Surface Reactivity of YSZ, Y₂O₃ and ZrO₂ Towards CO, CO₂ and CH₄:

A Comparative Discussion

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Abstract

The C1-surface chemistry of catalytically and technologically relevant oxides (YSZ, ZrO_2 and Y_2O_3) towards CH_4 , CO and CO_2 was comparatively studied by electrochemical impedance (EIS) and spectroscopic (FT-IR) methods. Highly correlated *in-situ* measurements yield a consistent picture with respect to qualitative and quantitative surface modifications as a function of temperature and gas phase composition. This includes a detailed study of carbon deposition in methane and adsorption of CO and CO_2 , but also proof of the strong influence of surface chemistry. On all studied oxides, carbon deposited during methane treatment grows dynamically forming interconnected islands and eventually a continuous conducting carbon layer at $T \geq 1073$ K. Before methane dissociation via gas phase radical reactions/H-abstraction and carbon growth, a complex redox interplay of total oxidation, formate and carbonate formation leads to associated surface and grain conductivity changes. For CO adsorption, these measurements yield data on the time- and temperature dependence of the adsorbate- and carburization-induced conductivity processes. In that respect, an equivalent circuit model in dry CO allows to disentangle the different contributions of grain interiors, grain boundaries and electrode contributions. For YSZ, temperature regions with different charge carrier activation energies could be identified, perfectly corresponding to significant changes in surface chemistry. Hydroxyl groups, carbonates or formates strongly influence the impedance properties, suggesting that the conductivity properties of YSZ e.g. in a realistic reforming gas mixture cannot be reduced to exclusive bulk ion conduction. 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: in contrast to ZrO_2 , the impact of the studied C1-gases on YSZ and Y_2O_3 is substantial. This also includes the re-oxidation/re-activation behavior of the surfaces.

1. Introduction

Zirconia-based oxides have been attracting much attention for a long time due to their potential in a variety of industrial and catalytic applications. Zirconia, especially when doped with Y_2O_3 , combines a high bulk ionic conductivity with a high mechanical and chemical stability, making it an ideal material for numerous applications. It has been used for gas sensors, oxygen pumps, thermal barrier coatings for gas-turbines, as an electrolyte and in combination with Ni as an anode material for solid oxide fuel cells.¹⁻¹⁷ In addition, hydrogenation, reforming and oxidative methane coupling activity have been reported for ZrO_2 materials.¹⁸⁻²¹ Recent catalytic applications include acting as an efficient growth template for distinct carbon materials such as nanotubes or disordered graphite layers.^{22,23} Unfortunately, despite the increasing interest and importance, so far comparably little is known about the surface chemistry of pure and doped ZrO_2 materials and its possible effect on materials or catalytic properties. Previous studies on the reactivity of the studied oxides in $\text{H}_2/\text{H}_2\text{O}$ mixtures infer an important role of the degree and nature of surface hydroxylation for the reactivity, especially in hydrogen. In fact, reduction of Y_2O_3 , YSZ and ZrO_2 has been shown to be a surface-bound phenomenon proceeding via reactive hydroxyl groups. This in turn caused associated changes in the conductivity of the oxides, indicating that their surface chemistry is strongly influencing the conduction behavior.²⁴⁻²⁷ Having said that, surface-related protonic conduction properties are of major interest because, in contrast to bulk proton conductivity, hydroxyl groups and water molecules on the surface of the oxide can also serve as a source of protons, giving rise to additional ionic charge carrier species. Interplay of these protonic species is suggested to play a fundamental part in the low- temperature proton transport properties in doped ZrO_2 materials, e.g. YSZ.²⁴ Connecting surface chemistry and catalytic applications directly, in previous works it was shown that the pure oxides under question can act as efficient nonmetallic substrates for methane or ethylene-induced growth of different carbon species.^{22,23} This as well caused associated changes in the surface conductivity. However, these conduction effects are so far discussed in a rather qualitative way, and

to date not much is known about the interplay between carbon growth species/deposited carbon and the reactivity of different surface-bound species.²³

To provide the most useful connection to catalytic applications, our aim is to focus on linking the electrochemical conduction properties to surface reactivity changes of pure and doped ZrO_2 materials, as well as Y_2O_3 as a ZrO_2 -free reference material in different C1 gas atmospheres (CH_4 , CO , CO_2). The choice of the respective C1-containing molecules is fueled by two reasons: At first, methane is chosen as one of the most relevant fuels with respect to abundance, existing infrastructure and high hydrogen-to-carbon ratio in energy conversion and also because a large data set on methane dissociation and subsequent carbon deposition at high temperatures ($T \geq 1023 \text{ K}$) already exists.²³ This renders it particularly useful to study the surface reactivity and properties before and during carbon growth, which has not been in the focus of research so far. In fact, before methane decomposition and carbon growth, a complex redox interplay of (total) oxidation, and the presence of different carbon-containing adsorbates, (e.g. formate and carbonates) might lead to associated surface and grain conductivity changes. Secondly, encompassing different catalytic aspects of the chosen oxides, the adsorption and reactivity of CO and CO_2 will be further scrutinized in a comparative discussion. This will help in understanding both the catalytic properties in hydrogenation or reforming reactions and also the complex interplay of bulk and surface charge transport processes upon internal reforming in zirconia-based solid electrolytes, being a core part of solid-oxide fuel cells. Especially regarding the latter, the composition of e.g. syngas mixtures has been shown to have a huge impact on the performance of the fuel cell.²⁸⁻³² Thus, the understanding of the performance of the solid electrolytes under the relevant comparatively harsh experimental conditions in e.g. pure CO is imperative. This particularly useful approach also allows to comparatively assess the performance of three different C1-containing gases under similar experimental conditions, eventually directly revealing similarities and common features of surface reactivity.

Speaking of the influence of surface properties – as shortly touched above - surface hydroxylation is expected to influence the C1-related adsorption/reactivity properties of the respective oxides crucially. Since all three oxides strongly differ with respect to water bonding and surface hydroxylation properties^{25,27}, they are perfect examples to also study this influence. As hydroxylation is expected to alter at least the surface- and possibly also the bulk conductivity properties, electrochemical impedance spectroscopy (EIS) is used for solid-state electrochemical characterization. As it is the method of choice to separate contributions of the different transport processes taking place on different time scales, frequency-dependent measurements in combination with simple impedance/conductivity experiments and FT-IR measurements will eventually allow to directly correlate the occurrence and reactivity of different adsorbed species with eventual changes in the electrochemical properties.

As it is potentially very difficult to keep track of the entangled surface chemistry and conductivity properties, we very briefly for the sake of clarity provide a very short conclusion about the main results already at this stage: As a general outcome, we were able to identify the temperature-dependent influence of different adsorbates and/or deposits on the oxide's surface reactivity. This is particularly obvious prior to the carbon deposition following methane or carbon monoxide adsorption. The complex interplay between total oxidation, formate and/or carbonate formation leads to temperature-dependent changes of grain interior, grain boundary and electrode contributions to the electrochemical properties, both for methane and carbon monoxide on Y_2O_3 , ZrO_2 , and YSZ.

2. Experimental

2.1. Materials and Sample Pre-treatment

Commercial powders of Y_2O_3 , ZrO_2 , and YSZ were used as starting materials. Cubic (bcc) Y_2O_3 (yttrium(III) oxide, nanopowder, < 50 nm particle size) and tetragonal YSZ (zirconium(IV)oxide yttria stabilized, nanopowder, containing 8 mol % Y_2O_3 as stabilizer) were supplied by Sigma-

Aldrich, and monoclinic ZrO₂ (zirconium(IV) oxide, 99.99%) by Alfa Aesar. To assure the same starting conditions for all experiments (and to guarantee that all samples are sintered), the samples were heated in pure O₂ up to 1273 K and held for 1 h 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 120 m²g⁻¹ (Y₂O₃), 32 m²g⁻¹ (YSZ), and 2 m²g⁻¹ (ZrO₂). Gases were supplied by Messer (Methane 3.5, CO 4.7, CO₂ 4.5 and O₂ 5.0).

For a typical experiment with the in situ EIS and FT-IR setup, the samples were heated at a rate of 10 K min⁻¹ up to 1173 K, held at 1173 K for 30 min, and subsequently cooled down to 300 K in the respective gas atmospheres under flowing conditions (≤ 1 mLs⁻¹). To ensure dry conditions, a liquid N₂-ethanol cooling trap at a temperature of ~ 163 K for O₂ and CO, and 233 K for CO₂ was used.

The structural stability and chemical purity of the samples was routinely checked by XRD²⁶ 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 especially metallic components, in particular Fe and Ni, were found to be below the detection limit. Purities of at least 99.99% were hence confirmed. This is of particular importance, since especially Fe and Ni, if present in a high impurity concentration, might act as metallic growth templates especially for carbon deposits, obscuring the surface properties of the oxide. Table S1 in the Supporting Information exemplarily shows an EDXRFA analysis for the used monoclinic ZrO₂ material.

2.2 Electrochemical Impedance Spectroscopy (EIS)

The in situ impedance cell consists of an outer quartz tube with two inner quartz tubes to which the sample and the electrodes are attached. Heating was 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. The impedance was measured by an IM6e impedance spectrometer (Zahner Messsysteme), which provides data on the impedance and the phase angle of the current as a function of voltage. The powder samples were pressed into pellets with a pressure of 2 t (5 mm diameter, ~ 0.2 mm thick, sample mass about 20 mg) and placed between two circular Pt electrodes forming a plate capacitor in mechanically enforced contact with the sample pellet.

For all temperature-programmed impedance measurements described in this article, 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 were applied to the Pt electrodes. Thus, the impedance of the pellet was effectively measured in an electrochemically unpolarized state. In all the temperature-dependent experiments the impedance modulus $|Z|$ value will be referred to as “impedance”.

A typical Nyquist plot is obtained isothermally at a given temperature in a frequency range between 100 mHz and 0.1 MHz at the same amplitude of the superimposed sinusoidal voltage signal that is also used for the temperature-dependent impedance measurements. The real and imaginary part of the impedance are first measured from 1 kHz up to 0.1 MHz (within 14 s) and then from 0.1 MHz down to 100 mHz (within 4 m 24 s; total measuring time: 4 m 38 s) to check for changes of the system during EIS.

Arrhenius analysis was performed to determine the activation energies for certain temperature regions. From the temperature-dependent EIS measurements the conductivity was calculated by taking the reciprocal of the impedance modulus value and plotting $\ln(\text{conductivity})$ vs. the reciprocal of the reaction temperature. This conductivity is proportional to the sum of the total charge carrier concentration and not specific for a certain kind of charge carrier. Hence, an “apparent” activation energy can be determined. This was done by using the formula: $E_A = -R \cdot k$ (R : ideal gas constant – 8.3145 J/mol·K; k : slope of the line). This calculated activation energy is the weighted sum of several contributions. Hence, there are too many parameters to extract the individual E_A of a single

process. Since there are many activated processes occurring simultaneously it is very difficult to assign one specific E_A to one process. In fact, we aim for identifying qualitative changes in the E_A that correspond to changes on the surface.

The resistance values gathered from the fit of the Nyquist plots for the different processes were also transformed into conductivities. As in the case of the temperature-dependent EIS measurements, the “apparent” activation energies were calculated with the same formula as above.

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 operando/in situ reactor cell.³³ This cell provides a chemically inert surrounding of the sample in the heated area and in situ measurements up to 1273 K under flowing and static conditions can be performed. Also measurements in vacuum with a minimum pressure of $3 \cdot 10^{-7}$ mbar are possible. The window material BaF_2 allows accessing wavelengths above 800 cm^{-1} . Experiments in flowing mode can be exactly correlated with associated EIS measurements. In static mode, the gases are pre-adsorbed on a $5 \text{ \AA}$ zeolite trap, binding water sufficiently strongly, before the dried gases are desorbed into the evacuated and thoroughly 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.

3. Results and Discussion

3.1. Methane

Linking surface reactivity and electrochemical impedance properties before and during carbon growth

As introduction to the chapter on methane and for the sake of clarity of discussion, it should be noted that the experiments presented here are in fact based on those discussed in a previous publication²³ entirely dealing with the structural consequences of gas-phase methane cracking at temperatures at and above 1023 K and the structure and morphology of the subsequently deposited carbon layer. Although temperature-dependent impedance measurements were also provided, the discussion of the complex interplay between impedance and surface reactivity before and during carbon growth was entirely spared. This, however, will form the core of results presented here.

It is known from literature by Chen et al.³⁴ that thermal decomposition of methane takes place at temperatures above 995 K. The initial stages of this reaction can be described by a homogeneous, nonchain radical mechanism with the main products C_2H_6 and H_2 . In some experiments, the pyrolysis has been limited to this stage. However, rapid secondary reactions may also set in yielding C_2H_4 , C_2H_2 and finally C.³⁴

Regarding our experimental data we can state that the first step is most likely the same as during the oxidative coupling reaction described in the work from Zavyalova et al.²⁰ From a previous study by Köck et al.³³ it is also already known that in the beginning of this redox reaction CO and CO_2 are formed (note that this process only concerns the surface of the sample). Re-oxidation does not occur since no oxygen is present - like in the case of the oxidative methane coupling reaction. Carbon deposition starts at $T \geq 1023$ K. However, the crucial question is: how does the further C-deposition proceed? At least two contributions for C-deposition are possible:

- via adsorbed methyl radicals
- via intermediate species (ethane, ethylene, acetylene which are good carburization agents)

However, at a certain point carbon has to begin to grow on carbon atoms, and it was stated that 3 to 4 C-layers catalyze the growth of carbon best³⁵, but even in this case this will be strongly dependent on the surface chemistry of the sample.

Figure 1 now highlights a temperature-dependent impedance experiment performed on Y_2O_3 in dry methane (similar to the one presented in ref.²³), where the impedance changes observed during heating have now been linked to associated changes in surface reactivity, as deduced from in parallel acquired FT-IR spectra shown as small insets at selected temperature.

Figure 1. Combined temperature-dependent EIS (large panel) and FT-IR (small panels) measurements on Y_2O_3 in dry CH_4 (flow $\sim 0.7 \text{ mLs}^{-1}$). Both methods were performed at linear heating and cooling rates of 10 Kmin^{-1} between room temperature (300 K) and 1173 K.

In short, semiconductive behavior and the reversible formation of thermally excited charge carriers is apparent upon exposure of the Y_2O_3 sample to dry methane and heating up to around 1023 K (steady decrease of impedance from the detection limit at $6 \cdot 10^9 \Omega$ to $\sim 4 \cdot 10^6 \Omega$). This region is followed by a

drastic decrease of the impedance at temperatures above 1023 K, leading to a final value of around 12 Ω at $\sim$ 1100 K. This value is associated with metallic conductivity and indicates a drastic material change at the surface/interface of the sample. Metallic conductivity is still preserved even after cooling the system to room temperature. As discussed in more detail in ref.²³ this is due to a graphitic carbon layer with a high degree of disorder following predominantly gas-phase dissociation of methane.

Linking the impedance changes now to surface reactivity, in the region below 1023 K, where the impedance measurements essentially exhibit semiconductive behavior, the infrared experiments in essence show typical gas phase spectra of methane (rotational vibration modes between 3940 - 3750, 3250 - 2300, 1730 - 1530 and 1510 – 1100 cm^{-1}). Noticeable are very strong negative signals in the region of the surface OH-groups (3800 cm^{-1} – 3200 cm^{-1}). This effect seems to be a lot more pronounced on Y_2O_3 treated in methane than compared to heating in other gases like CO or CO_2 .²⁵ Negative signals indicate that a species that was stable when the background was taken – in this case the fully oxidized sample at room temperature – is removed or changed during the subsequent heating in methane. When the impedance drops due to formation of graphitic carbon, the only effect on the spectra of Y_2O_3 seems to be a correspondingly strong decrease in the transmittance, which is in line with TEM and Raman results (discussed in ref.²³) of a disordered graphitic layer. No additional peaks for C-O bonds that are typical for graphite oxide or possible intermediate species arise. At 1023 K a transmittance of about 80% is measured, which is reduced to 20% at 1123 K and to almost zero at 1143 K. Similar to the EIS experiment, also the IR spectra now directly prove that the carbon layer is stable while cooling the sample back to room temperature.

Figure 2. Combined temperature-dependent EIS (panel A heating and cooling) and FT-IR (panel B heating, panel C cooling) measurements on YSZ in dry CH₄ (flow ~ 0.7 mLs⁻¹). Linear heating and cooling rates of 10 Kmin⁻¹ between room temperature and 1173 K were applied. The FT-IR spectra were collected every 10 K step.

Figure 2A shows the corresponding impedance experiment in dry methane on the YSZ sample. Even though it is known from a previous study²³ that the carbon deposition and the resulting disordered graphitic layer on YSZ is very similar to the ones on Y₂O₃ and ZrO₂, there are still some noticeable differences in the course of the impedance. These arise especially between 950 and 980 K as a small plateau (where the impedance seemingly does not change) and secondly, as a small increase in the impedance with a maximum at 1000 K and a corresponding value of $9.4 \cdot 10^3 \Omega$. In the temperature range between 1000 K and 1093 K, again a decrease of the impedance is visible. Further raising the temperature up to 1173 K finally leads to a significant drop in the impedance with a final value of 13 Ω , corroborating the presence of a conducting disordered graphitic carbon layer (see also ref.²³). In good correlation with the measurements on Y₂O₃, cooling down in dry CH₄ to 300 K does not lead to a reversibly high impedance value which is obtained for example in O₂.

Interestingly, the different impedance course (with respect to Y₂O₃) is also directly visible in the accordingly different FT-IR spectra. The transmission is not decreasing over the entire spectral region, but a broad characteristic feature below 2500 cm⁻¹ up to 800 cm⁻¹ is apparent in the heating experiment (Figure 2B). Interestingly, a slight, but obvious change in the overall transmittance at 973 K is observed, which can be directly associated with the plateau in the impedance course (Figure 2A). The characteristic changes for carbon deposition in the infrared signal start at 1073 K and a closer look at Figure 2B reveals a very fast acceleration of this process due to the strongly enhanced increase of the carbon feature at every 10 K step. In connection to the impedance trace this is the temperature region after the plateau, where the impedance drops again, but the decrease is not as

drastic. The representative signal for carbon deposition in the infrared spectra reaches a maximum above 1113 K and is not changing up to 1173 K, although this is the temperature region where the impedance drops drastically and the sample reaches metallic conductivity. From this behavior we may conclude that on YSZ the formation of carbon affects the infrared signal only during growth of the carbon islands. When these islands form a conducting, continuous layer, a characteristic IR fingerprint for this graphitic layer on YSZ arises (cf. spectrum in vacuum after re-cooling to room temperature without superimposed gas phase absorptions in Figure 2C, “RT vacuum”). Upon re-cooling – as on Y_2O_3 – there are hardly any changes in the impedance and the same is true for the infrared spectra (Figure 2C).

Figure 3. Combined temperature-dependent EIS (panel A heating and cooling) and FT-IR (panel B heating, panel C cooling) measurements on ZrO_2 in dry CH_4 (flow $\sim 0.7 \text{ mLs}^{-1}$). Linear heating and cooling rates of 10 Kmin^{-1} between room temperature and 1273 K were applied. The FT-IR spectra are shown every 50 K step.

A very similar trend of the temperature-induced impedance changes as in Figure 1 is visible on ZrO_2 (Figure 3 panel A), although a temperature shift in the onset of the impedance decrease (here at 1050 K) is obvious, again indicating the irreversible formation of the conducting carbon layer.²³ Even though it is clear that the dissociation of methane and the deposition of carbon took place just like on

Y₂O₃ and YSZ, there are hardly any changes that can be attributed to this carbon species in the infrared experiment. The variations in the transmittance during heating and cooling of ZrO₂ (Figure 3B and C) in methane can be exclusively assigned to heat radiation and thus, only show a gas phase signal of methane on this oxide for all temperatures. After re-cooling and methane removal, slightly negative signals for OH-groups and a comparatively small feature in the region between 1300 cm⁻¹ and 800 cm⁻¹ remains.

Methane chemistry before and during carbon deposition and growth

In a previous study²³, CH₄ measurements on all three oxides indicated that one can roughly divide the processes concerning the reaction of gaseous methane with the oxide surface into CH₄ oxidizing mechanisms below ~ 1023 K and carbon depositing behavior strongly related to gas phase radicals of methane above a temperature of ~ 1023 K. For a better understanding of especially the C1-related processes occurring at lower temperatures, we give a brief account of the previous results. For example on Y₂O₃, already above 600 K signals for gaseous CO and CO₂ have been detected during heating in 90 mbar static CH₄ up to 1143 K and re-cooling to room temperature.^{23,33} In a dedicated FT-IR experiment³³, this methane pressure was deliberately chosen to create a surface where the methane decomposition has already been induced to a rather small amount but at the same time the resulting carbon layer was not thick enough (i.e. complete) to affect the total transmittance and other surface-related signals of the spectra. However, as in these experiments gas phase methane obscures the surface reactivity of CO and CO₂ at lower temperatures, a connecting experiment with deliberate elimination of especially the gaseous CH₄ signals has been conducted and is presented here (Figure 4).

Figure 4. FT-IR measurements of formate evolution and reactivity during static heating (front) and re-cooling (back) between room temperature and 773 K on Y_2O_3 , starting in vacuum at a pressure of 10^{-6} mbar (start of series at the front of the waterfall plot). The inset magnifies the region between 2500 cm^{-1} to 2000 cm^{-1} . The FT-IR spectra were collected every 20 K step.

To do so, vacuum was applied after re-cooling the mixture of CH_4 and initially formed CO and CO_2 back to room temperature, which unravels the distinctive signals of formates and other surface-bound species. This state is represented by the starting spectrum at RT in Figure 4 (front of the waterfall plot). Note that re-cooling in the mixture of CH_4 , CO and CO_2 , would in principle imply the formation of formates and (bi-)carbonates, the latter especially on Y_2O_3 which is very sensitive to CO_2 . Interestingly, as it follows from Figure 4 (cf. RT spectrum in the front), the main species after this treatment are in fact formates (colored in red: $\nu_{\text{as}}(\text{OCO}) = 1595\text{ cm}^{-1}$, $\nu_{\text{s}}(\text{OCO}) = 1380\text{ cm}^{-1}$, $\delta(\text{CH}) = 1395\text{ cm}^{-1}$ and $\nu(\text{CH}) = 2845\text{ cm}^{-1}$) alongside a minor amount of strongly bound carbonates

($\nu_{\text{as}}(\text{CO}_3) = 1445 \text{ cm}^{-1}$).²⁵ Weakly bound (bi-)carbonates are absent. This indicates that the reduced state of the oxide surface, established during previous CH_4 oxidation at lower temperatures favor the formation of formates rather than (bi-)carbonates during re-cooling.

To shed more light on the molecular processes associated with this surface state and the related C1-chemistry below $\sim 1023 \text{ K}$, in Figure 4 the initially formate-covered sample was subsequently heated up to 773 K and re-cooled to room temperature (10 Kmin^{-1}) under static conditions (without continuous pumping), starting with a vacuum pressure of 10^{-6} mbar . This experiment can clarify the open question whether these formates contribute to CO_2 formation via de-carboxylation (CO_2 is also observed in experiments in pure CO) or if they are just reversibly formed species from the reaction of gaseous CO with surface OH -groups of the Y_2O_3 sample.²⁵ In this context, the mechanism of the formation of CO_2 from CO on oxides via the water gas shift reaction is also a frequently and generally discussed question in literature, as there are two principle reaction pathways³⁶: formation of surface formates when a CO molecule reacts with surface OH groups and the resulting adsorbates then de-carboxylate to CO_2 , or the reaction of the gaseous CO with lattice oxygen atoms to form defects/vacancy sites when releasing resulting gaseous CO_2 molecules. In either case, a reduced surface center is formed. However, with the experiment conducted here, the most likely mechanism can now be clarified. A closer look at the formate signal for the bidentate or bridged formates (colored in red in Figure 4) reveals that above a temperature of 593 K those signals decrease drastically and are completely removed at a temperature of 693 K . This can be perfectly correlated with the appearance of a gas phase signal for CO (see inset in Figure 4). Obviously, almost no signal for CO_2 in the gas phase could be detected although it has a stronger infrared absorbance than CO at the same pressure. Hence, the formate reaction pathway from CO to CO_2 on Y_2O_3 could be ruled out and the observed CO_2 is rather produced by surface vacancy formation. This is in line with the fact that de-carboxylation to carbon dioxide would further increase the already quite reduced state of the surface, which appears unlikely on a poorly reducible oxide. When re-cooling the sample under static

conditions from 773 K to room temperature the formate signals re-appear below a temperature of 673 K and reach the same intensity as compared to the starting conditions below 473 K. The corresponding gas phase CO signal disappears completely upon cooling. This behavior also indicates that the formates are not related to the methane decomposition because they are de-carbonylated at much lower temperatures as the methane-to-carbon decomposition itself takes place. Figure 4 also illustrates the interplay between formate and polydentate carbonate species, which are labeled in blue at a characteristic wavenumber of $1445\text{ cm}^{-1} = \nu_{\text{as}}$. The decrease of the formate signals seems to be correlated with the increase of the peaks of the polydentate carbonate, which is also observed in the heating experiment of YSZ in pure CO (Figure 10) and will be also discussed later in section 3.2.

The discussed processes of the obviously complex C1-chemistry on Y_2O_3 with CH_4 and its oxidation products CO and CO_2 in the lower temperature range $< 1023\text{ K}$, where a methane radical mechanism can be excluded, are also present on YSZ. Further investigations discussed in sections 3.2 and 3.3 pronounce the strong impact of the surface chemistry on the electrochemical behavior over a wide temperature range.

Dynamics of carbon growth

To get a better understanding of the dynamics of carbon layer growth and a qualitative impression on the time scale on which this carbon deposition/growth occurs and is finished, frequency-dependent impedance experiments in dry methane were conducted at different temperatures. The resulting Nyquist plots are shown in Figure 5. Figure 5A displays the plot for the Y_2O_3 sample in dry methane at 973 K. When compared to the temperature-dependent experiment shown in Figure 1, it is immediately obvious that this is exactly the temperature just before the drastic impedance drop occurs, i.e. ongoing slow carbon deposition can be assumed. From this complex frequency-dependent impedance spectrum it follows that the carbon deposited on the sample grows forming dynamically merging islands. The higher the temperature gets or the longer the system is held at a

high enough temperature (with respect to methane decomposition) the more those separated carbon atoms/small separated patches get interconnected forming larger percolated islands. At 1023 K, the carbon deposition on Y_2O_3 is already much faster (cf. Figure 1 large panel). Thus, upon further heating (or after longer decomposition times) the carbon islands fully percolate to form a continuous conducting carbon layer. As mentioned in the experimental section, the impedance was recorded starting from 1 kHz up to 0.1 MHz (within 16 s) and then from 0.1 MHz back to 100 mHz (within 4 m 22 s). Normally, this is performed to prove the stability of the system, because on an unaltered system the real and imaginary contributions to the impedance for the same frequencies should not differ. In this case, EIS helps to demonstrate the dynamics of island growth on the timescale of a single spectrum. Since it is very obvious that one does not attain the same impedance values for the same frequencies, this implies that the system is changing during the measurement. Between the first point in this experiment at 1 kHz (Z_R : $2.3 \cdot 10^5 \Omega$ and $-Z_{IM}$: $1.5 \cdot 10^4 \Omega$) and the second one also at 1 kHz (Z_R : $1.1 \cdot 10^5 \Omega$ and $-Z_{IM}$: $2.5 \cdot 10^3 \Omega$) there is only a time difference of 26 s. This shows that different contributions for the real and imaginary part of the impedance and consequently, also for the phase shift, are attained. At frequencies of 0.1 kHz and below (after 30 s) there is hardly any contribution of the imaginary part left, which means that only ohmic resistance is observed. This is due to the presence of a more or less complete conducting carbon layer and means that a change from a system with grain boundaries to a sintered, “closed” system has taken place. This again helps to show how fast this process of island growth (forming a fully percolated carbon layer) is taking place and when it is finished (frequencies < 0.1 kHz after 30 s). Consequently, a purely “ohmic” Nyquist plot is observed if the sample is treated in dry methane at a temperature of 1073 K (Panel 5B), i.e. carbon growth is much faster as compared to lower temperatures. The imaginary part of the impedance is basically zero and only a “real” resistance (without phase shift) is observed. This course of the Nyquist plot is also due to the fully interconnected conducting carbon layer which is

present already at the beginning of the EIS spectrum. Thus, the sample only exhibits ohmic resistance without phase-shifting intergrain capacitance effects as seen at 973 K (cf. Figure 5A).

To figure out if the hypothesis of the island growth following decomposition of CH_4 is also valid for YSZ and if so on which time scale these processes occur and are finished, associated Nyquist plots have been collected, too. Figure 5C in turn shows the complex impedance plot of YSZ in dry methane at 1073 K. Note that the temperature here is 100 K higher than compared to the Y_2O_3 sample in Figure 5A to induce carbon island coalescence on the timescale of a single impedance spectrum. It is already known from literature that methane dissociation starts on Y_2O_3 at lower temperatures than on YSZ and ZrO_2 .²³ Although the total measurement time (4m 38 s) for the experiment on Y_2O_3 and YSZ is exactly the same and in this case the temperature is higher, not the same result is obtained. At the beginning of the experiment (1 kHz up 0.1 MHz and back to 20 kHz within 17 s; minimum in the inset in Figure 5C) the real part of the impedance is decreasing. During this frequency range an impedance course with very little phase shift (i.e. contribution of the imaginary part of the impedance) is apparent. However, starting at frequencies below 20 kHz, the imaginary part of the impedance starts to increase again with another complex impedance course between 20 kHz and 10 Hz. This indicates that some form of capacitance has evolved, which is getting more and more pronounced during the measurement. In the beginning of this process, Z_R increases a little bit (up to 68 Hz), then starts to increase again with a plateau between 10 – 1 Hz. If the experiment is extended to even lower frequencies, the imaginary part of the impedance rises even further, leading to a final value of 523 Ω at 100 mHz. For the YSZ sample, the island growth can therefore also be observed as a function of time, but with the difference that the deposition process is does not end up with purely ohmic resistance, as it was the case for Y_2O_3 . This is due to the fact that carbon deposition is much slower in comparison to Y_2O_3 and hence in this case the final state of carbon island growth at this temperature and time scale is different. Obviously, not an interconnected, fully percolated carbon layer is formed, but the high imaginary part at low

frequencies indicates a high capacitance contribution to the 764 Ω ohmic resistance read out at 100 mHz on the x-axis. From this very high phase shift, and therefore a high imaginary part and high capacitance at 100 mHz, we can deduce the presence of not fully interconnected carbon islands at this temperature. This indicates that the carbon deposit (graphite flakes/grains) is a very effective dielectric with, in view of the small deposited amount, enormous charge storage capacity. To obtain specific values for the time-dependent resistance and capacitance values of the studied system during this carbon deposition/island growth leading to an eventually fully percolated carbon layer, a more sophisticated model has to be used. In fact, a more complex dynamical model, assuming the time-dependent increase of a parallel, carbon-induced conductivity, along with a very high and also time-dependent carbon-induced capacitance contribution at “percolating” C-grain boundaries, would be more justified but is of course very difficult to establish.

Note that the Nyquist plots outlined in Figure 6 strongly differ from the ones presented in literature for treatments of YSZ or ScSZ materials either in carbon-free (e.g. hydrogen at elevated temperatures) or carbon containing gas atmospheres or for Ni-YSZ materials and full operating SOFC's.^{12,13,15,16,21,37-40} These differences are obviously due to the growing carbon layer on top of the YSZ grains. This is also especially true for comparable measurements in CH₄ atmospheres⁷, which are conducted at lower temperatures than discussed here. Thus, carbon deposition did not start yet in these studies.

Figure 5. Nyquist plots of Y₂O₃ treated in dry CH₄ at 973 K and 1073 K (panel A and B) and the corresponding Nyquist plot for YSZ treated in dry CH₄ at 1073 K (panel C). Total measurement time: 4 m 38 s; measurement time between 1 kHz to 0.1 MHz and back down to 1 kHz: 27 s.

3.2. Carbon Monoxide

Linking surface reactivity and electrochemical impedance properties

As a general introductory note, for the most useful correlation of the studies in methane and carbon monoxide, the experiments in CO were restricted to the almost similar temperature region. The impact of the surface chemistry of YSZ in flowing CO on the electrochemical behavior is elucidated in Figure 6, where the impedance experiment during heating and cooling and for direct visibility of distinct activation regions provided as Arrhenius plot were correlated with the corresponding FT-IR measurements. In this plot the regions of the different activation energies (summarized in Table 1) for the different processes were fitted and they perfectly correspond to significant chemical changes on the surface being detected in the infrared experiment (for a magnification, see also Figure 7). Starting at room temperature, the surface of YSZ is covered with polydentate carbonates p-CO₃²⁻ (1410 cm⁻¹, marked in blue in Figure 7). In the low temperature region between 475 – 574 K, a very low activation energy of 25.3 kJ mol⁻¹ can be determined. Around 523 K, the formation of surface formates ($\nu_{as}(\text{OCO}) = 1576 \text{ cm}^{-1}$, $\nu_s(\text{OCO}) = 1342 \text{ cm}^{-1}$, $\delta(\text{CH}) = 1385 \text{ cm}^{-1}$, $\nu(\text{CH}) = 2884 \text{ cm}^{-1}$)^{19,41} starts, whereas the bands for p-CO₃²⁻ are decreasing (see also Figure 7). At 573 K – just at the beginning of the second temperature region with an activation energy of 107.7 kJ mol⁻¹ – the signals for the formate adsorbates and the signals for carbonates reach approximately the same intensity, and just 50 K higher, the polydentate carbonates are decomposed. This perfectly fits to the well-resolved alteration in the slope of the Arrhenius plot. The formates are stable up to a temperature of 873 K with a maximum intensity at 673 K. This maximum of intensity of the formates obviously also contributes to the much higher E_A as compared to the lower temperature region and a formate-

induced blocking of the low-temperature protonic surface conductivity. As shown in the FT-IR measurement, these formates are stable up to 873 K and this is exactly the onset temperature for the high temperature region with a slightly lower activation energy. Hence, the build-up of formates is considered detrimental to surface/grain boundary conductivity. At 738 K another change in the activation energy is observed and this can be attributed to the formation rate maximum of CO_2 temperature at that temperature (result of a static FT-IR experiment, not shown here). From the experiment in Figure 7 one can argue that the presence of formates and the formation of CO_2 from CO are not implicitly linked because the increasing CO_2 pressure is mostly initiated by reductive reaction with surface oxygen. Above 873 K this process is the only remaining reaction that can be detected by FT-IR in the investigated temperature region.

Figure 6. (A) Temperature-dependent EIS measurement and (B) combined Arrhenius plot (large panel) and FT-IR (small panels) measurements on YSZ in dry CO (flow $\sim 0.7 \text{ mLs}^{-1}$). Both methods were performed at a linear heating rate of 10 Kmin^{-1} between room temperature and 1073 K.

Figure 7. FT-IR measurements on YSZ in dry CO (flow $\sim 0.7 \text{ mLs}^{-1}$) during heating from room temperature up to 973 K. The FT-IR spectra are shown every 50 K step. Relevant signals for formates (red) and polydentate carbonates (blue) are colored and the absorbance region of gaseous carbon monoxide was omitted.

In Table 1 the determined “apparent” activation energies for the three different samples in dry and, for comparison and to mimic the influence of surface hydroxylation, moist conditions are jointly summarized. Note that these activation energies (E_A 's) not only depend on the measurement conditions but also on the temperature region where the linear fit was applied to. Upon comparing the E_A 's for dry CO it is quite obvious that there are always at least two processes with different activation energies. As mentioned before, this can always be related to the change of the surface of the sample as monitored by FT-IR. The removal or formation of OH-groups, carbonates or formates influences the electrochemical impedance and hence, the Arrhenius plot with its activation energies. This makes it immediately clear that the conductivity properties of a powder YSZ sample in a realistic CO-containing (e.g. reforming) gas mixture cannot be assigned to exclusive bulk ion conduction.

Table 1. “Apparent” activation energies for the three oxides in dry and moist CO

		E_A dry CO /kJmol ⁻¹	Temperature range /K	E_A moist CO /kJmol ⁻¹	Temperature range /K
Y₂O₃	heating	134.8	1005 – 1066	111.9	712 – 1070
		108.4	647 – 1005	69.5	605 – 712
	cooling	122.4	918 – 1073	123.7	777 – 1073
		129.2	649 – 918	82.9	663 – 777
YSZ	heating	96.9	873 – 1079	103.7	787 – 1084
		97.2	738 – 873		
		107.7	574 – 738		
		25.3	475 – 574		
	cooling	131.4	850 – 1083	103.0	788 – 1080
		60.1	723 – 850		
		96.4	542 – 723		
ZrO₂	heating	121.2	774 – 1074	102.0	785 – 1070
		52.9	625 – 764	34.3	714 – 785
				70.5	585 – 714
	cooling	153.0	919 – 1074	124.5	898 – 1074
		103.5	720 – 919	40.9	789 – 898
				72.1	611 – 789

By taking a closer look on the E_A 's another trend becomes visible: the determined activation energies are generally higher for the measurements in dry than for the ones in moist CO. This is due to the fact that in the beginning of the heating routine OH-groups are removed (likely due to formate formation), which are then partly recovered again upon cooling. Thus, several processes, including hydroxyl-mediated surface protonic conductivity²⁴, are superimposed on bulk anion transport, simultaneously altering the surface of the sample and hence, higher or lower activation energies result. Only for the cooling in Y₂O₃ and the heating routine in YSZ a very similar E_A is calculated. It is known from literature that Y₂O₃ is very hygroscopic and exhibits a high fraction of strongly bonded hydroxyls.²⁷ Hence, the contribution from the generation or removal of OH-groups is less pronounced. Also the high basicity of Y₂O₃ is expected to counteract protonic conductivity. For the YSZ sample the much higher bulk anion conductivity contribution additionally blurs these effects. Of course, another possibility is simply that there are many different processes occurring simultaneously, which can be better separated on the other samples.

Figure 8. Nyquist plots (data points) and simulated spectra (continuous lines) using the proposed equivalent circuit (see Figure 9) of YSZ treated in dry CO at selected temperatures. The lowest frequency of 100 mHz is at the right side and the highest one of 0.1 MHz at the left side of the x-axis. The inset in the upper right corner shows an enlargement of the plots at higher temperatures.

Figure 8 highlights the corresponding Nyquist plots (NPs) of the YSZ sample treated in flowing CO at different temperatures. At 773, 823 and 873 K two well-defined “semicircles”/arcs are apparent: a very large one at high frequencies (HF) and a smaller one at low frequencies (LF) with “tailing”. Numerous attempts⁴²⁻⁵⁸ have been made in order to find the most adequate fit for an ionic conductor such as YSZ. However, several obstacles have to be overcome in order to find the perfect fit model: grain size effects^{45,46,53,54,57,59,60} or the semicircles being a mixture of the involved processes, to name just a few. Hence, the collection of reliable information from this data becomes a difficult task.^{52,53}

Even though, there are some specifics that are already known from literature: the bulk (grain interior) contribution is usually observed at high frequencies in the Nyquist plot whereas the grain boundary and electrode contribution is located at mid and low frequencies, respectively.^{54,58} This means that the high frequency (HF) part of the Nyquist plot is assigned to the specific electrical conductivity of zirconia grains and the low frequency (LF) “semicircle” characterizes the electrical conductivity of grain boundaries, which results from the blocking effect of charge carriers due to internal interfaces of the material pores.^{3,42,61} The “tailing” of the LF arc is due to interaction between the electrode and the sample pellet. Note that this described “tailing” is actually the onset of another semicircle which is as mentioned before due to electrode contribution and will appear in the high temperature range. If the frequency range during the experiment would be adapted to even lower frequencies, a semicircle for the electrode might be completely represented in the complex impedance plot.

Already in 1969, Bauerle assembled an equivalent circuit for a ceramic electrolyte such as YSZ with platinum electrodes consisting of three parallel RC elements being connected in series, corresponding to grain interiors (gi), grain boundaries (gb) and electrode (e).⁶² However, the circuit that we used in this study to fit the experimental data is composed of constant phase elements (CPE's) instead of ideal (Debye) capacitors. This is generally done for polycrystalline samples due to sample inhomogeneity, surface defects (e.g. pores) or electrode roughness, giving rise to frequency dispersion and non-uniform distribution in the current density. Hence, these elements more accurately represent the capacitive behavior of this kind of cells in the whole studied frequency range.^{42,62-64} Therefore, the EIS ac equivalent circuit was modeled as shown in Figure 9. Since constant phase elements in the place of capacitances were used in the equivalent circuit model, the capacitances (C) were calculated from $C = (R^{1-\alpha} \cdot Q)^{1/\alpha}$ with Q being the value obtained for the respective CPE and α indicates whether the CPE behaves more like an ideal capacitor ($\alpha = 1$) or more like an ideal resistance ($\alpha = 0$).

The bigger arc at HF in Figure 8 attributed to grain interiors (bulk) significantly decreases during the measurement whilst heating the system to higher temperatures. Thus, a clear trend is visible: the higher the temperature, the lower the contribution of the bulk is – this is also shown in Figure 8. If the system is heated up to 873 K (this is the temperature where the formates are not present anymore), a different trend becomes visible: the intensity and hence the resistance of the first and second “semicircle” are seemingly the same. If the heating procedure is continued to even higher temperatures (see inset in Figure 8), the maximum of the intensity of the “semicircle” is exactly the opposite. Starting at temperatures of 873 K and above, the first “semicircle” (contribution of the bulk) of the NP is getting less and less pronounced in the chosen frequency range and hence, the maximum is getting smaller and smaller. At the highest temperature of 1073 K, only a few data points of the first “semicircle” are present. The parameters of the equivalent circuit model used to fit the experimental data are summarized in Table 2. The agreement of the simulated spectra with the experimental data supports the validity of the equivalent circuit diagram and also the comparison to other studies on and under similar materials and conditions.^{3,37,42,46,50,54,56,59,62,65-69}

Figure 9. Equivalent circuit model that was used for fitting the Nyquist plot data of the samples with contributions from the grain interiors (gi), grain boundaries (gb) and electrode (e) as shown in Figure 8.

Table 2. Circuit parameters used to generate the impedance spectra of Figure 8

Temperature /K	773	823	873	923	973	1023	1073
R_{gi}/Ω	$7.1 \cdot 10^5$	$2.4 \cdot 10^5$	$9.4 \cdot 10^4$	$4.1 \cdot 10^4$	$2.0 \cdot 10^4$	$1.0 \cdot 10^4$	$5.7 \cdot 10^3$
C_{gi}/F	$3.3 \cdot 10^{-11}$	$3.9 \cdot 10^{-11}$	$2.8 \cdot 10^{-11}$	$2.8 \cdot 10^{-11}$	$2.8 \cdot 10^{-11}$	$2.8 \cdot 10^{-11}$	$2.9 \cdot 10^{-11}$
R_{gb}/Ω	$3.3 \cdot 10^5$	$1.6 \cdot 10^5$	$1.1 \cdot 10^5$	$6.6 \cdot 10^4$	$3.9 \cdot 10^4$	$2.4 \cdot 10^4$	$1.2 \cdot 10^4$
C_{gb}/F	$3.2 \cdot 10^{-5}$	$5.7 \cdot 10^{-5}$	$7.1 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$4.9 \cdot 10^{-4}$
R_e/Ω	$1.2 \cdot 10^5$	$7.8 \cdot 10^4$	$6.9 \cdot 10^4$	$5.3 \cdot 10^4$	$4.1 \cdot 10^4$	$3.0 \cdot 10^4$	$1.9 \cdot 10^4$
C_e/F	$8.4 \cdot 10^{-4}$	$6.2 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$

With the help of the circuit equivalent model that was used to fit the experimental data in Figure 9 we were able to distinguish the different contributions for the grain interior, grain boundaries and the electrode. With this knowledge, the temperature dependence of these contributions could be accordingly elucidated. As seen in Table 2, at the lowest temperature of 773 K the highest contributions for the three different resistances are obtained. The higher the temperature, the lower the contributions are, converging to a final value.

Similar C_{gi} values have been found by Lacroix et al. on complex oxides ($SrZr_{0.9}Ln_{0.1}O_{2.95}$).⁵⁰ In case of the grain boundary capacitance, values for comparable samples are hard to find in literature. 8-ScSZ has been reported to exhibit a clear trend⁴⁹: the higher the temperature (in this case the maximum temperature was 723 K, which is 50 K lower than our lowest temperature of 773 K) the higher the value for the grain boundary capacitance. This work stated a C_{gb} of $1.71 \cdot 10^{-6}$ F at 723 K. Verkerk et al.⁵³ also studied the impact of grain size on the C_{gb} . A value of $\sim 3.0 \cdot 10^{-6}$ F at 673 K for an alkoxide sample $[(ZrO_2)_{1-x}(YO_{1.5})_x; x = 0.164]$ with a grain size of $\sim 13 \mu m$ and also $\sim 3.0 \cdot 10^{-6}$ F at 673 K for a Zircar sample $[(ZrO_2)_{1-x}(YO_{1.5})_x; x = 0.140]$ with a grain size of $\sim 11 \mu m$ was reported. It has also already been stated in literature⁵⁸ that for a Pt | YSZ | Pt cell, similar temperature regimes have been observed: a low temperature region up to 720 K, where the Pt electrode behaves as being

blocked and the capacitance assumes values between $10^{-12} - 10^{-10}$ F, and a high temperature region ($T > 720$ K; note that this is exactly the temperature region where our Nyquist plots were obtained) with capacitances up to 10^{-3} F, which fits very well with the values we obtained.

Using the same procedure as for the EIS data in Figure 6, an Arrhenius plot of the $\ln(\text{conductivity})$ vs. the reciprocal of the temperature could thus be created in the temperature region between 773 – 1073 K (Figure 10) and the “apparent” activation energies for the three contributions (gi, gb and e) calculated. The highest E_A is obtained for the grain interior process with 110.9 kJmol^{-1} , perfectly fitting to the activation energy for bulk anion conductivity in YSZ.⁴⁴ The second highest E_A is related to the electrode-interface system with 67.4 kJmol^{-1} , followed by the grain boundary contribution, providing the lowest E_A with 33.8 kJmol^{-1} .

Figure 10. Arrhenius plot of the grain interior, grain boundary and the electrode contribution of YSZ treated in dry CO at selected temperatures.

3.3. Carbon Dioxide

Linking surface reactivity and electrochemical impedance properties

The heating and cooling curves of the impedance in dry CO₂ as a function of temperature are illustrated in Figure 11A (blue and yellow dots). Between 297 and around 425 K the sample shows insulating properties with a high value for the impedance. Starting at temperatures above 700 K, semiconductive behavior in the decrease of the impedance is visible, leading to a final value of 1.2 MΩ. During the cooling routine a very similar trend as for the heating process can be observed, with the exception of the temperature range between 853 and 1050 K. Panel B of Figure 11 shows the FT-IR measurements of heating in CO₂ (starting at the front) which were conducted up to 1173 K. Subsequently, the temperature was held for 10 min (blue colored spectra) and then the system was re-cooled to room temperature (i.e. exact the same procedure as in the EIS experiment). The spectra were collected every 20 K and are marked red every 100 K, starting at 373 K. The green spectra represent the correlated temperatures where the EIS Arrhenius plots show significant changes.

Figure 11. Combined temperature-dependent EIS (panel A heating and cooling) and FT-IR (panel B) measurements on Y_2O_3 in dry CO_2 (flow $\sim 0.7 \text{ mLs}^{-1}$) and a subsequent O_2 treatment after CO_2

exposure (panel C). Linear heating and cooling rates of 10 Kmin^{-1} were applied between room temperature and 1173 K.

The waterfall plot reveals the development of the (bi-)carbonates formed by flowing CO_2 on Y_2O_3 when heated up to 1173 K. Striking is the fact that obviously in the whole temperature range distinct carbonate species are stable to very high amounts. Starting at room temperature with an ambient pressure of carbon dioxide, the main species are bicarbonates, represented by the signal at $1635 \text{ cm}^{-1} = \nu_{\text{as}}(\text{CO}_3)$, $1450 \text{ cm}^{-1} = \nu_{\text{s}}(\text{CO}_3)$ and $1223 \text{ cm}^{-1} = \delta(\text{OH})$.²⁵ HCO_3^- species are stable up to a temperature of 653 K. This perfectly corresponds to the starting point of the first linear region in the Arrhenius plot between 563 K to 844 K with an activation energy of 56.0 kJmol^{-1} . What can be monitored in detail by plotting the FT-IR spectra as a waterfall plot is the continuous change of the distribution of the different possible (bi-)carbonate species up to a temperature of 853 K. Although it is quite difficult to distinguish well-separated signals for the different kinds of (bi-)carbonates at ambient pressure conditions, where there is a broad distribution of those species and thus, an interfering overlap of the corresponding bands, a certain scenario of the temperature evolution of the (bi-)carbonates arises. With the continuous decrease of clear signals for bicarbonates from room temperature up to 693 K, there is an increase of bands for possible bidentate carbonates (1573 and 1340 cm^{-1}) that finally decompose at about 853 K. Note that this is the start of the second linear temperature region in the Arrhenius plot with an activation energy of 80.0 kJmol^{-1} . In the temperature range between 373 and 573 K there are two correlated signals at 1548 and 1380 cm^{-1} , which can be related to a potentially bridged carbonate species. At temperatures above 853 K, the remaining signals are found at wavenumbers of 1498 , 1450 , 1384 and 1352 cm^{-1} (polydentate carbonates and other strongly bound carbonate species). There is very little change in the distribution of those peaks upon further heating and even upon holding the temperature at 1173 K. However, the remaining carbonates do not decompose despite the very high temperatures – they actually are

getting more intensive the longer the sample is exposed to CO₂ even at the highest temperatures. Even though no great changes in the FT-IR can be observed in the high temperature region, there is a third linear range in the Arrhenius plot between 955 – 1176 K with an activation energy of 116.9 kJmol⁻¹. This could indicate that the formed carbonates must somehow contribute to this higher activation energy. During cooling, the fingerprint of those high-temperature carbonates is continuously getting overlaid by peaks for bridged and bidentate carbonates at temperatures below 1053 K, which also influences the course of the Arrhenius plot of the impedance measurement. In the temperature region between 1054 – 1176 K, an activation energy of 147.1 kJmol⁻¹ and between 753 and 1054 K an E_A of 98.5 kJmol⁻¹ can be determined. Below temperatures of 753 K, again bands for bicarbonate species arise, which can be monitored easily for example by the delta OH signal at 1223 cm⁻¹. Obviously, the distribution of the carbonates after the experiment is different in comparison to the starting conditions, because the contribution of more strongly bound species is significantly higher.

If a significant amount of carbonates is stable up to 1173 K the removal with oxygen is equally interesting. Focusing on the oxygen treatment after exposure of the sample to CO₂ (Figure 11A, pink and dark blue traces correspond to heating and cooling, the green trace represents the isothermal period at 1173 K) up to 935 K a very similar course of the impedance is evident. Starting at 935 K, a steeper decrease in the impedance occurs up to 1080 K with a plateau between 1080 and 1173 K, where the impedance hardly changes. During the isothermal period at 1173 K the impedance decreases further to a value of $2.0 \cdot 10^5 \Omega$. At the beginning of the cooling routine another plateau in the impedance arises between 1173 and 1010 K. Below 1010 K the impedance starts to increase very drastically, again leading to a final value in the GΩ region.

A closer look on the peculiar impedance vs. temperature behavior between 1080 and 1173 K upon re-oxidation after CO₂ treatment is also helpful. As it can be clearly seen, the heating-cooling routine in CO₂ follows almost the same trend. The same is true for the first part of the heating routine in O₂

up to ~ 900 K. At higher temperatures, the CO_2 and O_2 curves start to deviate until – as reported above – the impedance (and the conductivity) does not change. This behavior can most likely be interpreted in terms of formation of a molten state of a Y-carbonate related species at the surface of the Y_2O_3 grains. This is deduced from the fact that related FT-IR experiments show a large amount of strongly-bound carbonates after the CO_2 treatment and we note that the temperatures are well in the range of the melting points of corresponding alkaline and (rare) earth alkaline carbonates. The molten state is then probably entered upon re-oxidation in O_2 and a thin layer of an ionically conducting Y-carbonate species is formed. A bulk-related phenomenon or a thicker layer is excluded as the background in IR spectra hardly changes. The same is seen for the cooling traces: the electrochemical behavior of Y_2O_3 is superimposed on the Y_2O_3 grains with Y-carbonate “wetting”. Hence, the cooling traces of O_2 and CO_2 strongly differ.

The corresponding FT-IR experiment is shown in panel C of Figure 11 which highlights measurements of heating (starting in the back) up to 1173 K, holding this temperature for 60 min (blue colored spectra every 10 min) and re-cooling to room temperature (front, 10 K min^{-1}) of Y_2O_3 in flowing O_2 after exposure to flowing CO_2 up to 1173 K. The FT-IR spectra were collected every 20 K step and are marked red every 100 K, starting with 373 K. The green spectra represent the correlated temperatures where the EIS Arrhenius plot shows significant changes. Starting in the back of the waterfall plot in Figure 11 (i.e. (bi-)carbonate distribution after heating and cooling in CO_2) from room temperature, a signal for gas phase CO_2 is visible. Hence, even at room temperature some weakly-bound carbonates are released into the gas phase during the flowing O_2 treatment. With increasing temperature the absolute amount of carbonates is decreasing continuously and when holding the temperature at 1173 K, a slight decrease of the remaining surface species is visible. Nevertheless, even though using pure oxygen and holding the highest temperature for an hour, not all carbonates can be removed from the sample. The first species that is decomposed during heating is the bicarbonate, where the disappearance of the corresponding signals at 1610 cm^{-1} , 1425 cm^{-1} and

1223 cm^{-1} at 693 K fits with the first edge in the Arrhenius plot and a correlating activation energy of 105.4 kJmol^{-1} . A very interesting behavior occurs between 693 K and 953 K, where a peak at 1450 cm^{-1} is increasing although re-oxidation is taking place and the system is heated up continuously. Evidently, in this temperature region the conversion into p-carbonates is favorable in comparison to removal into the gas phase. Up to 1083 K, a distinct decrease for bands related to bidentate and bridged carbonate species arises. In this temperature range an E_A of 197.8 kJmol^{-1} is obtained, which is almost 100 kJmol^{-1} higher than in the low temperature region. From this temperature the same fingerprint is predominant as in pure CO_2 at the highest temperatures, i.e. signals at wavenumbers of 1498, 1450, 1384 and 1352 cm^{-1} for polydentate carbonates and other strongly bound carbonate species can be observed. During re-cooling the bands for (bi-)carbonates rise again to a certain extent, due to the fact that there is still CO_2 in the gas phase, because obviously it was not possible to remove all carbonates with the chosen re-oxidizing conditions. Therefore, the different calculated activation energies are due to different kinds of re-established carbonates or even a Y-carbonate layer being formed.

Table 3 shows the corresponding “apparent” activation energies for the different temperature regions. If the obtained E_A ’s for the Y_2O_3 sample are compared, a clear trend can be extracted: In the highest temperature regions the highest activation energies are found. Moreover, the values for the cooling processes are higher than for the heating routines. The same trend is visible for the ZrO_2 sample treated in flowing CO_2 . If this sample is re-oxidized in O_2 , a different trend is hence observed since the highest E_A ’s are not obtained at the highest temperature region, but somewhere in between. This is also true for the YSZ sample in flowing CO_2 as well as in O_2 , where obviously several different processes with diverging activation energies are taking place. At the highest temperatures, a lower E_A of around 85 kJmol^{-1} is deduced, followed by a region with an activation energy of > 130 kJmol^{-1} . In the medium temperature range ($\sim 645 - 813$ K) a comparatively low activation energy

(between 50 – 70 kJmol⁻¹) and at the lowest temperature region again a high E_A (between 90 – 110 kJmol⁻¹) can be calculated.

Table 3. “Apparent” activation energies of all three samples in dry CO₂ and in O₂ after CO₂ treatment

		CO ₂		O ₂ after CO ₂	
		T-range /K	E _A /kJmol ⁻¹	T-range /K	E _A /kJmol ⁻¹
Y₂O₃	heating	955 – 1176	116.9	950 – 1083	197.8
		844 – 955	80.0	687 – 950	105.4
		653 – 844	56.0		
	cooling	1054 – 1176	147.1	808 – 1016	131.3
		753 – 1054	98.5	723 – 808	102.9
				574 – 723	75.7
YSZ	heating	924 – 1173	88.9	1073 – 1173	86.9
		760 – 924	154.0	813 – 1073	155.8
		673 – 760	56.8	688 – 813	51.8
		471 – 673	92.0	451 – 688	91.8
	cooling	960 – 1173	80.4	1071 – 1173	85.6
		752 – 960	134.2	795 – 1071	145.7
		645 – 752	69.5	679 – 795	59.1
		465 – 645	107.1	476 – 674	103.6
ZrO₂	heating	1105 – 1173	113.6	1031 – 1071	101.6
		750 – 1105	91.7	801 – 1031	104.8
	cooling	1064 – 1174	131.3	1123 – 1173	109.8
		848 – 1064	116.1	1028 – 1123	89.0
				853 – 1028	119.0

If one compares the EIS curves for YSZ with the ones for Y₂O₃ (and ZrO₂, see Supporting Information Figure S7) it becomes clear that the impedance course looks very different. In Figure 12 for the YSZ sample semiconductive behavior is observed with a bump between 678 – 874 K, both during the heating and cooling treatment in dry CO₂. Also the final value for the impedance at the highest temperature is four magnitudes lower than for Y₂O₃, which is due to the fact that YSZ exhibits a high ionic conductivity. A very similar trend is visible for the oxygen treatment after CO₂. Also in the range of the impedance, where the material shows quasi-insulating properties, a clear difference between these two samples is visible: for Y₂O₃ treated in CO₂ this period is between 297

K and around 425 K, during re-oxidation between 297 – 677 K for the heating procedure and between 297 – 571 K for the cooling process. The ZrO₂ sample shows a very similar trend for the impedance as a function of temperature during the CO₂ treatment as Y₂O₃. After the insulating temperature range (296 – 788 K), semiconductive behavior is observed. Almost exactly the same impedance course, exhibiting the same plateau in the beginning, is seen during re-oxidation.

As for the FT-IR measurements, on YSZ the amount of (bi-)carbonates is remarkably lower than on Y₂O₃ due to the much lower quantity of hydroxyl groups. At a pressure of 1 bar flowing CO₂ the main species are bicarbonates (bicarbonate: $\nu_{\text{as}}(\text{CO}_3) = 1640 \text{ cm}^{-1}$, $\nu_{\text{s}}(\text{CO}_3) = 1390 \text{ cm}^{-1}$ and $\delta(\text{OH}) = 1224 \text{ cm}^{-1}$; bridged carbonate: $\nu_{\text{s}}(\text{CO}_3) = 1298 \text{ cm}^{-1}$; Figure 12B, black spectra).²⁵ Upon heating to 1173 K, the total amount of those surface species is easily removed continuously without conversion into more strongly bound carbonates like on Y₂O₃. Already above 873 K there is no noticeable amount of CO₂-related adsorbates left on the sample and there are no changes in the infrared spectra upon holding the temperature at 1173 K for 1 hour (the signal around 1355 cm^{-1} is not a carbonate species but a cell artefact that is visible in this graph due to the very low absorbance range), which very well fits with the EIS data (Figure 12A). Even though at $T > 873 \text{ K}$ there are no apparent changes in the FT-IR spectra, there are two temperature regions visible in the Arrhenius plot: the first one between 760 – 924 K with a comparatively high E_A of 154.0 kJmol^{-1} and the second one between 924 – 1173 K with an E_A of 88.9 kJmol^{-1} . In the temperature region $T < 873 \text{ K}$ where bicarbonates are present on the surface of the sample, again two temperature regions are apparent between 471 – 673 K (E_A of 92.0 kJmol^{-1}) and 673 – 760 K (E_A of 56.8 kJmol^{-1}). Upon cooling in flowing CO₂, signals for carbonates re-appear at 873 K and at room temperature the overall distribution of the re-generated carbonates is exactly the same as before heating (compare the grey and black spectra in Figure 12B). Just like for the heating routine, again four temperature regions with different activation energies could be identified, yielding almost exactly the same E_A 's as for the heating procedure. In both the infrared and the impedance experiment it is quite striking that this

experiment produces nearly perfectly reversible data when comparing heating and cooling behavior. Therefore, we can conclude that the course of the impedance is hardly influenced by CO₂ – although a certain amount of carbonates on the surface at lower temperatures can be detected in the infrared, those (bi-)carbonates can be easily removed during heating without conversion to other carbonate species that do have an impact to the electrochemical impedance course, as on Y₂O₃. Also the fact that the distribution of the carbonates after re-cooling the sample in flowing CO₂ is just exactly the same as before heating indicates that the surface has not changed upon treatment in CO₂. When re-oxidizing the sample in oxygen, the carbonates are removed immediately up to a temperature of 773 K (which is almost at the end of the second temperature region in the Arrhenius plot with an E_A of 51.8 kJmol⁻¹) and upon further heating, holding at 1173 K for one hour and re-cooling to room temperature no remarkable change in the infrared signal occurs (except for the cell-artefact around 1355 cm⁻¹). This spectroscopic information together with the comparison of the EIS course in O₂ and CO₂ emphasizes the fact that in this case surface chemistry is only of secondary importance when interpreting the course of the impedance. This is also emphasized in Table 3, where four different temperature regions during O₂ treatment after CO₂ with diverging activation energies are shown.

Figure 12. Temperature-dependent behavior of YSZ in flowing CO₂ (flow $\sim 0.8 \text{ mLs}^{-1}$) and subsequently in flowing O₂ (flow $\sim 0.5 \text{ mLs}^{-1}$). Each experiment includes heating up to 1173 K and cooling back to room temperature (heating/cooling rate 10 Kmin^{-1}); Panel A: EIS-measurements, Panel B: FT-IR spectra.

Although the respective data are only shown in the Supporting Information in Figure S6 and S7, it is necessary to state that in general the (surface) reactivity of the investigated pure ZrO₂ towards CO₂ is relatively low. This strongly depends on the pre-treatment of the used ZrO₂ sample - in this case calcination in air up to a temperature of 1173 K and pre-oxidation in pure oxygen at 1173 K. Literature gives many examples for zirconia samples that are prepared via different sol-gel procedures and calcined at much lower temperatures than in our case. Those resulting oxides have a much higher reactivity towards gaseous molecules like CO₂ or CO because they provide a certain amount of hydroxylation and defectivity.⁷⁰⁻⁷⁸ In the case of the high-temperature treated zirconia, there are almost no hydroxyl groups left and the dissociation of water at least into high-temperature stable surface OH-groups seems to be inhibited.²⁵ Also the BET surface of this monoclinic ZrO₂ is low at $2 \text{ m}^2\text{g}^{-1}$. As a result of this low surface reactivity, detecting any changes in the infrared and

impedance measurement when heating and cooling in CO₂ and CO, and especially when comparing to the other well-hydroxylated oxides Y₂O₃ and YSZ, is difficult and the resulting impact of those gases on the special ZrO₂ surface reactivity is extremely low.

4. Conclusions

The present contribution highlights the importance of a combined approach of different methods yielding complementary information on surface-dependent processes for technologically and catalytically relevant oxides. Only by combination of in situ electrochemical impedance spectroscopy (i.e. conductivity changes) and in situ FT-IR measurements (i.e. adsorption properties), the temperature-dependent influence of the presence or removal of distinct adsorbed or deposited species (e.g. carbon-containing adsorbates, formates or different carbonates) on the surface reactivity could be directly verified. The specific effects the adsorption of individual studied C1 molecules causes, vary, and also affect the re-oxidation and re-activation behavior of the individual oxides. While the carbon deposition following methane decomposition is a common feature on all three studied oxides and yields a dynamically grown conducting carbon layer at the highest temperatures, the individual properties of the oxides are best seen in a comparative discussion of CO and CO₂ adsorption and treatment.

One of the most crucial aspects is related to the changes of the surface chemistry during treatment in CH₄ between 600 and 1000 K before the actual methane decomposition leads to a percolated carbon layer. Depending on the temperature, a complex redox interplay of methane total oxidation, formate and carbonate formation leads to correlated surface and grain conductivity changes, which could be directly followed by EIS. For CO the time- and temperature dependence of the adsorbate- and carburization-induced conductivity processes are best disentangled on YSZ. An equivalent circuit model in dry CO allows to separate the different contributions of grain interiors, grain boundaries and electrode contributions. Temperature regions with different charge carrier activation energies

perfectly correlate with distinct changes in surface chemistry. As a major outcome, the conductivity properties of polycrystalline YSZ with grain boundaries in realistic catalytic gas mixtures can thus not be assigned solely to exclusive bulk ion conduction. The different degree of hydroxylation and the different ability to chemisorb CO and CO₂ hence steers the influence of the surface chemistry on the electrochemical properties. In contrast to the studied ZrO₂ material, the impact of the studied C1-gases on YSZ and Y₂O₃ is rather substantial and also affects the re-oxidation/re-activation behavior of the surfaces.

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TOC Graphic

Supporting Information

Reactivity of YSZ, Y_2O_3 and ZrO_2 towards CO, CO_2 and CH_4 :

A Comparative Discussion

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Table 1. EDXRFA Analysis of the ZrO₂ Sample with 99.99 % Purity (Commercially Available, Monoclinic, Aldrich, 99.99%)

Al	<	0.002 %
Si	<	0.001 %
P	<	0.001 %
S	<	0.010 %
Cl	<	0.010 %
K	<	0.005 %
Ca	<	0.001 %
Ti	<	0.001 %
V	<	0.001 %
Cr	<	0.001 %
Mn	<	0.001 %
Fe	<	0.001 %
Co	<	0.001 %
Ni	<	0.001 %
Cu	<	0.001 %
Y	<	0.001 %
Hf	<	0.001 %

Figure S1: Schematics of the in-situ Impedance Cell (A) as well as the impedance setup (B).

Interaction of Y_2O_3 and ZrO_2 with CO: Combined EIS and FT-IR experiments

Figure S2: Combined temperature dependent EIS (heating and cooling) and FT-IR (heating) measurements on Y_2O_3 (panel A and B) and ZrO_2 (panel C and D) in dry CO (flow $\sim 0.7 \text{ mLs}^{-1}$). Linear heating and cooling rates of 10 Kmin^{-1} between room temperature and 1073 K were applied. The FT-IR spectra were collected every 50 K step.

The heating and cooling traces of Y_2O_3 during exposure to dry CO show a very similar behavior. Between RT – 650 K a plateau is visible where the impedance hardly changes at all and starting at temperature $> 650 \text{ K}$ semiconductive behavior is apparent. An impedance value of $7.6 \cdot 10^5 \Omega$ at 1073 K is obtained.

A very similar behavior upon exposure of ZrO_2 to dry CO is apparent as for Y_2O_3 with a plateau between RT – $\sim 650 \text{ K}$ and semiconductive behavior at $T > 650 \text{ K}$. An impedance value of $2.2 \cdot 10^6 \Omega$ at the highest temperature is preserved, which is one magnitude higher than the value for Y_2O_3 .

Raman Spectroscopy Experiments

Confocal Raman spectra of the polycrystalline samples in the range of $50\text{-}3800 \text{ cm}^{-1}$ were recorded with a Horiba Jobin Yvon Labram-HR 800 Raman micro spectrometer. The samples were excited using the 532 nm (2.33 eV) emission line of a frequency-doubled 25 mW Nd:YAG laser under an Olympus 100 $\times$ objective lens with a numerical aperture of 0.9. The size of the laser spot on the surface was approximately 1 μm in diameter. The scattered light was dispersed by an optical grating with 1800 lines mm^{-1} and collected by a 1024×256 open-electrode CCD detector. The spectral resolution, determined by measuring the Rayleigh line, was better than 2 cm^{-1} . The spectra were recorded in unpolarized mode at ambient conditions. The accuracy of the Raman line shifts, calibrated by measuring a silicon standard, was in the order of 0.5 cm^{-1} . First – and second-order polynomial and convoluted Gaussian-Lorentzian

functions were fitted to a background and Raman bands using the built-in spectrometer software LabSpec.¹

Raman mapping of the sample surface on a representative large sample area has also been performed. For mapping the D and G-band intensity, 48 Raman spectra were recorded on a 8x12 μm area in 1x2 large grid. Mapping of the radial breathing mode region (100-300 cm^{-1}) has been performed by sampling 24 spectra over a 8x12 μm area using a 2x2 large grid.

To gather additional information about the nature of the carbon species, detailed Raman spectroscopic measurements have been conducted. On the one hand, Raman spectroscopy is one of the most efficient methods to discriminate the chemical nature of different carbon species², on the other hand, a rather qualitative discussion of the mere presence of those different species on Y_2O_3 , YSZ and ZrO_2 has been provided recently.³ Subsequently, we want to provide further details on the structure, chemical and spatial homogeneity of the carbon layer, in close correlation to the FT-IR and EIS experiments.

Figure S3 shows a representative Raman mapping experiment using the D- and G-band intensity ratio of a carbon layer on YSZ, obtained by decomposing methane at 1073 K. Ratio and internal structure of these two bands yield information on the structure and homogeneity of the carbon layer². Within the 12x8 μm -sized area, the D/G-band intensity ratio varies drastically, directly indicating a rather inhomogeneous carbon distribution. Three distinct areas can be easily distinguished: area 1 (blue) with a very high D/G band ratio, area 2 (red) with the lowest D/G-band ratio and finally area 3 (green) with an intermediate D/G-band ratio.

Figure S3. Raman mapping of the YSZ pellet sample surface on a 12x8 μm large area, showing the intensity ratio of the *D*- and *G*-band. 48 Raman spectra at a distance of 1 μm in *x*-direction and 2 μm in *y*-direction were collected.

In order to get a better overview, three different Raman spectra of the mapping are outlined in Figure S3. The first Raman spectrum represents the blue area of the Raman map. In this area highly disordered graphitic carbon is most abundant, as deduced from the high *D/G* intensity ratio. As follows from Figure S4-A, the so-called *D*-band at 1341 cm^{-1} exhibits an intensity twice as high as compared to the *G*-band at about 1605 cm^{-1} . The *D*-band shows a dispersive behavior with the frequency depending on the laser energy. In addition, the *D'*-peak is visible at 1626 cm^{-1} . The second selected Raman spectrum (Figure S4-B) represents the red area of the map showing a low *D/G* intensity ratio. In comparison to Figure S4-A the intensities of the *D*- (1337 cm^{-1}) and *G*-mode (1592 cm^{-1}) are reversed and a splitting of the *G*-mode (first-order Raman mode) can be observed. Additional Raman modes can be seen at 1528 cm^{-1} , 1572 cm^{-1} and a broad band ranging from $1700\text{--}1800\text{ cm}^{-1}$. These modifications indicate the presence of carbon nanotubes. The broad Raman band can be assigned to overtones (so-called M^- and M^+) of the out-of-plane transversal optical mode (oTO, $q = 2k$ and $q = 0$) around 867 cm^{-1} (only IR-active) of the carbon nanotube. The *G*-peak shows two different components: the lower frequency component, which is associated with the

confinement of the vibrational wave in the circumferential direction (G^-), and the higher frequency component (G^+), in correlation with vibrations along the direction of the nanotube axis¹⁵. The third Raman spectrum (Figure S4-C) displays the green area of the Raman map, where the intensities of the D - and G -peak are similar. In this spectrum the D -band is visible at 1337 cm^{-1} , the G -band at 1592 cm^{-1} and the D' -peak at about 1615 cm^{-1} . In contrast to the Raman spectrum in Figure S4-B, no broad band in the wavenumber range between $1700\text{--}1800\text{ cm}^{-1}$ (M-features) occurs and also the splitting of the G -band is not really detectable, indicating the presence of disordered carbon. In brief summary this means, that the surface of the sample is covered partially by carbon nanotubes and by nanocrystalline graphite with variable degree of disorder.

Figure S4. Raman spectrum of highly disordered graphitic carbon in the wavenumber range 1000-1800 cm^{-1} (A, area 1), of a carbon nanotube in the wavenumber range 1000-1900 cm^{-1} (B, area 2) and of disordered graphite (less than shown in 7A) in the wavenumber range 1000-1800 cm^{-1} (C, area 3).

The appearance of the so-called radial breathing mode (RBM) at low frequencies is a characteristic feature in Raman spectra of carbon nanotubes. The radial breathing mode is an out-of-plane phonon mode and corresponds to the coherent vibration of carbon atoms in the radial direction, which generates an effect similar to “breathing”.² The typical RBM range is from 100 to 350 cm^{-1} , which is obvious in Figure S5-A and Figure S5-B. Raman mapping of the sample surface on a 8x12 μm large area has been performed. 24 Raman spectra, in the wavenumber range between 100 and 350 cm^{-1} , at a distance of 2 μm in both x- and y-direction were excited. Figure S5-A shows a comparison of selected spectra of the Raman mapping. All spectra feature breathing modes (RBM) at 175 cm^{-1} , 182 cm^{-1} , 187 cm^{-1} and 190 cm^{-1} , indicating the excitation of a bundle of carbon nanotubes with different nanotube diameters (d_t). RBM frequencies between 120 and 350 cm^{-1} correspond to diameters in the range 0.7 nm $< d_t < 2$ nm. This means, the majority of the carbon nanotubes formed at the YSZ sample exhibit a nanotube diameter around 1 nm.

Figure S5. Selected Raman spectra of the RBM of a bundle of carbon nanotubes in the wavenumber range 100-300 cm^{-1} (A). Full 2-D representation of the 24 Raman spectra showing the distribution and presence of the RBM's of a bundle of carbon nanotubes in the wavenumber range 100-300 cm^{-1} (B).

Interaction of ZrO_2 with CO_2 : FT-IR experiments

Figure S6. Waterfall plot of FT-IR spectra of ZrO₂ in flowing CO₂ up to 1173 K; flow ~ 0,8 mLs⁻¹, heating and cooling rates: 10 Kmin⁻¹. The cell artefact was eliminated with an x-axis interruption at 1300 – 1410 cm⁻¹ to enhance the visibility of the small remaining peaks.

In general, the interaction between ZrO₂ and CO₂ in the temperature region between RT – 1173 K is suppressed due to low amount of hydroxylation. Bi- and higher coordinated carbonates (labelled red and blue) are observed upon heating, as well as a gradual transformation of the former into the latter at higher temperatures.

Figure S7. Electrochemical impedance spectra of ZrO_2 in flowing CO_2 (flow $\sim 0,8 \text{ mLs}^{-1}$) and subsequently in flowing O_2 (flow $\sim 0.5 \text{ mLs}^{-1}$) up to 1173 K; heating and cooling rates: 10 Kmin^{-1} .

The ZrO_2 sample shows a very similar trend for the impedance as a function of temperature during the CO_2 treatment as Y_2O_3 . After the insulating temperature range (296 – $\sim 788 \text{ K}$), semiconductive behavior is observed. Almost exactly the same impedance course exhibiting the same plateau in the beginning is seen during re-oxidation.

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