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Solid oxide fuel cell using Co doped La(Sr)Ga(Mg)O_3 perovskite oxide with notably high power density at intermediate temperature

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Power generation characteristics of fuel cells was greatly improved by using $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_3$ as electrolyte. In particular, the maximum power density attained a value of 1.53 and 0.50 W cm^{-2} at 1073 and 873 K, respectively, in an H_2–O_2 cell when the thickness of electrolyte was 0.18 mm.

Solid oxide fuel cells (SOFCs) represent a new and clean electric power generation system. At present, Y_2O_3 stabilized -ZrO_2 (YSZ) is commonly used as the electrolyte of solid oxide fuel cells. Since the oxide ion conductivity of YSZ is fairly low, a thin electrolyte film without gas leakage and an excessively high operating temperature (1273 K) are essential to achieve high power density. On the other hand, advantages for SOFCs such as high efficiency and increased variety of usable fuels can be obtained at decreased temperatures such as 1073 K. Furthermore, choice of the materials for cell stacking becomes wider; in particular, cheap refractory metals such as stainless steel are usable upon decreasing the operating temperature down to 900 K. Consequently, a decrease in operating temperature is of importance for the development of cheap but reliable cells.[1] It is, therefore, of great importance to develop new electrolyte materials which exhibit high oxide ion conduction over a wide oxygen partial pressure. In our previous study, oxide ion conductivity in perovskite oxides were investigated and it was found that the $LaGaO_3$-based perovskite type oxide exhibits high oxide ion conductivity,[7,8] comparable with that of CeO_2-based oxide. In particular, $LaGaO_3$ doped with Sr for La and Mg for Ga sites (LSGM) exhibits high oxide ion conductivity over a wide oxygen partial pressure.[9–12] Furthermore, it was found that doping a small amount of Co into Ga sites of $LaGaO_3$ was effective in improving the oxide ion conductivity, albeit with the appearance of a small amount of hole conductivity.[13] Although the electrical conductivity monotonously increased, the transport number of oxide ion decreased with increasing Co content. Considering the transport number and oxide ion conductivity, the optimized composition of Co doped $LaGaO_3$ was $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_3$ (denoted LSGMC). Power generation characteristics of SOFCs with LSGMC as electrolyte was thus studied.

All specimens used in this study were prepared by conventional solid state reaction techniques employing powders of La_2O_3, Ga_2O_3, MgO, $SrCo_3$ and CoO (99.5%, Kishida). Details of the preparation procedure can be found elsewhere.[4,13] Sintering was performed at 1773 K for 6 h in air. Platinum paste was applied on both faces of sintered sample disks followed by calcination at 1223 K for 30 min.

In our previous study, for the application of LSGM as electrolyte to SOFCs, it was found that $Sm_{0.5}Sr_{0.5}CoO_3$ and Ni were appropriate for the cathode and the anode, respectively.[12] Using the same cathode and anode in this study, LSGMC was chosen as the electrolyte to develop SOFCs operable at intermediate temperatures. The initial SOFC fabricated in this study consisted of a single planar type cell of 20 mm diameter and the anode and cathode were both of 5 mm diameter. Pure O_2 or dry air and H_2 mixed with H_2O (3 vol%) were fed to the cathode and the anode, respectively, at 100 ml min^{-1}. The power generation characteristics were measured by a four probe method and a galvanostat was used to provide the electrical load.

The temperature dependence of the maximum power density together with the open circuit potential are shown in Fig. 1. The power generation characteristics of the cells using air and pure oxygen are also compared at 1073 K (Fig. 1). Open circuit potentials were slightly smaller than the theoretical values owing to hole conduction at high oxygen partial pressure, however, they remain > 1.0 V at all temperatures for both H_2–O_2 and H_2–air cells. On the other hand, notably large power densities are exhibited at all temperatures. When O_2 is used as oxidant, maximum power densities at 1273 and 1073 K are 1.40 and 0.77 W cm^{-2}, respectively. Furthermore, even at 873 K, the maximum power density is as high as 0.19 W cm^{-2}. At present, YSZ is the most common electrolyte for SOFCs. However, the maximum power density of an H_2–O_2 cell using YSZ as the electrolyte under the same conditions is only 0.38 and 0.06 W cm^{-2} at 1293 and 1073 K, respectively. Since the ionic conductivity of YSZ at 1273 K is almost the same as that of LSGMC at 923 K, it is expected that equivalent performances would potentially be achieved at considerably lower temperatures for LSGMC. The power density of the cell was slightly decreased by changing the oxidant from O_2 to air as shown in Fig. 1, however, the maximum power density was still higher than 700 mW cm^{-2} at 1073 K. It is generally observed that the power density is greatly decreased by changing the oxidant from O_2 to air. However, in this case the decrease in the power density was not large. This may result from hole conduction in LSGMC at high oxygen partial pressure. Since an extremely large power density was exhibited for both H_2–O_2 and H_2–air cells, LSGMC is highly attractive as the electrolyte of intermediate temperature SOFCs.

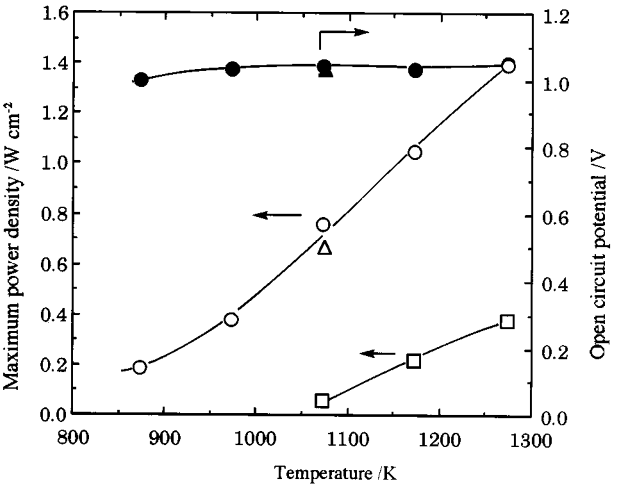

Fig. 1 Temperature dependence of electrical power generation characteristics of SOFCs containing $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_3$ as electrolyte. Thickness of electrolyte = 0.5 mm, $Sm_{0.5}Sr_{0.5}CoO_3$ cathode and Ni anode. (●) Open circuit potential and (○) maximum power density for an H_2–O_2 cell with LSGMC electrolyte. (△) Open circuit potential and (▲) maximum power density for an H_2–air cell with LSGMC electrolyte. (□) Maximum power density for an H_2–O_2 cell with $Zr_{0.84}Y_{0.16}O_4$ electrolyte.

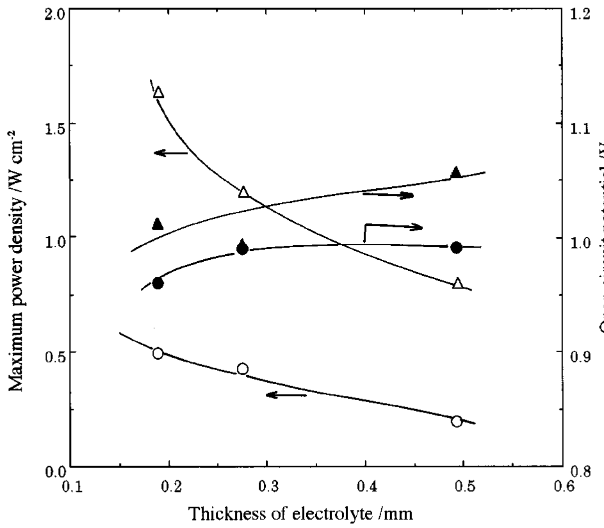

Fig. 2 Terminal voltage and power density of H_2–O_2 cells as a function of thickness of electrolyte. Ni and $Sm_{0.5}Sr_{0.5}CoO_3$ were used as anode and cathode, respectively. 873 K: (○) maximum power density and (●) open circuit potential. 1073 K: (△) maximum power density and (▲) open circuit potential.

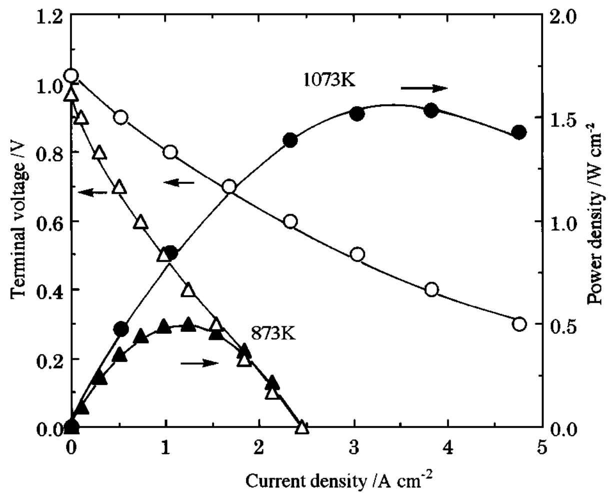

Fig. 3 Current–potential and current–power density curves of an SOFC utilizing 0.189 mm thick LSGMC at 873 and 1073 K with H_2 and O_2. (○) *I–V* curves and (●) *I–P* curves at 1073 K. (△) *I–V* curves and (▲) *I–P* curves at 873 K.

A large part of the internal resistance of the present cell is ohmic resistance which is almost comparable to that of ionic conductivity in LSGMC. Therefore, it is reasonable to expect higher power density from a thinner LSGMC electrolyte and thus the effect of electrolyte thickness was studied. Fig. 2 shows the open circuit potential and power density of H_2–O_2 cells as a function of thickness of electrolyte. The power density of the cell monotonously increases with decreasing thickness of the electrolyte. In particular, the maximum power density reached a value of 1.53 and 0.50 W cm^{-2} at 1073 and 873 K, respectively, when the thickness of electrolyte was 0.18 mm (Fig. 2). On the other hand, the open circuit potential was decreased with decreasing thickness of the electrolyte because the contribution of hole conduction was more significant upon increasing the gradient in oxygen partial pressure. However, the open circuit potential was always >1.0 V at 1073 K for an SOFC utilizing an LSGMC thin plate. At 0.18 mm electrolyte thickness, however, the open circuit potential was decreased to 0.94 V at 873 K, since the transport number of oxide ion was decreased. Fig. 3 shows the power generation characteristics of an LSGMC cell with 0.18 mm thick electrolyte. It is obvious that extremely large power density was attained for this cell even at 873 K. The current density at short circuited conditions at this temperature was 2.5 A cm^{-2} and furthermore, the power density at 0.7 V was as high as 352 mW cm^{-2}. This power density was comparable to that of a molten carbonate fuel cell operating at 923 K.

In light of the notably high oxide ion conductivity of LSGMC, we believe that today's SOFCs can be improved to yield higher power outputs at lower operating temperatures. The consequences of operation at low temperatures, are increased reliability of the cell with use of a reasonably priced metallic element, *e.g.* stainless steel, the removal of a requirement of an excessively thin electrolyte film and availability of more compact geometries which leads to easy maintenance and durability. These factors are major advantages arising from the use of the proposed electrolyte (LSGMC) for the next generation of power generators.

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