**Structure-Property Relationships in the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ Phase Diagram:
Influence of the Y-Content on Reactivity in C1 Gases, Surface Conduction and
Surface Chemistry**

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Abstract

The C1 chemistry of Y-doped ZrO_2 samples (3, 8, 20 and 40 mol% Y_2O_3 ; 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ) was comparatively studied with respect to the correlation of electrochemical properties and surface chemistry in CH_4 , CO and CO_2 atmospheres by electrochemical impedance (EIS) and spectroscopic (FT-IR) methods up to 1273 K to unravel the influence of the Y-doping level. A consistent picture with respect to qualitative and quantitative surface modifications as a function of temperature and gas phase composition evolves by performing highly correlated *operando/in-situ* measurements. A detailed study of carbon deposition in CH_4 and CO and adsorption of CO and CO_2 , but also proof of the strong influence of the surface chemistry, is included. Carbon deposition during treatment in CH_4 and CO at temperatures $T \geq 1023$ K is a common feature on all materials, irrespective of the Y content. On the 40-YSZ sample, the thinnest, but at the same time fully percolated carbon layer was generated and hence, “metallic” conductivity was apparent. This goes along with the fact that 40-YSZ is most unreactive towards adsorption, suggesting a direct link between homogeneous deposition and suppressed reactivity.

For all Y-doped samples, temperature regions with different charge carrier activation energies could be identified, perfectly corresponding to significant changes in surface chemistry. Due to the different degree of hydroxylation and the different ability to chemisorb CO and CO_2 , the influence of the surface chemistry on the electrochemical properties is varying strongly as a function of Y-content.

1. Introduction

Yttria-stabilized zirconia (YSZ) has been attracting a lot of attention recently due to its potential in a variety of industrial and catalytic applications. It combines a high bulk ionic conductivity and a high mechanical and chemical stability over a wide range of temperature and oxygen partial pressures.¹ These properties make it particularly attractive for solid oxide fuel cell (SOFC) applications. YSZ is the most widely studied and commonly employed oxide-ion electrolyte and (in combination with Ni) anode material in SOFC's.¹⁻¹⁸ It has been also used for gas sensors, oxygen pumps or thermal barrier coatings for gas-turbines.^{2,6,7,19} From a basic scientific viewpoint, it is already known that even pure zirconia-based materials (without metal) can act as efficient growth templates for distinct carbon materials, such as carbon nanotubes or disordered graphite layers, which can cause associated changes in the surface conductivity.²⁰⁻²² Furthermore, they also show activity for hydrogenation, reforming and oxidative methane coupling.^{17,23-25} As for catalytic applications in SOFC technology, several problems still have to be solved: materials incompatibility, low tolerance with respect to variations of operating conditions, fuel efficiencies and the overall performance and efficiency of SOFCs.¹⁸ By far, most of the experimental results have been obtained on high-temperature-sintered bulk polycrystalline YSZ samples with a doping level of 8 – 10 mol% Y_2O_3 . This is due to the fact that these samples supposedly exhibit the highest ionic conductivity.^{1,26-29} However, both from a fundamental understanding and an application-oriented viewpoint, a systematic approach towards understanding the relationship between composition, phase stability, electrical properties and surface chemistry of differently Y-doped (and, hence, differently structured) YSZ samples is necessary and imperative, as so far relatively little is known about the Y-dependence the surface chemistry of pure and doped ZrO_2 materials and its possible effect on materials or catalytic properties.

The aim of this paper is, therefore, to focus on linking the electrochemical conduction properties to surface reactivity changes of differently doped YSZ materials over a large compositional range from 3 – 40 mol% in different C1 gas atmospheres (CH_4 , CO , CO_2). This was done to provide insight on

why 8-YSZ is supposedly the “best” ionic conductor there is and to be able to compare the behavior of differently doped YSZ materials under operation in different C1 gases. CH₄ was chosen due to the fact that it is one of the most relevant fuels for “internal” reforming applications with respect to abundance, existing infrastructure and high hydrogen-to-carbon ratio in energy conversion and a complex redox interplay of (total) oxidation and the presence of different carbon-containing adsorbates (e.g. formates and carbonates), leading to associated surface and grain conductivity changes, is observed before methane dissociation and subsequent carbon deposition at high temperatures on pure oxides ($T \geq 1023$ K)^{22,30-32}

The studies on the adsorption and reactivity of CO and CO₂ will further help in understanding the complex interplay of bulk and surface charge transport processes upon internal reforming or hydrogenation in zirconia-based solid electrolytes. Especially regarding SOFC applications, the composition of e.g. syngas mixtures has been shown to have a huge impact on the performance of the solid oxide fuel cell.³¹⁻³⁵ Thus, the understanding of the performance of the differently doped YSZ materials under the relevant comparatively harsh experimental conditions in e.g. pure CO or CH₄ is essential.

The major outcome of this paper will link surface chemistry and electrochemical properties over the extended YSZ phase diagram, incorporating higher doping levels of Y₂O₃ and hence, providing this information for all known structures of the Y₂O₃-ZrO₂ phase diagram. The latter is currently comprised of four structures, which are reported experimentally and theoretically: monoclinic (less than 3 mol% Y₂O₃), tetragonal structures (for doping levels of 3 and 8 mol% Y₂O₃, 3-YSZ and 8-YSZ), cubic (at doping levels above 8 mol% Y₂O₃, e.g. 20 mol%, 20-YSZ) and a rhombohedral structure at 40 mol% Y₂O₃ (40-YSZ). The latter in fact is a new structure with the sum formula Zr₃Y₄O₁₂, which can not be simply derived from expanding and directly transforming the initial monoclinic ZrO₂ structure by simply increasing the Y₂O₃ doping level.³⁶

One particular goal therefore is to extract, if the surface chemical properties (and its influence on surface conduction) of the latter phase share a common behavior with the other YSZ phases and if particularly for the phases at lower Y_2O_3 doping levels a trend in these properties with increasing Y content becomes eventually visible. Exactly correlated combined *in situ* Fourier-transform infrared (FT-IR) spectroscopy and electrochemical impedance spectroscopy (EIS) in terms of experimental conditions will allow to directly link the structures and reactivity of different crystallographic phases with respect to adsorption to the associated changes in surface electrochemical properties.

2. Experimental

2.1. Materials and Sample Pre-treatment

Commercial powders of 3-YSZ (zirconium(IV) oxide yttria stabilized, nanopowder, containing 3 mol % Y_2O_3 as stabilizer; mixture of monoclinic ZrO_2 and tetragonal YSZ), tetragonal 8-YSZ (zirconium(IV) oxide yttria stabilized, nanopowder, containing 8 mol % Y_2O_3 as stabilizer), cubic 20-YSZ (zirconium(IV) oxide yttria stabilized, nanopowder, containing 20 mol % Y_2O_3 as stabilizer, 99.99%) and rhombohedral 40-YSZ ($\text{Zr}_3\text{Y}_4\text{O}_{12}$, zirconium(IV) oxide yttria stabilized, nanopowder, containing 40 mol % Y_2O_3 as stabilizer, 99.99%) were supplied by Sigma-Aldrich. The respective X-ray diffractograms of the initial materials after calcination are shown in Figure S1. To assure the same starting conditions for all experiments and to guarantee that all samples are equally sintered, all samples were heated in pure O_2 up to 1273 K and held at this temperature for 1 hour prior to each experiment. The surface areas after the pre-treatments were determined by nitrogen adsorption at 77 K using the Brunauer-Emmett-Teller (BET) method (using a Quantachrome Nova 2000 Surface Area and Pore Size Analyzer) as $17 \text{ m}^2\text{g}^{-1}$ (3-YSZ), $32 \text{ m}^2\text{g}^{-1}$ (8-YSZ), $3 \text{ m}^2\text{g}^{-1}$ (20-YSZ), and $0.5 \text{ m}^2\text{g}^{-1}$ (40-YSZ). Gases were supplied by Messer (Methane 3.5, CO 4.7, CO_2 4.5, O_2 5.0 and He 5.0).

For a typical experiment with the *operando/in situ* EIS and FT-IR setup, the samples were heated at a rate of 10 K min^{-1} up to 1273 K, held at 1273 K for 1 h, and subsequently cooled down to 300 K in

the respective gas atmospheres under flowing conditions ($\leq 1 \text{ mLs}^{-1}$). To ensure dry conditions, a liquid N_2 cooling trap for He at 77 K and a liquid N_2 -ethanol cooling trap at a temperature of ~ 163 K for O_2 , CH_4 and CO , and 233 K for CO_2 , was used.

The structural stability and chemical purity of the samples was routinely checked by XRD for structural changes upon annealing and by energy-dispersive X-ray analysis (EDXRFA) and X-ray photoelectron spectroscopy (XPS) before and after the treatments. Structural changes were absent and the impurity level of metallic components were found to be below the detection limit. Purities of at least 99.99% were hence confirmed.³⁷

2.2 Electrochemical Impedance Spectroscopy (EIS)

The *operando/in situ* impedance cell consists of an outer quartz tube with two inner quartz tubes to which the sample and the electrodes are attached to. Heating is provided by a tubular Linn furnace and controlled by a thermocouple (K-element), located in the reactor about 5 mm downstream of the sample, and a Micromega PID temperature controller. For impedance measurements an IM6e impedance spectrometer (Zahner Messsysteme) is used, providing data on the impedance and the phase angle of the current as a function of voltage. The pelletized powder samples are (pressure of 2 t, 5 mm diameter, ~ 0.2 mm thick, sample mass about 20 mg) placed between two circular Pt electrodes. These form a plate capacitor in mechanically enforced contact with the sample pellet.

For all temperature-programmed impedance measurements, an amplitude of 20 mV of the superimposed sinusoidal modulation voltage signal at an overall DC potential of 0 V and a frequency of 1 Hz is applied to the Pt electrodes. The impedance of the pellet is, thus, effectively measured in an electrochemically unpolarized state. In all temperature-dependent experiments the impedance modulus value $|Z|$ will be therefore further referred to as “impedance”.

Arrhenius analysis was performed to determine the activation energies for conduction (E_A 's) for selected temperature regions. The conductivity was calculated from the reciprocal of the impedance

modulus value and subsequently plotting $\ln(\text{conductivity})$ vs. the reciprocal of the reaction temperature. This conductivity is generally proportional to the sum of the total charge carrier concentration and not necessarily specific for a certain kind of charge carrier species. Hence, in the more frequent cases of mixed charge carrier conductance, only an “apparent” activation energy can be determined. As reported in this work, the calculated activation energy is usually a weighted sum of several contributions to the conductivity. Hence, there are generally too many parameters to unambiguously extract the individual activation energies of a single processes, as several activated processes may occur simultaneously with unknown relative contributions. It may be possible only in exceptional cases to refer one specific activation energy to a single charge transport process. Thus, our focus is identifying qualitative changes in the activation energy that can be eventually clearly related to changes in the surface chemistry.

A general remark on the temperature-dependent impedance behavior shown in the subsequent Figures should be given at this point. As the detection limit of the used EI spectrometer is in the $G\Omega$ range, this especially limits the measurement of the semiconductive behavior in the low-to-medium temperature regions. The usual appearance is then a quasi-constant impedance behavior at the instrumental limit as a function of temperature before the impedance decrease due to the already ongoing increase of thermally excitable charge carrier concentration can be detected. It is, thus, necessary to state that the actual threshold temperature for activation of these charge carriers might be overcome at even lower temperatures, which is out of the detection limit of the spectrometer.

2.3 Fourier Transform Infrared (FT-IR) Studies

FT-IR spectra were recorded in transmission mode using an Agilent Cary 660 spectrometer with a mid-infrared source and a DTGS detector. The powder samples were pressed into thin pellets using a pressure of 2 t (10 mm diameter, ~ 0.1 mm thick, sample mass about 20 mg) and subsequently

placed inside a home-built reactor cell,³⁸ providing a chemically inert environment of the sample in the heated area and allow *operando/in situ* measurements up to 1273 K under flowing and static conditions. Measurements in vacuum with a minimum pressure of 10^{-6} mbar are also possible. The window material BaF₂ allows to access wavelengths above 800 cm^{-1} . Most importantly, experiments under flowing conditions can be exactly correlated with associated EIS measurements. For static measurements, the gases are pre-adsorbed on a 5 Å zeolite trap, which binds water sufficiently strongly, before the dried gases are desorbed into the evacuated and degassed cell. All reported spectra are corrected by the spectrum of the dry pre-oxidized oxide pellet at room temperature and under vacuum prior to exposure to the gases.

Quantification of the carbon layer was also performed with the infrared setup, since the FT-IR reactor cell provides an essentially inert sample environment excluding any influences of metal or ceramic parts. Carbon deposition was induced by a flowing experiment (heating and cooling rates of 10 Kmin^{-1} , isothermal period at 1273 K for 1 h) in the respective gas. Afterwards, vacuum was applied and a static measurement with ~ 1000 mbar O₂ in the cell was subsequently performed to oxidatively remove the deposited carbon to form CO₂ (max. temperature of 1273 K, heating and cooling rates of 10 Kmin^{-1}). The spectrum at room temperature (RT) after cooling is the most important one because the obtained CO₂ peak was subsequently used for calibration. For this purpose, vacuum was applied and different pressures of CO₂ were measured with the same conditions (background) at room temperature. The areas under the CO₂ peaks were integrated and a calibration function of the peak area vs. the CO₂ pressure was established. The resulting pressure for the oxidation experiment was then converted into μmol and normalized to the respective sample mass. This procedure was done for each oxide in every single gas.

3. Results and Discussion

It should be noted in the beginning of the discussion of the results, that 8-YSZ will in the following be used as a “reference” material for the differently Y-doped samples. For the sake of clarity, data on 8-YSZ^{30,38} are included in some Figures to obtain the best correlation possible.

3.1. Treatment in helium

Figure 1. (A) Temperature-dependent EIS measurements on 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ and (B) Arrhenius plot of the EIS heating plot of 3-YSZ in dry He (flow $\sim 1.0 \text{ mLs}^{-1}$). Experiments were performed at linear heating and cooling rates of 10 Kmin^{-1} between room temperature and 1273 K.

For a better evaluation of simple intrinsic temperature effects and to elucidate the additional influence of carbon-containing gases such as CH_4 , CO or CO_2 on the surface chemistry, EIS measurements in an inert gas atmosphere (He) are shown in Figure 1A and 1B and subsequently used as a carbon free reference. Apparently, 3-, 20- and 40-YSZ behave similar to the reference material. This includes detection limit periods in the $\text{G}\Omega$ area between RT and 620 K (depending on the Y-

doping level) and visible semiconductive behavior manifesting itself in a more or less pronounced impedance drop (up to 1273 K). However, for the samples with lower Y-doping levels (3- and 8-YSZ), the semiconductive behavior is observable at lower temperatures and a smaller final impedance value at 1273 K is obtained (3- and 8-YSZ: $1.8 \cdot 10^2 \Omega$, 20-YSZ: $5.4 \cdot 10^2 \Omega$ and 40-YSZ: $2.4 \cdot 10^3 \Omega$). For 3- and 8-YSZ a characteristic impedance course (plateau-like feature) between 650 – 850 K is additionally visible. This peculiar feature, assigned to temperature-dependent dehydroxylation, is also observed for 8-YSZ in dry CH_4 and CO_2 and 3-YSZ in CO_2 and appears to be a common feature for YSZ samples at the lower end of Y-doping level ^{31,32}. A detailed discussion of the activation energies is included in the discussion of Table S1 in the Supporting Information (cf. also Figure 7).

3.2. Methane

In 1975 a study by Chen et al.³⁹ already proved that thermal decomposition of methane takes place at temperatures above 995 K. The first steps of this mechanism can be described by a homogeneous, non-chain radical mechanism resulting in C_2H_6 and H_2 as products, whereby the ability of the surface to abstract and bind H atoms is important (mixed heterogeneous/homogeneous mechanism). In some cases, the pyrolysis has been limited to this stage. However, eventual rapid secondary gas-phase reactions of the methyl radical species additionally yield C_2H_4 , C_2H_6 , C_2H_2 and finally carbon.²⁵ Putting this in the context of the discussed materials, we note that the onset temperature for such carbon deposition on Y_2O_3 , ZrO_2 and 8-YSZ could be already determined to be at temperatures $T \geq 1023 \text{ K}$.²²

Figure 2. (A) Combined temperature-dependent EIS measurements of 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ and (B) corresponding FT-IR spectra (heating between RT and 1273 K and vacuum after heating and cooling) on 3-YSZ in dry CH₄ (flow $\sim 0.7 \text{ mLs}^{-1}$). Both experiments were performed at linear heating and cooling rates of 10 Kmin^{-1} between room temperature and 1273 K. The FT-IR spectra are shown every 100 K between RT and 1073 K and every 20 K between 1073 and 1213 K.

Figure 2A highlights a comparative temperature-dependent impedance experiment performed on 3-YSZ, 20-YSZ and 40-YSZ in dry CH₄, correlated to 8-YSZ. Here, the impedance changes at selected temperatures observed during heating have now been linked to associated changes in surface reactivity, as deduced from in parallel acquired FT-IR spectra exemplarily shown for 3-YSZ in Figure 2B.

Generally, 3-YSZ (orange, yellow and red traces) behaves similar to the reference material (pink and purples traces) in the temperature-dependent EIS measurement in dry CH₄. The impedance slows down at higher temperatures, resulting in two characteristic temperature-invariant regions between 673 – 810 K and 893 – 990 K on 8-YSZ. For 3-YSZ, this first feature is not observed but only the second at higher temperatures between 1000 and 1050 K. Starting at $T > \sim 1023 \text{ K}$ (8-YSZ) and $T > 1050 \text{ K}$ (3-YSZ), a very steep impedance drop leads to a comparable final value of $\sim 14 \Omega$ at 1273 K on both samples. This value is associated with metallic conductivity and indicates a drastic material

change at the surface/interface of the sample, being due to the formation of a graphitic carbon layer with a high degree of disorder, as derived from TEM measurements on 8-YSZ^{22,30}.

Similar trends are observed in the measurements on 20-YSZ (blue traces) and 40-YSZ (green traces). A final value of 18 Ω and 15 Ω at 1273 K is obtained on both materials, respectively. 40-YSZ shows a rather pronounced impedance drop (about two orders of magnitude) between 773 K and 779 K, which might be due to a electrode contact artefact. As the corresponding FT-IR spectra show a small decrease in the total transmittance at the exact same temperature, it suggests that this drop may also be at least partially correlated with the intrinsic features of the studied 40-YSZ sample (Figure S2 D). Metallic conductivity is then still preserved even after re-cooling all samples to 300 K with a corresponding impedance value of $\sim 10 \Omega$. Already at this stage, we might conclude that on all YSZ samples independent of the Y-content a conducting carbon layer has been formed.

The FT-IR spectra are exemplarily shown for 3-YSZ in Figure 2B. CH₄ exposure leads to strong dehydroxylation of the sample from temperatures above ~ 593 K, expressed by negative peaks between $\sim 3750 \text{ cm}^{-1}$ and 3500 cm^{-1} (note that this coincides with the second temperature region in the Arrhenius plot between 495 – 723 K with an E_A 82 of kJmol^{-1} ; Table 1). To better illustrate this phenomenon, in Figure S3 the relative intensity of the OH signal was calculated (based on the total intensity between 4000 cm^{-1} and 3685 cm^{-1} of the raw data in transmittance) and plotted versus the temperature upon heating. This plot shows a very good correlation with the chosen temperature ranges of the Arrhenius fit in Table 1. Carbon deposition is visualized by a specific decrease of the total transmittance, which is pronounced in the region below 1800 cm^{-1} , where a distinct fingerprint for the carbon layer is visible in the FT-IR spectra (compare also the vacuum spectrum after heating and cooling marked in black in Figure 2B). This fingerprint is very similar to the one observed on the reference material 8-YSZ.³⁰ The changes in the spectra occur between 1073 and 1213 K and no further changes above 1213 K indicate a completed process and/or thickness saturation of the carbon layer. Again, this fits very well with the impedance data that show a first step in the drastic decrease

in the impedance starting at 1055 K and a second one at ~ 1073 K, resulting in metallic conductivity at 1213 K. As for the other oxides, no changes in the spectra upon cooling are observed. This includes no recovering of OH groups and indicates that the surface activity is blocked by the formed carbon layer, which seems to be structurally very similar on all Y-doped materials.

Extending the studies to 20-YSZ and 40-YSZ, investigations using the FT-IR setup clearly show that the surface chemistry of these phases is strongly suppressed, which leads to uninterpretable FT-IR spectra in all gases. In fact, essentially no surface species on these two oxides could be detected in any gas atmosphere. For the 40-YSZ sample this is not surprising since the harsh SOFC conditions – especially the high temperatures up to 1273 K – lead to a very small (sintered) surface area of $0.5 \text{ m}^2\text{g}^{-1}$. For “SOFC-treated” 20-YSZ, the BET surface could be estimated as $3 \text{ m}^2\text{g}^{-1}$, which is still quite low, but comparable to the surface of pure ZrO_2 ($2 \text{ m}^2\text{g}^{-1}$). However, on pure ZrO_2 small but distinct signals for (bi-)carbonates and formates could be detected, which is due to chemisorption of CO_2 and CO via reaction with surface OH groups.⁴⁰ This indicates that the 20-YSZ sample with a similar surface area is essentially de-hydroxylated with respect to reactive OH-groups. The only change in the spectra that can be assigned to carbon deposition is a slight irreversible decrease in the transmittance between 1253 K and the isothermal period at 1273 K for 4 minutes in the case of 40-YSZ (corresponding to the plateau where the impedance is more or less constant in Figure 2A, light green trace) and between 1013 K and 1253 K for 20-YSZ (corresponding to the onset of the steep impedance decrease in Figure 2A, light blue trace). In good correlation with the EIS measurements the change in the transmittance is not reversible upon cooling. For a better comparability and to relate this effect to the FT-IR spectra in Figure S2, the total transmittance at 2000 cm^{-1} is plotted vs. the temperature.

Table 1. Arrhenius-derived apparent activation energies of 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ in dry CH₄

		E_A dry CH₄ /kJmol⁻¹	Temperature range /K
3-YSZ	heating	39±2.4	723 – 898
		82±4.9	495 – 723
		54±3.2	414 – 495
8-YSZ	heating	39±2.4	799 – 893
		76±4.5	749 – 799
		42±2.5	684 – 749
		87±5.2	528 – 684
		50±3.0	410 – 528
20-YSZ	heating	122±7.3	621 – 895
40-YSZ	heating	207±12.4	850 – 900
		55±3.3	773 – 850
		107±6.4	643 – 773

Arrhenius plots for all temperature-dependent EIS experiments in Figure 2A have been established to determine the apparent activation energies before carbon deposition starts and hence, to take a closer look at the surface chemistry before the influence of the deposited carbon sets in. Thus, the highest temperature that was used for these linear fits was 900 K (this was also done accordingly for the fits in dry CO, see Table 2 and also compare to Figure 7). This means that no activation energies were calculated during cooling due to the presence of the conducting carbon layer.

If the calculated activation energies are compared to the ones in He (cf. Table S1 in the supporting information) the pronounced impact on the surface chemistry of the gas environment becomes evident, also affecting the conductivity. During treatments in He always four temperature regions for lower Y-doping levels (3- and 8-YSZ) were clearly seen. Exposure to CH₄ shows distinct differences upon comparing these two oxides, with respect to the number of changes in the impedance: three in the case of 3-YSZ and five for 8-YSZ during heating. These differences most likely arise due to the missing plateau-like feature between 673 – 810 for 3-YSZ. Nevertheless, similar values for the activation energies are obtained for similar temperature-regions for both samples. For 20-YSZ, only one linear temperature region with a comparably high activation energy (120 kJmol⁻¹) is visible (in contrast to He-treatment with two temperature-regions visible). In the case of the 40-YSZ sample, treatment in CH₄ gives rise to three temperature regions with distinctly different activation energies.

This suggests that the surface chemistry is severely, but differently affected, as discussed earlier. The so-obtained apparent activation energies are much lower as compared to the energy required for activation of O^{2-} bulk ion conduction in 8-YSZ samples (around $100 \text{ kJmol}^{-1} = 1 \text{ eV}$), at least for the samples at lower Y-doping levels. This suggests that the apparent activation energies must belong to a different - most likely surface-bound – conductivity process prior to carbon deposition. Naturally, the influence of the surface chemistry in this temperature region is significant and possibly comprises de-hydroxylation or other surface reduction processes.

3.3. Carbon Monoxide

The impact of the surface chemistry of the differently doped YSZ samples in dry CO on the electrochemical behavior is highlighted in Figure 3A, where the temperature-dependent impedance experiments during heating and cooling are displayed. Figure S4 in the Supporting Information will give a short reprise of the earlier findings on 8-YSZ,³⁰ which will serve as a scientific basis for the subsequent comparative discussion.

Even though the temperature-dependent impedance courses in He and CH_4 for 3- and 8-YSZ were very similar, or even almost identical, upon exposure to CO some differences arise: the first one is the temperature region between 583 - 1200 K (orange and red traces in Figure 3A), where differences in the heating and cooling procedure are apparent, which are much more pronounced on 3-YSZ than on 8-YSZ (temperature-invariant impedance between 623 – 1030 K). However, for both oxides starting at $T > 410 \text{ K}$, the impedance begins to decrease with associated thermal excitation of charge carriers. The second difference is the impedance value at 1273 K: for 3-YSZ it is almost one magnitude of order higher than on 8-YSZ. Below the chosen temperature limit of 900 K in the Arrhenius analysis, three temperature regions are present (cf. Table 2 and Figure 7C). Obviously, differences in the activation energies of 3- and 8-YSZ are apparent, since the impedance course

differs. For a detailed discussion of the possible mechanisms to explain the low activation energies we refer to that of Table 1.

The temperature-dependent FT-IR spectra of 3-YSZ (Figure 3B and Table 3) and the reference material 8-YSZ³² in CO show a quite similar trend concerning their surface chemistry. Starting at room temperature, the first adsorbate species that can be clearly assigned are polydentate carbonates. The signals for these carbonates increase up to 573 K, followed by a total decrease up to 633 K. Formate bands rise between 513 K and 673 K, followed by a continuous decrease up to 873 K. A fingerprint associated with carbon deposition can be seen above 1193 K. Similar to the CH₄ experiment on 3-YSZ, the signals for OH groups start to decrease continuously at 553 K and these negative bands stay constant from temperatures above ~ 1000 K. Upon re-cooling, these OH groups are not recovered.

Figure 3. (A) Combined temperature-dependent EIS measurements on 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ and (B) FT-IR experiments on 3-YSZ in dry CO (flow ~ 0.7 mLs⁻¹). Both experiments were performed at linear heating and cooling rates of 10 Kmin⁻¹ between room temperature and 1273 K. The FT-IR spectra are shown every 20 K.

Table 2. Arrhenius-derived apparent activation energies of 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ in dry CO

		E_A dry CO /kJmol ⁻¹	Temperature range /K
3-YSZ	heating	58±3.5	696 – 900
		97±5.8	527 – 696
		61±3.7	456 – 527
8-YSZ	heating	31±1.9	691 – 900
		63±3.8	644 – 691
		99±5.9	577 – 644
		76±4.6	458 – 577
20-YSZ	heating	97±5.8	746 – 900
40-YSZ	heating	132±7.9	694 – 900

Table 3 summarizes the observed peaks in the temperature dependent FT-IR spectra of 3- and 8-YSZ. Although the overall qualitative appearance is apparently the same, differences arise in the temperatures where the associated peak changes are observed. Whereas polydentate carbonates are present in a very similar temperature range, the formates on 8-YSZ are visible at a ~140 K lower temperatures than on 3-YSZ, and they start to decrease at a ~60 K higher temperature. In addition, the characteristic fingerprint of carbon deposition is visible on 3-YSZ at a ~140 K higher temperature as compared to 8-YSZ. In contrast, the temperature range where signals for OH-groups are decreasing (see also Figure S3), is more extended for 3-YSZ than for 8-YSZ. In fact, on 3-YSZ the removal of hydroxyl groups starts at ~60 K lower temperature and the process stops at ~140 K higher temperature. However, the characteristic CO₂ gas phase signal, associated with a direct (catalytic) vacancy-mediated mechanism (Mars-van-Krevelen mechanism: $\text{CO} + \text{O}_{\text{oxide}} \rightarrow \text{CO}_2 + \#$) has a similar onset temperature on both oxides. This could indicate that 3- and 8-YSZ have similar surface-chemical properties, despite their differing bulk structures (XRD data Figure S1): 3-YSZ is a mixture of monoclinic ZrO₂ and tetragonal YSZ phases and 8-YSZ is purely tetragonal. Comparing the increase of the CO₂ gas phase signal during carbon deposition/growth of the fingerprint (inverse Boudouard reaction) on 8-YSZ, this signal is – relative to the other signals – more pronounced than on 3-YSZ, where only a small increase during carbon deposition is observed. This observation is in

line with the fact that on 3-YSZ less carbon, only 42 % of the amount on 8-YSZ (cf. quantification in Figure 4), is deposited.

Table 3. Assignment of the FT-IR peaks of adsorbate species on 3- and, for comparison, on 8-YSZ upon heating in flowing CO.

	3-YSZ		8-YSZ	
p-CO₃⁻²	RT – 633 K	$\nu_{as}(\text{CO}_3) = 1446 \text{ cm}^{-1}$ $\nu_s(\text{CO}_3) = 1417 \text{ cm}^{-1}$	RT – 613 K	$\nu_{as}(\text{CO}_3) = 1444 \text{ cm}^{-1}$ $\nu_s(\text{CO}_3) = 1411 \text{ cm}^{-1}$
formate	513 – 873 K	$\nu_{as}(\text{OCO}) = 1577 \text{ cm}^{-1}$ $\delta(\text{CH}) = 1384 \text{ cm}^{-1}$ $\nu_s(\text{OCO}) = 1359 \text{ cm}^{-1}$ $\nu(\text{CH}) = 2879 \text{ cm}^{-1}$	373 – 933 K	$\nu_{as}(\text{OCO}) = 1583 \text{ cm}^{-1}$ $\delta(\text{CH}) = 1384 \text{ cm}^{-1}$ $\nu_s(\text{OCO}) = 1361 \text{ cm}^{-1}$ $\nu(\text{CH}) = 2877 \text{ cm}^{-1}$
CO₂ (g)	> 573 K	~2300 – 2400 cm^{-1}	> 553 K	~2300 – 2400 cm^{-1}
C	> 1193 K	feature < 1800 cm^{-1}	> 1053 K	feature < 1800 cm^{-1}
OH decrease	553 – 993 K	~ 3750 – 3500 cm^{-1}	613 – 853 K	~ 3810 – 3500 cm^{-1}

Summarizing, the surface chemistry of 3-YSZ toward CO seems to be gradually more hindered than on 8-YSZ. Especially the overall oxide ion conduction mechanism of 3-YSZ seems to be hampered by the impact of CO, especially at temperatures $T > 1100 \text{ K}$, which can probably be correlated with the more ineffective removal of hydroxyl species. This is also in good correlation with their impedance properties. Although almost identical EIS behavior in He and CH₄ is observed, clear differences arise in CO. These differences are also expressed in the activation energies derived from the Arrhenius fits. A tentative explanation of these differences could include the degree and stability of hydroxylation along with the intrinsic defectivities of the different oxides (8-YSZ: tetragonal, more defects, more OH-groups; 3-YSZ: mixture of monoclinic and tetragonal phase, less defects, less OH-groups in comparison to 8-YSZ). On 8-YSZ, sites with OH groups from H₂O dissociation are fully populated at ~600 K. At temperatures $T > 600 \text{ K}$ de-hydroxylation and reaction to other adsorbed species starts and is finished at around ~ 1023 K. This is in good correlation with the plateau-like feature in the impedance data (cf. Figure 3A) which is observed exactly in the same temperature range. The calculated activation energies in Table 2 also support this assignment. However, for 3-YSZ a noticeable decrease in the OH-signal starts at ~ 553 K and is finished also

around ~ 1000 K. From the EIS data it is known that semiconductive behavior starts at temperatures above 830 K. With this behavior it is conceivable that CO does not reduce 3-YSZ as effectively as 8-YSZ (at least not in the low temperature region up to 700 K) and hence, a longer induction period and no plateau-like feature is present in the impedance. However, once the temperatures are high enough, blocked reactive sites might become thermally reactivated, e.g. by depletion of formates visible in the FT-IR spectra of Figure 3B.

Regarding the 20-YSZ sample, basically an almost identical impedance course during the whole temperature treatment is apparent as for 3-YSZ (Figure 3A blue traces). For 20-YSZ, the impedance course in CO shows a strikingly different behavior. Essentially a perfectly correlated heating/cooling behavior without pronounced hysteresis is observed, with a much higher final impedance value of about $10^6 \Omega$. Corroborating these results, the FT-IR spectra of 20-YSZ obtained in CO do not show any surface activity despite a small amount of CO_2 formed as a consequence of direct surface reduction. The onset temperature for carbon deposition derived from distinct changes in the total transmittance (see also Figure S2 C) is 1053 K.

The light and dark green traces in Figure 3A finally represent the heating and cooling curves and the isothermal period (1273 K for 1 h) for 40-YSZ. The observed impedance trace is situated between 3-YSZ/8-YSZ and 20-YSZ. The impedance starts to drop significantly above ~ 700 K, yielding an activation energy of 132 kJmol^{-1} (measured in the temperature region 694 – 900 K). An overview of all E_A 's is given in Table 2 and Figure 7C. At a temperature of 1273 K almost the same impedance value as for 8-YSZ is obtained ($4.4 \cdot 10^3 \Omega$). During the isothermal period at this temperature the impedance drops by one magnitude to $3.1 \cdot 10^2 \Omega$, and after re-cooling to RT a final value of $1.4 \cdot 10^2 \Omega$ is obtained. Note that this is the only oxide that exhibits such an impedance course and hence, one could assume that more carbon or even more “layer-like” carbon was deposited, subsequently enhancing the conductivity (compare to pure Y_2O_3 in ref.³⁰, for which a value of $\sim 8 \Omega$ at RT after heating and cooling in dry CO was observed). In analogy to 20-YSZ, no surface reactivity can be

deduced from the FT-IR spectra, but in good correlation with the EIS data the carbon related changes of the transmittance (compare Figure S2 D) occur at the highest temperatures. A possible explanation of this behavior might be given in terms of the different bulk structure, and therefore, most likely different surface chemistry, of 40-YSZ. Whereas 3-YSZ, 8-YSZ and 20-YSZ are “true” intrinsically anion-vacancy doped YSZ phases with respect to obtaining stabilized tetragonal or cubic YSZ by successive substitution of ZrO_2 by Y_2O_3 , 40-YSZ (i.e. $\text{Zr}_3\text{Y}_4\text{O}_{12}$) represents a self-standing, peritectoidically melting rhombohedral structure in the Y_2O_3 - ZrO_2 phase diagram. Hence, a continuous trend in surface chemistry or surface conduction properties from 3-YSZ to 40-YSZ must not necessarily be expected.

Figure 4. FT-IR quantification of the oxide mass-normalized amounts of deposited carbon in pure CO and CH_4 on 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ, and for comparison, on the pure Y_2O_3 and ZrO_2 benchmark oxides.

To give a more quantitative analysis of carbon deposition, Figure 4 gives an overview of the total amount of deposited carbon on the oxides after treatment in flowing CO and CH₄ up to 1273 K. For the sake of clarity, the data on the pure benchmark oxides Y₂O₃ and ZrO₂ are also taken into account to provide full reference to the entire Y/Zr compositional range. On pure Y₂O₃ in CO, by far the largest amount of carbon (16556 μmol g⁻¹) was deposited, hence this value was set as 100% reference. Among the differently doped YSZ oxides it is striking that on 8-YSZ also a large amount of carbon (9652 and 10836 μmol g⁻¹, corresponding to around ~ 60 % of the maximum deposited carbon in CO on Y₂O₃) is deposited. Quantification of carbon on 3-YSZ results in values around ~ 30 %, on pure ZrO₂ ~ 15 % were deposited and below 10 % on 20- and 40-YSZ. This matches the surface activity derived from the tendency to form chemisorbed species and the amount of hydroxylation Y₂O₃ > 8-YSZ > 3-YSZ > ZrO₂ > 20-YSZ > 40-YSZ, which fits perfectly for the carbon deposition in CO. Mechanistic-wise, the island-forming carbon deposition mechanism in CO via the inverse-Boudouard reaction requires a more defect/vacancy –mediated catalytic participation of the surface, in contrast to the gas-phase – surface hybrid radical mechanism in CH₄. As a consequence, one can assume that more evenly distributed active sites lead to more islands and finally to more deposited carbon. Possible active sites for CO could be found around defects formed after de-hydroxylation, which is proven by the FT-IR measurements. Once removed and blocked by carbon, no re-hydroxylation is observed (even in moist conditions, not shown here), which is very striking due to the extremely high binding and dissociation affinity of these surface sites toward H₂O. Due to the fact that the carbon deposition in CH₄ primarily depends on the more isotropic gas-phase radical formation/surface H-abstraction, the resulting carbon layer covers the surface more evenly and the total amount of carbon therefore depends on the surface area to a certain extent.

3.4. Carbon Dioxide

3.4.1. Static FT-IR measurements at room temperature

To highlight the surface reactivity of the oxides toward CO₂, static experiments with increasing pressures of CO₂ between $1 \cdot 10^{-3}$ mbar – 950 mbar were performed (Figure 5A-C). Figure 5B and C show the resulting isothermal chemisorption behavior of 3- and 8-YSZ at room temperature.

Figure 5. (A) Comparison of FT-IR spectra in ~10 mbar CO₂ on 3-YSZ, 8-YSZ and ZrO₂ at room temperature. FT-IR spectra at different pressures of CO₂ ($1 \cdot 10^{-3}$ mbar – 950 mbar) on (B) 3-YSZ and (C) 8-YSZ.

Note that on 20- and 40 YSZ (similar to the behavior in CO) essentially no adsorbates of CO₂ can be observed at any temperature or pressure. The general chemisorption behavior in CO₂ is effectively related to the amount and nature of reactive surface OH-groups⁴⁰ and reflects the existence of basic sites or acid-base pair sites⁴¹, since the “acidic” CO₂ molecule adsorbs preferentially on basic surface

sites.⁴² Very simplified, chemisorption via reaction with an OH group leads to a bicarbonate and chemisorption via reaction with an unsaturated O²⁻ yields carbonate species.⁴⁰ The degree of coordination/distribution of the different kinds of carbonates (mono-, bi- or polydentate) contains information about the amount of closely spaced cus (cus = coordinately unsaturated) cationic centers, indicating an overall weaker binding of CO₂.⁴¹

Comparing the distribution of the (bi-)carbonates formed in ~10 mbar CO₂ on high temperature pre-treated 3-YSZ, 8-YSZ and ZrO₂ (the latter two as reference materials) in Figure 5A, distinct differences in the distribution of the chemisorbed species are obvious. On the monoclinic ZrO₂ sample, the only observed species is the bidentate bicarbonate (b-HCO₃²⁻) at 1624 cm⁻¹ ($\nu_{as}(\text{CO}_3)$), 1435 cm⁻¹ ($\nu_s(\text{CO}_3)$) and 1223 cm⁻¹ ($\delta(\text{OH})$), which is in good correlation with the fact that on this oxide only a few isolated terminal OH- groups are available for CO₂-adsorption and that on the undoped and annealed surface nearly no cus centers are present. On 3-YSZ and 8-YSZ also signals for b-HCO₃²⁻ are observed, whereas the relative amount of bicarbonates is higher on 8-YSZ, indicating a higher amount of reactive OH groups. Strikingly, on 3-YSZ a high amount of polydentate carbonates (p-CO₃²⁻) found at 1456 cm⁻¹ ($\nu_{as}(\text{CO}_3)$), and 1427 cm⁻¹ ($\nu_s(\text{CO}_3)$) is present, indicating a high amount of closely spaced cus centers on the surface of this oxide. On both oxides also a high amount of bidentate carbonates (b-CO₃²⁻) is formed, expressed by a quite broad peak for the $\nu_{as}(\text{CO}_3)$ band around 1550 cm⁻¹ and several peaks for the $\nu_s(\text{CO}_3)$ mode at 1377 cm⁻¹, 1342 cm⁻¹ and 1317 cm⁻¹. The different wavenumbers for the b-CO₃²⁻ species originate from the different adsorption sites at planes, terraces, edges and corners of the crystals.²⁴ Except for the different adsorption sites and thus the different distribution of (bi-)carbonates on 3- and 8-YSZ, the direct comparison also reveals variable adsorption behavior with increasing pressure. The lowest exactly measurable pressure in the FT-IR cell is 1·10⁻³ mbar. Already below this very low pressure (in terms of detectable chemisorption), very small doses of CO₂ lead to pronounced signals on 8-YSZ. According to the intensity of the absorbance, already below 1·10⁻³ mbar, 53 % of the absorbance

measured in 10 mbar is observed. At 10 mbar the most active surface sites for CO₂ chemisorption are saturated since the absorbance of 10 mbar is already 94 % of the absorbance at ambient pressure of 950 mbar. The affinity of 3-YSZ towards CO₂ chemisorption is not as pronounced as that of 8-YSZ, since on 3-YSZ a similar absorbance for (bi-)carbonates is only observed at $4.8 \cdot 10^{-2}$ mbar (as compared to $1 \cdot 10^{-3}$ mbar on 8-YSZ). In analogy to 8-YSZ, the relatively high (bi-)carbonate amount observed at 10 mbar amounts to ~80 % of the maximum amount of (bi-)carbonates at 950 mbar.

3.4.2. Temperature-dependent EIS and FT-IR measurements between room temperature and 1273 K under flowing conditions

Figure 6. (A) Temperature-dependent EIS measurements on 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ, (B) Arrhenius plots of heating and (C) cooling and (D) combined FT-IR and EIS experiments on 3-YSZ in dry CO₂ (flow $\sim 0.7 \text{ mLs}^{-1}$). Both types of experiments were performed at linear heating and cooling rates of 10 K min^{-1} between room temperature and 1273 K. The FT-IR spectra are shown every 20 K.

The heating and cooling curves of the impedance in dry CO₂ as a function of temperature are illustrated in Figure 6A. The temperature-dependence for 3-YSZ (orange and red traces in Figure

6A) is again similar to the reference material 8-YSZ, with the only notable difference of a less pronounced plateau-like feature between 693-873 K, which is also expressed in the different activation energies (cf. Table 4 and Figure 7D).

To correlate the surface conductivity with changes in surface chemistry (not possible for 20-YSZ and 40-YSZ due to suppressed CO₂ chemisorption) Figure 6B, C and D now show the Arrhenius analysis of the impedance course directly linked to the development of surface adsorbates. The specified temperature regions for the Arrhenius fit in Figure 6B and C are highlighted also in the combination plot of EIS and FT-IR data of CO₂ on 3-YSZ (Figure 6D). Upon heating, the first temperature region up to 673 K is characterized by a high amount of b-HCO₃⁻ and p-CO₃²⁻ species, along with a continuously decreasing amount of b-CO₃²⁻ species (see corresponding wavenumbers in section 3.4 above). Between 673 K and 893 K no b-HCO₃⁻ species are present anymore and the amount of carbonates is decreasing to zero. Above 893 K, no carbonates are visible. This is quite similar to 8-YSZ, on which no carbonates are observed above 873 K, too.³⁰

The temperature-dependent EIS experiments on 20-YSZ and 40-YSZ in dry CO₂ show hardly any differences, except for the visible onset temperatures of semiconduction and final impedance values at 1273 K (20-YSZ: 4.5·10² Ω, 40-YSZ: 2.0·10³ Ω). Also an impedance hysteresis during heating and cooling is absent.

In summary, the pronounced surface activity of 3- and 8-YSZ and the total absence of any surface activity on 20- and 40-YSZ are again confirmed by the comparison of the FT-IR data with the EIS analysis in flowing CO₂.

Table 4. Arrhenius-derived apparent activation energies of 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ in dry CO₂

		E _A dry CO ₂ /kJmol ⁻¹	Temperature range /K
3-YSZ	heating	73±4.4	893 – 1273
		127±7.6	773 – 893
		73±4.4	673 – 773
		89±5.3	444 – 673

	cooling	69±4.1 109±6.5 83±5.0 97±5.8	944 – 1275 773 – 944 676 – 773 447 – 676
8-YSZ	heating	61±3.7 99±5.9 178±10.7 47±2.8 87±5.2	1079 – 1273 873 – 1079 749 – 873 655 – 749 449 – 655
	cooling	63±3.8 106±6.4 156±9.4 56±3.4 110±6.6	1075 – 1279 873 – 1073 736 – 873 637 – 736 476 – 637
20-YSZ	heating	125±7.5 146±8.8 118±7.1	878 – 1273 776 – 878 571 – 776
	cooling	128±7.7 149±8.9 128±7.7	873 – 1273 790 – 873 571 – 790
40-YSZ	heating	137±8.2 111±6.7	751 – 1273 610 – 751
	cooling	141±8.5	628 – 1274

By taking a closer look on the E_A 's and comparing the four studied oxides, a definite trend becomes visible: there are always (except for 40-YSZ/cooling in CO_2) at least two or more different temperature regions with distinguishable activation energies observed. In case of 3- and 8-YSZ, a process with a comparably high activation energy ($>110 \text{ kJmol}^{-1}$) is visible in the “medium” temperature region. However, these activation energies are always higher for 8-YSZ than for 3-YSZ. A similar activation energy for 20-YSZ during heating and cooling in CO_2 is found in a similar temperature region (776 – 878 K E_A : $\sim 146 \text{ kJmol}^{-1}$). Another striking difference is, that both 20-YSZ and 40-YSZ exhibit a smaller number of distinguishable temperature regions as on the other two oxides. This can be ascribed to the fact that the characteristic plateau-like feature is absent in the medium temperature region (~ 600 to 800 K), which may eventually be related to the missing surface reactivity. In general, probably also applicable in the other gas environments, the peculiar impedance feature associated with the plateau might indicate two counteracting processes affecting the surface conductivity. On the one hand, the impedance obviously drops due to the increased thermal activation of charge carriers, but, as discussed earlier, surface and grain boundary chemistry plays a

vital role in the same temperature region. In due course, de-hydroxylation might lead to a diminished surface/grain boundary O^{2-} conduction, which would additionally increase the impedance again. Depending on the effectiveness of this de-hydroxylation step and the activation of charge carriers, and hence, their relative temperature-dependent contribution, a more or less pronounced “compensation” feature arises.

Figure 7. 3-D plot of activation energies versus the corresponding temperature regions and Y_2O_3 compositions for 3-YSZ, 8-YSZ, 20-YSZ and 40-YSZ in (A) He, (B) CH_4 , (C) CO and (D) CO_2 .

Figure 7A-D provides an overview of the various activation parameters observed in the different C1-gases and in He as a reference gas for the differently doped YSZ samples. What becomes immediately clear is that for 3-YSZ (orange and red bar-bells) during treatment in He and CO₂ in the low and high-temperature region very similar values for the E_A are obtained during heating and cooling (for detailed values see Tables 1, 2, 5 and S1, and additionally, Figure 7A and 7D). However, differences arise in the medium temperature region (discrepancies between 15 – 23 kJ mol⁻¹ depending on the gas, temperature-region and heating/cooling procedure). The same is also true for 8-YSZ treated in He and CO₂: the E_A values in the low temperature region correlate really well (for heating and cooling). However, for the high temperature region similar E_A 's are also obtained, but the temperature regions differ. During CO₂ treatment there are always five distinct temperature regions and during He exposure there are only four observed. Generally, there are less distinguishable temperature regions for 20-YSZ and 40-YSZ than for the other two oxides, which may again result from the poor surface reactivity of these samples. As for 8-YSZ, the values for 20-YSZ in the low temperature region and for 40-YSZ during heating and cooling (with the exception that there is a second temperature region during CO₂ treatment at lower temperatures with a lower E_A) are very similar for He and CO₂ treatment.

There are major differences in the E_A 's upon exposure to CH₄ and CO (before carbon deposition starts) for all oxides, which is most likely due to the different reduction degrees/gases differently affecting the surface chemistry. In order to interpret the values shown in Figure 7 – very much in line with the argumentation of explaining the plateau-like impedance feature – we might rise the question, which of the discussed Y-doped samples is essentially capable of oxide ion conduction. In essence, it appears that this is more pronounced for 3-YSZ and 8-YSZ, as the activation energies for 20-YSZ and 40-YSZ are generally much higher. Deviations from bulk oxide ion conduction might be then interpreted as a beneficial or detrimental contribution of surface or grain conduction to the overall bulk ion conduction, i.e. the individual kinetic barriers of surface, grain and bulk contribution

are increased or decreased, subsequently changing the rate-limiting step. Of course, this only holds if the chemical state of the surface remains unchanged, because simultaneous changes in the surface chemistry affecting the conduction mechanism might compensate these effects, virtually lowering the apparent activation energies.

4. Conclusions

The influence of the Y_2O_3 -doping level in different YSZ samples was investigated with spectroscopic techniques to yield complementary information on surface-dependent and electrochemical processes as a function of Y_2O_3 content. By combining *in situ* EIS (conductivity changes) and *in situ* FT-IR (adsorption properties), the temperature-dependent influence of the adsorption, desorption or deposition of various species (carbon-containing adsorbates, formates, carbonates) on the surface reactivity could be directly linked.

The summary of the interpretation of surface-chemistry related effects can be divided into two main parts – carbon deposition effects and gas-phase dependent correlated and entangled surface chemistry/(surface) conduction effects. On the one hand, carbon deposition following methane dissociation and carbon monoxide disproportionation is a common feature of the phases within the Y_2O_3 - ZrO_2 phase diagram (descriptors: fingerprint in FT-IR and changes in the total transmittance, quantification by FT-IR and onset of metallic conductivity/impedance drop in EIS) and yields a dynamically grown conducting carbon layer at the highest temperature. Differences arise in the EIS experiments due to the different deposition mechanisms in CH_4 and CO (gas phase radical reactions/H-abstraction and defect-mediated i-Boudouard reaction). Metallic conductivity via a fully percolated graphite film grown in CO is only seen on 40-YSZ despite the lowest amount of deposited carbon and not on the other oxides. However, a characteristic fingerprint of a non-percolated film is present for lower Y-doping levels and only distinct changes in the total transmittance due to carbon deposition are present on 20- and 40-YSZ.

On the other hand, the electrochemical behavior of 3-YSZ and 8-YSZ in He, CH₄ and also to some extent in CO₂, is very similar. Again, differences arise during treatment in CO due to the possibly stronger de-hydroxylation. This is also in good agreement with the FT-IR results, since these two oxides show pronounced surface activity due to a high amount of OH-groups. Upon CO and CO₂ adsorption, chemisorbed species could be clearly assigned. Temperature regions with different charge carrier activation energies before carbon deposition also perfectly correlate with distinct changes in the surface chemistry. The different degree of hydroxylation, and their different ability to chemisorb CO and CO₂, hence, steers the influence of the surface chemistry on the electrochemical properties. As for 40-YSZ, it appears that the discussed data essentially reflect the surface chemistry/surface conductivity properties of the particular Zr₃Y₄O₁₂ compound, but can be to a lesser extent derived from a simple reactivity trend by increased Y-doping of the ZrO₂ structure, but rather from the intrinsic defectivity/vacancy concentration. At least it appears that the impedance behavior in helium and CO₂ of 3-YSZ and 8-YSZ on the one hand, and 20-YSZ and 40-YSZ on the other hand, is somewhat similar and the surface activity regarding carbon deposition from CH₄ and CO (derived from the tendency to form chemisorbed species and the amount of hydroxylation) follows the trend 8-YSZ > 3-YSZ > 20-YSZ > 40-YSZ.

As a general concluding statement, we note that the presented results strongly suggest that the surface chemistry of the individual samples is the dominant steering factor for surface conductivity, adsorption and carbon deposition properties, but less so the morphology or even the crystallographic structure itself. The hydroxylation degree in due course is the most important reactivity descriptor. The synthesis procedure alone determines the extent of hydroxylation and hence, the surface reactivity. Seemingly bulk structure-wise identical samples may then exhibit strongly different surface reactivities due to deliberate steering of the hydroxylation degree (e.g. as has been proven for tetragonal or monoclinic ZrO₂^{30,37}).

Supporting Information available

X-ray diffractograms; additional correlated FT-IR and impedance measurements

5. Acknowledgments

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