Ni-CGO and Ni-YSZ cermet anodes for a Solid Oxide Fuel Cell were investigated. Cells were operated in the temperature range from 600 °C to 800 °C with both, humidified hydrogen and methane as fuel. The anodes were characterized by electrochemical impedance spectroscopy and current density-voltage characteristics. Ni-CGO anodes are superior to Ni-YSZ anodes especially at lower operating temperatures and when methane is used.

INTRODUCTION

State-of-the art solid oxide fuel cell anodes consist of a cermet made out of nickel and ytttria-stabilized zirconia (8 mol% Y₂O₃ in ZrO₂ solid solution, 8-YSZ). The nickel is intended to offer the catalytic activity for hydrogen dissociation and oxidation and the electronic conductivity. The ceramic component, 8-YSZ grains, hinder the coarsening and coalescence of the sintered Ni network during fuel cell operation and offers oxygen ionic conductivity. Optimization of the microstructure and the composition as well as the preparation technique lead to high quality anodes. The electrochemical performance is satisfactory when the electrodes are operated at temperatures around 900-1000 °C and when hydrogen or prereformed natural gas is used as fuel. Decreasing the operating temperature of solid oxide fuel cells to 600-800 °C offer the potential to reduce the system costs, less expensive materials for the interconnect and the gas supply can be used. In addition, the long-term stability of the cell components is increased, due to limited physical and chemical degradation. However with today’s anodes performance losses occur when the operating temperature is reduced or when the system works with unreformed natural gas and carbon is deposited on the anode. The lower operating temperature causes an increase of the ohmic and the polarization losses in the cell. The carbon deposition is a consequence of the nickel’s catalytic activity towards the dehydrogenation of hydrocarbons. Therefore an anode with a smaller electrochemical polarization and a higher catalytic activity, for the oxidation of hydrogen or hydrocarbons could overcome these problems. Furthermore a fine grain size increasing the amount of reactive triple phase boundary (tpb) is required.

Ceria solid solution, such as cerium gadolinium oxide (CGO), or cerium samarium oxide (CSO) were tested as alternative anode materials. Mixed ionic and electronic conductivity was observed under anode operating conditions with an ionic conductivity of 3 S m⁻¹ and an electronic conductivity up to 40 S m⁻¹ (700 °C) [1]. Compared to 8-YSZ the additional electronic conductivity might enhance the reaction zone over the triple
phase boundary. The picture of the anode reaction mechanism requires the contact of electrons, protons and oxygen ions at the so called triple phase boundary (tpb) and therefore an electronic conducting ceramic component might spread this reaction zone. Experiments by Watanabe et al. with samaria doped ceria anodes and small amounts of catalytic active noble metals, like Rh, Pd, showed the capacity of these materials (2). Without any percolating metallic network the anodic overpotential was around 125 mV at 500 mA cm\(^{-2}\) and 800\(^{\circ}\)C.

Furthermore the ceria provides a high catalytic activity towards hydrogen and hydrocarbon oxidation, which is used in the car exhaust catalyst (3). Park et al. reduced the function of the metal in the anode purely to electronic conduction, by producing a Cu-CGO-YSZ cermet (4). Copper is inert to any hydrogen or hydrocarbon oxidation. The cells could be operated with dry hydrocarbons like butene and toluene without any carbon deposition.

In this paper we will report on the microstructural and the electrochemical results for Ni-cerium-gadolinium-oxide (Ni-CGO) anodes and their use as an alternative SOFC anode material. The performance of several Ni-CGO anodes using hydrogen and methane as the fuel will be compared to a standard Ni-yttria-zirconia anode.

**Experimental**

**Anode Preparation**

The anodes were prepared by a screen-printing process. NiO-YSZ (8 mol % yttria stabilized zirconia, 8-YSZ) and NiO-CGO (Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{1.9}\)) with a metal oxide content of 70 wt%, were used as starting powders. The exact preparation method for the Ni-YSZ anode is described elsewhere (5). Commercially available NiO-CGO powder was used for the ceria anode [Praxair Speciality Ceramics, Woodinville, USA]. The organic paste was screen-printed on a 200 \(\mu\)m thick 8-YSZ electrolyte [Kerafol, Eschenbach, Germany]. The thickness of the anodes in the green state amounted 30 \(\mu\)m, the dimensions were 1 x 1 cm\(^2\). Pt gauze as current collector was slightly pressed onto the anode and contacted with thinned paste. Sintering the anodes and the Pt-current collector together ensures a good electrical contact. The anodes were sintered at temperatures between 1200 \(^{\circ}\)C and 1350 \(^{\circ}\)C in 50 \(^{\circ}\)C steps for two hours. The cells were completed with a Pt-paste, Pt gauze counter electrode symmetrically to the anode at the opposite side of the electrolyte.

**Microstructural Characterization**

The scanning electron microscope pictures (SEM) were obtained using a JEOL JSM 6400 microscope (JEOL, D) equipped with an X-ray analyzer for energy-dispersive X-ray spectroscopy (Z-Max 30, Tracer Northern, USA).

**Electrochemical Characterization**

The cells were characterized in a two gas chamber setup. A gaseous mixture of 40 vol% fuel (hydrogen or methane) and 60 vol% nitrogen humidified with 3 % water was used at
the anode side, air was used at the cathode side. The total flow of gases was 50 ml/min on each side at a pressure of one atmosphere.

Electrochemical analysis was performed in a three electrode setup with a Zahner IM6 impedance unit (Zahner, Kronach, Germany). The anode reference electrode is exposed to the same fuel atmosphere as the anode. Figure 1 shows the experimental arrangement for the electrochemical characterization described in (6).

Electrochemical impedance spectroscopy (EIS) measurements were performed under OCV conditions, with an excitation voltage of 10 mV. The frequency was varied ranging from 100 mHz to 100 kHz. The polarization resistance $R_p$ of the anode is derived as the difference between the two intercepts in the Nyquist plots. The electrolyte resistance $R_{el}$ is defined in the impedance spectra as the value of the real impedance at the high frequency x-axes intercept. DC current-voltage characteristics were measured with a polarization of the anode versus the reference electrode $\eta_{Anode}$. The overpotential curves were $I^*R$ corrected by substituting the ohmic part of the electrolyte $R_{el}$. The anode polarization $\eta_{Anode}$ is the potential difference between the anode and the reference electrode, which is including the electrochemical overpotential and the ohmic loss between anode and reference electrode.

![Fig. 1: Schematics of the measurement setup for the electrochemical characterization of the anodes.](image)

4-Point Conductivity Measurements

The in-plane conductivity was measured on screen-printed anodes with a size of 2 x 1 cm$^2$ and a thickness of 30 μm. Four parallel Pt wires were connected on the sample surface, the inner two for the voltage and the outer two for the current. The current and voltage was measured with a Keithley 197A multimeter [Keithley, Cleveland, USA]. The
conductivities were calculated by the geometrical dimensions of the sample. Measurements were performed in the same gas atmosphere that exists at the anode side.

RESULTS

Microstructure

The influence of the sintering temperature on the microstructure was investigated by SEM. Surface pictures of NiO-CGO anodes are shown in Figure 2. All pictures are top view pictures at the same magnification. With increasing sintering temperatures the microstructure became more open and the particle size increased as well. Graphical analysis resulted in an increase in the average pore size from 0.3 μm to 0.6 μm from 1200 °C to 1350 °C sintering temperature. Micrographs from cross-sections showed a good connection between the anode and the electrolyte for all sintering temperatures.

Fig. 2: Electron micrograph pictures of NiO-CGO surfaces sintered at different temperatures a) 1200 °C, b) 1250 °C, c) 1300 °C, d) 1350 °C.
The anodes were held for 8 hours under reducing operating conditions (800 °C, p(O₂): 10⁻²⁰ atm). An increase in the pore size was measured as a consequence of the volume reduction when NiO is reduced to metallic nickel. The ceramic framework remained unchanged during reduction. The average pore size in the reduced state was 0.5 μm for the samples sintered at 1200 °C and 1.2 μm for a sintering temperature of 1350 °C. Figure 3 shows a SEM picture of a reduced anode with a sintering temperature of 1350 °C. The microstructural requirements of a SOFC anode for an unhindered gas diffusion are an overall porosity of 40% and an average pore size of 1-2 μm. These requirements were best fulfilled for the Ni-CGO anodes sintered at 1350°C.

![Fig. 3: Electron micrograph of the Ni-CGO surface sintered at 1350 °C and reduced at 800 °C in hydrogen.](image)

**Electrochemistry**

In-plane conductivity measurements were performed to ensure the existence of a percolating metallic network. Under operating conditions Ni-CGO anodes reached a steady electronic conductivity of $1.7 \times 10^4$ S cm⁻¹. No significant difference in the conductivity was detected for anodes sintered at different temperatures. For all cases a continuous metallic network was present. Due to the stable conductivity over 30 hours of operation, it can be deduced that there is no coarsening of nickel.

**Anode Overpotential.** The comparison of an anode with a low sintering temperature and consequential a dense microstructure (average pore size: 0.5 μm) to one sintered at high temperature and an open microstructure (average pore size: 1.2 μm) is shown in Figure 4. The best results at 800 °C with hydrogen as fuel were obtained for an anode sintered at 1350 °C with less than 10 mV at 500 mA cm⁻². Sintering temperature of 1200 °C showed the worst performance with an anodic overpotential of 100 mV at 400 mA cm⁻². When using methane, the overpotential was 250 mA cm⁻² at 800 °C and 75 mV for the
anode sintered at 1350 °C and 170 mV for the one sintered at 1200 °C under the same conditions.

The results from the conductivity measurements and the existence of a stable microstructure lead to the conclusion that the difference in the performance are mainly caused by a limited fuel gas diffusion or H2O diffusion. The fine grain size of the anode sintered at 1200 °C builds up a network with a higher amount of triple phase boundary places, but the small pore size hinders an efficient gas transport to and from the anode. On the other hand, sintering at 1350 °C decreased the amount of triple phase boundary, but created a structure with pores large enough for a sufficient fuel supply and water removal.

A comparison of the overpotential of a standard Ni-YSZ anode and a Ni-CGO anode both sintered at 1350 °C with a comparable microstructure is shown in Figure 5. The cells were operated with hydrogen. The overpotential of the ceria based anode is at 800 °C and 500 mA cm⁻² only 20%, at 700°C and 250 mA cm⁻² only 60% of the Ni-YSZ anode. These results can be well explained with the model for the reaction mechanism and the materials properties of ceria proposed by Zhang et al. (7). Compared to a zirconia based anode a larger reaction area is available, the fuel can be oxidized at the nickel, as well as at the ceria surface. The transfer of the electrons from the ceria to the highly conductive nickel network is unhindered. A highly cross-connected network of metal and ceramic improves the performance due to short reaction paths. Additionally the supply of oxygen...
ions to the reaction zone must be as large as possible. Ceria solid solutions (ss) have a higher oxygen conductivity at 600-800 °C than doped zirconia. However a limited number of contact points between the electrolyte and the oxygen ion conducting ceramic can affect the anode performance like a bottleneck. Watanabe et al. considered this as a major hindrance for an anode operated at high reaction rates (8). A comparison of cross-section electron micrographs for the zirconia and ceria ss anode yielded in a similar good connection between the electrolyte and the anode.

The total polarization resistance of the anode was measured by electrochemical impedance spectroscopy. Figure 6 shows the Arrhenius plots of the reciprocal polarization resistance ($R_p^{-1}$), which is a measure of the electrochemical activity. The Ni-CGO anode was sintered at 1350°C. With both fuels, hydrogen and methane, the polarization resistance was lower and as a consequence the catalytic activity was higher for the Ni-CGO system. The catalytic activity of ceria was becoming more important when methane was used as fuel, what is documented in the larger difference in the curves. The similar decay of the curves when the system was operated with hydrogen, shows that the main catalytic activity in these cases was dominated by the nickel. This was different when methane is used as fuel. The decay in the plot differs by a factor of 2. The slopes of the Arrhenius curves shows the thermal activation energy of the overall anodic process. Obviously the rate determining step is different when the cell is operated with hydrogen and with methane. More data are necessary to get a better understanding of the underlying processes.
Fig. 6: Arrhenius plot of the total polarization resistance of Ni-CGO and Ni-YSZ anodes operated with hydrogen and methane.

CONCLUSIONS

Cerium-gadolinium oxide based anodes are an alternative to today’s state-of-the-art zirconia based anodes under lower temperature operation. The higher ionic conductivity compared to zirconium oxide and the mixed ionic electronic conductivity allows operating at reduced temperatures. Provided that a good microstructure was synthesized avoiding diffusion limitations, which was obtained with a sintering temperature of 1350°C, the performance for a Ni-CGO anode was better than that for a Ni-YSZ anode. The catalytic activity of ceria towards the reforming of hydrocarbons is clearly shown when the cells were operated with humidified methane as fuel. Lower polarization resistances and no carbon deposition were obtained for Ni-CGO anodes.

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