

Short communication

# Construction of fuel reformer using proton conducting oxides electrolyte and hydrogen-permeable metal membrane cathode

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## Abstract

We constructed a reformer of methane based on an electrochemical principle. This apparatus consists of the proton conducting ceramics electrolyte and the hydrogen-permeable metal membrane cathode. For methane reforming, a mixture of methane and oxygen gas is supplied to the porous Ag cathode. The hydrogen ions, which formed by the anode reaction:  $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$ , are transported through the proton conducting ceramics to the cathode. Then, the hydrogen is formed at the cathode by the reaction:  $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$ . The hydrogen, which permeates through the metal membrane cathode, is 100% purity.

The hydrogen separation ability of the reformer was investigated at 400–650 °C by measuring the electric current through the proton conducting oxide electrolyte. Since the ionic transport number of the proton conducting oxide is nearly unity, the current through the electrolyte corresponds to the proton flux through the electrolyte.

The current measurements showed that the extracted proton flux through the electrolyte increased with increasing the applied voltage as well as temperature as we expected. However, the current measurements under the low voltage revealed that the extracted current was lesser than the expected value from Ohm's law. The decrease of the current is possibly caused for the reduction of the effective voltage by the anode polarization. In order to separate the hydrogen with higher efficiency, the applied voltage must be as low as possible using the thinner electrolyte and the improved anode.

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**Keywords:** Methane reforming; Separation hydrogen from methane; Proton conducting ceramics; Hydrogen-permeable metal membrane

## 1. Introduction

At present, hydrogen serves as fuel for fuel cells in stationary and mobile power applications. For these fuel cell systems, reforming of methane or natural gas is considered to be favored process of  $\text{H}_2$  production. However, the reforming of gaseous hydrocarbons results in a product gas with differing fractions of hydrogen ( $\text{H}_2$ ), carbon dioxide ( $\text{CO}_2$ ), carbon monoxide (CO) and so on depending on the reforming process [1]. Since CO acts as a strong poison to the electrocatalyst, the amount of CO has to be reduced to only a few ppm by the selective oxidation [2].

We constructed a reformer of methane without the CO conversion using the proton conducting ceramics. Our apparatus is based on an electrochemical principle, and consists of the proton conducting ceramics electrolyte and the hydrogen-permeable metal membrane cathode. In this apparatus, proton conducting ceramics preferentially pump up hydrogen ions from methane or natural gas, and the hydrogen ions are transported through the proton conducting ceramics as reported by Iwahara [3].

In the present work, we have investigated hydrogen separation ability of the proton conducting ceramics by measuring the electric current through the  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  ceramics with different thickness. The results of the hydrogen separation show that the proton flux through the ceramics increased with increasing the applied voltage as well as temperature.

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Furthermore, it is revealed that amount of the extracted hydrogen per the consumed electric power depends on the electrolyte thickness and the reduction of the effective voltage by the anode polarization.

## 2. Experimental

The proton conducting  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  electrolytes used in the present study were the polycrystalline pellets with 0.6 mm thickness and the polycrystalline films of 42  $\mu\text{m}$  thickness. The  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  pellets were prepared by a solid state reaction and sintering process using appropriate oxides and carbonates as starting materials. The  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  films were prepared by the slurry coating method on the Pd membrane substrate of 0.1 mm thickness, which was used also as the cathode. The coating solution for the slurry coating was a mixture of  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  powder (<1  $\mu\text{m}$ ) and sol-gel precursor solution. Prior to the first coating step, the Pd membrane was cleaned in acetone by using an ultrasonic bath. 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  $\text{min}^{-1}$  and kept this temperature for 120 min, to drive out all organic compounds and to form chemical bonds between the film and the substrate. The resultant single layer films reached a thickness of approximately 2  $\mu\text{m}$ . The samples with desired thickness were finally sintered at temperatures between 1300 and 1450 °C for 10 h. The phase purity of the thin ceramics films was checked by X-ray diffraction. The diffraction pattern of  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  was only detected. The thickness of the ceramics films was determined by micrometer.

Fig. 1 illustrates schematically the principle of the hydrogen separator using proton conducting ceramics and hydrogen-permeable Pd membrane, with which only hydrogen can be extracted across the proton conducting  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  electrolyte driven by the dc power source. For methane reforming, a mixture of  $\text{CH}_4$  and  $\text{O}_2$  is supplied at the flow rate of 300  $\text{ml min}^{-1}$  to the anode. In this work, three kinds of anode materials, i.e. porous Ag film which

prepared by Ag-paste coating, Pt net of 100 mesh and Pt black-powder were tested.

The protons, which are formed by the anode reaction:  $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$ , migrate to the hydrogen-permeable Pd membrane cathode of 0.1–0.3 mm thickness, where hydrogen molecules are formed by the cathode reaction:  $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$ . Then, the hydrogen gas penetrates through the hydrogen-permeable Pd membrane cathode. In the present work, the results of the hydrogen separation using the mixed gas with a volume ratio of  $\text{CH}_4:\text{O}_2 = 0.5$  are presented.

## 3. Results and discussion

The amount of hydrogen extracted from methane was evaluated by measuring the electric charge through the proton conducting ceramics electrolyte. Since the ionic transport number for the  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  proton conducting ceramics is nearly unity [4], the current through the circuit corresponds to the proton flux through the electrolyte; electric charge of 1 C corresponds to  $6.24 \times 10^{18}$  protons. This amount of protons transforms to hydrogen gas of 0.117 cc under atmospheric pressure at ambient temperature.

In the separation of hydrogen by the electrochemical method, the electric power efficiency, i.e. the amount of hydrogen per the consumed electric power, is important from the economic point of view. Since the amount of extracted hydrogen is expressed by the extracted current, the efficiency of hydrogen separation is expressed by the following relation: hydrogen separation efficiency = current/electric power = current/current  $\times$  applied voltage = 1/applied voltage. From this relation, we notice that the applied voltage for the hydrogen separation must be as low as possible in order to increase the power efficiency of the hydrogen separation.

Figs. 2 and 3 shows the result of the dc current measurements under the applied voltage of 1 and 2 V using the porous Ag film anode prepared by Ag-paste coating and the Pt anode of 100 mesh, respectively. In these measurements, the same  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  pellet of 0.60 mm thickness is used as the electrolyte. The  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  ceramics were chosen as the electrolyte because of their high ionic conductivity and therefore their high proton mobility [5].

The results of Fig. 2 for the Ag anode indicate that the extracted currents, therefore the amounts of extracted hydrogen, increase exponentially with increasing temperature in agreement with the temperature dependence of the electrical conductivity of proton conducting ceramics [6]. However, the relation between applied voltage and extracted current does not obey Ohm's law; the current for 1 V are considerably smaller than half value of the current for 2 V as shown by the thin dotted line in Fig. 2. This result may be attributed to the loss of the applied voltage caused by the anode polarization.

On the other hand, the relation between the extracted current and the applied voltage nearly obeys Ohm's law as shown

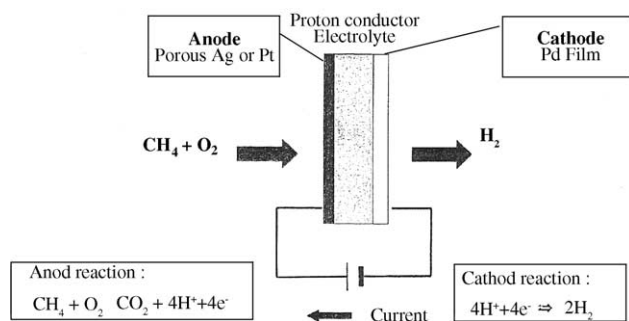


Fig. 1. Principle of the fuel reformer consisting of the proton conducting oxide electrolyte and the hydrogen-permeable metal membrane cathode.

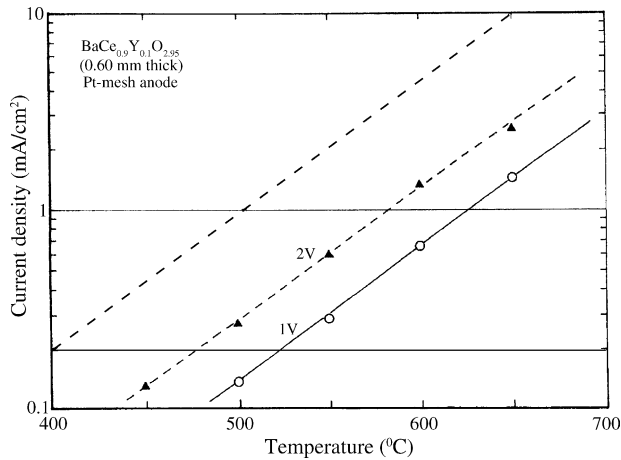


Fig. 2. Temperature dependence of the extracted current for the applied voltages of 1 and 2 V, where the BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>2.95</sub> pellet of 0.60 mm thickness, the porous Ag film and the Pd membrane of 0.3 mm thickness are used as the electrolyte, the anode and the cathode, respectively. The thin dotted line shows the half value of the thick line for the applied voltage of 2 V.

in Fig. 3 for the Pt mesh anode. This result indicates that the voltage loss caused by the polarization is less for the Pt anode than that for the Ag anode. In comparison to Fig. 2 with Fig. 3, however, the extracted currents of Fig. 2 are larger than that of Fig. 3. This result will be attributed to the difference of the effective electrode area; effective electrode area of the Pt mesh used in the measurement of Fig. 3 is about one-third of the porous Ag anode used in the measurement of Fig. 2.

Fig. 4 shows the variation of the dc current against temperature under the applied voltage of 1 and 2 V using the thin BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>2.95</sub> electrolyte of 42 μm thickness and the Pt powder anode. The extracted current of Pt powder anode is about fifty times larger than that of the Pt mesh anode, be-

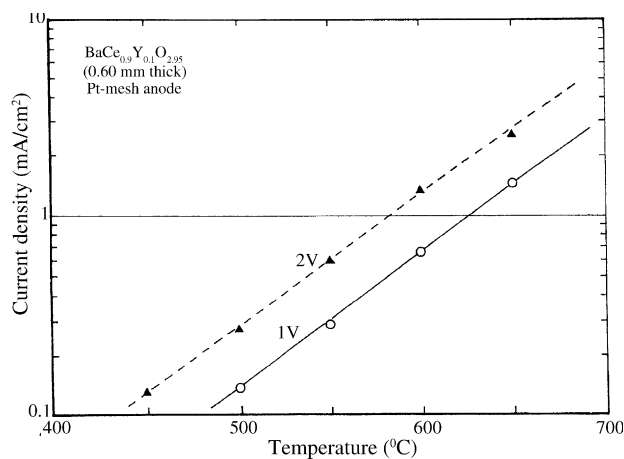


Fig. 3. Temperature dependence of the extracted current for the applied voltages of 1 and 2 V, where the BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>2.95</sub> pellet of 0.60 mm thickness, the Pt net of 100 mesh and the Pd membrane of 0.3 mm thickness are used as the electrolyte, the anode and the cathode, respectively.

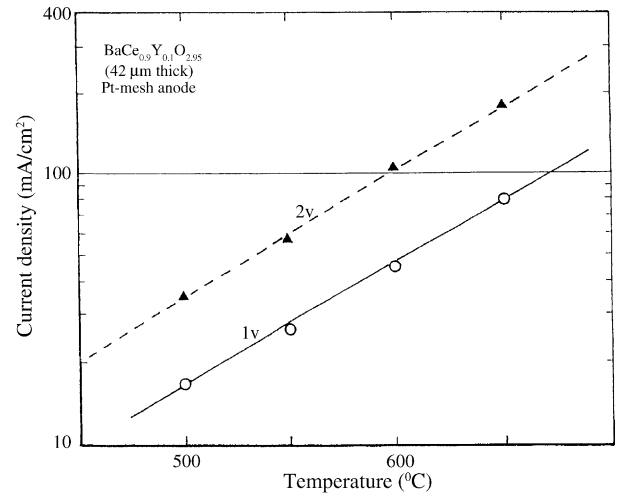


Fig. 4. Temperature dependence of the extracted current for the applied voltages of 1 and 2 V, where the BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>2.95</sub> film of 42 μm thickness, the Pt powder of 300 mesh and the Pd membrane of 0.1 mm thickness are used as the electrolyte, the anode and the cathode, respectively.

cause of the magnification of the effective electrode area as well as the decrease of the electric resistance which is proportional to the electrolyte thickness. In this measurement, the relation between the applied voltage and the extracted current almost obeys Ohm's law, since the voltage loss caused by the polarization at the Pt powder anode is small.

Taking into account of the voltage loss  $\eta$ , the relation between the applied voltage and the extracted current at temperature  $T$  may be expressed as,

$$I_T = \frac{V_T - \eta}{R_T}$$

where  $I_T$ ,  $V_T$  and  $R_T$  are the current, the voltage and the electric resistance of the electrolyte, respectively. Using this relation, we evaluated  $\eta$  and  $R_T$  from the experimental data by solving the simultaneous equations. The results are shown in Table 1, where  $R_T$  decrease with increasing temperature, while  $\eta$  are almost constant. These results suggest that we have to use the thinner electrolyte and the catalytic activity of the anode should be improved in order to increase the efficiency of the hydrogen separation.

Table 1  
Temperature dependence of electric resistance

	Temperature (°C)				
	450	500	550	600	650
BaCe <sub>0.9</sub> Y <sub>0.1</sub> O <sub>2.95</sub> ( $t=0.60$ mm) and Ag anode, $\eta=0.71$ V					
$R_T$ (k $\Omega$ )	4.35	1.85	0.93	0.49	0.17
BaCe <sub>0.9</sub> Y <sub>0.1</sub> O <sub>2.95</sub> ( $t=0.60$ mm) and Pt mesh anode, $\eta=0.13$ V					
$R_T$ (k $\Omega$ )	14.2	7.64	3.10	1.27	0.52
BaCe <sub>0.9</sub> Y <sub>0.1</sub> O <sub>2.95</sub> ( $t=42$ μm) and Pt powder anode, $\eta=0.16$ V					
$R_T$ (k $\Omega$ )	69.7	50.4	32.3	18.1	10.4

In the evaluation of the electric resistance, the difference of the effective area between the Ag anode and the Pt mesh anode did not revised.

#### 4. Conclusion

We separated hydrogen from methane by the electrochemical method using the proton conducting  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  electrolyte and the hydrogen-permeable Pd membrane cathode.

In order to separate the hydrogen economically, the applied voltage for the hydrogen separation has to be as low as possible using the thin electrolyte with the high ionic conductivity. It was recognized that the relation between the applied voltage and the extracted current through the electrolyte does not obey Ohm's law; the current decrease more radically with decreasing the applied voltage. The additional current decrease is attributed to the drop of the effective voltage by the anode polarization. In order to increase the efficiency of hydrogen separation under the low voltage, the catalytic activity of the anode should be improved.

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