The Contribution of Electrochemistry to the Industrial Development of the Future*

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Chlorine, with its innumerable compounds has become a measure of progress and civilization. Without chlorine and caustic, we would not have eliminated many diseases or controlled insects: We would not have had the fiber industry and the paper industry as they are today. We would not have had the petrochemical industry with plastic, solvents, dye-stuffs and so many other products which are part of our daily life and make our living safer and more comfortable. Together with chlorine and caustic, chlorate and hypochlorite, which are also obtained through brine electrolysis, find so many useful or even indispensable applications today.

The most important product of the other major electrochemical industry, the molten salt electrolysis, is aluminum, which so far is obtained by the electrolysis of alumina in a molten cryolite bath, and which together with magnesium is the basis of the light metal industry which is so important in the construction of aircrafts and other vehicles. Worldwide these two electrolysis processes utilize alone about 500 billion kWh per year of energy which, however, is only a very small percentage of the total electric energy produced. Nevertheless, the electrochemical industry has been deeply affected by the energy crisis of the last decade and Japan is among the nations having a serious energy problem affecting the electrochemical industry.

1 The Energy Problem

Going back in history to the discovery of fire, which historians place at half a million years ago, wood was man’s only source of energy and only much later coal was added to wood.

In the last century something extraordinary happened: The world discovered and begun to take advantage of oil and natural gas. Oil today covers half of the earth’s energy requirements, but trends indicate that oil will soon lose its central almost magical quality which has made it part of man’s economy and we know that the twilight nears for the age of oil. The role of oil in the economy is going to be substantially downgraded from now on also because at the rate of 60 million barrels per day, or 1000,000 ltrs per seconds, the proven oil reserves would last only a few decades. The Middle East has one quarter of these reserves, but supplies 40% of the oil traded among nations.

In the last few years, the economics of energy consumption have been radically transformed: We have been aware of the necessity of fuel conservation and we are making efforts in the search for alternative energy sources, including nuclear power and solar energy. Electrochemistry may in the future contribute considerably to the development of new energy sources, particularly from solar energy.

The utilization of solar energy for the generation of electricity in solar cells or otherwise is one of the high priority topics in electrochemical research today. The photochemical use of the sun for the production of hydrogen by water photolysis may become feasible before the end of this century and may one day solve radically the energy problem with hydrogen playing an important role in the energy of tomorrow. Unfortunately, the electrolysis of

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water is today still inefficient from the energetic point of view and even if new cells were developed, we still have to find a cheap, abundant source of electric energy to produce hydrogen and it will be a question of choice: Do we transport hydrogen or electricity.

If hydrogen and electric energy take a big share of tomorrow’s energy, hydrogen distribution systems will be available and fuel cells may constitute the the ideal electricity generators to be located near the utilization points. In addition to fuel cells, power cells, dry cells and other types of batteries will be required, in large number particularly for load levelling or for electric vehicles and there will be an increasing demand for high energy density, highly reliable primary and secondary batteries of low cost and long life and having a high efficiency. Electrochemical energy production and storage will therefore be important in the industrial development of the future.

It is difficult to say which type of battery will be the most economical. It is probable, however, that at least for electric cars the metal air batteries, utilizing oxygen cathodes, in which the metal is the fuel, or the metal-hydrogen batteries in which the hydrogen is the fuel will be those having greater chances of success. They are the simplest.

With electricity being an indispensable intermediate form of energy, whether derived from fossil fuels or the sun, the seas, the deep earth or from nuclear reactions, electrochemistry will play a major role in the world of tomorrow. Electrochemical processes however, to be economical, must have available efficient cells.

2 The Cell

Progress in industrial electrochemistry has brought the cell to a high degree of efficiency and to numerous, ingenious configurations permitting good operating conditions. To increase the efficiency of the cell, its components; structure, electrodes, separators, electrolytes must undergo substantial improvements and new cell designs have to be introduced.

i) Structure

The choice of the cell structure is important for cell operation and high capacity monopolar or bipolar cells having an horizontal or vertical geometry and easy connections to bus-bars are indispensable for economical operation. On the other side the choice of the materials of construction is important for cell life and cost.

ii) Dimensionally stable electrodes

It is the development of dimensionally stable electrodes that has greatly contributed in the recent years to better cell design and cell operation by increasing the current efficiency of the electrochemical process and decreasing the voltage required for cell operation. Highly selective D.S.E. permit to increase the energetic gap between the unwanted and wanted reactions and therefore improve the current efficiency. Highly electrocatalytic active D.S.E. have decreased the electrode potential. The bubble effect has been lowered or eliminated with a result of a lower voltage drop, by the choice of the right geometrical shape and location of electrodes.

High surface area activated D.S.E. are being developed to be used in many of the future cell designs. Promising are the electrode structures made of cellular conductive vitreous carbon, obtained by heat treating polyurethanes and other polymers under controlled atmosphere, or made of porous cellular metals or metal alloys. High porosity electrodes operating at apparently high but actually low current densities will also be manufactured utilizing sintered metallic powders, having low electrical resistivity and high mechanical and chemical stability.

Particulate electrodes made of powders with grains having a few tenths of a millimeter diameter will also be used in fluidized bed cells especially for the recovery of metals, treatment of effluents and electroorganic reactions.

Electrocatalytic active powders are also being applied to metal structures or directly to membrane acting as selective separators, to become the active electrode.

Coating and doping of electrodes is now a normal practice and will be used to a greater extent to improve the electrical conductivity and the selective electrocatalytic activity.

iii) Separators

The other great contribution to electrochemical technology has been the development of perma-ionic selective membranes. Separators with a high chemical and mechanical stability and low
ohmic drop are necessary for high energy efficiency. Ion selective separators, required in some electrochemical processes, having a high ionic conductivity and high ion selectivity, but no porosity or electronic conductivity will find large application in the future cell provided they have a long life and can be manufactured at low cost.

iv) Electrolytes

The heart of any electrochemical process is the electrolyte. Electrolytes with high conductivity, required for high cell efficiency and operating at high temperature in cells, having the narrowest possible gap, will permit great energy savings provided reactions between the product of electrolysis do not reduce the current efficiency.

v) Membrane cells

Let us review in more detail the manufacture of caustic or chlorine and the production of aluminum and see what practical solutions have been found to save energy in these processes.

In membrane chlorine cells, typical distributions of voltage with the cell operating at 3000 A/m², and having a current efficiency of 95% is given in Table 1.

Table 1 Distribution of cell voltage in membrane chlorine cells operating at 3000 A/m²

<table>
<thead>
<tr>
<th>Current efficiency</th>
<th>95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolysis potential</td>
<td>2.24 2.25 V</td>
</tr>
<tr>
<td>Anode overvoltage</td>
<td>0.15 0.05</td>
</tr>
<tr>
<td>Cathode overvoltage</td>
<td>0.20 0.10</td>
</tr>
<tr>
<td>Membrane and electrolyte drop</td>
<td>0.60 0.30</td>
</tr>
<tr>
<td>Structure drop</td>
<td>0.30 0.15</td>
</tr>
<tr>
<td>Total cell voltage</td>
<td>3.50 2.86 V</td>
</tr>
<tr>
<td>Electric energy per ton NaOH</td>
<td>2500 2000 kWh</td>
</tr>
<tr>
<td>Saving with oxygen cathode</td>
<td>0.00 0.55 V</td>
</tr>
<tr>
<td>Total Voltage with depolarized cathode</td>
<td>2.80 2.30 V</td>
</tr>
<tr>
<td>Electric energy per ton NaOH</td>
<td>1950 1600 kWh</td>
</tr>
</tbody>
</table>

1) Conventional modern cells with electrode gap, 2) MG or SPE cells

This drastic reduction in electric energy consumption to only 2000 kWh per ton of caustic soda has been possible thanks to:

1) The utilization of high porosity electrodes having coatings with a selective and high electrocatalytic activity and a configuration which eliminates the bubble effect.
2) The reduction of the gap between the electrodes to that corresponding to the thickness of the membrane.
3) The utilization of new ion selective membranes with lower ionic conductivity and less sensitivity to impurities.

An oxygen depolarizing cathode with no hydrogen produced at the cathode has been suggested and tested. If utilized, the energy consumption could further be reduced by almost 20%.

vi) Aluminum cell

The aluminum cell utilizes a carbon anode which is consumed at the rate of about 0.5 ton per ton of aluminum produced and a carbon cathode which, during operation, is covered by a thick layer of many centimeters of aluminum. Typical distributions of voltage for a modern cell operating at 10,000 A/m² and a cell with unsoluble anode and wettable cathode and operating at current efficiency of 90% is reported in the Table 2. The decrease in voltage correspond to the Membrane cells.
stable cathode and a stable anode.

An aluminum wettable stable cathode is necessary so that a thin layer of aluminum could be sufficient for the operation of the cell and therefore permitting the reduction of the gap between cathode and anode.

A stable cathode can only be realized if the cell is operated without a molten metal pad on the cathode. Unfortunately, carbon bare cathode operation is prevented by dissolution of the carbon cathode when alternately exposed to metal and electrolyte. The desirable properties of the new cathode material are:

- Inert to the environment: Electrolyte and molten aluminum
- Wet by aluminum
- Good electrical conductor and
- Withstand severe differential thermal gradients imposed during cell startup and operation.

A class of materials that seemed to meet all of these properties, except resistance to thermal shock, include the borides and carbides of Ti and Zr (refractory hard metals). Such materials are costly and must be fabricated using powder metallurgy technology with all its inherent disadvantages. Eltech is working to develop a stable cathode with sufficient life and low enough cost to be economically viable and permitting to gain maximum advantage from the interelectrode space reduction.

From the very inception, the aluminum industry has searched for a stable anode material having:

- Low reactivity with oxygen and the electrolyte
- High electronic conductivity
- Low oxygen overvoltage
- Mechanical strength and resistance to heat shock
- Easy electrical connections to bus
- Ability to be fabricated into the right shapes and which does not degrade the aluminum produced.

Permanent stable anodes would retain their shape and present a uniform surface to the electrolyte. However, the penalty in substituting an inert anode for a carbon anode would be 0.5 volts by keeping the same gap but by reducing the gap more than 1 volt could be saved.

A total energy balance, including expended gas or oil and electrical power in anode carbon manufacture and the energy content of the carbon, indicates an overall decrease in energy consumption of 5% if interelectrode spacing remains unchanged. However, if a 60% reduction in the interelectrode spacing can be achieved, the decrease in total energy consumption would be more than 20%.

3 Other Industrial Processes

In addition to improvements in the largely utilized existing processes of brine electrolysis, water electrolysis, molten salts electrolysis and the aqueous electrowinning or refining of metals, other processes will be developed and utilized in the future.

i) The electrowinning of metals

Not only aluminum, magnesium and sodium, but other metals will be manufactured by molten salt electrolysis.

Should an economical cell be developed there can be expected a big increase in the electrowinning of those metals which are now produced in small amounts such as beryllium, indium, tantalum, zirconium, hafnium, potassium, and a greater utilization of such metals as magnesium and sodium.

A wider range of metallurgical processes will one day be based on electrowinning methods. Ores, concentrated or dilute, will be treated to give solutions which after treatment by solvent extraction or ion exchange will give pure solutions containing sulphates and possibly mainly chlorides, ready for electrolysis.

Deep sea manganese nodules, as a potential source of nickel, copper and cobalt, when harvested, will utilize probably electrometallurgy for the recovery of their metal contents.

The electrochemical recovery of particular metals and/or metal oxides like uranium, rhenium, molybdenum, yttrium, vanadium, silver and other trace metals from ocean waters, rivers and lakes might also be possible. This is very attractive even though the proposed techniques, including biological extraction, may seem unrealistic today.

The development of DSA suitable to operate at apparently high current density, having a high active area, and without any appreciable
electrochemical passivation, will soon allow the electrowinning of these metals to become economical.

If a suitable electrochemical technology were to be developed, permitting the economical recovery of the most useful elements from the low concentration ores of the world, which are however enormous in volume, the availability of such elements to mankind could be assured well beyond the present estimates and certain elements could be made available in quantities larger than the presently known reserves now permit.

ii) Electrochemical organic syntheses
Finally many possibilities would exist in the field of electrochemical organic syntheses if suitable electrode materials were developed. Such electrodes should
a) contain an active coating with high valency dopants which catalise in situ the organic reactions (heterogeneous catalysis)
b) be able to regenerate the catalyst in solution or in suspension (homogeneous catalysis)
c) be able to dissolve themselves (sacrificial anodes) to generate active metal complexes and
d) be able to allow oxidation or reduction by having a high overpotential for the unwanted reactions, i.e. oxygen or hydrogen evolution.

The selected electrodes should also have very high active surfaces, very high reaction selectivity, high chemical and electrochemical stability, slow catalytic aging rate, high absorption rate of the reactants and high desorption rate of the products.

It should also be mentioned that the utilization of fluorine and bromine in the manufacture of chemicals and the use of interhalogens produced electrochemically (the most important being Br Cl) can be interesting for several processes such as selective halogenation, oxydation and hydroxylation.

The manufacture of perchlorates, persulphates, perborates, hydrogen peroxide and manganese dioxide are also important fields of industrial electrochemistry.

Of course, the electrochemical industry is also electroplating, electroforming, electrocleaning, electroflocculation, electroflotation, electrodialysis, electrophoresis, as well as anodic and cathodic protection. All these processes will find wider applications in the future.

4 Conclusion
One hundred years ago the invention of the dynamo gave an impetus to research in the electrochemical field, which until that time had been quite academic and permitted the development of the electrochemical industry. However, it was only the discovery of rectifiers, particularly the static rectifiers that provided industry with high currents and, therefore, permitted the design of modern cells of large capacity and the development of efficient electrochemical processes, essential to the future economy of the world.

To have electrochemists capable of detecting fields of major interest and inspiring young scientists, is just as important to the future development of the electrochemical industry. However, one should not expect spectacular successes, but continuous concrete improvements, and these can be best obtained, as in any technological search, by the teamwork of men of different minds and backgrounds: The pure scientists, the engineers, the researchers, the inventors, with some genius, and also the managers with experience and vision. Failure to recognize the problems, establish the goals, define objectives and strategies and have the grasp of the realities based on economical situations and feasible solutions would make progress slow.

With the energy crisis which really exists, we need a coherent global vision of an industrial world in which electrochemistry plays a big role. How fast, how soon, and how much will electrochemistry contribute to the industrial development of the world, I cannot forecast. However, I know that electrochemistry will have a bright future and electrochemists will have great goals, big incentives and an interesting challenge.