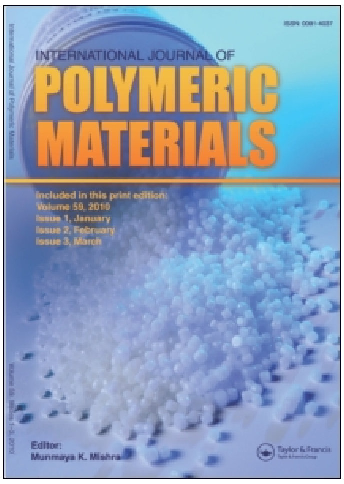

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Membrane Separator For Water Electrolysis: Characterization

H. S. Sodaye[a]; R. C. Bindal[a]; T. K. Dey[a]; B. M. Misra[a]
[a] Desalination Division, Bhabha Atomic Research Centre, Trombay, >Mumbai, India

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MEMBRANE SEPARATOR FOR WATER ELECTROLYSIS: CHARACTERIZATION

H. S. Sodaye
R. C. Bindal
T. K. Dey
B. M. Misra
Desalination Division, Bhabha Atomic Research Centre,
Trombay, Mumbai, India

The search for membrane separator for electrolysis of water in a radioactive environment has led to the development of solid oxide embedded polymer membranes. The present article discusses the preparation and characterization of TiO_2 *– polysulfone composite membrane. The membrane was prepared from dope solution of polysulfone, tetrabutyl orthotitanate (*$Ti[O(CH_2)_3CH_3]_4$*) in N-methyl-pyrrolidone. The membrane was prepared by phase inversion and was characterized for chemical and radiation stability, conductivity, pore structure, and pore size distribution. The membrane was found to be stable in alkaline environment. The membrane structure is that of ultra filtration membranes having asymmetric skin layer and macro voids.*

Keywords: polysulfone, membrane, titanium oxide, composite, electrolysis

INTRODUCTION

Water electrolysis uses electric current to split water into H_2 and O_2. The electrolysis cell consists of two electrodes, cathode and anode, and an electrolyte. During electrolysis of water H_2 is generated at the cathode whereas O_2 is generated at the anode. These cells operate with 20–40% aqueous alkali at around 70°C [1]. The electrolysis unit consists of porous Ni electrodes separated by porous diaphragm, which acts as a separator for the gases at the same time allowing passage for the electrolyte solution. The separator prevents the intermixing of H_2

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Address correspondence to H. S. Sodaye, Desalination Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India. E-mail: hemant@apsara.barc.ernet.in

and O_2, which is an explosive mixture. Commercially, asbestos is being used as an electrolytic separator. However, it loses its mechanical strength on radiation exposure. Therefore, it is necessary to have a separator that is stable to radiation damage. The present study aims at development of a separator having adequate porosity as well as chemical and radiation stability.

In the search of electrolytic separators to work in hot concentrated aqueous alkalis no material has been definitely proven as the alternative to crysotyle asbestos. Several synthetic organic polymers (i.e., polyphenylethylenes and polyphenylenes) have higher chemical stability than asbestos, but are non-wetable and/or mechanically rigid. Sulfonation, phosphonation, and carboxylation improve their wetability, but do not provide decisive overall improvements. Aromatic polymers charged with inorganic oxides (e.g., Sb_2O_3, MgO, or TiO_2) have been observed to display improved wetability and adequate mechanical strength [2–3]. In particular, membranes with TiO_2 generated *in situ* were proven to be a better alternative to crysotyle asbestos. These membranes were made from polysulfone, titanium ter-butyloxy as a precursor for TiO_2, and carbowax as pore-forming agent [3].

In the present work, the preparation and characterization of a composite separator membrane, consisting of polysulfone impregnated with hydrophilic inorganic oxide (TiO_2) is described.

EXPERIMENTAL

The composite membranes were prepared from solution of polysulfone (PS), tetrabutyl orthotitanate ($Ti[O(CH_2)_3CH_3]_4$) and a pore forming agent, that is poly(vinyl pyrrolidone) (PVP 30 K) of molecular weight 40,000 in N-methyl-pyrrolidone solvent. The weight ratios of TiO_2/PS and PVP/PS were $\approx 5.9\%$ and 25%, respectively [2].

The solution was poured onto a glass plate and spread evenly using a knife-edge. The height of the knife-edge was adjusted to get membranes of desired thickness, that is 0.1–0.9 mm. The membrane was gelled by phase inversion process by immersion in water. The final film porosity was achieved by leaching the PVP out of the film by boiling in water for 24 h. It was characterized for the chemical and radiation stability, conductivity, and pore structure.

CHARACTERIZATION

Pore Size Distribution

The bubble pressure breakthrough introduced by Bechhold uses a Washburn equation and is based on the measurement of the pressure needed to displace a fluid by another through a capillary of diameter d_p as [4]:

$$\Delta P = 2\gamma \cos\theta / d_p \tag{1}$$

ΔP being the applied pressure (Pascal), d_p the pore diameter, γ the surface tension of the liquid – liquid or air – liquid interface and θ the wetting angle with the solid matrix of the membrane ($\gamma \cos\theta$ is the Wilhelmy surface tension). If the fluid totally wets the membrane it can be assumed that $\cos\theta = 1$. Thus, according to Eq. 1 the largest pores open at the lowest pressure followed by the smaller pores, that is when different pores of diverse sizes are opened the volume flow, J_v, of air increases accordingly until all the pores are emptied. By monitoring the applied pressure and the flow of gas through the sample when liquid is being expelled a wet run is obtained. If the sample is then tested dry (without liquid in its pores) a dry run follows. Thus, the volume flow for the wet run J_v^w and for the dried one, J_v^d vs. the applied pressure allows evaluation of several parameters such as pores size and pore size distribution of the membrane. The details of the bubble point analysis are given elsewhere [5].

The bubble point apparatus was constructed in the authors' laboratory (Figure 1) and the method was standardized with membranes having known pore sizes. The separator membrane was characterized by this method using isopropyl alcohol ($\gamma = 0.0207\,\mathrm{N/m}$ at 25°C) as the pore liquid. The N_2 flux was measured for wet and dry membrane at different inlet gas pressure to obtain J_v^w and J_v^d, respectively.

Membrane porosity, determined gravimetrically from the weight difference in the wet and dry state using following equation, was found to be 70–80%.

$$\text{Porosity} = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100\% \tag{2}$$

Membrane Conductivity

The conductivity (S/cm) across the separator was measured using a simple apparatus as shown in Figure 2. The apparatus was constructed of plexiglass. The membrane was equilibrated with 1 N KCl overnight and sandwiched between two compartments and was held in place with the help of rubber gaskets. Both the compartments were filled with 1 N KCl and platinum plates coated with platinum black were immersed in each compartments. The conductivity was measured with and without membrane.

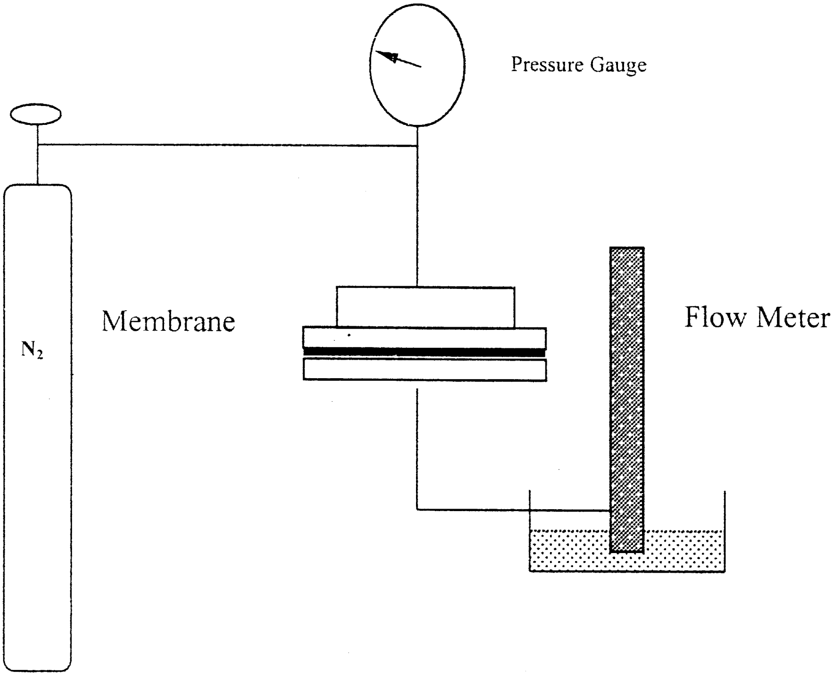


FIGURE 1 Schematics of bubble point pressure measurement apparatus.

Chemical Stability

The membrane stability in alkali was tested by exposing a weighed specimen of 6 cm. diameter to boiling KOH (30%) under N_2 atmosphere for 8 h. After the test, the specimen was withdrawn, washed with deionized water to neutral pH, dried for 24 h at 120°C, and reweighed.

Radiation Stability

The radiation stability of the membrane was studied by exposing wet membrane to the γ radiations from ^{60}Co source and monitoring the degradation of the membrane by determining the tensile strength at break. The maximum dose given was 0.20 MGy.

RESULTS AND DISCUSSION

The membrane was found to be chemically stable since no loss of membrane material was observed on boiling in KOH solution.

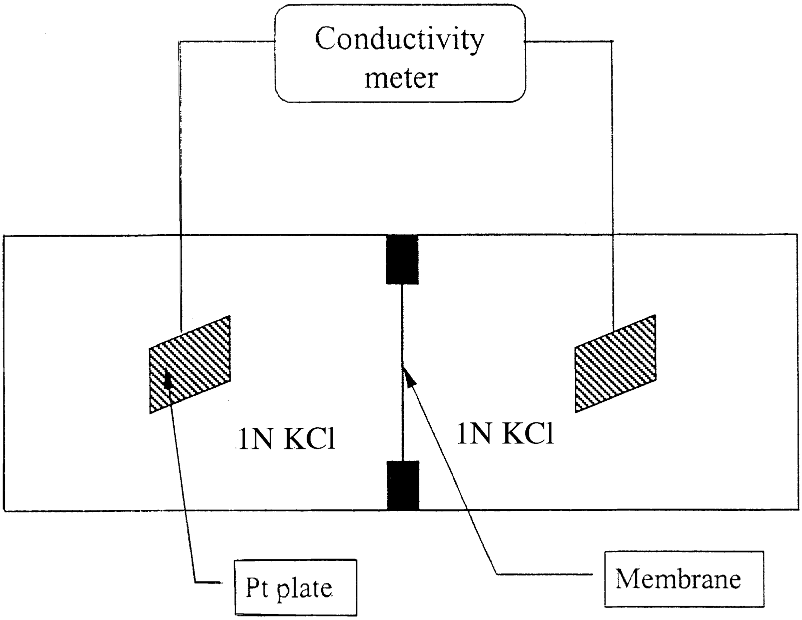


FIGURE 2 Schematic diagram of apparatus for measuring relative conductivity.

The radiation stability of the membrane for different doses is plotted against the tensile strength of the membrane in Figure 3. The tensile strength at break decreases linearly with the radiation dose and at 0.20 MGy it decreases by 29% from the unirradiated sample. It is reported that the addition of TiO_2 in polysulfone increases the radiation stability by about 54% [2]. This is because, in the membrane formation process tertbutyl orthotitane ($Ti[O(CH_2)_3CH_3]_4$) reacts with water to form orthotitanic acid, $Ti(OH)_4$ (or $TiO_2{\cdot}2H_2O$) and BuOH is washed out. During the process of boiling to leach out the pore-forming agent (PVP), orthotitanic acid is converted into meta titanic acid ($TiO(OH)_2$ or $TiO_2{\cdot}H_2O$), this voluminous and gelatinous precipitate plausibly encapsulates the polymer matrix, thereby providing shielding to the polymer matrix against radiation. The observed decrease of the tensile strength is therefore due to the degradation of the polysulfone matrix and in the present case remains above the breakdown strength of 19 kg/cm^2 reported by others (Figure 3) [2–3].

The separator was further characterized for its pore structure using scanning electron microscope (SEM) (submitted to the editor but not shown here). The film was freeze fractured to view the cross-section

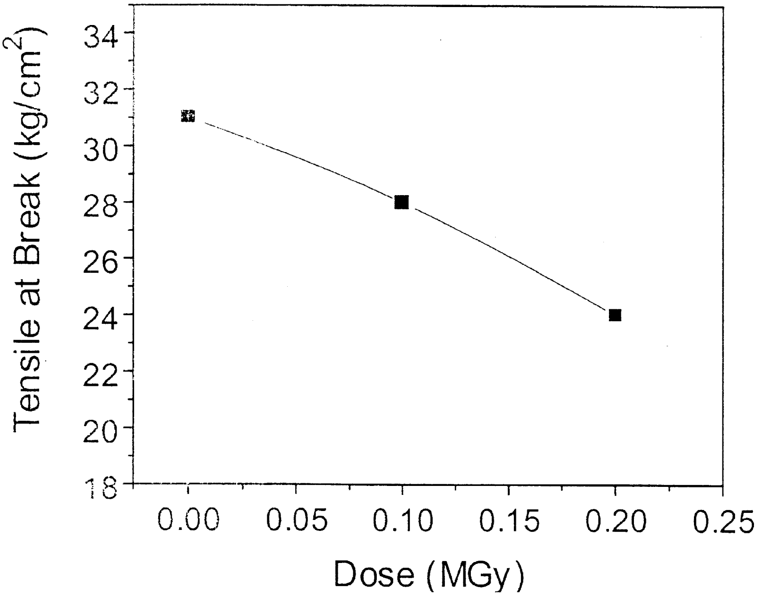
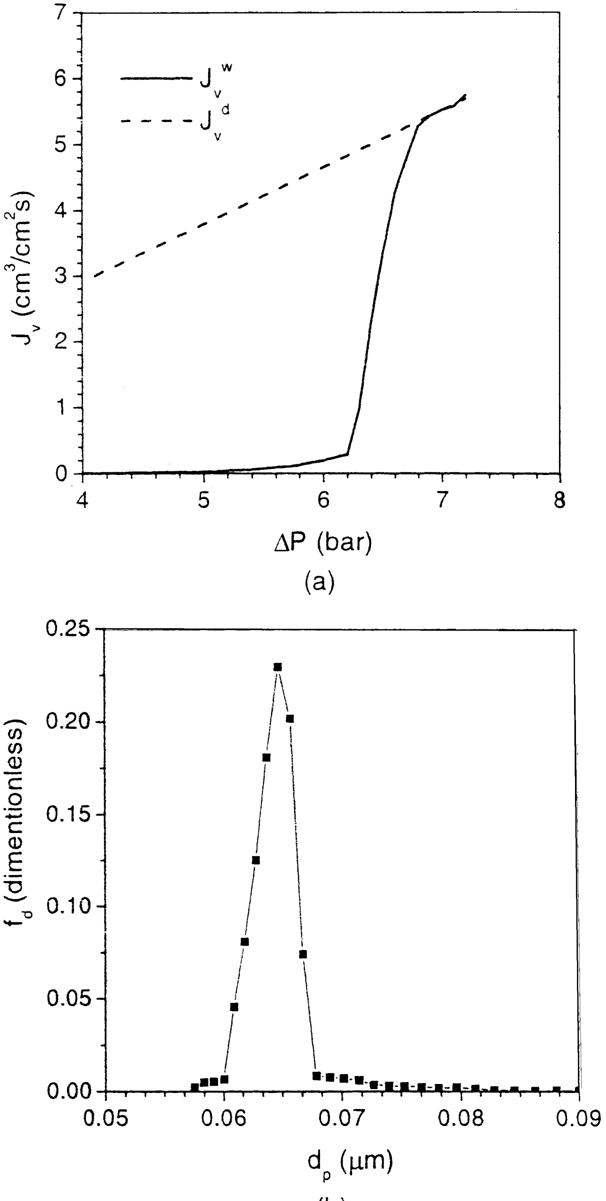


FIGURE 3 Tensile strength as a function of radiation dose.

and was coated with Ag by vacuum deposition. The photographs were taken at terminal voltage of 25 kV. The cross section view of the membrane reveals that the membrane is essentially that of ultra filtration (UF) type with a skin layer of about 10 µm thick and the rest are macro voids of 5–10 µm dia. It is therefore important to know the pore size distribution of the skin layer. Bubble point method was used to arrive at the pore size distribution as described in the experimental section. The distribution was calculated from the obtained N_2 flux through wet and dry membrane and plotted in Figure 4. The bubble point analysis reveals that the pore size distribution of the membrane is very narrow, centering around 0.065 µm. Considering water as the pore liquid ($\gamma = 0.072$ N/m at 25°C) the minimum gas pressure required to displace pore water from a 0.065 µm pores according to Eq. 1 is 22 bar. This ensures that intermixing of hydrogen and oxygen is prevented in the eletrolyzer cell.

The composite membrane was found to be highly conducting. The decrease in conductivity of 1 N KCl by introducing membrane was 5% for 500 µm thick membrane and 10% for 1000 µm membrane. This indicates that the bulk of the membrane is highly porous, which is corroborated by the observed porosity of 70–75%. Increasing the thickness of the membrane increases the thickness of the supporting



(a)

(b)

FIGURE 4 (a) Nitrogen flux through wet and dry membrane and (b) its corresponding pore size distribution.

TABLE 1 Physical Properties of PSul-TiO_2 Membrane

Measurement	Value
Porosity	70–75%
Drop in conductivity of 1 N KCl	5–10% (depending on thickness)
Tensile strength at break	31 kg/cm^2
Tensile strength after 0.20 MGy dose	24 kg/cm^2

layer whereas the thickness of the thinner top layer that controls the conductivity remains unchanged. This is reflected in minor change in conductivity values with varying thicknesses. All the aforementioned properties are summarized in Table 1.

In conclusion, the composite membrane of TiO_2-polysulfone is found to be very stable to radiation and chemical attack and has good conductivity and can be used safely for radiation dose <0.2 MGy. The smaller pores in the skin, resulting from the asymmetric structure of the membrane, prevent crossover of gas and at the same time provide passage to the electrolyte, leading to higher conductivity that does not strongly depend on the thickness of the membrane.

REFERENCES

[1] Casper, M. S. (Ed.) (1978). *Hydrogen Manufacture by Electrolysis, Thermal Decomposition and Usual Techniques* (Noyes Data Corporation, Park Ridge, New Jersey) p. 111.

[2] Pierini, G., Spelta, B., Maffi, S., Modica, G., Perez, G., and Possagno, E., *Nucl. Technol.* **81**, 415 (1988).

[3] Modica, G., Mafi, S., Montoneri, E., Tempesti, E., and Giuffre, L., *Int. J. Hydrogen Energy* **11**(5), 307 (1996).

[4] Bechhold, H., Schlesinger, M., Silbereisen, K., Maier, L., and Nurnberger, W., *Kolloid Z.* **55**, 172 (1931).

[5] Hernandez, A., Calvo, J. I., Pradanos, P., and Tejerina, F., *J. Membr. Sci.* **112**(1), (1996).