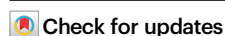


Unlocking stable intermediate states in $\text{SrFeO}_{3-\delta}$ through voltage control of oxygen non-stoichiometry

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Voltage-controlled ion insertion provides a powerful strategy for the analog tuning of material properties, enabling adaptive devices such as neuromorphic transistors and smart displays. Among tunable materials, mixed ionic-electronic conducting oxides undergoing topotactic phase transitions are particularly compelling due to their dramatic property changes between fully oxidized and fully reduced states. However, intermediate oxidation states remain largely underexplored because of significant control limitations. In this work, we investigate the topotactic phase transition in strontium ferrite ($\text{SrFeO}_{3-\delta}$) thin films by progressively and precisely modulating and quantifying oxygen non-stoichiometry via solid-state electrochemical pumping. This fine-tuning approach unveils the co-existence of multiple stable phases in equilibrium configurations across a broad range of oxidation states. A crystallographic mixing model that captures the structural–electronic coupling underlying this phenomenon is proposed, complemented by a defect chemistry framework that quantitatively describes the oxidation mechanism under applied voltage. These findings highlight the critical role of intermediate states in governing functional properties and open new pathways for designing advanced ionotronic oxygen-responsive devices.

The reversible control of metal-to-insulator transitions (MITs) in transition metal oxides via oxygen stoichiometry modulation has emerged as a powerful strategy to engineer materials for next-generation electronic and energy devices^{1–5}. One archetypal mechanism involves the topotactic transition between perovskite (PV, ABO_3) and brownmillerite (BM, $\text{ABO}_{2.5}$) crystal structures, which drastically alters the electronic and ionic transport properties of the material. The PV-to-BM transition is typically accompanied by a rearrangement of oxygen vacancies into ordered channels, and the associated changes in

the valence state of the transition metal cations lead to substantial shifts in functional properties^{4–8}. More broadly, oxygen vacancies are not merely passive defects but electronically active entities that strongly modify local coordination, oxygen diffusion pathways, band structure, carrier density, and transport, particularly near metal–insulator transitions⁹. Their ordering can further introduce structural anisotropy and stabilize distinct crystallographic and electronic states^{10,11}. As a result, structural, electronic, and defect degrees of freedom are intrinsically coupled, offering a pathway to stabilize

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and control emergent functional states through oxygen stoichiometry engineering. These reversible structural and functional modifications have been exploited in various contexts, including solid oxide fuel cells, memristors, and neuromorphic computing elements, where the ability to tune and retain a particular state is key to performance^{4,5,12–15}.

Among these materials, strontium ferrite ($\text{SrFeO}_{3-\delta}$, SFO) has gained increasing attention due to its rich redox chemistry and the accessibility of distinct topotactic phases. The end members of its MIT phase diagram, i.e., BM- $\text{SrFeO}_{2.5}$ and PV- SrFeO_3 , display sharply contrasting physical properties, ranging from insulating behavior in the BM phase to metallic conductivity in the fully oxidized PV state¹⁶. Beyond these end members, several nonstoichiometric phases of SFO are known to exist and have been structurally identified under specific thermodynamic or experimental conditions. In this regard, Mossbauer spectrometry studies have already identified four preferential stable phases at room temperature with formula $\text{SrFeO}_{3-1/n}$, where $n = \infty, 8, 4$, and 2 (see refs. 17–20). Intermediate phases were first reported by Tofield et al.²¹, and Takeda et al.¹⁸, who respectively confirmed the stability of the $\text{SrFeO}_{2.75}$ ($n = 4$) and $\text{SrFeO}_{2.875}$ ($n = 8$) phases at room temperature. $\text{SrFeO}_{2.75}$ has also been observed during the BM-to-PV transformation in in situ TEM experiments, supporting its role as an intermediate state along this transition²².

Importantly, the different SFO phases are not restricted to ideal stoichiometric compositions, but can accommodate oxygen non-stoichiometry over finite ranges²³. Oxygen content therefore acts as a primary thermodynamic variable in SFO, governing crystal symmetry, vacancy ordering, and functional response, while expanding the number of accessible intermediate states beyond the nominal BM ($3 - \delta = 2.5$) and PV ($3 - \delta = 3$) end configurations with coexisting crystallographic phases, depending on stoichiometry and thermodynamic conditions.

However, studies on SFO or similar materials have primarily focused on driving the system between these two extremes through a large oxygen chemical potential difference, for example, employing high-temperature annealing at different $p\text{O}_2$, wet-chemical oxidation, liquid electrochemical gating, or large electrochemical potentials^{24–30}. These approaches often target resistive-switching functionalities by associating the phase transition with binary ON/OFF states. While such binary schemes are technologically attractive, they do not exploit the broader spectrum of accessible intermediate states. This is particularly relevant for neuromorphic and analog devices, where continuous and distinguishable conductance levels are highly desirable. Indeed, intermediate and multiphase states can provide a larger number of stable resistance levels than filamentary switching mechanisms, while preserving the intrinsic structural stability associated with equilibrium or quasi-equilibrium configurations.

At the same time, the importance of intermediate states is not only technological but also fundamental. In many prior studies, these intermediate oxidation states are accessed transiently, under beam- or surface-driven conditions, or without clear evidence of equilibrium or reproducible macroscopic state control^{24–26}. As a result, the continuous evolution of material properties across intermediate equilibrium compositions remains insufficiently explored. In particular, beyond the large metal-to-insulator contrast between the BM and PV end members, the electronic conductivity of intermediate states and its relation to their structural character remain largely unclear. At the same time, the intrinsic complexity of the defect chemistry that stabilizes these states is still poorly understood³¹.

Despite dedicated efforts, the thermodynamic stability, transport properties, and the voltage-addressability of these non-stoichiometric SFO phases remain poorly characterized, especially within the intermediate temperature range spanning from ambient conditions up to 450 °C^{19,28}. Moreover, the defect chemistry of SFO is still under active debate, particularly regarding the origin and nature of its observed positive deviation from dilute-model predictions³¹. Establishing a

coherent picture across the PV–BM continuum is therefore essential for predictive control of the functional response of this family of materials.

Electrochemical oxygen pumping using an all-solid-state structure provides a powerful alternative for tuning oxygen stoichiometry in oxide thin films. By applying an external voltage across a solid electrolyte, the effective oxygen chemical potential in the active material can be precisely modulated^{32,33}. Crucially, this approach enables direct electrochemical potential control of the oxidation state, allowing macroscopic, reversible, and reproducible access to intermediate compositions that would otherwise be challenging to control, while simultaneously monitoring in situ changes in structure and functional properties. Previous studies on systems such as $\text{SrCoO}_{3-\delta}$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (LSF50) have demonstrated the viability of this approach and its potential to induce and stabilize PV–BM transitions via solid-state electrochemical pumping^{32–34}.

In this work, we apply a voltage-driven solid-state electrochemical approach to systematically probe the evolution of $\text{SrFeO}_{3-\delta}$ across a range of nonstoichiometric states. Using a platform previously developed for $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ ³², we modulate the oxygen content of SFO thin films via controlled electrochemical pumping and track the resulting changes in conductivity, lattice parameters, and phase composition. Rather than focusing on the mere existence of intermediate phases, our work emphasizes the ability to set, retain, and reversibly switch between multiple intermediate states in a controlled and continuous manner. Our results reveal a strong coupling between structural transitions and functional properties across the PV–BM continuum. We identify non-volatile, voltage-addressable intermediate states with distinct conductivity signatures and show that their stabilization is governed by an evolving thermodynamic landscape that departs from a simple first-order PV–BM transition. In particular, we show that oxygen non-stoichiometry not only controls phase stability but also reshapes the electronic structure and Gibbs free-energy landscape of $\text{SrFeO}_{3-\delta}$, thereby enabling the stabilization of intermediate states beyond the simple first-order PV–BM picture.

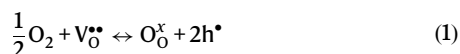
Results

SFO thin films were grown via pulsed laser deposition on (001)-oriented yttria-stabilized zirconia (YSZ) single-crystal substrate previously coated with 15 nm of Gd-doped ceria (CGO). This CGO coating acts as an interlayer, facilitating the epitaxial growth of the functional film. The thickness of the SFO functional layers ranged from 9 to 300 nm. Finally, an amorphous 200 nm Al_2O_3 capping layer was deposited to prevent direct oxygen incorporation from the atmosphere (see “Experimental section” for more details on the sample preparation).

Figure 1a shows a TEM cross-section of a 100 nm-thick $\text{SrFeO}_{3-\delta}$ sample. Well-defined interfaces, as well as CGO and SFO layers with high crystallinity and the desired thickness, were observed. Complementarily, the atomic force microscopy image in Fig. 1b shows a smooth as-deposited SFO surface, with a root mean square roughness of 0.58 nm, consistent with the uniformity observed with TEM. Figure 1c presents the high-resolution XRD $2\theta - \omega$ scan of the as-prepared sample. Note that the SFO orientation is described using pseudocubic (pc) notation, while the structural simulations are performed in the orthorhombic (o) setting. The correspondence between both descriptions is given by $[110]_{\text{pc}} = [100]_{\text{o}}$, $[\bar{1}10]_{\text{pc}} = [010]_{\text{o}}$ and $[001]_{\text{pc}} = [001]_{\text{o}}$ consistent with the alignment of oxygen vacancy channels along the $[100]_{\text{o}}$ direction. The pattern shows that the functional thin film grown on the CGO-coated YSZ is $(001)_{\text{pc}}$ -oriented. The emergence of half-order peaks $(00\frac{1}{2})_{\text{pc}}$ confirms the presence of the BM phase, with oxygen vacancy channels (OVC) lying in-plane, i.e., parallel to the substrate surface.

The in-plane (IP) structural relationship between $\text{SrFeO}_{3-\delta}$ and the substrate was examined using Selected Area Electron Diffraction (SAED). In general, perovskite oxides, and thus brownmillerite $\text{SrFeO}_{3-\delta}$ films, grow on (001)-oriented CGO with a 45° in-plane rotation of their pseudocubic cell to accommodate the substrate lattice parameter^{32,35}. Since the OVC align along the $[100]_o$ direction, lamellae were prepared along the $[100]$ and $[010]$ directions of the YSZ substrates. Figure 1d presents experimental SAED patterns acquired from two characteristic regions of the sample, together with the corresponding simulated patterns, showing excellent agreement. Relaxed SFO films are observed with two predominant IP orientations, corresponding to the two possible 45° in-plane rotations of SFO on CGO. This results in domains with 90° rotation difference in-plane where the OVC are aligned either along or across the lamella direction (see schematics in Fig. 1e). This growth mode has already been reported in other films and can act as a mechanism for strain relaxation^{36,37}. In contrast to other studies, the small compressive strain from the substrate is here relaxed by the coexistence of regions with two different in-plane OVC orientations, rather than by promoting an out-of-plane (OOP) orientation of the OVC as in Santana et al. for $\text{SrCoO}_{3-\delta}$ ³⁸.

Taking advantage of the oxide-ion electrolyte conduction of the YSZ substrate, an electrochemical cell for solid-state electrochemical pumping was fabricated, see schematic in Fig. 2a³². A silver paste counter electrode (Ag-CE) was painted at the opposite side of the YSZ substrate, which was used as a solid electrolyte, and 10 nm Ti/100 nm Au films were sputtered on top of the film for contacts. Oxygen (de) insertion into the film was induced by applying an electrochemical potential difference (V_W) between the top electrodes and the Ag-CE. The system will then act as a half-battery, and atmospheric oxygen (de) incorporation will be promoted by the Ag-CE, while oxygen will start to be (de)inserted at the SFO film. The oxidation reaction happening in the SFO thin film can be summed up as:



where $\text{O}_\text{O}^\times$, $\text{V}_\text{O}^\bullet$, and $\text{h}^\bullet$ denote the oxygen ions, oxygen vacancies and electronic holes species, respectively. The application of electrochemical potential modifies the equilibrium $p\text{O}_2$ of the thin films (see Nernst equation in “Experimental section”), thus driving substitution between $\text{O}_\text{O}^\times$ with $\text{V}_\text{O}^\bullet$ and, ultimately, the BM-PV phase transition in SFO.

In order to increase YSZ ionic conductivity, the temperature of the experiment was kept at 325°C . Different V_W comprised between -0.45 V and 0.1 V were applied in a staircase manner. Note that the CGO and Ti interlayer effect in the total integrated current has been demonstrated to be negligible³². No significant changes in oxygen stoichiometry were observed for $V_W < -0.45\text{ V}$, as evidenced by the absence of measurable current, indicating that the sample is fully reduced ($3-\delta=2.5$) under these conditions.

The oxygen stoichiometry was quantified from the integration of the coulometric current, see Fig. 2b (see “Experimental section” and section S1 in Supporting information for details on the oxygen stoichiometry quantification). Two distinguishable behaviors are observed. Starting from the stoichiometric $\text{SrFeO}_{2.5}$ state stabilized at the lowest potential, the material progressively incorporates oxygen following a dilute model³⁹, i.e., following a natural shift of the equilibrium of the reaction presented in Eq. (1). This trend is followed up to an oxygen stoichiometry of $3-\delta=2.7$, corresponding to an applied V_W of -0.175 V (area colored in purple in Fig. 2b). For higher applied electrochemical potentials, the material follows an oxidation behavior proportional to V_W . This deviation from the ideal solid-solution model, commonly referred to as positive deviation, will be analyzed in detail in the subsequent defect chemistry discussion.

For a better comparison with literature, the data are also plotted as a function of the equivalent $p\text{O}_2$ (calculated using the Nernst potential equation)^{39,40}. The $p\text{O}_2$ value corresponding to the change in behavior aligns with the abrupt loss of the pure $\text{SrFeO}_{2.5}$ -BM structure observed in bulk SFO studies^{23,41}. The oxygen stoichiometry in the positively deviated regime is also in excellent agreement with literature values. However, the dilute oxidation up to $3-\delta \approx 2.7$ has not been previously reported, highlighting the need to investigate the evolution of functional properties in this regime. It is important to stress out that these points are in equilibrium, as demonstrated by the reversibility and cyclability of the material through the application of varying ΔV_W (see section S1 in Supporting Information). Stoichiometries above $3-\delta=2.92$ were not accessed due to the limited voltage range, as higher V_W values degrade the capping layer.

In situ high-temperature XRD measurements were performed to investigate the evolution of the topotactic phase transition across the explored oxidation states (see Experimental Section for more details). Samples were stabilized at 325°C via the application of different V_W inside the X-ray diffractometer. Once stabilized, meaning when the current resulting from the V_W application relaxed to zero, scans were recorded. The evolution of the $00\frac{1}{2}$ and 002 peaks was tracked throughout the different $3-\delta$ values (see Fig. 2c and 2d, respectively). The X-ray diffraction pattern showed minimal changes for V_W below -0.45 V , proving that stable BM- $\text{SrFeO}_{2.5}$ had already been reached at that applied potential.

The BM-related $00\frac{1}{2}$ peak shows maximum intensity at $3-\delta=2.5$ and progressively decreases upon oxidation, with a shift to higher angles (Fig. 2c). At $3-\delta=2.7$, the intensity is strongly suppressed, indicating the loss of long-range vacancy order and the emergence of PV-like structures. The 002 peak, in contrast, maintains nearly constant intensity but shifts continuously, revealing a smooth evolution of the out-of-plane (OOP) lattice parameter across the transition (Fig. 2d). No peak splitting is observed, unlike in related systems such as $\text{SrCoO}_{3-\delta}$ ³³, suggesting a gradual transition rather than abrupt phase separation.

For a precise analysis of these two main peak evolutions, Fig. 2e, f presents the normalized peak intensity of the BM-SFO-related half-order $00\frac{1}{2}$ peak, and the evolution of the cell parameter as a function of the oxygen stoichiometry $3-\delta$, respectively. Both quantities evolve with oxygen incorporation but reflect fundamentally different aspects of the transition. The normalized $00\frac{1}{2}$ peak intensity acts as an order parameter, tracking the BM phase fraction, whereas the OOP lattice parameter reflects a structural average over coexisting BM and PV domains.

Both parameters change trend at the same transition point. In Fig. 2e, the normalized $00\frac{1}{2}$ intensity decreases from its maximum at reduced states and shows a sharp drop at $3-\delta=2.7$, consistent with an order-disorder transition and loss of BM phase fraction. In contrast, Fig. 2f exhibits a smooth evolution of the OOP lattice parameter with only a slight change in slope near $3-\delta=2.7$, reflecting an average over coexisting phases rather than a sharp transition.

The nearly linear decrease of the lattice parameter (see dashed lines in Fig. 2f) can be understood as a simple hard-sphere effect, i.e., the progressive replacement of larger Fe^{3+} ions by smaller Fe^{4+} ions³². Importantly, the OOP lattice parameter extracted from both the $00\frac{1}{2}$ (BM) and 002 (PV-related) peaks follows the same trend, supporting a continuous structural evolution despite the underlying phase transformation.

To discard any strain-induced or size-dependent effect⁴², samples with different thicknesses were studied following the same procedure. Results for the different samples are shown in Fig. 2e, f. No appreciable thickness-dependent difference was seen among the samples, reinforcing the idea that equilibrium intermediate oxidation states were being measured.

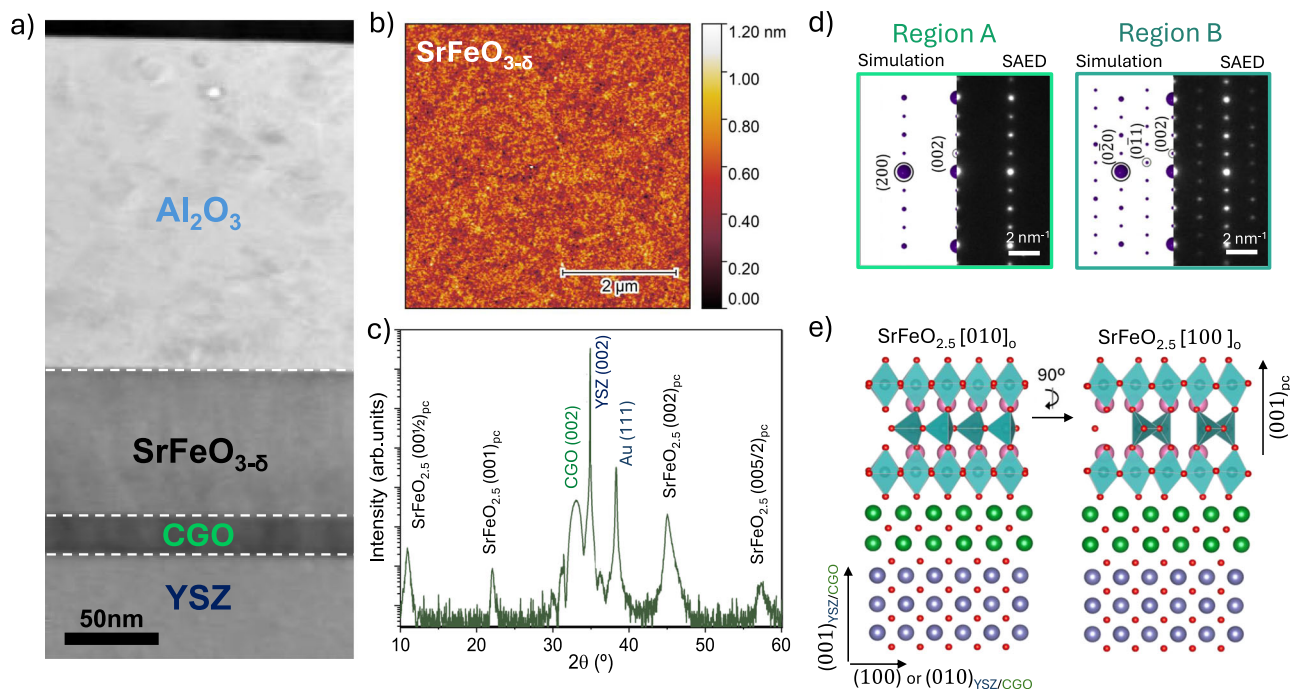


Fig. 1 | Structural characterization of $\text{SrFeO}_{3-\delta}$ thin films. **a** Cross-section TEM image of the yttria-stabilized zirconia (YSZ) / Gd-doped ceria (CGO)/ $\text{SrFeO}_{3-\delta}$ /Al₂O₃ system for the 100 nm-thick SFO sample. **b** AFM image of the SFO topography after deposition. **c** As-deposited X-ray diffractogram of the sample measured at room temperature (RT). **d** Experimental Selected Area Electron Diffraction (SAED) patterns measured at two different regions of the cross-section SFO lamella and corresponding simulated pattern along the orthorhombic (o) [010]_o and [100]_o zone

axes. **e** Schematic illustrating the two in-plane orientations of SFO on top of the substrate. Red spheres represent O, green Ce, purple Zr, magenta Sr. Cyan octahedra and dark cyan tetrahedra represent FeO₆ and FeO₄ units, respectively, defining the brownmillerite oxygen-vacancy channels along [100]_o. Structures were obtained with VESTA⁵⁶. Source data are available in the repository at <https://doi.org/10.34810/DATA3361>.

These results suggest that, in the most reduced states, dilute oxidation of the BM structure is followed. This initial regime corresponds to a single-phase over-stoichiometric BM structure, where oxygen is incorporated within the vacancy channels⁴³. The stability range of *over-stoichiometric* BM reaches a limit close to $3-\delta=2.7$, when the long-range order of the vacancies is lost. This point marks the transition from a single-phase regime to a regime where multiple crystallographic phases begin to coexist, as discussed below. Beyond this, the system transitions toward PV-like structures, accompanied by a change in thermodynamic behavior and a continued contraction of the lattice consistent with the increasing average Fe oxidation state. This is in line with DFT simulations, where O atoms were progressively incorporated into one oxygen vacancy plane of the BM- $\text{SrFeO}_{2.5}$, showing that such accumulation is thermodynamically favored up to $3-\delta \approx 2.7^{22}$.

To gain deeper insight into the observed trends, lamellae from three samples with predetermined oxidation states were fabricated using focused ion beam (FIB) milling and examined via transmission electron microscopy (TEM). Samples were initially equilibrated at 325 °C at their corresponding V_W and subsequently quenched to room temperature. The lamellae were prepared parallel to the [100] and [010] directions of the YSZ substrate (see “Experimental section” for more details). Samples’ oxidation states were selected based on their oxygen deficiency parameter ($3-\delta$), corresponding to: (i) the dilute BM region ($3-\delta=2.6$), (ii) transition region ($3-\delta=2.7$), and (iii) positive deviation region ($3-\delta=2.8$), respectively. Figure 3a–c shows cross-sectional TEM images of the SFO films for three different samples, all oriented with the out-of-plane direction vertical and the substrate at the bottom, while the corresponding FFT patterns of selected image regions are displayed below (Fig. 3d–f). An analysis of the cell parameter variation of the films at the different measured overall oxygen concentrations is given in section S2 in Supporting Information. The

result of the overall OOP cell parameter is in good agreement with the results from the in situ XRD results.

In Fig. 3a, TEM image of the $3-\delta=2.6$ sample is displayed. Although the overall oxidation state deviates from that of pure brownmillerite ($3-\delta=2.5$), characteristic OVC inherent to the brownmillerite structure are distinctly visible throughout the specimen. The TEM micrograph exhibits regions with two distinct crystallographic orientations: one with vacancy channels oriented perpendicular to the image plane, and another with vacancy channels aligned parallel to the image plane. This is further supported by the FFT patterns shown in Fig. 3d and the corresponding simulated diffraction (Fig. S8), consistent with the SAED results in Fig. 1d. The extracted out-of-plane Sr–Sr interatomic distances display the characteristic alternating BM structure in both regions (see Fig. S9), confirming a homogeneous over-stoichiometric BM phase.

In the transition region ($3-\delta=2.7$), the TEM images reveal the coexistence of BM domains with regions of distinct structural contrast (Fig. 3b). The corresponding FFT pattern (Fig. 3e) contains the reflections expected for BM, but also additional spots that cannot be indexed within either the BM or cubic PV structures. To further resolve this configuration, SAED of the whole layer was performed, see Fig. 3g. The experimental pattern is partly consistent with BM viewed along the [010]_o zone axis, confirming the presence of BM-related order, yet also displays extra superlattice reflections not captured by the BM model. These additional spots are instead well reproduced by simulations of $\text{SrFeO}_{2.75}$ along the same [010]_o zone axis, supporting the assignment of a distinct intermediate phase. This interpretation is reinforced by convergent beam electron diffraction (CBED) measurements (Fig. S10), as well as by the measured interplanar spacings and angular relations, which cannot be consistently indexed within the BM framework (Fig. S11).

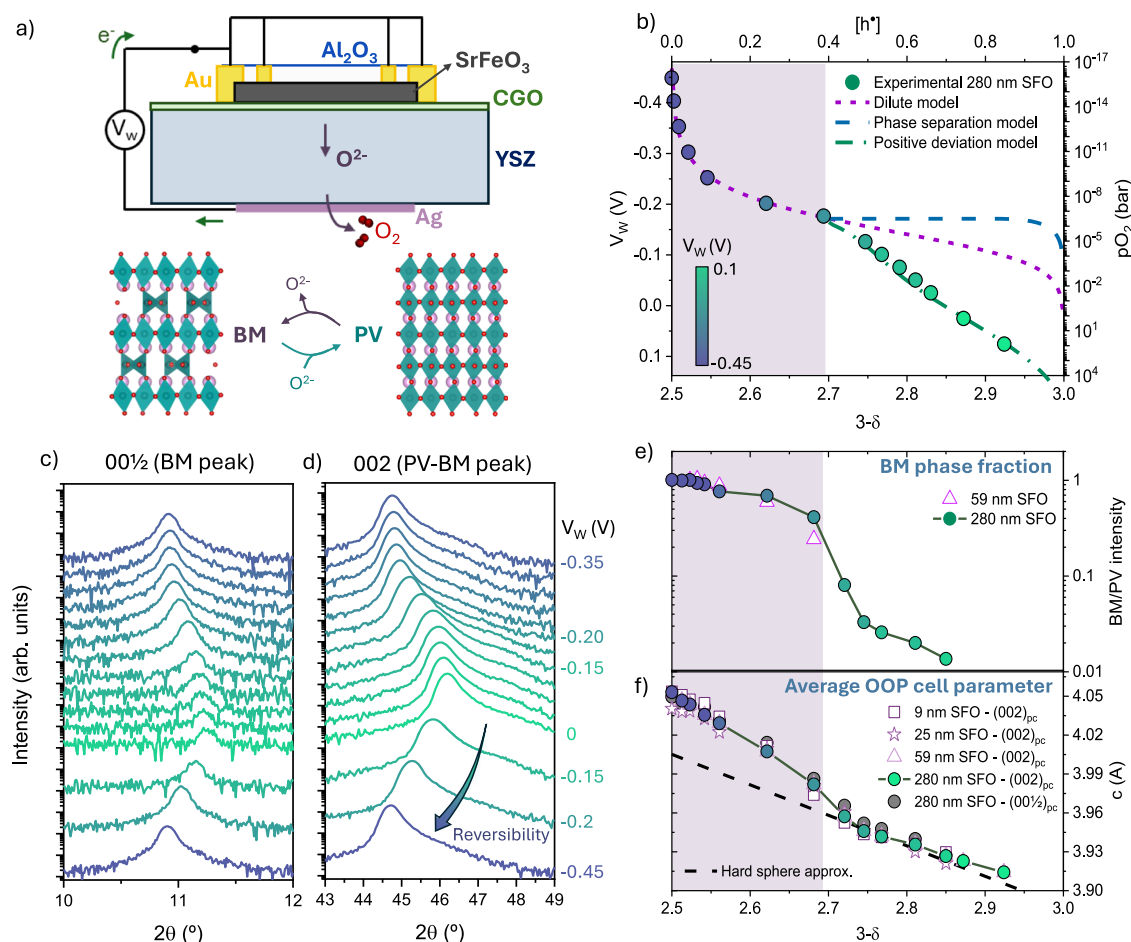


Fig. 2 | In situ tracking of structural evolution during electrochemical oxidation. **a** Sample schematic for electrochemical-potential-induced oxygen (de) insertion in SrFeO_{3-δ} during the reversible brownmillerite (BM) to perovskite (PV) phase transition. YSZ and CGO denote yttria-stabilized zirconia and Gd-doped ceria, respectively. Red spheres represent O, magenta spheres Sr, and cyan polyhedra FeO₆/FeO₄ coordination units in SFO. Structures were obtained with VESTA³⁶. **b** Oxidation curve extracted from current integration for SrFeO_{3-δ} at 325 °C. Fits according to dilute, phase-separation, and positive-deviation models are reported. The color scale of the data points indicates the applied electrochemical potential, V_W. **c, d** Evolution of the 00½ pseudocubic peak associated with BM long-range order and of the 002 pseudocubic SrFeO_{3-δ} peak, respectively, under different

electrochemical potentials at 325 °C. Measurements were performed from reducing (V_W = -0.35 V) to oxidizing (V_W = 0 V) conditions and then back to reducing conditions (V_W = -0.45 V) to test reversibility. Line colors follow the same V_W scale as in (b). **e** Semi-log plot of the normalized BM-associated peak intensity as a function of oxygen content for films with different thicknesses. Data-point colors follow the same V_W scale as in (b). **f** OOP cell parameter evolution for films with different thicknesses. Colored and empty points correspond to values extracted from the 002 pseudocubic peak, while grey points correspond to values obtained from the 00½ half-order peak. The dotted line indicates the expected variation considering a hard-sphere approximation, i.e., cell variation with the Fe³⁺/Fe⁴⁺ ratio. Source data are available in the repository at <https://doi.org/10.34810/DATA3361>.

Consistently, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Fig. 3h) reveals the coexistence of BM and IPh domains at the nanoscale. Comparison with HAADF-STEM simulations (Fig. 3i, j), together with analysis of Sr-Sr interatomic distances (Fig. 3k, l), highlights the absence of the characteristic alternating BM structure within the IPh regions. Altogether, these results provide compelling evidence for the presence and structural distinction of the intermediate SrFeO_{2.75} phase in the transition oxidation state (3-δ = 2.7) sample. This phase, known to be thermodynamically stable at low temperatures^{20,22,28}, exhibits a checkerboard-like ordering arising from partial occupation of oxygen vacancies within the Sr planes.

Finally, in the sample equilibrated within the region exhibiting positive deviation (3-δ = 2.8) areas exhibiting a cubic crystalline structure were observed (see Fig. 3c). Nevertheless, certain BM regions remained in the thin film. Moreover, clamping of the BM phase of a couple of nanometers was observed at the interface with CGO and Al₂O₃, explaining why a small (00½) peak intensity could still be seen at the most oxidized states (see section S2 in Supporting Information).

FFT reveals a cubic cell with no vacancy channel formation, characteristic of the cubic PV phase, where oxygen vacancies are randomly distributed throughout the lattice. Similar structure and consistent phase ratios were observed across the entire lamella, indicating that the analyzed regions in Fig. 3 exhibit representative behavior of each corresponding state.

As pointed out by the equilibrium oxidation experiments and the in situ XRD results, a more complex description than a first-order phase transition occurs in the material. As revealed by the TEM measurements, *over-stoichiometric* BM stable states start to transition towards PV-like structures with progressive domain crystallographic changes. This leads to the coexistence of multiple phases even in equilibrium with a precisely applied V_W. This observation aligns well with the continuous change in the out-of-plane cell parameter across the intermediate oxidation states seen in the XRD data. Based on these observations, we distinguish between two regimes within the intermediate oxidation range: (i) a single-phase regime at lower oxidation states, and (ii) a multiphase regime at higher oxidation states, where BM, IPh, and PV domains coexist.

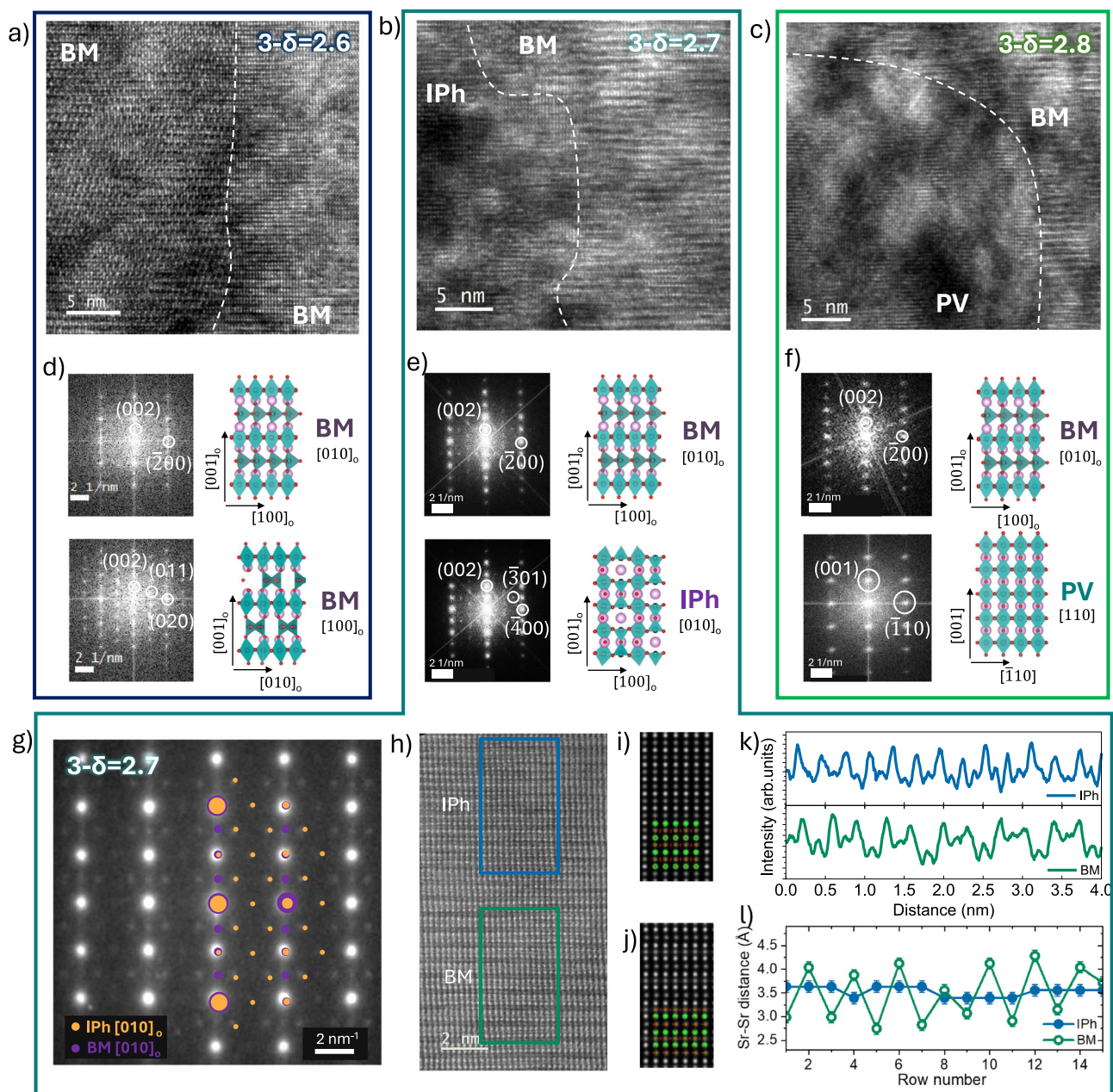


Fig. 3 | Ex situ short-range order. TEM images (a–c) and corresponding FFT patterns (d–f) acquired at different oxidation states. Panels a–c and d–f correspond to approximate $3-\delta$ values of 2.6, 2.7, and 2.8, respectively. The fast Fourier transform (FFT) patterns (d–f) are shown together with the indexed SFO structures/orientations. The TEM regions used to extract the FFT patterns in (d–f) are indicated in Fig. S7. Dashed lines in the TEM images indicate boundaries between phases or crystallographic orientations. g SAED pattern acquired from the whole SFO layer in the $3-\delta=2.7$ sample, together with simulated diffraction patterns of

the brownmillerite (BM) and intermediate (IPh) structures along the orthorhombic (o) $[010]_o$ zone axis, showing that the additional reflections are consistent with the IPh. h HAADF-STEM image of a region containing IPh (top) and BM (bottom) domains, compared with HAADF-STEM simulations along the $[001]$ zone axis (i, j). k Out-of-plane intensity profiles extracted from IPh and BM regions, and l corresponding Sr–Sr interatomic distances, highlighting the difference between the alternating BM structure and the homogeneous IPh phase. Source data are available in the repository at <https://doi.org/10.34810/DATA3361>.

To understand the effect of intermediate oxidation states on the electronic properties of the material, conductivity and optical property characterization were conducted (see Experimental Section). A color map showing the conductivity of the SFO films as a function of temperature at set oxygen stoichiometry is plotted in Fig. 4a. Again, the overall behavior can be interpreted following two distinct regimes. For the lowest measured oxygen content, i.e., $3-\delta=2.5-2.7$, the conductivity is highly temperature dependent. This is in line with dilute polaron hopping conductivity observed in other transition metal oxide materials. This behavior considers the holes to be localized over the

Fe–O bond length, and their hopping to the nearest neighbor to be assisted by phonons^{44,45}. The behavior of the conductivity follows an Arrhenius law with a given activation energy ($E_a \sim 0.3$ eV) related to the hopping process (see section S3 in Supporting Information). For states with $3-\delta > 2.85$, the temperature dependence of the conductivity is negligible. Besides, conductivity exhibits behavior characteristic of an ideal metallic conductor, indicating the absence of a thermally activated conduction mechanism. The insulator-metal transition is also highlighted by the optical conductivity measured by in situ ellipsometry, see section S4 in Supporting Information. Starting

with the fully reduced BM-SrFeO_{2.5} state, the material shows the expected behavior for an isolating material characterized by a band gap of 2.4 eV (see section S4 in Supporting Information). As the oxidation state increases, the gap gradually narrows, and a new in-gap transition emerges, driving the system towards metallic behavior²⁹.

A detailed visualization of conductivity variation as a function of the oxygen stoichiometry for the experimental isothermal conductivity at $T = 50^\circ\text{C}$ is shown in Fig. 4b. A change of nearly six orders of magnitude is observed from the fully reduced BM-SrFeO_{2.5} to the fully oxidized PV-SrFeO₃. This remarkable change at the two completely opposite extremes is the typically exploited ON/OFF resistive switching applications^{5,14}. Within this isotherm, distinct conductivity regimes can be identified. In the over-stoichiometric-BM range ($3 - \delta < 2.7$), conductivity increases when progressively incorporating oxygen in the OVC, reaching a saturation value of around 0.1 Scm^{-1} . This behavior is consistent with the polaron hopping mechanism, where the conductivity scales with $[h^*](1 - [h^*])$, corresponding to the probability of an occupied site adjacent to an unoccupied one^{44,45}. For the oxidized PV region ($3 - \delta > 2.85$), the conductivity follows a different trend, becoming proportional to $[h^*]$, as transport is dominated by band conduction through delocalized holes. The conductivity values of fully oxidized SFO reported in the literature match the trend observed for the conductivity measured for SFO within that range (see Fig. 4b)^{29,46}.

In contrast, the oxidation regime where multiple phases coexist ($2.7 < 3 - \delta < 2.85$), presents a sharp increase in conductivity of about four orders of magnitude, which cannot be explained by conventional single-phase models. Following these observations, a local mixture of insulating (polaronic-like) and conductive volumes was considered by employing the well-known Bruggeman's rule of mixing equation for a symmetric medium (see more details in section S3 in Supporting Information)⁴⁷:

$$f_{pol} \cdot \frac{\sigma_{pol} - \sigma}{\sigma_{pol} + \left(\frac{1-L}{L}\right)\sigma} + f_{met} \cdot \frac{\sigma_{cond} - \sigma}{\sigma_{cond} + \left(\frac{1-L}{L}\right)\sigma} = 0 \quad (2)$$

Where σ , σ_{pol} , σ_{met} correspond to the conductivity of the mixture, the polaronic-like phase and the metal-like conductive phase, respectively, and f_{pol} and f_{met} are the volume fractions for each phase. As shown in Fig. 4b (dashed black line), the model perfectly fits the sigmoidal increase of conductivity of the multiphase regime. Furthermore, this approach can be extended to all measured isotherms, allowing the stability regions of the different conductivity regimes to be mapped as a function of temperature (see Section S3 in Supporting Information). In general, increasing temperature stabilizes the conductive (PV-like) phase over a wider δ range, in agreement with bulk observations^{23,41}.

To investigate reversibility and long-term stability of coexistent-crystallographic-domain states, cyclability and conductivity evolution with time were addressed. Multiple electrical cycles were performed under controlled conditions, and the temporal evolution of conductivity in fixed states was monitored to assess domain retention, possible fatigue effects, and the degree of reversibility in the structural transitions. Figure 4c shows the conductivity values of SFO when cycling the material between three different states located in the mixture region: $3 - \delta = 2.7$, 2.75, and 2.8, respectively. The repeatability of the obtained conductivity values was confirmed by changing the state up to 25 times in a random order to check for any hysteretic behavior. No apparent changes in conductivity were observed when the state was equilibrated, and the results showed that the conductivity level could be set in a deterministic manner when applying the same V_W .

To investigate the temporal evolution of domains, the film's conductivity was monitored at room temperature after setting a state at 325°C of $3 - \delta = 2.7$, 2.75, and 2.8, respectively. Figure 4d shows conductivity retention over a 72-h experiment. The results indicate

excellent temporal stability, with variations below 2% and no evidence of oxygen redistribution or conductivity drift. These findings confirm that the intermediate states correspond to stable equilibrium configurations. This study is particularly relevant for device fabrication, as the materials and domain structures presented here exhibit promising performance characteristics, making them strong candidates for stable and reliable functional applications.

Overall, functional electronic properties of SFO could be linked to crystallographic changes happening along the different equilibrium states. Properties of SFO were modeled following two main extreme BM- and PV-stable regimes. The first presents dilute polaronic hopping behavior and a large band gap, and the last presents a closed band gap, due to the emergence of in-gap energy states, with a temperature-independent metallic conductivity. Notably, even within the BM regime alone, progressive oxygen incorporation produces a conductivity increase of over two orders of magnitude at 50°C , highlighting the strong functional tunability of the over-stoichiometric BM phase prior to the onset of phase coexistence. The experimental evolution of the properties in the mixed phase region could be reproduced by a combination of polaronic/metallic regions, in agreement with the crystallographic evolution results from XRD and TEM (see Fig. 4e). The overall change of nearly six orders of magnitude is comparable to that observed in LSF50³². However, unlike LSF50, where conductivity is governed by an antiferromagnetic-to-paramagnetic transition, in SFO thin films, this change originates from structural transitions and the associated band-structure modifications induced by oxygen content. Nonetheless, a contribution from the magnetic structure to the transport properties cannot be entirely excluded (see section S3 in Supporting Information).

Given the equilibrium nature of the attained oxidation states, it is possible to attempt a bulk defect chemistry description of SFO (full derivation is presented in Supporting Information S5). For a dilute mixture, the equilibrium of the oxygen incorporation reaction shown in Eq. (1) is:

$$\Delta G_{ox}^0 = 2\mu_h^0 + \mu_{O_o}^0 - \frac{1}{2}\mu_{O_2}^0 - \mu_{V_o}^0 = -RT \ln \left(\frac{\delta \cdot ([h^*])^2}{(3 - \delta) \cdot pO_2} \right) \quad (3)$$

Where ΔG_{ox}^0 refers to the standard free energy of the oxidation reaction, μ_h^0 , $\mu_{O_o}^0$, $\mu_{O_2}^0$, and $\mu_{V_o}^0$ are the standard chemical potentials of holes, lattice oxygen, gaseous oxygen, and oxygen vacancies, respectively. The different defect concentrations, i.e., $[h^*]$ and δ , can be calculated from site conservation and electroneutrality rules, while pO_2 can be obtained from μ_O . For an ideal solid solution, ΔG_{ox}^0 remains constant ($\Delta G_{ox}^{0,id}$) over the full range of oxygen stoichiometry. Experimentally, this behavior is observed in the BM region up to $3 - \delta \approx 2.7$ (Fig. 5a), consistent with the dilute regime identified in Fig. 2b. However, this model fails to capture the deviation observed for $3 - \delta > 2.7$, where the system departs from dilute behavior.

At that stoichiometry range, this classical dilute defect chemistry model needs to be extended to account for the potential coexistence of different phases, as observed by XRD and TEM, and the positive deviation of ΔG_{ox}^0 from $\Delta G_{ox}^{0,id}$. The enthalpy of mixing (h_{mix}) term is commonly added to describe phase separation and reproduce their deviation from the solid solution approach (see Supporting Information S5)⁴⁸. While this model performs well for phase-change materials such as SrCoO_{3- δ} ⁴⁹, it does not reproduce the distinctive behavior of SrFeO_{3- δ} . In particular, the phase-separation model fails to capture the progressive formation of the phases at different equilibrium V_W states (see Fig. 2b) and the experimentally observed positive deviation of ΔG_{ox}^0 (see Fig. 5a).

Several alternative approaches have been proposed to account for the positive deviations from the ideal dilute model, such as those observed in the experimental data for SFO^{31,50}. A common strategy

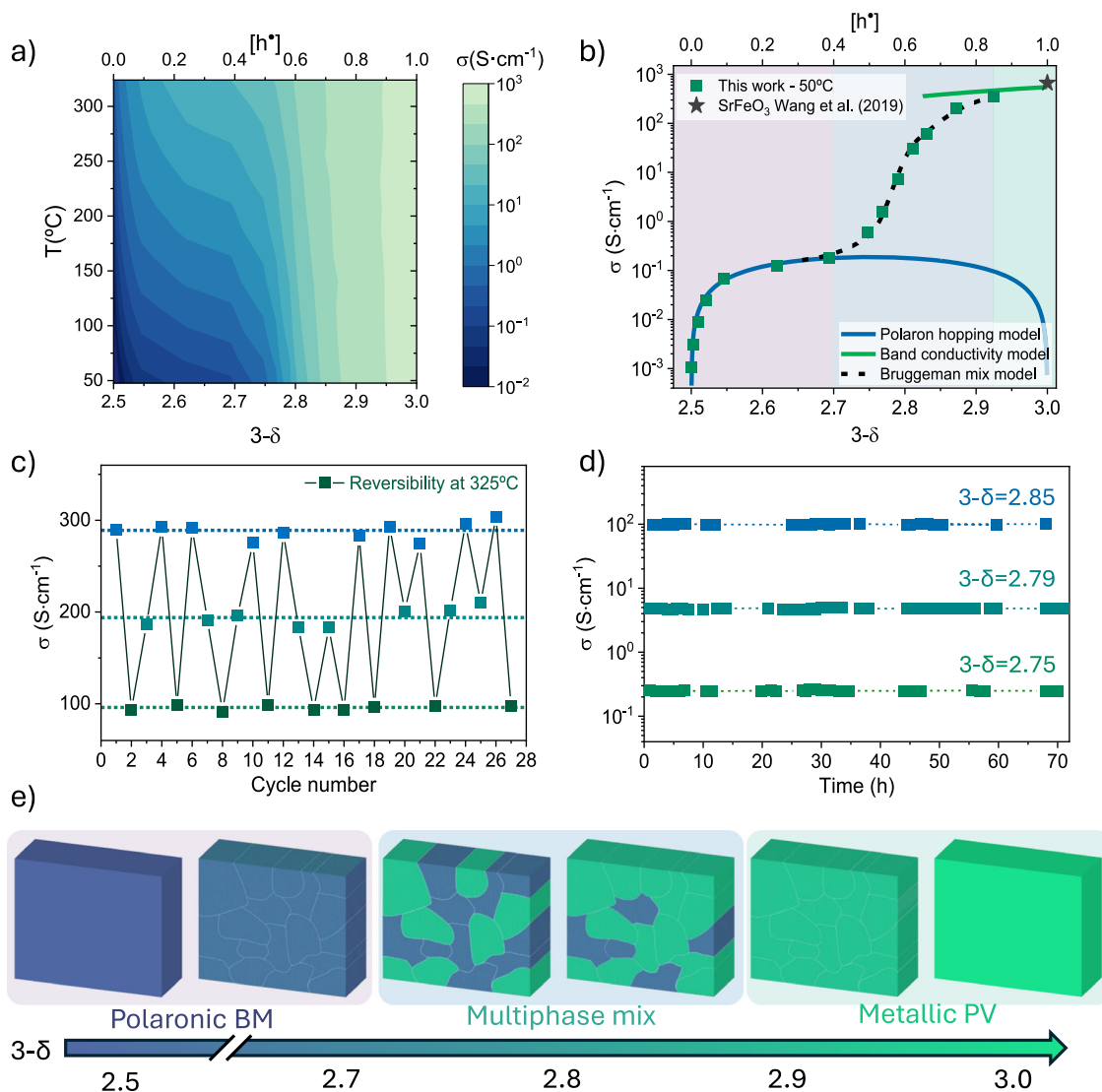


Fig. 4 | Electronic transport across intermediate oxidation states.

a Conductivity map of SFO as a function of oxygen non-stoichiometry and temperature. **b** Conductivity of SFO at 50 °C as a function of its defect concentration. Trends expected for the polaronic hopping, band conductivity, and Bruggeman mix of phases are shown. Reference conductivity for SrFeO₃ from Wang et al. is also included^{18,42}. **c** Conductivity of SFO measured at three oxidation states at $3-\delta = 2.75$, 2.8, and 2.85; after changing the material stoichiometry reversibly. The

dotted lines indicate the average conductivity levels during cycling. **d** Conductivity of SFO over time for the same states at room temperature. Square symbols correspond to experimental measurements, while dotted lines indicate the average conductivity levels. **e** Schematic evolution of the conductivity mechanism in SFO as a function of the oxygen stoichiometry. Source data are available in the repository at <https://doi.org/10.34810/DATA3361>.

involves introducing an activity coefficient for holes, $\gamma_{h^{\bullet}}$, which effectively modifies their standard chemical potential, $\mu_{h^{\bullet}}^{\circ}(h^{\bullet})$. This leads to a change in the equilibrium as:

$$\Delta G_{ox}^{\circ} = \Delta G_{ox}^{\circ, id} - 2RT \ln(\gamma_{h^{\bullet}}) = \Delta G_{ox}^{\circ, id} + 2\Delta\mu_{h^{\bullet}}^{\circ}([h^{\bullet}]) \quad (4)$$

Where $\Delta G_{ox}^{\circ, id}$ is the standard free energy for the ideal solid solution behavior, and $\Delta\mu_{h^{\bullet}}^{\circ}([h^{\bullet}]) = \mu_{h^{\bullet}}^{\circ}([h^{\bullet}]) - \mu_{h^{\bullet}}^{\circ}([h^{\bullet}] = 0)$ corresponds to the change in $\mu_{h^{\bullet}}^{\circ}$ as a function of the hole concentration. Here, we directly probed the variation of $\mu_{h^{\bullet}}^{\circ}$ by analyzing the variation of optical conductivity measured as a function of oxygen stoichiometry at 325 °C and its connection to the evolution of the band structure upon oxidation (see section S4 in Supporting Information). Specifically, we considered here the lower-energy transition A ($\hbar\omega = 0.6$ –1.3 eV), previously associated with electron transfer from the top of the valence band to the hole-induced in-gap band (see Fig. 5b)^{29,32,46}. Importantly, since the hole-induced level location in the energy

landscape corresponds to $-\mu_{h^{\bullet}}^{\circ}$ ⁵¹, the energy of Transition A is directly $\hbar\omega_A = (-\mu_{h^{\bullet}}^{\circ}) - E_{VB}$. Assuming the center of $\mu_{h^{\bullet}}^{\circ}$ and E_{VB} to remain fixed, $\mu_{h^{\bullet}}^{\circ}$ would change at half the rate of $\hbar\omega_A$. Consequently, the standard oxidation free energy evolve as:

$$\Delta G_{ox}^{\circ} = \Delta G_{ox}^{\circ, id} + 2\Delta\mu_{h^{\bullet}}^{\circ} = \Delta G_{ox}^{\circ, id} - \Delta\hbar\omega_A \quad (5)$$

where $\Delta\hbar\omega_A = \hbar\omega_A - \hbar\omega_A([h^{\bullet}] = 0)$. Figure 5a displays the evolution of the energy of its maximum, $\hbar\omega_A$, with non-stoichiometry as experimentally determined from optical conductivity measurements (see section S4 in Supporting Information for further details) together with the variation observed for ΔG_{ox}° obtained using Eq. (4). Notably, both quantities exhibit the same dependence on oxygen stoichiometry, matching in both trend and magnitude, as highlighted by the use of a common energy scale. This direct correspondence indicates that the evolution of ΔG_{ox}° follows that of the hole chemical potential. Importantly, incorporating this dependence into the defect chemistry

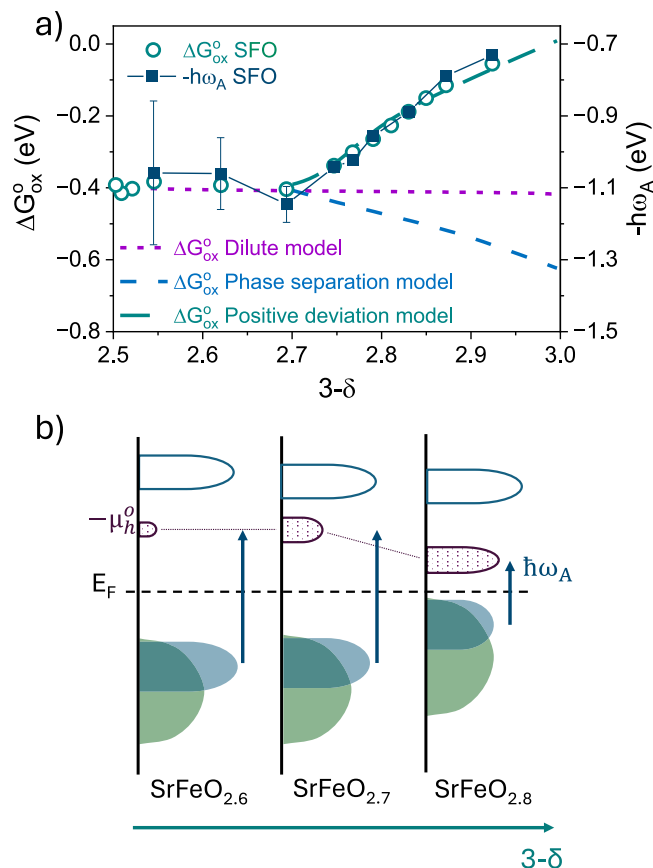


Fig. 5 | Oxidation thermodynamics across intermediate states. **a** Standard free energy of the oxidation reaction (ΔG_{ox}°) as a function of oxygen non-stoichiometry, showing the experimental data measured at 325 °C, together with the dilute solid-solution, phase-separation, and positive-deviation models. The energy evolution of optical transition A ($\hbar\omega_A$) is included for direct comparison with the experimental ΔG_{ox}° . **b** Schematic of the band evolution as a function of the oxygen stoichiometry. Filled regions represent occupied valence-band states, empty regions represent unoccupied conduction-band states, and dotted regions denote hole-induced in-gap band states. Green and blue indicate O 2p and Fe 3d character, respectively. Optical transition A ($\hbar\omega_A$), the Fermi level (E_F) and the standard chemical potential of holes ($-\mu_h^\circ$) are also indicated. Source data are available in the repository at <https://doi.org/10.34810/DATA3361>.

description reproduces the experimental oxidation behavior (Positive deviation model, see Fig. 2b), including the onset of the positive deviation beyond $3-\delta \approx 2.7$.

In summary, the defect chemistry of SFO deviates from ideal solid-solution behavior upon the dissolution of the BM phase and the formation of IPH/PV phases ($3-\delta > 2.7$). However, the standard phase-separation model fails to reproduce the observed behavior. Likewise, different defect models—such as O-interstitial, oxygen-centered hole, or iron-centered hole descriptions—cannot independently account for the observed behavior of the material (see section S5 in Supporting Information)^{52,53}. The presented positive deviation model successfully captures this shift, supported by experimental evidence that correlates the deviation with significant modifications in the material's band structure. Indeed, as the oxygen stoichiometry in the system overcomes $3-\delta = 2.7$, the material undergoes a transition from an extrinsic semiconducting regime to a degenerate regime, characteristic of heavily doped materials, which brings a narrowing of the bandgap. Based on optical conductivity measurements, it was observed that the polaronic hole level ($-\mu_h^\circ$) was highly dependent on non-stoichiometry. The introduction of the variation of μ_h° with hole concentration $[h^\bullet]$ in the defect chemistry model

accounted for the positive deviation from the ideal solid-solution behavior in SFO. The results from electrical and structural characterization suggest the presence of phase mixtures in this region, indicating that these phases lie close in the Gibbs free energy landscape. Under this premise, section S5 in Supporting Information presents a more detailed evaluation of the Gibbs free energy profile and proposes a description for the coexistence of the mixture of phases in the positive deviation region.

Discussion

This study reveals the critical role of intermediate oxidation states in shaping the structural, electronic, and transport properties of $\text{SrFeO}_{3-\delta}$. Through a combined experimental and modeling approach, this work demonstrates that these states can be reproducibly accessed, stabilized, and retained as equilibrium or quasi-equilibrium configurations under electrochemical potential control, with distinct defect chemistry and electronic structure.

The crystallographic order of the different equilibrium states was studied with in situ XRD and ex situ TEM. Our findings show the equilibrium coexistence of BM with other structures across a broad oxidation range, as well as the electrochemically addressable stabilization of an over-stoichiometric ($3-\delta > 2.5$) BM phase. The evolution of functional electronic properties across these states can be effectively described using a sequence of polaronic, phase-mixture, and metallic-like transport regimes. The temporal stability of these states was also demonstrated. Moreover, the evolution of the electronic hole level with overall non-stoichiometry modulates the oxidation thermodynamics of the material, giving rise to a positive deviation in Gibbs free energy.

From a device perspective, the ability to electrochemically access and stabilize multiple intermediate and coexisting states offers a promising route toward multilevel resistive switching. This can result in a larger number of stable and distinguishable resistance states, while preserving the intrinsic stability associated with equilibrium or quasi-equilibrium configurations.

Altogether, this study establishes a direct link between structural evolution and functional properties in SFO and highlights the potential of electrochemical control to unlock voltage-addressable, non-volatile regimes of phase stability and device functionality in oxygen-responsive materials. The importance of exploring the often-overlooked in-between states and their key role in understanding and tailoring the properties of correlated oxide systems is highlighted. Their intrinsic stability also makes their use promising for the development of robust and durable functional devices, particularly in fields such as solid-state electrochemistry, neuromorphic computing, and iontronics.

Methods

Sample fabrication: SFO thin films were epitaxially grown on gadolinium-doped ceria (CGO)-coated YSZ (001) $1 \times 1 \text{ cm}^2$ substrates using a large-area pulsed laser deposition (PLD) system, PVD products equipped with a KrF excimer laser ($\lambda = 248 \text{ nm}$) from Lambda Physik. The protective CGO layer ($\sim 20 \text{ nm}$) was deposited to prevent the formation of secondary phases at the interface of SFO with YSZ^{54,55}. Subsequently, SFO films of different thicknesses were deposited. During both depositions, the substrate temperature was kept at 600 °C, in an oxygen partial pressure of 0.0067 mbar during the deposition, and the substrate-target distance was set to 90 mm. The films were grown with an energy fluency of 0.8 J cm^{-2} per pulse at a frequency of 10 Hz. The deposition of the functional layer was done using a microfabricated Si mask with a size of $2.5 \times 3.5 \text{ mm}^2$ centered in the substrate. A conductive 10 nm Ti/100 nm Au electrode was microfabricated by photolithography and thermal evaporation. Finally, the alumina (Al_2O_3) capping layer of approximately 200 nm was also deposited via PLD following the same conditions as the other

PLD-deposited layers. The Al_2O_3 did not cover the entire sample area, allowing for direct contact between the tips and the Au stripes close to the edges. Silver paste was also used on the backside of the YSZ substrate as a counter electrode. The thickness and roughness of each deposition step were checked prior to the following, allowing for a precise thickness measurement after deposition.

Electrochemical characterization: Different V_W were applied to equilibrate the material at different potentials. The application of different V_W values results in distinct equilibrium shifts in reaction written in Eq. (1) of SFO, analogous to a modification of the equilibrium oxygen partial pressure ($p_{\text{O}_{2,eq}}$) through the Nernst potential:

$$p_{\text{O}_{2,eq}} = p_{\text{O}_{2,Ref}} \cdot \exp\left(\frac{4e\Delta V}{k_B T}\right) \quad (6)$$

Where $p_{\text{O}_{2,Ref}}$ is the reference ambient p_{O_2} . As a consequence, the change of oxygen stoichiometry induced when modifying oxygen equilibrium reads as a current (I_W) that reduces as the material reaches the equilibrium. The integration of this current along the transition between stable states is directly proportional to the change in oxygen non-stoichiometry ($\Delta\delta$) in the material⁵⁵:

$$\Delta\delta = -\frac{V_{u.c.}}{2eV_{film}} \int_0^t I_W(t) dt \quad (7)$$

Where e is the electron charge, $V_{u.c.}$ refers to the volume of the unit cell, and V_{film} is the volume of the film. Staircase chronopotentiometry was used to calculate the oxygen stoichiometry of the films as a function of the applied V_W . Measurements of the coulometric current and the applied potential are presented in section S1 of the Supporting Information.

In situ XRD setup: in situ evolution of the cell parameter during high-temperature electrochemical pumping was conducted in a heating stage provided by Anton Paar (DCS 1100), and the simultaneous voltage application with a Keithley 2401. Three platinum wires were used for electrical contacts. One was connected to the silver-painted plate of the stage holder to reach the counter electrode of the sample. The other two were attached to the top contacts with small drops of gold paint. The holder height and tilt were adjusted for proper alignment with the XRD beam, and the electrical connections were routed to the Keithley. The temperature was increased to 325 °C. Voltages ranging from −0.45 V to 0.1 V were applied stepwise in both directions, recording the current at each step. XRD spectra were acquired after the current had stabilized. All experiments were carried out in atmospheric air.

Lamellae preparation and local structural characterization: in-plane 45° rotation of the SFO cell with respect to CGO (and YSZ) is expected, in accordance with their respective cell parameter values, similar to $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ ³². This rotation translates to two possible equivalent in-plane orientations (right-handed and left-handed 45° rotated, respectively), separated by a total angle of 90°. To investigate the directional ordering of oxygen vacancies, two TEM lamellae were prepared at close region of each of the studied samples along perpendicular crystallographic orientations. First, a cross-sectional lamella was extracted using focused ion beam (FIB) milling, oriented perpendicular to the film surface to visualize the out-of-plane structure and following the (100)-plane direction of the YSZ substrate. A second orthogonal lamella was then prepared following the (010)-plane direction of the substrate. These two orientations allow for the perpendicular and/or parallel observation of the oxygen vacancy channels in SFO, as these follow the $[100]_0$ direction. This dual-directional approach enables the identification of anisotropic features and allows vacancy ordering to be resolved along the in-plane direction of interest. The lamellae were characterized in both a JEOL JEM2010F for High-Resolution Imaging (HRTEM) and Selected Area Electron Diffraction

(SAED), and a JEOL JEM-ARM200 (NeoARM) for High-Angle Annular Dark-Field Scanning TEM (HAADF-STEM) and 4D-STEM microdiffraction, both working at 200 kV. HRTEM offers information about the crystallographic planes in real space, at a sub-nanometric level, while HAADF-STEM actually shows the projection of atomic columns of cations in our sample. Regarding reciprocal space, on the one hand, 4D-STEM acquires an electron diffraction of each pixel in a STEM image, therefore obtaining order information at the nanometer level. SAED, on the other hand, extracts that information from a much larger area, but retains higher reciprocal space resolution and SNR, being therefore well suited for detecting weaker reflections. They have all been used to elucidate the phases present in the studied materials. Electron diffraction patterns along this zone axis were simulated using EjeZ software (TEM UCA).

Electrical characterization: Electrical conductivity measurements of the thin film were performed at different temperatures using a heating stage (Linkam instruments THMS600E-2) and 4-probe measurements with a Keithley 2400. Initially, the state was set by applying voltages from −0.45 V to 0.1 V across the YSZ at a temperature of 325 °C. Once the current was stabilized, the electronic conductivity of SFO was measured using the four microfabricated contacts following a 4-point probe method. Conductivity values were obtained by going up and down in temperature to attain for any hysteretic behavior and considering the geometrical characteristics of the sample.

Spectroscopic Ellipsometry Measurements: Spectroscopic ellipsometry was performed using a Horiba UVISEL system to measure the optical constants of SFO thin films from 0.6 to 5.0 eV (in 0.05 eV steps) with a 70° incident angle. The data were modeled and fitted using DeltaPsi2 software. Voltages from −0.45 V to 0.1 V were applied step by step in both directions, recording the current at each step. In situ measurements were taken at different temperatures after each voltage step equilibration.

Data availability

The datasets generated and analyzed during the current study, including the Source Data underlying the main and Supplementary Figs., have been deposited in CORA Repositori de Dades de Recerca and are available at <https://doi.org/10.34810/DATA3361>.

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Author contributions

Experiments were conceived by F.C., P.N. and A.T. Sample preparation was carried out by P.N., electrochemical characterization by P.N. XRD analysis was carried out by F.G., A.K., L.Z., R.D., F.C., P.N. and A.R.C. TEM lamella preparation was performed by A.R.C. and L.Y., TEM analysis by A.R.C., O.F., L.Y., S.E. and F.P. The original research plan was designed by F.C. and A.T.; P.N. prepared the initial draft. All the authors contributed to the interpretation and discussion.

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Competing interests

The authors declare no competing interests.

Additional information

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