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Intermediate temperature solid oxide fuel cell based on lanthanum gallate electrolyte

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Abstract

The Kansai Electric Power Co. Inc. (KEPCO) and Mitsubishi Materials Corporation (MMC) have been developing intermediate temperature solid oxide fuel cells (IT-SOFCs) which are operable at a temperature range between 600 and 800 °C. There are some significant features in IT-SOFC of KEPCO–MMC: (1) highly conductive lanthanum gallate-based oxide is adopted as an electrolyte to realize high-performance disk-type electrolyte-supported cells; (2) the cell-stacks with seal-less structure using metallic separators allow residual fuel to burn around the stack and the combustion heat is utilized for thermally self-sustainable operation; (3) the separators have flexible arms by which separate compressive forces can be applied for manifold parts and interconnection parts. We are currently participating in the project by New Energy and Industrial Technology Development Organization (NEDO) to develop 10 kW-class combined heat and power (CHP) systems. In FY2006, a 10 kW-class module was developed, with which the electrical efficiency of 50%HHV was obtained based on DC 12.6 kW. In the first quarter of FY2007, the 10 kW-class CHP system using the module gave the electrical efficiency of 41%HHV on AC 10 kW and the overall efficiency of 82%HHV when exhaust heat was recovered as 60 °C hot water. Currently, the operation has been accumulated for about 2500 h to evaluate the long-term stability of the system.

Keywords: Lanthanum gallate; Intermediate temperature solid oxide fuel cell; Power generation module; CHP system; Durability; Long-term stability

1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) operable at a temperature range between 600 and 800 °C have been drawing a great deal of attention, because the temperature range offers SOFCs several advantages, such as (i) choices of less expensive metallic materials for separators on cell stacking, (ii) higher stability and durability of cell stacks and the BoP components, and (iii) fast startup–shutdown due to high thermal conductivity of metallic components when used as separators, while preserving the possibility of internal reforming of hydrocarbon fuels. To develop practical IT-SOFCs, two approaches are under active investigation. 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 novel electrolyte materials which show high oxide ion conductivity at temperatures below 800 °C [4–7].

The Kansai Electric Power Co. Inc. (KEPCO) and Mitsubishi Materials Corporation (MMC) selected the latter approach to realize the high performance SOFC at the intermediate temperature range when they started the joint R&D in 2001.

This paper describes recent results obtained under the development of 10 kW-class disk-type IT-SOFC modules and the CHP system by KEPCO–MMC during the 4 years' project since FY2004, supported by New Energy and Industrial Technology Development Organization (NEDO).

2. Cell, stack, and module development

2.1. Cell using lanthanum gallate electrolyte

It is well-known that lanthanum gallate compounds, $La(Sr)Ga(Mg)O_{3-\delta}$ possess excellent oxide ion conductivity at intermediate temperatures over a broad range of oxygen

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partial pressures [8]. Furthermore, double-doping by a transient metals, e.g. Co, was proved to be the most effective 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]. The composition of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{3-\delta}$ (LSGMC) was chosen and the green-sheets obtained by tape-casting method were sintered at 1200–1300 °C, to give dense LSGMC electrolyte disks (120 mm in diameter and 200 μm in thickness).

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 use highly active electrodes that show sufficiently low polarization at intermediate temperatures. The cells were made up of 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. Ni-SDC cermet has been reported to become highly active in anodic reaction by controlling the microstructure [11–13]. And SSC has been demonstrated to show very small polarization as the cathode of SOFC [14]. Both electrodes were prepared by screen-printing onto each side of the LSGMC disk followed by sintering at the optimized temperatures. The thicknesses of both electrodes were 30–50 μm, respectively.

2.2. *Internal manifold seal-less cell stack*

It was demonstrated by MMC that the stainless steels could be utilized as separators for the planar type SOFCs [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 tubular type SOFC. Fig. 1 shows a conceptual drawing of the single cell stack-unit. A cell is sandwiched between two porous current collectors and the cell stack is made up by placing them alternately with metallic (stainless steel) separator plates. In general, one of the difficulties in stacking the planar-type cells has been ascribed to gas sealing. To eliminate this problem, the seal-less stack concept was adopted. Both fuel and air are flown out from individual center-holes at the separator surface. They are distributed in the porous current collectors and consumed for the electrochemical reaction. The remaining fuel after the electrochemical reaction is burned around the stack to supply the additional heat to maintain the cell stack temperature.

The separator has two flexible arms, each of which has a hole at the end. The holes constitute gas manifolds when stacked with ceramic rings between them. Inner gas channels in the separator connect the gas manifolds to two center-holes located at each side of the separator. The flexible arms have been designed in order to isolate the different levels of compressive forces needed for manifold parts and interconnection parts of separators. The manifold parts have to be tightened up by bolts strongly enough to make hermetic seals. On the other hand, the interconnection parts of the separators where cells and current collectors are layered need sufficient load to minimize electric contact resistance between separators, current collectors, and cells. This load on the interconnection parts is exerted by a weight at the top of the cell stack as shown in Fig. 1.

The cell stack-unit assembly with internal manifolds shown in Fig. 1 is the one for recently developed 4th generation 1 kW-class module which consists of 46 cells. There is a radiator plate between the upper stack and the lower stack, so that the stack temperature can be within moderate temperature range between 700 and 800 °C.

2.3. *Internal steam reforming module concept*

The module, a power generation unit, consists of the SOFC cell-stack and other components, such as a pre-reformer, a steam generator, a heat exchanger, and a startup burner. They are arranged around the stack and packed together in the thermally insulated housing, as schematically shown in Fig. 2. Desulfurized town gas is supplied to the module and mixed with steam in specified steam/carbon (S/C) ratios. Deionized water is supplied

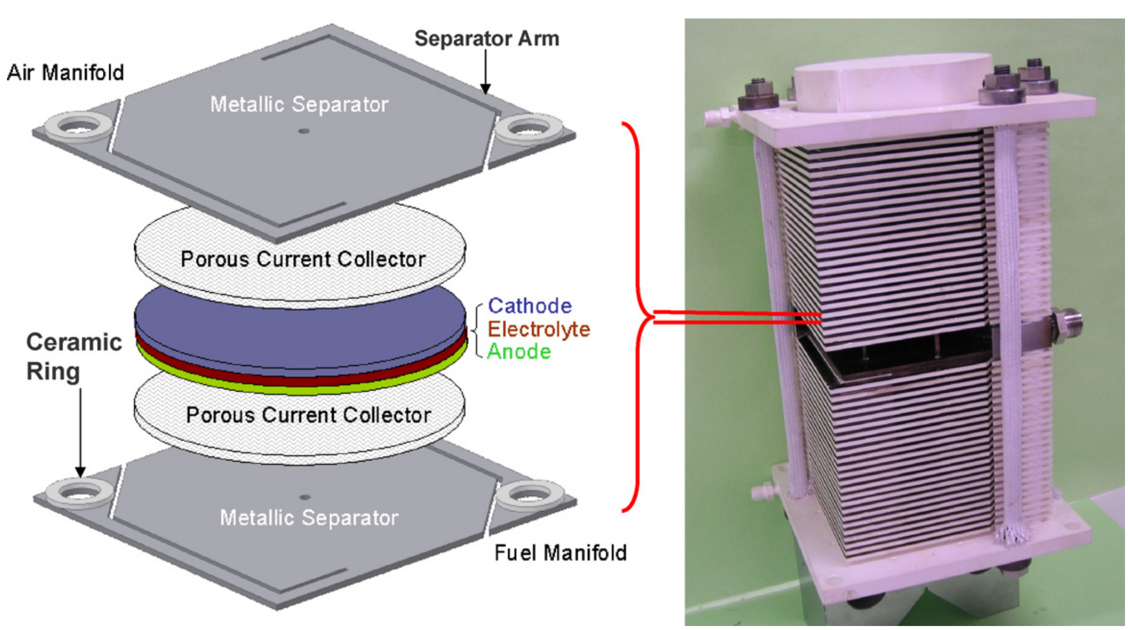

Fig. 1. Conceptual drawing of the single cell stack-unit and the cell stack.

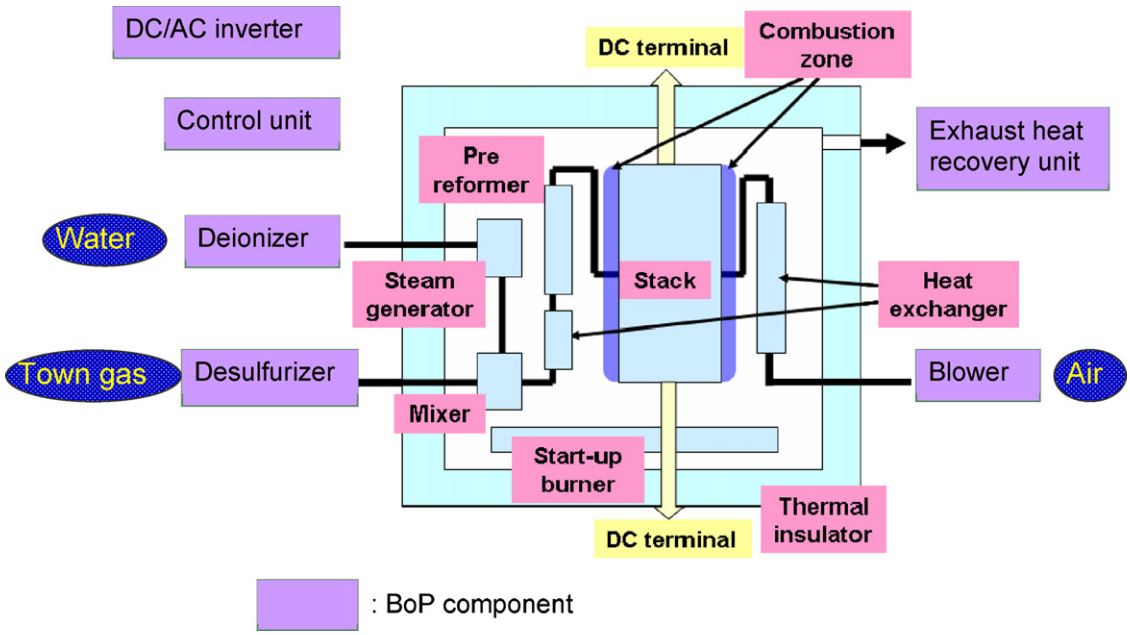

Fig. 2. Schematic view of SOFC module.

to the steam generator in the module. Steam reforming reaction takes place in the pre-reformer and the resulting reformate gas is supplied to the stack. Air is pre-heated in the heat exchanger before it goes into the stack. The heat obtained from the electrochemical fuel cell reaction and the combustion around the stack is efficiently utilized for those components.

We have developed four generations of 1 kW-class single stack modules so far. All of them have adopted internal reforming concept and the thermally self-sustained operation was possible. Using those modules, we accumulated knowledge to improve the technology concerned with the thermal management and the design-optimization of the stack and the auxiliary components to give the high electrical efficiency and the long-term stability [16–19].

3. 10 kW-class module development

In the NEDO project which was started in FY2004, the performance shown in Table 1 was targeted by the end of FY2007. The AC electrical efficiency higher than 40%HHV, overall efficiency higher than 80%HHV, and the voltage degradation rate lower than 0.25%/1000 h during the operation of 3000 h were targeted. We developed 10 kW-class IT-SOFC modules in FY2006, based on our basic technologies developed for multi-stack modules. As the target electrical efficiency of the CHP system is set as 40%HHV, it is necessary to develop the module which generates 12.6 kW-DC power output with electrical efficiency of 50%HHV under thermally self-sustained conditions, since the efficiency of DC–AC inverter which was manufactured to match the power output of the module specifically and the parasitic loss are estimated as 94 and 13%, respectively. The specifications of the 10 kW-class module are summarized in Table 2.

The module is composed of 16 stacks (an array of $2 \times 2 \times 4$) with 34 cells and hot BoP components, i.e. a pre-reformer, a steam generator, heat exchangers, start-up burners, and thermal insulator. The module size is about 1 m (W) × 1 m (D) × 2.4 m (H). A cross-shaped plate-type reformer was designed and positioned in the hottest region between the stacks to keep the reformer at temperatures as high as possible. Start-up burners utilizing town gas as fuel have been designed and located adjacent to the stack array. Those features were decided after giving consideration to the analysis and simulation results on the heat and material balance, the temperature and the gaseous species distributions inside the stack and module [20,21]. The conceptual view of the 10 kW-class module is shown in Fig. 3.

The performance test was carried out using the 10 kW-class module. Fig. 4 and Table 3 show the operational characteristics. Full load operation of 12.6 kW-DC was successfully demonstrated with DC electrical efficiency of 50%HHV and fuel

Table 1
Targeted values of NEDO project by the end of FY2007

	Target
Power output	10 kW-class (net AC)
Electrical efficiency	>40% (net AC/HHV) (at the rated output)
Overall efficiency	>80% (HHV) (exhaust heat is recovered as 60 °C hot water)
Long-term stability	Voltage degradation rate 0.25%/1000 h (through operation for >3000 h)

Table 2
The specifications of the 10 kW-class module

Fuel	Town gas (13 A)
Power output	12.6 kW-DC
Electrical efficiency	50%HHV
Maximum stack temperature	Below 800 °C

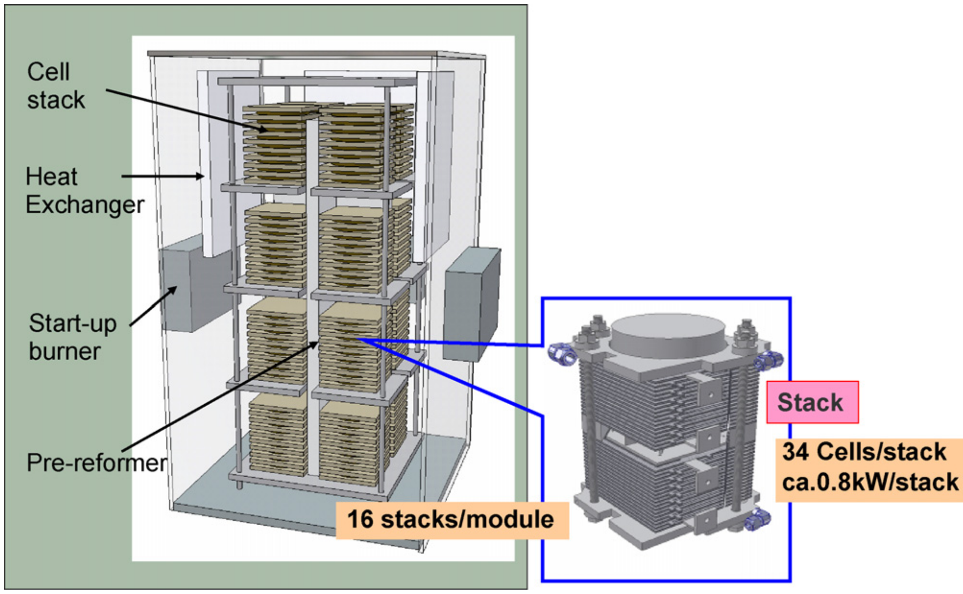

Fig. 3. The conceptual view of the 10 kW-class module.

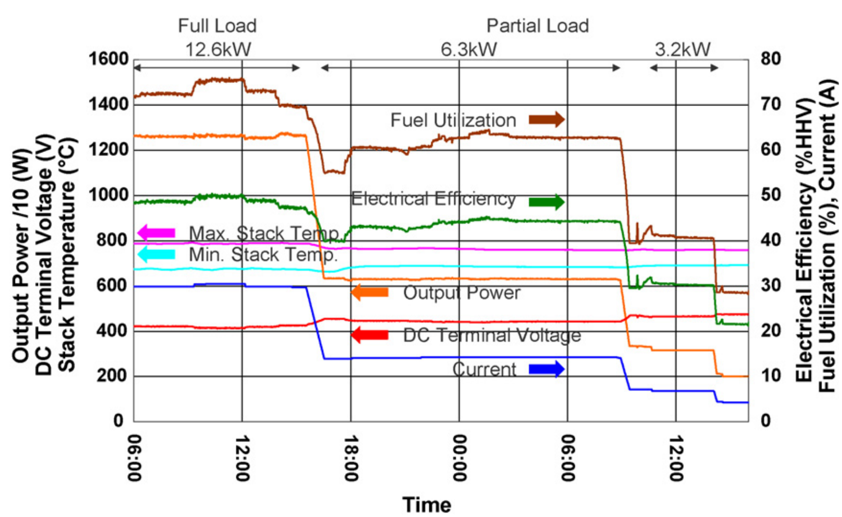

Fig. 4. The performance results using the 10 kW-class module.

utilization of 76% at stack temperatures below 800 °C. The efficiency met the specification shown in Table 2, and implies that the overall efficiency of 40%HHV could be possible when the module is installed for the system. Partial load operation was also achieved as shown in Fig. 4. DC electrical efficiency of 44%HHV with fuel utilization 63% for a half-load and 30% with 41% for a quarter-load were obtained under thermally self-sustained conditions. The stack temperatures for those operations were kept between 675 and 790 °C.

Table 3
The operational characteristics of 10 kW-class module

Operation mode	Full load	Partial load	
DC power output (kW)	12.6	6.3	3.2
Av. area specific power density (W cm^{-2})	0.208	0.103	0.051
DC terminal voltage (V)	415	443	466
DC electrical efficiency (%HHV)	50	44	30
Fuel utilization (%)	76	63	41
Air utilization (%)	53	36	17
Av. cell voltage (V)	0.77	0.82	0.86
Max. stack temperature (°C)	787	760	759
Min. stack temperature (°C)	675	684	690

4. Development of 10 kW-class CHP system

Fig. 5 shows the combined heat and power (CHP) system, which was installed at Rokko Testing facilities of KEPCO in FY2006. The system flow diagram is shown in Fig. 6 . The system contains a 10 kW-class SOFC module, a gas and water supply unit, a power conditioner, a control unit, and an exhaust heat recovery unit. The control unit has the function of automatic operation (i.e. start-up, power-generation, hot-standby, shut-down, and emergency stop). In the module, steam is generated using the purified water and mixed with desulfurized town

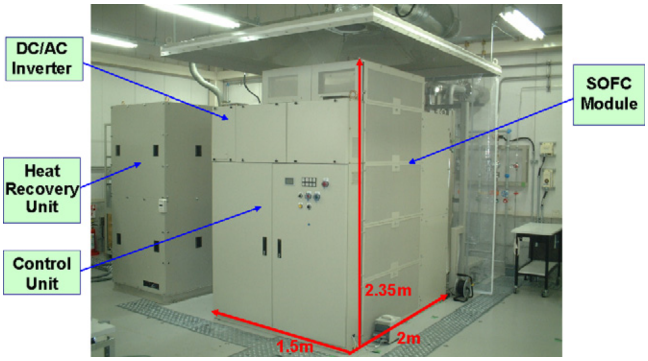

Fig. 5. The 10 kW-class CHP system of IT-SOFC.

gas fuel for the steam reforming. The exhaust heat is utilized to get hot water at the external heat recovery unit. The condensed water from the module exhaust can be recycled to be used for the reforming. The heat recovery unit has a hot water tank with the capacity of 370 L and a water pump. The unit can make hot water with the temperature between 60 and 90 °C. AC power output is obtained from the DC power at the DC/AC inverter, and then connected to the grid. The total heat energy utilized in the entire system includes not only sensible heat but also latent heat.

The operation results obtained in the first quarter of FY2007 are shown in Table 4, in which the NEDO target values are also shown. We obtained AC power output of 10.1 kW with AC electrical efficiency of 41%HHV as well as the overall efficiency of 82%HHV when exhaust heat was recovered as 60 °C hot water. When obtaining 90 °C hot water, AC electrical efficiency of 40%HHV and the overall efficiency of 79%HHV were recorded under stable operations. Those results clearly demonstrate that the IT-SOFC CHP system can generate the electricity and recover the heat with high efficiency.

After the initial performance was confirmed to qualify the NEDO project target, the long-term stability test started in FY2007. As shown in Fig. 7, the system has been under stable operation during the accumulated period of about 2500 h, except the trips twice at the accumulated time of around 1640 and 1930 h, both of which were unexpectedly occurred troubles in a

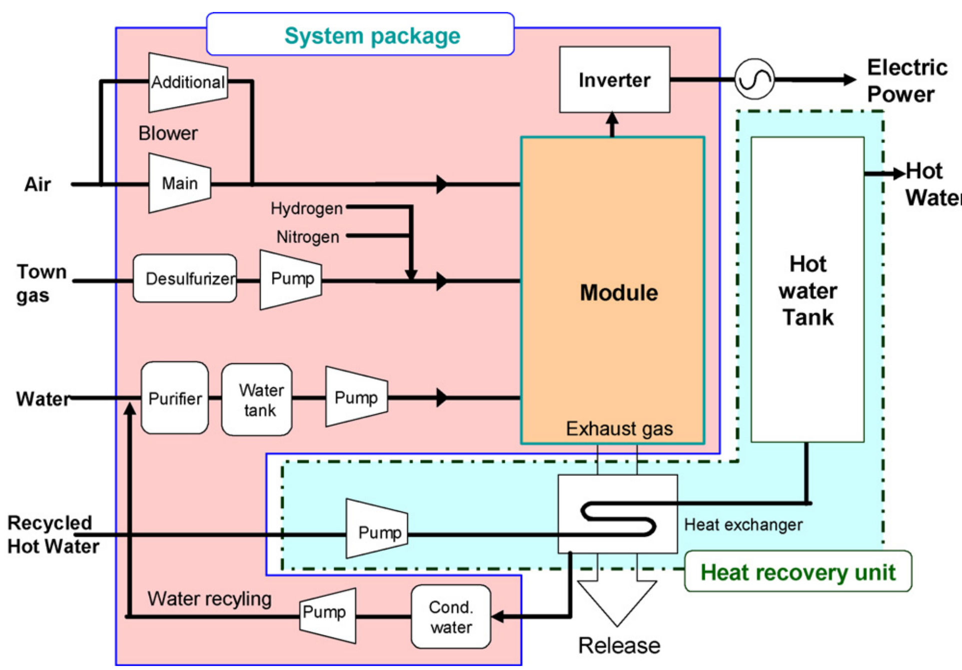

Fig. 6. The system flow diagram of 10 kW-class CHP system.

Table 4
The operation results obtained for 10 kW-class CHP system

		Target	Results	
			60 °C hot water	90 °C hot water
Fuel	–	Town gas	Town gas (13 A)	
DC power output	kW	–	12.4	12.4
DC electrical efficiency	%HHV	–	50	50
AC power output	kW	10	10.1	10.1
AC electrical efficiency	%HHV	40	41	40
Overall efficiency	%HHV	80[a]	82	79
Long-term stability	%/1000 h	0.25[b]	Under operation	–

[a] Exhaust heat is recovered as 60 °C hot water.
[b] Voltage degradation rate per 1000 h after 3000 h operation at the rated output.

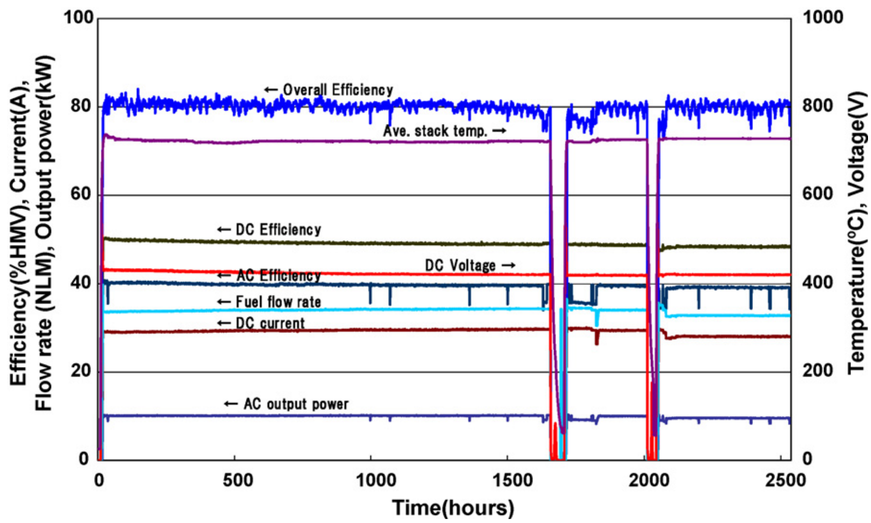

Fig. 7. The long-term operation test using 10 kW-class CHP system.

fuel flow controller and a thermocouple. It has been observed that the overall efficiency tends to fluctuate, mainly due to controlling delay for the heat recovery which is controlled on the inlet water temperature and the water flow rate. The long-term stability test is currently underway, aiming for >3000 h operation.

5. Conclusions

IT-SOFC has been developed under collaboration by KEPCO and MMC, which has significant features, such as: (1) highly conductive lanthanum gallate-based oxide is adopted as an electrolyte to realize high-performance disk-type electrolyte-supported cells; (2) the cell-stacks with seal-less structure using metallic separators allow residual fuel to burn around the stack and the combustion heat is utilized for thermally self-sustainable operation; (3) the separators have flexible arms by which separate compressive forces can be applied for manifold parts and interconnection parts. We are currently participating in the project by NEDO to develop 10 kW-class CHP systems. In FY2006, a 10 kW-class module was developed, with which the electrical efficiency of 50%HHV based on DC 12.6 kW was obtained. Partial load operations were also carried out under thermally self-sustained conditions. The 10 kW-class CHP system using the module gave the electrical efficiency of 41%HHV on rated output of AC 10 kW and the overall efficiency of 82%HHV when exhaust heat was recovered as 60 °C hot water, which accomplished the NEDO target. The field test has been underway for the elapsed period of about 2500 h aiming for >3000 h to evaluate the long-term stability of the system.

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