# Performance of fuel cells based on thin proton conducting oxide electrolyte and hydrogen-permeable metal film anode

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## Abstract

This work aims to construct the hydrogen–air fuel cells, which operate at intermediate temperature. In order to reduce the operation temperature, the fuel cells are constructed using a thin proton conducting $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte. The thin films of $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte are prepared by the multiple slurry coating on a hydrogen-permeable membrane used as the anode of fuel cell. In this work, we examine at first the applicability of the hydrogen-permeable metal membrane for the anode of the fuel cell. Then, we evaluate the performance of the fuel cells consisting of the thin electrolyte supported by the metal membrane anode.

It is recognized that the hydrogen-permeable metal membrane anode works well similar to the porous Ni anode. The voltage loss for the fuel cell with the hydrogen-permeable Pd membrane anode is lower than the fuel cell with the porous Ni anode. The fuel cells with the $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte of 45 $\mu$m thickness and the Pd membrane anode of 25 $\mu$m thickness operate stably giving an open circuit voltage of 1.0 V at 640 °C and the power density of 50 mW/cm$^2$ is derived.
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## 1. Introduction

Intermediate temperature (e.g. 600 °C) operation of fuel cells have several benefits such as fast electrode kinetics, no serious materials corrosion problems and low-cost for construction. When a proton conductor is used as an electrolyte of the fuel cells instead of an oxygen ion conductor, the operation temperature can be reduced to intermediate temperature. Many studies have been carried out to examine performance of the proton conducting oxide fuel cells [1–6]. However, the *I–V* plots for those fuel cells at 600 °C did not exceed the commercial target of 100 mW/cm$^2$ [7]. In the previous study [8], we evaluate each contribution of the electrolyte and the electrode to the voltage loss for the proton conducting oxide fuel cells from the dependence of the *I–V* characteristics on the electrolyte thickness. The contribution of electrolyte resistance to the voltage loss is dominant to some extent over the electrode reaction. Therefore, thin oxide membrane electrolytes ought to exhibit small voltage losses. Provided that these membranes are gas tight, they are good candidates

for solid electrolyte in solid oxide fuel cells. However, the fabrication of dense proton conducting oxide films on the porous substrate like the electrode of the fuel cells is very difficult; the oxide films deposited on the porous substrate contain too many pores to use for the electrolyte of the fuel cells. The substrate without open pore would be necessary to fabricate the dense proton conducting oxide films.

In this study, we examine at first applicability of the hydrogen-permeable metal membrane as the negative electrode (anode) in the hydrogen–air fuel cell. Then, we prepare the thin proton conducting oxide electrolyte by means of slurry coating method on the hydrogen-permeable metal membrane anode. Then, we measure the *I–V* characteristics for the fuel cell consisting of the thin $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte prepared on the hydrogen-permeable metal membrane anode. Results will be presented to demonstrate the thin $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte activity.

## 2. Experimental

The coating solution for the slurry coating was a mixture of $BaCe_{0.9}Y_{0.1}O_{2.95}$ powder ($<1$ $\mu$m) and sol–gel precur-

sor solution. The sol–gel precursor solution was purchased from Toshima, Matsuyama, Japan. Prior to the first coating step, the substrate was cleaned in acetone by using an ultrasonic bath. In order to prevent cracking of the thin ceramic film, the hydrogen-permeable metal substrates were supported by porous $Al_2O_3$ disc. The films were dried at 130 °C for 20 min to remove residual solvent. After drying the samples were heated to the calcining temperature of 640 °C with heating rate 5 °C/min and kept this temperature for 120 min, to drive out all organic compounds and to form chemical bonds between film and substrate. The resultant single layer films reached a thickness of approximately 2 µm. To obtain higher film thickness, multiple layer coating was successively performed on previous calcined layers. The samples with the desired thickness were finally sintered at temperatures between 1200 and 1450 °C for 10 h. The phase purity of the thin ceramic films was checked by X-ray diffraction with Cu Kα radiation. Only the diffraction pattern of $BaCe_{0.9}Y_{0.1}O_{295}$ [9] was detected. The thickness of the ceramic films was determined by micrometer.

The hydrogen–air fuel cell used in the present work is illustrated in Fig. 1. In this cell, both electrode components were separated by the solid electrolyte. Silver paste backed with silver mesh was used for the cathode and hydrogen-permeable metal (Pd and $Pd_{0.6}Ag_{0.4}$) membranes supported with porous $Al_2O_3$ was used for the anode. The contact lead of the anode was connected with the Pd membrane. Although the cathode was exposed to air, the anode component containing the metal hydride was sealed tightly using Ag and Cu gaskets to prevent the release of hydrogen. $TiH_2$ was used as hydrogen source for the cell operation at temperature near 600 °C. By using the metal hydride as the hydrogen source, we could investigate the performance of the fuel cell very easily and safely.

## 3. Results and discussion

At first, we examined the applicability of the hydrogen-permeable metal membrane for the anode. The fuel cells consisting of the metal membrane anode and the sintered $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte operated stably giving open circuit voltage of 1.1 V. The I–V characteristics at 640 °C for the fuel cells consisting of Pd membrane (25 µm), $Pd_{0.6}Ag_{0.4}$ membrane (80 µm) and porous Ni-paste anodes are shown in Fig. 2. It can be seen from this figure that the hydrogen-permeable metal membrane anodes work well similar to the porous Ni anode. Moreover, the voltage-current performance for the Pd membrane anode cell is better than the porous Ni anode cell.

When the cell is under load, the terminal voltage, V is depressed by an amount that depends on the current, electrolyte resistance and electrode kinetics. Under these conditions, the voltage can be described by the following expression:

$$V = E - IP_{\text{clyt}} - \eta_\alpha - \eta_\chi, \tag{1}$$

where E is the open circuit voltage, $R_{\text{clyt}}$ the electrolyte resistance, $\eta_\alpha$ and $\eta_\chi$ are the anode and cathode overvoltages, respectively. The difference of the I–V characteristics between the metal membrane cell and the porous Ni anode cell can be attributed to the difference of the overvoltage from the anode reaction, since the same electrolyte and the same cathode are used in these measurements.

The anode reaction in the proton conductor fuel cell is

$$2H \rightarrow 2H^+ + 2e^- \tag{2}$$

In the hydrogen-permeable metal, hydrogen exists in an atomic form. Then, the expected reaction for the hydrogen-permeable metal anode is

$$H \rightarrow H^+ + e^- \tag{3}$$

The dissociation process of hydrogen molecule is not included in this reaction. This may be the reason why the electrode reaction for the Pd membrane anode becomes faster
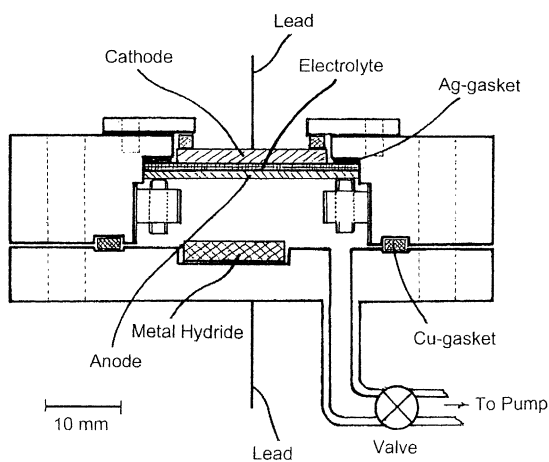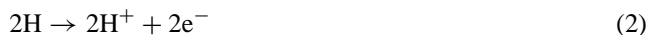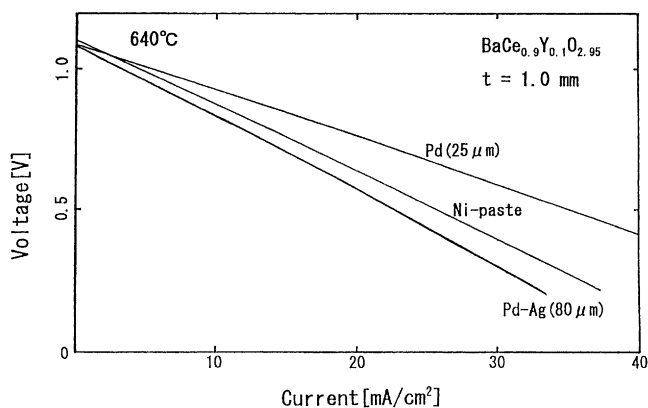


Fig. 1. Schematic illustration of hydrogen–air fuel cell consisting of the proton conducting oxide electrolyte and the metal hydride for hydrogen source.



Fig. 2. I–V characteristics of the fuel cells consisting of Pd membrane (25 µm), $Pd_{0.6}Ag_{0.4}$ membrane (80 µm) and porous Ni anodes. $BaCe_{0.90}Y_{0.1}O_{2.95}$ electrolyte and porous Ag cathode are used.

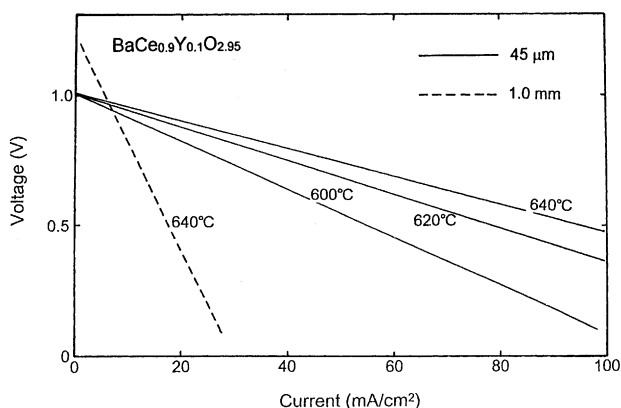Fig. 3. *I–V* characteristics of the fuel cell with $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte of 45 μm thickness. The previous result using $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte of 1.0 mm thickness is also shown.

than that for the porous Ni anode. The larger voltage loss for the $Pd_{0.60}Ag_{0.40}$ membrane anode cell, compared to that for the porous Ni cell, results from the difference of the permeation flux of protons through the anode membrane.

Disc-shaped $BaCe_{0.9}Y_{0.1}O_{2.95}$ thin films with 15 mm diameter and 20–50 μm thickness were fabricated by slurry coating method to use as the electrolyte in the fuel cell. The electrolyte films were prepared on the Pd membrane of 25 μm thickness supported by porous aluminum oxide disc, in order to prevent the cracking of the electrolyte films. The electrode area was $0.2 \, cm^2$.

It is revealed that the fuel cell using the thin $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte operates stably giving open circuit voltage of about 1.0 V, indicating negligible gas permeation through the thin electrolyte. Under load, the cell operates steady and stably giving almost constant current. The *I–V* characteristics of the fuel cell is measured at the temperature range of 600–640 °C.

Fig. 3 shows the *I–V* plots of the fuel cell using the $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte of 45 μm thickness together with our previous *I–V* result [8]. In the previous work, the $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte of 1.0 mm thickness prepared by the sintering at 1450 °C was used. In this figure, the *I–V* curves appear approximately as strait lines in accordance with Ohm's law. The voltage loss incurred in the thin electrolyte cell is considerably smaller than that in the thick electrolyte cell. However, the current densities achieved so far are very little against our expectation. The current densities could be increased by fabrication of the dense thin electrolyte with larger conductivity and improvement of the electrode performance. Studies to fabricate the thin electrolyte with high conductivity are now in progress.

## 4. Conclusion

We constructed a hydrogen–air fuel cell consisting of a thin proton conducting oxide electrolyte and a hydrogen-permeable metal (Pd and $Pd_{0.6}Ag_{0.4}$) membrane anode. Comparison of the *I–V* plots between the fuel cell with the metal membrane anode and that for the cell with the porous Ni anode revealed that the metal membrane anode worked well similar to the porous Ni anode except the voltage loss; the voltage loss for the fuel cell with the Pd membrane anode was smaller than that for the cell with the porous Ni anode. Discrepancy of the voltage loss would be associated with the difference of the anode reaction, since the same electrolyte and the same cathode were used in these measurements. In the anode reaction for the metal anode, the dissociation process of hydrogen molecule is not involved. This is the reason why the anode reaction for the Pd anode becomes faster than that for the porous Ni anode.

We fabricated the thin films of proton conducting oxide by the multiple slurry coating on hydrogen-permeable Pd membrane. It has been demonstrated that the fuel cell with $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte of 10–50 μm thickness and the hydrogen-permeable Pd anode of 25 μm thickness operated stably giving an open circuit voltage of 1.0 V indicating negligible gas permeation through the thin electrolyte. The performance of the fuel cell was evaluated from the measurement of the *I–V* characteristics and the current density of $50 \, mW/cm^2$ was obtained from the fuel cell using the $BaCe_{0.9}Y_{0.1}O_{2.95}$ electrolyte of 45 μm. However, this value was very little against our expectation. The performance of the fuel cell would be improved by fabrication of the dense thin electrolyte of high conductivity.

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