

***In situ* probing of voltage-driven metal exsolution in perovskite cathodes modulated by B-site composition**

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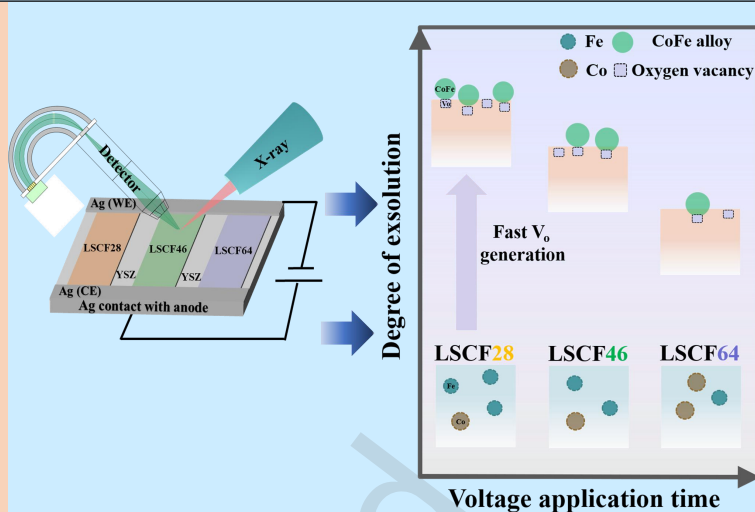
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This study investigates the effect of B-site composition on voltage-driven metal exsolution from perovskite cathodes, revealing that oxygen vacancy generation plays an important role in affecting the exsolution behaviors.

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ABSTRACT

Voltage-driven metal exsolution from perovskite (ABO₃) cathodes is a promising strategy for developing high-performance solid oxide electrolysis cells (SOECs). However, the effect of B-site composition on the exsolution process remains unclear due to the lack of direct and in situ comparison of the key parameters influencing exsolution. Herein, a multi-electrode model cell with graded potential distribution was constructed using La_{0.6}Sr_{0.4}Co_xFe_{1-x}O_{3-δ} (x = 0.2, 0.4 and 0.6, denoted as LSCF28, LSCF46 and LSCF64) as cathodes. Coupled with in situ spatially resolved X-ray photoelectron spectroscopy (μ-XPS), the effect of Co/Fe ratios on voltage-driven exsolution behaviors was investigated under the same conditions. The in-situ and comparative characterization results reveal preferential exsolution of Co⁰ compared with Fe⁰ under applied voltage. Moreover, the overall metal exsolution rates and oxygen vacancy generation rates follow the order LSCF28 > LSCF46 > LSCF64, suggesting that the oxygen vacancy plays an important role in linking Co/Fe ratios to voltage-driven exsolution. This work provides mechanistic insights for optimizing SOEC electrodes and establishes an efficient in situ strategy for comparative studies of multiple material systems.

KEYWORDS

solid oxide electrolysis cell (SOEC), voltage-driven exsolution, oxygen vacancy, in situ μ-XPS, multi-electrode model cell

1 Introduction

In situ exsolution of metal nanoparticles from perovskite (ABO₃) has recently emerged as an effective strategy for constructing metal/oxide heterointerfaces that enhance both catalytic activity and structural stability of electrodes in solid oxide electrolysis cells (SOECs) [1–6]. Among various influencing factors, the composition of B-site transition metals fundamentally influences exsolution behavior by modulating oxygen vacancy formation, lattice strain, and metal–oxygen bond strength [7–9]. For instance, increased Co incorporation in Pr- and Sr-based perovskites promotes oxygen vacancy generation and accelerates metal exsolution; however, excessive doping compromises structural stability, leading to particle coarsening or phase transformations [10,11]. Density functional theory (DFT) calculations reveal that Co doping enhances Fe–O octahedral distortions, weakens metal–oxygen bond strength and lowers the oxygen vacancy formation energy [12]. Collectively, these studies establish the importance of B-site regulation in exsolution under reducing atmospheres. Recently, voltage-driven exsolution under electrochemical polarization has also attracted increasing attention due to its faster exsolution rate and greater controllability [13–15]. However, the role of B-site composition in controlling voltage-driven exsolution and interfacial evolution remains insufficiently understood

[16–18].

Elucidating this issue requires both a compositionally tunable model system and a precise kinetic driving force. Among perovskite oxides, La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} (LSCF) and its derivatives serve as an excellent platform for the controllable exsolution of Co–Fe nanoparticles [19–21]. Previous work has demonstrated the effectiveness of voltage-driven exsolution strategy for LSCF. For instance, electrochemically exsolved nanoparticles on LSCF markedly decrease polarization resistance in SOECs [22] and similarly enhance product selectivity (C₂₊ and C₃H₆) during methane oxidative coupling [23]. Beyond these performance enhancements, fundamental studies have unraveled the unique mechanisms of this process. Koohfar et al. demonstrated that cathodic polarization promotes Co⁰ exsolution, triggering surface reconstructions and boosting intrinsic catalytic activity [24]. Kim et al. further revealed the ultrafast character of voltage-driven exsolution, showing that Co nanoparticles form within 2 min under –1.30 V at 700 °C. They also identified a critical electrochemical switching point (–0.98 V) associated with electrochemical reduction of the LSCF, which triggers the rapid progression of exsolution [25].

These studies predominantly rely on single and fixed LSCF compositions and, thus, the effect of Co/Fe ratios on voltage-driven exsolution remains unclear. Furthermore, it is known that oxygen vacancy generation is closely related to

the exsolution process [26,27]. Nevertheless, systematic and in situ studies linking B-site composition, oxygen vacancy formation, and voltage-driven exsolution under rigorously controlled comparative conditions are still lacking.

To address these challenges, a novel multi-electrode model cell with spatially graded potentials was designed using $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x = 0.2, 0.4$ and 0.6 , denoted as LSCF28, LSCF46 and LSCF64) as cathodes. By combining this model cell with in situ spatially resolved X-ray photoelectron spectroscopy (μ -XPS), direct and systematic investigation of voltage-driven exsolution behaviors across different cathodes under controlled comparative conditions was achieved. The results reveal that Co^0 exsolves preferentially, followed by Fe^0 exsolution. Moreover, the metal exsolution rates decrease in the order of $\text{LSCF28} > \text{LSCF46} > \text{LSCF64}$, consistent with the rates of oxygen vacancy generation. These findings reveal the compositional dependence of voltage-driven exsolution and provide guidance for rational designing of high-performance perovskite electrodes for SOECs.

2 Experimental

2.1 Sample preparation

2.1.1 Preparation of electrode slurries

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x = 0, 0.2, 0.4$ and 0.6 , denoted as LSF, LSCF28, LSCF46 and LSCF64, respectively) perovskite oxide powders were synthesized via a citric acid-assisted sol-gel method. First, $\text{La}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (Aladdin Industrial Corporation, AR), $\text{Sr}(\text{NO}_3)_2$ (Aladdin Industrial Corporation, AR), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aladdin Industrial Corporation, AR) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aladdin Industrial Corporation, AR) were dissolved in deionized water according to the stoichiometric ratio. Citric acid, at 1.5 times the total molar amount of metal ions, was then added to the solution, followed by ethylenediaminetetraacetic acid (EDTA) at 1.5 times the total molar amount of metal ions. Finally, the pH of the solution was adjusted to 9 using aqueous ammonia. The mixture was heated at 80°C under stirring until solvent evaporation yielded a yellow gel, which underwent self-propagating combustion to yield black powders. The powders were calcined at 1000°C for 5 h to obtain LSCF samples. The synthesized oxide powders were then combined with a solvent mixture of 94 wt% terpineol and 6 wt% ethyl cellulose at a 6:4 mass ratio to form the homogeneous electrode slurries.

2.1.2 Preparation of single-electrode model cell

The formed LSCF28 slurry was printed onto one side of a $10 \times 10 \times 0.5 \text{ mm}^3$ single-crystal Y_2O_3 -stabilized ZrO_2 (YSZ) electrolyte for the anode and dried under a heat lamp. Then LSF and LSCF28 slurries were coated with approximately equal thickness at opposite side of YSZ as the cathodes, respectively. The slurries were then dried under a heat lamp and sintered at 1100°C for 3 h, forming LSF|YSZ|LSCF28 and LSCF28|YSZ|LSCF28 cells.

2.1.3 Preparation of multi-electrode model cell with spatially graded potentials

The formed LSCF28 slurry was printed onto one side of a 10

$\times 10 \times 0.5 \text{ mm}^3$ single-crystal YSZ electrolyte for the anode and dried under a heat lamp. The opposite side was divided into three equal areas ($2 \times 10 \text{ mm}^2$) using masking tape, onto which LSCF28, LSCF46, and LSCF64 slurries were coated with approximately equal thickness. The sample was finally sintered at 1100°C for 3 h, forming three cathodes on the YSZ in one model cell. To investigate the effect of local potential on the metal exsolution behaviors of the three electrodes, a graded potential configuration reported in our previous work was employed [28]. Ag paste was applied to both ends of each electrode. One end served as the current collector for the working electrode (WE) during voltage application, whereas the other was connected to the LSCF28 anode (counter electrode, CE) on the backside of the YSZ through a lateral Ag conductive layer, thereby creating a continuous local potential gradient along the electrode surface.

2.2 Characterizations

In situ metal exsolution process was characterized using μ -XPS (PHI VersaProbe IV, ULVAC-PHI, Japan), which is equipped with a micro-area monochromatized Al $K\alpha$ radiation (1486.6 eV) source with the spot size ranging from 7.5 to 200 μm . The X-ray beam diameter chosen for this work was 100 μm . Photoelectron take-off angle was set at 45° , and the pass energy was set at 112 eV for the narrow scan under ultra-high vacuum condition (UHV, base pressure: $2 \times 10^{-8} \text{ mbar}$). Ar^+ ion beam was used to clean the sample surface with a sputtering voltage of 4 kV and an etching area of $1 \times 1 \text{ mm}^2$. Binding energies were calibrated using the lattice O 1s spectrum at 529.0 eV [29]. During the in situ XPS measurement, it takes ~ 10 min to complete the acquisition of the Co $2p_{3/2}$, Fe $2p_{3/2}$, and O 1s spectra on the three cathodes surface.

An electrochemical workstation (CHI660E, Chenhua, China) was used to apply a constant voltage to the samples in the XPS analysis stage, enabling in situ XPS characterization. Therefore, this setup allowed for the observation of the temporal evolution of elements on the sample surface upon applying voltage. The cells were first heated to 600°C under UHV condition and then a -3.0 V voltage was applied, resulting in currents of approximately $3.5 \sim 6.2 \text{ mA}$.

Scanning electron microscope (SEM: JSM-7900F, Japan) was utilized to characterize the surface morphology of cathodes after voltage-driven exsolution. ImageJ software was used to analyze the SEM images of the exsolved LSCF surface. X-ray diffraction (XRD) experiments were performed on the SmartLab X-ray diffractometer (Cu $K\alpha$ radiation source, $\lambda = 1.5418 \text{ \AA}$) with an operating current and voltage of 40 mA and 40 kV with scan rate of $10^\circ\text{C min}^{-1}$. High-resolution transmission electron microscopy (HRTEM) was performed on a JEM-F200 (JEOL, Japan) equipped with an FEI Tecnai G2 F20 EDS detector and operated at 200 kV.

3 Results and discussion

3.1 Role of B-site cation in voltage-driven exsolution

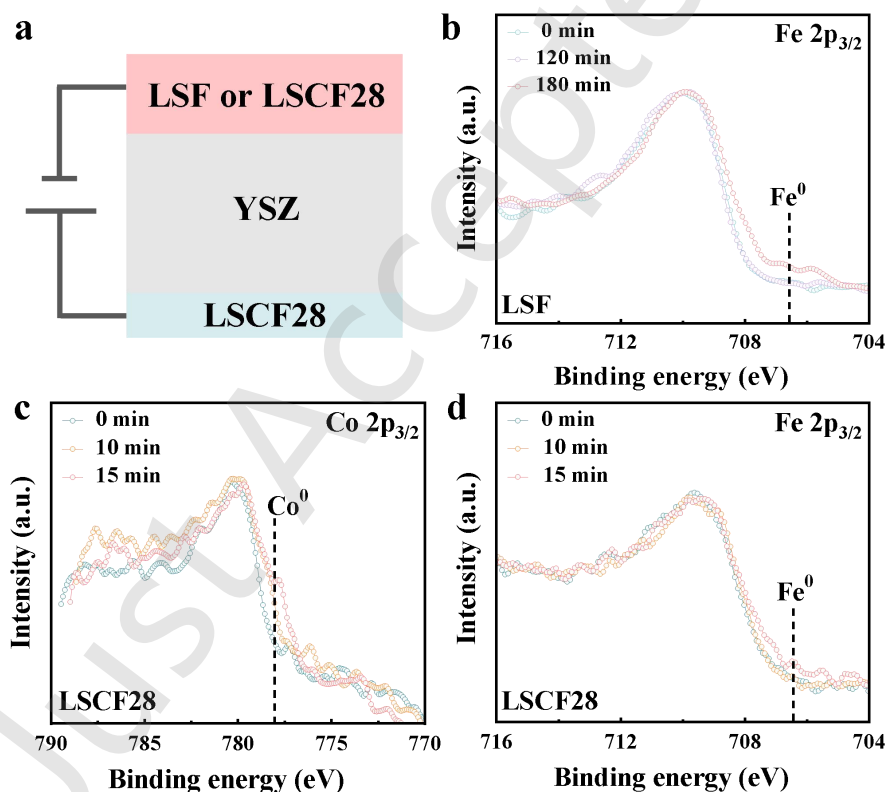
To gain fundamental insight into the role of B-site cations in voltage-driven exsolution, a simplified single-electrode

sandwich model system was first employed to systematically compare the exsolution behaviors of LSF and LSCF28 cathodes. The LSF|YSZ|LSCF28 and LSCF28|YSZ|LSCF28 model cells are shown in Fig. 1(a). While DFT predicts that the lower segregation energy of Co should thermodynamically favor its surface emergence over Fe, the actual kinetic response of these coupled cations under an applied voltage has yet to be experimentally validated in situ [7,30]. To address this gap, in situ XPS was employed to investigate the exsolution process of LSF and LSCF28.

For in situ XPS measurement, the model cell was mounted on the sample stage of XPS analysis chamber and resistively heated to $\sim 600^\circ\text{C}$ under UHV. The LSF and LSCF28 cathodes were first cleaned by Ar^+ etching to remove adventitious carbon, which does not induce reduction or exsolution of Co or Fe species. Subsequently, an external voltage was applied at 600°C using an electrochemical workstation. The shift of O 1s binding energy (ΔBE) from the open circuit voltage (OCV) condition was used as a direct

LSF and LSCF28 cathodes are -2.45 V and -2.55 V , respectively.

Time-resolved Fe $2p_{3/2}$ and Co $2p_{3/2}$ spectra of LSF and LSCF28 are shown in Fig. 1(b-d) and Fig. S1(a-c). The XPS signals of metallic Co^0 at 778.1 eV [23] and metallic Fe^0 at 706.5 eV [33–35] indicate the exsolution of Co^0 and Fe^0 with prolonged reaction time. For the model cell with the LSF cathode (Fig. 1(b)), the XPS signal of Fe^0 near 706.5 eV emerges after 180 min of applying voltage. In contrast, for the LSCF28 cathode (Fig. 1(c)) Co^0 signal near 778.1 eV is detected after only 10 min reaction under the same condition. Meanwhile, Fe element remains in an oxidized state during this period, and the Fe^0 signal appears after reaction for 15 min (Fig. 1(d)). These results demonstrate sequential exsolution in LSCF28, where Co^0 exsolves prior to Fe^0 under the applied voltage. Compared with LSF, the Co-containing cathode also exhibits a much faster evolution of metallic species. This comparison suggests that Co incorporation



indicator to evaluate the effective potential of each cathode [31,32]. When applying -3.0 V , the effective potentials of

effectively accelerates the reduction/exsolution behavior of LSCF under applied voltage.

Figure 1 In situ XPS characterization of metal exsolution under -3.0 V at 600°C . (a) Schematic of the single-electrode sandwich model cell. (b) Fe $2p_{3/2}$ XPS spectra of the LSF cathode. (c) Co $2p_{3/2}$ and (d) Fe $2p_{3/2}$ XPS spectra of the LSCF28 cathode.

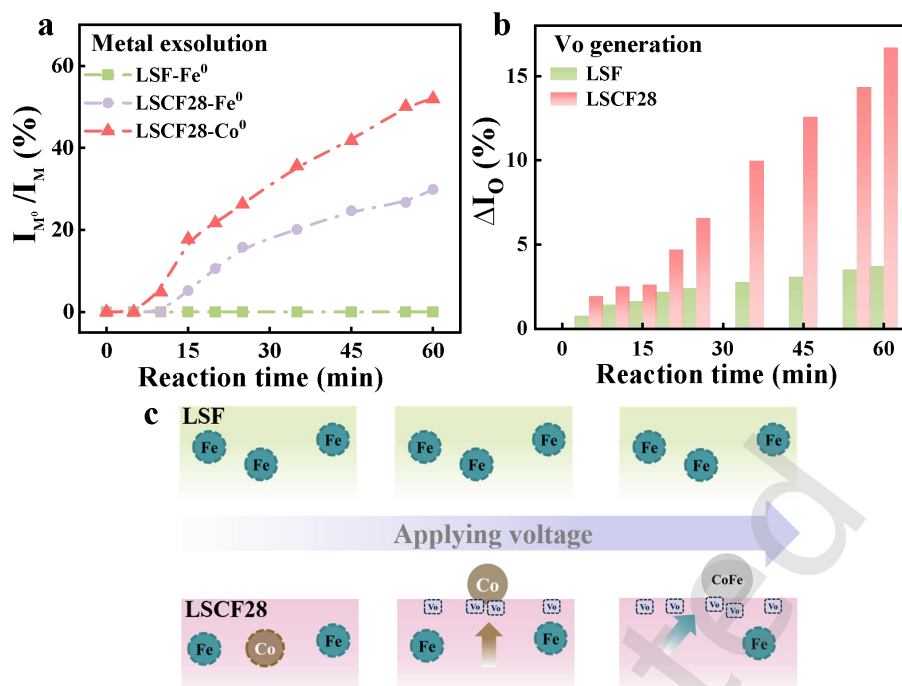


Figure 2 The role of B-site cation in voltage-driven exsolution. Time-dependent evolution of (a) the normalized peak intensity ratio (I_M^0/I_M) of Fe⁰ and Co⁰, and (b) oxygen vacancy concentration in LSF and LSCF28. Reaction condition: −3.0 V, 600 °C. (c) Comparison of voltage-driven exsolution behavior between LSF and LSCF28 cathodes.

To further verify this promoting effect, the temporal evolution of surface Co⁰ and Fe⁰ on LSF and LSCF28 at −3.0 V was semi-quantitatively analyzed. Due to overlapping Auger features arising from the monochromatic Al K α X-ray source (Fig. S2), Fe 2p and Co 2p spectra could not be reliably deconvoluted [36]. Therefore, the exsolution kinetics was semi-quantitatively evaluated using the peak intensities of the metallic Fe⁰ (706.5 eV) and Co⁰ (778.1 eV) species derived from Fig. S1(a-c). The temporal evolution of their normalized intensity ratios (I_M^0/I_M) is plotted in Fig. 2(a). Here, I_M^0 represents the peak height of the exsolved metallic phase (Fe⁰ or Co⁰), while I_M represents the sum of the peak heights of metallic and oxidized species. The I_M^0/I_M ratio is employed only as a semi-quantitative metric for relative comparison of exsolution behavior under the same experimental and measurement conditions. The results show that Co⁰ intensity in LSCF28 exhibits the fastest increase, followed by Fe⁰ in LSCF28, whereas Fe⁰ in LSF remains unchanged, confirming the promoting effect of Co incorporation on Fe⁰ exsolution.

Previous studies have revealed that oxygen vacancy (Vo) formation is closely related to metal exsolution [37,38]. Herein, the decrease in the O 1s peak intensity (ΔI_O) was employed as a semi-quantitative indicator of oxygen vacancy generation, which enables the comparative trend analysis across different cathodes under the same experimental and measurement conditions [39–41]. ΔI_O is defined as $(I_{O(OCV)} - I_{O(-3.0\text{ V})})/I_{O(OCV)}$, where $I_{O(OCV)}$ and $I_{O(-3.0\text{ V})}$ represent the O 1s peak intensity at 529.0 eV under OCV condition and after reaction for a period of time, respectively. Time-dependent O 1s spectra of LSF and LSCF28 are presented in Fig. S1(d-e). Derived from these spectra, Fig. 2(b) illustrates that LSCF28 exhibits a significant increase in oxygen vacancy under applied voltage, whereas LSF shows

negligible change, consistent with the trends in metal exsolution (Fig. 2(a)). The results indicate that oxygen vacancy formation is closely associated with the voltage-driven exsolution process. Overall, these findings demonstrate that Co incorporation in LSF accelerates oxygen vacancy formation, thereby promoting the subsequent exsolution of Fe⁰ under the applied voltage (Fig. 2(c)).

3.2 Construction of multi-electrode model cell with spatially graded potentials

To enable direct comparison of different cathodes within a single experiment, a multi-electrode model cell with spatially graded potentials was constructed. The top-view and cross-sectional view of the model cell are shown in Fig. 3(a) and Fig. 3(b), respectively. The detailed procedures for model cell preparation are presented in the Experimental section. Compared with conventional single-electrode measurements performed on separate cells, this configuration exhibits different local potentials on the three cathodes within a single cell. This design minimizes uncertainties arising from cell-to-cell differences in fabrication history, high-temperature condition, pretreatment, and experimental environment, thereby improving the reliability of comparative analyses.

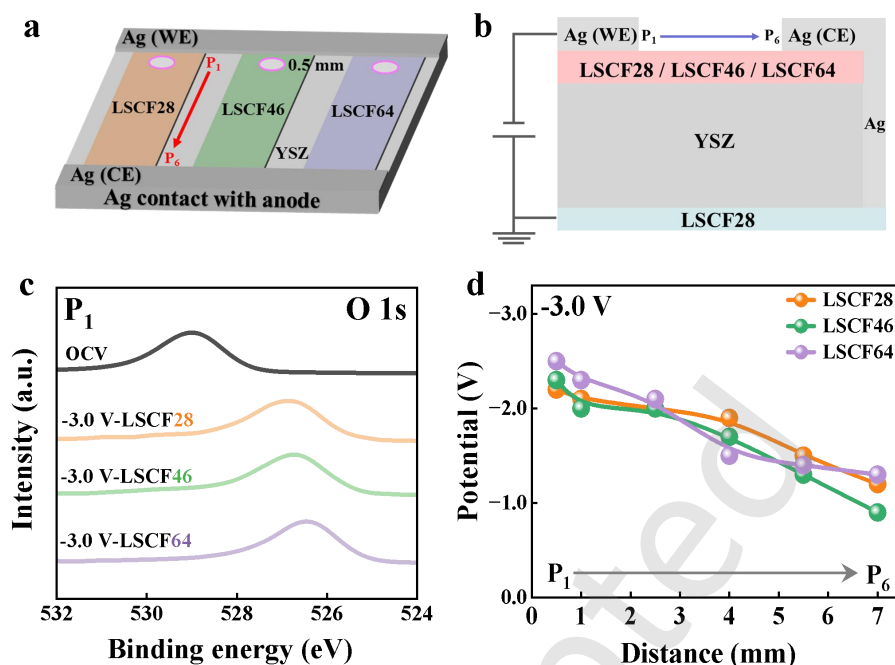


Figure 3 Construction of multi-electrode model cell with spatially graded potentials. Schematic illustration of (a) top-view and (b) cross-sectional view of the cell for in situ XPS characterization. The distance between Ag (WE) and Ag (CE) is ~ 7.5 mm. $P_1 \rightarrow P_6$ denote positions located at $x = 0.5, 1.0, 2.5, 4.0, 5.5,$ and 7.0 mm from the Ag (WE), respectively. (c) O 1s XPS spectra of the three electrodes at point P_1 under -3.0 V at 600°C and OCV. (d) Surface local potential distribution curves of the three cathodes in the multi-electrode model cell.

XRD was first performed to confirm that all electrode materials possessed a consistent perovskite structure before constructing the model cell. As shown in Fig. S3, all samples exhibit the characteristic diffraction peaks of a perovskite structure (LSF: PDF#49-0285) without any detectable secondary phases, demonstrating that varying the Co content preserves the perovskite framework. Dark-field scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) mapping results (Fig. S4(a-f)) reveal uniform distributions of La, Sr, Fe, and Co elements, without apparent segregation or phase separation, demonstrating excellent chemical homogeneity after synthesis and calcination. SEM cross-sectional images (Fig. S4(g-i)) show that all electrodes maintain a uniform thickness of $\sim 5\ \mu\text{m}$. The consistency of the initial materials and electrode thicknesses of different cathodes ensures the reliability of the subsequent comparative exsolution behaviors.

To verify the effectiveness of the model cell, μ -XPS was employed under -3.0 V at 600°C , while the ΔBE of O 1s served as a probe of the local potential. Upon applying -3.0 V, the ΔBE values at the region near Ag (WE) (P_1 , $x = 0.5$ mm) are -2.2 , -2.3 , and -2.5 eV for LSCF28, LSCF46, and LSCF64, respectively (Fig. 3(c)). These similar values confirm that all three cathodes experienced comparable

effective potentials near the Ag (WE). The local potential profiles of all cathodes (Fig. 3(d)) exhibit well-defined potential gradients, enabling simultaneous evaluation of exsolution behavior under multiple potential conditions within a single experiment.

3.3 Exsolution kinetics under a single potential in multi-electrode model cell

To compare the exsolution kinetics under an identical surface potential, in situ μ -XPS measurements were conducted on the comparable positions of the LSCF28, LSCF46, and LSCF64 electrodes in the multi-electrode model cell. The temporal evolution of Co $2p_{3/2}$ signals of the three cathodes at P_1 ($x = 0.5$ mm) is shown in Fig. 4(a-c). After applying -3.0 V for 10 min, a distinct Co^0 signal is already observed on LSCF28. In contrast, Co^0 exsolution on LSCF46 occurs after 60 min, while LSCF64 only exhibits a trace level of exsolution even after 120 min. Subsequent Fe^0 exsolution (Fig. S5(a-c)) follows the same sequence as Co^0 , indicating that the relative exsolution rates follow the order $\text{LSCF28} > \text{LSCF46} > \text{LSCF64}$ under the present experimental conditions. Meanwhile, all three cathodes exhibit a decrease in oxygen content (Fig. S5(d-f)), reflecting the formation of oxygen vacancy [40,41].

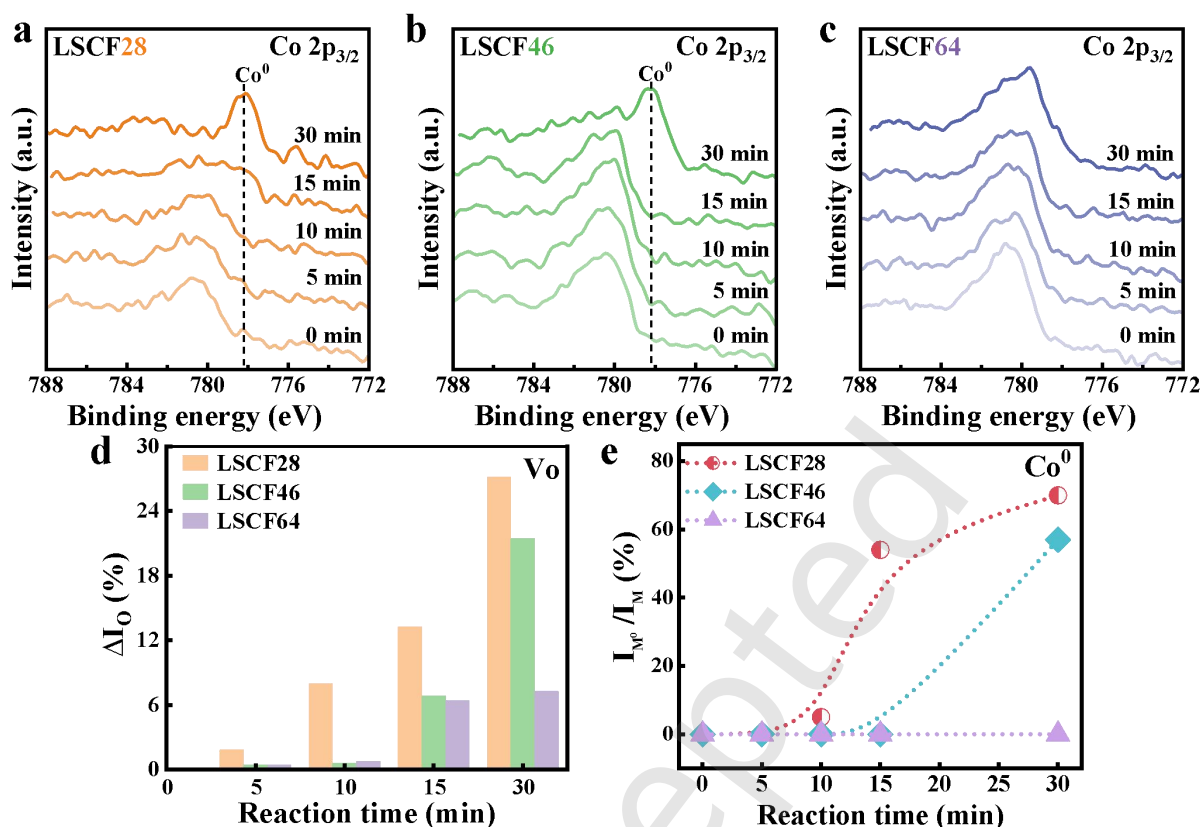


Figure 4 In situ XPS characterization of exsolution behaviors for three cathodes at P₁ ($x = 0.5$ mm) under the multi-electrode configuration. Temporal evolution of Co 2p_{3/2} XPS signals for (a) LSCF28, (b) LSCF46 and (c) LSCF64. Semi-quantified temporal evolution of (d) oxygen vacancy concentration and (e) Co⁰ content. Reaction condition: -3.0 V, 600 °C.

The time-resolved XPS results show that Co⁰ exsolves prior to Fe⁰ across all samples. Consequently, the temporal evolution of the Co⁰ signal was further semi-quantitatively analyzed. The corresponding time-dependent variations of oxygen vacancy concentration and Co⁰ content of three cathodes are presented in Fig. 4(d-e). Under the same conditions, LSCF28 exhibits the fastest oxygen vacancy generation, facilitating rapid and abundant Co⁰ exsolution. In contrast, LSCF64 shows the slowest oxygen vacancy formation, resulting in the lowest Co⁰ exsolution rate and content, while LSCF46 displays an intermediate exsolution rate. These results further suggest that oxygen vacancy formation is closely associated with the behaviors of metal exsolution.

To evaluate the surface morphology differences of exsolved nanoparticles among the three cathodes, SEM characterization was performed before and after in situ XPS experiments. As depicted in Fig. 5(a), the fresh cathode surface exhibits a smooth and clean morphology. After reaction for 120 min, the exsolved nanoparticles are uniformly distributed on all LSCF cathodes (Fig. 5(b-d)). The quantitative comparison of

particle size and density among the three cathodes are presented in Fig. 5(e-f). The average particle sizes are 10.1 ± 2.0 , 11.2 ± 1.8 , and 10.5 ± 2.4 nm for LSCF28, LSCF46 and LSCF64, respectively, indicating a relatively uniform size distribution independent of different cathodes (Fig. 5(e)). In contrast, the nanoparticle density differs markedly. As shown in Fig. 5(f), LSCF28 exhibits the highest nanoparticle density ($420 \mu\text{m}^{-2}$), followed by LSCF46 ($281 \mu\text{m}^{-2}$), whereas LSCF64 exhibits a substantially lower density ($62 \mu\text{m}^{-2}$). This trend aligns well with the exsolved metal content quantified by XPS.

HRTEM was performed to characterize the microstructure of the exsolved species. As shown in Fig. S6(a), the EDS elemental mapping of reacted LSCF28 shows homogeneous Co and Fe enrichment in the exsolved nanoparticles. Together with the metallic Co⁰ and Fe⁰ signals from XPS, these results corroborate the formation of the CoFe alloy. Further bright-field STEM image (Fig. S6(b)) shows a lattice spacing of 0.201 nm, corresponding to the (110) plane of CoFe alloy [21].

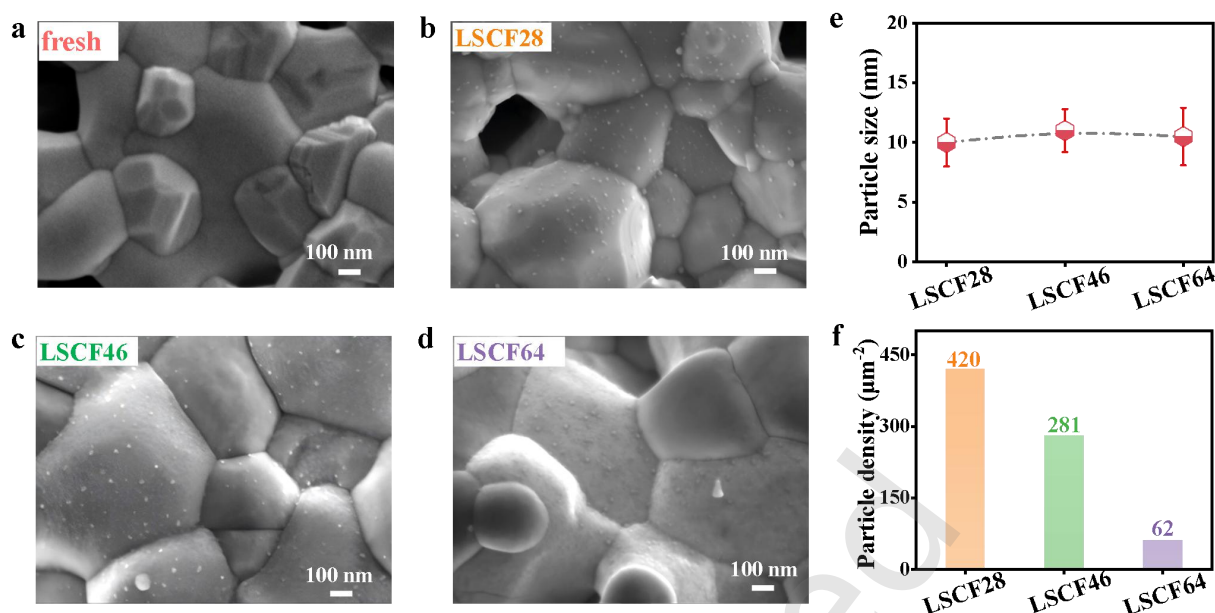


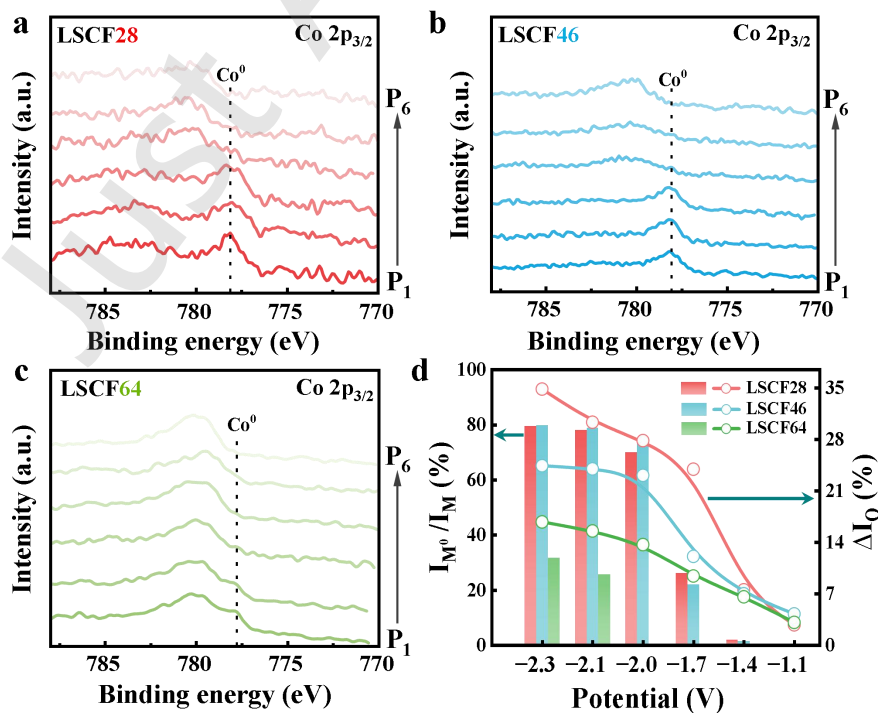
Figure 5 SEM characterization of LSCF cathodes at P_1 ($x = 0.5$ mm) before and after in situ XPS experiments. (a) Surface morphology of the fresh LSCF28 cathode. Surface morphology of different cathodes after in situ XPS experiments: (b) LSCF28, (c) LSCF46, and (d) LSCF64. (e, f) Variation in the size and density of exsolved nanoparticles among three cathodes. Reaction condition: -3.0 V, 600 °C, 120 min.

3.4 Exsolution kinetics under graded potentials

The specially designed configuration in Fig. 3 enables direct comparison of the exsolution behaviors of LSCF28, LSCF46, and LSCF64 under graded potentials within a single experiment. Fig. 6(a-c) show the Co $2p_{3/2}$ spectra of the three cathodes at different potential regions (P_1 – P_6 , Fig. 3(d)) after applying -3.0 V at 600 °C for 180 min. Corresponding Fe $2p_{3/2}$ spectra are shown in Fig. S7(a-c). The spatially resolved data reveal that, for all cathodes, the amounts of Co^0 and Fe^0

decrease significantly with decreasing local potential (i.e., farther from the WE). Meanwhile, the oxygen vacancy concentration also shows a pronounced decreasing trend (Fig. 6(d)), consistent with the semi-quantitative analysis of metallic Co^0 in each electrode at the final reaction state. These results indicate that, under a given applied voltage, regions with higher local potentials favor oxygen vacancy formation, thereby promoting the reduction and exsolution of B-site cations, in agreement with our previous findings [28].

Figure 6 In situ XPS characterization of three exsolved cathodes at different local potentials under the multi-electrode configuration. Co $2p_{3/2}$ XPS

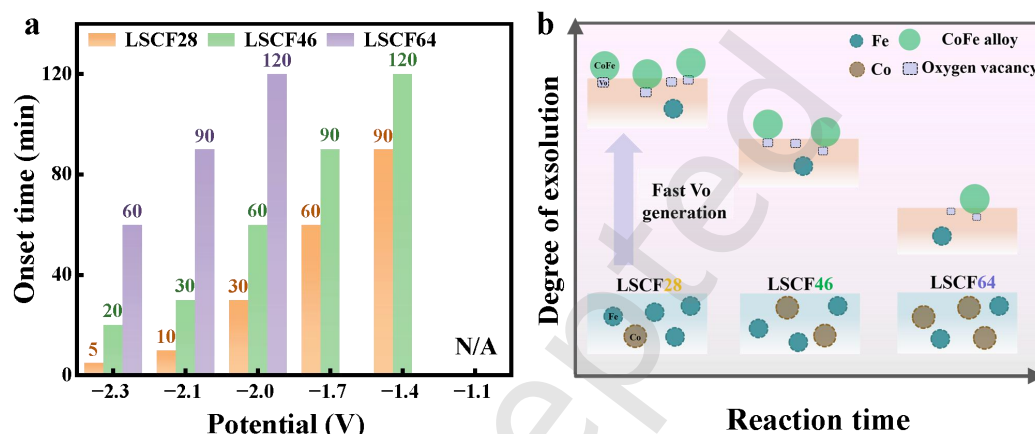


spectra of (a) LSCF28, (b) LSCF46 and (c) LSCF64. (d) Exsolved Co^0 contents and oxygen vacancy concentrations as a function of local potential at the final reaction states of three cathodes. Reaction condition: -3.0 V, 600 °C, 180 min.

The onset times of Co^0 exsolution on the three cathodes under similar potentials are compared to assess the differences in exsolution kinetics under the same measurement conditions. Here, the onset time of Co^0 exsolution is defined as the earliest reaction time at which Co^0 can be detected by XPS. As shown in Fig. 7(a), in regions with more negative local potentials (e.g., -2.2 , -2.3 and -2.5 V at P_1), Co^0 exsolution occurs after 5 min reaction on LSCF28, whereas 60 min is required for LSCF64. At less negative potentials (e.g., -1.3 , -1.4 and -1.5 V at P_5), exsolution appears after 90 min for LSCF28, while no

detectable exsolution is observed on LSCF64 even after 180 min. Thus, across the entire graded-potential region, the exsolution rates consistently follow the order $\text{LSCF28} > \text{LSCF46} > \text{LSCF64}$, demonstrating that the relative kinetics order among the three electrodes remains unchanged within the investigated potential window. Overall, the results obtained from the three electrodes under the graded potential further confirm the core mechanism: the Co/Fe ratio regulates the voltage-driven generation of oxygen vacancies, thereby affecting the rate of metal exsolution, as schematically summarized in Fig. 7(b).

Figure 7 The Co/Fe ratio-modulated exsolution kinetics under a multi-electrode configuration with graded potentials. (a) The onset times of Co^0



exsolution at different potentials for the three cathodes. (b) Schematic illustration highlighting the compositional dependence of the metal exsolution behavior. Reaction condition: -3.0 V, 600°C , 180 min.

4 Conclusion

In summary, this work clarifies how the Co/Fe ratios affect voltage-driven metal exsolution in LSCF cathodes. Using a multi-electrode model cell with graded potentials and in situ spatially resolved XPS characterization, we directly identify that Co^0 exsolves to the surface prior to Fe^0 under applied voltage, and the metal exsolution rates follow the order of $\text{LSCF28} > \text{LSCF46} > \text{LSCF64}$, positively correlating with oxygen vacancy formation. Furthermore, graded-potential experiments confirm that higher local potentials consistently promote faster exsolution over all electrodes with different compositions. These findings highlight the important role of oxygen vacancies in linking the Co/Fe ratio with voltage-driven exsolution behaviors. This work also establishes an efficient in situ strategy for comparative studies of multiple material systems and provides guidance for SOEC electrode optimization.

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Electronic Supplementary Material

In situ probing of voltage-driven metal exsolution in perovskite cathodes modulated by B-site composition

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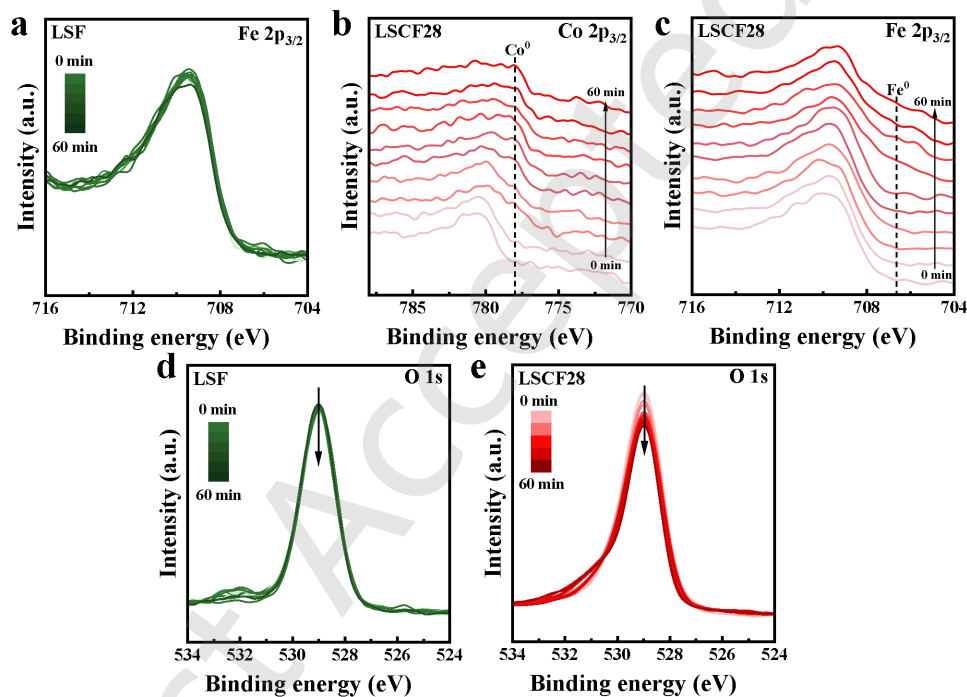


Figure S1 In situ time-resolved XPS spectra of surface elements of LSF and LSCF28 cathodes under the single-electrode configuration. (a) Fe 2p_{3/2} spectra of LSF. (b-c) Co 2p_{3/2} and Fe 2p_{3/2} spectra of LSCF28. (d-e) O 1s spectra of LSF and LSCF28. Reaction condition: -3.0 V, 600 °C.

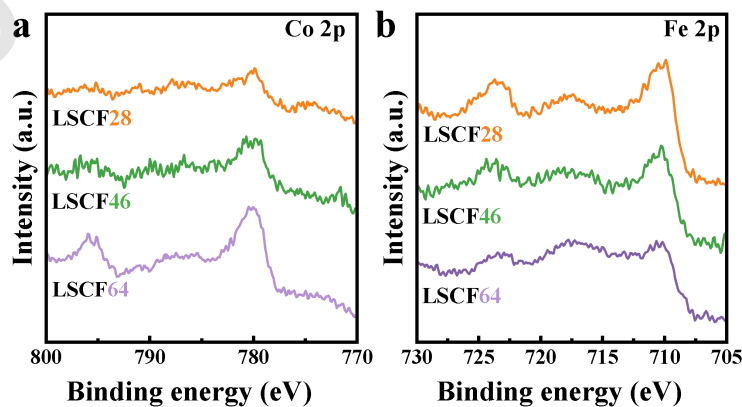


Figure S2 XPS spectra of fresh LSCF28, LSCF46 and LSCF64 cathodes: (a) Co 2p and (b) Fe 2p. Under a monochromatic Al K α X-ray source, the Co LMM Auger peak (~713 eV) overlaps with the Fe 2p region (700–740 eV), while the Fe LMM Auger peak (~784 eV) overlaps with the Co 2p region (770–815 eV), making reliable deconvolution of the Fe 2p and Co 2p spectra challenging.

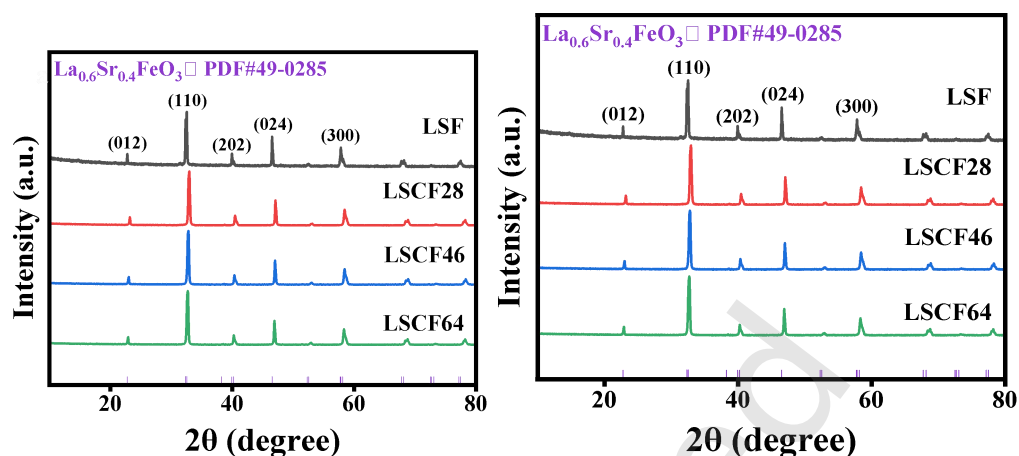


Figure S3 XRD patterns of LSF, LSCF28, LSCF46, and LSCF64 powders.

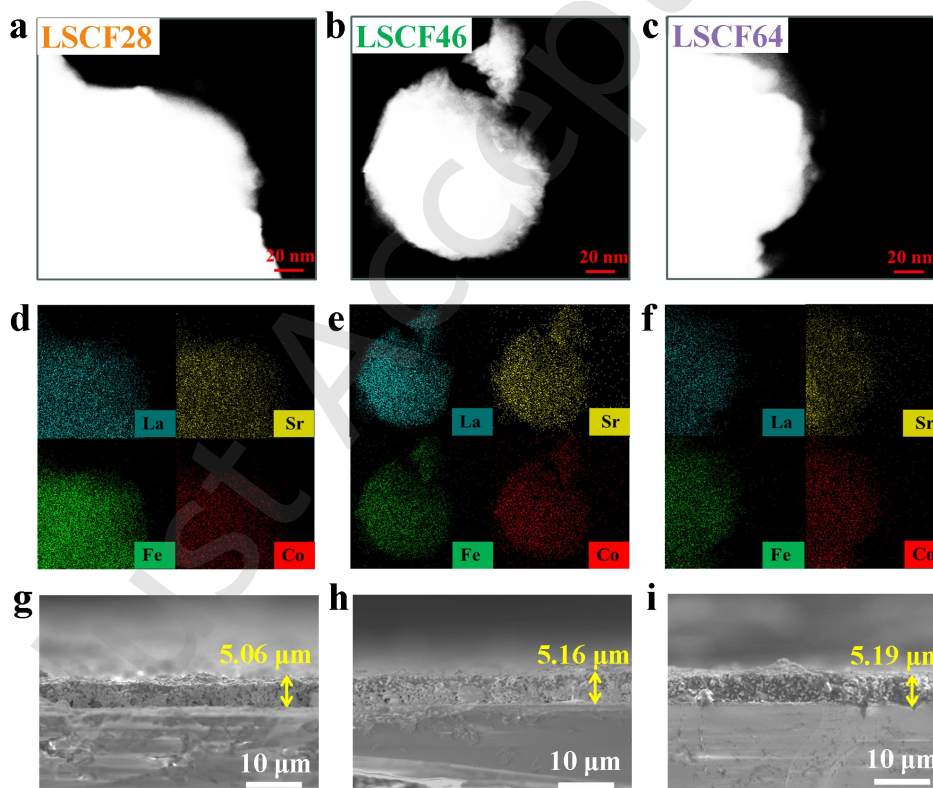


Figure S4 Dark-field STEM images and EDS-mapping of electrode materials: (a, d) LSCF28, (b, e) LSCF46, and (c, f) LSCF64. Cross-sectional SEM images of the three cathodes coated on the same YSZ: (g) LSCF28, (h) LSCF46, and (i) LSCF64.

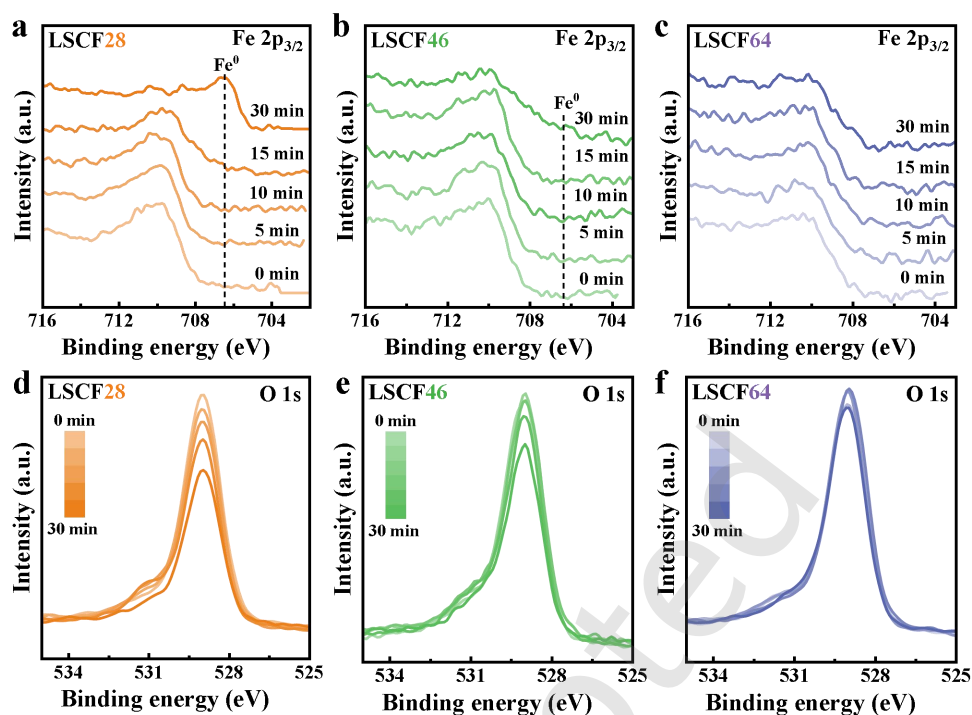


Figure S5 In situ time-resolved XPS spectra of surface elements of LSCF28, LSCF46, and LSCF64 cathodes under the multi-electrode configuration. (a-c) Fe 2p_{3/2} and (d-f) O 1s. Reaction condition: -3.0 V, 600°C .

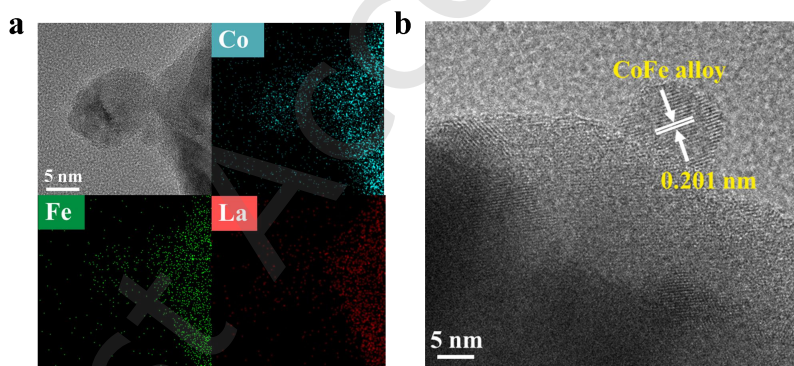


Figure S6 HRTEM characterization of the LSCF28 cathode after exsolution. (a) STEM-EDS elemental mapping. (b) Bright-field STEM image.

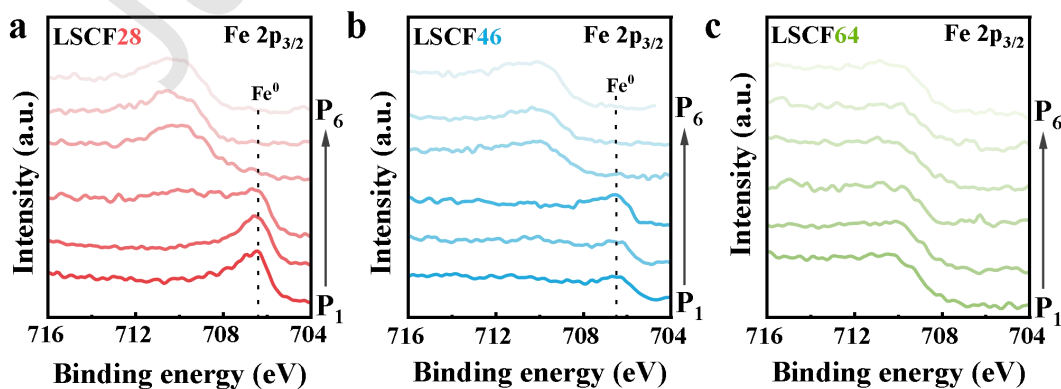


Figure S7 Fe 2p_{3/2} XPS spectra of the three cathodes at different local potentials after exsolution under the multi-electrode configuration. (a) LSCF28, (b) LSCF46, and (c) LSCF64. Reaction condition: -3.0 V, 600°C , 180 min.