Investigation of Current Leakage of Micro-tubular SOFCs with a Ceria Membrane for Low-intermediate Temperature Power-generation Applications

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In this work, current leakage of the micro-tubular cells with a 10-μm Ce0.95Gd0.05O1.95 (GDC) electrolyte based on cathode- and anode-supported configurations was investigated at 500 and 550 °C. It was found that the open circuit voltage (VOC) of the GDC membrane cell greatly corresponds to the cell structure, particularly influenced by the electrode polarization. Calculations derived from the experimental results showed that the leak current through the GDC electrolyte gradually vanished as the external current increased to a certain degree, which accordingly related to the polarizations, due to the cell structures. The anode-supported cell can be capable of generating a high power density with a reasonable maximum-efficiency. On the other hand, not only VOC but also cell output and efficiency were significantly lowered for the cathode-supported cell. It suggests that an appropriate cell structure is necessary to make the doped ceria a promising electrolyte for low-intermediate temperature power-generation applications.

Key Words : Solid Oxide Fuel Cells, Gadolinium Doped Ceria, Electrolyte Thickness, Open Circuit Voltage, Efficiency

1 Introduction

Doped ceria is a promising alternative to the current state-of-the-art electrolyte of stabilized zirconia for solid oxide fuel cell (SOFC) operating below 600 °C. However, the mixed conduction of doped ceria presents a major hindrance towards its applications. According to the transport equations for electrons and ions in a mixed conductor (Riess’model14), ionic and electronic currents (I and Jc) here I = -Jc occur under the open circuits for the ceria based SOFC, even there is no external current. The observed open circuit voltage (VOC), thus, is lower than the Nernst one (VM). This can be explained by the equation: VOC = VM - RJc - δVFin,C - δVFin,A, where δVFin,C and δVFin,A are the overpotential losses at the cathode and anode, respectively. R is the electrolyte resistance. The overpotential loss depends on Jc indicating that the electrode polarization greatly contributes to the VOC drops. The VOC has a strong dependency on the electrolyte thickness while the non-reversible electrodes are used.45 Riess et al.25 concluded the theoretical relations between the VOC and the electrolyte thickness. The thinner the electrolyte, the lower the VOC, due to the significantly increased internal short-circuit currents. Under power generation conditions, the influence of leak current can be reduced to some degrees. Several reports have discussed the cell output and efficiency of the low-intermediate temperature SOFCs based on a thin-film ceria electrolyte using the simulations, in which the leak current and efficiency can be well described in terms of various operating conditions according to a finite difference model.6-10 However, these have been mainly limited to the linear leakage current behavior based on an ideal electrode polarization. Few reports have experimentally investigated the influence of the mixed conduction of the ceria electrolyte on the cell current leakage and the relations between the cell structures and the leak currents. Recently, we have fabricated the micro-tubular cells with a thin Ce0.95Gd0.05O1.95 (GDC) electrolyte and demonstrated high power densities and good thermal expansion behaviors.11,12 In this study, leak current related to cell output and efficiencies of the micro-tubular cells were evaluated at the basis of the cathode- and anode-supported configurations.

2 Experimental

2.1 Preparations and measurements of the GDC electrolyte with different thickness

GDC electrolytes with different thickness were fabricated as electrolyte-, cathode- and anode-supported cells by a slurry coating and co-sintering process. The cathode, electrolyte and anode used were La0.8Sr0.2Co0.8Fe0.2O3-δ (LSCF)-GDC (Specific surface area : 23 m2g-1), GDC (10 m2g-1) and NiO-GDC (7 m2g-1), respectively. Preparation of the cathode-supported cell was previously reported.13 For the anode-supported cell, the anode substrate was prepared by uniaxially pressing the NiO-GDC composite with binder and pore former into discs under 23 MPa pressure. The electrolyte slurry that contains the GDC
powders and the organic ingredients was coated on the anode. The tapes were allowed to dry gradually at room temperature for 12 h. The bi-layers of the anode substrate and the coated GDC GDC tape were fired at 1400°C for 10 h. The heating and cooling rate was 5°C min⁻¹. The cathode slurry consisting of the 70 vol% LSCF-GDC powder was coated on the sintered electrolyte and fired at 1050°C for 2 h. For the electrolyte-supported cell, the GDC powder was pressed into a disc under 23 MPa pressure, and further sintered at 1400°C for 10 h. The dense samples (relative density >95%) were polished to obtain the desired thickness as 1 mm and 500 μm. The NiO-GDC slurry was coated on the electrolyte and sintered at 1400°C for 6 h. The LSCF-GDC slurry was coated on the opposite side of the electrolyte, and finally sintered at 1050°C for 2 h. The dimensions were 16 mm diameter × 2 mm thickness for the resulting cells, and the effective electrode area was 1 cm² for all the cells. Microstructures of the cells were observed using Scanning Electron Microscopy (SEM, Hitachi, S-3500H, Japan), and atom analysis was carried out using Scanning Transmission Electron Microscope (STEM, JEOL, JEM-2100F, Japan).

The total conductivities of the GDC electrolyte under different oxygen partial pressure (PO₂) were measured by a pseudo four-points (using four wires connecting two electrodes) AC impedance method. For the open circuit voltage measurements, Pt meshes used as the current collectors were attached to the electrodes with Pt paste and fixed with the ceramic binder. The cells were connected to a gas manifold and placed in an oven. The anode and the cathode compartments were separately sealed by melting a glass ring gasket at 900°C. Hydrogen (saturated with H₂O vapor at 20°C) and air were supplied to the anode and the cathode compartments, respectively. A flow rate of 100 mL min⁻¹ was used. The tests were carried out in the temperature range from 450 to 600°C. No gas leakage in the electrochemical measurements was confirmed using bubble-type gas flow meter.

2.2 Electrochemical measurement of micro-tubular cells

The fabrications of the micro-tubular cells with the GDC thin-film electrolyte based on the anode- and cathode-supported structures were reported elsewhere. The cathode, electrolyte and anode were LSCF-GDC, GDC and NiO-GDC (Ni to GDC = 50 : 50 in volume after reduction), respectively. Outer diameter and wall thickness of the anode-supported cell were 1.8 mm and 0.2 mm, respectively, whereas those of the cathode-supported one were 2.26 mm and 0.46 mm, respectively. The electrochemical performance of the micro-tubular was measured under the apparatus suggested in Ref. The current collection was done with a two-terminal mode where Pt meshes used as current collectors were covered to the support tube and Pt wires were well wound at two terminals of the tube as current collectors. These were fixed with Ag paste and further heated to 800°C for 5 h in air. 30 vol% H₂ - Ar (saturated with H₂O vapor at 20°C) and air gases were used as a fuel and oxidant with a flow rate of 100 mL min⁻¹. The electrochemical measurement was carried out at 500 and 550°C. Gas sealing was ensured by using the thermosetting sealants such as Aron ceramic C and C (TOAGOSEI CO., LTD, Japan). No gas leakage was confirmed using bubble-type gas flow meter. Power generation was measured using a current pulse generator (Nikkokaisoku, NCPG-105S, Japan) as a load, with an electrometer (Hokuto-denko, HC-104, Japan) to record the terminals voltages. Polarization was measured by current-interruption technique. During measurement, the effective reactive areas were 0.07 and 0.63 cm² for the cathode- and anode-supported cells, respectively.

3 Results and Discussion

3.1 Dependency of open circuit voltage upon electrolyte thickness and cell structure

Under open circuit, leak current through a thin-film GDC cell is greatly influenced by the electrolyte thickness and electrode polarization according to the theoretical assumptions. This can be experimentally confirmed by Figs. 1, in which the variety of Voc is linearly summarized as a function upon the electrolyte thickness

![Fig. 1](image-url)

**Fig. 1** Electrolyte thickness that relates to the cell structures as a function to the observed Voc at different temperatures. The calculated Voc based on Nernst and Schmalzried type equations are given as real lines and broken lines, respectively.
and cell structure. Theoretical $V_{OC}$ described by Nernst equation was marked as real line indicating a perfect electrolyte situation. For a mixed conductor of GDC, theoretical $V_{OC}$ cannot be simply calculated by Nernst equation because of internal short circuit caused by electronic conduction. Theoretical $V_{OC}$ of GDC can be estimated by Schmalzried type equation, $V_{OC} = RT/F \ln \left\{ \frac{P_{O_2}(\text{air})^{1/4} - (P_{O_2})^{1/4}}{P_{O_2}(\text{pure})^{1/4} - (P_{O_2})^{1/4}} \right\}$ $(P_{O_2})^*: a_{O_2} = a_{O_2}/(P_{O_2}/P_{O_2})^{1/2}$ $(5.5)$

where $R$, $T$, $F$, and $P_{O_2}$ are the gas constant, the sample temperature, Faraday's constant, and the oxygen partial pressure around the electrodes, respectively. $a_{O_2}$ and $\alpha$ are the ionic and electronic conductivities, respectively. By fitting the data of the measured conductivities of GDC and relatively $P_{O_2}$, the theoretical $V_{OC}$ of GDC was obtained and drawn as the broken line. A difference between Nernst $V_{OC}$ and Schmalzried value clearly reflects the influence of the mixed conduction of GDC in nature. The observed $V_{OC}$ accordingly decreased as the electrolyte thickness reduced at each temperature. This can be explained by the fact that the decrease in resistance for migration of the charge carries ($O^2-$ and electron) in ceria tends to increase the internal short circuit current.\cite{4,10} For thin-film GDC with a thickness of 50 and 10 $\mu$m, the anode-supported cell showed a relatively higher $V_{OC}$ of 0.1 V than the cathode-supported one. It can be attributed to the kinetic aspects of interfacial polarization between the electrode and the electrolyte. AC impedance analysis revealed that the non-ohmic resistances of the cathode-supported cell were 55 and 7.2 $\Omega$ cm$^2$ at 500 and 600 $^\circ$C, respectively. These are much larger than those of the anode-supported cells (13 $\Omega$ cm$^2$ at 500 $^\circ$C and 1.7 $\Omega$ cm$^2$ at 600 $^\circ$C), due to the mass transportation and the charge transfer limitation of cathode support. The internal short-circuit caused by the electronic conduction imposed the polarization loss for the cathode-supported cell under the open circuit conditions, leading to a low $V_{OC}$.

Elemental diffusion into the electrolyte during co-firing process could be also an influence on $V_{OC}$. Figure 2 shows the atom analysis near the cathode/electrolyte interface for a cathode-supported cell. Fe and La (ca. 4 mol%) were found in the electrolyte and their concentration distributions showed a linear dependency upon the distance deviating from the cathode/electrolyte interface. Traces of Fe and La (ca. 2 mol%) were further confirmed in an interior part of the electrolyte (5 $\mu$m depth from the interface). A small amount of additions (<2 mol%) of transition metal oxides (Fe) into doped ceria have been reported to considerably favor the densification.\cite{15,16} It can be explained by a formation of an amorphous transition metal rich grain boundary film that facilitates the densification via liquid phase with a minimum of grain growth. The minor dopant additions have no essential effect on total and ionic conductivity, but considerably increase the p-type electronic transport, which relates to the boundary layers.\cite{15}

3.2 Current leakage and efficiency of the cells under power generations

The current-voltage and power density characteristics of the micro-tubular anode-supported cell are given in Fig. 3. The ceria membrane on the anode tube showed a thickness of ca. 8 $\mu$m resulting in fairly low values of the open circuit voltages of 0.83 and 0.89 V at 500 and 550 $^\circ$C, respectively. This can be well explained by the observations of Figs. 1 due to the increased internal short-circuit as the ceria thickness is highly reduced. The maximum power densities of the cell reached at 0.68 W cm$^{-2}$ (0.39 V, 1.75 A cm$^{-2}$) and 0.97 W cm$^{-2}$ (0.47 V, 2.07 A cm$^{-2}$) at 500 and 550 $^\circ$C, respectively.

The leak current through the GDC electrolyte of the micro-tubular cells was calculated based the equation proposed by Gödecke and Gauckler.\cite{14}

![Figure 2](image2.png)  
**Fig. 2** Linear atom concentration and distribution as a function upon the distance deviating from the cathode/electrolyte interface based on the STEM analysis for a cathode-supported cell. The total atom concentration was 100% based on Fe, La, Sr and Co. The symbols of minus and plus in the x-axis represent the cathode and electrolyte regions, respectively.

![Figure 3](image3.png)  
**Fig. 3** Current density-voltage curves and power densities of the anode-supported micro-tubular cell at 500 and 550 $^\circ$C.
\[ j_e = \left( \frac{\text{PO}_2^*}{\exp \left( \frac{-4RT}{F(V_{\text{OCV}} + \delta V_C)} \right)} \right)^{1/4} \frac{1}{j_t} \exp \left( \frac{g}{RT} V_a - 1 \right) \frac{1}{1 - \exp \left( \frac{-g}{R T} V_a \right)} \]  

(1)

where \( j_e \) is the leakage current density, \( j_t \) the total current density, \( j_f \), the external current density (A cm\(^{-2}\)). \( \text{PO}_2^* \) indicates the oxygen partial pressure of \( \text{PO}_2 \) at \( \alpha = \alpha_0 \) for GDC electrolyte (bar). \( R \) means the ideal gas constant (J mol\(^{-1}\) K\(^{-1}\)), whereas \( T \) is the absolute temperature (K) and \( F \) is the Faraday constant (C mol\(^{-1}\)). \( V_{\text{OCV}} \) is the open circuit voltage calculated by Nernst equation (V), and \( V_{\text{cell}} \) is the observed voltage. \( \delta_{\text{C}} \) and \( \delta_{\text{VA}} \) mean the overpotentials at the cathode and anode (V), respectively, and \( L_{\text{exp}} \) the electrolyte thickness (m). \( \alpha \) is the conductivity of GDC in air (S m\(^{-1}\)).

By fitting the required parameters as measured, the leakage current was calculated at 500 and 550°C. Figure 4 shows the leak current density as a function of the external current density of a micro-tubular anode-supported cell at 500 and 550°C. Under open circuit, the current leakage reached the maximum. Loading of the cell is effectuated by reducing the external resistance, resulting in an increase of the external current and a decrease of peak current. This can also be explained by the chemical potential changes at the anode and cathode of the cells under operation. The leakage current density decreased rapidly and almost vanished as the external current density gets over 1.5 A cm\(^{-2}\).

The efficiency of the micro-tubular cells was further calculated by the following equations: \(^{(4)}\)

\[ \varepsilon_{\text{AG}} = \varepsilon_f \varepsilon_f = -\varepsilon_f V_{\text{cell}} \frac{j_t}{j_t} = \frac{V_{\text{cell}} j_t}{V_{\text{OCV, Nernst}}} \frac{j_t}{j_t} \]  

(2)

where \( \varepsilon_f \) is the voltage efficiency given by \( V_{\text{cell}}/V_{\text{OCV, Nernst}} \). \( V_{\text{OCV, Nernst}} \) is the calculated open circuit voltage by Nernst equation (V) and \( V_{\text{cell}} \) is the observed terminal cell voltage (V). \( \varepsilon_f \) is the faradaic efficiency, given by \( j_t/j_{\text{cell}} \). \( j_t \) is

the total current density and \( j_t \), the external current density (A cm\(^{-2}\)).

Assuming the fuel utilization of 100%, the overall efficiencies of the micro-tubular anode-supported cell at 500 and 550°C are thus calculated and shown in Fig. 5a and b, respectively. As can be seen, the efficiency of the cell was mainly determined by the leak current at a relatively low external current (<0.5 A cm\(^{-2}\)) and increased linearly as the \( \varepsilon_f \) increased. At relatively high external current (>1.0 A cm\(^{-2}\)), the GDC showed electrolytic behavior and the efficiency was exclusively determined by the loading and varied mainly according to the \( \varepsilon_f \). The maximum-efficiency of the cells reached at approximately 58% and 56% at 500 and 550°C, respectively.

Current-voltage and power generation characteristics of the micro-tubular cathode-supported cell at 500 and 550°C are shown in Fig. 5.\(^{(17)}\) The ceria membrane on the cathode tube had a thickness of ca. 12 μm. Open circuit voltages of 0.78 V at 500°C and 0.74 V at 550°C for the cathode-supported cell were relatively lower than those of the anode-supported cell.
of the anode-supported one. The cell polarization curves were almost linear in all current density range. The maximum power densities of the cell reached at 0.11 W cm$^{-2}$ (0.48 V, 0.23 A cm$^{-2}$) and 0.13 W cm$^{-2}$ (0.36 V, 0.36 A cm$^{-2}$) at 500 and 550 °C, respectively.

The leak current through the GDC membrane and the resulting efficiency were calculated according to the equation (1) and (2). Figure 7 shows the leak current density as a function of the external current density of the micro-tubular cathode-supported cell at 500 and 550 °C. The decrease of current leakage gradually accompanied with the increase of the external current, and finally faded away while the external current achieved at 0.5 A cm$^{-2}$. As can be seen, the efficiency shown in Fig. 8 has the maximum values of 40 and 33% at 500 and 550 °C, respectively, which are obviously lower than those of the anode-supported cells. The lower efficiency of the cathode-supported cell can be mainly attributed to a higher cathode-polarization, as discussed theoretically by Mogensen et al.$^{28}$ Additionally, the relatively low $\varepsilon_V$

![Fig. 6](image_url)  
**Fig. 6** Current density-voltage curves and power densities of the cathode-supported micro-tubular cell at 500 and 550 °C.$^{27}$

![Fig. 7](image_url)  
**Fig. 7** Calculated electronic leak current through the Ce$_{0.8}$Gd$_{0.2}$O$_{1.55}$ electrolyte for the cathode-supported micro-tubular cell.

![Fig. 8](image_url)  
**Fig. 8** Calculated efficiency of the cathode-supported micro-tubular cell at a) 500 °C and b) 550 °C.

could be also the consequence.

Both the cathode- and anode-supported cells presented a higher power density at a higher temperature (550 °C), due to the increase in ionic conductivity and decrease in the polarization resistance, but a higher maximum-efficiency at a lower temperature (500 °C), due to the lower concentration and mobility of the electronic charge carriers.

### 4 Conclusions

In this work, Ce$_{0.8}$Gd$_{0.2}$O$_{1.55}$ (GDC) electrolyte was evaluated under open circuit and power-generation conditions for low-intermediate temperature SOFCs. At certain temperature, the open circuit voltage ($V_{OC}$) of the GDC electrolyte varied mainly as a function of the electrolyte thickness and the cell structure. For the supported-ceria cells, the $V_{OC}$ obviously depended on the support electrodes. The anode-supported cell showed a relatively higher $V_{OC}$ than the cathode-supported one. Furthermore, the electrical performance and efficiency of the micro-tubular SOFCs with a 10-μm GDC electrolyte membrane based on the cathode- and anode-supported configurations were investigated at 500 and 550 °C. Calculations derived from the experimental results showed that the leak current through the GDC thin-electrolyte gradually
vanished as the external current increased to some degree, which accordingly related to the polarizations, due to the cell structures. The anode-supported cell can be capable of generating a high power density with a reasonable maximum-efficiency of 58 and 54% at 500 and 550°C, respectively. The cathode-supported micro-tubular cell, however, has much lower efficiency of 40% and 33% at 500 and 550°C, as well as lower power density. It suggests that the mixed conductor of the doped ceria would be promising for power-generation applications while designing an appropriate cell structure.

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References