Industrial Electrolysis and Electrochemical Engineering

by Morris Grotheer, Richard Alkire, and Richard Varjian

with modifications by Venkat Srinivasan and John Weidner

The introduction of the electrical dynamo in the early 1870s made large scale, relatively inexpensive electric power available for commercial scale chemical production. The early electrolytic products included the metals aluminum, potassium, and sodium; strong chemicals such as bleach, chlorine, bromine, and sodium hydroxide. Over the years, a wide variety of materials, primarily metals and strong oxidizing agents, have been produced electrolytically. Among those produced today are chlorine, sodium hydroxide, sodium chlorate, hydrogen, oxygen, aluminum, copper, magnesium, zinc, and adiponitrile, a raw material for the manufacture of nylon.

Electrochemical reactors are called electrolysis cells. The cells consist of a container, the cell body; two electrodes, the anode and cathode, where the electrochemical reactions occur; and an electrolyte. Some cells have a diaphragm or membrane between the anode and cathode compartments to separate the anodic and cathodic products. While general purpose electrolysis cells are available, cells are usually custom designed for a particular process. The electrolysis cells used to produce the various chemicals and metals cited above differ significantly from one another.

Electrolytic processes consume more than 6% of the total electrical generating capacity of the United States. It is the responsibility of the electrochemical engineer in industry to simultaneously manage electrical consumption and chemical production. He or she must apply relevant scientific and engineering principles to design, construct, and operate a process in an economical, safe, and environmentally conscious manner. Improved understanding of scientific principles and the application of new materials can lead to more efficient cell designs and processes. The constant evolution of technology provides challenging and rewarding careers to engineers and scientists in a range of disciplines.

Examples of Industrial Electrolytic Processes

While a summary of industrial activity follows, a more complete discussion of industrial activity is published annually in the *Journal of The Electrochemical Society*. Some specific references for additional reading are given at the end of this section.

Chlorine and Sodium Hydroxide

Two common chemicals produced by electrolysis of salt solutions are chlorine and sodium hydroxide. The principal electrode reactions that occur in the electrolysis of salt solutions are

$$\text{(Anode)} \quad 2Na^+ + 2Cl^- \rightarrow Cl_2 + 2Na^+ + 2e^-$$

$$\text{(Cathode)} \quad 2H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$$

The resulting overall reaction is

$$\underset{\text{salt}}{2NaCl} + \underset{\text{water}}{2H_2O} \xrightarrow{\text{DC Power}} \underset{\text{sodium hydroxide}}{2NaOH} + \underset{\text{chlorine}}{Cl_2} + \underset{\text{hydrogen}}{H_2}$$

Early production plants were located where electric power from hydroelectric or steam sources and solid salt or brine deposits were readily available. Over the years, two processes emerged. The first was the diaphragm cell, in which a porous asbestos mat separated the anode and cathode compartments. The second was the mercury cell, where the cathode was actually a pool of liquid mercury. The cathodic reaction involved the formation of a sodium amalgam which was separated in a second cell (the stripper cell). The mercury cell used more electrical energy but produced a product of higher purity than the diaphragm cell. Factors, including environmental concerns about mercury and asbestos, product purity of the diaphragm cell, and the availability of new electrodes and materials, currently favor a third system, the membrane cell. The membrane is an impervious separator that allows only sodium ions to pass between the anode and cathode compartments. This results in greater product purity than the diaphragm cell and lower energy consumption than the mercury cell. The membrane is the latest in a series of developments, which include catalytically coated titanium anodes, low voltage cathodes, and corrosion resistant polymers used for cell bodies, that have been incorporated into chlor-alkali cells in the past 30 years. Experience has shown that cell designs evolve constantly and it is expected that new technology will be incorporated into membrane cells in the years ahead.

One example of the constant evolution in design is the development of a process that produces chlorine by electrolyzing hydrochloric acid in cells that are similar to ones described above. Hydrochloric acid is produced as a by-product in various organic processes and its handling and disposal pose serious environmental problems. Electrolyzing the acid to supplement the chlorine produced from chlor-alkali cells allows for a viable means to dispose the chemical. Figure 1 describes a new development in this area where a significant reduction in the energy use was achieved by using an electrode material that allows for the use of oxygen as the feed (an oxygen depolarized cathode), along with a design to feed the oxygen into the system (a gas diffusion electrode). The concept described here is expected to be implemented in the next-generation electrochemical technologies to enhance energy savings.

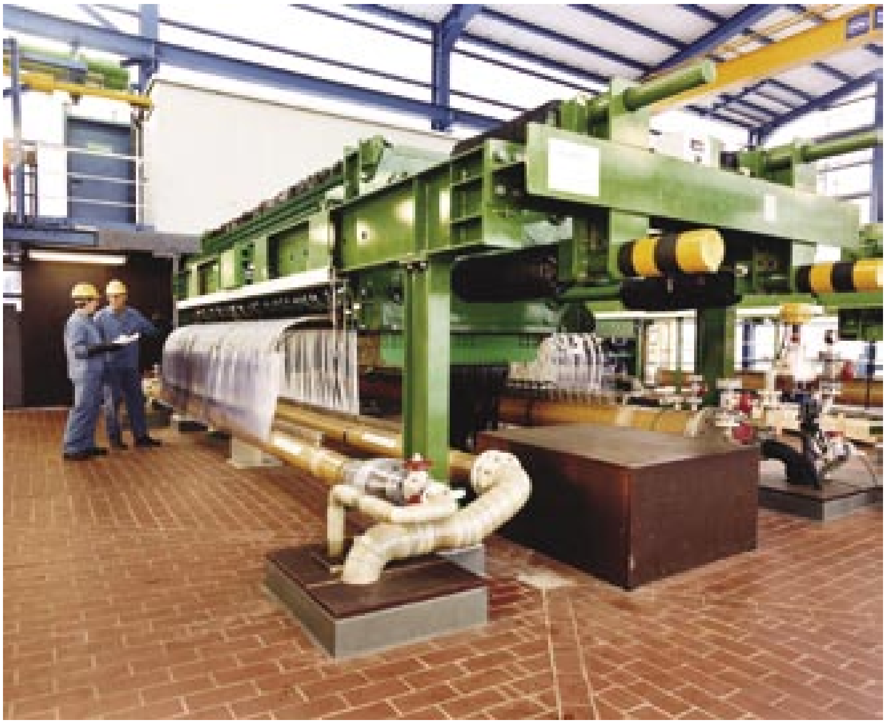

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Fig. 1. *A modern chlorine production cell installation using ion exchange membrane cells. Each electrolyzer consists of planar cell elements separated from each other by a sheet of ion exchange membrane. The cell uses hydrochloric acid and oxygen to produce chlorine gas and water. The cell shown above is the first plant built with a new electrode termed an oxygen depolarized cathode (ODC), and a gas diffusion electrode (GDE) to feed the oxygen. Developed by a joint cooperation of De Nora Tecnologie Elettrochimiche, Bayer Material Science, and Uhde, these changes reduce the energy demand from 1700 kWh per ton of chlorine to 1000 kWh per ton of chlorine. The companies involved received the New Electrochemical Technology Award of the ECS Industrial Electrolysis and Electrochemical Engineering Division in 2005 for this advance. The ODC electrolysis of HCl may be seen as the forerunner of a new family of electrochemical processes all based on the GDE technology and all characterized by lower energy consumption compared to conventional plants. (Picture courtsey of the three companies.)*

Aluminum

Prior to its manufacture by electrolysis, aluminum metal was extremely rare, as expensive as silver, and just as prized. Today aluminum is an inexpensive and widely available material valued for its corrosion resistant properties. The large demand for aluminum products is reflected in that aluminum production consumes more electrical power than any other electrolytic process.

$$\underset{\text{aluminum oxide}}{2Al_2O_3} + \underset{\text{carbon}}{3C} \xrightarrow{\text{DC Power}} \underset{\text{aluminum}}{4Al} + \underset{\text{carbon dioxide}}{3CO_2}$$

One electrode in the cell is made of carbon and is consumed in this high temperature process. Several unwanted reactions also occur, so the production efficiency based on electricity consumption is less than l00%. Among the considerations that influence cell efficiency and lower consumption are temperature, spacing between electrodes, electrode material, electrolyte consumption, cell size, source of raw material, and production rate. Clearly, engineering skill is required for understanding these effects and for achieving optimum production conditions.

In the aluminum industry, intensive research efforts are currently directed toward increasing cell efficiency and toward conserving energy by reducing cell voltage. Among the major research concepts are development of process sensors and control schemes for maintaining consistently high efficiency, and development of electrode materials that permit lower cell voltages and that are not derived from petroleum by-products.

Metal Winning and Refining

Many other metals are obtained from their ores (winning) or purified from impure stock (refining) by electrochemical processes. Among numerous examples are copper, nickel, zinc, magnesium, and titanium. In the copper industry, for instance, electrorefining is carried out by placing impure copper sheets in a cell, dissolving them by electrolysis in a bath of sulfuric acid, and electroplating pure copper at the other electrode. By judicious control of cell conditions, impurities are left behind, either as undissolved solids or as dissolved species that do not plate out. The scientific fundamentals that underlie copper electrorefining include thermodynamics, kinetics, mass transport, and current and potential distribution phenomena. However, fundamental concepts must be transformed into engineering designs to achieve economical operation and high quality product.

Membrane Processes

Membranes make possible an enormous variety of separation processes. Examples of membrane separations include desalting of brackish water and of seawater, demineralization of food products, separation of amino acids, and recovery of resources from wastewater streams. In these processes, the key component is a membrane that permits some chemicals to go through but not others, thus separating them.

Understanding of transport processes across membranes is far from complete, although many industrial processes have been established successfully. Extensive activity is currently directed toward obtaining better insight into how membranes work and toward achieving new membrane recipes that exhibit high selectivity, low ohmic resistance, and robust strength over wide ranges of pH and chemical environments. New industrial membrane processes are constantly emerging as this technology matures.

Electro-organic Synthesis

A commercial process for producing organic chemicals that is currently practiced on a scale comparable to the inorganic chemicals and metals cited above is the electrohydrodimerization of acrylonitrile to adiponitrile

Anode $H_2O \rightarrow 2H^+ + ½\, O_2 + 2e^-$

Cathode $2CH_2 = CHCN + 2H_2O + 2e^- \rightarrow NC(CH_2)_4CN + 2OH^-$

$$\underset{\text{acrylonitrile}}{2CH_2{=}CHCN} + \underset{\text{water}}{H_2O} \xrightarrow{\text{DC Power}} \underset{\text{oxygen}}{½\, O_2} + \underset{\text{adiponitrile}}{NC(CH_2)_4CN}$$

Specialty organic chemicals that are produced electrochemically include perfluorooctanoic acid [$CF_3(CF_2)_6COOH$] and perfluorooctanesulfonic acid [$CF_3(CF_2)_7SO_3H$]. Several electro-organic processes have been practiced on a semicommercial scale. Examples are the oxidation of benzene to benzoquinone and the epoxidation of propylene to propylene oxide. Many electro-organic reactions are facile, and scientific

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understanding is constantly improving. The reasons for the relative lack of large scale electro-organic processes are primarily economic. As feedstock and energy conditions change and technology progresses, additional electro-organic processes may achieve economic viability.

Electrochemical Engineering

While each of the processes above use cells designed for a specific purpose, they are all bound together by fundamental principles that govern the operation. Known collectively as the principles of electrochemical engineering, these concepts include transport processes, current and potential distribution phenomena, thermodynamics, kinetics, scale-up, sensing, control, and optimization. With use of quantitative methods, many salient features of cell operations can be modeled in concise mathematical form. Thus, it has been increasingly possible to predict cell behavior without the cost of an extensive empirical (trial and error) program of preliminary study. These principles cut across all electrochemical industries and can be applied with equal success whether they are used to design a plant to produce chemicals or to design a battery or a fuel cell for use in an electric car. While these concepts are well established in the electrolytic industry, their use in other areas has blossomed in the last few years. Concepts of current and potential distribution within cells, originally conceived by electroplaters, are now being applied throughout the field.

The impact on industry of these developments has been impressive. Beneficial cross fertilization of ideas has occurred recently at an explosive rate. For example, ion exchange membranes, originally developed for fuel cells in space capsules, have revolutionized chlor-alkali production. These same membrane materials have been readapted for use in redesigned fuel cells for terrestrial applications. Similarly, the oxygen depolarized cathode and the gas diffusion electrode, described in Fig. 1, are concepts borrowed from fuel cells and used for chlorine production.

Future of Electrochemical Technology

The development, design, and operation of electrochemical processes have seen enormous advances within the last few decades with profound changes in the recent past. The consequences of energy feedstock and pollution constraints have led to the need for dramatic process changes and reoptimizations. The introduction of new materials in electrolytic cells has led to evolution of wholly new cells and systems. These trends, which have been accompanied by a maturing and deepening of fundamental principles of electrochemical engineering and science, have generated an enormous number of new process options and technologies. For example, the introduction of high surface area porous electrodes into electrolytic cells significantly improves the recovery of metals from very dilute solutions such as occur in the rinse streams of electroplating operations. The opportunities for the future are exciting. ■

Additional Reading

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4. *Tutorials in Electrochemical Engineering-Mathematical Modeling*, R. F. Savinell, J. M. Fenton, A. C. West, S. L. Scanlon, and J. Weidner, Editors, PV 99-14, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).
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7. *Advances in Mathematical Modeling and Simulation of Electrochemical Processes - and - Oxygen Depolarized Cathodes and Activated Cathodes for Chlor-Alkali and Chlorate Processes*, J. W. Van Zee, T. F. Fuller, P. C. Foller, and F. Hine, Editors, PV 98-10, The Electrochemical Society Proceedings Series, Pennington, NJ (1998).

About the Authors

***Morris Grotheer**, a member of ECS since 1963, is retired from the Kerr McGee Corp.*

***Richard C. Alkire** holds the Charles J. and Dorothy G. Prizer Endowed Chair in the Department of Chemical and Biomolecular Engineering at the University of Illinois and is a Fellow and Honorary Member of ECS. He received three of the Society's most prestigious awards: the Carl Wagner Award in 1985, the Edward G. Acheson Award in 1996, and the Vittorio de Nora Award in 2004. He served as ECS President for the 1985-86 term. He may be reached at r-alkire@uiuc.edu.*

***Richard Varjian** is a Technical Leader in the New Ventures Business of The Dow Chemical Company in Midland, Michigan, where his role is developing new process technologies. He is a past chair of the ECS IEEE Division. He may be reached at rdvarjian@dow.com.*

***Venkat Srinivasan** is a scientist at the Lawrence Berkeley National Lab in Berkeley, California, where he works with a team of researchers solving the multitude of problems that prevent Li-ion batteries from being used in hybrid-electric vehicles. Venkat is a regular contributor to Tech Highlights (featured in* Interface*) and the author of the report of the Electrolytic Industries for the years 2001, 2002, and 2004. He may be reached at vsrinivasan@lbl.gov.*

***John W. Weidner** is a professor of chemical engineering at the University of South Carolina. He has published 53 refereed papers on the synthesis and characterization of electrochemically active materials, and the design and optimization of electrochemical systems. Professor Weidner is currently Secretary/Treasurer of the ECS Industrial Electrolysis and Electrochemical Engineering (IEEE) Division. He may be reached at weidner@engr.sc.edu.*