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Effect of Sintering Temperature on the Fabrication of Ceramic Hollow Fibre Membrane

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Recently, ceramic membrane gradually acquired attention from researchers due to the advantages of ceramic's behavior, which allows the ceramic to overcome the limitations of using polymeric membrane. This work focused on the fabrication of ceramic hollow fibre membrane from a ceramic suspension solution containing yttria-stabilized zirconia (YSZ), polyethersulfone (PESf), N-methylpyrrolidone (NMP) and dispersants using combined phase inversion sintering technique. In this study, ceramic hollow membrane precursors were sintered at different sintering temperature ranging between 1250°C and 1400°C. The influences of sintering temperature on the microstructure, porosity and pore size distribution, mechanical strength and pure water flux of ceramic hollow fibre membrane were investigated in detail. The results show an asymmetric structure of YSZ hollow fibre membrane containing finger-like structure and sponge-like structure. The sponge-like structure can serve as a separation layer, while finger-like-structure performs as a supported layer. It is observed that sintering process caused a significant densification of sponge-like structure (microstructure). Sintering at temperature 1400°C shows the formation of non-interconnected voids. Sintering at 1300°C is sufficient enough having a mechanical strength of 227.55MPa with an apparent porosity of 45.09% and PWF of 118.39L.m^{-2}.hr^{-1}.

Keywords: yttria-stabilized zirconia, ceramic hollow fibre membrane and sintering.

INTRODUCTION

Ceramic material is well known for its superior mechanical properties and is beneficial in fabricating into ceramic membrane with high mechanical strength that enable for high pressure operation. Besides, ceramic membranes also performed high thermal and chemical resistance which enables for high temperature operations and harsh environment such as in wastewater treatment facilities and processes (Khemakhem et al. 2009). For membrane filtration application, backwashing process to remove fouling particles on the membrane surfaces required a pressure twice than permeate pressure. Their

superior thermal, chemical and mechanical properties widen the range of application of ceramic membranes; membrane reactors (Rahman et al. 2011 and García-García et al. 2011), gas separation (Li et al. 2006), fuel cell (Wei and Li 2008 and Othman et al. 2010). From all the advantages of ceramic membrane over polymeric membrane, the reliability of ceramic membrane made it long-lasting while enables in reducing the maintenance which associated with cost saving and energy usage.

Developing ceramic hollow fibre membranes by using a combined phase inversion and sintering process allows the formation of an asymmetric structure of ceramic hollow fibre membranes as done by Kingsbury and Li (2009). The hydrodynamically unstable viscous fingering is a phenomenon that occurs during the mixing of two fluids with different viscosities. When the suspension solution is in contact with the non-solvent (coagulant bath), the hydrodynamically unstable viscous fingering takes place which later results in finger-like voids formation. In this circumstance, the solvent diffuses out from the suspension solution while the non-solvent diffuses into the suspension solution. The precipitation of polymer phase is taken place during solvent and non-solvent exchange and during this time, ceramic particles are immobilized once the precipitation of polymer binder occurs. Then, the polymer binders were burned off during sintering process.

Sintering is a heat treatment process at high temperature that plays a foremost part of fabricating ceramic membrane. Previous study confirmed that the sintering process does not change the general morphology of the ceramic precursors. Finger-like voids are remains and the sponge-like like voids with other small pores experienced densification. Sintering process composed of three stages which are; (1) pre-sintering, (2) thermolysis and (3) final sintering (Li 2007). At pre-sintering, it removes any liquid that remains inside the precursor after the formation or drying, and potential moisture absorbed from the atmosphere during transporting and setting (Li 2007). Then, the polymer binder that exists in the precursor is burn off and leaves the ceramic particles at thermolysis stage (Li 2007). Liu and Li (2005) study on the sintering process indicate the weight loss of the SCYb hollow fibre which is caused by the burning off of polymer binder. At the final sintering stage, experienced different features of particle movements, grain coarsening and pores closing that result in enhance the mechanical strength as the sintering temperature increases. It is agreed by Liu et al. (2003) in the study that shows the same patterned of increasing mechanical strength of fibres with increasing sintering temperature. According to the author, this may due to the neck growth of particles bonding that enhances the strength.

Membrane filtration which operates by a surface removal mechanism reject particles larger than the size of the largest pore, while particles finer than the largest pore can pass through the membrane to the filtrate side. As the targeting sintering temperature gives an impact at the surface morphology, grain growth and pore

evaluation or elimination, it may hinder the membranes to be used for the applications. In this work, the ceramic hollow fibre precursors prepared at same spinning conditions were sintered at different sintering temperature range 1250°C - 1400°C. The influences of the sintering temperature on morphology structure, porosity, pure water flux, and mechanical strength was investigated.

EXPERIMENTAL

Materials

Commercially available 8 mol% yttria-stabilized zirconia (YSZ) powder (d_{50} = 0.3μm) purchased from Fuel Cell Material were used as ceramic particles. Polyethersulfone (PESf) (Radel A300, Ameco Performance, USA), Arlacel P135 (Polyethyleneglycol 30 Dipolyhydroxystrearate, CRODA) and N-Methylpyrrolidone (NMP, QRëC TM) were used as polymer binder, additive and solvent respectively. Tap water was used as the external and internal coagulant.

Preparation of YSZ hollow fibre membrane

The YSZ powder and PESf were dried and Arlacel P135 was melted in oven overnight at 60˚C. Then, Arlacel P135 was first dissolved in NMP prior to the addition of YSZ powders. The mixtures were milled in planetary milling ball for 48 hours with 20 mm agate mill ball to ensure that the ceramic materials, solvent and additive are well dissolves. The milling was continued for another 48 hours after the addition of PESf. Prior to the spinning process, the suspension solution was degassed under vacuum while stirring until no bubbles observed. The ceramic powder/ polymer binder ratio is kept constant at 10:1.

The suspension solution was then transferred into a stainless steel container and extruded by syringe pump through a tube-in-orifice spinneret into an external coagulation bath. The spinning conditions were listed in Table 1. The hollow fibre precursors produced were left in the external coagulation bath overnight for the completion of phase inversion process. Then, the hollow fibre precursors were dried in room temperature for 24 hours.

After the pre-drying process, the YSZ hollow fibre precursors were sintered in a tubular furnace (MAGNA, XY-1700). The sintering process was run at two-step sintering process. The sintering temperature was increased from room temperature to 600˚C at a rate of 2˚C/min. Then, the sintering temperature is further increased to 1250 – 1400˚C at a rate of 5˚C/min. The temperature was later cold down to room temperature at a rate of 5˚C/min. In this process, the polymer binder will burn-off and leave the ceramic material only. Hence, the YSZ hollow fibre membranes were produced.

Characterization

The viscosity of suspension solution was collected immediately prior to spinning process by at shear rate between $1s^{-1}$ and $100s^{-1}$ at room temperature. SEM characterization was conducted using HITACHI Model TM 3000 and SEM images were taken at varying magnification. The surface roughness was determined using Atomic Force Microscopy (AFM). The mechanical strength of hollow fibres was

examined by three-points bending test using Instron Model 5544 tensile tester provided with a load cell of 1 kN. The bending strength (σ_F) is calculated using the Eq. (1) (Othman et al. 2010 and Liu et al. 2001):

$$\sigma_F = \frac{8FLD_o}{\pi(D_o^4 - D_i^4)} \quad (1)$$

Where F is the measured force at which the fracture occurred, L, D_o, and D_i are the span length (43mm), the outer diameter (D_o), and the inner diameter (D_i) of the hollow fibres, respectively.

The pure water flux of the YSZ hollow fiber membranes was measured with a cross-flow filtration system using 15cm length fibres. The apparatus was operated with a feed velocity of 3.0 m/s and trans-membrane pressure difference of 3.0bar. Before the measurements of permeate flux, all the samples were immersed in deionized water (1000μS/cm) for 20 minutes. All the measurements were conducted at room temperature.

RESULT AND DISCUSSIONS

Morphology of YSZ hollow fibre membrane

The YSZ hollow fibre membranes produced were prepared by using dope solution with a composition as listed in Table 1 and the SEM images is shown in Fig. 1. It can be seen that YSZ hollow fibre membranes having an asymmetric structure containing finger-like structure originating from the inner layer of the fibre and small finger-like voids exhibit at the outer layer approximately 50% and 10% respectively cross the fibre. While, sponge-like structure is occupying approximately 40% at the central of fibre. This type of structure enables the sponge-like structure to be functioned as a separation layer and the finger-like structure as a support and also contribute to enhance the permeability of membranes. Thus, this structure is suitable for membrane filtration applications.

Table 1. Composition of ceramic suspension solution and spinning conditions

Parameter	Value
Composition of ceramic suspension solution	
8%YSZ	65wt%
PESf	6.5wt%
Arlacel P135	0.5wt%
NMP	28wt%
Spinning conditions	
Internal Coagulant	Tap water
External Coagulant	Tap water
Spinneret dimension (o.d/i.d)	2.8mm/0.5mm
Temperature	Room temperature
Air-gap	20cm
Internal coagulant flow rate	10ml/min
External coagulant flow rate	7ml/min

As mentioned above, the sponge-like structure (microstructure) will undergo a densification during sintering process. The densification of sponge-like structure attributes to the neck growth between ceramic particles made it closely packed together and reducing the porosity of the

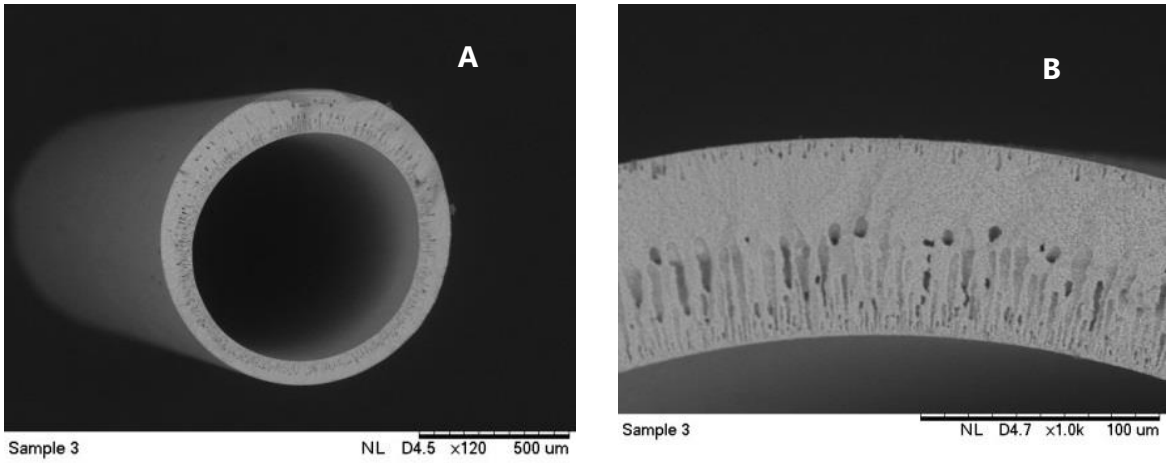

Fig. 1: The morphological structure of YSZ hollow fibre membrane after sintering at 1350°C for 6hrs; (A) overall image and (B) cross-sectional

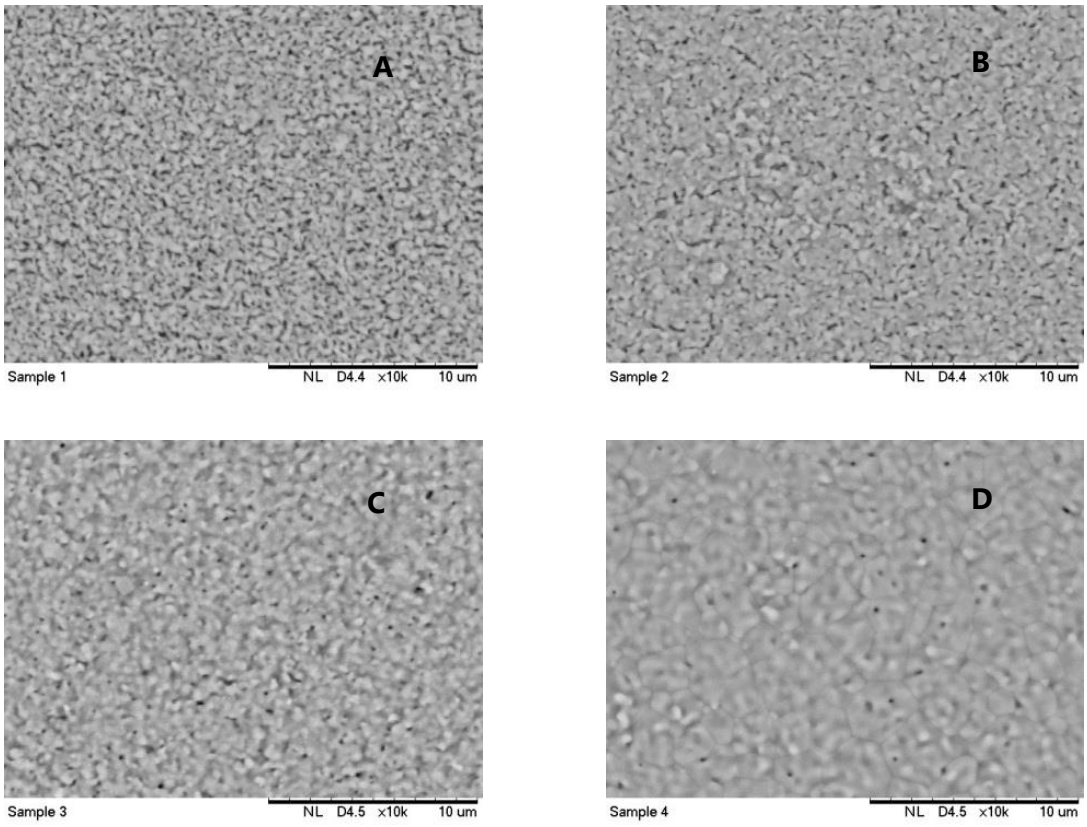

Fig. 2: Microstructure of YSZ hollow fibre membrane sintered at different sintering temperature for 6hrs; (A) 1250°C, (B) 1300°C, (C) 1350°C and (D) 1400°C

membranes. Fig.2 shows evolution of microstructure of YSZ hollow fibre membrane at different sintering temperature. It can be seen that the porosities of the microstructure reduced greatly as the sintering temperature increases. This simultaneously affects the properties of the membrane as the sponge-like structure plays as a separation layer. At sintering temperature 1250°C,

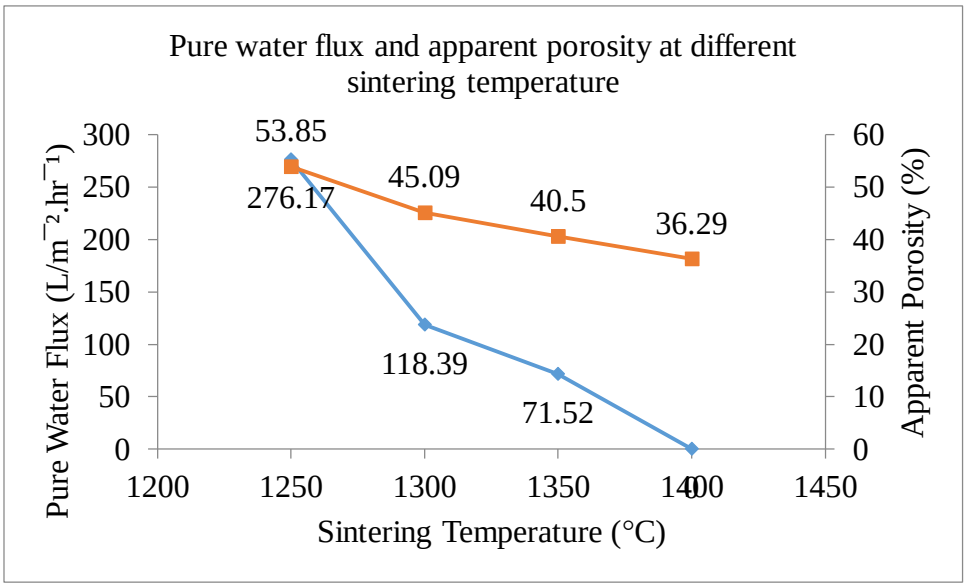

Fig. 3: Pure water flux and apparent porosity of YSZ hollow fibre membrane sintered at sintering temperature range between 1250°C to 1400°C.

the interconnected pores are observed at the microstructure as shown in Fig. 2A. At 1300°C and 1350°C the interconnected pores are still observed although the porosity is decreases compared to membrane sintered at 1250°C as shown in Fig. 2B and 2C. As the sintering temperature increase up to1400°C, the membrane microstructure shown in Fig. 3D becomes almost fully dense and non-interconnected pores are observed.

Apparent Porosity

The densification of microstructure during sintering process affects the porosity of YSZ hollow fibre membranes. Figure 3 shows the apparent porosity of fibres at different sintering temperature. As expected from the SEM results, increases of sintering temperature decreased the apparent porosity of YSZ hollow fibre membrane. The apparent porosity is decreased from 53.85% to 45.09% when sintered at 1250°C and 1300°C respectively. Further increase the temperature up to 1350°C and 1400°C, the porosity is keep on decreases from 40.50% to 36.29%, respectively. This result is parallel with the SEM images shown above. As porosity is crucial for a ceramic membrane to be used for separation while providing enough pores for a good permeation, the sintering temperature should be controlled for a good separation.

Pure Water Flux

In practical applications, ceramic hollow fibre membranes with high water permeability are preferable. In this study, sintering process plays an important role in controlling the porosity of the fibre. The experimental results of pure water flux of YSZ hollow fibre membranes sintered at different sintering temperature operating at 3 bar and in room temperature is presents in Figure 3. As the sintering temperature is increased, the pure water

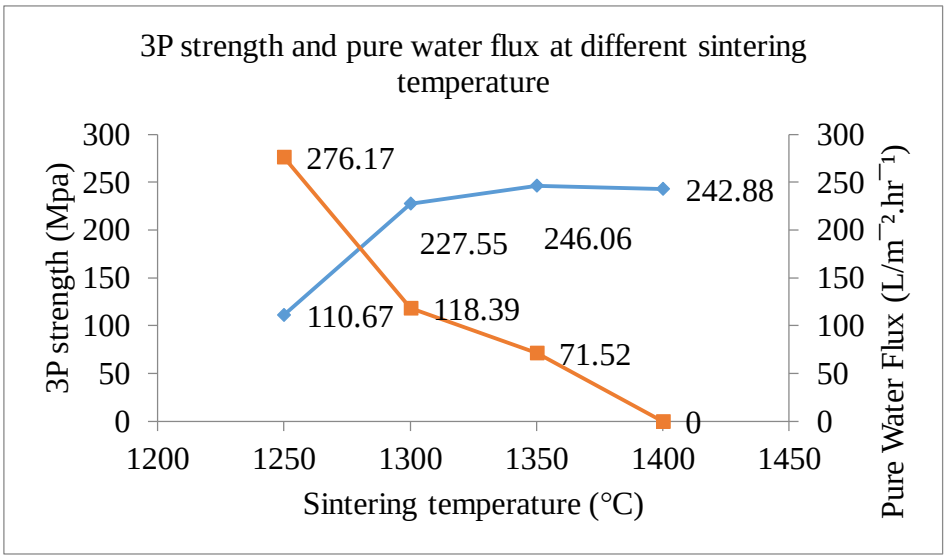

Fig. 4: The 3P strength and pure water flux of YSZ hollow fibre membrane at sintering temperature range between 1250°C to 1400°C.

permeation flux decreases. This pattern is same as shown by Yin *et. al.* (Yin et al. 2009) and Zhang *et. al.* (Zhang et al. 2010). Sintering fibre at 1250°C and 1300°C gives a water flux of 276.17L.m^{-2}.hr^{-1} and 118.39L.m^{-2}.hr^{-1}, respectively. This can be linked to the porosity of the fibres that decreases as the sintering temperature increases due to the densification effect. A significant drop of water flux between fibres sintered at 1350°C and 1400°C is clearly seen. At 1350°C the water flux measured is 71.52L.m^{-2}.hr^{-1} and is shown to be totally eliminated in fibres sintered at 1400°C (no water permeation is measured). Even though the fibres sintered at 1400°C having an apparent porosity of 36.29, the pores are an isolated pores that surrounded by the dense structure which hindered the water permeation.

Mechanical Strength

The experimental data shown in Figure 4 indicates the effect of sintering temperature on the mechanical strength of YSZ hollow fibre membranes. In general, it can be seen that the mechanical strength is increases as the sintering temperature increased. Sintering at temperature 1250°C gives the membrane a mechanical strength of 110.67MPa and increase up to 227.55MPa when sintered at 1300°C. The mechanical strength is kept on increasing up to 246.06MPa as further sintered to 1350°C. This may due to the closely pack of particles which simultaneously enhance the strength of fibres. However, at 1400°C the strength is slightly decreased to 242.88MPa. Besides, the mechanical strength also may be attributed by the wall thickness of YSZ hollow fibre membrane. The wall thickness of YSZ hollow fibre membrane sintered at 1250°C, 1300°C, 1350°C and 1400°C are 0.304mm, 0.256mm, 0.236mm and 0.211mm respectively. This decline also affects the mechanical strength of membranes. Thus,

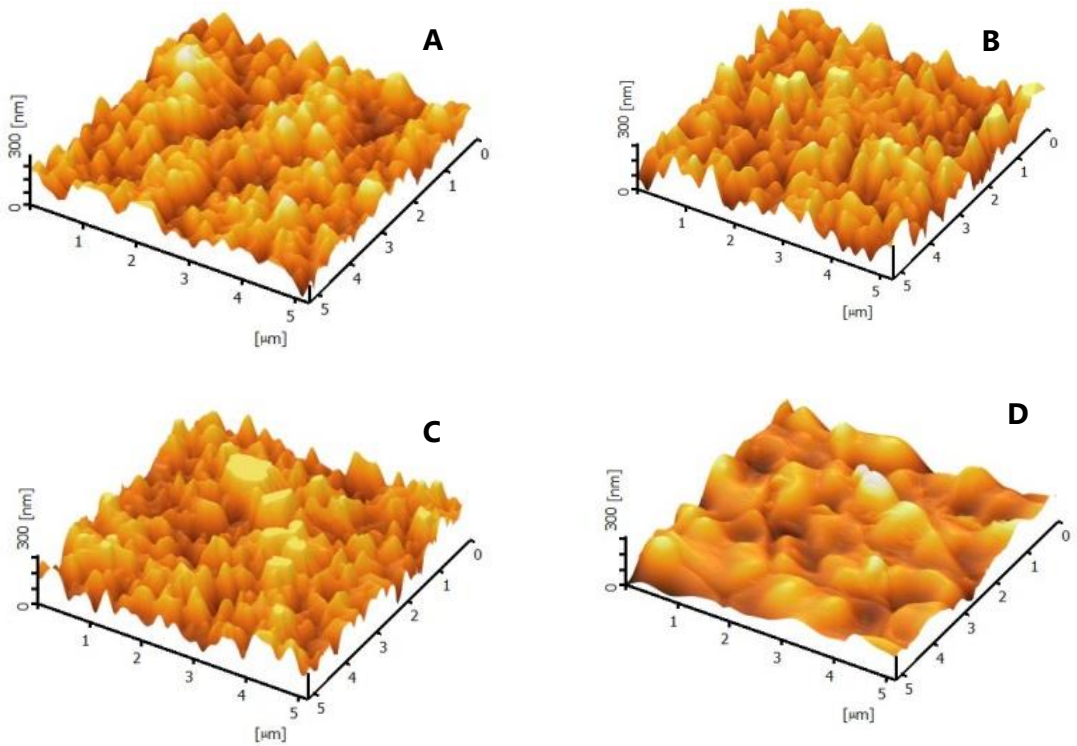

Fig. 5: AFM images of YSZ hollow fibre membranes sintered at (A) 1250°C, (B) 1300°C, (C) 1350°C and (D) 1400°C

it shows that sintered at higher temperature somehow will lower the mechanical strength of the membranes. In correlation with the pure water flux, limiting the sintering temperature below 1400°C is acceptable since there is no pure water flux indicates when sintered at 1400°C. Besides the mechanical strength sintered below 1400°C is sufficient enough for the fibres to be fabricated into a module without breaking and considerably losing its separation and permeation characteristics.

Surface Roughness

Figure 5 shows the AFM images of the outer surface of YSZ hollow fibre membrane in 5µm x 5µm scanning area. It can be seen that the outer surface of membranes is not smooth but consists of a mass of peaks (bright region) and valleys (dark region) when sintered at 1250°C, 1300°C, 1350°C. Further sintered at 1400°C, the outer surface membranes become smoother and it's also indicate the neck growth of ceramic particles. This result, parallel with SEM images of outer surface of fibres. The outer surface becomes less porous as sintering temperature increases. Thus, it is obviously shown the membrane's roughness may reflect the surface porosity of the membrane because the valleys may probably be the membrane's pores on the surface.

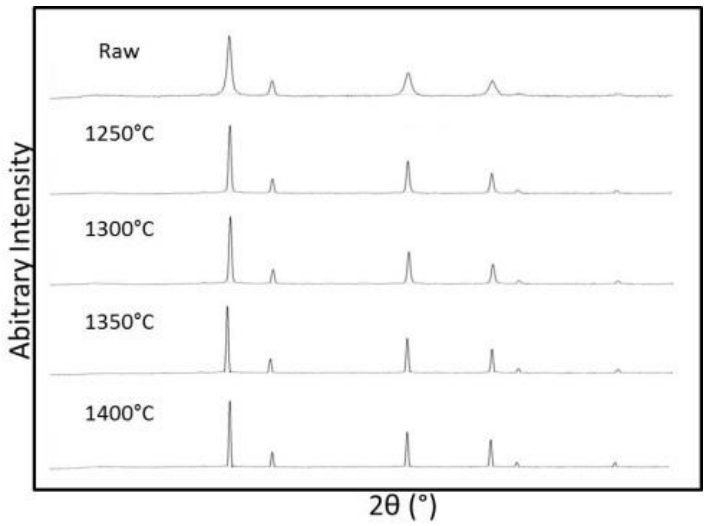

Fig. 6: XRD patterns of YSZ powder and YSZ hollow fibre membranes sintered at different sintering temperature

XRD Patterns

Figure 6 compares the XRD patterns of YSZ powder and YSZ hollow fibre membranes sintered at different sintering temperature (1250°C - 1400°C). It shows that the sintered YSZ hollow fibres membranes possess the same cubic fluorite crystal phase as the YSZ powders. In other words, the crystalline structure of the YSZ powders does not change after undergo a spinning process for hollow fibre fabrication and sintering process. Besides, the intensity peaks for the sintered hollow fibres is much higher original YSZ powders. This indicates that the YSZ crystals in the hollow fibre membrane have become larger after the high-temperature sintering.

CONCLUSION

In conclusion, an asymmetric structure of YSZ hollow fibre membranes is produced by using a combined phase inversion and sintering process. The experimental result shows that sintering process does effects the microstructure and the properties of the membranes. Increasing the sintering temperature leads to the densification of microstructure and thus, decreased the apparent porosity and the pure water flux of membranes. At sintering temperature of 1400°C, the formation of non-interconnected voids which inhibit the pure water permeation is observed. Thus, it can be draw that sintering temperature is limit <1400°C and sintering at 1300°C sufficient enough having a mechanical strength of 227.55MPa, apparent porosity of 45.09% and PWF of 118.39L.m^{-2}.hr^{-1}. Hence, controlling the sintering temperature is essential for controlling the properties of the YSZ hollow fibre membrane.

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