To significantly increase the amount of exsolved particles, the complete phase reconstruction from simple perovskite to Ruddlesden-Popper (R-P) perovskite is greatly desirable. However, a comprehensive understanding of key parameters affecting the phase reconstruction to R-P perovskite is still unexplored. Herein, we propose the Gibbs free energy for oxygen vacancy formation in Pr$_{0.5}$(Ba/Sr)$_{0.5}$TO$_{3-\delta}$ (T = Mn, Fe, Co, and Ni) as the important factor in determining the type of phase reconstruction. Furthermore, using in-situ temperature & environment-controlled X-ray diffraction measurements, we report the phase diagram and optimum ‘x’ range required for the complete phase reconstruction to R-P perovskite in Pr$_{0.5}$Ba$_{0.5-x}$Sr$_x$FeO$_{3-\delta}$ system. Among the Pr$_{0.5}$Ba$_{0.5-x}$Sr$_x$FeO$_{3-\delta}$ $(Pr_{0.5}Ba_{0.2}Sr_{0.3})_2FeO_{4+\delta}$ – Fe metal demonstrates the smallest size of exsolved Fe metal particles when the phase reconstruction occurs under reducing condition. The exsolved nano-Fe metal particles exhibit high particle density and are well-distributed on the perovskite surface, showing great catalytic activity in fuel cell and syngas production.
Tailoring the functionality of perovskite oxides (ABO₃) by decorating the surface with catalytically active particles plays an important role in energy-related applications such as fuel cells, electrolysis cells, metal-air batteries, and supercapacitors. The catalyst particles are typically prepared by deposition techniques (e.g. infiltration, chemical vapor deposition, and pulsed laser deposition), in which the catalysts are embedded onto the surface from external precursors. However, these techniques require redundant heat-treatments for preparation and often result in incomplete phase reconstruction, breaking the bottleneck of exsolution capability. Exsolution phenomenon on the basis of in-situ growth takes place in non-stoichiometric perovskite. In this approach, catalytically-active metal elements (e.g. Pd, Ru, Co, Ni, and Fe, etc.) are initially incorporated into the B-site of perovskite oxides, and then exsolved as metallic particles from the perovskite support under reducing atmosphere. As compared with the conventional catalyst preparation methods, the in-situ exsolution process provides benefits of time-efficient catalyst preparation, enhanced catalyst lifetime, and robust thermal stability. Notwithstanding the advantages, two major thresholds hinder the practical application of the exsolution process: (i) restricted diffusion of catalytically active cations to the surface due to preferential segregation within the bulk, and (ii) structural destruction and/or insulating phase evolution after excessive cation defect formation.

In order to address the challenges of the exsolution phenomenon, A-site deficient perovskites (A/B < 1) has been extensively employed as an attractive methodology. In A-site deficient perovskites, formation of oxygen vacancies is promoted by phase stabilization from non-stoichiometric perovskite to defect-free perovskite under reducing condition, facilitating the B-site exsolution. Hence, the B-site exsolution level is proportional to A-site deficiency range (α' for AₓBa₁₋ₓBO₃). Meanwhile, there exists restriction in the variation of A-site deficiency range (about 0 < α < 0.2 for AₓBa₁₋ₓBO₃) because excessive A-site deficiency may be accompanied by formation of undesirable A-site oxide phases. Given these aspects, an alternative corresponding method to further trigger the B-site exsolution is using the in-situ phase reconstruction from simple perovskite to Ruddlesden-Popper (R-P) perovskite oxides (Aₓₙ₋₁B₂O₃ₙ₋₁) with n = 1, 2, and 3) via reduction process. This strategy facilitates abundant formation of oxygen vacancies during the phase reconstruction, breaking the bottleneck of exsolution capability.

\[
\text{ABO}_3 \xrightarrow{\text{After reduction}} \frac{1}{2} \text{A}_2\text{BO}_4 + \frac{1}{2} \text{B} + \frac{1}{2} \text{O}_2
\]

From Eq. 1, it is probable that considerable number of cations at B-site will be reduced into metals without A-site segregation after phase reconstruction from simple perovskite (ABO₃) to n = 1 R-P perovskite (AₓBO₄). Although several perovskites have exhibited superior distribution of catalyst particles on the surface via phase transition to R-P perovskite, the comprehensive understanding of key factors modulating the phase reconstruction to R-P perovskite is still an open question.

Inspired by the above perspectives, the goal of this study is to identify the significant factors contributing to the phase reconstruction from simple perovskite to R-P perovskite. Here, we systematically report the Gibbs free energy for oxygen vacancy formation (G_{f,O}) of perovskite oxides with various cations as the unprecedented factor affecting the phase reconstruction. The type of phase reconstruction can be predicted with the G_{f,O} value from PrO and TO₂ networks in Pr₀.₅Ba₀.₅Sr₀.₅TO₃₋δ (T = Mn, Fe, Co, and Ni), in which the most appropriate cations for the complete reconstruction to R-P perovskite are determined. Afterwards, the phase diagram from in-situ temperature and environment-controlled X-ray diffraction (XRD) measurements reveals the phase reconstruction tendency of Pr₀.₅Ba₀.₅SrₓFeO₃₋δ (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5, abbreviated as PBSF in Supplementary Table 1) materials with respect to T and x value and reduction temperature. Furthermore, the as-exsolved Fe metal particle size and distribution for PBSF after reduction process are observed from microscopy analysis. In accordance with the theoretical calculations and experimental data, Pr₀.₅Ba₀.₅SrₓFeO₃₋δ (A-PBSF30) is adopted as the optimized electrode material for symmetrical solid oxide cell (S-SOC) and demonstrates exceptional electrochemical performance (1.23 W cm⁻² at 800 °C under fuel cell mode and ~1.62 A cm⁻² at 800 °C under co-electrolysis mode).

**Results**

**Density functional theory calculations.** The complete phase reconstruction from simple perovskite (ABO₃) to R-P perovskite (AₓBO₄) via reduction is considered as one of the efficient strategies to significantly boost the population of exsolved particles. However, the key factors contributing to the phase reconstruction to R-P perovskite has not been investigated. To determine the unexplored factor for the phase reconstruction for the first time, the Gibbs free energy for oxygen vacancy formation (G_{f,O}) and the oxygen vacancy formation energies (E_{f,O}) from the surface AO (A-site) and BO₂ (B-site) networks were calculated for Pr₀.₅Ba₀.₅TO₃₋δ and Pr₀.₅SrₓTO₃₋δ (T = Mn, Fe, Co, and Ni) perovskite oxides (Fig. 1 and Supplementary Fig. 1). For the perovskite oxides to undergo phase reconstruction without phase decomposition under reducing condition, the A-site G_{f,O} value should be positive (A-site G_{f,O} > 0 eV). Moreover, the B-site G_{f,O} value would be an important factor for determining the type of phase reconstruction. For instance, the B-site G_{f,O} should be in the vicinity of about −1.2 to 0 eV (−1.2 eV < B-site G_{f,O} < 0 eV) to demonstrate complete phase reconstruction to R-P perovskite in the reduction environment. Considering the aforementioned results and the experimental data, only Pr₀.₅Sr₀.₅MnO₃₋δ (PSM) and Pr₀.₅Sr₀.₅FeO₃₋δ (A-PBSF50) are the possible candidates for the complete phase reconstruction to R-P perovskite in this study (Supplementary Fig. 2). Among the two potential candidates, we adopted Fe cation as the more suitable B-site cation because of its much superior catalytic activity for fuel oxidation reaction rather than Mn cation. Accordingly, we systematically analyzed the phase reconstruction tendency of Pr₀.₅Ba₀.₅SrₓFeO₃₋δ (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5, abbreviated as PBSF in Supplementary Table 1) materials with respect to different Ba²⁺/Sr²⁺ ratio.

**Structural characterization.** Before examining the phase reconstruction tendency of PBSF, the crystalline structures after heat-treated in two different environmental conditions were analyzed by X-ray diffraction (XRD) and Rietveld refinement profiles (Supplementary Figs. 3, 4 and Supplementary Table 2). The air-sintered PBSF are all corresponded to simple perovskite structure without detectable secondary phases. On the other hand, after reduction in H₂ atmosphere, the PBSF samples were surprisingly changed to different types of phases depending on the Sr²⁺ concentration. As shown in Supplementary Fig. 4b, Pr₀.₅Ba₀.₅SrₓFeO₃₋δ (A-PBSF00), Pr₀.₅Ba₀.₅SrₓFeO₃₋δ (A-PBSF30), and Pr₀.₅SrₓFeO₃₋δ (A-PBSF50) were changed to Pr₀.₅Ba₀.₅FeO₃₋δ - Fe metal & Pr oxide (R-PBSF00), (Pr₀.₅Ba₀.₅SrₓFeO₃₋δ - Fe metal (R-PBSF30), and (Pr₀.₅SrₓFeO₃₋δ - Fe metal (R-PBSF50), respectively. Only catalytically active Fe metal peaks along with complete phase reconstruction to R-P perovskite are identified at the signiﬁcant range of A/B < 0.2 for AₓBa₁₋ₓBO₃. Given these aspects, an alternative correlation method to further trigger the B-site exsolution is using the in-situ phase reconstruction from simple perovskite to Ruddlesden-Popper (R-P) perovskite oxides (Aₓₙ₋₁B₂O₃ₙ₋₁) with n = 1, 2, and 3) via reduction process. The strategy facilitates abundant formation of oxygen vacancies during the phase reconstruction, breaking the bottleneck of exsolution capability.

\[
\text{ABO}_3 \xrightarrow{\text{After reduction}} \frac{1}{2} \text{A}_2\text{BO}_4 + \frac{1}{2} \text{B} + \frac{1}{2} \text{O}_2
\]
observed for R-PBSF30 and R-PBSF50, while R-PBSF00 shows Fe metal and Pr oxide segregation without phase reconstruction under reducing condition. Based on the further Rietveld refinement analysis in Supplementary Fig. 5, R-PBSF30 clearly exhibits the complete phase reconstruction to R-P perovskite with tetragonal structure (space group $I4/mmm$ with lattice parameters of $a = b = 3.879$ Å and $c = 12.704$ Å). The complete phase reconstruction could be also described by Eq. (2), of which considerable amounts of Fe metal are expected to be exsolved in the reduction environment.

$$\Pr_{0.5}Ba_{0.3}FeO_3 \rightarrow \frac{1}{2}(Pr_{0.5}Ba_{0.3}Sr_{0.3})FeO_4 + \frac{1}{2}Fe + \frac{1}{2}O_2 \quad (2)$$

Phase reconstruction tendency analysis from phase diagram. To precisely analyze the phase reconstruction tendency for $Pr_{0.5}Ba_{0.5-x}Sr_xFeO_3$ $(x = 0, 0.1, 0.2, 0.25, 0.3, 0.4$, and $0.5)$ materials, in-situ XRD measurements were systematically conducted in various reduction temperatures and $Sr^{2+}$ concentrations. (Fig. 2a and Supplementary Fig. 6). Figure 2b displays the proposed phase diagram and the corresponding plotted points after in-situ XRD measurements in $H_2$ with elevating temperature intervals of 10 °C. The A-PBSF00 sample remained simple perovskite structure for all reduction temperature range and co-segregation of Fe metal and Pr oxide was observed simultaneously at the reduction temperature higher than 840 °C (Region II in Fig. 2b). Even though there was noticeable phase reconstruction for all $Sr^{2+}$-doped samples, complete phase reconstruction to R-P perovskite was not accomplished for $Pr_{0.5}Ba_{0.5}Sr_{0.5}FeO_3$ (A-PBSF10), $Pr_{0.5}Ba_{0.25}Sr_{0.25}FeO_3$ (A-PBSF20), and $Pr_{0.5}Ba_{0.3}Sr_{0.2}FeO_3$ (A-PBSF25) even at the reduction temperature of 870 °C. (Region III in Fig. 2b). On the contrary, complete phase reconstruction to R-P perovskite is observed for A-PBSF30, $Pr_{0.5}Ba_{0.3}Sr_{0.2}FeO_3$ (A-PBSF40), and A-PBSF50 at the reduction temperature of approximately 850 °C (Region IV in Fig. 2b). These results indicate that the $x'$ value in PBSF should be at least approximately 0.3 along with the reduction temperature of about 850 °C to accomplish complete phase reconstruction, as illustrated in Fig. 2c.

Effect of $Sr^{2+}$ concentration on phase reconstruction and exsolution. The role of $Sr^{2+}$ concentration in PBSF in terms of phase reconstruction tendency to R-P perovskite was additionally explored using density functional theory (DFT) calculations. Figure 2d shows the required total energies for the phase reconstruction ($E_{\text{recon}}$) from simple perovskite to R-P perovskite of four model structures with different $Ba^{2+}/Sr^{2+}$ ratio. The $E_{\text{recon}}$ decreases with increasing $Sr^{2+}$ concentration in PBSF, indicating that the incorporation of $Sr^{2+}$ into $Ba^{2+}$ site promotes the phase reconstruction to R-P perovskite (Supplementary Fig. 7). Furthermore, the $E_{\text{f-O}}$ of four simple perovskite models were calculated in Fig. 2e. More negative $E_{\text{f-O}}$ value implies easier formation of oxygen vacancies in the reduction environment. The $E_{\text{f-O}}$ value becomes more negative after doping $Sr^{2+}$ into $Ba^{2+}$, revealing that the $Sr^{2+}$ doping facilitates the formation of oxygen vacancies in the reduction atmosphere. This trend could be
elucidated by the decrease in tolerance factor after replacement of Ba$^{2+}$ by Sr$^{2+}$ (Supplementary Table 3)\textsuperscript{36}. A co-segregation energy (E$_{co-seg}$) associated to the degree of exsolution for B-site transition metal cations under reducing condition was also calculated (Fig. 2e). Interestingly, E$_{co-seg}$ decreased as the Sr$^{2+}$ contents increased, suggesting the enhanced degree of Fe exsolution with increasing Sr$^{2+}$ concentration.

**Transmission electron microscopy analysis.** On the basis of proposed phase diagram and DFT calculations, the A-PBSF30, the minimum Sr$^{2+}$-doped sample demonstrating complete reconstruction to R-P perovskite, is selected as the target material for structural analysis. The transmission electron microscopy (TEM) and scanning TEM (STEM) analysis were successfully performed to visually probe the complete phase reconstruction.
from simple perovskite to R-P perovskite of A-PBSF30 material (Fig. 3 and Supplementary Fig. 8). From the high-resolution TEM images and corresponding fast-Fourier transformed (FFT) patterns, the lattice spaces between planes of A-PBSF30 and R-PBSF30 are 0.395 nm (Fig. 3a) and 0.634 nm (Fig. 3d), which are consistent with the lattice constant of (001) plane for simple perovskite and the lattice constant of (002) plane for R-P perovskite, respectively. Furthermore, the atomic-scale observations of A-PBSF30 and R-PBSF30 were definitely validated from high-angle annular dark-field (HAADF) STEM images, of which only technically elusive [100] direction is mandatory for R-P perovskite. The locations of cations are well-matched with the simple perovskite (Fig. 3b) and R-P perovskite (Fig. 3e) because the atomic column intensity is proportional to the Z−2 (Z is the atomic number)37, thereby the bright and dark columns are the A-site (i.e., Pr, Ba, and Sr (green)) and the B-site (i.e., Fe (purple)), respectively, in the HAADF-STEM mode.

**Electrochemical performance evaluation.** Prior to assessment of electrochemical performance for A-PBSF30 in the practical application of SOFCs, great thermo-chemical compatibility between all PBSF and the La0.8Sr0.2Ga2MgO4+δ (LSGM) electrolyte was confirmed by XRD measurement (Supplementary Fig. 14). Moreover, similar microstructures of air-sintered PBSF samples imply that the electrochemical performance would not be affected by surface morphology (Supplementary Fig. 15). Then, electrochemical performance of symmetrical solid oxide fuel cells (S-SOFCs) using PBSF as both electrodes was characterized by LSGM electrolyte-supported cells to identify the huge impact of the exsolved Fe metal particle size and surface distribution (Fig. 5a and Supplementary Figs. 16, 17). The peak power density of the A-PBSF30 symmetrical cell is 1.23 W cm−2 at 800 °C with humidified H2 (3% H2O) as fuel. This outstanding cell performance is the highest out of open literature based on LSGM electrolyte-supported S-SOFCs without any external catalysts at 800 °C under humidified H2 (3% H2O) as fuel to our best knowledge (Fig. 5b and Table 1)28,39,41–46. In addition, peak power output of 0.73 W cm−2 was demonstrated in humidified C3H8 (3% H2O) at 800 °C (Fig. 5c and Supplementary Fig. 18). Furthermore, the A-PBSF30 symmetrical cell demonstrated fairly stable current density without observable degradation for about 200 h in H2 and 150 h in C3H8 at 700°C (Fig. 5d, e). We also evaluated the electrochemical performance of the A-PBSF30 symmetrical cell in co-electrolysis mode. The excellent current density of −1.62 A cm−2 at a cell voltage of 1.5 V (close to thermo-neutral voltage)47 at 800 °C under co-electrolysis condition was demonstrated for the A-PBSF30 symmetrical cell (Fig. 5f), which is exceptionally high compared to other oxygen-conducting solid oxide electrolysis cell (SOEC) systems with different electrode materials19,31,48,49. The in-operando quantitative analysis of the synthetic gas products (H2 and CO) was further investigated via gas chromatography (GC) profiles for the A-PBSF30 symmetrical cell at 800 °C during co-electrolysis of H2O and CO2 (Supplementary Fig. 19). The amount of generated H2 and CO were measured to be 0.50 and 10.81 ml min−1 cm−2, respectively, implying that the A-PBSF30 symmetrical cell could efficiently produce synthetic gas during co-electrolysis50. Together with superior electrochemical performance and efficient synthetic gas production, relatively constant voltage was observed for about 700 h in H2 and 500 h in C3H8 at 700 °C in co-electrolysis mode (Fig. 5g), representing great durability in continuous SOEC operation. It is noteworthy that in-situ exsolution of well-dispersed Fe metal particles after complete phase reconstruction to R-P perovskite matrix acts as catalysts with promising electro-catalytic activity (Fig. 6), leading to outstanding electrochemical performances in various applications.

**Discussion**

In summary, this study successfully calculated G_{f(O) value} from PrO and TOx in Pr0.5(Ba/Sr)0.5TO3−δ (T = Mn, Fe, Co, and Ni) as the key factor for identifying the type of the phase reconstruction. Remarkably, the phase diagram acquired from in-situ examination and characterization of exsolved particle size. In general, particle size and surface distribution of catalysts have a considerable influence on the catalytic activity4,38. As such, the particle size and surface distribution of exsolved metal particles via reduction treatment could impact on the electro-catalytic activity of catalysts. Before examining the electro-catalytic effect of the in-situ exsolved Fe metal particles, an explicit comparison of exsolved particle size and surface distribution for R-PBSF00, R-PBSF30, and R-PBSF50 samples were presented in scanning electron microscope (SEM) images (Fig. 3c, f and Supplementary Figs. 9, 10). As shown in Fig. 3f, many small particles with size of about 100 to 200 nm are observed and uniformlyocketed onto the perovskite oxide matrix after reduction, which are speculated as Fe metal particles. In contrast, the size of exsolved particles was relatively larger for R-PBSF00 and R-PBSF50 (Supplementary Figs. 11, 12). The energy dispersive spectroscopy (EDS) spectrum and the elemental mapping images of R-PBSF30 also clearly revealed that Fe metal particle with size of about 150 nm is well-socketted onto the R-P perovskite after reduction (Fig. 3g, h). Furthermore, noticeable energy shift to the higher energy in X-ray absorption near-edge structure (XANES), much increase in Fe-Fe shell intensity from the Fourier-transformed extended X-ray absorption fine structure (EXAFS) spectra after reduction, and the presence of Fe2P1/2 peak for only R-PBSF30 from X-ray photoelectron spectroscopy (XPS) measurements confirm the exsolution of Fe metal onto the surface under reducing condition39, in coincidence with the above experimental results (Fig. 4). To investigate the electrically conductive properties of the exsolved Fe metal particles, the electrical conductivities as a function of temperature under reducing atmosphere were measured for PBSF (Supplementary Fig. 13). The A-PBSF30 displayed the highest electrical conductivity value compared to other PBSF in the reduction environment coupled with sufficiently high electrical conductivity in the air atmosphere (Supplementary Fig. 13b)40, suggesting that the A-PBSF30 is the potential electrode material for S-SOFC electrode material.
temperature and environment-controlled XRD measurements indicated that the complete phase reconstruction to R-P perovskite occurs at least approximately x = 0.3 above at the reduction temperature of 850 °C for PBSF system. Among PBSF with complete phase reconstruction, the highly-populated Fe metal particles socketed on R-PBSF30 attributed to excellent electrochemical performances under both fuel cell (1.23 W cm\(^{-2}\) at 800 °C under H\(_2\) fuel) and electrolysis cell (≈1.62 A cm\(^{-2}\) at 1.5 V and 800 °C under CO\(_2\) and H\(_2\)O fuels) modes coupled with great durability. Our investigations strongly provide a pathway to...
explore new factors for the phase reconstruction and offer a new opportunity to discover prospective candidates with customized functionalities for next-generation energy-related applications.

Methods

**Material synthesis.** Pr₀.₅Ba₀.₂Sr₀.₃FeO₄₋ₓ (Pr₀.₅Ba₀.₂Sr₀.₃)₂FeO₄₋ₓ (R-PBSF30) with two references (Fe foil and Fe₂O₃). Fourier-transformed Fe K-edge extended X-ray absorption fine structure (EXAFS) spectra of A-PBSF30 and R-PBSF30. X-ray photoelectron spectra (XPS) of Fe 2p for A-PBSF30 and R-PBSF30.

**Structural characterization.** The crystal structures of the Pr₀.₅Ba₀.₂Sr₀.₃FeO₄₋ₓ samples (x = 0, 0.1, 0.2, 0.25, 0.3, 0.4, and 0.5) and Pr₀.₅Sr₀.₅MnO₃ samples (Pr₀.₅Sr₀.₅)₂FeO₄₋ₓ were analyzed by X-ray diffraction (XRD) measurement using the GSAS II program. The surface analysis of the synthesized powders and their abbreviations were given in Supplementary Table 1.

**Electron microscopy analysis.** The microstructures of (1) Pr₀.₅Ba₀.₂Sr₀.₃FeO₄₋ₓ samples (x = 0, 0.3, and 0.5) sintered at 1200 °C for 4 h in air atmosphere, (2) Pr₀.₅Ba₀.₂Sr₀.₃FeO₄₋ₓ samples (x = 0, 0.3, and 0.5) sintered at 850 °C for 4 h in humidified H₂ environment (3% H₂O) and (3) all PBSF samples sintered at 850 °C for 4 h in humidified H₂ environment (3% H₂O) were analyzed by XPS analyses on ESCALAB 250 XI from Thermo Fisher Scientific with a monochromated Al-Kα (ultraviolet He1, He2) X-ray source. The X-ray absorption fine structure (XAFS) spectra of Fe K-edge for A-PBSF30, R-PBSF30, and Fe metal (R-PBSF30) were measured on ionization detectors under fluorescence mode at the Pohang Accelerator Laboratory (PAL, 6D extended XAFS (EXAFS)). The XAFS and Fourier-transformed (FT) EXAFS spectra analysis were performed using the Athena (Demeter) program.

**Electrical conductivity measurements.** The electrical conductivities of PBSF with respect to temperature were measured under air and 5% H₂ environments by the Thermo Fisher Scientific absolute humidity humidifier 2000 E. The measurement was conducted with a four-point probe method using a Keithley 2400 source-measurement unit.
4-probe method. The samples were pressed into pellets of cylindrical shape and then sintered at 1400 °C for 4 h in air environment to reach an apparent density of ~90%. The electrical conductivities were first measured in air atmosphere from 300 to 800 °C with intervals of 50 °C, and then measured in wet 5% H2 atmosphere (Ar balance, 3% H2O) from 300 to 800 °C with intervals of 50 °C. The current and voltage were recorded by a Biologic Potentiostat to calculate the resistance, resistivity, and conductivity of samples.

**Computational methods.** DFT calculations were performed to investigate the appropriate dopants for the phase reconstruction to $n = 1$ R-P perovskite along with the role of Sr$^{2+}$ concentration on phase reconstruction tendency of PBSF using the Vienna ab initio Simulation Package. For the exchange-correlation, the generalized gradient approximation (GGA) based Perdew-Burke-Ernzerhof functional was used. The electron-ion interactions were described using the projector augmented wave potential. A plane wave was expanded up to cutoff energy of 400 eV. Electronic occupancies were calculated using Gaussian smearing with a smearing parameter of 0.05 eV. For the bulk optimization, all internal atoms were relaxed using a conjugate gradient algorithm until the forces of each atom were lowered below 0.03 eV/Å with an energy convergence of $10^{-6}$ eV. GGA + $U$ approach was used to correct the self-interaction errors with $U_{Fe} = 4.0$ eV for Fe 3d orbital, $U_{Co} = 3.3$ eV for Co 3d orbital, $U_{Sr} = 2.5$ eV for Sr 3d orbital, and $U_{Pr} = 2.0$ eV for Pr 3d orbital.

![Graph](image_url)
Table 1 Comparison of the electrochemical performance of La1-xSrxGa0.5MgO3-δ (LSGM) electrolyte-supported symmetrical solid oxide fuel cells (S-SOFCs) reported in the literature and in the present study.

| Reference | Cell configuration (Air electrode | Electrolyte | Fuel electrode) | Electrolyte thickness (μm) | Maximum power density at 800 °C (W cm⁻²) |
|-----------|-----------------------------------|-------------|------------------|-----------------------------|----------------------------------------|
| Present study | A-PBSF30 | LDC | LSGM | LDC | R-PBSF30 |
| (28) | Pr0.6Sr0.4CoO3Fe2O7 | LSGM | | | |
| (39) | Sr2Ti0.5Co0.5FeO3 | LSGM | | | |
| (41) | SrFe1.5Mo0.5O6 | LSGM | | | |
| (42) | Pr0.6Sr0.4Fe0.8Ni0.2Mo0.2O3 | LSGM | | | |
| (43) | PrBa(Fe0.8Sc0.2)2O5 | LSGM | | | |
| (44) | SmBaMnO3 | LSGM | | | |
| (45) | La0.5Sr0.5FeO3 | LSGM | | | |
| (46) | La0.6Sr0.4Co0.5FeO3 | LSGM | | | |

A-PBSF30: Pr0.5Ba0.25Sr0.25FeO3, R-PBSF30: Pr0.5Sr0.5FeO3, LDC: Gd0.4Ce0.6O2, SDC: Sm0.4Ce0.6O2, GDC: Gd0.4Ce0.6O2, LSGM: La0.6Sr0.4Co0.2Fe0.7Mo0.1O3, LDC: La0.8Mn0.2O3.

Fig. 6 Schematic illustration of this work. Schematic illustration of the fuel electrode side of Pr0.5Ba0.5Sr0.5FeO3-δ (x = 0, 0.3, and 0.5) symmetrical cells and its relation to electrochemical performances.

Uid = 4.0 eV for Mn 3d orbital, Uid = 7.0 eV for Ni 3d orbital, and Uid = 6.0 eV for Pr 4f orbital. For the Brillouin zones of the formation energy calculation of cubic perovskite (2 × 2 × 2 super cell) and n = 1 R-P perovskite (2 × 2 × 1 super cell, 3 × 3 × 1 and 3 × 3 × 2 Monkhorst-Pack k-point sampling were used, respectively. For the oxygen vacancy formation energy calculations of BO2 layer between two AO layers, PrO-terminated (001) slab model (2 × 2 surface, 8 layers with 2 fixed bottom layers, vacuum layer of 16 Å) were used. For the co-segregation energy calculations, FeO2-terminated (001) slab model (2 × 2 × 2 surface, 8 layers with 3 fixed bottom layers, vacuum layer of 16 Å) were used. For the Brillouin zones of the oxygen vacancy formation energy and the co-segregation energy calculations, 3 × 3 × 1 and 1 × 1 × 1 Monkhorst-Pack k-point sampling were used. The optimized lattice parameters of four materials, A-PBSF00 (BaSr = 6.10), Pr0.5Ba0.25Sr0.25FeO3-δ (BaSr = 6.10), Pr0.5Ba0.25Sr0.25FeO3-δ (BaSr = 4.12), and A-PBSF50 (BaSr = 0.16) were used for model structures in the computational studies. For the Ba2+/Sr2+ mixed models, the most stable configurations among the total 5 different Ba configurations were used. The relative energies required for the phase reconstruction from simple perovskite to n = 1 R-P perovskite (Erecon) of six model structures with different Sr2+ concentration were calculated using the total energy difference between simple perovskite and n = 1 R-P perovskite by following equation:

\[ E_{\text{recon}} = \frac{1}{n} E_{\text{bulk}} + n E_{\text{simple perovskite}} - n E_{\text{perovskite}} \]

Where \( E_{\text{bulk}} \) and \( E_{\text{simple perovskite}} \) are the total energy of simple perovskite (2 × 2 × 4 super cell) and R-P perovskite (2 × 2 × 1 super cell), \( E_{\text{perovskite}} \) is total energy of body-centered cubic FeO2 metal unit cell, and \( E_{\text{bulk}} \) is the total energy of gas phase oxygen molecule.

The oxygen vacancy formation energies (\( E_{\text{recon}} \)) of Pr0.5Sr0.5FeO3-δ require the formation of both oxygen and B-site vacancies. For the Pr0.5Sr0.5FeO3-δ and Pr0.5Sr0.5To3-δ (T = Mn, Co, Fe, and Ni) models, the most stable structure configurations were utilized for the oxygen vacancy formation energy calculations. For the four computational models with different Sr2+ concentrations, the most stable vacancy sites were utilized for Ba2+/Sr2+ mixed models with BaSr = 6.10 and BaSr = 4.12. The E(δ) was calculated by following equation:

\[ E_{\text{O2-δ}} = E_{\text{perovskite}} - \frac{1}{2} E_{\text{O2}} - E_{\text{perovskite}} \]

Where \( E_{\text{perovskite}} \) and \( E_{\text{perovskite}} \) are the total energies of PrO-terminated (001) perovskite slab model with and without the oxygen vacancy, respectively.

The co-segregation energy (\( E_{\text{co-seg}} \)) is defined as the total energy difference of two surface models that have different vacancy site. The co-segregation energies of four computational models with different Sr2+ concentrations were calculated by following equation:

\[ E_{\text{co-seg}} = E_{(\text{Fe}−\text{V})_{\text{surface}}} − E_{(\text{Fe}−\text{V})_{\text{bulk}}} \]

Where \( E_{(\text{Fe}−\text{V})_{\text{surface}}} \) and \( E_{(\text{Fe}−\text{V})_{\text{bulk}}} \) are total energies of FeO2-terminated (001) perovskite slab model that have oxygen vacancy on surface FeO2 and bulk FeO2 layer, respectively.

Furthermore, the Gibbs free energy for oxygen vacancy formation of eight samples were calculated to include the temperature and oxygen partial pressure factors in the \( E_{\text{O2-δ}} \) calculations. The equations used for the \( G(T) \) calculations from the surface AO and BO2 layers in Pr0.5(Ba/Sr)0.5To3-δ (T = Mn, Co, Fe, and Ni) are as follows:

\[ G(T) = E_{\text{O2-δ}} + E_{\text{perovskite}} + \frac{1}{2} n T \mu_{O} \]

Where \( \mu_{O} \) is the oxygen chemical potential.
and H2O (Ratio of CO2:H2:H2O = 1:2:3).

The surface hydrogen oxidation reaction occurred via two elementary steps: (1) surface hydrogen oxidation reaction and (2) diffusion of oxygen. The diffusion step is the rate-determining step of the reaction. The rate of this reaction is given by the Arrhenius equation:

\[ \ln k = \ln A - \frac{E_a}{RT} \]

where \( k \) is the rate constant, \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, \( R \) is the gas constant, and \( T \) is the temperature. The activation energy \( E_a \) for the surface hydrogen oxidation reaction was calculated to be 0.95 eV.

The electrochemical performance measurements were carried out using a commercial electrochemical workstation (Princeton Applied Research) in a three-electrode configuration at a scan rate of 10 mV/s. The LDC layer was screen-printed between the electrode and electrolyte to prevent the electrolyte from contacting the electrode. The electrolyte-supported symmetrical S-SOC was fabricated by pressing stoichiometric amounts of La2O3 (Sigma, 99.9%) powders into a disc of desired stoichiometry, followed by sintering at 2 MPa and 800 °C for 2 h. After drying, the obtained LDC layer was polished to about 250 nm. The LDC layer was also prepared by ball-milling stoichiometric amounts of La2O3 (Sigma, 99.99%) and MgO (Sigma, 99.9%) powders to form a mixture with a desired composition. The mixture was then dried at 100 °C for 24 h and calcined at 1000 °C for 6 h. After formation of LSGM powder with desired stoichiometry, the electrolyte substrate was prepared by pressing at 50 MPa and 800 °C for 2 h. The electrolyte-supported symmetrical S-SOC was fabricated by press-sintering at 800 °C for 2 h. After drying, the obtained LDC layer was polished to about 250 nm. A La2O3-CeO2-O2 (LDC) as a buffer layer was also prepared by ball-milling stoichiometric amounts of La2O3 (Sigma, 99.99%) and CeO2 (Sigma, 99.99%) in ethanol for 24 h and calcined at 1000 °C for 6 h. Electrode slurries were prepared by mixing pre-calced powders of PBSF with an organic binder (Hercules V006) and aceton at a certain weight ratio. The electrode slurry was then coated on the LDC layer and dried at 100 °C for 24 h. After drying, the obtained electrode was glued on the LDC layer using a commercial adhesive (Ceramabond 552, Aremco). The electrochemical performance test of S-SOC with the cell composition of PBSF:La2O3 = 3:1 was carried out using a BioLogic Potentiostat. For the electrochemical performance test of S-SOC, the cell was first activated by cycling between 0.01 V and 1 V at a scan rate of 10 mV/s. After activation, the cell was placed inside a furnace and heated to the desired temperature. The temperature, p(O2), p(H2), and p(H2O) values are 750 °C, 10 atm, and 1 atm, respectively, for G. Eperov, T. Sengodan, S. et al. Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells. Nat. Mater. 14, 205–209 (2015).

The data measured, simulated, and analyzed in this study are available from the corresponding author on reasonable request.

**References**

1. Sengodan, S. et al. Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells. Nat. Mater. 14, 205–209 (2015).

2. Neagu, D., Tsekouoras, G., Miller, D. N., Menard, H. & Irvine, J. T. S. In situ growth of nanoparticles through control of non-stoichiometry. Nat. Chem. 5, 916–923 (2013).

3. Kang, K. N. et al. CoO2-exolved defective layered perovskite oxide for energy storage systems. ACS Energy Lett. 5, 3828–3836 (2020).

4. Joo, S. et al. Cation-swapped homogeneous nanoparticles in perovskite oxides for high power density. Nat. Commun. 10, 1–9 (2019).

5. Opitz, A. et al. Understanding electrochemical switchability of perovskite-type exsolution catalysts. Nat. Commun. 11, 1–10 (2020).

6. Irvine, I. T. S. et al. Evolution of the electrochemical interface in high-temperature fuel cells and electrolyzers. Nat. Energy 1, 1–13 (2016).

7. Ding, D., Li, X., Lai, S. Y., Gerdes, K. & Liu, M. Enhancing SOFC cathode performance by surface modification through infiltration. Energy Environ. Sci. 7, 535–574 (2014).

8. Schlupp, M. V. F., Evans, A., Martynczuk, J. & Prestat, M. Micro-solid oxide fuel cell membranes prepared by aerosol-assisted chemical vapor deposition. Adv. Energy Mater. 4, 1–7 (2014).

9. Kwak, N. et al. In situ synthesis of supported metal nanocatalysts through heterogeneous doping. Nat. Commun. 9, 1–8 (2018).

10. Jun, A., Kim, J., Shin, J. & Kim, G. Achieving high efficiency and eliminating degradation in solid oxide electrochemical cells using high oxygen-capacity perovskite. Angew. Chem. Int. Ed. 55, 12512–12515 (2016).

11. Choi, S. et al. A robust symmetrical electrode with layered perovskite structure for direct hydrocarbon solid oxide fuel cells: Pr0.5Ba0.5MnO3–δ/LSGM (Pr0.4Sr0.6)3(Fe0.85 Nb0.15)2O7 ceramic anode for direct hydrocarbon solid oxide fuel cells. Nat. Mater. 5, 528–531 (2016).

12. Neagu, D. et al. In situ observation of nanoparticle exsolution from perovskite oxides: from atomic mechanistic insight to nanostructure tailoring. ACS Nano 13, 12996–13005 (2019).

13. Sun, Y. et al. New opportunity for in situ exsolution of metallic nanoparticles on perovskite parent. Nano Lett. 16, 5303–5308 (2016).

14. Kwon, O. et al. Self-assembled alloy nanoparticles in a layered double perovskite as a fuel oxidation catalyst for solid oxide fuel cells. J. Mater. Chem. A. 4, 1747–1753 (2016).

15. Myung, J. H., Neagu, D., Miller, D. N. & Irvine, J. T. S. Switching on electrocatalytic activity in solid oxide cells. Nature 537, 528–531 (2016).

16. Zhang, J., Gao, M. R. & Luo, J. L. In situ exsolved metal nanoparticles: a smart approach for optimization of catalysts. Chem. Mater. 32, 5424–5441 (2020).

17. Kwon, O. et al. Exsolution trends and co-segregation aspects of self-grown exsolved catalysts. Adv. Energy Mater. 11, 1–9 (2020).

18. Liu, S., Liu, Q. & Luo, J. L. Highly stable and efficient catalyst with in situ exsolved Fe-Ni alloy nanoparticles on an oxygen deficient perovskite for direct CO2 electroxidation. ACS Catal. 6, 6219–6228 (2016).

19. Sun, Y. et al. A-site deficient perovskite: the parent for in situ exsolution of highly active, regenerable nano-particles as SOFC anodes. J. Mater. Chem. A. 3, 11048–11056 (2015).

20. Tsekouoras, G., Neagu, D. & Irvine, J. T. S. Step-change in high temperature steam electrolysiss performance of perovskite oxide cathodes with exsolution of 8-site dopants. Energy Environ. Sci. 6, 256–266 (2013).

21. Zhu, T., Troiani, H. E., Mogni, L. V., Han, M. & Barnett, S. A. Ni-substituted LDC | LSGM | LDC | A-PBSF30 during co-electrolysis, 50 ml min−1 of H2 and CO2 into a H2O-containing bubbler (with a heating tape) were co-fed to fuel electrode and 100 ml min−1 of air was fed to air electrode. The in-operando quantitative analysis of the generated synthetic gas (H2 and CO2) during co-electrolysis of CO2 and H2O (Ratio of CO2:H2O=45:45) for the A-PBSF30 symmetrical cell (580 °C and 1.5 V) was demonstrated by the gas chromatograph (Agilent 7820 A GC instrument) with a thermal conductivity detector and a packed column (Agilent carboxen 1000).
27. Lv, H. et al. In situ investigation of reversible exsolution/dissolution of CoFe alloy nanoparticles in a Co-doped SrFe$_2$$_3$Mo$_{6}$O$_{15}$ cathode for CO$_2$ electrolysis. Adv. Mater. 32, 1906193 (2020).
28. Yang, C. et al. Sulfur-tolerant redox-reversible anode material for direct hydrocarbon solid oxide fuel cells. Adv. Mater. 24, 1439–1443 (2012).
29. Du, Z. et al. High-performance anode material Sr$_2$FeMo$_{6.5}$O$_{15.5}$ with in situ exsolved nanoparticle catalyst. ACS Nano. 10, 8660–8669 (2016).
30. Chung, Y. S. et al. In situ preparation of a La$_{2}$Sr$_{2}$Mo$_{6}$O$_{15}$ Ruddlesden-Popper phase with exsolved Fe nanoparticles as an anode for SOFCs. J. Mater. Chem. A. 5, 6437–6446 (2017).
31. Park, S. et al. In situ exsolved Co nanoparticles on Ruddlesden-Popper material as highly active catalyst for CO$_2$ electrolysis to CO. Appl. Catal. B Environ. 248, 147–156 (2019).
32. Kim, K. et al. Mechanistic insights into the phase transition and metal exsolution phenomena of Pr$_3$Ba$_3$Mn$_{2.5}$Co$_{0.5}$O$_{12.5}$ from simple to layered perovskite under reducing conditions and enhanced catalytic activity. Energy Environ. Sci. 14, 873–882 (2021).
33. Višňovský, V. et al. Characterization of PrNi$_{2}$O$_{4}$ as oxygen electrode for SOFCs. Solid State Sci. 81, 26–31 (2018).
34. Choi, S. et al. Highly efficient and robust cathode materials for low-temperature solid oxide fuel cells: PrBa$_3$Sr$_2$Co$_5$Fe$_{10}$O$_{34+δ}$. Sci. Rep. 3, 1–6 (2013).
35. Chen, C. & Ciucci, F. Designing Fe-based oxygen catalysts by density functional theory calculations. Chem. Mater. 28, 7058–7065 (2016).
36. Brown, J. J., Ke, Z., Geng, W. & Page, A. J. Oxygen vacancy defect migration in titanate perovskite surfaces: effect of the A-site cations. J. Phys. Chem. C. 122, 14590–14597 (2018).
37. Kwon, O. et al. Probing one-dimensional oxygen vacancy channels driven by cation-anion double ordering in perovskites. Nano Lett. 20, 8353–8359 (2020).
38. Neagu, D. et al. Nano-sketched nickel particles with enhanced coking resistance grown in situ by redox exsolution. Nat. Commun. 6, 1–8 (2015).
39. Niu, B. et al. In-situ growth of nanoparticles-decorated double perovskite electrode materials for symmetrical solid oxide cells. Appl. Catal. B Environ. 270, 118842 (2020).
40. Kim, H., Joo, S., Kwon, O., Choi, S. & Kim, G. Cobalt-free Pr$_{0.5}$Ba$_{0.4}$Sr$_{0.1}$Fe$_{0.3}$O$_{3}$ as a highly efficient cathode for commercial YSZ-supported solid oxide fuel cell. ChemElectroChem 7, 4378–4382 (2020).
41. Liu, B. Q., Di, Z., Gu, C., Zhao, F. & Chen, F. A novel electrode material for symmetrical SOFCs. Adv. Mater. 22, 5478–5482 (2010).
42. Lu, X. et al. Mo-doped Pr$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$Ni$_{0.2}$O$_{3-δ}$ as potential electrodes for intermediate-temperature symmetrical solid oxide fuel cells. Electrochim. Acta 227, 33–40 (2017).
43. He, W., Wu, X., Dong, F. & Ni, M. A novel layered perovskite electrode for symmetrical solid oxide fuel cells: PrBa$_3$Sr$_2$Co$_{5}$Fe$_{10}$O$_{34+δ}$. J. Power Sources 363, 16–19 (2017).
44. Zhang, Y., Zhao, H., Du, Z., Swierczek, K. & Li, Y. High-performance SrBa$_3$Mn$_{6}$O$_{13+δ}$ electrode for symmetrical solid oxide fuel cell. Chem. Mater. 31, 3784–3793 (2019).
45. Cai, H. et al. Cobalt-free La$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$Mo$_{0.2}$O$_{3-δ}$ electrode for symmetrical SOFC operating on H$_2$ and CO fuels. Electroact. Acta 320, 134642 (2019).
46. Lu, C. et al. Efficient and stable symmetrical electrode La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$Mo$_{0.2}$O$_{3-δ}$ for direct hydrocarbon solid oxide fuel cells. Electrochim. Acta 323, 134857 (2019).
47. Hansen, J. B. Solid oxide electrolysis - a key enabling technology for sustainable energy scenarios. Faraday Discuss. 182, 9–48 (2015).
48. Zhu, J. et al. Enhancing CO$_2$ catalytic activation and direct electroreduction on in-situ exsolved Fe$_x$Mn$_{1-x}$O$_{2}$ nanoparticles from (Pr, Ba)$_3$Mn$_{2.5}$Fe$_{10}$O$_{34+δ}$ layered perovskites for SOEC cathodes. Appl. Catal. B Environ. 268, 118389 (2020).
49. Zhou, Y. et al. Enhancing CO$_2$ electrolysis performance with vanadium-doped perovskite cathode in solid oxide electrolysis cell. Nano Energy 50, 43–51 (2018).
50. Kim, C. et al. Highly efficient CO$_2$ utilization via aqueous zinc–or aluminum–CO$_2$ systems for hydrogen gas evolution and electricity production. Angew. Chem. Int. Ed. 58, 9506–9511 (2019).
51. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561 (1993).
52. Sholl, D. & Steckel, J. A. Density functional theory: a practical introduction. (John Wiley & Sons, Inc., 2011).
53. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
54. Bloch, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).
55. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B. 59, 1758–1775 (1999).
56. Kirdlin, S. et al. The open quantum materials database (OQMD): assessing the accuracy of DFT formation energies. npj Comput. Mater. 1, 1–15 (2015).
57. Bouadjemi, B., Bentata, S., Abbad, A., Benstaali, W. & Bouhafs, B. Half-metallic ferromagnetism in PrMnO$_3$ perovskite from first principles calculations. Solid State Commun. 168, 6–10 (2013).
58. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. Phys. Rev. B. 13, 5188 (1976).
59. Noskov, J. K. et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. J. Phys. Chem. B. 108, 17886–17892 (2004).
60. Wang, L., Maxisch, T. & Ceder, G. Oxidation energies of transition metal oxides within the GGA + U framework. Phys. Rev. B. 73, 195107 (2006).
61. Zhang, D. et al. Preparation and characterization of a redox-stable Pr$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$Mn$_{0.2}$O$_{3-δ}$ material as a novel symmetrical electrode for solid oxide cell application. Int. J. Hydrog. Energy 45, 21825–21835 (2020).