[AMT09] Synthesis of perovskite-alumina gel for membrane preparation by sol-gel technique

Nor Faeqah Idrus, Abdul Latif Ahmad, Mohd. Roslee Othman

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.

Introduction

The potential application of inorganic alumina membranes in separation, filtration and catalytic reactions has preferential research on synthesis, characterization and property improvement of inorganic alumina membranes because of their unique features. The sol gel technique is considered as he most practical method to prepare inorganic alumina membranes (Chen et al., 2001).

The sol-gel technique has attracted more attentions due to the intensive development of sol-gel technology. The advantages of sol-gel compared with other technologies are low process cost, low temperature of heat treatment and formed uniform pore size membrane (Chen *et al*., 2004). Sol-gel technique is a chemical synthesis of oxides involving hydrolizable alkoxides that undergo a sol-gel transition. In most of the sol gel processes for preparing microporous membranes, a stable sol is first prepared as an organometallic oxide precursor, followed by the addition of acid for peptization and binders.

In the limited studies related to thermal stability of ceramic membranes, some elements such as lanthanum, magnesium, silica, boron and metal oxide have been introduced into the alumina sol to improve the thermal stability of alumina membrane (Chen *et al*., 2004). In this study, perovskite was impregnated with alumina to form perovskite-alumina gel for preparation of membrane. Perovskite was used due to its potential application in separation of oxygen because of its high oxygen ion conductivity and high thermal and chemical stability (Tong *et al*., 2003).

The objective of this study is to synthesis the perovskite-alumina gel to form thin layer membrane. Polyvinyl alcohol (PVA) was used as a binder. The effect of temperature on membrane morphology was analyzed.

Materials and methods

Membrane preparation

The aluminum secondary butoxide was used as a precursor. Aluminum secondary butoxide and was dissolved in distilled water followed by the addition of perovskite. The type of perovskite used in this study is $SrCoFeO_x$. The sol was stirred at 90°C for 30 minutes. HNO_3 was added to peptize the sol. The molar ratio of Al^{3+}:H^+:H_2O is 1:0.07:100. The solution was stirred for 30 minutes before reflux at 90°C for 20 hours to ensure complete mixing and hydrolysis.

Polyvinyl alcohol (PVA) was used as a binder. PVA was dissolved in deionized water at 90°C. PVA with concentration 2g PVA/100 ml H_2O, 4g PVA/100ml H_2O and 8g PVA/100ml H_2O were prepared. The ratio of PVA in perovskite-alumina sol was varied from 1:50 to 4:50 for each concentration of PVA. PVA was added in initial solution before reflux for 20 hours.

The unsupported membrane gel layer was prepared by pouring the sol into Petri dish and dried for 24 hours at room temperature. The resulting gels were removed from Petri dish before sintered.

Membrane characterization

The gel viscosity was measured using Rheometer Brookfield.. The dried membrane gel was heated in carbolite furnace before analyze with X-ray Diffractometer (XRD) and Scanning Electron Microscope (SEM) to study the phase transformation and morphology of the membrane.

Results and Discussion

Effect of binder on gel viscosity

The binder used in this study is Polyvinyl alcohol (PVA). PVA was added to prevent the formation of crack during drying process. The effect of PVA addition on gel viscosity and

membrane appearance is presented in Tables 1, 2 and 3 respectively.

As observed from the tables, the gel viscosity increased as the amount of PVA in sol increase. The membrane appearance also affected by the amount of PVA in sol. The membrane gel layer tends to form many crack if small amount of PVA used. However, the increase of PVA amount in sol will formed high viscous gel. The high viscous gel will form thick membrane layer which is tends to crack during drying (Huang et al.,1997). The optimum ratio of PVA in sol to form thin membrane layer with slightly crack was 1:50 with PVA concentration was 4g PVA/100ml H_2O.

TABLE 1 Effect of binder (2g PVA/100ml H_2O)

Percentage of PVA in the sol	Speed, rpm	Viscosity, cP	Appearance of membrane
2	50	0.83	Crack, thin layer gel
4	50	0.70	Crack, thin layer gel
8	50	0.76	Slightly crack, thin layer gel

TABLE 2 Effect of binder (4g PVA/100ml H_2O)

Percentage of PVA in the sol	Speed, rpm	Viscosity, cP	Appearance of membrane
2	50	0.74	Slightly crack, thin layer gel
4	50	1.18	Slightly crack, thick layer gel
8	50	1.94	Slightly crack, thick layer gel

TABLE 3 Effect of binder (8g PVA/100ml H_2O)

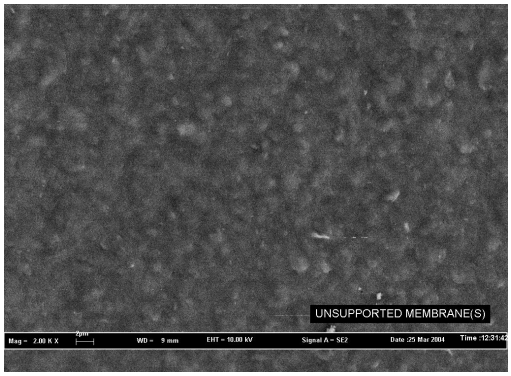
Percentage of PVA in the sol	Speed, rpm	Viscosity, cP	Appearance of membrane
2	50	1.19	Slightly crack, thick layer gel
4	50	1.59	Slightly crack, thick layer gel
8	50	1.88	Slightly crack, thick layer gel

Effect of temperature on membrane morphology

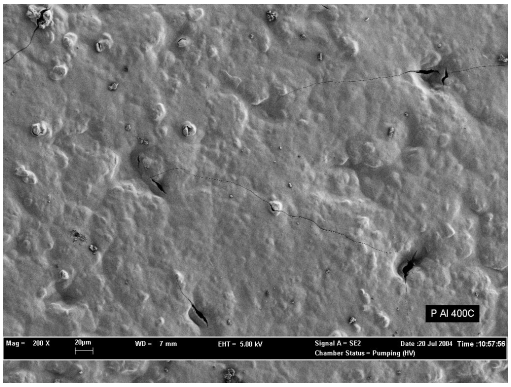
The effect of temperature on membrane morphology was analyzed using Scanning Electron Microscope (SEM). Figure 1(a) shows the SEM micrograph of membrane gel layer after sintered at 400°C. PVA contained in gel will burnt out during sintering and formed the white spot on the membrane surface (Othman et al., 2001).

The existence of cracks is clearly shown in Figure 1(b) after coated the gel layer on

alumina pellet. The texture of the membrane surface is irregular compared to unsupported membrane. It is because of the surface of the support material may not be smooth and contribute to the crater surface of membrane gel layer.



(a)



(b)

FIGURE 1 SEM micrograph of
(a) unsupported perovskite-alumina gel layer (b) supported perovskite-alumina gel layer after sintered at 400°C.

Figure 2 shows the thickness of membrane gel layer coated on alumina pellet. The thickness of membrane is about 5.74μm.

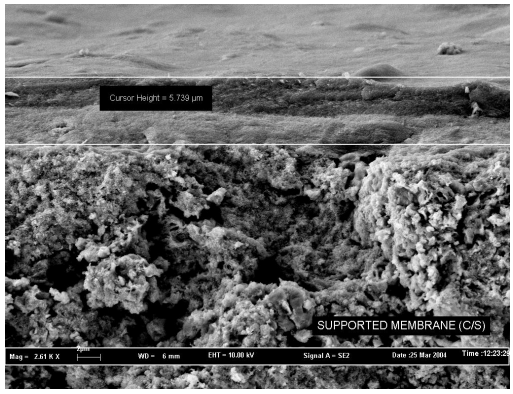


FIGURE 2 SEM cross-section of perovskite-alumina gel layer coated on alumina pellet after sintered at 400°C.

XRD analysis

XRD analysis of perovskite-alumina membrane after sintered at 400°C and 900°C was shown in Figure 3. There is no difference in phase transformation observed after sintered the membrane gel layer at 400°C and 900°C. The formation of $SrCoFeO_x$ perovskite phase is almost undetectable. The poor crystalline phase of perovskite is because of alumina was reacted with perovskite and formed $SrAl_2O_4$, $CoAl_2O_4$ and $Al_2Fe_2O_6$.

Alumina membranes generally have been obtain through several crystallographic modifications from aluminum hydroxide sols (γ-AlOOH) prepared by the hydrolysis of aluminum alkoxide (in this case aluminum secondary butoxide). Dehydration of γ-AlOOH occurs around 400°C-500°C to form γ-Al_2O_3. An increase of temperature generates the transformation of γ-Al_2O_3 to δ- Al_2O_3 and θ -Al_2O_3. Finally θ-Al_2O_3 transform to α-Al_2O_3 phase. α-Al_2O_3 usually obtained after sintered at 1200°C (Ersoy & Gunay, 2004). In this study, it was difficult to observe the existence of γ-, δ-, θ- and α-Al_2O_3 phase due to similarity in peak position and poor crystallinity. The introduction of perovskite into alumina can delay the phase transformation of γ-Al_2O_3 phase to α-Al_2O_3 phase.

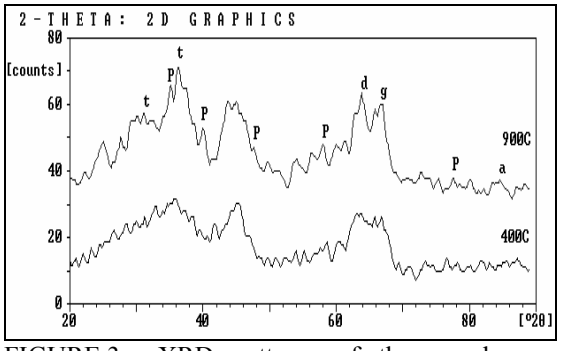


FIGURE 3 XRD patterns of the membranes processed at 400°C and 900°C. P: perovskite, a: α-Al_2O_3; d: δ-Al_2O_3; g: γ-Al_2O_3; t: θ-Al_2O_3.

Acknowledgements

The authors wished to thank the Ministry of Science, Technology and Innovation (MOSTI), Malaysia for the National Science Fellowship awarded to Nor Faeqah Idrus and for University Sains Malaysia (USM) short term grant for financial support of this research.

References

Chen, T.D., Wang, L., Chen, H.R. and Shi, J.L. (2001). Synthesis and microstructure of boron-doped alumina membranes prepared by the sol-gel method. *Material Letters* 50: 353-357.

Chen, W., Zhang, J., Fang, Q., Li, S., Wu, J., Li, F. and Jiang, K. (2004). Sol-gel preparation of thick titania coatings aided by organic binder materials. *Sensors and Actuators B: Chemical*, Vol 100: 195-199.

Tong, J., Yang, W., Cai, R., Zhu, B., Xiong, G. and Lin, L. (2003). Investigation on the structure stability and oxygen permeability of titanium-doped perovskite-type oxides of $BaTi_{0.2}Co_xFe_{0.8-x}O_{3-\delta}$(x=0.2-0.6). *Separation and Purification Technology*, 32: 289-299.

Huang, X.R., Meng, G.L., Huang, Z.T. and Geng, J.M. (1997). Preparation of unsupported alumina membrane by sol-gel techniques. *Journal of Membrane Science* 133: 145-150.

Othman, M.R., Ahmad, A.L. and Mukhtar, H. (2001). Characteristics of unsupported alumina membrane prepared using sol-gel technique. *ASEAN Journal Science and Technology Development* 18(2): 59-70

Ersoy, B. and Gunay, V. (2004). Effect of La_2O_3 addition on the thermal stability of γ-Al_2O_3 gels. *Ceramic International* 30: 163-170.