This is the peer-reviewed version of the following article:

[CO₂ Reduction on the Pre-reduced Mixed Ionic-Electronic Conducting Perovskites La_{0.6}Sr_{0.4}FeO_{3-δ} and SrTi_{0.7}Fe_{0.3}O_{3-δ}, Matthias Grünbacher, Thomas Götsch, Alexander K. Opitz, Bernhard Klötzer, and Simon Penner, ChemPhysChem 19(1) (2018) 93-107],

which has been published in final form at [https://doi.org/10.1002/cphc.201700970]. This article may be used for non-commercial purposes in accordance with Wiley-VCH Terms and Conditions for Self-Archiving.

<https://authorservices.wiley.com/author-resources/Journal-Authors/licensing-open-access/licensing/self-archiving.html>

CO₂ reduction on the pre-reduced mixed ionic-electronic conducting perovskites La_{0.6}Sr_{0.6}FeO_{3-δ} and SrTi_{0.7}Fe_{0.3}O_{3-δ}

Matthias Grünbacher,^[a] Thomas Götsch,^[a] Alexander K. Opitz,^[b] Bernhard Klötzer,^[a] and Simon Penner^{*[a]}

[a] M.G., T. G., B. K., S. P.
University of Innsbruck
Institute of Physical Chemistry
Innrain 52c, A-6020 Innsbruck
simon.penner@uibk.ac.at

[b] A. K. O.
TU Wien
Institute of Chemical Technologies and Analytics
Getreidemarkt 9/164-EC, A-1060 Vienna

Abstract: The activity of the pre-reduced perovskites $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF64) and $\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (STF73) for the CO_2 reduction to CO was investigated with special focus on the reactivity of oxide-dissolved hydrogen. This is of particular interest in hydrogen solid-oxide electrolysis cell (H-SOEC) technology, where proton-conducting ceramics are used and the reaction $2\text{e}^- + 2\text{H}^+ + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ is of central importance. To clarify if hydrogen dissolved in LSF64 and STF73 partakes in the CO_2 reduction, temperature-programmed reduction (TPR) in H_2 , followed by temperature-programmed reoxidation (TPO) in CO_2 and, moreover, temperature-programmed desorption (TPD) of ad- and absorbed species were utilized. The experiments reveal that 50 mol% of the CO_2 is converted by hydrogen dissolved in STF73 and reacts quantitatively. On the other hand, LSF64 converts less than 20 mol% of CO_2 *via* dissolved hydrogen and a residual of bulk OH is still detectable after CO_2 -TPO.

Table of contents entry

The reactivity of oxide-dissolved hydrogen in the CO₂ reduction to CO has been investigated using pre-reduced perovskite materials La_{0.6}Sr_{0.4}FeO_{3-δ} (LSF64) and SrTi_{0.7}Fe_{0.3}O_{3-δ} (STF73). This is of particular interest in hydrogen solid-oxide electrolysis cell technology, where proton-conducting ceramics and the reaction $2\text{e}^- + 2\text{H}^+ + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ are of paramount importance. Quantitative CO₂ conversion by hydrogen dissolved in STF73 is observed, whereas LSF64 converts only 20 mol% of CO₂ *via* dissolved hydrogen and bulk OH is still detectable after CO₂ conversion.

Introduction

As environmental concerns have been growing over the last years, renewable and low carbon energy sources, as well as highly efficient ways of power generation are getting more and more into the focus of research and development. Especially, solid oxide cells (SOC) have gained great attention over the past years. SOC can also be referred to as ceramic high temperature fuel cells, as they consist mainly of ceramic materials operating at temperatures of ~ 750 °C.^[1,2] One reason for the high temperatures is that SOC use solid oxide electrolytes – such as yttria stabilized zirconia (YSZ) –, which conduct oxide ions only at elevated temperatures.^[3,4] These devices are mostly constructed in a planar or tubular fashion^[3,5,6] and can be operated in two modes: Solid oxide fuel cells (SOFC) are devices that generate electricity by oxidizing fuel and utilizing O_2 from the air. Solid oxide electrolysis cells (SOEC) reverse the process by consuming electricity and heat.

In the case of SOFCs, the Carnot limitation of heat powered engines is obsolete, which is due to the fact that electrochemical cells directly transfer reaction's Gibbs free energy of the reaction into electric energy.^[1] Because of the resulting high efficiency – and therefore low CO_2 formation – as well as the low emission of toxic gases such as CO, NO_x , SO_x and particulate matter, SOFC technology provides one of the cleanest ways to generate electric energy.^[7] SOFCs can combust a wide range of fuels from hydrogen to hydrocarbons such as natural gas, diesel, alcohols and others.^[8] Therefore, SOFCs can work in a fossil-fuel based, as well as in a fully renewable and/or hydrogen based infrastructure, which might grow ever more important in the future.^[8]

SOECs can be used to produce H_2 by electrolyzing H_2O ^[5,9,10] or to produce syngas (CO/H_2) from moist CO_2 ^[11,12]. Especially for the electrochemical splitting of carbon dioxide the high operating temperatures of SOECs are highly beneficial allowing increased kinetics of CO_2 reduction.^[13,14] If SOECs can be powered by renewable energy supplies, this technology can potentially become very interesting for closing the renewable fuel cycle.^[11] Liquid hydrocarbons might be synthesized by processing the syngas derived from high temperature electrolysis by Fischer-Tropsch synthesis (gas to liquid process).^[15] As the infrastructure for H_2 production, storage, transmission and distribution is currently not sufficiently developed, synthetic fuels from renewable resources are the most attractive alternative in the medium term.^[16] Furthermore, operated at low temperatures and high pressures, electrolysis of CO_2/H_2O to syngas and methane synthesis can potentially be combined.^[10,16,17]

However, current Ni/YSZ-cermet based SOEC electrodes suffer from increased degradation rates compared to SOFC operation and microstructural changes of their electrodes under very high current densities.^[18-20] A potential approach to meet the above-mentioned requirements is to look for alternative materials that can be used in SOC technology.^[21,22] Perovskite-type oxides with mixed ionic and electronic conductivity, for example, have already been tested successfully to substitute Ni/YSZ in SOFCs.^[23] Perovskites are oxides with the general formula ABO_3 . A and B are metal cations with A having the larger ionic radius. In the perovskite structure, A is 12-fold coordinated by oxygen anions, while B is 6-fold coordinated. There is a wide variety of compositions that also include doping of A or/and B with other cations, which leads to versatile properties and applications.^[24] In addition, doped perovskites exhibit rich redox properties, which is reflected in their vital defect chemistry.^[24] Some perovskites undergo temperature-induced oxygen loss, which is a reversible process and can be used to split H_2O ^[25] or CO_2 ^[26] in terms of a redox cycling process, which is interesting for solar-thermochemical fuel production^[27]. The suitability of mixed conducting perovskite-type SOEC cathodes has already been explored in various studies,^[28-34] including $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF64) and $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ (STF73) for both water^[35] and CO_2 electrolysis^[36] using *operando* near-ambient pressure XPS. LSF64 and STF73 are

particular interesting for SOC research as they are mixed ionic-electronic conductors, have a well-known defect chemistry and relatively high thermodynamic stability even under reducing conditions.^[37-41]

In addition, our investigations were motivated by the relatively new idea of SOECs employing proton-conducting materials (H-SOEC).^[42,43] H-SOECs provide several advantages: First of all, H-SOECs are expected to operate at temperatures of 600 °C or lower^[42], which allows for the formation of higher CH₄ equilibrium concentrations as shown by Xie *et al.*^[17] Moreover, H-SOECs facilitate the production of syngas with a fine-tuned composition.^[42] In this context, LSF64 and STF73 can be very interesting materials for electrolyzers on basis of proton conducting ceramics, as they are capable of dissolving hydrogen^[44] and – as the present work clearly shows – this dissolved hydrogen is available for reducing CO₂ to CO.

The aim of the present work was to characterize the catalytic activity of the perovskite-type materials La_{0.6}Sr_{0.4}FeO_{3-δ} (LSF64) and SrTi_{0.7}Fe_{0.3}O_{3-δ} (STF73) for CO₂ reduction. To account for the reactivity of dissolved hydrogen, the oxides were pre-reduced by heating in reducing gas atmosphere followed by temperature-programmed oxidation experiments in CO₂ atmosphere. To distinguish contributions of dissolved hydrogen from oxygen vacancies as the reactive point defects in the materials, pre-reduction was performed in H₂ as well as in CO.

Results and Discussion

The goal of the following experiments was to clarify, whether pre-reduced LSF64 and STF73 are capable of converting CO₂ into CO and if the degree of reduction influences this capability. Moreover, the role of dissolved hydrogen in the CO₂ reduction was examined. For this purpose, LSF64 and STF73 powders were pre-reduced with flowing/dry H₂ at different maximum temperatures. The reduction of the perovskite *via* H₂ can either lead to the formation of oxygen vacancies V_O^{••} while water is released, or to the formation of bulk hydroxyls (OH)_O[•].^[45,46] The corresponding reactions are written in Kröger-Vink notation in equations (1) and (2), respectively:

Subsequently, the pre-reduced sample was tested by CO₂-TPO to detect whether CO₂ is consumed from the gas phase and CO accumulates in the reactor volume. The re-oxidation of the pre-reduced perovskites *via* CO₂ can occur by quenching of vacancies (equation (3)) or by reaction with protonic defects (equation (4)):

Additionally, the exsolution of metallic Fe, which was already observed on LSF64 under severe reducing conditions^[47], could play a role for CO₂ reduction.

CO₂ reduction *via* H₂ pre-reduced LSF64/STF73

The results of the CO₂-TPO experiments are depicted in Figure 1 (LSF64) and 2 (STF73). Panel A in Figures 1 and 2 shows the respective CO₂ conversion, while Panel B in Figs. 1 and 2 highlights the pressure drop-compensated (*via* addition of inert Ar) quadrupole mass spectrometry (QMS) signals reflecting the conversion of CO₂ and CO, where for the sake of clarity only one exemplary CO₂-TPO experiment is shown. Figure 1B represents the CO₂-TPO of LSF64 after H₂ treatment at 440 °C. Figure 2B shows the CO₂-TPO experiment collected from STF73 after H₂ treatment at 520 °C. The CO₂ conversion was normalized to the sample surface (left axis) and to the mol of oxide in the reactor (right axis).

Figure 1. CO₂-TPO of LSF64 after pre-treating the sample in flowing, dry H₂ at different maximum temperatures of 340 °C, 440 °C and 520 °C (as indicated by insets). The samples were allowed to cool down to RT in flowing H₂. For CO₂-TPO the sample was heated from room temperature to 800 °C at a rate of 10 °C min⁻¹. 800 °C was held for 10 min followed by a cooling ramp (10 °C min⁻¹). A dried gas mixture containing ca. 75 mol% CO₂ and ca. 25 mol% Ar was used for TPO. Initial pressure: ca. 200 mbar. End pressure: ca. 100 mbar. Panel A shows the surface-normalized molar CO₂ conversion (left axis) and the molar CO₂ conversion normalized to the mol of oxide used in the experiment (right axis). The details for CO₂ quantification are laid out in the Experimental Section. Panel B shows the Ar normalized CO₂/CO signals of the CO₂-TPO acquired after reducing the sample at 440 °C.

Figure 2. CO₂-TPO of STF73 after treating the sample in flowing and dry H₂ at different maximum temperatures of 340 °C, 440 °C and 520 °C (as indicated by insets). The samples were allowed to cool down to RT in flowing H₂. For CO₂-TPO the sample was heated from room temperature to 800 °C at a rate of 10 °C min⁻¹. 800 °C was held for 10 min followed by a cooling ramp (10 °C min⁻¹). A dried gas mixture containing ca. 75 %mol CO₂ and ca. 25 %mol Ar was used for TPO. Initial pressure: ca. 200 mbar. End pressure: ca. 100 mbar. Panel A shows the surface-normalized molar CO₂ conversion (left axis) and the molar CO₂ conversion normalized to the mol of oxide used in the experiment (right axis). The details for CO₂ quantification are laid out in the Experimental Section. Panel B shows the Ar normalized CO₂/CO signals acquired after reducing the sample at 520 °C.

The CO₂-TPO experiments (*cf.* Panel A in Figures 1 and 2) show a correlation between the overall CO₂ conversion at the end of the CO₂-TPO experiment and the maximum reduction temperature reached during previous H₂ treatment (*cf.* Table 1). In ref. ^[44] it was shown that the maximum reduction temperature during the H₂ treatment directly affects the degree of reduction of both LSF64 and STF73. The higher the temperature reached during H₂ pre-reduction, the more pronounced was the reduction of LSF64/STF73. Therefore, the presented experiments show that more deeply reduced LSF64/STF73 samples are capable of reducing more CO₂ during TPO.

A reason for this different activity can be due to different contributions of possible ionic charge carriers, such as oxygen vacancies or protons (see Equations 1-4). In other words, the overall degree of reduction after H₂ pre-reduction is not only defined by the concentration of O vacancies but also by the concentration of dissolved hydrogen (i.e., protonic point defects).^[44] In addition, segregated metallic Fe might add to the overall reduction capacity of the pre-reduced perovskites. However, metallic Fe was not detected on STF73 by XRD after H₂ pre-reduction at 530 °C and subsequent heating under TPD conditions (not shown). As no Fe exsolution was observed at the highest H₂ reduction temperature no Fe segregation is expected for lower H₂ reduction temperatures, either. In case of LSF64, however, Fe metal is present after H₂ pre-reduction at 440 °C and 520 °C, as verified by XRD (*cf.* Figure 3). The graph shows three diffractograms corresponding to oxidized LSF64 (black) as a reference and H₂ pre-reduced LSF64, which are colored blue (pre-reduced at 400 °C) and green (pre-reduced at 500 °C). Reflexes, that are assigned to metallic Fe, are marked by arrows. In addition, an inset shows the magnified region in between 34 ° and 38 ° (2 θ). The most intense Fe metal reflex can be found at 20.15 °. Also, a signal at 35.28 ° is expected for metallic Fe and appears as a peak shoulder in the diffractogram (see inset). The calculated reflexes of the perovskite structure of La_{0.6}Sr_{0.4}FeO_{2.976} and Fe metal are plotted as red and black bars, respectively. However, the amount of exsolved Fe⁰ is rather small (compare peak intensities of the two phases in Figure 3).

Figure 3. XRD patterns collected from LSF64 after O₂ pre-oxidation (for details see experimental section) and reduction in flowing/dry H₂ at 400 °C / 500 °C. For H₂ pre-reduction the perovskite samples were heated from room temperature to 400 °C / 500 °C. This temperature was then held for 1 h before the sample was allowed to cool back down to room temperature (see also experimental section). Reflexes assigned to metallic Fe are marked by arrows. The inset on the right side (black frame) shows the magnified region in between 34° and 38° (2θ) while the inset on the left side (blue frame) shows the magnified region in between 19° and 23° (2θ). For the assignment of the relevant reflexes the following software was employed: STOE Powder Diffraction Software Package WinX^{POW} (version PKS 2.01). The red and black bars depict the calculated reflexes of La_{0.6}Sr_{0.4}FeO_{2.976} (perovskite) and Fe⁰, respectively.

Moreover, it can be concluded from Figures 1 and 2 that LSF64 is a much more effective catalyst for CO₂ reduction than STF73, since the mol of converted CO₂ per mol oxide/acceptor-dopant are about one order of magnitude larger for LSF64 than for STF73. Since both oxides have only slight differences in terms of their doping level (40 *versus* 30 mol%) this significant activity difference can be explained by either strongly different reduction kinetics during pre-treatment, thus leading to insufficiently reduced powder or by a strongly different activity of the point defects, which are formed during this pre-reduction step. The first effect may explain the inactivity of both powders after pre-reduction at the lowest temperature at 340 °C (see black curves in Figures 1A and 2A): Even though both oxides are expected to be reduced after the described pre-treatment in dry H₂,^[37-39] they do not show CO₂ reduction activity since the kinetics for pre-reduction at 340 °C were too sluggish to form a sufficient amount of reactive point defects.

The degree of reduction of LSF64 and STF73 after H₂ pre-reduction at 520 °C and 530 °C, respectively, was determined by O₂ TPO and H₂ TPD (considering $V_O^{\bullet\bullet}$ and $(OH)_O^\bullet$): For La_{0.6}Sr_{0.4}FeO_{3-δ} the “delta” in oxygen was found to be *ca.* 0.3 and for SrTi_{0.7}Fe_{0.3}O_{3-δ} it is *ca.* 0.1 (see Table 2 and discussion below). In case of LSF64 this value is larger than the possible value of 0.2 given by the acceptor dopant, which can be explained by the observed Fe exsolution. Since these two nominal delta values only differ by about a factor of three, they can hardly explain the difference in CO₂ conversion by about an order of magnitude (see Table 1).

Also, since the amount of exsolved Fe is rather small (compare peak intensities of the two phases in Figure 3) it can be virtually excluded that solely oxidation of metallic Fe by CO₂ is responsible for the large differences in CO₂ reduction capacity between the two investigated oxides. A catalytic effect of the metallic phase is possible, but was excluded in a NAP-XPS study on CO₂ reduction on perovskite-type electrocatalysts.^[36] Consequently, a different reduction activity of ionic point defects generated upon reductive pre-treatment is the most likely explanation for the differences between Figures 1A and 2A. This potentially different contribution of oxygen vacancies and protons to the CO₂ reduction activity will be discussed in the following.

Table 1. Overall CO₂ conversion of LSF64/STF73 at the end of CO₂-TPO experiments after various sample treatments: (1) pre-reduced in flowing / dry H₂ at T_{max} = 440 °C and T_{max} = 520 °C. (2) To test the role of dissolved hydrogen on CO₂ reduction, samples were thermally depleted of H₂ after pre-reduction (LSF64: T_{max} = 520 °C / STF73: T_{max} = 530 °C) by heating under TPD conditions. (3) To clarify the reduction agent's influence on subsequent CO₂ reduction, LSF64 and STF73 were pre-treated in flowing and dry CO (including intermediate HV-TPD before CO₂-TPO). Maximum temperatures reached during CO treatment: 520 °C (LSF64) and 530 °C (STF73). Aside from changing the reduction gas, the pre-treatment protocol remained the same: pre-reduction in CO or H₂ followed by HV-TPD. This allows for direct comparison of CO₂-TPO measurements (2) and (3). The conversion of CO₂ is given in mol CO₂ m⁻² sample and mol CO₂ mol⁻¹ oxide.

Nr.	Treatment	LSF64			STF73		
		Max. Temp. / °C	CO ₂ con. / mol·m ⁻²	CO ₂ con. / mol·mol ⁻¹	Max. Temp. / °C	CO ₂ con. / mol·m ⁻²	CO ₂ con. / mol·mol ⁻¹
1	H ₂	340	---	---	340	---	---
		440	0.98·10 ⁻⁴	11·10 ⁻²	440	1.16·10 ⁻⁴	0.862·10 ⁻²
		520	1.27·10 ⁻⁴	13.5·10 ⁻²	520	2.05·10 ⁻⁴	1.52·10 ⁻²
2	H ₂ / Heating	520	1.05·10 ⁻⁴	11.2·10 ⁻²	530	0.78·10 ⁻⁴	0.58·10 ⁻²
3	CO / Heating	520	1.53·10 ⁻⁴	16.3·10 ⁻²	530	2.58·10 ⁻⁴	1.92·10 ⁻²

A comparison of the overall CO₂ conversion found by TPO and the amount of desorbed H₂ directly after H₂ treatment^[44] shows the following: In case of LSF64, the total amount of desorbed H₂ directly after pre-reduction with H₂ under identical conditions is $0.7 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 7 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$ (H₂ treatment at 440 °C) and $1.8 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 19 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$ (interpolated for H₂ treatment at 520 °C).^[44] In the case of STF73, the respective values are $8 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 6 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$ (H₂ treatment at 440 °C) and $11 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 8 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$ (interpolated for H₂ treatment at 520 °C).^[44] These values reflect the minimum amount of hydrogen bound by LSF64/STF73, since hydrogen equivalents desorbing as H₂O were neglected in this evaluation.^[44] However, H₂O desorption might be estimated from TPD experiments after H₂-TPR, where strongly reduced LSF64/STF73 desorbed up to $0.5 \cdot 10^{-5} \text{ mol H}_2\text{O m}^{-2} = 5 \cdot 10^{-3} \text{ mol H}_2\text{O mol}^{-1} \text{ oxide}$ and $1 \cdot 10^{-5} \text{ mol H}_2\text{O m}^{-2} = 7 \cdot 10^{-4} \text{ mol H}_2\text{O mol}^{-1} \text{ oxide}$, respectively. Based on that, the amount of bound hydrogen can be estimated to be *approx.* $1.2 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 13 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$ for LSF64 and $9 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 7 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$ for STF73 at most (calculated for H₂ treatment at 440 °C). After H₂ pre-reduction at 420 °C the respective numbers are $2.3 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 25 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$ (LSF64) and $12 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 8.9 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$ (STF73). The values are also depicted in Fig. 4, where the green bar shows the amount of desorbed H₂ and the blue bar shows the amount of desorbed H₂O found by TPD. The bars are stacked upon each other so the absolute height gives an idea of the total amount of dissolved hydrogen in LSF4 (left)/STF73(right) after H₂ pre-reduction at 440 °C and 520 °C.

The overall CO₂ conversion of pre-reduced LSF64 shown in Figure 1A (grey bars in Fig. 4) significantly exceeds the amount of bound hydrogen found by TPD, whereas the CO₂ conversion of pre-reduced STF73 (*cf.* Fig. 2A) is only slightly higher than the amount of bound hydrogen. An overview is also shown in Figure 4. This implies that most of the CO₂ converted by reduced LSF64 reacts with O vacancies and/or segregated metallic Fe, as H₂ pre-reduced LSF64 does not contain enough protonic charge carriers to reduce the full amount of CO₂. For STF73, on the other hand, this estimation shows that a higher fraction of CO₂ is converted by reaction with dissolved hydrogen than with O vacancies. Furthermore, dissolved hydrogen stored in STF73 reacts quantitatively with CO₂. This is deduced from the fact, that no H₂ desorbs during CO₂ TPO and subsequent TPD (discussed below).

Figure 4. A comparison between the total CO₂ conversion (grey bars) of LSF64 (left) and STF73 (right) found by CO₂-TPO (see also Fig. 1A and 2A) with the respective amounts of dissolved hydrogen found by H₂-TPR and TPD discussed in ref. ^[44]. The total H₂ desorption is colored green, while the H₂O desorption is colored blue. The bars are stacked upon each other. The values are given in mol m⁻² and mol mol⁻¹ oxide.

The obtained surface-normalized total CO₂ conversions of LSF64 and STF73 determined from CO₂-TPO are comparable, but the mass-normalized CO₂ conversions of the two perovskites differ from each other, as the specific surface areas of LSF64/STF73 vary by a factor of 10 (not shown). Hence, LSF64 shows a significantly higher mass specific CO₂ conversion than STF73. This becomes also clear when comparing the CO₂ conversion normalized to mol of perovskite of LSF64 and STF73 shown on the right axis of Figures 1A and 2A.

During TPO with carbon dioxide not only CO₂ but also the reaction product CO was detected. The Ar-normalized CO and CO₂ intensity curves for two exemplary temperature-programmed experiments are depicted in Panel B in Figures 1 (LSF64) and 2 (STF73). By comparing the CO and CO₂ signals, it is possible to distinguish CO₂ adsorption from a reactive conversion of CO₂ into CO. In the case of LSF64 (Figure 1B) the results suggest CO₂ adsorption between 100 °C and 400 °C during the heating phase of the experiment, as CO₂ is consumed from the atmosphere, but still no CO is formed. However, CO₂ adsorption on LSF64 was only observed on samples with a reduction degree that was high enough. After heating LSF64 in flowing H₂ up to 340 °C, no observable CO₂ adsorption occurs. This suggests an O-defect-related CO₂ adsorbate on LSF64. An adsorption of CO₂ to surface vacancies was also discussed in a recent electrochemical CO₂ splitting study on LSF64.^[36] For STF73 such a preceding CO₂ adsorption was not observable, which may be related to the significantly smaller surface area of the STF73 powder (see BET results).

CO₂ reduction/CO formation *via* LSF64/STF73 (pre-reduced at 440 °C/520 °C) starts at around 420 °C and 350 °C (*cf.* Panel B in Figs. 1 and 2), respectively. For LSF64 there seems to be a slight maximum in CO accumulation and CO₂ depletion in the atmosphere. The position of the extremum seems to depend on the maximum pre-reduction temperature. After H₂ treatment at 440 °C the peak shows up toward the end of the heating phase (*ca.* 750 °C), while a pre-reduction at 520 °C causes the extremum to move into the isothermic phase of the experiment (*cf.* Figure 1A). However, this seems to be a kinetic effect that could be explained by time-dependent depletion and accumulation of reactive O vacancies/oxide ions on the perovskite surface during the TPO experiments. In the case of LSF64, this would mean that the reduction of CO₂ by reduced surface-near regions is dominant at temperatures below 750 °C (heating phase). Beyond this point (at even higher temperatures) the increased mobility of oxide ions allows for a recognizable diffusion of the former from the bulk towards the surface resulting in the reoxidation of CO. There might be a similar effect on STF73. However, the extrema in the CO/CO₂ signals are not as well defined as for LSF64, even if the general course of the CO₂ conversion after H₂ pre-reduction at 520 °C suggests a back reaction at temperatures above ~450 °C (heating phase). This is also indicated by a quite abrupt stop in the smoothly increasing CO₂ conversion (starting at 350 °C) of STF73 at 450 °C (samples pre-reduced with H₂ at 440 °C and 520 °C / *cf.* Figure 2). However, the interpretation of this feature of the measurements is not straightforward.

Temperature-programmed desorption experiments were conducted directly after CO₂-TPO. Figure 5 depicts TPD spectra acquired from LSF64 (Panel A) and STF73 (Panel B). CO, CO₂ and H₂ desorb from LSF64 after pre-reducing the sample at 440 °C/520 °C and subsequent CO₂-TPO. Comparing the amounts of desorbing gases, CO₂ exhibits the largest integral desorption of all three. The CO₂-TPDs show three distinct maxima in the desorption rate. The first rate maximum occurs early during the heating program at around 100 °C. However, the CO₂ desorption up to *ca.* 200 °C is only minor in amount when compared to the CO₂ desorption in the mid-temperature regime (*ca.* 200 °C < T < *ca.* 600 °C) with two desorption rate maxima at around 380 °C and 460 °C. Therefore, the TPD shows carbon species with different thermal stability releasing CO₂ upon decomposition. CO desorption occurs between 400 °C and 600 °C. The start of CO desorption coincides with the start of H₂ desorption. This result suggests that

even during TPD, bound hydrogen might be used to reduce carbonate-type adsorbates, thereby releasing CO. However, the re-oxidation of O vacancies or metallic Fe by carbonate-type species during TPD can not be excluded. Moreover, the onset temperature of CO desorption in TPD corresponds well to the onset temperature of CO₂ reduction found in TPO experiments (*cf.* Fig. 1A). Both, the CO₂ and CO desorption rates decrease to zero at *ca.* 650 °C on LSF64 and at *ca.* 750 °C on STF73.

The fact that still some H₂ desorbs from LSF64 after pre-reduction with H₂ and subsequent CO₂-TPO indicates that H₂ was not consumed quantitatively *via* CO₂ reduction. Desorption of H₂ from reduced LSF64 during CO₂-TPO was not observed either. The H₂ TPD results shown in Figure 5A can be compared to H₂-TPD spectra acquired from LSF64 after H₂ reduction (under the same conditions but without CO₂-TPO): TPD experiments of LSF64 after H₂ treatment at 440 °C and 550 °C exhibit H₂ desorption starting at about 400 °C (*cf.* Figure 9A in ref. ^[44]), which is in very good agreement with the experiments shown in Figure 5A. However, the main H₂ desorption between room temperature and *ca.* 350 °C present after sole H₂ pre-reduction without subsequent CO₂-TPO (*cf.* Figure 9A in ref. ^[44]) is missing after H₂ preparation followed by CO₂-TPO. From this it also becomes clear, that a part (but not all) of the stored hydrogen reacts with CO₂. In terms of integral amounts of H₂ monitored by TPD, this indicates the following: After simple H₂ treatment of LSF64 at 440 °C (*cf.* Figure 9A in ref. ^[44]), five times more H₂ desorbs during TPD than after the same H₂ preparation followed by CO₂-TPO (*cf.* Figure 5A), indicating that CO₂ reacts with a great portion of the dissolved hydrogen.

As mentioned before, STF73 desorbs only CO₂ (*cf.* Figure 5B) after H₂ preparation followed by CO₂-TPO suggesting that hydrogen bound by STF73 after pre-reduction reacts quantitatively with CO₂. This could mean that STF73 dissolves hydrogen mostly in surface-near regions and/or that the transport processes important for CO₂ reduction are faster than on LSF64. The subsequent CO₂ thermal desorption spectrum acquired from STF73 resembles the CO₂-TPD from LSF64 in a qualitative way: CO₂-TPD spectra collected from both perovskites show three distinct maxima in the CO₂ desorption rate with a minor CO₂ desorption below 200 °C. However, the positions with respect to temperature of these maxima are shifted. Also, a persisting CO₂ desorption rate of STF73 is still measureable at 800 °C during TPD, suggesting incomplete desorption. The absence of CO desorption is a hint that there are no more utilizable reduction equivalents left on STF73 to further reduce highly oxidized (carbonate-like) carbon species.

Figure 5. TPD experiments as obtained after initial pre-reduction with H₂ and the subsequent CO₂-TPO experiments shown in Figures 1 and 2. The temperatures given in the legend refer to the maximum temperature during H₂ pre-reduction. Panels A and B show data collected from LSF64 and STF73, respectively. The samples were heated from room temperature to 800 °C at a rate of 10 °C min⁻¹.

CO₂ reduction via LSF64/STF73 after H₂ pre-reduction and HV heating

To further study the role of bulk hydroxyls (OH)_O^{*} for CO₂ reduction, additional experiments were conducted. LSF64 and STF73 were reduced in flowing/dry H₂ at 520 °C and 530 °C, respectively. Subsequently, a TPD experiment was performed directly after pre-reduction to desorb hydrogen from the specimens before CO₂-TPO and in due course to quantify the associated loss of CO₂ reduction equivalents. For this, only H₂ desorption was considered. H₂O desorption was not taken into account, since H₂ equivalents desorbing from the perovskite *via* H₂O formation should not affect the total CO₂ conversion during TPO, as for each H₂O molecule formed one H₂ equivalent is consumed and one O vacancy remains (assuming that the reactivity of bound hydrogen and O vacancies are comparable for CO₂ reduction). CO₂-TPO was done after H₂ pre-reduction followed by TPD to determine the CO₂ conversion as is shown in Figure 6.

Panel A in Figure 6 depicts data collected from LSF64. The red trace shows CO₂-TPO data from LSF64 after H₂ pre-reduction at 520 °C and subsequent TPD under high vacuum conditions. For direct comparison, the green curve depicts the TPO course measured directly after H₂ pre-treatment at 520 °C without intermediate TPD. The CO₂ conversion normalized to the mol of perovskite are shown additionally on the right axis of Figures 6A and B. The results show that the intermediate TPD cycle decreases the CO₂ conversion during subsequent CO₂-TPO. The exact values for the integral CO₂ conversion can be compared in Table 1. From the intermediate TPD after H₂ pre-treatment the amount of desorbed H₂ was estimated and found to be about $2.3 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 25 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$. The difference in CO₂ conversion in Figure 6A is *ca.* $2.2 \cdot 10^{-5} \text{ mol CO}_2 \text{ m}^{-2} = 23 \cdot 10^{-3} \text{ mol CO}_2 \text{ mol}^{-1} \text{ oxide}$, which fits well with the H₂ TPD derived value. These measurements clearly show that in the case of LSF64 < 20%mol of the converted CO₂ is reduced by dissolved hydrogen.

O₂-TPO of LSF64 (not shown) acquired after H₂ pre-reduction at 520 °C/HV heating reveals that the perovskite is heavily reduced as the integral O uptake was found to be $3.07 \cdot 10^{-4} \text{ mol O m}^{-2} = 0.327 \text{ mol O mol}^{-1} \text{ oxide}$ (see also Table 2). This is also indicated by the formerly mentioned segregation of metallic Fe found by XRD (*cf.* Figure 7). An XRD pattern was acquired from LSF64 in different states. The black curve in Figure 7 corresponds to LSF64 after O₂ pre-oxidation. The red /purple diffractogram was collected from a LSF64 sample after H₂ pre-treatment /CO pre-treatment, respectively (also discussed below). Reflexes assigned to metallic Fe are marked by arrows. The most intense Fe reflex shows up at 20.15° (2θ). A second Fe reflex can be found at 35.28° (see inset). In addition, the calculated reflexes for Fe metal (black bars) and La_{0.6}Sr_{0.4}FeO_{2.976} (red bars) are shown.

The O₂-TPO results of LSF64 also show that CO₂ is not capable of re-oxidizing the H₂ pre-treated (520 °C) sample completely. Additionally, O₂-TPO reveals the uptake of $0.04 \cdot 10^{-4} \text{ mol O m}^{-2} = 4 \cdot 10^{-3} \text{ mol O mol}^{-1} \text{ oxide}$ at room temperature. The amount of O₂ that is contained within one monolayer of LSF64 was estimated to be $0.04 \cdot 10^{-4} \text{ mol O m}^{-2} = 4 \cdot 10^{-3} \text{ mol O mol}^{-1} \text{ oxide}$. This calculation is based on the BET surface area of LSF64, the dimension of its unit cell and the assertion that one LSF64 unit cell binds one O atom. Based on this, the oxidation of reduced bulk LSF64 by O₂ at RT is not likely, but rather an oxidation of the reduced LSF64 surface.

However, other than the difference in overall CO₂ conversion of LSF64, the red and green curve exhibit similar features. By comparing the Ar-normalized CO and CO₂ signals (not shown), CO₂ adsorption between 200 °C and 400 °C is revealed. The quantification of this adsorption shows a value of $0.05 \cdot 10^{-4} \text{ mol CO}_2 \text{ m}^{-2} = 5 \cdot 10^{-3} \text{ mol CO}_2 \text{ mol}^{-1} \text{ oxide}$ which corresponds well with the O₂ room temperature uptake and hence suggests CO₂ adsorption. The CO₂ reduction starts at slightly lower temperatures (*ca.* 400 °C/heating phase) and is identified by the accumulation of CO in the gas phase. Also, a maximum in CO concentration is reached

and corresponds to a minimum in the CO₂ concentration (*ca.* 780 °C/heating phase). Passing the maximum, a part of the previously formed CO is re-oxidized to CO₂. As was mentioned before, this effect could be assigned to delayed release of lattice oxygen in the context of Figures 1 and 2. During the cooling phase, the CO₂ conversion remains constant.

Panel B in Figure 6 shows the CO₂ conversion of STF73 after various pre-treatments. The red trace exhibits the CO₂ conversion of STF73 after pre-reduction at 530 °C in flowing/dry H₂ and subsequent TPD, while the green curve shows the CO₂ conversion directly after H₂ pre-reduction at 520 °C. Again, the intermediate TPD cycle decreases the CO₂ conversion during subsequent TPO (*cf.* Table 1). The amount of removed H₂ during TPD after H₂ treatment is about $8 \cdot 10^{-5} \text{ mol H}_2 \text{ m}^{-2} = 6 \cdot 10^{-3} \text{ mol H}_2 \text{ mol}^{-1} \text{ oxide}$. This value fits well to the difference in CO₂ conversion which is found to be about $10 \cdot 10^{-5} \text{ mol CO}_2 \text{ m}^{-2} = 7 \cdot 10^{-3} \text{ mol CO}_2 \text{ mol}^{-1} \text{ oxide}$. Furthermore, no H₂ desorption was observed during CO₂ TPO or subsequent TPD, which proves that any stored hydrogen is consumed quantitatively by CO₂. H₂ reduced STF73 converts approximately 50 mol% of the CO₂ by stored hydrogen. Since no metallic Fe was detected on STF73 after H₂ reduction at 530 °C and subsequent TPD heating, CO₂ conversion can only occur *via* quenching of O vacancies in the absence of dissolved hydrogen. Again the amount of mol O m⁻² in one monolayer STF73 can be estimated using the BET surface area and the cell parameter of STF73. Furthermore, it is assumed that one O atom is consumed by one unit cell. Using these assumptions, it is found that H₂-reduced (at 530 °C and subsequent heating) STF73 consumes about 15 monolayers of O provided by CO₂, indicating bulk oxidation. The O uptake derived by O₂-TPO (after preparation of STF73 under the same conditions) exceeds the CO₂ conversion and reaches $15.57 \cdot 10^{-4} \text{ mol O m}^{-2} = 0.1158 \text{ mol O mol}^{-1} \text{ oxide}$ (see also Table 2). Hence, CO₂ can not quench all O vacancies on STF73 produced by H₂ reduction at 530 °C and HV heating. However, in the case of STF73, neither measureable CO₂ adsorption nor a peak in the Ar normalized CO₂/CO signals could be identified.

Table 2. Integral O uptake derived from O₂-TPO. LSF64 and STF73 were pre-reduced in flowing/dry H₂ (1) or CO (2) at 520 °C (LSF64) / 530 °C (STF73). The perovskite specimens were heated under TPD conditions after pre-reduction. The integral O uptake is given in mol O m⁻² surface and mol O mol⁻¹ Oxide.

Nr.	Treatment	LSF64			STF73		
		Max. Temp. / °C	O uptake / mol·m ⁻²	O uptake / mol·mol ⁻¹	Max. Temp. / °C	O uptake / mol·m ⁻²	O uptake / mol·mol ⁻¹
1	H ₂ / Heating	520	3.07·10 ⁻⁴	0.327	530	15.57·10 ⁻⁴	0.1158
2	CO / Heating	520	3.92·10 ⁻⁴	0.418	530	14.74·10 ⁻⁴	0.1096

CO₂ reduction via LSF64/STF73 after CO pre-reduction and HV heating

The influence of the reduction agent – used on the perovskites before CO₂-TPO – on the reduction of CO₂ was also tested. As a surrogate for hydrogen, carbon monoxide was selected, which has similar reduction capacity, but cannot deliver hydrogen to the bulk of the oxides. LSF64/STF73 was treated with CO (1.06 bar) under flowing/dry conditions at 520 °C and 530 °C, respectively. After CO reduction the samples were heated under HV-TPD conditions. This treatment procedure was selected as it allows for a direct comparison of the CO₂-TPO data after H₂ and CO reduction at 520 °C (LSF64, including intermediate HV heating) and 530 °C (STF73, including intermediate HV heating) as is shown in Figure 6 (red/purple traces).

The HV-heating before TPO was monitored by QMS and revealed a major CO and minor CO₂ desorption contributions from both perovskites (*cf.* Figure 8). This could indicate, that LSF64/STF73 is strongly depleted with respect to reactive lattice oxygen after CO pre-treatment, which is necessary to release CO₂. In the case of LSF64 also O₂ TPO after CO pre-treatment suggests a high reduction degree which exceeds the value of O consumption after H₂ reduction and HV heating (see also Table 2). The segregation of metallic Fe found by XRD confirms severe reduction of LSF64 (*cf.* Figure 7 / purple diffractogram). However, LSF64 desorbs about five times, STF73 about four times more CO than CO₂ directly after this CO pre-treatment. CO/CO₂ desorption from LSF64 is finished at *ca.* 720 °C (*cf.* Figure 8), which hints that all of the reactive C and/or O species are consumed. The QMS signals of CO and CO₂ of the STF73 TPD experiment were still well measurable at 800 °C. The major part of reactive C and/or O might have reacted by the end of the TPD experiment on STF73.

The CO₂-TPO experiments were eventually conducted after the respective CO pre-reduction/TPD procedure. The overall CO₂ conversion curves derived from CO₂-TPO are shown in Figure 6 in purple color. LSF64/STF73 data are depicted in Panels A and B, respectively. The CO₂ conversion of both samples is increased after CO pre-reduction followed by TPD (violet curve) when compared to samples treated in H₂ followed by TPD under otherwise identical conditions (red curve) and even samples that were not subjected to TPD before CO₂-TPO (green curve). The final CO₂ conversion values of LSF64/STF73 derived from TPO after CO/H₂ treatment are collected in Table 1.

The results show a CO₂ adsorption on LSF64 starting at *ca.* 200 °C and ceasing at *ca.* 340 °C, reaching a plateau. In this case, the CO₂ conversion of LSF64 reaches a maximum during the cooling phase of the experiment (*ca.* 670 °C). However, the position of this maximum in the CO₂ conversion of LSF64 is dependent on the specific pre-treatment (compare Figure 1A and Figure 6A). On the other hand, CO₂ adsorption and a CO₂ conversion maximum after CO pre-treatment and subsequent TPD was not observed on STF73. Both samples show the same qualitative behavior concerning the CO₂ conversion after CO pre-treatment (and intermediate HV heating) and H₂ pre-treatment (and intermediate HV heating).

The higher CO₂ conversion of CO pre-treated samples might be explained by the formation of more O vacancies and/or O vacancies that are chemically more reactive towards CO₂ reduction (1): O₂-TPO of LSF64/STF73 pre-reduced with CO or H₂ show the following: For LSF64 the O uptake is higher after the CO preparation routine than after the H₂ preparation routine. For STF73 the O uptake determined by O₂-TPO after H₂ preparation is slightly higher than the O uptake after CO preparation (see also Table 2). Comparing the O₂-TPO and CO₂-TPO confirms that CO₂ is not capable of re-oxidizing the pre-reduced perovskite samples completely as the O uptake from O₂ exceeds the CO₂ conversion clearly

Also segregated Fe⁰ has to be taken into account, as it increases the reduction capacity of a reduced perovskite sample (2): Segregation of Fe⁰ was verified for LSF64 after reduction with H₂ or CO and subsequent TPD heating (state of the sample before

CO₂-TPO) by XRD, but not for STF73 (*cf.* Figure 7 shown only for LSF64). XPS (*cf.* Figures 9 and 10) could not detect any metallic Fe (Fe 2p spectrum not shown) on either perovskite after the formerly mentioned treatments in H₂ or CO. This is most likely due to the fact that the sample was in direct contact with air before acquiring the XP spectra, which caused the segregated metallic Fe to quickly re-oxidize, as was shown in previous studies.^[41,48] Being a surface-sensitive method, XPS only detected the oxidic shell of the iron particles.

In addition, the deposition of carbon or any form of reduced carbon-containing species might contribute to the conversion of CO₂ *via* the Boudouard reaction (3): Whether carbon was deposited on LSF64/STF73 *via* CO treatment is not straight-forward to verify at first glance. Figure 9 panel A shows the Sr 3d and panel C the C 1s region of LSF64 after O₂ treatment, while panels B and D correspond to the CO-reduced state, respectively. XPS reveals the presence of low binding energy species in Sr 3d and C 1s spectra on LSF64 after CO reduction/TPD heating (*cf.* Figure 9 – panels B and D, respectively). This correlation may be interpreted as the appearance of strontium carbide, which would indicate that carbon was indeed deposited prior to its formation. The respective carbon component is located at a binding energy of 282.7 eV, which is significantly lower than that for the sp³-hybridized C-C component, and is in good agreement with literature values for other carbides, such as WC, SiC or Mo₂C.^[49-51] Since no literature data on strontium carbide can be found, no comparison can be drawn for the Sr 3d component of this species. It does, however, follow the trend exhibited by other metals, where the carbide peaks are found at significantly lower binding energies than those of the oxides,^[52-56] with the 3d_{5/2} component of the carbide species being located at 130.6 eV as compared to the 132.1 eV of the bulk oxide. The carbon deposition is also corroborated by the Sr/C ratio: for the oxidized sample, it is 1.8 (owing to adventitious carbon), whereas it drops to 0.3 for the specimen after CO treatment. Thus, there is a lot more carbon present on the surface after heating in carbon monoxide.

XPS data of STF73 (*cf.* Figure 10) show an increase of the degree of reduction after CO treatment/TPD heating, which can be deduced from the Ti 2p spectra: In panel E, the state of the specimen after O₂ treatment is shown and can be compared to the state of the sample after CO pre-treatment (panel F). The Ti³⁺/Ti⁴⁺ ratio obviously shifts towards Ti³⁺ by heating the sample in CO followed by TPD heating (62 % Ti³⁺ compared to 42 % for the oxidized sample). Furthermore, after CO reduction and intermediate HV heating no additional low binding energy components in the Sr 3d and C 1s region (*cf.* Figure 10 panel B and D) could be identified, suggesting that no carbide is present here. However, the quantification suggests an increased amount of carbon as well: after oxidation, the Sr/C ratio is 1.3, and it becomes 0.5 after treatment in CO. The Fe 2p region between 737 eV and 702 eV is not shown for neither LSF64 nor STF73, as no outstanding change occurs as the oxidized perovskite samples undergo the CO treatment.

The results imply that the increased CO₂ conversion of LSF64 after CO treatment can be caused by an overall deeper degree of reduction, which includes more pronounced exsolution of metallic Fe. Also the quality of O vacancies (*e.g.* the formation of singly charged oxygen vacancies, which may form under strongly reducing conditions^[57-59]), as well as the deposition of carbon might play a role. In the case of STF73 metallic Fe is not involved in the reduction of CO₂, as no detectable amount of metallic Fe was segregated by CO pre-treatment. Therefore, the increased CO₂ conversion could be explained by a different quality and/or quantity of O vacancies as well as by carbon deposition caused by CO pre-treatment.

Figure 6. CO₂ conversion after selected sample treatments: Specimen treated in flowing/dry H₂ (green curves). Specimen treated in flowing/dry H₂ and subsequent TPD in high vacuum up to 800 °C (red curves). Specimen treated in flowing/dry CO and subsequent TPD up to 800 °C (purple curves). For TPO a dry gas mixture containing ca. 75 mol% CO₂ and ca. 25 mol% Ar was used. Initial pressure: ca. 200 mbar. Final pressure: ca. 100 mbar. The samples were heated from room temperature to 800 °C being held isothermally for 10 min. The heating and cooling rate was 10 °C min⁻¹. Temperatures indicated in the graphs refer to maximum temperature reached during reductive pre-treatment. Panel A/B depict data collected from LSF64/STF73, respectively.

Figure 7. XRD patterns collected from LSF64 after O₂ pre-oxidation (black curve), H₂ pre-treatment (red curve) and CO pre-treatment (violet curve). Reflexes assigned to metallic Fe are marked by arrows. The inset on the right side (black frame) shows the magnified region in between 34 ° and 38 ° (2θ) while the inset on the left side (blue frame) shows the magnified region in between 19 ° and 23 ° (2θ). For the assignment of the relevant reflexes the STOE Powder Diffraction Software Package WinX^{POW} (version PKS 2.01) was employed. The red and black bars depict the calculated reflexes of La_{0.6}Sr_{0.4}FeO_{2.976} (perovskite) and Fe⁰, respectively.

Figure 8. TPD measurements directly after CO pre-reduction under flowing and dry conditions. Maximum temperatures during CO pre-treatment were 520 °C (LSF64) and 530 °C (STF73). Results acquired from LSF64 are depicted *via* continuous lines while STF73 data are depicted *via* dotted lines. For TPD experiments the samples were heated from room temperature to 800 °C at a rate of 10 °C min⁻¹ in HV.

Figure 9. XPS spectra of LSF64 in the oxidized state after O₂ pre-treatment at 800 °C (panels A and C) and after CO treatment involving CO pre-reduction (at 520 °C) and subsequent HV heating up to 800 °C (panels B and D). Panels A and B show the Sr 3d region of the spectrum, while panels C and D show the C 1s region. Red circle markers correspond to experimental data, while the envelope curve, resulting from the fitted peaks, is colored black.

Figure 10. XPS data acquired from STF73 specimens after O₂ pre-treatment (up to 800 °C) and after CO pre-reduction (at 530 °C) followed by heating under TPD conditions (up to 800 °C). The state of the oxidized STF73 samples is represented by the spectra shown in the panels A, C and E. XPS results acquired from CO pre-treated STF73 are depicted in the panels B, D and F. The shown spectra depict the Sr 3d region (panel A, B), the C 1s region (panel C, D) and the Ti 2p region (panel E, F) of the spectrum. Red circle markers correspond to experimental data, while the envelope is colored black.

A further set of TPD data from LSF64 and STF73 was recorded after a 3-step pre-treatment process: (1) H₂ or CO pre-reduction followed by (2) intermediate TPD from the pre-reduced samples (already shown in Figure 8) and (3) CO₂ TPO. The results are shown in Fig. 11, where Panels A and B represent LSF64 and STF73, respectively.

The CO/CO₂-TPD spectra obtained from LSF64 do not differ majorly after H₂ and CO pre-reduction followed by TPD and TPO. Both measurements show CO₂ and CO desorption to approximately the same extent, with a clear trend toward CO formation above ~400 °C, likely due to increasing reduction of CO₂ replacing simple desorption. Also, the thermal stability of the decomposing species is quite similar. Desorption of residual hydrogen, observable after H₂ treatment followed by TPD and CO₂-TPO is surely the main difference between the two experiments. Even after intermediate TPD and CO₂-TPO up to 520 °C, dissolved hydrogen is still present in LSF64. However, the maximum H₂ desorption yield reached during TPD is higher if intermediate vacuum heating after H₂ treatment is not performed (compare Figure 5A and Figure 11A). The experiments show that hydrogen dissolved in LSF64 only gases out slowly under HV conditions as already observed before.

TPD measurements obtained from STF73 after CO₂ TPO (*cf.* Figure 11B) on the other hand show distinct differences after H₂ *versus* CO treatment, in both cases followed by TPD and CO₂-TPO. CO pre-treatment seems to generate carbon-containing reactive species, that exhibit a rather high thermal stability as indicated by the strongly increasing CO/CO₂ desorption rate at and above 700 °C (*cf.* Figure 11B full lines). For comparison, the CO₂ desorption rate from STF73 during TPD after H₂ treatment followed by TPD and CO₂-TPO is clearly decreasing at this point (*cf.* Figure 11B dashed line); in addition, no CO desorption is measured. These TPD results imply that treating STF73 with CO under flowing and dry conditions generates chemically distinct reactive/binding sites with an additional rather strongly bonded carbon source, which is clearly absent on H₂ pre-reduced STF73. As mentioned before, TPD directly after CO pre-treatment of STF73 (*cf.* Figure 7) exhibits a major CO desorption starting at *ca.* 400 °C, that is not complete by the end of the TPD experiment. Therefore, the additional CO/CO₂ desorption shown in Figure 10B at T > 650 °C could be a residual from the previous CO treatment.

Figure 11. Comparison of TPD spectra acquired from LSF64/STF73 after pre-reduction in flowing, dry H₂ or CO, followed by HV heating under TPD conditions and CO₂ TPO. Maximum temperatures during H₂/CO pre-treatment were 520 °C (LSF64) and 530 °C (STF73). Panel A and B show data collected from LSF64 and STF73, respectively. For TPD experiments the samples were heated from room temperature to 800 °C at a rate of 10 °C min⁻¹.

Additionally, the reduction of LSF64/STF73 by CO was tested *via* volumetric CO TPR experiments under static conditions. The results are presented in Figure 12 showing the Ar normalized CO and CO₂ signals during TPR. The oxidation of CO by pre-oxidized LSF64/STF73 is characterized by CO depletion and CO₂ accumulation, as can be seen in Figure 12. The onset temperatures for CO oxidation are 280 °C and 200 °C for LSF64 and STF73, respectively. Furthermore, no precedent CO adsorption on LSF64 or STF73 was observed. The TPR data show that the CO concentration eventually reaches a minimum during the heating phase which corresponds to a maximum CO₂ concentration. The peak positions can be found at 750 °C (LSF64) and 580 °C (STF73). Passing these peak temperatures, the CO concentration starts to increase again as the CO₂ concentration decreases, which implies the partially reversible reduction of CO₂. However, this type of back reaction stagnates during the cooling routine for kinetic reasons, and does not proceed to set the system back to its initial state. An explanation of this effect *via* the time- and temperature-dependent variation in concentration of surface-near O vacancies in LSF64 and STF73 is not conceivable as an increase in temperature should cause the CO₂/CO proportion to increase steadily. However, this behavior could be explained by considering the Boudouard equilibrium: carbon could be deposited on LSF64/STF73 during the early stages of the heating phase, while the temperature is relatively low (bulk oxygen mobility still low). This would consume CO and cause CO₂ formation. Then, as the temperature is raised, CO₂ could react with deposited C to form CO. This would explain the observed back reaction of CO₂ to CO. Furthermore, an inhibited carbon nucleation could be responsible for the irreversibility of the reaction during the cooling phase. It must, however, be emphasized that the interpretation of the observed maximum in CO₂ concentration is not straightforward.

TPD experiments were conducted directly after CO-TPR (Figure 13). The results reveal a major contribution of CO₂ desorption, starting already at low temperatures (some CO₂ desorption already between room temperature and 200 °C, followed by two desorption rate maxima). In the case of LSF64 these peaks are found at 350 °C and 470 °C. For STF73 the peak temperatures are 350 °C and 560 °C. The CO₂ desorption from LSF64 is finished at around 650 °C, while STF73 still desorbs CO₂ at ~800 °C.

Only minor CO desorption is observed on both LSF64 and STF73. The CO desorption from LSF64 takes place in between 450 °C and 650 °C and exhibits only one rate maximum at 520 °C. However, in the case of STF73 the CO desorption is spread out from 400 °C to 800 °C showing two rate maxima at 520 °C and 610 °C. The desorption of CO from LSF64 and STF73 is finished at 650 °C and 750 °C, respectively. The integral amounts of desorbing C (CO+CO₂) after CO-TPR are $0.6 \cdot 10^{-5} \text{ mol m}^{-2} = 6 \cdot 10^{-3} \text{ mol mol}^{-1}$ oxide and $0.8 \cdot 10^{-5} \text{ mol m}^{-2} = 8 \cdot 10^{-3} \text{ mol mol}^{-1}$ oxide for LSF64 and STF73, respectively. The surface specific numbers are quite similar which implies a similar coverage on LSF64 and STF73. Also, TPD from STF73 after CO-TPR (*cf.* Figure 13) does not exhibit the high temperature CO₂/CO formation between 600 °C and 800 °C observed after the sequence CO pre-reduction (flowing) / HV vacuum desorption / CO₂-TPO (*cf.* Figure 11B). This shows that static CO-TPR treatment of STF73 does not generate the same high temperature persistent carbon species that become reactive around 700 °C.

Upon further comparison of the TPDs acquired after static CO-TPR shown in Figure 13 and those obtained directly after flowing/dry CO pre-treatment (520 °C for LSF64, 530 °C for STF73, *cf.* Figure 8), we find that the integral CO₂ desorption remains approximately the same and that the CO desorption is largely increased after the flowing CO pre-treatment (both LSF64 and STF73). The fact that so much more CO desorbs from LSF64/STF73 after flowing CO pre-reduction implies that the perovskites are more reduced than after static CO-TPR. This might be explained both by the continuous removal of CO₂ and the higher CO pressure under flowing conditions, while already formed CO₂ remains in contact with the perovskite samples during the static CO-TPR and therefore increased the effective O₂ partial pressure in the system defined by the ratio of CO and CO₂ in the gas phase.

Figure 12. CO-TPR experiments of oxidized LSF64/STF73 under static volumetric conditions. The specimens underwent the following temperature program, while exposed to a dry gas mixture initially containing ca. 75 mol% CO and ca. 25 mol% Ar: heating from RT to 800 °C with 10 °C min⁻¹, followed by isothermal heating for 10 min and by cooling at a rate of 10 °C min⁻¹ back to 30 °C. Initial pressure: ca. 200 mbar. End pressure: ca. 100 mbar. The graph shows the respective Ar normalized signals of CO and CO₂ of both LSF64 and STF73 during CO TPR in direct comparison.

Figure 13. TPD measurements directly after the static CO-TPR experiments. CO and CO₂ desorption acquired from LSF64 (continuous lines) and STF73 (dashed lines) are compared. The specimens were heated from room temperature to 800 °C at a defined heating rate of 10 °C min⁻¹.

Conclusion

In this work, the CO₂ reduction capability of two pre-reduced iron containing perovskite-type oxides – LSF64 (La_{0.6}Sr_{0.4}FeO_{3-δ}) and STF73 (SrTi_{0.7}Fe_{0.3}O_{3-δ}) – was tested. The central goal was to examine the contribution of dissolved hydrogen stored in pre-reduced LSF64/STF73 powders. It was clearly shown, that hydrogen stored in the LSF64 and STF73 bulk participates in CO₂ reduction. Hydrogen becomes both bulk-mobile and reactive for CO₂ reduction at temperatures around 420 °C/350 °C on LSF64 and STF73, respectively, suggesting a potential application of these perovskites for proton-transfer operated SOC's.

However, the extent to which dissolved hydrogen is consumed in CO₂ reduction varies between LSF64 and STF73: After pre-reduction of the perovskites at 520 °C in flowing H₂ STF73 converts slightly more than 50 mol% of the reacting CO₂ *via* reduction with dissolved hydrogen. LSF64, on the other hand, performs less than 20 mol% of the total CO₂ conversion by stored hydrogen. The total reduced amount of CO₂ per mol of oxide, however, is significantly larger on LSF64. This may be related to a higher reduction capacity of the defect species in LSF64 formed upon pre-reduction.

Briefly summarized, our investigations showed the following:

- A minimum degree of reduction is necessary for CO formation to occur. Only slightly reduced LSF64/STF73 does not show any measurable CO₂ conversion.
- Hydrogen dissolved in STF73 reacts quantitatively with CO₂ while LSF64 tends to hold remnants of dissolved hydrogen: This might be explained by differences between LSF64 and STF73 concerning the stability of (OH)_O[•], the kinetics of surface processes involved in CO₂ conversion to CO or diffusion limitation of dissolved hydrogen within the oxide bulk.
- CO₂ adsorption on LSF64 preceding to CO formation was observed.
- CO₂ is not able to completely re-oxidize pre-reduced LSF64 and STF73.
- Flowing H₂ and CO treatment cause Fe⁰ segregation on LSF64, but not on STF73.
- LSF64 showed a partial back reaction (CO → CO₂) during CO₂-TPO and both LSF64 and STF73 showed a partial reaction (CO₂ → CO) during CO-TPR.

Experimental

Perovskite Materials

Iron-doped strontium titanate with the composition $\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (STF73) is not commercially available and was synthesized *via* a solid state reaction. For this, the appropriate amounts of TiO_2 , Fe_2O_3 and SrCO_3 were ground manually for 30 min and subsequently calcined in air to form the perovskite. To guarantee complete carbonate reaction, the sample was heated to 800 °C (held for 30 min) followed by calcination at 1000 °C for 5 h. The resulting powder was ground for another 30 min before heating it to 1250 °C (dwell for 6 h). Finally, the product was powdered by grinding it for 30 min one last time. Lanthanum strontium ferrite powder ($< 0.5 \mu\text{m}$ particle size) with composition $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF64) was purchased from Sigma Aldrich. Using the BET method the surface areas of LSF64 and STF73 were found to be $4.8 \text{ m}^2 \text{ g}^{-1}$ and $0.4 \text{ m}^2 \text{ g}^{-1}$, respectively. Before BET measurements, the specimens were heated in air over night at 800 °C to account for sintering. The BET analysis was done using a Quantachrome Nova 2000e surface and pore size analyzer.

Volumetric Adsorption Apparatus

For temperature-programmed oxidation (TPO) and temperature-programmed desorption (TPD) experiments an all-quartz apparatus (*ca.* 33 ml chamber volume) equipped with a quadrupole mass spectrometer (QMS) from Balzers (QMA 125; QME 125-9) was employed. Electron impact was used for gas ionisation, while a channeltron (accelerating voltage 1600 V) works as a detector. The gas constituents CO , CO_2 , Ar and H_2 were analysed by QMS using their respective mass-to-charge ratios (m/z) of 28, 44, 40 and 2. The sample was heated *via* a Linn High Therm furnace, while the sample temperature was controlled by a Ni/CrNi thermocouple. For measuring pressures greater than 0.1 mbar in the reactor, a Baratron pressure transducer from MKS Instruments was used. Both, reactor pressure and sample temperature were recorded by National Instruments LabView[®] software. Pressures between 10^{-8} mbar and 10^{-4} mbar were detected by a cold-cathode ionization gauge from Balzers. High vacuum was generated by a Pfeiffer HiCube turbomolecular pumping station. Additionally, the gas flow during sample pre-reduction was regulated *via* flow controllers (MKS instruments). The dry powder sample was filled in a replaceable quartz tube and fixed with quartz wool to avoid contamination of the apparatus. As water might quench oxygen vacancies, a zeolite trap was used to bind released moisture during pre-treatment with H_2 . The zeolite and the sample were arranged in a way that either of them could be heated separately.

An oxidation pre-treatment in flowing/dry O_2 (0.8 ml s^{-1} / *ca.* 1100 mbar O_2) was applied in the very beginning of each measurement to ensure identical starting conditions – *e.g.* to start every experiment from an identical defect chemical state of the oxides as well as to remove moisture and/or organic contamination from the specimens. The O_2 feed gas stream was dried by an ethanol/liquid N_2 cooling trap (*ca.* -110 °C). The sample underwent the following temperature program while exposed to flowing/dry O_2 : Firstly, the sample was heated from room temperature to 800 °C within 30 min. Subsequently, the sample temperature was held constant at 800 °C for 30 min before allowing the sample to cool back down to room temperature in approximately 1 h. Afterwards, the zeolite – if present – was heated in high vacuum at 300 °C until the pressure decreased below 10^{-6} mbar.

In the following step, the specimens were reduced with dry/flowing H_2 or dry/flowing CO . H_2 was cooled to liquid N_2 temperature to remove residual moisture from the gas. CO , on the other hand, was dried *via* an ethanol/liquid N_2 cooling trap (*ca.* -110 °C). A previously dried zeolite was only present during experiments involving H_2 pre-reduction. The gas flow was regulated to 1 ml s^{-1} leading to a pressure around 1060 mbar. The sample was then heated from room temperature to maximum temperature (340 °C, 440 °C, 520 °C, 530 °C) at a rate of 10 °C min^{-1} . After dwelling at maximum temperature for 1 h the sample was allowed to cool back down to room temperature. The subsequent experiment was conducted as soon as the sample temperature decreased below 30 °C. Sample preparation for XRD examination was performed similarly. The maximum temperatures reached during H_2 preparation of LSF64 were 400 °C and 500 °C.

CO₂ Temperature-Programmed Oxidation (CO₂-TPO)

A gas mixture containing *ca.* 75 mol% CO_2 and *ca.* 25 mol% Ar was used for the static TPO experiments. Before filling the reactor, the gas mixture was cooled down to -40 °C to remove residual moisture using an ethanol/liquid N_2 cooling trap. Subsequently, about 250 mbar of the dry gas mixture

was filled into the reactor volume. Then, the gas was allowed to effuse slowly from the reactor into the QMS chamber. The QMS signals were given 40 min time to equilibrate. By then, the pressure in the reactor decreased to about 200 mbar and the temperature program was started. For TPO the following temperature program was used: Starting at *ca.* 25 °C the sample temperature was increased to 800 °C at a rate of 10 °C min⁻¹ followed by dwelling at 800 °C for 10 min. Then, the sample was allowed to cool to 100 °C with 10 °C min⁻¹. Since the sample was not actively cooled, the cooling rate decreased continuously from this point on. As soon as the sample temperature reached 30 °C, the experiment was finished. The final pressure in the reactor was usually about 100 mbar.

Since gas was continuously removed from the reaction chamber for the MS measurement, the absolute amounts of gas in the reactor volume were decreasing during TPO regardless of any reactive conversion or adsorption of CO₂. By calculating the QMS signal proportion of CO₂ and the inert gas Ar ($I_{\text{CO}_2}/I_{\text{Ar}}$), the superimposed decrease of the CO₂ QMS signal due to gas effusion was corrected accordingly. Subsequently, the partial pressure proportion of CO₂ and Ar ($P_{\text{CO}_2}/P_{\text{Ar}}$) was determined from $I_{\text{CO}_2}/I_{\text{Ar}}$. For this, the known starting values (before running the temperature program) of $I_{\text{CO}_2}/I_{\text{Ar}}$ (from QMS) and $P_{\text{CO}_2}/P_{\text{Ar}}$ (from known mixing ratio and total pressure) were used. The amount of reduced CO₂ ($n_{\text{con}}^0(\text{CO}_2)$) was obtained from $P_{\text{CO}_2}/P_{\text{Ar}}$ and the initial amount of Ar in the reactor volume (start temperature program) as a difference between the initial CO₂ amount and the remaining CO₂ in the system. Using this approach, the CO₂ conversion refers to a gas mixture at the start of the temperature program. The CO₂ conversion was normalized to the sample surface area, which allows for comparability with results discussed in ref. [44]. However, as bulk species take the major part in CO₂ reduction, the CO₂ conversion was also normalized to the molar amount of the respective oxide.

O₂ Temperature-Programmed Oxidation (O₂-TPO)

Static O₂-TPO was utilized to determine the reduction degree of the perovskite samples generated by reductive treatment. For this, a known amount of dry O₂ was expanded from a calibrated volume into the whole reactor. Typically, the O₂ pressure dropped during expansion to *ca.* 135 mbar. The system was given 5 min to equilibrate to account for possible room temperature O₂ uptake. Subsequently, the specimen was heated to 800 °C starting at room temperature where the heating rate was set to 10 °C min⁻¹. 800 °C was held for 10 min before the sample was allowed to cool at a rate of 10 °C min⁻¹. Since the sample was not actively cooled, the cooling rate continuously decreased below 100 °C. During TPO, the pressure evolution in the system was detected and recorded.

Quantification of changes in the amount of gas requires a calibration experiment using an inert gas such as He. However, since LSF64 and STF73 desorb O₂ at elevated temperatures, the specimens were heated under HV conditions up to 800 °C to avoid falsification of data by the release of gas. The calibration was conducted in exactly the same manner than the previous O₂-TPO. From the calibration data a temperature-dependent effective volume of the reactor is calculated, which is then used in the ideal gas equation to calculate the amount of gas in the reactor at a given sample temperature during O₂-TPO. This approach is necessary to account for the fact that not the entire apparatus is heated, but only the small compartment that contains the sample. Finally, the O₂ uptake was normalized to the sample surface area as well as to the molar amount of oxide.

Temperature-Programmed Reduction in CO (CO-TPR)

For static CO-TPR a gas mixture containing 75 mol% CO and 25 mol% Ar was prepared. Residual moisture was removed using an ethanol/liquid N₂ cooling trap at *ca.* -110 °C. The CO-TPR experiment was conducted analogously as described in the experimental CO₂-TPO section (see above).

Temperature-Programmed Desorption (TPD)

Before starting the temperature program, the reactor volume was evacuated and the decrease of the QMS signals were recorded for 30 min at room temperature and fitted for base line correction. After evacuation at room temperature the sample was heated with 10 °C min⁻¹ to a maximum temperature of 800 °C. The external calibration of H₂ is outlined elsewhere and the same method was used for CO/CO₂ calibration.^[44] The desorption rates were normalized to the sample surface. Desorption rates are obtained by differentiation of the respective MS signals.

X-ray powder diffraction (XRD)

XRD measurements were done with a STOE STADI P diffractometer using Mo K $_{\alpha 1}$ (17.5 keV) radiation. Furthermore, the system is equipped with a Mythen 1K detector and a curved germanium (111) monochromator. The diffractograms were measured in transmission mode. The software STOE Powder Diffraction Software Package WinX^{POW} (version PKS 2.01) was used to identify crystalline phases.

X-ray photoelectron spectroscopy (XPS)

For XPS analysis a Thermo Scientific MultiLab 2000 spectrometer was used. The base pressure in the chamber was in the low 10⁻¹⁰ mbar range. For measurements the Al-K $_{\alpha}$ line was selected. The kinetic energy of the photoelectrons was analyzed *via* a hemispherical Alpha 110 sector analyzer. To account for sample charging, a flood gun provided electrons with a kinetic energy of 6 eV. In the case of LSF64, finely dispersed graphite powder was used for energy calibration (the sp²-component in the C1s spectrum was set to 284.2 eV). The calibration, in this case, was done in a separate experiment in order to find the position of the Sr 3p peaks. This was done to prevent the falsification of the C quantification on LSF64 after CO treatment. For STF73 the C-C (sp³) component was set to 284.8 eV.

Acknowledgements

We thank the FWF (Austrian Science Foundation) for financial support under the project F4503-N16 of the SFB F45 „Functional Oxide Surfaces and Interfaces“ (FOXSI). This work has been performed within the framework of the research platform „materials and nanoscience“ and the special PhD program “Reactivity and Catalysis” at the University of Innsbruck.

Keywords: lanthanum strontium ferrite • iron doped strontium titanate • oxygen vacancies • adsorption • dissolved hydrogen

- [1] J. Richter, P. Holtappels, T. Graule, T. Nakamura, L. J. Gauckler, *Monatsh. Chem.* **2009**, 140, 985–999.
- [2] Z. Gao, L. V. Mogni, E. C. Miller, J. G. Railsack, S. A. Barnett, *Energy Environ. Sci.* **2016**, 9, 1602–1644.
- [3] N. H. Menzler, F. Tietz, S. Uhlenbruck, H. P. Buchkremer, D. Stöver, *J. Mater. Sci.* **2012**, 45, 3109–3135.
- [4] L. Blum, L. G. J. de Haart, J. Malzbender, N. Menzler, J. Rammel, R. Steinberger-Wilchens, *J. Power Sources* **2013**, 241, 477–485.
- [5] L. Qingshan, Z. Yifeng, G. Wanbing, X. Cheng, G. W. Wei, *Int. J. Hydrogen Energ.* **2014**, 39, 10833–10842.
- [6] S.-D. Kim, J.-H. Yu, D.-W. Seo, I.-S. Han, S.-K. Woo, *Int. J. Hydrogen Energ.* **2012**, 37, 78–83.
- [7] Y. D. Lee, K. Y. Ahn, T. Morosuk, G. Tsatsaronis, *Energy* **2015**, 79, 455–466.
- [8] H. Yokokawa, H. Tu, B. Iwanschitz, A. Mai, *J. Power Sources* **2008**, 182, 400–412.
- [9] M. Ni, M. K. Leung, D. Y. Leung, *Int. J. Hydrogen Energ.* **2008**, 33, 2337–2345.
- [10] S. H. Jensen, C. Graves, M. Mogensen, C. Wendel, R. Braun, G. Hughes, Z. Gao, S. A. Barnett, *Energy Environ. Sci.* **2015**, 8, 2471–2479.
- [11] C. Graves, S. D. Ebbesen, M. Mogensen, *Solid State Ion.* **2011**, 192, 398–403.
- [12] S. D. Ebbesen, S. H. Jensen, A. Hauch, M. B. Mogensen, *Chem. Rev.* **2014**, 114, 10697–10734.
- [13] S. D. Ebbesen, M. B. Mogensen, *J. Power Sources* **2009**, 193, 349–358.
- [14] H. J. Freund, M. W. Roberts, *Surf. Sci. Rep.* **1996**, 25, 225–273.
- [15] H. Schulz, *Appl. Catal., A* **1999**, 186, 3–12.
- [16] K. Xie, Y. Zhang, G. Meng, J. T. S. Irvine, *Energy Environ. Sci.* **2011**, 4, 2218–2222.
- [17] K. Xie, Y. Zhang, G. Meng, J. T. Irvine, *J. Mater. Chem.* **2011**, 21, 195–198.
- [18] A. Hauch, S. D. Ebbesen, S. H. Jensen, M. Mogensen, *J. Electrochem. Soc.* **2008**, 155, B1184–B1193.
- [19] O. A. Marina, L. R. Pederson, M. C. Williams, G. W. Coffey, K. D. Meinhardt, C. D. Nguyen, E. C. Thomsen, *J. Electrochem. Soc.* **2007**, 154, B452–B459.
- [20] K. Eguchi, T. Hataishi, H. Arai, *Solid State Ion.* **1996**, 86–88, 1245–1249.
- [21] M. Ni, M. K. H. Leung, D. Y. C. Leung, Prospect of solid oxide steam electrolysis for hydrogen production, Lyon France, **2006**.
- [22] J. B. Goodenough, Y.-H. Huang, *J. Power Sources* **2007**, 173, 1–10.
- [23] B. A. Boukamp, *Nat. Mater.* **2003**, 2, 294–296.
- [24] M. A. Pena, J. L. G. Fierro, *Chem. Rev.* **2001**, 101, 1981–2017.
- [25] A. Demont, S. Abanades, E. Beche, *J. Phys. Chem. C* **2014**, 118, 12682–12692.
- [26] S. Dey, C. N. R. Rao, *ACS Energy Lett.* **2016**, 1, 237–243.
- [27] A. H. Bork, M. Kubicek, M. Struzik, J. L. M. Rupp, *J. Mater. Chem. A* **2015**, 3, 15546–15557.
- [28] X. Zhang, L. Ye, J. Hu, J. Li, W. Jiang, C.-J. Tseng, K. Xie, *Electrochim. Acta* **2016**, 212, 32–40.
- [29] X. Yue, J. T. S. Irvine, *J. Electrochem. Soc.* **2012**, 159, F442–F448.
- [30] S. Liu, Q. Liu, J.-L. Luo, *ACS Catal.* **2016**, 6, 6219–6228.
- [31] Y. Li, Y. Wang, W. Doherty, K. Xie, Y. Wu, *ACS Appl. Mater. Interfaces* **2013**, 5, 8553–8562.
- [32] G. Tsekouras, D. Neagu, J. T. S. Irvine, *Energy Environ. Sci.* **2013**, 6, 256–266.
- [33] G. Walch, A. K. Optiz, S. Kogler, J. Fleig, *Monatsh. Chem.* **2014**, 145, 1055–1061.
- [34] G. Tsekouras, T. S. Irvine, *J. Mater. Chem.* **2011**, 21, 9367–9376.

- [35] A. Nenning, A. K. Opitz, C. Rameshan, R. Rameshan, R. Blume, M. Hävecker, A. Knop-Gericke, G. Rupprechter, B. Klötzer, J. Fleig, *J. Phys. Chem. C* **2016**, 120, 1461-1471.
- [36] A. K. Opitz, A. Nenning, C. Rameshan, M. Kubicek, T. Götsch, R. Blume, M. Hävecker, A. Knop-Gericke, G. Rupprechter, B. Klötzer, J. Fleig, *ACS Applied Materials and Interfaces* **2017**, submitted
- [37] A. Rothschild, W. Menesklou, H. L. Tuller, E. Ivers-Tiffée, *Chem. Mater.* **2006**, 18, 3651–3659.
- [38] W. Jung, H. L. Tuller, *Adv. Energy Mater.* **2011**, 1, 1184–1191.
- [39] M. Kuhn, S. Hashimoto, K. Sato, K. Yashiro, J. Mizusaki, *Solid State Ion.* **2011**, 195, 7–15.
- [40] S. Kogler, A. Nenning, G. M. Rupp, A. K. Oppitz, J. Fleig, *J. Electrochem. Soc.* **2015**, 162, F317-F326.
- [41] R. Thalinger, A. K. Opitz, S. Kogler, M. Heggen, D. Stroppa, D. Schmidmair, R. Tappert, J. Fleig, B. Klötzer, S. Penner, *J. Phys. Chem. B* **2015**, 119, 11739–11753.
- [42] E. Ruiz-Trejo, J. T. S. Irvine, *Solid State Ionics* **2013**, 252, 157–164.
- [43] E. Ruiz-Trejo, J. T. S. Irvine, *Solid State Ionics* **2012**, 216, 36–40.
- [44] M. Grünbacher, E.-M. Köck, M. Kogler, B. Klötzer, S. Penner, *Phys. Chem. Chem. Phys.* **2016**, 18, 26873–26884.
- [45] R. Merkle, J. Maier, *Angew. Chem. Int. Ed.* **2008**, 47, 3874–3894.
- [46] D. Poetsch, R. Merkle, J. Maier, *Adv. Funct. Mater.* **2015**, 25, 1542–1557.
- [47] A. K. Opitz, A. Nenning, C. Rameshan, R. Rameshan, R. Blume, M. Hävecker, A. Knop-Gericke, G. Rupprechter, J. Fleig, B. Klötzer, *Angew. Chem.* **2015**, 54, 2628–2632.
- [48] T. Götsch, C. Praty, M. Grünbacher, L. Schlicker, M. Bekheet, A. Doran, A. Gurlo, M. Tada, H. Matsui, N. Ishiguro, B. Klötzer, S. Penner, *ECS Trans.* **2017**, 78, 1771–1780.
- [49] L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman, C. Nordling, *J. Phys. Chem. Solids* **1969**, 30, 1835.
- [50] C. D. Stinespring, J. C. Wormhoudt, *J. Appl. Phys.* **1989**, 65, 1733.
- [51] S. Contarini, S. P. Howlett, C. Rizzo, B. A. De Angelis, *Appl. Surf. Sci.* **1991**, 51, 177.
- [52] E.-M. Köck, M. Kogler, T. Götsch, B. Klötzer, S. Penner, *Phys. Chem. Chem. Phys.* **2016**, 18, 14333–14349.
- [53] E.-M. Köck, M. Kogler, T. Götsch, L. Schlicker, M. F. Bekheet, A. Doran, A. Gurlo, B. Klötzer, B. Petermüller, D. Schilchammer, N. Yigit, S. Penner, *Dalton Trans.* **2017**, 46, 4554–4570.
- [54] K. L. Smith, K. M. Black, *J. Vac. Sci. Technol. A* **1984**, 2, 744.
- [55] K. Petkov, V. Krastev, T. Marinova, *Surf. Interface Anal.* **1992**, 18, 487.
- [56] W. A. Brainard, D. R. Wheeler, *J. Vac. Sci. Technol.* **1978**, 15, 1801.
- [57] M. Setvin, C. Franchini, X. Hao, M. Schmid, A. Janotti, J. Kaltak, C. G. Van de Walle, G. Kresse, U. Diebold, *Phys. Rev. Lett.* **2014**, 113, 086402.
- [58] C. N. Berglund, H. J. Braun, *Phys. Rev.* **1967**, 164, 790-799.
- [59] S. Yoon, J. Dornseiffer, Y. Xiong, D. Grüner, Z. Shen, S. Iwaya, C. Pithan, R. Waser, *J. Eur. Ceram. Soc.* **2011**, 31, 773-782.