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CHARACTERISTICS OF UNSUPPORTED ALUMINA MEMBRANE PREPARED USING SOL-GEL TECHNIQUE

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ABSTRACT

A laboratory scale alumina membrane was prepared using sol-gel technique. Results from the experiment demonstrate that the addition of PVA is important for viscosity adjustment to determine the appropriate coating time if the membrane is required for coating on the porous support. The effects of varying PVA content and sintering temperature on the characteristics of the sintered membrane are discussed. In this work, a 2 volume % of PVA solution containing 4g of PVA in 100ml of water was discovered to be adequate to achieve appropriate porosity level and avoid cracks in the gel layer. It was also discovered that the sol viscosity essentially increased as the PVA addition was increased. On the contrary, the coating time decreased as PVA content in the sol was increased. Generally, the pore size of the membrane increased with the increase in PVA addition. The density of the membrane increased with increase in sintering temperature. The porosity level however, decreased as the temperature was increased. The pore size became greater and pore size distribution wider at higher sintering temperatures.

1. INTRODUCTION

The sol gel technique is attractive for application on a porous filter support or preparation of composite/asymmetric membrane. In the process, a sol is first prepared using an organo-metallic oxide followed by addition of binders and acid. Later, the thickened sol is deposited or coated as a layer on the support by dip or spin coating, after which it is dried under controlled environment to form a gel. In the final process, the membrane is calcined and sintered before the composite ceramic membrane is obtained. The sol gel technique offers great promises for making porous membranes with extremely fine pores. It typically results in nano-scale structures unattainable by conventional methods.

In this work, alumina membrane was selected for several reasons. Firstly, alumina (Al_2O_3) is chemically inert and stable to its melting point of 2050°C. It has good mechanical strength and endurance. In its pure form, alumina has a high Young's modulus of ≈ 400 GNm^{-2} [1]. Secondly, alumina membranes with less than 4nm pore size can be produced successfully. Alumina membranes of pore size 2.5nm has been prepared successfully in the laboratory experiments[2,3]. Egan et al.[4] successfully refined the pore size of membrane

and produced the membrane with pore radii less than 1nm. And thirdly, alumina is chosen due to the fact that it is one of the most versatile refractory ceramic oxides. It has secured more than 50% of the world market for technical ceramic products[1].

2.   APPLICATION OF BINDER IN MEMBRANE SYNTHESIS

A common problem associated with the production of alumina membrane using sol gel technique is the formation of crack gel layer. The development of crack free alumina membrane requires the control of many factors, namely the film thickness, molar ratio or composition of the alkoxide, water, and acid. In addition, the use of correct amount of binder also helps determine the success of crack free alumina production from sol gel technique. Commonly, binders are introduced to add strength to the membrane and avoid cracks from forming in membrane layer. The purpose of using organic binders is to avoid particle aggregation, permit adjusting of viscosity and increase the mechanical strength of the material to prevent crack formation by maintaining its shape until it is sintered. The application of PVA to permit adjusting of viscosity[5] can be deliberately manipulated to modify the rheology of the sol in order to determine the appropriate membrane coating time.

It is well understood that a membrane support immersed in sol for a long period of time results in the formation of cracks in the top surface of the support due to the development of membrane layer that is too thick, whereas, too short a period of coating time produces a layer that is too thin to hold the support. Xia[6] has proposed a foundation for proper coating time using viscosity as a guide. For sol with relatively high viscosity (40×10^{-3} Pa.s or 40 cp), the appropriate coating time should be about 3 seconds. For less viscous sol (1.3×10^{-3} Pa.s or 1.3 cp), the appropriate coating time should be longer, of about 30 seconds.

3.   ALUMINA MEMBRANES PREPARATION FROM SOL GEL ROUTE

Unsupported alumina membrane can be prepared in the laboratory by hydrolisation of aluminium secondary butoxide with water and peptisation with acid at temperature of about 90°C under rigorous stirring condition. The peptised (stable) sol is then cooled down steadily to allow formation of gel. Later, the gel is fired to obtain aluminium oxide or alumina. This route to obtain alumina is referred to as sol-gel technique.

4.   MATERIALS AND METHODS

The composition of aluminium sec-butoxide, water, and HNO_3 used in the experiment follows the optimum molar ratio as recommended in the work of Yoldas[7] which is 1:0.07:100. The raw material and chemicals used in the experiment to develop alumina membrane are listed in Table 1.

Table1: Chemicals for alumina membrane development using sol-gel technique.

Chemicals	Formula	M. Weight (g/gmol)	Density (g/cm^3)	Supplier	Purity
1. Aluminium secondary butoxide	$Al(OC_4H_9)_3$	246.33	0.96	Merck (Malaysia)	>95%
2. Nitric acid	HNO_3	63.01	1.42	Merck (Malaysia)	1M
3. De-ionised water	H_2O	18	0.99705	-	-
4. Polyvinyl alcohol	PVA	72000	-	Merck (Malaysia)	>98%

4.1 PVA preparation

2, 4, 6 and 8g of PVA was weighed and dissolved in 100ml of distilled de-ionised water at temperature 70°C respectively. Then, the PVA solution was added to the boehmite sol during peptisation with concentration 1, 2, 3 and 4 volume % of the solution from the total volume of the boehmite sol (103.25ml).

4.2 Membrane preparation

Boehmite sol was prepared using 90.3ml de-ionized water heated on a hot plate at a temperature between 85-90°C, followed by addition of 12.8ml aluminum secondary butoxide stirred vigorously with magnetic stirrer. The temperature of the mixture was maintained at 90°C. Later, 3.1ml of acid and PVA solution with different concentrations were added to the mixture and refluxed under continuous stirring at temperature 90°C for 24 hrs. The sol was cooled down slowly and left aside for a few hours.

A small amount of the final sol mixture, approximately 0.3-1ml, was poured onto a 85mm diameter polypropylene petri dish. The sol was then dried under ambient and highly humid conditions for a minimum duration of 24 hrs until gelation and eventually hardened/dried gel was obtained. A sample of dried gel from the dish was transferred into a porcelain crucible for calcination/sintering at 400°C, after which the boehmite particles were transformed into γ-alumina[2,8].

An example of sintering profile at 400°C adopted from the Larbot's[9] procedure is illustrated in Figure 1. A programmable muffle furnace with computer PID control system supplied by Isuzu Seisakusho Co. Ltd. from Japan was used for the calcination process. The program setup for the calcinations process is given in Table 2. The complete flow diagram of membrane preparation is shown in Figure 2.
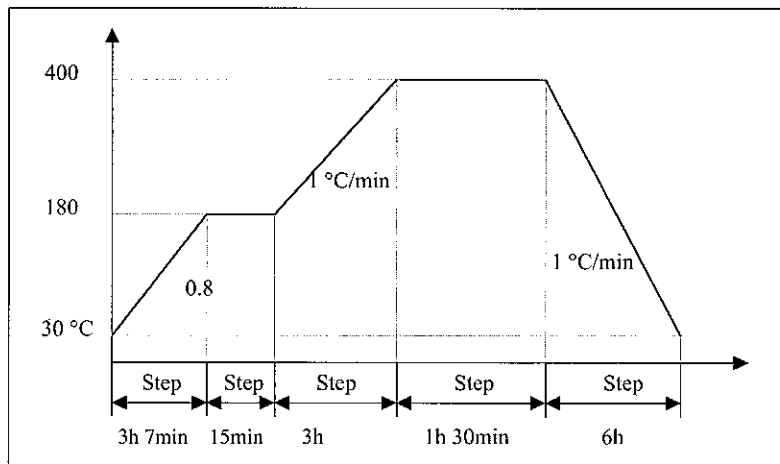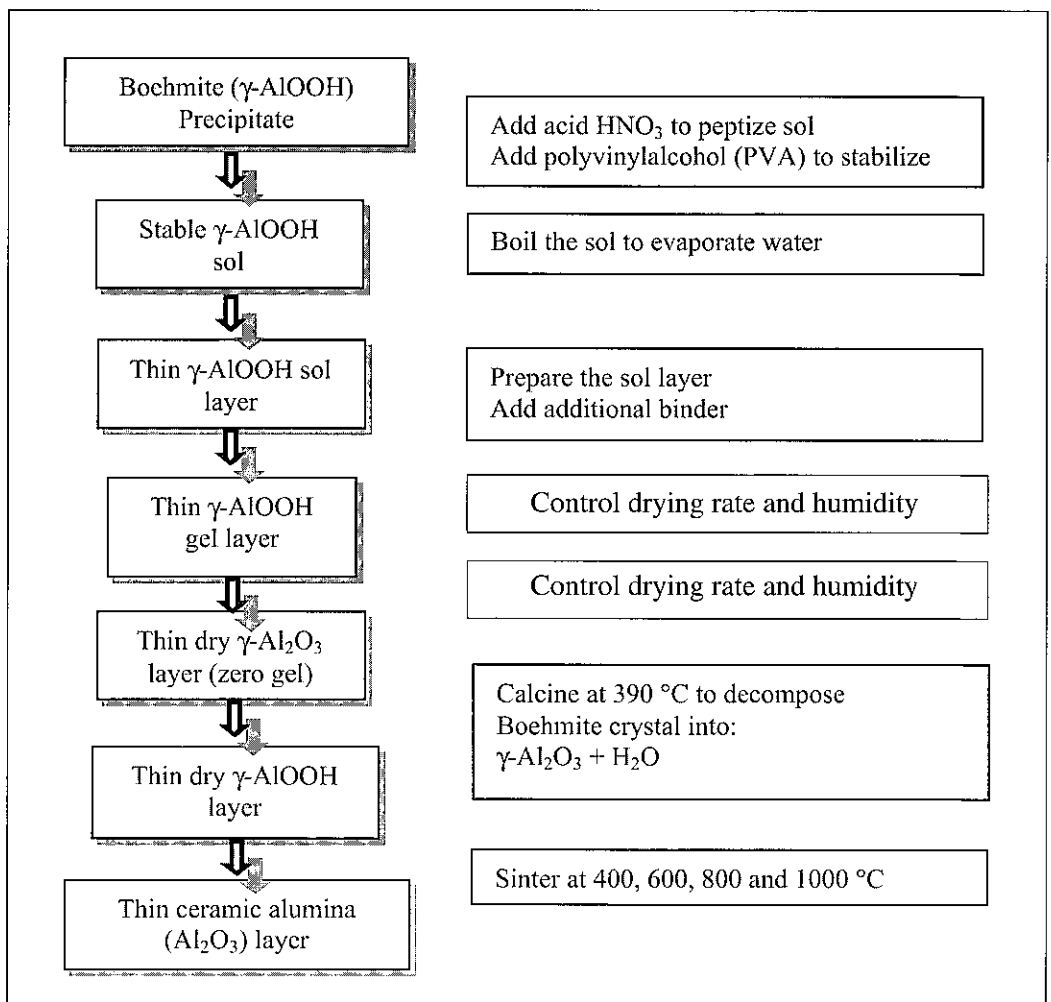
Figure 1: Membrane sintering profile.

Figure 2: Alumina membrane preparation using sol gel technique.

Table 2: Muffle furnace program setup for sintering process of the membrane.

Step	Key	Display	Status
1	POWER	"30"	PV lamp is lit to show temperature at sensor
2	MODE	"PrG.*"	Show previous program number
3	ENTER	"PrG.*"	Flashing digit
4	▲▼□	"PrG.4"	"4"entered
5	ENTER	"* * * *"	SV lamp, STEP 1 lamp lit indicated previous temperature. Highest digit flashes.
6	▲▼□	"0180"	0180 entered
7	ENTER	"0180" "**.^{H}**^{M}"	Flashing stops, set temperature entered, shift time set. Highest digit flashes
8	▲▼□	"03.^{H}"7.5^{M}"	3hrs 7.5min set
9	ENTER	"* * * *"	STEP 2 lamp lit, highest digit of temperature display flashes
10	▲▼□	"0180"	0180 entered
11	ENTER	"0180" "**.^{H}**^{M}"	Flashing stops, set temperature entered, shift time set. Highest digit flashes
12	▲▼□	"00^{H}"15^{M}"	15 min set
13	ENTER	"* * * *"	STEP 3 lamp lit, highest digit of temperature display flashes
14	▲▼□	"0400"	0400 entered
15	ENTER	"0400" "**.^{H}**^{M}"	Flashing stops, set temperature entered, shift time set. Highest digit flashes
16	▲▼□	"03.^{H}40^{M}"	3 hrs 40 min set
17	ENTER	"* * * *"	STEP 4 lamp lit, highest digit of temperature display flashes
18	▲▼□	"0400"	0400 entered
19	ENTER	"0400" "**.^{H}**^{M}"	Flashing stops, set temperature entered, shift time set. Highest digit flashes
20	▲▼□	"01.^{H}30^{M}"	1 hr 30min set
21	ENTER	"* * * *"	STEP 5 lamp lit, highest digit of temperature display flashes
22	▲▼□	"0030"	0030 entered
23	ENTER	"0030" "**.^{H}**^{M}"	Flashing stops, set temperature entered, shift time set. Highest digit flashes
24	▲▼□	"06.^{H}10^{M}"	6 hrs 10 min set
25	ENTER	"RP.**"	Number of repetition
26	▲▼□	"rP.01"	01 entered (1 time set)
27	ENTER	"PrG.4"	Show program 4
28	RUN/STOP	"30" "03.^{H}19^{M}"	Operation starts. Temperature of sensor inside the vessel is indicated. Time shows 3.19.PV, RUN/STOP, HEAT, STEP 1 lamp lit
29	Program finished		Buzzer sounding 5 times, all lamp of STEP 1 to 5 lit. Time is total from start to end

4.3   Membrane characterisation

The viscosity of the sol was determined using a Brookfield rheometer accompanied with Rheocalc V2.1 software. The measurement was made using spindle speed of 180RPM and temperature of 30°C. The pore distribution and surface area were determined using Quantachrome Autosorb automated gas sorption system and the accompanying Micropore version 2.48 data acquisition software.

5.   RESULTS AND DISCUSSION

5.1   Effect of PVA addition on the gel viscosity

The effect of PVA addition in boehmite sol during peptisation on the viscosity, interpolated coating time from the data in the literature, pore size and BET surface area is presented in Tables 3, 4, 5, and 6 respectively.

Table 3: Effect of PVA concentration on the sol and membrane characteristics (2g PVA dissolved in 100ml de-ionised distilled water).

Percent PVA in sol	Viscosity (cp)	Coating time (s)	Pore size (nm)	BET Area (m^2/g)	Membrane appearance
1	2.38	29	1.350	391	Translucent, many cracks with curl from edge.
2	4.80	28	1.525	373	Translucent, slight crack with curl from edge
3	13.1	22	1.700	226	Translucent, slight crack with curl from edge
4	15.2	20	1.725	219	Translucent, almost without crack.

Table 4: Effect of PVA concentration on the sol and membrane characteristics (4g PVA dissolved in 100ml de-ionised distilled water).

Percent PVA in sol	Viscosity (cp)	Coating time (s)	Pore size (nm)	BET Area (m^2/g)	Membrane appearance
1	3.02	29	1.450	355	Translucent, slight crack and curl from edge.
2	5.28	27	1.600	322	Translucent, without crack.
3	14.7	21	1.725	219	Translucent, without crack.
4	15.0	20	1.750	201	Translucent, without crack.

Table 5: Effect of PVA concentration on the sol and membrane characteristics (6g PVA dissolved in 100ml de-ionised distilled water)

Percent PVA in sol	Viscosity (cp)	Coating time (s)	Pore size (nm)	BET Area (m^2/g)	Membrane appearance
1	8.78	25	1.675	288	Translucent, without crack.
2	27.2	12	1.725	205	Translucent, without crack.
3	32.6	8	1.780	150	Translucent, without crack.
4	39.1	4	1.870	182	Translucent, without crack.

Table 6: Effect of PVA concentration on the sol and membrane characteristics (8g PVA dissolved in 100ml de-ionised distilled water).

Percent PVA in sol	Viscosity (cp)	Coating time (s)	Pore size (nm)	BET Area (m^2/g)	Membrane appearance
1	8.25	25	1.700	273	Translucent, without crack.
2	28.6	11	1.750	256	Translucent, without crack.
3	30.0	10	1.850	131	Translucent, without crack.
4	39.1	4	1.870	135	Translucent, without crack.

In general, different PVA contents in the sol give a grade of characteristic viscosity range. In this work, the sol viscosity essentially increased as the PVA addition was increased as observed from the tables. On the contrary, the coating time decreased as PVA content in the sol was increased.

5.2   Effect of PVA addition on the morphology

From Tables 3, 4, 5, and 6 respectively, it is found that the higher the PVA content and concentration in the sol, the less likely the resulting layer to form crack. Although slightly deformed shape was observed for the membrane developed using at least 2 volume % PVA solution containing 4g PVA dissolved in 100ml of de-ionised water, the membrane was free from defects such as cracks and pinholes when the membrane was observed under a microscope. The deformation existed was actually due to the fluctuation of humidity level during drying process.

The microstructure of a membrane sample prepared from 2 volume % PVA solution containing 4g of PVA dissolved in 100 ml of de-ionised water is shown in Figure 3. A hill was discovered to have developed from a dust on the petri dish as seen from the SEM micrographs. Despite its presence, the hill did not induce structural defection in the membrane.
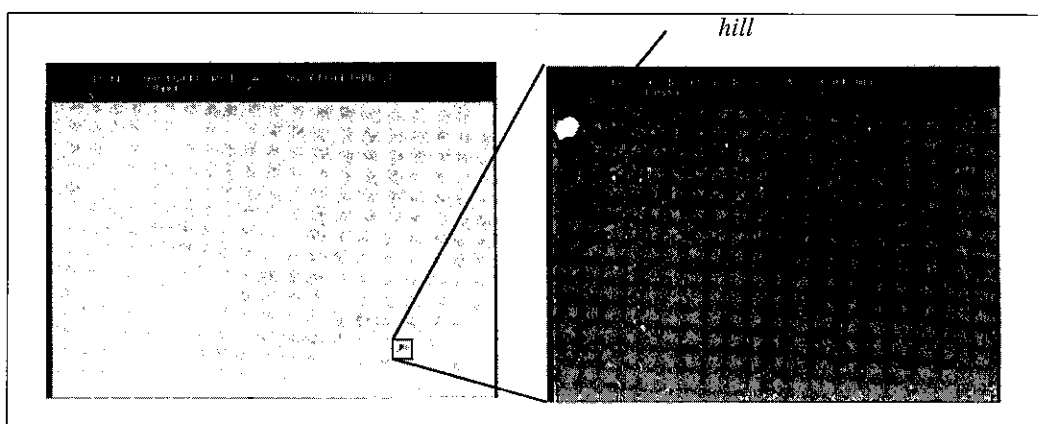
Figure 3: SEM micrographs of sintered alumina membrane from sol-gel technique.

It is not uncommon to develop hills in membrane because the surface of the support material (in this case a petri dish) may not be smooth, it may contain dust and tiny grains, which protrude from the dish surface and eventually contribute to the crater development. The presence of hills and craters have been reported in many literatures and some have suggested the use of subsequent coating and firing of the membrane to hinder the development of hills and craters[10,11].

5.3   Effect of PVA addition on the pore size

In general, the pore size of the membrane increased with the increase in PVA addition as observed from Tables 3-6. The results from this work appear to be consistent with that of the established work. Yang *et al.*[12] for instance, demonstrated that the range of pore size in their work actually increased with increasing PVA content. In a separate work, Das and Maiti[13] reported that higher PVA content promotes agglomeration of the ceramic particles, which on firing leads to wider pore size and formation of closed pores.

In essence, the minimum pore size was achieved when a minimum amount of PVA was used. This is demonstrated in Tables 3-6. Nevertheless, membrane produced using low PVA concentration normally results in cracks. Higher PVA concentration is therefore required for production of crack-free membrane, but this in turn results in larger pores. For successful production of membrane with reasonably small pore size and most importantly, without crack formation or other structural defections, it is found that 4g PVA dissolved in 100ml of water and 2% of this PVA solution from the total sol volume should be used.   The alumina membrane prepared using the recommended PVA concentration apparently exhibits very narrow pore distribution with mean pore diameter of about 1.6nm.

5.4   Effect of PVA addition on the BET surface area

The BET surface area of the sintered membrane (400°C) is given in Tables 3-6. For membranes prepared from 2 and 4g of PVA respectively, the surface area tends to decrease with the decrease of PVA content in the sol as observed from Table 3 and 4 respectively. However, for membrane prepared from 6g of PVA, the surface area increased

when 1 and 2% PVA solution were used, and then it decreased when 3 and 4% of PVA solution were used. Similarly for membrane prepared from 8g of PVA, the surface area increased when 1 and 2% PVA solution were used, and then it decreased when 3 and 4% of PVA solution are used as observed in Table 5 and 6 respectively.

5.5 Effect of sintering temperature on the density and porosity

The effect of sintering temperature on the density and porosity of the membrane in this work is shown in Table 7. The density increased from 2.0 to 3.0g/cm³ as the sintering temperature was increased from 400 to 1000°C. However, the porosity values calculated using the method proposed by De Lange et al.[14].

$$\varepsilon(\%) = \frac{V_p}{V_p + \frac{1}{\rho}} \times 100\% \tag{1}$$

where, ε, the porosity, and V_p, the micro pore volume determined from Autosorb analysis, decreased as the sintering temperature was increased. The decrease in porosity is due to the micro pore volume that decreased with increase in temperature because more of the micro pores evolved to form meso and macro pores at higher temperature.

Table 7: Effect of sintering temperature on the membrane characteristics (4g PVA dissolved in 100ml de-ionised distilled water and 2 volume % from the total sol volume).

Sintering temperature (°C)	BET surface area (m²/g)	Mean pore size (nm)	Density (g/cm³)	Porosity (%)
400	322	1.6	2.0	26.2
600	273	1.8	2.3	25.0
800	91	1.9	2.7	9.4
1000	81	2.0	3.0	8.2

5.6 Effect of sintering temperature on the pore size distribution

The effect of sintering temperature on the pore size and pore size distribution of the membrane in this work is shown in Table 7 and Figure 4 respectively. The pore size of the membrane appeared to increase with the increase in sintering temperature. The trend is consistent with the work of Leenaars et al.[2]. Nevertheless, the membrane developed in this work was more stable in that it only increased marginally from 1.6 to 2nm as the sintering temperature was raised from 400 to 1000°C compared to 4 to 78nm in the work of Leenaars et al.[2] for similar increase in temperature.

Figure 4 shows that the pore size distribution of the membrane amplified to a greater magnitude at a higher temperature. This indicates that much more coarse pores have been developed in the membrane at higher temperatures than at lower ones. More micro pores became meso pores and meso pores became macro pores after exposure to a higher sintering temperature.
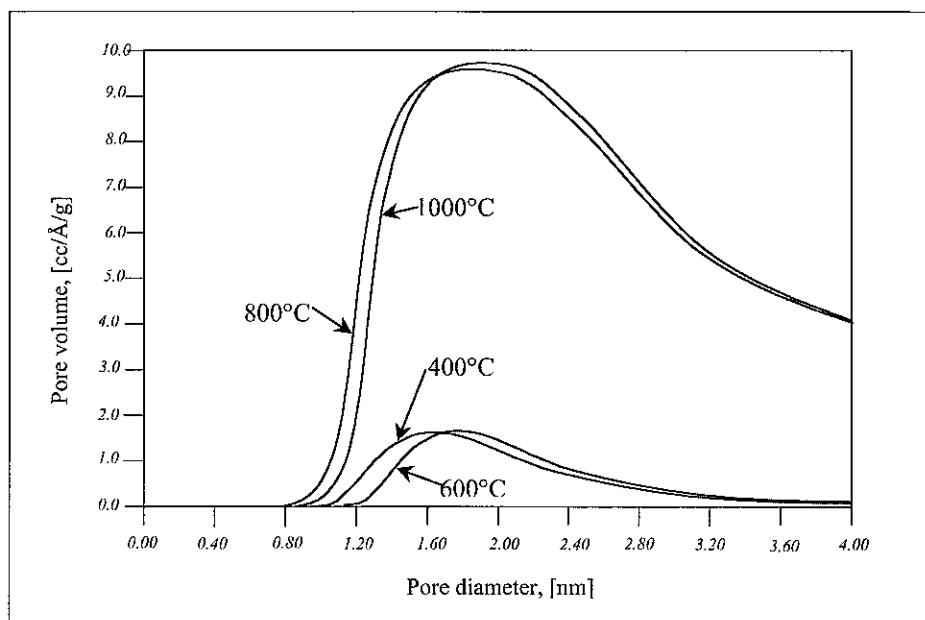
Figure 4: Pore size distribution of sintered alumina membrane from sol gel technique at different sintering temperatures (4g PVA dissolved in 100ml de-ionised distilled water and 2 volume % from the total sol volume).

The fact that the pore volume also evolved significantly as observed from the figure especially at high temperature reveals that the membrane may have experienced bloating, a phenomenon that usually occurs as a result of material being overfired as reported in the work of Mangles[15]. This phenomenon may also have taken place due to the coalescence of very fine agglomerates pores to form relatively large pores as reported in the work of Das and Maiti[13].

5.7 Effect of sintering temperature on the BET surface area

The effect of sintering temperature on the surface area of the membrane in this work is shown in Table 7. The surface area of the membrane decreased as the sintering temperature was raised which is in complete agreement with the work of Leenaars *et al.*[2] However, the decrease in the surface area for the membrane developed in this work appeared to be in a smaller range. In this work, the decrease of surface area, as temperature was increased from 400 to 1000°C, was $241m^2/g$, compared to $286m^2/g$ in the work of Leenaars *et al.*[2].

6. CONCLUSIONS

In this work, a 2 volume % of PVA solution containing 4 g of PVA in 100ml of water was found to be adequate in achieving an appropriate porosity level to avoid cracks in the gel layer. It was discovered that the sol viscosity essentially increased as the PVA addition was increased. On the contrary, the coating time decreased as PVA content in the sol was increased. Generally, the pore size of the membrane increased with the increase in PVA and the minimum pore size was achieved when a minimum amount of PVA was used. The

alumina membrane prepared using the recommended PVA concentration apparently exhibits very narrow pore distribution with a mean pore diameter of about 1.6nm. Although a slightly deformed shape was observed for the membrane developed in this work, the membrane was free from defects such as cracks and pinholes. In general, the density of the membrane developed in this work increased with increase in sintering temperature. The porosity level, however, decreased as the temperature was raised.

7. ACKNOWLEDGEMENT

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