RESEARCH AND DEVELOPMENT OF SOLID OXIDE FUEL CELL

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ABSTRACT

The solid oxide fuel cell(SOFC) using a ZrO_2-based electrolyte expected for a high efficient power generator that is effective in reducing pollution. There are many proposed structures and forming processes of SOFC. We have developed a fabrication process for planar SOFC. The SOFC was fabricated by using a cofiring process. The maximum current density of a single cell with an effective electrode surface area of 110 cm^2 was 0.3 A/cm^2 at the terminal voltage of 0.7 V. A 6-cell stack with same effective electrode surface area showed an electric power of 120 W. For the commercial usage, it is necessary to develop a large size electrolyte plate which has low ionic conductivity and excellent durability.

1. INTRODUCTION

The fuel cell is expected for a high efficient power generator which is effective in reducing pollution. The SOFC using a ZrO_2-based electrolyte is developed in many organizations, because it is expected long-term durability and simplification of generating system.

Murata Mfg. Co., Ltd. is a manufacturer of many ceramics-based electronic devices and maintains a broad technical background of ceramic processing. It has conducted the R&D activities for solid ions, such as an oxygen sensor. We have developed SOFC since FY1987 on the above mentioned technical backgrounds. Murata's R & D program for SOFC has been sponsored by New Energy and Industrial Technology Development Organization (NEDO) under the Moonlight Project of Agency of Industrial Science and Technology, MITI, since FY1989.

In this report, the principle of power generation for SOFC and the world-wide status of SOFC development are presented. Our status of SOFC development and the future subjects for commercialization of SOFC are also described.

2. PRINCIPLE OF FUEL CELL

A fuel cell is an energy conversion system using reverse reaction of the water electrolysis 1). Figure 1 shows a principle of fuel cell using an oxygen ion conductor(electrolyte). The oxygen received electrons on the cathode/electrode interface is changed to O^{2-} ions as shown the equation (1).

$$O_2 + 4e^- = 2O^{2-} \quad (1)$$

The oxygen ions conducted through the electrolyte react with hydrogen on the electrolyte/anode interface resulting in the formation of water as shown in the equation (2).

$$O^{2-} + H_2 = H_20 + 2e^- \quad (2)$$

The electrons are conducted from anode to cathode through an outer circuit with electrical load. This is the principle of the fuel cell power generation.

The fuel cells are power generators which are capable of directly converting the chemical energy of a fuel into electrical energy, so that they are anti-pollution and high efficiency generators. The energy conversion efficiency is independent to a

capacity of fuel cell. The noise level of fuel cells is extremely low comparing with the conventional generators using turbines or boilers. From these characteristics, fuel cells are expected to be used as cogeneration systems or dispersed power stations in towns or isolated islands.

There are tree types of fuel cells. The phosphoric acid fuel cell(PAFC), which uses phosphoric acid as an electrolyte, operates at about 200℃. The electric charge in electrolyte is H+. The world's largest 11 MW PAFC plant was constructed by Tokyo Electric Power Co. in 1991. The molten carbonate fuel cell(MCFC), which uses an alkali-carbonate mixture as an electrolyte, operates at about 650℃. The electric charge in electrolyte is CO_3^{2-}. The 100 kW class plant is under construction in Japan. The PAFC and MCFC use liquid state electrolytes which have the problem of cell corrosion. To alleviate this corrosion problem, the solid oxide fuel cell is developed. It is operated at about 1000℃, and ZrO_2-based materials are used as electrolytes. The electric charge in electrolyte is O^{2-} which is same as figure 1. There are many technical hurdles in order to realize SOFC because of their high temperature operation. The high operation temperature, however, causes the highest power generation efficiency among three types of fuel cells. From these advantages, the SOFC is developed all over the world.

3. CURRENT STATUS OF R&D ON SOFC

The world's largest 25 KW SOFC plant was developed by Westinghouse(WH) of the Unite State in 1992. The SOFC of WH is a tubular type cells shown in Figure 2. Another type of SOFC is a planar type shown in Figure 3. The inner impedance of the planar type cells is lower than that of the tubular type cells so that a power density of the former cells is expected higher than that of the latter cells. The low inner impedance of the planar type cells is caused by a short current passage which is at right angles to electrolyte plates. From this advantage, many organization in the world develop the planar type SOFC recently.

As the solid electrolyte, Y_2O_3 stabilized ZrO_2 is used in the almost developing organizations. The many processing to form electrolyte plate are tried. The typical processing methods are shown in Table 1.

4. R&D ON SOFC AT MURATA

4.1 CELL DESIGN

The schematic design of Murata's planar SOFC is shown in Figure 4. The single cell is composed of an anode(Ni-YSZ)/electrolyte(YSZ)/cathode($LaSrO_3$) multilayer, two distributors(Ni-YSZ and $LaSrO_3$) surrounded by gas tight materials (spacer, YSZ) and two interconnects($LaCaCrO_3$). The fuel gas or oxidant gas flows through the passages between neighboring distributors. The electric current between the electrode (anode or cathode) and the interconnect flows through the distributors. The stack assembly consists of several single cells.

Besides using the ceramics distributors and interconnects, monolithic bodies of distributors and interconnects of Ni-Cr alloys were also used. These bodies are called the bipolar plates.

4.2 FABRICATION PROCESS

We have developed a fabrication process for planar SOFC using a cofiring technique. The planar SOFC, fabricated by a cofiring process can be expected to achieve low cost, high power densities and good gas sealing capability. On the other hand, the cofiring technique requires that the sintering temperature, the shrinkage profiles and the thermal expansion characteristics of component materials should be compatible with each other.

We have developed a SOFC cofired whole cell components. However, it was difficult to fabricate a stack assembly with a larger effective electrode area. This was due to the slight mismatch of sintering shrinkage profiles and thermal expansion of the components. This mismatch causes stresses in the cell bodies during the cofiring process, resulting in cracking of cells and deterioration of performance.

In order to alleviate the above mentioned problems, we have developed a new cofiring process. The SOFC is fabricated by combining cofired anode/electrolyte/cathode multilayers, distributors and interconnects. By using the cofired anode/electrolyte/cathode multilayers, we can reduce the thickness of the electrolyte layers. The SOFC with thin electrolyte layers can be expected to achieve good performance due to a reduction in the inner impedance of the cells.

Fabrication of anode/electrolyte/cathode multilayers involves forming the thin green films, cutting, laminating and cofiring. The materials used for the electrolyte is 8 mol% Y_2O_3 stabilized-ZrO_2 (YSZ). The materials used for anode and cathode are Ni-YSZ cermet and $LaSrMnO_3$, respectively. The doctor blade technique was used for forming the thin green anode, cathode and electrolyte films. These green ceramic films were cut into desired sizes and laminated to form multilayers as the green bodies. The green multilayers were then cofired below 1400 ℃ and sintered into a rigid structure. The mismatch of sintering shrinkage profiles and the thermal expansion characteristics of anode, cathode and electrolyte materials were minimized to achieve good flatness of multilayer surfaces.

After cofiring process, we could maintained dense structure for electrolyte, and a porous structure for cathode. In Figure 5, the SEM images of electrolyte and electrode interfaces are shown.

The single cells and stacks were fabricated by piling up the anode/electrolyte/cathode multilayers and other cell components. The materials used for distributors are Ni-YSZ cermet for the anode side and $LaSrMnO_3$ for the cathode side. $LaCaCrO_3$ is used as the interconnects. The doctor blade technique was also used for forming green films of distributors and interconnects. These green ceramic films were then cut, laminated and sintered below 1400 ℃ into rigid bodies. After the assembly of rigid cell components, single cells or stacks were fabricated by cofiring at the temperature higher than the each sintering temperatures of cell components. The mismatch of the thermal expansion characteristics of the components materials was minimized to achieve good bonding characteristics between adjacent components. This process is called 2-step cofiring. A several cells stack with effective electrode surface area of 130 cm2 per cell was the final product as shown in Figure 6.

Besides using the ceramics distributors and interconnects, the bipolar plates of Ni-Cr alloys were also used. They were fabricated by the grinding process. By piling up the cell components, the single cells and stacks were fabricated. Glass sealing was used between the adjacent components. A several cells stack with effective electrode surface area of 110 cm2 was fabricated as shown in Figure 7.

4.3 PERFORMANCE

Until now, the performance of $LaCaCrO_3$ interconnect stacks have not been so good, for example the current density of 30 ma/cm2 at the terminal voltage of 0.7 V was observed. The reason of this poor characteristics might be due to slight mismatches among component material characteristics. More detailed study of cell components materials are required.

For the metal bipolar plate cells and stacks, the good performances are achieved. The single cell performances with an effective electrode area of 110 cm^2 were as follows. The I-V characteristics at constant flow rate was shown in Figure 8. The current density at the terminal voltage of 0.7 V was 0.3 A/cm^2 and the maximum electric power of the same single cell was about 25 W. The result of the fuel and air utilization tests at the current density of 0.3 mA/cm^2 were shown in Figure 9. The reduction of power with increasing gas utilization was not remarkably. The temperature dependence of the terminal voltage at the current density of 0.3 mA/cm^2 was shown in Figure 10. With decreasing temperature, the terminal voltage was

decreased because of the conductivity reduction of electrolyte and the polarization increase of electrodes.

It is suggested that CH_4 is used as fuel of commercial SOFC and CH_4 is reformed to H2 before the introduction to cells. The reforming reaction is expressed as follows.

$$CH_4 + H_2O = 4H_2 + CO_2 \quad (3)$$

We, therefore, estimated the I-V characteristics at constant flow rate using $4H_2/CO_2$ mixture gas which is called the model reformed gas. The result is shown in Figure 11. The current density was slightly decreased comparing that using pure H_2 gas for fuel.

The I-V characteristics of 6-cell stack with an effective electrode surface area of 110 cm^2 at constant flow rate is shown in Figure 12. The maximum electric power was about 120 W which is not proportional to the performance of single cell. The reason is supposed that the a self load of stack caused a breakdown of a portion of electrolyte/electrode multilayer. To alleviate this problem, the improvements of strength and flatness for the multilayers are required.

5. FUTURE ISSUES

The future issues of SOFC are as follows.

-Construction of large scale cells
-Improvement of power generating density
-Decreasing of operation temperature
-Improvement of durability

In this section, the present subjects in the field of solid electrolytes are discussed.

5.1 Large scale cells

In order to construct the large scale cells, the formation of large surface electrolyte plates and the increase of laminated cell layers are needed.

To alleviate increasing inner impedance, the thickness of electrolyte layer is not able to be increase. From this reason, the strengthening of electrolyte is investigated. The partially stabilized ZrO_2 and Al_2O_3 containing ZrO_2 are used for this purpose. To avoid stress concentrations resulting in the breakdown of electrolyte, the flatness of the plates must be achieved. For this purpose, the improvements of processing technology are required.

5.2 Power generating density and operation temperature

To improve a power generating density and to decrease operation temperature, the inner impedance of electrolyte should decrease. For this purpose, the development of processing technology for thin film formation is studied. The thin film, however, shows weak strength so that thin film formation on substrates such as a porous thick electrode plate is under development.

5.3 Durability

The durability of 5 years is required for SOFC. On this standing point, the thermodynamic stability of Y2O3 doped ZrO2 is studied. It is suggested that the inner impedance of partially stabilized ZrO2 is increased under the operating condition at 1000flC. The more detailed studies for stability of electrolyte materials are required.

REFERENCES

(1) T. Takahashi, "Nenryoudenti", p23, Kyouritu-shuppan, Tokyo(1984).
(2) S. P. S. Badwal, Proc. of 2nd International Symposium on SOFC, p.445, Athens (1991).

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Table 1. Procceing method of electrolyte layer

DC Plasma Spray	Tubular, Planar
RF Plasma Spray	Tubular, Planar
Hybrid Plasma Spray	Tubular, Planar
Laser Spray	Tubular
EVD	Tubular, Planar
Plasma CVD	Tubular, Planar
CVD	Tubular, Planar
RF Spatter	Tubular, Planar
Ion Plating	Tubular, Planar
Electron Beam Evapolation	Planar
Laser Evapolation	Planar
HIP	Tubular, Planar
Slurry Coating	Tubular, Planar
Doctor Blade	Tubular, Planar
Calender Roll	Planar
Slip Casting	Planar
Spray Hydrolysis	Tubular, Planar

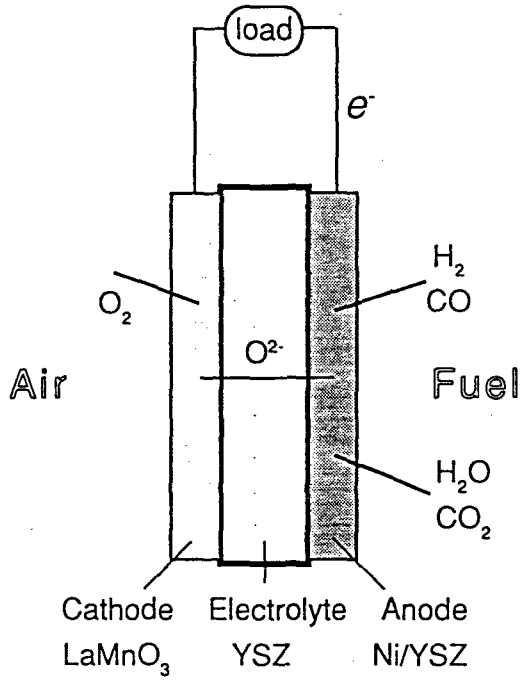


Figure 1. Principle of fuel cell

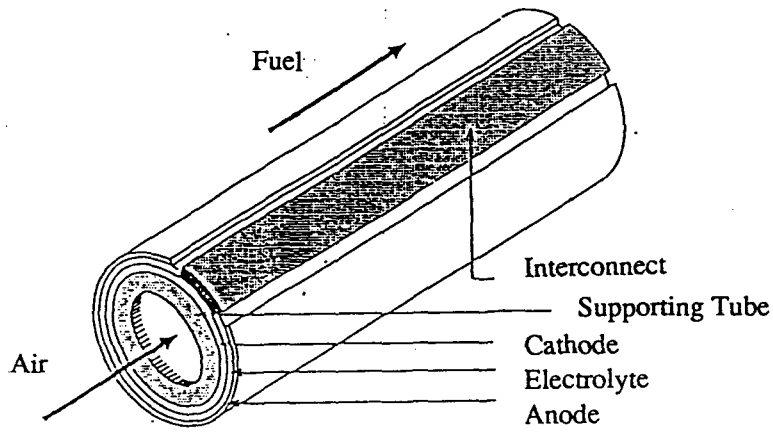


Figure 2. Schematic design of tubular SOFC

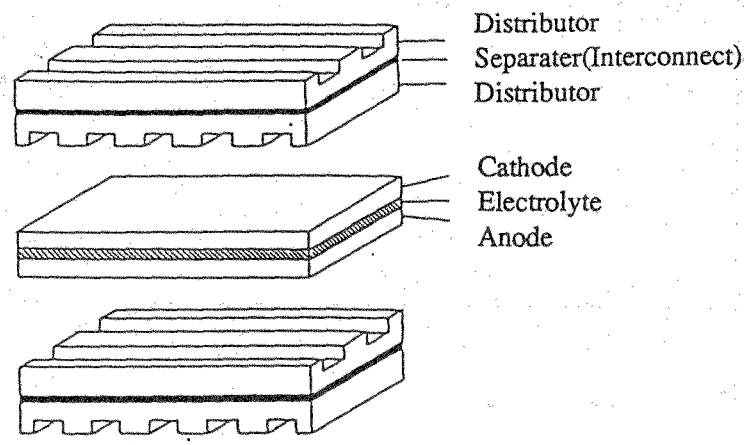


Figure 3. Schematic design of planar SOFC

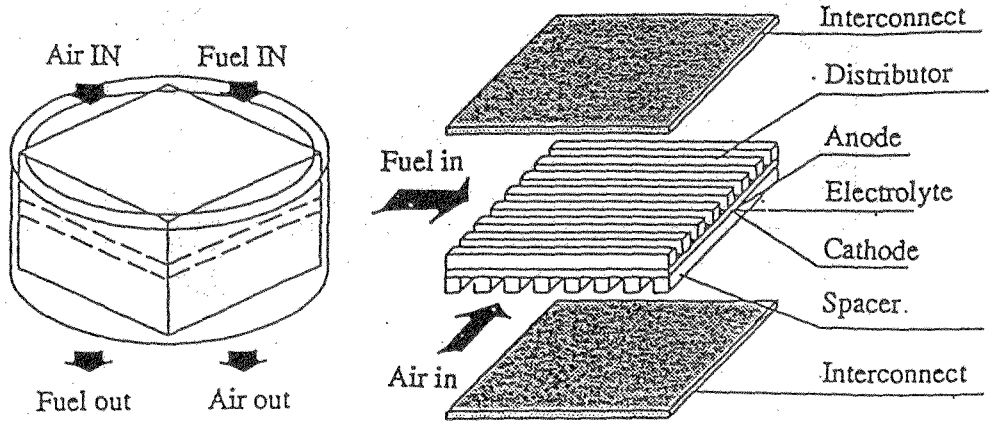
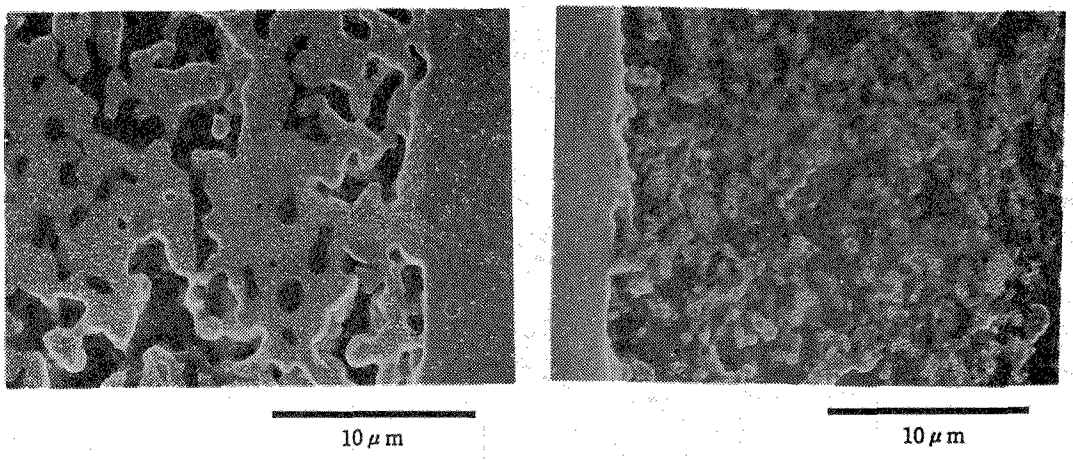


Figure 4. Schematic design of Murata's SOFC



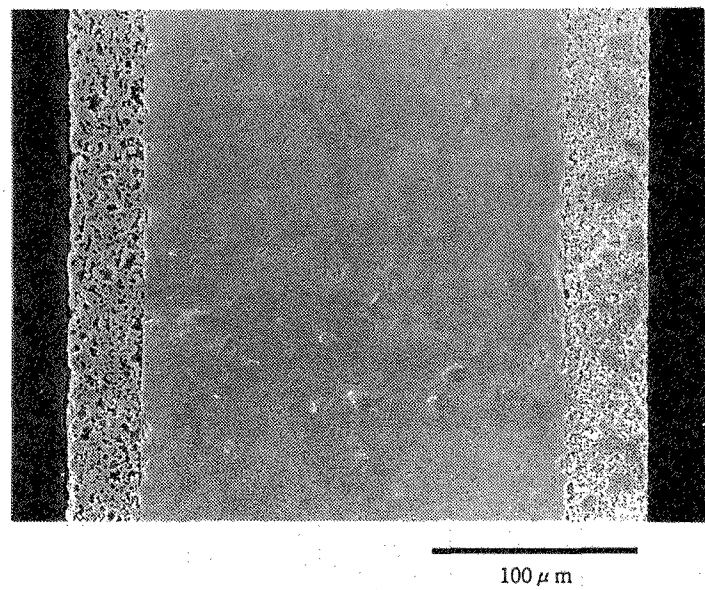


Figure 5. SEM image of electrolyte/electrode interface

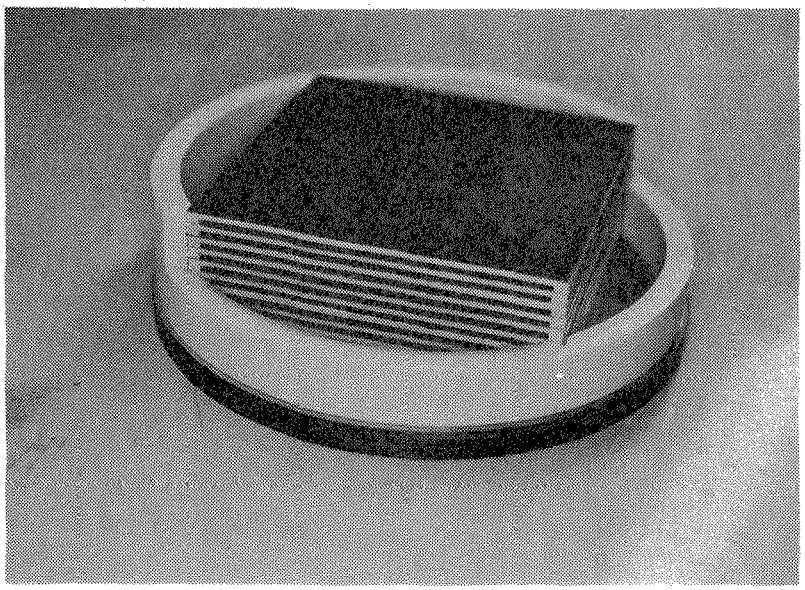


Figure 6. $LaCaCrO_3$ interconnect stack

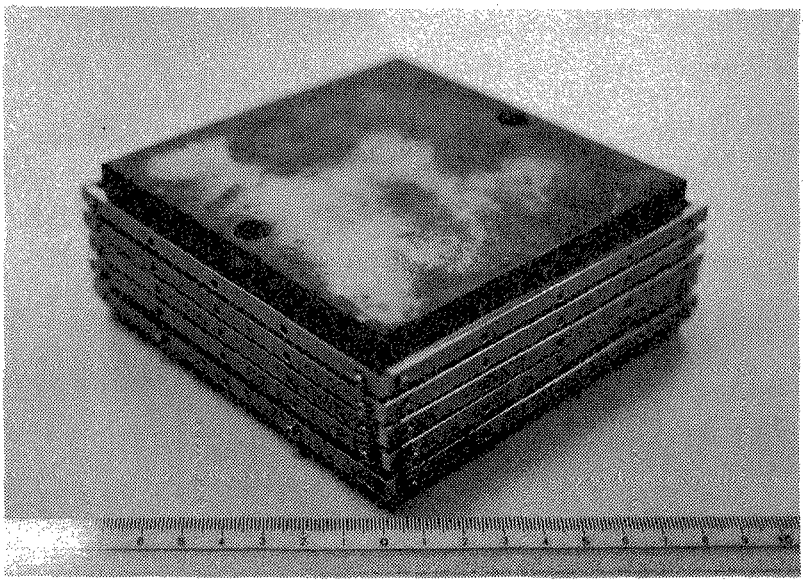


Figure 7. Metal bipolar plate stack

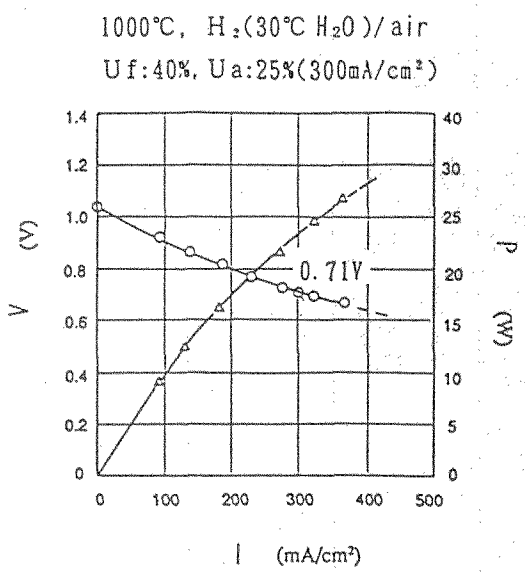


Figure 8. I-V characteristic of single cell

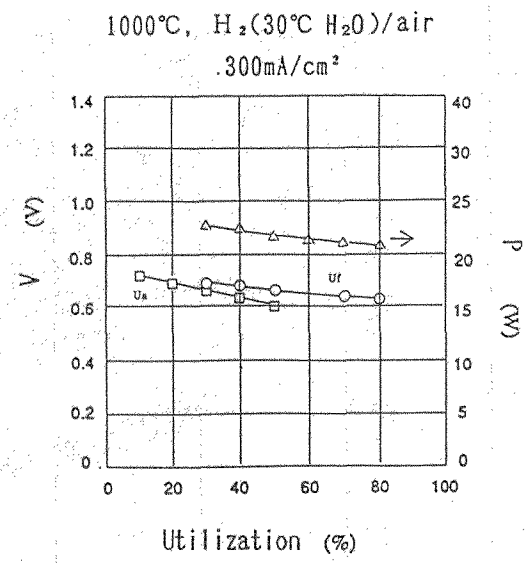


Figure 9. Effect of utilization

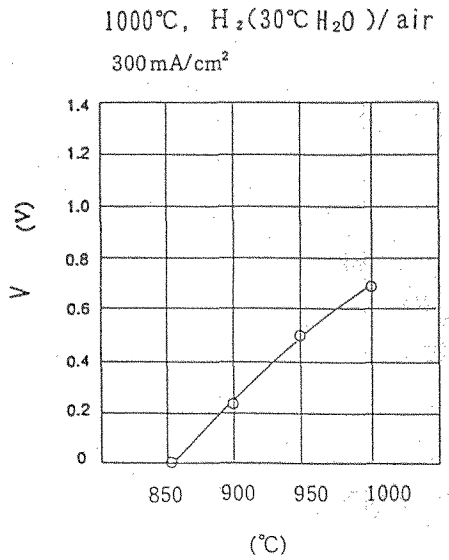


Figure 10. Effect of temperature

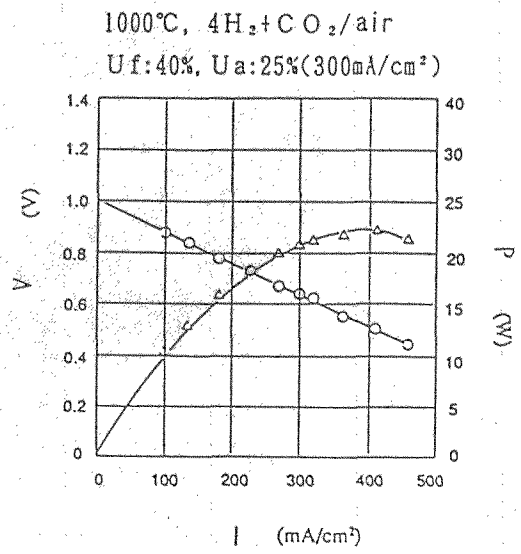


Figure 11. I-V characteristic of single cell

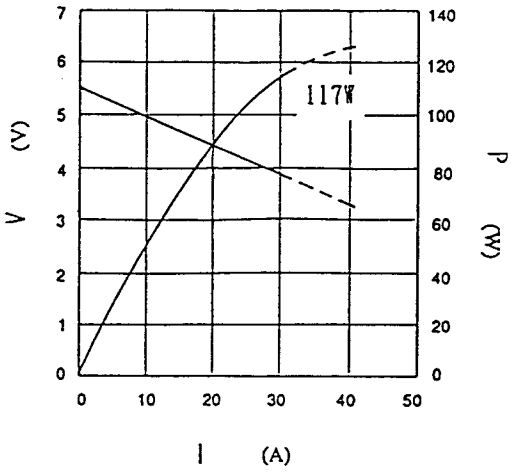


Figure 12. I-V characteristic of 6-cell stack