Effect of lanthanum tungstate hole-blocking layer for improvement of energy efficiency in anode-supported protonic ceramic fuel cells

Hiroki MATSUO¹, Kenta NAKANE¹, Yoshio MATSUZAKI²,³ and Junichiro OTOMO¹,†

¹Department of Environment Systems, Graduate School of Frontier Sciences, The University of Tokyo, 5–1–5 Kashiwanoha, Kashiwa, Chiba 277–8563, Japan
²Tokyo Gas Co., Ltd. Fundamental Technology Dpt., 1–7–7 Suehirocho, Tsurumi, Yokohama 230–0045, Japan
³Kyushu University, Next-generation Fuel Cell Research Center, 7–4–4 Motooka, Nishi-ku, Fukuoka 819–0395, Japan

Conduction of minority carriers in electrolytes is one of the key factors to be controlled to realize highly efficient protonic ceramic fuel cells (PCFCs). In this study, the performance of anode-supported PCFCs using a BaZr₀.₈Y₀.₂O₃₋₄ (BZY) monolayer electrolyte membrane and a bilayer electrolyte where a lanthanum tungstate (La₂₈₋ₓW₄₊ₓO₅₄₋₃₋₂ₓ; LWO) hole-blocking layer is deposited on the BZY membrane are investigated by theoretical calculations based on transport properties of the electrolytes and experimental electrochemical performance tests. The theoretical calculations indicated that the BZY/LWO bilayer cell can achieve higher open-circuit voltage (OCV) and energy efficiency than those of the BZY monolayer cell by suppressing the hole conduction in the electrolyte membrane. We experimentally confirmed that the BZY/LWO cell exhibited the OCV of 1.01 V while that of the BZY monolayer cell was 0.93 V at 600 °C. This study presents that the thin LWO hole-blocking layer is effective in the improvement of the OCV and the energy efficiency of the anode-supported PCFCs.

©2021 The Ceramic Society of Japan. All rights reserved.

Key-words : Protonic ceramic fuel cell, Leakage current, Hole conduction, Lanthanum tungstate, Bilayer electrolyte, Anode-supported cell

1. Introduction

Protonic ceramic fuel cells (PCFCs) are one of the attractive energy devices which can operate at lower temperatures compared to conventional oxide-ion conducting solid-oxygen fuel cells (SOFCs). Its low operating temperature will enable daily start and stop operation, a longer lifetime, and low operation cost.¹⁻⁴ Since water is generated at the cathode side, higher fuel efficiency than that of the SOFCs can be attained. In terms of efficient operation of PCFCs, suppression of a leakage current arising from non-negligible conduction of electrons and holes through electrolyte membranes has been an essential issue as well as the development of electrolyte materials with high protonic conductivity. While Ba-based perovskite-type proton conductors which have been widely recognized as the most promising electrolyte materials for practical cells because of their high protonic conductivity,⁵⁻⁷ they also exhibit significant hole conduction under oxidative atmosphere.⁵⁻⁹ The leakage current causes severe reduction of open-circuit voltage (OCV) because of electrical short between the cathode and the anode electrodes. Moreover, the high leakage current results in lowering of energy efficiency because electronic currents flowing through the electrolyte membrane cannot be utilized as an external current while hydrogen molecules equivalent to the leakage current are used to generate it.¹⁰⁻¹² Therefore, a novel approach to suppress the leakage current has been required to develop the high-efficiency PCFCs.

Lanthanum tungstate (La₂₈₋ₓW₄₊ₓO₅₄₋₃₋₂ₓ) with high La/W ratio of 6.7 (x = 0.156) is one of the attractive proton conductors with quite low hole conductivity.¹³⁻¹⁵ In this report, lanthanum tungstate with a composition of La/W = 6.7 is expressed as LWO. High protonic transport number under the oxidative atmosphere owing to the low hole conductivity is a great advantage of LWO though its proton conductivity is lower than that of the typical Ba₉Zr₀.₈Y₀.₂O₃₋₄ (BZY) monolayer electrolyte membrane. Our previous theoretical calculations suggested that the leakage current in a BaZr₀.₈Y₀.₂O₃₋₈ (BZY) electrolyte membrane can be well suppressed by introducing a thin LWO hole-blocking layer.¹¹ The introduction of the LWO hole-blocking layer changes an oxygen chemical

† Corresponding author; J. Otomo; E-mail: otomo@k.u-tokyo.ac.jp
potential profile in the electrolytes, which effectively prohibits the oxidation of the BZY membrane leading to the suppressed leakage current.

While LWO is a possible material for the hole-blocking layer because of its high protonic transport number even in the oxidative atmosphere, relatively low chemical stability which causes chemical reactions with other constituents in the cell is a barrier for application to the practical cell. We have reported that thin films of Gd-doped ceria (GDC) and La-doped ceria (LDC) can be utilized as an interlayer to protect the LWO electrolyte from the chemical reactions with the other constituents. We fabricated anode-supported PCFCs using LWO as the electrolyte membrane with a thickness of 1–3 μm such as Ni-GDC[GDC][LWO] GDC[LaFe0.95Nb0.05O3–δ] and Ni-GDC[LDC][LWO]LDC Lao.6Sr0.4Co0.2Fe0.8O3–δ (SCF), where the GDC layer and the LDC layer had a role to hinder the chemical reactions of the LWO electrolyte and the electrodes.10,17 We confirmed the successful operation of the cells with the thin LWO electrolyte membrane, but their performances were still low compared to the conventional PCFCs with the perovskite-type electrolyte membranes. Since LWO has the high protonic transport number while its proton conductivity is lower than that of the typical perovskites, a combination of LWO with the Ba-based perovskite oxides having high proton conductivity to form a bilayer electrolyte structure will attain high-performance cell with a high power density and the low leakage current. However, integration of LWO as the hole-blocking layer with Ba-based perovskite oxides with high proton conductivity has not been realized yet.

In this study, we introduced the LWO hole-blocking layer to the anode-supported PCFC using the BZY electrolyte membrane to form a BZY|LWO bilayer structure. We explored the influence of the LWO hole-blocking layer on the cell performances such as OCV and energy efficiency by theoretical calculations and experiments. In the theoretical calculations, we employed a model of the BZY|LWO bilayer structure in which the thin LWO layer was placed at the cathode side of the thicker BZY membrane. Moreover, we experimentally investigated the performance of the anode-supported cells with the BZY monolayer electrolyte and that with the BZY|LWO bilayer electrolyte to reveal the effect of the LWO hole-blocking layer.

2. Theoretical calculation and experimental

2.1 Theoretical estimation of cell performance

The OCV value, energy efficiency, and power density of the BZY monolayer cell, the LWO monolayer cell, and the BZY|LWO bilayer cells with various LWO layer thickness (L_LWO) were estimated from the transport properties of LWO and BZY based on a calculation method reported in the literatures.10,11,14,15 The total thickness (L_total) of the electrolyte membrane including both the LWO hole-blocking layer and the BZY layer were fixed as 10 μm, namely L_total = 10 μm. In the bilayer model, terminal voltage (V_T), can be calculated from the following equations.11

\[
V_T = \frac{RT}{4F} \left( \frac{\ln n_{P,\text{O}_2,\text{interface}}}{n_{P,\text{O}_2,\text{anode}}} \cdot \sigma_{\text{ion,1}} \cdot d \ln n_{P,\text{O}_2} + \frac{\ln n_{P,\text{O}_2,\text{cathode}}}{n_{P,\text{O}_2,\text{cathode}}} \cdot \sigma_{\text{ion,2}} \cdot d \ln n_{P,\text{O}_2} \right)
\]

\[
\sigma_{\text{elec}} = \sigma_{\text{elec}}^{p,1} + \sigma_{\text{elec}}^{\text{O}_2,0,1}
\]

\[
r = I_{\text{ion}}/I_{\text{leak}}
\]

where, R, T, F, P_{O_2}, I_{leak} and I_{ion} and I are gas constant, temperature, Faraday constant, oxygen partial pressure, leakage current density, and ionic current density, respectively. \(\sigma_{\text{ion,1}}\) and \(\sigma_{\text{elec}}\) are ionic conductivity, and electronic conductivity including hole conduction \(\sigma_{\text{elec}}^{p,1}\) and electron conduction \(\sigma_{\text{elec}}^{p,0}\) of the electrolyte “i”. The subscript “1” expresses BZY when i = 1 and LWO when i = 2. The conductivity parameters are summarized in Table 1.

| Electrolyte | \(\sigma_{\text{ion}}\) (S cm\(^{-1}\)) | \(\sigma_{\text{elec}}^{p,1}\) (S cm\(^{-1}\) atm\(^{-1}\)) | \(\sigma_{\text{elec}}^{\text{O}_2,0,1}\) (S cm\(^{-1}\) atm\(^{-1}\)) | Ref. |
|-------------|-----------------|-----------------------------|--------------------------|-----|
| BZY         | 4.00 x 10\(^{-3}\) | 6.00 x 10\(^{-3}\)          | 1.18 x 10\(^{-10}\)     | 19  |
| LWO         | 1.22 x 10\(^{-3}\) | 1.66 x 10\(^{-5}\)          |                          | 14  |

Open-circuit condition is reproduced by \(r = -1\) because \(I_{\text{ion}} = -I_{\text{leak}}\) should be held. We defined energy efficiency (\(\epsilon\))

\[
\epsilon = V_T I_{\text{elec}}/V_{\text{th}} I_{\text{ion}}
\]

where \(I_{\text{elec}}\) and \(V_{\text{th}}\) are external current density and theoretical Nernst potential, respectively. We assumed the following operation conditions; operation temperature of 600°C, 3% H2O + 97% H2 for anode gas, and 3% H2O + 19.4% O2 + 77.6% Ar for cathode gas. An L_WO dependence of the OCV in the BZY|LWO bilayer model was calculated from Eq. (1) with \(r = -1\). Dependences of \(\epsilon\) and the power density on the L_WO/L_total ratio are calculated for the bilayer model at a fixed I_{elec} of 250 mA cm\(^{-2}\) and at a fixed \(V_T\) of 1.05 V, respectively. The detailed calculation procedure are presented in Ref. 10). Though \(V_T = 1.05\) V is higher than practical operation voltage, we selected this value since our calculation takes only ohmic polarization by electrolyte resistance into consideration while activation polarization and concentration polarization cause further voltage drop of the practical cells.

2.2 Experimental procedures

BZY powder was prepared by solid-state reaction. BaCO₃ (99.9%), ZrO₂ (99.9%), Y₂O₃ (99.9%) powders were ball milled in ethanol and the mixed powders were calcined at 1300°C for 4 h. The calcined powders were then ball-milled again and uniaxially pressed into disks. The BZY disks were sintered at 1600°C for 10 h. The sintered BZY disks were crushed into powders using an aluminum pestle and mortar. The resulted powders were ball-milled again in ethanol and pressed by uniaxial pressing at 70 MPa followed by cold-isostatic pressing (CIP) at
150 MPa. The obtained disk was sintered at 1600 °C for 10 h to form a BZY target for the pulsed laser deposition (PLD) method. LWO powders and Lanthanum-doped ceria (La2.6Ce1.4O8−δ, LDC) powders were also synthesized by the citrate complexation method as reported in our previous reports.16,17]

The NiO–BZY anode substrate was prepared by the following procedure. The BZY powders sintered at 1600 °C were mixed with NiO powders by ball milling in ethanol. The obtained NiO–BZY powders were prepared into disks with a diameter of 10 mm by uniaxial pressing followed by CIP at 150 MPa for 15 min. The NiO–BZY disks were sintered at 1450 °C for 5 h. The sintered NiO–BZY disks were mirror-polished to obtain a smooth surface. For the fabrication of the BZY monolayer cell, the BZY electrolyte membrane was deposited on the NiO–BZY substrate by the PLD method under the following deposition conditions; a substrate temperature 650 °C, the PLD method under the following deposition condition; a substrate temperature 650 °C, pO2 = 2.7 Pa, laser fluence of 2 J cm−2, and repetition frequency of 10 Hz. The NiO–BZY|BZY sample was annealed at 1200 °C for 3 h in air to improve adhesiveness between the NiO–BZY substrate and the BZY electrolyte. The thickness of the BZY membrane of the monolayer cell was 3.5 μm. To fabricate the BZY|LWO bilayer cell, the LWO and the LDC interlayers were deposited by the PLD on the annealed NiO–BZY|BZY membrane by the following procedure. Firstly, a 3 μm thick BZY membrane was deposited and annealed under the same condition as the BZY membrane for the monolayer cell was made. Then, a thin LDC interlayer with a thickness of 40 nm was prepared on the BZY membrane followed by the deposition of the LWO layer with a thickness of 1 μm. Finally, the LDC interlayer with a thickness of 40 nm was deposited again on the LWO layer. Both the LWO layer and the LDC interlayers were deposited by the following deposition condition; the substrate temperature 600 °C, pO2 = 1 Pa, laser fluence of 3 J cm−2, and repetition frequency of 10 Hz. Commercial LSCF powders (AGC Seimichemical) were used for the cathode. The LSCF powders were pasted on the electrolyte layer and sintered at 930 °C for 1 h in air to obtain test specimens for the power generation test. The resulted structures of the monolayer cell and the bilayer cell were NiO–BZY|BZY|LSCF and NiO–BZY|BZY|LDC|LWO|LDC, respectively, as shown in Fig. 1. Crystal structures of the deposited films were investigated by X-ray diffraction (XRD) measurement (SmartLab, RIGAKU).

The cell performance was evaluated using the commercialized equipment (FC-400H, CHINO). A PYREX glass ring was used for gas sealing. The anode support was reduced under 3 % humidified H2 gas at 600 °C in the test chamber before the power generation tests while 3 % humidified 20 % O2 + Ar gas was supplied to the cathode. Firstly, 3 % humidified 20 % H2 + Ar gas was fed to the anode and the hydrogen concentration was gradually increased to 3 % humidified pure H2 in an hour. Then, the reduction of the anode substrate with 3 % humidified pure H2 gas was continued for more than 300 min. The current density–voltage (I–V) measurement was performed at 500

![Image](320x684 to 530x759)

**Fig. 1.** Schematics of the structures of the anode-supported (a) BZY monolayer cell and (b) BZY|LWO bilayer cell.

![Image](318x342 to 330x344)

**Fig. 2.** Calculated dependence of the OCV of the BZY|LWO bilayer model on L_{LWO}/L_{total} ratio.

and 600 °C using potentiostat/galvanostat system (Autolab PGSTAT30, Metrohm AutoLab Inc.). The impedance data were obtained in the frequency range of 107–10 Hz with an amplitude of 20 mV. The data were analyzed using Z-view software (v3.5h, Scribner Associate Inc.).

### 3. Results and discussion

#### 3.1 Theoretical estimation of cell performance

The calculated dependence of the OCV on $L_{LWO}/L_{total}$ for the bilayer model was shown in Fig. 2. The OCV of the BZY monolayer model ($L_{LWO}/L_{total} = 0$) and the LWO monolayer model ($L_{LWO}/L_{total} = 1$) were 1.082 and 1.102 V, respectively. By the introduction of the LWO layer, a sharp increase in the OCV was observed with increasing $L_{LWO}/L_{total}$ and the OCV mostly saturated at $L_{LWO}/L_{total} = 0.125$, which indicated that even small LWO thickness was effective in the improvement of the OCV. The OCV of the bilayer model with $L_{LWO}/L_{total} = 0.125$ reached 1.132 V which was mostly comparable to the Nernst voltage of 1.135 V. The increase in the OCV was attributable to a reduction of the leakage current density. The calculated $|I_{leak}|$ values for the BZY monolayer model and the bilayer model with $L_{LWO}/L_{total} = 0.125$ were 208 and 7 mA cm−2, respectively. Since the calculated $pO_2$,interface value for the model with $L_{LWO}/L_{total} = 0.125$ was 2.6 × 10−8 atm, which was much lower than the cathode atmosphere, the drastic reduction of the leakage current density was provided by the suppression of the oxidation of the BZY layer by the introduction of the thin LWO layer.

Calculated $L_{LWO}/L_{total}$ dependences of energy efficiency $\varepsilon$ and the power density for the bilayer model are shown
in Fig. 3. The energy efficiency and the power density showed a steep increase with increasing \( L_{\text{LWO}}/L_{\text{total}} \). They showed maximum values at certain \( L_{\text{LWO}}/L_{\text{total}} \) values, and then gradually decreased as \( L_{\text{LWO}}/L_{\text{total}} \) approached 1. This calculation result indicates that the cells exhibiting both the high \( \eta \) and the high-power density can be designed by employing the LWO hole-blocking layer with an optimal thickness. At \( L_{\text{LWO}}/L_{\text{total}} = 0.05 \), the \( \eta \) value and the power density reached 89% and 300 mW cm\(^{-2} \) which were 1.5 times and 1.6 times as high as those of the BZY monolayer model at the given calculation condition. The improvements were provided by the suppression of the leakage current through the electrolyte membrane. Moreover, as the performance of the bilayer cell can be tuned by changing \( L_{\text{LWO}}/L_{\text{total}} \) as presented in Figs. 2 and 3, the bilayer structure increases a degree of freedom for cell design to satisfy various performance requirements.

3.2 Structural characterization of cell

XRD patterns of the LWO target and the BZY|LWO bilayer cell before depositing the LSCF cathode are shown in Figs. 4(a) and 4(b), respectively. In Fig. 4(b), the major diffraction peaks were derived from the BZY layer. The strong peak intensity of 200 diffraction from the BZY membrane was probably because of (100) preferential orientation of the BZY layer. In Fig. 4(c), the scale of the vertical axis of Fig. 4(b) is converted to a logarithmic scale. We confirmed that the LWO layer was successfully formed by comparing the diffraction pattern of the BZY|LWO bilayer cell [Fig. 4(c)] and that of the LWO target [Fig. 4(a)]. The relatively weak peak intensity of the LWO layer can be attributable to the small thickness of the LWO layer compared with the BZY membrane.

Figure 5 shows cross-sectional SEM images using backscattered electron imaging of the BZY monolayer cell [Fig. 5(a)] and the bilayer cell [Fig. 5(b)] after the performance tests, respectively. Dense electrolyte layers were observed for both the cells. Boundary of the LWO hole blocking layer and the BZY layer was not apparently observed in the SEM image, which indicated fine interfacial adhesion between the two layers.

3.3 Electrochemical performance of cell

Figure 6 shows time dependence of the OCV during the reduction treatment of the anode substrates. For the BZY monolayer cell [Fig. 6(a)], the OCV value basically continued to increase during the reduction treatment and eventually reached 0.93 V. For the BZY|LWO bilayer cell, [Fig. 6(b)], the OCV value of 1.05 V was observed after 60 min of the start of the reduction treatment. The high OCV of 1.05–1.06 V was retained for about 170 min. Though a small decrease in the OCV was observed in about 240 min, the BZY|LWO bilayer cell exhibited stable OCV of 1.01 V even after 400 min treatment. We note that, to the best of our knowledge, the high OCV exceeding 1.05 V at 600 °C has not been reported for the anode-supported PCFCs using the BZY electrolyte membrane. The improvement of the OCV in the bilayer cell compared with the BZY monolayer cell demonstrated the theoretical calculation results suggesting that the suppression of the leakage current by the introduction of the LWO hole-blocking layer provides higher OCV than the monolayer cell.

We also investigated the performance of a bilayer cell without LDC interlayers. Instead of the LDC interlayers, a thin BZY layer with a thickness of 100 nm was inserted between the LWO layer and the LSCF cathode to prevent direct contact of them. The resulted structure of the bilayer
cell without LDC interlayers was Ni–BZY|LWO|BZY|LSCF. In contrast to the stable OCV of the bilayer cell with the LDC interlayers, the OCV of the bilayer cell without LDC interlayers was quite unstable as shown in Fig. 6(c). Though the OCV of 0.91 V was instantaneously observed, the OCV continued to decrease during the reduction treatment and eventually dropped to 0.1 V. The contrasting OCV behavior during the reduction treatment for the bilayer cell with the LDC interlayers and that without the LDC interlayers indicated that the LDC interlayers played an important role for the stable operation of the bilayer cell. We consider that the introduction of the LDC interlayer suppressed undesirable chemical reaction between the BZY layer and the LWO hole-blocking layer during the reduction treatment. The bilayer cell with the LDC interlayers is expressed as “the bilayer cell” otherwise stated in the following text.

Figure 7 shows the $I$–$V$ and the power density–voltage ($P$–$V$) properties of the BZY monolayer cell and the BZY|LWO bilayer cell. The maximum power density of the monolayer cell and the bilayer cell at 600 °C were 54 and 41 mW cm$^{-2}$, respectively. While the OCV was improved by the introduction of the LWO hole-blocking layer as presented in Fig. 6, the current density of the bilayer cell was smaller than that of the monolayer cell. The lower power density of the bilayer cell is probably due to the lower conductivity of LWO and LDC compared to BZY.

To analyze overpotentials during the cell operation, AC impedance measurements were performed under the OCV condition and the polarized condition at 600 °C. During the EIS measurement under polarized condition, the terminal voltage was controlled to be lower than OCV by 200 mV with the potentiostat. Nyquist plots under the OCV condition and the polarized condition were shown in Figs. 8(a)–8(d). Basically, two distorted semicircles were found in all the impedance data. Fitting analyses for the impedance data were carried out assuming an equivalent circuit model, $LR_{\text{sho}}(R_{\text{HF}}Q_{\text{HF}})(R_{\text{LF}}Q_{\text{LF}})$, where $L$ is the inductor, $R_{\text{sho}}$ is the ohmic resistance, $R_{\text{HF}}$ and $R_{\text{LF}}$ are resistances in the high-frequency and the low-frequency regions, and $Q_{\text{HF}}$ and $Q_{\text{LF}}$ are corresponding capacitive elements replaced by constant phase elements (CPE) [Fig. 8(e)]. $(RQ)$ represents a parallel combination of a resistor $R$ and a CPE with a pseudocapacitance $Q$. The impedance of CPE is expressed by $Z = 1/(jω)^nQ$, where $n$ is a CPE parameter in the range of 0 to 1. The parameters
obtained from the fitting analyses are presented in Table 2. The calculated $R_{\text{ohm}}$, $R_{\text{HF}}$, and $R_{\text{LF}}$ are summarized in Fig. 8. The value of $R_{\text{ohm}}$ was around 2.2 $\Omega \cdot \text{cm}^2$ for the monolayer cell while that for the bilayer cell was around 3.8 $\Omega \cdot \text{cm}^2$ under both the OCV condition and the polarized condition. The increase in $R_{\text{ohm}}$ may be caused by the lower conductivity of LWO than BZY. Since theoretical calculation suggested that even quite thin LWO layer with $L_{\text{LWO}}/L_{\text{total}}$ smaller than 0.1 can effectively improve the OCV and the energy efficiency, the bilayer cell with smaller LWO thickness than that of the present bilayer cell will be favorable for more efficient operation. Therefore, reducing the thickness of the LWO layer of the present bilayer cell with $L_{\text{LWO}}/L_{\text{total}} = 0.25$ will enable further improvement of the performance owing to a reduction of $R_{\text{ohm}}$. We consider that $R_{\text{HF}}$ and $R_{\text{LF}}$ are associated with reactions at the cathode and the anode, respectively, according to a dependence of the impedance data on a partial hydrogen pressure in the fuel gas. The $R_{\text{LF}}$ values for both the monolayer cell and the bilayer cell increased under the polarized condition, which suggested that poor fuel gas diffusion in the anode support even after the reduction treatment. Actually, we confirmed that the performance can be improved by increasing the porosity of the anode substrate in the monolayer cell. The detailed analysis of the polarization resistance will be discussed elsewhere. Besides, the larger $R_{\text{LF}}$ and smaller $n_{\text{LF}}$ values in the bilayer cell than those of the monolayer cell reflecting severely distorted semicircle in the low-frequency region may imply the existence of additional semicircles associated with the complex stacking structure of the bilayer cell.

4. Conclusions

The Influence of the LWO hole-blocking layer on the performance of the anode-supported PCFC using the BZY electrolyte membrane was evaluated by theoretical calculations based on the transport properties of the electrolyte.

Table 2. Fitted parameters for AC impedance data of the monolayer cell and the bilayer cell under the OCV condition and the polarized condition

| Condition         | $L_{\text{LWO}}$ (H cm$^{-2}$) | $R_{\text{ohm}}$ (H cm$^{-2}$) | $R_{\text{HF}}$ (H cm$^{-2}$) | $Q_{\text{HF}}$ (F cm$^{-2}$ | $n_{\text{HF}}$ | $R_{\text{LF}}$ (H cm$^{-2}$) | $Q_{\text{LF}}$ (F cm$^{-2}$ | $n_{\text{LF}}$ |
|-------------------|-------------------------------|-------------------------------|-------------------------------|------------------------------|----------------|-------------------------------|-------------------------------|----------------|
| Monolayer (OCV)   | $3.4 \times 10^{-7}$          | 2.20                          | 0.39                          | $2.8 \times 10^{-3}$        | 0.92           | 3.3 $\times 10^{-2}$         | 0.42                          |                |
| Monolayer (Polarized) | $3.4 \times 10^{-7}$          | 2.24                          | 0.64                          | $2.6 \times 10^{-3}$        | 0.89           | 4.5 $\times 10^{-2}$         | 0.35                          |                |
| Bilayer (OCV)     | $3.0 \times 10^{-7}$          | 3.79                          | 0.41                          | $2.8 \times 10^{-3}$        | 0.94           | 3.41 $\times 10^{-2}$        | 0.31                          |                |
| Bilayer (Polarized)| $3.1 \times 10^{-7}$          | 3.79                          | 0.42                          | $2.7 \times 10^{-3}$        | 0.96           | 4.07 $\times 10^{-2}$        | 0.31                          |                |
materials and experimental investigations. The theoretical calculations indicated that the BZY/LWO bilayer model, where the LWO layer is placed at the cathode side of the BZY layer, can exhibit higher OCV value and higher energy efficiency than those of the BZY monolayer model and the LWO monolayer model. In the bilayer model with the thin LWO hole-blocking layer with $L_{LWO}/L_{total} = 0.05$, the energy efficiency at a fixed external current density of 250 mA cm$^{-2}$ reaches 89% which is 1.5 times as high as that of the BZY monolayer model as a result of the suppressed leakage current through the electrolyte membrane.

We fabricated the BZY monolayer cell (Ni–BZY|BZY| LDC) and the BZY/LWO bilayer cell (Ni–BZY|BZY| LDC|LWO|LDC|LSCF) to experimentally evaluate the effectiveness of the LWO-hole blocking layer suggested by the theoretical calculations. We presented that the bilayer cell exhibited OCV of 1.01 V which was higher than the BZY monolayer cell exhibiting OCV of 0.93 V, thus, the calculation results were supported by the experimental performance tests. Besides, we found that the bilayer cell with the LDC interlayer exhibited stable performance whereas the bilayer cell without the LDC interlayer showed a gradual decrease of the OCV as the reduction of the anode substrate proceeds. The LDC layer enables integration of the BZY membrane and the LWO hole-blocking layer leading to the stable operation of the bilayer cell. Though the maximum power density of the bilayer cell was lower than that of the monolayer cell owing to the relatively thick LWO layer with $L_{LWO}/L_{total} = 0.25$ in our present cell, further improvement will be attained by reducing $L_{LWO}/L_{total}$ down to the optimal value as suggested by the calculations. Our theoretical calculations and experimental investigations present that the integration of the LWO hole-blocking layer with the BZY membrane will be a reliable approach to realize highly efficient anode-supported PCFCs.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP17H00801 of Japan Society for the Promotion of Science (JSPS), JST COI Grant Number JPMJCE1318 of Japan Science and Technology Agency (JST). XRD and SEM measurements were performed using the facilities of the Institute of Solid State Physics, the University of Tokyo.

References

1) S. Hossain, A. M. Abdalla, S. N. B. Jamain, J. H. Zaini and A. K. Azad, *Renew. Sust. Energ. Rev.*, 79, 750–764 (2017).
2) C. Duan, J. Tong, M. Sheng, S. Nikodemi, M. Sanders, S. Ricote, A. Alamansoori and R. O’Hayre, *Science*, 349, 1321–1326 (2015).
3) H. An, H.-W. Lee, B.-K. Kim, J.-W. Son, K. J. Yoon, Y. Kim, D. Shin, H.-L. Ji and J.-H. Lee, *Nat. Energy*, 3, 870–875 (2018).
4) Y. Matsuzaki, Y. Tachikawa, T. Somekawa, T. Hatae, H. Matsumoto, S. Taniguchi and K. Sasaki, *Sci. Rep.*, 5, 12640 (2015).
5) E. Fabbri, D. Pergolesi and E. Traversa, *Chem. Soc. Rev.*, 39, 4355–4369 (2010).
6) P. Sawant, S. Varma, B. N. Wani and S. R. Bharadwaj, *Int. J. Hydrogen Energ.*, 37, 3848–3856 (2012).
7) M. Scholten, J. Schoonman, J. Vanmilitenburg and H. Oonk, *Solid State Ionics*, 61, 83–91 (1993).
8) K. Kato, D. Han and T. Uda, *J. Am. Ceram. Soc.*, 102, 1201–1210 (2019).
9) D. Han, Y. Noda, T. Onishi, N. Hatada, M. Majima and T. Uda, *Int. J. Hydrogen Energ.*, 41, 14897–14908 (2016).
10) T. Somekawa, Y. Matsuzaki, Y. Tachikawa, H. Matsumoto, S. Taniguchi and K. Sasaki, *Int. J. Hydrogen Energ.*, 41, 17539–17547 (2016).
11) Y. Matsuzaki, Y. Tachikawa, Y. Baba, K. Sato, G. Kojo, H. Matsuo, J. Otomo, H. Matsumoto, S. Taniguchi and K. Sasaki, *J. Electrochem. Soc.*, 167, 084515 (2020).
12) X. Wang, T. Zhang, J. Kang, L. Zhao, L. Guo, P. Feng, F. Zhou and Y. Ling, *Electrochim. Acta*, 248, 356–367 (2017).
13) S. Erdal, L. Kalland, R. Hancke, J. Polfus, R. Haugsrud, T. Norby and A. Magrasso, *Int. J. Hydrogen Energ.*, 37, 8051–8055 (2012).
14) G. Kojo, R. Tsukimura and J. Otomo, *Solid State Ionics*, 306, 89–96 (2017).
15) G. Kojo, Y. Shono, H. Ushiyama, Y. Oshima and J. Otomo, *J. Solid State Chem.*, 248, 1–8 (2017).
16) G. Kojo, X. Wei, Y. Matsuzaki, H. Matsuo, K. Hellgardt and J. Otomo, *Solid State Ionics*, 337, 132–139 (2019).
17) H. Matsuo, G. Kojo, K. Sakata, Y. Matsuzaki and J. Otomo, *ECS Trans.*, 91, 1019–1028 (2019).
18) N. S. Choudhury and J. W. Patterson, *J. Electrochem. Soc.*, 118, 1398–1403 (1971).
19) K. Nomura and H. Kageyama, *Solid State Ionics*, 178, 661–665 (2007).