Short communication

New intermediate temperature fuel cell with ultra-thin proton conductor electrolyte[☆]

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Abstract

A new approach for intermediate temperature fuel cells is tried and discussed in this paper. The essence of this new approach is an ultra-thin proton conductor coated on the solid metal anode. The $BaCe_{0.8}Y_{0.2}O_3$ perovskite was chosen for the electrolyte material. The electrolyte layer, which is 0.7 μm in thickness, was coated on Pd film by pulse laser deposition. Test cells were operated from 400 to 600 °C. The open circuit voltages were close to theoretical value in all operating temperatures. The power density was 0.9 and 1.4 W cm^{-2} at the operating temperature of 400 and 600 °C. It is shown that this new type fuel cell is an attractive new technology not only for vehicle applications but also stationary applications.
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1. Introduction

Recently, the trend of fuel cell vehicles is polymer electrolyte fuel cells (PEFCs) with on-board hydrogen storage. But the use of an on-board reformer with a fuel cell system is a very attractive option for fuel cell vehicles because of its long cruising range and no need for new hydrogen infrastructure, and high total efficiency. Two characteristics are essential for an on-board fuel cell used with a reformer, high power density and an intermediate operating temperature, which matches with the reformer. Bernay et al. reported that the PEFC and the solid oxide fuel cell (SOFC) are two candidate fuel cells for vehicle applications because they have enough power density [1]. The PEFC is an excellent FC with on-board hydrogen storage, but is not suitable with a reformer because PEFC and reformer have different operating temperatures. Solid oxide fuel cells are not suitable either because its operating temperature is too high as an on-board FC.

Intermediate temperature fuel cells with high power density have not been realized because there is not a "good" electrolyte with high ion conductivity in this temperature region. So research has been focused on decreasing electrolyte resistance because major part of fuel cell resistance derived from electrolyte resistance. There have been two main research approaches for intermediate temperature fuel cells. One approach is a search for a new electrolyte material with high ion conductivity. Ishihara et al. found that $LaGaO_3$-based perovskite oxides are good oxygen ion conductors in intermediate temperatures and they are working on SOFCs using it as electrolyte materials [2,3]. The major challenge of this approach is a trade-off between conductivity and chemical stability. Haile et al. proposed proton conducting solid acids, such as $CsHSO_4$ and CsH_2PO_4, for intermediate temperature fuel cells [4,5]. Poor physical properties, chemical stability and temperature limit (around 250 °C) are three major issues for solid acids. The other approach is an attempt for a thinner electrolyte supported on a porous electrode [6–9]. The main difficulty regarding this approach lies in making solid thin film on porous material.

Our approach is different from these approaches. The essence of this approach is an ultra-thin proton conduc-

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$$2H^+ + 1/2\,O_2 + 2e^- \Rightarrow H_2O$$

Cathode
Electrolyte 0.7μm
Pd Hydrogen Membrane 40μm

e^- H^+

Anode
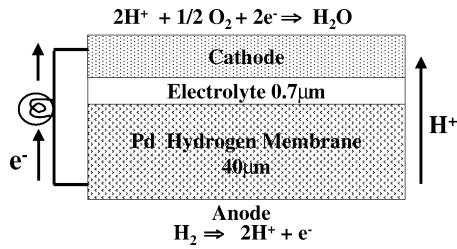$$H_2 \Rightarrow 2H^+ + e^-$$

Fig. 1. Schematic diagram of hydrogen membrane fuel cell structure.

tor electrolyte supported on solid hydrogen membrane. We named this new type fuel cell a hydrogen membrane fuel cell (HMFC). The schematic diagram of the HMFC structure is shown in Fig. 1. A much thinner electrolyte can be easily realized because it is formed on a solid, non-porous membrane. Another advantage of this approach is an ease of high density stacking because the physical base of this fuel cell is a metal film, not ceramics as in the case of SOFCs. The HMFC can use only proton conductors as an electrolyte because the hydrogen membrane layer only permeates hydrogen. We chose perovskite type proton conductor for the electrolyte. This type of material is suitable for HMFC electrolyte because it has enough proton conductivity in the intermediate temperature range. Our target position of the HMFC is shown in Fig. 2. We set the target operating temperature of the HMFC from 400 to 600 °C.

2. Experimental

2.1. Preparation of fuel cells

The test cell was prepared as follows. The $BaCe_{0.8}Y_{0.2}O_3$ electrolyte was deposited on a Pd film (40 μm in thickness) by pulse laser deposition. The approximate thickness of the electrolyte was from 0.7 μm. Then the perovskite cathode paste was screen-printed on the coated Pd structure and dried by a heat gun. This procedure was repeated for three times to make a complete cathode layer, which is 30 μm in thickness. The size of the Pd film was 15 mm × 15 mm. The electrolyte and electrode were coated on the Pd film as a 6 mm circle in diameter to make a 0.283 cm^2 effective fuel cell area.
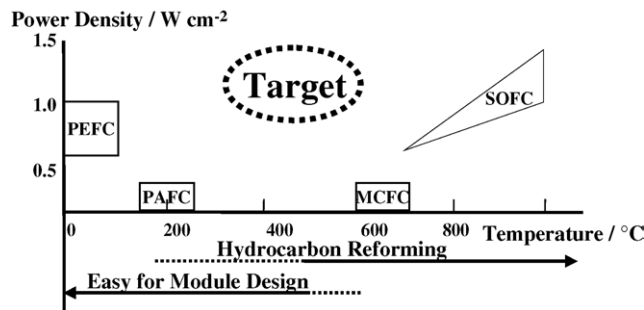
Fig. 2. Target of hydrogen membrane fuel cell.

2.2. Characterization of fuel cells

The electrolyte was characterized by SEM (JEOL, JSM-6700F) and XRD (RIGAKU, RINT2500). The cross-section SEM photograph of the electrolyte was obtained to check the quality of the membrane. Before preparation of the cross-section sample, the tungsten protection layer was coated on the electrolyte layer to avoid damages. The XRD measurement was carried out to check the crystal structure of the membrane. Both the Pd film and the electrolyte coated Pd film were measured to compare because the electrolyte layer is very thin.

2.3. Operation and evaluation of fuel cells

The single cells were sealed by ceramic adhesive (White Seal by Taketuna Corporation) and heated to operating temperatures. During this period, dry air (400 cc min^{-1}) was supplied to both anode and cathode sides. The single cells were operated at various temperatures between 400 and 610 °C. Humidified hydrogen (200 cc min^{-1}, 40 °C humidified) was supplied to the anode side. Hydrogen concentration was varied from 10 to 100% for open circuit voltage (OCV) measurement, and kept to 100% for all other measurement. Humidified air (400 cc min^{-1}, 40 °C humidified) was supplied to the cathode side during operation. Electrochemical measurement was carried out by a Solatron SI 1287 + 1255B system. The AC impedance measurement was carried out in a frequency range of 0.1–1 MHz.

3. Results and discussion

3.1. Characterization of the electrolyte

Fig. 3 shows the cross-section SEM image of the electrolyte. As seen, a solid and uniform electrolyte layer without any pores, peeling or flaking was formed on Pd sub-
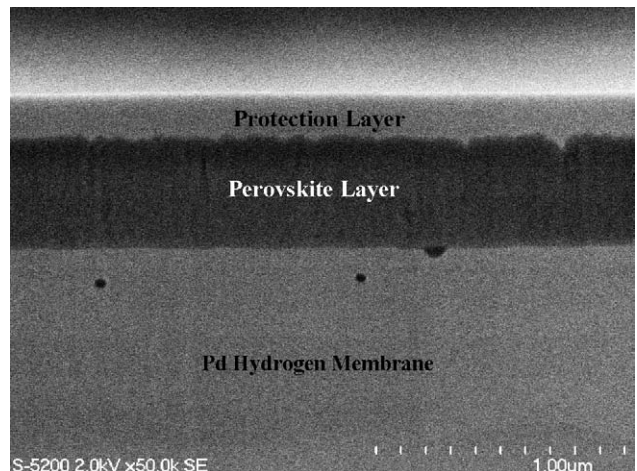
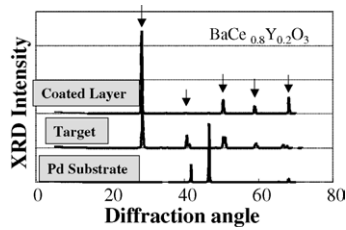Fig. 3. SEM image of cross-section of perovskite thin film on Pd substrate.

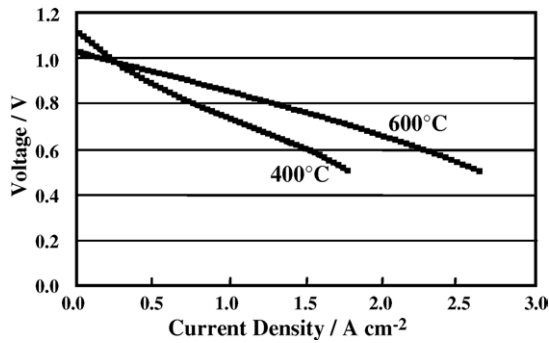Fig. 4. X-ray diffraction pattern of the perovskite thin film on Pd substrate.

Fig. 5. I–V characteristics of single cell at various temperatures. Anode gas was moist H_2 and cathode gas was moist air (both $40\,°C$ humidified).

strate. Fig. 4 shows the X-ray diffraction pattern of the electrolyte film. All the peaks of the electrolyte sample match the $BaCe_{0.8}Y_{0.2}O_3$ target peaks when the Pd peaks are excluded. From these data, it is confirmed that a good perovskite layer can be formed on Pd film by pulse laser deposition.

3.2. Evaluation of fuel cells

The open circuit voltage of single cell was measured at various temperatures and hydrogen concentrations. The results of OCV measurement are shown in Table 1. Measured OCVs are close to theoretical voltages and much higher than typical PEFCs. This result shows that the HMFC structure, which has a hydrogen membrane as the anode, works without any critical problem as a fuel cell. The difference between measured OCVs and theoretical values is almost independent from operating conditions. Iwahara et al. reported that the Y doped $BaCeO_3$ perovskite is almost a pure proton conductor under $600\,°C$ [10]. The high OCV of the HMFC is a substantial advantage over PEFCs especially in low current density region.

The V–I characteristic of a single cell is shown in Fig. 5. The power density was 0.9 and $1.4\,W\,cm^{-2}$ at the operating
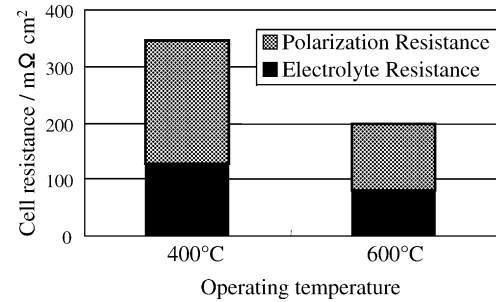

Fig. 6. Composition of cell resistance.

temperatures of 400 and $600\,°C$, respectively. This performance of the HMFC is higher than typical PEFCs and as high as that of high temperature SOFCs, even though it is operated at intermediate temperatures. The temperature sensitivity of the HMFC performance is smaller than SOFCs [11]. This can be explained by the fact that the proton conductivity has smaller temperature dependence than the oxygen ion conductivity. It is shown that the HMFC has a relatively wide operation temperature window and allows for further temperature decrease if system design or fuel choice requires.

The cell resistance was divided into an IR resistance and a polarization resistance by AC impedance method. Although measured polarization was not ohmic, a polarization resistance here is calculated as an average resistance between an OCV and 0.5 V for comparison purpose. The composition of cell resistance is shown in Fig. 6. At each temperature, the polarization resistance was about two-third of the cell total resistance and this result shows that further improvement of performance can be expected by the improvement of the electrode activities. A reference electrode was introduced to the cathode side to try to clarify anode and cathode polarization, but it was not successful because cathode and reference electrode showed almost the same potential. The dependence of AC impedance spectra to $P(H_2)$ in anode and $P(O_2)$ in cathode suggests the existence of both anode and cathode polarization. More detailed and specially designed work is necessary to clarify the ratio of polarization of the HMFC. Although the cathode material used in our fuel cell is popular in SOFCs, the polarization is much smaller than those reported in SOFC researches using bulk electrolyte [12]. Hibino et al. also measured anode and cathode polarization of fuel cells using a perovskite proton conductor as a bulk electrolyte and the polarization was much larger than our result [13]. These facts suggest that electrolyte thickness may affect the polarization.

Table 1
Open circuit voltage of single cell in various conditions

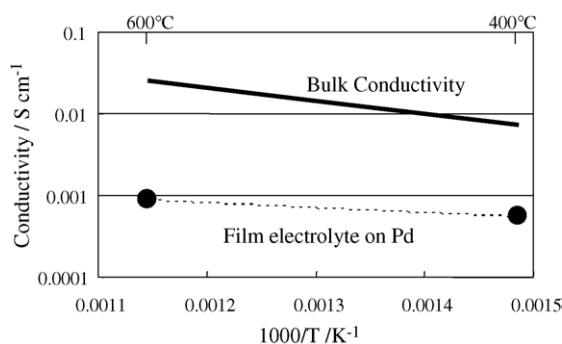| Temperature (°C)	Anode gas	Cathode gas	Measured OCV (mV)	Theoretical voltage (mV)
440	$H_2 = 100\%$	Air	1103	1140
440	$H_2 = 50\%$	Air	1082	1120
440	$H_2 = 10\%$	Air	1036	1073
530	$H_2 = 100\%$	Air	1081	1120
610	$H_2 = 100\%$	Air	1051	1100

Fig. 7. Temperature dependence of $BaCe_{0.8}Y_{0.2}O_3$ electrolyte conductivity.

In Fig. 7, the conductivity of the film electrolytes are calculated from measured IR resistances and compared with the bulk conductivity reported in literature [14]. Even though the HMFC structure can decrease the total electrolyte resistance, the conductivity of the film electrolyte is about one order of magnitude lower than bulk electrolyte, and the temperature dependence is more moderate than bulk electrolyte. These results suggest that measured IR resistance may include an interface resistance.

4. Conclusion

A new approach, hydrogen membrane fuel cell, is proposed for intermediate temperature fuel cells. The essence of the HMFC is an ultra-thin proton conductor electrolyte supported on metal hydrogen membrane. The performance of the HMFC is as high as that of high temperature SOFCs, even though it is operated at intermediate temperatures. It is shown that HMFC is an attractive new technology not only for vehicle applications but also stationary applications. Further improvement of performance is expected by the improvement of electrode performance.

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