ELECTROCHEMICAL PROCESSING, ORGANIC

1. Introduction

An electroorganic reaction is the chemical transformation of an organic substance by the action of an electric current. It takes place at an electrode and is therefore a heterogeneous process. Like other processes taking place at surfaces, its selectivity is influenced by the nature of the electrode material, mass transport, mixing rates, and the nature and composition of the surface and bulk regimes. Successful development of a viable large-scale electroorganic reaction is best effected by application of chemical engineering methods. Electrochemical engineering began to develop as a discrete field in the mid-1950s. It is an interdisciplinary field (1) involving consideration of such factors as current distribution and interfacial electrochemistry as well as chemical engineering process principles. There are a number of texts covering electrochemical engineering and technology (2–14). A significant theme in recent years has been process design to minimize environmental impact or to replace environmentally undesirable chemical processes with more benign electrochemical ones (7–9).

In an electrochemical cell electrons are given up to some component of the medium (reduction) at the cathode and taken up from another component (oxidation) at the anode, both processes driven by a power source. Of necessity therefore, reduction and oxidation take place simultaneously. Most organic electrode reactions involve initial one-electron reduction to a radical anion or one-electron oxidation to a radical cation, although there are processes that can involve direct addition or loss of two electrons. The radical ions generally react rapidly, often producing intermediates which undergo further electrochemical transformation, resulting in overall consumption of two or more electrons. Many such reaction cascades have been reported and analyzed in the organic electrochemical literature (15–24). Not surprisingly, the nature of the reactions which take place is a function of the substance and electrolysis conditions such as concentration, pH, and the nature of the electrode material, particularly where starting materials, intermediates, or products are adsorbed on the electrode surface.

Electrochemical processes must compete with standard reduction or oxidation reactions using reformer hydrogen, atmospheric oxygen, or chemical reagents. An electrochemical process can be a viable alternative to such chemical redox reactions if it involves a cheaper feedstock, reduction of the number of steps or elimination of a difficult, hazardous, or environmentally adverse reaction step, avoidance of waste disposal, toxic materials, permits recycling of reagents, or permits the possibility of generating useful products simultaneously at both anode and cathode. For an electroorganic process to be profitable, desirable features are high product yield and selectivity, current efficiency >50%, electrolysis energy consumption less than about 8 kWh/kg of product, lifetime >1000 hours, ease of isolation of product and ease of recycling of the electrolyte, product stream having >10% concentration of product, and of course production of a useful material.

Most successful applications have been in the fine chemical area, though one successful commodity-scale synthesis, that of adiponitrile, has been operated successfully for many years (see below). Numerous applications, some of which have been commercialized, have been developed in medium-to-small scale processing. Especially attractive on this scale is production of special intermediates in pharmaceutical synthesis or high added-value chemical synthesis (see Fine Chemicals). In these processes multistep reactions are common, and an electrochemical reaction step can aid in process simplification. Off-the-shelf laboratory cells with scaled-up counterparts are now available from a variety of sources, and their components are compatible with most organic reagents and solvents.

2. Cell Design

2.1. Materials.

Cell Construction and Composition. Because most electroorganic syntheses are carried out at or near room temperature, a wide range of plastics can be used in cell construction. A number of readily available polymers such as polyethylene, poly(vinylidene fluoride (PVDF), polypropylene, polytetrafluoroethylene (PTFE; Teflon) are used for cell frames or vessels, while elastomers (qv) such as neoprene, Viton, ethylene–propylene–diene monomer (EPDM) and PTFE are used as gaskets to seal cell parts. Because the cell contents are often good solvents, materials used in cell construction must be tested for long-term stability in the electrolysis mixture. Testing must consider not just the solubility of the materials but also dimensional stability to avoid problems such as swelling at tracks and joints. The materials should also be tested for conductivity because some polymers and elastomers have conductive fillers that preclude their use for insulated cell parts. Whereas machining can be used for fabrication, injection molding is often the preferred method for manufacture. Cells can be reinforced externally if strength is required.

Electrodes. Choice of electrode material is more critical for commercial cells than for those used in laboratory electrolyses. At least three factors have to be considered: (*1*) Cost: the lowest cost form of the electrode material that produces the desired electrode reaction; (*2*) Stability: the electrode material must be stable over long times. Slow dissolution or physical breakdown of the electrode may be unnoticeable in the laboratory but become a significant problem over months of use; (*3*) Conductivity: if the electrode material is not a good conductor, energy losses during electrolysis will add to the costs of operation. Another point to consider is the possibility that the electrode may participate chemically in the overall electrode process (electrocatalysis). Comprehensive discussions of electrode materials are available (25–27).

Electrode Materials. A cell contains both an anode and a cathode and it is common to use different materials for the two. The most widely used cathode materials are C, Fe, Ni, Al, Hg, Pb, Pb, Zn, Cu, Sn, and Cd. Typical considerations in choice of electrode material include the following. Mercury and lead have high hydrogen overvoltage, which may be needed for some transformations. Because it is a liquid, mercury presents mechanical problems and can be lost during electrolyses, resulting in environmental damage, though conversion to an amalgam can mitigate the problem. Lead is soft and readily deforms, presenting mechanical problems which can be overcome by hot dip or electroplating onto iron, steel, or other rigid materials or by alloying with a few percent of silver, antimony, calcium, or copper. Alloying may change the selectivity and efficiency of the electrode, however. Steel is often used as an electrode material because of its low cost and strength and where the cathode is the counter electrode and hydrogen evolution is desired as the cathode reaction. If a lower hydrogen overvoltage is desired, nickel or the more expensive Raney Ni coated cathode, as developed for chlor-alkali cells by Dow and Eltech, may be used instead of steel.

Corrosion problems are common for anode materials, thus the list is shorter than for cathodes. Stoichiometric anode corrosion (a so-called sacrificial anode) may be acceptable where the cathode product is of sufficient value. Frequently-used anode materials include Pt, C, and PbO_2 or NiO_2 (for fabrication see Ref. 28). Ag, Au, Cu, Fe, and Ni anodes can be used for easily oxidized organics. Fe and Ni are relatively stable and have been widely used in high pH aqueous electrolytes. Platinum-clad or platinum-coated titanium can be used for processes such as the Kolbe synthesis, which generally give best results on smooth platinum. Certain types of carbon (29) have also been found to afford good yields in the Kolbe process. Magnetite can be used as an oxygen-evolving anode material; it presents some fabrication problems but methods of preparing it for use as an anode have been reviewed (30). The plasma spray technique is attractive (see Plasma Technology). Because magnetite is a ceramic material, fabricating it as a coating on titanium is probably best.

Steel and nickel are generally used in making anodes for oxygen evolution in alkaline electrolytes. Graphite or nickel is frequently used as anodes for anodic halogenation of organics. Platinum cannot be used as an anode in the presence of halide ions because of dissolution to form tetrahaloaluminates. A major development in anode technology was introduction of the so-called dimensionally stable anode (DSA) in the chlor-alkali process for chlorine and sodium hydroxide production, which represents the largest use of electricity for electrochemical processing world-wide. DSA anodes generally use a metal oxide coated on a metal support. The Beer process uses a coating of ruthenium oxide [12036-10-1] (RuO_2) and titanium oxide[13463-67-7] (TiO_2) on titanium for chlorine production. However, this electrode is not very long-lived as an oxygen generator. Companies that offer coated anodes are Eltech, Engelhard, and Electrocatalytic in the United States, ICI in the United Kingdom, Conradty in Germany, and Permelec in Europe (see Metal Anodes).

Stability. The best way to view the electrode is as a catalyst in the process. Its costs and effectiveness should be assessed on the amount of electrode required per kg of product produced. With time, the nature of the active surface is likely to change either chemically or physically. The leaching out of a component from an alloy can change the electrode composition as can surface contamination from an insoluble or strongly adsorbed by-product or electrodeposition of extraneous metals. In laboratory experiments involving short runs at small scale, low concentrations, and reagent-grade chemicals, electrode surface contamination may not be recognized as a problem. It may however turn out to be a critical consideration when developing a commercial process. Surface contamination can be circumvented by: (*1*) periodic mechanical and/or chemical cleaning; (*2*) periodic current reversal; (*3*) stringent raw material specifications with respect to problem impurities; (*4*) purging and processing the electrolyte recycle stream; or (*5*) periodic replacement of the electrodes.

Corrosion or erosion may cause mechanical deterioration of the electrode surface. To minimize such problems, electrode materials should be chosen with care. Pourbaix diagrams, ie, plots of potential vs pH, point to conditions that might lead to corrosion (12,25). Because the diagrams for metal-water alone can give only an approximate idea of corrosion conditions, the Pourbaix diagram should be generated with all components of the electrolyte present (31). Possible corrosion conditions examined should include measurements at open circuit, ie, without current passing, since it must be known how long electrolytes can remain inside the cell without causing damage when power is removed from the cell for maintenance. Intermediates in the organic electrode process may also cause corrosion. Radical intermediates, including the initially produced radical ions, may attack the anode and/or cathode to form organometallics. High rates of circulation of electrolyte containing solid particles, eg, reaction products or electrode corrosion materials, may cause physical erosion. This problem can be contained by removal of the solids external to the cell. Electrode coatings may be removed chemically or physically, requiring new bonding methods.

Conductivity. Electrical conductivity is important and the cell conditions should be arranged to maximize it. Energy losses and the consequent heating of electrode and electrical connectors are to be avoided. For cell design using a monopolar electrode configuration, pure electrode materials require a resistivity of less than 10^{-4} Ω-cm (26). This helps not only to avoid energy losses, but also to maintain a uniform current distribution (26,32). Because it involves only short current paths through the electrode materials, bipolar design is better for more resistive electrodes such as oxides and conductive polymers.

Diaphragms. In many electroorganic systems, the use of a diaphragm to separate anolyte and catholyte is necessary to minimize possibility of substances formed at the anode migrating to the cathode and being reduced, or *vice versa*. In the development of a commercially feasible process, the selection of a diaphragm for large-scale cells often presents a serious obstacle. The preferred electrolysis diaphragm would have low cost, low electrical resistance, high resistance to mass transfer between anolyte and catholyte while allowing movement of ions to carry the current, long operating life, good dimensional stability, and be resistant to plugging and fouling. The likelihood of finding all of these properties in a single material is small. Diaphragm materials are available in two types: permeable and permselective. The permeable material is a porous matrix offering a limited barrier to all species in an electrolyte and having little variation in transport numbers (and hence little selectivity) among different species. Permselective materials, or ion-exchange membranes, allow the passage of ions of one charge, either negative or positive, with a high degree of exclusion of ions of the opposite charge. Cation-exchange membranes allow greater mobility to cations than anions, and *vice versa* for anion-exchange membranes (see Ion Exchange; membrane Technology). Because of significantly lower cost, permeable materials may be preferable to permselective membranes.

Permeable Diaphragms. A permeable separator is entirely satisfactory when a small amount of flow between the anolyte and catholyte can be tolerated or perhaps even desired. Alundum cups and glass frits are often used in simple laboratory cells. In production cells, however, alundum and other forms of unglazed porcelain are not very practical on account of their fragility (see Enamels, Porcelain Or Vitreous). A variety of alternative porous media are available and in a range of porosities. These have been manufactured as separators or filters in electrical batteries. Available materials include porous thermoplastics of polyethylene or polypropylene, PVC, PTFE, polycarbonate, and isoprene rubber, filter cloth of glass, polyethylene or polypropylene, PVC, and PTFE, and nonwoven fabrics (qv) of polyethylene and polypropylene or vinyl chloride–acrylonitrile copolymer. The electrical and diffusional resistances of porous materials are related to permeability, pore size, and thickness. Methods of evaluating and correlating the electrical conductivity of different porous materials have been described (33). Other factors to consider are that the hydrophobic character of some membranes makes them unsuitable for many applications, and that too high a current density can lead to local boiling of the electrolyte within the membrane.

Permselective Diaphragms. There has been considerable activity in development of permselective diaphragms or ion-exchange membranes, especially for electrodialysis and the chlor-alkali processes. Several general reviews have been published on commercially available membranes (27,34,35). Commercial ion-exchange membranes range from 0.1–0.6 mm in thickness, 40–150 cm in width, and 100–300 cm in length; other properties include 1.5–2.0 Ω-cm resistance and 0.8–0.99 transport number when measured in 0.5 N NaCl; 10–60% water content; 2–20 kg/cm^2 mullen burst strength; and \$50–500/m^2 cost. One method of preparing thin ion-exchange membranes involves the casting of a finely divided powder of ion-exchange resin in a plastic binder. Because of their heterogeneous character, these membranes have several disadvantages.

Relatively large channels usually exist through the matrix between resin particles leading to high rates of electroosmotic water/solvent transfer and molecular diffusion. In contrast, homogeneous ion-exchange membranes are available that are essentially a continuous polymeric structure. Several membrane manufacturers use a matrix of copolymer of styrene and divinylbenzene to produce a cross-linked structure. This is then aminated for anion exchange or sulfonated for cation exchange. Alternatively, the styrene and divinylbenzene can also be grafted to a polymer film and then aminated or sulfonated. To improve its mechanical properties, the polymer is frequently reinforced with a screen of Teflon, Saran, glass, or PVC. Tosoh Corp. (Tokyo). A number of companies produce ion-exchange membranes, including Aqualytics Inc. (Warren, N.J.), Aquatech Intl. Corp. (Canonsburg, Pa.), Asahi Chemical (Tokyo), Asahi Glass Co. (Tokyo), Chem-Solv, Inc. (St. Louis, Mo.), Dais Corp. (Odessa, Fl.), E. I. du Pont de Nemours & Co., Inc. (Wilmington, Del.), Electropure, Inc. (Laguna Hills, Calif.), Ionics (Watertown, Mass.), Koch Membrane Systems, Inc. (Wilmington, Mass.), Pall RAI Research Corp. (Long Island, N.Y.), PCA GmbH (Heusweiler, Germany), Solvay S.A. (Brussels), Sybron Chemicals Inc. (Birmingham, N. J.), and Tokuyama Soda (Tokyo). The variety of substances available may be seen by the following examples. Asahi Chemical of Japan produces perfluorocarboxylic acid-type cation-exchange membranes. Tokuyama Soda of Japan produces a fluorocarbon-based cation-exchange resin. RAI Research Corp. (U.S.) produces a range of anion- and cation-exchange membranes on polyethylene or polyfluoroethylene matrixes. Grafting techniques are used by RAI to build in the ion-exchange properties. Properties of ion-exchange membranes can be varied by altering polymer porosity, polymer composition, backing material, thickness, and exchange capacity. It is conceivable that a membrane can be tailor-made to fit the specific requirements of a particular electroorganic synthesis. Examples of membrane evaluations are available (36,37). Mechanical properties are important, as well as problems of unwanted transport of solvent or reactant. The latter not only constitutes a loss of materials, but could result in degradation of the counter electrode. Perfluorinated matrixes have been converted into ion-exchange membranes for the more rigorous environments of the chlor-alkali industry. The first of these, Nafion, a sulfonated membrane for cation exchange, is marketed by Du Pont. These membranes have found application in electroorganic synthesis because of excellent chemical and physical stability as well as success in the chlor-alkali industry (38). A range of perfluorosulfonic membranes for various cell applications is available (39)

Electrolyte. The ideal electrolyte, ie, the conductive solvent of the cell, for organic synthesis would have high solubility for the organic component(s), possess good conductivity, have low cost, be easily recovered and purified, and be noncorrosive. Quaternary ammonium salts provide many of the above criteria in aqueous systems. A concise compilation of solvents and salts used in electroorganic chemistry is available (40).

2.2. Transport Phenomena. Electrochemical reactions are heterogeneous and are governed by various transport phenomena, which are important features in the design of a commercial electroorganic cell system. As for other heterogeneous reactions, the electrochemical reaction is affected by heat and mass transport. The electrochemical reaction, however, is unique in that it also has charge-transport characteristics. More comprehensive works on transport phenomena are available (2-14,41).

Mass Transport. Probably the most investigated physical phenomenon in an electrode process is mass transfer in the form of a limiting current, ie, one that is controlled by the rate at which the electroactive arrives at the electrode surface, not by the applied electrode potential (42). For a simple analysis using the limiting current characteristics of various correlations for flow conditions in a parallel plate cell, see Reference 43. The limiting current in the direction of fluid flow for free upward convection at a vertical planar electrode is proportional to the 1/4 power of the distance up the electrode (43). The limiting current density becomes independent of electrode length for the horizontal configuration. An electrode under free convection, but having gas evolution, produces results that are similar to those seen under forced convection. In most electroorganic syntheses, forced convection environments provide the best cell conditions. Flow can be under either laminar conditions, ie, Reynolds No. (Re) <1000, or turbulent flow (Re >2500). When one considers the parallel plate electrode cell (which can be considered a duct) for laminar flow conditions, the limiting current is inversely proportional to the 1/3 power of the distance along the electrode. Entrance effects are not included in this estimate; a further correction must be determined for this region.

Eddy diffusion as a transport mechanism dominates turbulent flow at a planar electrode in a duct. Close to the electrode, however, transport is by diffusion across a laminar sublayer. Because this sublayer is much thinner than the layer under laminar flow, higher mass-transfer rates under turbulent conditions result. Assuming an essentially constant reactant concentration, the limiting current under turbulent flow is expected to be independent of distance in the direction of electrolyte flow.

Methods proposed for improving mass-transfer rates in large-scale cells are (*1*) rotation of cylindrical or disk electrodes including wiping of the surface; (*2*) use of turbine or propeller agitators; (*3*) fluidized beds of electrode particles; (*4*) fluidized beds of nonconducting particles; (*5*) vibration of the electrode; (*6*) gas sparging; and (*7*) external pumping of electrolyte in open channels or channels having turbulence promoters. In laboratory work, rotating-type electrodes are attractive. However, these run the risk of being an expensive solution to the mass-transfer problem in commercial cells. Costs include operation, initial investment, maintenance, and corrosion in crevices. The use of rotating cylinder electrodes as an approach to the mass-transfer problem in cell design for electroorganic synthesis has been examined (44).

For many electrode reactions, it is just as important to transfer the products away from the vicinity of the electrode as it is to move the reactants to the electrode. For example, cathodic reductions in aqueous solution generate base. This local shift in pH can lead to unwanted side reactions such as in the electrohydrodimerization of acrylonitrile (45,46). In that process the formation of biscyanoethyl ether, the formation of which is pH controlled, is minimized by increasing the mass-transfer rate within the cell by increased electrolyte velocity. Using the same electrode reaction, Asahi employed turbulence promoters, similar to those used in dialysis cells, in the catholyte compartment (46). General

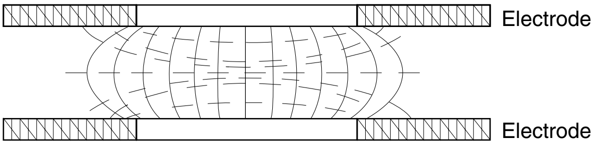


Fig. 1. Current flow (—) and electrical potential distribution (– –) between two planar electrodes separated by an insulated channel. Courtesy of Marcel Dekker, Inc., (45).

discussions of mass-transfer problems for a range of cell designs are available (10,47).

Charge Transport. Side reactions can occur if the current distribution and therefore electrode potential along an electrode is not uniform. The side reactions can take the form of unwanted by-product formation or localized corrosion of the electrode. The problem is addressed by the analysis of charge transport in cell design. The path of current flow in a cell is dependent on cell geometry, activation overpotential, concentration overpotential, and conductivity of the electrolyte and electrodes. Three types of current distribution can be described (48) when these factors are analyzed, a nontrivial exercise even for simple geometries (11).

Primary Current Distribution. As shown in Figure 1, current flow is normal to lines of equipotential. Primary current distribution is influenced only by geometric factors, and in most cells of this arrangement, results in high current density at an edge of an electrode. The primary current distribution at the edges of the electrode is theoretically infinite. Depending on the angle the insulator makes with the electrode, the current density at the edge is lower for an electrode not mounted flush in a cell (11), and for a crevice it approaches zero. The tendency for corrosion to occur where plastic spacers meet an electrode is explained by this local depolarization.

Secondary Current Distribution. When activation overvoltage alone is superimposed on the primary current distribution, the effect of secondary current distribution occurs. High overpotentials would be required for the primary current distribution to be achieved at the edge of the electrode. Because the electrode is essentially unipotential, this requires a redistribution of the electrolyte potential. This, in turn, redistributes the current. Therefore, the result of the influence of the activation overvoltage is that the primary current distribution tends to be evened out. The activation overpotential is exponential with current density. Thus the overall cell voltages are not ohmic, especially at low currents.

Tertiary Current Distribution. The current distribution is again affected when the overpotential influence is that of concentration, ie, at limiting current density. The result is that the higher current density is distorted toward the entrance of the cell. Because of the nonuniform electrolyte resistance, secondary and tertiary current distribution are further complicated when there is gas evolution along the cell track. Examples of investigations in this area are available (49-51).

Heat Transfer. Cells are designed to minimize electrical power consumption. Heat removal, however, is generally also a requirement because of the electrical resistive heating of the electrolyte. Although not economical, this becomes a convenient method of cell temperature control. Heat removal for a commercial electrolysis system is generally carried out by internal or external evaporative cooling, circulation of electrolyte through external heat exchangers, or internal cooling with coils, jackets, or tubes that may also act as electrodes. Standard chemical engineering practice (52,53) is followed for other aspects of cooling system design.

2.3. Reaction Engineering. Electrochemical reaction engineering considers the performance of the overall cell design in carrying out a reaction. The joining of electrode kinetics with the physical environment of the reaction provides a description of the reaction system. Both the electrode configuration and the reactant flow patterns are taken into account. More in-depth treatments of this topic are available (3,6,10-14).

Electrochemical Cells as Reactors. The electrochemical reactor readily parallels the chemical reactor of which there are two types used as ideal models. The first is the plug flow reactor (PFR) where reactants and products move through the reactor in a plug-like manner. No mixing occurs in the PFR, which presumes that concentration changes occur only in the direction of electrolyte flow. The second model is referred to as a back-mix or stirred tank reactor (STR). The STR assumes perfect mixing and uniform composition in all zones of the reactor. An E is inserted for the electrochemical version of these abbreviations to produce PFER and STER. Idealized models are not attained in practice: mixing occurs in the PFER, whereas imperfect mixing occurs in the STER. Thus reactors are often described as having either PFER or STER features.

The PFER and STER reactor types are influenced by mode of operation. The PFER can be used as shown (Fig. 2). Alternatively, a circulation loop can be added so that the inlet composition contains product. It is possible to shorten the length of the reactor and have higher mass-transfer rates using this latter configuration. The change in composition in these reactors is dependent on electrode length or flow rate. The plug flow model can be of use in estimation of electrode lengths. Reference 55 provides an example of this reactor model analysis.

As shown in Figure 3, the STER can be configured for four modes of operation. A narrow gap divided cell is depicted in these schematic drawings. This narrow gap divided cell is shown in a circulation loop containing a surge tank and

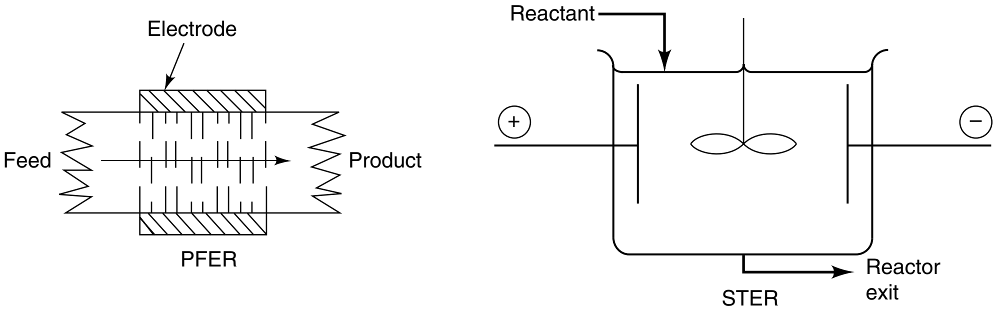


Fig. 2. Schematic models of a plug flow electrochemical reactor (PFER) and a stirred tank electrochemical reactor (STER). Courtesy of Marcel Dekker, Inc. (54).

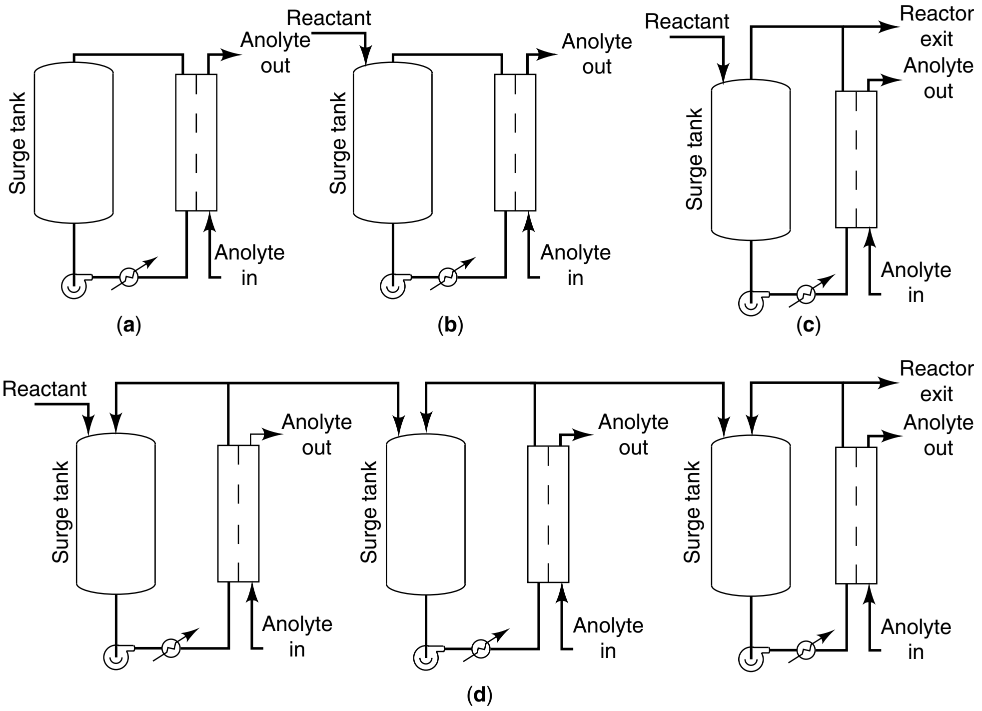


Fig. 3. Configurations for the stirred tank electrochemical reactor (STER). The surge tank contains both reactant and product. (**a**), Batch; (**b**), semibatch; (**c**), continuous; and (**d**), cascade. Courtesy of Marcel Dekker, Inc. (54).

heat exchanger. Because of the dominant need for low cell resistance and good mass transfer through forced convection, this is probably the most likely general cell arrangement for the STER. Acceptable current distribution is provided by parallel plates. Figure 4 shows the reactor compositions for the various modes of operation. A single charge of reactant is made for the batch reactor. After sufficient reaction time, the charge, which has now been converted into product, is removed. As seen in Figure 4**b**, conversion depends on time. With the exception

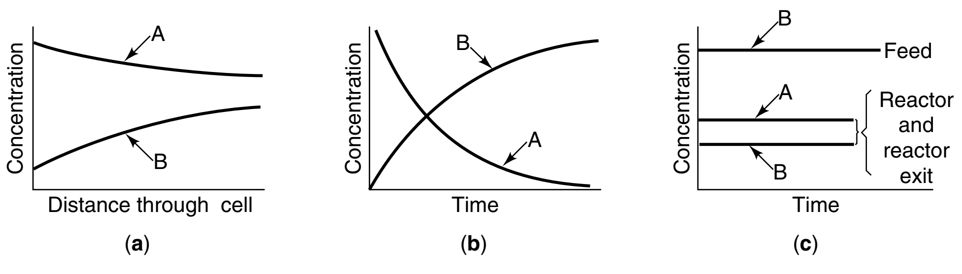


Fig. 4. Representations of reactor compositions for modes of cell operation where A represents product and B, reactant. (**a**), PFER; (**b**), batch STER; and (**c**), continuous STER. Courtesy of Marcel Dekker, Inc. (56).

of the reactant composition in the batch being kept constant with time, the semibatch reactor configuration has the same feature. For the continuous STER (Fig. 4**c**), the compositions are constant with time. The first step in product refining with this arrangement is recovery of reactant for recycle back to the reactor. When continuous reactors are linked in a cascade, the final scheme for STER is produced. This arrangement gives an overall performance similar to that of the PFER, such that each reactor is at a point on the curves of the PFER. Some work on modeling the STER is available (57).

Economics and key characteristics of the electrode process govern the choice of reactor configuration and mode of operation. Where reaction rates have to be matched, engineering design can be critical in reaction schemes that involve electrochemical regeneration of a reactant. The regeneration of Mn^{3+} in the reaction sequence of butadiene to sorbic acid (58) is an example. Continuous operation is preferred for commercial cells. However, pharmaceutical products are usually made in batches so that materials can be accumulated for subsequent steps. Reactor choice is determined when a feature of the reaction significantly determines yield. The electrohydrodimerization of acrylonitrile to adiponitrile is an example. In this case, there is an optimum concentration of acrylonitrile in the electrolyte for minimum by-product formation (59). Thus the continuous STER-type reactor is used. The product refining first goes through a reactant recovery step (60). Electrochemical cell design in the context of reaction engineering and electroorganic synthesis has been reviewed (10,61).

Scale-Up of Electrochemical Reactors. The intermediate scale of the pilot plant is frequently used in the scale-up of an electrochemical reactor or process to full scale. Dimensional analysis (qv) has been used in chemical engineering scale-up to simplify and generalize a multivariant system, and may be applied to electrochemical systems, but has shown limitations. It is best used in conjunction with mathematical models. Scale-up often involves seeking a few critical parameters. For electrochemical cells, these parameters are generally current distribution and cell resistance. The characteristics of electrolytic process scale-up have been described (62,64).

In standard chemical engineering, scale-up is sometimes achieved by a number of small reactors rather than one large one. This is normal in the case of electrochemical cells, but it is common to use many small cells. This is an attractive form of scale-up because it gives reliable performance. However, it loses the cost advantage of the large reactor. A variety of options for hydraulic and electrical connections are possible with multiple cells and are shown in Figures 5 and 6, respectively. The electrolyte may be run in parallel from one manifold to another in a given stack of cells. Alternatively, electrolyte can flow in series. Parallel flow has the general advantages of small temperature rise, lower gas fraction problems, low pressure drop, and low conversion per pass (some reactions are optimum at a constant reactant concentration). Parallel flow has the possible disadvantages, however, of nonuniform flow distribution, large volumetric flows, low conversion per pass (keeping recycle of reactant to a minimum), and higher bypass currents. Electrical connection to the cell bank can be monopolar or bipolar. Bipolar cell connection has the advantages of fewer busbar connections, more uniform current in each cell, better matching to rectifier equipment, lower voltage losses because of fewer connections, and no

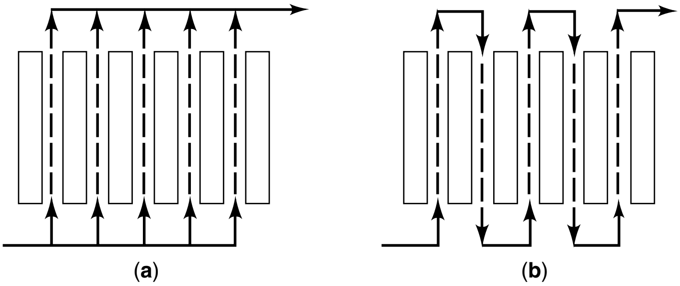


Fig. 5. Options for electrolyte flow through parallel plate cells: (**a**), parallel, and (**b**), series flow. Courtesy of Marcel Dekker, Inc. (65).

problem of current distribution down a plate because of plate resistance. The bipolar arrangement has the disadvantages of hazard present with high d-c voltages, disruption of a whole bank of cells in case of a cell malfunction, and current losses from bypass currents in the manifolds.

Over the years, a number of workers have included bypass currents (also known as shunt, leakage, or parasitic currents) in the modeling of bipolar cell stacks. These models have been based on analysis of an analog resistance network of the cell bank. Although a simpler but more approximate model may be used (67), Reference 68 gives a more comprehensive modeling. The fraction of leakage, ie, wasted current, increases with approximately the square of the number of cells, but decreases with increased current density, because of the nonlinearity of overpotential and electrode length. Manifold design is a compromise between constricted high resistance channeling and tolerable pressure drop to achieve low current bypass at the cell inlet and exit. Corrosion of exposed metal may occur in this manifold region because of considerable voltage gradients.

2.4. Cell Geometries. Uniform electrode potential, short interelectrode gaps, and good mixing and mass transport benefit many electrochemical reactions. These are best achieved with narrow spaced rectangular plates with turbulent flow electrolyte. Reviews of electrolytic cell design are available in the literature (10,69,70). Several types of cell designs are reviewed herein. Design

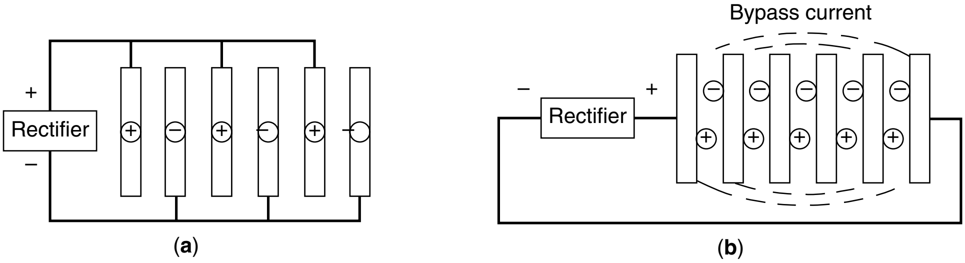


Fig. 6. Options for electrical connections to parallel plate cells: (**a**), monopolar and (**b**), bipolar connection. Courtesy of Marcel Dekker, Inc. (66).

features in standard chemical engineering hardware are often used in various electrochemical cell designs. This is especially true if that equipment has a desired feature such as mass transfer, heat transfer, or gas absorption. The familiar filter press cells are made more sophisticated with internal manifolds such as plate heat exchanger, fluidized and packed bed from catalytic reactors, etc.

Tank Cells. One can directly extrapolate a laboratory beaker cell to larger scale by the use of plate electrodes immersed in a lined rectangular tank, which may be fitted with a cover for gas collection or vapor control. The tank cell, which is usually undivided, is used in batch or semibatch operations. It has the attraction of being both simple to design and usually inexpensive. However, it is not the most suitable for large-scale operation or where forced convection is needed. Rotating cylinders or rotating disks have been used to overcome mass-transfer problems in tank cells. An example for electroorganic synthesis is available (45).

Two-Dimensional Electrode Flow Cells. The simplest and least expensive cell design is the undivided parallel plate cell with electrolyte flow by some form of manifold. Electrical power is monopolar to the cell pack (71). An exploded view of the Foreman and Veatch cell is shown in Figure 7. Note that electrolyte flow is in series and that it is not easily adapted for divided cell operation.

A possible problem of sealing the electrolyte path is found in the Foreman and Veatch cell. This can be avoided by placing the cells in a vessel. The best known example of this is the Beck and Guthke cell shown in Fig. 8 (72). The cell consists of a stack of circular bipolar electrodes in which the electrolyte is fed to the center and flows radially out. Synthesis experience using this cell at BASF has been described (73,74). This cell exhibits problems of current by-pass at the inner and outer edge of the disk cells. Where this has become a serious problem, insulator edges have been fitted. The cell stack has parallel electrolyte flow; however, it is not readily adaptable to divided cell operation.

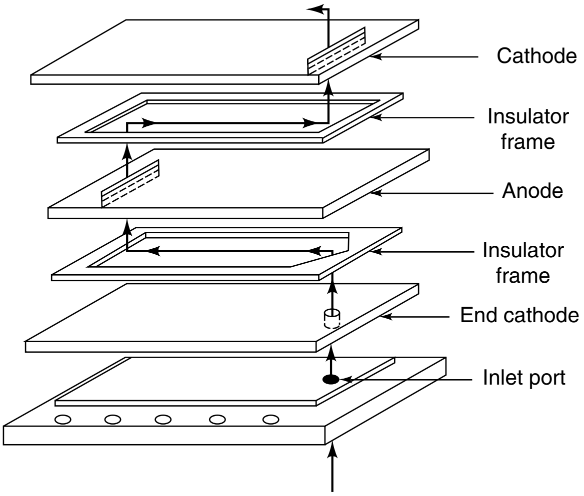


Fig. 7. Foreman and Veatch cell (71).

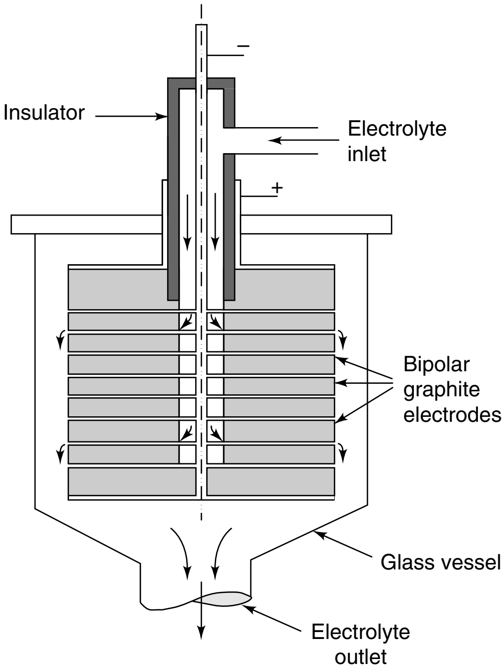
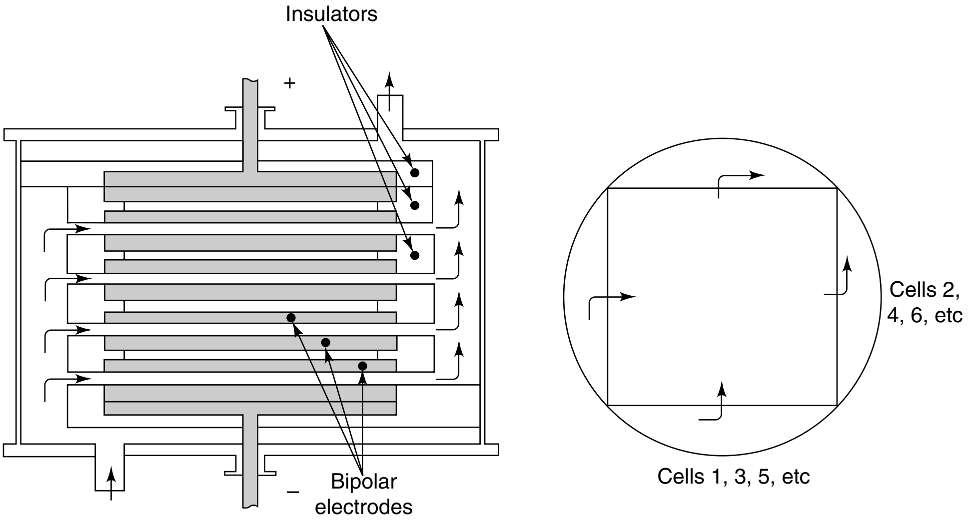


Fig. 8. BASF capillary gap cell (75).

Cell design work at Monsanto has also moved in the direction of vessel enclosed electrode stacks. As shown in Figure 9, one design (75) utilizes square rather than circular electrodes set in a cylindrical vessel. Manifolds are formed by the four segment cavities. To minimize current bypass in the bipolar operation, plastic electrode spacers insulate the cell edges. The advantages of this cell over the disk stack cell are uniform electrolyte flow and square electrodes that can be economically cut from sheets. Adaptation for divided cell operation (77) provides an interesting variation of this cell design. In this mode, the four manifolds are paired to give anolyte and catholyte flow paths. Alternate electrodes are replaced by diaphragm material. A further variation of the stacked electrode system is achieved by placing the electrodes vertically in the cylindrical vessel (78).

The divided cells often involve plate and frame construction. An example of a cell used at Monsanto can be found in Reference 79. Plate and frame cells have also been used by other workers, including BASF (73). In addition, there are commercially available cells of this type.

Three-dimensional-Electrode-Flow-Cells. Three-dimensional electrode flow cells have attracted attention for a number of years as electrode systems that give a high electrode area to cell volume ratio. In addition, they can have good mass-transfer characteristics. These cells are similar to heterogeneous catalytic reactors in being packed or fluidized beds of electrode material. Each may also function as monopolar or bipolar electrodes. The current distribution on the



(a) (b)

Fig. 9. Monsanto stack cell. (**a**), Side view of cell stack; (**b**), top view of flow paths across cells (76).

electrode surface is nonuniform for both of these electrical configurations. This may be undesirable. Electrolyte pressure drops through an electrode bed can be large. The possibility of handling electrode material as a process stream is an attractive feature of the packed-bed particulate electrode. The Nalco process for the manufacture of tetraalkyllead carried out this type of electrolysis on a large scale (80).

3. Commercially Available Cells

The lack of commercially available electrochemical cells was formerly a significant obstacle to electrode process development. This has changed because a number of companies now fabricate a range of cells for general use in electroorganic synthesis. These are parallel plate cells that may be divided or undivided. All use electrolyte recirculation for convection, and some include turbulence promoters to enhance mass transport. They follow the plate and frame design with external or internal electrolyte manifolding. A variety of electrode materials is offered, eg, pure metals, PbO_2, DSA, graphite, and alloys. The cells are constructed of polypropylene, polyvinylidenedifluoride, or Teflon, and a range of elastomers. Peripheral components such as pumps, piping, etc, are also made available from the cell manufacturers. Brochures on these cells are available from the respective companies, which also offer some consulting and support services. Manufacturers of commercial cells include ElectroCell AB (Karlskoga, Sweden), Electrochemical Technology Business (a branch of Ineos Chlor Ltd, previously part of ICI, Runcorn, Cheshire, UK), and USFilter Electrocatalytic (Union, N.J.).

Table 1. **Characteristic ElectroCell AB Cells**[a]

Cell	Micro Flow	ElectroMp	ElectroSyn	ElectroProd
electrode area[b], m^2	0.001	0.01	0.04	0.4
module area[c], m^2	0.001	0.2	1.04	16
current density[c], mA/cm^2	400	400	400	400
interelectrode gap, mm	3–6	6–12	5	0.5–4
electrolyte flow per cell, L/min	0.18–1.5	1–5	5–15	10–30
electrolyte velocity per cell, m/s	0.05–0.4	0.03–0.3	0.2–0.6	0.15–0.45

[a] Ref. 82.
[b] Value given is minimum.
[c] Value given is maximum.

3.1. ElectroCell AB. Cells developed through the cooperation of the Swedish National Development Co. (SU) and the foundation for Industrial Organic Chemistry at the University of Lund, Sweden, are marketed by ElectroCell AB (Akersberga, Sweden), jointly owned by SU and Investment AB Eken. The North American agent for these cells is Electrolytica (Alpharetta, Georgia). A range of cell size is offered from a small benchtop unit to commercial-size modules. The statistics of these cells are outlined in Table 1 and an example is shown in Figure 10. The cells are of the plate and frame design using internal manifolding similar to a plate heat exchanger. With the exception of the Micro Flow cell,

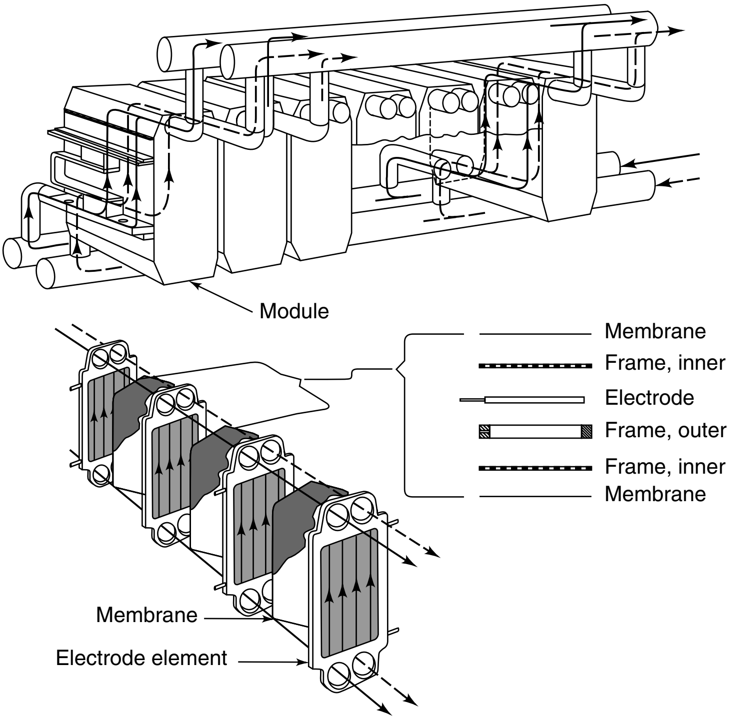


Fig. 10. The ElectroSynCell of ElectroCell AB (81).

multiple cells are packed to form a module in which the electrolyte flows in parallel. The electrodes are electrically connected in monopolar fashion to avoid current bypass. The modules can be hydraulically fitted together as shown in Figure 10 for the ElectroSynCell model. Turbulence promoters are used to enhance mass transfer, and a cell divider is optional. The ElectroSynCell has been demonstrated in the production of glyoxylic acid from oxalic acid with current efficiencies of 84%. This, coupled with the low cell voltage, gives a power usage of 4.3 kWh/kg glyoxylic acid formed. As part of an indirect electrochemical process, the oxidation of cerous to ceric ion has also been performed with a 90% current efficiency (81,82). The purchase price of these cells falls in the range of \$7,000−15,000 per square meter. These prices are dependent on quantity of cells and materials of construction.

3.2. Electrochemical Technology Business (part of Ineos Chlor). In 1981 ICI made available the FM 21 cell for the chlor-alkali industry. FM 21 referred to filterpress, monopolar, 21 dm^2 membrane area. This successful cell was soon modified to the FM 21-SP (superior performance) for general electrolysis processes and particularly electroorganic synthesis by ICI C&P Ltd. In the UK and is now manufactured as the FM1500 cell by Electrochemical Technology Business, Cheshire, United Kingdom.An overall view of the cell is shown in Figure 11. The cell can be either divided or undivided, and uses internal manifolding of electrolyte which is fed to the cell pack in parallel. Electrodes can be flat plate, bladed, or other enhanced surface area forms. The electrodes are spaced as closely as 2 mm, and have a nominal projected area of 0.21 m^2. Electrical connection is monopolar by a copper bus attached along the long edge of the

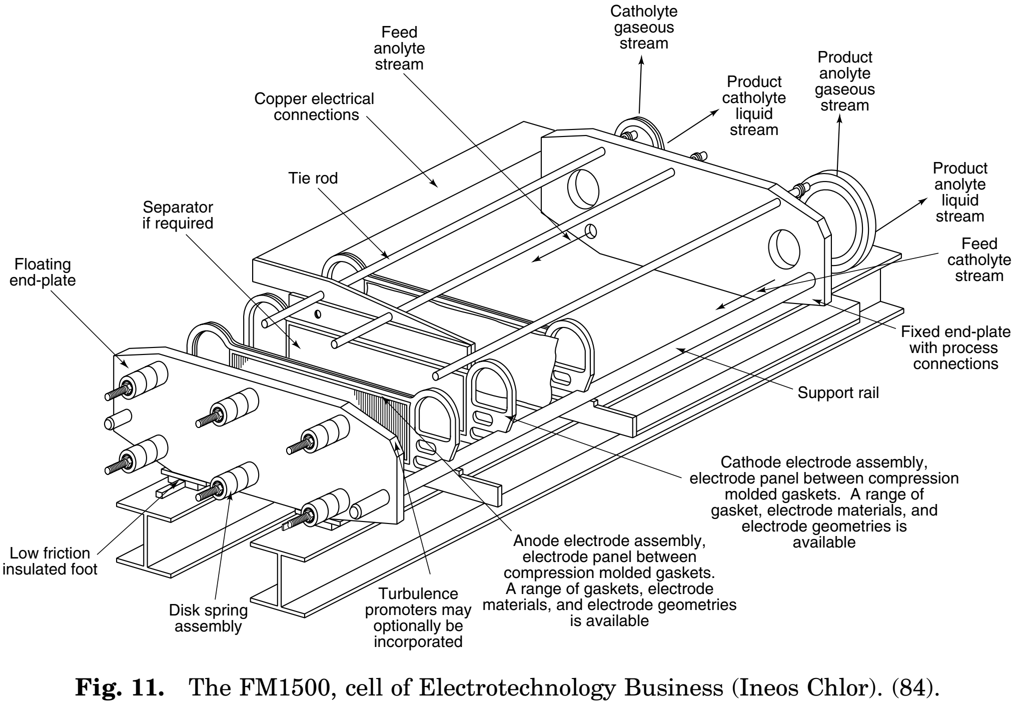


Fig. 11. The FM1500, cell of Electrotechnology Business (Ineos Chlor). (84).

Table 2. **Features of the Electrochemical Technology Business Electrolysis Cells**[a]

Cell	FM01-LC	FM1500
electrode area, m^2	0.0064	0.21
interelectrode gap, mm	1–10	1–10
electrolyte velocity per cell, m/s	0–0.2	0–0.2

[a] Electrode geometries may be plate, blade, or extended surface.

electrode. The cathode connection is on top and the anode on the underside. Several organic processes have been described as run in this cell (83,84). This design and other cells have been developed for lab to commercial-scale use. Some features of the range of cells available are summarized in Table 2. The benchtop cell version of the FM 21-SP is the FM01-LC unit. The FB series cells also have internal manifolding and are of a filter press design. However, they are bipolar in electrical connection, allowing a wider range of electrode materials to be used. As with the ElectroCell AB cell, lab bench to pilot-plant-scale operation can be carried out in the same cell design. The cost of these cells is in the range of $7,000–15,000 per square meter depending on quantity and materials used. The cells are available through Electrotechnology Business, Ineos Chlor Enterprises Ltd, ETB Technical Centre, Cheshire, U.K.), which also manufactures a bipolar divided electrolysis cell for the production of chlorine and caustic soda.

USFilter Electrocatalytic. The cell manufactured by USFilter Electrocatalytic (Union, N.J.) was developed and patented (85) by the Electricity Council, Capenhurst, U.K. The cell design, which is now out of patent, is referred to as dished electrode membrane (DEM) cell, and is of the plate and frame type. The electrodes are dished to produce a wide entrance in the frame for the electrolyte supply. The design overcomes the problem of externally manifolding for a narrow gap parallel plate cell. The electrode and diaphragm spacing is about 4 mm and turbulence promoters can be used, although high electrolyte velocity can be applied. Cell hardware comes in four electrode area sizes: 0.01, 0.05, 0.175, and 1.00 m^2. The external manifolding gives parallel electrolyte flow with a long electrolyte path to avoid current bypass. Electrical connection can be monopolar or bipolar. The current density is up to 500 mA/cm^2, or in special cases up to 100 mA/cm^2. Complete packages are available with pumps, tanks, piping and rectifier. Examples of this cell's use in electroorganic synthesis can be found in Reference 86. The cost of these cells is in the range of $10,000–15,000 per square meter depending on quantity and materials used. The cells are available from USF Electrocatalytic (Union, N.J). C-Tech Innovation Ltd (Chester, U.K.), the successor to the Electricity Council, still offers development work and testing on the DEM cell. Other cells designed for *in situ* generation of sodium hypochlorite from seawater at coastal plants are also available from USFilter Electrocatalytic.

CerOx. CerOx Corporation (Santa Maria, Calif.) offers cells intended for destruction of organics in aqueous streams (87). Ce^{+3} in the stream is oxidized to Ce^{+4}, a potent oxidant, which then oxidizes the organic materials electrocatalytically. A schematic view of the cell is provided in Fig. 12. The cell could in

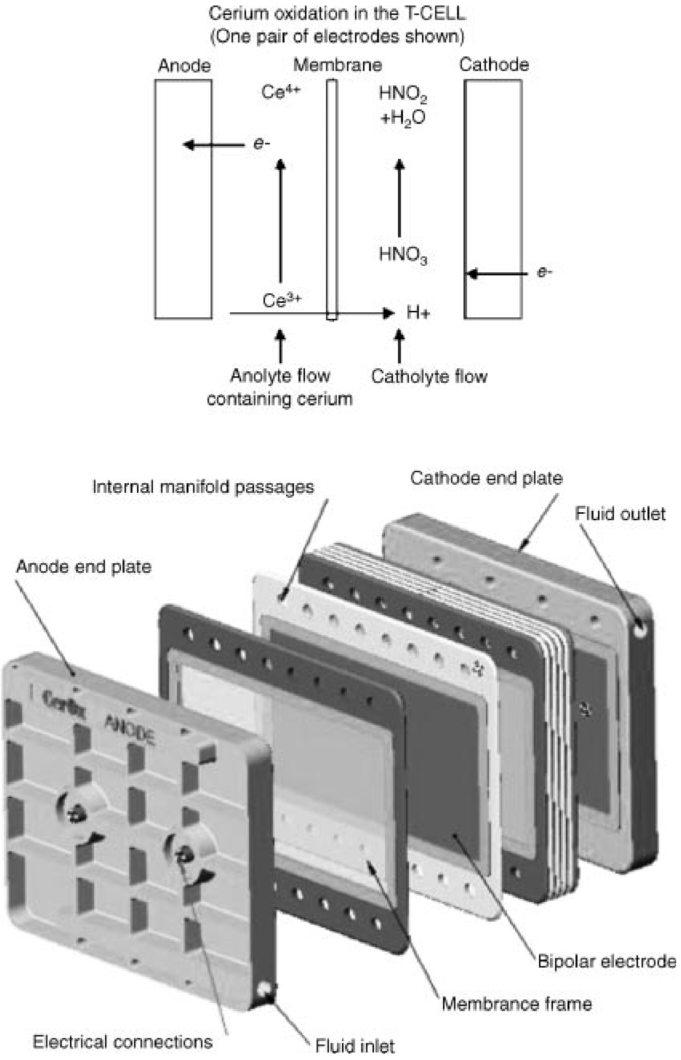


Fig. 12. The Cerox cell (87).

principle be used as an electrosynthetic cell as well. More details can be found at the following web site: http://www.cerox.com/systems_treatment.html#ecell

4. Product Recovery

Comparison of the electrochemical cell to a chemical reactor shows the electrochemical cell to have two general features that affect product recovery. Cell product is usually liquid, can be aqueous, and is likely to contain a salt, ie, a supporting electrolyte added to improve conductivity. In addition, there is a second product from the counter electrode, even if this is only a gas. Supporting electrolyte conservation and purity are requirements. Because product separation from the starting material may be difficult, carrying out the reaction to completion is desirable; cells would be run batch or plug flow. The water balance over the whole flow sheet needs to be considered, especially for divided cells where membranes transport a number of moles of water per Faraday. At the inception of a proposed electroorganic process, feasibility and cost of product recovery and refining should be included in the evaluation to determine true viability. Thus early cell work needs to be carried out with the preferred electrolyte/solvent and degree of conversion. The economic aspects of product recovery strategies have been discussed (88). Some process flow sheets are also available (60).

5. Economic Aspects

Several publications probe the various areas of electroorganic process cost. Cells (89), overall process costs (41,90,91), economic optimization (92,93), and a comparison between the chemical and electrochemical methods (94) are all discussed. Of the three key criteria that govern electrode processes, ie, product selectivity, electric power usage, and electrolysis system capital, any one of these may become paramount in the cost analysis. For instance, power cost is critical in a large-scale process such as the hydrodimerization of acrylonitrile. On the other hand, in small-scale high value-added processes product selectivity is foremost. An important factor in the design of an electrolysis process is the intensity with which the cells can be driven, ie, how high a current density can be used. If it is assumed that the selectivity of the process is independent of current density, then capital and power costs are determining factors. The higher the current density, the less cell related capital is required. To balance this, the higher current density requires an increased power cost. When these two main factors are computed, a minimum total process operating cost is found at a particular current density. Thus the optimum capital and electrical energy usage point is found, and is used to size cells and rectifiers, etc.

Economic analyses including both a detailed cost estimate as well as a factored estimate of a generalized electroorganic process have been worked out (41). These estimates produce a similar result. A detailed breakdown of a cost estimate for a hypothetical electroorganic process using the factored method (41) is given in Table 3 for a process producing 10,000 tons of product annually. The estimates are those from the 1994 edition of the *Encyclopedia*, corrected for an estimated 3% inflationary rate (33.3% overall) over the 10-year interval 1992–2002. The reaction is assumed to take two electrons per mole with a molecular weight of 100. In this analysis, only the cell related capital and operations are considered; product extraction or refining costs are not included. Electrical power, electrolyte cooling, rectifiers, pumps, tanks, and cells with membranes and electrodes, and maintenance and operating costs of the cell area are included. The cost of capital is taken to be 30% of the total investment. Although the process is hypothetical, Table 3 permits analysis of some of the factors involved in the economic estimates. For example, Figure 13 shows that the cost of capital falls steeply with increasing current density, but tends to level out at the higher current densities. Electrical power costs increase continuously with current density because of the linear nature of cell voltage and current at

Table 3. **Current Density Optimization of a Hypothetical 10,000 t/yr Organic Process**[a]

Factor	1	2	3	4
cell current, A	1,050	2,100	4,200	8,400
current density, A/cm^2	0.125	0.25	0.5	1.0
voltage per cell, V	4.9	5.8	7.5	11.0
number of cells	800	400	200	100
equipment cost, \$ $\times$ 10^3				
cells[b]	4,262	2,131	1,066	533
rectifier	573	675	880	1,292
heat exchangers	442	222	286	361
pumps and tanks	597	325	181	104
Total capital cost incl installation \$ $\times$ 10^3	*23,700*	*14,300*	*10,250*	*9,500*
operating cost, \$ $\times$ 10^3/yr				
electricity[c]	1,788	2,105	2,748	4,029
cooling water	75	88	115	169
membranes	480	240	120	60
cell maintenance	280	280	280	280
other maintenance	778	487	367	359
cell labor[d]	1,067	534	267	134
Total operating cost, \$ $\times$ 10^3/yr	*4,468*	*3,734*	*3,897*	*5,031*
capital charges at 30%	7,110	4,290	3,075	2,850
production cost, \$ $\times$ 10^3/yr	11,578	8,024	6,972	7,881

[a] Costs are estimated for 2002 using those in the 1994 edition, assuming a 10-year inflation rate of 3% (overall 33 1.3% increase, which is unlikely to be valid for all items) and do not involve special materials or special cell design. Data were developed by the factor method (41) and do not purport to be any particular process. Equivalent weight of the reactant is 50, and 100% current efficiency is assumed.

[b] Cost is \$5,328 per cell, corresponding to a cell cost of \$6,270/m^2 electrode area.

[c] Cost is \$0.02/kWh.

[d] Cost is \$50,000 per operator.

well above reversible current densities. The membranes, maintenance, and labor factor fall with increasing current density, but are flat for much of the range. The total conversion cost, excluding raw materials, is seen to go through a minimum at about 0.5 A/cm^2. This is the optimum operating current density for this cost model.

Costs for the three factors are lowered substantially for electrode processes that can be run in undivided cells. The cell voltage is lower, cells are less complicated and thus cheaper, and maintenance is simplified. Using a stack cell design, a new production cost for minimum current density is produced. This is shown in Figure 14 together with the total curve for the plate and frame cell. Here the undivided cell gives the lower cost and lower optimum current density of about 0.3 A/cm^2. In this last example, if for some reason the cell had remained an expensive design but the power was still significantly lowered, then the current density minimum point would have been moved higher. Lowering the cost of capital related items moves the current density minimum down, and lowering the electrical power needs moves the current density minimum up.

Similarly, the optimum cost model for three cell designs including separation and refining costs has been examined (95). Using these cost models, it becomes clear where research and development is most advantageous. In most instances, there are clear advantages in carrying out the process in narrow

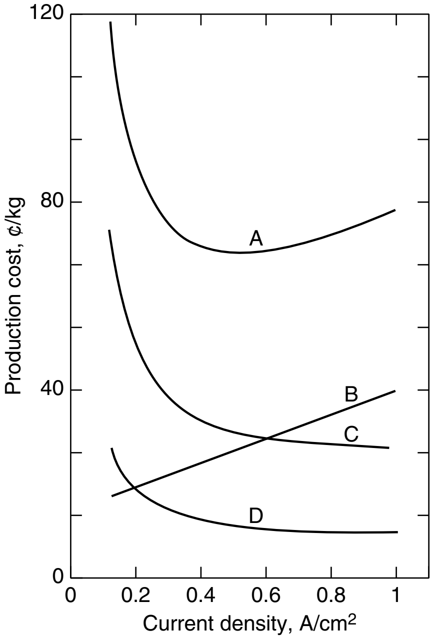


Fig. 13. Economic optimization of conversion costs for a plate and frame cell where A is total divided cell, B is electricity, C is capital, and D is membranes, maintenance, and labor.

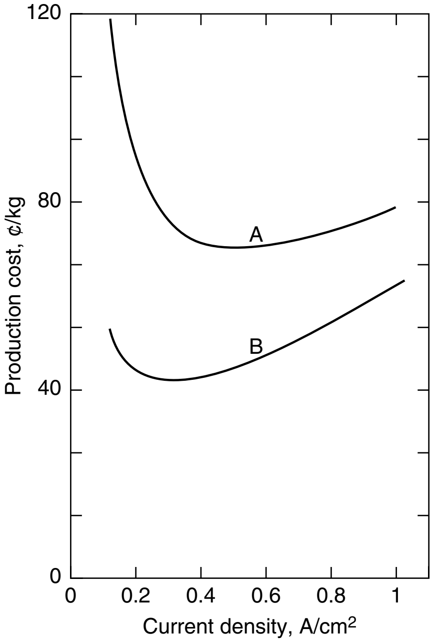


Fig. 14. Economic optimization comparison. Total cost of A, plate and frame, and B, stack cells.

gap undivided cells if possible. Product separation and refining may dominate the cost model, as is the case of the sebacic acid process. Here the demands of the cell reaction require the half ester which has to be recycled. Some general comments on product recovery have been made. Regarding the cost split between reaction area and the product work-up for electrochemical and conventional reactions (60), generally there is not much difference. However, in the scale-up of the cell/reactor, the electrochemical method is at a disadvantage because of the near linear nature of cell scale-up. The cost model may require further complication for bipolar cells to take into account current leakage. Also, although product selectivity may remain constant, the current efficiency may change with current density, and should also be included in the cost model.

6. Commercial Electroorganic Processes

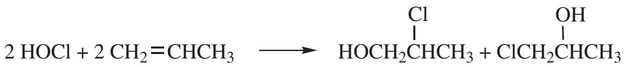
6.1. Commodity-Scale Processes. Some processing of organic chemicals by electrolysis for commercial purposes was carried out in the first half of the twentieth century. These were limited in number and mostly small-scale applications. The industrial uses of electroorganic synthesis on a large scale have been very few. The first large plant was built by Atlas Powder Co. in 1937 for the manufacture of sorbitol and mannitol using the cathodic reduction of glucose (see Sugar Alcohols) (96).

Production was at the rate of 1400 t/yr, but by 1947 this process was superseded by a high pressure catalytic hydrogenation method. In 1964, Nalco's tetraalkyllead process at Freeport, Texas came on stream. It had an original capacity of 14,000 t/yr tetramethyllead [75-74-1], $C_4H_{12}Pb$, or 18,000 t/yr tetraethyllead [78-00-2], $C_8H_{20}Pb$. The primary use of tetraalkylleads was as gasoline additives. Increasing concerns over the environmental implications of the large-scale emission of lead from automobiles resulted in the use of these additives being banned in the U.S. and final doscontinuation of the Nalco process. In 1965, Monsanto started production of adiponitrile [111-69-3], $C_6H_8N_2$, by the electrohydrodimerization of acrylonitrile [107-13-1] at Decatur, Alabama, at similar rates. At the present time only two substances are produced electrochemically in commodity amounts (defined here as production of 10,000 tons/year or more), adiponitrile and bleached montan wax (used to impart a hard, shiny coating to a wide variety of commercial products).

Adiponitrile. The most significant commercial electroorganic synthesis process is Monsanto's electrohydrodimerization (EHD) of acrylonitrile to adiponitrile [111-69-3]. The importance of adiponitrile is as a precursor to hexamethylenediamine [124-09-4], which is used in the manufacture of nylon-6, 6. More than 340,000 metric tons of adiponitrile are produced annually by this process. Monsanto (Decatur, Ala.) is the largest producer, followed by BASF (Teesside, U.K.), Asahi Chemical (Nobeoka, Japan), and Rhodia (Camaciri, Brazil). The cost of manufacturing nylon-6,6 is critically dependent on the cost of the intermediates used, and this has maintained the pressure to produce improvements in the EHD process. In using concentrated solutions of quaternary ammonium salts (QAS), such as tetraethylammonium-*p*-toluenesufonate [733-44-8], $C_8H_{20}N \cdot C_7H_7O_3S$, yields of about 90% were demonstrated at lead and mercury cathodes (97). The principal reactions are as follows: *Main cathode reaction*

$$2\ Cl^- \rightarrow Cl_2 + 2e^-$$

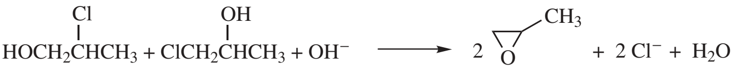
$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$



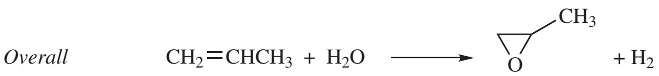
$$2\ HOCl + 2\ CH_2{=}CHCH_3 \longrightarrow HOCH_2\overset{Cl}{C}HCH_3 + ClCH_2\overset{OH}{C}HCH_3$$

Anodic water decomposition

$$2\ e^- + 2\ H_2O \rightarrow 2\ OH^- + H_2$$



Two principal cathode by-products



Propionitrile [107-12-0], C_3H_5N, and an acrylonitrile trimer, 1,3,6-tricyanohexane [1772-25-4] are also produced at the cathode as by-products.

The key cell parameters of Monsanto's divided and undivided cell processes are given in Table 4. The divided cell process is no longer used. The cell was of the plate and frame type (36) with external manifolding. Electrolyte flow was in parallel and recirculated through external heat exchangers; the anolyte was dilute sulfuric acid; the electrolysis system consisted of 16 cell presses, each containing 24 bipolar cells, and a current of 3000 A at 300 V was distributed to each cell bank. Four separate catholyte systems were used to feed the cell banks to minimize contamination in the event of a significant diaphragm rupture (38,78,98). The catholyte in the divided cell EHD process was relatively expensive

Table 4. **Monsanto Adiponitrile EHD Cell Configurations**

Property	Divided cell[a]	Undivided cell[b]
cathode	Pb	Cd
anode	Pb	steel
membrane	ionics CR 61	none
temp, °C	50	55
electrode gap, mm	7	1.8
electrolyte velocity, m/s	2	1.2
current density,[c] A/dm^2	45	20
cell voltage, V	11.7	3.8
power usage, k Wh/kg	6.6	2.3

[a] The electrolyte contains 40 wt% $(C_2H_5)_4N^+C_2H_5SO_4^-$.

[b] The electrolyte consists of 0.4 wt% hexamethylene N,N′-*bis*(ethyldibutyl)ammonium ion, 10 wt% Na_2HPO_4, 2 wt% $Na_2B_4O_7$, and 0.5 wt% tetrasodium ethylenediaminetetracetic acid.

[c] Containing 1 wt% Ag.

and a poor electrical conductor. Furthermore, the ion-exchange membrane was an added cost and gave added voltage drop, and the plate and frame cell was expensive to construct and maintain. These problems were addressed in the development of the process employing an undivided cell (Table 4) (41,78). The electrolyte in the undivided cell has good electrical conductivity and only low concentrations of the quaternary ammonium salt (QAS); this facilitates the dimerization. Sodium EDTA is present to solubilize the iron and cadmium electrode corrosion products and maintain cathode quality. Additionally, the cell structure was very much simplified. The membrane was eliminated, and the bipolar electrode structure was simplified by using cadmium-coated steel sheets. These rectangular sheets were simply stacked with insulator spacers in packs of 100–200 cells. The cell packs were then placed in an insulated vessel in such a manner as to give uniform electrolyte flow in the direction of the longer side.

To recover the adiponitrile product, the organic layer, containing acrylonitrile, adiponitrile, and by-products is decanted from the electrolyte and the QAS is extracted using water. The water-containing QAS is returned to the cell operation. The organic stream leaving the extraction column is sent to a stripping column. There, following removal of by-product propionitrile, the acrylonitrile is recycled to the process. The tails from the acrylonitrile stripper are further refined by distillation to produce a 99+% pure product. This product is suitable for hydrogenation into hexamethylenediamine. To remove the organic and metal ion impurities from the aqueous part of the electrolyte that can adversely affect the reaction selectivity and current efficiency, a portion of this is purged from the electrolyte circulating system. Adiponitrile is recovered from this stream by extraction with acrylonitrile. The aqueous part is then concentrated by evaporation and crystallized to recover phosphate and borate salts. The crystallizer mother liquor containing cadmium salts is removed by precipitation.

It is clear from Table 4 that the undivided cell has considerable power usage savings over the divided cell operation. Also, there are no membrane costs and cell fabrication is much cheaper. In addition, it was possible to simplify the product recovery in the undivided cell process.

Asahi Chemical EHD Processes. In the late 1960s, Asahi Chemical Industries in Japan developed an alternative electrolyte system for the electroreductive coupling of acrylonitrile. The catholyte in the Asahi divided cell process consisted of an emulsion of acrylonitrile and electrolysis products in a 10% aqueous solution of tetraethylammonium sulfate. The concentration of acrylonitrile in the aqueous phase for the original Monsanto process was 15–20 wt%, but the Asahi process uses only about 2 wt%. Asahi claims simpler separation and purification of the adiponitrile from the catholyte. A cation-exchange membrane is employed with dilute sulfuric acid in the anode compartment. The cathode is lead containing 6% antimony, and the anode is the same alloy but also contains 0.7% silver (44). The current efficiency is 88–89%, with an adiponitrile selectivity of 91%. This process, started by Asahi in 1971 at Nobeoka City, Japan, is also operated by the Rhône Poulenc subsidiary Rhodia in Brazil under license from Asahi.

Asahi has also reported an undivided cell process employing a lead alloy cathode, a nickel–steel anode, and an electrolyte composed of an emulsion of 20 wt% of an oil phase and 80 wt% of an aqueous phase (99). The aqueous phase is 10 wt% K_2HPO_4, 3 wt% $K_2B_4O_7$, and 2 wt% $(C_2H_5(C_4H_9)_3N)_2HPO_4$. The oil phase is about 28 wt% acrylonitrile and 50 wt% adiponitrile. The balance of the oil phase consists of by-products and water. The cell operates at a current density of 20 A/dm^2 at 50°C. The electrolyte is circulated across the cathode surface at a superficial velocity of 1.5 m/s. A 91% selectivity to adiponitrile is claimed at a current efficiency of 90%. The respective anode and cathode corrosion rates are at about the mg/ A-h level.

Bleached Montan Wax. Montan wax is a plant fossil product found in certain coal deposits. As found in nature it is a dense, hard, shiny black substance which can be separated from the coal by extraction with an organic solvent. Certain applications, eg, coatings of pharmaceutical tablets, require elimination of the color. An electrochemical bleaching process was developed by Hoechst and the material is now produced by Clariant GmbH (Sulzbach am Taunus, Germany). More than 10,000 tons of bleached montan wax are produced annually using this process.

6.2. Smaller-Scale Processes. Reports of bench-scale electroorganic reactions date back to the nineteenth century (18). Although the Monsanto process is the only really large-scale operation, there has been significant growth in processes on a small scale. More than 50 processes appear to be commercial worldwide (4) and about an equal number have been shown to be feasible in the pilot plant. A listing of some processes can be found in Table 5; further details and a listing of more processes are also available (4,5,25,86,100-105). It is difficult to be comprehensive, because activity in this area is brisk as new processes are brought on line and others are discontinued for one reason or another.

Table 5. **Some Representative Industrial Electrochemical Processes**

Product	Starting material	Company	Scale[a]
adiponitrile	acrylonitrile	Monsanto, Asahi, BSF	L
bleached montan wax	unbleached montan wax	Hoechst (Aventis)	L
dimethyl sebacate	monomethyl adipate	Asahi, others	M
4-anisaldehyde, 4-tolualdehyde	4-methoxytoluene	BASF	M
diacetone-2-keto- gulonic acid	diacetone-L-sorbose	Hoffmann-LaRoche, Merck	M
calcium gluconate	glucose	Sandoz, others	M
anthraquinone	anthracene	L. B. Holliday, ECRC	S
3-hydroxybenzyl alcohol	3-hydroxybenzoic acid	Mitsui Toatsu	S
4-*t*-butylbenzaldehyde	4-*t*-butyltoluene	BASF, Givaudan	S
fluorocarbons and perfluorinated substances	alkanes, etc	3M, Phillips Petroleum, Bayer, DuPont, Hoechst	S
2,5-dimethoxy-2,5-dihydrofurfuryl-1-ethanol	1-furfurylethanol	Otsuka	S
alkyl aryl ketones	2-arylpropionic acids	Searle, Solutia, SNPE, Monsanto	P
propiolic acid	propargyl alcohol	BASF	P
sorbic acid	butadiene, acetic acid	Monsanto	P
3,6-dichloropicolinic acid acid	3,4,5,6-tetrachloropicolinic	Dow	P

[a] L = >10,000 tons/year; M = >1,000–10,000 tons/year; S = >10–1000 tons/year; P = >pilot scale.

Substances produced in quantities greater than 1000 tons/yr include substituted benzaldehydes such as anisaldehyde, tolualdehyde, and 4-*t*-butylbenzaldehyde, anthraquinone, and calcium gluconate (Many other substances are produced in smaller quantities (10–1000 tons/yr) by processes whose value lies in the fact that the electrochemical transformation adds sufficient substantial value to the material to warrant small-scale production. A few of these are described below to illustrate the diversity of the electrochemical process designs represented among these syntheses.

Fluorination. Perfluorinated organic compounds are important industrial surfactants (qv) and textile treating agents (see Fibers, Survey). Ammonium perfluorooctanoate [3825-26-1], $C_8H_4F_{15}NO_2$, has been employed as an emulsifying agent in the polymerization of tetrafluoroethylene (106). Other perfluorocompounds have been used to prepare a firefighting foam that has proven effective in smothering petroleum fires (107). A polymer formed from dihydroperfluorooctyl acrylate has been reported to provide dirt repellency in a formulation applied to textile fabrics (108).

The discovery that a number of organic compounds can be fluorinated by electrolysis in a solution of anhydrous hydrogen fluoride (HF) [7664-39-3] was made around 1940 (109) (see Fluorine Compounds, Inorganic, Hydrogen). In the Simons process, fluorination of the dissolved organics takes place at a nickel anode, generally without generation of free fluorine; hydrogen is evolved at the iron cathode of diaphragmless cell. Alkali fluorides may be added for improved electrolyte conductivity. Typically, the electrolysis is carried out at low (0–20°C) temperatures, low (1–2 A/dm^2) current densities, and operating cell voltages of 5–6 V. Generally, a large number of products are formed, and the yields and current efficiencies are poor by commercial standards. Electrochemical fluorinations of a wide range of compounds including hydrocarbons, alcohols, ketones, carboxylic acids, and amines have been studied (110). A comprehensive review of the field has been published (111).

The first commercial production of electrofluorinated organics was carried out by 3M Co. at Hastings, Minnesota, in 1951. This facility employed a 10 kA cell and had a capacity of about 115 kg/d of fluorocarbon products. The cell employed alternating planar nickel and iron sheets at 12.5 mm spacing, immersed in a cylindrical steel vessel 180 cm high by 120 cm diameter. Cooling was generally provided by coils of tubing within the cell vessel. Vapors consisting of hydrogen, hydrogen fluoride, and light fluorocarbons were passed through a condenser to remove the HF for return to the cell. This cell was used to produce a wide variety of fluorochemicals.

The electrofluorinated organics of principal industrial importance are perfluorooctanoic acid [335-67-1], $CF_3(CF_2)_6COOH$, and perfluorooctanesulfonic acid [1763-23-1], $CF_3(CF_2)_7SO_3H$. Typical conditions for preparation of the latter compound involve batch electrolysis of a 10 wt% solution of *n*-octanesulfonyl chloride in anhydrous liquid hydrogen fluoride at 101 kPa(1 atm) and 17–19°C, employing an anode current density of $2A/dm^2$. An insoluble liquid phase is formed during electrolysis and is readily withdrawn from the bottom of the cell; distillation of this material gives perfluorooctanesulfonyl fluoride in 30–35% molar yields. The potassium salt may be formed by hydrolysis of the sulfonyl fluoride with KOH and the corresponding acid is prepared by distilling from a mixture of the salt in 100% H_2SO_4.

An improved electrofluorination system of Phillips Petroleum Co. has received extensive study. Instead of the flat nickel anode of the 3M cell, a porous carbon (qv) anode is employed, and the organic feedstock is introduced through the pores (111). By judicious control of the organic feed rate and anode current, varying degrees of fluorination can be achieved within the porous anode. Typically, a mixture of potassium fluoride and hydrogen fluoride (1:2 mole ratio) is employed as the electrolyte at operating temperatures of 60/105°C. Current densities of 6–30 A/dm^2 are used, and cell voltages are generally 4–12 V. Current efficiencies to fluorinated products of 80–100% are reported using light hydrocarbon feedstocks. Whereas the 3M process prefers soluble organic reactants, the Phillips' process gives best results using insoluble organic reactant.

Sebacic Acid. Sebacic acid [111-20-6], $C_{10}H_{18}O_4$, is an important intermediate in the manufacture of polyamide resins (see Polyamides, General). It has an estimated demand worldwide of approximately 50,000 t/yr. The alkaline hydrolysis of castor oil (qv), which historically has shown wide fluctuations in price, is the conventional method of preparation. Because of these price fluctuations, there has been considerable interest in an electrochemical route to sebacic acid based on adipic acid [124-04-9] (qv) as the starting material. The electrochemical step involves the Kolbé-type or Brown-Walker reaction where anodic coupling of the monomethyl ester of adipic acid forms dimethyl sebacate [106-79-6]. The three steps in the reaction sequence from adipic acid to sebacic acid are as follows:

Formation of half-ester of adipic acid

$$HOOC(CH_2)_4COOH + CH_3OH \longrightarrow CH_3OOC(CH_2)_4COOH + H_2O$$

Kolbé
coupling of half-ester

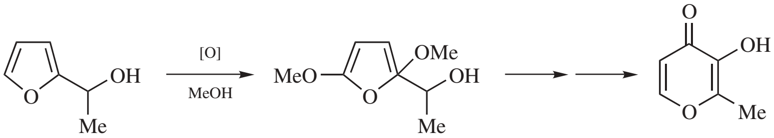
$$CH_3OOC(CH_2)_4COO^- + H^+ \longrightarrow \frac{1}{2}\,CH_3OOC(CH_2)_8COOCH_3 + CO_2 + \frac{1}{2}\,H_2$$

Hydrolysis of diester

$$CH_3OOC(CH_2)_8COOCH_3 + 2\ H_2O \longrightarrow HOOC(CH_2)_8COOH + 2\ CH_3OH$$

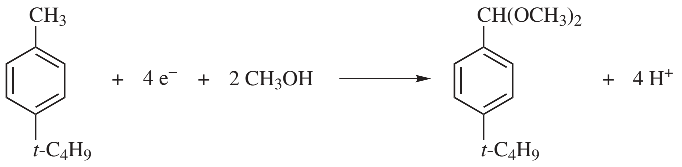
BASF (73), Asahi Chemical Industry (112), and a CIS group (113,114) have carried out pilot-plant studies of the electrochemical route to sebacic acid. Yields of dimethyl sebacate reported for the BASF and CIS processes are in the range of 80–85%. Asahi claims product yields as high as 92% at current efficiencies in the range of 85–90%. The use of high electrolyte velocity (3–4 m/s) through the cell is evidently the key to achieving these superior results. A 20 wt% aqueous solution of monomethyl adipate [627-91-8], having 30 mole per 100 mole of the organic acidity neutralized with sodium hydroxide, comprises the electrolyte and cell temperature is 55°C. A bipolar plate and frame cell with a platinum-plated titanium anode and a steel cathode is used in the Asahi process. Typically, the cells are operated at a current density of 20 A/dm^2 and 14 V. The electrode spacing is 2 mm. A flow diagram for the Asahi manufacture of sebacic acid from adipic acid is given in Reference (112). From the complexity of the process flow diagram, it appears that the sebacic acid process has significant investment and operating costs to overcome. The 1976 economic study by Chem Systems showed a slightly better than 10% cost advantage of the electrochemical route over the conventional process from castor oil in an 11,000 t/yr plant. This technology was demonstrated by Asahi at a 100 t/yr scale. As of this writing, Asahi has not commercialized the process. Sebacic acid was produced electrochemically on a large scale in the former USSR (113,114).

Maltol. Otsuka Chemical Co. in Japan has operated several electroorganic processes on a small commercial scale. It has used plate and frame and annular cells at currents in the range of 4500–6000 A (115). The process for the synthesis of maltol [118-71-8], a food additive and flavor enhancer, starts from furfural [98-01-1] (see Food Additive; Flavors). The electrochemical step is the oxidation of α-methylfurfural to give a cyclic acetal. The remaining reaction sequence is acid-catalyzed ring expansion, epoxidation with hydrogen peroxide, and then acid-catalyzed rearrangement to yield maltol, ie:

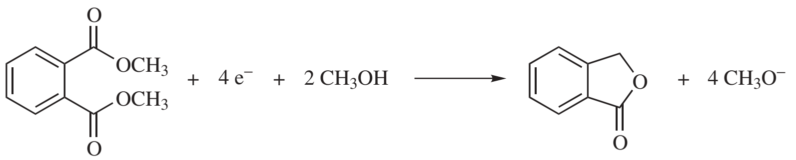


Paired Synthesis of phthalide and 4-t-butylbenzaldehyde. This BASF process is interesting synthetically, economically, and environmentally. It will be recalled that every electrochemical cell requires both an anode and a cathode. In almost all processes the product of interest is formed at one of these, and the product at the other electrode is of little interest and may even be deleterious, requiring separation of the two electrodes by a diaphragm. If one could design a process where both products are desirable materials, then the electrical power would in effect be used twice, saving overall operational costs as well as eliminating the need to dispose of the undesired counter electrode product. Baizer has discussed the advantages and disadvantages of such “paired syntheses” (116). There are stringent requirements for such a process to be feasible commercially, eg, that the two substances be produced under the same conditions, the two half reactions must not interfere with each other and the overall cell reaction must be balanced including consumption of the same amount of current at each electrode, and the two products must be in approximately equal market demand. The chlor-alkali process, in which an aqueous sodium chloride solution is electrolyzed to produce sodium hydroxide at the cathode and chlorine or hypochlorite is formed at the anode, is a good example of a commercial paired inorganic synthesis. A number of paired syntheses have been reported on the laboratory scale (117,118), including even a few which produce the same product at both electrodes, thus doubling the current efficiency (119,120). The first commercial example of a paired organic electrosynthesis was reported by BASF in 1999 (121). Dimethyl phthalate is reduced to phthalide at the cathode of an undivided cell while 4-*t*-butyltoluene is oxidized to 4-*t*-butylbenzaldehyde dimethylacetal at the anode according to the following reactions. Both are important commercial products. Not only is the current used at both electrodes to produce useful products, but the process avoids the formation of hydrogen, with its hazards and disposal costs, that had previously been generated at the cathode before the introduction of dimethyl phthalate as the new cathode electroactive species; likewise, the previous BASF synthesis of phthalide.

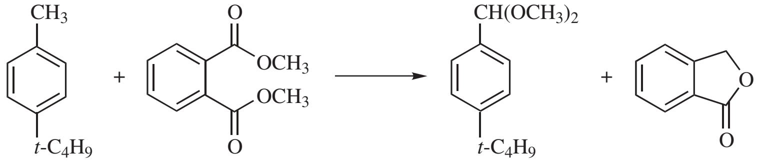
Anode



Cathode



Net cell process



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