ELECTROCHEMICAL CHARACTERISATION OF SUPPORTING SOFC ANODES

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ABSTRACT

In order to get a detailed insight into the electrochemical performance of the single anode in an anode supported SOFC cell, symmetrical cells consisting of two nominally identically prepared electrode and support layers have been prepared. Different electrode layers were investigated: Ni-yttria stabilized zirconia (Ni-YSZ) with different ratios of the fine and coarse YSZ, Ni-gadolinium modified ceria (Ni-CGO), and Ni-yttria-titania modified zirconia (Ni-YZT). High quality impedance data are obtained in this set-up and the influence of the Ni-YSZ cermet microstructure corresponds well to results reported earlier. The impedance indicates that the electrode performance is limited rather by electrochemical reaction steps in the Ni-cermet electrode than by gas transport phenomena.

INTRODUCTION

The anode supported cell design is becoming the most frequently used concept for flat plate planar SOFCs to date. It consists of a 10-40 micron thick electrolyte layer, whereas the anode support is between 300 micron and 2 mm in thickness, depending on the cell manufacturer. In order to get a detailed insight into the electrochemical performance of the single anode in an anode supported SOFC cell, symmetrical cells consisting of two nominally identically prepared electrodes and support layers have been prepared. Using this cell concept, there is no need for a reference electrode, which would have been impossible to place on the thin electrolyte. Moreover, Adler showed that using a three-electrode-setup can very easily lead to wrong interpretations, because impedances from the counter and work electrode cannot always be separated [1].

The state-of-the-art Ni/YSZ anode of today's still has some problems. Among these are redox-stability, Ni-agglomeration at high temperatures and fuel inflexibility [2]. These limitations all come down on the use of nickel in the anode. Furthermore, the fuel oxidation in Ni/YSZ anodes can only take place in the vicinity of the so-called triple phase boundary (TPB), where the gas phase, the electronic and ionic conducting phase meet. Anodes without the limitation of a TPB would mean a big improvement. Mixed
electronic and ionic conducting materials are of great interest in this perspective. Gadolinium doped ceria and titania doped yttria stabilized zirconia have been suggested as alternatives for the YSZ in Ni/YSZ. Gadolinium modified ceria (CGO) is specifically interesting for intermediate temperature SOFC, because they already show high activity at low temperatures and because they are compatible with the CGO electrolytes in these cells [3,4,5,6]. Titania-yttria modified zirconia becomes mixed conducting in reducing atmospheres and is interesting due to its chemical and thermal compatibility with YSZ, which is still one of the most used electrolyte material [7,8,9]. In this work, three different materials have been used as electrodes in symmetrical cells: Ni-YSZ, Ni-CeO$_{0.8}$GdO$_{0.2}$O$_{1.80}$ (Ni-CGO), and Ni-Y$_{0.20}$Ti$_{0.18}$Zr$_{0.62}$O$_{1.90}$ (Ni-YZT). These electrodes were tested for their anodic performance using impedance spectroscopy.

EXPERIMENTAL

The supporting electrode substrates have been prepared by cold die pressing of NiO-YSZ. Polymer bounded NiO-YSZ granules with 50w% NiO and 50w% YSZ (8 mol% Yttria) have been prepared with different grades of YSZ and NiO powders. They were pressed to pellets of 14 mm diameter and a thickness of 0.8 mm. One side of the pellets was coated subsequently with the electrode layer by air spraying. Different electrode layers were prepared: NiO-YSZ with different ratios of the fine and coarse YSZ, NiO-CeO$_{0.8}$GdO$_{0.2}$O$_{1.80}$ (Ni-CGO), and NiO-Y$_{0.20}$Ti$_{0.18}$Zr$_{0.62}$O$_{1.90}$ (Ni-YZT). All electrodes contain 40 vol% nickel after reduction. The electrodes were subsequently coated with an 8-YSZ (Unitec) electrolyte layer by air spraying. Two nominally identically prepared half-cells were then pressed together and fired at 1430°C for 2 h in air to form the symmetrical electrode supported cells. The principle structure of the symmetrical cells is shown in Fig 1.

![Figure 1. Schematic drawing of the symmetrical cells consisting of 2 anode materials including the support.](image)

The as prepared symmetrical cells have been electrochemically characterized by using impedance spectroscopy. The impedance was measured in the frequency range of 30 kHz - 10 mHz, using a Solartron 1255 Frequency Response Analyzer and Solartron 1287 Electrochemical Interface. The cells were mounted in a single-atmosphere quartz reactor and in situ reduced at 800°C in hydrogen. Measurements were performed in wet hydrogen at different pH$_2$, pH$_{2O}$ and different temperatures. The validity of the impedance data has been checked by performing a Kramers-Kronig transformation. The EQUIVCRT software was used to further analyze the impedance spectra [10,11].
RESULTS AND DISCUSSION

Microstructure

Figure 2 shows a cross-section of a symmetrical cell. It clearly distinguishes the support, functional electrode layer and electrolyte, with their respective microstructures. The thickness of the different functional electrode layers is 20 – 30 μm, whereas the electrolyte has a thickness of 30 – 40 μm.

Three different Ni-YSZ electrodes have been tested, differing in the fine/coarse YSZ ratio. The electrodes contain 15%, 33% and 70% fine YSZ (0.2 μm), respectively. Figure 3 shows the microstructure of the electrode, containing 70% fine YSZ. Although this is the electrode with the highest amount of fine particles, its microstructure is still relatively coarse.

The microstructures of the different electrodes (Ni-YSZ, Ni-CGO, Ni-YZT) are compared in Figure 3 at a larger magnification. Remarkable are the very fine microstructure of the Ni-CGO electrode, compared to the other electrodes, and the quite dense and coarse microstructure of the Ni-YZT electrode. The CGO has a particle size of ~0.5 μm, which creates a large surface area for the hydrogen oxidation reaction. The YSZ in the Ni/YSZ electrodes has a bimodal particle size. The small particles have a particle size of ~ 1.0 μm, whereas the larger particles and sintered agglomerates have a particle size of 5 – 10 μm. The YZT in the Ni/YZT electrodes has sintered to quite dense structures with a particle size of 5 – 10 μm. Lower sintering temperatures would possibly give electrode structures with finer particles and more porosity. However, co-sintering with the electrolyte material becomes problematic at lower temperatures, since dense electrolytes are required.

Figure 2. SEM fracture cross-section of a symmetrical electrode supported cell. The electrolyte thickness is 30-40 micron followed by a fine porous Ni-CGO electrode layer and subsequently the coarser Ni-YSZ electrode support.
Figure 3. Microstructures of the different electrodes. Upper left: Ni/YSZ; Upper right: Ni/YZT; Lower left: Ni/CGO.

Electrochemical Testing

A typical impedance response of a symmetric Ni-YSZ/Ni-YSZ electrode cell is shown in Figure 4. The ohmic resistance in the symmetrical cells at 800°C was found to be between 0.4 and 0.7 Ω with an activation enthalpy of 0.72 – 1.0 eV and attributed to the YSZ electrolyte layer (s. Fig 4). The electrode impedance is the sum of the polarization resistance of two nominally identical electrodes, expressed as “2 Rp” in Fig 4. By dividing the real part of the impedance by two, an average polarization resistance $R_{p,av}$ for the single supported electrode is obtained.

The average single electrode polarization resistance $R_{p,av}$ for Ni-YSZ cermet electrodes with 15, 33, and 70wt% fine YSZ was 7.4 $\Omega$cm$^2$, 3.2 $\Omega$cm$^2$, and 2.0 $\Omega$cm$^2$, respectively. The activation enthalpy was 1.20 – 1.40 eV. The decrease of polarization resistance with
increasing amount of fine YSZ in the electrode is in agreement with findings of De Boer [12]. The value of 3.2 $\Omega$cm$^2$ and the activation enthalpies are in fair agreement with data reported earlier for Ni-YSZ cermets by Holtappels [13] but also Ni-pattern electrodes, investigated by Bieberle et al. [14].

The relatively high value for the impedance (please note that the average polarization resistance attributed to the SOFC electrode exceeds the total specific resistance of state-of-the-art anode supported cells) can partly be explained by the coarse microstructure of the Ni/YSZ electrodes.

Two processes are obvious in the impedance for which the maximum frequencies are around 20 Hz and 0.1 Hz. Contributions by gas conversion are not considered due to the symmetrical setup and also gas diffusion usually is observed at a faster rate (e.g. at frequencies around 100 -200 Hz [15]). Therefore it is most likely that the impedance is dominated by the electrochemical processes inside the electrode. A further analysis of the partial pressure and temperature dependence of the impedance is in progress to better understand the impedance response.

The impedance spectra of the Ni/YSZ electrode with 70% fine YSZ in different pH$_2$ and pH$_2$O atmospheres are shown in Figure 5. The single electrode impedance is shown here, expressed by plotting half of the area specific impedance (1/2 $Z_{im}$ vs 1/2 $Z_{re}$.)

Figure 4. Example of an Impedance spectra for a Ni-YSZ/Ni-YSZ/YSZ cell, fine fraction of YSZ was 70%, T = 800°C, p(H$_2$) = 0.99 bar, p(H$_2$O) = 0.023 bar.

Figure 5. Impedance spectra of a symmetrical Ni-YSZ/Ni-YSZ/YSZ cell at 800°C. Left: p(H$_2$O) = 0.023 bar; Right: p(H$_2$) = 0.81 bar.
The tested samples showed an increase in the resistance with time. The highest degradation rate was found for the cermet electrode with the highest amount of fine YSZ. Within 50 hours, its original polarization resistance had increased with ~100%. After this initial increase the degradation rate dropped. However, systematic variations of the atmosphere and temperature were performed in a time frame of ~6 hours, which comes down on an average error of ~8% in the data, which is caused by the decay. This is considered within an acceptable range.

The lowest polarization resistance was found for Ni-CGO electrodes showing an average polarization resistance of 1.1 Ωcm², which slightly increased with decreasing hydrogen partial pressure. The polarization resistance is more dependent on water partial pressure as can be seen from Figure 6. For a water vapor partial pressure of 0.20 bar and a hydrogen partial pressure of 0.81 bar, the average polarization resistance has decreased to 0.83 Ωcm². The impedance spectra at different water and hydrogen partial pressure are shown in Figure 6.

![Figure 6. Impedance spectra of a symmetrical Ni-YSZ/Ni-CGO/YSZ cell at 800°C. Left: p(H₂O) = 0.023 bar; Right: p(H₂) = 0.81 bar.](image)

A more detailed investigation with EQUIVCRT leads to the suspicion that adsorption/desorption of H₂O and/or OH⁻ species causes an important contribution to the electrode impedance. The arc in the mid-frequency range (0.1 – 1 Hz) has an activation energy of 1.2 eV which was also observed by Primdahl [5] for the hydrogen adsorption on the CGO surface. Hydrogen adsorption however doesn't seem to be limiting, since adding only small amounts (0.8 – 2.5 w%) on Ni should already solve this problem [5,6]. In our case we have 40 vol% Ni in the electrode, which should cover this problem. Therefore identifying the nature of the mid frequency arc needs further investigations.

The impedance spectra for the Ni/YZT electrodes in different pH₂ and pH₂O atmospheres are shown in Figure 7. The Ni/YZT electrodes exhibit the highest polarization resistance. The polarization resistance of 11 Ωcm² can be attributed to the coarse and dense microstructure of the electrode layer. Probably the sintering temperature of 1430°C is too high for YZT. Gonzalez Cuenca [16] already found that the anodic performance decreases when the sintering temperature for Ni/YZT electrodes is increased from 1300°C to 1400°C. Unfortunately, high sintering temperatures are required to guarantee a dense electrolyte. Another serious problem with this anode material could be the ionic conductivity of the YZT. Skarmoutsos [8] found that the ionic conductivity of a material...
with a slightly different composition, $Y_{0.25}Zr_{0.60}Ti_{0.15}O_{2-x}$, was a factor 10 lower than that of 8-YSZ. This decrease in ionic conductivity could seriously obstruct the oxygen ion release from the electrolyte into the anode. The activation energy for the total electrode polarization amounts 1.1 eV, which is close to the activation energy for ionic conduction in YZT [7]. This is another indication that the ionic conductivity in YZT becomes limiting for proper anodic performance.

Figure 7. Impedance spectra of a symmetrical Ni-YSZ/Ni-YZT/YSZ cell at 800°C. Left: $p(H_2O) = 0.023$ bar; Right: $p(H_2) = 0.81$ bar.

SUMMARY

The results indicate clearly that symmetric cells consisting of two nominally identically prepared electrodes provide information on the single electrode performance in thin supported electrolyte cells and thus allow the evaluation and comparison of different SOFC anode materials for anode supported cells. Besides the total electrode performance of a supporting anode, a further insight into the electrochemical processes can be obtained from a kinetic analysis of the partial pressure, temperature and frequency response. A detailed analysis of the impedance based on appropriate models reflecting the ionic and mixed ionic electronic conductivity of Ni-YSZ, Ni-CGO and Ni-YZT cerments is the next step in order to better understand the electrochemical processes in SOFC anodes.

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REFERENCES

1. S. B. Adler, *J. Electrochem. Soc.*, 149, E166-E172 (2000).
2. S. Tao, J. T. S. Irvine, *The Chemical Record*, 4, 83-95 (2004).
3. C. Xia, M. Liu, *Solid State Ionics*, 152-153, 423-443 (2002).
4. S. Zha, et al., *Solid State Ionics*, **166**, 241-250 (2004).
5. S. Primdahl, Y. L. Liu, *J. Electrochem. Soc.*, **149**, A1466-A1472 (2002).
6. S. Primdahl, M. Mogensen, *Solid State Ionics*, **152-153**, 597-608.
7. L. S. M. Traqueia, et al., *J. Eur. Ceram. Soc.*, **17**, 1019-1026 (1997).
8. D. Skarmoutsos, et al., *Solid State Ionics*, **170**, 153-158 (2004).
9. M. Mori, et al., *Solid State Ionics*, **160**, (2003).
10. B. A. Boukamp, *Solid State Ionics*, **72**, (1986).
11. B. A. Boukamp, *J. Electrochem. Soc.*, **142**(6), (1995).
12. B. De Boer, *Hydrogen oxidation at porous nickel and nickel/yttria stabilised zirconia cermet anodes*, Thesis, University of Twente, Enschede, NL, (1998).
13. P. Holtappels, et al., *J. Electrochem. Soc.*, **146**, 2976-2982 (1999).
14. A. Bieberle, et al., *J. Electrochem. Soc.*, **148**, A646-A656 (2001).
15. S. Primdahl, M. Mogensen, *J. Electrochem. Soc.*, **145**, 2431-2438 (1998).
16. M. Gonzalez Cuenca, *Novel anode materials for solid oxide fuel cells*, Thesis, University of Twente, University Press, Enschede, NL, (2002).