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Development of segmented-in-series-type solid oxide fuel cells for residential applications

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ABSTRACT

Segmented-in-series-type solid oxide fuel cells (SIS-SOFCs) have been developed for residential applications. The average stack voltage of the SIS-SOFC with a fuel consisting of CH_4 (steam/carbon = 2.5) was 0.75 V and 0.24 A/cm^2 at fuel utilisation = 70.1%, yielding a direct current lower heating value (LHV) energy conversion efficiency of 50.6%. The degradation ratio, the ratio for thermal cycling, and the ratio for redox cycling were 0.62%/1000 h, 0.11% per cycle, and 0.04% per cycle, respectively. A micro combined heat and power (m-CHP) SOFC system was fabricated and successfully demonstrated for over 4000 h. The degradation ratio of 0.75%/1000 h was almost the same as that of the stack in a furnace. An LHV alternating current electrical efficiency of over 40% and LHV heat recovery efficiency of over 35% was achieved. Thus, SIS-SOFCs are suitable for m-CHP SOFC systems.

Keywords: Solid oxide fuel cell; Segmented-in-series; m-CHP system

1. Introduction

As a result of increasing consciousness about the global environment, the reduction of greenhouse gas emissions has become necessary to prevent global warming. Solid oxide fuel cells (SOFCs) are expected to evolve into electrochemical devices that exhibit high electrical conversion efficiencies because they can convert chemical fuels directly into electrical power. In recent years, a high-efficiency, large-scale hybrid system based on SOFC technology has been developed [1–4]. However, its output voltage during regular operation is only 0.7–0.8 V, and each single cell has to be connected in series in order to obtain

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sufficiently high voltage that is necessary for creating a large-scale SOFC generation system. Therefore, this conventional large-scale SOFC system faces many challenges with regard to its electrical connections and uniform fuel distribution. For monolithic SOFCs (m-SOFCs), the number of stacks is small and they are relatively easy to put together. However, heat loss from the surface of an m-SOFC becomes large in comparison to the evolution of heat that takes place inside, and it therefore becomes difficult to sustain its proper operating temperature. In order to realise the thermally self-sustaining operation of such a device, it is necessary to increase its power density by using a compact SOFC system. When considering uses in residential applications, many challenges must be addressed, such as the need for high efficiency, long-term durability, thermal cycling, redox tolerance, and cost. In general, anode-supported fuel cells (ASCs) are prepared from a thick substrate with Ni-YSZ cermet. The Ni content in the cermet is over 60%, because the substrate needs to have high electrical conductivity. The thickness of the substrate and the Ni content affect the residual stresses in the electrolyte, owing to the different thermal expansion coefficients of the substrate and the electrolyte. It has been reported that the failure probability of the electrolyte increases with decreasing substrate thickness [4, 5]. It is therefore necessary to fabricate a thin substrate and reduce the Ni content. The substrate in segmented-in-series-type solid oxide fuel cells (SIS-SOFCs) is prepared by using an insulating porous substrate which permits the realisation of low Ni content and the use of a thin anode. To increase its reliability, the design of an SOFC stack and the control conditions in the system are very important. In this paper, we describe the performance of an SIS-SOFC and a micro combined heat and power system.

2. Experimental

2.1. SIS-SOFC preparation

An SIS-SOFC was designed with the aim of achieving a low cost and high degree of reliability [6–12]. A schematic representation of the SIS-SOFC is shown in Fig. 1.

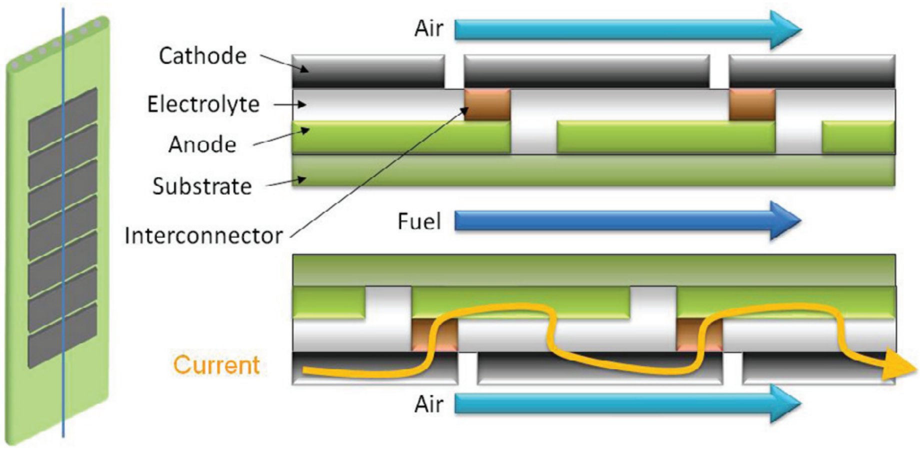

Fig. 1. Schematic representation of a segmented-in-series-type solid oxide fuel cell (SIS-SOFC) stack and a cross-sectional view of the SIS-SOFC.

The substrate was made of an electrically insulating material which was prepared from an MgO-based material. It exhibited high chemical stability and mechanical strength [7–9]. The substrate was prepared by an extrusion process and moulded into the form of a flattened tube. Anode cermet was prepared from NiO and 8 mol% yttria-stabilised zirconia (YSZ). Anode sheets, which were prepared by tape casting, were arrayed on the substrate. The substrate with the anode was then dipped in an YSZ slurry and co-fired at 1200°C. The cathode was a screen composed of $(La,Sr)(Co,Fe)O_3$ that was printed on the dense electrolyte and sintered at 1150°C. Sixteen single cells were linked electrically in series by ceramic interconnects. For the SIS-SOFC, reducing the ohmic polarisation of the cathode and the anode is important for obtaining high electrical efficiency. Thus, we optimised the dimensions of the components of the SIS-SOFC stack. Details on the preparation and the stack design are reported elsewhere [10, 11].

2.2. SIS-SOFC performance

The current-voltage-power density (*I–V–P*) characteristics and the fuel utilisation (U_f) dependencies of the voltage and the electrical efficiency of the SIS-SOFC stack were measured every 25°C from 675°C to 825°C with steam-reformed methane (steam/carbon (S/C) = 2.5) used as a fuel. Additionally, the U_f dependences of the current density were measured at 775°C. Long-term durability tests were conducted at 775°C and U_f = 70%, 825°C and U_f = 70%, and 775°C and U_f = 80% using 20% H_2O-H_2 as a fuel. The effects of thermal cycling on the *I-V* characteristics and the U_f dependences were measured every five cycles at 775°C. The stack was heated at temperatures of up to 775°C for 2 h in 4% H_2-N_2 as a reducing gas on the anode side, and then cooled down to room temperature. The redox tolerance of the SIS-SOFC was estimated at 775°C by supplying air as a re-oxidising gas to the anode side of the cells. The re-oxidation reaction time dependence of the SIS-SOFC voltage was examined. Following this, the open-circuit voltage (OCV), *I-V* characteristics, and ohmic drop (IR) were measured after reduction reaction for 30 min using steam-reformed methane (S/C = 2.5). Next, we investigated the performance stability with respect to shutdown operation without any reducing gas. The stack was cooled down to room temperature by supplying air as a re-oxidising gas to the anode side. The reduction process was carried out in a furnace by supplying 4% H_2-N_2 as the reducing gas at a temperature of 775°C for 2 h. The stack voltage of the SIS-SOFC were measured at 0.24 A/cm^2 and U_f = 70% when 20% H_2O-H_2 was used as a fuel. An emergency shutdown cycle test along with the redox reaction was carried out over 50 times.

2.3. Configuration of SIS-SOFC CHP system

A schematic illustration of the configuration of the CHP system is shown in Fig. 2.

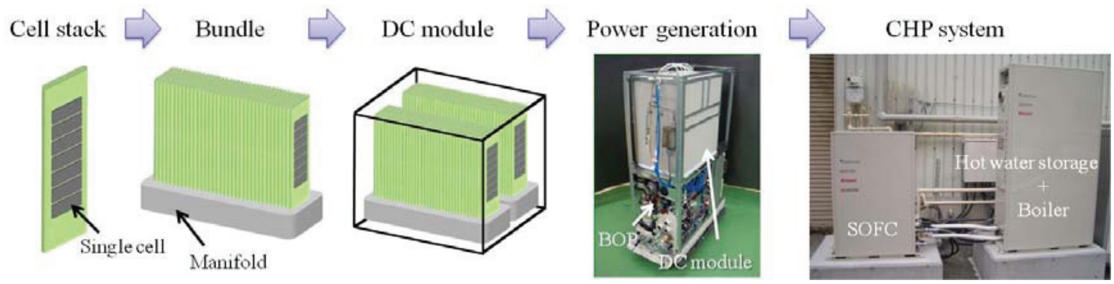

Fig. 2. Schematic representation of a segmented-in-series-type solid oxide fuel cell combined heat and power (CHP) system configuration.

To obtain a high output power, a bundle was fabricated using 36 cell stacks embedded in an alloy manifold with a glass sealant. A direct current (DC) module which involved a pre-reformer was contained within two bundles. A power generation unit consisted of the DC module, balance-of-plant, and a power conditioner. The SIS-SOFC CHP system for residential applications was configured with a power generator and a hot water storage unit including a backup boiler. The system could operate using city gas as fuel. The size of the power generator and hot water storage unit were 350 mm long × 650 mm wide × 1040 mm high, and 350 mm long × 890 mm wide × 1620 mm high, respectively. The SIS-SOFC CHP system could operate automatically for startup and shutdown depending on the power demand, and generate according to the power demand. When a lack of exhaust heat from the generator occurred, hot water was supplied by the backup boiler, and when the exhaust heat was sufficient for the storage tank, the excess heat was dissipated by a radiator.

2.4. SIS-SOFC CHP performance

The initial performance of the SIS-SOFC CHP system was investigated in the laboratory. The alternating current (AC) output power dependencies of the AC efficiency and the operating temperature were obtained during thermally self-sustaining operation. Next, the SIS-SOFC CHP system was installed in an actual residential house, and its effectiveness in terms of small-scale power generation was examined. The AC efficiency, exhaust heat recovery efficiency, and AC output power of the system were monitored during automatic operation. The heat recovery efficiency was calculated from the temperature difference between the inlet hot water and the outlet water.

3. Results and discussion

Fig. 3(a) shows the *I–V–P* characteristics of the SIS-SOFC stack at various temperatures. A power density of 0.186 W/cm^2 was obtained at a current density of 0.24 A/cm^2 at 825°C. For a low current density, the power density exhibited almost the same value as observed during our previous development of planar ACSs [13]. The power density slightly decreased with temperature, and a value of 0.176 W/cm^2 was observed at 725°C. Within the temperature range from 725°C to 825°C, the performance exhibited relatively low temperature dependence. Fig. 3(b) shows the U_f dependencies of the voltages at various temperatures and current densities when reformed methane was used as a fuel.

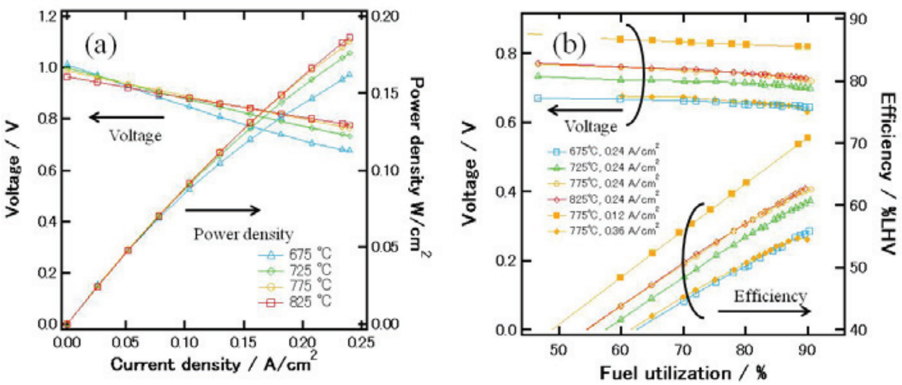

Fig. 3. (a) *I–V–P* characteristics of the segmented-in-series-type solid oxide fuel cell (SIS-SOFC) stack at various temperatures, and (b) fuel utilisation dependences of the average cell-stack voltage and electrical efficiency of the SIS-SOFC stack that used steam-reformed methane (S/C = 2.5) as fuel.

A maximum LHV conversion efficiency of over 70% was obtained at an average voltage of 0.819 V and a current density of 0.12 A/cm^2 at U_f = 90.0%. The SIS-SOFC exhibited stable operation at U_f up to 90% for every condition, and achieved uniform fuel distribution. The voltage at 0.36 A/cm^2 for $U_f > 90\%$ slightly decreased due to the low gas diffusivity of the substrate. However, the efficiency at 0.36 A/cm^2 was the almost same as that at 675°C and 0.24 A/cm^2. Thus, the rated current density, temperature, and U_f for the system were taken to be 0.24 A/cm^2, 750°C, and 70%, respectively.

In general, the SOFC performance exhibited modest degradation during long-term operation because of impurities, structural changes, chemical interactions, and diffusion on the component materials and at the interfaces [14–21]. The degradation ratio is considered to be affected by the operating temperature and U_f. Additionally, accurate control of the temperature and U_f is difficult, and an acceptable error range is therefore important for producing a reliable system. Thus, we conducted durability tests at U_f = 80% and a temperature of 850°C, for which the results are shown in Fig. 4(a). A degradation ratio of 0.62%/1000 h was observed under normal conditions of 775°C and U_f = 70%, and degradation ratios of 0.88%/1000 h and 0.65%/1000 h were obtained at U_f = 80% and 850°C, respectively. In conventional ASCs, a decreasing OCV and an increasing IR loss were confirmed by observing the degradation of the glass sealant and increased oxide scale on the metallic interconnector. The degradation ratio and behaviour exhibited almost the same tendencies under various conditions. The SIS-SOFC durability performance can contribute to attaining a reliable and robust system in terms of local high U_f operation due to the temperature, current density, and fuel distribution.

Tolerance towards thermal cycling is required for an m-SOFC in order for it to be forced into shutdown for maintenance and long idling periods. The durability performance of the SIS-SOFC stack as a function of thermal cycling is shown in Fig. 4(b). The SIS-SOFC exhibited stable performance after 120 thermal cycles. The voltage decreased slightly with increasing thermal cycling and a degradation ratio of 0.11% per cycle was obtained for U_f = 80%. It has been reported that degradation caused by thermal cycling is mainly due to mechanical failure caused by differences in the TEC in the various components, and that the failure probability depends on the thickness of the substrate [4–5]. Thus, slight degradation was considered to be the operation time due to maintain the OCV.

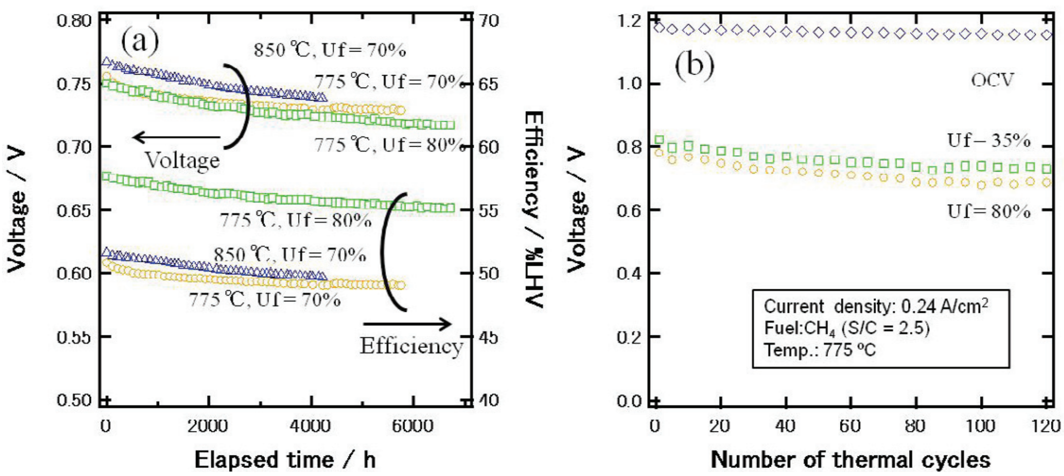

Fig. 4. (a) Durability test results for the segmented-in-series-type solid oxide fuel cell (SIS-SOFC) at a constant current density of 0.24 A/cm^2, and (b) SIS-SOFC average cell voltage at 0.24 A/cm^2, 775°C, and open-circuit voltage (OCV) after thermal cycling.

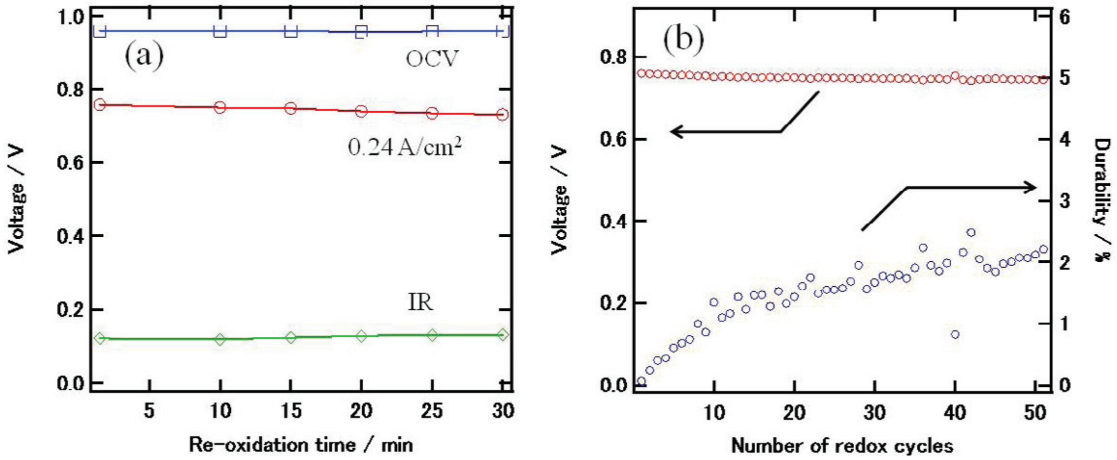

Fig. 5. (a) Segmented-in-series-type solid oxide fuel cell (SIS-SOFC) performance after redox cycling at 775°C, where the ohmic resistance characteristics were measured using a current interrupt method, and (b) SIS-SOFC performance after start-and-stop operation without the reducing gas supply.

In the case of a reliable SOFC system, a high redox durability is important for commercial and safety reasons [11, 22–23]. The redox durability of a conventional ACS is believed to be related to the bulk expansion of the anode, which causes cracks to form in the electrolyte [5]. Fig. 5(a) shows the performance of the SIS-SOFC after re-oxidation. The voltage slightly decreased with increasing re-oxidation time and a voltage drop of 26 mV and increasing IR of 9 mV were observed after an oxidation time of 30 min. The SIS-SOFC was able to successfully generate electricity after a total oxidation time of 100 min, and exhibited high tolerance toward redox cycling. The high tolerance was considered to be due to the substrate functioning as an oxidation barrier layer, which restrained the dimensional changes in the thin anode.

When the redox phenomena were confirmed for the system, the system cooled down to room temperature without the need for reducing gas. The anode expanded on re-oxidation, but the other component materials contracted with decreasing temperature. Thus, it was considered that a large residual stress had manifested compared to the stress associated with normal thermal cycling or redox cycling. The CHP system will lose its safety and reliability when the residual stress causes cracks to appear in the SOFC stacks. Fig. 5(b) shows the results of the shutdown test without using the reducing gas, assuming that the operation of the CHP system was halted using an emergency protocol. The average cell voltage at a current density of 0.24 A/cm^2 decreased slightly, and the degradation ratio of the shutdown cycles was approximately 0.04% per cycle. The high tolerance was considered to result from the substrate preventing the oxidation of the anode for a short oxidation time. Therefore, degradation due to shutdown was almost the same as that for normal start-and-stop operation. In addition, the high durability of the SIS-SOFC suggests that it is possible to develop such a system without using purge gas.

SIS-SOFC power generation can respond to demands for power automatically. However, it is difficult for SIS-SOFCs to remain at their operating temperature with a high degree of U_f during partial load operation. SIS-SOFC power generation is designed for thermally self-sustaining operation at low U_f during partial load operation. The AC electrical efficiency, heat recovery efficiency, operating temperature, and U_f as a function of the AC output power are shown in Fig 6(a). The highest LHV conversion efficiency of 40.7% was obtained at 530 W and 750°C with U_f = 66%. SIS-SOFC power generation was maintained at an operating temperature of 640°C with a partial load of 173 W, and an LHV conversion efficiency of 26.2% was obtained at U_f = 26.2%. Thus, we proved that the SIS-SOFC could be suitable for use in an m-SOFC system. The SIS-SOFC CHP system was therefore installed in a residential house, and its successful operation was demonstrated for over 4000 h. Long-term durability test results on its AC electrical efficiency, exhaust heat recovery efficiency, and AC output power are shown in Fig. 6(b). The data were extracted for a rated current density of 0.24 A/cm^2. The AC electrical efficiency decreased slightly, and the exhaust heat recovery efficiency remained almost the same. The SIS-SOFC CHP system achieved an overall LHV efficiency of 75%. The voltage degradation ratio of 0.75%/1000 h was about the same as that for the durability test in the furnace. Thus, it was considered that the degradation ratio of the SIS-SOFC CHP system was relatively small.

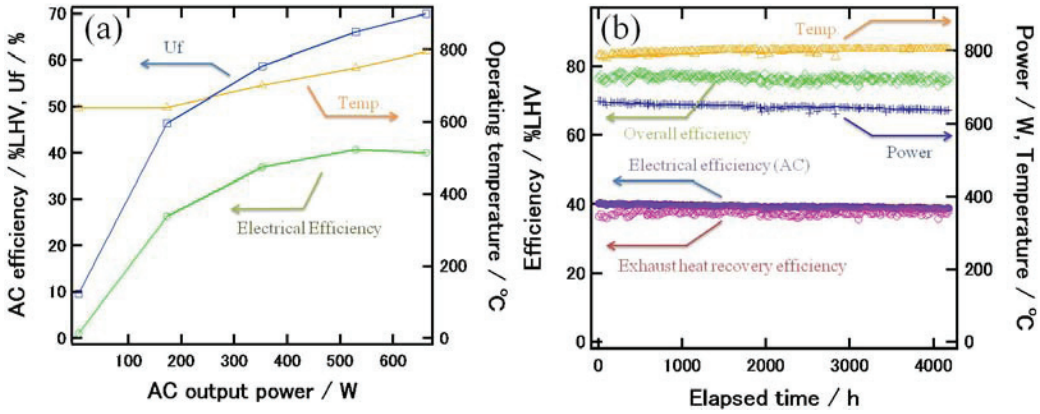

Fig. 6. (a) Alternating current (AC) output power dependences of AC efficiency, operating temperature, fuel utilisation (U_f), and exhaust heat recovery efficiency of the segmented-in-series-type solid oxide fuel cell combined heat and power system, and (b) durability test results for the SIS-SOFC combined heat and power system. The plotted dates were extracted for a rated current density of 0.24 A/cm^2.

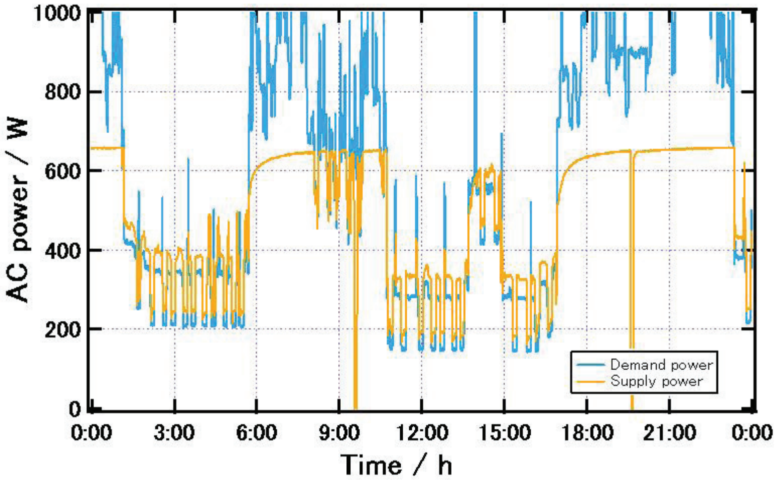

Fig. 7. Results for the load of the home installed segmented-in-series-type solid oxide fuel cell combined heat and power system during operation.

The SIS-SOFC CHP was able to follow the load demand in the residential house. Results for one day's worth of operation are shown in Fig. 7. The supply power covered the demand power of over 75%. The general SOFC had difficulty in responding to the load change, because a change in the current affected the local current density, temperature, and fuel distribution. The SIS-SOFC operated at a low rated current density of 0.24 A/cm^2 and the temperature change was small, as shown in Fig. 6(a). Therefore, it was easy to follow the load demand of the SIS-SOFC CHP system.

Additionally, the SIS-SOFC could operate automatically including during start-and-stop operation. The AC output power, AC efficiency, operating temperature, and flow rate of the fuel during the normal shutdown and restart sequence are shown in Fig. 8(a). During the normal shutdown sequence, the fuel was supplied to prevent oxidation of the anode at temperatures up to 300°C. Following this, the system restarted automatically and obtained almost the same efficiency as before the shutdown sequence. The system exhibited high tolerance towards thermal cycling, which was the same as for the results in the furnace. Next, the emergency shutdown sequence was conducted, as shown in Fig. 8(b). The fuel and electrical power that were supplied to the system were stopped suddenly. During the shutdown sequence, the power for a data logger was not supplied and the operating temperature was not reached. The system was cooled down to room temperature without the methane fuel. After the emergency shutdown, the system was restarted and exhibited good performance. These shutdown sequences did not affect the degradation ratio, and the SIS-SOFC system exhibited high tolerance towards the sudden power and fuel outages.

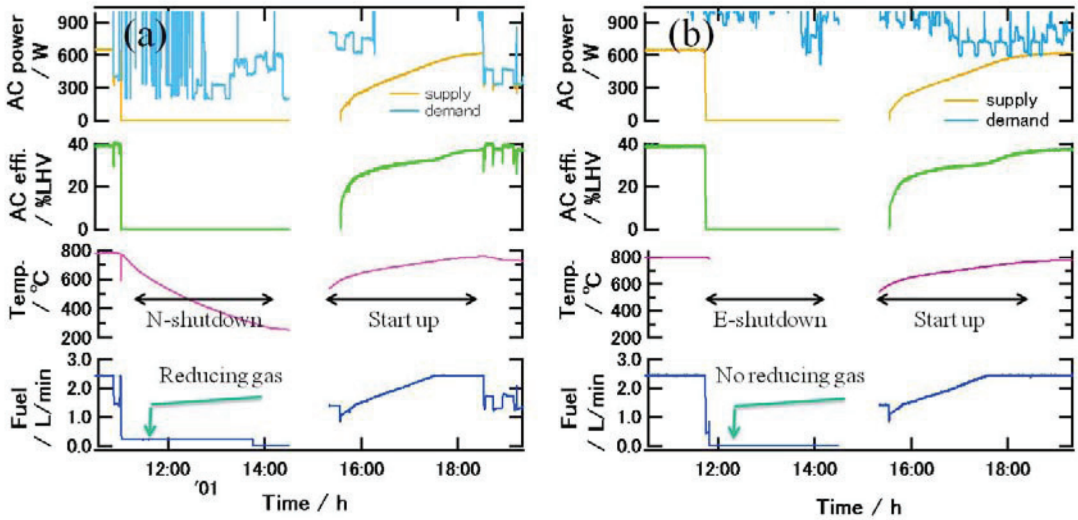

Fig. 8. (a) Segmented-in-series-type solid oxide fuel cell combined heat and power system (SIS-SOFC CHP) performance after a normal shutdown operation; the system supplied a small quantity of fuel to the anode side of the cells to inhibit their re-oxidation. (b) SIS-SOFC CHP system performance after the emergency shutdown operation. The system was cooled down to room temperature without any reducing gas.

4. Conclusions

SIS-SOFCs exhibit long-term durability and high tolerances towards thermal cycling and redox cycling. We have developed a small-scale SIS-SOFC CHP system that can automatically operate and accommodate the demand for power. It exhibited an AC LHV efficiency of over 40% and an LHV heat recovery efficiency of over 35% at its rated output power. The SIS-SOFC CHP system was installed in a residential house, and its operation was successfully demonstrated for 4000 h. It is therefore considered to be suitable for small-scale power generation because of its robustness.

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