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From the Editor's Desk

Membranes and Diaphragms for Electrochemical Processes (Part - II)

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Hydrogen Production

In the production of hydrogen by water electrolysis, a diaphragm is used to prevent the passage of gas from one electrode compartment to another without offering appreciable resistances to the passage of current. To prevent the passage of gas bubbles, the pores of the diaphragm must be smaller than the diameter of the gas bubbles in the electrolyte and must also poses a low contact angle with respect to the electrolyte. To prevent the passage of dissolved gas especially in pressure electrolysis, the diaphragm must have considerable resistance to flow of the electrolyte and at the same time a low resistance to current.

Asbestos is the most common material for diaphragm although in certain designs metal diaphragms are also used. A metal diaphragm will be satisfactory and will not act as an electrode unless the ohmic drop across it becomes greater than the decomposition voltage. Woven asbestos blankets are used as diaphragm in electrolyser working at atmospheric pressure. In the largest cells the same is usually reinforced with a fine nickel wire. Asbestos fibers in the form of mat or felt which produce a fine pore structure and have a high resistance to the flow of the electrolyte, are usually employed in the pressure electrolysers. Asbestos, though commonly made use of as the material for diaphragm, is not the ideal one, since loose of fibres can give enough trouble. The electrolyte attacks the asbestos and the rate increases with increase of temperature. Plastic materials such as PTFE are not suitable because of their non-wettability. Recently Nafion® has been used as a diaphragm with added advantage like lowering of energy consumption and longer life. Based on this Nafion® membrane, PEM based electrolyzers are developed and very encouraging results has been obtained, especially the lowering of energy consumption.

The development of PEM water electrolyser was taken up at the Central Electrochemical Research Institute, Karaikudi during 1996. Hydrogen generation units of 100W (0.02 Nm^3/hr) to 25kW (5.0 Nm^3/hr) capacity have been developed (see figure).

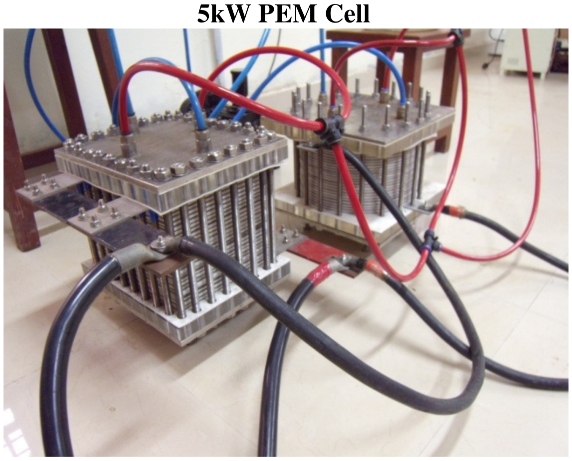
The prototype has additional features, such as, hydrogen collection and drying units, pressure regulator, water feed container, level and purity indicator etc. The entire operation is controlled electronically. The unit is conveniently designed to be portable. The cell can operate at a very low voltage even at 100 $A.dm^{-2}$ (<2.25V) and the corresponding energy consumption is much lower than what is observed with conventional electrolysers.

100W – PEM Cell

200W PEM Cell

400W PEM Cell

5kW PEM Cell



25 kW PEM Cell

Ceramic diaphragms based on Teflon-bonded barium titanate, or sintered nickel oxide can be made use of in water electrolysers.

Other Inorganic Chemicals

Among other inorganic chemicals, the production of fluorine is important. Diaphragm made of monel metal have been employed in the production of fluorine using molten mixtures of KF-HF of varying proportions, to separate mixing of gases.

In the production of persulphates, asbestos (blue) diaphragms are employed either in the form of cloth or fibres wound on cathode. While producing cuprous oxide, the cloth diaphragm is employed to avoid the reduction of cuprous oxide formed into copper powder. The preparation of permanganate, periodates can be done both in diaphragm or non-diaphragm cells and asbestos is normally used as diaphragm material. In the oxidation of ferrocyanide to ferricyanide, as well as in the reduction of titanic sulphate or chloride to titanous salt, asbestos diaphragm white in the former and blue in the latter is employed. Nafion® membranes have been employed in the production of potassium stannate with the reduction of electrical energy. Ceramic diaphragms have been reported in the *on-site* production of hydrogen peroxide by the reduction of oxygen employing the trickle bed reactor. High purity uranium tetrafluoride is being made from uranium solutions by electrolytic reduction using cation exchange membranes, which effectively prevents the oxidation process.

Organic Electrochemicals: Among the organic electrochemicals only a few processes employ diaphragms in the form of either porous membrane and/or ion-exchange membranes. As typical examples the following processes are considered.

Adiponitrile from Acrylonitrile: Adiponitrile, which is an intermediate in the production of Nylon-66, has become an industrially viable process only after Baizer established the electrochemical route and the same is now a multimillion dollar production unit. In the hydrodimerisation of acrylonitrile to adiponitrile, the use of cation exchange membrane (Nafion®) in the place of porous separators prevents the migration and oxidation of tetraalkyl ammonium p-tolune sulponate used as supporting electrolyte and thereby increasing the anode life. Now the process has been worked out using diaphragm less cell.

Reduction of Nitrobenzene: Nitrobenzene is reduced electrolytically to p-aminophenol or aniline in acid medium where blue asbestos or any cation exchange membrane is used as diaphragm material. However, under alkaline conditions, hydrazobenzene is obtained and in this process also, white asbestos cloth is used as diaphragm material.

Glyozalic Acid from Oxalic Acid: During the reduction of oxalic acid for obtaining glyoxalic acid the efficiency of the process is decreased due to migration of both the oxalate and glyoxalate anions through the porous separators to the anode compartment thereby leading to oxidation. However, the replacement of porous separators with cation exchange membrane prevented the migration of anions and enabled a quantitative reduction.

Salicylic Acid to Salicylaldehyde: In the reduction of salicylic acid to salicylaldehyde, porous pot, blue asbestos or cation exchange membrane is employed as diaphragm material.

Hydrometallurgy and Electroplating

Regeneration of Cupric Chloride Etchant from Printed Circuit Boards: The basis of this regeneration system is the use of electrolysis to achieve twin objectives i. the reduction of cuprous ions produced in the etching process and ii. the plating out of the etched copper from the etching solution. For this a divided cell utilizing a cation exchange membrane as the cell divider is employed.

Purification of Chromic Acid Solution: For spent chromic/sulfuric acid etch baths where chromium is present in Cr^{3+} in printed circuit board production, an electrolytic method of oxidizing Cr^{3+} to Cr^{6+} has been developed on a large scale. Fluorocarbon membranes or porous ceramic separators are employed in the cells to allow passage of protons for discharge at the cathode, while hindering Cr^{3+} access to the cathode.

Nickel and other Plating: To prevent the sludge from anode to deposit on the cathode, it is the usual practice to employ diaphragm in the form of cloth or asbestos cloth or felt.

Electrowinning of Manganese and Other Metals: Generally cloth or asbestos felt diaphragm is employed to prevent oxidation.

Batteries: In almost all the batteries, separators are essential to prevent shorting of the electrodes. Cloth, Nylon, Terylene, PVC, microporous rubber, wooden separators, poly vinyl alcohol crosslinked with aldehyde, radiation grafting membranes are employed as diaphragm materials or separators in all the batteries. With the advent of conducting polymers, interest in the use of the same for battery application is increasing. In the case of high temperature Na-S batteries β-alumina membrane are employed.

Electrodialysis and Pollution Control: In these processes, the ion exchange membranes are invariably employed as diaphragm materials. Depending upon the process of the reaction, either anion exchange membrane or cation exchange membranes or both can be employed in two compartment or three compartment or multi compartment cells. In this processes, the desired products are formed purely by ion transport through the membranes as a result of impressed voltage.

Desalination of Brackish Water: The recovery of water is certainly the major use of electrodialysis. A multi compartment cell having alternate anion and cation permselective membranes between two end electrodes is normally used for desalination process. When a potential is applied, anions and cations move in opposite directions. But each membrane allows one of the species. In installations containing ten to hundreds of compartments between one pair of electrodes at the end compartments, the passage of electric current produces water depleted of salt and enriched brine in neighboring compartment. In other words while half of the compartments carry water depleted salts, the other half carry enriched salts. At the electrode, oxygen and chlorine evolution at the anode with the formation of acid in the anode compartment and hydrogen evolution at the cathode with the formation of alkali at the cathode compartment will take place.

Concentration of Salts: The same principle as described in electrodialysis is being made use of to concentrate the brine to get salt. A suitable membrane called univalent – selective ion exchange membrane has been employed. Divalent ions like Ca^{2+}, Mg^{2+} and SO_4^{2+} are prevented.

Metathesis: One of the methods of preparation of chemicals is by metathesis or double decomposition employing the same multi compartment cell with alternate anion and cation permeable membranes. Examples are (a) preparation of sodium hydroxide from NaCl and $Ca(OH)_2$, (b) $BaCl_2$ and Na_2S were prepared from BaS and NaCl, (c) photographic emulsions have been produced from NaBr and $AgNO_3$ with a gelation emulsion being fed into the compartment where double decomposition reaction takes place, (d) preparation of salts from unstable or insoluble parent compounds (eg) Na_2CO_3 from $(NH_4)_2CO_3$ and NaCl and uranyl sulfate from uranyl nitrate and (d) sebacic acid from sodium sebacate.

Waste Recovery and Purification Processes
Another major field where permselective membranes are extensively used is in the process for purification and thereby eliminating or minimizing waste disposal problems. The examples are: i. recovery of sulfuric acid from pickle liquor, ii. recovery of salts from electroplating waste liquor, iii. recovery of gold from rinse water in gold plating, iv. recovery of sulfuric acid and sodium hydroxide from waste sodium sulfate, v. for removing ionized impurities from whey and amino acids, vi. for deashing of sugar solutions and glycerol, vii. fractionate and recover the spent liquor from the pulp industry and viii. removal of inorganics from sewage effluents, etc.

Conclusion

Although man is quite aware of the use of membrane processes in the human system, yet the development of membranes especially permselective membrane processes to achieve desired products in industrial applications, particularly in electrochemical cells, is relatively recent. The development of plastics, the increased knowledge of polymer morphology enabled advances in the development of technology of synthetic ion-exchange membranes and these advances enabled the electrolytic processes employing such membranes to compete with or replace the old established method.