Synthesis and hydrogen permeation properties of membranes based on dense SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$ thin films

Satoshi Hamakawa$^1$, Lin Li, Anwu Li, Enrique Iglesia*

Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720-1462, USA
Division of Materials Sciences, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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Abstract

Dense SrZr$_{0.95}$Y$_{0.05}$O$_{3-x}$ and SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$ thin films with perovskite structure were prepared on porous SrZr$_{0.95}$Y$_{0.05}$O$_{3-x}$ substrates by spin coating colloidal suspensions of powders prepared by combustion methods. Porous substrates were prepared by treating carbon/SrZr$_{0.95}$Y$_{0.05}$O$_{3-x}$ composites in air at 1273–1573 K in order to combust the carbon and partially sinter the resulting porous oxide. This procedure led to strong porous solids with a high gas permeability. Matching the shrinkage of the porous substrate and of the thin film by this pre-sintering of the porous substrate led to thin films free of fissures and other defects. Thin films prepared by these methods did not transport He at ambient temperature or N$_2$ at 900–1000 K. H$_2$ permeation rates through SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$ thin films at 950 K were as high as 500 times larger than on 1-mm disks and reached values of $6 \times 10^{-4}$ mol H$_2$/cm$^2$ min for 2 $\mu$m films. H$_2$ permeation rates were proportional to the inverse of the membrane thickness, indicating that permeation in SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$ thin films is controlled by bulk diffusion and not by H$_2$ dissociative chemisorption or by boundary layer transport, even for 2 $\mu$m films. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$; Hydrogen permeation; Thin films

1. Introduction

High-temperature proton conductors based on mixed oxides with perovskite structures have attracted considerable attention. Early studies focused on exploratory development of new compositions and on their characterization by total conductivity measurements in various environments [1–5]. More recent reports have included hydrogen permeation measurements, which are critical in order to assess the function of these materials as hydrogen-permeable membranes [6,7]. Proton conduction through dense solids involves migration through the crystalline oxide lattice. Selective H$_2$ permeation requires a low diffusivity of lattice oxygen, which is normally associated with electronic insulators [8] that cannot be used for proton transport in open circuit modes because of the additional requirement for electron or hole conduction through the solid. The requirement of low oxygen conductivity also requires that proton conduction occur at practical rates at relatively low temperatures (< 1100 K).

Significant advances in the proton conductivity have been brought forth by the development of doped...
perovskite structures, but permeation rates remain unattractive for non-electrochemical removal of H₂ from dilute streams. Typically, these materials are used as 1–2 mm thick disks or as tubes with thick walls (>2 mm). Permeation rates are inversely proportional to the thickness of the membrane when permeation across the membrane is controlled by transport through the solid phase and not by boundary layer transport or by the activation of H₂ at membrane surfaces. Therefore, membranes consisting of dense films supported on porous substrates should lead to much higher permeation rates than the larger structures currently used. Several methods have been used for the synthesis of ion-conducting oxides as thin films, but most previous studies focused on structural characterization or conductivity measurements, without detailed measurements of permeation rates.

Itoh et al. [9] prepared Ca(Ti,Fe)O₃ thin films by spin-coating Ca(Ti,Fe)O₃ powders dispersed in isopropanol onto CaTiO₃ porous substrates, and subsequently treating these composites at 1473–1573 K in air for 2 h to form 20–50 µm thin films impermeable to N₂. The O₂ permeation rates of 1–6 × 10⁻⁷ mol/cm² min at 1273 K were significantly higher than for disks of identical composition. Visco et al. [10] coated NiO–YSZ substrates with colloidal suspensions of yttria-stabilized zirconia (YSZ) powders prepared by glycine–nitrate methods. Dense YSZ thin films (4–10 µm) were obtained after treatment in air at 1673 K for 1 h. Fissures and cracks were minimized by partial shrinkage of a nonporous mechanical support in order to match its subsequent shrinkage with that of the coated powders. The NiO-based supports were nonporous during film deposition, but became porous (and electrically conducting) by subsequent reduction of the NiO. Eschenbaum et al. [11] prepared SrZr₀.₉₅Yb₀.₀₅O₃₋ₓ thin films on nonporous silicon substrates by depositing a precursor formed via sol–gel methods, treating the composites in air at 873 K in order to remove organic residues, and then sintering at 973–1273 K. X-ray diffraction measurements detected crystalline SrZrO₃. Scanning electron micrographs revealed highly irregular defective films with a high density of fissures. Kosaki and Anderson [12] prepared SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ thin films with perovskite structure (~1 µm) on dense silicon or Al₂O₃ substrates using a polymer precursor method. Only the structure and electrical conductivity of the films were reported. The higher total conductivity of the films compared with dense polycrystalline SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ disks was attributed to smaller grains in the thin films than in the larger dense structures.

Here, we describe procedures for the synthesis of nonporous SrZr₀.₉₅Y₀.₀₅O₃₋ₓ and SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ thin films prepared on porous substrates by spin coating colloidal suspensions of powders prepared by combustion methods. We also describe methods for the synthesis and partial sintering of perovskite substrates with high porosity and for the deposition and densification of thin films. The structure and H₂ permeation properties of these dense films were determined by scanning electron microscopy and high-temperature permeation measurements, respectively. Films with 2–140 µm thickness led to H₂ permeation rates up to 500 times greater than for 1 mm disks of identical composition.

2. Experimental

2.1. Synthesis of dense films and disks and of porous supports

Combustion methods were used in order to prepare SrZr₀.₉₅Y₀.₀₅O₃₋ₓ and SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ precursor powders. Glycolic acid and citric acid were used as complexing agents and fuels for the synthesis of SrZr₀.₉₅Y₀.₀₅O₃₋ₓ and SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ powders, respectively. The powders were treated in ambient air at 0.0825 K/s to 1273 K for 2 h. X-ray diffraction detected the expected perovskite structures in all powders. Detailed synthesis procedures have been reported previously [13,14]. A dense SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ disk (1 mm thickness) was prepared by treating powders compacted at ~120 MPa in a 2.5 cm die for 10 h at 1873 K in ambient air.

Porous disks with SrZr₀.₉₅Y₀.₀₅O₃₋ₓ composition and perovskite structure were used to support dense films of both SrZr₀.₉₅Y₀.₀₅O₃₋ₓ and SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ. These porous substrates showed good mechanical integrity and stability in both oxidizing and reducing environments. They remained porous even after treatment at 1873 K in ambient air, a procedure required in order to densify the perovskite powders coated onto their surfaces into dense films. These films and substrates remained intact in H₂ (1 bar) at 1073 K. Porous substrates were prepared by ultra-
sonically dispersing SrZr_{0.95}Y_{0.05}O_{3-\delta} powders and carbon black (Fisher) in isopropanol for 0.5–1.0 h. The slurry was filtered, dried in ambient air at \sim 300 K, and then the SrZr_{0.95}Y_{0.05}O_{3-\delta} powders (1.6 g) were compacted at \sim 120 MPa using a 2.5 cm die. These disks were partially sintered in ambient air and the carbon black combusted by heating in flowing ambient air at a slow ramping rate (0.033 K/s) in order to avoid cracking. The carbon black content and the sintering temperature of the carbon-perovskite composites were varied in order to determine conditions that accurately matched the shrinkage profile of the porous substrates with that of the deposited perovskite films during the final sintering of the composite membrane, as discussed in detail below.

The synthesis of thin films involved grinding of oxide powders (SrZr_{0.95}Y_{0.05}O_{3-\delta} or SrCe_{0.95}Yb_{0.05}O_{3-\delta}, 2–5 wt.%) in a mortar and pestle for 30 min and ultrasonically dispersing these powders as an isopropanol slurry for 1 h in order to break up loose agglomerates and to form a homogeneous dispersion. About 1 cm\textsuperscript{3} of the colloidal dispersion was added dropwise onto a pre-sintered porous substrate as the porous substrate rotated at 30–50 Hz. After each coating step, the sample was dried in ambient air at room temperature for 1 h. After three coatings, the membrane was partially sintered in ambient air at the same heating rate and final pre-sintering temperature and time used for the synthesis of the substrate. This was done in order to prevent the development of cumulative stresses during sequential coating steps. The coating–drying–sintering cycles, which can be used to deposit \sim 2 \mu m films during each cycle, were repeated several times in order to vary the film thickness. After coating, the film–substrate composite was treated in Ar (7 kPa) by increasing the temperature to 1873 K at 0.033 K/s and holding for 2 h. The composite was cooled to ambient temperature at a slow rate (0.067 K/s) in order to prevent thermal stresses, which tend to develop during rapid or nonuniform cooling. The samples were then treated at 1273 K for 2 h in ambient air in order to replace any lattice oxygen atoms removed during the Ar treatment and to restore the stoichiometric perovskite composition. The synthesis procedure is shown schematically in Fig. 1.

2.2. Characterization of the structure and permeation properties of thin films and porous substrates

The permeability of the porous substrates and the integrity of the dense films were examined at ambient temperature by sealing the edges of the substrates and

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**Synthesis of porous supports**

- ultrasonically mixing of powder with carbon black (10–25wt%)
  - uniaxially pressing of disks 120MPa
  - partial sintering of substrates at 1273–1573 K, 2 h, 0.033 K/s

**Synthesis of thin films**

- ultrasonically mixing of powder with isopropanol 60 min
  - spin coating of suspension onto substrate for 3 times (drying at room temperature for 60 min between each coating), 3000 rpm
  - drying in flowing ambient air at 1273–1573 K for 2 h, 0.033 K/s
  - sintering at 1873 K for 2 h in Ar 0.033 K/s
  - pre-treatment at 1273 K for 2 h in ambient air 0.033 K/s

Fig. 1. Procedures for the synthesis of porous substrates and thin films.
composites using O-rings and a silicone sealant. Helium permeation rates through either the porous substrates, to measure their permeability, or through the composites, to confirm their dense nature, were obtained using a bubble meter at various pressure differences across the materials (50–350 kPa). The shrinkage rates of these porous substrates were determined by measuring the diameter of the disk before and after thermal treatments. A dual-stage ISI-DS130C scanning electron microscope (SEM) was used to examine the morphology of the substrates and the composites, as well as the thickness of the top layer. The perovskite structure was confirmed by X-ray diffraction using a Siemens Diffractometer D5000 and Cu Kα radiation.

The H₂ flux through SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ films was measured using a high-temperature permeation apparatus. Gas flow rates were metered using electronic mass flow controllers in both sides of the membrane (Porter). The membrane disk was held between two alumina tubes and sealed with a glass ring that softens at 873 K. One side of the membrane (upstream) was exposed to H₂ (99.99%) diluted to the desired concentration using He (99.999%) or N₂ (99.999%). The other side (downstream) was swept with N₂/O₂ and He, as a sweep gas. The flow rates of upstream and downstream gases were 50 and 60 cm³/min, respectively. When the permeate side was swept with He or N₂, a make-up O₂ stream (10 ml/min) was introduced downstream of the membrane module and of the mass spectrometer sampling point in order to convert H₂ to water using a Pt mesh (Alfa Aesar, 100 mesh) at 973 K. H₂ permeation rates through the membrane were measured using a mass spectrometer (Transpector, Leybold-Inficon) to analyze the permeate stream and confirmed by a humidity meter (HMI 38, Vaisala).

3. Results and discussions

3.1. Synthesis of porous substrates

The synthesis variables that influence the porosity and permeability of the porous substrates were systematically examined in order to obtain strong and stable substrates and to match their shrinkage profiles with those of the dense top layer. These variables included the carbon content in the composites, the temperature of the thermal treatment in ambient air, and the pressure used in order to compact the perovskite–carbon composite.

The amount of carbon, the time held at the maximum sintering temperature, and the heating rate influenced the permeability of the porous support. Fig. 2 shows the results of permeation measurements at ambient temperature on porous substrates obtained by varying these three variables. These substrates were prepared as described in Section 2.2, but sintered to 1873 K in order to simulate the treatment that would be ultimately required to form thin films from powders coated on their surfaces. The permeability of the porous substrate increased as the amount of carbon black (Fig. 2a) or the heating rate increased (Fig. 2c). It decreased with increasing holding time at the maximum temperature (Fig. 2b).

The porosity of these substrates arises from voids created by the combustion of carbon black. Therefore, higher carbon black concentrations lead to larger void fractions in SrZr₀.₉₅Y₀.₀₅O₃₋ₓ substrate and to higher permeation rates. The heating rate and the time held at the highest sintering temperature also influence the extent of densification; the pore volume and the average pore size decrease as densification occurs. The temperature at which powder precursors were treated before pressing into disks and the extent of mixing between SrZr₀.₉₅Y₀.₀₅O₃₋ₓ and carbon black (with or without ultrasonic mixing) also influenced porosity and permeation rates. Higher treatment temperatures before pressing increased the particle size of the oxide component, which led to larger voids between perovskite crystallites and to slower densification. The elimination of the ultrasonic dispersion step led to larger pores because the composite material contained much larger carbon and oxide agglomerates. The flexibility introduced by the systematic control of these variables confirmed that porous substrates with a wide range of morphologies, permeation rates, and mechanical strength can be prepared in order to match the densification requirements of films with a wide compositional range.

The initial partial sintering of the substrate before film deposition is required in order to (1) ensure the formation of solid bridges between the particles, required for structural integrity and mechanical strength, (2) decompose the carbon black precursors and form the required voids, and (3) match the shrinkage of the
substrate to that of the thin film. Substrates partially sintered above 1273 K were sufficiently strong for spin coating procedures. The combustion of the carbon black must occur before deposition of thin films in order to avoid the significant temperature gradients and the rapid gas evolution caused by this combustion step, which can lead to nonuniform densification of the films and to the formation of fissures or defects. Temperature-programmed oxidation studies showed that the carbon component mixed with SrZr0.95Y0.05O3−x oxidizes to CO2 at ~ 970 K. Thus, pre-sintering in air at 1273 K is sufficient to achieve the required strength and to create the porosity resulting from the combustion of the carbon component.

Large differences between the densification rates of the thin films and of the porous substrates lead to fissures and defects, which were easily detected by optical microscopy and by high He permeation rates at ambient temperature through the film–substrate composites. Fig. 3 shows that significant densification of the porous substrate (34% vol.) occurs between 1473 and 1873 K. Thin films deposited on this porous substrate must shrink to similar extents when treated at 1873 K in order to form dense and defect-free thin films with good adherence to the porous substrate. There is no method to measure directly and during synthesis the shrinkage rate of the thin films in order to accurately match that of the substrate as it is heated from the pre-sintering temperature (1273 K) to the final temperature required to form dense films (1873 K). The relative shrinkage rates of the thin films and the substrates can be inferred after sintering, however, by inspection of the curvature of the film–substrate composites. Concave film surfaces indicate that the thin film densified faster than the porous substrate, while a convex film surface reflects the faster densification of the porous substrate. The pre-sintering of the porous SrZr0.95Y0.05O3−x substrates at 1273–1573 K before film deposition slows down the subsequent densification of these substrates during subsequent treatment of

Fig. 2. Helium flux through porous substrates at ambient temperature as a function of the pressure difference across the disk. Permeate side at ambient pressure. (a) Effect of carbon black content, heating rate: 0.0167 K/s to 1873 K, holding time 2 h. (b) Effect of holding time at 1873 K, carbon black: 25 wt.%, heating rate: 0.0167 K/s. (c) Effect of the heating rate to 1873 K, carbon black: 25 wt.%, 2-h holding time at 1873 K.
the film–substrate composites at 1873 K and leads to the coincident shrinkage of the two layers and to flat film–substrate composites.

The extent of densification of the porous substrate can also be controlled by varying the compaction pressure used to form the carbon–perovskite precursors. Fig. 4 shows that the extent of densification after treatment at 1873 K in air for 2 h decreased from 35% to 30% as the compaction pressure increased from 50 to 200 MPa. These effects are small compared with those achieved by varying the pre-sintering temperature. Therefore, compaction pressures were used only to fine-tune the density of the porous substrates before film deposition. This compaction pressure influences the initial void volume of carbon-containing disks which leads to variations in the residual void volume after sintering. As reported previously, more extensive compaction of the perovskite–carbon composite leads to smaller losses in pore volume during subsequent thermal treatment [14].

3.2. Synthesis and structure of thin films supported on porous substrates

Based on the densification behavior of the porous substrates and the films, SrZr$_{0.95}$Y$_{0.05}$O$_{3-x}$ and SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$ thin films were successfully prepared by spin coating powders synthesized via combustion methods onto pre-sintered porous substrates. SrZr$_{0.95}$Y$_{0.05}$O$_{3-x}$ powders were used to prepare the porous substrates for both film compositions, because SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$ formed much weaker porous disks. Substrate synthesis and treatment conditions must be tailored for each film layer material in order to match the shrinkage characteristics of the corresponding film. Table 1 shows the procedures used for the synthesis of the porous substrates in each case. For SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$ films, lower carbon contents and higher pre-sintering temperatures were required.

![Fig. 3. Effect of sintering temperature on the shrinkage of porous substrates. Carbon black: 25 wt.%, heating rate: 0.0825 K/s, 2 h holding time at final temperature.](image1)

![Fig. 4. Effect of compaction pressure on the shrinkage of porous substrates. Carbon black: 25 wt.%, heating rate: 0.0825 K/s, 2 h holding time at 1873 K.](image2)

<table>
<thead>
<tr>
<th>Composition of film</th>
<th>SrZr$<em>{0.95}$Y$</em>{0.05}$O$_{3-x}$</th>
<th>SrCe$<em>{0.95}$Yb$</em>{0.05}$O$_{3-x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black (wt.%)</td>
<td>25</td>
<td>10 or 20</td>
</tr>
<tr>
<td>Pressing pressure (MPa)</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Pre-sintering protocols</td>
<td>0.0167 K/s to 1273 K in flowing ambient air and 2-h hold</td>
<td>0.033 K/s to 1573 K in flowing ambient air and 2-h hold</td>
</tr>
</tbody>
</table>
because the shrinkage for SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ films was significantly less than for SrZr₀.₉₅Y₀.₀₅O₃₋ₓ films.

Scanning electron micrographs of representative SrZr₀.₉₅Y₀.₀₅O₃₋ₓ thin films on porous substrates are shown in Fig. 5. The micrograph shown in Fig. 5 is that of a 20 μm film prepared by nine coatings of SrZr₀.₉₅Y₀.₀₅O₃₋ₓ (Table 2). This film shows excellent adhesion to the substrate and no detectable porosity or surface imperfections. Room temperature permeation tests showed that this material was impermeable to He at ambient temperature and 200 kPa. The successful synthesis of nonporous thin films by partial sintering of porous substrates suggests that the spin coating procedures used were able to deposit powder precursors uniformly on the porous substrate surfaces.

Dense top layers of SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ (80–140 μm) prepared by the method described in Table 2 are evident from the micrographs in Fig. 6b,c. The structure of the film in Fig. 6a differed from those in the other two samples shown. The total thickness of the SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ top layer was about 20 μm, but all but the lowest 2 μm showed a structure with large pores, with a dense 2 μm film at the interface between the SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ top layer and the SrZr₀.₉₅Y₀.₀₅O₃₋ₓ porous substrate. Thus, the perme-

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**Table 2**

<table>
<thead>
<tr>
<th>Top layer</th>
<th>SrZr₀.₉₅Y₀.₀₅O₃₋ₓ</th>
<th>SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (μm)</td>
<td>20</td>
<td>(a) 2, (b) 80, (c) 140</td>
</tr>
<tr>
<td>Spin coating cycles</td>
<td>9</td>
<td>(a) 9, (b) 6, (c) 9</td>
</tr>
<tr>
<td>Final sintering protocols</td>
<td>0.033 K/s to 1873 K in flowing ambient air, hold for 2 h and quench to room temperature; (b,c) 0.033 K/s to 1873 K in flowing Ar, hold for 2 h and 0.067 K/s to room temperature and then treatment by ambient air (air treatment) at 1273 K for 2 h</td>
<td></td>
</tr>
</tbody>
</table>
The H₂ permeation properties of these materials are likely to reflect the thickness of this thin film, as confirmed by the H₂ permeation data shown in the next section. The reasons for the unusual structure of the material in Fig. 6a remain unclear at this time.

3.3. H₂ permeation rates in SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ thin films

The H₂ flux through a 1 mm SrZr₀.₉₅Y₀.₀₅O₃₋ₓ disk at 973 K and 200 kPa H₂ was smaller than 10⁻⁸
mol/cm² min. H₂ transport in this open circuit non-electrochemical mode requires mixed conduction (protons and electrons or holes) and the permeability of one or both of these charge carriers appears to be very low in SrZr₀.₉₅Y₀.₀₅O₃₋ₓ; as a result, it is not an attractive material for H₂ separations. SrZr₀.₉₅Y₀.₀₅O₃₋ₓ materials may be useful, however, as gas sensors or as fuel cell electrolytes, for which only one of the two charge carriers must diffuse, but even as thin films, their permeabilities are too low for accurate measurements.

At similar conditions, the H₂ flux through a 1 mm SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ disk is more than 10 times greater than for SrZr₀.₉₅Y₀.₀₅O₃₋ₓ, making the SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ a more attractive choice for the permeation improvements expected by using thin films. Therefore, only H₂ permeation rates on SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ films are reported below. Fig. 7 shows H₂ permeation rates at 950 K for SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ thin films of varying thickness as a function of H₂ pressure. Permeation rates increased with increasing H₂ pressure and with decreasing thickness of the dense perovskite layer (Fig. 7). The film with a 2 μm dense layer showed a H₂ flux ~ 500 times greater than the 1 mm disk at each H₂ partial pressure. The nonporous nature of the films was confirmed by using N₂ as the diluent in the H₂ stream and ensuring that N₂ concentrations remained below the detection limit in the permeate side.

Fig. 8 shows the ion yields for H₂ (2 amu) and N₂ (28 amu) in the permeate side with concurrent changes in the H₂ and N₂ partial pressures (0 – 100 kPa) in the process side (80 μm SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ films; 950 K).

Permeation rates through dense ceramic membranes depend on the mobility of charge carriers in the mixed conductors [6–8]. Occasionally, they also depend on the rate of diffusion of the permeating species through a porous substrate or a gaseous boundary layer and on the rate at which molecules, such as H₂, dissociate at membrane surfaces to form atomic hydrogen. When permeation is not controlled by diffusion through the solid, permeation rates become independent of the
thickness of the dense conductor. This is likely to occur as materials become thinner and total permeation rates increase. In order to clarify the mechanism of hydrogen permeation with mixed conduction in SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ thin films, the thickness dependence of the H$_2$ permeation rates was examined. The dependence of H$_2$ permeation rates at 950 K and 20 kPa H$_2$ on membrane thickness is shown in Fig. 9. In previous studies [15–18], permeation rates were found to vary linearly with the reciprocal of the sample thickness for mixed conductors, when permeation was controlled by bulk diffusion. In Fig. 9, hydrogen permeation rates are shown as a function of the reciprocal of the film thickness for the samples in our study. These data show that even for the thinnest films tested, the bulk protonic and electronic conductivities of the dense perovskite films control the H$_2$ permeation rates through SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ thin films at 950 K and 0–60 kPa H$_2$ partial pressures.

Chen et al. [18] have reported that La$_{0.3}$Sr$_{0.7}$CoO$_3$ mixed oxygen–electronic conductors become limited by adsorption processes for membranes thinner than 80 μm at 1273 K. In our study, 2 μm SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ films remained limited by bulk transport. The thickness at which this transition occurs depends on the relative rates of bulk transport and of activation processes at surfaces. Generally, H$_2$ dissociation is fast on metal oxides than for O$_2$ dissociation, which often require significant oxygen mobility to generate neighboring vacancies. In addition, proton conductivities in SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ at 950 K are much smaller (≈ 5 × 10$^{-3}$ S cm$^{-1}$ in pure hydrogen [1]) than the oxide ion conductivity in La$_{0.3}$Sr$_{0.7}$CoO$_3$ at 1273 K (0.5 S cm$^{-1}$ in air [18]), and the required electronic conduction is also likely to be smaller in SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ at 950 K than in La$_{0.3}$Sr$_{0.7}$CoO$_3$ at 1273 K, leading to lower overall permeation rates via mixed conduction processes. Boundary layer or surface processes are unlikely to control hydrogen permeation of 2 μm SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ films at 950 K because of the slow nature of the bulk transport processes through the dense membrane material. This study confirms the limiting step of proton permeation phenomena in SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ with a proton and electron mixed conduction at relatively low temperatures (950 K). This assumption was made without direct experimental evidence in previous studies. The results presented show that significant improvements in H$_2$ permeation rates are possible by decreasing the thickness of mixed proton–electron conductors.

4. Conclusions

A synthesis procedure to form nonporous SrZr$_{0.95}$Y$_{0.05}$O$_{3-\delta}$ and SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ thin films on a porous substrate was developed using spin coating methods. In order to avoid fissures or pinholes, the shrinkage rate of the porous substrate and of the thin film were carefully matched by varying the carbon content, the pre-sintering temperature, and the compaction pressure in carbon–perovskite composites used as precursors for the porous substrates. Undetectable He permeation at ambient temperature and N$_2$ permeation at 950 K and scanning electron microscopy confirmed the nonporous nature of SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ thin films. H$_2$ permeation rates for 2 μm SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$ films were more than 100 greater than for 1 mm dense disks of identical composition.
Permeation rates were inversely proportional to the thickness of the dense layers deposited on the porous substrates. This indicates that $\text{H}_2$ permeation rates at 950 K were controlled by bulk diffusion through the dense solids even for $2 \mu\text{m}$ $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\text{x}}$ films.

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