Operation of anode-supported thin electrolyte film solid oxide fuel cells at 800°C and below

L.G.J. de Haart*, K. Mayer, U. Stimming[1], I.C. Vinke

Institut für Energieverfahrenstechnik, Forschungszentrum Jülich, D-52425 Jülich, Germany

Abstract

The influence of the fuel composition and fuel utilisation on the performance of an anode-supported solid oxide fuel cell (SOFC) have been studied as function of time by DC-methods both on single cells and on short stacks. For a single cell the influence of the water/hydrogen ratio in the fuel can mainly be attributed to the change in the open cell voltage. The performance of a single cell fed with a mixture of methane and water (1:2) (internal reforming) is in the current density range up to 0.3 A/cm^2 comparable to the performance of the cell under hydrogen/water (2:1) having the same open cell voltage. The influence of the water content in the hydrogen on the performance of a short stack is also mainly caused by the difference in open cell voltage. The influence of a prolonged galvanostatic load on the performance of a short stack was measured. A short stack driven at 375 mA/cm^2 and 800°C for 1000 h (fuel H_2/H_2O = 99:1 fuel utilisation 9%) showed an ageing of 64 $\mu\Omega \cdot$cm^2/h. This value is typical for these anode-supported cells under these conditions. A stack running under high humidity (H_2/H_2O = 1:1) lost 53 mV during the first 100 h of operation. After this period the stack voltage increased to values comparable to the starting values. © 1998 Elsevier Science S.A.

Keywords: Solid oxide fuel cell; Internal reforming; Degradation; Thin films

1. Introduction

In order to increase life time and to allow cost reduction by using less expensive materials the operating temperature of solid oxide fuel cells (SOFCs) must be lowered. One way to achieve this objective is to lower the cell resistance by using a thin electrolyte layer. The Jülicher substrate concept incorporates a thin electrolyte layer of 15 μm 8YSZ on a porous nickel/8YSZ substrate [1,2]. The coarse pored support is 1.7 mm thick and a 5–10-μm thick, fine pored anode functional layer with the same composition is applied on top [3]. The cathode consists of a strontium doped lanthanum manganite/8YSZ composite layer [4]. These type of single cells have been produced as large as 25 × 25 cm^2 [1,2].

2. Experimental

For regular testing, cells of 10 × 10 cm^2 or 5 × 5 cm^2 are used. For cell testing, these single cells are placed in a ceramic testing housing. Contacts are provided by a nickel mesh on the anode and a platinum mesh on the cathode. Sealing of the fuel gas compartment is obtained by a gold seal.

For stack tests, the cells are stacked with bipolar plates of a ferritic steel, in which the gas channels were machined [3]. Contact on the anode side is provided by a nickel mesh. On the cathode side a contact layer of lanthanum cobaltite is provided. For standard tests these stacks contain two single cells. Gas seals consist of a glass ceramic. The stack is built into a metallic housing of the same ferritic steel providing the gas manifold [3].

The operating temperature for both single cell and stack measurements is maintained by a furnace. Gases are provided from bottles using mass flow controllers. Humidification is provided either by controlled water injection into a heated chamber or by supersaturation and condensation.

All electrochemical data are obtained by DC-methods using galvanostatic control.

3. Results and discussion

Short-term experiments with 'dry' hydrogen (1–3% H_2O) and low fuel utilisations were performed on a single anode-

---

* Corresponding author.
[1] Present address: Institut für Festkörperphysik und technische Physik, Technische Universität München, D-85747 Garching, Germany.
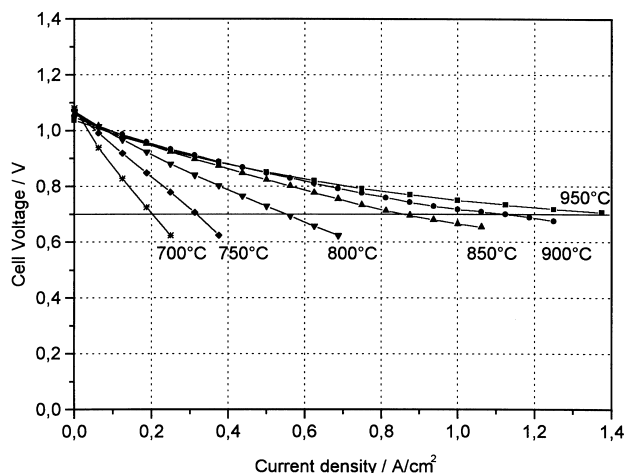
Fig. 1. Current–voltage curves for a 16-cm^2 anode-supported single cell as a function of temperature (H_2 = 1000 ml/min, H_2O = 3%, oxidant = air).
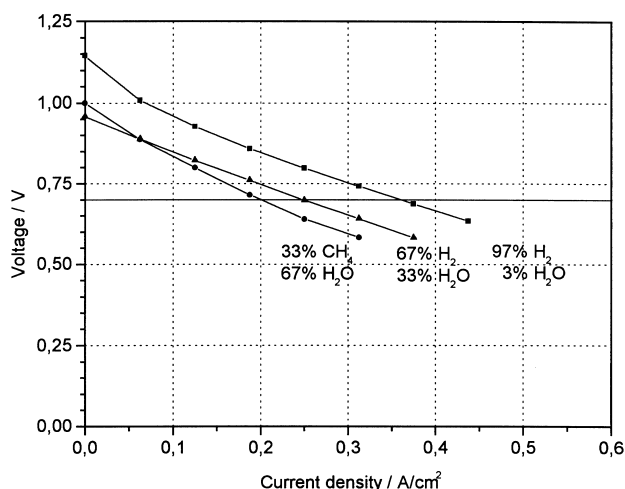

Fig. 2. Comparison of the current–voltage curves for water/hydrogen (H_2 = 2000 ml/min) and water/methane mixtures (CH_4 = 500 ml/min) at 800°C for an anode-supported single cell of 16 cm^2.

supported electrolyte cell of 16 cm^2 active surface area. A set of current–voltage curves for different temperatures is presented in Fig. 1. The current density at 950°C comes to 1.38 A/cm^2 at 0.7 V. More important, the current density at 750°C still reaches 0.32 A/cm^2 at 0.7 V (for details see Table 1).

Table 1

Electrochemical data from the analysis of Fig. 1

Temperature (°C)	Current density at 0.7 V (A/cm^2)	Area specific resistance ($\Omega \cdot$cm^2)
950	1.375	0.269 ± 0.012
900	1.125	0.301 ± 0.005
850	0.860	0.365 ± 0.003
800	0.550	0.594 ± 0.008
750	0.318	1.190 ± 0.032
700	0.203	1.677 ± 0.026

Table 2

Electrochemical data from the analysis of Fig. 3

Temperature (°C)	Current density at 0.7 V (A/cm^2)	Area specific resistance ($\Omega \cdot$cm^2)
950	0.485	0.418 ± 0.012
900	0.434	0.579 ± 0.011
850	0.320	0.762 ± 0.025
800	0.200	1.326 ± 0.034
750	0.132	1.816 ± 0.069

One of the future objectives for the SOFC is the use of natural gas as fuel, preferably utilising internal reforming [5]. In order to obtain a better understanding of the electrochemical performance with natural gas as feed, experiments were performed on a single cell of 5 × 5 cm^2. Current–voltage curves for this cell were measured using different
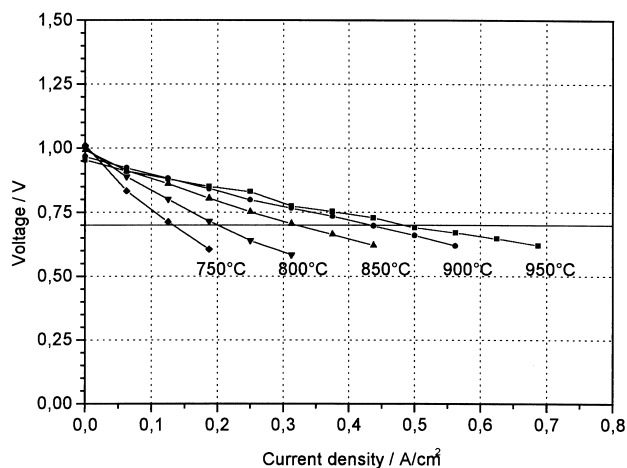

Fig. 3. Current–voltage curves for a 16-cm^2 anode-supported single cell as function of temperature under CH_4/H_2O (ratio 1:2) (CH_4 = 500 ml/min, oxidant = air).
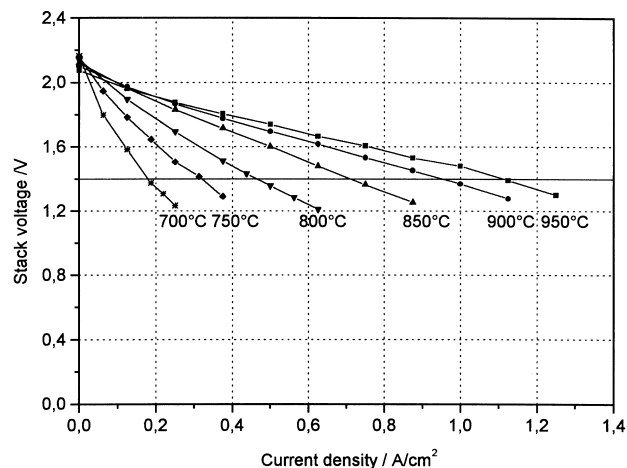

Fig. 4. Current–voltage characteristics of a 2-cell stack as function of temperature (16 cm^2 cell area, fuel H_2/H_2O = 1000:10 ml/min, fuel utilization = 7% at 0.31 A/cm^2, oxidant = air).
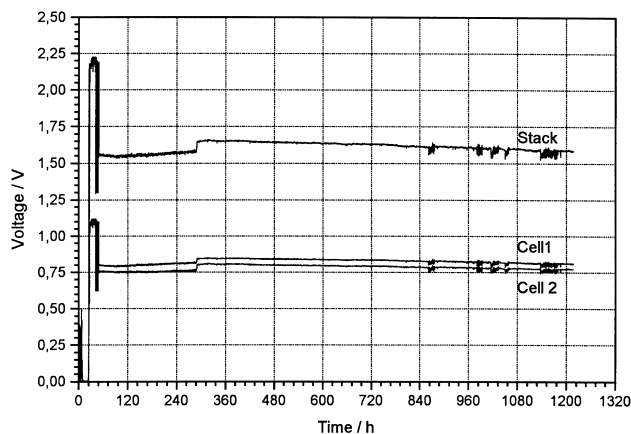
Fig. 5. Time plot of a 2-cell stack at 800°C (16 cm^2 cell area, fuel H_2/H_2O = 1000:10 ml/min, fuel utilization = 7% at 0.31 A/cm^2, oxidant = air).

gas mixtures at 800°C (see Fig. 2). Using conditions comparable to the measurements of Fig. 1, a current density of 0.36 A/cm^2 at 0.7 V was found. These lower values are caused by contact problems between the metal mesh current collectors and the electrodes. When using internal reforming, the fuel gas contains a large amount of water resulting in a high oxygen partial pressure, i.e. a lower open cell voltage (OCV). A fuel gas with 33% water in hydrogen produces an oxygen partial pressure approximately equal to the oxygen partial pressure in the methane/water (1:2) fuel. Due to a lower OCV the current–voltage curve for 'wet' hydrogen only reaches 0.25 A/cm^2 at 0.7 V. The cell resistance however is comparable to the resistance of 'dry' hydrogen as can be obtained from the slope of both curves at 0.7 V. For 'dry' hydrogen the resistance is 0.88 $\Omega \cdot cm^2$ and for 'wet' hydrogen 0.93 $\Omega \cdot cm^2$.

When using a methane/water (1:2) mixture as fuel, the cell performance decreases some what compared to 'wet' hydrogen. A current density of 0.20 A/cm^2 at 0.7 V can, however, still be reached. Comparison of the curves for 'wet' hydrogen and methane shows that the cell resistance increases when using methane (see Fig. 2). The temperature influence on the current–voltage curves of this cell under methane/water (1:2) is shown in Fig. 3. The analysis of these curves is presented in Table 2.

Combining single cells to a stack introduces a number of parameters that can influence the electrochemical perfor-
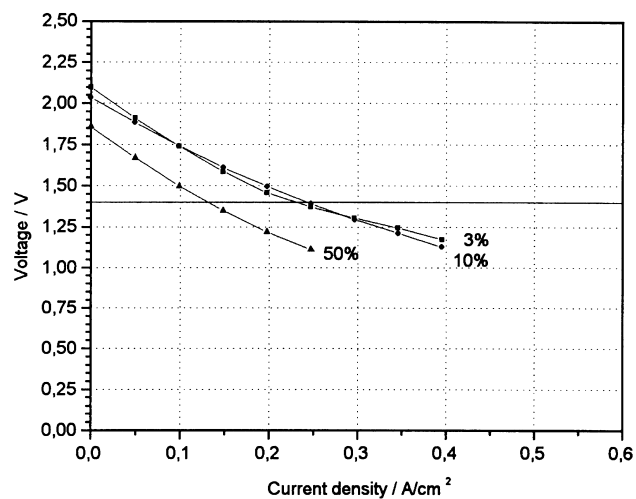

Fig. 6. Influence of the H_2O concentration in the fuel gas on the electrochemical performance of an anode-supported SOFC stack at 800°C (81 cm^2 cell area, fuel H_2 = 3000 ml/min, oxidant = air).

mance of this stack. To study these influences the following experiments were performed.

Using the standard conditions of hydrogen fuel humidified with 1% of water, current–voltage measurements were performed on a short stack containing two cells of 5 × 5 cm^2. At 950°C the current density reaches 1.1 A/cm^2 at our reference potential of 1.4 V (see Fig. 4). This value is somewhat lower than the value of 1.5 A/cm^2 obtained for the single cell of Fig. 1. This difference is caused by the high air utilisation at these current densities. This causes the stack resistance to increase, as can be seen from the bending of the current–voltage curve. At 750°C the current density reaches 0.32 A/cm^2 at 1.4 V (see Table 3). This value is comparable to the value obtained for a single cell (0.318 A/cm^2).

The influence of galvanostatic load on the performance of these short stacks was studied (see Fig. 5). A stack was run for 900 h at 0.38 A/cm^2 and 800°C (fuel = 1% H_2O in H_2, H_2 = 1000 ml/min, utilisation = 7%, oxidant = air). During this period the stack lost 0.073 V. Related to the starting voltage, this represents a degradation of 5% in 1000 h. From current–voltage measurements performed at the start and at the end of these 900 h, a degradation of 64 $\mu\Omega \cdot cm^2$/h could be calculated. This degradation behaviour is typical for these stacks running under these conditions.

Table 3

Electrochemical data from the analysis of Fig. 4

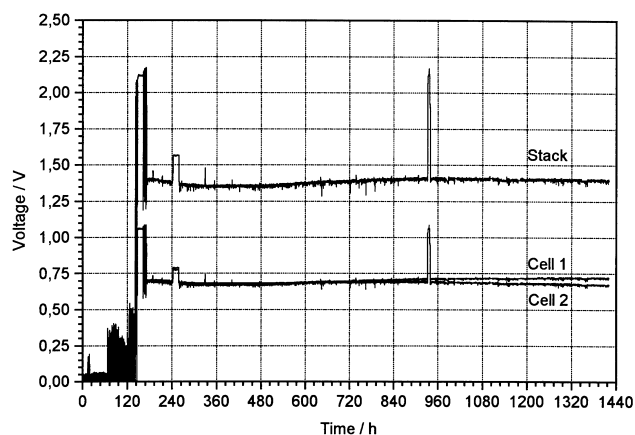| Temperature (°C)	Current density at 0.7 V/cell (A/cm^2)			Area specific resistance ($\Omega \cdot cm^2$)	
	Stack	Cell 1 (top)	Cell 2 (bottom)	Cell 1 (top)	Cell 2 (bottom)
950	1.112	1.073	1.153	0.273 ± 0.003	0.258 ± 0.004
900	0.951	0.922	0.974	0.341 ± 0.004	0.314 ± 0.003
850	0.710	0.700	0.721	0.482 ± 0.004	0.445 ± 0.005
800	0.464	0.464	0.470	0.733 ± 0.007	0.646 ± 0.018
750	0.320	0.321	0.309	0.997 ± 0.037	0.898 ± 0.045
700	0.177	0.180	0.177	1.421 ± 0.104	1.381 ± 0.100

Fig. 7. Stack and cell voltage as function of time of a 2-cell stack running at 0.25 A/cm^2 at 800°C under 50% H_2O (16 cm^2 cell area, fuel H_2 = 1000 ml/min, fuel utilization = 6.1%, oxidant = air).

The influence of the water concentration in the fuel on the performance of the anode-supported cells was studied using a 2-cell short stack of 10×10 cm^2 cells at 800°C. For 'dry' hydrogen (3% H_2O) a current density of 0.25 mA/cm^2 is obtained at 1.4 V (see Fig. 6). This value is lower than expected from previous experiments. This is most likely due to problems with the electrical contact between the bipolar plates and the electrodes. Due to a lower open cell voltage, the current density at 1.4 V will be lower for higher water concentrations. A comparison of the stack voltage at 0.13 A/cm^2 (the 1.4 V point for 50% H_2O) between the curve for 3% H_2O and 50% H_2O shows a potential difference of 0.241 V. This value is almost equal to the value of the difference in open cell voltage of 0.239 V under these conditions. This result is comparable to the results for the single cell. This indicates that the current controlling processes are not influenced by the water vapour concentration.

In order to study the influence of the water vapour concentration on the stability of the electrochemical performance, a short stack has been running at 800°C and 0.25 A/cm^2 (fuel = 50% H_2O in H_2, H_2 = 1000 ml/min, utilisation = 6.2%, oxidant = air). During the first 100 h of constant current operation, the stack voltage dropped rapidly at a rate of 0.2 V/1000 h (see Fig. 7). This process stopped and after 300 h of operation, the stack voltage climbed to values comparable to or better than the starting values. This short stack has now been running for more than 1400 h. After approximately 800 h of operation, cell 2 starts to degrade at a rate comparable to the rates for 'dry' hydrogen. The voltage of cell 1 seems to reach a maximum value after 1300 h of operation. For this cell no degradation rates can be determined. The different behaviour of these two cells can have several causes, like a bad (and worsening) contact of one cell or a gas leakage in the sealing near one cell, not affecting, however, the other.

4. Conclusions

- Both the anode-supported thin electrolyte single cells as well as the short stacks built with these cells show excellent electrochemical characteristics compared to electrolyte-supported cells, especially at temperatures of 800°C and below. A large problem, however, is the electrical contact between the current collectors and the electrodes.
- The amount of water in the fuel gas lowers the open cell voltage due to the increased oxygen partial pressure. The cell resistance, however, is virtually unaffected.
- When driven on 'dry' hydrogen (1–3% H_2O) and low fuel utilisation (<10%), a degradation of 5% in 1000 h is observed.
- When using 50% H_2O in hydrogen as fuel gas, the behaviour of the cells is quite different. The degradation seems slower than observed for 'dry' conditions.
- Internal reforming using methane/water (1:2) is possible with these anode-supported thin film electrolyte cells. The current densities obtained are somewhat lower than under operation with hydrogen/water mixtures of comparable oxygen partial pressures. The cell resistance for methane/water is only slightly higher than for hydrogen/water up to current densities of around 0.3 A/cm^2.

Acknowledgements

References

[1] H.P. Buchkremer, U. Diekmann and D. Stöver, in B. Thorstensen (ed.), *Proc. 2nd Eur. SOFC Forum 1996*, U. Bossel, Morgenacherstrasse 2F, CH-5452 Oberrohrdorf, Switzerland, 1996, pp. 221–228.

[2] L.G.J. de Haart, Th. Hauber, K. Mayer and U. Stimming, in B. Thorstensen (ed.), *Proc. 2nd Eur. SOFC Forum 1996*, U. Bossel, Morgenacherstrasse 2F, CH-5452 Oberrohrdorf, Switzerland, 1996, pp. 229–235.

[3] H.P. Buchkremer, U. Diekmann, L.G.J. de Haart, H. Kabs, U. Stimming and D. Stöver, in U. Stimming, S.C. Singhal, H. Tagawa and W. Lehnert (eds.), *Proc. 5th Int. Symp. on SOFC*, Vol. 97–40, The Electrochemical Society, Pennington, NJ, 1997, pp. 160–170.

[4] R. Wilkenhöner, W. Mallener, H.P. Buchkremer, Th. Hauber and U. Stimming, in B. Thorstensen (ed.), *Proc. 2nd Eur. SOFC Forum 1996*, U. Bossel, Morgenacherstrasse 2F, CH-5452 Oberrohrdorf, Switzerland, 1996, pp. 279–288.

[5] J. Meusinger, E. Rienche and U. Stimming, *J. Power Sources, 71 (1–2)* (1998) 315.