Interaction of a ceria-based anode functional layer with a stabilized zirconia electrolyte: considerations from a materials perspective

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Abstract

We report on the materials interaction of gadolinium doped ceria (GDC) and yttria stabilized zirconia (YSZ) in the context of high temperature sintering during manufacturing of anode supported solid oxide fuel cells (AS-SOFC). While ceria-based anodes are expected to show superior electrochemical performance and enhanced sulfur and coking tolerance in comparison to zirconia-based anodes, we demonstrate that the incorporation of a Ni-GDC anode into an ASC with YSZ electrolyte decreases the performance of the ASC by approximately 50% compared to the standard Ni-YSZ cell. The performance loss is attributed to interdiffusion of ceria and zirconia during cell fabrication, which is investigated using powder mixtures and demonstrated to be more severe in the presence of NiO. We examine the physical properties of a GDC-YSZ mixed phase under reducing conditions in detail regarding ionic and electronic conductivity as well as reducibility, and discuss the expected impact of cation intermixing between anode and electrolyte.

1. Introduction

Solid oxide cells are electrochemical energy conversion devices that can convert hydrogen or hydrocarbon fuels into electricity (fuel cell, SOFC) or vice-versa (electrolysis cell, SOEC). Typical operation temperatures for anode supported cells (ASC) are 700°C in fuel cell mode and 800°C in electrolysis mode.[1] ASC stacks operated at 700°C with stainless steel interconnects have demonstrated high power densities (>1 W/cm^2 at 0.7 V)[2] and excellent stability (>80.000 h operation time[*]) using humidified hydrogen as fuel and laboratory air as oxidant.[3] Since the operating temperature is high enough for internal reformation of hydrocarbon fuels into CO_2 and H_2 in the anode substrate, the fuel flexibility of SOFCs makes them attractive as a transition technology on the road toward a sustainable, low-emission energy supply. One environmentally friendly approach is to use SOFCs to convert bio-fuels into electricity, effectively reducing the CO_2 emission to zero. However, bio-fuels can include significant amounts of sulfur-containing compounds or tars such as phenyl or naphthalene. A well-known degradation effect of the commonly-used Ni-YSZ anode is the poisoning of the anode by sulfur deposition or carbon deposition (coking).[4, 5, 6, 7] The sulfur atoms show a propensity towards deposition at the three-phase boundaries (TPB) in the anode, leading to a fast performance degradation, while massive coking can block the gas diffusion in the anode substrate in addition to blocking the TPBs. To improve the stability toward sulfur poisoning and cooking, Ni-GDC anodes have been suggested.[8, 9, 10, 11, 12] Since a fraction of Ce^{4+} ions reduce to Ce^{3+} ions in the fuel gas, the electronic conductivity of GDC under anode conditions extends the TPBs and increases the active area of the anode, mitigating the effect of coking and sulfur deposition.

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[*] The stack reached 70.000 hours of operation in 2016 and is still running, having reached more than 80.000 hours of operation in 2017.

Both ceria and zirconia crystallize in the fluorite structure and show complete miscibility.[13] Ceria-zirconia solid solutions are a popular oxygen storage material, since the oxygen storage capacity of CeO_2-ZrO_2 is increased compared to pure CeO_2.[14] However, the increased storage capacity (reducibility) is accompanied by a decrease of the ionic conductivity of CeO_2-ZrO_2 solid solutions as well as mixtures of doped ceria and zirconia.[15, 16, 17] Since GDC interlayers are routinely used in SOFCs to avoid the reaction between Sr-containing cathodes like $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) and the zirconia electrolyte, the effect of GDC-YSZ intermixing on the air side of SOFCs is well studied.[18, 19, 20, 21, 22, 23] However, dedicated investigations to elucidate the influence of an YSZ-GDC mixed phase under the reducing conditions of the fuel gas remain scarce.

In this paper, we examine the decreased power density of an anode supported SOFC that uses Ni-GDC instead of the Ni-YSZ anode. Our investigation focuses on the materials interaction between the GDC in the anode and the YSZ of the electrolyte and anode support during the fabrication process. Based on investigations of the conductivity in both air and Ar/H_2 atmosphere as well as the reducibility of GDC-YSZ mixed phases, we suggest that the decreased power density of the cell with a Ni-GDC anode is caused by interdiffusion of the Zr- and Ce-phases during the high temperature sintering of the electrolyte and the concomitant loss of ionic conductivity.

2. Experimental

2.1. Cell fabrication and powder preparation

The NiO-YSZ anode support was fabricated using tape casting as described in detail elsewhere, and pre-sintered at 1230°C in air.[24, 25] Commercial NiO (Vogler, The Netherlands) and $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC, Treibacher, Austria) powders were used for the electrochemically active anode layer. The powders were mixed with a NiO/GDC weight ratio of 50:50 to prepare screen-printing paste, which contained terpineol (Sigma Aldrich Chemie GmbH, Taufkirchen, Germany) as solvent and Nuosperse FX9086 (Elementis Specialities Inc., East Windsor, NJ 08512, USA) as dispersant. The anode layer was dried in air and calcined at 1000°C for 1 h with a heating rate of 3 K min^{-1}. Except for the substrate, all layers (NiO-GDC (50wt% NiO) anode layers, $Y_{0.148}Zr_{0.852}O_{1.926}$ (8YSZ) electrolyte, GDC diffusion barrier layer, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode functional layer) were fabricated using screen-printing and adapted sintering. The sintering temperature of the 8YSZ electrolyte, the 20GDC barrier layer and the LSCF cathode were 1400°C, 1300°C and 1080°C, respectively. The active cathode area for cell testing was 16 cm^2.

The powders used for the interdiffusion study were identical to those used for cell fabrication. In a first experiment, equal weight percentages of 8YSZ (Tosoh, Japan) and 20GDC (Treibacher Industries, Austria) powder were mixed and ball milled in ethanol with zirconia balls for 24 hours. The particle sizes of both primary powders were very similar after ball milling: d_{10} = 0.58 µm, d_{50} = 0.64 µm, d_{90} = 0.75 µm and d_{10} = 0.5 µm, d_{50}= 0.71 µm, d_{90} = 0.99 µm for 20GDC and 8YSZ, respectively. In a second experiment, equal weight percentages of 20GDC, 8YSZ and NiO were ball milled together to assess the influence of NiO on the interdiffusion of 20GDC and 8YSZ. After drying, the mixtures were uniaxially pressed into pellets and sintered at different temperatures for 5h in air. The sintering time was chosen to mimic the exact sintering conditions of anode supported cells, which necessitate a sintering temperature of 1400°C for 5 hours to densify the electrolyte and achieve the desired shrinkage of the anode substrate.

2.2. Cell testing

Cell performance was investigated in a test bench at the Institute for Applied Materials (IAM-WET), KIT, described by Timmermann *et* al.[26] The cells were contacted with Ni-mesh on anode side and Au-mesh on cathode side, respectively. After a defined heat-up and reduction procedure, current-voltage characteristics were recorded at 820°C using laboratory air (1000 sccm) as oxidant and dry hydrogen (1000 sccm) as fuel.

2.3. X-ray diffraction (XRD)

X-ray diffraction measurements on powder mixtures were performed using a Bruker D4 diffractometer. Powder mixtures were ball-milled prior to uniaxial pressing, and sintered at temperatures between 1000°C and 1400°C for 5 hours. The phase composition was analyzed using a combination of a polynomial fit to determine the position of diffraction lines, and a subsequent Rietveld refinement method.

2.4. X-ray photoelectron spectroscopy (XPS)

XPS was performed in a VersaProbe photoelectron spectrometer (Physical Electronics) utilizing a monochromated Al K_α source and a hemispherical photoelectron analyzer with a pass energy of E_{pass} = 23 eV. In order to remove surface carbonate contamination without a heat treatment that would oxidize the sample surface, ceramic samples were polished on fine grained sand paper prior to analysis and cleaned with ethanol. It is not expected that this pre-treatment induces artifacts into the measurement. An electron flood gun was used to provide charge neutralization for insulating samples. Where neutralization was insufficient, the charging effect was corrected for by using the binding energy of the Zr *3d* doublet. XPS spectra were evaluated using the CasaXPS software package.

2.5. 4-point conductivity

Electrical conductivity in air and Ar/H_2 was investigated using a custom-built setup inside a tube furnace. Conductivity experiments were performed on ceramic bars after sintering at 1400°C for 5 h in air. The density of the sintered bodies was investigated using the Archimedes method and cross-sectional electron microscopy, and the conductivity was corrected for the porosity using the procedure outlined by Mizusaki et al.[27]

2.6. Thermo-gravimetric analysis

Thermogravimetric measurements were performed in a NETZSCH STA 449 F3 Jupiter, using Al_2O_3 crucibles. Buoyancy was corrected through a reference measurement. Oxygen stoichiometry was calculated from the weight loss measured in Ar/H_2 atmosphere.

3. Results

3.1. Cell tests

Anode supported cells with Ni-YSZ and Ni-GDC AFL were tested in a test rig using dry H_2 as fuel and laboratory air as oxidant. Figure 1 shows the current-voltage curves of two cells with Ni-GDC (red triangles) and Ni-YSZ (black squares) anode at 820°C. Apart from the anode layer, the two cells had nominally identical structures. At 820°C, the current density of the cell with Ni-GDC anode at a cell voltage of 800 mV is ~700 mA, approximately 50% of that of the cell with Ni-YSZ anode. The decreased current density motivated the following studies on the interdiffusion on YSZ and GDC and the physical properties of the 20GDC-8YSZ mixed phase.

3.2. Interdiffusion during sintering

The interdiffusion of doped zirconia with doped ceria during high temperature sintering has been the subject of a number of studies, and the high solubility of each phase in the other is well documented.[13, 18, 21, 23] The amount of interdiffusion depends on the powder properties and their processing history, as well as sintering time and temperature. It is therefore necessary to investigate the phase content as a function of temperature with the actual powders used in this study in order to obtain insight into the amount of interdiffusion that can be expected in this study. In order to investigate whether the addition of NiO influences the interdiffusion, the experiments were conducted for mixtures of equal amounts of YSZ and GDC, as well as for mixtures of YSZ and GDC with NiO.

Figure 2 a) shows the X-ray diffraction patterns of the crushed pellets of the GDC-YSZ mixtures after sintering at different temperatures. The Bragg reflections corresponding to oxidized the (111), (200) and

(220) crystallographic planes of 20GDC and 8YSZ are indicated with a red dashed line and a blue dotted line, respectively.

From the XRD patterns of the YSZ-GDC mixtures, an increasing amount of intermixing is apparent with increasing sintering temperature. After heat treatment at 1000°C, the 8YSZ and 20GDC phases are still well separated, indicating that intermixing is negligible. With increasing sintering temperature, the intermixing of the two phases is easily visible by the shifting reflections. The larger 20GDC lattice contracts with an increasing amount of Zr- and Y-ions dissolving into it, shifting the reflections to higher 2θ angles according to Bragg's law ($\sin(\Theta) \sim 1/a$). This phase is denoted as GDC'. Correspondingly, the smaller unit cell of 8YSZ expands with increasing amounts of interdiffusing Ce- and Gd-ions, shifting the reflections to lower angles (YSZ'). After sintering at 1300°C, only a single fluorite phase with broad reflections (due to high lattice disorder) is visible. The reflections sharpen after heat treatment at 1400°C, resulting from less microstrain effects and bigger crystallite sizes of the mixed phase at this temperature.

Rietveld analysis was performed to investigate the development of the relative phase content as a function of sintering temperature. The lattice constant of the YSZ-GDC solid solution follows Vegard's law very closely and shows a linear relationship between stoichiometry and lattice constant.[15] It is therefore possible to first determine the lattice constant of each phase visible in the diffraction pattern, calculate the stoichiometry of this phase and subsequently use this information to determine the phase content via Rietveld refinement. The results of this procedure are shown in Figure 3 a) for the GDC-YSZ powder mixture. It appears that the amount of pure 20GDC (black, solid squares) decreases more rapidly than that of 8YSZ (red, solid circles), while the amount of the GDC-rich mixed phase (GDC', hollow black squares) increases faster than the amount of the YSZ-rich mixed phase (YSZ', hollow red circles). The phase content of the YSZ-GDC mixed phase (blue, solid triangles) is in between the two mixed phases with either Zr- or Ce-majority for sintering temperatures up to 1200°C. For higher sintering temperatures, only the single YSZ-GDC phase is observed. The analogous analysis for the NiO-GDC-YSZ mixtures shows a strong influence of the presence of NiO in the powder mixture, as depicted in Figure 3 b). The presence of NiO accelerates the interdiffusion kinetics of GDC and YSZ, resulting in a more complete intermixing at lower temperatures compared to the GDC-YSZ mixture. This effect could be related to an increase in grain boundary mobility and grain growth kinetics of 8YSZ in the presence of NiO.[28, 29]

The experimental procedure employed does not allow to determine *a priori* whether the observed intermixing is limited kinetically (the system strives for equilibrium, but does not reach it in the given timeframe) or reaches thermodynamical equilibrium for each investigated temperature. Further experiments show that the phase composition is a function of annealing time as well as temperature (data not shown), therefore it is conceivable that the GDC' and YSZ' phases are kinetically stabilized intermediates. This is in line with the expectations for a diffusion-driven intermixing.

3.3. Reducibility

In order to investigate the reducibility of YSZ-GDC solid solutions, ceramic samples were reduced at 900°C for 3 hours in Ar/H_2. The valence state of the Ce-ions of the reduced samples was investigated by XPS. Using peak fitting routines, it is possible to quantify the amount of tri- and tetravalent ceria ions in the surface region of each sample. Using the electroneutrality condition:

$$2[V_O^{\bullet\bullet}] = [Ce'_{Ce}] \tag{1}$$

the ratio of Ce^{3+}/Ce^{4+} ions (Ce'_{Ce} and Ce^{x}_{Ce}in Kroeger-Vink notation, respectively) can be used to calculate the oxygen non-stoichiometry δ in YSZ-GDC.

The Ce 3*d* spectrum exhibits a complex shape for mixed valence compounds. The Ce 3*d* level is split into a doublet (denoted as *u* and *v*) by the spin orbit interaction. In addition, each doublet shows multiple emission lines related to different final states of the excitation process, with Ce^{3+} showing 2 multiplets and Ce^{4+} showing 3 multiplets per spin-orbit split state. For mixed-valence ceria compounds, a physically correct description therefore contains a total of 10 emission lines that make up the Ce 3*d* spectrum.[30] Emission lines corresponding to Ce^{3+} are denoted as v^0, v', u^0 and u', whereas those corresponding to Ce^{4+} are denoted as v, v'',v''', u, u'' and u''' (in order of ascending binding energy).

Figure 4 shows an exemplary Ce 3*d* spectrum of an YSZ-GDC powder mixture that was sintered at 1400°C and reduced at 900°C. Due to the inherent widths of each emission line and the limited energy resolution of the photoelectron analyzer, there is significant overlap between the emission lines. In order to obtain a physically sound least-square fit of the experimental spectrum with these many components, it is important to reduce the amount of free fitting parameters. Table 1 shows the restrictions that were imposed upon the fit for each spectrum in order to enable the comparison of different spectra. The binding energy of the lowest-energy component of both $3d_{5/2}$ and $3d_{3/2}$ lines was kept as a free fitting parameter, while all other binding energies were set to defined energy distances to this component. The intensity ratio was kept at $3d_{5/2} / 3d_{3/2} = 1.5$. In addition, it was necessary to model the background using a Shirley background function in three different regions (as indicated by the vertical dashed lines in Figure 4). As a consequence of these constraints, the numerical fit to the experimental data is not ideal for all spectra. However, the parameter restrictions prevent unphysical modifications to the model caused by the least-squares fit. The fits for YSZ-GDC mixtures sintered at 1200°C and 1300°C, as well as for 20GDC sintered at 1400°C, are shown in the supplementary information available online in Figures S1-S3, respectively. We note that YSZ-GDC mixtures sintered at less than 1200°C were too insulating to measure reliably with XPS, even after reduction at 900°C in Ar/H_2, which is a result of the significant amount of the insulating 8YSZ phase that is still present in these samples (see Figure 3 a)). The XPS analysis reveals that the amount of Ce^{3+} ions after reduction increases with increasing sintering temperature. Considering the XRD results, the reducibility is correlated to the amount of the YSZ-GDC mixed phase present in the sample. These findings are in line with previous findings that ceria-zirconia mixtures are more reducible than pure CeO_2.[31, 32]

Another suitable technique to quantify the oxygen loss during reduction is thermo-gravimetric analysis (TGA). Sintered samples were first ground to a powder to increase the surface area of the sample, and heated to 1100°C in air to remove residual organics and carbonates. The subsequent heat treatment switched between air and Ar/H_2 atmosphere at different temperatures. Figure 5 shows the TGA curves for 20GDC and GDC-YSZ. Knowing the relative weight loss after reduction, the oxygen non-stoichiometry δ can be calculated for each compound under the assumption that the only volatile species under the experimental conditions is oxygen. Once δ is known, the concentration of Ce^{3+} can be calculated using equation 1. The values of δ obtained from XPS and TGA at 900°C are compared in Table 2. YSZ-GDC and pure GDC sintered at 1400°C show a very similar degree of reduction according to both XPS and TGA.

We note that due to the fact that TGA probes the entire sample and XPS probes only a few monolayers at the sample surface, there is not a good quantitative agreement between the values derived by XPS and TGA. The fact that the surface is more deficient of oxygen than the bulk is in general agreement with the reduction behavior of oxides, however. The values derived by TGA should be regarded as more accurate in assessing the overall oxygen stoichiometry in the sample.

3.4. Conductivity

The DC conductivity of 8YSZ, 20GDC and YSZ-GDC after sintering at 1400°C in air was investigated using a 4-probe geometry in air and Ar/H_2 as a function of temperature. Figure 6 shows the isobaric measurements of 8YSZ, 20GDC, YSZ-GDC (black, red and blue symbols, respectively) in oxidized state in air (closed symbols) and in reduced state on Ar/H_2 (open symbols). The lines are a guide to the eye.

The total conductivity σ_{tot} of mixed ionic-electronic conducting (MIEC) oxides is the sum of the partial conductivities σ_i of each mobile species:

$$\sigma_{tot} = \sum_i \sigma_i = \sum_i n_i q_i \mu_i \quad (2)$$

where n_i, q_i and μ_i denote the charge carrier density, the electrical charge and the mobility, respectively, of species i. The mobility of each charge carrier species is thermally activated and can be described by the analytical relation:

$$\mu_i = \frac{\mu_i^0}{T} \exp\left(-\frac{H_{m,i}}{kT}\right) \quad (3)$$

where μ_i^0 and $H_{m,i}$ are the pre-exponential factor of the mobility and the migration enthalpy of species i, respectively, while k and T denote Boltzmann's constant and the absolute temperature. In the investigated temperature range, the apparent activation energy of the mobility equals the migration enthalpy, since contributions of the association enthalpy between oxygen vacancy and the ionized donors are typically observed at lower temperatures only. No changes in effective activation energy are observed in the investigated temperature range, indicating the absence of association effects.

Since the investigated ceramics are acceptor doped, all measured conductivities in the oxidized state are purely ionic, i.e. the ionic transference number $\tau_{ion} = \sigma_{ion}/\sigma_{tot}$ is very close to 1.[17] Keeping in mind that the self-ionization of both ceria and zirconia is negligible at these temperatures in air ($n \ll [A_A']$), it is possible to calculate the oxygen vacancy concentration from the charge neutrality condition given in equation 1. The pre-exponential factor μ_V^0 and migration enthalpy $H_{m,V}$ of oxygen vacancies can then be extracted from the conductivity data using equations 2 and 3.

In the reduced state, the Ce-containing ceramics show increased conductivity due to the reduction of ceria:

$$Ce_{Ce}^x \rightarrow Ce_{Ce}' + n \quad (4)$$

Due to the loss of oxygen, the concentration of oxygen vacancies is increased in the material. The compensating electrons are located on the Ce^{3+} ions and can conduct electrical charge through a polaron hopping mechanism. Using TGA data to determine the oxygen vacancy concentration at 900°C in Ar/H_2, the electron density can be calculated using equation 4. Under the assumption that the mobility of oxygen vacancies is not affected by their increased concentration, it is then possible to calculate the pre-exponential factor μ_{el}^{0} and migration enthalpy $H_{m,el}$ of the electronic charge carriers using equations 2 and 3. Table 3 summarizes the calculated parameters. Numbers printed in italics were calculated for the oxidized state and then used to calculate the ionic conductivity in the reduced state. The effective activation energy E_A is also noted in Table 3, which is identical to the migration enthalpy of oxygen vacancies in the oxidized state, but is a combination of the migration enthalpies for oxygen vacancies and electrons in the reduced state. The measurement uncertainty is $\pm$ 0.01 for all values in (eV) and $\pm$ 1 for all mobility values.

The extracted value for the migration enthalpy for 20GDC and 8YSZ are in good agreement with values reported in literature.[33, 34, 35] Wang *et* al. report a migration enthalpy for oxygen vacancies and electrons in 20GDC as 0.71 eV and 0.52 eV, respectively, in excellent agreement with both the measured and calculated result for 20GDC.[33]

The YSZ-GDC system behaves analogous to pure GDC. The effective activation energy in the oxidized state agrees well with values reported in literature.[15, 16] While the effective activation energy in the reduced state is slightly higher than for 20GDC, the calculated migration enthalpy for electrons is identical within the measurement uncertainty to that of 20GDC. The mobility of electrons is significantly smaller in YSZ-GDC than in 20GDC, which is intuitive since there are fewer available Ce-sites in YSZ-GDC. Interestingly, while the mobility of both oxygen vacancies and electrons is lower in YSZ-GDC than in pure 20GDC, the cause is different in that an increased migration enthalpy $H_{m,V}$ of oxygen vacancies and a reduced pre-exponential factor μ_{el}^{0} for electrons is observed. The increased migration enthalpy $H_{m,V}$ is likely related to the increased disorder in the crystal lattice of YSZ-GDC as compared to 20GDC. The difference in ionic radii of the cations surrounding an oxygen vacancy lifts the degeneracy of the energy barriers for a jump to the adjacent sites around the vacancy, as discussed by Rührupp and Wiemhöfer.[16] In other words, the mobility of the oxygen vacancies is reduced because the local crystal structure is not isotropic around the vacancy. In contrast, the mobility of the electrons is decreased due to a decrease in the pre-exponential factor μ_{el}^{0} , while the migration enthalpy of electrons is the same as that of 20GDC. The constant migration enthalpy is not surprising, given the fact that the only available sites for electron transport are Ce ions, both in pure 20GDC and YSZ-GDC. The reduced pre-exponential factor is most likely related to the much lower availability of Ce-ions, since the amount of Ce in the lattice is approximately 35% with respect to the cation stoichiometry. It is therefore likely that there are Ce-ions in the lattice that do not have another Ce-ion as a next neighbor, effectively trapping electrons localized on the isolated Ce-ion.

4. Discussion

The integration of a ceria-based anode into an ASC with an 8YSZ electrolyte leads to a strong intermixing of YSZ and GDC during the high temperature sintering step necessary to densify the electrolyte. Rührupp and Wiemhöfer discussed the effect of varied Ce/Zr ratios with a fixed amount of acceptor dopants ($(Ce_xZr_{1-x})_{0.8}RE_{0.2}O_{1.9}$) on the electrical conductivity in some detail, and found a minimum of the conductivity when $x = 0.5$.[16] The investigation by Tsoga et al. of the physical properties of YSZ-GDC mixed phases as a function of the mixing ratio under oxidizing conditions came to the same conclusion.[15] We have therefore focused on this mixing ratio to study the reducibility and the electrical conductivity. Going beyond the previous investigations, we have studied the YSZ-GDC mixed phase under reducing conditions since the intermixing layer is located on the fuel side of the cell.

The intermixing of the two fluorite phases YSZ and GDC is diffusion-driven and therefore the kinetics are strongly temperature dependent. Our model powder mixtures of YSZ and GDC show a complete interdiffusion after the standard electrolyte sintering procedure at 1400°C, which implies an interdiffusion zone of the order of a micrometer or larger. As a consequence, an YSZ-GDC mixed layer can be assumed to form during sintering at the contact points of AFL and electrolyte.

We therefore investigated the physical properties of the YSZ-GDC mixed phase under anode conditions, in order to assess the consequences of the intermixing process on the conductivity. Our dedicated investigation reveals that not only the ionic conductivity, but also the electronic conductivity of the GDC phase is negatively affected. This implies that beyond the reduced ionic conductivity, the advantage of using a GDC anode to extend the size of the three-phase boundaries will be negatively impacted.

The reducibility of the YSZ-GDC mixed phase is comparable to that of pure GDC, as determined by XPS and TGA. Therefore, better catalytic properties of the anode cannot reasonably be expected, in contrast to undoped CeO_2 and CeO_2-ZrO_2 mixtures.[14]

5. Conclusions

It is possible to examine plausible effects on the cell performance based on the material properties outlined in this paper.The impact of the GDC-YSZ interdiffusion on cell performance can be divided into the ionic conductivity of the electrolyte (ohmic resistance) and the electrochemical processes in the anode function layer (polarization resistance).

i) The <u>ohmic resistance</u> of the cell depends on the ionic conductivity and the thickness of the electrolyte. Since the intermixed YSZ-GDC phase shows an ionic conductivity almost an order of magnitude lower than that of YSZ at 700°C (0.0034 S/cm and 0.02 S/cm, respectively), even a small interdiffusion layer can significantly increase the electrolyte resistance. An interdiffusion layer of 1 µm thickness could thus double the ohmic resistance of a 10 µm thin supported electrolyte.

ii) The <u>polarization resistance</u> of the cell depends strongly on the length of the three-phase boundaries (TPBs) between the metal catalyst, the ionic conductor and the fuel gas. A major advantage of GDC is the extension of the TPBs due to the electronic conductivity under fuel atmosphere, and thus a higher density of active sites compared to YSZ-based anodes. However, the reduction in electronic as well as ionic conductivity upon diffusion of Zr into the GDC anode will reduce the electrochemical activity of the anode. Furthermore, interdiffusion between YSZ and GDC may lead to changes in the microstructure of the AFL due to the Kirkendall effect.[21] One possible result of microstructural changes would be NiO coarsening and a concomitant reduction of the length of the TPBs. All of these effects can be expected to increase the polarization resistance of the anode.

It is beyond the scope of this investigation to pinpoint which one of the discussed mechanisms is the reason for the observed performance loss compared to a Ni-YSZ anode. The effect of the cell microstructure and the electrochemical performance of the cells with Ni-GDC anodes will be discussed in detail in a forthcoming paper.

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References

1. Steinberger-Wilckens, R., Blum, L., Buchkremer, H. P., et al., Recent Results in Solid Oxide Fuel Cell Development at Forschungszentrum Juelich. *ECS Transactions* (2011);35:53-60.

2. Han, F., Mücke, R., Van Gestel, T., et al., Novel high-performance solid oxide fuel cells with bulk ionic conductance dominated thin-film electrolytes. *Journal of Power Sources* (2012);218:157-162.
3. Blum, L., de Haart, L., Malzbender, J., et al., Anode-Supported Solid Oxide Fuel Cell Achieves 70 000 Hours of Continuous Operation. *Energy Technology* (2016);4:939-942.
4. Rasmussen, J. F. B. and Hagen, A., The effect of H_2S on the performance of Ni–YSZ anodes in solid oxide fuel cells. *Journal of Power Sources* (2009);191:534-541.
5. Offer, G. J., Mermelstein, J., Brightman, E., et al., Thermodynamics and Kinetics of the Interaction of Carbon and Sulfur with Solid Oxide fuel Cell Anodes. *Journal of the American Ceramic Society* (2009);92:763-780.
6. Lorente, E., Berrueco, C., Millan, M., et al., Effect of tar fractions from coal gasification on nickel–yttria stabilized zirconia and nickel–gadolinium doped ceria solid oxide fuel cell anode materials. *Journal of Power Sources* (2013);242:824-831.
7. Lorente, E., Millan, M., and Brandon, N. P., Use of gasification syngas in SOFC: Impact of real tar on anode materials. *International Journal of Hydrogen Energy* (2012);37:7271-7278.
8. Zhang, L., Jiang, S. P., He, H. Q., et al., A comparative study of H_2S poisoning on electrode behavior of Ni/YSZ and Ni/GDC anodes of solid oxide fuel cells. *International Journal of Hydrogen Energy* (2010);35:12359-12368.
9. Kavurucu Schubert, S., Kusnezoff, M., Michaelis, A., et al., Comparison of the performances of single cell solid oxide fuel cell stacks with Ni/8YSZ and Ni/10CGO anodes with H_2S containing fuel. *Journal of Power Sources* (2012);217:364-372.
10. Xu, C., Gansor, P., Zondlo, J. W., et al., An H_2S-Tolerant Ni-GDC Anode with a GDC Barrier Layer. *Journal of The Electrochemical Society* (2011);158:B1405-B1416.
11. Lee, K. T., Vito, N. J., Camaratta, M., et al., Effect of Ni-GDC AFL Composition on Performance of IT-SOFCs. *ECS Transactions* (2010);28:151-163.
12. Gerstl, M., Nenning, A., Iskandar, R., et al., The Sulphur Poisoning Behaviour of Gadolinia Doped Ceria Model Systems in Reducing Atmospheres. *Materials* (2016);9:649.
13. Varez, A., Garcia-Gonzalez, E., and Sanz, J., Cation miscibility in CeO_2–ZrO_2oxides with fluorite structure. A combined TEM, SAED and XRD Rietveld analysis. *J. Mater. Chem.* (2006);16:4249-4256.
14. Kašpar, J., Fornasiero, P., and Graziani, M., Use of CeO_2-based oxides in the three-way catalysis. *Catalysis Today* (1999);50:285-298.
15. Tsoga, A., Naoumidis, A., and Stöver, D., Total electrical conductivity and defect structure of ZrO_2–CeO_2–Y_2O_3–Gd_2O_3 solid solutions. *Solid State Ionics* (2000);135:403-409.
16. Rührup, V. and Wiemhöfer, H. D., Ionic conductivity of Gd- and Y-doped Ceria-Zirconia solid solutions. *Z. Naturforschung* (2006);61b:916-922.
17. Eufinger, J.-P., Daniels, M., Schmale, K., et al., The model case of an oxygen storage catalyst - non-stoichiometry, point defects and electrical conductivity of single crystalline CeO_2-ZrO_2-Y_2O_3 solid solutions. *Physical Chemistry Chemical Physics* (2014);16:25583-25600.
18. Wilde, V., Störmer, H., Szász, J., et al., Effect of $Gd_{0.2}Ce_{0.8}O_2$ Sintering Temperature on Formation of a $SrZrO_3$ Blocking Layer between $Y_{0.16}Zr_{0.84}O_2$, $Gd_{0.2}Ce_{0.8}O_2$ and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$. *ECS Transactions* (2015);66:103-107.
19. Szász, J., Wankmüller, F., Wilde, V., et al., High-Performance Cathode/Electrolyte Interfaces for SOFC. *ECS Transactions* (2015);68:763-771.
20. Tsoga, A., Gupta, A., Naoumidis, A., et al., Gadolinia-doped ceria and yttria stabilized zirconia interfaces: regarding their application for SOFC technology. *Acta Materialia* (2000);48:4709-4714.
21. Tsoga, A., Naoumidis, A., Gupta, A., et al., "Microstructure and interdiffusion phenomena in YSZ-CGO composite electrolyte," pp. 794-799 in Materials science forum. Vol. 308. (1999).

22. Mitsuyasu, H., Nonaka, Y., and Eguchi, K., Analysis of solid state reaction at the interface of yttria-doped ceria/yttria-stabilized zirconia. *Solid State Ionics* (1998);113–115:279-284.
23. Somekawa, T., Matsuzaki, Y., Tachikawa, Y., et al., Study of the solid-state reaction at the interface between lanthanoid-doped ceria and yttria-stabilized zirconia for solid-oxide fuel cell applications. *Solid State Ionics* (2015);282:1-6.
24. Blum, L., de Haart, L. G. J., Malzbender, J., et al., Recent results in Jülich solid oxide fuel cell technology development. *Journal of Power Sources* (2013);241:477-485.
25. Schafbauer, W., Menzler, N. H., and Buchkremer, H. P., Tape Casting of Anode Supports for Solid Oxide Fuel Cells at Forschungszentrum Jülich. *International Journal of Applied Ceramic Technology* (2014);11:125-135.
26. Timmermann, H., Sawady, W., Reimert, R., et al., Kinetics of (reversible) internal reforming of methane in solid oxide fuel cells under stationary and APU conditions. *Journal of Power Sources* (2010);195:214-222.
27. Mizusaki, J., Waragai, K., Tsuchiya, S., et al., Simple Mathematical Model for the Electrical Conductivity of Highly Porous Ceramics. *Journal of the American Ceramic Society* (1996);79:109-113.
28. Delaforce, P. M., Yeomans, J. A., Filkin, N. C., et al., Effect of NiO on the Phase Stability and Microstructure of Yttria-Stabilized Zirconia. *Journal of the American Ceramic Society* (2007);90:918-924.
29. White, J., Reimanis, I. E., Menzer, S., et al., The Enhanced Stabilization of the Cubic Phase in Yttria-Stabilized Zirconia with the Addition of Nickel Oxide. *Journal of the American Ceramic Society* (2011);94:2030-2036.
30. Bêche, E., Charvin, P., Perarnau, D., et al., Ce 3d XPS investigation of cerium oxides and mixed cerium oxide ($Ce_xTi_yO_z$). *Surface and Interface Analysis* (2008);40:264-267.
31. Zhou, G., Shah, P. R., Kim, T., et al., Oxidation entropies and enthalpies of ceria–zirconia solid solutions. *Catalysis Today* (2007);123:86-93.
32. Ozawa, M., Kimura, M., and Isogai, A., The application of Ce[redacted] oxide solid solution to oxygen storage promoters in automotive catalysts. *Journal of Alloys and Compounds* (1993);193:73-75.
33. Wang, S., Kobayashi, T., Dokiya, M., et al., Electrical and Ionic Conductivity of Gd-Doped Ceria. *Journal of The Electrochemical Society* (2000);147:3606-3609.
34. Avila-Paredes, H. J., Choi, K., Chen, C.-T., et al., Dopant-concentration dependence of grain-boundary conductivity in ceria: A space-charge analysis. *Journal of Materials Chemistry* (2009);19:4837-4842.
35. Steele, B. C. H., Appraisal of $Ce_{1-y}Gd_yO_{2-y/2}$ electrolytes for IT-SOFC operation at 500°C. *Solid State Ionics* (2000);129:95-110.

Figure 1: Current-voltage curves recorded on anode supported cells with Ni-YSZ (black squares) and Ni-GDC (red triangles) anode function layers, and the corresponding power density (open symbols).

Figure 2: XRD patterns of YSZ-GDC mixtures after sintering at different temperatures for 5 hours in air. The positions of the (111), (200) and (220) lattice reflections are marked by red, dashed lines for GDC and dashed, blue lines for YSZ.

Figure 3: Relative phase content after sintering as a function of the sintering temperature for a) GDC-YSZ powder mixtures and b) NiO-GDC-YSZ powder mixtures.

Figure 4: XPS spectrum of a YSZ-GDC mixed phase sintered at 1400°C in air and reduced in Ar/H2 at 900°C.

Figure 5: TGA analysis of the reduction of GDC (blue line) and a GDC-YSZ mixed phase sintered at 1400°C (black line). Vertical, dashed green lines indicate a change of the gas atmosphere.

Figure 6: 4-point conductivity measurements of YSZ (black squares), 20GDC (red circles) and a YSZ-GDC mixed phase (blue triangles) in the oxidized and reduced state (closed and open symbols, respectively). The lines are a guide to the eye. All samples were sintered in air at 1400°C.

Table 1: Restrictions on area and binding energy for all components used in the least-squares fit of the Ce 3*d* spectra

Component	v	v’’	v’’’	u	u’’	u’’’	v^0	v’	u^0	u’
Area	-	-	-	v*2/3	v’’*2/3	v’’’*2/3	-	-	v^0*2/3	v’*2/3
Binding energy (eV)	Free	v+5.8	v+15.6	v+18.6	v+24.6	v+34.2	Free	v^0+4.3	v^0+18.2	v^0+22.5

Table 2: Comparison of Ce^{3+} concentrations from XPS and TGA

Sample	**$[Ce^{3+}]$ (%) - XPS**	**$[Ce^{3+}]$ (%) – TGA 900°C**
YSZ-GDC 1200	33.2	-
YSZ-GDC 1300	51.1	-
YSZ-GDC 1400	59.2	35,5
20GDC 1400	50.3	37

Table 3: Conductivity parameters in oxidized and reduced state

Sample	E_A [eV]	$H_{m,V}$ [eV]	μ_V^0 K cm²/Vs	μ_V *(700°C)* *cm²/Vs*	$H_{m,el}$ [eV]	μ_{el}^0 K cm²/Vs	μ_{el} *(700°C)* *cm²/Vs*	$[V_O^{**}]$ [10^{21} cm^{-3}]	*n* [10^{21} cm^{-3}]
20GDC ox.	0.79	0.79	446	$3.9\cdot10^{-5}$	-	-	-	2.52	-
20GDC red.	0.5	*0.79*	*446*	$3.9\cdot10^{-5}$	0.48	155	$1.6\cdot10^{-4}$	6.03	12
YSZ ox.	1.01	1.01	5937	$3.4\cdot10^{-5}$	-	-	-	2.18	-
YSZ red.	0.99	0.99	3463	$2.8\cdot10^{-5}$	-	-	-	2.18	-
YSZ-GDC	1.10	1.10	2618	$5.26\cdot10^{-6}$	-	-	-	2.22	-

ox.									
YSZ-GDC red.	0.60	*1.10*	*2618*	$5.26\cdot10^{-6}$	0.47	2	$8.16\cdot10^{-6}$	4.16	8.32