High-Efficiency Direct Ammonia Fuel Cells Based on $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}/\text{Pd}$ Oxide-Metal Junctions

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A direct ammonia-type intermediate temperature fuel cell is examined by means of a hydrogen membrane fuel cell (HMFC) comprising 1-μm-thick $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) thin-film electrolyte and Pd solid anode. It generates the maximum power density of 0.58 W cm$^{-2}$ at 600 °C with ammonia fuels, and this value is found to be three times larger than the champion data of the recently reported direct ammonia-type proton-conducting ceramic fuel cells (PCFCs). AC impedance spectroscopy is performed to determine the interfacial polarization resistances, disclosing that the anodic overpotentials of HMFCs are at least one order of magnitude smaller than those of anode-supported PCFC under relatively high DC outputs. The anode reactions are driven by the oxidation of monomolecular hydrogen dissolving at the BZCY/Pd solid–solid interface, mediated via proton transfer from Pd to BZCY. The electrochemical analysis reveals that the BZCY/Pd junction forms Ohmic contact without growth of wide depletion layer and thus facilitates the proton transfer reactions because the interfacial region beneath Pd electrode can accommodate amounts of protonic defects as well as the bulk of BZCY due to the small depletion of holes under hole–proton thermodynamic equilibrium.

1. Introduction

There is widespread consensus that the fossil fuel reserves will be exhausted to a large extent within next few decades due to accelerated growth of worldwide energy consumption. In the face of the energy crisis, hydrogen is attractive alternative fuel since it can be renewable by the water splitting driven with the solar energy. With the advent of hydrogen economy, however, cannot be realized until technical issues related to hydrogen production, transportation, and storage infrastructure are clear. Ammonia is a highly efficient hydrogen carrier since it can be easily liquefied to store and transport at room temperature, is widely available, is carbon-free, and has hydrogen capacity larger than the liquid hydrogen. Hence, it is strongly motivated to utilize ammonia in fuel cells for the direct conversion of ammonia chemical energy to electricity in a high efficiency. The proton conducting ceramic fuel cells (PCFCs) using proton-conducting oxide electrolytes, such as $\text{BaZr}_{x}\text{Ce}_{0.8-x}\text{Y}_{0.2}\text{O}_{3-\delta}$, is promising as a direct ammonia type fuel cell operating at the intermediate temperature (IT) range (400–600 °C) for stationary applications. Because water formation in PCFCs is mainly progressive at the cathode side, unlike solid oxide fuel cells (SOFCs), and therefore, mixing of the ammonia fuels into the exhaust water is precluded, thereby eliminating repurification of water exhaust and simplifying total systems. Moreover, formation of environmentally hazardous substances NOx at the anode is discouraged if the proton conductivity is much higher than the minor oxide ion conductivity.

Although the resistivity and related activation energy of proton conductors are smaller than oxide ion conductors used in SOFCs, the performances of the current PCFCs, however, are far behind the SOFCs even with pure H2 fuels because of large interfacial polarization due to a lack of suitable cathode and the deteriorated microstructural electrolyte. Meanwhile, exceptionally high power output has been reported in the IT range for hydrogen membrane fuel cell (HMFC), which comprises a thin proton conducting ceramic electrolyte supported on a dense hydrogen permeable metal anode with the anode reactions driven by separation of the monatomic hydrogen dissolves into protons and electrons at electrolyte/nonporous-anode solid–solid interfaces (Figure 1a). Regardless of its simple cell structure, the HMFC based on $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3}$ (BCY) thin film and Pd foil has achieved the maximum power density of 1.4 W cm$^{-2}$ at 600 °C, which is still higher than the average performances of recently reported highly efficiency PCFCs at the temperatures. Here, we report on the highly...
efficiency power generation of direct ammonia type HMFC with BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY) electrolyte due to enhanced proton incorporation into BZCY at the BZCY/Pd oxide-metal junctions. The cell gained an open-circuit voltage of about 1.0 V and maximum power density of 0.58 W cm$^{-2}$ at 600 $^\circ$C, which were much higher than the champion data of the recently reported direct ammonia type PCFCs.

2. Results

2.1. Fuel Cell Performances

BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ films were successfully fabricated by RF cosputtering with BaCe$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ and ZrO$_2$ double targets in the deposition conditions listed in Table 1. X-ray diffraction patterns of deposited films were identical to BaCeO$_3$-$\delta$ phase (JCPDS 22-0074) (Figure S1, Supporting Information), and the chemical composition determined by the wavelength dispersive X-ray (WDX) analysis equaled Ba/Zr/Ce/Y = 1.0/0.16/0.69/0.19, which was in agreement with the objective one. The densely packed BZCY electrolytes thin films were uniformly formed over a wide area of the Pd foil anode without any microclacks and pinholes. The films have “bamboo” like microstructures, in which pillar grains of 10’s nm width are grown up perpendicular to the substrate and they are tightly adhered to each other. Such a columnar microstructure is frequently developed in the sputter-deposited oxide films.

HMFC comprising a 1 $\mu$m thick BZCY thin film offers excellent cell performances at 600 $^\circ$C, generating the peak power density ($P_{\text{max}}$) of 0.81 W cm$^{-2}$ and open-circuit voltage (OCV) of 1.1 V with a pure H$_2$ fuel (Figure 2a). This value is similar to the values of highly efficiency PCFCs comprising from 10's $\mu$m thick electrolytes and porous cermet anode supports. The HMFC retains OCV over 0.9 V if the hydrogen partial pressure ($p_{H_2}$) in the anode is decreased to 0.3 $p_0$ ($p_0$ = 101 kPa; Figure 2a). Moreover, the HMFC also enables highly efficient power generation by a direct use of NH$_3$ fuels, providing OCV of 0.95 V and $P_{\text{max}}$ of 0.58 W cm$^{-2}$ at 600 $^\circ$C (Figure 2b). The power output is very stable and the current remains at about 0.6 A cm$^{-2}$ at 0.75 V for a few hours (Figure 3c) without deterioration of the current–voltage ($I$–$V$) and current–power ($I$–$P$) characteristics (Figure 2b). It is warrant to note that the power output of NH$_3$ type HMFC is identical to that of H$_2$ type HMFC using H$_2$ gases at $p_{H_2}$ = 0.6 $p_0$ in the anode.

Figure 3 shows the $I$–$V$ and $I$–$P$ relationships of BZCY-HMFC operating with H$_2$ and NH$_3$ fuels at various temperatures. The power outputs abruptly drop by decreasing the operation temperatures, with $P_{\text{max}}$ gaining 0.81, 0.49, 0.24, and 0.085 W cm$^{-2}$ at 600, 550, 500, and 450 $^\circ$C, respectively for hydrogen fuel cells and $P_{\text{max}}$ equaling 0.58, 0.34, 0.21, and 0.071 W cm$^{-2}$ at 600, 550, 500, and 450 $^\circ$C, respectively for ammonia fuel cells. The OCV of ammonia fuel cells would be increased with elevating temperatures if the following oxidation reaction of NH$_3$ electrochemically takes place:

$$4\text{NH}_3(g) + 3\text{O}_2(g) \rightarrow 6\text{H}_2\text{O}(g) + 2\text{N}_2(g)$$

(1)

However, the actual OCV is shifted to opposite direction by elevated temperatures, increasing with reducing the operation temperature like hydrogen fuel cells, with the values at 600, 550, 500, and 450 $^\circ$C equaling 0.95, 1.0, 1.03, and 0.98 V, respectively. These results propose that the decomposition of

Table 1. Optimal conditions for RF co-sputtering deposition of BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ thin films.

| Conditions                       | Value                  |
|----------------------------------|------------------------|
| Sputtering atmosphere            | Ar [50 cm$^3$ min$^{-1}$] |
| Substrate temperature            | 500 $^\circ$C          |
| Target-substrate distance        | 70 mm                  |
| RF power                         | BaCe$_{0.8}$Y$_{0.2}$:70 W, ZrO$_2$:30 W |
| Chamber pressure                 | 2.0 Pa                 |
| Postannealing temperature        | 700 $^\circ$C          |
| Postannealing atmosphere         | O$_2$ [$p_{O_2}$ = 0.7 Pa] |
| Postannealing time               | 1 h                    |

Figure 1. a) Scheme of a hydrogen membrane fuel cell (HMFC). b) Cross-section TEM image of BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ thin films (500 nm) sputter-deposited on a Pd anode substrate.
ammonia in the cell probably follows a two-step process: initial decomposition of ammonia to hydrogen and nitrogen, and subsequent dissolution of hydrogen into Pd anode as follows

\[ \text{NH}_3 \rightleftharpoons \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \]  

H₂ → 2H⁺

Here, H⁺ denotes hydrogen dissolves in Pd.

In order to evaluate the effective hydrogen partial pressure in the anode of NH₃-fed HMFC at 600 °C, the ammonia decomposition rate was determined by acid–base titration for the 1 m H₂SO₄ solution equilibrated with the exhaust gases from the anode of NH₃-fed HMFC, indicating that about 65% of NH₃ feeds were decomposed by reaction (2) with yielding a mixed gas of H₂/N₂/NH₃ = 60/20/20. This value is consistent with the thermodynamic equilibrium data, since ammonia decomposition is favored at temperatures above ≈200 °C. Based on this analysis, the results of Figure 2b reveal that efficiency of NH₃ type HMFC is corresponding to that of the H₂ type using equivalent-pH₂ hydrogen fuel gases.

2.2. Polarization Behavior

To provide further verification for the efficient power generation of direct ammonia type HMFC, the interfacial polarization
resistances were evaluated by electrochemical impedance spectroscopy. In our previous report, spectra of the BCY-based HMFC with H₂ fuels had been deconvoluted by a systematic survey of the electrochemical impedance responses. The HMFC exposes three distinct arcs in Nyquist plots: relatively large S₀ arc in a high frequency region at around 10⁴–10² Hz due to the cathode interfacial charge transfer, very small S_m arc in a middle frequency region at around 10²–10¹ Hz due to the charge transfer at Pd/electrolyte interfaces and small S₁ arc in a low frequency region at around 10¹–10⁻¹ Hz related to the hydrogen diffusion-limited terms for the anodic charge transfer reactions (see the inset of Figure 4a).

These spectral features have been replicated well by using an equivalent circuit depicted in Figure 4f, where the Ohmic resistance, \( R_b \), cathodic interfacial charge transfer, (\( R_c Q_c \)), and anodic charge transfer correlated with the mass transfer in Pd bulk, (\( Q_a (R_a Z_{mt}) \)), are connected in series. \( R \) is a resistance and \( Q \) is a constant phase element representing a time-dependent capacitance with the parallel-connected \( R_i \) and \( Q_i \) being related to the capacitance \( C_i \) by

\[
C_i = (R_i \cdot Q_i)^{1/m} \cdot R_i^{-1}
\]

(4)

\( Z_{mt} \) denotes the hydrogen mass transfer impedances, which is associated with the perturbation of hydrogen permeation flux across Pd membrane and is represented with an admittance \( Y_{mt} \) and a time decay constant \( B_{mt} \) by

![Figure 4](https://www.global-challenges.com)

**Figure 4.** Impedance responses of H₂ type HMFC (H₂, Pd | BCY | LSCF, wet air) operating at 200 mA cm⁻² DC current by changing a) oxygen partial pressure (\( p_{O_2} \)) in cathode gas and b) hydrogen partial pressure (\( p_{H_2} \)) in anode gas. In (a), the inset shows a reference spectra of BCY-based HMFC operating in 200 mA cm⁻² DC current at \( p_{O_2} = 0.2 p_0 \) in the cathode and \( p_{H_2} = 1.0 p_0 \) in the anode. Responses of HMFC under various DC conditions with c) pure H₂ fuel, d) NH₃ fuels, and e) diluted H₂ fuel (\( p_{H_2} = 0.6 p_0 \)). In (d,e), circles show the observed spectra and solid lines show the fitting curves calculated with an equivalent circuit model depicted in Fig. 4f. In (a–e), the decades of the frequencies at each highlighted point are shown.
\[ Z_{\text{mt}} = \left( Y_{\text{mt}} \sqrt{j\omega} \right)^{-1} \tanh \left\{ B_{\text{mt}} \sqrt{j\omega} \right\} \] \tag{5}

\[ B_{\text{mt}} = \frac{L}{D_{\text{H}}^{0.5}} \] \tag{6}

where \( L \) is the thickness of membranes, \( D_{\text{H}} \) diffusion coefficient, \( j \) a square root of \(-1\), and \( \omega \) angular frequency. Equations (5) and (6) are called Nernst circuit element, which provides the mass transfer resistance, \( R_{\text{mt}} \), and capacitance, \( C_{\text{mt}} \), by following \cite{24}:

\[ R_{\text{mt}} = B_{\text{mt}} Y_{\text{mt}}^{-1} \] \tag{7}

\[ C_{\text{mt}} = Y_{\text{mt}} B_{\text{mt}} \] \tag{8}

In H\(_2\)-fed HMFC \cite{21} cathodic \( S_h \) arcs could be represented very well by \((R_{\text{c}},Q_{\text{c}})\) elements, and the \( R_{\text{c}} \) thus determined were found to be proportional to \( p_{\text{O}_2}^{-1/4} \) in cathode gases, indicating that \( R_{\text{c}} \) could be assigned to the interfacial charge transfer reaction controlled by oxide ion transfer at gas-electrode–electrolyte triple phase boundary zones. \cite{35} The anode reaction of HMFC can be deconvoluted into three elemental steps: Step (i) hydrogen dissolution, step (ii) diffusion of hydrogen dissolves in Pd and step (iii) oxidation of hydrogen dissolves

Step (i): \( \text{H}_2 \rightarrow 2\text{H}^{\text{pd}} \) \tag{9}

Step (ii): \( \text{H}^{\text{pd}} \rightarrow \text{H}^{\text{int}} \) \tag{10}

Step (iii): \( \text{H}^{\text{int}} \rightarrow \text{H}^{\text{int}} + e^- \) \tag{11}

Here \( \text{H}^{\text{int}} \) are hydrogen dissolves in Pd/BCY interface, and \( \text{H}^{\text{int}} \) is proton in the interface. Based on the theoretical circuit model for the electrochemical hydrogen insertion into Pd membrane electrodes, \cite{24} anodic \( S_m \) arcs could be assigned to the charge transfer step at Pd/BCY interfaces (Step (iii)) and \( S_i \) arc to the hydrogen diffusion in Pd bulk (Step (ii)), and thus the anodic polarization is replicated by \((Q_{\text{c}}(R_{\text{c}},Z_{\text{int}}))\) with parallel-connected \( Q_{\text{c}} \) and \( R_{\text{c}} \) representing \( S_m \) arc and \( Z_{\text{int}} \) expressing \( S_i \) arc. \cite{21,22} \( R_{\text{c}} \) and \( R_{\text{int}} \) determined by fitting roughly correlated with \( p_{\text{H}_2}^{-1/2} \), which is in agreement with the reaction orders of steps (ii) and (iii) with respect to \( p_{\text{H}_2} \). \cite{21,22}

Figure 4a,b shows the impedance responses of BZCY-based HMFCs with adjusting oxygen partial pressure in the cathode \((p_{\text{O}_2}^c)\) or hydrogen partial pressure in the anode \((p_{\text{H}_2}^a)\), confirming that the spectral features are essentially same as ones of the BCY-based HMFC (Figure 4a). Hereafter, prime and double prime denote cathode \((\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3\text{O}_1\), LSCF side) and anode (Pd side), respectively. \( S_i \) arc is clearly assigned to the contribution of the cathodic interfacial charge transfers, because it increases with decreasing \( p_{\text{H}_2}^a \) (Figure 4a) and systematically decreases with DC currents, i.e., LSCF being polarized more cathodic (Figure 4c). BZCY-based HMFC clearly shows the anode contributions of \( S_i \) and \( S_m \) arcs, because \( S_i \) is drastically enlarged and \( S_m \) as a tail in high frequency side at around \( 10^2–10^3 \) Hz becomes more evident with reducing \( p_{\text{H}_2}^a \) in the anode although \( S_m \) is too small and so unclear by overlapping with \( S_i \) and \( S_h \) in \( p_{\text{H}_2}^a \geq 0.8 \) \( p_{\text{O}_2} \) (Figure 4b).

In \( p_{\text{H}_2}^a = 1.0 \) \( p_{\text{O}_2} \), anodic impedance arcs are not sensitive to DC current, indicating that anodic overpotentials are much smaller than voltage losses at cathodes or electrolytes albeit with high DC outputs (Figure 4c). However, both anodic arcs \((S_i \text{ and } S_m)\) of HMFC are much enhanced when \( p_{\text{H}_2}^a \) is changed from 1.0 \( p_{\text{O}_2} \). This mass transfer-related polarization arcs remarkably grow up with increasing DC currents at \( p_{\text{H}_2}^a = 0.6 \) \( p_{\text{O}_2} \) disclosing that larger DC output potentiates anodic concentration overpotential in the operation with a diluted H\(_2\) fuel. Impedance responses of NH\(_3\)-type HMFC are identical to those of H\(_2\)-type HMFC operating at the equivalent \( p_{\text{H}_2}^a (0.6 \) \( p_{\text{O}_2} \) under any DC conditions, with involving a large anodic \( S_i \) arc as much as cathodic \( S_h \) arc and significant growth of anodic \( S_i \) and \( S_m \) arcs with increasing DC current (Figure 4d), which implies that the anode polarization resistances of NH\(_3\)-type HMFC are almost same as those of the H\(_2\) type with equivalent \( p_{\text{H}_2}^a \).

All impedance responses could be nicely replicated with the equivalent circuit model depicted in Figure 4f regardless of the fuel types and DC current conditions (Figure 4c,d). The fitting parameters are listed in Tables S1–S3 (Supporting Information) and the related resistances are plotted as a function of DC current in Figure 5. At \( p_{\text{H}_2}^a = 1.0 \) \( p_{\text{O}_2} \), \( S_m \) arc is much smaller than \( S_h \) and \( S_i \) arcs (Figure 4c), and thus the corresponding spectrum is fitted without including \( R_{\text{c}} \) and \( Q_{\text{c}} \). \cite{21,22}

For H\(_2\)-type HMFC, \( R_{\text{mt}} \) is much smaller than \( R_{\text{c}} \) at any DC conditions in \( p_{\text{H}_2}^a = 1.0 \) \( p_{\text{O}_2} \), whereas the anodic resistances given by a sum of \( R_{\text{c}} \) and \( R_{\text{int}} \) are predominant to the cathodic \( R_{\text{c}} \) in \( p_{\text{H}_2}^a = 0.6 \) \( p_{\text{O}_2} \) (Figure 5). Moreover, all resistances of NH\(_3\)-type HMFC are in close agreement with those of the H\(_2\)-type with \( p_{\text{H}_2}^a = 0.6 \) \( p_{\text{O}_2} \) in the all DC range, proving that NH\(_3\)-type HMFC can undergo power generation by utilizing hydrogen products via ammonia pyrolysis without large overpotentials for the direct electrooxidation and/or surface poisoning of ammonia chemisorbed. Hence, current-enhanced anodic polarization resistances of NH\(_3\)-fed HMFC can be mainly attributed to the concentration overpotentials due to the delay of the hydrogen mass diffusion inside Pd bulk under relatively low \( p_{\text{H}_2}^a \).

### 2.3. Electronic Properties of BZCY/Pd Oxide-Metal Junctions

Since BZCY has been reported to show partial hole conductivity in relatively high \( p_{\text{O}_2} \) atmosphere, \cite{36,37} the BZCY/Pd junction essentially acts as a p-semiconductor/metal junction. It is well known that a potential energy barrier for electron, so called, Schottky barrier, is formed at metal–semiconductor junctions, \cite{38} where the bands of the p-semiconductors are bended upward by a contact with metals for alignment of Fermi energy levels, leading to the depletion layer of hole carriers in the semiconductor/metal interfaces (Figure 7b,c). \cite{38} Such devices tend to show the current rectification with allowing nominal current flow only by applying a positive bias on p-semiconductor (i.e., forward bias). In order to clarify the electronic properties of the BZCY/Pd junctions, \( I–V \) characteristics were tested for the cell: dry Ar, Pd | BZCY | LSCF, dry air (Figure 6a). In this case, the main charge carriers are electron holes because of the absence
of proton sources in the atmosphere. The devices exhibit symmetric, nonlinear \( I-V \) characteristics without occurrence of remarkable current rectification (Figure 6a), confirming that depletion layer at the BZCY/Pd interfaces is very narrow so that the junction allows a large tunneling current in both bias directions, thereby, establishing Ohmic contact.[38]

In order to evaluate the proton transfer number of HMFC under a presence of oxygen in the cathode side, OCV were measured for pseudo hydrogen concentration cells: H\(_2/\)Ar, Pd \( \mid \) BZCY \( \mid \) LSCF, wet 0.1%-O\(_2/\)Ar (Figure 6b). Here, H\(_2\) in the anode is adjusted in a range of 0.2 to 1.0 \( p_0 \) and the humidified, 0.1%-O\(_2\) gas (\( p'_0 = 0.001 p_0 \)) is supplied to the cathode side. In the general case, the thermodynamic OCV value of such cells can be defined as follows[39]

\[
OCV = t_O \frac{RT}{4F} \ln \left( \frac{p'_O}{p'_0} \right) + t_H \frac{RT}{2F} \ln \left( \frac{p''_H}{P''_H} \right)
\]  

(12)

Here, the prime' and double prime'' denote cathode (LSCF side) and anode (Pd side), respectively, \( t_O \) and \( t_H \) are the transfer number of oxide ion and protons, \( F \) a Faradaic constant, and \( R \) a gas constant. \( P''_H \) can be defined by coupled with water dissociation reaction as follows

\[
P''_H = K_w p'_H O_p O_{-0.5}
\]  

(13)

Effective hydrogen partial pressure at the BZCY/Pd interface (\( p''_H \)) must equal \( p''_H \) under OCV condition in order to keep zero hydrogen flux in Pd foils. In both humidified conditions (\( p''_H = 0.03, 0.09 p_0 \)), the observed OCVs are in agreement with

Figure 5. Ohmic and polarization resistances of NH\(_3\) and H\(_2\) type HMFCs under various DC conditions at 600 °C, determined by impedance equivalent circuit analysis. a) Electrolyte resistances, \( R_b \), b) cathode polarization resistances, \( R_c \), and c) anode interfacial charge transfer resistances, \( R_a \), and d) hydrogen mass transfer terms \( R_{mt} \). NH\(_3\) (○), diluted H\(_2\) (\( p_{H2} = 0.6 p_0 \)), and pure H\(_2\) (\( p_{H2} = 1.0 p_0 \)).

Figure 6. a) \( I-V \) characteristic of the cell with the following configuration: Ar, Pd \( \mid \) BZCY \( \mid \) LSCF, dry air. Here, the bias on Pd metal is controlled. b) OCV of the "pseudo" hydrogen concentration cells, measured at 600 °C with the configuration H\(_2/\)Ar (\( p''_H \)), Pd \( \mid \) BaZr\(_0.1\)Ce\(_0.7\)Y\(_0.2\)O\(_3-\delta\) \( \mid \) LSCF, H\(_2\)O/\( O_2/\)Ar (\( p'_O, p'_0 \)). Here, \( p''_H \) is varied in the range of 0.2 to 1.0 \( p_0 \), \( p'_O \) is adjusted at 0.03 or 0.09 \( p_0 \), and \( p'_0 \) is fixed at 0.001 \( p_0 \). Symbols (○) show the observed, and solid lines are calculated by Equation (14). The details of calculation is mentioned in main text.

Here, \( K_w \) is an equilibrium constant and \( p''_H \) water partial pressure. BZCY electrolyte is well known to exhibit mixed oxide ion and proton conduction under fuel cell conditions.[40] Nonetheless, the contribution of partial oxide ion conduction must be limited in HMFC because the Pd solid electrodes act as a blocking electrode of oxide ion, and thus \( t_O \) can be assumed to be nearly zero. Finally, OCV of the HMFC is given by the following

\[
OCV = t_H \frac{RT}{2F} \ln \left( \frac{K_w p'_H O_p O_{-0.5}}{p''_H} \right) = t_H \frac{RT}{2F} \ln \left( \frac{K_w p'_H O_p O_{-0.5}}{p''_H} \right)
\]  

(14)
the calculated by Equation (14) with \( l = 1.0 \) in \( p_{H_2}^\mu > 0.4 \ p_0 \), whereas they are deviated downward from the calculated in \( p_{H_2}^\mu < 0.2 \ p_0 \) (Figure 6b), revealing that HMFC would cause hole leakage when the \( p_{H_2}^\mu \) is sufficiently decreased with the cathode exposed to oxygen.

3. Discussion

3.1. Performance Comparison for Direct Ammonia Type Fuel Cells

The preceding results unequivocally demonstrate that HMFCs exhibit superior fuel cell performances to other fuel cell systems by direct NH\(_3\) feeds. For direct comparison, electrochemical performances of the direct ammonia type PCFCs and SOFCs reported in recent studies\(^{[41–47]}\) are summarized in Table 2. To best of our knowledge, the highest \( P_{\text{max}} \) at 600 °C (0.4 W cm\(^{-2}\)) is achieved by an anode-supported SOFC comprising 20 µm thick \( \text{Ce}_0.8\text{Sm}_0.2\text{O}_3 \) electrolyte and Ni-Ce\(_{0.9}\)Sm\(_{0.1}\)O\(_2\) cermet anode.\(^{[41]}\)

The performances of the NH\(_3\) type PCFCs are still low and the \( P_{\text{max}} \) is in most cases less than 0.2 W cm\(^{-2}\), as listed in Table 2. Apparently, the \( P_{\text{max}} \) of our HMFC is higher than the champion data, revealing that polarization resistances of NH\(_3\) type HMFCs is much lower than those of the PCFCs and SOFCs with porous cermet anodes.

The largest voltage losses in HMFC are assigned to the Ohmic losses mainly due to electrolyte resistances (\( R_\text{el} \); Figure 5a). 1 µm thick BZCY thin films possess \( R_\text{el} \) of about 0.27 Ω cm\(^{-2}\) at OCV conditions, and the corresponding proton conductivity \( \sigma \) becomes 2.7 \( \times \) 10\(^{-4}\) S cm\(^{-2}\), which is two orders of magnitude lower than the values of the sintered pellets (4.9 \( \times \) 10\(^{-3}\) S cm\(^{-2}\)).\(^{[36]}\) The deteriorated \( \sigma \) of the films must be owing to the precipitates in a grain boundary region, deviation of the stoichiometry, and high resistivity of grain boundaries, and so on.\(^{[48,49]}\) \( R_\text{el} \) of HMFC is remarkably decreased with DC currents, indicating that the proton conductivity of electrolyte is enhanced by an applied field. Several authors reported on the modification of ion carrier profiles by biasing in ion-conducting thin films sandwiched by ion-blocking electrodes.\(^{[50,51]}\) In such case, the cationic or anionic ion carriers tend to be accumulated in the region beneath oppositely charged electrodes and depleted in another side by the drifts under applied fields, and thus the overall ion conductivity of films is varied by the modified ion profiles. Because the anode of fuel cells is more positively biased if DC current is higher, i.e., cell voltage is lower, the mobile O\(^{2-}\) anions must be accumulated in the BZCY layer in vicinity of Pd blocking electrodes under DC conditions, altogether with protons for charge compensation, which may improve the proton conductivity by the increment of proton concentrations in the interfacial layers.

Previously, we have demonstrated that BCY-based HMFC has significantly lowered cathode polarization resistances \( R_c \), which is 20 times smaller than that of the anode-supported type PCFCs comprising same BCY/LSCF cathode configuration.\(^{[21,52]}\) \( R_c \) of the current BCY-based HMFC is lower than 0.1 Ω cm\(^{-2}\) in both H\(_2\) and NH\(_3\) types at any DC conditions (Figure 5), which is similar as those of BCY-HMFC.\(^{[21]}\) The mechanism for lowering cathodic interfacial resistances would be reported in next paper.

The impedance fitting analysis clearly demonstrated that a large concentration overpotential takes place at the anode by using NH\(_3\) or diluted H\(_2\) fuels particularly in high DC current conditions owing to the limited hydrogen mass transfer in Pd bulk (Figure 5c,d). The fundamental studies on the anodic polarization behavior of ammonia fuel cells have been still quite a few. Yang et al. reported that NH\(_3\) type PCFC made of a BaCe\(_{0.75}\)Y\(_{0.25}\)O\(_3\)-δ electrolyte and Ni-BaCe\(_{0.75}\)Y\(_{0.25}\)O\(_3\)-δ cermet anode had the anodic overpotential of 0.08 V under 0.06 A cm\(^{-2}\) at 600 °C.\(^{[53]}\) The corresponding anodic resistance is calculated to be 1.2 Ω cm\(^{-2}\), which is at least one order of magnitude larger than the sum of \( R_\text{el} \) and \( R_{\text{mt}} \) of the HMFC operating at 0.6 A cm\(^{-2}\), revealing that the anode reaction of NH\(_3\)-type HMFC is significantly faster than the reaction at the Ni-BZCY-gas triple phase boundaries of NH\(_3\) type PCFC despite the former going on with mediated via mass diffusion in metal anode.

In order to output 1 A cm\(^{-2}\) DC currents, hydrogen flux \( (J_{H2}) \) in Pd is required to 1.05 \( \times \) 10\(^{-5}\) mol cm\(^{-2}\) s\(^{-1}\), which can be given by the following with hydrogen permeability \( \varphi \) and thickness \( \beta \):

\[
J_{H2} = \varphi \Delta P_{H2} \Delta m_{H2} = \varphi \Delta \rho_{H2} \Delta m_{H2} (15)
\]

Here \( \Delta m_{H2} \) is the \( m_{H2} \) gap between both Pd edges, which is corresponding to \( p_{H2}^\mu - p_{H2}^\mu \). By using \( \varphi = 4 \times 10^{-8} \) mol cm\(^{-2}\) s\(^{-1}\) Pa\(^{-0.5}\)\(^{[55]}\) and \( l = 30 \) µm, the \( \Delta m_{H2} \) is calculated to about 13 kPa for the \( J_{H2} \) value, clarifying that \( p_{H2}^\mu \) is still as high as 0.45 \( p_0 \) under operating in 1.0 A cm\(^{-2}\) DC currents by NH\(_3\) fuels, i.e., \( p_{H2}^\mu = 0.6 \ p_0 \). This analysis strongly suggests that NH\(_3\)-type HMFC can generate sufficiently high DC powers by utilizing only pyrolytic H\(_2\) products due to the high hydrogen permeability of Pd anode. It is clearly concluded that HMFC is viable fuel cells enabling efficient power generation by direct ammonia feeds at around 600 °C.

3.2. Proton Transfer at Oxide-Metal Junctions

In BZCY, the proton carriers are in equilibrium with moisture in the atmosphere as follows\(^{[56,57]}\):

Table 2. Summary of the recent literatures for NH\(_3\)-type PCFCs and SOFCs operating at 600 °C.

| Electrolyte    | Anode cermet | OCV [V] | \( P_{\text{max}} @ 600 ^\circ \text{C} \) [mW cm\(^{-2}\)] | Ref. |
|----------------|--------------|---------|-------------------------------------------------|-----|
| BaCe\(_{0.75}\)Gd\(_{0.25}\)O\(_3\) (10 µm) | Ni-Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_3\) | 1.1 | 150 | [44] |
| BaCe\(_{0.75}\)Gd\(_{0.25}\)O\(_3\) (10 µm) | Ni-Ce\(_{0.75}\)Gd\(_{0.25}\)O\(_3\) | 1.0 | 210 | [46] |
| BaZr\(_{0.2}\)Ce\(_{0.8}\)Y\(_{0.2}\)O\(_3\) (20 µm) | Ni-Ce\(_{0.8}\)Zr\(_{0.2}\)Ce\(_{0.2}\)O\(_3\) | 1.15 | 190 | [42] |
| BaCe\(_{0.7}\)Zr\(_{0.3}\)O\(_3\) (60 µm) | Ni-BaCe\(_{0.7}\)Zr\(_{0.3}\)O\(_3\) | 1.07 | 165 | [43] |
| Zr\(_{0.3}\)Sc\(_{0.7}\)O\(_3\) (20 µm) | Fe/Ni-Zr\(_{0.3}\)Sc\(_{0.7}\)O\(_3\) | 1.1 | 240 | [45] |
| Ce\(_{0.8}\)Sm\(_{0.2}\)O\(_3\) (20 µm) | Ni-Ce\(_{0.8}\)Sm\(_{0.2}\)O\(_3\) | 0.9 | 410 | [41] |
| Ce\(_{0.8}\)Sm\(_{0.2}\)O\(_3\) (50 µm) | Ni-Ce\(_{0.8}\)Sm\(_{0.2}\)O\(_3\) | 0.88 | 170 | [47] |
| BaZr\(_{0.2}\)Ce\(_{0.8}\)Y\(_{0.2}\)O\(_3\) (1 µm) | Pd foil | 0.98 | 580 | This work |

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\[ V_2^- + H_2O \rightarrow 2H^+ + O_2 \]  

(16)

The corresponding equilibrium constant \( K_1 \) is given by

\[ K_1 = \left[ H_2^+ \right]^2 \left[ O_2^- \right] \left[ V_2^- \right] - \frac{1}{2} p_{O_2} \]  

(17)

Here, according to Kröger–Vink notations, \( V_2^- \), \( O_2^- \), and \( H_2^+ \) represent oxygen vacancies, lattice oxygens, and proton defects, respectively, and \( [ \cdot ] \) denotes the concentration of each specie. The hole carriers, \( h^\bullet \), are incorporated into BZCY by the following defect reactions

\[ V_2^- + 1/2O_2 \rightarrow O_2^- + 2h^\bullet \]  

(18)

\[ K_2 = \left[ O_2^- \right] \left[ h^\bullet \right]^2 \left[ V_2^- \right] - \frac{1}{2} p_{O_2} \]  

(19)

Proton and hole carriers are in equilibrium by the following reactions

\[ H_2O + 2h^\bullet \rightarrow 2H^+ + 1/2O_2 \]  

(20)

\[ K_3 = \left[ \left[ H_2^+ \right]/\left[ h^\bullet \right]^2 \right] p_{O_2}^{1/2} \]  

(21)

\[ K_4 = \left[ \left[ H_2^+ \right]/\left[ h^\bullet \right]^2 \right] K_e p_{O_2} \]  

(22)

Ohmic contacts between Pd and BZCY (Figure 6a) would not be convenient to block the electron (hole) charge transfer across the interface. In fact, the HMFC increases hole transfer number when \( p_{O_2} \) in the anode is significantly lowered (<0.2 \( p_{O_2} \)) with increasing \([h^\bullet]\) in relation to equilibrium (22) (Figure 6b). Nevertheless, Equation (22) suggests that the absence of wide depletion layer at the junction is advantageous for the anodic charge transfer reactions of HMFC. In BZCY electrolyte, protons' jumping to neighbor sites leaves an excess hole behind for the local charge neutrality (Figure 7c,e). Therefore, moving away of protons from the interfacial sites gives rise to unequilibrated \([H^\bullet]/[h^\bullet]\) ratio within the interfacial regions, which exerts incorporation of the proton intermediates formed on the Pd surface into BZCY layer in order to recover the \([H^\bullet]/[h^\bullet]\) thermodynamic equilibrium (22) (Figure 7e). In case of the “Ohmic” BZCY/Pd junctions, the \([H^\bullet]\) in the interfacial region of BZCY electrolyte is not depleted according to the hole-proton equilibrium (22) because Ohmic contact accepts relatively high \([h^\bullet]\) in the interfacial region (Figure 7c,e), whereas allowable \([H^\bullet]\) in the interfacial region of the Schottky-type junction would be much lower than that of the Ohmic contact because of lowering \([h^\bullet]\) in the interfaces (Figure 7d,f). In fact, it has been reported that the SrZr\(_{0.9}\)Y\(_{0.1}\)O\(_3\)/Pd junction which forms Schottky-type potential barrier with wide depletion layer at the interface shows lessened conductivity because the proton concentrations in the interfacial layer becomes smaller than those of the SrZr\(_{0.9}\)Y\(_{0.1}\)O\(_3\) bulk.\(^{58,59}\) These imply that the proton incorporation via “Ohmic” BZCY/Pd junction is much faster than that via Schottky-type junction due to the relatively large acceptable concentrations of hydrogen defects (\([H^\bullet]\)) in the interfacial region (Figure 7e). Although the physical model mentioned above is purely analytical, however, it strongly suggests that Ohmic contact between BZCY electrolytes and Pd anodes is indispensable for the fast charge transfer reaction mediated via proton–hole exchanges at the BZCT/Pd interfaces.

4. Conclusion

It is demonstrated that hydrogen membrane fuel cells based on the BZCY-Pd oxide-metal junction enables efficient power generation by direct feed of NH\(_3\) fuels at intermediate temperatures. The corresponding anode reactions are found to proceed via the thermal decomposition of NH\(_3\) and the subsequent oxidation of the hydrogen products. In HMFCs, Pd metal anodes can efficiently capture pyrolytic hydrogen products from the mixed fuel gases with subsequently transferring them to the reaction interface due to the excellent hydrogen permeability. Moreover, Ohmic contact of BZCY/Pd junction allows to accommodate large amounts of protons in the interfacial region and thus promotes the incorporation of proton from Pd into BZCY according to the hole–proton thermodynamic equilibrium, thereby accelerating the anodic charge transfer reaction. Accordingly, NH\(_3\)-fed HMFCs possess significantly lowered anodic polarization resistance, which lead the superior fuel cell performances to the corresponding SOFCs and PCFCs with gaining stable power outputs of 0.58 W cm\(^{-2}\) at 600 °C. It is concluded that the HMFC comprising highly conducting ceramic electrolytes and hydrogen sorption alloys is greatly advantageous for power generation with not only NH\(_3\) but also other hydrogen carriers by utilizing efficiently their pyrolytic hydrogen products at intermediate temperatures. The current results exert a great influence on the direction in the developments of the next-generation intermediate-temperature fuel cells.

5. Experimental Section

Previously, a BCY thin film was successfully fabricated by RF cosputtering technique with BaCe\(_0.9\)Y\(_{0.1}\)O\(_{3-\delta}\) and CeO\(_2\) double targets.\(^{21,28}\) BZCY thin films were also fabricated by the same method with BaCe\(_0.9\)Y\(_{0.1}\)O\(_{3-\delta}\) and ZrO\(_2\) targets. Phase purity and crystallinity of the deposited films were checked by X-ray diffraction patterns with a RIGAKU diffractometer (RIGAKU Rint2000). The scanning electron microscopy was conducted with JEOL JSM-7100F. The chemical composition of BCY thin films was determined by WDX with a JEOL JXA-8530F. The scanning transmission electron microscopy (STEM) was carried out in a HITACHI HD-2000. The specimens for TEM observation were prepared by a focused ion beam microfabrication (HITACHI FB-2100). The HMFCs were fabricated by depositing a BZCY thin film of 1 µm thickness on a Pd foil (0.05 × 12 × 12 mm, Tanaka Co.). The foil was polished with alumina particles (1.0 µm diameter) and was cleaned by sonication in acetone and pure water before deposition. LSCF button electrode (7 mm\(^2\)) was screen-printed on the surfaces of the BZCY films as a porous cathode by using a commercial LSCF paste (FuelcellMaterials) with subsequent heating by a heat-gun for 2 min.
The performances of the HMFCs were evaluated by measuring the current–voltage (I–V) relation and electrochemical impedance spectra at elevated temperatures. The specimen was sealed in a specially designed sample holder with a mica gasket (FuelCellMaterials). Both cathode and anode were contacted with Pt meshes, and a thermocouple was placed in close proximity to the cell to obtain temperature data as accurate as possible. Normally, dry H₂ or NH₃ gases were fed to the Pd anode side at a flow rate of 100 cm³ min⁻¹, and wet air gas was fed to the cathode side at a rate of 100 cm³ min⁻¹. The wet gas (pH₂O = 3 kPa) was prepared by passing the gases through water at 25 °C. The pH₂ and pO₂ in anode and cathode gases, respectively, were adjusted with Ar balance gases. Electrochemical impedance spectroscopy and I–V characteristics were obtained by using a Solartron 1260/1287 system in the frequency range of 10⁶ to 0.1 Hz with AC amplitude of 30 mV under several DC bias voltages. The effective hydrogen partial pressures in the anode gases of NH₃-fed HMFC were determined by acid–base titration for the 1 m H₂SO₄ solution equilibrated with exhaust gases from the anode sides of NH₃-fed HMFC. For this, anode exhausts were bubbled in H₂SO₄ solution for 1 h during power generation under 0.75 V potentiostatic condition at 600 °C, and the resultant solutions were titrated with 0.1 m NaOH standard solutions and a pH meter (Horiba D-71LAB).

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**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This research was supported by JST, PRESTO, “Creation of Innovative Core Technology for Manufacture and Use of Energy Carriers from Renewable Energy” program (Grant No. JPMJPR1341). This work was conducted at Hokkaido University, supported by “Nanotechnology Platform” Program of the MEXT Japan.
Conflict of Interest

The authors declare no conflict of interest.

Keywords
direct ammonia fuel cells, hydrogen membrane fuel cells, PCFC, RF sputtering deposition

Received: September 15, 2017
Revised: October 9, 2017
Published online: December 14, 2017