

A Novel Method for Preparation of SrFeCo_{0.5}O_x Membranes on Porous Substrates for Oxygen Permeation

Masayuki Ikeguchi¹, Masayuki Kaneko¹, Yasushi Sekine², Eiichi Kikuchi^{1,2},
and Masahiko Matsukata^{1,2*}

1) Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, JAPAN

*2) Advanced Research Institute for Science and Engineering, Waseda University

3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, JAPAN, Tel & Fax: 81-3-5286-3850, e-mail: mmatsu@waseda.jp

High temperature oxygen permeable membrane needs to have both high permeability and mechanical strength. In this study, we developed an asymmetric membrane possessing a SrFeCo_{0.5}O_x (SFC-2) thin dense layer on an SFC-2 porous support layer. The porous support was prepared by calcining a disk made of a mixture of SFC-2 powder and ethyl cellulose. The porous support was treated by dip coating with an SFC-2-ethanol slurry to fill up large defects which were observed on its surface. Fine SFC-2 powder used for an evacuating deposition was separately prepared by a Pechini method in order to obtain powder with small particle size. The dense layer was prepared by repeated deposition of the fine powder and calcination. The gas-tightness of the membrane greatly increased by repeating the evacuating deposition. Finally, a gas-tight membrane was successfully obtained by repeating dropping of a solution containing constituent metals of SFC-2 on the membrane and calcination.

Key words: Ceramic, asymmetric membrane, oxygen permeation, SrFeCo_{0.5}O_x, slurry, solution

1. INTRODUCTION

Dense membranes made of oxide ionic-electronic mixed conducting ceramic have been investigated by many groups in recent years as means to separate oxygen from air at high temperatures. As applications of oxygen permselective membranes, oxygen production process, membrane reactors for partial oxidation of methane to syngas (CO + H₂) or oxidative coupling of methane to C₂ chemicals have been proposed.

Since Teraoka et al. first reported oxide ionic-electronic mixed conducting membranes with high oxygen permeabilities [1], many kinds of mixed conducting oxides mainly with perovskite or its related structure have been reported as membrane materials. La_xA_{1-x}Fe_yCo_{1-y}O_{3-δ}, A=Sr, Ba (Teraoka et al. and many groups [1]-[5]), SrFeCo_{0.5}O_x (Balachandran et al. [6]), Ba_{0.5}Sr_{0.5}Fe_{0.2}Co_{0.8}O_{3-δ} (Shao et al. [7]), and La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-δ} (Ishihara et al. [8]) have exhibited comparatively higher oxygen permeabilities.

The oxygen permeability can be enhanced by reduction of the membrane thickness, which reduce, however, the mechanical strength. Since most of these membranes reported are symmetric and self-supporting, the membrane thickness is as large as 0.5 to 2 mm, and it is difficult to decrease membrane thickness further. Asymmetric membranes, in which a thin dense mixed conducting membrane for oxygen separation is formed on a porous support layer for increasing mechanical strength of the membrane, would be a solution to obtain a thin membrane with high mechanical strength [9]. In case porous substrate made of commercial materials such as α-alumina are used, the dense layer can peel off from the porous support because of the thermal expansion mismatch of both layers. And oxygen permeation would be disturbed by a formation of new phase due to the solid state reaction between both layers

at high temperatures during calcination or oxygen permeation.

Our group already reported an easy and novel technique (solid-state synthesis) to prepare a mechanically stable asymmetric membrane by using SrFeCo_{0.5}O_x (SFC-2) for dense layer and porous support layer [10]. SFC-2 powder for dense layer and a mixture, which was obtained by mixing SFC-2 powder and ethyl cellulose powder in an agate mortar, for a porous support layer were simultaneously compressed into a disk and calcined. Combustion of ethyl cellulose resulted in the formation of the porous support layer. The asymmetric membrane with the dense layer thickness of about 100 μm was obtained, and asymmetric membranes gave greater oxygen flux than a symmetric membrane. It was, however, difficult to prepare the asymmetric membrane thinner than 100 μm, and it was observed that the porous support layer would act as resistance for oxygen permeation.

The purpose of this study was to prepare a thin SFC-2 membrane with slurry or solution on an SFC-2 porous support with high gas diffusivity. Since the porous support mentioned in the solid-state synthesis possessed pores of more than 100 μm, it would be difficult to prepare a thin membrane on the porous support. Therefore, an SFC-2 porous support with pore sizes of micrometer order was prepared by using another technique. The dense layer was prepared by three methods, a dip coating, an evacuating deposition, and a dropping of solution. Each method was used properly according to the membrane state.

2. EXPERIMENTAL

2.1 Preparation of porous support

Stoichiometric amounts of the constituent metal nitrates, Sr(NO₃)₂, Fe(NO₃)₃ · 9H₂O, and Co(NO₃)₂ ·

6H₂O, were dissolved in water. The solution was heated and stirred on a hot stirrer until dried. The obtained solid was calcined in air at 1123 K for 16 h and was ground for 2 h in an agate mortar. Then the powder was again calcined at 1423 K for 10 h and ground for 2 h, and we obtained the SFC-2 powder for preparation of the porous layer and the dip coating. The SFC-2 porous support was prepared by calcining a disk made of a mixture of the SFC-2 powder and ethyl cellulose. The mixture was obtained by dispersing the SFC-2 powder in an ethanol solution of ethyl cellulose, drying the slurry, and grinding the powder. The mixture was pressed in a 13 mm diameter die to make a disk, and then the disk was calcined at 1373 K for 10 h at heating and cooling rates of 1 K/min.

2. 2 Dip coating

The porous support was treated by dip coating to fill up large defects on the surface. The SFC-2 powder was ultrasonically dispersed in ethanol at 0.2 g/ml-ethanol. The SFC-2 porous support was dipped in the slurry, and calcined in air at 1373 K for 10 h at heating and cooling rates of 1 K/min.

2. 3 Evacuating deposition

SFC-2 fine powder used in the evacuating deposition was prepared by a Pechini method [11] in order to obtain powder with small particle size. Citric acid, ethylene glycol, and stoichiometric amounts of constituent metals Sr(NO₃)₂, Fe(NO₃)₃ · 9H₂O, and Co(NO₃)₂ · 6H₂O were dissolved in water. The solution was heated at 353-363 K with stirring in a water bath until a gel was formed. The gel was precalcined at 673 K for 2 h. The obtained powder was calcined in air at 1073 K for 2 h, and was ground in an agate mortar for 2 h. In this method, metal cations were distributed and fixed in the polymeric network formed with citric acid and ethylene glycol. After the polymer was removed by heating, small and homogeneous powder would be obtained. The obtained powder was ultrasonically dispersed in ethanol and the slurry was stood for 30 min in order to remove large particles. The fine SFC-2 powder was obtained by recovering and drying the supernatant.

The bottom of membrane was connected to a glass tube with epoxy resin. The connected membrane was dipped in ultrasonically dispersed slurry of an SFC-2 fine powder and ethanol at 0.5 mg/ml-ethanol, and the SFC-2 fine powder was deposited by evacuating from glass tube for 1 min. After removing the epoxy resin by heating at 773 K for 1 h, the membrane was calcined in air at 1373 K for 10 h at heating and cooling rates of 1 K/min. The procedure of deposition and the calcination was repeated several times.

2. 4 Dropping of solution

2.5 mmol of Fe(NO₃)₃ · 9H₂O and 1.25 mmol of Co(NO₃)₂ · 6H₂O were dissolved in 10 ml of ethanol. Strontium was not contained in the solution because many kinds of strontium salts were slightly soluble to ethanol. The solution was dropped onto the membrane heated on a hot plate. The membrane was calcined in air at 1373 K for 10 h at heating and cooling rates of 1 K/min. The procedure of dropping and the calcination

was repeated several times.

2. 5 Nitrogen permeation measurement

The gas diffusivity through porous support and the gas-tightness of asymmetric membrane were evaluated with the N₂ permeance (P) which is measured by N₂ permeation measurements at room temperature for the pressure difference of 1.0 kgf cm⁻². The membrane whose N₂ permeance was less than the detection limit; about 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹, was defined as gas-tight membrane.

3. RESULTS AND DISCUSSION

Figure 1 shows the change of N₂ permeance through the membrane due to the successive preparation by dip coating, evacuating deposition, and the dropping of solution.

The SEM images for the porous support were shown in Figure 2. The porous support with pore sizes of micrometer order was obtained. Ethyl cellulose contained in the mixture used for the preparation of porous support was burnt at low temperature during calcination, and spaces were formed between SFC-2 particles remained. Therefore, particles did not connect completely together by sintering at higher temperatures, and the porous structure shown in Figure 2 was formed. This porous support showed high gas diffusivity.

As shown in Figure 2(b), some defects larger than 10 μm were observed on the top of porous support. These defects would disturb the formation of thin membrane. The porous support was treated by the dip coating with SFC-2 powder, which was used for the preparation of porous support, to fill up such defects. Figure 3 shows the SEM images for the membrane after the dip coating. Defects disappeared, and a uniform porous structure of about 2 μm pore size, which was similar to that of the porous substrate, was formed. The N₂ permeance slightly decreased by the dip coating as shown in Figure 1.

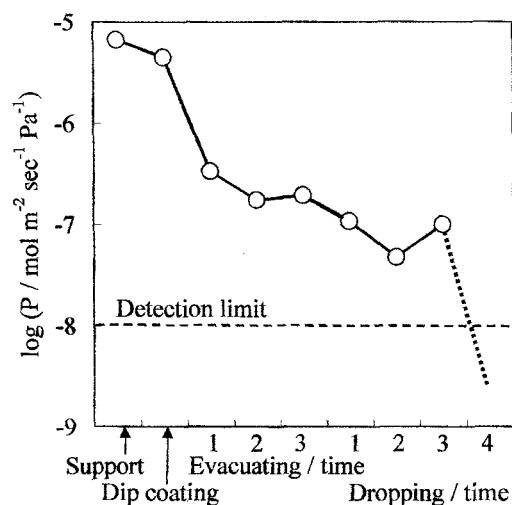


Fig. 1 Change of N₂ permeance through the membrane due to the successive preparation by dip coating, evacuating deposition, and the dropping of solution.

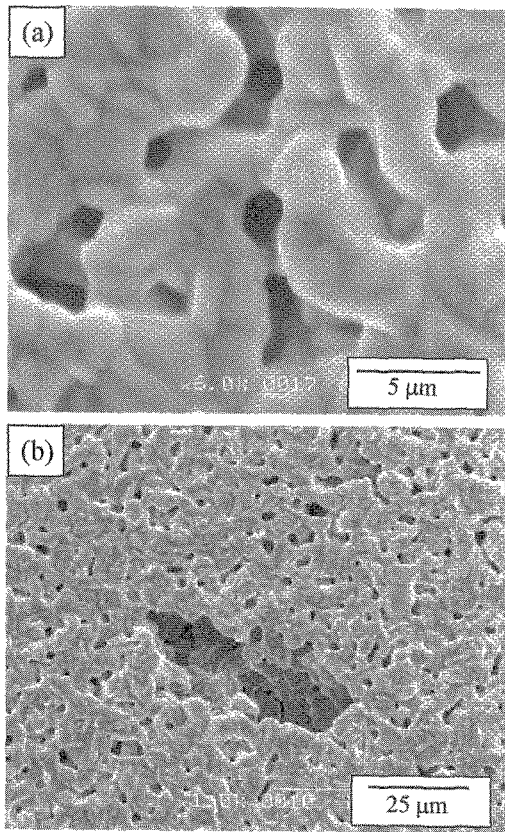


Fig. 2 SEM images for the top of the SFC-2 porous support.

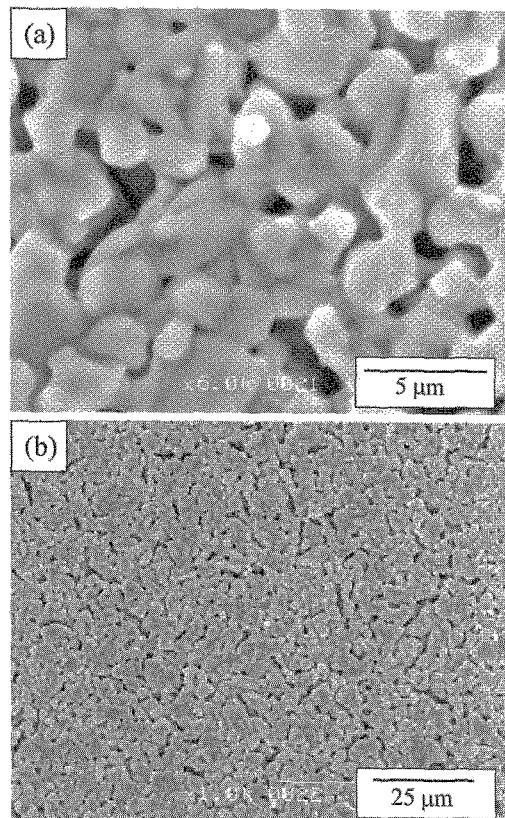


Fig. 3 SEM images for the top of the membrane after the dip coating.

The evacuating deposition was repeated to close pores on the membrane with the SFC-2 fine powder, which is smaller than pores formed after the dip coating. Figure 4 shows the SEM image for the membrane after the first deposition before calcination. It was observed that the SFC-2 fine powder closed pores by evacuation. Pores which were not closed, however, still remained. As shown in Figure 1, by repeating the evacuating deposition, the N_2 permeance decreased greatly up to about $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, however, it did not decrease further. The remaining pores were filled up by repeating the evacuating deposition, and the N_2 permeance decreased. After the remaining pores decreased and the N_2 permeance decreased, however, the evacuation of the slurry became hard, and decrease in the N_2 permeance stopped. It was also confirmed by the fact that the amount of permeating ethanol through the membrane during evacuation decreased by repeating the preparation and finally the permeation of ethanol was not observed. Figure 5 shows the SEM image for the membrane, through which the N_2 permeance was decreased up to about $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ by repeating the evacuating deposition. Though the pores were decreased, pinholes which could not be closed by the evacuating deposition were observed on the top of the membrane.

We investigated to provide constituent metals of SFC-2 into pinholes by the dropping of solution. Though the solution which contained only Fe and Co was used in this method, it would be a few influences on oxygen permeation to close pinholes only with Fe and Co because most of dense layer was already formed with SFC-2 by the dip coating and the evacuating deposition. The gas-tight membrane through which N_2 permeance was less than $10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ was obtained by repeating the dropping of solution as shown in Figure 1. XRD pattern for the gas-tight membrane was shown in Figure 6, and SEM image for this membrane after oxygen permeation measurement was shown in Figure 7. Though reflection peaks of perovskite, which were similar to that of SFC-2, were observed, large reflection peaks of CoFe_2O_4 were also appeared. As shown in Figure 7 deposits were formed on the membrane. The composition of the deposits measured by EDX were Sr: Fe: Co=5.85: 55.52: 38.63. Much amount of Fe and Co were contained in the

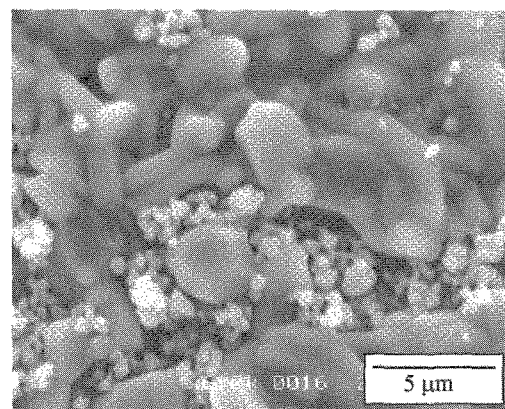


Fig. 4 SEM image for the top of the membrane after first deposition before calcination.

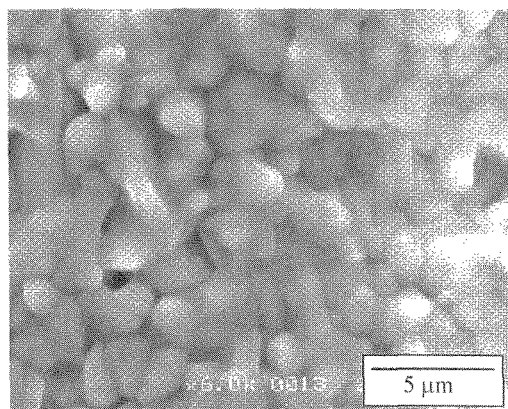


Fig. 5 SEM image for the top of the membrane after repeating the evacuating deposition.

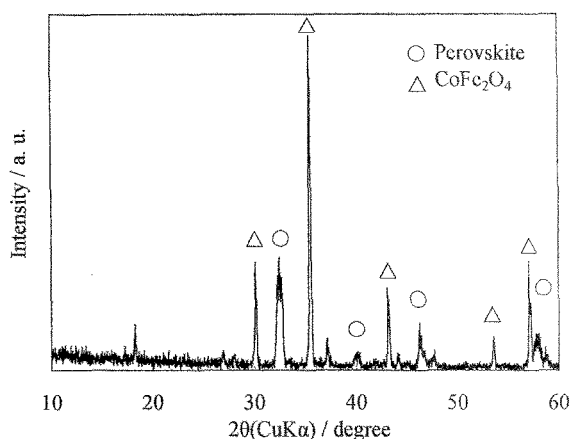


Fig. 6 XRD pattern for the gas-tight membrane after repeating the dropping of solution.

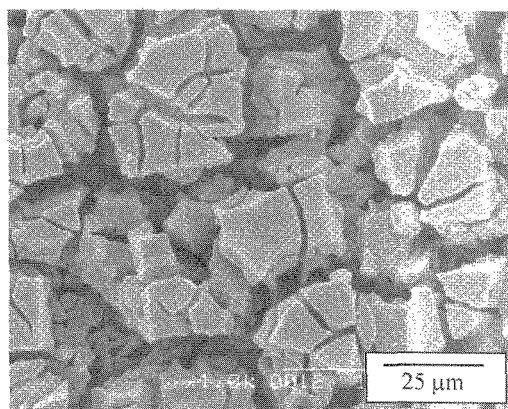


Fig. 7 SEM image for the top of the gas-tight membrane after repeating the dropping of solution.

deposits compared with ideal composition of SFC-2; Sr:Fe: Co=40: 40: 20, and the result was corresponded with the XRD result. To prevent such undesirable distribution of composition, proper solution which contains all of the constituent metals should be used. Though the composition difference was found on the top

of the membrane, the composition of the inside of the membrane was similar to the ideal composition of SFC-2.

4. CONCLUSIONS

We investigated the preparation of a $\text{SrFeCo}_{0.5}\text{O}_x$ (SFC-2) porous substrate with high gas diffusivity and to deposit a thin SFC-2 membrane on the substrate by using slurry or solution. The porous substrate with high gas diffusivity was obtained by calcining a disk made of a mixture of SFC-2 powder and ethyl cellulose. Defects, which was larger than 10 μm , were closed by the dip coating with the slurry of SFC-2 powder, pores of about 2 μm diameter were closed by the evacuating deposition with the slurry of SFC-2 fine powder, and pinholes were closed by the dropping of solution which contains constituent metals of SFC-2. The gas-tight asymmetric membrane was successfully prepared by selecting preparation methods properly according to the membrane state.

5. ACKNOWLEDGEMENTS

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