[Review Paper]

Low Temperature Solid Oxide Fuel Cells Using LaGaO₃-based Oxide Electrolyte on Metal Support

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Solid oxide fuel cells (SOFCs) can directly convert the chemical energy of various fuels to electric power with unmatched energy conversion efficiency. The oxide ion conductivity of LaGaO₃ doped with Sr and Mg (LSGM) is introduced and application of LSGM to low temperature SOFCs is explained. Power density at lower temperature was dramatically increased by application of LSGM film manufactured with laser ablation techniques. By application of a suitable buffer layer, the cell using LSGM thin film electrolyte had reasonable power density (0.2 W cm⁻²) at 773 K. Ce_{0.6}Mn_{0.3}Fe_{0.1}O₂ (CMF) oxide had high activity for the anodic reaction and insertion of a CMF layer much improved the maximum power density (0.17 W cm⁻² at 673 K). Oxide anode consisting of Ce_{0.6}Mn_{0.3}Fe_{0.1}O₂ (CMF)–La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O₃ (LSFM) (= 12.5 : 87.5 wt%) enabled the use of dry hydrocarbon for fuel with almost no coke deposition.

Keywords

Low temperature SOFC, Lanthanum gallate, Thin film, Nickel-iron porous metal, Oxide anode, Direct hydrocarbon SOFC

1. Introduction

Energy demand is growing rapidly worldwide because of the increasing global population and the desire for higher standards of living. However, terrestrial hydrocarbon natural resources (*e.g.*, fossil fuels and biomass) are finite, and fossil fuel consumption is causing climate change, so efficient use of these resources is critical to global sustainability. Unfortunately, the current efficiency of energy conversion from fossil fuels is only about 36 % with the rest of the energy wasted as heat¹⁾. In contrast, fuel cells directly convert fuel energy to electric power with significantly higher efficiency^{2)–5)}.

Various types of fuel cells have been developed, but the polymer-based proton exchange membrane fuel cell (PEMFC) is the most extensively studied, largely due to the lower operating temperature (~353 K) allowing application to portable and transportation (automobile) applications which require rapid start-up from ambient temperature. However, PEMFCs consume pure H₂ (extremely low CO content), so requiring a H₂ fueling infrastructure that does not currently exist. Moreover, H₂ production from natural gas (the source of H₂ today) involves considerable energy losses, so the “well to

wheels” efficiency of PEMFCs is less than 45 % at best⁶⁾.

Solid oxide fuel cells (SOFCs) use an oxygen-ion (instead of proton) conducting electrolyte to transport oxygen from the (cathode) air electrode to oxidize fuel at the anode (fuel electrode), so can directly convert various hydrocarbon fuels with high fuel to electricity conversion efficiency (>55 % Lower Heating Value (LHV))³⁾. Moreover, SOFCs can exceed 85 % efficiency in combined heat and power (CHP) applications, unmatched by any other energy conversion technology. The SOFC electrolyte of choice has been Y₂O₃ stabilized ZrO₂ (YSZ) for the last 30 years^{2)–4)}. However, early SOFCs operated at ~1273 K due to the limited conductivity of YSZ. Such high temperatures result in high cell costs, long start-up and shut down cycles, and unacceptable performance degradation rates due to reactions between the component materials and electrode sintering. Operating temperatures for commercially developed SOFC stacks have since been decreased to around 1073 K. These so-called intermediate temperature SOFCs (ITSOFCs) are based on thin film electrolytes and more active anode and cathode materials in especially developed composite structures^{7),8)}. ITSOFCs now have numerous applications to convert various hydrocarbon fuels.

Oxides with the perovskite structure are anticipated to be superior oxide ion conductors, but typical

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perovskite oxides such as LaCoO_3 and LaFeO_3 are well known to be mixed electronic and oxide ionic conductors, which can be used for the cathode of SOFCs. Therefore, such mixed conducting perovskite oxides are promising candidates for the cathode catalysts of SOFCs or oxygen permeating membranes. Previously, we identified high oxide ion conductivity in doped LaGaO_3 electrolyte, and this oxide has higher pure oxide ion conductivity than YSZ by an order of magnitude⁹⁾. This report introduces the application of LSGM electrolyte to low temperature SOFCs.

2. Oxide Ion Conductivity in LaGaO_3 Doped with Sr and Mg

In this section, oxide ion conductivity in LaGaO_3 perovskite oxide is briefly introduced⁸⁾. LaGaO_3 -based perovskite is the first pure oxide ion conductor described in 1994⁹⁾. The high oxide ion conductivity of this oxide is achieved by double doping of lower valence cations into A and B sites of perovskite oxide, ABO_3 . Clearly the oxide ion conductivity strongly depends on the cations at the A sites, which is similar to the case of Al-based oxide, and the highest conductivity is achieved with LaGaO_3 , which also has the largest unit lattice volume among the Ga-based perovskites. The electrical conductivity of Ga-based perovskite oxides is almost independent of the oxygen partial pressure in the range from 1 to 10^{-21} atm (1 atm = 1.01325×10^5 Pa). Therefore, oxide ion conduction should be dominant in all Ga-based perovskite oxides.

Doping with a lower valence cation generally forms oxygen vacancies to satisfy electrical neutrality, so the oxide ion conductivity will increase with higher number of oxygen vacancies. Therefore, doping of alkaline earth cations to La sites was investigated and the resultant effects on oxide ion conductivity are shown in Fig. 1⁸⁾. The electrical conductivity of LaGaO_3 depends strongly on the alkaline earth cations doped at the La sites and increases in the order $\text{Sr} > \text{Ba} > \text{Ca}$. Therefore, strontium, with almost the same ionic size as La^{3+} , is the most suitable dopant for the La sites in LaGaO_3 . This effect may also be explained by the formation of local stress in the lattice caused by the mismatch in ionic size. Theoretically, higher doping of Sr will increase the number of oxygen vacancies resulting in increased oxide ion conductivity. However, the solid solubility of Sr into the La sites of LaGaO_3 is poor, and secondary phases SrGaO_3 or La_4SrO_7 form if the concentration of Sr exceeds 10 mol%. Therefore, the number of oxygen vacancies introduced by La site doping is not large.

Doping with Mg is highly effective for increasing the oxide ion conductivity, since additional oxide ion vacancies are formed. The oxide ion conductivity is further increased by higher amounts of doped Mg, and

Fig. 1 Electrical Conductivity of LaGaO_3 with Alkaline Earth Cations Doped at La Sites

reaches the maximum at 20 mol% Mg. Mg doping also increases the limit of Sr solid solution in La sites¹⁰⁾, possibly due to the enlarged crystal lattice. The highest oxide ion conductivity in LaGaO_3 -based oxide is obtained with the composition of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ ¹¹⁾.

LaGaO_3 -based oxide contains four elements, so the optimum reported composition varies slightly. Oxide ion conductivity in LaGaO_3 -based oxide was investigated by several groups^{12),13)} and various cations were examined as the dopant. The oxide ion conductivity for various compositions¹³⁾ was investigated and expressed in contour maps¹⁴⁾ as shown in Fig. 2, which also shows the optimum composition reported by two other groups. The highest oxide ion conductivity was obtained with the composition of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3$ ¹⁵⁾. On the other hand, the optimized composition was also reported as $\text{La}_{1-X}\text{Sr}_X\text{Ga}_{1-Y}\text{Mg}_Y\text{O}_3$ at $X = 0.2$, $Y = 0.17$ ^{15),16)}. However, the optimized compositions of the three groups are close and achieved between $Y = 0.15$ to 0.2 in $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{1-Y}\text{Mg}_Y\text{O}_3$. Any differences may be attributed to the uniformity of composition and grain size.

Figure 3 compares the oxide ion conductivity of doubly doped LaGaO_3 with those of conventional oxide ion conductors. Clearly the oxide ion conductivity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ is higher than the typical conductivity of ZrO_2 - or CeO_2 -based oxides and somewhat lower than those of Bi_2O_3 -based oxides. The n-type semiconduction mechanism is dominant in CeO_2 - or Bi_2O_3 -based oxides under a reducing atmosphere, and thermal stability is not satisfactory for Bi_2O_3 -based oxides. In contrast, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ exhibits only ionic conduction under $P_{\text{O}_2} = 10^{-21}$ to 1 atm. Therefore,

doubly doped LaGaO_3 perovskite oxide is highly promising for the solid electrolyte of fuel cells and oxygen sensors.

The diffusivity of oxide ions in LSGM was further studied with ^{18}O tracer diffusion measurements¹⁷⁾. LSGM has higher diffusion coefficient than fluoride oxide, which could originate from the higher mobility of the oxide ions compared with fluoride oxide (Table 1). Therefore, the perovskite structure is considered to have a large free lattice volume resulting in the high diffusivity of oxide ions, and consequently high oxide ion conductivity.

Recently, visualization of oxygen transport has been simulated in perovskite based on quantum chemistry, in particular for LaGaO_3 perovskite¹⁸⁾. The migrating ion must pass through the opening of a triangle defined by two A sites (La^{3+}) ions and one B site ion in perovskite. The geometrical constraints on lattice relaxation suggest that a small deviation from the direct path for

vacancy migration occurs as illustrated schematically in Fig. 4. The calculations reveal a curved route around the octahedron edge with the saddle point distant from the adjacent B site cation. Therefore, the large free volume is the cause of the high mobility of oxide ion and the consequent high oxygen ion conductivity in perovskite.

3. Preparation of LSGM Thin Film by the Laser Ablation Method on Porous Ni-Fe Metal Substrate for Low Temperature SOFCs¹⁹⁾

LSGM has acceptably high oxide ion conductivity, but a thin film electrolyte is required to achieve high power density at low temperatures. In a previous study, porous oxide electrodes such as NiO-YSZ cermet were used for the substrate. However, the thickness of

Fig. 2 Contour Plot of the Conductivity in $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$ at 1073 K^{12),13)}

Fig. 3 Comparison of Oxide Ion Conductivity in LaGaO_3 Doped with Sr, Mg, and Co with that of Fluorite Oxide Ion Conductor in N_2 Atmosphere

Table 1 Comparison of Mobility of Oxide Ion in Various Fluorite and LSGM Oxides at 1073 K

	D_t [cm^2/s]	E_a [eV]	δ	$[\text{Vo}^{\bullet\bullet}]$ [cm^3]	D [cm^2/s]	μ [cm^2/Vs]
$\text{Zr}_{0.81}\text{Y}_{0.19}\text{O}_{2-\delta}$	6.2×10^8	1.0	0.10	2.95×10^{21}	1.31×10^6	1.41×10^5
$\text{Zr}_{0.85}\text{Ca}_{0.142}\text{O}_{2-\delta}$	7.54×10^9	1.53	0.142	4.19×10^{21}	1.06×10^7	1.15×10^6
$\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{2-\delta}$	1.87×10^8	1.22	0.15	4.43×10^{21}	2.49×10^7	2.69×10^6
$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$	2.70×10^8	0.9	0.05	1.26×10^{21}	1.08×10^6	1.17×10^5
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	3.24×10^7	0.74	0.15	2.53×10^{21}	6.4×10^6	6.93×10^5
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	4.13×10^7	0.63	0.20	3.34×10^{21}	6.12×10^6	6.62×10^5
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_{3-\delta}$	4.50×10^7	0.42	0.1645	2.78×10^{21}	8.21×10^6	8.89×10^5

D_t : Tracer diffusion coefficient, D : Self diffusion coefficient.

Fig. 4 Calculated Path for Oxygen Vacancy Migration¹⁷⁾

Fig. 5 Schematic for Preparation of SOFC Supported by Porous Ni-Fe Metal Substrate

the electrolyte film has some limitations depending on the thickness and pore size of the substrate because dense electrolyte film without gas leakage is essential. In contrast, use of a dense substrate allows the preparation of a thin but dense film. This study used the so-called selective reduction method for preparation of metal-supported LSGM thin film cells. **Figure 5** shows the preparation procedure for these cells. Our previous study found that Ni-Fe bimetallic anode is highly active for the electrochemical oxidation of fuel.

Fig. 6 Change in the Shrinkage and Porosity as a Function of Reduction Temperature

Fig. 7 Power Generation Properties of the SOFC Reduced at Different Temperatures

The precursor of the Ni-Fe mixed oxide substrate was prepared by impregnation of Fe_3O_4 on NiO particles followed by calcination. The LSGM film with thickness of a few micrometers was deposited by the pulse laser deposition method followed by reduction with hydrogen. During reduction, the dense NiO- Fe_3O_4 substrate was reduced to porous metals, because reduction of NiO is faster and easier, and so reduction of NiO occurs initially followed by reduction of Fe_3O_4 . Consequently, the reduction of NiO- Fe_3O_4 results in porous metal with little change in shape based on the use of the Fe_3O_4 -coated NiO particles. **Figure 6** shows the changes in the shrinkage and porosity as a function of reduction temperature. The volumetric shrinkage increased and the porosity decreased with higher reduction temperature. Large porosity and small shrinkage are necessary to achieve high performance and stable operation. Therefore, the optimum reduction temperature is 973 K for the NiO- Fe_3O_4 substrate.

Further detailed investigations on the effect of reduction temperature measured the power generation properties in three cells prepared by reduction at different temperatures as shown in **Fig. 7**. The cell at reduced

Fig. 8 SEM Image of the Surface Morphology of the SOFC after Power Generation Measurement

Fig. 9 Effects of Thermal Cycles on Power Generation Characteristics of the SOFC

973 K showed almost theoretical open circuit voltage (OCV) and high power density. In contrast, the cells reduced at 873 K and 1072 K showed low OCV and the power density. Such low OCV values may have originated in fuel leakages resulting from cracking or delamination of the electrolyte.

Figure 8 shows the scanning electron microscope (SEM) image of the surface morphology of the cell after power generation measurement. Clearly the substrate has developed small pores with diameter of a few micrometers. In contrast, no cracks or pin holes were formed in the dense film of about 5- μm thickness deposited on the porous Ni-Fe substrate during reduction. Therefore, LSGM film can be successfully formed on Ni-Fe porous metal substrate and cells manufactured using the obtained LSGM film have high power density at low temperatures.

High mechanical strength is a great advantage of metal-supported SOFCs. **Figure 9** shows the effects of thermal cycles on the power generation characteristics of the cell. In this experiment, the cell was quenched from 973 K to room temperature and then heated up to 973 K. No serious decrease in power density was

caused by the thermal cycle, showing that the cell is highly resistant to thermal cycling and indicating the suitability for use in sturdy and reliable SOFCs. The small degradation in power density caused by the thermal cycle test was probably due to delamination of the cathode based on measurement of the internal resistance. Therefore, metal-supported cells using LSGM electrolyte thin film have high tolerance to thermal shock and high power density at low temperatures.

4. Oxide Anode for Further Improvement in Power Density

Ni mixed with oxide called cermet is widely used for the anode in conventional fuel cells²⁾, but Ni is easily aggregated under normal operating conditions resulting in reduced power density. Oxide anodes may be a new type of anode material for SOFCs to overcome such problems with the conventional Ni anode. Therefore, development of anode materials tolerant to re-oxidation is very important for durable and reliable electrodes for SOFCs. In addition, nickel has high catalytic activity, in particular for electrochemical oxidation of hydrocarbon fuel, but nickel catalyst requires excess steam for fuel reforming due to carbon deposition on the metal catalyst.

Various research groups have investigated anode materials to overcome the disadvantages of current commercial anode materials for a few decades. Cu-ceria base and some perovskite oxides, which are highly tolerant to the redox cycle, have been widely investigated as oxide anode materials for SOFC. Ceria-based ceramic anodes with small amounts of metal additives such as Cu or Pd perform reliably and Cu-ceria seems to be suited for hydrocarbon fuel^{20),21)}. However, Cu has a lower melting point and so is not compatible with typical SOFC fabrication methods, as well as providing lower electro-catalytic activity than nickel. High power density could be achieved by using $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ for the anode with fairly good stability under redox cycling because of the oxide characteristics^{22),23)}. However, further improvement in anodic performance is still very important for adaptable oxide anodes for SOFCs. The present study investigated the anodes of CeO_2 -based oxide and found that Mn and Fe doped CeO_2 provides high performance, so the application of Fe, Mn doped CeO_2 for anode of Ni-Fe metal support cell was studied²⁴⁾.

Figure 10 shows the temperature dependence of the maximum power density and the internal resistance of the cell using $\text{Ce}_{0.6}\text{Mn}_{0.3}\text{Fe}_{0.1}\text{O}_2$ (CMF) anodes. Unlike metal-based anodes, the current collecting effect is not high enough due to the low electrical conductivity of the oxide anode, particularly at low temperature. Therefore, the power density of cells using the oxide anode was lower than that of cells using the Ni anode. For exam-

IR loss and η of anode was at 0.2 A cm^{-2} .
 (▲) M.P.D., (◆) IR loss, (⊕) anodic overpotential.
 $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_3$ was used for electrolyte.

Fig. 10 Temperature Dependence of Anodic Overpotential, IR Loss and Maximum Power Density of the SOFC Using $\text{Ce}(\text{M} = \text{Mn}, \text{Fe})\text{O}_2$ for the Anode

Fig. 11 (a) Schematic of the SOFC Prepared in this Study and (b) SEM Images of the Prepared Cell and the Sectioned Film

ple, the cell using Ni-Fe anode exhibited maximum power density of *ca.* 800 mW cm^{-2} at 1073 K , whereas the cell using CMF anode achieved only 330 mW cm^{-2} . Such low power density of the cell using oxide anode can be explained by the large IR loss resulting from insufficient conductivity of CMF. Evidently, the potential drop caused by IR loss at the anode was more dominant than that caused by overpotential at the CMF anode as shown in **Fig. 10**. However, a small anodic overpotential was still sustained at lower temperatures such as 873 K , suggesting that the surface activity of this oxide was adequate for anodic reaction in the intermediate temperature range.

The power density of the cell using CMF is still lower than that of the cell using Ni, but higher power density can be expected by improving the electrical conductivity of the anode by using a thin film anode. **Figure 11** shows the concept and SEM image of the thin film anode.

Fig. 12 *I-P* and *I-V* Curves of the Metal-supported Cell with SSC-LSGM-CMF Thin Films at Intermediate Temperatures

The limited reaction zone is a large disadvantage of the porous Ni-Fe metal because of the limited three phase boundary, so that insertion of a mixed conducting CMF layer will extend reaction area as schematically shown in **Fig. 11(a)**. The SEM image of the sectioned film obtained with field ion beam micromachining equipment clearly shows that the thin CMF layer was successfully deposited between the Ni-Fe porous metal substrate and LSGM film in **Fig. 11(b)**. Energy dispersive X-ray fluorescence spectrometer (EDX) analysis showed the thickness of the film was just a few 100 nm with tight contact to the LSGM film.

Figure 12 shows the *I-V* and *I-P* curves of the metal-supported cell with $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC)-LSGM-CMF thin films at intermediate temperatures. The cell exhibited high open circuit voltage (OCV) of 1.08 V , which is close to the theoretical value (1.14 V), and extremely high power density of 3.1 W cm^{-2} at 973 K . Evidently the obtained film was dense without gas leakage because the OCV was close to the theoretical voltage (1.14 V). The power generating property of the metal-supported cell was slightly lower than that of cermet-supported cell using LSGM- $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_2$ (SDC) thin films¹⁹, but was much improved compared to the metal-supported cell using SSC-LSGM-SDC thin films²⁴. The SDC thin layer has been used for preventing counter diffusion of cations such as lanthanum and nickel between the LSGM electrolyte film and Ni-Fe metal substrate. However, SDC may also be regarded as a functional anodic layer based on analysis of CeO_2 -based oxides in the anodes of SOFCs which found significantly decreased activation overpotential for oxidizing hydrogen²⁵. However, the SDC layer has inadequate anodic characteristics to achieve high power density in the intermediate temperature range suitable for power generation with a metal-supported cell using LSGM-SDC. Therefore, this study investigated co-doped ceria (CMF) to achieve superior anodic characteristics and high power generation. Clearly

Fig. 13 *I-P* and *I-V* Curves of the Cells Using the CMF-LSFM Composite Oxide and Ni-Fe Anodes, Respectively

SOFCs using CMF dense anode and LSGM thin film electrolyte are highly promising as a low temperature SOFC with high reliability.

5. Direct Hydrocarbon Type SOFC Using Oxide Anode

Development of the direct hydrocarbon SOFC is another important issue for development of SOFC to achieve the highest energy conversion efficiency with simplified gas supply system. However, the use of hydrocarbon fuel for current SOFCs has been limited due to deactivation by carbon coking. Ni-based anodes have good electrochemical conductivity and catalytic performance for hydrogen oxidation, but Ni is easily deactivated by carbon formation with directly exposure to hydrocarbons²⁾. Under the most serious conditions, the cells fracture as a result of deposited coke. Consequently, replacing Ni-based anodes with a more reliable anode material such as Cu-based metals or ceramics has recently attracted a great deal of attention. Methane is generally considered as the fuel for the direct hydrocarbon type SOFC. However, both methane and liquid petroleum gas have various advantages as fuels for portable SOFC power generating systems and auxiliary power units for vehicles. Therefore, this study examined the use of various hydrocarbon fuels in SOFCs with $\text{Ce}_{0.6}\text{Mn}_{0.3}\text{Fe}_{0.1}\text{O}_2$ (CMF)- $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Mn}_{0.1}\text{O}_3$ (LSFM) composite oxide anodes. Since simple benefit of plant (BOP) was expected, dry condition was used for the hydrocarbons, which is an extremely difficult condition for coke deposition.

Figures 13 shows the *I-P* and *I-V* curves of the cells using CMF-LSFM composite oxide and Ni-Fe anodes, respectively, with various hydrocarbons, *i.e.*²⁶⁾, hydro-

gen, methane, ethane, propane, and butane, as the fuel. Fairly good power density was achieved using hydrogen fuel in this as reported previously, but the value was much lower than that for the cell using Ni-Fe (9 : 1) bimetal anode. On the other hand, the maximum power density increased with higher carbon number of the hydrocarbon fuel for the cell using the CMF-LSFM oxide anode, reaching approximately 1 W cm^{-2} at 1073 K using C_3H_8 or C_4H_{10} as the fuel as shown in Fig. 13. In contrast, power density decreased with higher carbon number with the conventional Ni-Fe anode. Power density drastically decreased over the measurement period using C_3H_8 as the fuel, suggesting deactivation of the anode by coke deposition. The finding of increasing power density with higher carbon number in the cell using the CMF-LSFM oxide anode is very interesting. This power density was also extremely high compared to the results reported for ceramic or even metal anodes; the power density of the oxide anode is always smaller than 0.5 W cm^{-2} at 1073 K for hydrogen or methane. Therefore, the cell using the CMF-LSFM composite anode showed highly advantageous characteristics which allow direct use of hydrocarbon as the fuel.

6. Conclusion

The current trends in SOFC development were reviewed. SOFC has high potential as a power generator with high energy conversion efficiency, but the excessively high operating temperature limits the applications as well as service life of the conventional SOFC system. Lower operating temperature and increased reliability are important to solve such problems. Our previous study proposed a new preparation method for fabricating metal supported SOFC, which is based on the different reduction rates of NiO and Fe_3O_4 . By using selective reduction, a metal support SOFC using a LSGM/SDC bilayer thin film electrode film was successfully prepared. The prepared metal support cell has reasonably high power density (1.8 W cm^{-2} at 973 K) and high mechanical strength against thermal shock. Insertion of a CMF dense anode layer between the LSGM electrolyte and Ni-Fe porous anode decreased the anodic overpotential and much improved the power density, with maximum power density of 3.1 W cm^{-2} and 0.17 W cm^{-2} at 973 K and 673 K, respectively. Consequently, low temperature SOFCs can be successfully manufactured by using fast oxide ion conducting electrolyte film such as LSGM, which will extend the applications of SOFC.

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要 旨

金属基板上に製膜された LaGaO₃系酸化物薄膜を用いる低温作動型固体酸化物電解質燃料電池

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低温作動型燃料電池のために Sr と Mg を添加した LaGaO₃系酸化物 (LSGM) の酸素イオン伝導度の紹介を行った。SOFC は多様な燃料を用いることの可能な高効率な電力発生装置である。本稿では Sr と Mg を添加した高酸素イオン伝導体の低温作動型 SOFC の電解質への応用を検討した。低温での出力密度は LSGM の応用により大きく向上したが、さらに大きな出力を達成するには LSGM の薄膜化が必要である。レーザーアブ

レーションにより、LSGM の薄膜化が可能であり、緩衝層を最適化することで、0.2 W cm⁻² の出力を 773 K で達成できた。一方、Ce_{0.6}Mn_{0.3}Fe_{0.1}O₂ (CMF) が優れたアノード特性を示すことを見出し、CMF 薄膜をアノードとした SOFC は 673 K でも 0.17 W cm⁻² の出力を示した。さらに、CMF と La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O₃ (LSFM) を 12.5 : 87.5 wt% で混合した酸化物をアノードとすると、炭化水素を直接燃料として用いることが可能なことを示した。