## **Supporting Information**

# Structural and Chemical Degradation Mechanisms of pure YSZ and Its Components ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> in Carbon-Rich Fuel Gases

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#### *Carbon Deposition in CH*<sub>4</sub>

EIS investigations on YSZ (red and dark blue trace),  $ZrO_2$  (pink and light green trace) and  $Y_2O_3$  (yellow and light blue trace) in CH<sub>4</sub> (Figure 1A) show metallic conductivity of all samples above 1173 K due to formation of a fully percolated graphitic carbon layer (start of carbon deposition: ~ 1023 K). During heating, in the temperature region <1000 K only the intrinsic semiconductive behavior of the individual materials is observed. For YSZ a much more pronounced decrease in the impedance is measured prior to carbon deposition, as thermal excitability of anionic charge carriers (predominantly O<sup>2-</sup>) is drastically increased relative to undoped  $Y_2O_3$  and  $ZrO_2$ . Metallic conductivity is still preserved after re-cooling to 300 K with a corresponding impedance value of ~ 10  $\Omega$ , implying that the C-layer is still present on the surface of all three oxides. Consequently, all subsequent gas treatments discussed below start at an impedance value of metallic conductivity and upon carbon removal/detachment in general, the impedance increases drastically.

All three oxides were also investigated with FT-IR but in this work only spectra of YSZ are shown. YSZ was highlighted as it is the oxide that is actually used as an SOFC component and it is the most illustrative in terms of spectral display due to the formation of a distinct fingerprint of the carbon layer (features < 2000 cm<sup>-1</sup>) in both gases, CO and CH<sub>4</sub> (Figures 1E and 2E vacuum spectra at RT, thick black lines). For detailed discussion of this feature see also reference <sup>1</sup>. Basically, this reflects not discrete adsorption bands but rather an enhanced selective depression of transmission in this spectral region in the presence of a carbon layer. In the case of  $Y_2O_3$ , carbon deposited carbon is too low to affect the spectra characteristically. What can be directly extracted from Figure 1E is that in parallel with a strong decrease of the impedance this characteristic fingerprint increases between 1073 K and 1123 K. When the impedance reaches metallic conductivity, no further changes are observed, indicating no further growth of the C-layer. All further FT-IR investigations subsequently to the deposition

therefore start with this distinct fingerprint (< 2000 cm<sup>-1</sup>) and effective carbon removal is accompanied by the decrease of this feature.

#### Carbon Deposition in CO

Carbon deposition of highly distorted carbon takes place above ~1100 K on all three oxides via the inverse Boudouard reaction (2CO  $\rightarrow$  C + CO<sub>2</sub>). In EIS measurements (Figure 2A) this reaction manifests itself only on Y<sub>2</sub>O<sub>3</sub> by a conducting C-layer with an impedance value of  $\sim$ 13  $\Omega$  at 1273 K (yellow and light blue traces, persisting upon re-cooling to RT). In case of YSZ and ZrO<sub>2</sub>, a metallic impedance value as for the Y<sub>2</sub>O<sub>3</sub> sample could not be obtained. On the contrary, there is a 2 magnitudes larger impedance observed on YSZ and even 4 magnitudes larger value on ZrO<sub>2</sub>. This does not mean that there is also orders of magnitude less carbon deposited, since quantitative determination of the total carbon amount per sample mass (compare Figure 9) demonstrates that in some cases even a higher total amount of carbon does not necessarily lead to a conducting layer or a drop in the impedance spectra. In fact, on  $Y_2O_3$  by far the most carbon is deposited – twice as much as in  $CH_4$  – which in both cases leads to metallic conductivity. For YSZ and ZrO2, where no metallic resistance is observed in CO, the general amount of carbon is roughly comparable to the one resulting from CH<sub>4</sub>. This is caused by the different deposition mechanisms. On the one hand, Cdeposition is mediated by thermally induced methyl gas phase radicals in CH<sub>4</sub>, resulting in a successful "isotropic" C-deposition. In CO, on the other hand, an active catalytic involvement of the surface is necessary (inverse Boudouard reaction), i.e. the surface is locally reduced and graphite nucleation and growth is rather locally triggered, e.g. by structural surface defects. Although for YSZ the same impedance value is obtained after re-cooling as for the starting conditions, the impedance courses for the heating and cooling procedure differ in some temperature areas (especially in the T-range between 650 – 1000 K). These differences arise from the different processes that are taking place on the surface of the sample, since upon

cooling there is an active surface (carbonates and formates, see FT-IR discussion below) and upon heating the surface is largely blocked by a carbon layer.

When taking a closer look at the FT-IR spectra in Figure 2E, the reduction of the surface by reaction of lattice oxygen with CO is proven by the occurrence of a CO<sub>2</sub> gas phase signal  $(2400 \text{ cm}^{-1} - 2240 \text{ cm}^{-1})$  at temperatures above 573 K, which further increases during C-deposition (same fingerprint as in CH<sub>4</sub>) between 1053 K and 1173 K. This confirms that the inverse Boudouard reaction initially occurs on a pre-reduced, i.e. vacancy-doped, oxide surface. In the lower temperature region, distinct signals for p-carbonates and formates are observed, which appear to precede surface reduction and the subsequent carbon deposition. Nevertheless, they are characteristic for the general activity of the surface (chemisorption of CO) and this surface reactivity influences the course of the impedance, as was characterized in detail elsewhere.<sup>2</sup>



**Figure S1.** FT-IR spectra of YSZ in flowing O<sub>2</sub> after carbon deposition in CH<sub>4</sub>. Displayed temperature region: 593 K – 733 K; gas flow  $\leq 1$  m Ls<sup>-1</sup>, heating rate = 10 K min<sup>-1</sup>.



**Figure S2.** Static measurement of carbon-pre-covered YSZ (after carbon deposition in flowing  $CH_4$  up to 1273 K) in 50 mbar  $CO_2$ ; heating/cooling rates = 10 K min<sup>-1</sup>, isothermal period at 1273 K for 1 h; FT-IR spectra are shown every 20 K (time-steps: 2 minutes), starting in the background of the waterfall plot.



**Figure S3.** FT-IR spectra of YSZ in flowing CO<sub>2</sub> after carbon deposition in CH<sub>4</sub>. Displayed temperature region: 1273 K – RT upon cooling; gas flow  $\leq 1$  m Ls<sup>-1</sup>, cooling rate = 10 K min<sup>-1</sup>.



Figure S4. Resulting FT-IR spectra at RT of YSZ after removing deposited carbon with flowing CO<sub>2</sub> after carbon deposition in CH<sub>4</sub> and CO. gas flow  $\leq 1$  m Ls<sup>-1</sup>, heating/cooling rate = 10 K min<sup>-1</sup>.

Table S1: Overview of the removal/detachment temperatures of carbon deposited from  $CH_4$  and CO in  $O_2$ ,  $CO_2$  and  $H_2O$ .

| oxide                         | depositing<br>gas | removing<br>gas  | temperature<br>of significant<br>CO <sub>2</sub> FT-IR<br>signal | temperature<br>of maximum<br>removal | start<br>temperature<br>of EIS<br>change | max<br>temperature<br>of EIS change<br>during heating |
|-------------------------------|-------------------|------------------|--|--------------------------------------|--|---|
| Y <sub>2</sub> O <sub>3</sub> | СО                | O <sub>2</sub>   | 653 K  | 753 K                                | 627 K                                    | 710 K   |
|                               |                   | CO <sub>2</sub>  | -  | 1273 K                               | 720 K                                    | 1065 K  |
|                               |                   | H <sub>2</sub> O | 1173 K   | 1273 K                               | 1050 K                                   | 1144 K  |
|                               | $CH_4$            | O <sub>2</sub>   | 673 K  | 723 K                                | 565 K                                    | 716 K   |
|                               |                   | CO <sub>2</sub>  | -  | 1273 K<br>2min                       | 1220 K                                   | isoth. per.   |
|                               |                   | $H_2O$           | 1173 K   | 1273 K                               | 980 K                                    | 1171 K  |
| YSZ                           | СО                | O <sub>2</sub>   | 533 K  | 693 K                                | -  | -   |
|                               |                   | CO <sub>2</sub>  | -  | 1253 K                               | -  | -   |
|                               |                   | H <sub>2</sub> O | 1113 K   | 1273 K<br>2 min                      | -  | -   |
|                               | $\mathrm{CH}_4$   | O <sub>2</sub>   | 593 K  | 643 K                                | 565 K                                    | 610 K   |
|                               |                   | CO <sub>2</sub>  | -  | 1273 K<br>2 min                      | isoth. per.                              | isoth. per.   |
|                               |                   | H <sub>2</sub> O | 1193 K   | 1273 K<br>2 min                      | isoth. per.                              | isoth. per.   |
| ZrO <sub>2</sub>              | СО                | O <sub>2</sub>   | 613 K  | 713 K                                | -  | -   |
|                               |                   | CO <sub>2</sub>  | -  | -                                    | -  | -   |
|                               |                   | H <sub>2</sub> O | 773 K  | 1273 K                               | -  | -   |
|                               | CH4               | O <sub>2</sub>   | 673 K  | 753 K                                | 520 K                                    | 700 K   |
|                               |                   | CO <sub>2</sub>  | -  | -                                    | isoth. per.                              | isoth. per.   |
|                               |                   | H <sub>2</sub> O | 1273 K   | 1273 K<br>6 min                      | 610 K                                    | 740 K   |



Figure S5. FT-IR spectra of YSZ in flowing CO<sub>2</sub>:CO (1:1); (A) heating spectra every 100 K step between RT and 1273 K, (B) cooling spectra every 100 K step between 1273 K and RT; gas flow  $\sim 1 \text{ m Ls}^{-1}$ , heating/cooling rate = 10 K min<sup>-1</sup>.





**Figure S6.** *Operando* FT-IR spectra of YSZ in flowing (A)  $CO:H_2$  (1:1), (B) moist  $CO:H_2$  (1:1), (C) moist CO; gas flow ~ 1 mL s<sup>-1</sup>, heating and cooling rates = 10 K min<sup>-1</sup>.

Comparing the progress of the IR-active species observed in the experiments on YSZ in the gas mixtures discussed in the context of Figure S6 (dry syngas S6A, moist syngas S6B and

moist CO S6C), the smallest amount of carbon dioxide (gas phase infrared signal labeled in dark blue) is formed during exposure to dry syngas over the entire temperature range. Upon heating, the evolution of the surface species observed in dry syngas is well comparable to the one in dry CO (Figure 2E, compare also <sup>1, 2</sup>): increasing formation of polydentate carbonates (labelled in light blue in Figure S6A) up to ~593 K, followed by a very drastic decomposition of the carbonates upon further heating. Formates (labeled in red) are observed between 393 K and 993 K with maximum signals at 673 K. As already mentioned, the amount of formed CO<sub>2</sub> is generally low. However, a gas phase signal for CO<sub>2</sub> (labelled in dark blue) can be seen at temperatures above 553 K. The only remarkable change of the gaseous CO<sub>2</sub> during heating is a slight increase between 773 K and 1053 K with a maximum at 913 K, which can be explained by decomposition of formates and carbonates. This is not observed upon cooling, where the formate signals re-appear below 893 K and the p-CO<sub>3</sub><sup>2-</sup> adsorbates above 653 K. No CO<sub>2</sub> formation is observed below 533 K during cooling.

For moist syngas and moist CO, under flowing conditions the water gas shift reaction (CO +  $H_2O \rightarrow CO_2 + H_2$ ) can be expected, which is also expressed by the pronounced CO<sub>2</sub> signal in Figure S6B and S6C. In detail, in both cases there is a strong increase of gaseous CO<sub>2</sub> above 773 K upon heating, which steadily increases up to 1273 K and stays constant during holding at 1273 K. When cooling back to room temperature, in both measurements this signal decreases reversibly between 1273 K and 773 K. The total amount of CO<sub>2</sub> (related to the signals of gaseous H<sub>2</sub>O and the formates) is higher in moist CO than in moist syngas since the H<sub>2</sub> content shifts the water gas shift equilibrium. Like for the dry syngas experiment there are formates observed (labelled in red in Figure S6B and S6C), but eventually, carbonate signals are superimposed by the signals of gaseous H<sub>2</sub>O. Definite signals for formates are visible between 573 K and 973 K upon heating and below 973 K upon cooling.

### References

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