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Preparation of asymmetric perovskite-type membranes by a settlement method

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Abstract

Asymmetric $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ (SCYb) membranes were prepared by using a settlement method to deposit a thin dense SCYb layer on the green porous SCYb support, followed by conventional dry pressing and co-sintering. SCYb powder was mixed in a liquid media (isopropanol) and directly poured onto the pre-pressed green porous SCYb support placed in a beaker. After the powder fully settled onto the support, the green asymmetric sample was dried and co-sintered. The cross-sectional images of the asymmetric systems indicate that thin dense SCYb films in the asymmetric membranes had uniform thicknesses at this level of analysis and show excellent adhesion to the porous support without any undesirable defects, delamination or cracking. Further, different dense layer thicknesses (80–20 μm) were readily obtained by altering the amount of the SCYb powders in the liquid media. The minimum dense layer thickness obtained by the settlement method, with the synthesis conditions utilised in this study, was around 20 μm.

Keywords: A. Pressing; D. Perovskite; E. Membranes; Settlement method

1. Introduction

More than 85% of the current world energy sources are from non-renewable sources, which have led to significant environmental impacts such as greenhouse gas emissions. The greenhouse gas emissions from the stationary and transport energy sectors, and fugitive emissions, are the largest sources of greenhouse gases in Australia [1]. These data strongly indicate the necessity of developing alternative renewable, clean and reliable energy sources, such as hydrogen fuel.

One of the main difficulties in the production of hydrogen fuel is the cost of the separation of hydrogen from gas mixtures such as gasification syngas. There are three major hydrogen separation processes, namely pressure swing adsorption, cryogenic distillation, and membrane separation. Hydrogen separation membranes can include polymer, dense metal, nanoporous inorganic, dense cermet and dense ceramic membranes [2,3]. Dense ceramic membranes with mixed protonic–electronic conduction seem to be one of the most promising technologies for high temperature hydrogen separation. It offers advantages over the alternative technologies, such as low energy consumption, relatively inexpensive material, and simple and compact equipment and operation, and no requirement for an external electric supply [2,4]. However, the attainment of high hydrogen separation rates of such membranes is still the greatest barrier to commercially viable hydrogen separation membranes. There are several approaches that can be employed to improve hydrogen permeation flux through mixed protonic–electronic conducting dense ceramic membranes: (1) optimisation of membrane compositions to increase proton and electron conductivities; (2) deposition of a thin film on a porous support to decrease the dense membrane thickness [4]; (3) coating of a dense membrane with a porous layer to increase effective surface area for hydrogen dissociation/re-association reactions; (4) coating of a dense membrane with catalyst to increase the surface exchange reactions of hydrogen [5]; and (5) reduction of the grain boundary resistance.

When bulk diffusion is the limiting factor in the hydrogen permeation process, reducing the dense membrane thickness may be one of the most simple but effective techniques to obtain improved hydrogen permeation flux. For example, Hamakawa

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et al. [6] verified that hydrogen permeation rates through a 2 μm-thick $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ dense layer at 677 °C were approximately 500 times larger than through 1 mm-thick $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ membrane. This can be described with the Wagner equation where the hydrogen permeation flux is proportional to the reciprocal of the thickness of the membrane. Therefore, there have been many studies on fabrication of thin dense layers on porous supports (not limited to hydrogen separation membranes). Ma et al. [7] prepared 60–150 μm-thick dense $BaCe_{0.9-x}Zr_xYb_{0.1}O_{3-\alpha}$ membranes on porous Ni–$BaCeO_3$ supports by air plasma spraying. Etchegoyen et al. [8] used tape casting to obtain asymmetric membranes with a 120 μm dense $La_{0.6}Sr_{0.4}Fe_{0.9}Ga_{0.1}O_{3-\alpha}$ layer on a thick porous support layer of the same material. Other studies include for example, dip coating (20 μm thin $La_{0.2}Sr_{0.8}CoO_{3-\alpha}$ films on porous MgO supports) [9], pulsed laser deposition (0.6–1.5 μm yttria-stabilised zirconia layers on platinum and sapphire supports) [10], and spin coating (2–140 μm dense $SrCe_{0.95}Yb_{0.05}O_3$ thin films on $SrZr_{0.95}Y_{0.05}O_3$ support) [6].

Despite there being a number of sophisticated techniques available for the deposition of thin dense layers on porous supports, some of the techniques can be very complex and difficult to replicate. In contrast, conventional dry pressing is known to be a simple, reproducible and cost-effective method to fabricate asymmetric membranes [11,12]. For example, Cheng et al. [12] fabricated asymmetric membranes consisting of 150–800 μm dense $SrCe_{0.95}Tm_{0.05}O_{3-\alpha}$ layers on $SrCe_{0.95}Tm_{0.05}O_{3-\alpha}$ porous supports by conventional dry pressing, which is the currently achievable thickness using such simple techniques. Xia and Liu [11] prepared an 8 μm $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) dense film on a porous NiO-GDC substrate by traditional dry pressing with unique ‘foam’ (highly porous) GDC powder. However, they reported that the GDC ‘foam’ powder had very poor flow behaviour due to its high porosity and particle sizes, resulting in non-uniform distribution of powder and low packing density. They suggested that improvements can be made by improving the flow behaviour of the powder or by improving the filling techniques to obtain a uniform and reproducible filling. Therefore the focus of the present work is the improvement of the filling techniques to aid the conventional dry pressing, by developing a method of depositing a thin uniform dense layer on a green porous support. The layers so generated will need to overcome difficulties of cracking and non-uniformity, and also need to be readily reproducible.

2. Experimental

Preparation of asymmetric membranes can be complicated due to differences in shrinkage or thermal expansion rates in the dense and porous layers, resulting in cracks, reactions and/or delamination. Etchegoyen et al. [8] co-sintered (i.e. no pre-sintering of porous supports) asymmetric perovskite membranes prepared by tape casting and lamination, which contained cornstarch particles as the pore forming agent in the porous supports. In that study, the shrinkage behaviour of a dense membrane and of a porous support containing cornstarch particles was measured by dilatometry during the co-sintering of the asymmetric system. The result showed identical shrinkage behaviour of the asymmetric system, indicating successful co-sintering of the dense and porous layers. Scanning electron microscope images of the co-sintered membranes also confirmed flat and crack-free asymmetric membranes with no delamination or interfacial reaction between the two layers. This suggests that there will be less/no complications with the control of shrinkage behaviours in preparation of asymmetric membranes [8,13]. Therefore, green dense SCYb membranes and green porous SCYb supports containing cornstarch particles were co-sintered in this study.

2.1. Precursor powder synthesis

The $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ (SCYb) powder was synthesised by solid-state reaction. Appropriate amounts of oxide powders, $SrCO_3$ (99.9+%, Sigma–Aldrich) and CeO_2 (99.9%, Strem Chemicals) and Yb_2O_3 (99.9%, Alfa Aesar) were mixed in a ball mill. The mixture was calcined in an alumina crucible in air at 1300 °C for 12 h with the heating and cooling rates of 5 °C/min. The calcined powder was then ground with a mortar and pestle, and sieved. The calcination, grinding and sieving were repeated.

2.2. Preparation of porous supports

The same ceramic materials were utilised in the dense layer and porous support, and the porosity of the porous support was controlled by cornstarch particles which leaves pores after the combustion, as mentioned above. The SCYb powder was mixed with an appropriate amount of cornstarch particles in a ball mill. The mixture was put into a die of 25 mm diameter and uniaxially pressed with a pressure of approximately 80 MPa to obtain a green porous SCYb support. The different cornstarch contents of 10, 20, and 30 wt% in the porous supports were preliminarily examined and for the preparation of the asymmetric membranes, the porous supports with 20 wt% cornstarch were adopted. This amount of cornstarch results in a suitably porous support.

2.3. Asymmetric membrane fabrication

Green dense SCYb membranes and green porous SCYb supports containing cornstarch particles were co-sintered in this study. As mentioned in Section 2.2, the different cornstarch contents in the porous supports were first examined to determine the suitable amount of cornstarch in order to avoid delamination. In order to deposit a thin dense SCYb layer on the green porous SCYb support, a ‘‘settlement method’’ described in the work by Agranovski et al. [14], was employed, instead of tape casting and lamination utilised in the study by Etchegoyen et al. [8]. The settlement method was then followed by conventional dry pressing to produce the asymmetric SCYb membranes, and co-sintering. In this study, isopropanol (Merck, viscosity: 1.96 cP at 25 °C) was utilised as the liquid media for the settlement method. Accurately weighed SCYb powder was added to 6 ml of isopropanol and mixed with a magnetic stirrer for 1 h. After the powder was uniformly dispersed in the isopropanol, the mixture was directly poured onto the green porous SCYb support placed in a beaker. They were left until the powder fully settled and then the excess isopropanol was removed from the beaker. The green asymmetric sample was dried at room temperature overnight. The green asymmetric membrane was carefully removed from the beaker and pressed again with a final pressure of 230 MPa. The green membrane was sintered in air at 1500 °C for 12 h, with the heating rate of 2 up to 550 °C, 5 °C/min from 550 to 1500 °C and the cooling rate of 5 °C/min. The heating rate of 2 °C/min was essential during the combustion of cornstarch (up to 550 °C) to avoid the separation of the dense layer from the porous support, due to significant temperature changes or rapid generation of gas due to the combustion of cornstarch. The heating rate of 5 °C/min was acceptable for heating over 550 °C, and for cooling. The samples were placed on a platinum foil in an alumina crucible to avoid the reaction between the samples and the alumina, as strontium can react with alumina to form $SrAl_2O_4$ at temperatures higher than 1200 °C, possibly leading to loss of strontium and an excess of cerium [15]. The thickness of the dense layer was controlled by the concentration of SCYb powder in isopropanol. Prior to the powder settlement, it was essential to ensure that (1) the diameter of the beaker was slightly larger than the diameter of the green support to avoid any edge effect from the beaker wall and (2) the liquid media provided enough height for particles to settle in order to obtain uniform settlement of the powders. The uniformity of the settled dense layers was verified with a scanning electron microscopy (SEM, FEI Quanta 200).

2.4. Characterisation

The elemental compositions of the synthesised powder was analysed with inductively coupled plasma mass spectrometry (ICP-MS). The particle sizes of SCYb powder and cornstarch particles were determined by a volume based particle size analyser (Malvern, Mastersizer S). Phase crystallographic structures of the SCYb powder were determined by X-ray diffraction analysis (XRD) using Cu Kα radiation. The microstructure of the asymmetric membranes and the thicknesses of the dense layers were analysed using SEM (JEOL 840A and FEI Quanta 200) [8]. The gas tightness of the dense layers of the asymmetric membranes was determined by helium gas permeation at room temperature using a bubble test. The samples tested are categorised into two groups: (A) asymmetric membranes which were sintered at 1465 °C and (B) asymmetric membranes sintered at 1500 °C. Bulk density, true density, theoretical density, true porosity, and apparent porosity of porous supports with various cornstarch contents, were calculated by using the modified Archimedes method [16,17]. Bulk density (density of samples containing pores), ρ_b, was calculated from:

$$\rho_b = \frac{W_d}{W_w - W_s} \tag{1}$$

where W_d is the weight of the dry sample (kg m/s^2), W_s is the weight of the ceramic suspended in water (kg m/s^2), which is measured as W_d minus the buoyancy force, F_B (kg m/s^2), W_w is the weight of the ceramic removed from water (kg m/s^2). The true density of ceramic, ρ, was determined from:

$$\rho = \frac{W_d \rho_w}{F_B}, \tag{2}$$

where ρ_w is the density of water. Theoretical density, ρ_T, was calculated from:

$$\rho_T = \frac{zA}{V_C N_A} \tag{3}$$

where z is the number of formula units per unit cell (4 formula units/cell for perovskite), A is the formula weight (g/mol), V_C is the volume of the unit cell calculated from lattice parameters of the unit cell (cm^3/cell) and N_A is Avogadro's number (formula units/mol). Percent theoretical density was determined as

$$\text{theoretical density } (\%) = \frac{\rho_T - \rho}{\rho_T} \tag{4}$$

The true porosity which includes both interconnected and closed pores, was calculated from:

$$\text{true porosity} = \frac{\rho - \rho_b}{\rho} \tag{5}$$

The apparent (interconnected) porosity which relates permeability of gases through the support, was calculated from:

$$\text{apparent porosity} = \frac{W_w - W_d}{W_w - W_s} \tag{6}$$

The fractions of pores closed were determined by

$$\text{fraction pores closed} = \frac{\text{true porosity} - \text{apparent porosity}}{\text{true porosity}}. \tag{7}$$

The downside of the settlement method may be the non-uniformity of the particle settlement, due to the fact that the particle settlement depends on the density and diameters of settling particles. This possibly leads to non-uniform distribution of the powders across the vertical cross-section of the dense layers. Therefore, energy dispersive X-ray spectroscopy (EDX) was employed in order to confirm the uniformity of the elemental compositions across the vertical cross-section of the deposited dense layers. Approximately every 10 μm along the vertical cross-section of the dense layers, was scanned, from the top surface of the dense layer to the interface with the porous support. The average atomic fractions of strontium, cerium and ytterbium at each location were normalised to the values obtained at the top surface of the dense layer. Non-uniformities may also arise from differential settling near the walls of the settling chambers. The examination of the SEM images did not detect any evidence of variation across the asymmetric membranes.

3. Results and discussion

3.1. Precursor powder synthesis

The compositions of the SCYb precursor powder were determined by ICP-MS and the results are approximately in accordance with the desired compositions of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$. Therefore the chemical formula of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ is used to represent the composition of the precursor powder utilised in this study, assuming the valencies of Sr^{2+}, Ce^{4+} and Yb^{3+} and no cation vacancies. The particle size distribution of the SCYb powder and cornstarch particles was analysed with the volume based particle size analyser and is shown in Fig. 1. The particle size distributions of the SCYb powders and the cornstarch particles were determined as approximately 0.1–70 and 0.2–40 μm, respectively. The volume median diameters (the diameter where 50% of the distribution is above and 50% is below) are about 11 μm for the SCYb powders and around 18 μm for the cornstarch particles. The XRD patterns of the SCYb powder exhibit perovskite structures as shown in Fig. 2.

3.2. Sintering process

The sintering process plays an important role in the fabrication of dense ceramic membranes, since it influences not only the microstructures and mechanical strength but also the transport properties of the membranes. The sintering process generally consists of distinct stages; densification/consolidation, removal of the pores between starting particles, shrinkage of the components, and grain growth. It is essential to carefully control these sintering processes, as remaining pores can behave like grains of different materials, affecting the uniformity and the transport properties of the membranes. Fig. 3(A) and (B) shows the surface morphology of the dense top layer of asymmetric membranes sintered at 1465 and 1500 °C, respectively. Comparing the membrane surfaces in Fig. 3(A1) and (B1), it can be seen that there is a significant difference in the extent of the sintering processes in the samples. The sample sintered at 1465 °C (Fig. 3(A1) and (A2)) has undergone the densification process and has a smooth surface with no distinct individual particles remaining, however, there are still many pores remaining on the surface. On the other hand, the sample sintered at 1500 °C (Fig. 3(B1) and (B2)) has a much denser and smoother surface with little remaining pores and consists of bigger grains. This indicates that the pore closing process and further grain growth occurred between 1465 and 1500 °C. This agrees with Liu and Li [18] who reported that fully dense membrane surface was obtained at sintering temperature of 1500–1600 °C for their SCYb samples.

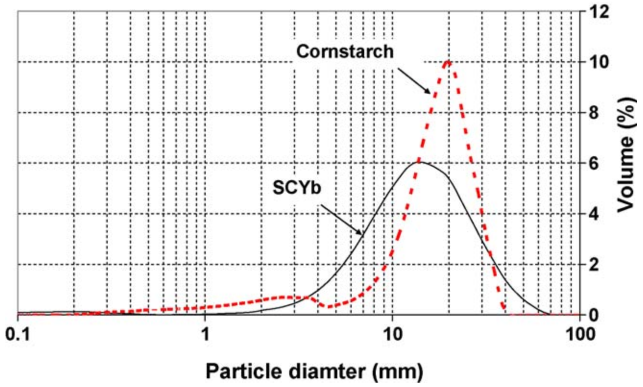

Fig. 1. Particle size distributions of the precursor SCYb powder and cornstarch particles.

3.3. Porous support fabrication

The porous supports with the different cornstarch contents of 10, 20, and 30 wt%, referred to as porous support A, B and C, respectively, were prepared in order to demonstrate the porosity control with the use of cornstarch particles. Table 1 summarises the densities and porosities of the porous supports A, B and C. The true densities of the supports A, B and C are 5.3, 5.5 and 5.4 g/cm^3, respectively, which are on average approximately 93% theoretical density of SCYb (5.8 g/cm^3). Bulk densities of the supports are proportional to the cornstarch concentrations in the supports. The pre-sintering porosities of the green porous supports A, B and C and the true porosities (including both

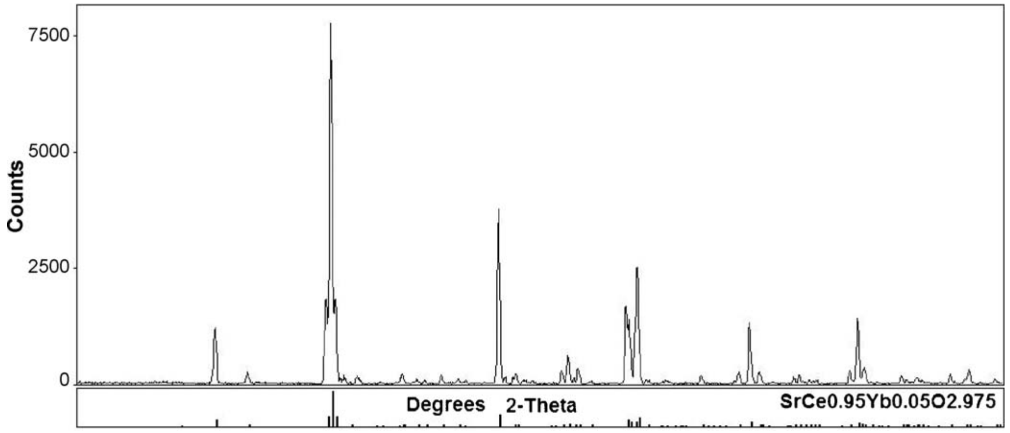

Fig. 2. XRD patterns of the SCYb precursor powder.

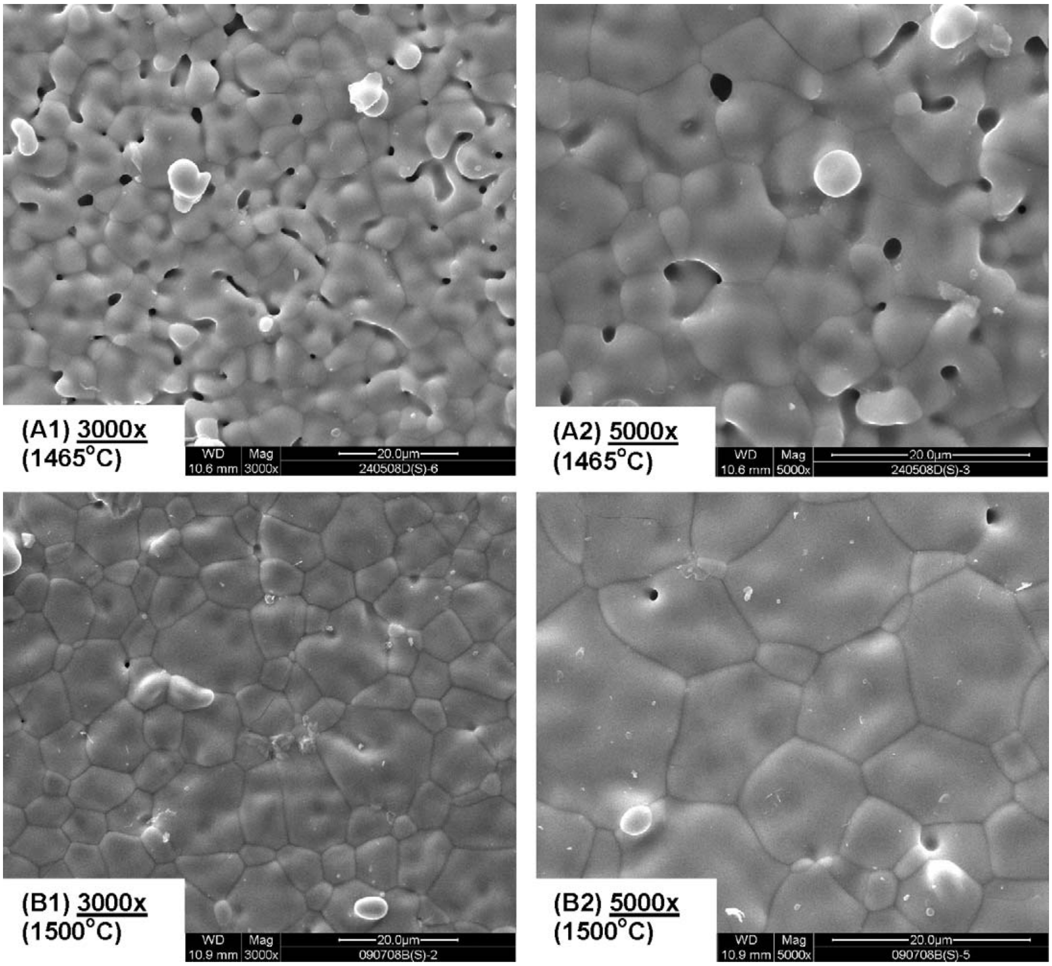

Fig. 3. SEM photographs of surface morphology of the dense top layer of the asymmetric membranes sintered at (A) 1465 °C and (B) 1500 °C (1 and 2 correspond to the 3000× and 5000× magnifications, respectively).

interconnected and closed pores) of the sintered supports A, B and C indicate that 1.7%, 12%, and 19% of the pores were lost during the sintering process, respectively. The apparent (interconnected) porosities of the sintered porous supports suggest that approximately 25% of the pores in the support A are closed pores, on the other hand, only 10% for the supports B and C. This indicates the support B and C (containing 20 and 30 wt% cornstarch particles, respectively) would likely ensure easy gas transport through the supports.

3.4. Asymmetric membrane fabrication

Asymmetric membranes were prepared by deposition of thin dense SCYb layers on the green porous SCYb supports by the settlement method, followed by conventional dry pressing and co-sintering. Membrane microstructures of cross-sections of co-sintered asymmetric membranes were observed using SEM [8]. Fig. 4(A)–(C) shows the SEM cross-sectional images of the asymmetric membranes with different dense layer thicknesses

Table 1
Density and porosity of porous supports.

Support no.	A		B		C	
Pre-sintering porosity	29.3 vol% (10 wt% cornstarch)		48.4 vol% (20 wt% cornstarch)		61.6 vol% (30 wt% cornstarch)	
Post-sintering	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
True density (g/cm^3)	5.28	0.029	5.51	0.025	5.40	0.035
Bulk density (g/cm^3)	4.20	0.06	3.67	0.05	3.35	0.06
True porosity (vol%)	27.7%	1.1%	36.8%	0.8%	42.3%	1.1%
Apparent porosity (vol%)	20.7%	1.2%	33.6%	0.8%	38.1%	1.4%
Fraction pores closed	0.25	0.020	0.09	0.007	0.1	0.012
Porosity lost during sintering (%)	1.7%	–	11.6%	–	19.4%	–

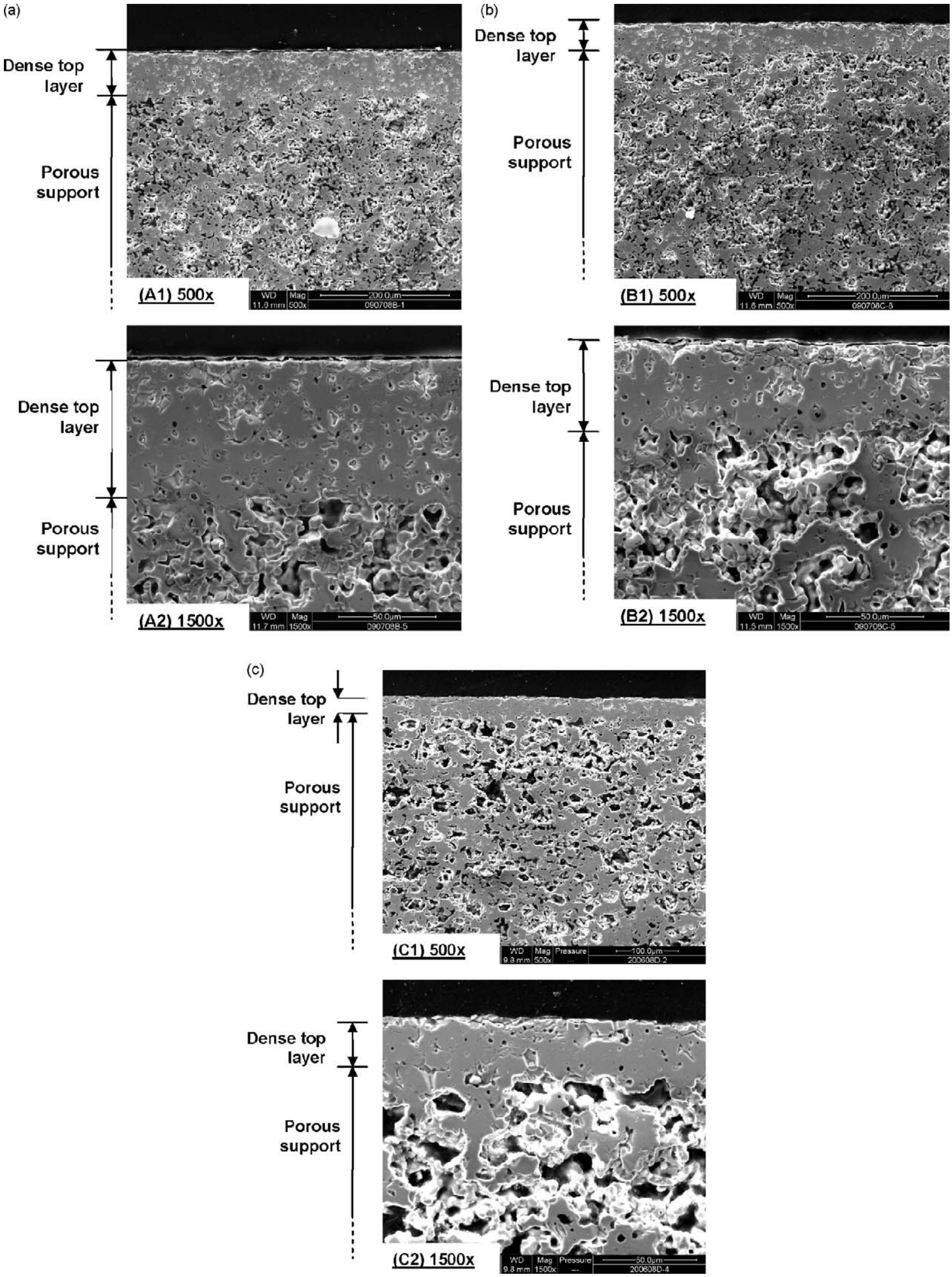

Fig. 4. SEM photographs of cross-sections of asymmetric membranes sintered at 1500 °C, showing different dense layer thickness: (A) 65 μm, (B) 40 μm and (C) 30 μm (1 and 2 correspond to the 500× and 1500× magnifications, respectively).

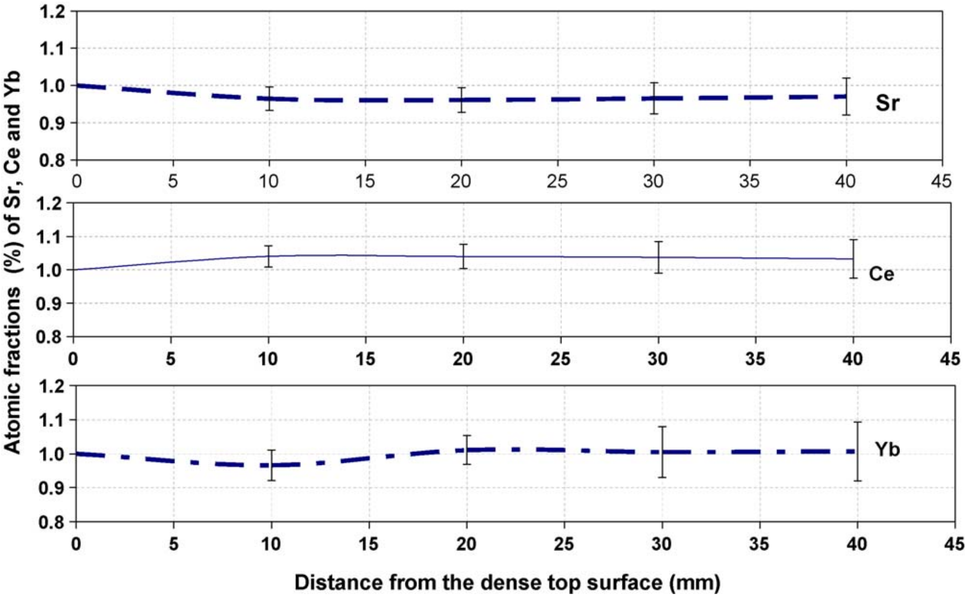

Fig. 5. Atomic fractions of strontium, cerium, and ytterbium along the vertical cross-sections of the settled dense layers as evaluated from EDX.

of 65, 40 and 30 μm, respectively. From these figures, it is apparent that thin dense SCYb films were successfully prepared on the porous SCYb supports by the settlement method.

The different dense layer thicknesses were easily obtained by altering the amount of the SCYb powders suspended in the liquid media. The use of the same ceramic material in the dense layer and green porous support and co-sintering have been demonstrated as effective in producing crack-free asymmetric membranes, as shown in Fig. 4. The dense layer and the porous support in the asymmetric system densified at the same, or at a similar, rate during the sintering and there was no reaction between the two layers. As can be seen in Fig. 4, the asymmetric systems are distinctive and the transition from the dense membranes to porous supports does not show any signs of delamination. The creation and control of the pores in the support have also been effective through the use of cornstarch particles. Cornstarch particles did not interfere with the sintering behaviour of the asymmetric system, and the co-sintering of the green asymmetric membranes resulted in no delamination or cracks.

The downside of the settlement method may be the non-uniformity of the particle settlement, due to the fact that the particle settlement depends on the density and diameters of settling particles. This possibly leads to non-uniform microstructures of the dense layers. However, these layers in Fig. 4(A)–(C) shows uniform thicknesses at this level of analysis, homogenous microstructures, and excellent adhesion to the porous supports with no signs of undesirable defects, cracks or delamination.

The elemental compositions across the vertical cross-section of the deposited dense layers were examined with EDX, in order to determine the uniformity of the SCYb powder distributions. The normalised atomic fractions of strontium, cerium, and ytterbium along the vertical cross-sections are displayed in Fig. 5, for the 40 μm layer. Atomic fractions at each section of the dense layers, for each element, are normalised to one at the top surface of the dense layer. The result indicates consistency in the settled dense layers, with a standard deviation of 5% for strontium, 6% for cerium and 9% for ytterbium. This suggests the overall uniform distribution of the SCYb powders across the deposited dense layers.

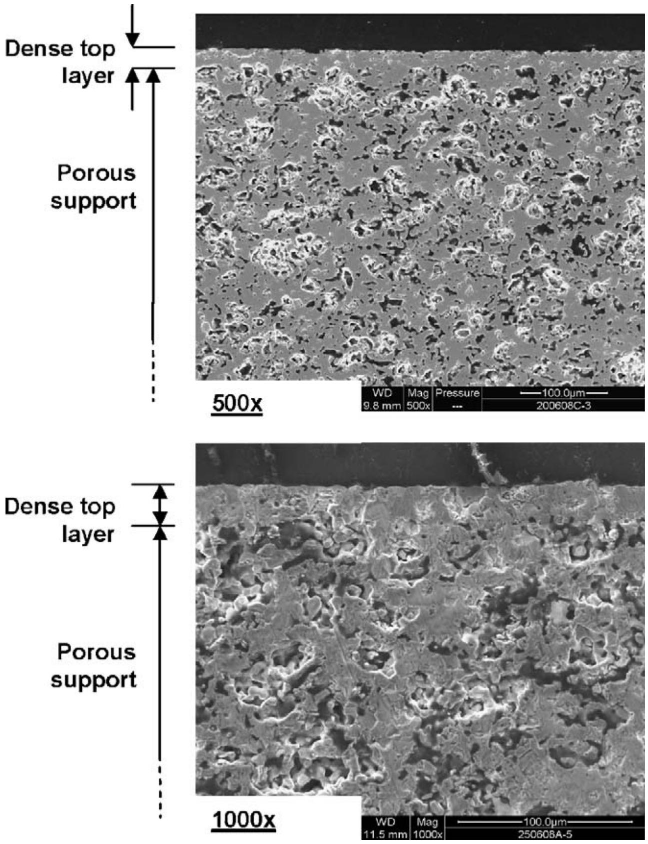

Fig. 6. SEM photographs of cross-sections of asymmetric membranes sintered at 1500 °C, showing the minimum thickness (20 μm) (shown at two magnifications, 500× and 1000× magnifications).

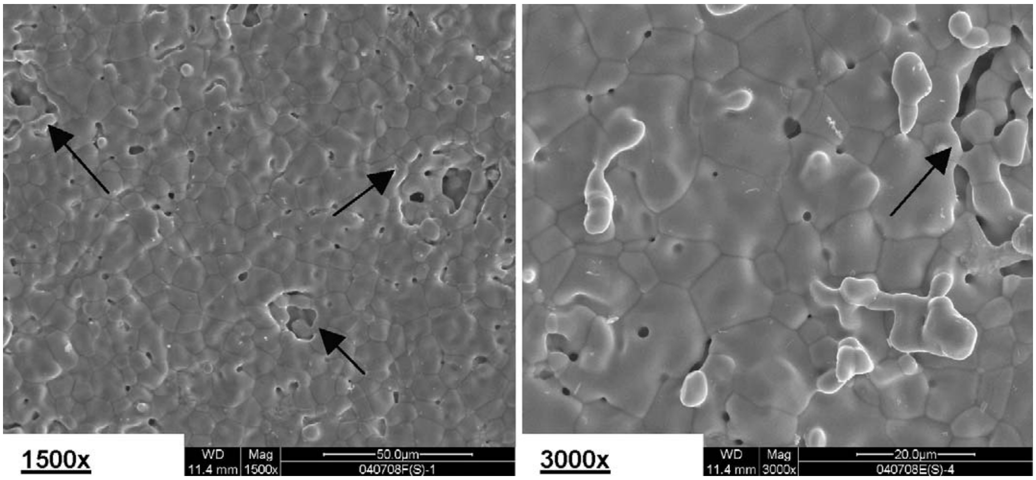

Fig. 7. SEM photographs of surface morphology of the thinner dense top layer (7–18 µm, below the minimum thickness), sintered at 1500 °C (shown at two magnifications, 1500× and 3000× magnifications). The arrows show non-uniformities in the dense layer.

The minimum thickness of the dense layer obtained by the settlement method, with the synthesis conditions utilised in this study, is around 20 µm, as shown in Fig. 6. From the figure, it is apparent that the thin 20 µm dense layer is still distinctive and has a uniform thickness at this level of analysis with no delamination or cracks on the interface. Further, the SEM cross-sectional images of the edges of the asymmetric membranes, indicates that there is no evidence of edge effects from the settling process. Although the SCYb powder utilised in this study included particles with sizes up to 70 µm, the thin 20 µm dense layer was successfully prepared on the porous support by the settlement method, conventional dry pressing and sintering.

By further reducing the amount of SCYb powders in the liquid media, thinner dense layers (7–18 µm) were prepared on the porous supports. However the 7–18 µm dense layers showed less uniform thickness and occasional gaps on the surface of the top dense layers, as shown in Fig. 7. The surface morphologies shown in Fig. 7 indicate that most of the surface is dense and smooth, however there are apparent gaps on the surfaces due to an insufficient amount of SCYb powder being deposited on the surface. Therefore, it is concluded that the minimum thickness which can be prepared by the settlement method with the synthesis conditions utilised in this study is approximately 20 µm.

The gas tightness of the dense layers in the asymmetric membrane samples was determined by helium gas permeation at room temperature using a bubble test and the results are shown in Table 2. It should be noted that Table 2 does not include the result for the samples sintered at 1465 °C (i.e. group A), as all of the samples sintered at 1465 °C are not helium gas tight, regardless of the dense layer thicknesses. This agrees with the findings in Section 3.2. The visual inspection of the surface morphology of the dense top layer of asymmetric membranes sintered at 1465 and 1500 °C (Fig. 3(A) and (B), respectively) indicates that the pore closing process and further grain growth occurred between 1465 and 1500 °C and that a sintering temperature of at least 1500 °C is required to obtain fully dense membrane surface for SCYb samples. This confirms the results of Liu and Li [18].

Although there are some variations in the results shown in Table 2, it can generally be concluded that thicknesses greater than 30 and less than 20, are not helium gas tight. Dense layers thinner than 20 µm are not helium gas tight, which can be explained by the findings in Fig. 7. Fig. 7 shows the surface morphologies of the 7–18 µm-thick dense layers where there are apparent gaps on the surfaces due to insufficient amounts of SCYb powders deposited on the surface. Those gaps obviously result in a lack of gas tightness of the dense layers.

The dense layers which are thicker than 30 µm, are also found to not gas tight for helium. This may be seen in Fig. 4(A)–(C), which show the SEM cross-sectional images of the

Table 2
Helium gas tight test results for group B (samples sintered at 1500 °C).

Sample no.	Areal concentration (g/cm^2)	Estimated dense layer thickness (µm)[a]	Helium gas tightness
1	0.0566	80.7	No
2	0.0448	65.0[b]	No
3	0.0286	41.3[b]	No
4	0.0285	41.2[b]	No
5	0.0283	41.5	No
6	0.0251	36.4	No
7	0.0212	30.9	Tight
8	0.0197	30.4	No
9	0.0170	24.9	Tight
10	0.0157	20.6	Tight
11	0.0142	20.2	Tight
12	0.0141	20.1[b]	Tight
13	0.0143	20.5	Tight
14	0.0129	20.5	No
15	0.0129	18.3[b]	Tight
16	0.0114	16.2[b]	No
17	0.0114	16.1[b]	No

[a] The thicknesses of the dense layers were estimated either from the SEM images when the dense layers in the SEM images are clear.

[b] Otherwise the thicknesses were estimated from the equation for the trend-line in Fig. 8, $y = 1463.5x - 0.5415$, where x is the areal concentration (g/cm^2).

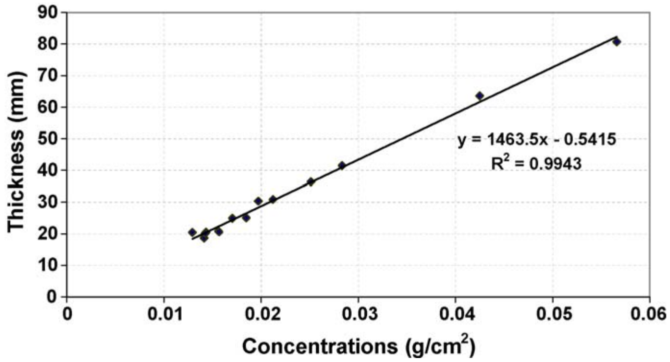

Fig. 8. Relationship between the concentrations of the SCYb powder in the liquid media and the corresponding dense layer thicknesses in the sintered asymmetric membranes.

asymmetric membranes with different dense layer thicknesses of 65, 40 and 30 μm, respectively. The 65 μm- and 40 μm-thick dense layers (Fig. 4(A) and (B), respectively) contain more pores than the 30 μm-thick dense layer (Fig. 4(C)). It is suggested that the non-gas tightness may result from insufficient sintering temperature or time for the gas seal to be attained for the thicker samples.

Fig. 8 summarises the thicknesses of the dense thin layers prepared on the porous supports by the settlement method. It plots the areal concentration (g/cm^2) of the SCYb powders in the liquid media against the corresponding thickness of the dense layer on the porous support obtained after sintering. It should be noted that the areal concentration, rather than volumetric concentration (g/cm^3), is utilised in Fig. 8. This metric is used because the reason that the critical factor is the amount of SCYb powder in the liquid media per unit area of the support (for example, 1 cm^3 of 1 g/cm^3-solution provides 1 g of SCYb powder for settling on the support, while 2 cm^3 of 0.5 g/cm^3-solution also provides 1 g of SCYb powder). The coefficient of determination (R^2) value is 0.99 which shows an excellent fit. This suggests the effective control of the dense layer thickness by this method and the layers so generated are readily reproducible. This study has verified that settlement methods are an effective filling technique which aids the conventional dry pressing, in order to prepare a thin uniform dense layer on a porous support.

4. Conclusions

Thin dense SCYb films were successfully prepared on the porous SCYb supports by the settlement method. These dense layers have uniform thicknesses at this level of analysis, and show excellent adhesion to the porous support without any undesirable defects or crack. The settlement method provides a uniform distribution across the membranes without any major edge effects on the deposited surfaces. Further, different dense layer thicknesses were easily controlled by altering the amount of the SCYb powders in the liquid media. The settlement method can provide the advantages that (1) the control of the dense layer thickness is very easy and effective; (2) it does not require pre-sintering of supports or sequences of coatings, and hence is less labour consuming; (3) the liquid media can be any liquid which does not interfere or react with the powder; (4) the method requires simple mixing of powder and the liquid media, and does not require any additions such as dispersant; and (5) the method includes only a few process variables making it less complex and suitable for a larger scale application. So in conclusion, this study has demonstrated settlement methods as the effective filling technique which aids the conventional dry pressing, in order to prepare a thin uniform dense layer on a porous support.

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