Oxygen Permeability of Mn/Fe-Based Perovskite-Type Oxide and Its Application to Methane Partial Oxidation Membrane Reactor

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1. Introduction

Dense membranes of mixed ionic-electronic conductive (MIEC) perovskites with oxygen semi-permeability at elevated temperatures can be applied to membrane reactors for partial oxidation[1] and oxidative coupling of methane[2], NOx removal[3] and so on. Cobaltite perovskites such as $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF2882) and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF82) show high oxygen permeability and used most frequently for oxygen separators. However, they are easily reduced when exposing to reducing atmosphere, making it difficult to apply them for membrane reactors with the construction of, for example, air/membrane/CH_4. Therefore, development of materials with high permeability and reduction tolerance is indispensable to realize the MIEC membrane reactors involving CH_4 as a reactant.

In this study, we have revealed that Mn/Fe-based perovskite-type oxides are new oxygen-permeable materials with high oxygen permeability and resistance against the reduction and that they can be successfully applied to the membrane reactor for partial oxidation of methane (POM, $O_2 + 2CH_4 \rightarrow 2CO + 4H_2$).

2. Experimental

Perovskite-type oxides were prepared from nitrates or acetates of constituent metal cations. A mixed aqueous solution containing appropriate amounts of metal salts was evaporated to dryness, followed by the calcination at 850 ºC for 5h in air. The powder product was ground well in an agate mortar, compressed into a disk (20 mm in diameter, 1.5 mm thick) under the uniaxial pressure of 400 MPa, and sintered at 1300-1450 ºC for 5h in air.

For oxygen permeation measurements, the both sides of sintered disk were polished with an emery paper to 1 mm thick. The disk sample was fixed to a quartz-tube reactor by welding with a silver ring at 965 ºC. The cell constructions of air/membrane/He and air/membrane/ 20vol.%CH_4-Ar were used for oxygen permeation membrane and POM membrane reactor, respectively. Concentration of gaseous components was measured by a TCD gas chromatograph.

3. Results and discussion

A series of (A, Sr)-(Mn, Fe)-O (A=La, Ba, Ca) perovskites in the Sr/Fe-rich composition region were prepared. Figure 1 shows temperature dependences of oxygen permeability through BSF37 ($Ba_{0.3}Sr_{0.7}FeO_{3-\delta}$), SF ($SrFeO_{3-\delta}$), BSMF3719 ($Ba_{0.3}Sr_{0.7}Mn_{0.1}Fe_{0.9}O_{3-\delta}$), CSMF 1919 ($Ca_{0.1}Sr_{0.9}Mn_{0.1}Fe_{0.9}O_{3-\delta}$), SMF19 ($SrMn_{0.1}Fe_{0.9}O_{3-\delta}$) and LSMF1919 ($La_{0.1}Sr_{0.9}Mn_{0.1}Fe_{0.9}O_{3-\delta}$) membranes; they all were single-phase cubic perovskite-type structure (XRD). Among oxides examined in this study, Ba-substituted oxide (BSF37) exhibited the highest oxygen permeability of 3.0 $cm^3(STP)cm^{-2}\cdot min^{-1}$ at 900 ºC, which is larger than that of SCF82 or LSCF2882. On the other hand, La and Ca substitution for Sr and Mn substitution for Fe caused a decrease in the oxygen permeation rate.

Thermogravimetric (TG) analysis in 5%H_2/N_2 stream was carried out to evaluate the reduction tolerance up to 1000ºC. Perovskite-type structure of LSCFs was completely destroyed under the TG experimental condition. Mn/Fe-based perovskites, on the other hand, were found to be more stable against the reduction. The reduction tolerance of SF was enhanced by the substitution of adequate amounts of Ba and Mn, and BSMF3719 was the most stable against reduction; its cubic crystal structure was intact after the TG experiment. It can thus be concluded that the Mn/Fe-based perovskites, especially BSMFs, are promising materials for membrane reactor application with excellent oxygen permeability and reduction tolerance.

Figure 2 shows time courses of performance of POM membrane reactor (BSMF3719 with $LaNiO_3$ catalyst) at 900ºC. After reaching the steady-state at around 150 min, the performance was not deteriorated even after 450 min on stream. CH_4 conversion, H_2 selectivity and CO selectivity was 60, 84 and 95% at the steady state, respectively. Note that the LSCF1991 membrane was destroyed after 240 min on stream under the same reaction condition. Although the Ni-based POM catalyst should be optimized in terms of materials and pre-reduction condition, etc, the present results demonstrated the high potentiality of BSMF membrane in POM membrane reactor application.

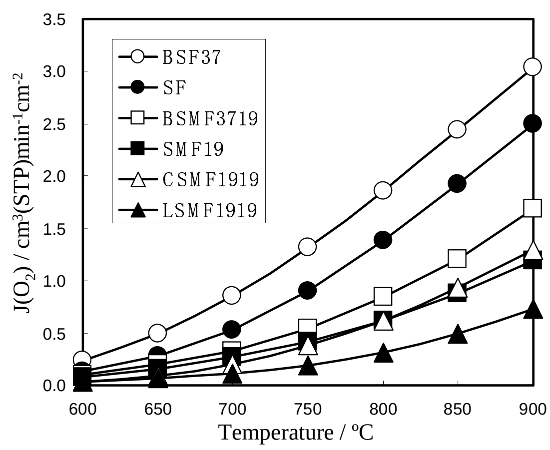

Fig. 1 Oxygen permeability through Mn/Fe-based perovskite membranes.

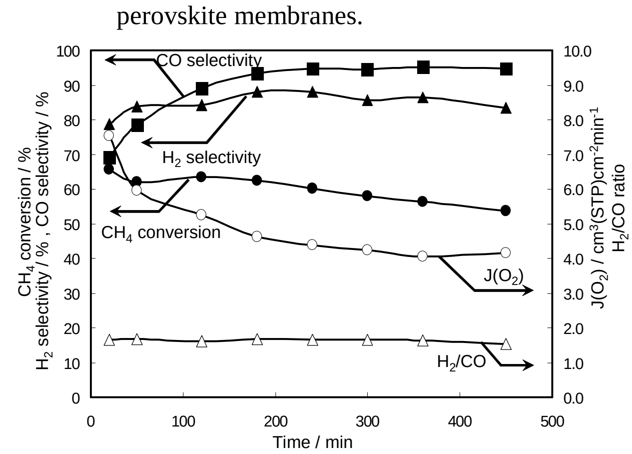

Fig.2 Time courses of performance of POM membrane reactor at 900ºC. Membrane; BSMF3719, Catalyst; $LaNiO_3$.

References

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