Gd-doped ceria with transition metal oxide co-doping is especially interesting for catalytical applications in the intermediate temperature range between 400–600°C. Ce0.9xFe0.05Gd0.05O2–δ samples with x = 0.0 to 0.05 were produced via a sol-gel synthesis route. XRD measurements proved the materials to be single phase with fluorite structure, but electron microscopy investigations showed enrichment of Gd and Fe at the grain boundaries and the existence of small-scale secondary phases for 5 mol% Fe. The effect of Fe co-doping on the ionic and electronic conductivity was monitored using impedance spectroscopy and DC polarization-relaxation measurements applying ion blocking micro contacts (Hebb-Wagner setup). Already the addition of 1 mol% Fe raised the total conductivity of the material by two decades (about 10−4 S/cm at 750°C compared to 5 · 10−6 S/cm for Ce0.95Gd0.05O2–δ). In addition, already for 1 mol% Fe, but very clearly for 2 and 5 mol% Fe addition, a temperature and oxygen partial pressure dependent maximum in the p-type conductivity has been found, which is attributed to the Fe2+/3+ redox reaction and a related small polaron hopping process.

Doped CeO2 is a very versatile material. Due to its high oxide ion conductivity and the considerable electronic conductivity it is applied or tested for various industrial applications, ranging from fuel cells, oxygen sensors and oxygen permeation membranes3,4 in the intermediate to room temperature range. Especially rare earth element (Gd3+, Sm3+, Pr4+) doped materials have been widely investigated in the last years, as these materials are chemically very stable, easy to fabricate and show oxide ion conductivities in the range of yttria-stabilized zirconia already at about 800°C. Apart from a rise of the conductivity due to Fe addition in Gd-doped ceria can at least partly be attributed to the formation of hematite and GdFeO3 species at the grain boundaries even at Fe concentrations of 2 mol%. Hence, the Fe solubility in acceptor doped ceria was estimated to be somewhere below 2 mol%. This is in accordance to findings by Zheng et al.28 who found secondary phase formation in 20 mol% Sm doped ceria for Fe contents of more than 1.5 mol% and Wang et al.29 who observed similar values for 10 mol% Gd doped samples. For other transition metals, a comparably low solubility in acceptor doped ceria has been reported as well.19 Wang et al., on the other hand report a solubility of up to 10 mol% Fe in 10 mol% Gd co-doped ceria.

Individually from the observed solubilities, an increase of the electrical conductivity of acceptor doped ceria with increased Fe addition was reported by several groups.15,19,28,31 Fagg et al. were the first to trace the effect back to an increased p-type conductivity,19 which was confirmed by Zheng et al.28 The measurements of the electronic conductivity were only performed regarding a comparably small temperature and oxygen partial pressure range, though.

In addition to the observed acceptor doping effect, a small polaron hopping contribution to the electron conductivity similarly to that observed e.g. for Pr3+/4+ doping,18,32,33 can be expected. A significant increase of the Fe2+/3+ concentration is expected below a p(O2) of about 10−4 bar (depending on temperature), hence the maximum of a possible small polaron hopping contribution should occur in this partial pressure regime, assuming a high enough concentration of Fe2+/3+ incorporated in the ceria structure. Apart from a rise of the oxygen vacancy and hole concentrations by increasing Fe2+/3+ addition, a general increase of the electronic conductivity is also expected as well: Khare et al. observed the development of an additional small polaron hopping process.
ture at the binding energy position of 2.6 eV in the valence band of CeO₂ after doping with 2–6 mol% iron.⁵ This feature is related to the introduction of an additional Fe-d level, which can work as a “stepping stone” for electrons within the wide ceria bandgap.

In our study, 10 mol% Gd doped ceria was co-doped with an additional small amount of iron oxide (Ce₀.₉ₓGd₀.₁ₓFe₂O₅₋ₓ with x = 0.01, 0.02, 0.05). Gd was used to fix the oxygen vacancy concentration at a certain level for a better evaluation of the effect of small amounts of Fe. A comprehensive evaluation of the effect of Fe addition especially on the electronic part was possible by measuring over a wide temperature and partial pressure range using a Hebb-Wagner type measurement approach and collecting complementary data regarding grain boundary conductivity and grain boundary chemistry by impedance spectroscopy and electron microscopy-based measurements.

**Theoretical Considerations**

Gd⁴⁺ works as an acceptor dopant when introduced into the ceria structure.¹,³⁻⁵ By adding an acceptor dopant, the p-type (defect electron or hole) conductivity of ceria can be increased and is dominant compared to the electron conductivity down to low oxygen partial pressures. At the same time, the oxide ion conductivity is increased and oxide ion transport is the majority charge transport process. By addition of a fixed amount of Gd⁴⁺ acceptor dopant, a fixed “basic” oxygen vacancy concentration [V'O] is established in the materials investigated in this study, as we can assume:

\[ [V'O'] \approx 2 [Gd_{Ce}] \]  
with Gd_{Ce} = trivalent Gd substituting for tetravalent cerium. In all cases, the electroneutrality of the sample has to be kept, which gives the electroneutrality constraint:

\[ [V'O] + [h^+] = 2[O₂⁻] + [e^-] + 2 [M_{Ce}'] \approx [e^-] + 2 [M_{Ce}'] \]  
(with [h^+] = defects on electrons or holes and M_{Ce}' = trivalent M substituting for tetravalent cerium) under the assumptions that the oxygen interstitial concentration [O'] is roughly zero, as [V'O'] >> [O'] at p(O₂) ≤ 0.01 bar. The fixed vacancy concentration by stable Gd dopant composition has the advantage that the partial conductivities of the investigated sample compositions should be in any case high enough to be easily measured.

For 20 mol% Gd doping, p-type conductivity has previously been reported to dominate in the range of p(O₂) > 10⁻⁷ bar at T ≥ 600°C¹⁸,³³,³⁴ therefore the following equation holds in this partial pressure range:

\[ \frac{1}{2} O₂⁻ + V'O^- \rightleftharpoons O₂^0 + 2h^+ \]  

For lower oxygen partial pressure, a n-type (electron) conductivity can be assumed.

\[ \frac{1}{2} O₂⁻ + V'O^- + 2e^- \rightleftharpoons O₂^0 \]  

In contrast to the stable valence of the acceptor dopant Gd⁴⁺, Fe⁴⁺ can be reduced to Fe²⁺ at oxygen partial pressures slightly below the ambient pressure. At first instance, this should lead to a further increase of the acceptor doping effect as the concentration of oxygen vacancies (V'O') has to increase with Fe²⁺ content in order to keep electroneutrality.

**Experimental**

**Powder synthesis, sample preparation and microstructure analysis.**—Precursor solutions for Gd doped ceria samples with different amounts of Fe were prepared via sol-gel synthesis route.³⁶⁻³⁸ Altogether, three samples with different nominal Fe concentrations were synthesized: Ce₀.₉ₓFe₀.₁ₓGd₀.₀ₓO₂₋ₓ with x = 0.01, 0.02, and 0.05. For comparison Ce₀.₉ₓGd₀.₁ₓO₂₋ₓ without Fe doping was also synthesized.

Ce(NO₃)₃ · 6H₂O (abcr, 99.9%), Gd(NO₃)₃ · 6H₂O (abcr, 99.9%) and Fe(NO₃)₃ · 9H₂O (Sigma Aldrich, 99.99%) were dissolved in the right ratio in distilled water and stirred for 30 min at 70°C. Then, 3.3 eq. citric acid dissolved in distilled water was added and the obtained solution was stirred at constant temperature. After 30 min, 6 eq. of ethylene glycol was added and stirred at 70°C for another 30 min. The clear solution was evaporated to dryness until an orange foam was formed. The obtained solid was calcined in air at 600°C for 2 h and subsequently at 800°C for 3 h. The powders were thoroughly ground in an agate mortar, uniaxially pressed into pellets of 1.5 mm thickness and sintered at 1200°C in air for 8 h for samples with Fe content and at 1600°C for 8 h for solely Gd doped samples. Sintering tests showed that annealing at 1000 and 1100°C led to suboptimal densities, which is in agreement to reports by Wang et al.,³⁹ while samples fired at 1300°C were very brittle for the Fe doped samples.

XRD measurements (Fr 552 by Enraf-Nonius, Delft) were performed on the sintered pellets, which were ground in an agate mortar, using Cu Kα-radiation in order to gain information concerning the phase composition of the material. By using the relation sin²θ = λ²/(4d0²) · (h² + k² + l²) with λ = wavelength of X-rays, d₀ = length of unit cell edge, h, k, l = Miller indexes of respective reflex, the scattering angle, which is valid for cubic phases, was able to determine the unit cell volume and hence the theoretical density of the samples from the position of the (111) and (200) reflexes. The real density of the received samples was measured using a hydrostatic balance working according to Archimedes principle.

For SEM and EDX imaging the samples were monitored one time as received and one time after polishing. Samples in both cases were sputtered with Au. SEM measurements were performed with a JEOL JSM-6510 with a Bruker EDX detector. In addition to conventional microstructure analysis, Ce₀.₉ₓFe₀.₁ₓGd₀.₀ₓO₂₋ₓ was also investigated by transmission electron microscopy. The TEM specimen was prepared by focused ion beam (FIB) milling using a FEI Helios NanoLab 400S system with a Ga ion beam.³⁹ Further thinning and cleaning were performed with an Ar ion beam in a Fischione Nanomill 1040 at 900 eV and 500 eV beam energy respectively.

TEM investigations of the sintered pellets with the nominal composition Ce₀.₉ₓFe₀.₁ₓGd₀.₀ₓO₂₋ₓ were performed on FEI Tecnai F20 at 200 keV (bright field (BF) imaging and energy filtered (EF) imaging) and on Zeiss Libra at 200 keV (energy dispersive X-ray (EDX) elemental mapping).

**Impedance spectroscopy.**—The total conductivity as well as its separation into the contributions from grain boundary and bulk conductivities was determined from an analysis of temperature dependent impedance spectra using a Novotherm HT 1200 frequency analyzer. The samples were coated with a Pt resinate paste (RP 070107, Heraeus GmbH, Germany) and Pt sheet contacts were attached at both sides of the sample. Before measurement, the Pt paste was annealed at 120°C for 10 minutes and at 850°C for 5 minutes. Measurements were then started from 800°C to lower temperatures.

All measurements were performed in air. An AC voltage peak-to-peak amplitude of 40 mV was applied for all measurements. Evaluation of the measurements was executed as already described in Refs. 11,12, using an equivalent circuit with a series connection of one single resistance to account for the electrode processes and two resistors in parallel connection with a constant phase element each, to account for bulk and grain boundary resistivity, respectively (cf. Fig. 1).

**Bulk (σ_b) and grain boundary conductivities (σ_gb) have the following connection in the analyzed frequency range:**

\[ R_{total} = R_b + R_gb = \frac{n}{A} \left( \frac{1}{\sigma_b} \cdot L_g + \frac{1}{\sigma_gb} \cdot L_gb \right) = \frac{1}{\sigma_t} \]  

where n is the number of grains perpendicular to the electric field, A is the contact area, L_g is the average grain size, L_gb is the average thickness of the grain boundary (for this type of analysis, the electrode interface resistance is negligible in the observed frequency range.)
Figure 1. Selected impedance spectroscopy raw data in a Nyquist plot for the composition Ce$_{0.88}$Fe$_{0.02}$Gd$_{0.1}$O$_{2-δ}$ at selected temperatures as well as raw data for all samples at 600$^\circ$C. Below, the equivalent circuit which was applied for data analysis is depicted.

range, see also selected raw data in Fig. 1). In our study, $L_{gb}$ was assumed to be 1 nm.\textsuperscript{40,41} The grain boundary conductivity was corrected with the factor $\frac{L_{gb}}{L_{g}}$ and the corrected grain boundary conductivity $\sigma_{gb}$ according to the brick layer model was plotted.\textsuperscript{40,42} Activation energies were calculated from Arrhenius diagrams of the respective conductivities.

**Oxygen partial pressure dependent electronic conductivity.**—Measurements of the electronic conductivity were executed using a modified Hebb-Wagner setup.\textsuperscript{9,11,18,33} The top of the sample pellet was contacted with a Pt micro contact with a diameter of about 300 nm, which is surrounded by a gastight encapsulation (IP 041 glass paste by Heraeus GmbH). The bottom part of the sample was contacted with a Pt sheet as a counter electrode. Additionally, Pt resinate paste (RP 070107, Heraeus GmbH) was applied to reduce the contact resistance. Before measurement, the Pt paste was annealed at 120$^\circ$C for 10 minutes and at 850$^\circ$C for 5 minutes. Measurements were then started from 800$^\circ$C to lower temperatures. By investigating I-V-curves at different temperatures, the oxygen partial pressure and temperature dependent electron conductivity of the sample can be derived over a large continuous $p$(O$_2$) range using this method.

For Hebb-Wagner measurements, oxygen partial pressure of air is used as a reference, so by applying a voltage, the oxygen partial pressure near the micro contact can be changed according to the Nernst equation:

\[
V_{\text{appl}} = R \cdot \frac{T}{z \cdot F} \cdot \log \left( \frac{p(O_2)_{\text{contact}}}{p(O_2)_{\text{air}}} \right) + V_{\text{contact}}
\]  

The abbreviations are: $V_{\text{appl}}$ = applied voltage, $R$ = gas constant, $T$ = temperature in K, $z$ = atomic number, $F$ = Faraday constant, $p(O_2)_{\text{induced}}$ = induced oxygen partial pressure in bar, $p(O_2)_{\text{air}}$ = 0.21 bar, and $V_{\text{contact}}$ = contact resistance. The contact resistance can be calculated from subsequent polarization relaxation measurements, as already described in detail in previous publications;\textsuperscript{9,11,18} the sample is first polarized for 30 minutes with a constant potential and then the potential drop within the sample is measured when the polarization is switched off. The ohmic contribution from the contact resistance vanishes in the first few moments after switching of the polarization, while the contribution from local ionic movement takes longer and can be used to calculate the chemical diffusion coefficient $D_0$ of a sample, if three requirements are fulfilled:

(i) The conductivity of the majority charge carrier has to be much higher than for the minority charge carrier, e.g. in our case: $\sigma_{e} \gg \sigma_{i}$.

(ii) Hence, no ionic current can be measured during an instationary movement as $|\nabla \bar{\mu}_i| \ll |\nabla \bar{\mu}_e - \nabla \bar{\mu}_e|$.
Figure 2. XRD measurements reveal pure fluorite phase for all compositions. The detection limit for secondary phases is in the range of 1–3 mol%, so these results cannot finally exclude a Fe accumulation at the grain surfaces either in the form of a nanocrystalline or amorphous phase for the higher Fe concentrations.

(iii) Although the ionic current is zero, still the stoichiometry can be re-equilibrated to the state before pre-polarization by coupled diffusion of electrons and holes.

By measuring either in the range of p- or n-type conductivity, we can also assume that either \([\text{h}^+] \gg [\text{e}^-] \) or \([\text{e}^-] \gg [\text{h}^+]\). Here, we will focus on the latter case, as in our experiments, the pre-polarization was always in the n-type range of the material (see also Diffusion coefficients section) and the electron conductivity is not influenced by the \(\text{Fe}^{2+/3+}\) redox process. Therefore, holes can be neglected in the description to simplify the physical connections, giving us \(D_{\text{O}} = D_{\text{K-}}\).

For the description, a hemispherical semi-infinite symmetry was assumed for solving Fick’s second law:

\[
\frac{\delta c_{\text{O}}}{\delta t} = D_{\text{O}} \left( \frac{\delta^2 c_{\text{O}}}{\delta r^2} + \frac{2}{r} \frac{\delta c_{\text{O}}}{\delta r} \right)
\]

with \(r\) = distance from the center of the hemispherical micro contact used as working electrode, \(t\) = time, \(c_{\text{O}}\) = concentration of oxygen atoms. This equation can be solved for the following initial and boundary conditions:

A steady state with a homogeneous distribution of oxide ions was reached during polarization:

\[
c(r, t = 0) = c_{\text{O}}
\]

At large distances from the micro contact working electrode, the concentration of oxygen atoms \(c_{\text{O}}\) is not changed:

\[
\left( \frac{\delta c_{\text{O}}}{\delta r} \right)_{r=\infty} = 0
\]

The chemical potential \(\mu_{\text{O}}\) is assumed as fixed. Hence, the oxygen concentration at the interface of the micro electrode must be constant and independent of time with a radial limitation at \(r = a\):

\[
\left( \frac{\delta c_{\text{O}}}{\delta r} \right)_{r=\text{a}} = 0 \quad f o r \quad t > 0
\]

With Eqs. 8–10, the following solution is obtained from Fick’s law for the time dependent oxygen concentration in ceria at \(r = a\), i.e. directly in front of the hemispherical micro contact interface, is:

\[
c_{\text{O}}(a, t) - c_{\text{O}}(0, 0) = -\exp \left( \frac{D_{\text{O}} t}{a^2} \right) \text{erf} \left( \frac{\sqrt{D_{\text{O}} t}}{a} \right)
\]

The respective concentrations equal to the Nernst equation to the electrical potential differences \(V = \Phi(r = a) - \Phi(c.e.)\), i.e. between the micro contact and the counter electrode, which are measured in the open circuit experiment. \(V\) is in this case the voltage applied in the pre-polarization experiment \((V' = V(t = 0))\). By inserting this into the above equation, we can derive:

\[
\frac{\text{exp}(\frac{V(t')}{R T}) - \text{exp}(\frac{V' F}{R T})}{1 - \text{exp}(\frac{V F}{R T})} = 1 - \frac{D_{\text{O}} t}{a^2} \text{erf} \left( \frac{\sqrt{D_{\text{O}} t}}{a} \right)
\]

Using this relation, the chemical diffusion coefficient \(D_{\text{O}}\) can be calculated by taking the slope from a linear part of the plot of \(\text{ln}|V_{\text{meas}}(t)|\) vs. \(t^{1/2}\), where \(V_{\text{meas}}(t)\) is the measured voltage during the open circuit experiment.

### Results

#### Sample chemistry and microstructure—XRD and microstructure.

XRD measurements showed a single fluorite phase for all samples (cf. Fig. 2). The lattice constants calculated from the XRD spectra show a consistent trend: they become smaller for higher Fe concentrations (cf. Table I). In accordance to findings by other groups,\(^{19,43}\) we found an increasing density of our samples compared with the theoretical density for 1 mol% Fe doping. The density of the \(\text{Ce}_{0.88}\text{Gd}_{0.1}\text{Fe}_{0.02}\text{O}_{2.3}\) is nearly equal to that of the purely Gd doped sample, while a remarkable decrease can be found for 5 mol% Fe doping (cf. Table I). For control sintering tests of samples with the composition \(\text{Ce}_{0.88}\text{Gd}_{0.1}\text{Fe}_{0.02}\text{O}_{2.3}\) (overstoichiometric Fe addition), which were prepared by solid state sintering of the respective oxides, an increase of the density was found up to 2 mol%.\(^{19}\) For 4 mol% Fe addition, the density stayed similar and 6 mol% showed a decreased density as well.\(^{13}\)

Grain sizes for the unpolished iron doped samples were analyzed from SEM images using the lineal intercept method\(^{26}\) (cf. Table II and Fig. 3). It can be seen, that increasing iron oxide addition leads to a coarsening of the microstructure and to increasingly inhomogeneous grain sizes.

SEM/EDX analysis of polished samples was performed to compare nominal and real composition by performing single point measurements in several grains. Average results of 5 EDX point measurements per sample are shown in Table II: the iron content is lower than in the nominal composition, especially for the nominally 5 mol% doped sample. For sake of clarity and because for the 5 mol% doped sample, additional slight enrichment of Fe was found at the grain boundaries, which were not especially addressed during SEM/EDX analysis (see also TEM analysis in the next paragraph), we will refer to the nominal compositions throughout the paper.

#### Analysis of secondary phase formation.

As can be seen from the SEM-EDX maps in Fig. 4, already at 1 mol% Fe addition the distribution of Fe is not entirely homogeneous. This inhomogeneity increases with increasing Fe content, supporting the theory that Fe is

| Composition | lattice constant \(a/\text{nm}\) | density |
|-------------|-------------------------------|---------|
| \(\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2.3}\) | 0.5441 ± 0.0005 | 96 ± 1% |
| \(\text{Ce}_{0.85}\text{Fe}_{0.05}\text{Gd}_{0.1}\text{O}_{2.3}\) | 0.5406 ± 0.0005 | 98 ± 1% |
| \(\text{Ce}_{0.85}\text{Fe}_{0.05}\text{Gd}_{0.1}\text{O}_{2.3}\) | 0.5406 ± 0005 | 95 ± 1% |
| \(\text{Ce}_{0.85}\text{Fe}_{0.05}\text{Gd}_{0.1}\text{O}_{2.3}\) | 0.5387 ± 0.0005 | 88± 1% |

in the pre-polarization experiment \((V' = V(t = 0))\). By inserting this into the above equation, we can derive:

\[
\frac{\text{exp}(\frac{V(t')}{R T}) - \text{exp}(\frac{V' F}{R T})}{1 - \text{exp}(\frac{V F}{R T})} = 1 - \frac{D_{\text{O}} t}{a^2} \text{erf} \left( \frac{\sqrt{D_{\text{O}} t}}{a} \right)
\]

Using this relation, the chemical diffusion coefficient \(D_{\text{O}}\) can be calculated by taking the slope from a linear part of the plot of \(\text{ln}|V_{\text{meas}}(t)|\) vs. \(t^{1/2}\), where \(V_{\text{meas}}(t)\) is the measured voltage during the open circuit experiment.
not entirely solved in the ceria structure, although the XRD spectra show a single-phase material.

An overview of the Ce$_{0.85}$Gd$_{0.1}$Fe$_{0.05}$O$_{2-\delta}$ membrane, which was additionally investigated using TEM, is shown in Fig. 5a. The varying contrast among different grains is due to their different orientation. A few secondary phases, as shown exemplary in Fig. 5b, and enrichments of Gd and Fe at grain boundaries, as shown in Fig. 5c, were noticed. Fig. 5b shows exemplarily, that by EF imaging, the lower grain can be determined as secondary phase containing negligible Ce but a significant Gd concentration. This in good accordance to findings by TSIPIS et al. who considered GdFeO$_3$ to be the most abundant secondary phase in the Fe/Gd co-doped systems, even at very low concentrations of Fe co-dopant. The EDX elemental mapping in Fig. 5c shows considerable enrichment of Gd and Fe located at the junction of three ceria grains. This is also in accordance to reports from literature as segregation of Gd at the grain boundaries is a commonly observed feature and similar features have also been found for Co.

**Impedance spectroscopy.**— As can be seen from Fig. 6, the total conductivity of the samples was raised considerably by addition of 2 mol% of Fe but sinks again for 5 mol% Fe addition. This is in good accordance to findings from Ref. 19. The total conductivity of the 1 mol% doped sample is comparable to the solely Gd doped sample, whereas for 5 mol% doping the total conductivity is less than for the sample without iron doping.

There is a clear trend visible for the activation energies derived from the impedance spectroscopy data (cf. Table III): The grain boundary conductivity is increasing with increasing Fe content for 1 and 2 mol% Fe addition but shows a sharp decrease for 5 mol% Fe addition. At the same time, the activation energy for bulk transport increases steadily. This is an indication for Fe segregation and second phase formation at the grain boundaries as found by TSIPIS et al. 15

**Hebb-Wagner measurements.**— All Hebb-Wagner measurements show a distinct transition for p- to n-type conduction behavior, which appears as a minimum of $\sigma_e$ in the graphs shown in Fig. 9. As expected, the minimum is shifting to lower oxygen partial pressure with decreasing temperatures. Also, a very slight shift of the minimum to smaller oxygen partial pressures with increasing Fe content can be seen, supporting our initial theory that Fe acts as an acceptor dopant in ceria and that therefore Fe addition enhances the p-type conductivity. In addition, an increase of the overall electron conductivity can be found for increasing Fe addition.

Apart from these very basic observations, a strong influence of Fe can be observed in the p-branch of the conductivity graphs. An additional maximum can be found which is shifting from low to higher oxygen partial pressures with increasing temperature. For 1 mol% Fe addition, this can only be seen very faintly but for 5 mol% Fe addition, the additional maximum becomes prominent, leading to a complete distortion of the nominally V-shaped electron conductivity graph at low temperatures.

By comparing the electron conductivities at 600 °C (cf. Fig. 10) it becomes clear that the maxima for 2 and 5 mol% Fe addition occur in the same oxygen partial pressure regime, while for 1 mol% Fe addition, the position of the maximum is shifted to a position near the ambient oxygen partial pressure. Furthermore, it can be observed, that the p-branch of the conductivity graphs between the minimum and the Fe-induced maximum shows a much steeper slope (about 1/3) than the 1/4 slope, which is normally anticipated for acceptor doped ceria.

By evaluating the electron conductivity of the different samples at two selected partial pressures in the n- and in the p-type conduction range (p(O$_2$) = 10$^{-11}$ bar and p(O$_2$) = 10$^{-2}$ bar, respectively) at 500–800 °C, activation energies for electron ($E_{A,e}$) and hole transport...
Figure 5. (a) Bright field (BF) TEM image of the Ce$_{0.85}$Gd$_{0.1}$Fe$_{0.05}$O$_{2-\delta}$ membrane. (b) Top to bottom: BF image shows two neighboring grains, corresponding to the right rectangle in (a); energy filtered image from Ce N$_{4,5}$ edge and Gd N$_{4,5}$ edge respectively. (c) Left to right: high angle annular dark field image corresponding to the left rectangle in (a); energy dispersive X-ray elemental mapping of Ce L line, Gd L line and Fe K line.

$E_{A,h}$ were obtained (cf. Fig. 11). It can be seen, that both activation energies are significantly decreasing up to 2 mol% Fe content. For 5 mol% Fe content, $E_{A,e}$ stays on the same level while $E_{A,h}$ increases drastically, reaching an even higher value than for the primary Gd doped material. This is in good accordance to previously published data with Fe addition to commercially available CGO.$^{13}$

**Diffusion coefficients.**—Diffusion coefficients for the purely Gd doped sample and the sample with 2 mol% Fe doping were calculated from polarization-open circuit experiments (cf. Fig. 12). Samples with 2 mol% Fe addition showed the best performance (high total conductivity paired with high electron conductivity), which made further investigation into oxygen transport especially interesting.

For these measurements, a pre-polarization with $-0.5\,\text{V}$ for 30 minutes was executed before starting the open circuit measure-

Table III. Activation energies for grain boundary, bulk and total transport calculated from Arrhenius diagrams of the impedance spectroscopy measurements. Activation energies for bulk transport for 1 mol% Fe were not determined as the data set was incomplete. Data for pure CGO$^{46}$ and Fe-Gd co-doped material received by solid state reaction at 1300°C$^{13}$ and by precipitation from nitrates$^{29}$ are shown for comparison.

| Composition | $E_{A,\text{GB}}$ / (kJ mol$^{-1}$) | $E_{A,\text{bulk}}$ / (kJ mol$^{-1}$) | $E_{A,\text{total}}$ / (kJ mol$^{-1}$) |
|-------------|----------------------------------|----------------------------------|----------------------------------|
| x = 0.00 $^{29}$ | 108 ± 2                          | 90 ± 20                          | 108 ± 2                          |
| x = 0.00 $^{26}$ | 89 ± 2                           | 73 ± 1                           | -                               |
| x = 0.01 $^{29}$ | 109 ± 4                          | -                                | 109 ± 4                          |
| Ce$_{0.9}$Gd$_{0.09}$Fe$_{0.01}$O$_{2-\delta}$ $^{29}$ | -                               | -                                | 88                              |
| x = 0.02 $^{13}$ | 117 ± 2                          | 100 ± 2                          | 117 ± 2                          |
| Fe$_{0.02}$Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$ $^{13}$ | 117 ± 9                          | 98 ± 8                           | 117 ± 9                          |
| Fe$_{0.04}$Ce$_{0.9}$Gd$_{0.1}$O$_{2-\delta}$ $^{13}$ | 144 ± 3                          | 84 ± 5                           | 140 ± 2                          |
| x = 0.05 $^{13}$ | 95 ± 1                           | 114 ± 12                         | 98 ± 1                           |
| Ce$_{0.9}$Fe$_{0.1}$O$_{2-\delta}$ $^{29}$ | -                               | -                                | 141                             |
ments. A decrease of 0.5 V translates to a oxygen partial pressure of \(10^{-13.7}\) bar at 500°C and \(10^{-10.07}\) bar at 800°C. This means that the measurements were conducted in the n-type conduction range in all cases (\([I^<'] \gg [I^>']\)).

From the slopes of the chemical diffusion coefficients vs. temperature graphs which were obtained for Ce₀.9Gd₀.1O₂₋ₓ and Ce₀.98Fe₀.02Gd₀.1O₂₋ₓ (cf. Fig. 12), migration enthalpies for electron transport were calculated. The migration enthalpy for Ce₀.9Gd₀.1O₂₋ₓ lies with \(H_{\text{mig,e}} = 45\) kJ/mol somewhat higher than that of Ce₀.98Fe₀.02Gd₀.1O₂₋ₓ with \(H_{\text{mig,e}} = 40\) kJ/mol.

**Discussion.**—The impedance spectroscopy measurements showed a behavior of the different samples which was already expected: the grain boundary conductivity of the samples was found to increase with increasing amount of Fe dopant, but it sinks back to a level comparable to the primary Gd doped material for 5 mol% Fe addition. Considering the bulk and grain boundary conductivity contribution to the total conductivity, it can clearly be seen that the bulk as well as the grain boundary conductivity is increased by small amounts of Fe addition (cf. Fig. 7 and Fig. 8), although it was not in all cases possible to evaluate the bulk and grain boundary contribution to the total conductivity separately. Obviously, the grain boundary conductivity decreases for 5 mol% addition reaching lower values than the primary Gd doped material. This can be taken as a hint, that only part of the excess Fe develops a nanocrystalline or amorphous phase, this theory also fits to the XRD results, where no additional phase was detected. TEM results showed only a minute amount of secondary phases at the grain boundaries of the sample with 5 mol% Fe addition and a small degree of enrichment of Gd and Fe, which is mainly located at grain boundary triple junctions (cf. Fig. 5). Another possible explanation for the decreased electrical conductivity would therefore be an increase of the potential difference between grain boundary core and grain bulk by segregation of Gd and Fe cations, which would not necessarily include the formation of secondary phases. An according effect by Gd segregation has already been reported.

At the same time, the bulk conductivity of the 5 mol% doped sample also decreases drastically. This cannot be explained by secondary phase formation or increase of the Schottky potential barrier. A third possibility for the observed behavior could be an increased trapping of mobile oxygen vacancies by formation of Fe-related defect associates, but this cannot be validated by our data.

By comparing the total conductivity \(\sigma_{\text{tot}}\) from impedance spectroscopy measurements and electron conductivity \(\sigma_e\) from Hebb-Wagner experiments at ambient oxygen partial pressure, the transference number can be derived:

\[
\tau_{O^2{}^−} = \frac{\sigma_{\text{tot}} - \sigma_e}{\sigma_{\text{tot}}} \tag{13}
\]

The results for 600°C are shown in Table IV: with increasing Fe content the transference number decreases, but the still values indicate a very high oxygen transport for 1 and 2 mol% Fe addition. At the same time, the sample with 5 mol% Fe doping still shows an increase compared to pure Ce₀.9Gd₀.1O₂₋ₓ, but a lowered transference number in comparison with the samples with lower Fe concentrations. The observed transference numbers for the Fe-doped material are roughly

| Composition Ce₀.9ₓGd₀.1FexO₂₋ₓ | Transference Number (\(\tau_{O^2{}^−}\)) |
|-------------------------------|----------------------------------|
| \(x = 0.00\)                | 0.85                             |
| \(x = 0.01\)                | 0.99                             |
| \(x = 0.02\)                | 0.99                             |
| \(x = 0.05\)                | 0.94                             |

Fe is solved in the ceria lattice acting as an acceptor dopant and the rest of the material is segregated at the grain boundaries, similar to the behavior found for Co and other Fe doped ceria samples. If the excess Fe develops a nanocrystalline or amorphous phase, this theory also fits to the XRD results, where no additional phase was detected. TEM results showed only a minute amount of secondary phases at the grain boundaries of the sample with 5 mol% Fe addition and a small degree of enrichment of Gd and Fe, which is mainly located at grain boundary triple junctions (cf. Fig. 5). Another possible explanation for the decreased electrical conductivity would therefore be an increase of the potential difference between grain boundary core and grain bulk by segregation of Gd and Fe cations, which would not necessarily include the formation of secondary phases. An according effect by Gd segregation has already been reported.

At the same time, the bulk conductivity of the 5 mol% doped sample also decreases drastically. This cannot be explained by secondary phase formation or increase of the Schottky potential barrier. A third possibility for the observed behavior could be an increased trapping of mobile oxygen vacancies by formation of Fe-related defect associates, but this cannot be validated by our data.

By comparing the total conductivity \(\sigma_{\text{tot}}\) from impedance spectroscopy measurements and electron conductivity \(\sigma_e\) from Hebb-Wagner experiments at ambient oxygen partial pressure, the transference number can be derived:

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Figure 9. From left to right and top to bottom: pure Ce₀.₉Gd₀.₁O₂₋δ, 1, 2 and 5 mol% Fe addition. For Ce₀.₉Fe₀.₀₁Gd₀.₁O₂₋δ, the measurements at 700°C were not evaluated. All measurements were corrected for the contact resistance obtained from polarization and subsequent open circuit measurements.

According to the expectations but in parts in contradiction to previous findings, the electron conductivity of the samples - especially in the p-type conductivity regime - was severely influenced by the addition of Fe (cf. Fig. 9 and Fig. 10). On the one hand, the total electron conductivity was increased by a factor of 15–20 comparing to pure CGO. Also, the p-n-transition was shifted slightly to lower partial pressures. Both is in accordance to previously published reports. On the other hand, a very strong effect of Fe on the p-type conductivity was found. The slope of the p-type branch of the electron conductivity graph was raised from a typical 1/4 to a 1/3 slope and moreover, an additional maximum of the p-type conductivity, which showed a temperature-dependent shift over the partial pressure range, was observed. The occurrence of an additional maximum of the p-type conductivity was already well described for Pr-doped ceria and is normally attributed to a small polaron hopping process. In contrast to our results, Pr-doped ceria always shows a slope of 1/4 or 1/6 for the p-type conductivity as it is according to the acceptor dopant theory. We assume, that an explanation for the especially steep slope of more than 1/4, which was observed for the p-type branch of the electronic conductivity in the present study, could be an overlap of ceria-dominated hole mobility and additional electron formation/annihilation by the Fe²⁺/³⁺ redox process. Then again, the observed steep increase of electron conductivity with oxygen partial pressure decrease cannot by explained so easily, but several contributions can be ruled out:

i) Fe²⁺, Ce³⁺, and Gd³⁺ should dominate the sample’s behavior at low oxygen partial pressures and no additional redox process should occur, which can also affect the n-type conductivity.
ii) The amount of secondary phases (<5 mol%) is too small to build an own electron percolation network, which could than show overlapping effects with the ceria phase.
iii) The development of immobile dopant-defect associates, as proposed to explain the decrease of the bulk conductivity for Ce₀.₈₅Fe₀.₀₅Gd₀.₁O₂₋δ should generally lead to trapping of electrons. A decreased slope or bending of the n-type branch of the curve would be the result.

The observation of the redox-related maximum in p-type conductivity and the significant increase of the p-type and n-type conductivity slope is especially interesting, as it stands in contradiction to previously reported behavior of Fe-Ge co-doped materials prepared by solid state reactions. Further, a similar behavior also has not been described in literature before, even if the groups used nitrate dissolution and reprecipitation or sol-gel synthesis as preparation routes.

In Ref. 13, Fe₂O₃ was added to commercially available CGO10 and sintered at 1300°C. Here, no indication for a redox-related peak

Figure 10. Comparison of electronic conductivity at 600°C of Ce₀.₉₋ₓFeₓGd₀.₁O₂₋δ with x = 0.01, 0.02, and 0.05.
was found in the electronic conductivity measurements throughout the whole measurement range, although the same measurement conditions were applied. It has been reported, that at sintering temperatures of 1200 °C or lower, Fe is immiscible in the ceria matrix,31,47,48 leading to an almost exclusive segregation of Fe-rich phases at the grain boundaries. In our case, we made contradicting observations: the Ce0.8Gd0.2O2-δ samples investigated in our study showed only a minute amount of secondary phases and a small degree of enrichment of Fe at triple grain boundaries. A sample from Ref. 13 with the composition Ce0.8Gd0.2Fe0.06O2-δ, which was also investigated with TEM for comparison, in contrast was found to have a considerable amount of secondary phases (namely GdFeO3) and also considerable enrichment of Fe cations at the grain boundaries, which is in good accordance to findings from T SIPIS et al.15 We assume, that the high degree of dissolution of Fe cations in the ceria host matrix, which was found for the present samples, is the explanation for the strong difference in electronic conductivity compared to previous findings. This is therefore further indication that the synthesis method and ion dispersion in electronic conductivity compared to previous findings. This is already an established fact, which already has been widely observed.

Fe addition with concentrations of c(Fe) ≤ 2 mol% was in the present study also found to considerably lower the activation energy for p-type (Ea,h) as well as n-type (Ea,e) conductivity (cf. Fig. 11), while for 5 mol%, Ea,h increases drastically. In contrast to our measurements, FAGG et al.19 report a slight decrease of the p-type conductivity for Fe0.02Ce0.9Gd0.1O2-δ compared to Ce0.8Gd0.2O2-δ. Also, they observed an activation energy of EAon = 72.9 ± 0.8 kJ/mol for the ionic conductivity and an activation energy for the p-type conductivity of EA,h = 145 ± 8 kJ/mol for Ce0.8Gd0.2O2-δ compared to a slightly increased EAon of 78 ± 1 kJ/mol and steady EA,h of 145 ± 3 kJ/mol for Fe0.05Ce0.95Gd0.05O2-δ. In our experiments, EA,h for the pure Ce0.9Gd0.1O2-δ was comparable to the results from FAGG et al.,19 and the strong increase of EA,h and EA,e already for 2 mol% Fe is in good accordance to data from Ref. 13, but has not been reported otherwise, so far. The different behavior could arise from the influence of Gd doping, which is stronger for the 20 mol% Gd doped samples which were investigated by FAGG et al.

Conclusions

The increased mixed conductivity makes Ce0.9-xGd0.1Fe0.05O2-δ, in general and especially the composition Ce0.85Gd0.1Fe0.02O2-δ, a very promising material for permeation membranes and for high-temperature catalytic applications, where high sinterability, mixed conductivity and surface exchange are essential for a good performance. Addition of Fe is in this case advantageous compared to the widely used Co addition as Fe is more environmentally friendly. The observed maximum in the p-type conductivity can be explained by electron trapping/generation by Fe2+/3+ redox reaction taking place at slightly decreased oxygen partial pressures. For the observed increase of the oxygen partial pressure dependence for electron as well as hole conductivity, which results in slopes higher than the expected 1/4 slope, there is so far no satisfying explanation.

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References

1. M. B. Mogensen, N. M. Sammes, and G. A. Tompsett, Solid State Ionics, 129, 63 (2000).
2. H. Inaba and H. Tagawa, Solid State Ionics, 83(1–2), 1 (1996).
3. H. L. Tuller and A. S. Nowick, J Electrochem Soc, 122(2), 255 (1975).
4. V. V. Kharton, F. M. Figueiredo, L. Navarro, E. N. Naumovich, A. V. Kovalsky, A. A. Yaremchenko, A. P. Viskup, A. Carneiro, F. M. B. Marques, and J. R. Frade, J Mater Sci, 36, 1105 (2001).
5. A. Khare, R. J. Choudhary, D. M. Phase, and S. P. Sanyal, J Appl Phys, 109(12), 123706 (2011).
6. A. Y. Estevez, S. Pritchard, K. Harper, J. W. Aston, A. Lynch, J. J. Lucky, J. S. Ludington, P. Chatani, W. P. Mosenthal, J. C. Leiter, S. Andrews, and J. S. Ehrlichman, Free Radical Biol Med, 51(6), 1155 (2011).
7. S. Patil, A. Sandberg, E. Heckert, W. Self, and S. Seal, Biomater, 28(31), 4600 (2007).
8. R. W. Tanner, J. Colon, S. Patil, and S. Seal, Nano Lett, 5(12), 2573 (2005).
9. J-P. Eufinger, M. Daniels, K. Schmale, S. Berendts, G. Ulbrich, M. Lerch, H.-D. Wiemhöfer, and J. Janek, Phys Chem Chem Phys, 16(46), 25583 (2014).
10. D. P. Fagg, V. V. Kharton, and J. R. Frade, J Electroceram, 9(3), 199 (2002).
11. K. Schmale, M. Daniels, A. Buchheit, M. Grünebaum, L. Haase, S. Koops, and H.-D. Wiemhöfer, J Electrochem Soc, 160(9), F1081 (2013).
12. K. Neuhaus, S. Baumann, R. Dolle, and H.-D. Wiemhöfer, Crystals, 8(1), 40 (2018).
13. K. Neuhaus, R. Dolle, and H.-D. Wiemhöfer, J Electrochem Soc, 165(7), F533 (2018).
14. S. Taub, K. Neuhaus, H.-D. Wiemhöfer, N. Ni, J. A. Kilner, and A. Atkinson, Solid State Ionics, 282, 54 (2015).
15. E. V. Tsipis, J. Wacrenbergh, and V. V. Kharton, J Solid State Electrochem, 1 (2017).
16. C. M. Kleinlogel and L. J. Gauckler, Solid State Ionics, 135, 567 (2000).

Figure 11. Comparison for activation energy for hole and electron transport (Ea,h and Ea,e) of Ce0.9-xGd0.1Fe0.02O2-δ with x = 0, 0.01, 0.02, and 0.05. Data for hole transport were obtained at p(O2) = 10-13 bar and data for electron transport was obtained at p(O2) = 10-11 bar. Open symbols show data for Fe0.02Ce0.9Gd0.1O2-δ and Fe0.04Ce0.9Gd0.1O2-δ from Ref. 13.

Figure 12. Diffusion coefficients for Ce0.85Gd0.1Fe0.02O2-δ and Ce0.8Gd0.2Fe0.02O2-δ at temperatures between 750°C and 600°C. Measurements for lower temperatures had a too high noise-signal ratio for evaluation.
17. C. M. Kleinlogel and L. J. Gauckler, *Journal of Electroceramics*, 5(3), 231 (2000).
18. K. Schmale, M. Grünbaum, M. Janssen, S. Baumann, F. Schulze-Kuppers, and H.-D. Wiemhöfer, *Phys Stat Sol B*, 248(2), 314 (2011).
19. D. P. Fagg, V. V. Kharton, and J. R. Frade, *J Electroceram*, 9(3), 199 (2002).
20. T. Zhang, P. Hing, H. Huang, and J. A. Kilner, *J Mater Process Tech*, 113(1), 463 (2001).
21. T. Zhang, P. Hing, H. Huang, and J. A. Kilner, *J Eur Ceram Soc*, 21(12), 2221 (2001).
22. G. Hua, X. Ding, W. Zhu, and J. Li, *J Mater Sci - Mater El*, 26(6), 3664 (2015).
23. E. Aneggi, C. de Leitenburg, G. Dolcetti, and A. Trovarelli, *Catal Tod*, 114(1), 40 (2006).
24. O. H. Laguna, M. A. Centeno, G. Arzmendi, L. M. Gandía, F. Romero-Sarria, and J. A. Odríozola, *Catalysis Today*, 157(1), 155 (2010).
25. F. J. Perez-Alonso, I. Melián-Cabeera, M. López Granados, F. Kapteijn, and J. L. G. Fierro, *J Catal*, 239(2), 340 (2006).
26. W. Cai, F. Chen, X. Shen, L. Chen, and J. Zhang, *Appl Catal B*, 101(1–2), 160 (2010).
27. L. Zhao, S. R. Bishop, J. Hyodo, T. Tishihara, and K. Sasaki, *ECS Trans.*, 50(40), 53 (2013).
28. Y. Zheng, M. Zhou, L. Ge, S. Li, H. Chen, and L. Guo, *J Alloy Compound*, 509(2), 546 (2011).
29. Z. Wang, Y. Zeng, C. Li, Z. Ye, L. Cao, and Y. Zhang, *Ceram Internat*, 44(9), 10328 (2018).
30. H. J. Avila-Paredes, C.-T. Chen, S. Wang, R. A. De Souza, M. Martin, Z. Munira, and S. Kim, *J Mater Chem*, 20, 10110 (2010).
31. C. Zhang, J. Sunarso, Z. Zhu, S. Wang, and S. Liu, *Solid State Ionics*, 310, 121 (2017).
32. S. R. Bishop, T. S. Stefanik, and H. L. Tuller, *Phys Chem Chem Phys*, 13(21), 10165 (2011).
33. S. Libke and H.-D. Wiemhöfer, *Solid State Ionics*, 117, 229 (1999).
34. S. Wang, T. Kobayashi, M. Dokiya, and T. Hashimoto, *J Electrochem Soc*, 147(10), 3606 (2000).
35. B. C. H. Steele, *Solid State Ionics*, 129(1–4), 95 (2000).
36. A. Rosario and E. Pereira, *J Sol-Gel Sci Technol*, 38(3), 233 (2006).
37. S. A. M. Lima, F. A. Sigoli, M. R. Davolos, and M. Jafelici Jr, *Journal of Alloys and Compounds*, 344(1–2), 280 (2002).
38. M. Alifanti, B. Baps, N. Blangenois, J. Naud, P. Grange, and B. Delmon, *Chem Mater*, 15(2), 395 (2003).
39. D. Meertens, M. Kruth, and K. Tillmann, *Journal of large-scale research facilities ILSRF*, 2, 60 (2016).
40. A. Jasper, J. A. Kilner, and D. W. McComb, *Solid State Ionics*, 179(21), 904 (2008).
41. J.-H. Hwang, D. S. McLachlan, and T. O. Mason, *J Electroceram*, 3(1), 7 (1999).
42. G. M. Christie and F. P. F. Van Berkel, *Solid State Ionics*, 83(1), 17 (1996).
43. E. Jud, Z. Zhang, W. Sigle, and L. J. Gauckler, *Journal of Electroceramics*, 16, 191 (2006).
44. J. C. Wurst and J. A. Nelson, *Journal of the American Ceramic Society*, 55(2), 109 (1972).
45. H. B. Lee, F. B. Prinz, and W. Cai, *Acta Materialia*, 61(10), 3872 (2013).
46. H. J. Avila-Paredes, K. Chot, C.-T. Chen, and S. Kim, *J Mater Chem*, 19(27), 4837 (2009).
47. M. Hrovat, J. Holc, S. Bernik, and D. Makovec, *Materials Research Bulletin*, 33(8), 1175 (1998).
48. R. R. Kondakindi and K. Karan, *Mat Chem Phys*, 115(2–3), 728 (2009).