

Designing Iron-Based Layered Perovskite Oxides with Optimized Oxygen Storage Performance and Structural Stability

*Taiki Kosuge¹, Chika Yamazoe², Shogo Kawaguchi³, Shintaro Kobayashi³, Naoto Nagata⁴,
Masaki Azuma^{5, 1, 6}, Saburo Hosokawa^{2*}, and Takafumi Yamamoto^{1, 7*}*

¹Laboratory of Materials and Structures, Institute of Integrated Research, Institute of Science
Tokyo, Yokohama, Kanagawa, 226-8501, Japan

²Faculty of Materials Science and Engineering, Kyoto Institute of Technology, Sakyo-ku,
Kyoto, 606-8585, Japan

³Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Sayo-gun, Hyogo, 679-5198,
Japan

⁴Higashifuji Technical Center, Advanced Material Engineering Div., Toyota Motor
Corporation, 1200, Mishuku, Susono, Shizuoka 410-1193, Japan

⁵Research Center for Autonomous Systems Materialogy (ASMat), Institute of Integrated
Research, Institute of Science Tokyo, Yokohama, Kanagawa, 226-8501, Japan

⁶Kanagawa Institute of Industrial Science and Technology, Ebina, Kanagawa, 243-0435, Japan

⁷Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502,
Japan.

KEYWORDS: Oxygen storage material, Perovskite oxide, Time-resolved XRD measurement,
Topochemical reaction

ABSTRACT

Oxygen storage materials (OSMs) play a significant role in automotive catalyst and oxygen separation systems. Here, we examine the oxygen storage ability of Ruddlesden-Popper-type layered perovskites $A_{n+1}Fe_nO_{3n+1-\delta}$ ($A = \text{Sr, La}$) using temperature-programmed reduction with H_2 (H_2 -TPR) and thermogravimetry (TG) measurements. As a result, we found that oxygen storage capacity exhibited an increasing trend with the number of perovskite layers. Furthermore, time-resolved X-ray diffraction measurements revealed reaction dynamics during the redox reactions, visualizing the process of the phase changes and reaction times. Among the compounds we examined, $LaSr_3Fe_3O_{10-\delta}$ with triple perovskite layer ($n = 3$) has high structural stability and good oxygen storage characteristics. From this perspective, we propose a perovskite-based OSM design guideline to combine oxygen-storage perovskite layers and robust rock-salt layers. These findings provide new insights into the design of novel OSMs.

1 INTRODUCTION

2 Oxygen storage materials (OSMs) can reversibly undergo redox processes in response to
3 environmental changes, such as fluctuations in atmosphere or temperature. Due to this feature,
4 OSMs are crucial in various applications, including automotive catalyst system^{1, 2, 3}, oxygen
5 separation^{4, 5, 6}, and chemical looping reactions^{7, 8, 9}. Developing high-performance OSMs is
6 essential for advancing sustainable technologies, especially in improving energy efficiency.

7 In practical applications like automotive catalysis, materials are often exposed to rapidly
8 changing gas environments, with atmospheric switching occurring at frequencies up to about
9 5 Hz. Under these conditions, high oxygen storage capacity, fast response, and excellent
10 reversibility are crucial. To enable efficient and reversible oxide ion exchange, oxygen storage
11 materials (OSMs) need to release and store oxide ions without substantial alteration of their
12 original structural framework. For example, the CeO₂-ZrO₂ system is a widely used OSM as a
13 cocatalyst of a three-way catalytic converter for automotive exhaust purification^{2, 10, 11}. The
14 CeO₂-ZrO₂ system exhibits a topochemical reaction, where the Ce/Zr cationic sequence is
15 maintained during redox processes¹⁰. These reactions are inherently fast (≤ 10 s at 500°C) due
16 to the absence of cation rearrangement.

17 Oxygen-deficient perovskite oxides with the general formula ABO_{3- δ} (δ represents oxygen
18 vacancies) have attracted attention as promising OSMs because of their high oxygen storage
19 capacity⁷. In these materials, a fast oxygen release/absorption rate is often achieved by ordering
20 oxygen defects in addition to the topochemical reaction. Motohashi et al. investigated the
21 oxygen-deficient perovskite Ca₂AlMnO_{5+ δ} and reported the large oxygen storage capacity¹².
22 Ca₂AlMnO₅ has a brownmillerite structure, which consists of alternating stacking of MnO₆
23 octahedral layers and AlO₄ tetrahedral layers. This structure is a defect-ordered perovskite in
24 which every other BO₆ octahedral layer is replaced by a corner-sharing BO₄ tetrahedral layer,

1 forming ordered vacancies along the $[110]_p$ direction. These $[110]_p$ defects are associated with
2 enhanced oxygen mobility of $\text{Ca}_2\text{AlMnO}_5$ ¹³.

3 Sr-Fe-based perovskite $\text{SrFeO}_{3-\delta}$ also has a defect-ordered structure depending on the
4 amount of oxygen defects¹⁴. $\text{SrFeO}_{3-\delta}$ exhibits cyclic redox reactions between the cubic phase
5 ($\delta \sim 0.25$) and the brownmillerite phase ($\delta = 0.5$) at 500°C (**Figure 1a**). Since it can be reduced
6 at low temperatures, its application in air separation and chemical looping has already been
7 investigated^{15, 16, 17}. However, the disadvantage of $\text{SrFeO}_{3-\delta}$ for automobile gas purification is
8 its structural instability in a reducing atmosphere at high temperatures. In reducing atmospheres
9 above 700°C, the structural framework cannot be maintained and decomposes due to the
10 reduction of Fe ions to metallic Fe. Therefore, it is unsuitable for automotive catalysts that are
11 exposed to high-temperature reducing atmospheres of nearly 1000°C¹⁸.

12 To address this issue, we have investigated the layered perovskite oxide $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ and
13 found that it has improved thermal stability under high-temperature reduction conditions¹⁸.
14 $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ has the Ruddlesden-Popper (RP)-type layered perovskite structure with intergrowth
15 of double perovskite and rock-salt layers (**Figure 1a**). $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ has superior thermal stability,
16 but its oxygen storage capacity is inferior to $\text{SrFeO}_{3-\delta}$, while Pd-loading¹⁹ improves oxygen
17 storage properties. Therefore, further structure optimization is required to obtain optimal
18 oxygen storage material.

19 This study focuses on the oxygen storage ability depending on the number of perovskite
20 layers in RP-type layered perovskites $\text{A}_{n+1}\text{Fe}_n\text{O}_{3n+1-\delta}$ ($\text{A} = \text{Sr}, \text{La}$). $\text{SrFeO}_{3-\delta}$, $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$, and
21 $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ are $n = \infty$ and 2, 3 series, respectively, and show topochemical oxygen
22 release/storage capability. Here, we report the superior oxygen storage capacity and the
23 stability under high-temperature reduction conditions for RP-type $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$. We also
24 investigated the reaction dynamics during the fast oxygen intercalation/deintercalation

processes for Pd-supported $A_{n+1}Fe_nO_{3n+1-\delta}$ using in-situ synchrotron time-resolved X-ray diffraction (XRD) techniques. Notably, Pd/LaSr₃Fe₃O_{10- δ} exhibited a fast reaction time in the oxidation and reduction processes. Hence, LaSr₃Fe₃O_{10- δ} has the advantageous properties of both Sr₃Fe₂O_{7- δ} and SrFeO_{3- δ} . Our findings provide the structural design of efficient OSM by combining structural blocks with separate roles.

RESULTS

We compared the oxygen storage ability of Pd-loaded Sr-Fe-based layered perovskite oxides, Pd/Sr₃Fe₂O_{7- δ} ($n = 2$), Pd/LaSr₃Fe₃O_{10- δ} ($n = 3$), and Pd/SrFeO_{3- δ} ($n = \infty$). These compounds are RP-type layered perovskites $A_{n+1}Fe_nO_{3n+1-\delta}$, where n corresponds to the thickness of the perovskite blocks (**Figure 1a**). All of these phases are capable of topotactic redox reactions. In Sr₃Fe₂O_{7- δ} , the oxygen atom at the center of the two perovskite blocks is removed during reduction, leading to a change in the Fe coordination environment from an FeO₆ octahedron to an FeO₅ pyramid. For SrFeO_{3- δ} , reduction induces ordered defects along the [110]_p direction, resulting in a brownmillerite-type structure characterized by alternating layers of FeO₄ tetrahedral coordination and FeO₆ octahedral coordination. In the case of LaSr₃Fe₃O_{10- δ} , reduction introduces defects in the central perovskite block. The defects align along the [110]_p direction, similar to those in SrFeO_{3- δ} . In this way, redox reactions occur within the perovskite block, and this part contributes to oxygen storage. In addition, the improvement in reduction tolerance in Sr₃Fe₂O_{7- δ} suggests that the presence of the rock-salt layer has the effect of increasing reduction resistance in the high-temperature region¹⁸.

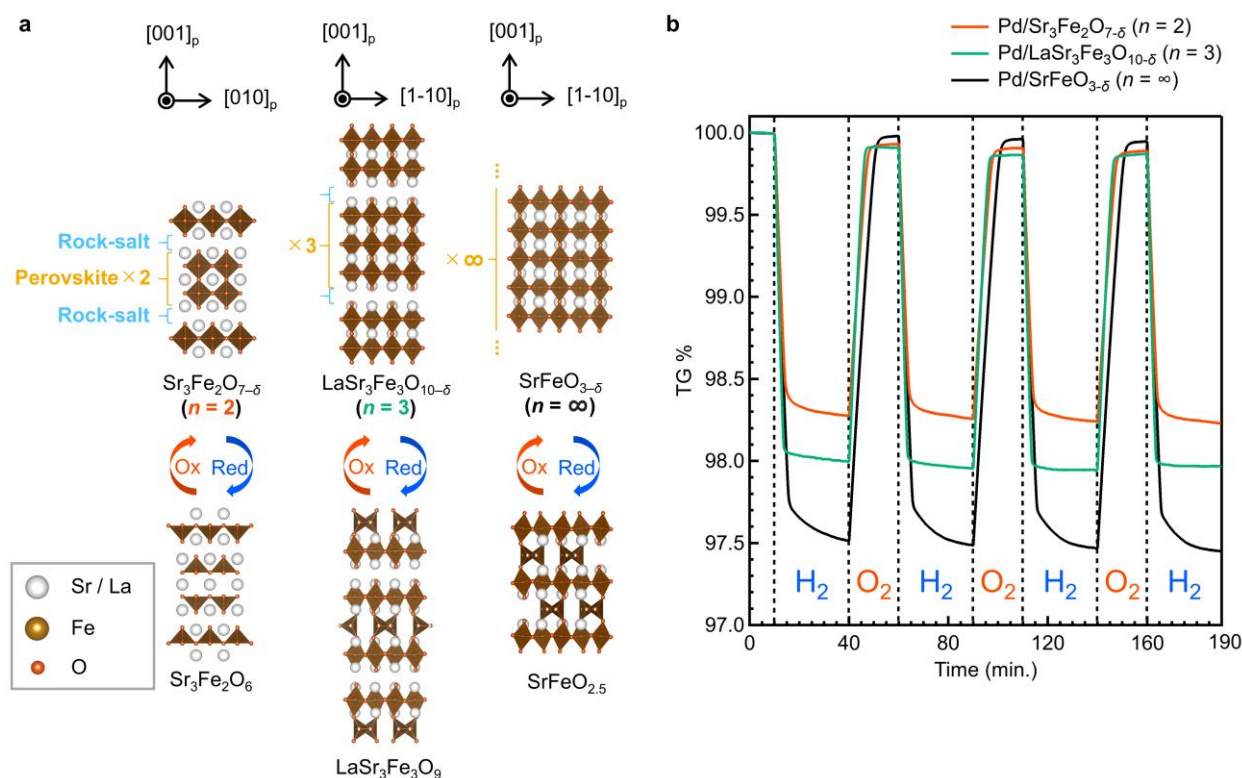


Figure 1. a) Schematic images of Sr-Fe-based layered perovskite redox reaction. White, brown, and red atoms represent Sr / La, Fe, and O, respectively. Crystal structures were depicted by using the *VESTA3* program²⁰. b) Isothermal oxygen-storage capacity profiles of Sr-Fe-based layered perovskites at 500°C. The red, green, and black lines represent $\text{Pd}/\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$, $\text{Pd}/\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$, and $\text{Pd}/\text{SrFeO}_{3-\delta}$, respectively. The gas atmosphere around the sample was switched between 2% H₂/Ar (30 min) and 2% O₂/Ar (20 min) alternately.

Sr-Fe-based samples with particles ranging from a few hundred nanometers to a few micrometers in size (**Figure S1**) were synthesized by the polymerization complex method. Pd loading was then performed using the impregnation method. Transmission electron microscopy measurements of the $\text{Pd}/\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ sample after an oxidation-reduction cycle at 500°C revealed that a few nanometer-sized Pd particles are dispersed on the surface (**Figure S2**), which is roughly consistent with $\text{Pd}/\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ reported previously¹⁹.

In order to evaluate the oxygen storage capacity of the Pd-loaded Sr-Fe-based samples, cyclic thermogravimetry (TG) measurements were performed. The atmosphere around the sample was alternately switched between H₂/Ar and O₂/Ar, and the weight changes associated with the reaction were measured. As shown in **Figure 1b**, all samples show good and reversible oxygen storage capacity. Pd/SrFeO_{3-δ} has the largest oxygen storage capacity of 2.5 wt%, and Pd/LaSr₃Fe₃O_{10-δ} and Pd/Sr₃Fe₂O_{7-δ} show capacities of 2.0 wt% and 1.7 wt%, respectively. As expected, the oxygen storage capacity is in the order of the proportion of perovskite blocks in the structure. The valence of iron in Sr₃Fe₂O_{7-δ}, LaSr₃Fe₃O_{10-δ}, and SrFeO_{3-δ} at 500°C oxidation states are estimated to be about +3.5, +3.6, and +3.6, respectively. These values are consistent with previous reports under room temperature conditions (Sr₃Fe₂O_{6.64}²¹: +3.64, LaSr₃Fe₃O_{9.9}²²: +3.6, SrFeO_{2.875}¹⁴: +3.75).

To assess the structural robustness at high temperatures, we carried out H₂-TPR measurements (**Figure 2a**). The sample was brought to 900°C at a heating rate of 5°C/min in a 2% H₂/Ar flow. The amount of hydrogen consumption during the reaction was estimated using a thermal conductivity detector. In the low-temperature region, a steep peak corresponding to hydrogen consumption was observed around 100°C in all three samples. This indicates that all samples have good oxygen release characteristics under low-temperature regions. However, in Pd/SrFeO_{3-δ}, the intensity gradually increased with temperature above 650°C, corresponding to the decomposition, whereas no clear sign of decomposition was observed in Pd/Sr₃Fe₂O_{7-δ} and Pd/LaSr₃Fe₃O_{10-δ}. Powder XRD measurements clearly showed the difference in the robustness of the three samples (**Figure 2b**). After annealing in 5% H₂/Ar at 900°C for 3h, Pd/SrFeO_{3-δ} fully decomposed into metallic iron and Sr-containing compounds, while Pd/Sr₃Fe₂O_{7-δ} showed partial decomposition under the same conditions. In these samples, the intensity has significantly decreased due to the non-crystalline phase produced by decomposition during reduction. Remarkably, Pd/LaSr₃Fe₃O_{10-δ} did not undergo

decomposition or reduction of its crystallinity, suggesting high structural stability at high temperatures. It seems that the presence of a rock-salt layer in $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ prevents structural decomposition at high temperatures.

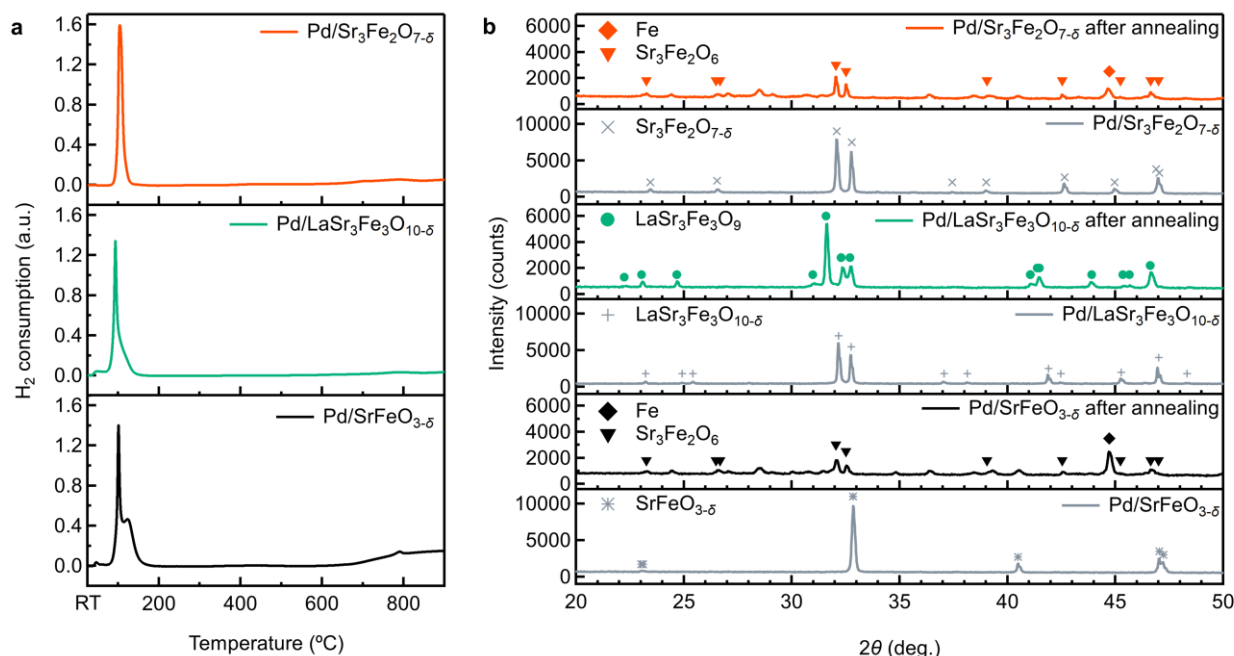


Figure 2. a) H₂-TPR measurement of the Sr-Fe-based layered perovskites. The sample was heated to 900°C at 5°C / min, under 2% H₂/Ar flowing. b) Powder XRD patterns of Sr-Fe-based layered perovskites after annealing at 900°C for 3h under 5% H₂/Ar flowing. A detailed analysis of XRD patterns about the containing compounds after annealing is shown in **Figure S3**.

Time-resolved synchrotron XRD measurements for Sr-Fe-based layered perovskites

We measured time-resolved XRD for the three samples to reveal the reaction dynamics. **Figure 3h** illustrates the experimental setup of the XRD measurements at SPring-8 BL13XU. The silica capillary with the sample inside was evacuated, and the temperature was set to 500°C. Pure O₂ / H₂ (≈ 100 kPa) was introduced instantly, 1.2 seconds after the start of the XRD

measurement. The measurement interval is 12 milliseconds, which is sufficiently fast for observing solid-gas reactions. **Figures 3a ~ 3g** show time-resolved XRD profiles around the main peaks during the redox process. Whole powder diffraction patterns are shown in **Figures S4 ~ S9**. The reduction reaction of $\text{Pd}/\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ is given in **Figures 3b** and **3c**. Note that we reported the same reaction at the different beamline (with relatively low resolution) in the previous study²³, where the time resolution of the measurement was a few hundred milliseconds. Focusing on the 110 reflection (**Figure 3b**), we can see that the peak shifts to the low-angle side as soon as the gas is introduced. In addition, looking at the 0010 peak (**Figure 3c**), which reflects the *c*-axis length, a peak jump is observed, corresponding to the disorder-to-order transition of the oxygen defects. These results are in line with our previous studies²³. In contrast, the oxidation reaction (**Figure 3a**) shows no peak jumps, indicating its structure continuously changes.

Figures 3d and **3e** present the redox reactions of $\text{Pd}/\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$. At the beginning of the reduction reaction (**Figure 3e**), $\text{Pd}/\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ has a tetragonal structure, represented by double main peaks (110 and 107). In the reduction reaction (**Figure 3e**), we observed a prominent jump of the peaks, suggesting a discontinuous structure change; the 110 reflection splits into 200 and 020 reflections for orthorhombic $\text{LaSr}_3\text{Fe}_3\text{O}_9$ ²⁴. This corresponds to the disorder-to-order transition where the brownmillerite-type defects ($[\text{110}]_p$ defects) are introduced in the center of the perovskite block anisotropically in phase $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ (**Figure 1a**). This behavior is qualitatively consistent with the static result that a two-phase region appears between $0.51 < \delta < 0.85$ ²⁴. In contrast, the oxidation process (**Figure 3d**) shows a continuous shift in the peaks, without an obvious jump. This suggests continuous change in the structure and stoichiometry. This is different from static behavior²⁴ and, thus, includes dynamic phases.

Figures 3f and 3g illustrate the redox reactions of $\text{Pd}/\text{SrFeO}_{3-\delta}$ without a rock-salt layer. Reduction and oxidation reactions exhibit discontinuous and continuous changes, respectively, between cubic $\text{SrFeO}_{3-\delta}$ and brownmillerite $\text{SrFeO}_{2.5}$. Note that there are no intermediate phases (**Figure S10**), even though several oxygen defect-ordered phases, such as $\text{SrFeO}_{2.875}$ and $\text{SrFeO}_{2.75}$, are reported statically²⁵.

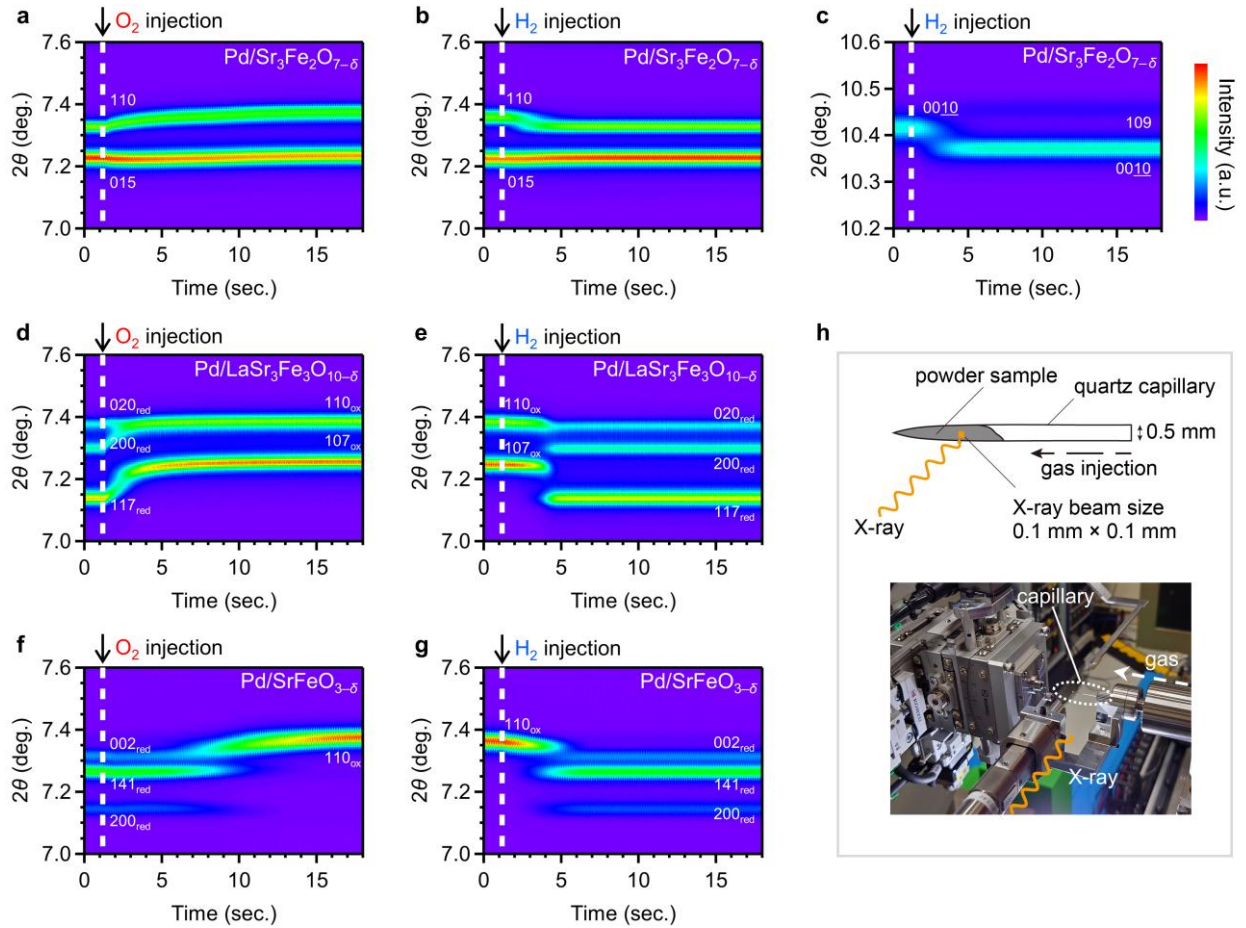


Figure 3. High-speed time-resolved synchrotron XRD measurement at 500°C. Contour plots of a) d) f) the oxidation and b) c) e) g) reduction process of $\text{Pd}/\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$, $\text{Pd}/\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$, and $\text{Pd}/\text{SrFeO}_{3-\delta}$. b) and c) show two different 2θ ranges for the same reaction. The white dotted lines represent the timing of gas injection. h) Schematic illustration of the sample and the image of the SXR setup around the sample at BL13XU beamline.

1 DISCUSSION

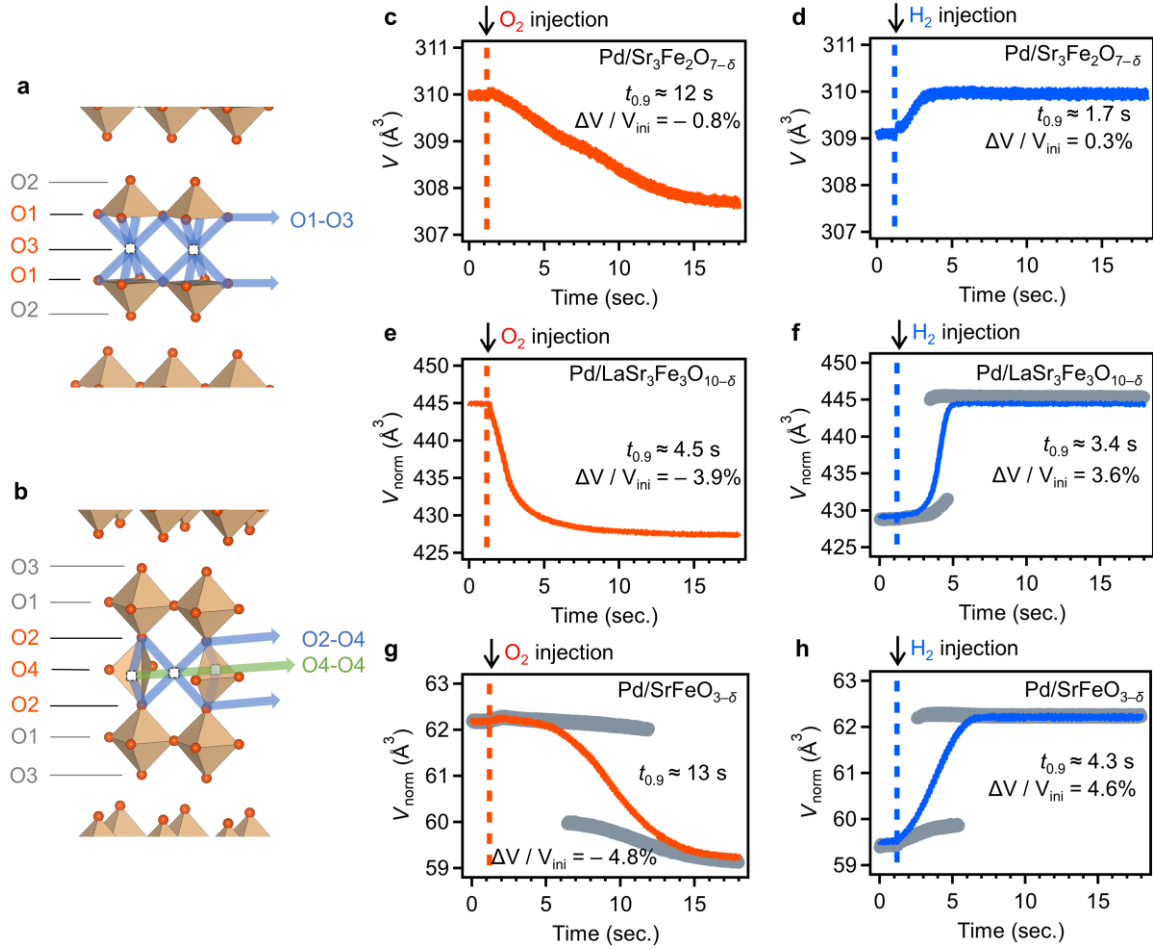


Figure 4. a) b) Schematic images of the conduction paths of a) $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ and b) $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$. δ . Sr atoms are omitted. The $\square$ at anion sites represent oxygen vacancies, and the blue and green lines represent predominant conduction paths. c) ~ h) Average volume changes in c) e) g) the oxidation and d) f) h) reduction process of $\text{Pd/Sr}_3\text{Fe}_2\text{O}_{7-\delta}$, $\text{Pd/LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$, and $\text{Pd/SrFeO}_{3-\delta}$. The red and blue lines indicate the average volume changes under the oxidation and reduction conditions. The gray lines represent the volume changes of each phase. The dotted lines represent the timing of gas injection. V_{norm} represents the normalized lattice volume.

In order to evaluate the quantitative reaction rates for each reaction, we carried out Rietveld refinements of the time-resolved XRD measurement patterns. The average volume changes during the reactions are shown in **Figures 4c ~ 4h**. $t_{0.9}$ in the figures represents the time required for the reaction progress to reach 90%, estimated from the volume changes.

Compared to the oxidation (**Figures 4c, 4e, 4g**) and reduction (**Figures 4d, 4f, 4h**) rates, the reduction reaction rates tended to be faster than in the oxidation reactions in all the compounds. This may be attributed to differences in the structures when diffusion occurs. In the oxidation reactions, all the reactions start from the defect-ordered structures; thus, oxygen conduction in the ordered structure is necessary. In contrast, all the reduction reactions start from the defect-disordered structures. In addition, the disorder-to-order transitions of oxygen defects occur just before the reactions finish. This means that the oxygen conduction in the reduction reaction occurs only in defect-disordered structures. Typically, disordered defects enhance ion conductivity, and diffusion is faster in a disordered structure than in an ordered structure. Thus, the differences in the reaction pathway could be responsible for the reaction rates.

Among the oxidation reactions (**Figures 4c, 4e, 4g**), Pd/LaSr₃Fe₃O_{10-δ} reacted significantly faster than the other two. This fast oxidation reaction in Pd/LaSr₃Fe₃O_{10-δ} can be attributed to its defect-ordered structure. In brownmillerite-type defects, it has been reported that the conduction pathway involves oxygen atoms at the apical site of FeO₆ octahedra (O2 site) migrating to the oxygen-deficient site (O4 site) at high temperatures²⁶. Therefore, potential conduction paths for LaSr₃Fe₃O_{10-δ} are the O2-O4 and O4-O4 paths, as shown in **Figure 4b**, which is attributed to the vacancies at the O2 and O4 sites. Compared to the other conduction paths, the O2-O4 and O4-O4 conduction paths are more promising with larger bottleneck areas, and the O4-O4 conduction is dominant at high temperatures²⁷. In Sr₃Fe₂O_{7-δ} with [001]_p ordered defect, a previous study suggested that the main conduction path is O1-O3 along the edges of the FeO₆ octahedron²⁸ (**Figure 4a**). This conduction path potentially has a high energy

1 barrier because all the defects are isolated in the ordered structure. In other words, the defects
2 do not form channels, in contrast to the brownmillerite-type defects. Therefore, the oxidation
3 in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ is considered to be slower than $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ with the brownmillerite-type
4 defects.

5 With regard to the comparison between $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ and $\text{SrFeO}_{3-\delta}$, both compounds have
6 brownmillerite-type defects^{14, 24} and are expected to have a similar conduction mechanism.
7 However, the reaction rate is superior to $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$. This may be attributed to the difference
8 in phase transition mode. As seen in oxidation reactions of these materials (**Figures 3d and**
9 **3f**), the reaction in $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ is changing in a second-order-like phase transition (a
10 continuous phase change), whereas in $\text{SrFeO}_{3-\delta}$, the reaction is a first-order-like phase
11 transition (a coexistence region of the two phases). Thus, in $\text{SrFeO}_{3-\delta}$, it is possible that there
12 is a large activation barrier associated with the drastic (first-order-like) phase transition, which
13 may hinder the fast reaction.

14 The performance of the three perovskite-based oxygen storage materials is summarized in
15 Table 1. The oxygen storage performance of $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ was also evaluated under the same
16 conditions, as a comparison to Sr-Fe-based materials (**Figures S11, S12, and Table S1**). Our
17 experiments revealed that $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$, with $n = 3$ series of RP-type perovskite structure, has
18 a good oxygen storage capacity, high structural stability, and quick response to atmospheric
19 changes. The high oxygen storage capacity comes from thick perovskite blocks with a high
20 oxygen storage capacity. In addition, $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ has a rock-salt layer, unlike $\text{SrFeO}_{3-\delta}$,
21 which prevents structural decomposition at high temperatures. Thus, combining oxygen-
22 storage perovskite and robust rock-salt layers enables the design of an oxygen-storage material
23 with high robustness and fast conduction.

Table 1. Oxygen storage characteristics of Pd-loaded Sr-Fe-based layered perovskites

	$\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ ($n = 2$)	$\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$ ($n = 3$)	$\text{SrFeO}_{3-\delta}$ ($n = \infty$)
Oxygen storage capacity at 500°C ^a	≈ 1.7 wt%	≈ 2.0 wt%	≈ 2.5 wt%
Stability under high-temperature reduction ^b	Partially decomposed	Stable	Decomposed
Oxidation speed at 500°C ^c	≈ 12 s	≈ 4.5 s	≈ 13 s
Reduction speed at 500°C ^d	≈ 1.7 s	≈ 3.4 s	≈ 4.3 s

^a Cyclic-TG measurement with switching gas atmosphere between 2% H₂/Ar (30 min.) and 2% O₂/Ar (20 min.).

^b H₂-TPR measurement with heating to 900°C at 5°C / min, under 2% H₂/Ar flowing.

^{c, d} Time for reaction to progress to 90%, estimated from Time-resolved XRD data at 500°C under pure O₂ / H₂ (≈ 100 kPa).

CONCLUSIONS

In this study, we discussed the oxygen storage characteristics of Sr-Fe-based layered perovskite. H₂-TPR measurement revealed that a rock-salt layer enhanced the stability under the high-temperature reduction condition. Cyclic TG measurement uncovered that the oxygen storage capacity showed an upward trend with the increase in perovskite layers. Time-resolved XRD measurement showed the dynamic structural change during the reaction. Within the compounds we examined, LaSr₃Fe₃O_{10- δ} has a good oxygen storage ability and high structural stability. These results provided that combining structural blocks with separate roles in oxygen storage materials is a valid strategy for the development of high-performance OSM.

1 EXPERIMENTAL SECTION

2 *Synthesis of Sr-Fe-based (layered) perovskite oxides and κ -Ce₂Zr₂O₈*

3 Polycrystalline samples of Sr₃Fe₂O_{7- δ} , and SrFeO_{3- δ} were prepared using the Pechini
4 method. 333.33 mmol of citric acid (Kanto Chemical, $\geq 99.0\%$) was dissolved in 180 ml of
5 water, and then SrCO₃ (20 mmol, FUJIFILM Wako Pure Chemical, 99.0%) and
6 Fe(NO₃)₃·9H₂O (13.33 mmol for Sr₃Fe₂O_{7- δ} , 20 mmol for SrFeO_{3- δ} , Nacalai Tesque, $\geq 99.0\%$)
7 were added to it. The solution was stirred and heated at 80°C for 2 hours to obtain the metal
8 oxide complexes. 333.33 mmol of ethylene glycol (FUJIFILM Wako Pure Chemical, 99.0 +%)
9 were added to this solution and stirred at 140°C for 3 h. This operation produces a gel-like
10 solution. This solution was heated with a mantle heater at 350°C for 3 h, and the powder
11 obtained was calcined at 1000°C for 5 h with flowing O₂ to prevent the formation of SrCO₃.

12 Polycrystalline sample of LaSr₃Fe₃O_{10- δ} were prepared by the same procedure. 400 mmol of
13 citric acid (Kanto Chemical, 99%) was dissolved in 180 ml of water, and then SrCO₃ (20 mmol,
14 FUJIFILM Wako Pure Chemical, 99.99%), Fe(NO₃)₃·9H₂O (20 mmol, FUJIFILM Wako Pure
15 Chemical, 99.9%) and La(NO₃)₃·6H₂O (6.67 mmol, FUJIFILM Wako Pure Chemical, 99.9%)
16 were added to it. The solution was stirred and heated at 70°C. 400 mmol of ethylene glycol
17 (FUJIFILM Wako Pure Chemical, 99.5%) were added to this solution and stirred at 130°C for
18 2 h. This solution was heated at 350°C for 2 h, and the powder obtained was calcined at 1400°C
19 for 2 h.

20 Pd-loading was conducted by an impregnation method. (CH₃COO)₂Pd (Sigma-Aldrich, $\geq$
21 99.0%) was dissolved in acetone, and then the sample was added to the solution. The solution
22 was evaporated by heating at 80°C. The remaining powder was heated at 800°C for 5 h to
23 obtain the Pd-loaded sample. The loading amount of Pd species was 1 wt% on a metal basis.

Polycrystalline samples of κ -Ce₂Zr₂O₈ were synthesized by following the procedure. Ce(NO₃)₃·6H₂O (20 mmol, Nacalai Tesque, ≥ 35.0% as CeO₂) and ZrO(NO₃)₂ · 2H₂O (20 mmol, Kanto Chemical, ≥ 99.0%) were added to a beaker and dissolved in 400 mL of distilled water. A 28% aqueous ammonia solution (32 mL) was diluted with 900 mL of distilled water under stirring, followed by the dropwise addition of the cerium and zirconium solution. The mixture was stirred at room temperature for one day. The resulting precipitate was transferred to a centrifuge tube and centrifuged at 3000 rpm for 5 minutes. The supernatant was decanted, and the precipitate was redispersed in 500 mL of distilled water. This washing and centrifugation process was repeated twice. The obtained precipitate was dried at 110°C for one day and then calcined at 250 °C for 2 hours. The calcined powder was ground in a mortar and further calcined at 800 °C for 5 hours. The resulting powder was pressed at 2 tons, then reduced at 1400 °C for 5 hours under a flow of 10% H₂/N₂ gas at 5 L/min. The reduced sample was ground again and re-calcined in air at 500 °C for 5 hours to obtain κ -Ce₂Zr₂O₈. Pd loading was performed using the same impregnation method with Pd(NO₃)₂.

Characterization of Powder Samples

The sample quality was examined by XRD measurements by a D8 ADVANCE diffractometer (Bruker AXS) with Cu K α radiation. The temperature-programmed reduction (H₂-TPR) measurement was conducted using a fixed-bed flow reactor. A 2% H₂/Ar gas mixture was introduced at a total flow rate of 30 mL·min⁻¹ over a 50 mg sample, and the temperature was increased from room temperature to 900°C at a rate of 5°C·min⁻¹. The hydrogen concentration in the outlet gas was measured with a thermal conductivity detector (TCD), and the hydrogen consumption was quantified. The oxygen storage capacity of the sample was measured using a thermogravimetric analyzer (NETZSCH STA2500 Regulus). A 100 mg sample was placed in an alumina pan, and a reaction gas (2% H₂/Ar or 2% O₂/Ar) was flowed

at a total volume of 100 mL with a $W/F = 0.06 \text{ g} \cdot \text{s} \cdot \text{mL}^{-1}$. Initially, the sample was heated to 500°C at a rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ under an oxygen flow, and the temperature and gas flow were maintained until the sample weight stabilized. Subsequently, the gas flow was alternated between 2% H_2/Ar for 30 min and 2% O_2/Ar for 20 min at a flow rate of $100 \text{ mL} \cdot \text{min}^{-1}$. The oxygen storage capacity was determined based on the weight change of the sample during the redox reactions. The analysis of sample size was performed using an S-4800 field-emission scanning electron microscope (Hitachi High-Tech), with an accelerating voltage of 5 kV for $\text{Pd}/\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$, and $\text{Pd}/\text{SrFeO}_{3-\delta}$, 15 kV for $\text{Pd}/\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$. To evaluate the loading state of Pd, Bright-field STEM (BF-STEM), High-Angle Annular Dark-Field STEM (HAADF-STEM), and energy-dispersive X-ray spectroscopy (STEM-EDX) for elemental mapping were conducted using a JEM-2100F transmission electron microscope (JEOL) operated at an accelerating voltage of 200 kV. The sample dispersed in ethanol was dropped onto a carbon-coated copper mesh and then dried for observation.

Time-resolved synchrotron XRD measurements

Time-resolved synchrotron XRD measurements were conducted to monitor structural changes and assess the reaction speed under redox conditions. This experiment was performed using a powder diffractometer equipped with two-dimensional CdTe (LAMBDA 750k) detectors at the beamline BL13XU²⁹ (SPring-8). The time-resolved data were collected by single-step mode. The synchrotron radiation from standard-type SPring-8 in-vacuum undulator was monochromatized to the photon energy of 35 keV ($\lambda = 0.35424 \text{ \AA}$ for $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ and $\text{SrFeO}_{3-\delta}$, $0.35447 \text{ \AA}$ for $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$). The samples were packed into a quartz capillary with a diameter of 0.5 mm. The sample temperature was controlled by a hot N_2 gas flow device, and the gas atmosphere of the samples was controlled by a remote gas- and vapor-pressure control (RGVPC) system³⁰. First, the samples were heated to 700°C in pure H_2 and then pretreated with pure O_2/H_2 conditions to remove the impurities at the surface. Then, the sample space

was evacuated, and the temperature was set to 500°C. The data acquisition was started 1.2 s before the O₂/H₂ gas injection ($\approx$ 100 kPa). The time window of the measurement is 12 milliseconds. To improve the intensity homogeneity along the Debye–Scherrer rings, the capillary was rotated at 400 rpm during the measurement using the high-speed capillary spinner cell. The collected XRD profiles were analyzed by TOPAS6 software³¹. Atomic positions and atomic displacement parameters were fixed to prevent parameter divergence during Rietveld refinement.

Supporting Information.

The following files are available free of charge.

Additional SEM/TEM images of the samples (**Figures S1 and S2**), additional XRD patterns (**Figures S3-S10**), and details of experiment on κ -Ce₂Zr₂O₈ (**Figures S11 and S12, Table S1**)

AUTHOR INFORMATION

Corresponding Author

Takafumi Yamamoto: yama@kuchem.kyoto-u.ac.jp

Saburo Hosokawa: hosokawa@kit.ac.jp

Author Contributions

S. Hosokawa and T. Yamamoto contributed equally to this paper. S. Hosokawa and T. Yamamoto designed the research. T. Kosuge and C. Yamazoe, and N. Nagata synthesized and characterized the samples. T. Kosuge, C. Yamazoe, S. Kawaguchi, S. Kobayashi, S. Hosokawa, and T. Yamamoto conducted the synchrotron XRD measurement. N. Nagata and M. Azuma were involved in the discussion of the paper. The initial versions of the

manuscript were written by T. Kosuge, and reviewing and editing of the final versions of the manuscript was done by T. Kosuge, S. Hosokawa, and T. Yamamoto, with comments from all authors.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Transformative Research Areas (A) “Supra-ceramics” (JSPS KAKENHI Grant Number JP22H05147), Grant-in-Aid for Scientific Research (JSPS KAKENHI Grant Number JP23H03673), Grant-in-Aid for JSPS Fellows (JSPS KAKENHI Grant Number JP24KJ1089), and Toyota Motor Corporation. This work was also supported by the Institute of Science Tokyo Academy for Convergence of Materials and Informatics (TAC-MI) by MEXT. The authors thank Ms. Chisa Iwasaki (Kyoto University), Mr. Ryosuke Sugimoto (Kyoto Institute of Technology) and Yuna Ueda (Kyoto Institute of Technology) for their assistance with sample preparation, TG analysis, and H₂-TPR measurement. The synchrotron XRD experiments were conducted at the BL13XU of SPring-8 with the approval of JASRI (2023A1502, 2023B2012, 2024A1853, 2024B2001).

REFERENCES

- (1) Kašpar, J.; Fornasiero, P.; Hickey, N. Automotive Catalytic Converters: Current Status and Some Perspectives. *Catal. Today* **2003**, *77*, 419–449.
- (2) Sugiura, M. Oxygen Storage Materials for Automotive Catalysts: Ceria-Zirconia Solid Solutions. *Catal. Surv. from Asia* **2003**, *7* (1), 77–87.
<https://doi.org/10.1023/A:1023488709527>.
- (3) Wang, J.; Chen, H.; Hu, Z.; Yao, M.; Li, Y. A Review on the Pd-Based Three-Way Catalyst. *Catal. Rev. - Sci. Eng.* **2015**, *57* (1), 79–144.
<https://doi.org/10.1080/01614940.2014.977059>.

- (4) Vieten, J.; Bulfin, B.; Call, F.; Lange, M.; Schmücker, M.; Francke, A.; Roeb, M.; Sattler, C. Perovskite Oxides for Application in Thermochemical Air Separation and Oxygen Storage. *J. Mater. Chem. A* **2016**, *4* (35), 13652–13659. <https://doi.org/10.1039/c6ta04867f>.
- (5) Yang, Z.; Lin, Y. S.; Zeng, Y. High-Temperature Sorption Process for Air Separation and Oxygen Removal. *Ind. Eng. Chem. Res.* **2002**, *41* (11), 2775–2784. <https://doi.org/10.1021/ie010736k>.
- (6) Xu, M.; Wu, H. C.; Lin, Y. S.; Deng, S. Simulation and Optimization of Pressure Swing Adsorption Process for High-Temperature Air Separation by Perovskite Sorbents. *Chem. Eng. J.* **2018**, *354* (August), 62–74. <https://doi.org/10.1016/j.cej.2018.07.080>.
- (7) Zhu, X.; Li, K.; Neal, L.; Li, F. Perovskites as Geo-Inspired Oxygen Storage Materials for Chemical Looping and Three-Way Catalysis: A Perspective. *ACS Catal.* **2018**, *8* (9), 8213–8236. <https://doi.org/10.1021/acscatal.8b01973>.
- (8) Zhu, X.; Imtiaz, Q.; Donat, F.; Müller, C. R.; Li, F. Chemical Looping beyond Combustion-a Perspective. *Energy Environ. Sci.* **2020**, *13* (3), 772–804. <https://doi.org/10.1039/c9ee03793d>.
- (9) Taylor, D. D.; Schreiber, N. J.; Levitas, B. D.; Xu, W.; Whitfield, P. S.; Rodriguez, E. E. Oxygen Storage Properties of La_{1-x}Sr_xFeO_{3-δ} for Chemical-Looping Reactions - An in Situ Neutron and Synchrotron X-Ray Study. *Chem. Mater.* **2016**, *28* (11), 3951–3960. <https://doi.org/10.1021/acs.chemmater.6b01274>.
- (10) Di Monte, R.; Kašpar, J. Nanostructured CeO₂–ZrO₂ Mixed Oxides. *J. Mater. Chem.* **2005**, *15* (6), 633–648. <https://doi.org/10.1039/B414244F>.

- (11) Kašpar, J.; Fornasiero, P.; Graziani, M. Use of CeO₂-Based Oxides in the Three-Way Catalysis. *Catal. Today* **1999**, *50* (2), 285–298. [https://doi.org/10.1016/S0920-5861\(98\)00510-0](https://doi.org/10.1016/S0920-5861(98)00510-0).
- (12) Motohashi, T.; Hirano, Y.; Masubuchi, Y.; Oshima, K.; Setoyama, T.; Kikkawa, S. Oxygen Storage Capability of Brownmillerite-Type Ca₂AlMnO_{5+δ} and Its Application to Oxygen Enrichment. *Chem. Mater.* **2013**, *25* (3), 372–377. <https://doi.org/10.1002/chin.201322200>.
- (13) Matsumoto, U.; Kuwabara, A.; Fisher, C. A. J.; Moriwake, H.; Tanaka, I. Oxide-Ion Diffusion in Brownmillerite-Type Ca₂AlMnO₅₊: Δ from First-Principles Calculations. *Phys. Chem. Chem. Phys.* **2022**, *24* (3), 1503–1509. <https://doi.org/10.1039/d1cp05174a>.
- (14) Hodges, J. P.; Short, S.; Jorgensen, J. D.; Xiong, X.; Dabrowski, B.; Mini, S. M.; Kimball, C. W. Evolution of Oxygen-Vacancy Ordered Crystal Structures in the Perovskite Series Sr(n)Fe(n)O(3n-1) (n = 2, 4, 8, and ∞), and the Relationship to Electronic and Magnetic Properties. *J. Solid State Chem.* **2000**, *151* (2), 190–209. <https://doi.org/10.1006/jssc.1999.8640>.
- (15) Bulfin, B.; Lapp, J.; Richter, S.; Gubà, D.; Vieten, J.; Brendelberger, S.; Roeb, M.; Sattler, C. Air Separation and Selective Oxygen Pumping via Temperature and Pressure Swing Oxygen Adsorption Using a Redox Cycle of SrFeO₃ Perovskite. *Chem. Eng. Sci.* **2019**, *203*, 68–75. <https://doi.org/10.1016/j.ces.2019.03.057>.
- (16) Ikeda, H.; Nikata, S.; Hirakawa, E.; Tsuchida, A.; Miura, N. Oxygen Sorption/Desorption Behavior and Crystal Structural Change for SrFeO_{3-δ}. *Chem. Eng. Sci.* **2016**, *147*, 166–172. <https://doi.org/10.1016/j.ces.2016.03.034>.

- 1 (17) Lau, C. Y.; Dunstan, M. T.; Hu, W.; Grey, C. P.; Scott, S. A. Large Scale in Silico
2 Screening of Materials for Carbon Capture through Chemical Looping. *Energy*
3 *Environ. Sci.* **2017**, *10* (3), 818–831. <https://doi.org/10.1039/c6ee02763f>.
- 4 (18) Beppu, K.; Hosokawa, S.; Teramura, K.; Tanaka, T. Oxygen Storage Capacity of
5 Sr₃Fe₂O_{7-δ} Having High Structural Stability. *J. Mater. Chem. A* **2015**, *3* (25), 13540–
6 13545. <https://doi.org/10.1039/c5ta01588j>.
- 7 (19) Beppu, K.; Hosokawa, S.; Shibano, T.; Demizu, A.; Kato, K.; Wada, K.; Asakura, H.;
8 Teramura, K.; Tanaka, T. Enhanced Oxygen-Release/Storage Properties of Pd-Loaded
9 Sr₃Fe₂O_{7-δ}. *Phys. Chem. Chem. Phys.* **2017**, *19* (21), 14107–14113.
10 <https://doi.org/10.1039/c7cp01614j>.
- 11 (20) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal,
12 Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *44* (6), 1272–1276.
13 <https://doi.org/10.1107/S0021889811038970>.
- 14 (21) Dann, S. E.; Weller, M. T.; Currie, D. B. Structure and Oxygen Stoichiometry in
15 Sr₃Fe₂O_{7-y}, 0 ≤ y ≤ 1.0. *J. Solid State Chem.* **1992**, *97* (1), 179–185.
16 [https://doi.org/10.1016/0022-4596\(92\)90023-O](https://doi.org/10.1016/0022-4596(92)90023-O).
- 17 (22) Lee, J. Y.; Swinnea, J. S.; Steinfink, H.; Reiff, W. M.; Pei, S.; Jorgensen, J. D. The
18 Crystal Chemistry and Physical Properties of the Triple Layer Perovskite Intergrowths
19 LaSr₃Fe₃O_{10-δ} and LaSr₃(Fe_{3-x}Al_x)O_{10-δ}. *Journal of Solid State Chemistry*. 1993, pp
20 1–15. <https://doi.org/10.1006/jssc.1993.1072>.
- 21 (23) Yamamoto, T.; Kawaguchi, S.; Kosuge, T.; Sugai, A.; Tsunoda, N.; Kumagai, Y.;
22 Beppu, K.; Ohmi, T.; Nagase, T.; Higashi, K.; Kato, K.; Nitta, K.; Uruga, T.;
23 Yamazoe, S.; Oba, F.; Tanaka, T.; Azuma, M.; Hosokawa, S. Emergence of

Dynamically-Disordered Phases During Fast Oxygen Deintercalation Reaction of Layered Perovskite. *Adv. Sci.* **2023**, *10* (19), 1–8.
<https://doi.org/10.1002/advs.202301876>.

(24) Fjellvåg, Ø. S.; Øygarden, V.; Sørby, M. H.; Sjøstad, A. O. Crystal Structure of $\text{LaSr}_3\text{Fe}_3\text{O}_9$ and Its Phase Relation with $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$. *J. Solid State Chem.* **2019**, *275* (February), 56–62. <https://doi.org/10.1016/j.jssc.2019.03.050>.

(25) Takeda, Y.; Kanno, K.; Takada, T.; Yamamoto, O.; Takano, M.; Nakayama, N.; Bando, Y. Phase Relation in the Oxygen Nonstoichiometric System, SrFeO_x ($2.5 \leq x \leq 3.0$). *J. Solid State Chem.* **1986**, *63* (2), 237–249. [https://doi.org/10.1016/0022-4596\(86\)90174-X](https://doi.org/10.1016/0022-4596(86)90174-X).

(26) Paulus, W.; Schober, H.; Eibl, S.; Johnson, M.; Berthier, T.; Hernandez, O.; Ceretti, M.; Plazanet, M. Mobility in Solid Oxide Ion Conductors. *J. Am. Chem. Soc.* **2008**, *130* (10), 16080–16085.

(27) Kagomiya, I.; Jimbo, K.; Kakimoto, K. I. Distribution Change of Oxygen Vacancies in Layered Perovskite Type $(\text{Sr}, \text{La})_{\text{N}+1}\text{Fe}_\text{n}\text{O}_{3\text{n}+1}$ ($\text{N}=3$). *J. Solid State Chem.* **2013**, *207*, 184–189. <https://doi.org/10.1016/j.jssc.2013.08.030>.

(28) Ota, T.; Kizaki, H.; Morikawa, Y. Mechanistic Analysis of Oxygen Vacancy Formation and Ionic Transport in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$. *J. Phys. Chem. C* **2018**, *122* (8), 4172–4181. <https://doi.org/10.1021/acs.jpcc.7b11904>.

(29) Kawaguchi, S.; Kobayashi, S.; Yamada, H.; Ashitani, H.; Takemoto, M.; Imai, Y.; Hatsui, T.; Sugimoto, K.; Sakata, O. High-Throughput and High-Resolution Powder X-Ray Diffractometer Consisting of Six Sets of 2D CdTe Detectors with Variable

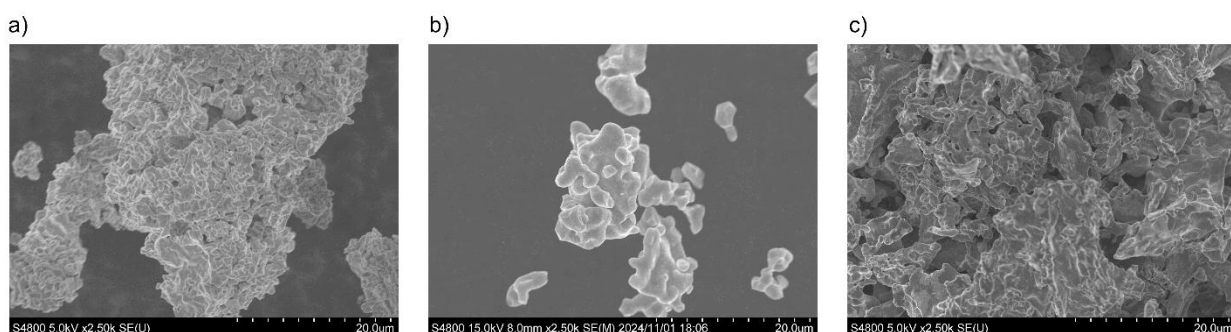
1 Sample-to-Detector Distance and Innovative Automation System. *J. Synchrotron*
2 *Radiat.* **2024**, *31* (Pt 4), 955–967. <https://doi.org/10.1107/S1600577524003539>.

3 (30) Kawaguchi, S.; Takemoto, M.; Tanak, H.; Hiraide, S.; Sugimoto, K.; Kubota, Y. Fast
4 Continuous Measurement of Synchrotron Powder Diffraction Synchronized with
5 Controlling Gas and Vapour Pressures at Beamline BL02B2 of SPring-8. *J.*
6 *Synchrotron Radiat.* **2020**, *27*, 616–624. <https://doi.org/10.1107/S1600577520001599>.

7 (31) Coelho, A. A. TOPAS and TOPAS-Academic: An Optimization Program Integrating
8 Computer Algebra and Crystallographic Objects Written in C++: An. *J. Appl.*
9 *Crystallogr.* **2018**, *51* (1), 210–218. <https://doi.org/10.1107/S1600576718000183>.

1 Supporting information

2



3 **Figure S1. SEM images of Sr-Fe-based materials. a) Pd/Sr₃Fe₂O_{7-d}, b) Pd/LaSr₃Fe₃O_{10-d},**
4 **c) Pd/SrFeO_{3-d}.**

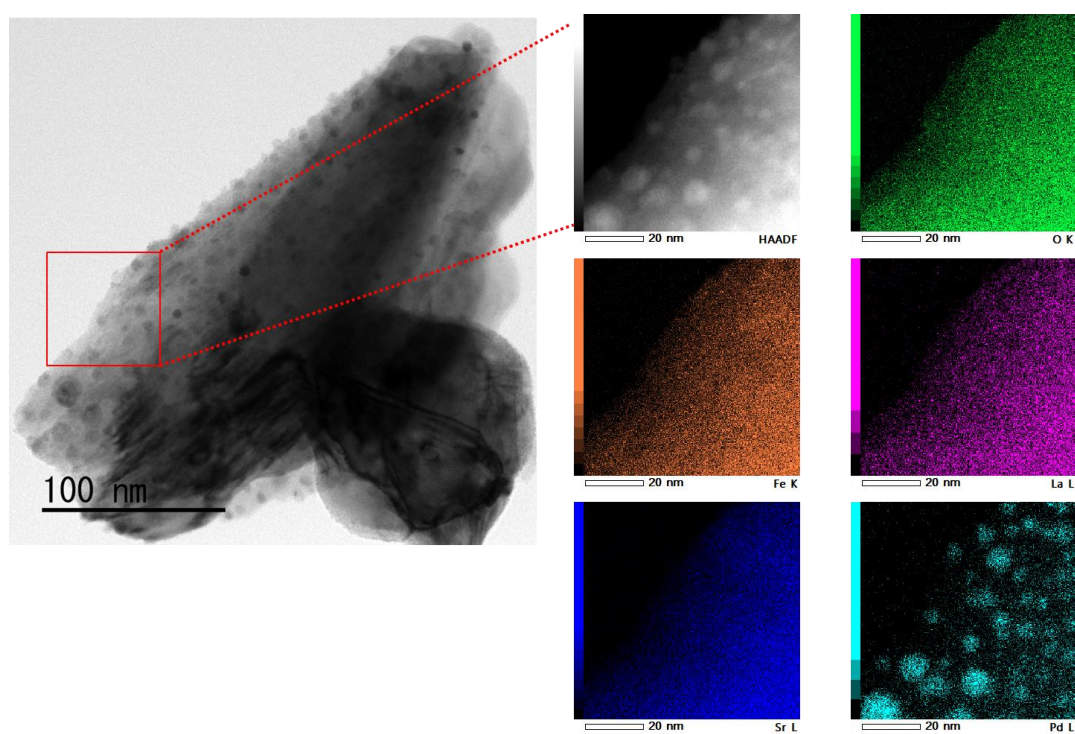


Figure S2. BF-STEM image, HAADF image, and EDS intensity mapping image of Pd/LaSr₃Fe₃O_{10-d} sample after oxidation-reduction cycle at 500°C.

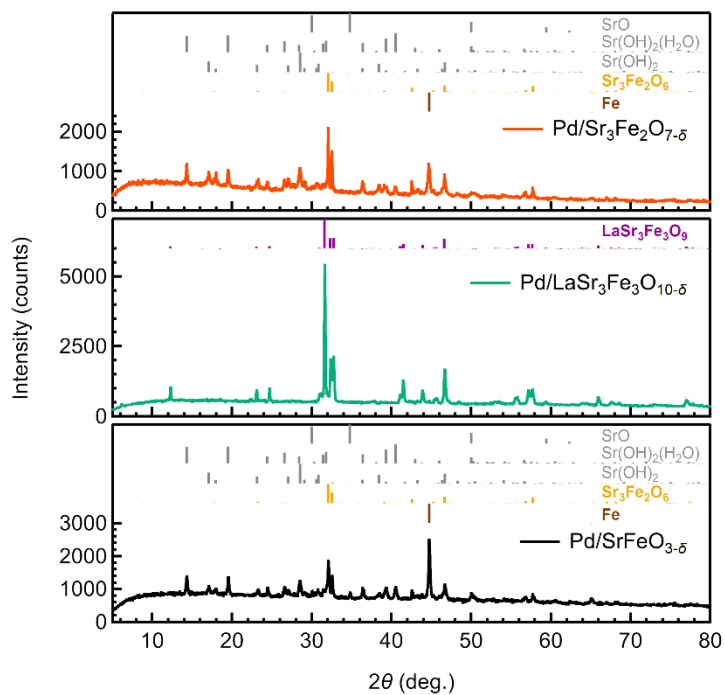


Figure S3. The detailed description of XRD pattern after annealing. The diffraction peaks were identified based on PDF: SrO (PDF 01-075-6979), SrO(OH)₂·H₂O (PDF 01-072-0057), Sr(OH)₂ (PDF 01-071-2365), Sr₃Fe₂O₆ (PDF 01-082-0426), Fe (PDF 01-085-8654), LaSr₃Fe₃O₉ (PDF 01-087-4448).

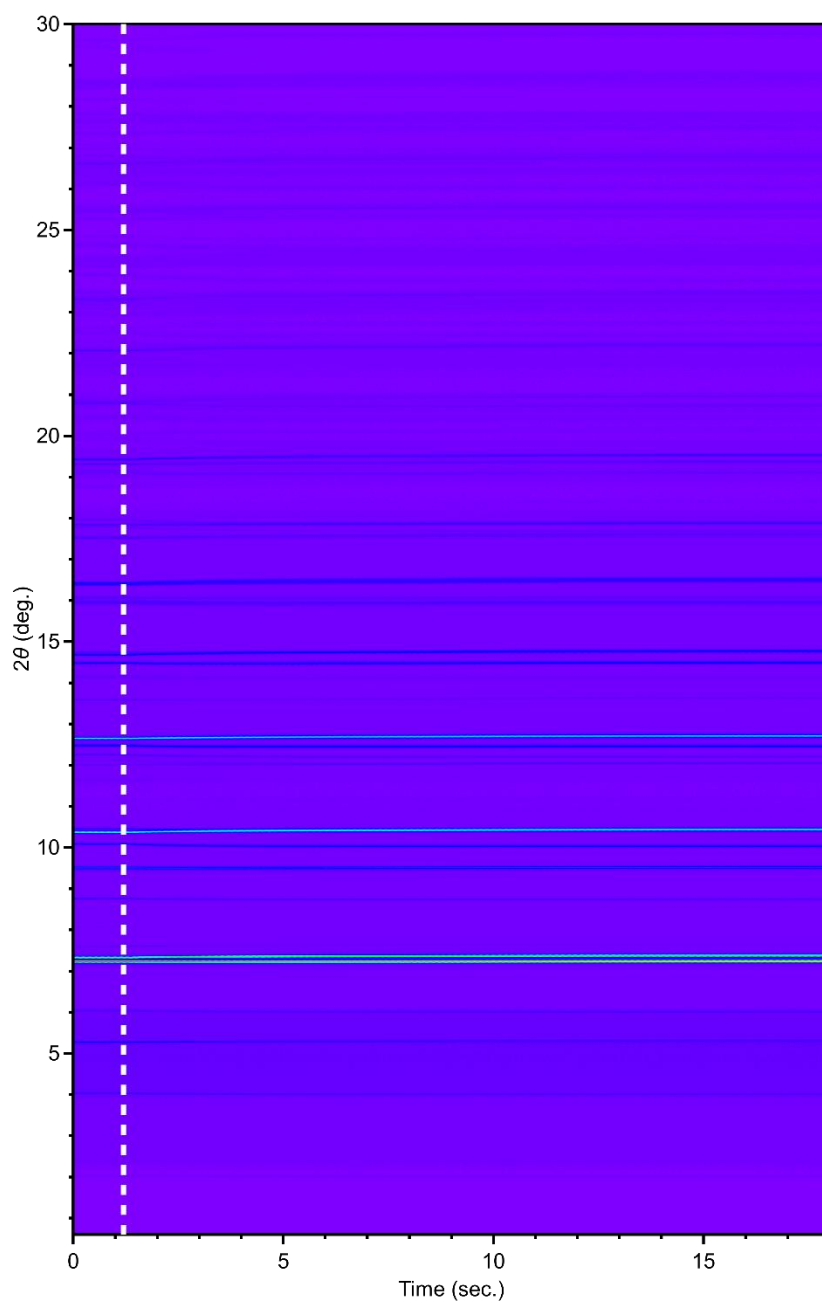


Figure S4. Whole powder diffraction patterns of oxidation reaction for Pd/Sr₃Fe₂O_{7-δ} at 500 °C. The white dotted lines represent the timing of gas injection.

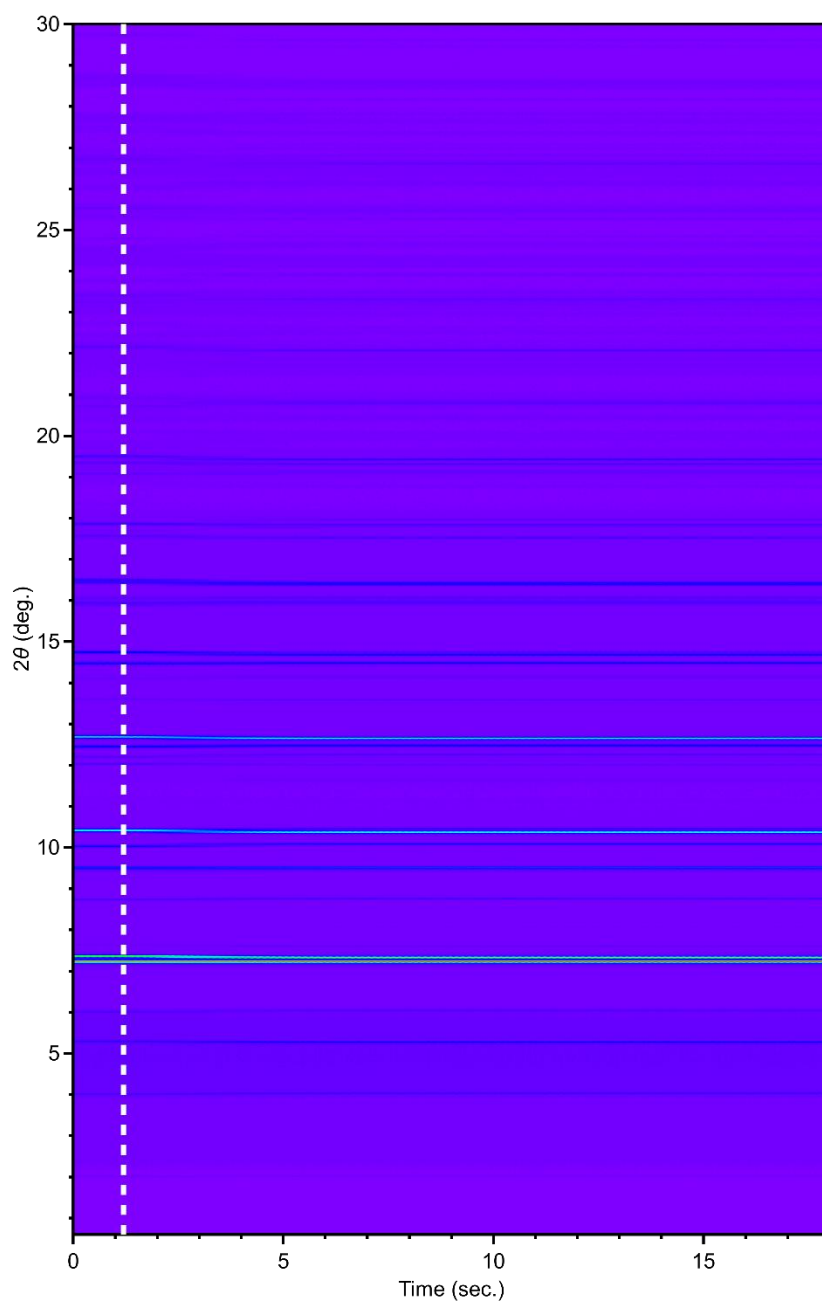


Figure S5. Whole powder diffraction patterns of reduction reaction for Pd/Sr₃Fe₂O_{7-δ} at 500 °C. The white dotted lines represent the timing of gas injection.

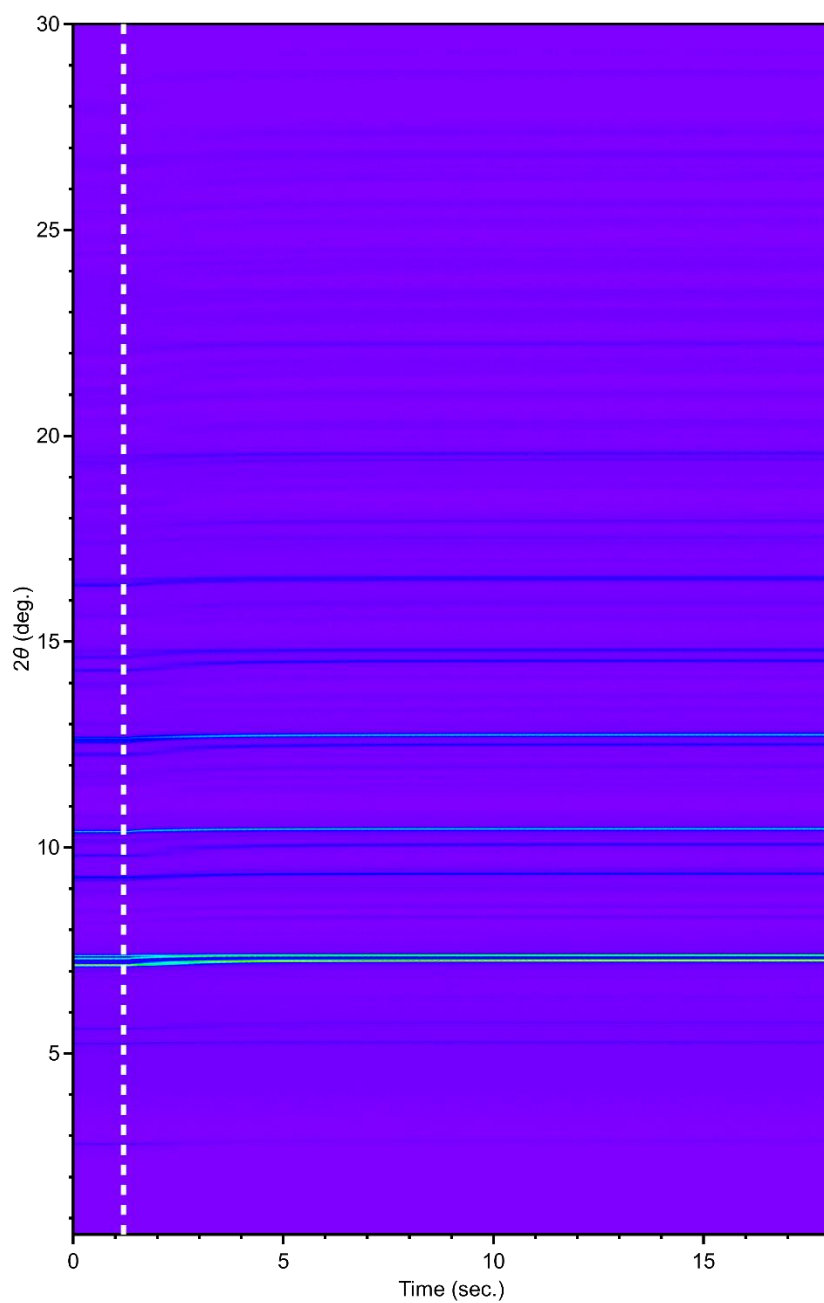


Figure S6. Whole powder diffraction patterns of oxidation reaction for Pd/LaSr₃Fe₃O_{10-δ} at 500 °C. The white dotted lines represent the timing of gas injection.

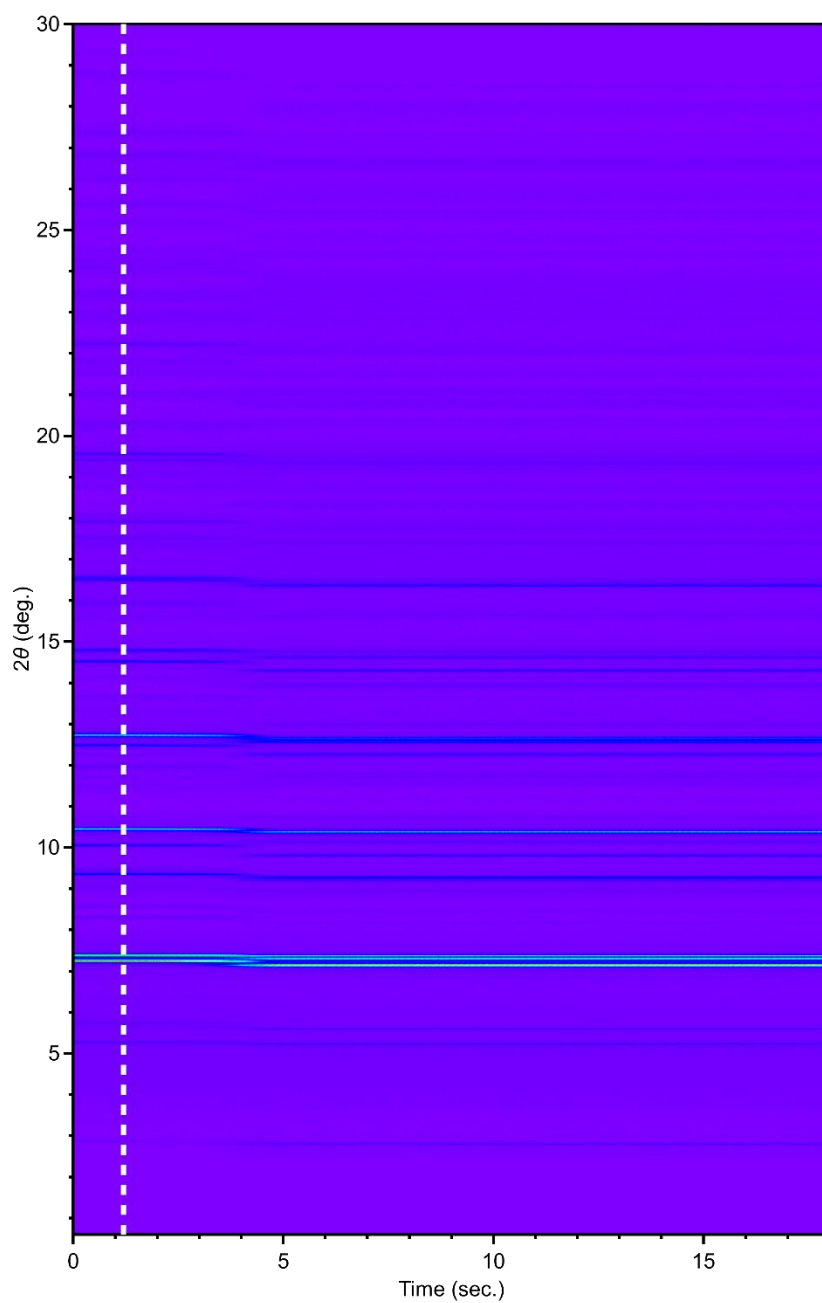


Figure S7. Whole powder diffraction patterns of reduction reaction for Pd/LaSr₃Fe₃O_{10-δ} at 500 °C. The white dotted lines represent the timing of gas injection.

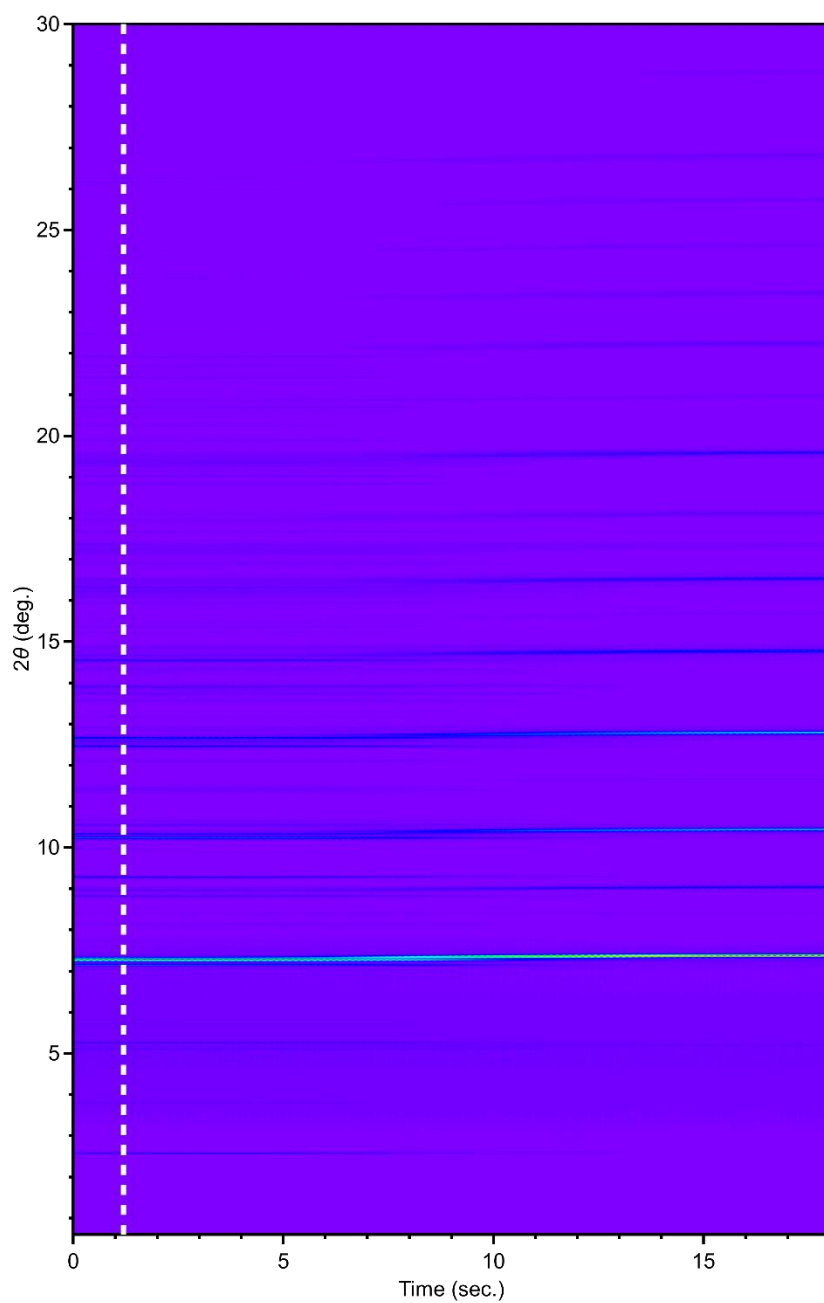


Figure S8. Whole powder diffraction patterns of oxidation reaction for Pd/SrFeO_{3-δ} at 500 °C. The white dotted lines represent the timing of gas injection.

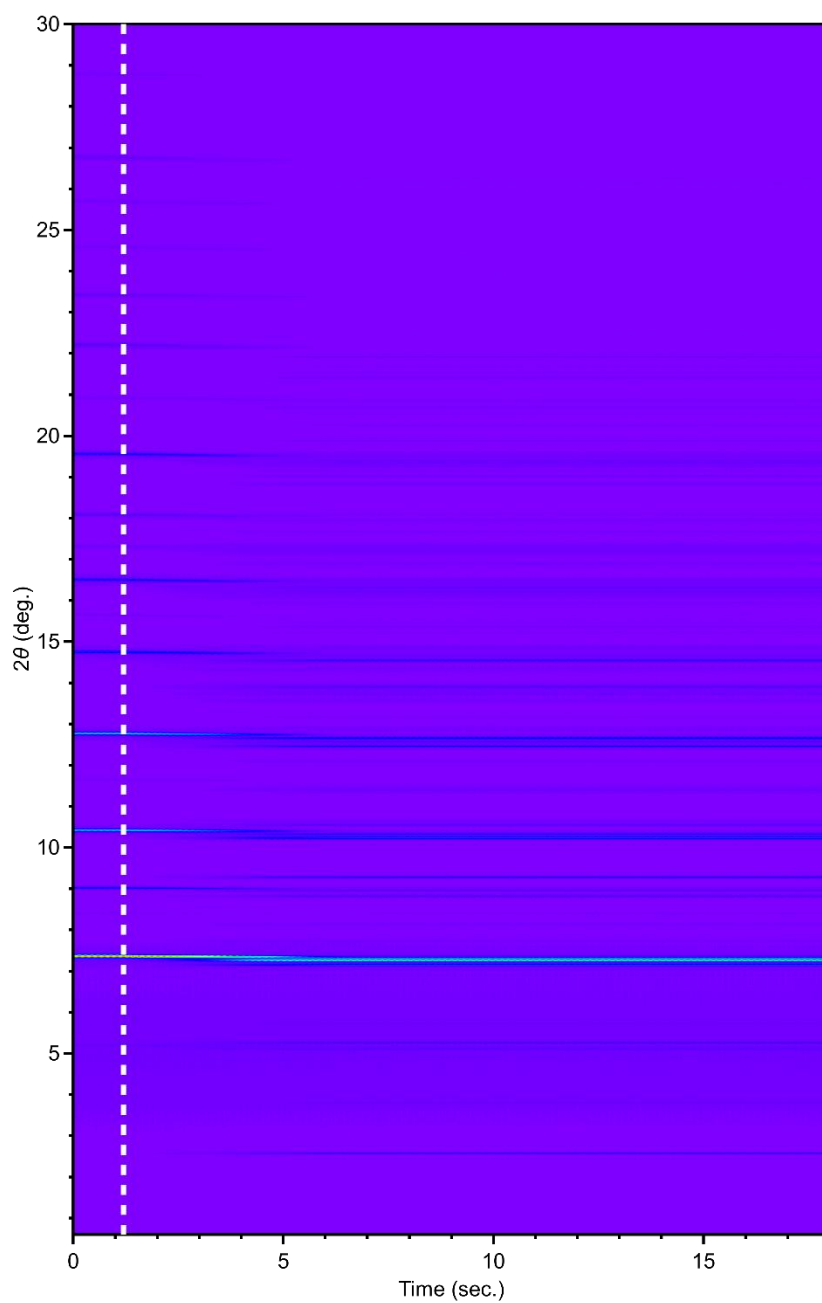


Figure S9. Whole powder diffraction patterns of reduction reaction for Pd/SrFeO_{3-δ} at 500 °C. The white dotted lines represent the timing of gas injection.

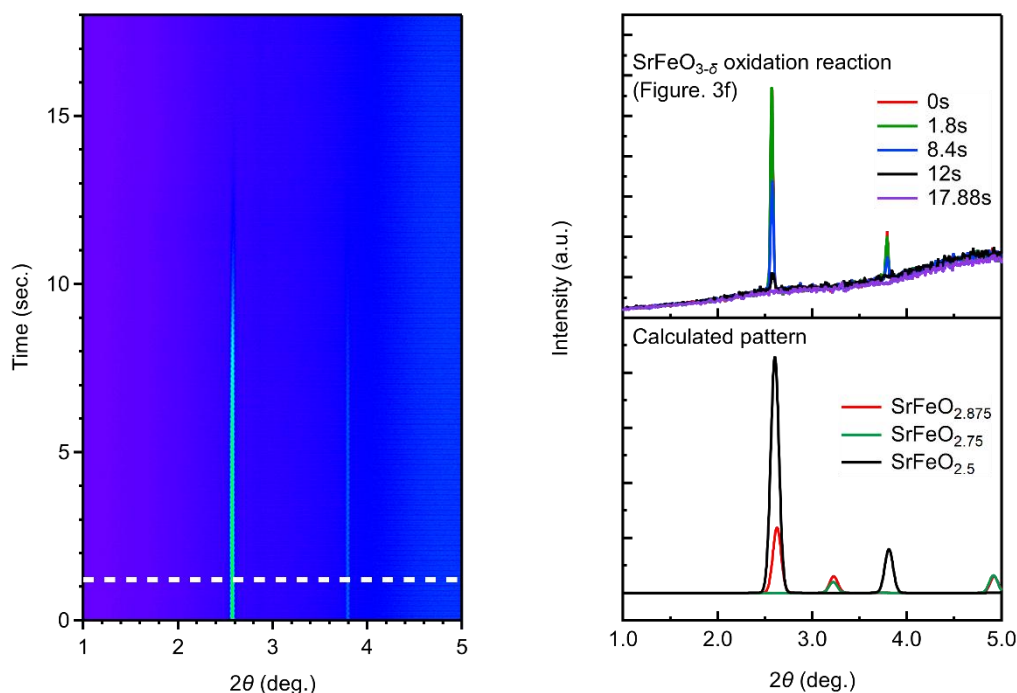


Figure S10. Comparison of XRD patterns of the experimental and reported defect-ordered structures. a) Low-angle Time-resolved XRD data of oxidation reaction for Pd/SrFeO_{3-δ} at 500 °C. The data is the same as Fig. 3f and Fig. S6. The white dotted lines represent the timing of gas injection. b) Comparison of the experimental XRD pattern and calculated pattern in the oxidation reaction of Pd/SrFeO_{3-δ} at 500 °C. There are no peaks around 3 deg. or 5 deg., which correspond to the reported defect-order phase (SrFeO_{2.875} and SrFeO_{2.75}).

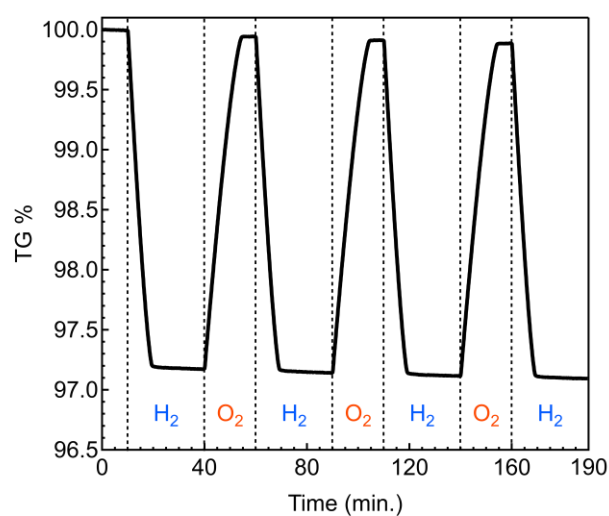


Figure S11. Isothermal oxygen-storage capacity profiles of Pd/κ-Ce₂Zr₂O₈ at 500°C. The gas atmosphere around the sample was switched between 2% H₂/Ar (30 min) and 2% O₂/Ar (20 min) alternately.

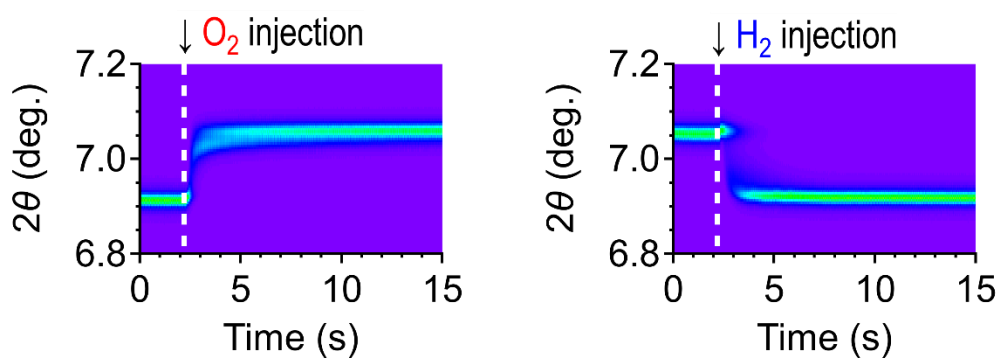


Figure S12. Time-resolved XRD patterns of Pd/κ-Ce₂Zr₂O₈ redox reaction at 500°C. The white dotted lines represent the timing of gas injection.

Table S2. Oxygen storage characteristics of κ -Ce₂Zr₂O₈

	Sr ₃ Fe ₂ O _{7-δ} ($n = 2$)	LaSr ₃ Fe ₃ O _{10-δ} ($n = 3$)	SrFeO _{3-δ} ($n = \infty$)	κ -Ce ₂ Zr ₂ O ₈
Oxygen storage capacity at 500°C ^a	≈ 1.7 wt%	≈ 2.0 wt%	≈ 2.5 wt%	≈ 2.8 wt%
Stability under high-temperature reduction ^b	Partially decomposed	Stable	Decomposed	Stable
Oxidation speed at 500°C ^c	≈ 12 s	≈ 4.5 s	≈ 13 s	≈ 1.8 s
Reduction speed at 500°C ^d	≈ 1.7 s	≈ 3.4 s	≈ 4.3 s	≈ 2.3 s

^a Cyclic-TG measurement with switching gas atmosphere between 2% H₂/Ar (30 min.) and 2% O₂/Ar (20 min.).

^b H₂-TPR measurement with heating to 900°C at 5°C / min, under 2% H₂/Ar flowing.

^{c, d} Time for reaction to progress to 90%, estimated from Time-resolved XRD data at 500°C under pure O₂ / H₂ (≈ 100 kPa).