



**From the Editor's Desk**

## Membranes and Diaphragms for Electrochemical Processes (Part - I)

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### Introduction

A membrane or a diaphragm is a microporous material with average pores less than one micron. They allow passage of either solvent from one chamber to other or electrical flow and passage of solute through the same. To carry out any electrolysis, it is absolutely essential that the cell should comprise of two electrodes (conductors of electricity or electrons). The electrode at which the oxidation takes place resulting in the loss of electrons by atoms or ions is termed as anode and electrode at which the reduction takes place resulting in the gain of electrons by atoms or ions as cathode. In certain electrochemical processes, these two electrodes have to be divided to segregate the anolyte and catholyte zone as well as to prevent mixing of the gases. This process is commonly done by introducing a material which allows the passage of electricity and at the same time separating the anolyte and catholyte. Such a material is called the diaphragm or separator.

The diaphragm material should possess the following properties: i. low resistance, ii. good chemical and physical stability, iii. high resistance to diffusion of electrolytes between compartments except for transport of the desired current carrying ion and iv. low cost.

### Types of Diaphragm

Two types of diaphragm or membranes are employed in electrolytic cells i. Porous media membranes and ii. ion-exchange membranes. Porous membranes pose a barrier to the transport of molecular and ionic species between the electrolyte compartments by limiting convective flow and molecular diffusion. Ion exchange (a permselective) membranes provide a high degree of mobility for either anions or cations while offering a very effective barrier for counter ions and perhaps to neutral molecule.

In general, microporous materials with average pores less than one micron can be used as diaphragm. However, it is

necessary to have sufficient pores in order to permit the passage of electricity when the pores are filled with electrolyte. But at the same time it should be sufficient to prevent the hydraulic flow through the diaphragm.

### Diaphragm Materials

Membranes may be natural products or modified natural products. Porous pots or plates made of unglazed porcelain or porous sintered glass are commonly used and these are, however, not suitable for industrial/commercial scale operations, because of their fragile natures. Sometimes, woven fabrics made of cloth, fiberglass, nylon, terylene are employed as diaphragm in electrochemical cells. Microporous rubber or microporous plastic sheets of polyethylene, polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE) are also being used as diaphragm materials.

Ion exchange membranes are thin sheets of polymeric material containing pendant groups capable of exchanging selectively either anions or cations. Generally the polymer contains sulphonic acid or carboxylic acid groups for cation exchange membranes and amine groups for anion exchange membranes. Earlier polystyrene cross linked with divinyl benzene (DVB) formed the polymeric form of membrane to which suitable groups are provided depending on the exchange of ions. Recently perfluoro type membranes are available which are chemically inert and have other advantages for their use in chlor alkali cells as well as water electrolyzers for the production of hydrogen.

In addition, metallic diaphragms are employed in certain processes (fluorine production). Certain refractory materials like  $\beta$ -alumina or Nascioon act as the electrolyte and separator in some of electrochemical devices. Wooden separators are used in batteries to act as diaphragm.

Osmotic membranes allow passage of solvent from one chamber to the other. Cellulose acetate is employed in Reverse Osmosis processes. Some of the earlier membranes of this type are egg membrane, pig's bladder, thin biological membrane, parchment paper and also some other natural products are used as membranes.

In analytical methods, special type of glass as in the case of glass electrodes or the membranes prepared for ion selective electrodes act as diaphragm or membrane allowing to interact with ions that electrode is designed to sense. There are liquid ion exchange membranes for ion selective electrodes.

For non-electrochemical processes, liquid membranes as well as membranes to prevent certain gases (preventing air pollution) are also in vogue.

## General Preparation of Membranes

**Physical Method:** Physical methods are employed to make membranes of both thermoplastic and ceramic materials. The base materials are ground to desired fineness and then either fired or sintered to fuse the particles in rigid structures. The spaces left between the particles then become the effective pores. Membranes have been sintered of poly vinyl chloride, polyethylene, alumina and a wide variety of inorganic materials.

**Leaching or 'cook-out' Method:** Membranes may be made either a leaching or 'cook-out' method, where salt or starch is normally employed. The materials are ground to the desired mesh size and then dispersed in molten plastic or a solution of plastic. This plastic solid mixture is then extruded or cast into sheet form. Salt particles are removed with hot water, starch by digestion in sulfuric acid. Holes are formed wherever salt or starch solid particles were before treatment. Microporous PVC, polyethylene, rubber and cellulose acetate are made by this procedure.

**Gelatin Process:** The easiest synthetic membranes are produced by gelatin process, in which very uniform pore size can be maintained. Gelatin can be made into a membrane by casting a solution on glass plate into thin film. The water within the gel structure is removed by washing with ethyl alcohol. This disrupts the gel walls leaving a microporous structure. The gelatin can be insolubilized by "tanning". Gelatin concentration controls the pore size. The earliest synthetic membrane produced by this process was from nitrocellulose. Commercial cellulose ester membranes and membranes based on

various polyvinyl alcohol derivatives and copolymers employ the same basic process mentioned above.

Ion selective membranes are manufactured by some of the following techniques, i. Casting plastics in sheet form and then reacting with the material made to form ion exchange resin, ii. Mixing resin with other polymers to form heterogeneous ion selective membrane, iii. Coating of membrane with ion selective material.

Some of the polymer formulations employed for perm-selective or ion exchange membranes in electrolytic processes are: i. Polystyrene cross-linked with divinylbenzene and sulphonated to provide cation exchange sites or by chloromethylation and subsequent amination to get anion exchange membrane, ii. A fluorocarbon polymer with either sulphonic acid or carboxylic acid.

## Applications for Electrochemical Processes

**Inorganic Electrochemicals: Chlor Alkali:** The preparations of ideal chlor alkali membrane separators are: i. High tear strength, ii. Minimal swelling changes, iii. Low thickness, iv. Chemically inert to  $\text{Cl}_2$  and  $\text{NaOH}$  at  $100^\circ\text{C}$ , v. Highly permselective to  $\text{Na}^+$  and no ion-transport, vi. Minimal water permeability, vii. Low cost, viii. High resistance to fouling from brine impurities and ix. Good conductivity.

In the conventional production of chlor alkali, diaphragm cells are employed using asbestos diaphragm. Although asbestos has been in use for more than 50 years, it suffers from swelling, poor shelf life and is affected by variations in operating conditions. Latter researches on the improvement of asbestos diaphragm make the asbestos fibers to suitably admix with polymer, possibly fluoropolymer to obtain "polymer-stabilized asbestos diaphragm". These have the following advantages: i. Thinner, ii. Possess lower electrical resistance due to minimal hydrogen occlusion, iii. Permit closer interelectrode distance with expandable metal anodes giving advantage in cell voltage, iv. Posses longer shelf life and v. Have extended service life. An energy saving of 10% or more has been achieved at a current density of  $2.1 \text{ KA m}^2$ .

Recent reports indicate the complete replacement of asbestos with microporous separators based on PTFE (Teflon). However, the quality of brain for these cells must be significantly better than that used in conventional diaphragm cells. Thus these new diaphragms possess the

advantages of possibility of retrofitting to the existing diaphragm cells.

A major break-through was made in sixties with large scale production of polytetrafluoroethylene type of plastics. Pioneering work in the field of perfluorinated ionomer membranes was done Du Pont, USA resulting in the development of perfluorosulphonic acid type cation exchange membrane called 'Nafion<sup>®</sup>'. Later three Japanese Companies viz., Asahi Chemicals, Ashi Gals Co (Flemion) and Tokyama soda Co. (Neosepta-F) have also developed perfluoro membranes, but having carboxylic acid type, which favors the hydrophobicity leading to higher concentration of alkali. The latest introduction of carboxy-sulphonate bimembrane with unique reinforcement is capable of sustained stable performance for any membrane electrolysis. "Nafion<sup>®</sup>" is a copolymer of tetra-fluoroethylene with a perfluorovinyl ether sulphonyl fluoride. If carboxylate perfluorovinyl ether is employed then caboxylate ionomer membrane is obtained. In general, the overall objective in using membrane cell-both monopolar and bipolar is to get optimum utilization of power which means achieving highest possible current efficiency with the lowest

possible voltage. High concentration of alkali is also obtained. Thus the new membrane cells fulfill the twin objectives of attaining higher concentration of alkali with lower energy consumption and the avoidance of mercury/asbestos pollution. However, the brain has to be purified to have Ca<sup>2+</sup> and Mg<sup>2+</sup> content at less than 50ppb.

The Solid Polymer Electrolyte (SPE) cell process for chloralkali forms the logical consequence of the ion exchange membrane process. The SPE electrolysis cell is unique in that the electrodes in the form of catalytic particles are bonded on to the ionically conductive perfluoro type ion exchange membrane, so that the SPE is the only electrolyte in the cell. The minimum thickness (0.25 to 0.3mm) of perfluorine cation exchange membrane allows the electrolyte resistance in this cell to be much lower than it is in the conventional type of cell. The charge carriers in the electrolyte are Na<sup>+</sup>. A slash of 15-20% of energy consumption, compared to membrane cell, is achieved due to the elimination of ohmic drops due to anolyte and catholyte solutions as well as gas bubble effects of the gases evolved.

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