CHAPTER 2

PREPARATION OF MEMBRANES

2.1 SOL-GEL ROUTE

Titania and zirconia membranes were prepared by sol-gel process by the destabilisation of the respective colloidal solutions.

The different steps involved in the preparation process by the sol-gel route can be summarised as follows: (Andre Larbot 1987).

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Metal alkoxide → hydrolysis
Metal hydrous oxide → peptisation
Sol → binder
Viscous sol →
   i) filtration through microporous support
   ii) gelation
   iii) sintering
   permanent membrane layer
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2.1.1 Preparation and Characterisation of Membrane Materials

AR grade samples of tetra butoxide of titanium (Merck-schuchardt) and zirconium (Aldrich) and secondary butoxide of aluminium (Fluka) were used as source materials for the preparation of titania, zirconia and alumina respectively (Yanane et al 1979).

The hydrous oxides of titanium and zirconium were prepared by complete hydrolysis with 100 mole of distilled water per mole of tetra butoxide at room temperature with constant stirring (Andre Larbot et al 1989). Boehmite was prepared by adding aluminium secondary butoxide to water in the same molar ratio which was heated at 80°C for 16 hours with efficient stirring (Leenars et al 1984). The resultant materials were filtered, washed with distilled water and dried at 110°C. The dried materials were sintered at 400°C, 600°C and 1200°C (titania), 470°C, 720°C and 1200°C (zirconia) and 400°C, 900°C and 1200°C (alumina) for five hours. The sintered and unsintered powders of titania, zirconia and alumina were characterised by XRD using Philips pw 1710 X-ray diffractometer using nickel filtered Cu $K_{\alpha}$ radiation ($\lambda=1.5410$ A) at 200 cps and scan speed of $2^\circ$/min and the XRD patterns of titania, zirconia and alumina are shown in Figs.2.1, 2.2 and 2.3 respectively. Temperature and duration of heating strongly influence the phase composition. The XRD pattern of titania dried at 110°C shows amorphous phase and those sintered at 400°C and 600°C show formation and retention of anatase phase, whereas the sample sintered at 1200°C shows the transformation to rutile phase. The XRD pattern of zirconia dried at 110°C and sintered at 470°C show the formation of amorphous and tetragonal phases respectively, whereas those sintered at 720°C and 1200°C show monoclinic phase. The XRD pattern of alumina dried at 110°C, and those sintered at 400°C, 900°C and 1200°C show the formation of boehmite, gamma, delta and alpha phases respectively.
Figure 2.2 XRD patterns of untreated and heat treated zirconia

(a) untreated (b) 470°C (c) 720°C & 1200°C
Figure 2.3 XRD patterns of untreated and heat treated alumina

(a) untreated (b) 400°C (c) 900°C (d) 1200°C
The specific surface area and pore size distribution measurements of the samples sintered at different temperatures were analysed by surface area monitor (Quantosorb Jr. sorption system, USA) using helium as the non adsorbate gas and nitrogen as adsorbate at liquid nitrogen temperature. The lower part of the adsorption isotherm, ie. \(0.05 < p/p_0 < 0.35\) was used for the measurements of specific surface area, whereas the entire desorption isotherm was used for determining the pore size distribution. Fig.2.4 shows the variation in specific surface area of the materials with sintering temperatures. It is observed from this figure that titania and zirconia show drastic reduction in specific surface area with temperature, whereas alumina shows less reduction. For instance, the specific surface area in \(m^2/g\) of titania, zirconia and alumina sintered respectively at 400°C, 470°C and 400°C were found to be 120, 28 and 218 respectively which decreased to 10, 2 and 141 respectively on increasing the sintering temperature to 1200°C. Ramarao et al (1989) have also reported less reduction in specific surface area with sintering of alumina powders. Large decrease in specific surface area of titania and zirconia on sintering implies that they would form good membranes on a support. Hence these membranes were prepared by sol-gel route involving sintering for radioactive waste treatment purpose.

The pore size distributions of sintered titania, zirconia and alumina were calculated using Kelvin radius and the thickness of the adsorbed layer using Kelvin and Halsey equations (Lowell 1979). Figs.2.5, 2.6 and 2.7 show the pore size distributions of titania, zirconia and alumina respectively. It is observed from these figures that the peak positions of the pore radius is shifted to larger side with increase in sintering temperature.

### 2.1.2 Preparation of Sol

The sols of the hydrous oxides of titanium or zirconium was prepared by hydrolysing the respective alkoxide followed by peptisation using nitric acid or perchloric acid as peptising medium (Yoldas 1975).
Figure 2.4 Variation of specific surface area of the membrane materials with temperature

**Materials**

- **Titania**
- **Zirconia**
- **Alumina**

Specific surface area (m$^2$/g)

Temperature (K)
Figure 2.5 Pore size distribution of untreated and heat treated titania

Figure 2.6 Pore size distribution of untreated and heat treated alumina

Figure 2.7a Pore size distribution of untreated and heat treated zirconia

Figure 2.7b Pore size distribution of heat treated zirconia
Experiments were conducted to choose the suitable medium between the two and to fix the pH of the sol, concentration of the sol and concentration of the electrolyte to stabilise the sol.

### 2.1.2.1 Selection of medium

The peptization is caused by electrostatic repulsion of the electrical double layers around the colloidal particles (Verwey-Overbeek 1948). These double layers are produced from the arrangement of electrolytes (NO$_3^-$ or ClO$_4^-$) around the particles (Deryaquin and Levi 1964). The repulsion depends essentially on the pH, nature and concentration of the electrolyte. The stability range of the colloidal particles was determined by measuring the mobility in an electrical field (zeta potential) of the particles as a function of pH in the two media. Figs. 2.8a and 2.8b show the variation of zeta potential of titania and zirconia sol respectively in the two media, with pH. It shows that nitric acid is a better medium than perchloric acid since the zeta potentials in nitric acid are larger than in perchloric acid medium. Hence nitric acid medium was chosen for peptisation.

### 2.1.2.2 Optimisation of pH

It was observed that the sols of titania and zirconia were unstable when the pH was around 5 since this is nearer to the point of zero charge. Same observation was reported by Partlow and Yoldas (1981). This means that pH of the sol must be away from the point of zero charge to prevent flocculation. Moreover, this condition is the best starting point to give defect free membranes. From Figs. 2.8a and 2.8b, it is observed that the zeta potential decreases with increase in pH and changes sign beyond pH=5 for both titania and zirconia. Since the maximum zeta potential was observed at pH=1, and also since the point of zero charge is far away from pH=1, the pH of the sol was optimised at pH=1 to obtain stable sol for both
Figure 2.8a Variation of zeta potential of titania in different media as a function of pH

Medium
- Nitric acid
- Perchloric acid

Figure 2.8b Variation of zeta potential of zirconia in different media as a function of pH

Medium
- Nitric acid
- Perchloric acid
titania and zirconia. pH beyond 5 was not considered due to the possible degradation of the binder near alkaline pH.

2.1.2.3 Optimisation of electrolyte concentration

Surface charge on a solid particle can be established by the adsorption of ions from solution. Preferential adsorption of one species over another can result from electrostatic attraction, London-Van der Waals interaction and hydrogen bonding. The anion chosen for the electrolyte and peptizing acid must not form a complex with the metal ion of the membrane to be formed (Wnek and Davies 1977). Based on this, sodium nitrate was chosen as stabilising electrolyte. The stability range of the sol in $10^{-4}$ to $10^{-1}$ M sodium nitrate was studied by measuring the zeta potential of the sol.

Fig. 2.9 shows the zeta potential of titania and zirconia sol in nitric acid medium at pH=1 as a function of sodium nitrate concentration in the range $10^{-1}$-$10^{-1}$ M. It is seen that the zeta potential first increases from the electrolyte free sol to $10^{-3}$ M and attains almost constant value from $10^{-3}$ M - $10^{-1}$ M of sodium nitrate. Hence, the electrolyte concentration was fixed at $10^{-3}$ M to stabilise the sol.

2.1.2.4 Fixation of sol concentration

The particle size of titania and zirconia in the respective sol was determined over a concentration range of 100-500 ppm in the aqueous medium containing $10^{-3}$M sodium nitrate as electrolyte at pH=1 using nitric acid. Fig. 2.10 shows the mean particle size of titania and zirconia as a function of sol concentration.

From the Fig. 2.10, it is observed that the particle size varies between 476-1080 nm for titania and 350-850 nm for zirconia in the concentration range 100-500 ppm. For both titania and zirconia, the mean
Figure 2.9 Optimisation of electrolyte concentration in the sol preparation.
Figure 2.10 Variation of particle size with concentration of sol

Materials
Titania | Zirconia

Concentration of the sol (ppm)

Particle size (nm)

Figure 2.10 Variation of particle size with concentration of sol
Figure 2.11a  Particle size distribution of 300 ppm titania

Figure 2.11b  Particle size distribution of 300 ppm zirconia
particle size was found to be almost equal at 300 ppm of the sol concentration. Hence, the sol concentration was fixed at 300 ppm for the preparation of titania and zirconia membranes for the purpose of comparison. The particle size distributions of titania and zirconia at 300 ppm are shown in Figs. 2.11(a) and 2.11(b) respectively.

### 2.1.2.5 Selection of binders

Binders are used to serve two purposes viz., 1) they allow the adjustment of sol viscosity and 2) they protect thin layer from cracking during sol-gel transition at the drying stage. The following are the desirable properties of good binders, (Soheng W.U 1982) viz., i) low molecular weight, ii) higher chain flexibility iii) less number of functional groups which can form interfacial chemical bonding or hydrogen bonding vi) lower degree of cross linking v) devoid of bulky side groups vi) good wettability vii) compatibility with the medium and viii) easy pyrolysis at relatively low temperatures without leaving carbon residue.

Nitrogen containing groups, hydroxyl and methylol groups promote adhesion to inorganic and organic adherend. Based on these criteria, polyvinyl alcohol, polyacrylamide and polyethyleneimine were chosen as binders. They are soluble in water. Tsuchiya and Sumi (1969) have reported that polyvinyl alcohol undergoes two stages of decomposition, the first at 240°C with formation of water and carbonyl compound as the main decomposition product. The second stage of decomposition takes place at 300°C with the formation of a series of n-alkanes, n-alkenes and aromatic hydrocarbons. Polyacrylamide undergoes three stages of weight loss (Mark et al 1985). The first stage is due to loss of ammonia at 290 C, the second stage at 430 C with loss of water, carbon monoxide and ammonia and the third stage at 550°C also with the loss of the above materials. The losses at the three stages are to the extent of 98.5% by wt. Decomposition of
polyethyleneimine in air does not occur below 300°C (Mark et al 1985b). Hence the sintering temperature was chosen from 400°C and above.

Viscosity

The membrane formation rate and the thickness of the membrane layer depend on the viscosity of the sol (Deryaquin and Levi 1964). The viscosity of the sol is mainly due to the binder and hence the viscosity of the binders at various concentrations were determined by measuring the power associated with the rotation of paddle agitator within the laminar region using glycerol as standard (Shinghi Nagata 1975). Aqueous glycerol solutions of various concentrations from 30 to 100 wt % were prepared. 500 ml of the solution was taken in a beaker and thermostated at 3°C. Paddle agitator with impeller of 3 cms length was immersed in the solution without touching the sides or bottom of the beaker. The paddle agitator was connected to powermeter which read directly the power involved in the rotation of the agitator in Watts. At each concentration, the power consumed in air without the viscous medium was measured which was subtracted from the total power consumed at a given RPM for various concentrations. The effective power at each concentration for various RPM was determined. The power consumed in the glycerol solution increases as the square of the rotation speed as shown in Fig.2.12 for various concentrations of glycerol. This behaviour is expected in the laminar flow region (Shinghi Nagata 1975). The viscosity of the glycerol solutions of different concentrations are known (Norbert Adolph Langes 1970). Fig.2.13a shows the consumed power of glycerol as a function of viscosity at 30 RPM. 30 RPM was chosen since it is very well within the laminar region. Power consumed at 30 RPM in the aqueous solutions of the three binders viz., polyvinyl alcohol, polyacrylamide and polyethyleneimine at various concentrations are shown in Figs.2.13b, 2.13c and 2.13d respectively. Power consumed depends on the viscosity of the solution irrespective of the polymer present in it. Using Figs.2.13a-d,
Figure 2.12 Effective power as a function of square of RPM in glycerol
Figure 2.13a Effective power as a function of viscosity of glycerol.

Figure 2.13b Effective power as a function of concentration of polyvinyl alcohol.

Figure 2.13c Effective power as a function of concentration of polyacrylamide.

Figure 2.13d Effective power as a function of concentration of polyethyleneimine.
the relation between the concentration of binder in the solution and its viscosity was obtained and the values are given in Table-2.1. The viscosity of polyvinyl alcohol vary from 50-80 cp in the concentration range 0.765 to 3.8 wt%. The corresponding concentration range for polyacrylamide and polyethyleneimine are 0.051 to 0.069 and 6.7 to 25 wt% respectively.

Table 2.1 Variation of viscosity with concentrations

<table>
<thead>
<tr>
<th>Viscosity (cp)</th>
<th>Polvinylalcohol (Wt %)</th>
<th>Polyacrylamide (Wt %)</th>
<th>Polyethyleneimine (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.765</td>
<td>0.051</td>
<td>6.7</td>
</tr>
<tr>
<td>60</td>
<td>1.826</td>
<td>0.059</td>
<td>14.0</td>
</tr>
<tr>
<td>70</td>
<td>3.000</td>
<td>0.064</td>
<td>23.0</td>
</tr>
<tr>
<td>80</td>
<td>3.800</td>
<td>0.069</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Surface tension

Low energy materials having surface tension below 100 dynes/cm (eg. organic polymers and water) tend to adsorb strongly on to high energy surfaces having surface tension in the range 200-5000 dynes/cm (eg. oxides, nitride, silica and diamond) as this will greatly decrease the surface energy of the system (Smith 1962).

For polymeric binders, adhesion is a two stage process, wetting as the first stage followed by inter diffusion. Hence, the binder with low surface tension in the solution is preferable for good adhesion. With this in view, the surface tension of the binders of various concentrations were determined using torsion balance (M/s.Hardson, Calcutta).

The surface tension in dynes/cm of the polyvinyl alcohol, polyacrylamide and polyethyleneimine vary between 58-45, 65-62 and 59-52 in the viscosity range 60-80 cp. It is clear from these measurements that polyvinyl alcohol solution has low surface tension. Hence polyvinyl alcohol was preferred as binder.
To evaluate the binding capacity of different binders with the support, the IR frequency shift in the functional group of the binder when bonded to the support was studied (Nakamoto 1978).

80 cp viscous solutions of polyvinyl alcohol, polyacrylamide and polyethyleneimine were filtered separately through the porous support for 30 minutes at 5 Kg/cm² using the filtration setup as shown in Fig.2.14. The same set up was used for the preparation as well as the application of the membranes. It consists of a small mild steel tank of one litre capacity closed at the top with three holes, one for connecting the nitrogen gas cylinder for pressurisation, the seconld for pressure gauge and the third for introducing the sol for filtration. The fittings are made air tight to avoid any pressure leakage.

The coated surface was dried at 100°C, cooled to room temperature and the IR spectra was recorded. The IR spectra of polyvinyl alcohol, polyacrylamide and polyethyleneimine with and without the support are shown in Figs.2.15a, 2.15b and 2.15c respectively. Polyvinyl alcohol shows -OH band at 3500 cm⁻¹ (λ 3.5 μm) in free state. When it is bonded to alumina support, the -OH band of the polyvinyl alcohol decreases to 3472 cm⁻¹ (λ 2.88 μm) giving rise to negative shift of 28 cm⁻¹ in the band position (Fig.2.15a). The bonding between the electron pair available on the oxygen of the -OH group of the polyvinyl alcohol to the support decreas the bond strength of the -OH group of the polyvinyl alcohol. This results in the negative IR frequency shift of the functional group -OH of polyvinyl alcohol.

Polyethyleneimine shows NH stretching band at 3355 cm⁻¹ (λ 2.98 μm) in the free state. It decreases to 3333 cm⁻¹ (λ 3.0 μm) when bonded to alumina support. This results in the negative shift of 22 cm⁻¹ in the band position (Fig.2.15b). The electron pair available on the nitrogen of the imino group in polyethyleneimine to the support decreases the bond strength of the
Figure 2.15 IR spectra of binders with and without the porous support

(a) Polyvinyl alcohol  (b) Polyacrylamide  (c) Polyethyleneimine

(1) with support  (2) without support
imino group. This results in the negative IR frequency of the functional group -NH of the polyethyleneimine. Polyacrylamide shows carbonyl absorption band at 1650 cm\(^{-1}\) (\(\lambda\) 6.06 \(\mu\)m) in the free state. When bonded to alumina support, it increases to 1666 cm\(^{-1}\) (\(\lambda\) 6.0 \(\mu\)m) giving rise to positive shift of 16 cm\(^{-1}\) in the band position (Fig.2.15 c). The bonding of the electron pair available on the nitrogen of the amide group to the support increases the double bond nature of the carbonyl group of the amide group which reflects in the IR frequency of the carbonyl group of the amide group (when bonded to the alumina support) in the positive direction. Since among the binders, polyvinyl alcohol shows the highest frequency shift, it is expected to show the best binding to the alumina support because of relatively larger interaction. The frequency shift is attributed to the coordination between the oxygen of the -OH group present in the alcohol to the metal atom of the oxide in the support. Considering the magnitude of the frequency shift, Polyvinyl alcohol was chosen as the binder.

2.1.3 Characterisation of support

High refractory porous alumina tube procured from BHEL, India, was used as support for coating the membrane material to obtain membrane layer. This porous alumina support was formed by packing of coarse-grained materials (micron range) with additions of organic binders. After burning away the organic binders, the compact form was sintered to obtain this support. The geometry of the support was a cylinder of 3 cm length and 1 cm internal diameter. The wall thickness was 3 mm. This gives rise to internal surface area of 9.45 cm\(^2\).

Pore size, pore density, and porosity of the support

The pore size distribution of the support was determined using the SEM (Fig.2.16) and the pore size distribution is shown in Fig.2.17. The pore size distribution range from 2000 to 8000 nm. The mean pore size and pore
Figure 2.16 Scanning electron micrograph of porous support
Figure 2.17 Pore size distribution of porous support
density were found to be 5400 nm and $2.6 \times 10^6$/cm² respectively. The porosity of the support was determined by estimating the water content of the support as follows: Porous alumina support was weighed after keeping in an oven at 110°C for 3 hours and cooling in desiccator. Let the weight be $W_1^*$. The support was immersed in boiling water for 6 hours to completely fill up the pores present in the support with water, the tube was taken out, outer surface wiped and re weighed in air ($W_2^*$) and in water ($W_3^*$). Care was taken that the tube did not touch the sides or bottom of the beaker while weighing in water. The weight loss in each case was equated to the volume of water displaced (since the density of water is 1 gm/cc). The volume of the pores in the support ($V_{ps}$) was calculated from $(W_2^* - W_1^*)$ and the volume of the support ($V_s$) was calculated from $(W_1^* - W_3^*)$. Hence the porosity of the support defined as the ratio of the volume of the pores present in the support to the total volume of the pores and the support was calculated using the equation

$$\alpha_s = \frac{V_{ps}}{V_s + V_{ps}} = \frac{W_2^* - W_1^*}{W_2^* - W_3^*} \quad (2.1)$$

The porosity of the support was found to be 0.5499

**Permeability**

The permeability of the support was determined from the flux of porous support using water as the permeating species at gas pressures 1, 3, and 5 Kg/cm². Fig.2.18 shows the permeability of the support as a function of pressure. The permeability expressed as L/m²/hr was found to be 4535 and 10,990 at 1 and 5 Kg/cm² respectively. Increase of permeability with pressure is expected. The theoretical permeability was calculated using Hagen Poiseuille equation 2.2 (Munir Cheryan 1986) at these pressures.

$$J = \frac{\varepsilon d_r^2 \Delta p}{32 \tau \eta} \quad (2.2)$$
Figure 2.18 Permeability studies of porous alumina support
where \( \varepsilon \) is the porosity, \( d_p \) is pore diameter, \( \Delta p \) is the applied pressure, \( t \) is the thickness and \( \eta \) is the viscosity of the solution.

The theoretical permeabilities calculated using the equation 2.2 in L/m\(^2\)/h are 5800 and 28,960 at 1 Kg/cm\(^2\) and 5 Kg/cm\(^2\) respectively. The low experimental values might be due to the deviation from the assumption that the pores are cylindrical and through and through in the support.

2.1.4 Filtration characteristics during membrane growth

The membrane preparation was done by clogging the pores of the support with the particles present in the colloidal sol followed by membrane layer formation by filtering the colloidal viscous sol through the support under pressure. Since the binding of the membrane materials with the porous support will increase with pressure, the preparation of the membrane by using gas pressurisation was employed (Souhenge, 1980). 500 ml of the sols of 300 ppm titania or zirconia in nitric acid medium at pH=1 with \( 10^{-3} \) M sodium nitrate as stabilising electrolyte and viscosity 80 cp (with polyvinyl alcohol as binder) was filtered through the porous alumina support using the filtration set up as shown in Fig.2.14. To know the filtration characteristics, the flux of the filtrate was measured as a function of time. Figs.2.19a and 2.19b show \( t/v \) versus \( t \) plots for titania and zirconia sols respectively, where \( t \) is the time of contact of sol with the support and \( v \) is the volume filtered at every 5 minutes. Figs.2.20a and 2.20b show \( t/v \) against \( v \) for titania and zirconia at 5 Kg/cm\(^2\). The amount of titania or zirconia present in the filtrate at every 15 minutes was determined spectrophotometrically (Vogel 1961) and the % of the material rejected was calculated. They are presented in Figs.2.21a and 2.21b respectively.
Figure 2.19a Filtration mechanism during clogging of the support pores in the titania membrane formation.

Figure 2.19b Filtration mechanism during clogging of the support pores in the zirconia membrane formation.
Figure 2.20a Filtration mechanism during titania membrane formation

Figure 2.20b Filtration mechanism during zirconia membrane formation
Figure 2.21a Percentage rejection of titania

Figure 2.21b Percentage rejection of zirconia
2.1.5 Results and Discussion

Figs.2.19a and 2.19b show linear increase of \( \frac{t}{v} \) with \( t \) during initial period and subsequently it deviates from the linearity at 5 Kg/cm\(^2\). The deviation from linearity is not observed at pressures less than 5 Kg/cm\(^2\) during the time of filtration of our study. Also, \( \frac{t}{v} \) versus \( v \) shows linearity at 5 Kg/cm\(^2\) in the later period of time as shown in Figs.2.20a and 2.20b. This behaviour is consistent with the model involving two stages of membrane growth (Freilich and Tanny 1977). The first stage is the pore clogging step in which the pores present in the support are clogged and the second stage is the formation of the membrane by bridging with colloidal particles.

The pore clogging step is governed by the equation

\[
k \frac{t}{2} = \frac{t}{v(t)} - \frac{1}{J_0}
\]

where \( v(t) \) is the volume of filtrate passing through the support at the contact time \( t \), \( J_0 \) is the flux at \( t=0 \) and \( k \) is a constant. It is clear from this equation that \( \frac{t}{v} \) is linear with \( t \) as shown in Figs.2.19a and 2.19b. The membrane growth is governed by the equation

\[
\frac{t}{V} = \frac{(V + 2V_f)}{K}
\]

where \( V_f \) is the volume of filtrate which must pass in order to create a membrane of resistane equal to that of the original support and \( K \) is the membrane resistance. Hence \( \frac{t}{v} \) versus \( v \) is a straight line at the second stage which is represented in Figs.2.20a and 2.20b.
Figs.2.19a and 2.19b show that the pore clogging mechanism operates up to 35 minutes for titania sol and 40 minutes for zirconia sol at 5 Kg/cm$^2$. Then the membrane growth mechanism takes over.

The particle size distribution of the 300 ppm titania and zirconia sols (Figs.2.11a and 2.11b) show that even though the mean particle size is almost comparable, titania sol contains relatively more number of larger sized particles compared to zirconia. This resulted in faster clogging of the support pores with titania and the consequent reduction in the flux during the filtration of titania sol compared to zirconia sol. The experimental observation that the pore clogging step continued for 35 minutes in the filtration of titania sol as against 40 minutes in the filtration of zirconia sol is consistent with the earlier observation with respect to clogging of the pores. Also observation from these figures that the less filtrate volume in the formation of titania membrane compared to that in the formation of zirconia membrane is understandable from this result.

The percentage rejection of the material is defined as

\[
\text{\% rejection} = \frac{[\text{Feed}] - [\text{Filtrate}]}{[\text{Feed}]} \times 100 \quad (2.5)
\]

where \([\text{Feed}]\) and \([\text{Filtrate}]\) represent the concentrations of feed and filtrate respectively. The percentage rejection was plotted as function of time as Fig.2.21a for titania sol and as Fig.2.21b for zirconia sol. It shows that the percentage rejection increases with time, reaching almost 100% at 60 minutes in the filtration of the sols. Because of the clogging and consequent reduction in the pore size of the support, the amount of the material in the filtrate came down with time. Hence the percentage rejection of the material in the filtrate increased with time.
The filtration of the sols was continued for 60 minutes and the porous support coated with titania and zirconia were subjected to sintering after gelling at 20°C for 24 hours. Titania membrane coated support was sintered at 400°C, 600°C and 1200°C for 5 hours. Zirconia membrane coated support was sintered at 470°C, 720°C and 1200°C for 5 hours. The sintering was done to increase the adhesion and to remove the binder. The membranes so obtained were characterised and discussed in Chapter 3.

2.2 ANODIZATION ROUTE

Because of the high affinity of aluminium surfaces for oxygen, the metal is always covered with a highly resistant oxide film (Hoar and Mott 1959). This oxide layer will be very thin of the order of 10 nm. This will be excellent in corrosion resistance and gives attractive finish to the material. Anodization of aluminium is used to prepare porous oxide membrane (O’sullivan and Wood 1970) of the required thickness and porosity.

The type of anodic oxide film that can be produced on aluminium anode in an electrolytic cell depends upon several factors, the most important of which is the nature of electrolyte. Electrolytes in which the formed oxide film is completely insoluble are those electrolytes which produce barrier type films without pores (Diggle et al 1968). Examples of this type of electrolytes include neutral boric acid solution, ammonium borate or tartarate aqueous solutions (pH 5-7), ammonium tetraborate in ethylene glycol, and several organic electrolytes including citric, malic and glycolic acids. Electrolytes in which the anodically formed oxide films is slightly soluble are those electrolytes which produce porous-type films. Examples of this types of electrolytes are sulphuric, phosphoric, chromic and oxalic acids at almost any concentration. These two types of films differ in thickness and porosity.
Since the present study concerns with the porous oxide membranes, the anodization of aluminium in pore forming electrolyte is carried out.

2.2.1 Experimental procedure

Aluminium anodizing is normally far easier in acids with divalent or trivalent anions than with those having monovalent anions. Trivalent or divalent ions could adsorb much more easily than monovalent ions on the positively charged alumina surfaces, especially at high electric fields. Hence the alumina membranes were prepared in a tribasic, phosphoric acid and a dibasic, oxalic acid. Additional advantage of using phosphoric acid lies in the fact that it permits anodization at high voltages without excessive current flow and heat evolution (Furneaux et al 1989).

99.96 % pure aluminium pieces procured from E.Merck, Germany was used for anodization. A U-shaped glass tube with an external jacket for circulating water was used as an electrolytic cell for preparing the alumina membrane (Fig.2.22). The aluminium piece of 1 cm × 1 cm was used as anode with 0.5 cm² of the piece immersed in the electrolyte. A graphite rod was used as cathode and it was kept at a distance of 9 cm from the anode. The two electrodes were connected to a D.C. power supply. Phosphoric acid or oxalic acid was used as electrolytes. Same sized aluminium pieces were used for carrying out separate experiments for different time durations. The aluminium pieces were electropolished at 20°C employing a current density of 10 mA/cm² at 20 volts using a mixture of 34.5 % volume of perchloric acid and 65.5% by volume of acetic anhydride. For the selective removal of metal for obtaining the oxide layer, a solution of 2 ml of bromine in 100 ml of dry methanol was used (Henley 1982). The pieces were weighed (w₁) and anodised in phosphoric acid or oxalic acid at 325 volts for 2 minutes at four different temperatures, 20°, 30°, 40° and 50° C. One side of the piece, not facing the cathode, was covered with cellotape to avoid formation of oxide layer on that side. The aluminium pieces with the oxide coatings were weighed (w₂). The aluminium oxide formed was selectively dissolved in
Figure 2.2: Anodization setup

CATHODE - CARBON ROD

ANODE - ELECTRO POLISHED ALUMINIUM

WATER IN

WATER OUT

(+)

(-)
phosphochromic acid prepared by dissolving 20 g of chromic anhydride and 35 ml of phosphoric acid in 1 litre of water and the pieces were re-weighed ($w_3$). From the above weights, the weight of oxide formed was calculated as ($w_2 - w_3$). The coating ratio (C.R), defined as

$$\text{C.R} = \frac{\text{(weight of oxide formed)}}{\text{(weight of aluminium lost)}} = \frac{w_2 - w_3}{w_1 - w_3},$$

was calculated in each case.

In order to study the effect of current strength on the membrane formation, the current was changed from 0.15 - 0.5 A at the same voltage (325 V) by adjusting the concentrations of the electrolyte. Similarly, to correlate the voltage with the pore size, the anodization was carried out at voltages of 150, 200, 250 and 325 at the same current strength (0.5 A). The current-time characteristics in phosphoric acid and oxalic acid are plotted for the four different temperatures (Figs. 2.23a and 2.23b). The coating ratio are plotted as a function of time at various temperatures in these media (Figs. 2.24a and 2.24b).

2.2.2 Results and discussion

Current time characteristics

From Figs. 2.23a and 2.23b it is found that the current density decreases with increase of time due to the insulating nature of the oxide layer formed. Since the weight of oxide formed is less in the case of oxalic acid medium as compared to phosphoric acid medium, the drop in the current is slower in the former case. The relatively thicker oxide formation in phosphoric acid is due to the trivalent anion (phosphate) in phosphoric acid as compared to the divalent anion (oxalate) in oxalic acid. The current-time characteristics show that, the current reduces from the initial formation current to a steady value. It is so due to the insulating nature and
Figure 2.23a Current-time characteristics during membrane formation in phosphoric acid medium.

Figure 2.23b Current-time characteristics during membrane formation in oxalic acid medium.
Figure 2.24a Coating ratio in phosphoric acid medium at different temperatures

Figure 2.24b Coating ratio in oxalic acid medium at different temperatures
the porous structure of the oxide layer. Since the oxide layer is porous, the current does not drop to zero but attains a steady value.

Coating ratio

It is found from Figs.2.24a and 2.24b, that the coating ratio lies in the range 1.6-1.7 in the case of phosphoric acid and 1-1.4 in the case of oxalic acid. The experimentally observed C.R values for both phosphoric and oxalic acids are lower than the theoretical value of 1.89. Similar observation was reported by Diggle et al (1989) also. In both the cases, it is more at lower temperatures indicating that the formation of oxide is more probable than dissolution at lower temperatures. Higher coating ratio in phosphoric acid is due to the larger valency of the phosphate anion. The possible reasons for the low coating ratio are the following:

a) Some aluminium may go directly into solution without recourse to oxide formation.
b) Outer surface dissolution of the porous film.

The low coating ratio was explained by Diggle et al (1968) by considering the following reactions with formation of Al⁺ and Al³⁺ as the first stage (reaction 2.7). The presence of Al⁺ was confirmed by the experimental observation of Raijola (1956).

\[
2 \text{Al} \rightarrow \text{Al}^+ + \text{Al}^{3+} + 4e^- \quad (2.7)
\]

Reaction 2.7 could then be followed by reactions 2.8 or 2.9 and 2.10.

\[
\begin{align*}
\text{Al}^+ + 2\text{H}_3\text{O}^+ &\rightarrow \text{Al}^{3+} + \text{H}_2 + 2\text{H}_2\text{O} \quad (2.8) \\
\text{Al}^+ + 2\text{H}_2\text{O} &\rightarrow \text{Al}^{3+} + \text{H}_2 + 2\text{OH}^- \quad (2.9) \\
2\text{Al}^{3+} + 9\text{H}_2\text{O} &\rightarrow \text{Al}_2\text{O}_3 + 6\text{H}_3\text{O}^+ \quad (2.10)
\end{align*}
\]
Diggle et al (1968) have proposed that the Al$^{3+}$ produced in reaction 2.8 and reaction 2.9 diffuse into the bulk without forming the oxide. Only the Al$^{3+}$ produced in the reaction 2.7 forms the oxide. Moreover the ratio of Al$^{+}$/Al$^{3+}$ is found to increase with temperature and so there is less availability of the Al$^{3+}$ to form the oxide at higher temperatures. Hence the coating ratio was found to come down with increase in temperature. But one can not rule out the possibility of outer surface dissolution of the membrane layer which also increases with temperature.