Journal of the European Ceramic Society 21 (2001) 1813–1816

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Modelling and DC-polarisation of a three dimensional electrode/electrolyte interface

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Received 4 September 2000; received in revised form 7 December 2000; accepted 15 December 2000

Abstract

A finite element model (FEM) was developed which is able to calculate and predict the electrical performance of a solid oxide fuel cell (SOFC) with a three dimensional interface between cathode and electrolyte. An enlargement of the electrochemical active surface leads to a significant increase of the electrical performance of a SOFC. Various three dimensional electrolyte/electrode interfaces have been realized by first screen printing of individual 10YSZ particles onto a flat and dense 8YSZ substrate. Surface enlargements between 10 and 50% have been realised and investigated. Second, a screen printed cathode (LSM) layer was applied as a current collector and gas distribution layer. In order to develop a FEM-model for this type of cathode/electrolyte interface, several electrical properties of cathode (LSM) and electrolyte (8YSZ) were examined. Further on, measurements of symmetrical cells (LSM/8YSZ/LSM) to evaluate the electrode resistance R_0 were carried out for different symmetrical cells. Taking into account the enlargement of the interface surface, electrical conductivity and electrode resistance R_0, the entire DC polarisation-resistance R_{pol} could be calculated by FEM.

Keywords: Electrical properties; Fuel cells; Impedance spectroscopy

1. Introduction

Fuel cells are an attractive alternative for stationary energy production applications because of their high power generation efficiency. A main part of the power losses in planar solid oxide fuel cells (SOFCs) occurs due to the polarization resistance of the cathode/electrolyte interface [1]. The electrochemical reaction in a porous LSM-cathode is restricted to the three phase boundary (tpb) between cathode, oxidant and the electrolyte surface. Therefore a decrease of the cathode resistance is achievable by an increase of the tpb or/and the effective electrolyte surface area.[2]

A decrease of the polarisation resistance and therefore an increase of the electrical output is possible by a well defined three-dimensional penetration structure between cathode and electrolyte. An additional screen-printed LSM-layer with large LSM-grains and a high porosity was applied as a current collector and gas distribution layer. A schematic sketch of the modified cathode is given in Fig. 1.

In the first part of this paper the preparation of SOFC-single cells and symmetrical cathode cells with a structured cathode is reported, the second part deals with the comparison between electrical measurements and calculations of the polarisation resistance by FEM. The calculations by FEM has been carried out with regard to the electrical conductivities of the interface materials at elevated temperatures and by implementation of the geometrical size of the interface. The calculation of the electrochemical active interface of cathode and electrolyte by the FEM provides an opportunity to tailor the shape of the interface in order to lower internal losses and therefore to increase the electrical power output.

2. Experimental

SOFC and symmetrical cathode cells were prepared using an 8YSZ-green tape (8YSZ: Tosoh TZ-8Y) which was covered with an appropriate YSZ-layer by screen printing. The covered substrates were sintered at 1550°C for 1 h. The sintered substrates had a size of 50×50 mm

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0955-2219/01/$ - see front matter
PII: S0955-2219(01)00121-2

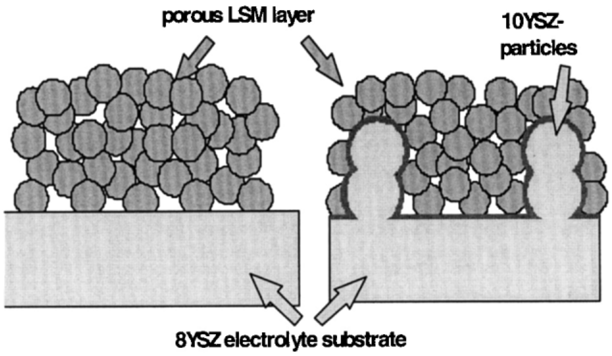

Fig. 1. Scheme of a standard (left) and a modified (right) cathode.

and a thickness of 200 μm. The influence of the effective interface area was increased stepwise by preparing a series of specimens with varied YSZ-particle content in the screen printing paste to increase the electrochemical active area. The electrolyte surface enlargement was determined by optical microscopy and image analysis, assuming that the sintered individual particles have a spherical shape. A conventional cermet anode consisting of a mixture of 75% NiO and 25% 8YSZ, was screen printed on the opposite side and sintered at 1350°C for 5 h, was used. An ULSM-layer (ULSM: Lanthanum deficient LSM $La_{0.75}Sr_{0.2}MnO_3$) was screen printed onto the structured electrolyte, working as a current collector and gas distribution layer. This layer, consisting of larger ULSM-particles ($d_{50} \approx 3$ μm), exhibited a thickness of about 30 μm and a porosity of about 35%, after sintering at 1000°C for 2 h.

The SOFC-single cells with different structured cathodes were tested under realistic operating conditions using specially designed equipment. They were installed in a alumina-housing, the electrodes were contacted with a platinum-grid. The alumina-housing was located in a furnace which operating between 500 and 1000 °C.

An electronic load was used to adjust the current. The impedance measurements were performed using a SOLARTRON 1260 Frequency Response Analyzer in a frequency range from 100 mHz to 1 MHz. Investigating symmetrical cells and SOFCs by impedance spectroscopy, a current amplitude $I_{amp=}$40 mA and $I_{bias=}$40 mA bias, under open circuit conditions (OCC), were applied.

The FEM calculations were carried out with the Maxwell-software.[3] Using the experimental cell geometry and electrode arrangements. In each calculation an insulating surrounding atmosphere at the circumference of the sample was applied and the electrodes were considered as ideal electrical conductors ($S > 10^5$ S/cm).

3. Results

Fig. 2 shows the impedance spectra of symmetrical cells at 950°C with different cathodes, whereas a decrease of the polarisation resistance, due to the enlargement of the electrolyte surface is observed. This is reasonable insofar that the particles had a good adhesion to the electrolyte and the total surface was covered with the LSM cathode material (Fig. 3).

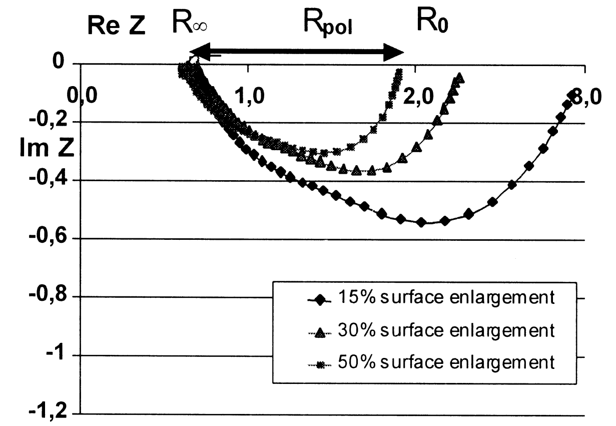

Fig. 2. Impedance spectra of symmetrical cells with different modified cathodes.

Additionally, impedance measurements of SOFCs at operating conditions (950°C, Anode H_2: 0.5 l per min, Cathode: air 0.5 l per min, OCC) show a direct influence of surface enlargement and decrease of the polarisation resistance (Fig. 4). Impedance spectra of single-cells with a modified cathode show that the polarization resistance of the cell strongly depends on the degree of the structuring of the electrolyte surface. The electrolyte resistance, i.e. the ohmic resistance determined from the point of intersection of the abscissa at high frequencies, exhibited a value of approximately 150 mΩ cm^{-2}. This value is in good agreement with values determined by four probe measurements on appropriate 8YSZ-bulk-ceramics. Hardly any influence of the 8YSZ-structure on the ohmic resistance of the cell was observed. To calculate the polarisation resistance of a three dimensional interface by FEM the electrical conductivity and

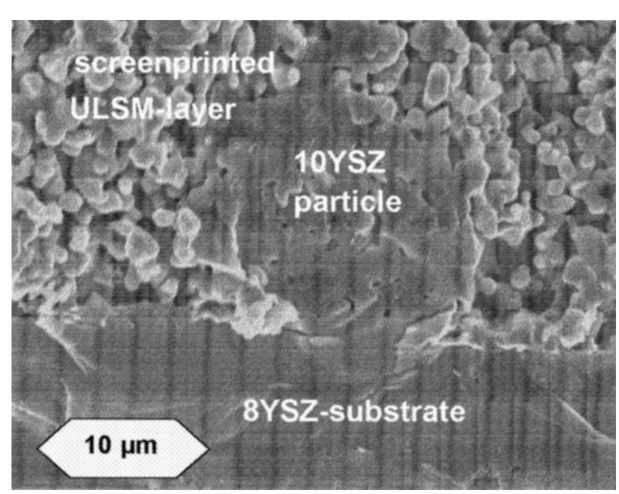

Fig. 3. Cross-section SEM image of a structured cathode.

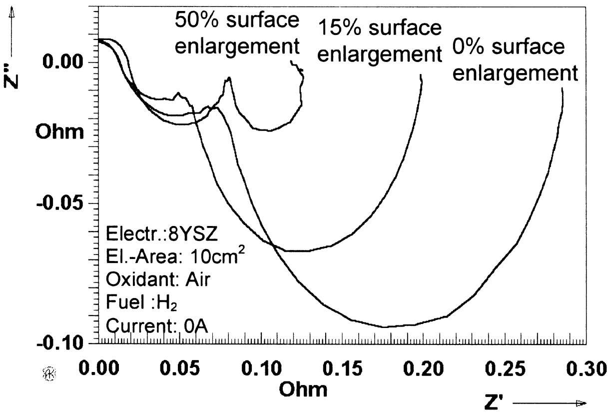

Fig. 4. Impedance measurements of SOFC with different structured cathodes (1223 K, OCC, anode: 0.5 l/min H_2, Cathode: 0.5 l/min air).

the geometrical size of the assumed interlayer have to be known. The DC polarisation resistance occurs at the interface between the cathode and the electrolyte. A thin layer (referred to as "current transfer layer" in the following) was considered in the FEM calculations. The electrical properties of the current transfer layer were determined by investigating the polarisation resistance of a standard symmetrical cell. The impedance measurement were carried out at 950°C with air supplied to both electrodes. The total measured DC-polarisation resistance of a symmetrical cell consists of an ohmic and a polarisation part. The ohmic part could be determined from the intersection of the abscissa at high frequencies. The difference of DC-polarisation resistance and ohmic resistance gives the polarisation resistance which occurs at the interface of cathode and electrolyte. Additional electrical measurements of the materials, i.e. the electrical conductivities of the ULSM screen printed layer and of the electrolyte material 8YSZ at elevated temperatures ($\sigma_{LSM}(T), \sigma_{8YSZ}(T)$) had to be performed to evaluate the basic data which are necessary to obtain the electrical property of the current transfer layer. The assumption of a thickness of 1 μm and the measured polarisation resistance leads to the electrical conductivity σ_{CTL} of the current transfer layer by following formula: $\sigma_{CTL} = \frac{l_{CTL}}{R_{pol} \cdot A}$ (R_{pol} = polarisation resistance, A = electrode area, l_{CTL} = assumed current transfer layer thickness).

After evaluation of the electrical conductivities of the employed materials and the conductivity of the current transfer layer, a calculation of a three dimensional electrode/electrolyte interface (interface for a structured cathode) made by FEM was possible. Fig. 5 show a section of the FEM-model, the cathode, the electrolyte and the "current transfer layer" were the polarization resistance occurs. The included calculation-mesh is additionally shown in Fig. 5. The FEM-calculations were performed for various amount of particles, according to the investigated symmetrical cells.

Fig. 6 shows the comparison of the DC-polarisation resistance between the FEM calculations and the measured values from symmetrical cells at 950°C. A correlation between the calculations and the measurements can be achieved. The FEM-model provides an tool which helps to limit the number of time consuming experiments preparation of SOFC cathodes could be avoided. Applying a structured cathode for SOFC a significant increase of the electrical output in comparison to a standard type of cell is observed (Fig. 7). The variation of the electrolyte surface structure showed, that the cathode performance depends on the effective electrolyte surface area i.e. the area where the cathodic reaction takes place. A further increase of the SOFC performance by an optimization of the structure of the electrolyte surface ought to be possible.

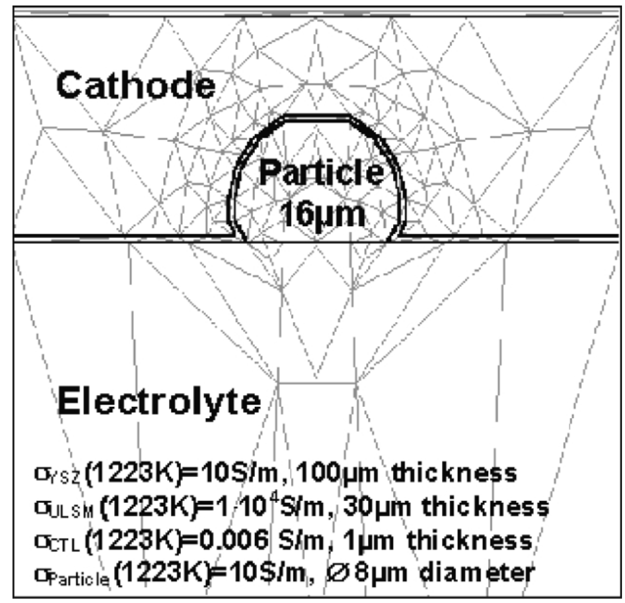

Fig. 5. FEM model of a structured cathode with calculation mesh.

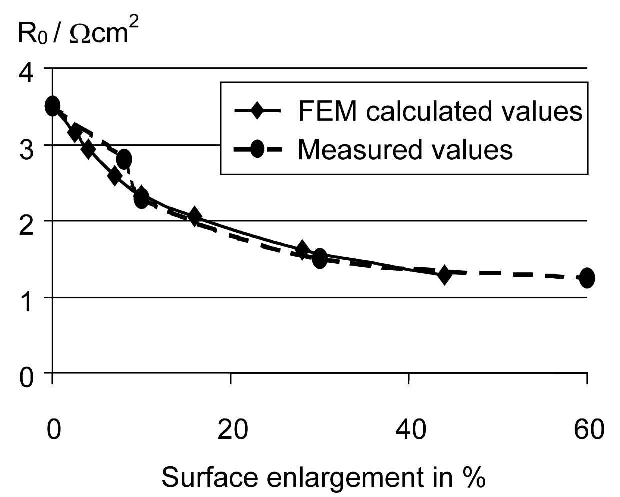

Fig. 6. Comparison of FEM calculated polarisation resistance and measured polarisation resistance.

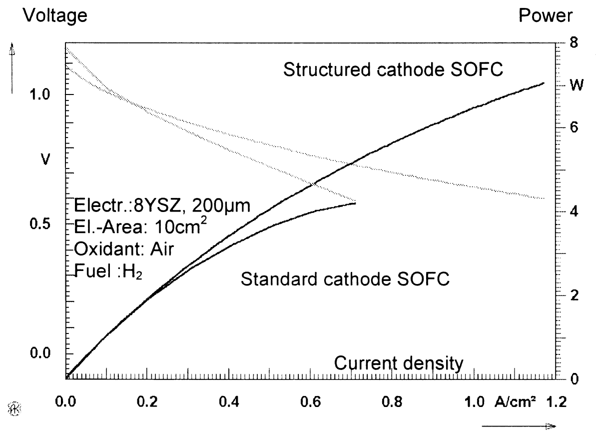

Fig. 7. I/V-characteristics of SOFC single-cells with standard and modified cathode.

4. Conclusion

A finite element model (FEM) to evaluate the polarisation resistance of a cathode cell (LSM/8YSZ/LSM) was developed. The basic data which were included into the FEM model were measured at a standard type of symmetrical cathode cell by impedance spectroscopy to evaluate the polarisation- and ohmic-resistance. The FEM-calculation were made under the assumption, that the polarisation resistance occur at a so called "current transfer layer", with a self-determined thickness of 1 μm. A series of symmetrical cathode cells with a three dimensional penetration structure were electrically characterized and FEM calculations performed to evaluate the DC polarisation resistance. The determination of the polarisation resistance by FEM correlates with the measurements. The FEM model provides the opportunity to calculate a high effective interface i.e. for a SOFC cathode to decrease internal losses.

Acknowledgements

The authors gratefully acknowledge the Deutschen Forschungsgemeinshaft (DFG) for financial support.

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