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APPLICATION OF ELECTROCHEMICAL ENGINEERING PRINCIPLES TO ENERGY CONSERVATION PROBLEMS

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Application of Electrochemical Engineering Principles to Energy Conservation Problems

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Even since continuous electric power has become available on a large scale through the introduction of rotating generators, electrochemical processes have become significant users of power for the manufacture of essential materials by synthesis, separation, or modification of surface properties (1). The present interest in the examination of the role of electrochemical processes is not only due to the relatively large fraction of electric power presently consumed by processes currently in use.* Rather, it appears likely that as a consequence of gradual shift from fossil fuels toward nuclear, solar, or geothermal energy sources, incentives for the use of electrochemical process alternatives will increase.

Electrochemical processes are characterized by high energy efficiency and high material yield. They offer the possibility of virtually limitless oxidizing or reducing power, equivalent to hypothetical catalytic reduction or oxidation in the presence of 10^{20} - 10^{30} atmospheres pressure of hydrogen or of oxygen, respectively. Because the electrode potential can be closely controlled, electrode processes are capable of high selectivity, and can achieve very high separation factors. Further, electrochemical reduction of metals from their ions in solution allows a control of shape, of crytalline structure, and of surface finish.

These advantageous characteristics are counterbalanced by some adverse features: electrochemical reactors, compared to "ordinary" chemical reactors have low space-time yield, primarily because of the low mobility of the charge carrying species in electrolytes. As a

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*Currently close to 7% of the electrical energy and 1.5% of the total energy used in the USA is devoted to manufacture of materials by electrolysis.

consequence, plants usually comprise hundreds, even thousands of identical reactor units (cells); area requirements, capital investments, as well as labor and maintenance charges are high.

The most widely applied electrochemical processes involve the reduction of metal ions to metal, or oxidation of the metal to some ionic state or to an oxide adhering to the surface. Virtually all metals of the periodic table may be so processed, and in fact, most are commercially won, refined or plated solely by this method. The most remarkable feature of the electrochemical metal treating industry is the tremendous variety of technological objectives it satisfies in terms of variety of metals and their combinations, the substrate used, and the nature of the surface layer produced. The number of industrial organizations employing these techniques ranges in the thousands.

Among the electrochemical synthesis processes those requiring high oxidation potentials are most prevalent. Chlorine and fluorine and certain of their derivatives are solely manufactured by electrolysis. Although electrolytic decomposition of water to hydrogen and oxygen has lost its economic appeal ever since hydrogen could be obtained from liquid and gaseous hydrocarbons at an unrealistically low cost, it is very likely that this process alternative will regain its significance in the future. Electro-organic synthesis, primarily reduction, oxidation, or halogenation, has had early beginning, but with the exception of a few commercial applications exploitation of this promising technology has been disappointingly modest (2). Certain separation processes involving permselective membranes (e.g. desalination) have already proven to be economically viable. Other special processes, e.g. treatment of waste waters, dehydration of clay, electrophoretic deposition of suspended solids, or of colloids, have reached commercialization, and are used with increasing frequency. Finally, mention must be made of the electrochemical techniques employed for the prevention of corrosion by cathodic or anodic protection (2).

The aggregate economic and social significance of these processes, and of others yet to be advanced to broad application justifies consideration of the present and projected role of "electrochemical engineering".

Electrochemical processes have reached industrial application far before electrical power has become available on a large scale. The beginning of electroplating occured in the first half of the 19th century, and successful processes have been introduced many decades before an even rudimentary understanding of the thermodynamics and kinetics of electrode reactions, or of the nature of electrolytes was available. Large scale industrial electrolysis, electrorefining, chlorine, aluminum and sodium had its beginnings in the 1880-1900 period. This development preceded the elucidation of the EMF series, the Nernst Equation, the nature of the kinetics of electrode processes, and comprehension of transport limitations. There has been a vigorous spirit of exploration, largely by trial and error, of what useful materials may be produced by applying a d.c. potential across two electrodes plunged in a bewildering variety of electrolyte compositions. A wealth of discoveries were made in the laboratory, and quite a few of these reached commercial exploitation. In the absence of rational understanding of the laws governing electrode phenomena, and of transport in electrolytes, translating a process from the laboratory bench to economically significant scale involved purely empirical procedures. Paucity of available materials for electrodes, cell casings, separators, placed a severe restraint on possible cell designs. The role of convection of electrolyte was not even qualitatively understood, in fact supply and removal of reactants and products occured often solely by free convection; a phenomenon responsible for that continued electrolysis was at all found possible.

Scale-up, along with the development of final cell design required painfully small increments in size, and in the absence of understanding of simultaneous phenomena occuring in electrolysis cells the resulting final hardware represented a unique accomplishment. It could not be reproduced by a rational sequence of a priori decisions based on the comprehension of the functional dependence of design parameters. As a consequence, the development of a commercially successful large scale electrolysis process was justly regarded as a unique achievement, a result of ingeneous experimentation, of mistic touch, something that had to be kept secret, because no one could be expected to arrive at similar results unless by devine miracle the same inspiration (and the same luck) were to be granted to him.

The beginnings of the electrochemical process industries, which so far preceded the comprehension of the laws of nature governing their processes, may be responsible for the secrecy surrounding their operations. This industry remained excessively secretive and unwilling to engage in discussions of even the basics relevant to its own processes, and for this reason it failed to inspire scientific advancements needed for a broader adaptation of electrochemical technology. Considering the gamut of potentially interesting and profitable electrochemical processes, many of them proposed already 60-80 years ago, the development of new processes has, in my opinion been lagging far behind the promise inherent in this technology.

Other branches of chemical technology "took off" early in this century, following the path outlined by the ammonia synthesis, and contact sulfuric acid, employing at an accelerating pace modern concepts of thermodynamics, kinetics, and of transport phenomena. The introduction of analysis of chemical processing along the lines of unit operations and unit processes in the 1920's marked the beginnings of chemical engineering science, and resulted in an unparalled expansion of the modern chemical process industries. Design and optimization have gradually become scientific disciplines which have eliminated to a large degree the necessity of empirical scale up and experimentation on the plant scale. The performance of equipment and of entire plants could be predicted with astonishing accuracy, reducing the risk in investment in new facilities and in new process schemes. A parallel development relevant to what would be appropriate to call "electrochemical cell engineering" was late to come.

Not until the 1940's has there been an approach suggested for the engineering analysis of elementary cell phenomena relevant to the prediction of performance of the integral cell processes, and for the establishment of criteria of scale up. [Mantell's book (1960) on "Electrochemical Engineering" is entirely descriptive revealing no awareness of the principles of transport involved in cell processes.]

The first definitive writing on mass transport in convective flow at electrodes (1942) and the first coherent exposition of the effect of electric field on distribution of current on electrode surfaces (1940) set the course for the emergence of "electrochemical engineering science". Following the lucid analysis of Wagner in the 1950's of a number of classical models relevant to component processes occuring in cells (3), investigations of an increasing range of cell phenomena important for rational design and optimization have been forthcoming. Although the flow of this work has gradually increased, the rate of progress has been less than what one would desire considering the potential impact it should have on improvements of existing processes and on the introduction of new electrochemical technology. Just where we stand today in the science of electrochemical engineering can be assessed by what is reflected in Newman's text "Electrochemical Systems" (4), and in recent presentations at the ECS Symposium on Electrochemical Engineering in May 1976, Washington, D.C. (5).

The central task of electrochemical engineering is the realization of electrochemical processes with maximum benefit to society: the development, optimization, design and operation of cell processes which produce materials at the lowest possible overall cost. It is important to recognize that the electrolysis cell represents but one step in an overall process scheme, and that therefore it is the economy of the complete process that is decisive, rather than that of the cell operation alone. In most cell processes the current (charge) efficiency is inherently high, and therefore when one considers energy economy the primary concern is the magnitude of the cell voltage required for a desired production rate. The excess cell voltage (i.e. the increment required over the thermodynamic minimum) is determined by the rate processes within the electrolyte (migration, and convective mass transport) and by the kinetics of the electrode reactions (related to surface catalysis).

A rational design and scale-up procedure therefore depends on the availability of methods for predicting the effects of cell geometry, flow characteristics, surface morphology, and electrolyte composition on cell voltage. In addition, the distribution of reaction rates (current distribution) on the electrode may also be of critical importance. Further, in potential sensitive processes, the range of current density dependent electrode potentials occuring along an electrode has to be kept between preset limits. The electrolyte contained between the electrodes not only provides the electrical conducting path between the electrodes, it also serves as a source for reacting species, and in many instances, as a sink for reaction products. The interfacial composition of electrolyte will in all practical situations be significantly different from the bulk composition. Movement of electrolyte is essential to assure adequate rates of supply and removal of reactants and products. Not only the current energy efficiency, but also the distribution and quality of surface products are sharply dependent on factors determining transport to and from the electrode surfaces. The interfacial composition and the maximum specific rate at an electrode surface (limiting current density) are dependent on geometry, solution properties and hydrodynamics, just as are rates of mass and heat transport in ordinary chemical reactors.

A major area of development in electrochemical engineering science in the past 20-25 years has been the gradual establishment of quantitative relationships which allow the prediction of transport conditions at electrode surfaces (6). This is one of the essential components of any scale-up and design procedure. In high-rate processes mass transfer represents the key limitation to cell capacity.

The distribution of current over electrode surfaces on both the micro- and macro scale is the other significant scale dependent phenomenon. To control shape, and surface structure, current densities must be maintained within narrow limits. The combined effects of geometry, composition, transport and surface kinetics can be predicted by use of advanced numerical techniques requiring large computing facilities. Realistic simulation of transient states (e.g. growths of a metal profile upon cathodic deposition, cutting of a metal surface by anodic dissolution) have recently been achieved, allowing replacement of purely empirical adjustment of process conditions by rational design procedures (7).

The mechanism of gas evolution at electrode surfaces is still poorly understood, and we haven't as yet arrived at the definition of the criteria for the most favorable gas-electrode configurations and flow conditions consistent with the best achievable energy economy.

For the processing of electrolytes which are dilute with respect to the reacting species, and for processes which require close control of electrode potential, porous (or packed bed) electrodes promise to provide interesting design possibilities. The analysis of performance of these three dimensional electrode structures, although not complete, is relatively well advanced, and it is expected that useful applications will soon follow.

The electrochemical engineer faces a special difficulty in the area of prediction of transport properties of concentrated electrolytes, particularly those involving more than one solute. Available theories on electrolytes already fail at low concentrations, and there are no methods by which transport properties of concentrated solutions may be predicted from molecular properties or from dilute behavior.

Advancements in electrode materials, including catalytic surfaces, separators (membranes) and polymers suitable for structural elements [containment and seals] open up entirely new possibilities in cell design. Such new materials as the dimensionally stable (inert) electrodes, and permselective, chemically resistant membranes, have greatly brightened the prospects of improvements in energy efficiency. By providing materials designed to satisfy well defined criteria material science and technology can be expected to continue to play a key role in the advancements of electrochemical process technology.

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A program aimed at energy conservation by advancement of electrochemical process technology should recognize the following three domains of activity:

1. Improvement of existing cell processes by modification of design, and/or of operation conditions (e.g. Cl_2, H_2/O_2 electrowinning, refining).
2. Replacement of existing electrochemical cell processes by new alternatives (e.g. chloride process for Al, electrowinning by through-flow electrodes).
3. Replacement of existing "ordinary" chemical synthesis processes by more efficient and cost effective electrochemical alternatives. (e.g. organic synthesis, high speed electroforming, treatment of radioactive wastes, waste-water treatment).

For progress to occur at a rate commensurate with our rapidly developing needs, efforts in education, research and development must be significantly increased. Considering the economic and social importance of already existing electrochemical processes, and of those demonstrated to have future promise, the commitment of man-power and funds to research in electrochemistry and in engineering is far from adequate. Only a handful of universities offer training in electrochemistry, and in chemical engineering the offerings are equally meager. Support of research devoted to advance the base level of knowledge necessary for developments in technology has been modest, to say the least. There is still an inadequate recognition among funding agencies that a variety of seemingly unrelated technological areas involve electrochemical reactions, and that the advancement of electrochemical science and engineering should have beneficial effects on such economically significant problem areas as corrosion, energy storage and conversion, air and water pollution abatement, in addition to the synthesis, separation, and surface treatment of materials (2,8).

Electrochemical technology provides materials and devices essential for sustaining our civilization. Because of their unique capabilities and inherently high efficiencies, electrochemical processes should achieve an increasing importance in the years to come.

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