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Journal of Alloys and Compounds 408–412 (2006) 512–517

Journal of ALLOYS AND COMPOUNDS

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Demonstration of high efficiency intermediate-temperature solid oxide fuel cell based on lanthanum gallate electrolyte

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Available online 1 July 2005

Abstract

The Kansai Electric Power Co., Inc. (KEPCO) and Mitsubishi Materials Corporation (MMC) have been jointly developing intermediate-temperature solid oxide fuel cells (SOFCs). The operation temperatures between 600 and 800 °C were set as the target, which enable SOFC to use less expensive metallic separators for cell-stacking and to carry out internal reforming of hydrocarbon fuels. The electrolyte-supported planar-type cells were fabricated using highly conductive lanthanum gallate-based electrolyte, $La(Sr)Ga(Mg,Co)O_{3-\delta}$, Ni-$(CeO_2)_{1-x}(SmO_{1.5})_x$ cermet anode, and $Sm(Sr)CoO_{3-\delta}$ cathode. The 1 kW-class power generation modules were fabricated using a seal-less stack of the cells and metallic separators. The 1 kW-class prototype power generation system with the module was developed with the high performance cell, which showed the thermally self-sustainability. The system included an SOFC module, a dc–ac inverter, a desulfurizer, and a heat recovery unit. It provided stable ac power output of 1 kW with the electrical efficiency of 45% LHV based on ac output by using city gas as a fuel, which was considered to be excellent for such a small power generation system. And the hot water of 90 °C was obtained using high temperature off-gas from SOFC.

Keywords: Lanthanum gallate; Ni–SDC; Intermediate temperature solid oxide fuel cell; Power generation module; System

1. Introduction

The solid oxide fuel cell (SOFC) is one of the most attractive energy conversion systems because of its high efficiency, low pollution and fuel flexibility. The SOFCs are usually operated at high temperatures near 1000 °C, so as to give the electrolyte materials conductivity high enough to be used. Recently, the reduction of the operation temperatures of SOFC has been drawing a great deal of attention, because it gives several advantages (i.e. wider choices of low-cost and high performance component materials, higher stability, reduced amount of degradation and increased freedom for structural design, etc.). The Kansai Electric Power Company Inc. (KEPCO) and Mitsubishi Materials Corporation (MMC) have been jointly developing intermediate temperature SOFC since 2001. The operation temperatures between 600 and 800 °C were set as the target, which enable SOFC to use less expensive metallic separators for cell-stacking and to carry out internal reforming of hydrocarbon fuels.

To develop a practical intermediate temperature SOFC, two approaches are under active consideration. One is to use an extremely thin YSZ membrane to make the ohmic loss due to the electrolyte as small as possible [1–3]. Another is to use a new electrolyte material that shows high oxide ion conductivity at temperatures below 800 °C [4–7], comparable to that of YSZ at 1000 °C. It has been reported that doped lanthanum gallate compounds, $La(Sr)Ga(Mg)O_{3-\delta}$ possess excellent oxide ion conductivity at intermediate temperatures over a broad range of oxygen partial pressures [8]. Furthermore, double doping by a transition metal, e.g. Co,

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doi:10.1016/j.jallcom.2005.04.158

was proved to be the most appropriate in further improving the oxide ion conduction in La(Sr)Ga(Mg,Co)$O_{3-\delta}$, which was reported by Ishihara et al. [9,10].

Since lowering the operation temperature increases not only the ohmic loss but also the polarization loss at the anode and the cathode, it is also necessary to develop highly active electrodes that show sufficiently low polarization at intermediate temperatures. KEPCO and Japan Fine Ceramics Center developed the highly active Ni-$(CeO_2)_{1-x}(SmO_{1.5})_x$ (Ni–SDC) cermet anodes, which were prepared using highly dispersed composite particles synthesized by spray pyrolysis technique [11–13]. On the other hand, Samarium cobaltite compounds, Sm(Sr)$CoO_{3-\delta}$ have been demonstrated to show very small polarization as the cathode material [14]. The high performance intermediate temperature SOFC was fabricated and the highly efficient 1 kW-class system, along with multi-kilowatt-class power generation modules were developed and demonstrated.

2. Development of high performance cell

The coin-shaped cells with the electrode area of 2 cm^2 were fabricated with $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{3-\delta}$ (LSGMC) electrolyte, Ni-$(CeO_2)_{0.8}(SmO_{1.5})_{0.2}$ (Ni–SDC) cermet anode, and $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) cathode. Production of 100 μm-thick LSGMC was realized by tape casting technique to give green-sheets, which were dried, cut to a disk shape, and then sintered at 1400–1500 °C for several hours. The diameter of the resulting disks was 32 mm, and the observed densities of the disks were higher than 98% of the theoretical value.

NiO–SDC composite particles were synthesized by spray pyrolysis technique (Fig. 1). Aqueous solutions containing the desired composition of corresponding cations were prepared by dissolving $Ni(OCOCH_3)_2 \cdot xH_2O$, $Ce(NO_3)_3 \cdot xH_2O$, and Sm_2O_3 in the presence of nitric acid. These solutions were atomized with an ultrasonic vibrator operating at 1.7 MHz. The droplets were transported into a reaction furnace using air as a carrier gas with a fixed flow rate of 1 L/min. The reaction furnace consisted of four independent heating zones, temperatures of which were set at 200, 400, 800, and 1000 °C, respectively. The particles were collected using an electrostatic precipitator or membrane filter, and were calcined at 1000 °C for 24 h. Fig. 2 shows the NiO–SDC composite particles synthesized with the spray pyrolysis method before the calcination. It was found that these composite particles were spherical particles with mean particle size of about 1 μm, and some particles were consisted of much smaller sub-micron particles. X-ray diffraction analysis showed the composite particles were two-phase mixture of NiO and SDC, and that the crystallization of the composite particles was increased by the calcination at 1000 °C. The compositions of synthesized particles were confirmed by X-ray fluorescence analysis.

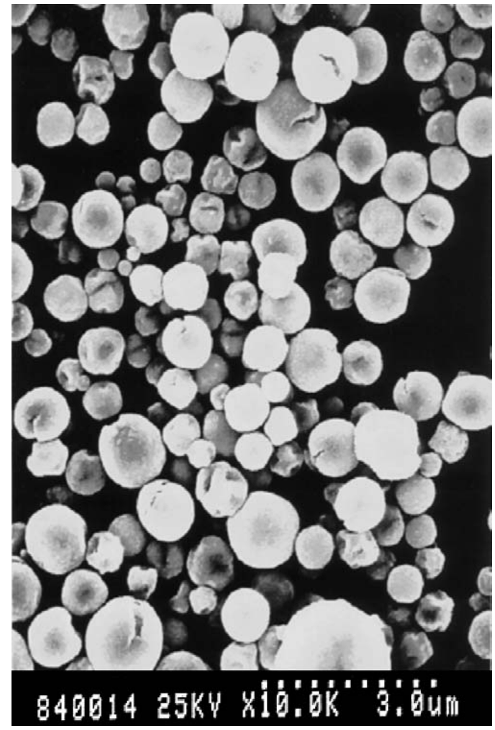

Fig. 2. SEM image of NiO–SDC composite particles prepared by spray pyrolysis.

NiO–SDC composite particles thus obtained were deposited onto LSGMC disks by the screen-printing method, followed by sintering at 1250 °C for 3 h. The temperature was optimized to give the best microstructure for anode reaction. For the cathode, the slurry containing cathode particles of SSC was also screen-printed onto the opposite side of the electrolyte and was sintered at 1100 °C. The single cell tests were carried out at temperatures between 650 and 800 °C. Air was used as an oxidant, and 3% moisturized hydrogen gas (H_2 + 3 vol.% H_2O) was used as a fuel. NiO in the anode was reduced to Ni under fuel atmosphere prior to measuring

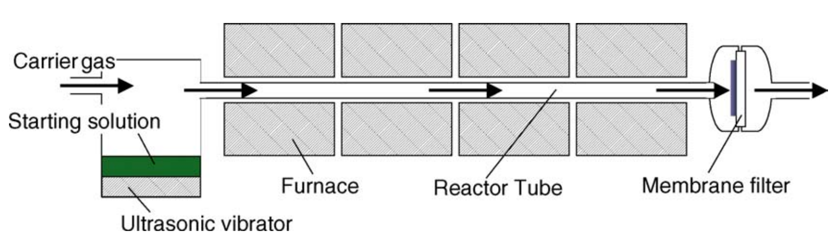

Fig. 1. Schematic diagram of synthesis of composite particles by spray pyrolysis.

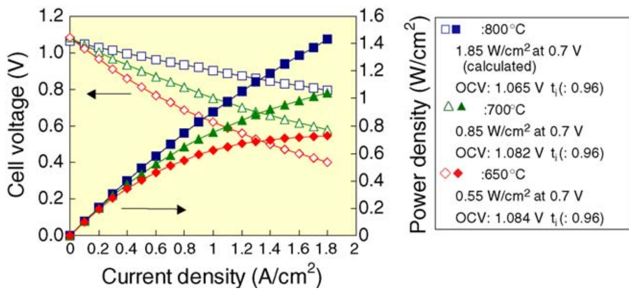

Fig. 3. Power generation characteristics of Ni–SDC/LSGMC/SSC cell at 650, 700 and 800 °C with 3 vol.% humidified hydrogen fuel.

the power generation characteristics. Fig. 3 shows the typical result on power generation characteristics of the single cell. The ion transport number t_i was 0.96 in the temperature range between 650 and 800 °C. It was found that the initial power density at the cell voltage of 0.7 V was as high as 1.85 W/cm^2 at 800 °C, and 0.85 W/cm^2 at 700 °C. The power density with 0.7 V at 800 °C was obtained by the extrapolation of the *I*–*V* curve, because it could not be measured due to the current limit by the electric load instrument. This result was considered to be one of the best among the ones reported [1–3,7] on the SOFC operated at such a low temperature region. This extremely high power density of the cell could be the result of the combination of the thin electrolyte of LSGMC, the composition- and sintering temperature-optimized Ni–SDC cermet anode [11–13], and the highly active SSC cathode.

Fig. 4 shows the internal resistance of the cell measured by the current interruption method at each temperature, which shows that both anodic and cathodic overpotentials are quite low, for example, the anodic overpotential with 0.3 A/cm^2 at 800 °C is less than 20 mV and the cathodic one is about 10 mV. It was also found that the *iR* drop is in good agreement with the one calculated from the conductivity of the LSGMC, shown as $iR_{\text{electrolyte}}$ in Fig. 4, which means that the *iR* drops due to the electrodes are negligible for the cell used in this study. Further investigation on the anode using the composite particles synthesized by the spray pyrolysis is needed.

3. Single cell stack-unit performance

One of the biggest advantages of the reduction of the operation temperature of SOFC is the applicability of stainless steels for the material of the separators, which leads to a lowering of the manufacturing cost. MMC reported that the stainless steels were applicable as the separators to the planar type SOFC [15]. It is also expected that high power output per unit volume could be achieved by the planar type SOFC due to its advantage of packed configuration over the cylindrical type SOFC. In general, the difficulty in stacking the planar type cells has been ascribed to gas sealing as well as the management of the differences in the thermal expansion coefficients between the cell and the separator on the thermal cycles.

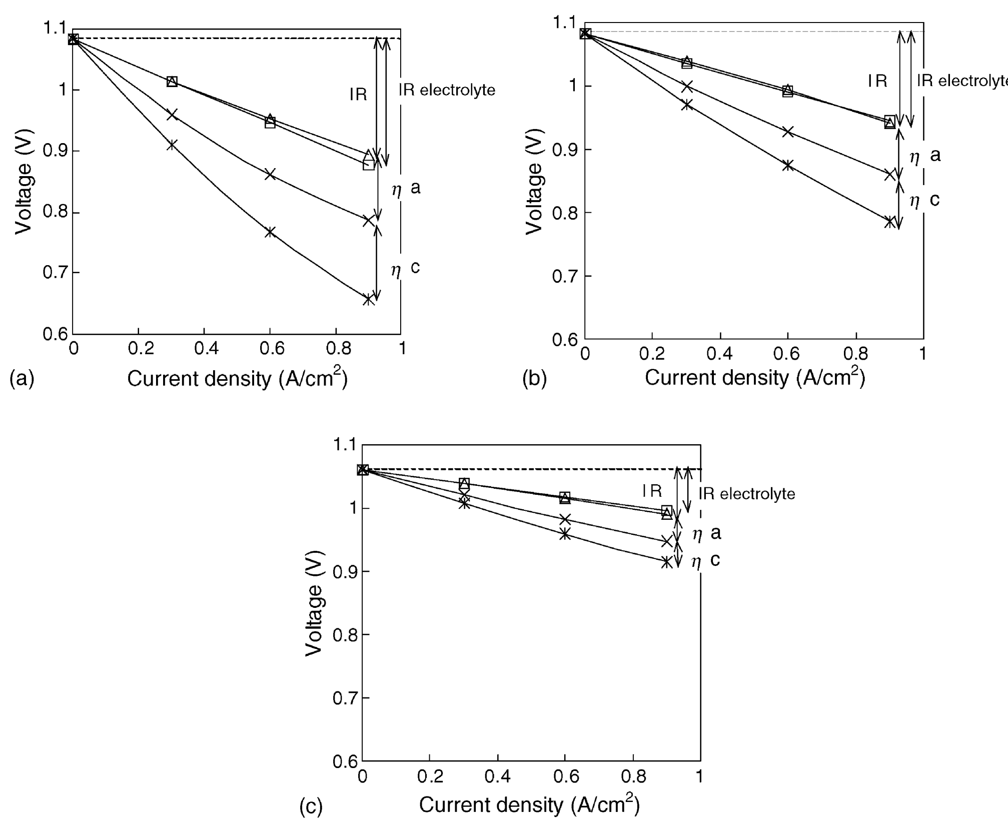

Fig. 4. Internal resistance of Ni–SDC/LSGMC/SSC cell at (a) 650 °C, (b) 700 °C and (c) 800 °C with 3 vol.% humidified hydrogen fuel.

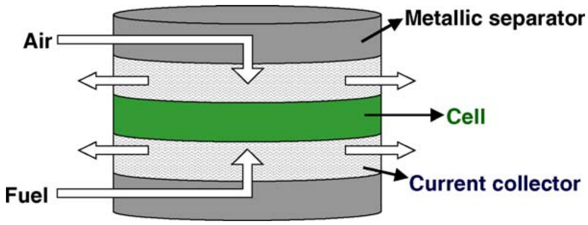

Fig. 5. Conceptual design of seal-less stack-unit.

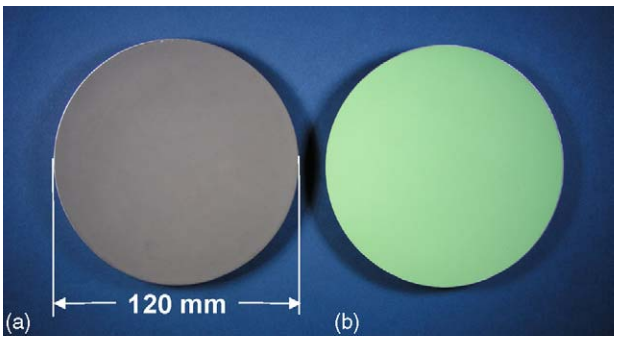

Fig. 6. Disk-type single cell: (a) cathode side and (b) anode side.

The seal-less stack concept, as shown schematically in Fig. 5, was adopted to keep away from the gas-sealing problems. Both fuel and air are supplied through inlets located at the side edge of each separator, and flow out from individual center-holes at the separator surface. The remaining fuel after the fuel cell reaction is burned around the stack to supply the additional heat to maintain the cell stack temperature.

On the other hand, it was confirmed that Ni–SDC/LSGMC/SSC cell had great potentiality to realize excellent performance by modifying the small size cell technology, mentioned above, to practical size cell fabrication. The anode was prepared using mixture of NiO and SDC for the cell with 120 mm in diameter. The electrolyte thickness of 200 μm have been employed as a standard for the SOFC module development (Fig. 6).

The typical performance data obtained with the single cell stack-unit at various operation temperatures are shown in Fig. 7. The cell voltage was measured at the current density of 0.3 A/cm^2 with pure H_2 as a fuel (the flow rate of 340 NmL/min, fuel utilization of 70%). The obvious temperature dependence of the cell performance was not observed, and the best performance was obtained at 750 °C in the temperature range between 650 and 800 °C. The reason of this behavior is not clear at this moment. It might be somehow due to the seal-less structure of the single cell stack-unit or the cell size, because the small size cell performance using the sealant shows the clear temperature dependence (Fig. 3). Furthermore, the electrical efficiency of 54% was attained at 750 °C with 90% hydrogen utilization. The power density of 0.69 W/cm^2 was also obtained at 750 °C with 84% fuel utilization.

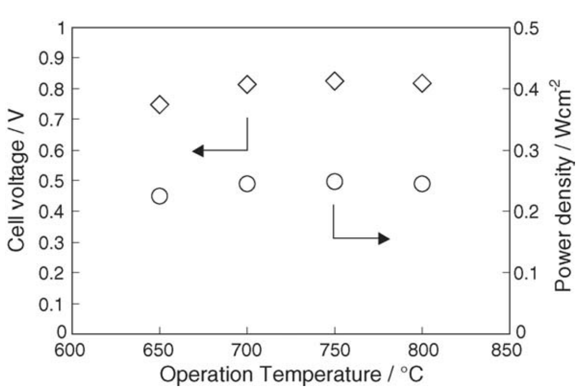

Fig. 7. Power generation characteristics of the single cell stack-unit.

4. Demonstration of 1 kW-class SOFC system

After two types of 1 kW-class power generation modules with either hydrogen or internally steam-reformed methane as a fuel were confirmed to give the high performance under thermally self-sustained conditions, KEPCO and MMC jointly developed a prototype 1 kW power generation system with the city gas as a fuel to demonstrate the potential for commercial use. The chemical composition of the city gas used in this study is as follows: CH_4 89%, C_2H_6 7%, C_3H_8 3%, and C_4H_{10} 1%. The schematic diagram of the system is shown in Fig. 8 and the external view of the module in Fig. 9. The system, along with the SOFC module which has 46 cells with 120 mm in diameter, is composed of four sub-units. One is the reactant supply unit, which controls the flow rate of city gas, air and water. The sulfur-based odorant contained in the city gas is removed by means of desulfurizer. The water is purified through the column of ion exchange resin. The second unit is dc/ac inverter to give ac current of 100 V and 60 Hz. The third one is the heat recovery unit utilizing the high temperature off-gas from SOFC module. The last one is a control and monitoring unit. The entire system is controlled automatically. The open circuit voltage of each cell at the average temperature of 600 °C was at around 1 V, indicating the uniformity of the environment of each cell. The typical performance data obtained with

Table 1
Operation results of 1 kW SOFC system

	Result
Fuel	City gas 13A (CH_4 89%, C_2H_6 7%, C_3H_8 3%, C_4H_{10} 1%)
S/C	3.80
Fuel utilization (%)	68
Average temperature (°C)	778
Output dc power (W)	1099
Output ac power (W)	1019
dc voltage (V)	34.3
dc efficiency (LHV) (%)	48
ac efficiency (LHV) (%)	45
Inverter efficiency (%)	93
Produced hot water temperature (°C)	90

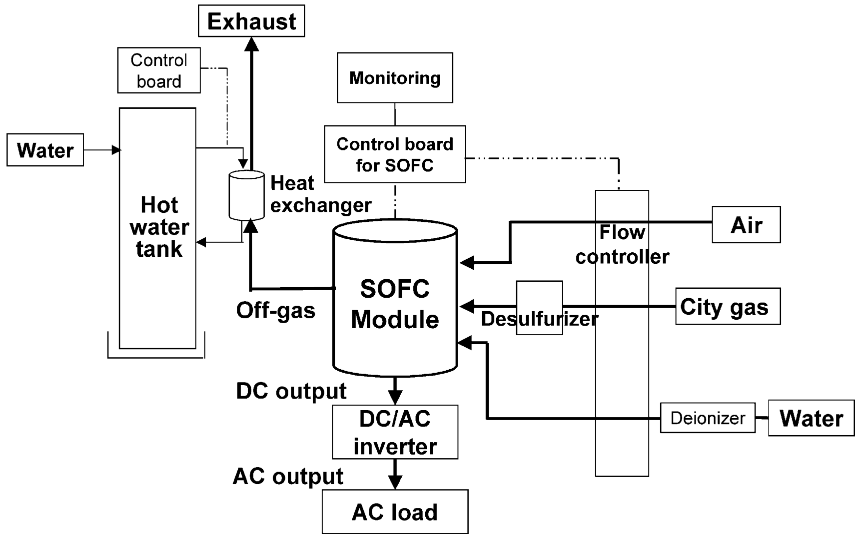

Fig. 8. Schematic diagram of 1 kW SOFC system.

the SOFC system is shown in Table 1. It was operated successfully with city gas as a fuel to provide stable ac power output of 1019 W under thermally self-sustained conditions. The electrical efficiency obtained with this system was 45% LHV based on ac output. The efficiency was calculated by dividing the power output energy by the combustion energy of the fuel fed to the system. The parasitic loss is not included in the calculation, because the system components are not optimized with respect to their power consumption. The electrical efficiency was raised to 50% LHV using a duplicated module whose thermal balance was improved, by which the ac efficiency is expected to be enhanced further. The hot water of 90 °C was obtained using high temperature off-gas from SOFC. The partial load performance test using the 1 kW system to demonstrate that even 10% partial power, 100 W (ac), was obtained under thermally self-sustained conditions. This result implies that the hot-standby condition can be achieved without using any external electric power.

Fig. 9. 1 kW SOFC system (the module part).

5. Multi-stack SOFC module development

The triple-stack module for multiple-kilowatt output was developed in parallel with 1 kW system. The module consists of three seal-less stacks assembled electrically in either series or parallel depending upon the test conditions. Each stack has 41 cells with 120 mm in diameter. The thermally self-sustaining power generation results with methane as a fuel is summarized in Table 2. The dc electrical efficiency of 55% LHV was obtained at the power output of 2970 W with the fuel utilization of 77%. The improvement of the efficiency of multi-stack module compared with the dc efficiency of 1 kW system is considered to be due to the improvement of the thermal balance. The results lead us to the development of the higher power output module.

Table 2
Operation results of triple-stack SOFC module

	Result
Fuel	Methane
S/C	3.6
Fuel utilization (%)	77
Average temperature (°C)	773
Output dc power (W)	2970
dc efficiency (LHV) (%)	55

6. Summary and future plan

KEPCO and MMC have been jointly developing intermediate temperature SOFC, composed of the high performance materials, specifically, highly oxide ion conductive LSGMC, Ni–SDC cermet anode, and SSC cathode. The operation temperatures between 600 and 800 °C were set as the target, which enable SOFC to use less expensive metallic separators for cell-stacking and to carry out internal reforming of hydrocarbon fuels. The 1 kW-class power generation modules were fabricated using a seal-less stack of the cells and metallic separators. The 1 kW-class prototype power generation system using city gas as a fuel was developed with the module, which showed the thermal self-sustainability. The system included an SOFC module, a dc–ac inverter, a desulfurizer, and a heat recovery unit. It provided stable ac power output of 1 kW with the electrical efficiency of 45% LHV based on ac output and 48% LHV on dc output, which was considered to be excellent for such a small power generation system. And the hot water of 90 °C was obtained using high temperature off-gas from SOFC. The evaluation tests of the long-term stability of SOFC module and system are scheduled. The preliminary design of 10 kW-class modules is under way based on the results obtained with 1 kW single-stack and triple-stack modules. The first milestone will be a completion of the development of several 10 kW-class SOFC system by the end of FY2006.

Acknowledgements

Authors would like to thank Professor Yusaku Takita of Oita University, Professor Tatsumi Ishihara of Kyusyu University, and Japan Fine Ceramics Center for their great contribution to the development of high performance materials.

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