

# Influence of Calcination Temperature and Perovskite Concentration on the Morphology, Gas Permeance and Selectivity of Perovskite-Titania Membranes

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## Abstract

Defect-free titania membranes doped with different concentrations of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  perovskite were successfully prepared using a sol-gel technique combined with a wet impregnation process. The titania membranes were immersed in a perovskite solution, dried, and calcined to obtain perovskite affixed inside the porous titania membranes. The phase transformation of titania and perovskite was investigated by varying the calcination temperature from 300 to 500 °C. The effect of perovskite concentration on the titania membrane morphology is described in detail. The results showed that calcination at 400 °C was preferable for preparing a perovskite-titania membrane with fully crystallized anatase and perovskite phases. The performance of the perovskite-titania membranes with various perovskite concentrations in terms of the  $\text{O}_2$  and  $\text{N}_2$  permeances and  $\text{O}_2/\text{N}_2$  selectivity was also studied. We determined that the perovskite concentration affected the gas permeation performance of the membrane and that the P3/titania membrane provided the highest gas permeance and selectivity.

*Keywords:* Titania membrane, perovskite, calcination temperature, concentration, morphology, phase structure

## I. Introduction

The perovskite-type oxide  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  is a typical mixed ionic electronic conducting membrane material that has garnered a significant amount of attention and has been applied in the chemical and petroleum industries. Owing to its high oxygen ion and electron conductivity, it can operate steadily for long periods of time at high temperatures and has been used widely as a membrane for oxygen separation in the oxidative coupling of methane and the partial oxidation of methane<sup>1</sup>. Usually, the perovskite membrane is used independently and is prepared with a conventional solid state method to form a perovskite powder. This powder is compressed into a disc and sintered before application in gas-separation processes<sup>2</sup>.

Ceramic membranes made with a variety of materials, such as alumina, titania, silica, zeolites, and zirconia, have been extensively studied. Among them, titania has gained considerable attention owing to its high chemical resistance and several unique characteristics, including semi-conductivity, catalytic and photocatalytic behaviour, and high water flux. The potential applications of titania membranes are numerous. They include ultrafiltration processes, catalytic/photocatalytic membrane reactors, gas separations/reactions, and gas sensors<sup>3-6</sup>.

Titania membranes are usually prepared in porous form with the sol-gel process. This method is considered the most practical one. The sol-gel process is based on the controlled hydrolysis of alkoxides and condensation-poly-

merization reactions at low temperature. The produced membrane has a very high specific area, and additional elements can be added to further modify its properties. This method has demonstrated excellent compositional control, homogeneous microstructure, and feasibility in producing thin films on complex shapes when dip-coating is used<sup>6,9,10</sup>.

Although titania membranes can offer various advantages, they possess one drawback with regard to their anatase-rutile phase transformation. This phase transformation causes large volume and energy changes, leading to large variations in particle size and, therefore, in the membrane pore size and porosity<sup>11</sup>. The transformation from the anatase to the rutile phase is not favoured because the anatase phase has a higher specific surface area compared to the rutile phase. Thus, the anatase phase is more useful as a membrane material in gas-separation applications<sup>12</sup>.

Another problem relating to titania membranes in gas-separation processes is their selectivity. Titania membranes with porous structures have a high permeability but low selectivity. Hence, one of the objectives of this study was to improve the selectivity of the membrane by affixing perovskite materials in the membrane pores in a wet impregnation process. This is a well-known method in the development of heterogeneous catalysts and has been utilized to deposit nano-sized particles into the electrode structures of solid oxide fuel cells<sup>13</sup>. Thus, we believed that it would impart highly uniform perovskite into the titania matrix.

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To the best of our knowledge, there are no reports on the preparation of titania membranes containing perovskite, especially using the sol-gel method in combination with a wet impregnation process. In this paper, the main emphasis is on how the membrane morphology and performance are affected by changing the synthesis parameters (calcination temperature and perovskite concentration). The two major membrane performance characteristics of concern in the present study were gas permeance and the selectivity of O<sub>2</sub> and N<sub>2</sub> transport across the membrane.

## II. Methodology

### (1) Preparation of titania support and binders

The porous titania disc prepared from titanium (IV) oxide powder was used as a support for a perovskite-titania membrane. The disc dimensions are 20 mm in diameter and 2 mm in thickness. About 1.75 g of titania powder was loaded into the stainless steel mould. The mould was then pressed using hydraulic press equipment under 20 MPa pressure. The disc was then dried at 70 °C, followed by a calcination process at 965 °C for 4 h respectively. In the calcination process, low heating and cooling rates of 2 °C/min were applied to prevent cracking on the support surface.

Polyvinyl alcohol (PVA) and hydroxypropyl cellulose (HPC) were used as binders in this study to prevent the formation of cracks on the thin membrane layer surface. They were also used to achieve excellent adhesion of the titania membrane to the titania support. For the preparation of PVA solution, 0.1 g of PVA with molecular weight of 22,000 g/mol was dissolved in 100 mL of distilled water and stirred for about 1 h. While for the preparation of HPC solution, 0.7 g of HPC with molecular weight of 88,000 g/mol was dissolved in 100 mL of distilled water and stirred for 1 h.

### (2) Preparation of titania membrane

The starting materials for the preparation of the titania sol were titanium tetra-isopropoxide (TTIP) as the titania precursor, nitric acid as a catalyst for the peptization, distilled water as a dispersing media and isopropanol as the solvent. 2.38 mL of TTIP was dissolved in 18.62 mL of isopropanol, and this solution was added drop-wise into 3.35 mL of distilled water and 41.38 mL of isopropanol with vigorous stirring. After the hydrolysis reaction was complete, the remaining white precipitate of titanium hydroxide (Ti(OH)<sub>4</sub>) was filtered and subsequently washed with water to remove the alcohol. Then, the filtrate was dispersed in 28.33 mL of distilled water and about 0.29 mL of nitric acid was added to stabilize the solution. The solution was then peptized for 2 h at 70 °C. The solution was peptized in a closed beaker to enhance the peptization rate. To break the weak bonds of the agglomerated particles, the sol was treated ultrasonically for 30 min. A blue, semi-opaque colloidal dispersion with a concentration of 0.325 M was the final product. Lower concentrations could be achieved by simple dilution with distilled water.

The dipping solution for the titania membrane contained 30 mL of 0.05 M titania sol mixed with 10 mL of PVA solution and 20 mL of HPC solution. An adequate amount of dipping solution was coated onto a porous titania support

disc by dip-coating to form the supported titania membranes. Subsequently, the membranes were dried and calcined at different temperatures (300, 400 and 500 °C) for 2 h.

### (3) Preparation of perovskite-titania membrane

Perovskite was prepared as described in a previous publication<sup>15</sup>. Sr(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and FeCl<sub>3</sub>·6H<sub>2</sub>O were weighed in equimolar amounts and dissolved in distilled water (0.7 M). The solution was stirred for approximately 1 h to ensure complete dissolution and mixing. The concentration of perovskite solution was varied according to Table 1. The perovskite phase was only obtained after the membrane was calcined. The type of perovskite obtained in this study was SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>. In the perovskite impregnation process, the titania membrane was immersed into the perovskite solution for 10 min. Subsequently, the membrane was dried and then calcined in air at 400 °C for 2 h.

**Table 1:** Names and concentrations of perovskite.

Label	Concentration of perovskite (M)
P1	0.7
P2	2.1
P3	3.5

### (4) Membrane characterization

The phase transformation of the membrane during the calcination process was observed with an XRD (Philips PW1729 X-ray generator with a Philips PW1820 diffractometer) with Cu K $\alpha$  radiation. TEM (Philips CM12) measurements were performed to investigate the dispersion of the particles in the membrane. The membrane surface and thickness were observed by FESEM (Leo Supra 50VP).

### (5) Gas permeation measurements

The experimental apparatus for the gas permeation measurements is illustrated in Fig. 1. Permeance was determined for a single gas (O<sub>2</sub> and N<sub>2</sub>), and selectivity was defined as the ratio of permeances. The permeance of the membrane ( $\kappa$ ) in mol Pa<sup>-1</sup> m<sup>-2</sup> s<sup>-1</sup> was obtained using Eq. (1)<sup>15</sup>:

$$\kappa = \frac{\alpha_p}{A_m \Delta P} \quad (1)$$

where  $\alpha_p$  is the gas flow rate of the permeate stream,  $A_m$  is the membrane's effective surface area, and  $\Delta P$  is the pressure difference between the feed and permeate streams. The selectivity (separation factor) of the membrane  $\alpha_{O_2/N_2}$  is equal to the ratio of permeances between O<sub>2</sub> and N<sub>2</sub> under mixed gas feed conditions, as shown in Eq. (2)<sup>15</sup>:

$$\alpha_{O_2/N_2} = \frac{\kappa_{O_2}}{\kappa_{N_2}} \quad (2)$$

Analysis of the permeation of individual gases across the perovskite-titania membranes of different concentrations was conducted at 28 °C and an operating pressure of 1 bar.

### III. Results and Discussion

#### (1) Effect of calcination temperature on the phase structure of titania

The titania membranes were first prepared by means of the sol-gel and dip-coating processes on titania support discs. In this study, the calcination process was studied in a range from 300 to 500 °C to ensure formation of the anatase phase of titania after calcination. Fig. 2 shows the XRD patterns of titania samples calcined at 300, 400 and 500 °C. It can be seen that the membrane showed a partially crystallized (mainly amorphous) structure at 300 °C, whereas at higher temperature (400 °C) transformation into the anatase phase was complete, as observed by the dominant XRD peak of anatase at  $2\theta=25.3^\circ$ . The titania membranes with the anatase phase had smaller particle and pore sizes, which are important for gas-separation applications<sup>16</sup>. In contrast, the membrane calcined at 500 °C showed a partial rutile phase transformation with a dominant XRD peak at  $2\theta=27.4^\circ$ . This was due to the crystal lattice expansion and recrystallization accompanied by the formation of rutile nuclei and crystallite growth. Owing to this phase transition phenomenon, the titania specific surface area was assumed to decline<sup>17</sup>. Thus, from the XRD observations, the membrane calcined at 400 °C was considered to have only the anatase phase.

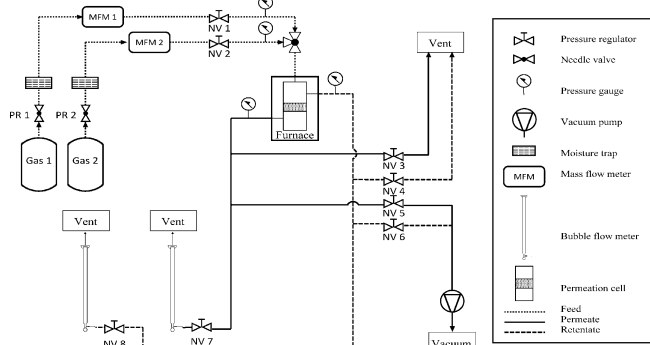


Fig. 1: Schematic diagram of membrane permeation test rig.

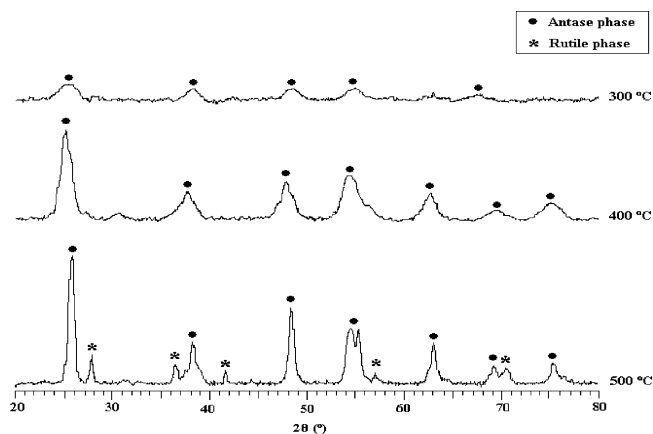


Fig. 2: XRD patterns of titania membranes calcined for 2 h at 300, 400 and 500 °C.

#### (2) Effect of calcination temperature on the phase structure of perovskite

Fig. 3 shows the XRD patterns of perovskite calcined at 300, 400 and 500 °C. It can be seen that the perovskite calcined at 300 °C consisted of  $\text{SrCO}_3$  (strontium carbonate),  $\text{Fe}_2\text{O}_3$  (iron oxide), and  $\text{CoO}$  (cobalt oxide). In the preparation of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  perovskite, the perovskite needs to be calcined until the perovskite phase is fully achieved. The observations at 300 °C were attributed to an incomplete oxidation process of the perovskite. At 400 and 500 °C, transformation of the perovskite had occurred based on the dominant XRD peak at  $2\theta=40.7^\circ$ . Based on our experiment results, the presence of a perovskite-type  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  structure readily occurs at 400 °C. This finding is consistent with results obtained by Mohammadi and Fray (2009)<sup>18</sup>, who prepared a low-temperature perovskite-type cadmium titanate membrane.

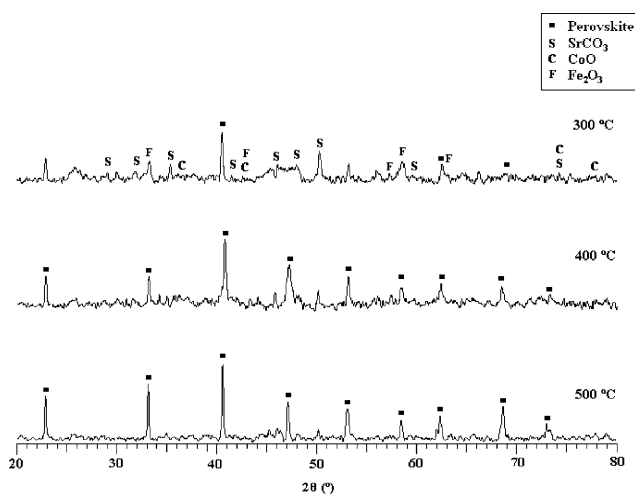


Fig. 3: XRD patterns of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  perovskite oxide calcined at 300, 400 and 500 °C.

#### (3) Effect of perovskite concentration on the titania membrane morphology

Based on the above results, a calcination temperature of 400 °C was chosen to prepare the perovskite-titania membrane in order to inhibit anatase-rutile phase transformation. The dried membrane gel was calcined at 400 °C, and the perovskite was then dispersed in the titania membrane by means of a wet impregnation process. These two processes were repeated three times.

Fig. 4a shows that the titania particles were roughly spherical in shape and nearly equal in size (8 – 5 nm). The image of all of the perovskite-titania (Figs. 4b-d) revealed that the membrane consisted of a composite of two distinct phases, roughly spherical titania particles and perovskite particles between or on the surface of the titania particles. However, some perovskite particles were aggregated between the titania particles; this increased with an increase in perovskite concentration. The size of the perovskite particles ranged from 20 – 40 nm, whereas that of the titania particles ranged from 5 – 10 nm in all the samples. Alexandrescu *et al.* (2007)<sup>19</sup> observed a similar phenomenon with iron (Fe) in titania nanopowders. The perovskite material did not have any effect on the titania

phase transformation or titania particles because the perovskite was not directly added to the titania sol. Normally, an increase in the perovskite concentration can promote agglomeration of the perovskite, leading to the growth of larger perovskite clusters. However, the reverse was observed in this study. The sizes of the perovskite particles were not altered with increasing levels of perovskite. This finding is consistent with that observed for palladium dispersed in alumina membranes by Chen *et al.* (2003)<sup>20</sup>.

#### (4) Membrane performance

Before further testing of the membrane performance, the membranes were scanned under FESEM to confirm the presence of perovskite in the titania membrane, as shown in Figs. 5a and b. The surface area of the membrane showed a homogeneous dispersion of perovskite particles on the titania layers without cracking (Fig. 5a). However, there were agglomerations of perovskite particles that were likely formed during the dip-coating, which can result in the localized aggregation of perovskite particles. The thickness of the perovskite-titania membrane on the titania support was estimated to be approximately 0.5  $\mu\text{m}$ . This multiple coating technique can avoid the formation of irregularities on the membrane surface (Fig. 5b).

The membrane performance was studied based on the permeance of  $\text{O}_2$  and  $\text{N}_2$  and the selectivity of  $\text{O}_2/\text{N}_2$ . The

$\text{O}_2$  and  $\text{N}_2$  permeances and  $\text{O}_2/\text{N}_2$  selectivity were calculated using Eqs. (1) and (2), respectively. The permeance and selectivity obtained with different perovskite concentrations are tabulated in Table 2.  $\text{O}_2$  exhibited a higher permeance compared to  $\text{N}_2$ . This is due to the kinetic diameter of  $\text{N}_2$  (3.64 Å), which is larger than that of  $\text{O}_2$  (3.46 Å)<sup>21</sup>. Although the titania membranes showed high gas permeances, they exhibited lower selectivities compared to the P3/titania membrane, which had a high gas permeance and selectivity. Regardless of the perovskite concentration, the gas permeance and selectivity were increased owing to the increased perovskite concentration ( $\text{P1} < \text{P2} < \text{P3}$ ). This phenomenon was also observed by Tan *et al.* (2004)<sup>22</sup> in the case of an Ag-perovskite membrane. The perovskite material contains several transition metal oxides (iron and cobalt oxides), which have been reported to be high-temperature adsorbents for gas separation, and theoretically have an infinitely high selectivity for  $\text{O}_2$  over  $\text{N}_2$  or other non-oxygen species<sup>23</sup>. The mechanism of transport of  $\text{O}_2/\text{N}_2$  separation predominantly involves the Knudsen diffusion mechanism because the value (selectivity) was higher than the theoretical Knudsen diffusion (1.07), which is defined as the square root of the ratio of the heavier molecular weight gas ( $\text{O}_2$ ) to the lighter molecular weight gas ( $\text{N}_2$ ).

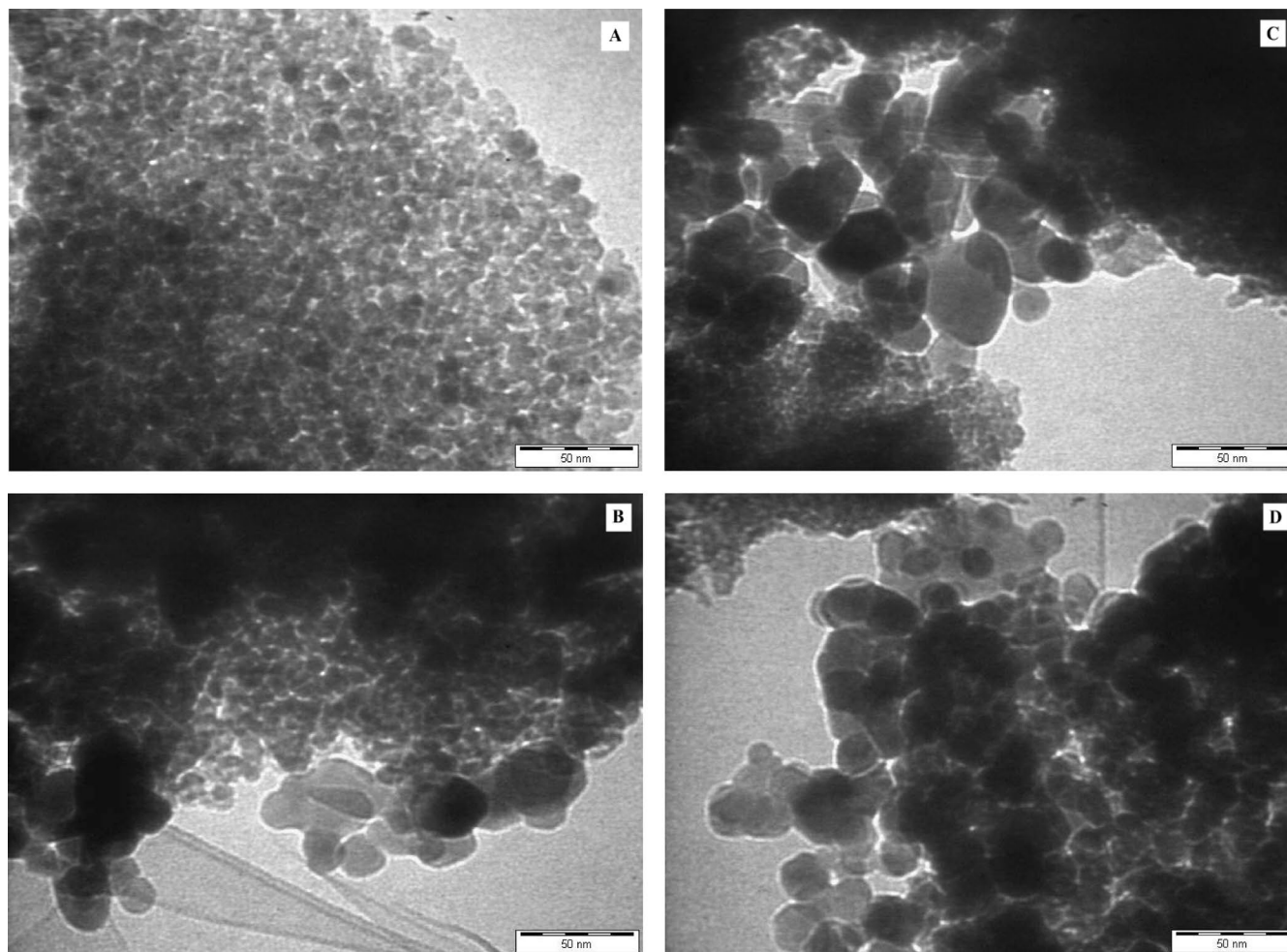


Fig. 4: Titania and perovskite-titania particles calcined at 400 °C as a function of perovskite concentration change: (a) titania, (b) P1, (c) P2, and (d) P3.

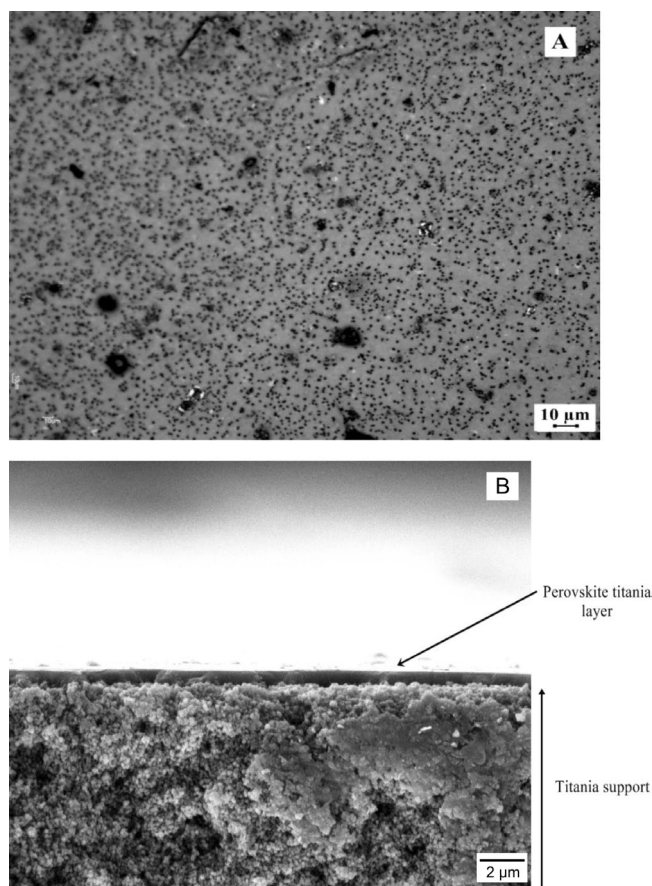


Fig. 5: SEM images of multiple-coated perovskite-titania membrane calcined at 400 °C: (a) surface and (b) cross-section.

**Table 2:** Effect of perovskite concentration on the gas permeation performance of the perovskite-titania membranes.

Membrane	Single gas permeance (mol Pa <sup>-1</sup> m <sup>-2</sup> s <sup>-1</sup> )		Selectivity
	O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>
Titania	7.42E-07	6.55E-07	1.13
P1/titania	1.16E-07	1.00E-07	1.16
P2/titania	3.34E-07	2.86E-07	1.17
P3/titania	7.70E-07	6.42E-07	1.20

#### IV. Conclusions

Titania-based membranes containing a perovskite dispersion were successfully prepared by means of a sol-gel process combined with a wet impregnation process. Based on our findings, the optimal calcination temperature for the titania and perovskite was 400 °C, where the titania is fully transformed to the anatase phase and the oxidation process of perovskite is complete. The particle size of titania was found to be significantly independent of the perovskite concentration. This was attributed to the perovskite particles not directly incorporating in the titania lattice. The perovskite consisted of particles that were four times larger than the titania particles. A crack-free and homogeneous surface of the perovskite-ti-

tania membrane was obtained after multiple dip-coatings of the titania layer followed by repeated wet impregnations. In studying the effect of perovskite concentration on the membrane performance using the perovskite-titania membranes and titania membranes, we found that increasing the perovskite concentration leads to an increase in the O<sub>2</sub> and N<sub>2</sub> permeance and O<sub>2</sub>/N<sub>2</sub> selectivity. The highest permeance and selectivity was achieved with a P3/titania membrane. Therefore, perovskite in a titania membrane, which acts as a filler phase, has been shown to have potential for the separation of oxygen and could be of use as an oxygen enrichment membrane.

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#### References

- Tong, J., Yang, W., Cai, R., Zhu, B., Lin, L.: Titanium-based perovskite-type mixed conducting ceramic membranes for oxygen permeation, *Mater. Lett.*, **56**, 958-962, (2002).
- Etchegoyen, G., Chartier, T., Del-Gallo, P.: An architectural approach to the oxygen permeability of a La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.9</sub>Ga<sub>0.1</sub>O<sub>3-δ</sub> perovskite membrane, *J. Eur. Ceram. Soc.*, **26**, 2807-2815, (2006).
- Ahmad, A.L., Othman, M.R., Mukhtar, H.: H<sub>2</sub> separation from binary gas mixture using coated alumina-titania membrane by sol-gel technique at high-temperature region, *Int. J. Hydrogen Energy*, **29**, 817-828, (2004).
- Tan, X., Pang, Z., Gu, Z., Liu, S.: Catalytic perovskite hollow fibre membrane reactors for methane oxidative coupling, *J. Membr. Sci.*, **302**, 109-114, (2007).
- Bayraktar, D., Clemens, F., Diethelm, S., Graule, T., Herle, J.V., Holtappels, P.: Production and properties of substituted LaFeO<sub>3</sub>-perovskite tubular membranes for partial oxidation of methane to syngas, *J. Eur. Ceram. Soc.*, **27**, 2455-2461, (2007).
- Mohammadi, M.R., Fray, D.J., Cordero-Cabrera, M.C.: Sensor performance of nanostructured TiO<sub>2</sub> thin films derived from particulate sol-gel route and polymeric fugitive agents, *Sens. Actuators B: Chem.*, **124**, 74-83, (2007).
- Ding, H., Lin, B., Liu, X., Meng, G.: High performance protonic ceramic membrane fuel cells (PCMFCs) with Ba<sub>0.5</sub>Sr<sub>0.5</sub>Zn<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> perovskite cathode, *Electrochem. Comm.*, **10**, 1388-1391, (2008).
- Wang, Y.H., Liu, X.Q., Meng, G.Y.: Preparation and properties of supported 100% titania ceramic membranes, *Mater. Res. Bull.*, **43**, 1480-1491, (2008).
- Pierre, A.C., Introduction to Sol-Gel Processing. Kluwer Academic Publishers, The Netherlands, (1998).
- Agoudjil, N., Benkacem, T.: Synthesis of porous titanium dioxide membranes, *J. Desal.*, **206**, 531-537, (2007).
- Gestal, V.T., Decastele, V.C., Buekenhoudt, A., Dotremont, C., Luyten, J., Leysen, R., Bruggen, V.B., Maes, G.: Alumina and titania multilayer membranes for nanofiltration: preparation, characterization and chemical stability, *J. Membr. Sci.*, **207**, 73-89, (2002).
- Mohammadi, M.R., Fray, D.J., Mohammadi, A.: Sol-gel nanostructured titanium dioxide: controlling the crystal structure, crystallite size, phase transformation, packing and ordering, *Micro. Meso. Mat.*, **112**, 392-402, (2008).
- Jiang, S.P.: A review of wet impregnation-an alternative method for the fabrication of high performance and nano-

- structured electrodes of solid oxide fuel cell, *Mater. Sci. Eng. A*, **418**, 199-210, (2006).
- 14 Ahmad, A.L., Idrus, N.F., Othman, M.R.: Preparation of perovskite alumina ceramic membrane using sol-gel method, *J. Membr. Sci.*, **262**, 129-137, (2005).
- 15 Li, K.: Ceramic Membrane for Separation and Reactions. John Wiley & Sons, Ltd., England, (2007).
- 16 Alem, A., Sarpoolaky, H., Keshmiri, M.: Titania ultrafiltration membrane: preparation, characterization and photocatalytic activity, *J. Eur. Ceram. Soc.*, **29**, 629-635, (2009).
- 17 Grznil, B., Kic, B., Rabe, M.: Inhibition of the anatase-rutile phase transformation with addition of  $K_2O$ ,  $P_2O_5$ , and  $Li_2O$ , *Chem. Pap.*, **58** (6), 410-414, (2004).
- 18 Mohammadi, M.R., Fray, D.J.: Low-temperature perovskite-type cadmium titanate thin films derived from a simple particulate sol-gel process, *Act. Mater.*, **57**, 1049-1059, (2009).
- 19 Alexanrescu, R., Morjan, I., Scarisorenu, M., Birjega, R., Popovici, E., Soare, I., Gavrilă-Florescu, L., Voicu, I., Dumitrache, F., Vasile, E., Figgemeier, E.: Structural investigations on  $TiO_2$  and Fe-doped  $TiO_2$  nanoparticles synthesized by laser pyrolysis, *Thin Solid Films*, **515**, 8438-8445, (2007).
- 20 Chen, H.I., Shiau, J.D., Chu, C.Y., Huang, T.C.: Synthesis and characterization of palladium clusters dispersed alumina membranes, *Sep. Pur. Tech.*, **32**, 247-254, (2003).
- 21 Kusworo, T.D., Ismail, A.F., Mustafa, A., Budiayoni: Application of activated carbon mixed matrix membrane for oxygen purification, *Internat. J. Sci. Eng.*, **1**(1), 21-24, (2010).
- 22 Tan, L., Yang, L., Gu, X., Jin, W., Zhang, L., Xu, N.: Structure and oxygen permeability of Ag-doped  $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$  oxide, *Amer. Inst. Chem. Engrs.*, **50** (3), 701-707, (2004).
- 23 Hao, H., Zhao, L., Hu, J., Hu, X. and Hou, H.: Oxygen adsorption/desorption behavior of  $YBaCo_4O_{7+\delta}$  and its application to oxygen removal from nitrogen, *J. Rare Earths*, **27** (5), 815-818, (2009).