability, selectivity, energy consumption, and electrolyzer design requirements. Much of our practical experience of electrode materials comes from the large inorganic processes, and hence the discussion of some aspects of chlorine, hydrogen, and oxygen electrodes is an essential element of the section.

A. Hydrogen Evolution

The cathodic evolution of hydrogen is, of course, probably the most widely studied electrode reaction. The mechanism and the overpotential required depend strongly on the choice of cathode, and this is known to reflect the strength of the M–H bond. Table VI reports typical kinetic data, and other data are available.[246-248] Such tabulations are useful for selecting both electrocatalysts for hydrogen evolution cathodes and also high-overpotential materials for other electrode reactions where hydrogen evolution would be considered an unwanted competing reaction.

In acid solution, the noble metals and alloys are the best electrocatalysts although, because of cost, they would normally be present as a coating. There are, however, few possible substrate materials stable in acid solution during any period off load (when the catalyst and substrate are no longer cathodically protected) and also not suffering from the formation of hydrides (e.g., Ti, Ta, and Zr all form hydrides that restrict their application as cathodes). Hence, the choice of substrate is limited to lead and perhaps carbon. Indeed, the same materials are probable candidates as the electrode if the decision is made to use a cathode for evolving hydrogen which is stable and cheap but to accept a high overpotential.

TABLE VI. Exchange Current Densities (i_0) and Tafel Slopes for the H_2 Evolution Reaction at Various Materials in Acidic and Basic Solutions at Room Temperature[a]

	acid			base		
	$[H^+]$/ M	i_0/ (A cm^{-2})	Tafel slope/ mV	$[OH^-]$/ M	i_0/ (A cm^{-2})	Tafel slope/ mV
Ag	5	5×10^{-6}	120	1	3.2×10^{-7}	120
C				40%[b]	2.9×10^{-5}	148
Cu	0.1	1.5×10^{-7}	114	0.1	1×10^{-7}	120
Cd	0.25	1.7×10^{-11}	135	6	4×10^{-7}	160
Cr	1	5×10^{-6}		6	1×10^{-7}	120
Fe	0.5	6.6×10^{-6}	133	0.1	1.6×10^{-6}	120
Hg	0.1	7.8×10^{-13}	116	0.1	3×10^{-15}	120
Ni	0.25	6.0×10^{-6}	24	0.5	7.9×10^{-7}	96
Pb	0.05	1.3×10^{-13}	118	0.5	3.2×10^{-7}	130
Pt	1	6.9×10^{-4}	30	0.1	6.7×10^{-5}	114
Ir	1	2.0×10^{-3}		0.1	5.5×10^{-4}	125
Sn	1	1×10^{-9}		6	3.2×10^{-7}	150
Ti	0.5	8.5×10^{-7}	135	6	1×10^{-6}	140
Zn	0.5	1.6×10^{-11}	120	6	4.0×10^{-7}	210

[a] Data compiled from ref 14. [b] 313 K.

In alkaline solutions, many more materials are stable, even on open circuit. Factors such as cost, availability, and overpotential favor the choice of nickel, a mild steel, or a stainless steel (e.g., 316 grade). Minimizing the energy consumption of chlor-alkali and water electrolysis cells has become very important, and this has led to developments in electrocatalysts for hydrogen evolution in basic solutions (see below). The success has also led to new theories that attempt to rationalize the relationship between activity and catalyst structure.[249]

(i) Water Electrolysis, Chlor-Alkali, and Related Processes

The cathode chemistry in these processes is discussed in detail elsewhere.[4-10,246,250,251] Commonly, the cathode is mild steel if the sodium hydroxide concentration remains below 15% w/w and nickel for higher concentrations or for high-temperature operation. When possible, the cost is reduced by using nickel-plated mild steel.[252]

The reduction of cathode overpotential constitutes a powerful way to reduce power consumption in these processes. This can be achieved in several ways with these materials. The surface may be roughened[253-255] or the nickel can be applied as a porous, sintered coating[256,257] or by plasma spraying.[258] Another approach employs a Raney nickel coating,[259] but in early electrolyzers, the mild steel did not provide a sufficiently stable substrate and the overpotential advantage was lost with time. The advent of membrane electrolyzer technology promoted the introduction of more stable substrates (Ni, Ni plated on mild or stainless steels) and performance improved.[260-263] Additives to the Raney nickel (e.g., Ti and Cr) have been included to improve long-term stability. Precious metal coatings also perform very well in membrane cells;[255,264] typical coatings would be based on Pt and/or Ru coatings on nickel. The cost of precious metal coatings has led to the search for less expensive alternatives, and coatings of Ni/Mo, Co/Ni, and Ni/Mo/V each have their proponents.[265-270]

All cathode coatings have to be used in carefully controlled conditions. Problems that arise include (a) deactivation due to nickel hydride formation,[271,272] (b) the deposition of less active metals (particularly iron) or organics on the cathode,[273,274] and (c) corrosion due to current reversal when the cell is taken off load (particularly in diaphragm cells).

Acid electrolytes are met in solid polymer electrolyte cells for water electrolysis and hydrochloric acid electrolysis. In the former the cathode is generally a precious metal dispersed onto a corrosion-resistant material that does not hydride, typically carbon.[4,246] In hydrochloric acid electrolysis, the cathode is a carbon to ensure a long operating life[275] but it has a large overpotential and appropriate coatings are being studied.[276]

In chlorate manufacture, the electrolyte is close to neutral and, despite concerns about hydriding, titanium is a convenient cathode.[277-279] Titanium has also been used in seawater electrolysis[280] and as a substrate for a La/Mo coating for electrolyzers for chlorate;[266] the coating probably reduces hydrogen migration into the titanium.

(ii) Other Processes

Hydrogen evolution can be a very convenient counter electrode reaction for a process involving an anodic oxidation. In alkaline solutions, for example in processes for the manufacture of peracid salts of bromine or iodine or potassium permanganate, the preferred cathodes are again nickel or a steel.[4,280] Acid electrolyses are used for manufacture or regeneration of dichromate, persulfate, cerium(IV), and manganese(III) but then lead and carbon are generally used despite their poor electrocatalytic properties;[4,47,280,281] in some conditions, a grade of stainless steel is possible.

Hydrogen evolution is also a useful counter electrode reaction in nonaqueous solvents; it can be convenient and also maintain the electrolyte pH constant. Carbon is the cathode in processes for the acetoxylation of aromatics in acetic acid,[14,282] nickel or stainless steel is used in fluorination or fluorine evolution in KHF_2 or HF media,[4,283] and stainless steel or carbon (for bipolar electrodes) is used for methoxylations[284,285] or Kolbe couplings[286-291] in methanol. In all cases, the cathode reaction is the reduction of the solvent

$$2SH + 2e^- \rightarrow H_2 + 2S^- \qquad (25)$$

with $S^- = OAc^-$, F^-, or CH_3O^-.

B. Chlorine Evolution and Related Reactions

The technology of chlorine generation has been thoroughly reported.[3-9] The anodes have been highly optimized, and the kinetics and mechanism of chlorine evolution at many materials have also been widely studied. Trasatti has reviewed the literature for oxide electrodes,[292] and Tarasevich and Khrushcheva[276] have considered the reaction at carbon. Some kinetic data are reported in Table VII and it can be seen that the reaction is rapid at precious metal oxide surfaces. Bromine and fluorine have been studied less[14] and only the latter is commercially important. Nickel or carbon anodes are selected for fluorine evolution largely because of their relative inertness in the aggressive fluoride melt used for the electrolysis.

TABLE VII. Kinetic Data for the Cl_2 Evolution Reaction at Various Materials[a]

	medium (temp/K)	i_0/ (A cm^{-2})	Tafel slope/mV
Pt	0.2 M Cl^- + 1.2 M H^+ (298)	4.0×10^{-3}	120
	3 M NaCl (303)	6.7×10^{-3}	40
Ir	0.2 M Cl^- + 1.2 M H^+ (298)	0.2×10^{-3}	120
RuO_2	5 M NaCl (293)	6.3×10^{-4}	30 at low η
		3.5×10^{-4}	40 at high η
IrO_2	5 M NaCl (298)	4.0×10^{-2}	120 at low η
		1.2×10^{-3}	40 at high η
graphite	satd NaCl, pH 0.5 (323)	1.2×10^{-3}	40–120
	4 M NaCl + 1 M HCl (323)	0.3×10^{-3}	101

[a] Compiled from ref 14.

(i) The Chlor-Alkali Industry

The changeover from graphite to coated titanium anodes is now almost complete. Titanium is universally used as the substrate because of the passive oxide film that results if its surface is exposed under anodic conditions. The coatings are based on platinum group metal oxides.[3-8,293,294] The commonest catalyst is RuO_2, which is combined with other oxides (e.g., TiO_2, SnO_2, and IrO_2) in the commercial electrode coatings. Their composition and structure determine the overpotential, the selectivity (vs O_2 evolution, which is the thermodynamically preferred reaction), and lifetime as well as behavior on shut down or nonoptimum conditions. Although the performance of the RuO_2-based anode coatings for chlorine evolution is excellent, it is again necessary to control conditions, particularly impurities in the brine. The effects may be illustrated by (a) enhanced corrosion of titanium due to F^-, (b) increased rate of loss of coating in the presence of organic acids, and (c) scaling due to precipitation of $BaSO_4$ in the coating. Beck[295] has reviewed these failure processes.

Less expensive oxides have also been examined; the main system has been Co_3O_4 and related materials.[5,296,297] Amorphous metals also show great stability in brine and have good catalytic properties[298-300] but are not yet available in a form suitable for large electrodes of the complex shapes demanded by modern chlor-alkali cell design.

In hydrochloric acid electrolysis, carbon anodes remain standard[275] but the concentration must exceed 3 M (otherwise O_2 evolution and enhanced corrosion occur), while impurities have a detrimental influence on performance.[301]

(ii) Other Processes

Electrolyses of brine solutions at higher pH are used to manufacture chlorate and also for low-tonnage generation of hypochlorite (e.g., for swimming pools and water purification). A much wider range of anode materials is employed; these include carbon, platinized titanium, and lead dioxide in addition to RuO_2-based coatings.[4] The evolution of chlorine at an anode forms the basis of the epoxidation of olefins. The most widely studied synthesis is that of propylene oxide;[302] one version uses a RuO_2-coated anode and a membrane cell with a NaCl anolyte. The application of hypobromous acid for epoxidation has also been described. For example, an undivided cell with a RuO_2-coated anode and an electrolyte based on ammonium bromide in 95/5% DMF/water has been used for the epoxidation of a substituted diphenylethylene.[44,303]

Anodically generated chlorine has also been used as an in situ oxidant in a number of reported syntheses. An illustrative example is the selective oxidation of alcohols in a cell with a carbon anode and a sodium chloride electrolyte containing RuO_2/RuO_4 as a second phase.[304] The yields are good but the exact mechanism is unclear.

Halogen evolution is seldom used as a counter electrode reaction in electrosynthesis. Its rapid kinetics would make it attractive from the viewpoint of energy consumption, but the properties of halogens make them difficult to handle or dispose of unless the electrosynthesis process is part of a chemical plant already handling them.

C. Oxygen Evolution

The evolution of oxygen is a relatively slow reaction but it has an essential role in water electrolysis and is a convenient counter electrode reaction in metal extraction and synthesis cells. Traditionally, anodes for the latter processes have been selected for stability rather than low overpotential although recent developments are changing this situation.

(i) Water Electrolysis

Normally, the electrolyte in water electrolysis cells is 20–30% w/w KOH and, in such media, the preferred anode materials are nickel or nickel-plated mild steel, provided the chloride concentration is low enough that pitting of the oxide layers does not occur. As with hydrogen evolution, various methods are used to increase the anode area.[9,10] In addition, several coatings capable of reducing the oxygen overpotential by 100–150 mV have been reported; they are transition-metal oxides,[305,306] spinels,[307–309] or perovskites.[310] Little has been reported about long-term stability or the durability of their performance. The electrolysis of acid electrolytes is unusual (because of the additional corrosion problems throughout the system) but precious metal oxides (RuO_2/IrO_2) dispersed on carbon/PTFE composites are used in solid polymer electrolyte cells.

(ii) Metal Winning and Processing

Processes such as zinc electrowinning and galvanizing use acid electrolytes and require oxygen-evolving anodes. Provided the electrolyte is sulfate, the favored anode has been lead, which forms a brown layer of PbO_2 during operation, and this reduces further corrosion. The PbO_2 layer is electrically conducting and relatively stable under oxygen-evolving conditions but has a high overpotential. Nor can these anodes be regarded as completely stable[311] although the use of alloys (e.g., Pb with 5% Ag) increases lifetime and reduces the overpotential to some extent. Recently, the electrogalvanizing industry has been reequipped with new continuous steel strip coating plants with coated titanium anodes. Key objectives were to increase production rates by using higher current densities and to improve product quality by maintaining a more uniform gap.[312] RuO_2 was found not to be a suitable coating[313,314] because of insufficient lifetime due to both dissolution of the coating and formation of TiO_2 at the titanium/coating interface. Instead, coatings based on IrO_2 have been developed and described in a large number of patents.[315,316] Examination of their electrochemical properties[317–319] shows that their overpotentials for O_2 evolution are not low, and a value of 0.47 V at 0.3 A cm^{-2} is typical for acid electrolytes. Their advantage lies in the lifetimes that may be achieved, and several thousand hours has been reported.[312,320]

This durability makes the IrO_2-coated Ti anodes of interest as replacements for PbO_2 anodes to the designers of electrosynthetic processes. But it should be emphasized that Cl_2 evolution is always favored if chloride ion is present, and the lifetime depends on control of the environment. The rate of dissolution of the coating depends on current density and temperature (as well as coating preparation),[321] while insulating layers can form at the substrate/coating interface.[322] Impurities can lead to attack on the titanium (e.g., F^-[323]), scaling (e.g., Mn^{2+}[324]), or enhanced loss of coating (e.g., organic acids[325]).

(iii) As Counter Electrode in Synthesis

Oxygen evolution is a very convenient counter electrode reaction for a cathodic reduction in aqueous solution. In many electrosyntheses, the process has been designed so that the anode is in contact with sulfuric acid (if necessary, by using a membrane). Then, lead (or PbO_2) anodes are frequently used. The overpotential is not low but such anodes are inexpensive and can be designed to have lifetimes above 1 year. Corrosion is, however, continuous and accelerated if many organic compounds are present in solution. Problems have been described based on experience with the Mark I Monsanto adiponitrile process[326] and the reduction of oxalic acid to glyoxylic acid.[327] In the former case, the difficulties (and also the oxygen overpotential) were reduced to some extent by using a Pb/Ag alloy, while in the latter process, the engineers resorted to platinized titanium. In the future, it is likely that the IrO_2 anodes described above will be tested for such duties. A titanium mesh with a Pt/Ir coating was the anode chosen in a process for the pinacolization of acetone,[328] but such anodes are also not necessarily immune from corrosion. Thus, a platinized titanium anode was found to lose coating during the reduction of (trichloromethyl)carbinol.[329]

There is much less experience of oxygen-evolving anodes in non-sulfuric acid media. Clearly, materials for use in alkaline solution could be designed from knowledge obtained from water electrolysis. In neutral solution the literature is sparse although Monsanto (for their Mark II adiponitrile process) has found a mild steel satisfactory as an anode in a neutral phosphate buffer, provided corrosion inhibitors are present.[26,330] The organic compounds present in the undivided cell appear to pose no problems.

D. Oxygen Reduction

The cathodic reduction of oxygen has been widely studied at a broad range of cathode materials. The reaction occurs via two types of mechanism.[4,20,331,332] In the first, complete reduction to water takes place

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (26)$$

while in the second, reduction occurs in two stages

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \xrightarrow{+2e^- + 2H^+} 2H_2O \quad (27)$$

and, indeed, in some conditions hydrogen peroxide may be the stable product. Universally, oxygen reduction is a slow reaction, and good catalysts have been very difficult to find. The problems of finding a good electrocatalyst (and a stable, inert substrate) are compounded by the instability of most materials to corrosion close to the reversible potential for the O_2/H_2O couple. Corrosion can be accelerated by the presence of trace hydrogen peroxide, and the lifetimes of potential candidate catalysts can be reduced by poisoning and sintering. All practical applications of oxygen cathodes also require the development of porous gas electrodes because, otherwise, the solubility of oxygen is too low to maintain a reasonable current density.

These problems are unfortunate since oxygen reduction potentially has an important role in fuel cells and batteries as well as a counter electrode for synthesis. The technology that has been developed is described in several reviews.[4,20,331,332] The electrocatalysts currently considered promising may be divided into three groups: (a) noble metals, particularly Pt, (b) carbon with or without organometallic coatings (e.g., Co macrocycles), and (c) transition-metal oxides (e.g., perovskites). Studies also continue in both acid and alkaline media. The latter is easier because materials are more stable but the oxygen feed has to be CO_2 free. Substrate corrosion is as difficult to avoid as dissolution of the catalyst.

Platinum is the preferred noble metal for oxygen reduction. It is used in a highly dispersed form, usually on a carbon substrate. The Pt loading is now typically below 1 mg m^{-2}. At least in the laboratory, it is possible to obtain current densities as high as 0.9 A cm^{-2} at an overpotential of 400–500 mV with PTFE-bonded Pt/C cathodes.[333-336] While long-term testing of such electrodes has been carried out in both fuel cells and pilot plant chlor-alkali facilities, we are not aware that they are commercially available.

Other cathodes are based on sintered nickel or, more frequently, carbon. A recent review has looked at carbon as an oxygen cathode[276] but usually a catalyst is considered necessary. Several transition-metal macrocycles have been shown to be moderate catalysts[20,332,337] but their stability is insufficient. Heat treatment has been shown to produce better oxygen cathodes,[332,337,338] and, indeed, their activity can then compare with platinum at a similar loading. The exact species active on the surface is, however, not clear.

Oxide cathodes, for example, perovskites,[340,341] manganese oxides,[342] and lead pyrochlores,[343] also threaten to rival the performance of platinum (on a cost basis), but much less is known about long-term stability, including selectivity to poisons.

(i) Hydrogen Peroxide Synthesis

The reduction of oxygen provides a route for the synthesis of hydrogen peroxide.[4,280] In particular, Dow has described a process for the manufacture of 5% hydrogen peroxide in sodium hydroxide that employs a carbon sphere bed through which the electrolyte trickles. The carbon spheres are modified by using a proprietary process to produce a high-area carbon surface.

(ii) As a Counter Electrode in Synthesis

A cell for the production of ozone and employing an oxygen cathode has been described.[344] It is an undivided cell with an internally cooled, cylindrical vitreous carbon anode, and the air-breathing cathode surrounds the anode. The electrolyte is 48% HBF_4. The system can generate concentrated ozone without the coproduction of hydrogen, and the air cathode greatly reduces energy consumption.

Successful oxygen cathodes would attract considerable attention from engineers designing electrosynthetic processes. So far, the only extensive testing is in membrane cells for the chlor-alkali industry, where the oxygen cathode must operate in strong caustic soda. The replacement of hydrogen evolution by oxygen reduction (with the formation of the same products) leads to a substantial decrease in equilibrium cell voltage and hence, potentially in energy consumption. The reduction in energy consumption must be traded against the increased complexity of cells with oxygen cathodes and to the present, the overpotential leads to insufficient improvement in energy consumption to warrant plant application.

E. Electrosynthetic Reactions

So far in this section, the discussion has been largely limited to counter electrode reactions and to background intended to indicate the type of performance that can be achieved with materials specifically designed for particular reactions.

We now consider the working electrode in synthetic reactions. A wide range of electrosyntheses are now carried out commercially but their scale is commonly small. Hence electrode materials will not be developed specifically for each process. Indeed, the designer of a process must not expect to achieve a low overpotential. Rather, he will concentrate on selecting a material whose corrosion rate is low in the process conditions (and there is little literature information on corrosion under realistic process conditions, maybe a nonaqueous solvent with an anode strongly polarized) and that will give good material yield and current efficiency for the reaction of interest. How will the electrode be selected? The initial choice will be based on experience, both from the literature and from industrial practice (particularly the large-scale industries). The performance of candidate electrode materials will first be compared in the laboratory; special attention will be paid to material yields, current efficiencies, and obvious signs of corrosion. The better materials will then be tested in a pilot plant for an extended period. Special attention will be paid to the following factors:

(i) The rate of corrosion of the anode material or the rate of loss of coating together with the rate of corrosion of the substrate in realistic process conditions (including temperature and flow rate as well as electrolyte). Do these processes increase in rate with time, changes in process conditions, or accumulation of impurities or products in the electrolyte?

(ii) Does electrode deactivation occur? This may happen due to adsorption of impurities or minor products, slow formation of polymer on the electrode surface, or formation of insulating layers either on the surface or at the substrate/coating interface.

(iii) Does any metal from the electrodes end up in the products? What is the metal level in the product? Trace metals can necessitate the introduction of expensive, additional purification stages or even negate the use of the product for some purposes.

(iv) Does the material yield, current efficiency, product quality, or energy consumption change with time? For example, slow deposition of transition metals on a cathode, resulting from metal ion impurities in solution or transfer from the anode to cathode, can have a catastrophic effect on performance.

The literature describing each process is relatively small and certainly there are few papers discussing the relative performance of electrode materials for any process (the exception is the hydrodimerization of acrylonitrile to adiponitrile[26,98,326,330]). Hence it is more convenient to discuss the available electrode material rather than to review the literature by reaction.

(i) Anode Materials for Acid Electrolytes

A number of inorganic and organic reactions employ aqueous acid electrolytes. As far as the anode is concerned, the common features are (a) the need for stability under oxidizing conditions where thermodynamics would predict that the anode materials would not be stable and (b) the formation of oxygen as a possible competing reaction. For such conditions, the candidate anodes are Pt, Pt on Ti (Nb and Ta can also be used as the substrate), PbO_2, and perhaps carbon.

(*a*) *Pt and Pt/Ti.* Smooth Pt can be very stable to corrosion and also has a very high oxygen overpotential. It is obviously very expensive but has found application in some older processes (e.g., persulfate manufacture). The cost can be reduced by bonding thin foil to a conducting base. It is, however, much more common to use Pt as a coating on Ti; Nb and Ta can also be used but are only considered where Ti shows deficiencies because of their greater cost. The coatings are usually prepared by electrodeposition as it allows complete coverage of complex shapes and requires only a low weight of platinum per unit area of anode.

The electrodeposition of Pt onto titanium is an established technology.[345] The coatings are smooth with low porosity, adhere well to the substrate, and have good stability and high oxygen overpotentials. While their stability under anodic conditions is good, there is also a finite loss rate that depends on the electrolyte. Impurities can increase the loss rate markedly and, for example, the addition of 2.5–5 g dm^{-3} of chloride ion to sulfuric acid can accelerate the corrosion by a factor of 5.

Several inorganic reactions use Pt/Ti as the anode. Examples are the synthesis of perchlorate, periodate, and persulfate, while it has been reported that it is the only anode suitable for the generation of Ce(IV) in nitric and perchloric acids.[346] Pt/Ti is also a natural choice for organic reactions that do not go well on PbO_2.

(*b*) *Lead Dioxide.* Lead dioxide has several attractive features. In sulfate media of low pH, it is chemically stable and the oxygen overpotential is high. Its electrical conductivity is good so that it can be used as a thick layer and it is inexpensive. On the other hand, its corrosion rate is high under reducing conditions and also in some other acids, particularly hydrochloric acid. It exists in two crystal forms, orthorhombic and tetragonal, which have different electrochemical properties. In addition, the form and quality of its deposits can depend on slight differences in the manufacturing process. Because of poor mechanical properties, it is usually electroplated onto titanium or carbon or prepared in situ by anodizing lead. An extensive review of lead dioxide anodes was written in 1977,[347] and much recent work has sought to prepare improved electrodes[157–164,348–352] by, for example, pretreatment of the substrate,[160–162] examination of failure mechanisms,[348] the use of an interlayer between Ti and PbO_2,[349,350] and improving the adhesion.[352] While the production of reproducible and high-performance PbO_2 anode requires the use of carefully selected and controlled conditions, there is no generally accepted recipe. Typical procedures are described by Thangappan et al.[157] and by Rifi and Covitz,[353] but modifications may be necessary to achieve the required selectivity and durability for a particular application. When lead is anodized in situ, the coating cannot peel off but continuous corrosion does occur. Commonly, an alloy is used; <5% calcium improves the mechanical strength while silver or antimony reduces the rate of corrosion.

The most extensive use of PbO_2 is as an anode for the oxidation of chlorate to perchlorate.[4,151,347] It is also used for the regeneration of redox reagents including dichromate[149,150,281] and manganese(III)[281] where PbO_2 generally gives better selectivity than Pt/Ti. PbO_2 is the anode material selected for a solid polymer electrolyte system for the production of high-purity water via ozone.[354] PbO_2 has been used for the oxidation of several organic compounds in sulfuric acid. Examples would include the oxidation of 2-picoline to 2-picolinic acid,[355] of benzenes to quinones,[152–154,356] and of perfluoroalkenes.[285]

Some data on corrosion rates in such electrolyses have been reported,[347] and rates can vary between 0.01 to 10 mm $year^{-1}$, depending on conditions and current density. Generally, however, the design and optimization of a new process will require further testing.

(*c*) *Carbon.* Carbon is another material that always merits consideration as an anode in acid solution. Corrosion and/or erosion resulting from the lattice expansion following anion intercalation must always be of concern.[357,358] In very oxidizing conditions, glassy or vitreous carbons are advantageous because of their inertness and high oxygen overpotential. Glassy carbon is, for example, used for the generation of ozone.[4,344]

(ii) Anode Materials in Neutral and Alkaline Solutions

In aqueous alkaline solution, nickel is an excellent anode material and has been used for the manufacture of permanganate[4,280] and in pilot plants for the oxidation of a protected sorbose.[138,139] Organic reactions at nickel in base have been discussed in section V.C. Monel is a less expensive, possible alternative to nickel.

There is surprisingly little experience of synthetic oxidations in neutral solution but Pt/Ti and carbon would be the likely starting point for the search for an anode.

(iii) Anode Materials for Nonaqueous Media

An increasing number of organic electrosyntheses use an organic solvent, particularly methanol and acetic acid. Again the choice of anode will be based almost entirely on cost, stability to corrosion, and the ability to support the desired reaction selectively and seems to lie between Pt, Pt/Ti, and a carbon.

(*a*) *Pt and Pt/Ti.* Platinum is the preferred material for the Kolbe reaction, a number of which are used commercially. It has to be used as thin foil on a conducting base or Pt/Ti. The former has been used.[359] Platinum is found to undergo significant corrosion under conditions of the Kolbe reaction,[360,361] and this is one of the major factors restricting the wider use of such processes. Pt/Ti has been used as an anode for methoxylation reactions.

(*b*) *Carbon.* Carbon is increasingly used as the anode in nonaqueous solvents. It is inexpensive, relatively inert to corrosion, and often gives better selectivities. It is, however, available in many forms[87-89,276] and it is usually wise to test materials with different porosities and structures and even from different suppliers. Graphite is the least expensive form and has been widely used for the methoxylation of furans.[329,359] Vitreous (or glassy) carbon is more expensive but is more resistant to corrosion under strongly oxidizing conditions. It sometimes gives an acceptable selectivity for the Kolbe reaction.[362] The properties of carbon may be modified by various treatments including selective fluorination[363] and inclusion of polymers. Thus, a graphite/polypropylene composite has been shown to give a good selectivity for the acetoxylation of naphthalene in acetic acid.[359,364]

The use of poorly conducting organic solvents encourages the design of narrow-gap and three-dimensional electrode cells. With this in mind, it should be noted that carbon is available in many disparate forms, including felts,[365,366] reticulated foam,[52-54,367] powder,[368] and spheres.[369,370] The cell design must, however, take into account the low conductivity and brittleness of many carbons, and it is also a difficult material to fabricate into complex structures and to make electrical connections.

Processes for the selective fluorination of small organic molecules and based on carbon anodes have been developed.[371,372] The Phillips technology[372] may be an alternative to the Simons process and allows the preparation of partially fluorinated products. It uses a porous carbon tube and gaseous reactants are fed through the carbon. Reaction is thought to occur at the three-phase interface between the gas phase, the carbon, and the molten KHF_2 medium at 360 K.

(iv) High Hydrogen Overpotential Cathodes

The majority of cathodic reactions require an electrode with a high hydrogen overpotential because they take place at a potential negative to the equilibrium hydrogen potential for the electrolyte medium. Materials that are considered commonly include Hg, Pb, Cd, Zn, Sn, and carbon. For reactions requiring only moderately reducing conditions Cu, Al, Fe, steels, Ni, Hastelloy-C alloys, monel, and Ag may also be considered. For electrosynthesis, the factors dominating the thinking of the design engineer will be material yield, current efficiency, stability of the cathode (both on load and on open circuit), and for the preparation of some compounds (e.g., pharmaceuticals), fear of toxic contamination.

Historically, mercury occupies a special position. It has a very high hydrogen overpotential and has been widely used in the laboratory and, as a liquid, its surface can easily be renewed continuously. On the other hand, it is highly toxic to handle (and may lead to toxic materials in the products—elemental mercury or one of the many readily formed organomercury compounds; see sections V.E and V.F) and greatly increases the problems of cell design. Even so, it still sometimes finds application as an amalgam. For example, lead amalgam is used in a process for the reduction of VO^{2+} to V^{2+} for a nuclear decontamination process.[373]

Lead is the most common cathode. It also has a high hydrogen overpotential and is especially stable in sulfuric acid solutions. Its mechanical properties are not ideal for large-area electrodes and hence it is often used as an alloy (although, for example, Sb added to improve its corrosion resistance and machinability also lowers the H_2 evolution overpotential) or on a steel backing plate. Typical applications include the reduction of oxalic acid to glyoxylic acid,[327] of indoles to dihydroindoles,[359,374] of phthalic anhydride to dihydrophthalic acid,[359] and in the Mark I Monsanto process.[98,326,330]

Cadmium is a good alternative to lead although it is more toxic. Electroplated onto mild steel, it is the cathode in the Monsanto Mark II process.[4,26] It was selected, after extensive testing, as the best compromise taking into account selectivity and corrosion resistance although the success of these electrodes is very dependent on the quality of the electrodeposits. As noted earlier, the conditions are, in fact, controlled so that slow dissolution continues to occur.

The other metals listed above only find application in particular electrolyses where lead, cadmium, and carbon have disadvantages or the metal appears to have special activity. Examples of the latter include the reduction of nitrate, which occurs especially efficiently at nickel and Pt/Ni,[375] and the reduction of nitrobenzene to *p*-aminophenol, which has superior selectivity at copper or monel in concentrated sulfuric acid.[225-227] In general, copper and monel operate very satisfactorily in acid solutions,[376] and nickel and iron merit consideration in alkaline solution.

Carbon attracts increasing attention because of its nontoxic properties. It may be considered for most cathodic reductions although on some occasions it shows unusual properties. Thus, for the electrohydrodimerization of formaldehyde to ethylene glycol it has been found that graphite is the only cathode giving good selectivity.[232,233,377] A complex mechanism where the surface mimics an active enzyme center has been proposed; it has also been suggested that the graphite surface catalyzes the dimerization of radical intermediates.

(v) Other Cathodes

As discussed in section V.B, cathodes that operate by mechanisms involving absorbed hydrogen atoms are showing great promise in the laboratory. Such reactions show excellent selectivity and low overpotentials but we are, as yet, not aware of any examples of industrial exploitation.

F. Electrodes for Industrial Processes

As a summary, Tables VIII and IX report the conditions and electrode materials for a selection of processes that have been operated commercially or for extended periods in a pilot plant.

VII. New Developments in Electrode Materials

In this final section, some concepts and materials presently belonging only to the research laboratory are reviewed.

A. Polymer-Modified Electrodes

The past 20 years has seen intense activity aimed at developing chemically modified electrodes, i.e., metal or carbon surfaces coated with a layer of a conducting organic polymer.[128,378-380] Some conducting polymers (e.g., polypyrrole, polythiophene, polyaniline, and polyacetylene) show metallic conductivity while others constructed from monomers containing a redox center where both the oxidized and reduced forms of the couple are stable (e.g., a ferrocene, a nitro aromatic group, a quinone, and a ruthenium complex) conduct by the electron hopping between redox centers.

One driving force for the study of such electrodes was the belief that they could be used in synthesis. It is to be expected that the bound redox centers might show the specific chemistry typical of their solution-free counterparts while not needing to be recovered during the product isolation procedure. It was also hoped that the organic polymer might be used to engineer chiral environments for asymmetric synthesis and to act as hosts for redox enzymes that could be driven electrochemically.

While much progress has been made in the design and synthesis of conducting polymer layers and there are many examples in the literature of polymers that may be cycled between oxidation states over a prolonged period of time, no modified electrode suitable for large-scale synthesis has yet been described. The present status is perhaps best illustrated by a few examples.

Two papers[381,382] have described the preparation of electrodes coated with poly(4-vinyl-4′,4″-dibromotriphenylamine) and shown that the amine cation radical may be used for the decarboxylation of acetate and octanoate in acetonitrile while another[383] discusses the oxidation of carbinols to carbonyl compounds using a polymer prepared from a pyrrole substituted with a nitroxyl group (triphenylamines substituted in the 4-position and nitroxyl compounds are reagents known to carry out such reactions selectively in homogeneous solution). Typical redox groups used to mediate reductions are the viologens, and several polypyrroles based on monomers with a viologen substituent have been prepared.[384-386] These have been used for the debromination of 1,2-dibromo-1,2-diphenylethane to *trans*-stilbene in acetonitrile[384,385] and the reduction of hexachloroacetone to tetrachloroacetone in aqueous solution.[386] All these reactions occur with high selectivity and good current efficiency. The problems, however, are the low current density and particularly the short lifetime of the electrodes. A turnover number of 1000 must currently be regarded as good, and such rapid loss of activity does not allow synthesis on any scale even when the substrate for the polymer is a high-area carbon felt. The loss of activity seems to occur because of changes to the structure of the polymer layers rather than chemical destruction of the redox centers. The same polymers containing Pt or Pd microparticles are promising cathodes for electrohydrogenation.[387]

B. Continuously Deposited Cathodes

At a meeting during 1985, two papers described advantages of carrying out electrolyses with a low concentration of a metal in the catholyte so that fresh cathode surface was created continuously by electrodeposition. One presentation[388] suggested that the selectivity of organic reactions might be different at "clean", freshly created surfaces from bulk metal. The reaction used in the study was the reduction of acetone at copper deposits on lead; it was shown that the yield of the pinacol was 55% when copper was slowly electrodeposited during the reduction but only 2-propanol was formed at bulk lead or copper cathodes. The second paper[389] described a pilot plant for the reduction of nitrostyrenes to phenethylamines using a catholyte containing zinc ions. The role of the zinc ions was to cause the continuous electrodeposition of zinc and hence maintain the current efficiency by preventing contamination of the cathode surface with transition metals that would catalyze hydrogen evolution.

The continuous regeneration of the cathode surface also leads to the possibility of controlling the morphology and catalytic activity of the surface. Preliminary studies of the deposition of a hydrogenation catalyst, nickel, have been reported, and it was shown that the reduction of both acetophenone and benzaldehyde gave alcohol with good selectivity.[102] Having noted that the products from the reduction of carbon dioxide at copper in bicarbonate buffer were sensitive to impurities in the metal and its metallurgical preparation, Cook et al.[390,391] used continuous deposition of the copper on glassy carbon to produce an active and reproducible surface. Such cathodes gave good yields of hydrocarbon products at relatively high current density (e.g., 68% methane and 11% ethylene at 25 mA cm^{-2} or 73% methane and 25% ethylene at 8 mA cm^{-2}).

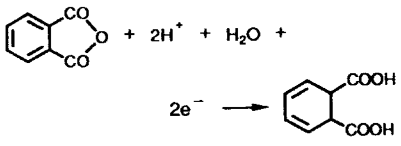
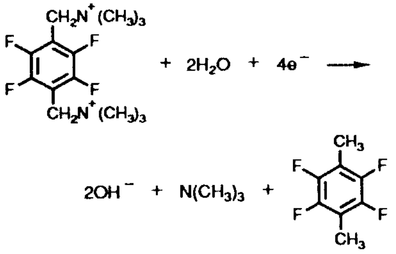
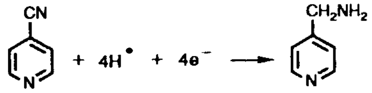
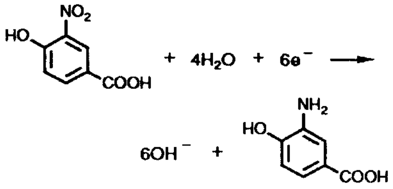
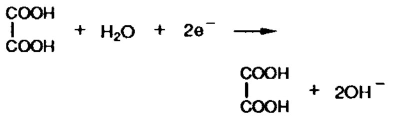
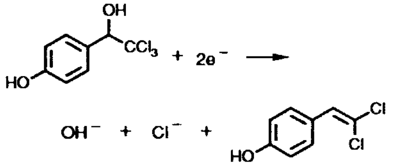
C. Electrodes with Underpotential Metal Coverages

The electrodeposition of submonolayer amounts of metals, particularly Pb, Tl, and Bi, has also been shown to have a marked influence on the performance of electrodes. Underpotential deposits of these metals on Pt surfaces have been shown to catalyze electron-transfer reactions[392] and also change products.[393-397] It is believed that the underpotential deposits form an organized array on the surface and that the mixed Pt/M surface is less able to adsorb either impurities or the electroactive species. Certainly, the reduction of nitrobenzenes seems to occur via electron-transfer mechanisms rather than by hydrogenation mechanisms as at Pt itself. The major problem with the use of such electrode surfaces in synthesis would be the long-term control of adatom coverage.

D. Ceramic Electrode Materials

For several decades a group of materials including carbides, borides, and nitrides have attracted attention as electrode materials. They are hard, wear resistant, and refractory materials that also have high conduc-

TABLE VIII. Conditions and the Choice of Electrodes for Some Organic Electrosyntheses

		cathode			anode		
manufacture of	cell	electrode	reaction	electrolyte	electrolyte	reaction	electrode
adiponitrile	undivided bipolar narrow-gap stack	Cd	$2CH_2CHCN + 2H_2O + 2e^- \rightarrow (CH_2CH_2CN)_2 + 2OH^-$	neutral phosphate buffer + additives		$2H_2O - 4e^- \rightarrow O_2 + 4H^+$	carbon steel
1,2-dihydrophthalic acid	membrane cell	Pb		5% H_2SO_4 in dioxane/H_2O	5% H_2SO_4 in H_2O	$2H_2O - 4e^- \rightarrow O_2 + 4H^+$	PbO_2/Pb
tetrafluoroxylene	FM21 cell with membrane	Pb or Zn		none added	satd NaCl	$2Cl^- - 2e^- \rightarrow Cl_2$	RuO_2/Ti
4-pyridylmethylamine	membrane cell with lead shot cathode	Pb shot		H_2SO_4 in MeOH/H_2O	H_2SO_4 in H_2O	$2H_2O - 4e^- \rightarrow O_2 + 4H^+$	PbO_2/Pb
3-amino-4-hydroxybenzoic acid	membrane cell	Cu		NaOH	NaOH	$4OH^- - 4e^- \rightarrow O_2 + 2H_2O$	Ni
glyoxylic acid	membrane cell	Pb		none added	H_2SO_4	$2H_2O - 4e^- \rightarrow O_2 + 4H^+$	PbO_2/Pb
intermediate to *p*-hydroxyphenylacetic acid	membrane cell	Pb		H_2SO_4 in CH_3CN/H_2O	H_2SO_4 in H_2O	$2H_2O - 4e^- \rightarrow O_2 + 4H^+$	PbO_2/Pb

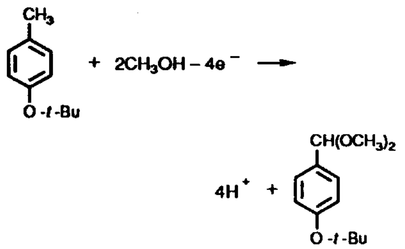
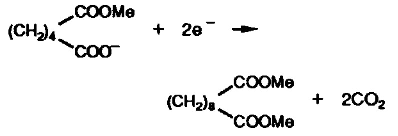
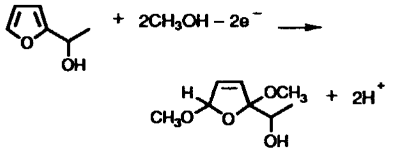
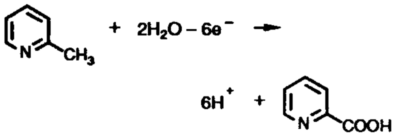
intermediate for 4-hydroxy-benzaldehyde	undivided bipolar carbon stack	C	$2CH_3OH + 2e^- \rightarrow 2CH_3O^- + H_2$.	CH_3OH/KF			C
sebacic acid	undivided narrow-gap cell	graphite or steel	$2CH_3OH + 2e^- \rightarrow 2CH_3O^- + H_2$	partial neutralized carboxylic acid			Pt/Ti or Pt
substituted dimethoxyfuran	undivided narrow-gap cell	steel	$2CH_3OH + 2e^- \rightarrow 2CH_3O^- + H^+$	$CH_3OH/NaBr$			C
picolinic acid	membrane cell with lead shot anode	Pb	$2H^+ + 2e^- \rightarrow H_2$	H_2SO_4	$H_2SO_4/NaHSO_4/H_2O$		PbO_2

TABLE IX. Conditions and Choice of Electrodes for the Electrosynthesis of Some Inorganic Compounds

manufacture of	cell	cathode			anode		
		electrode	reaction	electrolyte	electrolyte	reaction	electrode
bromate	undivided parallel plate with external holding tank	steel or Cu	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	NaBr, pH 11		$Br^- + 3H_2O - 6e^- \rightarrow BrO_3^- + 6H^+$	C, Pt/Ti or PbO_2/C
perchlorate	undivided parallel plate	stainless steel	$2H^+ + 2e^- \rightarrow H_2$	$NaClO_3$, pH 0–1		$ClO_3^- + H_2O - 2e^- \rightarrow ClO_4^- + 2H^+$	Pt/Ti or PbO_2/C
persulfate	undivided tubular cell	stainless steel	$2H^+ + 2e^- \rightarrow H_2$	$NaSO_4$, pH 1		$2SO_4^{2-} - 2e^- \rightarrow S_2O_8^{2-}$	Pt or Pt/Ti
ceric sulfate	bipolar membrane cell stack	Pb alloy	$2H^+ + 2e^- \rightarrow H_2$	H_2SO_4	H_2SO_4	$Ce^{3+} - e^- \rightarrow Ce^{4+}$	Pb alloy
manganese dioxide	Undivided open-tank cell	stainless steel	$2H^+ + 2e^- \rightarrow H_2$	H_2SO_4		$Mn^{2+} + 2H_2O - 2e^- \rightarrow MnO_2 + 4H^+$	graphite, Ti PbO_2/Pb
hydrogen peroxide	diaphragm cell with trickle bed cathode	carbon black on graphite	$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$	NaOH		$4OH^- - 4e^- \rightarrow 2H_2O + O_2$	Ni
silver nitrate	membrane cell	stainless steel	$2H^+ + 2e^- \rightarrow H_2$	HNO_3	pure HNO_3	$Ag - e^- \rightarrow Ag^+$	Ag
stannate	membrane cell	steel	$2H_2O - 2e^- \rightarrow H_2 + 2OH^-$	KOH	KOH	$Sn + 4OH^- - 2e^- \rightarrow SnO_2^{2-} + 2H_2O + O_2$ oxidation	Sn
dichromate	membrane cell	stainless steel	$2H^+ + 2e^- \rightarrow H_2$	H_2SO_4	$H_2SO_4^{2-}$	$2Cr^{3+} + 14H_2O - 6e^- \rightarrow Cr_2O_7^{2-} + 14H^+$	PbO_2/Pb alloy
ozone	undivided tubular cell	dispersed Pt on C (porous)	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	48% HBF_4		$3H_2O - 6e^- \rightarrow O_3 + 6H^+$	vitreous carbon
permanganate	undivided parallel plate; anode/cathode areas = 100/1	Fe or steel	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$K_2MnO_4 + KOH$		$MnO_4^{2-} - e^- \rightarrow MnO_4^-$	Ni or monel

tivities. They have been investigated as potential electrocatalysts[18] and a few papers[398–400] have also considered the kinetics of electron-transfer reactions. In general, the properties of the materials depend strongly on chemical composition but little is understood about the reasons.

Within the past 5 years a nonstoichiometric titanium oxide of approximate composition Ti_4O_7 and widely known as Ebonex has been shown to have very interesting properties as an electrode material.[401] It is very stable in many aqueous media and appears to be an excellent substrate for electrocatalytic layers. On the other hand, redox couples commonly show very slow kinetics at its surface,[401,402] and this leads to various possibilities for its use as a counter electrode in undivided cells. For example, it has been suggested that Ebonex may be used as the cathode in an undivided cell for regenerating ceric ion or as an anode in an undivided cell for the recovery of copper from a process stream containing cupric ion and EDTA (very readily oxidized at other anodes).

Ceramic electrodes are likely to become much more important in electrosynthesis.

E. Other Oxides

Ruthenium dioxide, iridium oxide, spinels, perovskites, tungsten bronzes, etc. are materials that have all been widely investigated as electrodes in other fields of electrochemical technology. Little attempt has been made to use them in synthesis or, indeed, to investigate the electrochemistry of organic or inorganic molecules (excluding, of course, the obvious exceptions!) at these materials. We believe that much more attention should be paid to these materials. For example, the excellent performance of Ni/Co spinels for oxidations in aqueous base was noted earlier.[143]

F. Carbons

Throughout this review we have noted the importance of a growing number of forms of carbon, ranging from traditional graphites to vitreous carbons, various structures based on carbon powders, and engineered forms such as reticulated carbon. Already the variation in carbons in terms of surface area and chemical properties is very large. Moreover, the number of forms available is likely to increase. In addition, for other objectives (e.g., fuel cells and oxygen electrodes), carbon has been widely investigated as a substrate for dispersed Pt and other metals. Its structure also makes it very suitable for intercalation or impregnation by organic and inorganic materials; e.g., intercalation by both anions[403–405] and cations[406] has been reported. Such electrodes have interesting properties but the swelling of the graphite during intercalation is also a mechanism for electrode disintegration. Technological success with electrodes of these types would impact rapidly on the technology of electrosynthesis.

G. Engineering Concepts

Many electrode reactions only give a good selectivity and current efficiency at low current densities, ca. <10 mA cm^{-2}. In order for these to be commercially viable it is essential to have a suitable high surface area electrode technology. At least two companies, ElectroCell AB and Reilly Tar and Chemicals Corp., now offer systems that can utilize a packed bed electrode[407–409] and fulfil this need. Pilot-scale operation has been demonstrated for syntheses at low current density. When the reactant is a poorly soluble gas, an alternative approach to increasing the cell current is to use a porous gas electrode. A recent paper[410] describes a cell for the reduction of carbon dioxide to formic acid based on a Pb-impregnated, PTFE-bonded carbon cathode. With a cathode containing 50% lead, it was possible to obtain 100% current efficiency at a current density of 150 mA cm^{-2}.

Solid polymer electrolyte cells are another development from elsewhere in electrochemical technology now being adapted for electrosynthesis. In an SPE cell the two porous electrodes are fabricated onto the opposite sides of an ion-conducting polymer film, e.g., a Nafion membrane. The chief advantage of such cells is their compactness and, because it is the polymer that provides ionic conduction, it is possible to have reactant feeds and therefore product streams that are free of electrolyte. This greatly simplifies product extraction. SPE cells were first developed for water electrolysis.[411] Another system, commercially available, is for the synthesis of ozone;[354,412–414] pure water is fed to the anode and the exit stream is an aqueous solution of ozone with oxygen gas. The only other cell product is hydrogen from the cathode. The system is particularly suited to the sterilization of water for hospitals, drug preparations, etc. Laboratory experiments have also considered organic electrosynthesis in such cells; Ogumi et al.[415–417] have attempted several reactions including the hydrogenation of olefins, the reduction of nitrobenzenes to anilines, and the Kolbe reaction. The promise for such syntheses can be seen from the study of the oxidation of monomethyl adipate to dimethyl sebacate. Using a 60% solution of the adipate ester in methanol and and SPE cell based on Nafion and a porous Pt anode, it was possible to obtain the desired product with a current efficiency of 55% and a selectivity >80%. The product extraction is very straightforward. The major drawback of SPE cells for organic electrosynthesis is the stability of the membrane/electrode combination but, as far as we are aware, there has, as yet, been little development work.

Registry No. H_2, 1333-74-0; O_2, 7782-44-7; Cl_2, 7782-50-5; C, 7440-44-0.

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