Mechanical properties and structural stability of perovskite-type, oxygen-permeable, dense membranes

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Abstract

Mechanical properties are considered as critical factors for electrochemical applications of ion conducting oxides because chemically induced stresses can cause component degradation, and it also needs to reduce the thickness of conductors for higher performance. Mechanical properties and structural stability under a reducing environment of oxygen-permeable, dense membranes were investigated. The mechanical properties such as fracture strength and toughness of the membrane could be explained with microstructural features and relative density. Reasons for membrane failure occurring during an oxygen permeation experiment were discussed with viewpoints towards lattice parameter change caused by nonstoichiometry, phase instability under the reducing environment, and stresses induced by reactor configuration. Stress analysis and fractographical investigation were conducted to support the discussions. It was found that a Sr- and Fe-doped LaGaO₃ membrane is reliable under a reducing environment at elevated temperature.

Keywords: Mechanical property; Mixed ionic electronic conductor; Membrane; Structural stability

1. Introduction

Perovskite-type, oxygen-permeable membranes, which can permeate oxygen molecules selectively, have been widely investigated for applications such as oxygen generators, catalytic membrane reactors and electrodes of solid oxide fuel cells [1,2]. Perovskite-type conductors have not only higher ionic conductivity than fluorite-structured oxides such as ZrO₂, but also have good electronic conductivity (so-called, mixed
ionic-electronic conductor, MIEC). Accordingly, there is no need to provide an electron path to keep oxygen ion conduction as long as an oxygen chemical potential gradient is maintained [3].

The most effective MIEC perovskite oxides should have high ionic conductivity, surface reactivity, and structural stability under operating conditions. Although perovskite-type conductors have been reported to have high oxygen permeability, their low reliability under operating conditions is a serious limiting factor [4]. Because of chemical and structural instability, oxygen permeation flux decreased and membranes failed in a severe reducing environment.

In the present study, \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \) was selected as a representative composition and evaluated mechanical properties as functions of microstructural features. When the intention is to prepare membranes as thin as possible to get the highest oxygen flux, mechanical properties should be considered. Fracture strength is an important factor because it determines crack initiation when critical stress, caused either by mechanical or chemical source, is applied on membranes. Furthermore, the reliability of the membrane is related to fracture toughness or propagation of initiated cracks. Resistance to crack propagation could be a criterion of membrane qualification because membrane lifetime is determined by whether pre-existing crack size reaches high enough critical values to induce a catastrophic failure. Finally, possible origins are discussed of membrane failure by stress analysis and fractographic investigation.

Throughout the paper, \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \) and \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Ga}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta} \) composition is designated by the abbreviation LSCF and LSGF, respectively.

2. Experimental

Perovskite-type mixed conducting oxides, LSCF and LSGF, were prepared using a conventional solid-state reaction. Synthesis procedures were described elsewhere in detail [5]. A rectangular mold of \( 40 \times 40 \text{ mm}^2 \) was used to form specimens for a strength test and an indentation-strength test. Uniaxially pressed powder cake was cold-isostatically pressed at \( \approx 140 \text{ MPa} \) to enhance green density. The green bodies were sintered at \( 1200–1400^\circ\text{C} \) for LSCF and \( 1350–1550^\circ\text{C} \) for LSGF with changing the holding time for 1–10 h in air.

Bar specimens with a nominal dimension of \( 2.5 \times 3 \times 15 \text{ mm} \) were cut from sintered blocks and edge-chamfered. Surfaces subjected to tensile stress during a flexure test were polished to 0.1 \( \mu\text{m} \) finish. A four-point flexure test was done using a universal testing machine (Hounsfield, S-series, UK) with a fixture of an outer span of 12.7 mm and inner span 6.35 mm, at a constant crosshead speed of 30 mm/min at room temperature. Hardness and fracture toughness of the membranes were evaluated by the Vickers indentation method. Indentation was performed on polished surfaces at specific load \( P \) and diagonal length of the impression \( 2a \) and length of radial cracks \( 2c \) were measured.

Oxygen permeation and partial oxidation of methane (POM) experiments were performed under He/air or a \( \text{CH}_4+\text{He}/\text{air} \) environment at temperatures below \( 950^\circ\text{C} \) with disk-shaped, 1.7-mm-thick specimens. The membrane was attached on an alumina tube with an Ag-ring, gas-tight seal. In the POM experiment, a gas mixture ratio of the permeate-side was \( \text{CH}_4:\text{He} = 22.4:36.9 \text{ (ml/min)} \); metallic Ni was used as a catalyst. The membrane surface exposed to air was coated with a “surface-reactive” \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta} \) composition using a screen-printing method.

Stresses induced by thermal expansion mismatched between the membrane and the alumina tubes were analyzed using a finite element code, TEXPAC (Texas Austin University), with nine-node rectangular elements. After the permeation experiment, surfaces were qualitatively analyzed using XRD (Rigaku).
3. Results and discussion

3.1. Mechanical properties

The mechanical properties of the LSCF membrane, sintered at 1200–1400°C for 5 h, are represented in Table 1. With increasing sintering temperature, the fracture strength of the membrane showed a tendency to increase, representing a maximum value of 195 MPa for the specimen sintered at 1300 °C. The dependence of fracture strength on sintering temperature is similar to that of relative densities (Table 2), implying that fracture strength is mainly determined by the degree of densification. Fracture toughness of the membranes increased from 1.4 to 1.9 MPa·m$^{1/2}$ with increasing sintering temperature, as shown in Table 1. The hardness of the membrane, on the contrary, tends to decrease with sintering temperature. These trends seem to be related to grain size variations. In polycrystalline ceramics, the nature of fracture damage can be controlled by events occurring at the microstructural level. Generally, larger grains can impede crack propagation by crack deflection or crack bridging mechanism, which absorbs much of the energy of microcrack expansion, and finally fracture toughness increases [6–8]. The sintering temperature dependence of the fracture strength for the LSGF membrane was similar to the case for the LSCF membrane (Table 1). However, relatively low strength and slightly high hardness were evident for LSGF, showing the highest strength of 107 MPa for the specimen sintered at 1450°C for 5 h.

3.2. Structural stability

The photograph of the LSCF disk membrane, taken after an oxygen permeation experiment in a helium/air atmosphere at 950°C, is shown in Fig. 1. A few facts can be inferred from the crack configurations. Firstly, the crack was evidently initiated at the surface exposed to helium. Also the crack profile developed on the surface is similar to that observed at typical biaxially-fractured ceramics, MgF$_2$, shown at the right side of Fig. 1. As the maximum tensile stress is induced at the center of a specimen when biaxial loads act, the crack is assumed to be originated from the center of the specimen. Prior researchers have suggested some probable causes of cracking during the permeation experiments: the gradient in lattice expansion across membranes caused by nonstoichiometry, and phase decomposition under a reducing environment. The stresses caused by reactor configuration can be considered as well.

Table 1

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sintering temp. (°C)</th>
<th>Fracture strength (MPa)</th>
<th>Fracture toughness</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCF</td>
<td>1200</td>
<td>86</td>
<td>1.4</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>95</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>195</td>
<td>1.8</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>91</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>55</td>
<td>1.9</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>32</td>
<td>1.8</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>107</td>
<td>1.9</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>1550</td>
<td>46</td>
<td>1.7</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Table 2
Mean grain size and relative density variation of LSCF and LSGF membranes sintered at various temperatures for 5 h

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sintering temp. (°C)</th>
<th>Mean grain size (µm)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCF</td>
<td>1200</td>
<td>0.9</td>
<td>96.6</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>2.0</td>
<td>98.3</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>4.8</td>
<td>98.3</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>6.7</td>
<td>97.2</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>16.4</td>
<td>92.9</td>
</tr>
<tr>
<td>LSGF</td>
<td>1400</td>
<td>2.1</td>
<td>98.1</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>3.3</td>
<td>98.1</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>5.5</td>
<td>97.8</td>
</tr>
</tbody>
</table>

3.2.1. Lattice expansion by nonstoichiometry

When mixed conducting membranes are under a low-oxygen partial-pressure condition, the lattice parameter and overall dimension increased [3, 9–11]. Oxygen vacancies can be created in the membrane by exposure to an environment having a low thermodynamic oxygen activity. These extra vacancies are sometimes regarded as nonstoichiometric vacancies since they represent a deviation from a nominal composition of the membrane. In order to form extra vacancies, it is necessary to have some variable cations in the structure to accept the electrons from the extracted oxygen ions. The ease with which these ions change valency, as reflected in their oxidation/reduction enthalpies, makes an important contribution to determining the concentration of extra vacancies. Mixed ionic-electronic conducting oxides, LSCF and LSGF, contain transition metal cations to provide high electronic conductivity and, hence, are likely to become oxygen deficient under reducing conditions [12]. Each extra vacancy is associated with an increase in the lattice parameter of the oxide crystal. Thus, the lattice expands as the oxide becomes more nonstoichiometric. For most application conditions, an oxygen-conducting membrane is under a gradient of oxygen partial pressure and is subject to strain differences across its thickness, caused by the gradient in concentration of oxygen vacancies. This, in turn, might induce mechanical...
stress that could ultimately cause a fracture of the membranes. If this mechanism acted on the membrane solely and uniformly, a crack would begin at the center of the disk because the edge of the disk is constrained [9].

3.2.2. Phase decomposition

The phase decomposition can be one of the reasons for membrane failure. Fig. 2 is the XRD pattern of the LSCF membrane measured after the POM experiment — CH4+He/air environment at 950°C. The occurrence of non-perovskite phases was evident in the surface exposed to methane, which implies that stability is not so good enough under a reducing atmosphere. Elshof et al. had reported that XRD analysis of LSCF membranes indicated the presence of SrCO3 and SrSO4 when the sample was treated in a CH4+He/air gradient [13]. Tsai et al. found that the Co content in a LaBaCoFeO3 membrane increased on the reducing side of the membrane surface after partial oxidation of methane, whereas the composition of the membrane surface exposed to air was similar to that of a fresh membrane [14]. They assumed that the change in the structure and composition of membranes led to a decrease in oxygen permeation flux. On the other hand, Jin et al. observed that the surface of LaSrCoFeO3 membranes exposed to a reducing environment contained a small amount of metallic lanthanum [3]. It might be possible that some of the oxides were reduced to La and Sr, which were subsequently sublimated at an elevated reaction temperature. They suggested that the metal ion reduction, metal sublimation and element segregation occurred on the membrane surfaces during the reaction at high temperature, providing the driving force for the redistribution of the metal ions across the membranes. This redistribution might weaken the mechanical strength of the membrane tube, leading to a fracture of the membrane [15]. Fig. 3 is the XRD pattern of the LSGF membrane measured after the POM experiment: CH4+He/air environment at 950°C. While the air-side surface of the membrane retained a perovskite structure, the non-perovskite, decomposed phases were observed at the surface exposed to methane. Non-
perovskite phases were analyzed as La$_2$O$_3$, La$_2$O$_2$(CO$_3$)$_2$, SrCO$_3$, and some unidentified ones. Carbonates might be formed by the reaction of the metallic ion with the deposited carbon [13]. Reduced metals were not observed in the present study, but the detrimental effects of the non-perovskite, decomposed phases on the electrochemical and dimensional stability could be expected.

3.2.3. Thermal expansion mismatch

Another possibility of cracking is a thermal expansion mismatch between the membrane and the sustaining alumina tubes. The thermal expansion coefficient of LSCF is relatively high with respect to other ceramic materials, ranging from 13 to 20 ppm/°C according to cation composition [16,17]. High lattice expansions seem to be caused by the loss of lattice oxygen at high temperatures. Accordingly, the mismatch in the thermal expansion coefficient of the membrane with that of alumina tubes (approximately 8 ppm/°C) might cause stress on the membrane.

To investigate the effect of expansion mismatch quantitatively and qualitatively, a finite element analysis code was used. Change in temperature $\Delta T$ was assumed to be 50°C and the thermal expansion coefficients used in this calculation were 15.3 and 8.0 ppm/°C for the membrane and alumina, respectively [17]. The deformation of the Ag sealant, which was placed between the membrane and the tube, was ignored by constraining the membrane to $x$ and $y$ directions for simplicity in calculation. Fig. 4(a) is a schematic diagram of the oxygen permeability measuring system. An alumina cap was fastened with a screw to the sustaining tube, which ensured a gas-tight seal. The part indicated by the dotted line was investigated axis-symmetrically. A contour of maximum principal stresses acting on the membrane and the sustaining tube is shown in Fig. 4(b). The maximum tensile stress, 81.1 MPa, was induced at the outermost boundary between the specimen and the tube, and the center of the membrane is under a slight tension applied uniformly along radial direction. Thus, if

![Fig. 4. (a) Schematic diagram of oxygen permeability measuring system. The area, bounded by dotted line was considered for FEM calculation. (b) The distribution of the principal stress induced by the thermal expansion difference between the membrane and the sustaining alumina tube.](image)


the difference in thermal expansion between the two materials was operated as a main factor for the failure of the membrane, the crack would begin at the edge of the disk-shaped membrane.

It is difficult to conclude definitely what is the main contributor to the failure of the membrane because there are some inconsistencies in fracture origin observation. How much the metal sealant, Ag, could deform plastically at a specific temperature seems to be another critical factor.

3.3. Long-term stability

The long-term stability of disk-shaped LSCF and LSGF membranes was evaluated under the CH₄+He/air condition at 950°C for 600 h. As methane reacts with the permeated oxygen to give H₂ and CO, the reaction is called “partial oxidation of methane” or “syngas production”. The variations in methane conversion and syngas yields are represented in Figs. 5 and 6 for LSCF and LSGF, respectively. The methane conversion, (CH₄ₛ_in−CH₄ₛ_out)/CH₄ₛ_in and the CO selectivity, (COₐₒut−CO₂ₒut)/COₒᵤt, were extremely low for the LSCF membrane. Furthermore, there was a significant gas leakage after a 6-h exposure to the environment. On the other hand, there was no significant degradation in conversion and yield of the LSGF membrane for 600 h, as shown in Fig. 6. Interestingly, the H₂/CO ratio (in concentration) was greater than 2; in other words, the yield of H₂ is higher than that of CO. This is probably due to carbon deposition on the membrane surface. A high ratio of CH₄ to O₂ could cause a deposition of large amounts of carbonic species that filled catalyst pores with reducing catalytic activity. It is noteworthy that the decomposed phase, shown in Fig. 3, did not exert an influence on overall syngas productivity. As discussed elsewhere [5], the surface-modified, 1.7-mm-thick LSGF membrane is rate-controlled by bulk diffusion. It seems that the depth of the decomposed surface was relatively so small compared to specimen thickness that the decomposed phases did not affect the overall oxygen permeation flux, the syngas yield and the methane conversion.

4. Conclusions

Fundamental mechanical properties of LSCF and LSGF membranes were evaluated. The reasons for membrane failure during the permeation experiment were discussed: dimensional discord, caused by the difference in nonstoichiometry between the surfaces of the membrane; surface weakening or phase decomposition due to the
instability of the perovskite structure in a severe reducing environment for a long time; and the mismatch in thermal expansion between the membrane and the sustaining tube. Although there are still some inconsistencies in the fractographical configuration, it might be inferred that each mechanism could be responsible for cracking under specific experimental conditions. In the case of the LSGF membrane, even though there were decomposed phases after the exposure to a highly reducing environment, CH$_4$+He, at 950°C for 600 h, the syngas yield and the methane conversion were unaffected.

References