

# Feasibility of Ni-based cermet anode for direct HC SOFCs: Fueling ethane at a low S/C condition to Ni–ScSZ anode-supported cell<sup>☆</sup>

Katsuhiko Yamaji<sup>\*</sup>, Haruo Kishimoto, Yueping Xiong,  
Teruhisa Horita, Natsuko Sakai, Manuel E. Brito, Harumi Yokokawa

*National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

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## Abstract

The feasibility of a Ni-based cermet anode for direct hydrocarbon (HC) SOFCs was investigated with ethane fuel as a step towards utilizing higher HCs such as propane and butane. The possibility of stable operation of SOFCs with ethane fuel at a low steam/carbon (S/C) ratio of 1.2 mol% H<sub>2</sub>O–98.8 mol% C<sub>2</sub>H<sub>6</sub> was investigated with anode-supported SOFCs utilizing a scandia stabilized zirconia (ScSZ) electrolyte and a Ni–ScSZ anode. Severe carbon deposition was observed around the anode especially at the fuel injection port during the cell tests at  $T=973$  K. The amount of deposited carbon became smaller with decreasing operation temperature, and a stable cell operation was achieved at  $T\approx 823$  K without severe carbon deposition over a week. However, at a low fuel utilization rate ( $U_f$ ) around 20%, nickel was heavily disintegrated accompanied by severe carbon deposition even at  $T\approx 823$  K. With increasing  $U_f$ , the disintegration became less, and a stable cell operations were achieved only with a small amount of deposited carbon for over a week at high  $U_f > 46\%$ .

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## 1. Introduction

Efficient power generation is expected for solid oxide fuel cells (SOFCs) because SOFCs can directly use many kinds of hydrocarbons (HCs) without any external reformers. Normally, a large amount of steam must be supplied with HC fuels at high steam/carbon (S/C) ratios  $>2$  to avoid carbon deposition on and around the anodes in SOFCs. The steam addition is effective to avoid coking, but the total SOFC system is enlarged because a large amount of water must be fed with systematic control. Accordingly, direct fuelling with HCs under non- or low-humidified conditions for SOFCs was extensively investigated to simplify the SOFC system [1–13], especially for

mobile use. However, SOFC operation with HC fuels in low S/C ratios generally results in degradation of the performance due to severe coking; especially, general Ni-based cermet anodes are considered to be unsuitable for these SOFCs because the high catalytic activity of Ni promotes cracking of HCs. Therefore, many researchers abandoned use of a Ni-based anode for low- or non-humidified HCs, and utilized new materials such as another metal-based cermet, all ceramic anode, and so on. These new anodes are stable for HC fuels but the catalytic activity is still lower than that of a Ni-based anode at the present time.

We believe the superior catalytic activity of nickel is required for utilizing HCs, and therefore, the feasibility of Ni-based cermet anode for direct HC SOFCs has been investigated. To suppress carbon deposition on the Ni-based anode in direct HC SOFCs, two approaches have been reported. The first is the utilization of a scandia stabilized zirconia (ScSZ) for the cermet anode [5] and the second is to decrease the operation temperature [4]. In addition, the effect of the fuel utilization rate ( $U_f$ ) for carbon deposition is also observed because H<sub>2</sub>O and CO<sub>2</sub> molecules produced by the electrochemical reaction during

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<sup>\*</sup> Corresponding author at: Fuel Cell Group, Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.  
Tel.: +81 298 61 9411; fax: +81 298 61 4540.

E-mail address: [k-yamaji@aist.go.jp](mailto:k-yamaji@aist.go.jp) (K. Yamaji).

power generation will be expected to suppress carbon deposition and/or remove deposited carbon. In our previous study [12], single cell tests for low S/C methane fuels were successfully carried out for about a 100 h by decreasing the operation temperature below 973 K and by increasing the  $U_f$  around 50% with Ni–ScSZ anode-supported cells.

The aim of this study is to investigate the feasibility of a Ni-based cermet anode for direct HC SOFCs. The feasibility of stable cell operation with ethane at a low S/C ratio with a Ni–ScSZ anode was investigated as a step to utilizing higher HCs for SOFCs. An anode-supported structure with a ScSZ electrolyte was adopted to improve the cell performance at lower temperatures. The effects of fuel utilization rate on carbon deposition were investigated in this study.

## 2. Experimental

A ScSZ (1 mol% CeO<sub>2</sub>–10 mol% Sc<sub>2</sub>O<sub>3</sub>–89 mol% ZrO<sub>2</sub>, Daiichi Kigenso Kagaku Kogyo Co. Ltd., hereafter ScSZ) was utilized for the electrolyte and the Ni-based cermet anode. The weight ratio of ScSZ/NiO was fixed at 40/60. Anode-supported electrolytes with a diameter of 35 mm, which were supplied by Japan Fine Ceramics Co., Ltd., were used in this study. The anode-supported electrolytes were fabricated by a screen printing method and a subsequent co-firing process. The anode and electrolyte thicknesses were 0.5–1 mm and 20 μm, respectively. As the cathode, an Ag–Pt–ScSZ paste (fabricated by Tanaka Kikin-zoku Kogyo K.K., the weight ratio of Ag/Pt/ScSZ was 5/5/7) was painted at the center of the electrolyte with a diameter of 24 mm and was fired at 1123 K for an hour. It should be noted that the Ag–Pt–ScSZ cathode was used only as a test electrode for lower temperatures such as a porous platinum cathode and not for practical use.

A schematic drawing of the arrangement of single cell test is shown in Fig. 1. A single cell was symmetrically placed between double alumina tubes with an alumina jig. A common soft glass sealant was used for fuels as shown in the figure. A platinum mesh welded with two platinum lead wires and a gold mesh welded with two gold lead wires were pushed onto the cathode and the anode, respectively, as current collectors with porous alumina plates. During cell tests, air was fed to the cathode at 100 cm<sup>3</sup>/min as the oxidant and the fuel (H<sub>2</sub> or C<sub>2</sub>H<sub>6</sub>) was fed to the anode after being humidified at  $T=283$  K; this humidified temperature means the fuel gas contains 1.2 mol% H<sub>2</sub>O. The single cell tests were operated with a potentio/galvano stat (Electrochemical Interface, Solartron Analytical, SI-1287) and an impedance analyzer (Impedance/Gain-Phase Analyzer, Solartron Analytical, SI-1260).

Before fueling C<sub>2</sub>H<sub>6</sub>, the power generation test was operated with H<sub>2</sub> in a potentiostatic mode until the current density became almost constant. After the current was stabilized, H<sub>2</sub> was changed to C<sub>2</sub>H<sub>6</sub> and the power generation was continued in the same potentiostatic condition. According to the chemical equivalent in the reaction with oxygen, the flow rate of C<sub>2</sub>H<sub>6</sub> was usually set at one-seventh of the flow rate of H<sub>2</sub>. The anode outlet gas was measured with gas chromatography equipment (VARIAN Micro-GC, CP-2002) to detect a leakage of air to the anode.

## 3. Results and discussion

Single cell tests with ethane were started at  $T=973$  K because a stable cell operation with low S/C methane was achieved at that temperature for about 100 h at a high fuel utilization rate around 50% but not achieved above  $T=1023$  K as shown in our previous study [12]. Single cell tests with ethane fuel have been

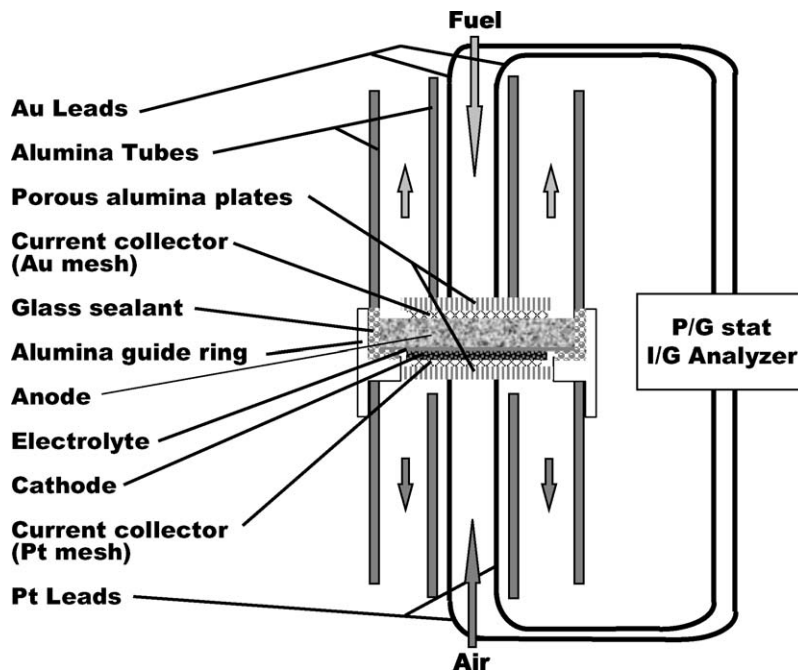


Fig. 1. Schematic drawing of the cell test arrangement.

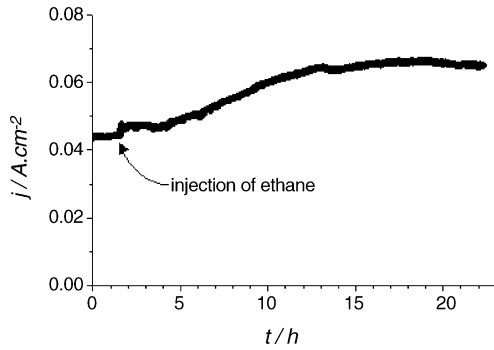


Fig. 2. Time dependency of current density  $j$  during a power generation test with low S/C ethane at a low  $U_f$  around 20%.

worked out with a nickel mesh current collector for the anode at  $T=973\text{--}873\text{ K}$  [13]. The cell performance rapidly decreased after fuelling ethane and the cell was finally broken; which caused a large amount of carbon to be deposited on and in the anode. The nickel mesh current collector was also covered with deposited carbon and was partly disintegrated near the fuel injection port accompanying with formation of a hole. However, the rate of the carbon deposition and the disintegration of the nickel mesh near the fuel injection port decreased with decreasing temperature.

In this study, the current collector of the anode was changed from nickel to gold to prevent the effects of carbon deposition on it, and the operation temperature was reduced at  $T\approx 823\text{ K}$ . Fig. 2 shows the result of a power generation test at a fixed terminal voltage of 0.5 V and  $T=823\text{ K}$ . The current density ( $j$ ) was too low because the porosity of the anode support was small due to the high sintering temperature of 1673 K. Because of the low current density, the fuel utilization rate was lower than that we expected; the fuel utilization rate ( $U_f$ ) was between 15 and 23% during the test. The current density  $j$  was gradually increased and finally became constant. By gas chromatography

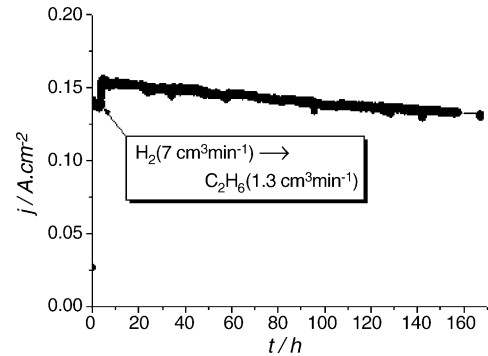


Fig. 4. Time dependency of current density  $j$  during a power generation test using an improved cell with low S/C ethane at a high  $U_f$  around 50%.

measurement, it was confirmed that the leakage of air gradually increased with time as well as  $j$  in Fig. 2, and finally became constant. Accordingly, it was considered that the improvement of the cell performance was due to the leakage of air via the broken cell from the cathode to the anode; the air enhanced the reforming reaction of ethane and  $\text{H}_2$  was provided to the anode reaction zone as fuel. After the cell test, the anode-supported cell near the fuel injection port was blackened and swelled. Fig. 3 shows photograph, schematic drawing and SEM images of the fractured surface. The anode-supported cell was swelled and clogged by a huge amount of carbon deposited near the fuel injection port. It was easily estimated that the electrolyte was broken by the mechanical stress in the swelled part.

In order to increase the porosity of the anode, the sintering temperature of the cell was reduced from 1673 to 1623 K and the porosity of the anode supports was about 30% before reduction of NiO to Ni. The cell tests hereafter were operated with the improved cells. Fig. 4 shows the results of a power generation test at a fixed terminal voltage of 0.5 V and  $T=826\text{ K}$ . The flow rate of  $\text{C}_2\text{H}_6$  was  $1.3\text{ cm}^3\text{ min}^{-1}$ . The total current and  $U_f$  were 0.705 A and 54%, respectively, just after fueling  $\text{C}_2\text{H}_6$ . The

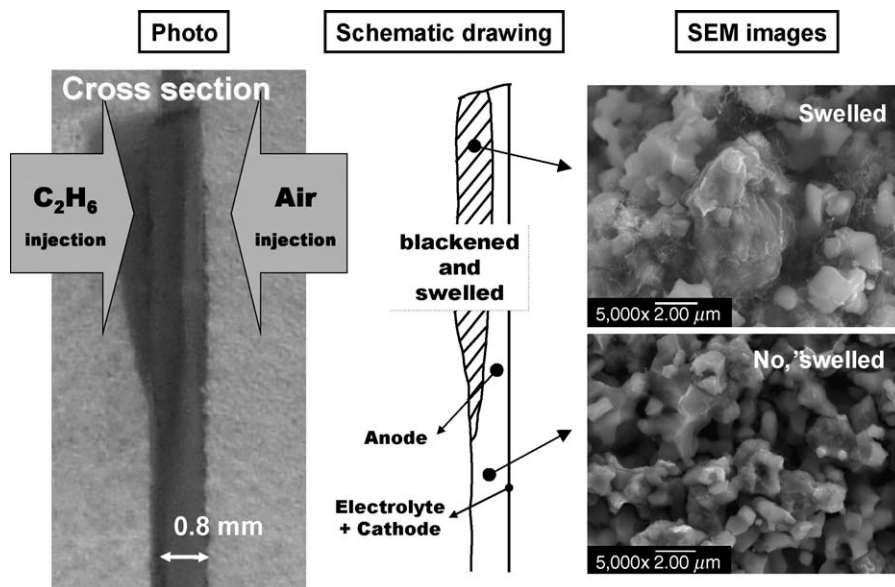


Fig. 3. Photograph, schematic drawing, and SEM images of the anode-supported cell after the power generation test shown in Fig. 2.

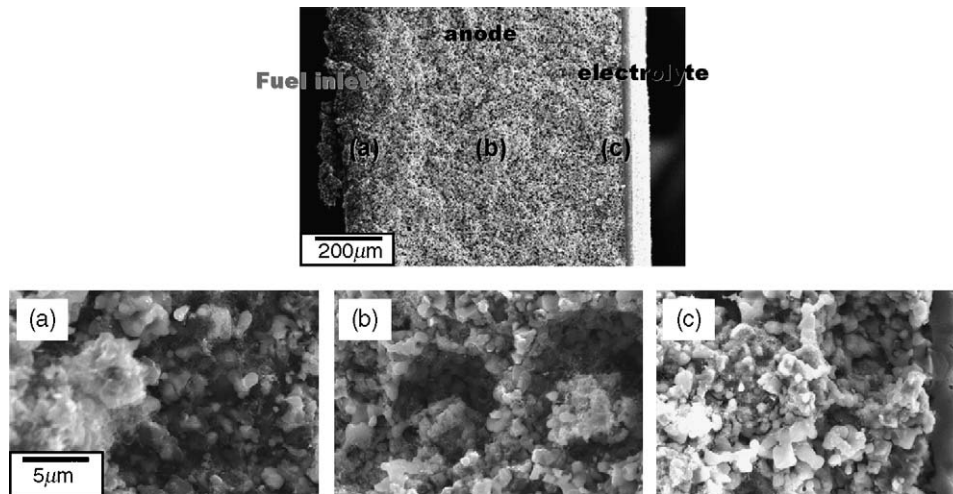


Fig. 5. SEM images of the fractured surfaces of the anode-supported cell after the power generation test shown in Fig. 4.

cell performance gradually decreased with time, and the current and  $U_f$  became 0.595 A and 46%, respectively, after 163 h operation. In our recent study using a reference electrode, it was confirmed that the gradual degradation of the cell performance was mainly due to the degradation of the cathode performance. By gas chromatograph measurement, the amount of air leakage into the anode was too small to be neglected during the cell operation. After the operation with ethane for 163 h, a slight amount of visible carbon was deposited near the fuel injection port, but there was no carbon on the Au mesh current collector and alumina components. Also in SEM measurements on the anode surface, the deposited carbon was observed in the vicinity of the ethane injection port, but was not in the area away from there on the porous Ni–ScSZ anode. Fig. 5 shows the SEM images of the fractured cell near the fuel injection port. At point (a) in Fig. 5, which is near the fuel injection port, a huge amount of carbon was deposited and filled the pore of the anode. Away from the fuel injection part into the anode, the amount of deposited carbon became smaller as shown in Fig. 5(b). Near the anode/electrolyte interface as shown in Fig. 5(c), the deposited carbon was small.

From our results with low S/C HCs with anode-supported cells, two competitive reactions are proposed to discuss the carbon deposition. First reaction is cracking of the fuel near the fuel injection port; in most of our tests, severe carbon deposition was observed in the vicinity of the anode surface near the fuel injection port. The second reaction is the removal of deposited carbon or protection against carbon deposition by the electrochemically produced  $H_2O$  (and/or  $CO_2$ ) near the anode/electrolyte interface; as shown in Figs. 3 and 5, the amount of carbon deposition decreased away from the fuel injection port. If the velocity of the first reaction is much faster than the second reaction, severe carbon deposition should occur on the anode. On the other hand, if the velocity of the second reaction is much faster than the first reaction, the carbon deposition should be eliminated.

Even with using a typical nickel-based anode, we confirmed a stable power generation for over a week with low S/C ethane at a lowered temperature and a high fuel utiliza-

tion rate. We consider that the application of a ScSZ to the cermet anode and the electrolyte of SOFCs should be effective in suppressing carbon deposition for low S/C ethane. However, no comparisons between ScSZ and the other materials were carried out in this study. In order to avoid carbon deposition and/or to remove deposited carbon with a Ni-based anode, two remedies were confirmed in this study as follows:

1. Decreasing operation temperature of SOFCs, which decreases the carbon deposition rate.
2. Increasing fuel utilization rate to increase oxidants ( $H_2O$  and  $CO_2$ ) which will be supplied to the carbon deposition part in the anode and remove the carbon.

It should be noted that as the fueling rate decreases with increasing the  $U_f$  in this study; the decrease in fueling rate will also increase the apparent diffusion rate of  $H_2O$  and  $CO_2$  to the fuel injection port where the most severe carbon deposition occurs.

In thermodynamic equilibrium, the  $U_f$  around 50% is a condition accompanying carbon deposition, and therefore, reduction

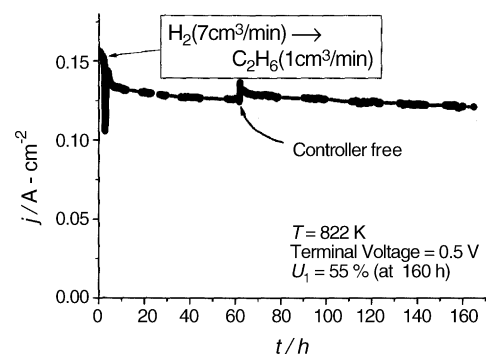


Fig. 6. Time dependency of current density  $j$  during a power generation test using an improved cell with low S/C ethane at a high  $U_f$  of around 60%.



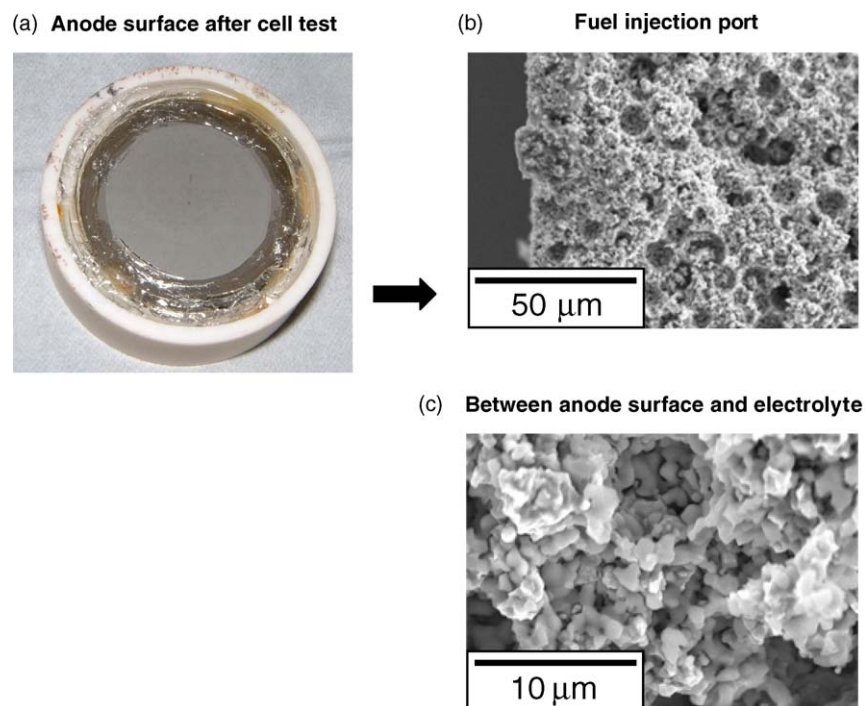


Fig. 7. Photographs and SEM images of the anode-supported cell after the power generation test shown in Fig. 6.

of carbon deposition around the fuel injection port is expected by increasing the  $U_f$ . Fig. 6 shows the result of a power generation test at a fixed terminal voltage of 0.5 V and  $T = 822$  K; which was operated at the highest  $U_f$  in a series of cell tests with ethane. The flow rate of  $C_2H_6$  was  $1.0 \text{ cm}^3 \text{ min}^{-1}$ . The total current and  $U_f$  were 0.55 A and 55%, respectively, after 160 h operation; the  $U_f$  was 10% higher than that the previous result shown in Fig. 4. The time dependency of current density  $j$  was similar to the previous result. After long-term operation with  $C_2H_6$ , the cell was applied to a power generation test in 1.2%  $H_2O-H_2$  atmosphere for a few hours, and the cell test was finished. After the cell test, there was no visible carbon on the surface of the anode, and SEM images of the fractured surface of the anode did not show any deposited carbon except near the fuel injection port as shown in Fig. 7. The amount of the deposited carbon was small even at the fuel injection port. In order to explain why the carbon deposition was suppressed in this cell test at the highest fuel utilization rate, we considered two reasons as follows:

1. Higher fuel utilization rate decreased the carbon deposition rate.
2. Deposited carbon was removed by  $H_2O$  during the additional power generation test with  $H_2$  fuel.

At the present time, we cannot conclude which process was dominant in eliminating carbon deposition. However, the Ni-based anode successfully performed without severe carbon deposition for a week in spite of fueling with low S/C ethane.

Recently, Ishihara et al. showed good performance of a single cell using thin LSGM electrolyte films around  $T = 773$  K [14]. With such a high performance electrolyte at lower temperatures, much higher HC fuels could be utilized at low S/C conditions.

#### 4. Conclusions

The feasibility of nickel-based cermet anode for a direct ethane SOFC was confirmed by increasing the fuel utilization rate at  $T = 826$  K. Although a small amount of carbon was partly deposited on the anode, a stable cell operation with slightly humidified ethane fuel was achieved over a week.

#### References

- [1] S. Park, J. Vohs, R. Gorte, J. Electrochem. Soc. 146 (1999) 3603.
- [2] H. Kim, S. Park, J. Vohs, R. Gorte, J. Electrochem. Soc. 148 (7) (1999) A693.
- [3] E. Murray, T. Tsai, S. Barnett, Nature 400 (1999) 649.
- [4] E. Murray, S. Barnett, Proceedings of the SOFC-VI, The Electrochem. Soc. Proc. Ser., PV 99-19, 1999, p. 1001.
- [5] K. Ukai, Y. Mizutani, Y. Kume, Proceedings of the SOFC-VII, the Electrochem. Soc. Proc. Series, PV2001-16, 2001, p. 375.
- [6] T. Norby, P.A. Osborg, O. Dyrlyie, R. Hildrum, M. Seiersten, R. Glenne, Proceedings of First European SOFC Forum, 1994, p. 227.
- [7] S. Primdahl, J. Hansen, L. Grahl-Madsen, P. Larsen, J. Electrochem. Soc. 148 (2001) A74.
- [8] G. Pudmich, W. Jungen, F. Tiez, Proceedings of the SOFC-VI, the Electrochem. Soc. Proc. Series, PV 99-19, 1999, p. 567.
- [9] C.M. Reich, A. Kaiser, J. Irvine, Proceedings of Fourth European SOFC Forum, 2000, p. 567.
- [10] O. Marina, L. Pederson, Proceedings of Fifth European SOFC Forum, 2000, p. 481.

- [11] J. Liu, B. Madsen, Z. Ji, S. Barnett, *Electrochem. Solid-State Lett.* 5 (2002) A122.
- [12] K. Yamaji, H. Kishimoto, Y. Xiong, H. Horita, N. Sakai, M.E. Brito, H. Yokokawa, in: *Proceedings of Sixth European SOFC Forum, European Fuel Cell Forum* 418 (2004).
- [13] K. Yamaji, H. Kishimoto, Y. Xiong, T. Horita, N. Sakai, M.E. Brito, H. Yokokawa, *Proceedings of the SOFC-IX, the Electrochem. Soc. Proc. Series, PV2005-07*, 2005, p. 585.
- [14] J. Yan, H. Matsumoto, M. Enoki, T. Ishihara, *Electrochem. Solid-State Lett.* 8 (2005) A389.