LONG TERM STABILITY OF SOFC WITH SC DOPED ZIRCONIA ELECTROLYTE

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ABSTRACT

10 mol% scandium doped ZrO₂ (10ScSZ) was investigated as an electrolyte material for electrolyte supported single cells. The cells with an electrolyte thickness of 200 μm and an electrode area of 10 cm² have been characterised by I/V- measurement and impedance spectroscopy. To decrease the ohmic losses, 10ScSZ was applied for the electrolyte substrate as well as in the anode cermet and the multilayer cathode. To decrease the cathodic polarisation losses a LSM thin film cathode layer covered by a screenprinted LSM layer was applied. A maximum power density of 0.35 W/cm² at 800 °C was achieved in air (0.7 l/min) and hydrogen (0.5 l/min). Long term measurements at 950 °C for more than 3500 h at a current density of 400 mA/cm² showed a significant increase in electrical power output during the first 1000 h.

INTRODUCTION

A main part of the power losses in the state of the art single-cells which consists of a 8YSZ-electrolyte-substrate (8YSZ: 8 mol% Y₂O₃ doped ZrO₂) with LSM cathode- and Ni/8YSZ-cermet anode-layers, occurs due to the polarisation resistance of the cathode/electrolyte interface. For lower temperatures the ohmic part increases with decreasing temperature. To minimise the ohmic losses the single cell (10ScSZ) should be subsequently applied for the electrolyte as well as the cermet anode and the composite cathode (1). The polarisation resistance which occurs mainly at the cathode side directly correlates with the number of three phase boundaries (TPBs) or/and the effective electrolyte surface area. The electrochemical reaction in a porous LSM-cathode is restricted to the (TPB) among cathode, oxidant and the electrolyte surface (2). Some improvement of LSM-cathodes have been realised by several groups using additional intermediate layer consisting of mixtures of LSM- and 8YSZ-particles (3,4). These interlayers show a better compatibility to the electrolyte because of the matched thermal expansion coefficient and the increased effective electrolyte surface area due to the 8YSZ-grains in this layer which exhibit a direct contact with the electrolyte surface, that is, the electrochemical reaction can take place all over the surface of this particles. Cathodes consisting of a mixture of electrolyte- and cathode-particles show a disadvantaged effect. The 8YSZ-particles which have no direct contact with the electrolyte in the cathode decrease the electronic conductivity as insulators.

To optimise the electrochemical active surface area, a well defined three-dimensional penetration structure between the cathode and the electrolyte was applied (5) by screen
printing of individual particles consisting of 10ScSZ. All 10ScSZ-particles in the cathode are in contact with the electrolyte, which obtains a significant increase of the electrolyte surface. To obtain a large amount of TPBs, a thin, nanoporous, electrochemical active cathode-layer which completely covers the electrolyte surface is applied. This layer has a high electronic conductivity, a sufficient thickness and continuity to avoid ohmic losses due to the electron transport. An additional LSM-layer with a high porosity are applied as a current collector and gas distribution layer. A schematic image of such a modified cathode is given in Fig. 1.

![Fig. 1 Scheme of a standard (left) and a modified (right) cathode. In case of the standard cathode, the TPBs are restricted to the surface of the electrolyte substrate. The modified cathode has a large number of TPBs all over the enlarged electrolyte surface.](image)

**EXPERIMENTAL**

Electrolytes were prepared using 10ScSZ-green tapes (Kerafol) and 10ScSZ-powder (Kerafol). The ceramic particles were prepared by sintering the 10ScSZ-powder at 1350 °C for 1 h. The agglomerated particles were afterwards manually ground and sieved (Rotary sieve shaker). After the preparation the particles which have an average diameter of approx. 14μm, were screen printed on green tapes and sintered at 1550 °C for 2 hours to get a structured 10ScSZ electrolyte. The sintered substrates had a size of 50 x 50 mm² and a thickness of 200 μm. A cermet anode consisting of a NiO/10ScSZ-mixture, was screen printed on the opposite side and sintered at 1400 °C for 5 hours. The electrode area was 10 cm².

To prepare a cathode which exhibits a decreased polarisation loss, a metal organic deposition-layer (MOD) was applied on top of the structured electrolyte by a spin coating process. The thin MOD-layer consists of A-side deficient LSM (LSM: La₀.₇₅Sr₀.₂MnO₃). The metal organic precursors are synthesised using La₂(CO₃), Mn(II)-acetate and Sr metal. The synthesis is performed by reacting these components solely in propionic acid. After precipitation and filtration the metal organic precursors are isolated as storable powders and mixed in the target stoichiometry. A subsequent heat treatment leads to the formation of the oxide ceramic film with perovskite type structure. An additional LSM-layer was screen printed on the MOD-layer as a current collector and a gas distribution layer. This layer, consisting of larger LSM-particles (d₅₀ = 3 μm), had a thickness of 350 μm.
about 30 µm and a porosity of about 35% after sintering at 1000 °C for 2 hours. In addition similar cells were prepared using 8YSZ for the structured electrolyte substrate and the cermet anode.

Both types of single cells were tested under realistic operating conditions using a specially designed equipment. They were installed in a Al₂O₃-housing, the cathode and the anode were contacted with a platinum-grid and a Ni-mesh respectively. The Al₂O₃-housing was located in a furnace which enables operating temperatures between 500 °C and 1000 °C. The gas supply to the electrodes was realised by channels in the housing, the flow rate was controlled by digital mass flow controllers. The anode was fed with a mixture of H₂ and H₂O (0.5 l/min at standard conditions 0 °C, 1013 mbar (slm), 0 ~ 80 % H₂O to simulate the fuel utilisation of preceding cells in a stack). On the cathode side 0.7 slm air was supplied. An electronic load was used to adjust the current. I/V-characteristics and impedance spectra were recorded as a function of temperature, fuel utilisation and operating time. During the cell test the cell voltage, the open circuit voltage and the voltage losses of the anode and the cathode were observed by a Keithley DMM 2000 voltmeter. The impedance spectra were measured in a frequency range from 100 mHz to 1 MHz with an amplitude I_{amp} = 60 mA under current flow conditions (0.5 to 10 A) and I_{amp} = 40 mA, I_{bias} = 40 mA under open circuit conditions.

The conductivity of the electrolyte materials was characterised as a function of temperature by 4 point dc conductivity measurement (6). In addition long term 4 point conductivity measurements with typical current densities (300 mA/cm²) for SOFC single cells have been performed for about 400 h.

The microstructure of the different modified cathode layers were characterised by optical and scanning electron microscopy before and after operation.

RESULTS AND DISCUSSIONS

After sintering the structured 10ScSZ-substrate, the morphology of the applied 10ScSZ-layer was investigated. The 10ScSZ-particles exhibited a good mechanical adhesion on the 10ScSZ-substrate. The good contact between the particles and the substrate was only achieved if the 10ScSZ-layer is printed onto the green tape. The SEM image of a structured MOD-cathode (Fig. 2) shows a ScSZ-particle sintered onto the 10ScSZ-electrolyte substrate.

Fig. 2 The scheme and the SEM image of a modified cathode. The LSM-MOD-layer is not visible due to its thickness of only 80 nm.

Electrochemical Society Proceedings Volume 2001-16

351
The LSM-MOD-layer, which covers the whole electrolyte surface, is not visible in this magnification, because the thickness of this layer is only about 80 nm. On top of the layer the porous LSM-layer is visible.

The power density of the single cells with the 10ScSZ-electrolyte was slightly larger than that with the 8YSZ-electrolyte at 950°C (Fig. 3). This increase is explained by the higher ionic conductivity of 10ScSZ compared with that of 8YSZ at 950 °C. On the other hand it must be considered that the microstructure and the density of the 10ScSZ-electrolyte substrate is quite poor compared to the 8YSZ-substrate. The lower OCV of the 10ScSZ-cell can not be explained by an open porosity or an electronic conductivity of the 10ScSZ-electrolyte. It occurs due to the poorer sealing of the ceramic sealing frames of the single cell, resulting in the roughness of the 10ScSZ substrate.

![I/V- characteristics of SOFCs with 10ScSZ- and 8YSZ-electrolyte at 950 °C.](image)

At 800°C the electrical performance of the 10ScSZ-electrolyte single cell is significantly higher than that of 8YSZ (Fig. 4). This can be explained by the high conductivity of 10ScSZ at lower temperatures (Fig. 5). Due to the continuous application of 10ScSZ for the electrolyte as well as the cermet anode and the multilayer cathode, not only the ohmic losses within the electrolyte substrate have been decreased. The improved transport property of the electrolyte material within the electrode structures results in decreased losses due to the improved oxide ion transport via the electrolyte particles. The influence of the current constriction within the structured electrolyte will be lowered, and therefore the current via the surface of the electrolyte particles is increased i.e. the current density distribution at the enlarged electrolyte surface will be more homogeneous.
To evaluate the suitability for electrical power generation, the long term stability at reasonable electrical load (400mA/cm²) was examined for the 8YSZ and 10ScSZ single cells. Due to the enhanced degradation at high operating temperatures the cells were operated at 950 °C for 3500 h. Impedance spectra were also recorded during the long term measurements. The initial impedance spectra and the impedance spectra after the operation for 3500 h of a 10ScSZ single cell is shown in Fig.6. The high polarisation...
resistance in the low frequency part of the spectra is due to the zero load conditions of the cell. The slight decrease of the polarisation resistance during the operation for 3500 h in the medium frequency part is attributed to a decrease in the cathodic polarisation resistance. No degradation of the electrolyte was observed (see Figure 6). In case of the 8YSZ cells an increase of the electrolyte resistance as well as of the polarisation resistance was observed after the operation for more than 1000 h (Fig. 7). The long term 4-point conductivity measurements of 10ScSZ and 8YSZ electrolyte substrates at 300mA/cm² and 900°C revealed the same behaviour on the electrolyte conductivity (Fig.10).

Fig. 6 Impedance spectra of a 10ScSZ single cell before and after long term testing.

Fig. 7 Impedance spectra of an 8YSZ single cell before and after long term testing.
The long term measurements of 10ScSZ single cells at 950 °C and 400 mA/cm$^2$ showed a significant increase in power density during the first 1000 h (Fig. 8). The cell voltage increases from 0.7 V to 0.85 V. This might be due to a formation of the cathode (7) and an in situ sintering of the electrolyte substrate which initially showed a slight porosity. The significant decrease of the power density for 1000 to 3180 h caused a failure in the gas supply system. After the fuel flow rate was set to its initial value at 3180 h, the high cell performance returned.

Fig. 8 Long term measurement of a 10ScSZ-single cell at 950 °C and 400 mA/cm$^2$.

Fig. 9 Long term measurement of a 8YSZ-single cell at 950 °C and 400 mA/cm$^2$. 
The long term stability of an 8YSZ single cell is shown in Fig. 9. The degradation of this type of cell seems to be quite similar. In consideration of the "degradation" due to the gas supply failure including a partial oxidation of the anode during the gas supply breakdown and the fact that a not optimised Ni/10ScSZ cermet anode was applied, the 10ScSZ cells can be respected to have a better long term stability than 8YSZ cells. Long term measurements of the different electrolyte substrates showed nearly no degradation of 10ScSZ whereas a significant decrease in conductivity was observed for 8YSZ (see Fig. 10).

![Graph](image-url)

Fig. 10 Comparison of long term conductivity measurements of 8YSZ and 10ScSZ-electrolyte substrates at 900°C.

**CONCLUSION**

The comparison of electrolyte supported single cells based on 8YSZ and 10ScSZ, which were used for the electrolyte substrate as well as the Ni/YSZ cermet anodes and the multilayer cathodes revealed that 10ScSZ cells show only a slight better performance at 950 °C and a significantly better performance at 800 °C than 8YSZ cells. The long term stability of the single cells is improved by the application of 10ScSZ instead of 8YSZ. Impedance spectroscopy measurements of the single cells as well as long term conductivity measurements showed that no degradation of the conductivity of the 10ScSZ electrolyte occurs. 10ScSZ seems to be superior than YSZ due to not only its higher conductivity but also the improved long term stability.

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