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Simplification of Solid Oxide Fuel Cell System Using Partial Oxidation of Methane

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The solid oxide fuel cell, Ni-YSZ cermet | YSZ | Au, could supply the stable electric power in an uniform atmosphere, namely, a methane + air mixture. At operating temperature of 950 ℃, the electromotive force (EMF) was 350 mV, and the terminal voltage was 159 mV at 14.7 mA cm^{-2} with 2.36 mW cm^{-2}. The working mechanism of the fuel cell was based on the difference in catalytic activity for partial oxidation of methane between Ni-YSZ cermet and Au electrode materials.

High temperature-type solid oxide fuel cell (SOFC) is an energy conversion system with a high energy efficiency and an environmental advantage. However, since fuel and oxidant gases must be supplied separately in the conventional fuel cell, this brings about the intricate and expensive apparatus. On such problems, a novel fuel cell system, which can work in an uniform atmosphere, have been proposed in principle by Gool1) and demonstrated in practice by Dyer.2) This system consisted of Pt | thin membrane | Pt, in which the membrane was gas-permeable and ionically conducting, and worked in a mixture of hydrogen and oxygen at room temperature. However, because of the low operation temperature, hydrocarbons such as methane can not be used as a fuel gas. Here, we report an alternative fuel cell system which works at high temperatures and uses a methane + air mixture as an energy source.

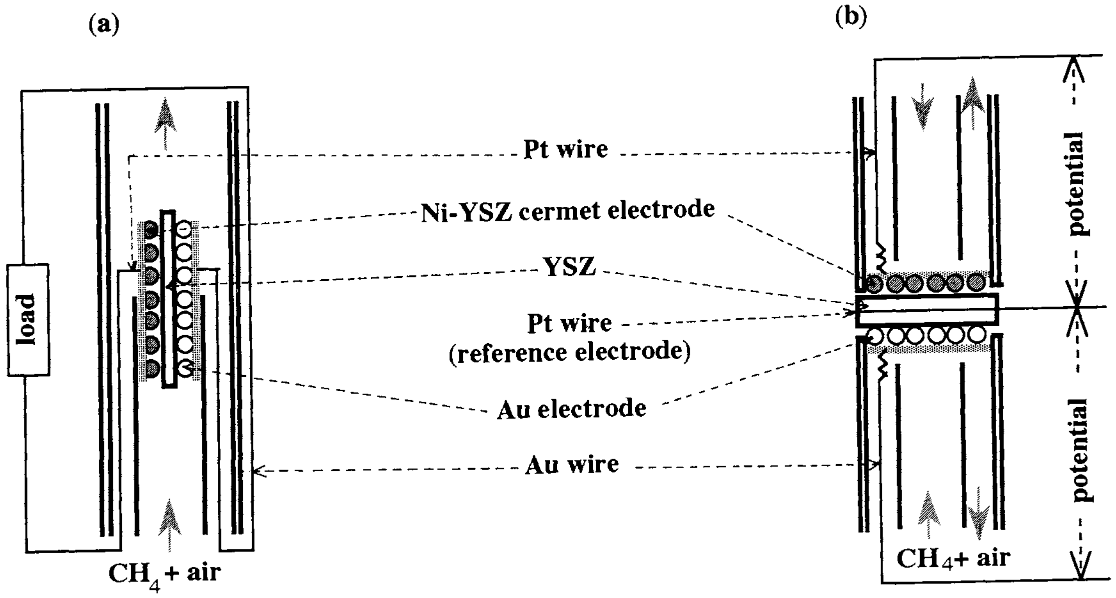

Fig. 1. The schematic illustrations of the test cells.

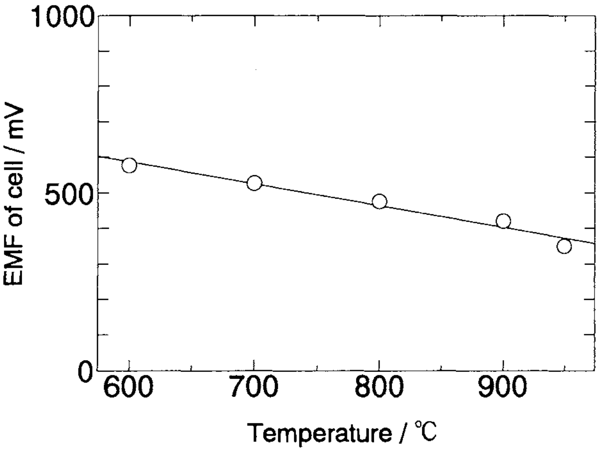

Fig. 2. The EMFs of the cell (a).

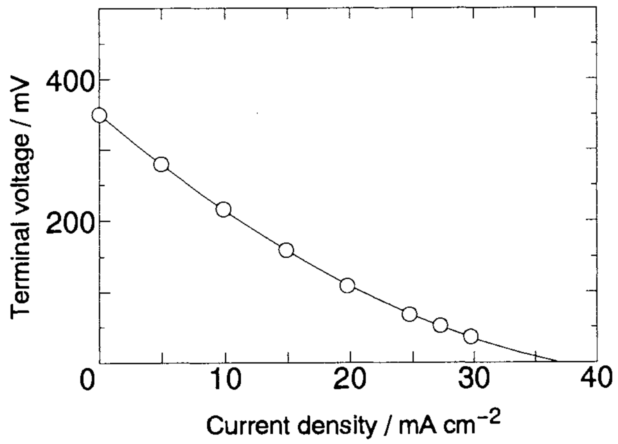

Fig. 3. The discharge characteristics of the cell (a): the thickness of electrolyte = 0.5 mm; the operation temperature = 950 ℃.

The structure of the test cell is shown in Fig. 1 (a). The disc of 8 mol% Y_2O_3-doped zirconia (YSZ) with 8 mm in diameter and 0.5 mm in thickness was used as a solid electrolyte. Ni (80 wt%)-YSZ (20 wt%) cermet was baked on one surface of the YSZ disc at 1400 ℃, and then Au metal was done on another face at 900 ℃. These electrodes were porous enough to allow the ambient gas to diffuse. The electrode area was 0.25 cm^2. Pt and Au lead wires served as output terminals for Ni-YSZ cermet and Au electrodes, respectively. The atmospheric gas was prepared by mixing methane with air (CH_4 : O_2 mole ratio = 2 : 1), and the flow rate was 210 ml min^{-1}. The operating temperature was in the range from 600 to 950 ℃.

Another test cell was used to measure the catalytic activity, potential or polarization characteristics of each electrode, as shown in Fig. 1 (b). The methane + air mixture with the same composition (CH_4 : O_2 = 2 : 1) was supplied to two electrode compartments. Pt wire was wound around the side of the YSZ disc as a reference electrode. The overpotential of each electrode was measured by current interruption method. The composition of each outlet gas was analyzed with gas chromatography, in which Porapak Q and molecular sieve 5A were used as column packings.

Figure 2 shows EMFs of the test cell (a) on introducing the methane + air mixture at 600–950 ℃. All EMFs were rather stable, and the potentials of Au electrode were always positive against Ni-YSZ cermet. On the other hand, this cell gave little EMF in air, nitrogen or hydrogen flow. The current could be stably drawn from this cell, as shown in Fig. 3. The maximal power output was 2.36 mW cm^{-2} at 14.7 mA cm^{-2} current density and 159 mV terminal voltage at 950 ℃. This value is two orders of magnitude smaller than observed in the conventional hydrogen-air fuel cell using YSZ with the same thickness. The reason will be discussed below.

In order to understand the working mechanism of this cell, the outlet gas of each electrode was analyzed with the cell (b). The result is shown in Fig. 4. In the Ni-YSZ cermet electrode compartment, oxygen almost disappeared, and methane was consumed to one-half from its inlet value. Hydrogen, carbon monoxide and a small amount of carbon dioxide were observed as products. On the other hand, the potential of Ni-YSZ cermet electrode was close to −900 mV against the reference electrode. According

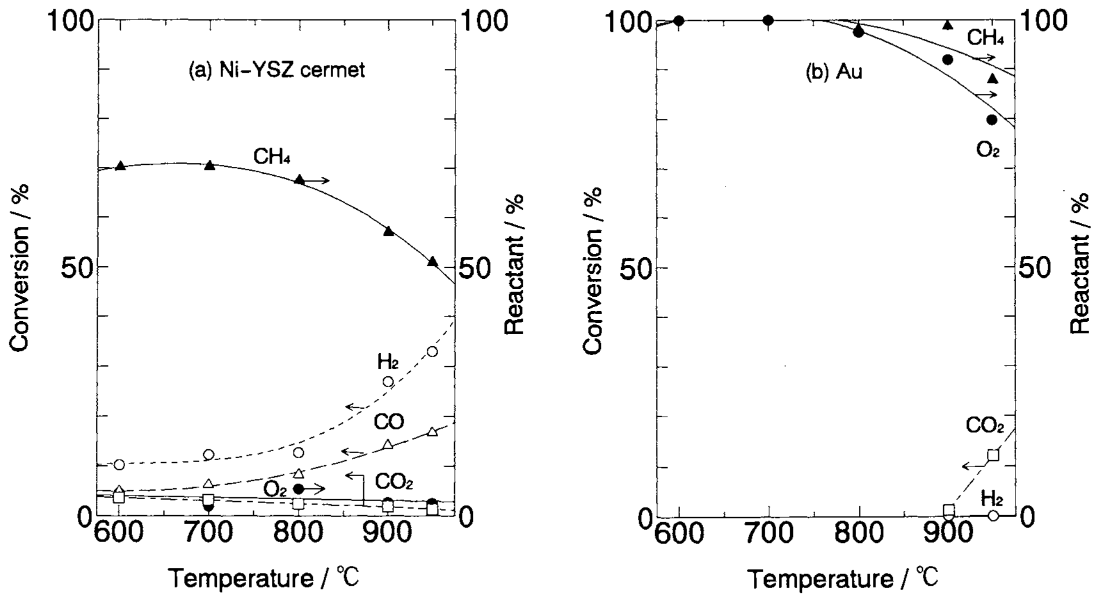

Fig. 4. The catalytic characterizations of Ni–YSZ cermet and Au electrodes in the cell (b).

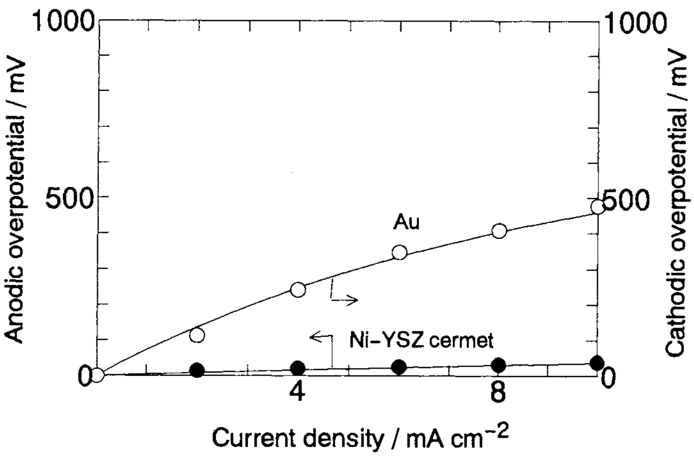

Fig. 5. The polarization characterizations of Ni–YSZ cermet and Au electrodes in the cell (b) at 950 ℃.

to the Nernst relationship, the partial pressure of oxygen at Ni–YSZ cermet electrode is calculated to be about 3 × 10^{-16} atm. This value will be reasonable to the above-mentioned composition of the outlet gas. Vernon et al.$^{3)}$ and Nakamura et al.$^{4)}$ have reported on methane-air reaction over Ni catalyst as follows:

$$CH_4 + 1/2O_2 \rightarrow 3/4CH_4 + 1/4CO_2 + 1/2H_2O \quad (1)$$

$$1/4CH_4 + 1/4CO_2 \rightarrow 1/2CO + 1/2H_2 \quad (2)$$

$$1/2CH_4 + 1/2H_2O \rightarrow 1/2CO + 3/2H_2 \quad (3)$$

Accordingly, Ni–YSZ cermet electrode, though not so active, catalyzes these reactions.

On the other hand, Au electrode scarcely exhibited the catalytic activity for the partial oxidation of methane: most of reactants were observed in the outlet gas; only small amount of hydrogen and carbon dioxide were detected. Hence, the potential of Au electrode was only −200 mV against the reference electrode. From the above findings, one can conclude that EMF observed in the cell (a) is ascribed to the difference in catalytic activity for the partial oxidation of methane between Ni–YSZ cermet and Au electrodes.

The electric power of the cell (a) was a low level, as described above. So, the overpotential of each electrode was measured with the cell (b) at 950 ℃ (Fig. 5). On the contrary to the anodic overpotential of Ni–YSZ cermet electrode, the cathodic overpotential of Au electrode was some hundreds mV. This indicates that the voltage drop observed in the cell (a) is mainly ascribed to the polarization characteristics of Au electrode. It is often said that Au metal is inactive to the adsorption, diffusion or ionization of oxygen gas. If these behaviors are the reason for the large cathodic overpotential, the polarization characteristics of Au electrode will be improved by using proton conductor, in which the above processes do not play an important role, as a solid electrolyte. In fact, we have recently constructed the fuel cells using $SrCeO_3$– and $BaCeO_3$–based ceramics as a proton conductor with 21 and 166 mW cm^{-2} at 950 ℃, respectively.

The present system, though unsatisfactory for its electric power, will make it possible for the fuel cell to simplify its construction and lower its cost. As an alternative advantage, this system can also produce synthesis gas (H_2 + CO) with the electric power supplying. Furthermore, water vapor and carbon dioxide evolved at Ni–YSZ cermet electrode on discharging the cell will react residual methane to form hydrogen and carbon monoxide according to Eqs. (2) and (3), respectively. If so, one can apply this system to a co-generation for electric power and chemicals.

References

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