CHARACTERIZATION OF CATHODE SUPPORTED THIN FILM ELECTROLYTES

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ABSTRACT

The lower operating temperature limit of SOFCs is governed by the thermally activated conductance of the electrolyte as well as by the polarization resistance of the electrodes. For operating temperatures lower than 800°C, supported thin film electrolytes can be applied to reduce the ohmic losses within a single cell. In this work, cathode supported thin film electrolytes from state-of-the-art ceria and zirconia electrolyte powders were realized using mass production technologies. The conductivity of the electrolyte thin film was determined by impedance spectroscopy and the microstructure was characterized by electron microscopy methods (SEM). The conductivity of the electrolyte thin film (thickness < 10 μm) depends on grain size and porosity. The conductivity values of state-of-the-art electrolyte substrates (thickness > 150 μm) have not been achieved so far. However, the contribution of the electrolyte thin film to the area specific resistance is significantly smaller compared to the ASR of an electrolyte supported single cell.

INTRODUCTION

For SOFCs operated at low and intermediate temperatures (500 - 800°C), single cell elements with a low area specific resistance (ASR) have to be developed. Since the internal resistance is governed by the thermally activated conductivity of the electrolyte, alternative electrolyte materials with improved conductivity have to be developed (1-5) and/or the thickness of the electrolyte has to be reduced drastically.

Anode supported cells (ASC) with dense electrolyte thin films have been developed using mass production technologies (6,7). An ASC can be sintered at elevated temperatures (cofiring of anode and electrolyte at 1300 to 1500°C) thus leading to a dense thin film (< 20 μm) electrolyte (YSZ, GCO or a two layer compound). After reducing the NiO to metallic Ni, a supporting anode cermet with a high porosity is created. However, the thermal expansion mismatch between supporting anode cermet and supported thin film electrolyte induces mechanical stress, thus leading to cracks within the ASE structure during thermal cycling. The redox-cycling (repeated oxidation and reduction of the supporting anode cermet, combined with a volume change) is even more serious. Last but not least, high fuel utilization of 80%, as required for a commercial system, results in high gas diffusion polarization losses at the interface anode/electrolyte when a supporting anode cermet (thickness > 500 μm) is used.
A cathode supported cell with a thin film electrolyte (CSC) can avoid or minimize most of these problems, successfully demonstrated by Westinghouse when changing from ASC to CSC more than 20 years ago. The development of a supporting cathode structure with a supported thin film electrolyte at Westinghouse is based on CVD/EVD processing of the electrolyte (8) and avoids high processing temperatures. The CSC processing temperatures are restricted to prevent interdiffusion and reactions at the cathode electrolyte-interface as well as a densification of the cathode substrate. Nevertheless, a major drawback of the CSC fabrication is the dependence on rather expensive fabrication technologies. This paper presents a first approach using mass production technologies for CSC, like tape casting for the supporting cathode substrate and screen printing for the supported thin film electrolyte.

EXPERIMENTAL

LSM (La$_{0.75}$Sr$_{0.3}$MnO$_3$) cathode substrates with a porosity of 35% and a thickness of 500 μm were produced by tape casting and sintering at 1250°C. The thin film electrolyte layers were applied in two consecutive steps. At first, a layer of YSZ (8 mol% Y$_2$O$_3$ doped ZrO$_2$) or GCO (10 mol% Gd$_2$O$_3$ doped CeO$_2$) was screen printed onto the cathode substrate and sintered at temperatures between 1000 °C and 1250°C. Depending on screen printing parameters and sintering temperature, the layer thickness could be varied between 5 and 10 μm. In a second step, the screen printed and sintered electrolyte layer was densified and coated using a Metallo Organic Deposition (MOD) process (9).

The microstructure of the cathode supported two layer electrolyte was characterized in a LEO 1530 scanning electron microscope. The ASR of the various cathode supported two layered thin film electrolyte was evaluated by impedance spectroscopy using a Solartron 1260 frequency response analyzer. The impedance of the samples was acquired as a function of temperature in a frequency range between 100 mHz to 1 MHz in air. The measurement set-up is shown in Fig. 1.

Figure 1: IS measurement set-up and simplified equivalent circuit diagram of a cathode supported thin film electrolyte.
The conductivity of the cathode supported electrolyte thin film was calculated using the sample geometry i.e. the electrode area and the thickness of the electrolyte and the high frequency intercept point $R_0$ of the impedance spectra. This point was obtained by fitting the left semicircle in Fig. 2 with an $RQ$-element using the “equivalent circuit” software (10). The ohmic resistances of the electrodes were neglected ($R_{\text{cathode}}, R_{\text{Pt}} < R_{\text{electrolyte}}$).

RESULTS AND DISCUSSION

Microstructure

Fig. 3 shows the top view and the cross section view of cathode supported screen printed and sintered YSZ electrolyte thin films, sintered for 5 h at 1000°C (left hand side), 1100°C (center), and 1200°C (right hand side). It is obvious that all screen printed and sintered electrolyte thin films exhibit smaller pore size and less overall porosity compared to the supporting cathode substrate.

The sintering behavior and the dependence of microstructure properties on sintering temperature were similar for screen printed GCO and YSZ electrolyte thin films. With sintering temperature the average grain size increased, resulting in a decrease in porosity and layer thickness.

Cathode supported GCO and YSZ electrolyte thin films, which were sintered at 1000°C exhibited a rather high porosity (~ 40 %) combined with a rather small average pore size (~ 100 nm) (see Fig. 3, left). Increasing the sintering temperature to 1200°C results in an increased average pore size (~ 0.8 μm). On the other hand the porosity decreases (~ 25 %) but remains as an open porosity. Therefore the screen printed and sintered electrolyte thin films are not gas tight.
Figure 3. Microstructures of cathode supported screen printed and sintered YSZ-layers ($T_{sinter}$: 1000°C left, 1100°C middle, 1200°C right).

In a second step, the cathode supported screen printed YSZ or GCO electrolyte thin films (5 μm to 10 μm and porous) were densified and coated with a YSZ electrolyte thin film (< 500 nm) by a MOD process followed by RTA. Fig. 4 shows SEM-images of a cathode supported (screen printed and sintered) GCO electrolyte thin film spin coated with a (MOD and RTA) YSZ electrolyte thin film. The MOD-YSZ appears to be dense and crack free with good adhesion to the porous screen printed and sintered GCO. The porosity of the screen printed and sintered GCO thin film was lower. The interface between GCO and the supporting cathode substrate is shown as well.

Figure 4. Top view of the sample (left) and cross view section (right) of a cathode supported (screen printed and sintered: 1000°C) GCO electrolyte coated and densified with a MOD YSZ electrolyte thin film.

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Electrical properties

Fig. 5 compares the electrical conductivity of a dense YSZ electrolyte substrate (150 μm) with the values measured for cathode supported screen printed and sintered porous YSZ electrolyte thin films (thickness from 5 μm to 10 μm). The conductivity values are at least 1 order of magnitude lower compared to the self supporting YSZ substrate, which can be attributed to the porosity of the cathode supported thin films. The variation in conductivity among the thin films can be explained by the variation in microstructure (overall porosity, as well as pore size and grain size distribution), due to different sintering temperatures applied (1550 vs. 1100 and 1000°C, resp.).

Figure 5. Conductivity of cathode supported screen printed and sintered porous YSZ electrolyte thin films (thickness 5 μm to 10 μm) compared to self supporting YSZ electrolyte substrates (150 μm).

Figure 6. Conductivity of cathode supported two layer thin film YSZ electrolytes (screen printed and sintered porous YSZ electrolyte thin film topped with a MOD and RTA dense YSZ electrolyte thin film) compared to a cathode supported single layer porous thin film YSZ electrolyte (screen printed and sintered).
The electrical conductivity could be improved by the application of a spin coated and annealed MOD electrolyte thin film on top of the porous screen printed and sintered YSZ electrolyte thin film. Best results have been obtained so far with screen printed electrolyte thin films sintered at 1000°C. The microstructure (grain size and pore size distribution) as shown in Fig. 3, allows the application of a dense MOD layer. Nevertheless, as can be seen in Fig. 6, the electrical conductivity of this two layer thin film electrolyte is still one order of magnitude lower compared to a dense self supported YSZ substrate.

The electrical characterization (EIS) of this cathode supported two layer thin film electrolyte showed that at 700°C, ASR values equivalent to those of dense YSZ electrolyte substrates at 900°C can be realized.

CONCLUSIONS

The electrical conductivity and the microstructure of cathode supported YSZ and GCO thin film electrolytes were investigated. The electrolyte thin films were prepared on top of a porous cathode substrate using mass production technologies such as tape casting, screen printing and spin coating. Sintering temperatures as low as 1000°C resulted in an electrolyte thin film with rather high porosity, which could only be densified by the application of a spin coated and annealed MOD layer on top. The electrical conductivity of this two layer thin film electrolyte is still one order of magnitude lower compared to a dense self supported YSZ substrate.

The electrical characterization (EIS) of the cathode supported thin film electrolytes showed that at 700°C ASR values equivalent to those of dense YSZ electrolyte substrates at 900°C can be realized.

It has clearly to be stated, that thin films with the as presented microstructure properties are not expected to be successfully operated in a single cell. Further investigations will be necessary to process dense cathode supported electrolyte thin films with improved and reliable electrical properties.

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