J Mater Sci (2011) 46:7056–7066
DOI 10.1007/s10853-011-5674-6

Sol–gel synthesis and characterization of mesoporous yttria-stabilized zirconia membranes with graded pore structure

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Received: 7 February 2011 / Accepted: 30 May 2011 / Published online: 16 June 2011

Abstract Mesoporous yttria-stabilized zirconia (YSZ) membranes can be used for liquid phase applications in harsh environments and as supports for ultra-thin dense ceramic, carbonate, or metallic membranes. This article reports on the synthesis and characterization of three-layer mesoporous ceramic membranes consisting of a mesoporous YSZ layer, a macroporous YSZ intermediate layer, and macroporous α-alumina support. The macroporous YSZ intermediate layer was coated on the alumina support using a suspension of submicron-sized YSZ powders, and the mesoporous YSZ layer was obtained by dip-coating with diluted zirconia sol doped with yttrium nitrate. The mesoporous YSZ layer has desired cubic phase structure. Crack-free mesoporous YSZ membranes could be obtained by multiple dip-coating, drying, and calcination using a dilute YSZ sol at a concentration of 0.014 M with the help of using a drying control chemical additive. The 5 times dip-coated mesoporous YSZ membranes were about 1 μm in thickness with an average pore diameter of 3 nm. The mesoporous YSZ membranes exhibited Knudsen separation factor. The characteristics of the dip-coating process for the mesoporous YSZ membranes on the macroporous YSZ support are similar to those on the macroporous alumina support.

Introduction

Yttria-stabilized zirconia (YSZ) is a widely used material because of its unique characteristics. YSZ has a better chemical stability in comparison to alumina and titania membranes making it more suitable for liquid phase applications under harsh conditions such as treatment of waste-water at extreme pH [1]. Compared with pure zirconia membranes which may form cracks due to the stresses developed associated with phase transformation from metastable tetragonal to stable monoclinic phase during heating treatment [2, 3], YSZ membrane could maintain a stable cubic fluorite structure between room temperature and 3000 K. As a result, it is more promising for high temperature applications such as membrane reactors and gas separation by Knudsen flow.

The YSZ membranes also exhibit a considerable oxygen ionic conductivity and an extreme low thermal conductivity at high temperature. Dense YSZ layers could be used as the electrolytes for solid oxide fuel cells, oxygen sensors, and oxygen pumps [4–7] while porous ones could be applied as barriers for thermal insulation and insulated engine components [8–10]. YSZ mesoporous membranes are attractive as the support, not only for ultra-thin dense YSZ but also for other ceramic or metallic membranes because of their chemical inertness, ionic conductivity, and thermal expansion coefficient which matches closely with that of many dense membrane materials [11].YSZ macroporous membrane could be used as an intermediate layer to improve the thermal stability of MFI-type zeolite membrane structure on porous alumina support [12].

The sol–gel method is considered to be the most common method for fabrication of porous ceramic membranes [1, 13]. The sol–gel synthesis of YSZ mesoporous membranes was previously reported by several investigators

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[14–16]. These studies were mainly focused on the phase and pore structures of YSZ. Recently, many researchers presented the synthesis and characterization of YSZ powders by the sol–gel process [17–19]. However, information on preparing crack and defect-free membranes and permeation data is limited. A few researchers reported on the preparation of defect-free supported YSZ membranes [20–22]. Okubo et al. [20] synthesized YSZ membranes by mixing a particulate sol and a polymeric sol to improve the film formation process and the film property. Kim and Lin [21] reported on the synthesis of porous YSZ membranes with a particulate sol that was obtained by hydrolysis and peptization of zirconium *n*-propoxide. The YSZ layer was determined to be pin-hole free by helium permeation tests. The zirconia sol used by Changrong et al. [22] was prepared by hydrolysis and condensation of zirconium tetra-*n*-propoxide.

All of these mesoporous YSZ membranes described above were synthesized directly on macroporous alumina supports. In these membranes the mesoporous YSZ layers, which is only 1–3 μm thick, is in direct contact with alumina support. For some applications of the mesoporous YSZ membranes, it is more desirable to have an intermediate macroporous YSZ layer as a buffer between the thin mesoporous YSZ layer and less costly alumina support. One application is to use the mesoporous YSZ layer as the support for preparation of dual-phase membranes (with the pores infiltrated either by Pd [23]or carbonate [24]), the macroporous intermediate layer would prevent infiltration of the second phase into alumina support, resulting in synthesis of thin dual-phase membranes for oxygen or carbon dioxide separation. The objective of this article is to report synthesis and characterization of the three-layer mesoporous YSZ membranes with a macroporous YSZ intermediate layer on alumina support by the methods of sol–gel [21] and suspension coating [25].

Materials and methods

Suspension preparation and YSZ macroporous membrane synthesis

Porous α-alumina supports were made by pressing α-alumina powder (A16, Alcoa) into disk shape under 150 MPa of hydraulic pressure, followed by sintering at 1150 °C for 30 h in programmable-temperature furnace. The alumina supports were polished sequentially by SiC polishing paper (Struers) #500, #800, and #1200, each for 5 min, after sintering. A stable YSZ suspension was made according to the procedures described by Kim and Lin [25]. YSZ powders (8-mol% Y_2O_3-stabilized ZrO_2) (TZ-8Y, Tosoh Co., Tokyo, Japan), mixed with dilute nitric acid (pH = 3–4) at a weight ratio of 1:2, were ball milled in polyethylene (PE) pots with ZrO_2 balls 0.5 mm in diameter. The suspension was treated ultrasonically to break up the agglomerates and was then ball milled for 7–10 days. After the ball-milling process, the YSZ suspension was diluted to 10 wt% by adding more dilute nitric acid.

Supported YSZ macroporous membranes were prepared by dip-coating a stable YSZ suspension on the α-alumina porous supports. Polyvinyl alcohol (PVA) was used as drying control chemical additive (DCCA) to prevent crack formation in the membranes during the drying step. PVA solution was prepared by dissolving 3 g of PVA (Fluka, MW = 72,000) in 95 mL water and 5 mL of 1 M nitric acid. The optimum amount of PVA solution to be added into the suspension was determined to be at a volume ratio of 1:4. The YSZ suspension with PVA was dip-coated on alumina supports and dip-coated disks were dried in air at a relative humidity (RH) of 50–60% and a temperature of 40 °C. After the drying process, the supported membrane was sintered in air at 1000 °C for 3 h with a heating and cooling rate of 100 °C/h. The dip-coating, drying, and sintering processes were repeated to ensure the preparation of crack-free supported YSZ macroporous membranes.

Sol preparation and YSZ mesoporous membrane synthesis

Mesoporous YSZ layer was coated on the macroporous YSZ/alumina supports, and for comparison on alumina supports, by the sol–gel method [21]. Stable 0.25 M zirconia sol was prepared by hydrolysis and condensation of 0.25 mol zirconium *n*-propoxide (Alfa, MW = 327.56) in a water (900 mL)/isopropanol (500 mL) solution. The white zirconia precipitates were filtered with vacuum suction and washed in water several times to remove the isopropanol. A small amount of water was added to help facilitate the filtering in the process. The filtered zirconia cake was diluted in 1L of water and peptized with 125 mL 1 M nitric acid at 90–100 °C overnight. The sol was ultrasonically treated for at least 30 min before it was used. A 0.07 M yttrium nitrate solution was made by mixing 2 g of $Y(NO_3)_3$ (Alfa) with 95 mL water and 5 mL 1 M nitric acid solution at 50 °C. The PVA solution was prepared using the same procedure as the one that was previously mentioned. Hydroxypropyl cellulose (HPC) (Aldrich, MW = 100,000) solution was prepared by dissolving 0.35 g powder in 95 mL water and 5 mL of 1 M nitric acid.

A solution-sol mixing method was used to coat the dopant on the grain surface of the zirconia membranes. The 0.07 M yttrium nitrate solution was mixed with the stable zirconia sol in a desired proportion to make 8 mol% YSZ. The optimum amount of DCCA at the specific concentration was found to be about 30% in volume of 0.25 M zirconia sol [21].The YSZ sol was made by mixing the zirconia sol, yttrium nitrate solution, and DCCA with an approximate volume ratio of 35:11:11. The concentration of yttria-doped zirconia sol with DCCA was 0.154 M. Unsupported YSZ mesoporous membranes were made by pouring the sol into petri-dishes. Supported membranes were made by dip-coating YSZ sol on α-alumina support and supported YSZ macroporous membranes previously synthesized, respectively. The membranes were dried at the same condition as the YSZ macroporous membranes. The membranes were calcined at 450 °C for 3 h with a heating and cooling rate of 0.5 °C/min. For the supported membranes, the procedure of coating, drying, and calcination was repeated to ensure the synthesis of crack-free membranes and formation of a membrane with the proper thickness. Some of the unsupported YSZ samples were heat treated at 700 °C 30 h.

Characterization

The surface area, pore volume, and pore size distribution of sol-gel derived YSZ powders were obtained from nitrogen ad(de)sorption isotherms using an adsorption porosimeter (Micrometrics, ASAP 2020). The phase structures of the membranes were identified by X-ray diffractometry (XRD) (Bruker AXS, D8 Focus Diffractometer) with Cu Kα radiation. The morphology and thickness of supported mesoporous and macroporous YSZ membranes were studied by examining the cross section and top layer of the membrane disks using scanning electron microscopy (SEM) equipment (Philips, FEI XL30 FEG). Helium permeation through the membrane was measured by a steady-state permeation setup shown in Fig. 1 to examine the quality of the membranes [27].

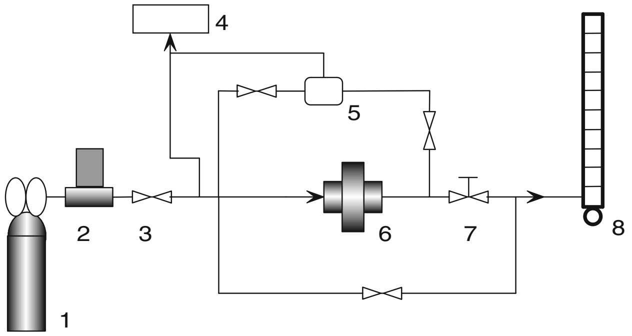

Fig. 1 Steady state helium permeation setup. (*1*) Helium cylinder, (*2*) mass flow controller, (3) valve, (*4*) pressure sensor, (*5*) gas reservoir, (*6*) permeation cell, (*7*) needle valve, (*8*) bubble flow meter

Results and discussion

Good quality, macroporous YSZ membranes were obtained by dip-coating the YSZ suspension on the α-alumina support, followed by drying and heat treatment. Figure 2 shows the SEM images of surface and cross section of a YSZ macroporous membrane on the alumina support prepared by dip-coating, drying, and calcination for 3 times. It can be seen that a crack-free and uniform YSZ layer, of about 20 μm in thickness, was formed. The cross sectional BE image shows a clear double layer structure in which the macroporous YSZ membrane can be distinguished from the α-alumina support due to the difference in the atomic weights. Figure 3 shows an XRD pattern of YSZ macroporous membrane prepared on an α-alumina support. Peaks assigned to the 111, 200, 220, 311, and 400 deflections correspond to cubic YSZ [26]. No XRD peaks for the alumina support can be seen due to the large thickness (at least 10 μm) of the YSZ layer.

Helium permeance data for the alumina support and for the supported macroporous YSZ membrane at different mean pressures cross the membrane are given in Fig. 4. Coating of the YSZ layer caused about 5% reduction in helium permeance. The helium permeance data for the alumina support can be correlated by straight line as [27, 28]

$$\frac{F}{L} = \alpha + \beta P_{\mathrm{av}} \quad (1)$$

Permeability coefficients α and β account for Knudsen flow and viscous flow, respectively, and can be used to calculate the pore radius of the membrane by:

$$r_{\mathrm{p}} = 8.47\mu \left(\frac{RT}{M}\right)^{1/2} \left(\frac{\beta}{\alpha}\right) \quad (2)$$

In these equations L is the disk thickness (m), M and μ are the molecular weight (kg/mol) and viscosity (kg/m/s) of the permeating gas (helium), and r_{p} is the average pore radius (m). The values for the permeation parameters obtained by linear regression and the pore size for the alumina support are given in Table 1.

The permeance for the supported YSZ layer was obtained from the flux data for the composite membrane (alumina support + YSZ layer) by the resistance-in-series model [27]. For a given helium flow through the composite membrane at Q_i with an upstream pressure of P_h on the surface of the YSZ side, the permeance for the YSZ top layer can be obtained by:

$$F_{\mathrm{t}} = \frac{Q_i}{S(P_{\mathrm{h}} - P_{\mathrm{m}})} \quad (3)$$

at the average pressure of $P_{\mathrm{av}} = (P_{\mathrm{h}} + P_{\mathrm{m}})/2$. Here P_{m} is obtained by:

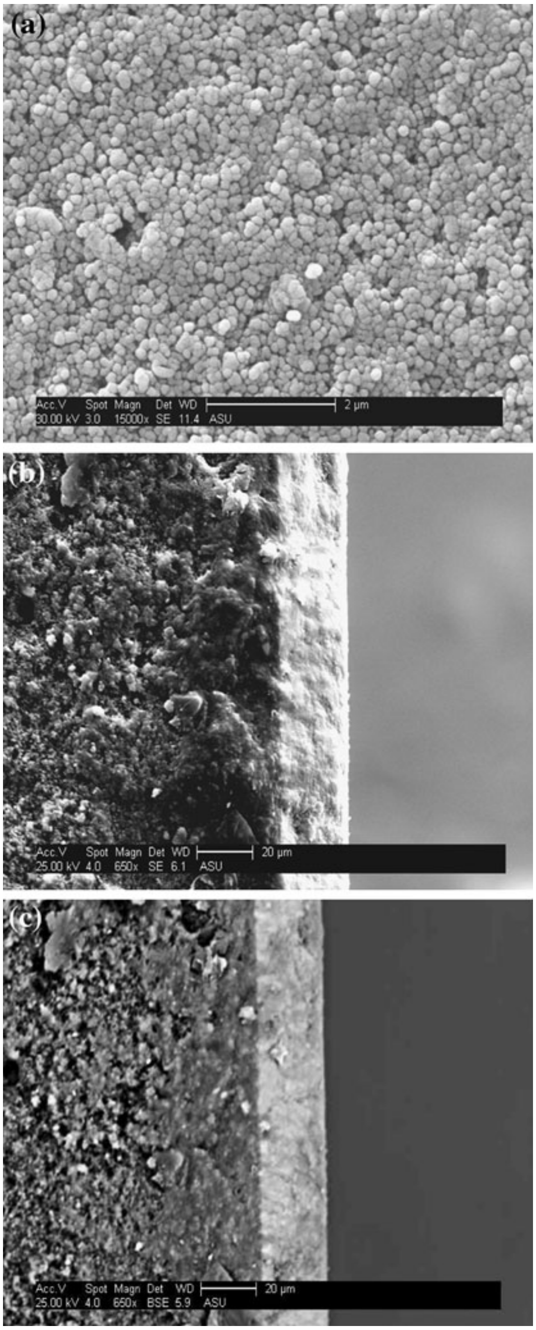

Fig. 2 SEM images of the surface (**a**) and cross section of YSZ macroporous membrane [**b** secondary-electron (SE) image and **c** backscattered-electron (BE) image]

$$P_{\mathrm{m}} = \frac{\sqrt{\alpha_{\mathrm{s}}^2 + 2\beta_{\mathrm{s}}\left(\frac{Q_i}{S} + \alpha_{\mathrm{s}} P_l + \frac{\beta_{\mathrm{s}}}{2} P_l^2\right)} - \alpha_{\mathrm{s}}}{\beta_s} \quad (4)$$

where the subscript “s” is for the properties for the support, P_l is the pressure on the downstream surface (alumina support surface), and S is the membrane permeation area. The results for the permeance for the YSZ top layer at various average pressures are plotted in Fig. 4b. As shown,

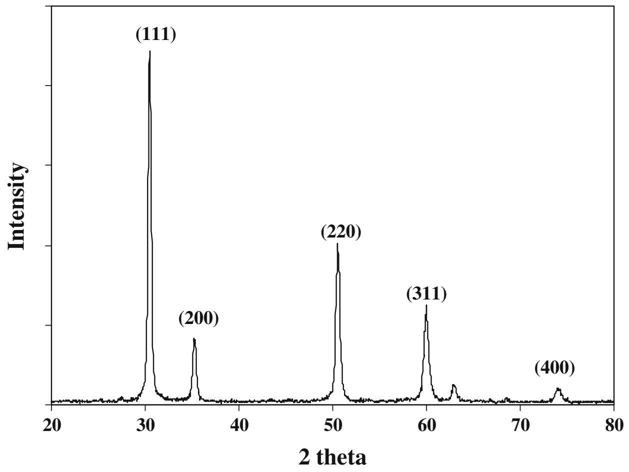

Fig. 3 XRD pattern of YSZ macroporous membrane supported by α-alumina support after 3 times dip-coating

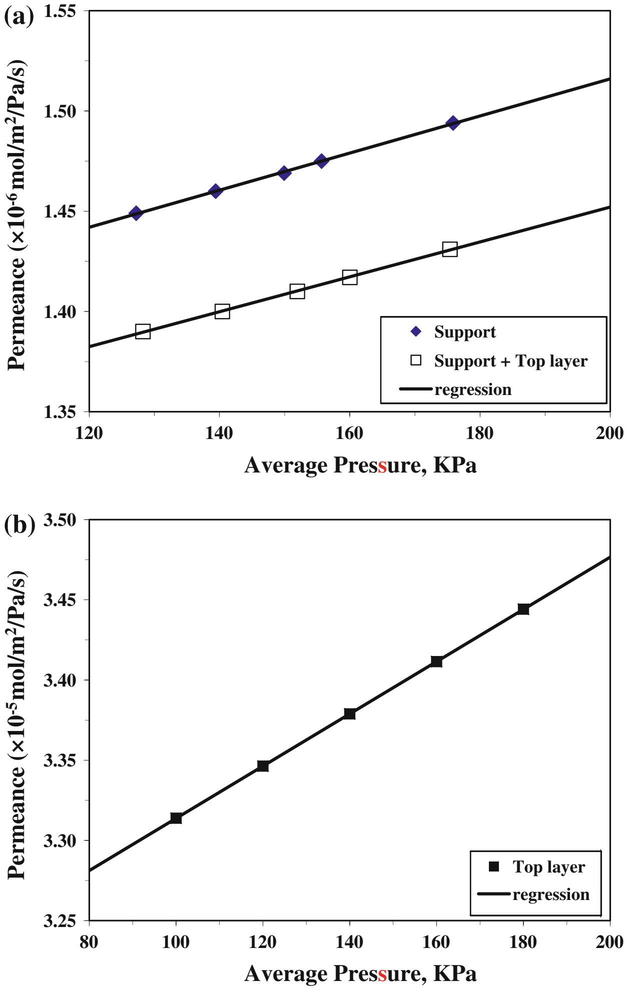

Fig. 4 Helium permeance versus average pressure of a supported YSZ macroporous membrane **a** support and YSZ top layer and **b** calculated top layer

Table 1 Values of α, β, and β/α for α-alumina support and 3 time-dip-coated top YSZ macroporous layer

Component	α (10^{-6} mol m^{-2} s^{-1} Pa^{-1})	β (10^{-12} mol m^{-2} s^{-1} Pa^{-2})	β/α (×10^{-6} Pa^{-1})	Calculated pore diameter (nm)
α-alumina support	1.332	0.92	0.69	180
YSZ top layer	31.51	14.29	0.45	116

the data can be correlated by a straightline, Eq. 1, with the values for the permeability coefficient for the YSZ top layer and the pore size calculated by Eq. 2 is given in Table 1. Average pore diameter calculated for YSZ macroporous membrane is about 116 nm which is in agreement with previously reported results [25]. The pore size of the macroporous YSZ layer is close to that of the alumina support. Therefore, it is suitable to coat mesoporous YSZ layer on the surface of the macroporous YSZ layer.

Stable zirconia sol was much more difficult to obtain [2] due to the extremely rapid reaction of zirconia alkoxide with water. The most important conditions for synthesis of zirconia sol include: (1) the dilution degree of the metal alkoxide, (2) the amount of water used for hydrolysis of the alkoxide, and (3) the peptization conditions. Kim and Lin [21] developed a promising method to make stable zirconia sol based on the conditions above and it was followed in this study. Environmental humidity was strictly controlled and steam formed during the experiment was removed to prevent the reaction between metal alkoxide and water.

Figure 5 shows pore size distribution (PSD) of unsupported mesoporous YSZ membranes after calcination at 450 °C for 3 h and after further heat treatment at 700 °C for 30 h. The PSD after calcination is rather narrow, but becomes much broader with an increased pore size after further heat treatment. The pore structure data of the YSZ mesoporous membrane are consistent with previous results [21] and are shown in Table 2. Figure 6 shows the XRD data of unsupported YSZ mesoporous membranes after calcination and further heat treatment. The peak positions

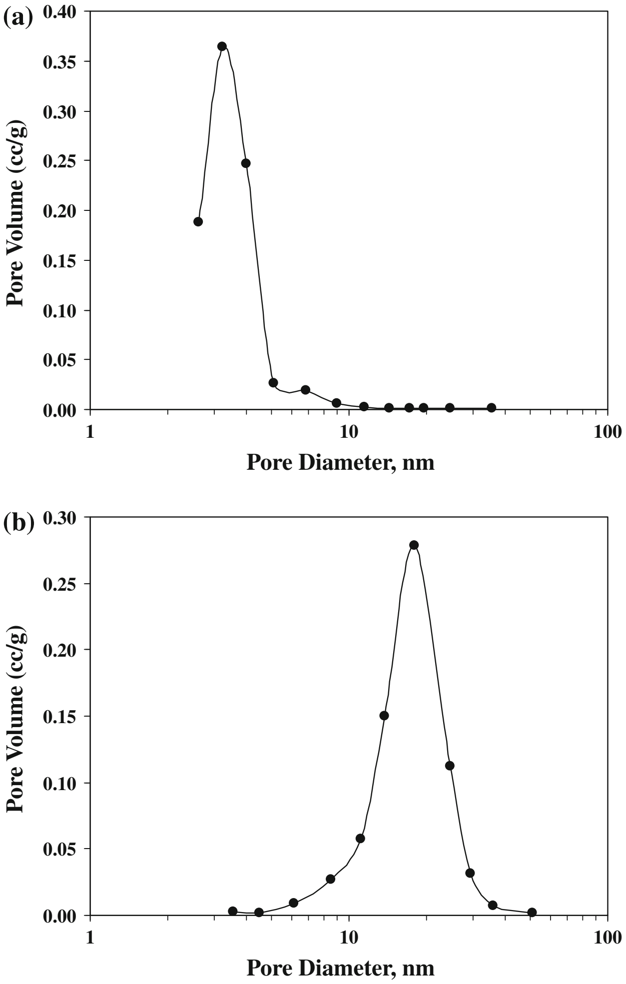

Fig. 5 Pore size distribution of unsupported YSZ sol membranes after calcination at 450 °C for 3 h (**a**) and after further heat treatment at 700 °C for 30 h (**b**)

Table 2 Pore structure data of YSZ membranes calcination at 450 °C for 3 h and after further heat treatment at 700 °C for 30 h

	After calcination	After sintering
Pore size (nm)	3.3	22.3
Surface area (m^2/g)	110.2	14.7
Pore volume (cc/g)	0.087	0.081

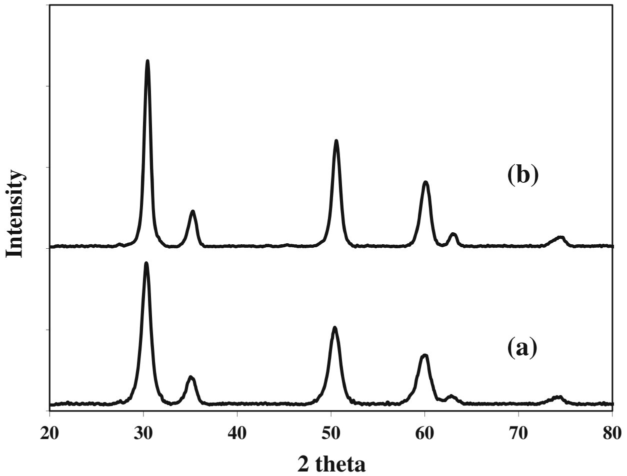

Fig. 6 XRD patterns of unsupported YSZ mesoporous membrane (*a*) after calcination at 450 °C for 3 h and (*b*) after further heat treatment at 700 °C for 30 h

of mesoporous YSZ membranes are consistent with those of macroporous YSZ membranes, showing a cubic structure.

Supported mesoporous YSZ membranes were first prepared by dip-coating the 0.154 M YSZ sol on supported macroporous YSZ membranes. The dip-coating, drying, and calcination steps were repeated several times to ensure the formation of YSZ layers of a proper thickness. There were, however, many cracks observed on the surface of the as-synthesized mesoporous YSZ membrane after three repetitions of the dip-coating, as shown in Fig. 7. From the figure, it is observed that the cracks are about 5–10 μm in length and 1–2 μm in width. The cracks form even on one-dip-coating layer. The cracks on the membrane are likely caused by the drying stress (σ_x) developed during the drying process. The larger the stress, the more likely cracks are to form. The drying stress on the membrane could be approximately fitted into equation as follows [28]:

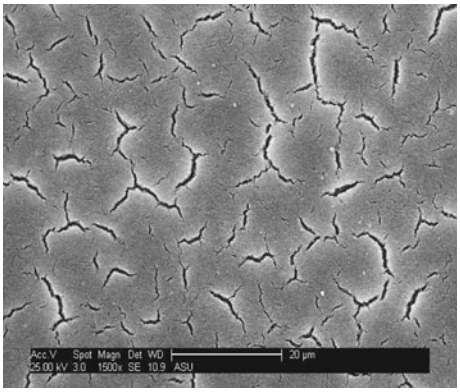

Fig. 7 SEM images of surface morphology of YSZ mesoporous membrane prepared with original 0.154 M sol on YSZ macroporous membrane after 3 times dip-coating

$$\sigma_x \approx L\eta_L \dot{V}_E / 3D \tag{5}$$

L is the thickness (m) of the membrane, η_L is the viscosity of the solvent (Pa s), $\dot{V}_E$ is drying rate (m/s), and D is the permeability of the membrane (m^2).

In this study, the membranes were dried in a humidity-controlled chamber at a relative humidity (RH) of 50–60% and a temperature of 40 °C. A further increase in humidity was not effective to prevent crack formation. The other effective way to reduce the stress is to decrease the membrane thickness and perform multiple dip-coating, drying, and calcination processes. The membrane thickness for each dip-coating is proportional to the sol concentration. In this study, the original 0.154 M YSZ sol was diluted to 0.026, 0.013, and 0.0087 M. Both PVA and HPC were studied as the DCCA to strengthen the gel structure and reduce the solvent viscosity. For comparison, mesoporous YSZ membranes were also prepared on macroporous alumina support as reported in our previous study [21]. Table 3 summarizes nine membrane samples prepared and the characteristics of these samples. For each sample, the dip-coating, drying, and calcination process was repeated by 5 times.

Figures 8 and 9 are surface and cross section SEM images of mesoporous YSZ membranes on YSZ macroporous membranes prepared from the sol with a concentration of 0.026, 0.013, and 0.0087 M, respectively, with PVA and HPC as DCCA. Comparing the surfaces in Fig. 8 with that in Fig. 7, it could be seen that crack formation was improved by virtue of the fact that the cracks

Table 3 Summary of the YSZ mesoporous membranes prepared and result observed and measured from SEM images

Sample no.	YSZ sol concentration (M)	Support	DCCA	Crack width range (μm) *L* length *W* width	Top layer thickness (μm)
1	0.026	YSZ macroporous membrane	PVA	*L*: 1–1.7 *W*: 0.16–0.34	3.35
2	0.013	YSZ macroporous membrane	PVA	*L*: 0.17–0.3 *W*: 0.09–0.16	1.35
3	0.0087	YSZ macroporous membrane	PVA	No cracks	1.02
4	0.026	YSZ macroporous membrane	HPC	*L*: 2–5 *W*: 0.5–1	3.33
5	0.013	YSZ macroporous membrane	HPC	*L*: 0.15–0.3 *W*: 0.1–0.15	1.37
6	0.0087	YSZ macroporous membrane	HPC	No cracks	1
7	0.026	Alumina support	PVA	*L*: 1–1.8 *W*: 0.15–0.36	3.5
8	0.013	Alumina support	PVA	*L*: 0.17–0.3 *W*: 0.1–0.21	1.4
9	0.0087	Alumina support	PVA	No cracks	1.1

decreased in size quite drastically after using the sol with a lower concentration. Cracks on the membranes prepared from 0.154 M sol were about 5–10 µm in length and 1–2 µm in width. Here, the cracks are just 1–1.7 µm in length and 0.16–0.34 µm in width for the membranes prepared from 0.026 M sol and about 0.17–0.3 µm in length and 0.09–0.16 µm in width for the membranes from 0.013 M sol. In some ways, it could be inferred that the size of cracks decreased reciprocally to the sol concentration. The membranes made from 0.0087 M sol are crack free. From Fig. 7b, d, and e, a clear triple-layer structure of the composite membrane can be observed. The top YSZ layers are about 3.35, 1.35, and 1.02 µm thick corresponding to 0.026, 0.013, and 0.0087 M. The thicknesses of the membranes decrease with a reduction of sol concentration, hence lessening the stresses and preventing crack formation. This is evident when the sol concentration is very low (0.0087 M) which led to the formation of a crack-free mesoporous YSZ membrane.

Comparing the cross sections shown in Fig. 9 (membranes prepared with HPC as DCCA) with those in Fig. 8 (PVA as DCCA), it was found that the film formations are

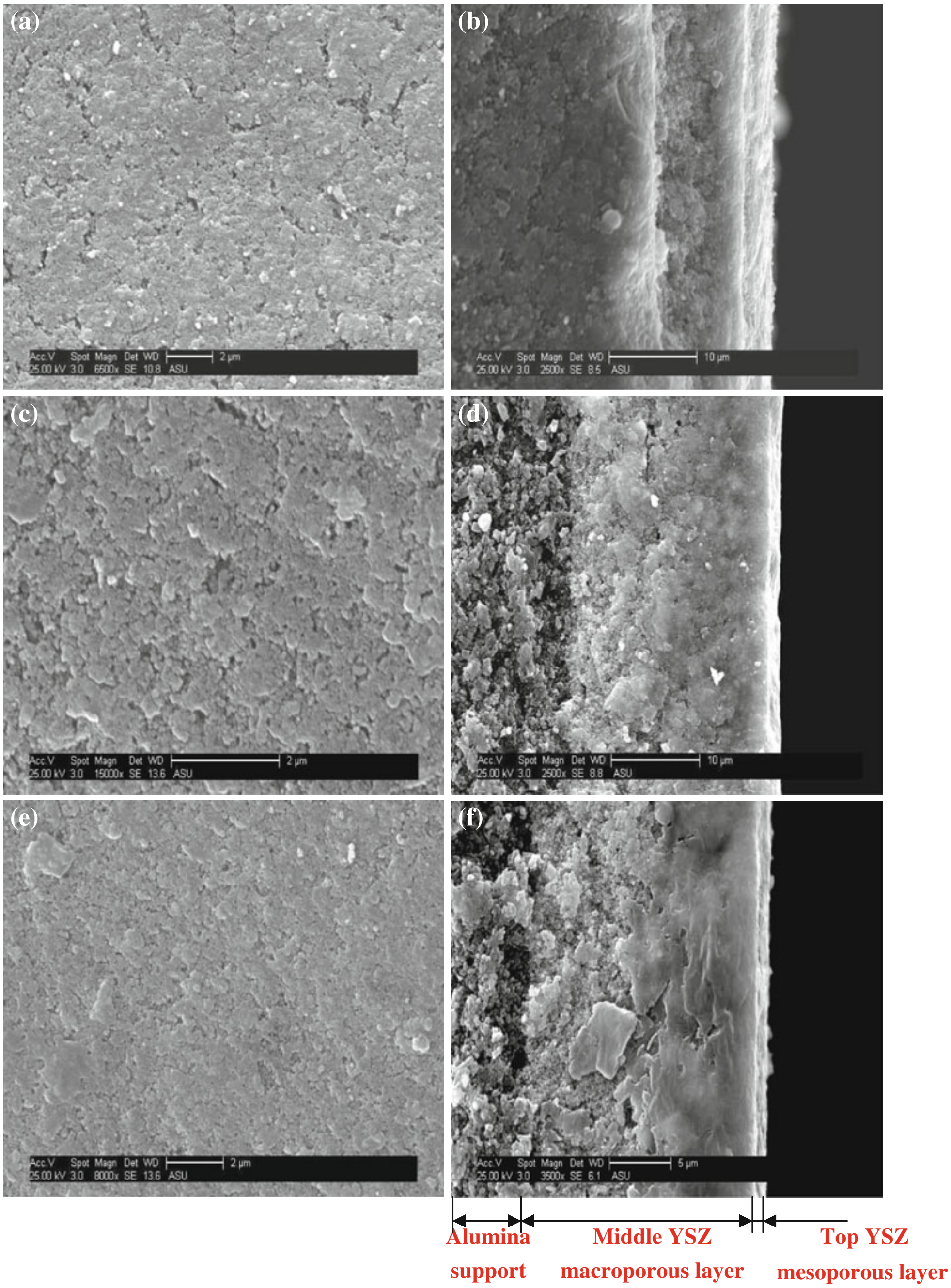

Fig. 8 SEM images of top surface and cross section of YSZ mesoporous membrane prepared on YSZ macroporous membrane with PVA after 5 times dip-coating by a sol concentration of 0.026 M (**a**, **b**), 0.013 M sol (**c**, **d**), and 0.0087 M (**e**, **f**)

very similar regardless of what DCCA is used. The membranes become thinner when the lower concentrations of sol are used. The thicknesses of the YSZ mesoporous membranes prepared with HPC are about 3.37, 1.33, and 1 μm, which are almost same as those obtained from the sol with PVA added. However, despite the similarity in thickness, differences in surface morphology can be distinguished from the SEM images. By comparing Figs. 9a and 8a, when the 0.026 M sol is used, the cracks on the sample with HPC are about 2–5 μm in length and 0.5–1 μm in width which are much larger than those on the membranes with PVA added as DCCA. It looks like the use of PVA is better than HPC in terms of limiting crack formation. When a lower concentration sol is used, crack formation is drastically improved for the sol with HPC and the quality of the membrane is very similar to that from the sol with PVA. When the concentration of the sol with HPC added is 0.013 M, the cracks are about 0.15–0.3 μm long and 0.1–0.15 μm wide. This size is smaller than those made from 0.026 M sol. Finally, when the concentration is

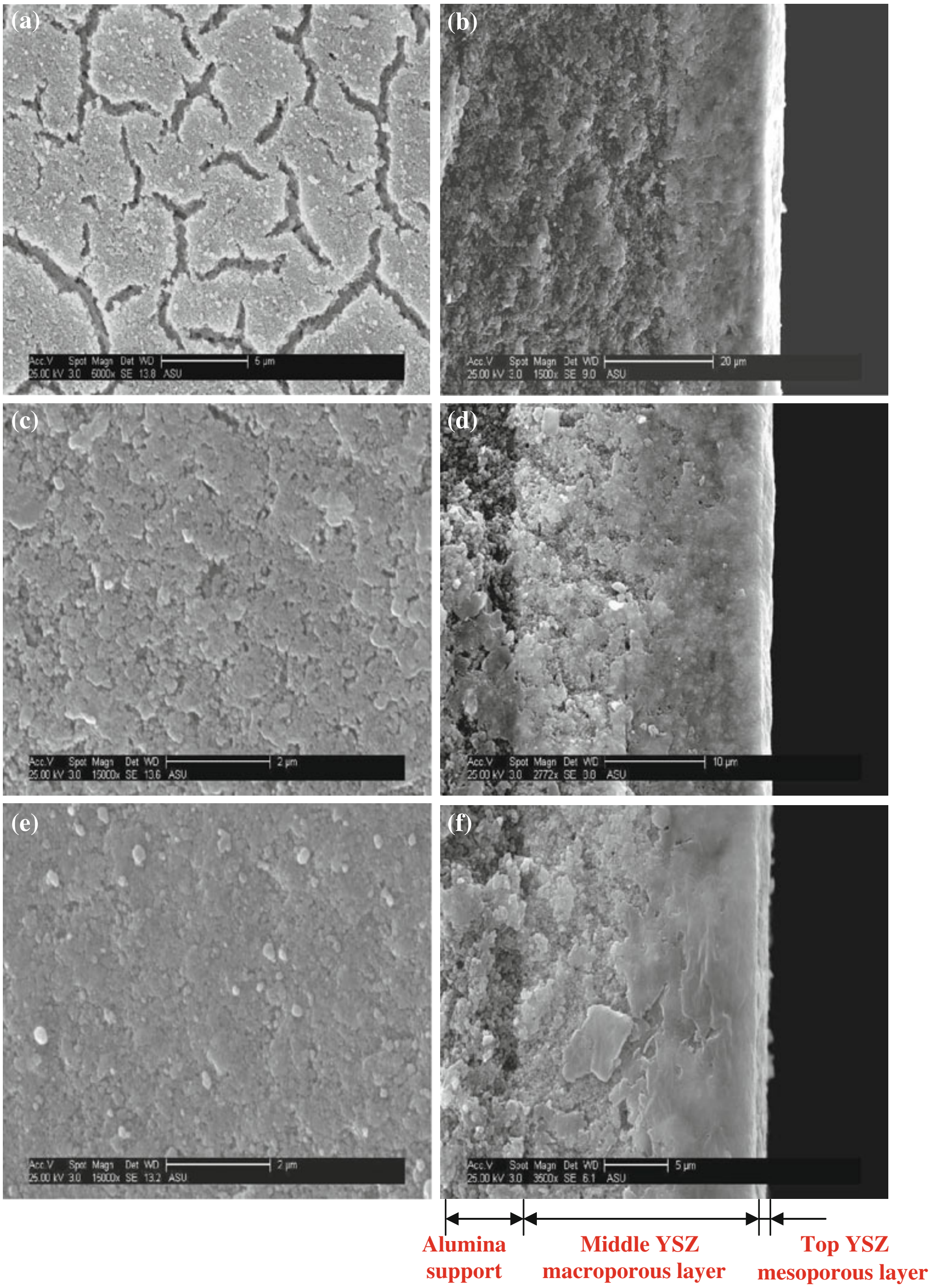

Fig. 9 SEM images of top surface and cross section of YSZ mesoporous membrane prepared on YSZ macroporous membrane with HPC after 5 times dip-coating by a sol concentration of 0.026 M (**a**, **b**), 0.013 M sol (**c**, **d**), and 0.0087 M (**e**, **f**)

0.0087 M with HPC, crack-free membranes could be obtained, as was also the case when PVA was used.

SEM images of mesoporous YSZ membranes directly prepared on alumina supports with PVA added are shown in Fig. 10a–f. Compared with Fig. 7, it can be seen that, with the same YSZ sol concentration used, the size of the cracks formed and the film thickness of the mesoporous YSZ membranes on macroporous YSZ membranes or alumina supports are almost same. This indicates that the difference in support properties does not influence the synthesis of mesoporous YSZ membranes, and that sol concentration remains the key factor in film preparation. The membrane prepared from 0.026 M YSZ sol on alumina support after 5 times dip-coating is around 3.5 µm, which is the same as that from our previous study [21]. However, the previous study showed that mesoporous YSZ

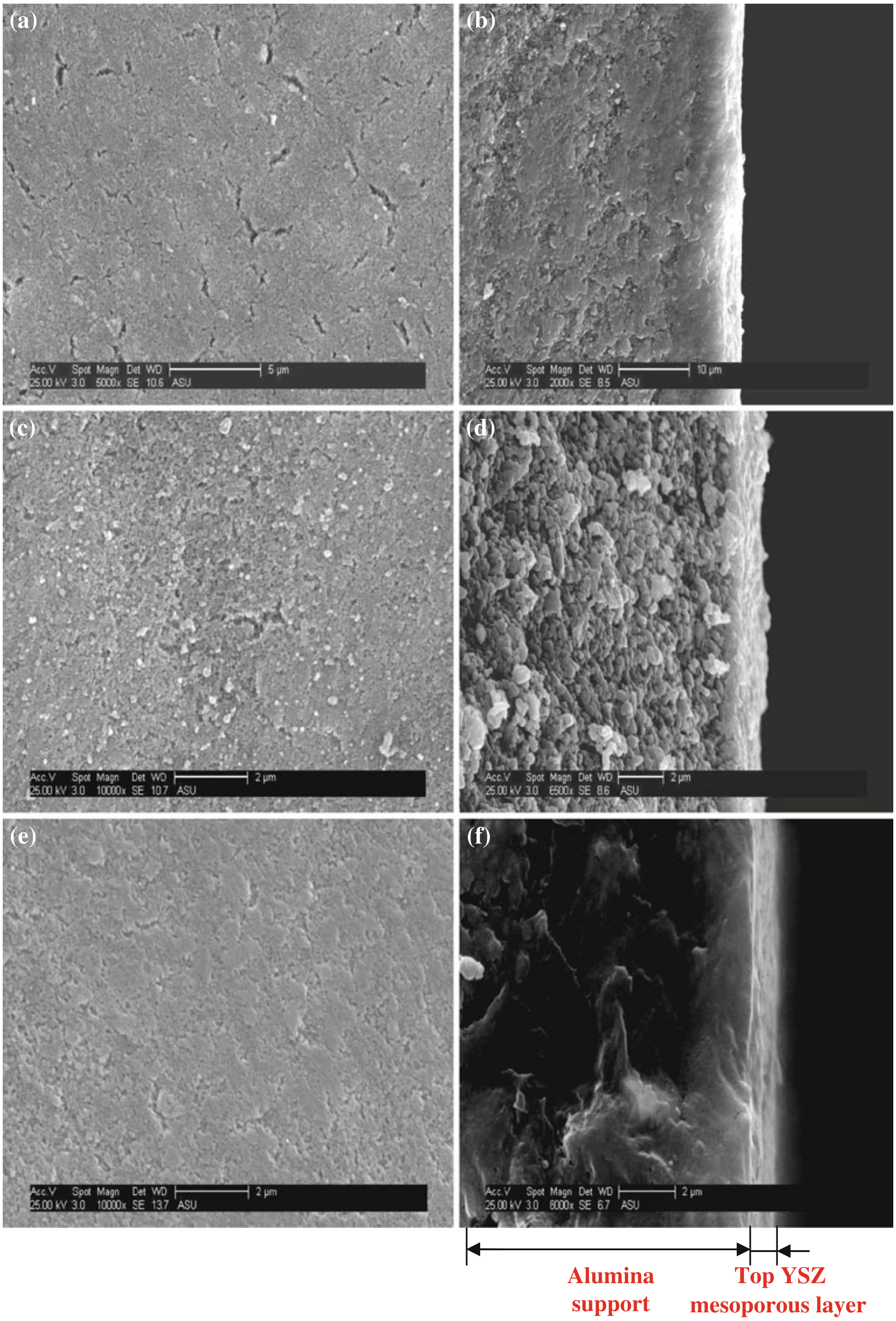

Fig. 10 SEM images of top surface and cross section of YSZ mesoporous membrane prepared on alumina support with PVA after 5 times dip-coating by a sol concentration of 0.026 M (**a**, **b**), 0.013 M sol (**c**, **d**), and 0.0087 M (**e**, **f**)

Table 4 Helium and nitrogen permeances through YSZ mesoporous membranes and gas separation ratio of the two gases

	Helium permeance P_{He} (10^{-6} mol m^{-2} s^{-1} Pa^{-1})	Nitrogen permeance P_{N_2} (10^{-6} mol m^{-2} s^{-1} Pa^{-1})	P_{He}/P_{N_2}
YSZ mesoporous membrane on alumina support	1.112	0.421	2.64
YSZ mesoporous membrane on YSZ macroporous membrane	1.085	0.408	2.66

membrane of this thickness on alumina support was crack-free. Although, in both studies drying was conducted in a humidity-controlled chamber, the dip-coating process was conducted in the air. The air humidity in the location of the previous study (Cincinnati, Ohio) is about 50–70%, much higher than that in the location of this study (Tempe, Arizona) (10–20%). The initial exposure of the dip-coated YSZ gel to the air of different humidity is the main reason for the different extent of cracks for the mesoporous YSZ membranes prepared in this and previous study. The results suggest a need to perform dip-coating in a humidity-controlled chamber in a relatively dry location if one wants to obtain crack-free thick membranes.

Gas permeation tests were done to check for the presence of the defects in the mesoporous YSZ membranes. Based on the PSD, the gas permeation mechanism through the mesoporous YSZ membrane should obey the rule of Knudsen flow. Consequently, gas separation factor should be equal to reciprocal of the square root of the molecular weight of the permeating gases. Helium and nitrogen permeation test were done through the crack-free mesoporous YSZ membrane prepared on YSZ macroporous membrane and alumina support. Gas permeance data and the calculated separation factors are shown in Table 4. The theoretical Knudsen separation factor of helium and nitrogen is 2.65. From Table 4, it is seen that the helium and nitrogen permeance through mesoporous YSZ membrane on alumina support is 1.112 and 0.421 (10^{-6} mol/m^2/Pa/s) with a separation ratio of 2.64. While for mesoporous YSZ membrane prepared on macroporous YSZ membrane, the permeances are 1.085 and 0.408 (10^{-6} mol/m^2/Pa/s) with a separation ratio of 2.66. For both membranes, the He/N_2 separation factor are approximately equal to the theoretical value, indicating the YSZ mesoporous membranes prepared on both supports are defect and pin-hole free.

Conclusions

High-quality, crack-free supported YSZ macroporous membranes were prepared from a stable suspension under optimum condition. The membrane prepared was of a cubic fluorite structure and average pore size was 116 nm measured by helium permeance test. Supported, crack-free, high-quality YSZ mesoporous membranes could be prepared from an YSZ sol with a lower concentration by dip-coating on supported YSZ macroporous membrane. The average pore size of the membrane was found to be about 3 nm, as measured by nitrogen adsorption porosimeter. The optimum concentration of the YSZ sol was determined to be 0.0087 M in this study. Concerning the use of the DCCA, there were no difference between using PVA and HPC on crack improvement and film formation of the YSZ membrane. At a relatively high concentration, PVA had a better effect on minimizing crack formation than HPC. Crack-free YSZ mesoporous membranes were around 1 μm thick after 5 times dip-coating. Crack-free YSZ mesoporous membranes were also prepared on alumina supports. The membrane properties were similar to those made on YSZ macroporous membranes and the quality of the membranes was not influenced by supports. Helium permeance experiments show Knudsen gas separation factor confirming that the supported YSZ mesoporous membranes are free of defects and pin-holes.

Acknowledgements The authors would like to acknowledge the support of NSF (CBET-0828146) and the DOE (DE-FE000470) on this project.

References

1. Bhave R (1991) Inorganic membranes synthesis, characteristics, and applications. Van Rostrnd Reinhold, New York
2. Chang CH, Gopalan R, Lin YS (1994) J Membr Sci 91:27
3. Gopalan R, Chang CH, Lin YS (1995) J Mater Sci 30:3075. doi:10.1007/BF01209219
4. Priyatham T, Bauri R (2010) Mater Charact 61:54
5. Mercera PDL, Ommen VJG, Doesburg EBM, Burggraaf AJ, Roos JRH (1991) Appl Catal 78:79
6. Birkby I, Stevens R (1996) Key Eng Mater 122:527
7. Minh NQ, Takahashi T (1995) Science and technology of ceramic fuel cells. Elsevier, Amsterdam
8. Hu LF, Wang CA, Huang Y (2010) J Mater Sci 45:3242. doi:10.1007/s10853-010-4331-9
9. Hu LF, Wang CA, Huang Y (2011) J Mater Sci 46:623. doi:10.1007/s10853-010-4783-y
10. Thery PY, Poulain M, Dupeux M, Braccini M (2009) J Mater Sci 44:1726. doi:10.1007/s10853-008-3108-x
11. Kueper TW, Visco SJ, Jonghe LCD (1992) Solid State Ion 52:251
12. Kanezashi M, O'Brien J, Lin YS (2007) Microporous Mesoporous Mater 103:302
13. Burggraaf AJ, Bouwmeester HJM, Boukamp BA, Uhihorn RJR, Zaspalis VT (1991) Science of ceramic interface. North-Holland, Amsterdam
14. Wen TL, Herbert V, Vilminot S, Bernier JC (1991) J Mater Sci 26:3787. doi:10.1007/BF01184972

15. Herbert V, His C, Guille J, Vilmiont S, Wen TL (1991) J Mater Sci 26:5184. doi:10.1007/BF01143211
16. Okubo T, Nagamoto H (1995) J Mater Sci 30:749. doi: 10.1007/BF00356338
17. Kuo CW, Lee YH, Hung IM, Wang MC, Wen SB, Fung KZ, Shih CJ (2008) J Alloys Compd 453:470
18. Farhikhten S, Maghsoudipour A, Raissi B (2010) J Alloys Compd 491:402
19. Heshmatpour F, Aghakhanpour RB (2011) Powder Technol 205:193
20. Okubo T, Takahashi T, Sakadata M, Nagamoto H (1996) J Membr Sci 118:151
21. Kim J, Lin YS (1998) J Membr Sci 139:75
22. Changrong X, Huaqiang C, Hong W, Pinghua Y, Guangyao M, Dingkun P (1999) J Membr Sci 162:181
23. Lin YS, Kim J (2000) Ind Eng Chem Res 39:2124
24. Anderson M, Lin YS (2010) J Membr Sci 357:122
25. Kim J, Lin YS (1999) J Am Ceram Soc 82:2641
26. Garcia G, Figueras A, Casado J, Llibre J, Mokchah M, Petot-ervas G, Calderer J (1998) Thin Solid Films 317:241
27. Lin YS, Burggraaf AJ (1993) J Membr Sci 79:65
28. Scherer GW, Brinker CJ (eds) (1990) Sol–gel science. Academic Press, Boston