Overview and Current Status

Advances in Solid Oxide Fuel Cells II
Narottam P. Bansal

DEVELOPMENT OF TWO TYPES OF TUBULAR SOFCS AT TOTO

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ABSTRACT

The current status of two types of SOFC R & D at TOTO is summarized. We have developed 10kW class tubular SOFC modules for stationary power generation using Japanese town gas (13A) as fuel. A small module which consisted of 5 stacks (a stack consisted of 2 × 6 cells) generated 1.5kW at 0.2A/cm^2 and achieved 55%-LHV efficiency at an average temperature of 900°C. A thermally self-sustaining module consisting of 20 stacks achieved 6.5kW at 0.2A/cm^2 and 50%-LHV.

We have also developed micro tubular SOFCs for portable application, which operate at relatively lower temperatures. The single cell generated 0.85, 0.70, and 0.24W/cm^2 at 700°C, 600°C, and 500°C, respectively. We built and evaluated a stack consisting of 14 micro tubular cells, and it successfully demonstrated 43W, 37W and 28W at a temperature of 700°C, 600°C, and 500°C, respectively.

INTRODUCTION

TOTO is the top sanitary ware manufacturer in Japan and highly experienced in traditional and advanced ceramic products. Solid Oxide Fuel Cells (SOFCs) are mainly composed of ceramics, and our fabrication technology has been utilized to produce high performance SOFCs at a low cost. TOTO started the research and development of tubular type SOFCs in 1989. From 2001 to 2004, we successfully completed a 10kW class thermally self-sustaining module test in a New Energy and Industrial Technology Development Organization (NEDO) project[1)]. Since 2004, TOTO started a new collaboration with Kyushu Electric Power Co., Inc. and Hitachi, Ltd. in a new NEDO project. We are developing a co-generation system by integration with the TOTO stack. On the other hand, TOTO also started the development of micro SOFCs using micro tubular cells (diameter is less than 5mm) from 2002 under another NEDO project. In this paper, we summarized the current status of two types of SOFCs R & D at TOTO, i.e. tubular SOFC for stationary power generation and micro tubular SOFC for portable power application.

TOTO TUBULAR SOFC

Cell development

The schematic viewgraphs of the TOTO tubular cell are shown in Figure 1. A perovskite cathode tube is formed by extrusion molding. A zirconia electrolyte and a nickel/zirconia cermet anode are coated onto the tube by the TOTO wet process[2]. A vertical interconnector is coated along the tube in a strip. The diameter of the cell is 16.5mm and the active length is 660mm. Fuel gas is supplied to the outside of the cell, and air is supplied to the inside by a thinner air supply tube. Recently, the materials used for cells are changed as shown in Table 1. The new material configuration resulted in the improvement of cell performance as shown in Figure 2, especially in lower operating temperatures. Our latest cell worked best at temperatures over 850°C.

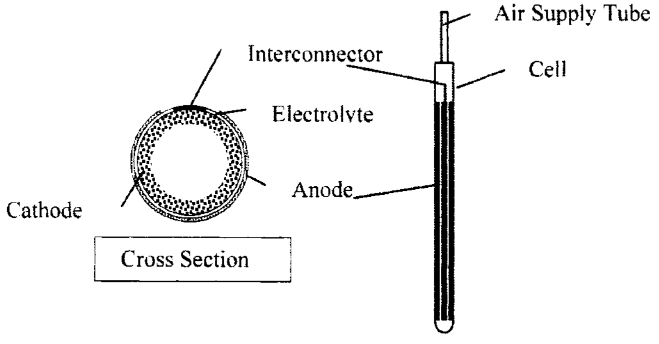

Figure 1. Schematic view of TOTO tubular cell.

Table 1. Materials used in TOTO tubular cell.

Components	Previous Type Cell	New Type Cell
Cathode Tube	$(La,Sr)MnO_3$	$(La,Sr)MnO_3$
Electrolyte	YSZ	ScSZ
Anode	Ni/YSZ	Ni/YSZ
Interconnector	$(La,Ca)CrO_3$	$(La,Ca)CrO_3$

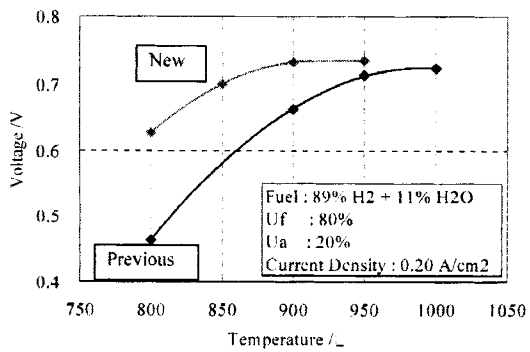

Figure 2. Cell performances as a function of operating temperature.

Stack development

Twelve tubes are bundled in a 2×6 stack with nickel materials connecting an interconnector of one cell and the anode of the next (Figure 3). A stack was installed in a metal casing and heated by an electric furnace. Simulated fuel of partially steam reformed town gas was supplied to the stack. The town gas was assumed to be 50% steam reformed under S/C (steam carbon ratio) =3.0. A stack generated 0.34kW at a current density of 0.2A/ cm^2 at a temperature of 940°C. The maximum efficiency for DC output of the stack was 57%-Lower Heating Value (LHV) calculated on the basis of equivalent town gas (Figure 4).

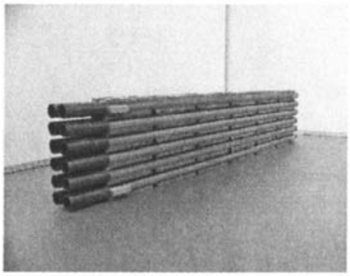

Figure 3. Appearance of TOTO stack.

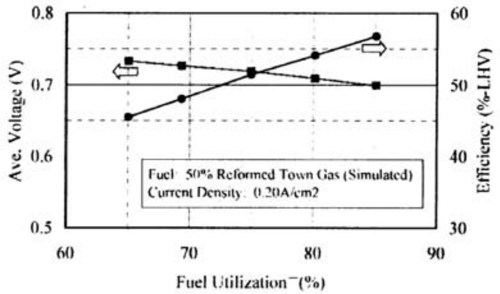

Figure. 4 Performance of 2×6 stack.

Small module (quarter size module)

The thermally self-sustaining operation indicates that the modules generate power without any external heat supply. A quarter-size small size modules, which consisted of 5 stacks were made and tested for basic evaluations to realize the thermally self-sustaining operation. The small module and its metal casing were covered with a ceramic insulator. In this test, the desulfurized town gas was partially steam reformed through a reactor. The reformer was installed outside of the module with an electric furnace as shown in Figure 5. The conversion of steam

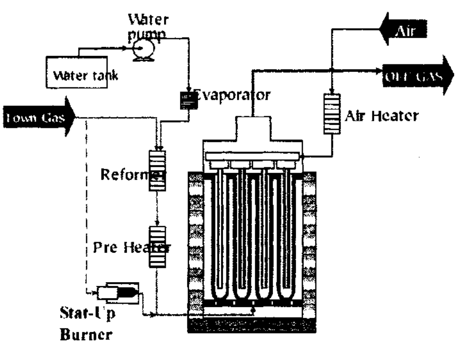

Figure 5. Flow diagram of small SOFC module.

reforming can be controlled independently with reformer temperature. However the higher hydrocarbons such as ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) were completely converted. The residual CH_4 was internally reformed on the anode, and the endothermic effect was utilized to maintain the homogeneous temperature distribution of the module. The outlet fuel and air were mixed and burned above the module, and this combustion heat was used for air pre-heating. Those improvements in temperature distribution and fuel gas distribution strongly affected on the module performance. We succeeded to operate a module with 1.6kW at 0.2A/cm^2 at an average temperature of 900°C which corresponds to the efficiency of 40%-LHV for 3000 hours. The maximum efficiency was 55 %- LHV, which obtained for different module.

Thermally self-sustaining module

A ten kW class module consisting of four quarter-size modules is fabricated for thermally self-sustaining operation (Figure 6). An integrated heat exchanging steam reformer was mounted above the module. It consisted of an evaporator, pre-heater and reformer. However, the stability of the evaporator was not clearly demonstrated, therefore steam was supplied by another evaporator with an electric furnace. The gas flow was simple, and it does not include any gas recycles as shown in Figure 7. The module, the after-burning zone, and the reformer were covered with a ceramic insulator. A commercial steam reforming catalyst was embedded in the reforming section. The desulfurized town gas was supplied to the modules after being partially steam reformed. In the test, the heat of exhaust gases was used for steam reforming through the reformer. The module was heated by a partially oxidation burner and air heaters from room temperature.

The voltages of each stack, and of the 2-cells in a quarter module, were monitored, and the variation of the voltages was quite small. The module generated 6.5kW at 0.19A/cm^2 and 46%-LHV (Table 2 Test 1). The improved module generated 6.5kW at 0.2A/cm^2 and 50%-LHV (Table 2 Test 2). The thermally self-sustainability of both operating condition were confirmed. The test was shifted to evaluation of long-term stability under the condition of Test 1. No degradation was observed in the module or the integrated heat exchanging steam reformer during the operating time of 1000 hours (Figure 8).

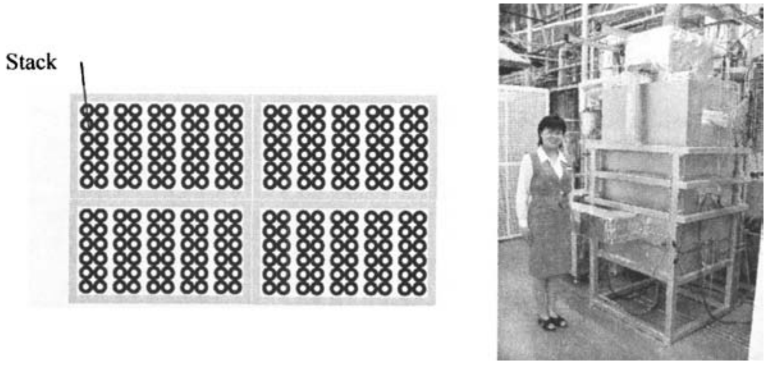

Figure 6. Stack layout and appearance of thermally self-sustaining SOFC module.

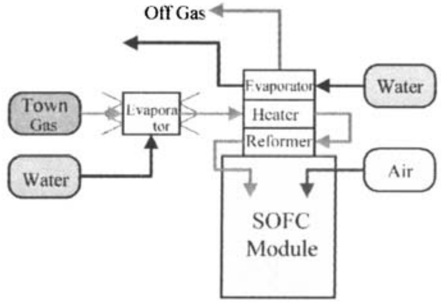

Figure 7. Flow diagram of thermally self-sustaining SOFC module system.

Table 2. Performance of thermally self-sustaining SOFC module.

Items	Test 1	Test 2
Power(kW)	6.4	6.5
Uf (%)	70	75
Current Density (A/ cm^2)	0.19	0.20
Ave. Cell Voltage (V)	0.69	0.70
Efficiency (%-LHV)	46	50

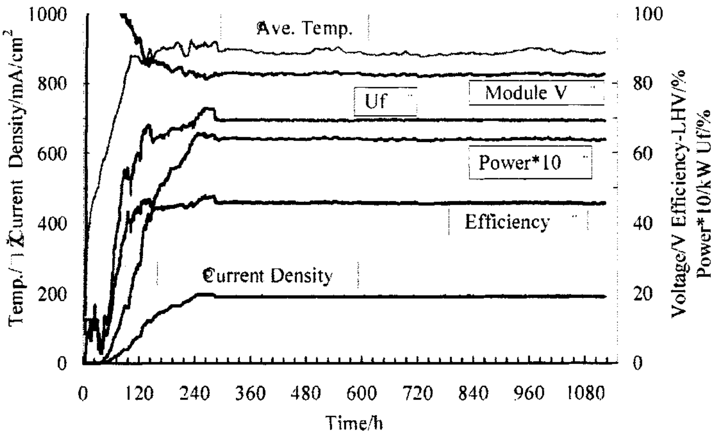

Figure 8. Long term stability of thermally self-sustaining SOFC module.

TOTO MICRO TUBULAR SOFC

Background

A micro tubular SOFC has potential for portable and transportation applications because of its advantages, including high volumetric power density and high thermal shock resistance which enables rapid start up[3]. We started the development of micro SOFCs using micro tubular cells (diameter is less than 5mm) from 2002 under a NEDO project[4]. The objectives of this project are to lower operation temperature to 500-700°C and to develop a compact stack that will achieve downsizing and rapid start up (in minutes or less) for the SOFC system. One of the significant advantages of SOFCs is its fuel flexibility compared to other kinds of fuel cells. Liquid petroleum gas (LPG) or dimethyl ether (DME) was selected as fuels because they can be easily handled and stored in portable cartridges.

To achieve high power density at lower temperatures, the anode-supported design with thin lanthanum gallate with strontium and magnesium doping was selected. The single cells and cell stacks were tested with various fuels, i.e. hydrogen, simulated reformate gas of LPG, and direct fueling of DME.

Micro tubular cell development

Table 3 shows materials and fabrication processes of the TOTO micro tubular cell. The anode substrate tube made of $NiO/(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ (NiO/YSZ) was formed by extrusion molding. The anode interlayer and the electrolyte were subsequently coated onto the anode substrate by slurry coating, and co-fired. These techniques are suitable for mass production and cost reduction. $NiO/(Ce_{0.9}Gd_{0.1})O_{1.95}$ (NiO/GDC10) anode interlayer was inserted between the substrate and the electrolyte to enhance the performance at lower temperatures. $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ (LSGM) was selected for the electrolyte material, which is considered as promising material for the intermediate temperature operating SOFCs [5)-6)]. An important point in cell fabrication is the insertion of a dense $(Ce_{0.6}La_{0.4})O_{1.8}$ (LDC40) layer between LSGM and NiO/GDC10 layer to prevent the undesirable nickel diffusion from the anode to LSGM during the co-firing procedure[7]. However, there was a problem that sintering temperature required for the preparation of dense LDC40 layer was much higher than that required for co-firing temperature. Therefore, we investigated the various additives for the sintering promotion of LDC40. As a result, it was found that the addition of a small amount of Ga_2O_3 to LDC40 was effective in obtaining a fully dense LDC40 layer at the co-firing temperature and it also improved electrical conductivity of LDC40 itself. From energy dispersed X-ray analysis (EDX) and X-ray diffraction analysis (XRD), it was seen that the reaction between LSGM and Ni was avoided by the introduction of LDC40 layer, and there was no obvious element diffusion between LSGM and LDC40. For the cathode material, $(La_{0.6}Sr_{0.4})(Co_{0.8}Fe_{0.2})O_3$ (LSCF) was coated by slurry coating and fired.

Table 3. Materials and fabrication process of micro tubular cell.

Component	Material	Fabrication	Firing
Anode Tube	NiO/YSZ	Extrude Molding	Co-Firing
Anode Interlayer	NiO/GDC10	Slurry coating	
Electrolyte	$LDC40(Ga_2O_3)$-LSGM (Double Layered)		
Cathode	LSCF		Firing

Figure 9 is a picture of a micro tubular single cell. The diameter of cell is 5mm, and the active length is 50mm. The single cell was jointed to the current collector cap with silver braze metal and its performance was tested in a furnace. Figure 10 shows the evaluation method for single cell performance. A fuel gas was supplied inside the cell, and air was supplied to the outside of the cell. The current voltage and impedance of the single cells were measured using a potentiostat and a frequency response analyzer in the 500 to 700°C temperature range.

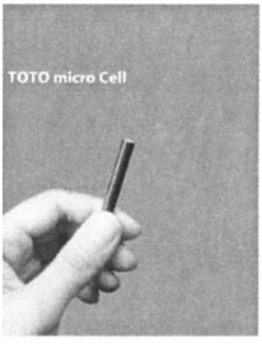

Figure 9. TOTO micro tubular cell.

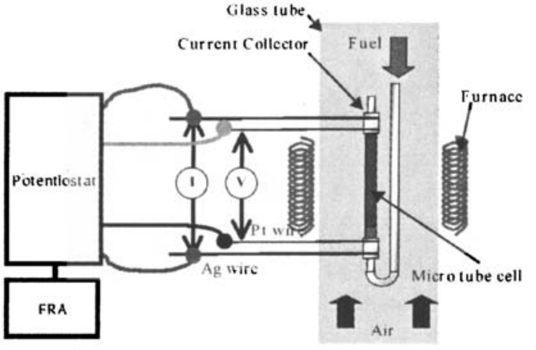

Figure 10. Evaluation method for single cell performance.

Figure 11 shows the typical I-V curves of a micro tubular single cell using dry H_2 in N_2 as fuel. H_2 flow was fixed at 0.12L/min. The open circuit voltage (OCV) was close to the theoretical value. It indicated that the electrolyte has a good gas tightness, and the chemical reaction between LSGM and Ni are effectively avoided by the LDC40 layer. The maximum

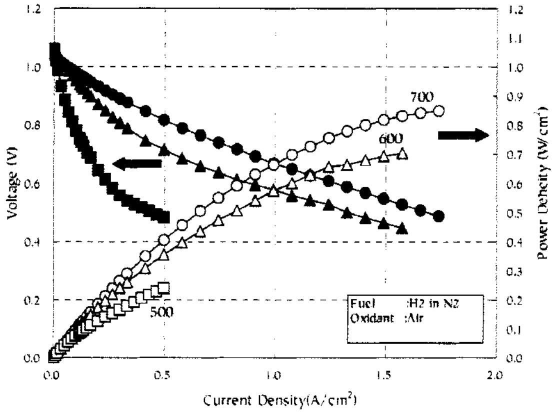

Figure 11. I-V characteristic of micro tubular single cell.

power densities were 0.85, 0.70, and 0.24W/cm^2 at 700°C, 600°C, and 500°C, respectively. Figure 12 shows the impedance spectra of a micro tubular cell measured under 0.125A/cm^2 at various temperatures. It has been generally assumed that the intercept with the real-axis at the highest frequency represents the ohmic resistance, and the width of low frequency arc represents the electrode resistance. The electrode resistance increased significantly with decreasing operation temperature, and ohmic resistance at 500°C was very high. The most likely cause of the high resistance is the low ionic conductivity of LDC40. Therefore, it is expected that the cell performance can be improved by optimizing the anode electrode and the thickness of LDC40 layer.

Figure 13 shows the fuel utilization effects on micro tubular cell performance measured under 0.125A/cm^2 at 700°C and 600°C. The observed cell voltage was close to the theoretical value calculated by the Nernst equation. It indicates that the micro tubular cell can be operated at a high efficiency.

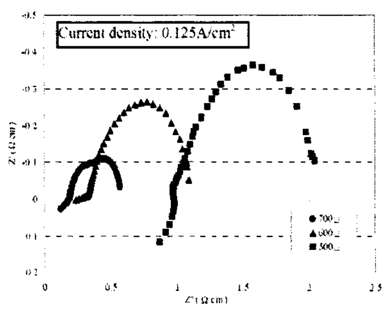

Figure 12. Impedance of micro tubular cell.

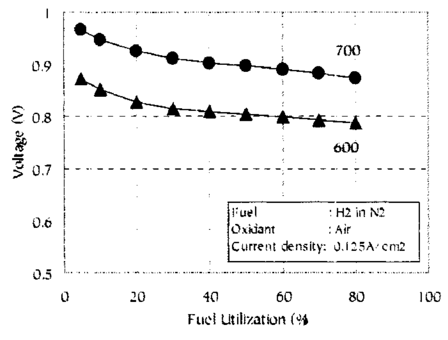

Figure 13. Fuel utilization effect on micro tubular cell performance.

The cell performances using H_2 in N_2 (1:1) gas mixture or simulated reformate gas were compared in Figure 14. The composition of simulated reformate was 32%H_2, 13%CO, 5%CO_2, and 50%N_2 based on the preliminary experiment of the catalytic partial oxidation (CPOX) reforming of LPG. As shown in the figure, the difference in cell performances was small at lower current densities. However, the performance using reformate gas was lower at higher current densities at temperatures of 600°C and 700°C. The differences became significant with increasing operating temperatures. To identify the differences, the impedance spectra were measured under a current density of 0.8A/cm^2 at 700°C (Figure 15). The electrode resistance on simulated reformate was higher than that on H_2 in N_2, and it was thought that this difference was caused by the CO transport resistance from the anode in the high current density area. Therefore, we are now trying to improve the anode performance.

Figure16 shows the cell performance using DME + air mixture as fuel at 550°C. The DME flow rate was fixed at 85ml/min and the excess air ratios (air-fuel ratio/ theoretical air-fuel ratio) were 0.1, 0.2, 0.3, and 0.4 respectively. Direct use of fuel without a reformer in SOFCs will simplify the system greatly, and this is important for SOFCs, especially in portable and transportation applications. DME is an attractive fuel because it is highly active and easily

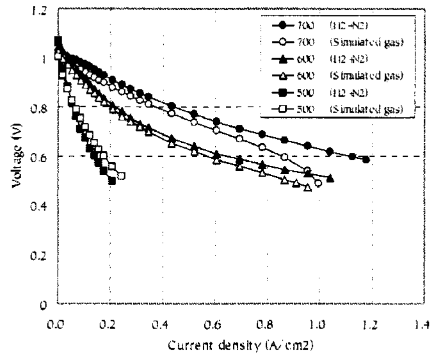

Figure 14. I-V curve tested on H_2 in N_2 and simulated reformate gas.

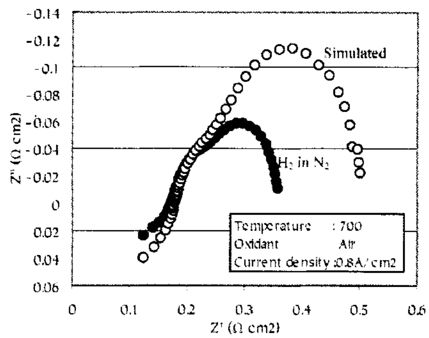

Figure 15. Impedance tested on H_2 in N_2 and simulated reformate gas.

liquefied and stored. As shown in the figure, the use of DME + air as fuel resulted in higher performance than that of H_2 in N_2 and no carbon deposition was observed during operation. Figure 17 shows the DME conversion rate and the exhaust gas composition analyzed by a gas chromatography. (The water content was not measured.) The DME conversion rate and CO_2 content increased with excess air ratio. Therefore, the increased performance achieved by using DME + air mixture is probably due to the raising cell surface temperatures caused by the decomposition and the combustion of DME. (The furnace temperature was kept at 550°C). These results demonstrated the high possibility of micro tubular cells being used for direct fueled operations.

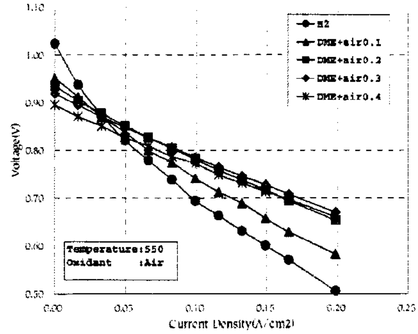

Figure 16. I-V curve tested on DME+air mixture as fuel at 550°C.

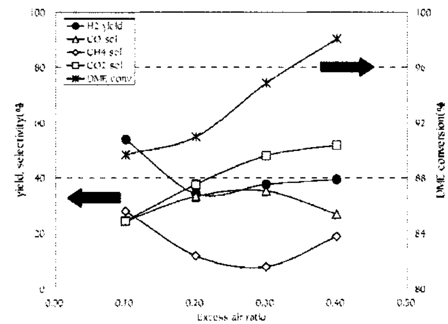

Figure 17. DME conversion rate and exhaust gas composition tested on DME+air mixture.

Micro tubular stack development

In order to evaluate the performance of cells in a bundle, we built the stack consisting of 14 micro tubular cells as shown in Figure18. This stack was evaluated in a furnace using hydrogen as a fuel, and successfully demonstrated 43W, 37W and 28W power generation at a temperature of 700°C, 600°C, and 500°C, respectively (Figure19). Table 4 summarizes the results we have obtained from the stack evaluation. The maximum stack power densities were 478W/L and 239W/kg at 700°C. These results demonstrated that micro tubular SOFCs have a high potential for portable and transportation applications.

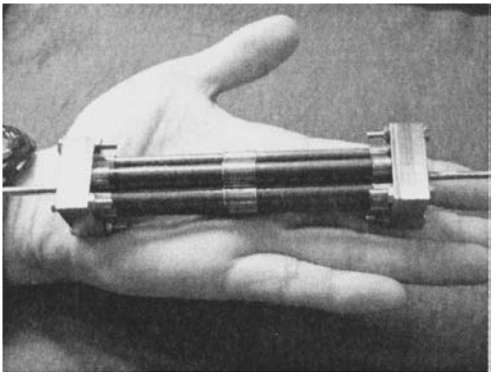

Figure 18. Appearance of micro tubular SOFC stack.

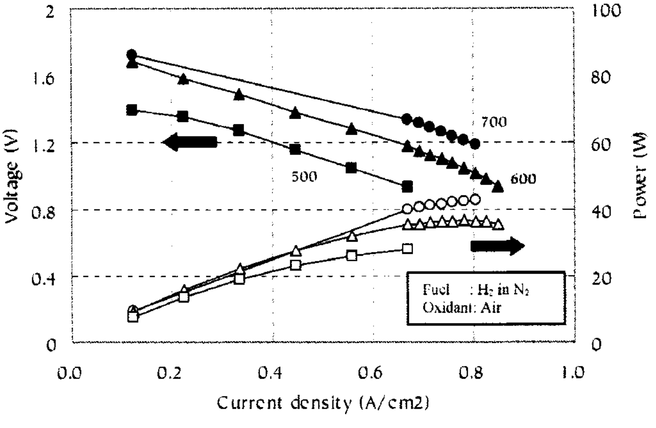

Figure 19. Performance of micro tubular SOFC stack.

Table 4. Performance of micro tubular SOFC stack at 700°C.

Item	Result
Maximum power (W)	43
Stack volume (L)	0.09
Stack weight (kg)	0.18
Stack power density (W/L)	478
Stack power density (W/kg)	239

SUMMARY

TOTO tubular SOFC

The 2×6 stack, small module and thermally self-sustaining module of the TOTO tubular SOFC were designed and made. They were evaluated using town gas or simulated fuel and showed excellent performance. We continually improve the cell performance and the durability to advance the module performance. TOTO started the small-scale production of SOFC and trial delivery in 2004. The SOFC can be supplied as a stack for the development of stationary power generation systems. In 2004, TOTO started a new collaboration with Kyushu Electric Power Co., Inc. and Hitachi, Ltd. in a new NEDO project. We are developing a co-generation system by integration with the TOTO stack.

TOTO micro tubular SOFC

The anode-supported micro tubular cells with thin lanthanum gallate with strontium and magnesium doping were developed. The single cells and the cell stack were tested using various fuels, i.e. hydrogen, simulated reformate gas of LPG, direct fueling of DME, and they showed excellent performance at lower temperatures from 500-700°C. These results demonstrated that micro tubular SOFCs have a high potential for portable and transportation applications. Further development on durability, quick start up, and compactness of the stack is being undertaken.

ACKNOWLEDGMENT

The development was supported by NEDO in Japan.

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