**Evidence for dissolved hydrogen in the mixed ionic-electronic conducting
perovskites $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ and $\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$**

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Abstract

Two mixed ionic-electronic conducting, Fe-containing perovskites were investigated regarding their reducibility in dry H_2 , namely lanthanum strontium ferrite (LSF4, $La_{0.6}Sr_{0.4}FeO_{3-\delta}$) and strontium titanium ferrite (STF3, $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$). Upon treatment under comparable reduction conditions, LSF4 is by far more affected by reduction and is reduced more deeply than STF3. Thermal treatments of fully oxidized or slightly reduced LSF4/STF3 at decreased O_2 partial pressure lead to spontaneous desorption of O_2 . Temperature-programmed desorption (TPD) spectra of H_2 reveal distinct differences in H_2 and H_2O desorption. A simple mass balance of H_2 reveals that oxygen vacancies formed on STF3 are more resilient towards O_2 re-oxidation compared to those on LSF4. The results also imply that substantial amounts of hydrogen are dissolved in the bulk of LSF4 or STF3. $4.9 \cdot 10^{-2}$ mol H_2 per mol LSF4 and $1.6 \cdot 10^{-2}$ mol H_2 per mol STF3 are incorporated if the specimens are heated in flowing/dry H_2 up to 550 °C and 612 °C, respectively. For LSF4 this equals about 13 hypothetical ML of H_2 and for STF3 about 20 hypothetical ML of H_2 . This conclusion is also supported by Fourier-transform infrared spectroscopy (FT-IR). FT-IR reveals water formation during static H_2 treatment of LSF4/STF3, which indicates perovskite reduction. Furthermore, both samples behave extraordinarily hydrophobic and no chemistry involving surface hydroxy groups was observed.

1. Introduction

Since the idea that greenhouse gases damage our environment was accepted, interest in low carbon and renewable power generation has grown massively.¹ Upon looking for alternatives, solid oxide cell (SOC) technology has gained more and more attention over the last years. SOCs are using an oxygen-ion conducting oxide-type electrolyte and are working at about 900 °C. In principle two modes are feasible: Solid oxide fuel cells (SOFC) efficiently generate electricity by oxidizing fuel¹, while solid oxide electrolyser cells (SOEC) consume electrical energy and moist CO₂ (co-electrolysis), forming industrially utilizable CO and H₂ e.g. useful for Fischer-Tropsch synthesis² or methanation. Therefore, SOECs might be the key for closing the renewable fuel-cycle.² Via reversible solid oxide fuel cell technology excessive electrical energy can be chemically stored (SOEC-mode) and buffer electric energy congestions by switching to SOFC-mode.³

As the economical interest in SOFC/SOEC grows, so does the motivation to improve these devices. Especially, the substitution of Ni-YSZ as an anode material in SOFC is aspired, as Ni-YSZ suffers from several drawbacks including carbon deposition, sulphur poisoning and nickel agglomeration.¹ In addition, Ni-YSZ undergoes irreversible degradation during high-temperature electrolysis (SOEC) of steam due to Ni mobility and migration during long term operation.³ This leads to decrease in Ni-YSZ contact area and loss of Ni percolation which result in an increasing ohmic resistance, especially at high current densities.⁴ This is a huge obstacle in efficiently using reversible solid oxide fuel cell technology.³ Due to their ease of production, flexibility and sheer variety of properties, perovskites are in this focus of research.¹

Fe-doping was shown to positively affect redox stability, electrical properties and electrochemical performance of SmBa_{0.5}Sr_{0.5}Co₂O_{5+δ}, used as cathode material in SOFC.⁵

Also Fe-substitution of Cr in (La,Sr)(Cr,Mg)O_{3-δ} resulted in better electrochemical performance compared to the Mn-substituted equivalent as SOFC anode.⁶

La-substituted (A-site-doped) SrTiO₃ is a promising material for anode uses in SOFCs due to its high electronic conductivity in reducing atmosphere, outstanding dimensional and chemical stability upon redox cycling and excellent sulfur and coking tolerances. Unfortunately, it shows poor ionic conductivity and electro-catalytic activity.⁷ Ferrites show a better performance in this respect. For example, an Fe⁰ species was shown to form on the surface of cathodically polarized LSF4.⁸ This Fe⁰ species leads to an enhanced activity for electrochemical water-splitting of the LSF4 surface.⁸

In general, LSF4 and STF3 are interesting alternatives, because they are so-called mixed ionic and electronic conductors (MIEC)^{9,10}, which is appreciated when used as electrode, but not for electrolyte applications (leak current). Also, LSF4/STF3 both exhibit a rich redox chemistry and considerable high chemical stability.^{11,12}

Some perovskites show proton conductivity at elevated temperatures (500 – 1000 °C), as it was first reported for SrCeO₃-based materials in 1981.¹³ Proton migration is determined by the Grotthuss mechanism and strongly depends on oxygen dynamics.¹⁴ However, the chemical characteristics of dissolved hydrogen are still under debate. Aside from protons – which is in accordance with chemical intuition – neutral hydrogen and even hydride species were proposed to exist in certain oxides.¹⁴ As for technical applications, high temperature proton conductors can be used as sensors, hydrogen separators, proton conducting membrane reactors, hydrogen isotopes separators, steam electrolyzers and fuel cells.¹³ Solid oxide fuel cells are of course more prominent than fuel cells that feature proton-conducting materials as electrolytes (H-SOFC).¹⁵ However, as the lowering of the operation temperature is very much aimed for, proton-conducting materials for electrolyte usage might become an interesting alternative to typically used YSZ compounds.^{14,15}

In this work, we aim at providing details on the hydrogen-perovskite interaction and to clarify the mechanisms of adsorption, incorporation and reactivity. For this purpose, two representative perovskite materials, $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF4) and $\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (STF3), with different reducibility and hence, different reactivity towards H_2 , are chosen as „model“ perovskite structures. Temperature-programmed reduction (TPR) and desorption (TPD) studies are, thus, coupled with *in situ* volumetric studies and Fourier-transform infrared spectroscopy (FT-IR) to correlate the surface and bulk reactivity with the quality and quantity of the associated number of oxygen vacancies.

2. Experimental

2.1. Perovskite materials

Lanthanum strontium ferrite, LSF4 ($\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$), with a particle size of less than $0.5\ \mu\text{m}$ was purchased from Sigma Aldrich. As strontium titanium ferrite, STF3 ($\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$), is not commercially available, it was synthesized via a solid state reaction: SrCO_3 , Fe_2O_3 and TiO_2 were used as raw materials. After the ingredients were mixed in appropriate amounts, they were ground manually for about 30 min. The powder was then heated to $800\ ^\circ\text{C}$ and held for 30 min for the carbonate to react. Subsequently, the temperature was increased to $1000\ ^\circ\text{C}$ (held for 5 h). Thereafter, the sample was ground again for 30 min and heated to $1250\ ^\circ\text{C}$ (held for 6 h). Finally, the sample was ground for 30 min one last time. BET surface areas were measured with a Quantachrome Nova 2000e surface and pore size analyzer. Before the BET measurement the perovskites were heated in air at $800\ ^\circ\text{C}$ overnight to account for sintering during the actual measurements. For LSF4 and STF3 surface areas of $4.8\ \text{m}^2\ \text{g}^{-1}$ and $0.4\ \text{m}^2\ \text{g}^{-1}$ were determined, respectively.

2.2. Volumetric Adsorption Apparatus

An all-quartz apparatus (ca. 33 ml) was used for experiments. The powder sample was filled into a quartz tube and fixed by quartz wool. Hence, the sample is only in direct contact to inert quartz. Moisture, formed and released from the specimen during H₂ treatment, was removed using a zeolite. The zeolite and the sample were arranged in a way, that either of them could be heated separately. The gas flow was regulated by flow controllers (MKS Instruments). The pressure in the reactor was measured via a Baratron pressure transducer (MKS Instruments), while a cold-cathode ionization gauge (Balzers) measured pressures in high vacuum (10^{-8} – 10^{-4} mbar). A Pfeiffer HiCube turbomolecular pumping station was used for high-vacuum pumping. A furnace from Linn High Therm was employed for heating. The temperature was measured via a Ni/CrNi thermocouple placed in direct vicinity to the sample. The reactor pressure and the sample temperature were controlled via the National Instruments “LabVIEW” software. For TPD, a quadrupole mass spectrometer (QMS) and software from Balzers was used (QMA 125; QME 125-9). Ionisation occurred by electron impact and a channeltron detector (accelerating voltage 1600 V) was used for quantitative analysis. H₂O/H₂/O₂ were quantified via externally calibrated mass signals at m/z 18.05/2.00/32.00.

An oxidation pre-treatment in flowing O₂ (0.8 ml s⁻¹ / ca. 1100 mbar O₂) was applied before each measurement. Residual moisture was removed from O₂ by an ethanol/liquid N₂ cooling trap (-110 °C). The sample was heated from room temperature to 800 °C in 30 min followed by an isothermal period at 800 °C for 30 min. Finally, the sample was allowed to cool down to room temperature in ca. 1 h. Afterwards, the zeolite was heated in high vacuum at 300 °C until the pressure decreased below 10^{-6} mbar.

Temperature-programmed reduction in H₂ (TPR)

At the start of the experiment a well-defined amount of dry H₂ (liquid N₂ cooling trap) was admitted in a separate, calibrated volume. From this separate volume the gas was expanded

into the reactor volume to a final pressure of ca. 100 mbar. Subsequently, the following temperature program was applied: The sample was heated from room temperature with $10\text{ }^{\circ}\text{C min}^{-1}$ to the final (maximum) temperature, which thereafter was held for 10 min. After this isothermal phase the sample cooled down with $10\text{ }^{\circ}\text{C min}^{-1}$ until ca. $200\text{ }^{\circ}\text{C}$. Because the sample was not actively cooled, the cooling rate decreased steadily below $200\text{ }^{\circ}\text{C}$. On the basis of the ideal gas equation, mbar H_2 was converted into mol H_2 . However, this required a calibration experiment with He as an inert gas in order to determine effective volumes depending on the sample temperature. For this He was expanded from a known volume into the reactor under otherwise identical experimental conditions. The consumed amount of H_2 was then normalized to the sample surface area for better comparison. For the static experiments, sample masses of 80 mg LSF4 and 170 mg STF3 were used.

Temperature-programmed reduction in flowing H_2

Some experiments involve pre-treatment of oxidized specimens with flowing H_2 (1 ml s^{-1}). Again, a liquid N_2 cooling trap ensured dry conditions when the sample was heated with $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to the desired maximum temperature. These maximum temperatures were then held for 1 h, after which the sample was allowed to cool down again. The system was evacuated as soon as the sample temperature decreased below $30\text{ }^{\circ}\text{C}$. For the flowing experiments, sample masses of 50 mg LSF4 and 110 mg STF3 were used.

Temperature-programmed desorption (TPD)

The reactor chamber was evacuated for 30 min and the (still slightly decreasing) intensities of the O_2 , H_2 and H_2O MS signals ($m/z = 32.00/2.00/18.05$, respectively) were recorded for base line correction. Subsequently, the sample was heated from room temperature to $800\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The temperature was held at $800\text{ }^{\circ}\text{C}$ for either 10 min or 1 h, depending

on the specific experiment. Also, in order to detect H₂O desorption, the zeolite was removed before TPD (only after H₂ TPR). The H₂ and O₂ MS signals were calibrated via a separate effusion experiment where H₂ or O₂ were pumped from the reactor chamber (without sample) via a capillary leak into the QMS chamber. This way, an effusion rate – calculated from absolute pressure decrease vs. time in the reactor chamber – was obtained in [mol s⁻¹] and correlated to the respective H₂/O₂ MS signal. Based on this calibration function, H₂/O₂ desorption rates were calculated from TPD MS signals. For H₂O calibration a slightly different approach was used, since H₂O adsorbs on glass. H₂O gas was admitted to a known volume and the pressure was detected immediately. Then, the vapor was pumped quantitatively into the QMS chamber. The H₂O signal was integrated and assigned to the initially admitted amount of H₂O. Furthermore, to ensure comparability, the quantified H₂, O₂ of H₂O desorption was normalized to the specimen surface.

O₂ titration measurements

For O₂ titration two types of experiments were performed. To quantify “elevated” temperature vacancy quenching only, initially, 200 mbar of dry O₂ was filled in the reactor volume. After the pressure ceased decreasing due to isothermal uptake at room temperature (not detected), the sample was heated linearly to 700 °C within 25 min. The temperature of 700 °C was held for 5 min. Subsequently, the sample was allowed to cool down to room temperature again in the residual O₂ atmosphere. The oxygen uptake was then calculated from the pressure difference (start/end). However, in this way only oxygen vacancies that can be oxidized at elevated temperatures were titrated. In order to quantify the integral amount of oxygen vacancies, O₂ was filled in a separate, known volume and then expanded to the reactor volume leading to an O₂ pressure of about 100 mbar. Therefore, the overall oxygen uptake is measured (“room temperature” uptake + “elevated temperature” uptake = integral uptake). Specific O₂ titration experiments below show the integral (after H₂ TPR / TPD) or the

“elevated“ oxygen uptake (after pre-reduction with flowing H_2 / TPD). In the present work the oxygen uptake is indicated as equivalents of O (not O_2) and from this point on referred to as O uptake.

In order to test the reducibility and to determine the amount of bound hydrogen, the following approach was used:

- 1.) H_2 TPR: integral H_2 uptake = oxygen vacancies + bound hydrogen
- 2.) TPD: amount of bound hydrogen = desorbed H_2 + desorbed H_2O
- 3.) O_2 titration: integral O uptake = “room temperature“ uptake + “elevated temperature“ uptake

 O_2 titration after H_2 TPR and TPD quantifies oxygen vacancies formed not only during H_2 TPR but also formed during TPD (H_2O desorption).
- 4.) Oxidation in flowing O_2 (1100 mbar): This step guaranteed full oxidation of the perovskite in case the O_2 titration is not quantitative. Also, this step is essential for self-control as is laid-out below.

This procedure can be used to determine the oxygen nonstoichiometry and the amount of bound hydrogen (“integral“). It enables self-control as the results can be mass-balanced (cf. Figure 1 / panel A). The equivalents of H_2 desorption and “integral“ O uptake add up to the integral H_2 uptake (TPR), provided the O_2 titration is quasi-quantitative. In this context the term quasi-quantitative is used to respect the fact, that O_2 titration was conducted with 100 mbar of O_2 (static) while subsequent re-oxidation was conducted with 1000 mbar O_2 (flowing). Since the oxygen nonstoichiometry (δ) depends on the oxygen pressure and the temperature – and this of course neglects kinetic considerations –, it is most likely that after re-oxidation δ is decreased to a certain degree. However, the mass balance shows whether this change of δ is negligible (quasi-quantitative) or not (not quantitative) and hence, whether O_2 titration is quantitative. This information is crucial for calculating the oxygen

nonstoichiometry. The in-principle evolution of the oxygen nonstoichiometry is shown in Figure 1 (panel B). δ_0 was estimated to be close to 0 for both perovskites on the basis of references^{10,11}. Kuhn *et al.*¹¹ showed that δ of LSF4 is close to 0 at 800 °C and 1 bar of O₂. As for STF3, the electrical conductivity of the material is p-type at 850 °C and 1 bar O₂, implying the Fe-doping is compensated mostly by electron holes not oxygen vacancies.¹⁰

The amount of bound hydrogen (“integral”) after H₂ TPR is derived from integration of subsequent TPD. H₂ and H₂O desorption defines the “integral” amount of bound hydrogen. It has to be emphasized, that H₂O desorption was not detected after pre-treatment in flowing H₂, because the zeolite was not removed before TPD. Hence, the “integral” amount of bound hydrogen after treatment in flowing H₂ is not known but only a minimum value since H₂O desorption is neglected. A more detailed discussion of the respective experiments is laid-out below.

Figure 1: Panel A shows the principle of H₂ mass-balance. Panel B shows the evolution of the oxygen nonstoichiometry during one experimental cycle.

2.3. Fourier-transform infrared spectroscopy (FT-IR)

An Agilent Cary 660 spectrometer equipped with a DTGS detector and a mid-infrared source was used to acquire FT-IR spectra. All spectra were recorded in transmission mode and are shown as absorbance vs. wavenumber. For *in situ/operando* sample analysis, a home-built reactor cell was used.¹⁶ All hot parts of the cell are constructed from quartz glass to ensure chemically inert conditions. The powder samples were pressed into pellets (diameter 10 mm). After inserting the sample, the cell was sealed with two ZnS windows. To clean the samples from remaining organic impurities and remove residual water, they were heated in dry, flowing O₂ up to 800 °C within 30 min followed by isothermic heating at 800 °C for 30 min. After this pre-treatment the cell was evacuated down to 5×10^{-7} mbar. H₂ experiments were conducted under static conditions. Initially, 100 mbar of dry H₂ were admitted to the cell. The heating and cooling rates were both 10 °C min⁻¹ and the maximum temperature was 600 °C and 800 °C for LSF4 and STF3, respectively. The maximum temperature was held for 10 min.

2.4. XRD

For XRD analysis a STOE XRD diffractometer (model STDI P) was used. The system uses Mo K_{α1} radiation (17.5 keV) and is equipped with a Mythen1K detector and a curved germanium (111) monochromator. Measurements were conducted in transmission.

3. Results and Discussion

The H₂ TPR uptake courses on LSF4 and STF3 are shown in Figure 2. The onset temperatures for major H₂ consumption are 250 °C and 300 °C for STF3 and LSF4, respectively. Before

that, H₂ consumption of LSF4 reaches a first plateau of ca. 2.7 μmol H₂ m⁻² at about 100 °C. For STF3 this plateau also occurs and reaches even 13 μmol H₂ m⁻². The plateaus are shown in the inset of Figure 2. For better interpretation, the maximum amount of adsorption sites for H₂ on LSF4 and STF3 was estimated using the BET surface area, as well as the molar mass and the density of the perovskites. It was assumed, that one H atom adsorbes on one surface unit cell and that the unit cells of LSF4 and STF3 are cubic. Based on this assumptions, the formerly mentioned initial H₂ uptake plateaus of LSF4 and STF3 correspond only to about 2 monolayers H₂. Having said that, the slight H₂ uptake between 100 °C to 200 °C does not necessarily correspond to H₂ chemisorption, but might as well indicate a “reactive“ reduction of near-surface regions of the perovskites. As will be shown later, FT-IR does not reveal any hydrogen chemisorption at 200 °C. La_{0.8}Sr_{0.2}FeO₃ (LSF2), for example, shows a similar pre-consumption of H₂ and this H₂ uptake at low temperatures was also explained via reduction of near-surface regions of the perovskite.¹⁷

However, after about 300 °C the H₂ consumption of LSF4/STF3 increases drastically. Subsequently, at about 520 °C, the H₂ consumption of STF3 slows down promptly. This might be due to two different reduction mechanisms being dominant in different temperature regimes and states of reduction of the perovskite. As this is a kinetic effect and the reactor is a closed system, the slowing down of hydrogen consumption appears to depend on the ongoing depletion of H₂, along with potentially delayed bulk oxygen supply. The TPR of LSF4 in Figure 2 depicts no such pronounced delay in the H₂ consumption. But the occurrence of a bend generally depends on the ratio of the amounts of H₂ and perovskite in the system.

Moreover, both samples consume H₂ during the isothermal period at a maximum temperature of 600 °C, as shown for the selected experiments below. Isothermal H₂ uptake is a general phenomenon occurring in all H₂ TPR experiments discussed later on and was more pronounced if the maximum temperature was kept lower. However, chemical equilibrium is not reached during the isothermal phase of the experiment. Subsequently, H₂ consumption

stagnates during the cooling phase. STF3 and LSF4 consume $1570 \mu\text{mol H}_2 \text{ m}^{-2}$ (ca. 300 monolayers H_2) and $327 \mu\text{mol H}_2 \text{ m}^{-2}$ (ca. 180 monolayers H_2), which indicates pronounced bulk reduction. Also, samples that were reduced with H_2 and re-oxidized at least once, tend to show a slightly higher integral H_2 consumption than fresh samples.

Figure 2: Temperature-programmed H_2 uptake of STF3 and LSF4. Heating from room temperature to 600°C was performed with a rate of $10^\circ\text{C min}^{-1}$. The maximum temperature was held for 10 min followed by a cooling period ($10^\circ\text{C min}^{-1}$). Initial H_2 pressure: ca. 100 mbar. Moisture was removed by a zeolite trap as discussed in the experimental section. The inset shows an enlargement of the temperature region between room temperature and 400°C (black box).

Figure 3 depicts the integral H_2 and O uptake in $[\text{mol m}^{-2}]$ (given as equivalents of O (not O_2)) during H_2 TPR and subsequent O_2 titration, respectively. Panel A shows the data regarding LSF4 and panel B for STF3. As can be seen, the H_2 and O uptake grows for LSF4/STF3 with increasing maximum temperature during TPR. Especially for STF3 a rather linear increase of H_2 uptake is observed in the TPR-treatment temperature region between 500°C and 800°C . Fresh samples seem to exhibit a slightly different behavior than samples that at least went once through the full experimental cycle (H_2 TPR $\rightarrow$ TPD $\rightarrow$ O_2 titration $\rightarrow$ O_2 re-oxidation).

This might be due to irreversible Fe-segregation (Fe-rods) on the surface of LSF4 upon reduction with dry H₂, as was discussed by Thalinger *et al.*^{9,18}. For STF3, similar Fe-segregation is not known, however, both perovskites seem to be predominantly terminated by SrO (STF3) and (La,Sr)O (LSF4) after H₂-reduction and water-gas shift or inverse water-gas shift reaction.⁹ It was shown by XRD that oxygen vacancies are formed in STF3 and LSF4 upon treatment in dry H₂. Furthermore, these bulk changes seem to be reversible – indicated by the fact that the shifting of the XRD reflexes is reversed when the specimens are re-oxidized in dry O₂.⁹ Since there seems to be no hysteresis effect on the perovskite bulk structure during redox cycling, the deviant behavior of fresh and re-used LSF4/STF3 samples observed in H₂ TPR and TPD is most likely due to irreversible changes of the surface.

Based on the quantification of H₂ TPR, TPD and subsequent O₂ titration the processed amounts of H₂ can be mass-balanced for the sake of self-control. In the latter case, the isothermal phase during the TPD experiments at 800 °C was 1 h to desorb H₂ quantitatively. The mass-balance of H₂ holds when the sum of the O equivalents from the O₂ titration (integral O uptake) and the H₂ desorption equals the integral H₂ uptake from the TPR experiment. Given the integral amount of desorbed H₂ (TPD) is negligible, compared to the equivalents determined from O₂ titration, Figure 3 reflects the H₂ balance adequately. For LSF4 (cf. Figure 3 / panel A), H₂ uptake and O uptake show a fairly good (ca. 5 % deviation) and certainly a better coincidence than for STF3 (cf. Figure 3 / panel B) (ca. 15 % deviation). This difference in the case of STF3 can only be explained by assuming the formation of oxygen vacancies during H₂ TPR and TPD that are not quantified adequately by O₂ titration, but can be only quenched during re-oxidation. Most likely this is due to the different conditions for O₂ titration (100 mbar O₂ / static) and O₂ oxidation (1100 mbar O₂ / flowing) (see also experimental section). The difference in O content of the perovskites when in equilibrium with 1100 mbar and 100 mbar of O₂ at 800 °C can be estimated from the results of Kuhn *et al.* For STF3¹² a value of about $0.2 \cdot 10^{-3}$ mol O m⁻² was found – for LSF4¹¹ about

$0.02 \cdot 10^{-3} \text{ mol O m}^{-2}$. Both values fit the discrepancy well. Also, a kinetic delay of vacancy quenching is not observed under O_2 titration conditions on STF3. This was determined by temperature programmed oxidation of STF3 (not shown). Therefore, O_2 titration is not the most reliable way to determine the change in oxygen nonstoichiometry ($\Delta\delta$). It seems more useful to calculate $\Delta\delta$ as a difference between the integral H_2 uptake (TPR) and the sum of integral H_2 and H_2O desorption (TPD) (cf. Figure 4). Since the oxygen nonstoichiometry at the start of the H_2 TPR (δ_0) is close to 0 (discussed in the experimental section), this way a correct oxygen nonstoichiometry δ after H_2 TPR is obtained, given hydrogen is removed from the perovskite quantitatively as H_2 and/or H_2O . However, the amount of additional oxygen vacancies formed during TPD adds only a small fraction. The majority of oxygen vacancies are formed during H_2 TPR.

Additionally, it should be emphasized that after H_2 TPR of LSF4 at 400°C , still O_2 desorption during subsequent TPD (cf. Figure 5) was observed, implying the perovskite is only reduced to a minor extent after H_2 TPR. Therefore, the O uptake exceeds the H_2 uptake at this point (cf. Figure 3 / panel A), when the obvious restriction for these experiment holds that not more oxygen vacancies can be formed during H_2 TPR as H_2 is apparently consumed. However, the mass balance also holds for this experiment. The O uptake shows the anticipated value, which is the sum of integral H_2 uptake (TPR) plus the integral O_2 desorption (TPD) in equivalents of O as well as the H_2O desorption during TPD. However, the amount of H_2O desorbed during this particular TPD was found to be negligible.

Figure 3: Integral H₂ and O uptake of LSF4 (panel A) and STF3 (panel B) as a function of the maximum temperature of the respective H₂ TPR. Experimental details of H₂ TPR and O₂ titration are described in the main text. Black framed points were acquired from fresh samples.

Figure 4: Oxygen nonstoichiometry (δ) of LSF4 and STF3 after H₂ TPR up to different maximum temperatures. The difference between the H₂ uptake (TPR) and the integral amount of desorbed H₂ and H₂O (TPD) was used to calculate δ . Measurements obtained from fresh samples are depicted separately (black frame).

H₂ TPR up to ca. 400 °C leaves LSF4 slightly reduced at best, as is indicated by the small integral H₂ uptake and still observable O₂ desorption during subsequent TPD (cf. Figure 5). Thereby, δ after H₂ TPR does reach 0.1 only. However, if 500 °C/600 °C are reached, respectively, upon performing the H₂ TPR, the oxygen nonstoichiometry rapidly increases to exceed 0.3, implying the perovskite is strongly reduced. Since 0.2 for absolute δ (La_{0.6}Sr_{0.4}FeO_{3- δ}) marks the limit of stability of LSF4¹¹, the results suggest the risk of partial destruction of the perovskite structure during reduction. XRD investigations of such a highly reduced LSF4 sample, on the other hand, prove that the perovskite structure, although distorted, remains intact after H₂ TPR up to 600 °C maximum temperature (a fresh LSF4 sample was prepared for XRD by heating in H₂ under TPR conditions up to 600 °C). However, it is important to emphasize, that the starting value for δ after re-oxidation in 1100 mbar flowing O₂ at 800 °C is not known accurately, even when it is estimated to be close to 0 (see experimental section).

STF3 is not as easily reduced as LSF4. Even after heating STF3 up to 800 °C during H₂ TPR, δ does only reach 0.13 (cf. Figure 4), which should be well within the structural limit of STF3 stability. For the STF3 perovskite, decomposition starts when the oxygen nonstoichiometry exceeds ca. 0.15.¹² As was emphasized before, also for STF3 δ after re-oxidation is assumed to be close to 0 (see experimental section). Again, the perovskite structure remains intact after H₂ TPR up to 800 °C, as was shown by XRD (a fresh STF3 sample was prepared for XRD by heating in H₂ under TPR conditions up to 800 °C).

Figure 5: TPD showing O₂ desorption from LSF4 after H₂ TPR (maximum temperature 400 °C). The specimen was heated with 10 °C min⁻¹ from room temperature to 800 °C, followed by an isothermal period at 800 °C for 1 h (not shown). An effusion experiment was used to calibrate the O₂ MS signal ($m/z = 32.00$), as described in the experimental section.

After H₂ TPR the zeolite was removed from the system to examine H₂ and H₂O desorption during TPD (cf. Figure 6 / 7, respectively). Dry Ar was used as an inert gas to backfill the TPR sample tube in order to avoid exposing the sample to O₂ and H₂O from ambient air while the reactor was open. Subsequent TPD shows H₂O as well as H₂ desorption, as will be discussed below. Hence, hydrogen can be bound by LSF4 and STF3 in such way, that molecular H₂ can desorb again.

The H₂ TPD spectra collected from fresh LSF4 (cf. Figure 6 / panel A) after H₂ TPR (500 °C and 600 °C maximum temperature) depict two distinct and well separated desorption rate maxima, which might indicate a certain difference with respect to binding energies of bound hydrogen species on LSF4 and STF3. The first desorption process reaches its rate peak in between 220 °C and 250 °C, which is comparable to STF3. The second peak in H₂ TPD of LSF4 (460 °C – 475 °C) is much more pronounced than it is for STF3.

The H₂ desorption rate from STF3 (cf. Figure 6 / panel B) reaches a first maximum at about 230 °C. The exact position depends on the maximum temperature formerly reached during the H₂ TPR. Aside from this rather weakly bonded hydrogen, a second hydrogen species seems to

be present after H₂ TPR, which manifest itself as a shoulder in the medium temperature region between 350 °C and 500 °C. Again, the exact position of its peak is shifting as the maximum temperature of the H₂ pre-treatment is varied. However, after H₂ treatment at about 500 °C the medium temperature H₂ desorption is clearly present and then is continuously overlapped by the low temperature desorption as the maximum treatment temperature increases. Also, a higher TPR maximum treatment temperature increases mainly the amount of weakly bonded hydrogen below 300 °C, not the the amount of H₂ desorbing in the medium temperature region.

However, the difference between fresh and re-used samples is distinct in the H₂ TPD spectra of LSF4 (cf. Figure 6 / panel A). While fresh LSF4 samples desorb H₂ after H₂ TPR (maximum H₂ treatment temperature 500 °C/600 °C), re-used samples exhibit a strongly reduced H₂ desorption capability (maximum H₂ treatment temperature 500 °C) to the point where no H₂ desorption is detected at all (maximum H₂ treatment temperature 600 °C). This is evidence for irreversible alteration of LSF4 during the first reduction/oxidation cycle. In accordance with Thalinger *et al.*¹⁸, this change most likely concerns the perovskite surface. Fresh and re-used STF3 specimens, however, do not exhibit such a drastically different H₂ desorption behavior, for H₂ desorption is always measurable. In addition, a fresh STF3 sample shows a lower integral H₂ desorption than a re-used STF3 sample which is exactly opposite to LSF4.

For both perovskites the H₂O desorption after H₂ TPR (cf. Figure 7) starts early during TPD. The H₂O TPD of LSF4 (cf. Figure 7 / panel A) shows a complex behavior. After an initial H₂O desorption peak, a shoulder occurs on the high-temperature side extending the H₂O desorption past 300 °C. According to the TPD data, it is assumed there is only one H₂O species present on STF3 (cf. Figure 7 / panel B) and at least two H₂O species adsorbed on LSF4 after H₂ TPR. Also, the higher the maximum H₂ TPR temperature is, the more H₂O desorbs from fresh LSF4 specimen. After H₂ TPR up to 400 °C almost no H₂O desorbes from

re-used LSF4. More H₂O desorbs from re-used LSF4 after H₂ TPR up to 500 °C / 600 °C, but the amounts essentially stay constant. For STF3 (cf. Figure 7 / panel B) basically all H₂O desorbs between 25 °C and 300 °C, indicating weakly bonded water. There seems to be an inverse relationship between the amount of desorbed H₂O and the maximum H₂ TPR temperature. The higher STF3 is heated during H₂ TPR, the less H₂O desorbs subsequently, although the effect is minor.

The integral amount of desorbed H₂ during TPD is plotted in Figure 8 (panel A). Besides the trend of increasing H₂ desorption with maximum TPR temperature (STF3) and the effect of the sample history on H₂ and H₂O desorption (especially LSF4), the discrepancy between the integral H₂ desorption from LSF4 and STF3 has to be emphasized. If the samples are treated during H₂ TPR up to 500 °C, eight times more H₂ per unit surface area desorbs from STF3 than from LSF4 (re-used samples). Aside from that, after H₂ treatment up to 600 °C no H₂ desorbs from LSF4, which is in strong contrast to STF3. However, this result can most likely be explained by the difference in the residual H₂ pressures at the end of H₂ TPR experiment. Accordingly, a low residual H₂ pressure after static TPR limits the total H₂ desorption to levels in the ML range. Under flowing H₂-conditions, the amount of desorbed H₂ becomes much larger, as will be shown later. Given the estimation for 1 ML (monolayer) of hydrogen adsorbed on STF3 (see above) we find that 2 - 3 ML of H₂ (depending on maximum H₂ TPR temperature) desorb from the specimen during TPD (cf. Figure 8 / panel A). For LSF4, however, less than 1 estimated ML of H₂ desorbs after H₂ TPR (500 °C maximum temperature) at most. After treating both perovskites in flowing H₂, the amount of absorbed H₂ is much higher (LSF4: ca. 12 times / STF3: ca. 10 times), as is discussed below.

Figure 8 / panel B shows the integral amount of H₂O that desorbed during TPD. Both perovskites show a weak trend with respect to the maximum temperature reached during previous H₂ TPR. Interestingly, these trends are inverse for LSF4 and STF3. While the amount of desorbed H₂O grows with maximum pre-reduction temperature for LSF4, it

decreases for STF3. The surface specific amounts of H₂O desorbed from LSF4/STF3 are rather different. However, for both perovskites a maximum amount of not more than 2 hypothetical ML of chemically bound water was found. The assumptions for this estimation can be found at the very beginning of this section. Furthermore, in the case of water it is assumed that one H₂O molecule occupies two binding sites. The results imply that for neither STF3 nor LSF4 a profound additional reduction during TPD occurs on behalf of H₂O desorption.

Table 1 presents an overview of the oxygen nonstoichiometry (δ) and the amount of bound hydrogen (y) of LSF4/STF3 after H₂ TPR experiments with different maximum temperatures. Additionally the ratio of bound hydrogen (y) and remaining oxygen ($3-\delta$) in LSF4/STF3 after H₂ TPR was calculated. The integral amounts of bound hydrogen were computed by adding up the integral amounts of desorbed H₂ and H₂O during TPD after H₂ TPR. LSF4 shows no clear tendency of the H/O ratio depending on the maximum H₂ TPR temperature, which is not true in the case of STF3. The increase of the H/O ratio on STF3 with respect to the maximum H₂ TPR temperature is not surprising since the oxygen nonstoichiometry and the integral amount of bound hydrogen (y) is increasing with growing H₂ TPR maximum temperatures. Comparing the H/O ratios of fresh and re-used LSF4 samples again shows a major difference. However, for STF3 the effect is not as pronounced. The O/H ratio of LSF4 is generally higher than that of STF3.

Figure 6: Quantified H_2 desorption after H_2 TPR from LSF4 (panel A) and STF3 (panel B). A H_2 -effusion experiment from the calibrated reactor volume was used to calibrate the H_2 signal ($m/z = 2.00$). The temperatures indicated in the figure are the maximum temperatures reached during H_2 TPR. Full lines show the H_2 desorption rate (left axis); broken lines depict the integral H_2 desorption (right axis). The specimens were heated from room temperature to 800 °C with a rate of 10 °C min^{-1} . An isothermal phase at 800 °C for 1 h followed (not shown).

Figure 7: Quantified H_2O desorption after H_2 TPR from LSF4 (panel A) and STF3 (panel B). The temperatures indicated in the figure are the maximum temperatures reached during H_2 TPR. Full lines show the desorption rate of H_2O (left axis). Broken lines show the integral H_2O desorption (right axis). The samples were heated from room temperature up to $800\text{ }^\circ\text{C}$ with a rate of $10\text{ }^\circ\text{C min}^{-1}$. An isothermal phase at $800\text{ }^\circ\text{C}$ for 1 h followed (not shown). 18.05 (m/z) was used to detect H_2O . Calibration is described in the experimental section.

Figure 8: Integral H_2 desorption (panel A) from LSF4/STF3 after TPR – 1 h isothermal heating at $800\text{ }^\circ\text{C}$ – as a function of the maximum treatment temperature during previous H_2 TPR. Panel B shows the integral H_2O desorption during the same TPD experiments. Values found for fresh samples are depicted separately (symbol with black frame).

Table 1: Amounts of bound hydrogen (y) and the oxygen nonstoichiometry (δ) as a function of the maximum TPR temperature. The amounts of bound hydrogen was calculated from the sum of H_2 and H_2O desorption during TPD after H_2 TPR. δ was calculated from the difference between integral H_2 uptake during H_2 TPR and H_2 / H_2O desorption during subsequent TPD. Additionally, the H/O ratio is given as $y / (3-\delta)$.

$La_{0.6}Sr_{0.4}FeO_{3-\delta}H_y$	$y \cdot 10^{-3}$	δ	H/O ratio $\cdot 10^{-3}$
Maximum TPR Temperature / °C			
398	0.38	0.103	0.13
498	9.9	0.316	3.7
506	8.1	0.329	3.0
598	8.0	0.351	3.0
604	6.0	0.348	2.3
501 (fresh)	11	0.309	4.1
599 (fresh)	16	0.328	6.0

$SrTi_{0.7}Fe_{0.3}O_{3-\delta}H_y$	$y \cdot 10^{-3}$	δ	H/O ratio $\cdot 10^{-3}$
Maximum TPR Temperature / °C			
509	2.8	0.109	0.97
600	3.3	0.115	1.1
695	3.4	0.122	1.2
803	3.6	0.129	1.3
507 (fresh)	2.6	0.100	0.90

Perovskite specimens were also treated in a H_2 -abundant environment (flowing conditions). The H_2 pressure was about 1000 mbar and therefore at least ten times higher than during H_2 TPR experiments (static conditions). As before, a zeolite was used to trap reaction-induced water. However, information regarding H_2 uptake as a function of temperature during reduction in H_2 stream is not accessible, as is information about H_2O desorption during subsequent TPD because the zeolite was not removed after H_2 treatment. The quantified H_2 TPD experiments are shown in Figure 9. Panel A shows data concerning LSF4 – Panel B STF3.

It is not surprising, that also these experiments show that the H_2 treatment temperature has some impact on the subsequent H_2 desorption properties. For example, if the H_2 treatment

temperature is 300 °C (LSF4/STF3), a subsequent TPD shows no H₂ desorption. A temperature of 388 °C on the other hand is high enough to adsorb hydrogen on both perovskites at least under dry and flowing conditions. Hence, a minimum temperature between 300 °C and 388 °C has to be exceeded during treatment for H₂ desorption to occur. Additionally, the higher a sample is treated temperature-wise, the more H₂ is desorbed during TPD at least for the tested H₂ treatment conditions (cf. Figure 9). A similar behavior exhibits LaNiO₃, which was explained by H₂ adsorption on exsolved Ni⁰.¹⁹ Metal segregation from LSF4 is also well known. Thalinger *et al.*¹⁸ tested LSF4 and found Fe⁰ segregation when treating the perovskite with flowing (1 ml s⁻¹), dry H₂ at 600 °C. Also, Kuhn *et al.*¹¹ showed that Fe⁰ is formed when the perovskite starts to decompose at low oxygen partial pressures and elevated temperatures.

It has not yet been clarified how hydrogen is bound by the LSF4 and STF3. However, no evidence has been found in FT-IR (see below) that hydrogen actually adsorbs on metal centers and/or surface oxygen, as it was found for example on β-Ga₂O₃.²⁰ The amounts of desorbed H₂, however, do exceed the hypothetical single ML of hydrogen by factors of ~12 (LSF4) and ~20 (STF3) at most (flowing, dry reduction) (cf. Figure 10), which indicates that there are not enough binding sites for these amounts of H₂ on both perovskites. Since H₂O desorption was not detected, these amounts give a minimal amount for bound hydrogen on LSF4/STF3. The results imply that hydrogen is dissolved in the perovskite bulk.

It is important to emphasize, that different conditions were used during H₂ TPR and treatment with flowing H₂, which of course is reflected in the TPD spectra. For example, TPD exhibits no H₂ desorption but O₂ desorption instead after heating LSF4 up to 398 °C under H₂ TPR conditions, which is not the case after reducing LSF4 at 388 °C in flowing H₂. In other words, the depth of reduction most likely not only depends on temperature, but also on the final H₂ pressure after flowing or static (TPR) conditions.

LSF4 shows a H₂ desorption pattern after pre-reduction in flowing/dry H₂ (cf. Figure 9 / panel A) similar to the TPD spectrum after H₂ TPR (cf. Figure 6 / panel A). A main desorption peak with its maximum at about 190 °C occurs. The peak temperature seems to be independent from the H₂ treatment temperature. However, more weakly adsorbed hydrogen desorbs in the region between 25 °C – 400 °C, if LSF4 is treated at higher temperatures during reduction. The desorption features above 400 °C are quite complex. Seemingly, there are at least two H₂ desorption processes occurring between 400 °C and 800 °C. Additionally, the H₂ desorption rate is sometimes persisting during the isothermal phase of the TPD experiment at 800 °C implying the desorption process has not yet finished. Also, the H₂ desorption from both perovskites after flowing and dry reduction with H₂ is basically non-zero in the temperature region between room temperature and 800 °C (cf. Figure 9). This may suggest a diffusion controlled desorption process extending over a very wide temperature range. However, a higher H₂ pressure and H₂ abundance during LSF4 pre-treatment yields quantitatively and qualitatively different H₂ TPD spectra, than obtained after H₂ TPR (cf. Figure 6 / panel A), especially between 350 °C and 800 °C (TPD temperature).

After H₂ treatment of STF3 at ca. 300 °C the sample does not desorb H₂ but O₂ (cf. Figure 11) indicating STF3 is only weakly reduced at best. As anticipated, more O₂ desorbs from STF3 when it is heated up to 296 °C (350 μmol O₂ m⁻²) than when the maximum pre-reduction temperature reaches 310 °C (250 μmol O₂ m⁻²), showing the increase of the reduction degree when treatment temperature is raised by only 14 °C. Again the BET surface area, the molar mass of STF3 as well as its density was used to estimate the hypothetical coverage of 1 ML of O₂ on STF3. It was assumed, that one O atom adsorbes on one surface unit cell and that the unit cells of STF3 are cubic. This estimation indicates that after H₂ treatment at 296 °C and 310 °C more than 50 ML of O₂ desorb during TPD. Hence, it is clear that we observe the desorption of bulk oxygen. Again, H₂ desorption was measurable after reduction with flowing/dry H₂ at 388 °C for the first time. The desorption behavior of H₂ is rather complex,

as there are no especially striking features except of being also very broad (cf. Figure 9 / panel B). Therefore, they appear different from the H₂ TPD spectra obtained after H₂ TPR (cf. Figure 6 / panel B).

Figure 9: H₂ desorption after H₂ treatment under flowing and dry conditions. Panel A depicts TPD spectra collected from LSF4, panel B from STF3. An effusion experiment was used to calibrate the H₂ MS signal ($m/z = 2.00$). The temperatures indicated in the figure are the maximum temperatures reached during H₂ pre-treatment. Full lines show the desorption rate (left axis); broken lines show the integral desorption (right axis). The specimens were heated from room temperature to 800 °C with 10 °C min⁻¹. An isothermal phase at 800 °C for 10 min followed (not shown). An H₂O-absorbing zeolite was present during TPD (between sample and QMS), hence the H₂O signal is not shown.

Figure 10: Integral H₂ desorption plotted as [mol m⁻²] and ML equivalents from LSF4/STF3 (TPD) after treatment in flowing H₂ at distinct maximum temperatures. The specimens were heated during TPD with 10 °C min⁻¹ from room temperature to 800 °C, followed by an isothermal phase at 800 °C for 10 min. Panel A shows data concerning LSF4 – panel B STF3.

Figure 11: O₂ desorption from STF3 after a mild H₂ treatment (flowing, dry conditions up to ca. 300 °C). An effusion experiment was used to calibrate the O₂ MS signal (m/z = 32.00).

The temperatures indicated in the figure are the maximum temperatures reached during H₂ pre-treatment. Full lines show the desorption rate (left axis); broken lines show the integral desorption (right axis). The specimens were heated from room temperature to 800 °C with 10 °C min⁻¹. An isothermal phase at 800 °C for 10 min followed.

After sample treatment in flowing dry H₂ and subsequent TPD the “elevated temperature” O uptake was measured (cf. Figure 12). Ca. 200 mbar of dry O₂ was expanded into the reactor volume. After the pressure ceased decreasing due to room temperature oxygen uptake (not detected), the sample was heated up to 700 °C and allowed to cool down again. Hence, only oxygen vacancies oxidized at elevated temperatures were titrated (elevated temperature vacancy quenching). The trends are extractable from Figure 12. This explains, also, why after streaming H₂ treatment / TPD, less O₂ was consumed than after H₂ TPR / TPD, where the integral O uptake (oxygen vacancies + oxygen adsorption) was measured (cf. Figure 3). Also, for STF3 it is questionable whether the O₂ titration is quantitative as was shown in Figure 3 / panel B.

The higher the pre-reduction temperature, the more O₂ is consumed subsequently, which is a strong indication that more oxygen vacancies are formed if the sample is heated higher. For LSF4 the increase of the maximum treatment temperature from 300 °C to 390 °C leads to a rapid growth of O uptake before reaching a plateau at 440 °C. Past 500 °C the oxygen uptake starts to increase again. STF3 does not exhibit such a rapid increase of the O uptake, which probably is due to the already mentioned O₂ desorption after H₂ treatment at ca. 300 °C during TPD, which means the perovskite undergoes a temperature induced thermal O₂ loss. The additional oxygen vacancies obviously increase the subsequent O uptake. Comparing the integral amount of desorbed O₂ from STF3 (cf. Figure 11) with the O₂ uptake (cf. Figure 12), we see a clear difference: the amount of desorbed O₂ is smaller than the O₂ uptake. This

means that already during H₂ treatment of STF3 at about 300 °C the perovskite becomes additionally reduced to some extent.

Figure 12: O₂ titration after H₂ treatment (flowing / dry) at distinct temperatures and TPD. The specimen were heated in 200 mbar dry O₂ up to 700 °C and allowed to cool down to room temperature again. Only oxygen vacancies quenched at temperatures above room temperature were quantified and O₂ uptake at room temperature is not included.

FT-IR spectroscopy was applied to extract information regarding the surface chemistry of LSF4/STF3 when treated with H₂ at elevated temperatures. The perovskite specimens were treated with 100 mbar of H₂ (static conditions). Eventually formed reaction water remained in the FT-IR cell, since there was no zeolite present. Figure 13 exhibits FT-IR measurements of LSF4 (panel A) and STF3 (panel B) after H₂ treatment up to 600 °C and 800 °C, respectively. FT-IR spectra were acquired at selected temperatures during heating in 100 °C steps. In addition one spectrum was measured at room temperature after the temperature program was finished (RT cooling) and another spectrum was measured subsequently at room temperature after the reactor cell was pumped down to below 10⁻⁵ mbar (RT pumping), in order to remove gas phase signals.

In the temperature region between room temperature and 400 °C (heating phase) no water formation or evidence for reactivity related to surface hydroxy groups was observed in FT-IR

spectra. H₂ TPR however shows some H₂ uptake in this temperature region (cf. Figure 2 / inset) indicating the reduction of surface near regions of the perovskites as was discussed above. This indicates that the reduction of the perovskites – at least in the temperature region between room temperature and 400 °C – does not lead to notable change in the population of surface hydroxy groups. Of course this includes the possibility, that there are no stable surface hydroxy groups on LSF4/STF3, which is most likely. The FT-IR results of both perovskites show the formation of notable amounts of water starting in between 400 °C and 500 °C during the heating phase which is in good agreement with H₂ TPR experiments (cf. Figure 2). This can be deduced from the apparently “noisy” signals in the region between 4000 cm⁻¹ and 3500 cm⁻¹ (rotational broadening of symmetric and antisymmetric stretching modes of H₂O_(g)). In this regard, the formation of water indicates the beginning bulk reduction of LSF4/STF3.

Furthermore, the formed water vapour can be evacuated quantitatively, suggesting that there is no significant interaction between the perovskite surface and the reaction water. Both, LSF4 and STF3, behave quite hydrophobic, which is in strong contrast to oxides like yttria-stabilized zirconia (YSZ) or Y₂O₃.²¹ From our TPD experiments (see above) it is clear that hydrogen is bonded by LSF4/STF3, but obviously in a spectroscopically invisible form. The absence of reactive hydroxyl groups is also an indication for dissolved hydrogen. Instead of surface hydroxyl groups the reduced perovskites might be OH defective (OH_i / Kröger-Vink notation).¹⁴

Figure 13: FT-IR spectra of LSF4/STF3 when treated with 100 mbar H₂ under static conditions. Reaction-water formed remained in the system. FT-IR spectra were acquired during the heating phase of the experiment at distinct temperatures. One spectrum was measured at room temperature after the temperature program was finished (RT cooling). A second spectrum was measured at room temperature after pumping the system down to below 10⁻⁵ mbar (RT pumping). Panel A shows the spectra regarding LSF4 – the specimen was heated up to 600 °C maximum temperature; panel B depicts the spectra regarding STF3 – the specimen was heated up to 800 °C maximum temperature.

5. Conclusions

In the present study two Fe-containing perovskites – La_{0.6}Sr_{0.4}FeO_{3-δ} (LSF4) and SrTi_{0.7}Fe_{0.3}O_{3-δ} (STF3) – were investigated with respect to their H₂-reduction properties. LSF4 is an extension of the simple perovskite LaFeO₃ (A site doping with Sr²⁺), whereas STF3 is obtained by partial substitution of Ti by Fe in SrTiO₃ (B site doping). Both perovskites are mixed ionic electronic conductors (MIEC) and are therefore investigated for H₂-related applications in SOFC technology.

Temperature programmed reduction (TPR) was used to investigate the reducibility of LSF4 and STF3 by H₂. STF3 shows a higher surface specific H₂ uptake than LSF4. However, this is

due to very different BET surface areas of LSF4 and STF3 and the results imply that actually LSF4 can be reduced more deeply than STF3. Surface-near (RT to ca. 300 °C) and deeper bulk reduction (ca. 300 °C to maximum temperature) could be distinguished in H₂ TPR. No H₂ adsorption was observed in FT-IR in the temperature region between room temperature and 400 °C. Temperature-programmed desorption experiments revealed H₂, H₂O and – if the perovskites are only minorly reduced – O₂ desorption. Generally, a higher treatment temperature, a higher H₂ pressure and flowing/dry conditions during sample treatment yields a higher integral amount of desorbed H₂. However, the history of sample treatment and H₂ concentration during H₂ treatment affects desorption properties as well, as was shown especially for LSF4. Also, the amount of desorbed H₂ during TPD in combination with the estimated ML of hydrogen bound to STF3/LSF4 indicates the presence of dissolved hydrogen, especially if the specimen are treated under flowing H₂ conditions. We found that at least 49 μmol H₂ per mol LSF4 ($2.3 \cdot 10^{-5}$ mol H₂ m⁻²) are bound after treatment in flowing /dry H₂ at 550 °C. This amount equals about 13 hypothetical ML of H₂ on LSF4. STF3 dissolves at least 16 μmol H₂ per mol STF3 ($11 \cdot 10^{-5}$ mol H₂ m⁻²) when heating up to 612 °C in flowing/dry H₂ which equals about 20 hypothetical ML of H₂ on STF3. FT-IR measurements agree with this conclusion, since aside from gaseous water formation during H₂ treatment no surface water chemistry whatsoever could be observed on these very hydrophobic perovskites.

A detailed mass balance of H₂ implies that O₂ titration of oxygen vacancies in reduced LSF4 and STF3 is not quantitative, especially for STF3. Hence, the data show that STF3 is not only harder to reduce by H₂ than LSF4, but also oxidation of oxygen vacancies by O₂ is somewhat more inhibited on STF3. Nevertheless, both perovskites consume more O₂ if the samples are treated with H₂ at increasing temperatures. However, it seems not reliable to use the O uptake for determination of the change in oxygen nonstoichiometry caused by H₂ treatment ($\Delta\delta$). Therefore, $\Delta\delta$ after H₂ TPR was better estimated from both the integral H₂ uptake (TPR) and

integral $\text{H}_2/\text{H}_2\text{O}$ desorption (TPD). It was found that δ of LSF4 exceeds 0.3 after H_2 TPR at 500 °C and 600 °C (maximum temperature). XRD of a such a highly reduced LSF4 sample evidenced no structural decay or Fe^0 exsolution. Also, STF3 seems to remain stable even after H_2 TPR up to 800 °C, at least what can be deduced from δ . Again, XRD showed an structurally intact perovskite structure for a maximum reduced STF3 specimen. This further confirms that dissolved hydrogen species in the bulk crystal structures are generated via H_2 reduction.

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Graphical Abstract

Evidence for dissolved hydrogen in mixed ionic-electronic conducting A- and B-site substituted perovskites