CHARACTERIZATION OF SOFC SINGLE CELLS

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ABSTRACT

The characterization of SOFC-materials and single cells with respect to their performance in an SOFC-system exhibits many sources of errors. The influence of the test setup like electrode arrangement, gas distribution, sealing and current collection, as well as the realization of the different operating conditions like operating temperature, gas supply and fuel utilization, on the electrical properties of a single cell have been studied by testing the same types of cells using different testing equipment and conditions. Furthermore the usability of in situ impedance spectroscopy and characterization with reference electrodes to obtain additional information about the different losses and degradation mechanisms under realistic working conditions has been investigated. Errors due to the application of reference electrodes in planar single cells in case of an electrode misalignment have been evaluated by FEM-modeling and testing appropriate cells. The testing environment and conditions have a significant impact on the apparent single cell performance and electrode properties.

INTRODUCTION

In the development of SOFC-materials and components, live tests of single cells are one main focus (1). The electrical characterization of single cells under realistic operating conditions is often conducted in a ceramic housing with noble metal current collectors and sealing namely in an "inert" testing environment using materials which should not affect the single cell (2,3). Nevertheless there might be some problems due to the gas tightness in sealing or the contact resistance in between the electrode and the current collector, which may have an influence on the single cell performance and the long term stability. Another way for the electrical characterization of single cells are short stack tests. The cell integrates an arrangement of functional interlayers, sealant and ceramic or metallic interconnectors. In this testing environment the influence of the materials for the setup might be more significant but much close to reality of the SOFC-system (4,5). In case of single cell tests the operating temperature has to be adjusted by an electrical furnace, because the waste heat in a single cell is not sufficient for keeping an appropriate operating temperature. The heat produced by the internal losses of the cell or by the combustion of fuel due to leakage as well as the heat consumed for heating up the gases or internal methane reforming has to be considered. Choosing an appropriate gas supply is an additional problem for single cell tests. Depending on the size of the single cells and the active electrode area reasonable gas flow rates have to be chosen. Operating on an oxidant (air) excess is quite realistic for SOFC-systems. The required fuel
utilization (~80%) may be achieved by applying a small fuel flow rate (5). In that case there will be lateral gradients in the fuel composition and therefore an inhomogeneous current density distribution. If the testing setup exhibits no ideal gas tightness a part of the fuel will be consumed due to the leakage. The fuel utilization can also be simulated by mixing an appropriate amount of reaction products (H₂O, CO₂) to the fuel. In that case, a high fuel flow rate can be applied to the cell resulting in a homogeneous fuel composition and current density all over the electrode area. Varying the simulated fuel utilization (0 to 80%) allows the calculation of the average current density of this type of cell in a stack (6).

**Materials**

| Cr | 5Fe | 1 Y₂O₃ |
| (La,Sr)CrO₃ |

**Components**

- bipolar plate
- protective coating + functional layer (c)
- single cell
- functional layer (a)
- joining material
- housing
- contact grid
- sealant
- Pt, Au
- Au, Al₂O₃
- Ni

**Problems**

- corrosion
- Cr-evaporation
- contact resistance
- interdiffusion of sealant
- contact resistance
- Pt-segregation
- Au-segregation
- gas tightness
- carbon deposition

![Fig. 1 Test setups for single cells: short stack (top) resp. "inert" setup (bottom).](image)

To obtain additional information about electrochemical processes and loss mechanisms the overall losses occurring in the cell have to be split up into several parts. These parts have to be attributed to the different cell components i.e. the electrolyte, the interlayers and the electrodes. In case of a special test cell geometry it is easier to obtain precise information of the individual electrodes because anode and cathode can be characterized separately using reference electrodes. Depending on the single cell concept and the applied production technology the properties of the electrodes significantly depend on the processing. Therefore it is often impossible to use the optimized test cell geometry. The characterization of the individual electrode properties under operating conditions in single cells with thick (50...200 µm) or thin film electrolyte (< 50 µm) with reference electrodes exhibits many sources of error (7). The objective of the present investigations is to clarify the influences of the testing environment on the performance and the long term stability of single cells.

**EXPERIMENTAL**

The experiments were carried out using electrolyte supported single cells based on a 150 or 200 µm thick 8YSZ-substrate with a size of 50 x 50 mm². A Ni/YSZ-cermet-anode and a single layer LSM-cathode (La₀.₇Sr₀.₃MnO₃) were screenprinted onto the substrate using an EKRA Microtronic 2-K screenprinting machine with optical positioning system and sintered at 1300 °C (8). Some of the experiments have been conducted using single cells with an high performance cathode (9). The active area of the working electrode was 16, 10 or 1 cm², the reference electrode area was about 0.25 cm².
The single cells were mounted into ceramic housings, the electrodes were contacted by platinum, gold or nickel meshes. Gold- or ceramic frames were used for sealing. Additional measurements were performed using a non sealed short stack testing setup with metallic current collectors. The single cells were operated under different operating conditions. I/V-characteristics and impedance spectra were taken at different gas flow rates (0.02 slm to 0.5 slm, p ≈ 1 atm), oxidant- and fuel-gas compositions (air, N₂, O₂ / H₂, H₂O) and temperatures.

Fig. 2 Test rig for single cell tests.

The contact resistance, i.e. the additional ASR (area specific resistance) due to the contacting meshes used as a current collector for single cell testing was examined by mounting an about 500 μm thick LSM- or Ni/YSZ-substrate in the fuel cell testing rig. Pt-mesh, Au-mesh and Pt-mesh + Pt-Paste on the LSM-substrate surface and a Ni-mesh

Fig. 3 Electrode configuration for measurements via reference electrodes.

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on the Ni/YSZ-substrate surface was used as a current collector. The substrate was contacted with the same arrangement on both sides. The contact resistance was obtained at a current density of 1 A/cm² (see Fig. 4). Single cells with different electrode configurations have been prepared to clarify the influence of an electrode displacement on the individual electrode losses determined with reference electrodes. Single cells with an electrode configuration shown in Fig. 3 were produced with well defined electrode displacements, i.e. the working and the reference cathodes were shifted against the working and the reference anodes. Additional FEM-calculations for the investigated electrode configurations using appropriate values for the conductivity of the different materials and the polarization resistance were carried out with the software tool Maxwell. An electrical model of the cell consisting of different layers with appropriate electrical conductivities was established. The polarization resistance of the electrodes was modeled by a 1 μm thick layer with a corresponding resistivity.

RESULTS AND DISCUSSION

Sealing and open circuit voltage

After mounting the cell in the ceramic housing, the furnace was heated up to 1000 °C to obtain a sufficient contact between the current collectors and the electrodes. In case of sealing with gold-frames a temperature near the melting point of gold is necessary to get a gas tight contact between the housing and the electrolyte because of softening the gold seal. In the next step the fuel gas (usually H₂ + H₂O) is applied to reduce the NiO in the anode cermet to Ni metal. Applying a H₂- and an air-flow of 0.5 slm each, an open circuit voltage of about 1.1 V to 1.2 V is achieved. Operating the cell in dry hydrogen leads to significant OCV-gradients due to an inhomogeneous distribution of water vapor arising from leakage in sealing. The lateral OCV-variations were measured at different hydrogen flow rates (Table 1). This values can be used to calculate the leakage of the setup resulting in an additional fuel consumption due to the oxygen admitted to the fuel gas at the anode.

| fuel flow rate | H₂ 0.5 slm | H₂ 0.25 slm | H₂ 0.1 slm | H₂ 0.05 slm | H₂ 0.02 slm | O₂-leakage / slm |
|---------------|-----------|-----------|-----------|-----------|-----------|-----------------|
| OCV₁          | 1166      | 1138      | 1099      | 1066      | 1016      | 0.0008 - 0.0014 |
| U₉(0 A)       | 1170      | 1140      | 1098      | 1062      | 1008      | 0.0009 - 0.0013 |
| OCV₂          | 1156      | 1125      | 1083      | 1048      | 996       | 0.0012 - 0.0017 |

Table 1 OCV at different positions in the testing setup shown in Fig. 3.

Disregarding other problems discussed later, the use of reference electrodes for determining the individual electrode losses in dc-measurements is possible if the oxygen chemical potential at the reference electrode is the same as at the working electrode. Otherwise the electrode losses (U_cathode 1,2 and U_anode 1,2 in Fig. 3) will be falsified due to an offset voltage. In case of operation on humidified hydrogen (10 % H₂O at H₂ flow rates of 0.1 to 0.5 slm) the OCV-variation of the different electrodes was within 2 mV. This means that appropriate gas flow rates and compositions are required to be achieved a homogeneous lateral potential distribution and current density over the whole electrode area. A lateral gradient of the oxygen chemical potential over the electrodes of a single cell will result in a compensation current even under OCV conditions.
Contact resistance between current collector and electrode

The initial contact resistance in between a cathode and a current collector was about 1 $\Omega \text{cm}^2$ in case of a Pt- or Au-mesh in direct contact with an LSM surface. It decreased by about 2 orders of magnitude during heating up to about 980 °C. The contact resistance significantly depends on the applied load. The contact weight (Fig. 2) was about 80 g/cm². In case of the substrate with Pt-Paste on the surface the initial contact resistance was significantly small (~ 0.1 $\Omega \text{cm}^2$). The temperature dependence of the ASR of the different current collectors (Fig. 4) was evaluated during cooling down. The resistance of the porous Ni/YSZ- and ULSM-substrate, evaluated by 4-point dc conductivity measurements, were more than one order of magnitude smaller than the contact resistance values and therefore were neglected. Provided that the electrode surfaces are completely contacted with the current collectors, at typical SOFC operating temperatures (600 ... 1000 °C) the overall contact resistance is about two orders of magnitude smaller than the total ASR of the cell. The additional voltage losses due to the contact resistance will be less than 10 mV at a current density of 1 A/cm².

Fig. 4 Additional area specific resistance (contact resistance) between electrode and each current collector as a function of temperature.

Impact of the test setup on the (long term) stability of the cell

One aim of single cell tests in an "inert" environment is to get information about the performance and the long term stability of the investigated cells without any influence due to the surroundings. The losses and the degradation should be restricted to the layers and the interfaces within the cell, i.e. there should be no interdiffusion or segregation of materials from the testing equipment. For short time tests with operation times of some hundred hours this requirement is adequately fulfilled, whereas there might be a significant influence on the cell performance during long term tests. For example, a segregation of gold from the sealing frame in the anode and on the anode surface, as well as a segregation of platinum from a current collector to the cathode/electrolyte interface, has been observed during long term tests.
Fig. 5 Segregation of gold from the sealing frame during operating at 1030 °C for 800 h. Microprobe analysis revealed, that Ni/Au-crystallites were formed in and on the anode. The segregation of gold is restricted to the electrode area near the sealing frame.

These effects are enhanced with operating temperature and time. The formation of Ni/Au-alloy particles might have an influence on the anode performance due to the depletion of nickel in the cermet, whereas the platinum deposition showed no significant influence on the cell performance. In case of Au-meshes used as the current collector on the cathode the cell showed the same performance and a similar long term stability. The use of gold meshes for current collection is advantageous because no deposition of gold was found within the cathode.

Fig. 6 Segregation of Pt to the cathode/electrolyte interface after 4500 h of operation at 850 °C / 200 mA/cm². The Pt-deposition is restricted to the interface area.

Operating temperature, fuel- and oxidant-utilization

The influence of the gas flow rate and the simulated fuel utilization on the performance of a single cell is shown in Fig. 7 and Fig. 8, respectively. With increasing fuel flow rate, the cell voltage at I = 0 A/cm² significantly increased, whereas the oxidant flow rate has no significant influence (Fig. 7). The power density of the cell as well as the shape of the I/V-characteristic is strongly depending on the fuel and oxidant utilization as well as on the way the gas utilization is realized. Especially for basic electrode and single cell tests, operating the cell with a simulated fuel utilization by adding 3 to 90 % water vapor to the fuel at a high fuel flow rate is advantageous because in that case the oxygen chemical potential is nearly constant all over the electrode. Therefore a homogeneous current density and temperature distribution associated with the same amount of ohmic and polarization losses can be achieved.
Fig. 7 I/V-characteristics of a single cell at different gas flow rates.

Fig. 8 I/V-characteristics of a single cell at different simulated fuel utilization.

Fig. 9 shows the I/V-characteristics of a single cell with high performance cathode in different testing setups. The properties of the cell significantly depend on the testing equipment as well as on the applied gas composition and flow rate. Due to the absence of a standardized technical regulation for single cell tests, a comparison of the performance of different types of single cells characterized in different testing environments is almost impossible. The I/V-characteristics in Fig. 9 show a significant hysteresis due to the increase in temperature at high current densities. In this setup the operating temperature was acquired by a thermocouple in the cell housing (i.e. 5 mm underneath the fuel gas channel) which suggests the operating temperature of the cell to be significantly higher. If the I/V-characteristics are analyzed disregarding the ohmic heating there might be significant errors in the determined electrode properties.
Fig. 9 I/V-characteristics of one type of electrolyte supported single cell logged in two different testing setups with different gas flow rates and compositions.

**Planar single cells with reference electrodes**

Single cells with different electrode arrangements as shown in Fig. 3 have been characterized by dc- and ac measurement techniques. In case of a large electrode displacement of about 1 mm significant errors were observed \( (U_{\text{cathode,1/2}}, U_{\text{anode,1/2}} \) in Fig. 10, right), whereas in case of a slight displacement of about 100 μm the errors of the electrode losses \( (U_{\text{cathode,1/2}}, U_{\text{anode,1/2}} \) in Fig. 10, left) were very smaller than the ohmic loss of the electrolyte i.e. the electrolyte losses are not equally distributed to the electrodes.

Fig. 10 I/V-characteristics of single cells with different electrode displacement.

These results are in good agreement with FEM calculations shown in Fig. 11. In case of slight electrode displacements the given equivalent circuit can be used as an approximation. The ohmic losses in the electrolyte are divided into two parts \( (I R_{\text{electrolyte,1}}, I R_{\text{electrolyte,2}}) \) which have to be subtracted from the measured cathodic and anodic overvoltage to calculate the polarization resistance of the individual electrodes. The electrolyte losses \( R_{\text{electrolyte,1}} \) and \( R_{\text{electrolyte,2}} \) can be determined with impedance spectra (Fig. 12).
The influence of the electrode displacement on the impedance spectra is shown in Fig. 12 and Fig. 13. Fig. 14 shows the cross sections of the corresponding cells. Only in case of a slight electrode displacement and a constant gas composition at the working and the dedicated reference electrodes no significant influence of electrode arrangement on the impedance spectra were observed (Fig. 12, top). The spectra acquired via the reference electrodes RE1 and RE2 are shifted according to the potential distribution within the electrolyte. In case of operating on dry hydrogen the shape of the impedance spectra is influenced by the position of the reference electrode due to the lateral inhomogeneity in the gas composition (Fig. 12, bottom). In case of large electrode displacements the impedance spectra are seriously affected (Fig. 13) and can not be used for determining the individual electrode properties.
Fig. 13 Impedance spectra of a single cell with an electrode displacement of 1 mm (see Fig. 14, top).

![Impedance spectra](image)

Fig. 14 SEM images of the cross sections of the investigated single cells with different electrode displacement.

![SEM images](image)

CONCLUSIONS

The performance of single cells characterized under "realistic operating conditions" significantly depends on the way how these conditions were achieved. The design of the test setup and the single cell as well as the realization of the operating parameters like gas flow, composition and temperature might result in a broad variation in cell performance of the same type of single cell. Even an "inert" testing environment might have an impact on the long term stability of the cell. The usability of reference electrodes for the characterization of the individual electrodes of a planar electrolyte supported single cell depends on the electrode arrangement and the precision the electrodes are aligned. The results obtained by DC- and AC-measurement techniques via reference electrodes on planar single cells will be deteriorated with increasing electrode displacement. In case of electrode supported single cells the application of reference electrodes is not suitable.
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