

Development of High Performance Anodes for Metal-Supported Fuel Cells

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Metal-supported solid oxide fuel cells (MSCs) offer various potentials like cost reduction and abuse tolerance, which make them attractive for mobile applications such as auxiliary power units (APUs). The implementation of the metallic substrate requires specific adaption of SOFC processing technologies since sintering of functional layers at high temperatures under oxidizing atmosphere is restricted by the substrate. Therefore, one of the current challenges is the development of an anode layer, which can be sintered under reducing atmospheres, which improves i.a. the performance, the ageing behavior and the ability of the anode to withstand sulfur contaminations of the fuel gas. In the present work, a new anode concept is presented, which is based on a Ni/GDC cermet replacing the established Ni/YSZ cermet. The sintering study is supported by some preliminary results of characterizing the electrochemical performance of the Ni/GDC anodes by impedance spectroscopy. In addition, a thin GDC layer is currently used as diffusion barrier layer between the anode and the metallic substrate. A systematic study of the stability of this barrier layer under anode sintering conditions is given.

Introduction

In future energy concepts, metal-supported solid oxide fuel cells (MSCs) are promising candidates for the highly efficient conversion of chemical energy into electrical energy whereby the development work has been pursued for more than two decades (1). In comparison to ceramic-supported fuel cells, MSCs offer various attractive qualities, i.e. reduced production costs, and improved mechanical stability and robustness, which makes them particularly attractive for mobile applications such as auxiliary power units (APUs). Since 2008, Plansee has been developing a proprietary MSC concept aiming to extend its portfolio of innovative SOFC components. Since the electrochemical performance of current MSCs is still lower than in the state-of-the-art ceramic-supported fuel cells, and since MSC specific degradation phenomena are still not fully understood, Plansee has decided to intensify fundamental research on MSC-related issues (2-4).

The present study was conducted within the framework of the Christian Doppler Laboratory “Interfaces in Metal-Supported Electrochemical Energy Converters”, which pursues a research concept reflecting the major challenges of current MSC technology. The Laboratory is implemented at Forschungszentrum Jülich (Jülich, Germany), one of the pioneers and leading research institutes in SOFC technology worldwide. Vienna University of Technology acts as external research partner and contributes by its widely recognized expertise in electrochemistry.

Currently, the anode of the Plansee MSC concept is based on the established Ni/YSZ cermet material. One beneficial property of Ni anodes is their catalytic activity for the steam reforming of hydrocarbons (5-7), which enables a high fuel flexibility of SOFCs. The possibility to use hydrocarbon fuels is highly attractive from an economic point of view. The products of the internal steam reforming process – mainly H₂ and CO – can be utilized electrochemically. One of the main drawbacks of current Ni/YSZ anodes is their sulfur intolerance. In the presence of H₂S- and SO₂-containing fuels (e.g. diesel or kerosene reformates or biogenic fuel gases), an increase in the anodic polarization resistance and thus a performance loss of the SOFC is observed. This effect is commonly referred to as sulfur poisoning of SOFC anodes and the following sulfur-related poisoning effects on Ni/YSZ were already reported in literature: The extent of poisoning increases with increasing H₂S concentration and decreasing temperature (8-9). Moreover, the sulfur poisoning process is reported to consist of two stages: a first very quick and reversible degradation, which is usually followed by a second slower and irreversible degradation process (5, 10-11). The poisoning effect is explained to be caused by adsorption of sulfur on Ni surface sites, which are active in the electrochemical oxidation of hydrogen (5).

A promising strategy to circumvent at least the second irreversible sulfur related degradation process is the replacement of the ionically conducting phase in common Ni/YSZ anodes by oxides with mixed ionic electronic conductivity (MIEC), e.g. Ce_{1-x}Gd_xO_{2-δ} (GDC). GDC based anodes exhibited a significantly lower performance loss when H₂S was added to the fuel (12-13). Since GDC is also catalytically active for the oxidation of common SOFC fuels, the high electrocatalytic activity of the metal phase (Ni) becomes less important, which makes Ni/GDC electrodes more resistant against sulfur poisoning. Moreover, owing to the mixed conductivity of GDC in reducing atmospheres, the electrochemically active region extends along the entire MIEC surface, and thus beyond the three-phase boundary usually discussed as the active site of Ni-based anodes. The metal in a GDC based anode mainly has to act as an electronically conducting phase for current collection. Moreover, the positive effect of ceria is probably also related to the formation of Ce₂O₂S (14). Thus, the ceria captures the sulfur and lowers the degree of sulfur poisoning of the Ni phase. Long-term stability tests with Ni/ceria cermet anodes, however, have not yet been reported.

Plansee is one of the leading companies in MSC development and industrialization, which includes establishing MSC pilot production to meet customer requirements and offering “ready-to-stack” components. The current Plansee MSC design is shown schematically in Figure 1. It acts as technical reference for the work described in this study.

The basis of the Plansee MSC is a porous sintered plate with a thickness of 1mm, which is manufactured by powder metallurgy starting from mechanically alloyed ITM powders (ITM = intermediate temperature metal, Fe-26Cr-Mo,Ti,Y₂O₃). A diffusion barrier layer (DBL-1) with a thickness of 1–2μm is applied on the metallic substrate by magnetron sputtering. DBL-1 is made of gadolinium-doped ceria Ce_{1-x}Gd_xO_{2-δ} (GDC).

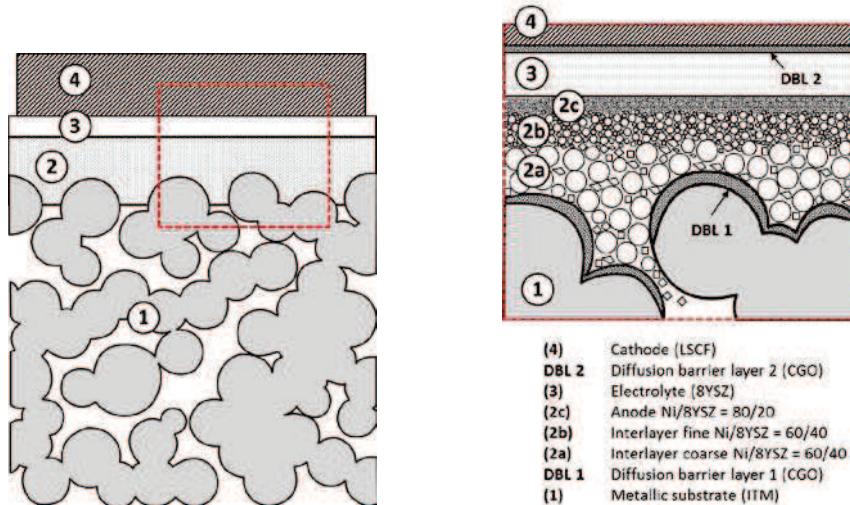


Figure 1. Schematic of the MSC developed by Plansee representing the current status of development (4).

On the top of DBL -1, a bi-layered intermediate structure made of Ni/8YSZ composite is deposited by screen printing. Afterwards, the electrochemically active anode containing the same materials is applied again by screen printing. The overall thickness of all three layers is 40–60μm. Pore size and surface roughness are reduced by decreasing the particle size. Furthermore, the Ni/8YSZ ratio is changed from 60/40 (in wt.%) in the first two intermediate layers to 80/20 in the top layer (active anode; thickness approximately 7μm). Enhanced Ni content in the top layer leads to improved surface quality for subsequent coatings. As a disadvantage, the electrochemical performance of this layer is lowered due to the reduction of the triple-phase-boundary (TPB) length compared to standard ASC anodes (anode-supported cell, ratio usually 60/40). Furthermore, the high Ni content of the active anode layer makes it more susceptible to sulfur poisoning and Ni coarsening. The latter effect is a well-known degradation phenomenon in SOFCs, in particular during long-term operation (15). Afterwards, a thin-film electrolyte with a thickness of 4–5μm is deposited by innovative physical vapor deposition combined with gas flow sputtering (PVD-GFS) (16-17). Another diffusion barrier layer (DBL-2) with a thickness of 0.5–1μm is deposited on the electrolyte by magnetron sputtering. This layer is required when cathodes on the basis of La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} (LSCF) are used to avoid the formation of electrically insulating interlayers such as SrZrO₃ (18-19) at the electrolyte-cathode interface during MSC operation. Finally, the electrochemically active cathode layer is coated on DBL-2 by screen printing.

Goal

The main goal of the present study is the introduction of a new sulfur-tolerant Ni/GDC anode (replacing layer 2c). In addition, a study on the stability of DBL-1 during the

processing of layer 2a, 2b, 2c has been conducted. So far, the knowledge about the sintering behavior of GDC and GDC/Ni in reducing atmospheres is rather scarce. Therefore, a systematic sintering study was carried out in the first step to obtain information on basic material properties under these atmospheric conditions. To monitor the progress in development the novel anodes were analyzed by preliminary electrochemical impedance spectroscopy experiments in the second step of the study.

Material and Methods

The ceramic powders GDC and YSZ, and the metallic powder Ni are commercially available and were used as received from the manufacturer. The ceramic powders were compacted at a pressure of 150 to 250MPa into cylindrical samples ($d=0.25\text{ mm}$, $t \approx 4\text{ mm}$, $m=5\text{ g}$), using an automated press (KOMAGE Gellner KG, Germany). Subsequently, the samples were sintered in a temperature range between 1000°C to 1300°C for 3h in H_2 . The sintering temperatures were chosen to provide an overview of the sintering behavior above and underneath standard sintering temperature of 1200°C . Then, the changes in geometry were measured, and the microstructures were analyzed using SEM to obtain information about the shrinkage behavior. X-ray diffraction measurements were performed to prove phase stability.

The screen printing inks were prepared accordingly to the reference ink, whereas adjustment of the solid content was based on rheological properties (3). Then, the free standing Ni/YSZ (ref.) and Ni/GDC anode layers with different ratios (80/20wt.% and 60/40wt.%) were screen printed on transfer paper (Rullis Russer Coaters Limited, England) utilizing a semi-automated screen printer (Asys Group, Germany). The samples were dried at 60°C for 1h. The layer were detached in warm water and dried for 20min at room temperature. Then, the samples were sintered on powder bed varying the temperature in the range of 1000°C to 1300°C , for 3h in H_2 -atmosphere. The shrinkage was calculated from the change in diameter.

For electrochemical characterization symmetrical electrolyte-supported cells were prepared. Therefore anode layers were screen printed onto both sides of YSZ-electrolyte films ($d=150\mu\text{m}$, Kerafol GmbH, Germany). Subsequently the samples were sintered at 1000°C – 1300°C for 3h in H_2 . For impedance measurements the symmetrical cells were mounted between two Pt sheets, which acted as current collectors. For simulating SOFC anode conditions a gas with $\sim 2.5\% \text{ H}_2/\sim 2.5\% \text{ H}_2\text{O}/\text{Ar}$ was fed through the experimental setup with a flux of about 50 ml/min. The electrochemical polarization resistances of the anodes were characterized by four-wire impedance measurements (Solartron Group, United Kingdom) in a frequency range between 1 MHz and 3 mHz with an ac voltage of 10mV (rms). The measurements were conducted under open-circuit conditions and operating temperatures from 650°C to 850°C .

Results and Discussion

Sintering Study on GDC in Reducing Atmosphere with respect to YSZ Reference

In the available dilatometer device, measurements could be only conducted in air. Therefore, an additional sintering study was done on powder compacts in H_2 atmosphere to estimate the sintering behavior of GDC under reducing atmosphere.

The results reveal that in air the sintering of GDC starts around 1100°C, which means that sintering activity is quite low compared to YSZ in the same temperature range. A different sintering behavior of GDC was expected in H₂ atmosphere with respect to related literature (20-22). During the sintering process GDC specific sintering mechanisms (i.e., oxygen removal) are discussed, which might dominate the shrinkage behavior of GDC in reducing atmosphere.

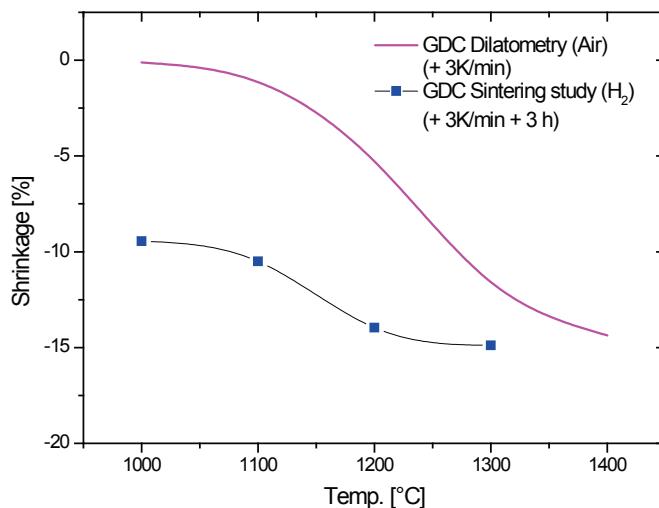


Figure 2. Shrinkage of GDC pellets in H₂ and air (dilatometry).

Figure 2 shows the dilatometry measurements of GDC in air and the related results from the sintering study on pellets in H₂. Obviously, already at 1000°C the GDC pellet (green density $\rho_{\text{rel}}=58\%$) is subjected to strong shrinkage by approx. -10%. The curve (blue data points) has an asymptotical approach to approx. -15% for 1300°C with a density $\rho_{1300^\circ\text{C}}>90\%$. In comparison, the shrinkage of a GDC compact (green density $\rho_{\text{rel}}=57\%$, pink curve) in air is not significant for $T<1100$ °C, but reaches about -15% and $\rho_{1400^\circ\text{C}}>90\%$ at 1400°C without dwell time (dilatometry). In reducing atmosphere, the shrinking process probably already starts at lower temperature than 1000°C and the resulting shrinkage may be observed to a small extent in the given temperature range. Additionally, a single attempt was performed by sintering a pellet in H₂ at 1200°C without dwell time to improve comparability to dilatometry results in air. This experiment confirms the observations discussed above, whereas a negligible dependence of dwell time on the sintering behavior of GDC is stated. Considering the green density of the pellet of $\rho_{\text{rel}}=55\%$, a shrinkage of -13% and a density $\rho_{1200^\circ\text{C},0\text{min}}=82\%$ was achieved.

In contrary, the reference YSZ shows similar sintering behavior for sintering in air and reducing atmosphere. But here, the shrinkage strongly depends on the dwell time. An increase of shrinkage to -12% was noted for sintering at 1200°C for 3h compared to sintering at 1200°C without dwell time, which leads to a shrinkage of YSZ by -3% only.

The different sintering behavior of GDC compared to YSZ is explained by atmosphere-dependent viscoelastic properties of the GDC (21). Accordingly, while sintering in reducing atmosphere, electronic defects are generated in the structure coupled with the reduction of Ce⁴⁺ to Ce³⁺. This phenomenon plays an important role in the thermally activated solid-state diffusion and leads to higher shrinkage rates (23).

In order to evaluate the influence of the shrinkage on the microstructure of the samples, starting powders and sintered pellets were analyzed by SEM (Figure 3 and 4). Hence, the reducing atmosphere influences thermally activated particle growth at the grain boundaries as observed by a densified microstructure. After sintering at 1000°C, (Figure 4 left), a negligible coarsening of the microstructure was observed.

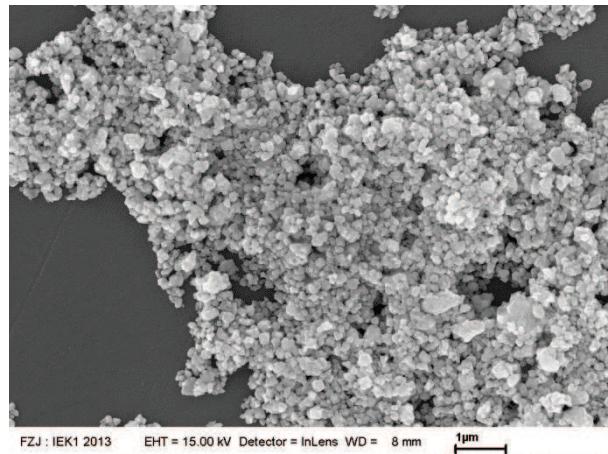


Figure 3. GDC, Pt-sputtered loose powder as delivered $d_{50}=0.35\mu\text{m}$.

With increasing sintering temperature, however, a strong, abnormal particle growth is observed as for example shown after sintering at 1200°C for 3h in H₂ (Figure 4 right). Interestingly, the grains show rod-shaped growth, which supported the effect of *micro cracking* along grain boundaries. Sintering at even higher temperatures leads to unacceptable coarsening and extensive *micro cracking*.

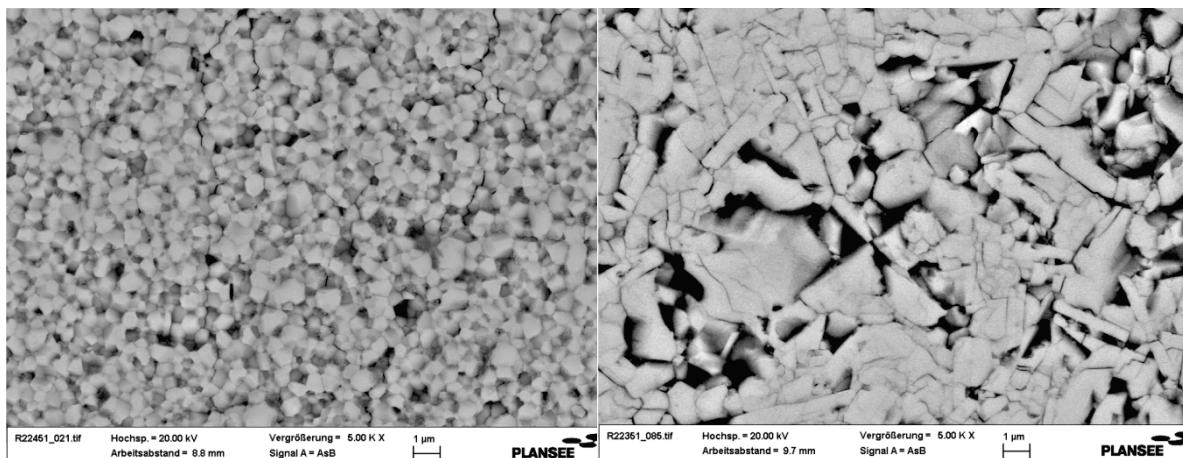


Figure 4. Compacted GDC pellet sintered at 1100°C/3h/H₂, $d\varnothing=0.4\text{--}0.8\mu\text{m}$, compacted GDC pellet sintered, 1200°C/3h/H₂, $d\varnothing=1\text{--}10\mu\text{m}$.

In literature, the loss of mechanical integrity of bulk specimen by *micro cracking* and separation of the particles at the grain boundaries is already described (20). In the present study, related defects were already visible at a sintering temperature of 1100°C becoming more pronounced at higher sintering temperatures coupled with extensive abnormal grain growth. In summary, both effects are less desirable due to decrease of mechanical and structural integrity. Nevertheless, the micro cracking behavior might be significantly

changed if an additional ductile Ni phase is present in the case of sintering cermet anodes in the same temperature range. Related experiments are currently under way.

GDC as delivered is a colorless powder. It has been observed that at sintering temperatures above 1200°C, the pellet turns to yellow-brown. Moreover, the samples radiate heat ($T > 80^\circ\text{C}$) upon removal from the furnace whereas the reference pellets have room temperature. Along with the observation that the samples were also fractured, those facts could be explained by an exothermic re-oxidation in air of Ce^{3+} species back to Ce^{4+} (25-26). Theoretically, this would involve an increase in weight through replacement of oxygen in the lattice structure. Unfortunately, the mechanical instability of the samples (measurement of the actual weight not possible) anticipated any weight analysis. Nevertheless, the assumption will be further investigated by means of chemisorption studies.

In conclusion, it becomes obvious that GDC shows a higher sintering activity in H_2 than in air. Therefore careful adaption of sintering parameters to lower temperatures and/or shorter dwell times is required with respect to the standard sintering conditions used for the Ni/YSZ anode of the MSC.

Non-constrained Shrinkage of Anode Compositions by Means of Free Standing Layers

The state-of-the-art of Plansee MSC anode is a Ni/YSZ-anode (layer 2c) with a metal-ceramic ratio of 80:20wt.%, which was found to be already critical regarding the risk of extensive Ni coarsening at MSC operating conditions. Considering even the improved sintering activity of GDC compared to YSZ, the Ni/GDC ratio was reduced to 60/40 wt.% in the subsequent sintering study, which was done on free-standing anode layers.

The Ni/YSZ reference showed at 1100°C a shrinkage of approx. -7%, which increases strongly to -28% at 1300°C, as given in Figure 5 (black dashed line). This behavior corresponds to the average shrinkage observed in compacted powder specimen.

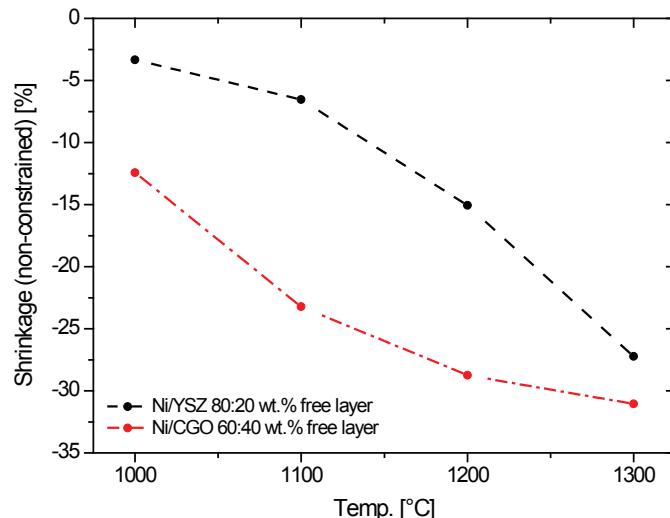


Figure 5. Non-constrained shrinkage investigated on free standing anode layers.

However, comparing the non-constrained shrinkage of Ni/GDC 60:40wt.% (red dot-dashed line), a significant difference to the reference and a similarity to shrinkage of pure

GDC is observed. As already mentioned above, a strong shrinkage of approx. -10% was measured already at 1000°C .With increase of temperature the shrinkage achieves a value of about -30% at 1300°C. Those results confirm again, that Ni/GDC anodes must be sintered at lower temperatures than the Ni/YSZ standard anode. Hence SEM sample preparation of free standing Ni/GDC layer was not successful, microstructural investigation was done on a Ni/GDC anode, which was supported by the MSC standard substrate, consisting of a porous ITM substrate covered with two Ni/YSZ interlayers as sketched out in Figure 1.

The cross-sections of Ni/YSZ reference and Ni/GDC anodes with different cermet ratios support the generated data. A Ni/GDC anode with a ratio of 80:20wt.%, which was sintered at 1200°C, showed the expected strong coarsening of Ni particles and highly reduced open porosity of the layer, which both decrease the catalytically active surface drastically. As a consequence, best results were achieved when not only the Ni amount was reduced but also the sintering temperature lowered for Ni/GDC cermets. On that account the most promising microstructure was found in an anode with a Ni/GDC ratio of 60:40wt.%, which was sintered at 1100°C for 3h in H₂, finally. The related cross-section is given in Figure 6.

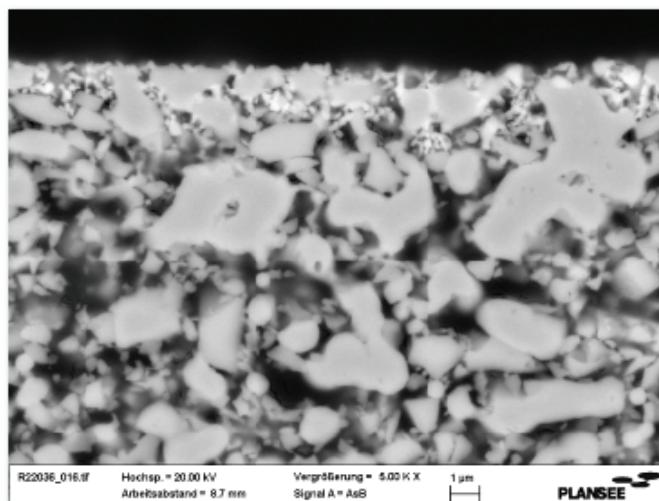


Figure 6. SEM cross section of real anode with Ni/GDC 60:40 wt.% anode sintered at 1100°C for 3h in H₂.

Further improvement of microstructure and Ni/GDC ratio requires systematic impedance spectroscopy studies enabling to evaluate the influence of the individual polarization processes, such as the gas diffusion.

Another important task less discussed in literature so far is the investigation of the phase stability of GDC in the Ni/GDC anode cermet if sintered under reducing atmospheres. In this regard X-ray diffraction studies were conducted on compacted powder specimen and the influence of the sintering temperature on the phase stability is given in Figure 7. It becomes obvious that under the given conditions no significant influence of sintering temperature or reducing sintering atmosphere, on the phase stability of neither GDC nor Ni is observed.

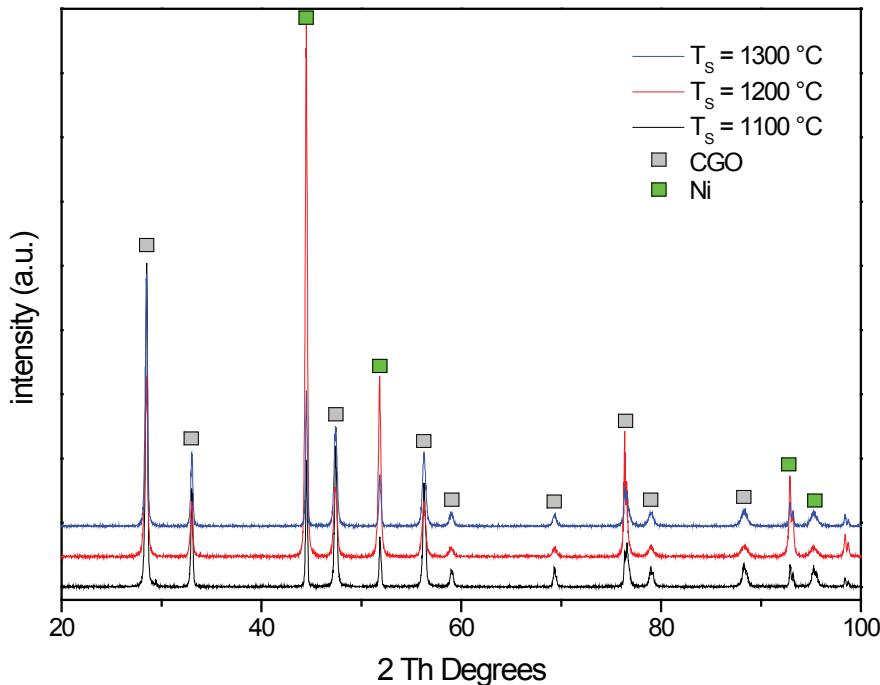


Figure 7. X-ray diffraction study on Ni/GDC 60:40wt.% compacted powder specimen in a temperature range of 1100°C to 1300°C.

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Electrochemical Results Obtained on Symmetrical Cells

As already mentioned above, Ni/GDC 60:40wt.% sintered at 1100°C was specified as best choice anode and thus also electrochemically characterized. Figure 8 shows the impedance spectra measured on GDC in an operating temperature range between 676°C and 855°C. Each spectrum consists of at least two features – a high frequency axis intercept and an asymmetric and depressed low frequency arc. The high frequency intercept consists of contributions from an ion transport resistance in the electrolyte as well as of electronic current collection and possible contact resistances (27). (The temperature dependence of the high frequency intercept being much too low for an ionic transport resistance suggests large contributions of the latter two.)

The low frequency feature can be assigned to the polarization resistance of the porous anodes and the chemical capacitance of GDC. (28). We are aware that the measured anode polarization resistances of 15 – 35 Ωcm^2 are too high for an application in an SOFC. However, it should be again emphasized that the shown spectra are preliminary results and thus no unambiguous interpretation of the results is possible yet.

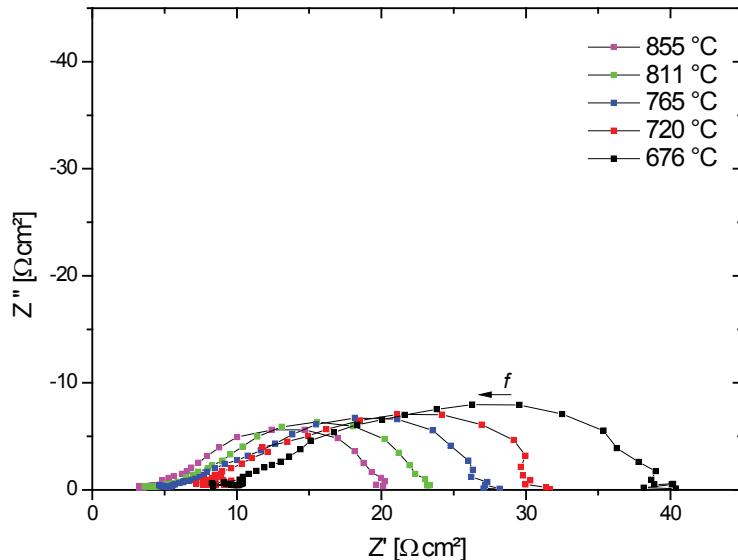


Figure 8. Impedance measurement on symmetrical cells consisting of Ni/GDC 60:40wt.% anode sintered at 1100°C for 3h in H₂.

Summary and Outlook

The present investigation aims on replacing the YSZ by GDC in the cermet anode for metal-supported SOFCs. Firstly, the chemical and physical stability of GDC in reducing atmosphere was questioned, but disproved by a sintering study on GDC with respect to YSZ reference. Secondly, the thermomechanical behavior was investigated by measuring the non-constrained shrinkage of anode compositions. The preliminary results reveal the potential of the anode based on Ni/GDC, but further systematic studies are required to implement the concept to current MSC technology. Preparation of symmetrical cells with alternative Ni/GDC and preliminary characterization of these samples by means of impedance spectroscopy was successfully performed. The first results are promising but further electrochemical studies of Ni/GDC anodes with improved sample preparation are required for lowering polarizations and improving reproducibility of the measurements. At first the electrochemistry will be continued on symmetrical cells and then pursued on complete metal-supported cells, with and without sulfur contaminations in the fuel gas. As mentioned before, GDC as anode material is promising due to mixed-ionic-electronic conductive properties opening alternative reaction pathways which increase i.a. the cell performance. Therefore an investigation of the specific surface area of Ni and GDC in the Ni/GDC anode by chemisorption experiments is planned.

Acknowledgments

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