

Supporting Information

Entropy-Driven Oxygen Transport Anisotropy and Spin-State

Manipulation for High-Performance Reversible Solid Oxide Cells

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1. Intrinsic physicochemical properties

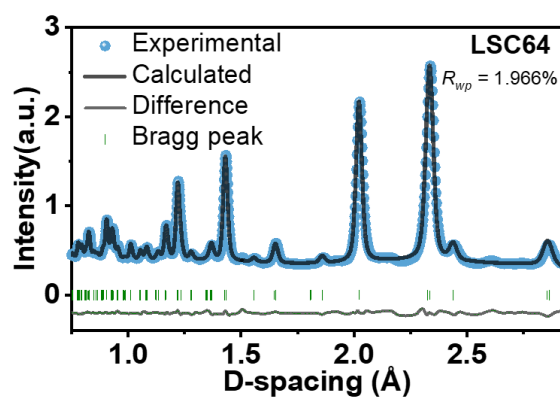


Figure S1. Neutron refinement of LSC64 ($R-3c$).

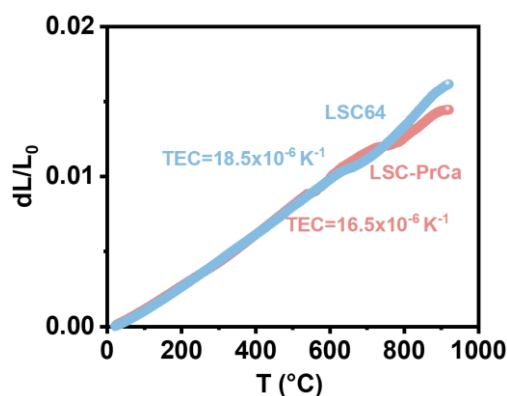


Figure S2. Thermal expansion of dense specimens in air (25~900 °C).

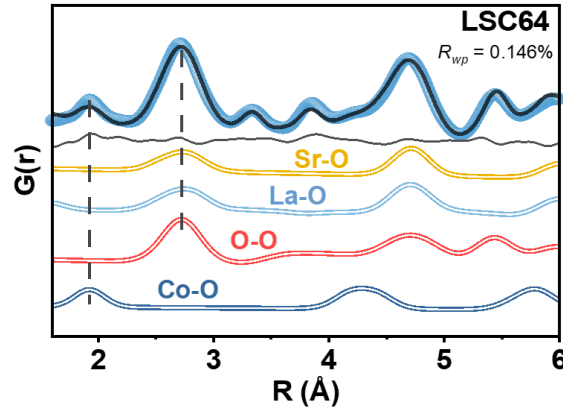


Figure S3. Total scattering fits (black lines) to experimental data (symbols) and corresponding residuals (gray lines), together with partial pair distribution functions (PDFs) for A-O, Co-O, and O-O correlations for LSC64.

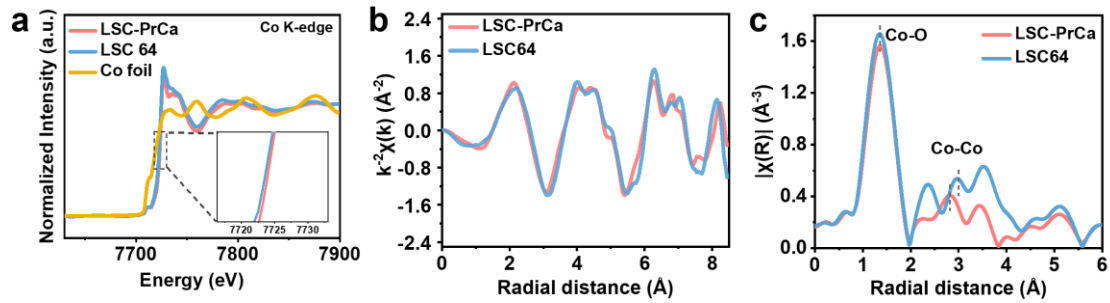


Figure S4. (a) Co K-edge XAFS spectra of samples and reference samples Co foil (yellow). (b) FT k^2 -weighted transformation of the Co-K edge EXAFS in k -space. (c) FT k^3 -weighted EXAFS spectra in R -space.

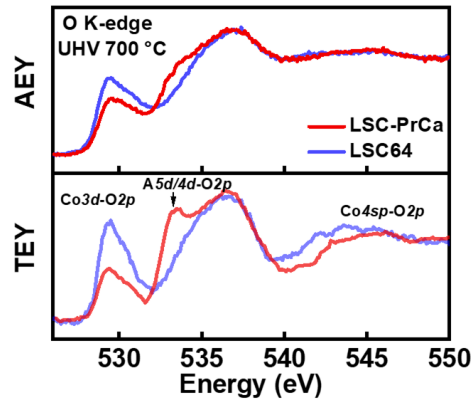


Figure S5. (a) AEY and (b) TEY O-K edge of LSC-PrCa in 700 °C.

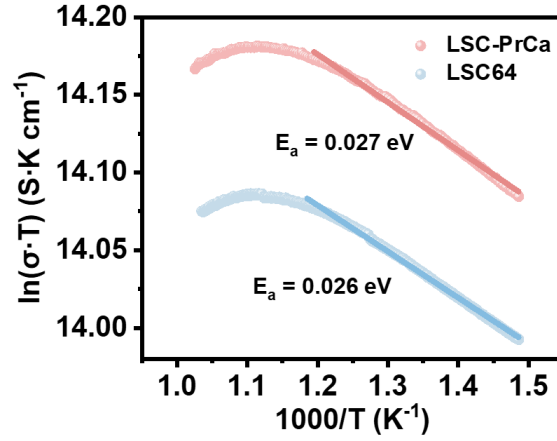


Figure S6. Arrhenius plots of total conductivity (σ_{total}) for dense LSC-PrCa and LSC64 in air (400~900°C).

Oxygen isotope exchange experiments coupled with time-of-flight secondary ion mass spectrometry (TOF-SIMS). Samples were pre-annealed at 600 °C for 8 h under ultra-high vacuum (UHV) conditions (1.7×10^{-8} mbar), followed by $^{18}\text{O}_2$ isotope exchange at 592°C for 1 h (80.96% $^{18}\text{O}_2$). The ^{18}O concentration profiles were analyzed by TOF-SIMS (Figure S6) and fitted using Fick's second law:

$$C'(x, t) = \frac{C(x, t) - C_{bg}}{C_g - C_{bg}}$$

$$= \text{erfc}\left(\frac{x}{2\sqrt{D^*t}}\right) - \left[\exp\left(\frac{k^*x}{D^*} + \frac{k^{*2}x}{D^*}\right) \times \text{erfc}\left(\frac{x}{2\sqrt{D^*t}} + k^*\sqrt{\frac{t}{D^*}}\right) \right] \quad (1)$$

Here, $C(x, t)$ represents the $^{18}\text{O}_2/(^{16}\text{O}_2+^{18}\text{O}_2)$ ratio at depth x and time t . C_{bg} is the natural ^{18}O isotopic background (0.002), C_g is the isotope fraction in the gas phase. At 600 °C, LSC-PrCa exhibited an order-of-magnitude higher tracer diffusion coefficient D^* ($8.34 \pm 1.75 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) than LSC64 ($8.53 \pm 2.32 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$), confirming intrinsically faster oxygen ion diffusion in LSC-PrCa.

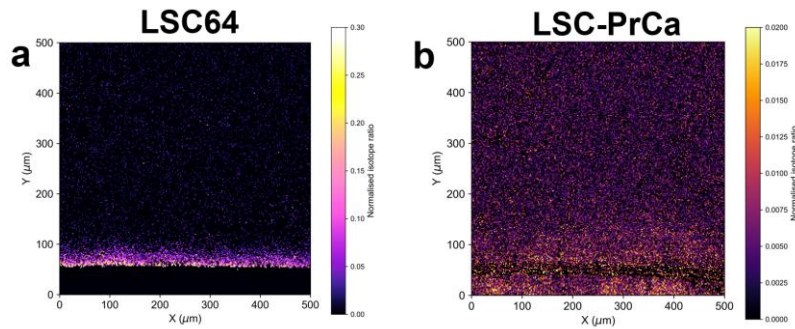


Figure S7. Secondary electron image of (a) LSC64 and (b) LSC-PrCa.

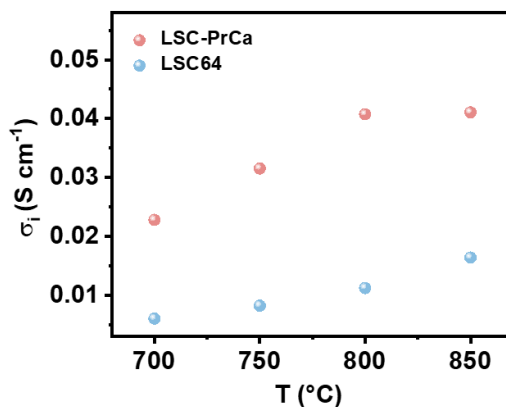


Figure S8. Oxygen ion conductivities (σ_i) measured via Hebb-Wagner method (700~850 °C).

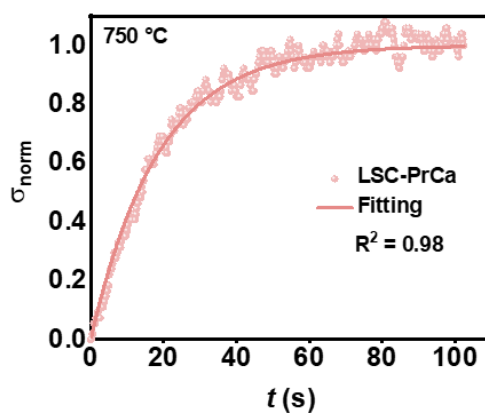


Figure S9. The representative ECR fitting curve of LSC-PrCa (750 °C)

2. Surface chemistry and electronic structures

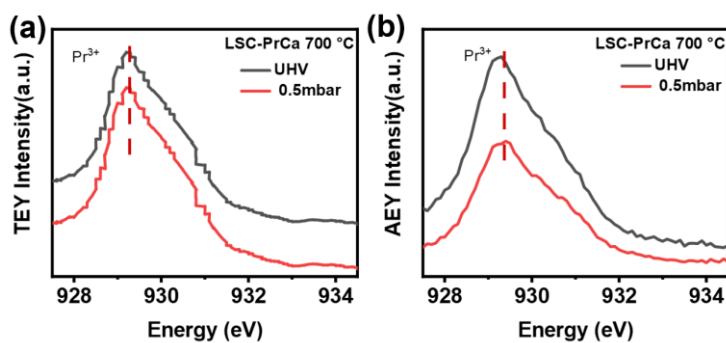


Figure S10. (a) AEY and (b) TEY Pr-M₄ edge of LSC-PrCa at 700 °C.

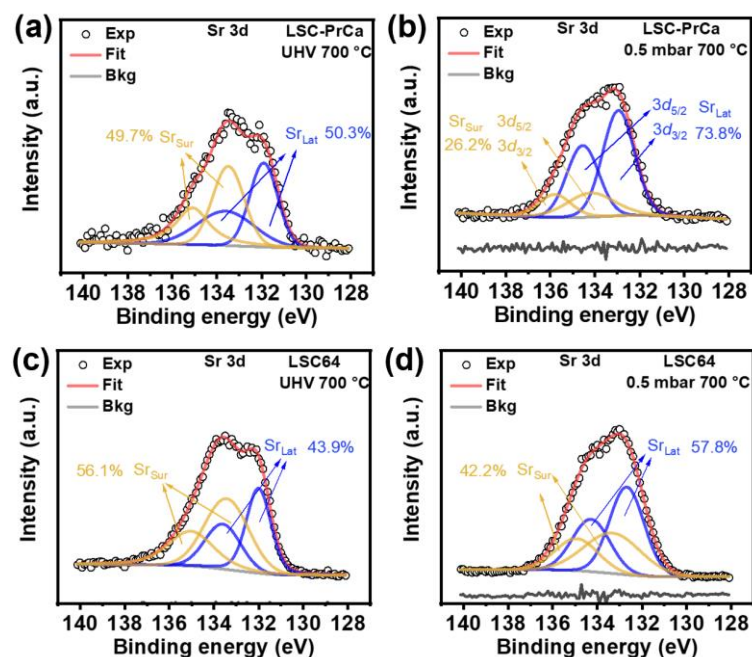


Figure S11. Sr 3d XPS spectra of LSC-PrCa (a: UHV, b: 0.5 mbar) and LSC64 (c: UHV, d: 0.5 mbar) in 700 °C.

The Co 2p XPS spectra at RT (Figure S12a) show similar peak positions and shapes for LSC-PrCa and LSC64, indicating comparable Co valence states at RT. The O 1s spectra at RT (Figure S12b) reveal a higher surface oxygen vacancy (V_o) concentration in LSC-PrCa (25.5%) than in LSC64 (10.4%).

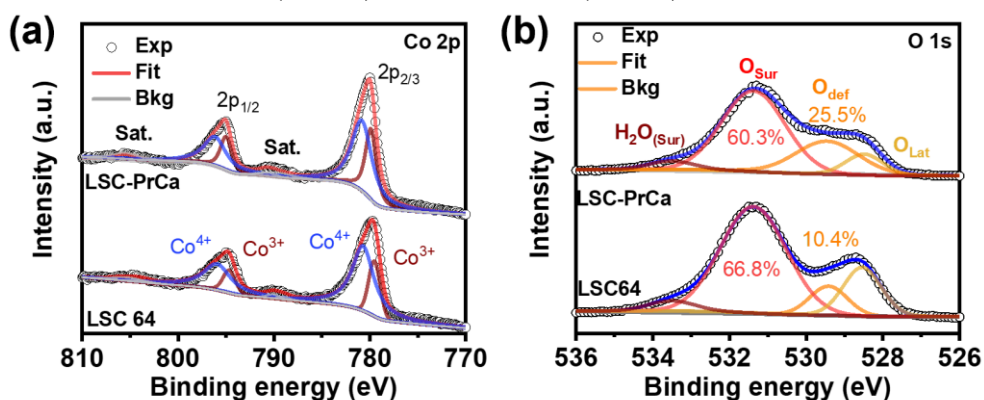


Figure S12. (a) Co 2p spectra and (b) O 1s spectra of samples at RT.

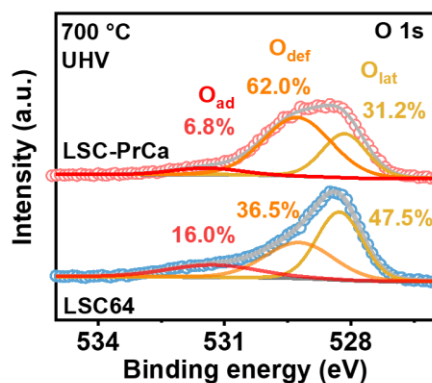


Figure S13. O 1s spectra of samples at 700 °C under UHV.

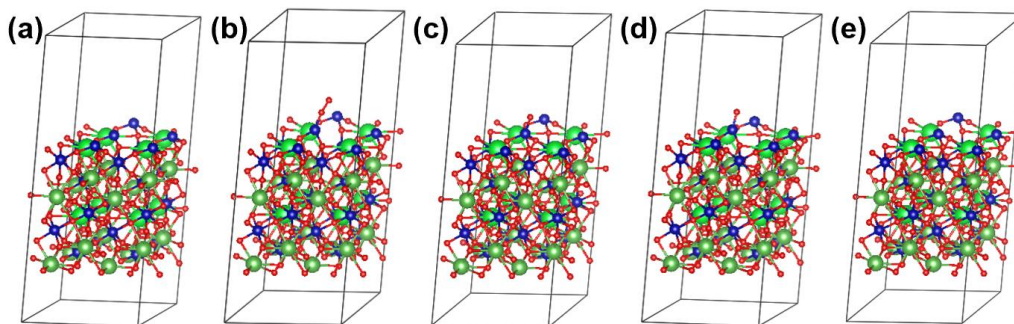


Figure S14. Optimized surface of the LSC64 (001) with free O_2 , adsorbed O_2^* and O^* , and adsorbed bulk $O_{O^\times}$ intermediates.

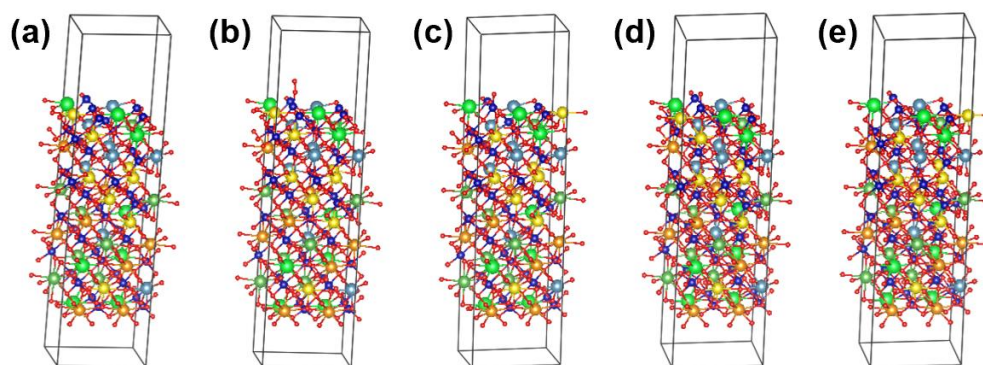


Figure S15. Optimized surface of the LSC-PrCa (001) with free O_2 , adsorbed O_2^* and O^* , and adsorbed bulk $O_{O^\times}$ intermediates.

3. Electrochemical process analysis

Microstructure of air electrode. Cross-sectional morphologies of electrolyte-supported (3YSZ) single cells with LSC-PrCa and LSC64 air electrodes were examined by high-resolution scanning electron microscopy (SEM) analysis (Figure S16). Both air electrodes exhibited similar porosity, pore connectivity, and sintered thickness ($25 \pm 2 \mu m$), confirming comparable microstructure and excluding its influence on the observed performance differences.

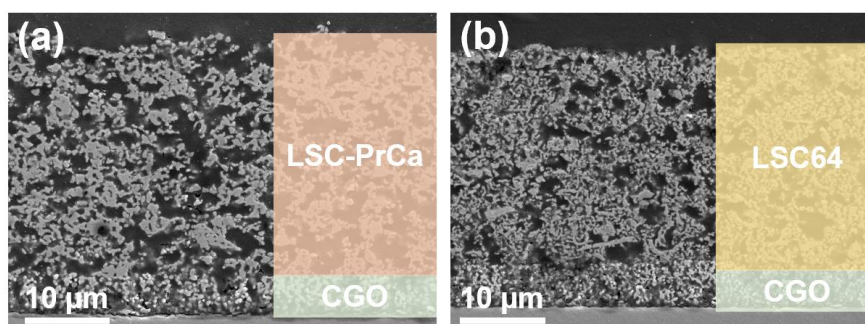


Figure S16. SEM diagram of LSC-PrCa (a) and LSC64 (b) single cell.

Electrochemical process analysis. Electrochemical impedance spectroscopy (EIS) was conducted on LSC-PrCa single cells under controlled gas compositions ($P_{O_2} = 0.05 \sim 0.21$ atm; flow rates = 100~200 sccm) in both fuel cell (FC) and electrolysis cell (EC) modes.

In FC mode, both ohmic resistance (R_o) and polarization resistance (R_p) decrease

with increasing gas flow rate and P_{O_2} (Figure S17a). A marked rise in R_p at low P_{O_2} (0.05 atm) reflects slower oxygen exchange kinetics. The trend was confirmed by three-electrode EIS isolating the air electrode response (Figure S17b).

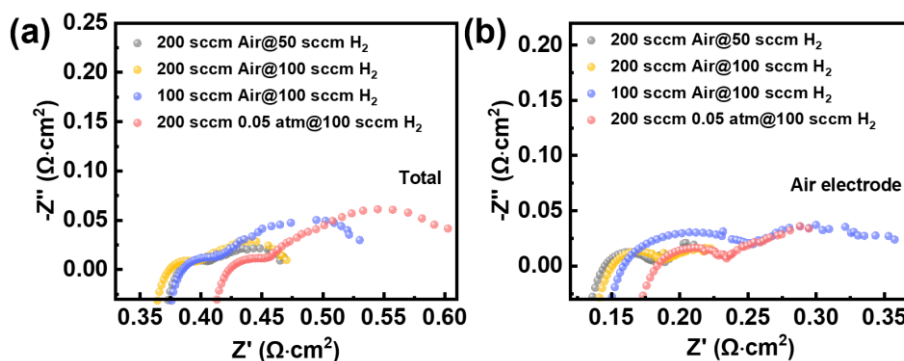


Figure S17. EIS of the LSC-PrCa full cell (a) and isolated air electrode (b) obtained by auxiliary partial pressure under varied atmospheres in FC mode at 850 °C.

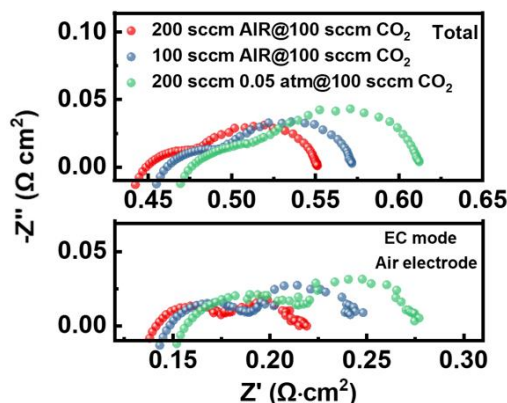


Figure S18. EIS of the electrolysis mode and isolated air electrode under varied atmospheres (100 sccm air vs. CO_2) in EC mode.

Bode spectra under varying gas compositions (Figure S19a) show contributions from both electrodes at low frequencies. Isolated air-electrode responses (Figure S19c) exhibit three primary processes: air electrode reaction, oxygen-ion conductivity (IC), and gas diffusion. Differential Bode analysis (Figure S19d) shows that lowering P_{O_2} (0.21 to 0.05 atm) significantly increases impedance below 1 Hz, confirming the P_{O_2} dependence of surface exchange kinetics. The ~ 10 Hz remains nearly constant, while gas diffusion contributions at ~ 100 Hz increase with reduced air flow. Characteristic frequencies are summarized in Table S6. Similarly, the air electrode contribution was obtained under electrolysis mode (Figure S20).

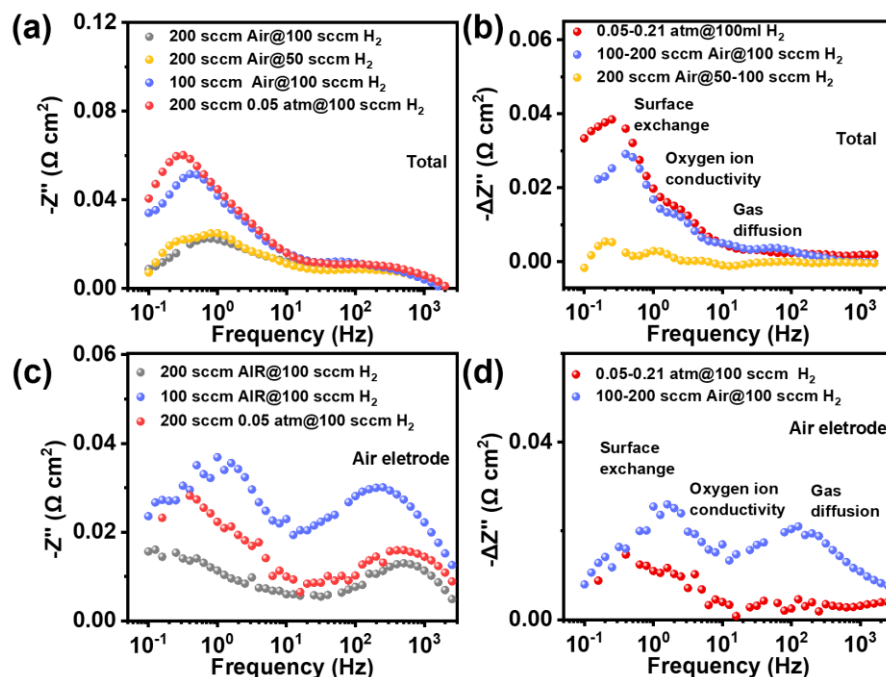


Figure S19. The corresponding Bode plots of the total LSC-PrCa full cell (a) and air electrode (c) under varied atmospheres in FC mode at 850 °C. The difference of Bode plots in LSC-PrCa total full cell (b) and air electrode (d) under varied atmospheres in FC mode at 850 °C. DRT plots quantifying oxygen partial pressure (P_{O_2}) effects: 0.05 atm oxygen and air in air electrode vs. 100 sccm 5 wt% wet H_2 in fuel electrode.

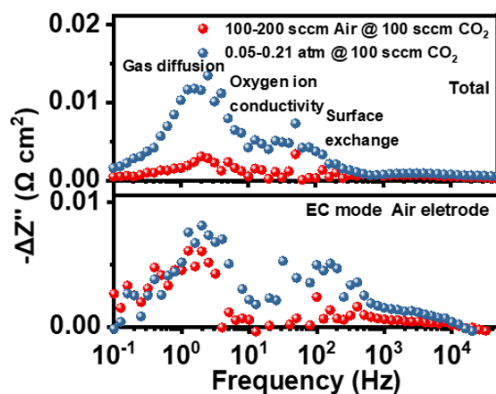


Figure S20. Difference Bode plots comparing 100 sccm air vs. 200 sccm air (red), and 0.05 atm P_{O_2} vs. air (blue) for the total single cell and isolated air electrode under electrolysis mode.

Bode plots of LSC-PrCa single cells before and after stability testing at 850 °C (Figure S20) show nearly unchanged features at ~10 Hz (ionic conduction) and ~1 Hz in FC; ~100 Hz in EC mode (surface exchange). Minor performance degradation arises from a slight increase in R_o due to interfacial delamination between the fuel electrode and 3YSZ, and a modest rise in R_p associated with diffusion and Ni-TPB impedance (100-1000 Hz).

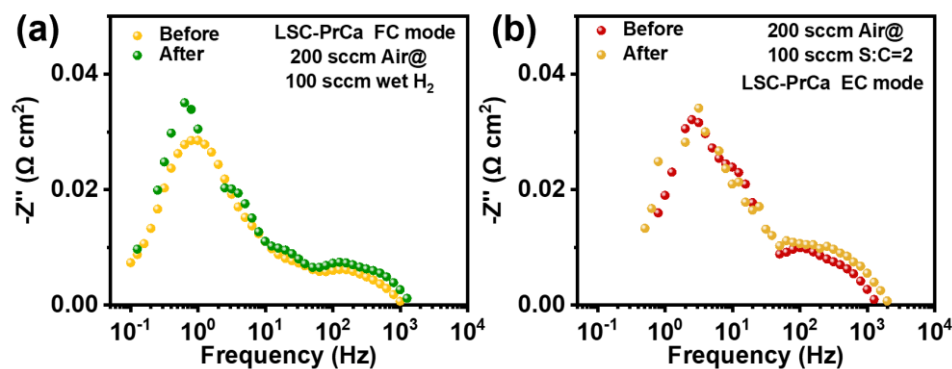


Figure S21. Bode plots of LSC-PrCa single cell before test and after test in (a) FC mode and (b) EC mode at 850 °C

SEM images of LSC-PrCa cell before and after testing (Figure S22) show that the air electrode remains structural integrity, while the fuel electrode exhibits interface delamination and degraded $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (CGO) connectivity after 68 hours of operation.

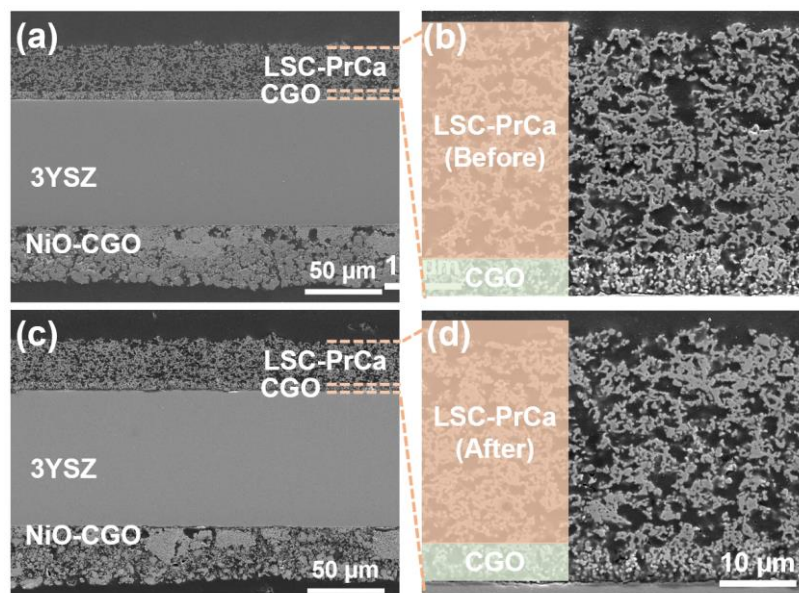


Figure S22. Comparison of cross-sectional SEM image for the electrolyte-supported Ni-CGO|CGO|3YSZ|CGO|LSC-PrCa single cell (a,b) before and (c,d) after testing.

Table**Table S1.** The atomic ratios of each element in the synthesized LSC-PrCa were measured by ICP.

Sample	La	Nd	Pr	Ca	Sr
Theoretical stoichiometric	0.2	0.2	0.2	0.2	0.2
As-synthesized	0.219	0.220	0.200	0.209	0.199

Table S2. Neutron diffraction refinement results of LSC samples.

Samples	LSC64	LSC-PrCa
Space	<i>R-3C</i>	<i>Pnma</i>
a (Å)	5.73020	5.38418
b (Å)	5.73020	7.61837
c (Å)	13.95200	5.42587
V (Å ³)	396.740	222.565
O1		<i>x</i> =0.51440 <i>y</i> = 0.25000 <i>z</i> =0.54790
	<i>x</i> =0.00000 <i>y</i> =0.53377 <i>z</i> =0.25000	<i>f</i> _{occ} =0.9881
O2	<i>f</i> _{occ} =0.973	<i>x</i> =0.22090 <i>y</i> =0. 03510 <i>z</i> =0.28040 <i>f</i> _{occ} =0.9751
3- δ	2.919	2.9591
<i>U</i> _{iso} (O1) (Å)	0.013	0.0125
<i>U</i> _{iso} (O2) (Å)	0.013	0.0121
<i>U</i> _{iso} (Co) (Å)	0.006	0.00295
R _{wp}	1.966%	3.552%

Table S3. Oxygen ion conductivities (σ_i) measured via Hebb-Wagner method (700~850 °C).

Temperature	LSC-PrCa (S cm ⁻¹)	LSC64 (S cm ⁻¹)
700 °C	0.02278	0.00599
750 °C	0.03152	0.00819
800 °C	0.04074	0.01120
850 °C	0.04106	0.01638

Table S4. k_{chem} measured via ECR (650~750 °C).

Temperature	LSC-PrCa (S cm ⁻¹)	LSC64 (S cm ⁻¹)
650 °C	1.01×10^{-3}	1.46×10^{-4}
700 °C	1.73×10^{-3}	2.14×10^{-4}
750 °C	1.82×10^{-3}	3.23×10^{-4}

Table S5. Comparison of the bulk O 2p band center of the bulk LSC-PrCa and LSC64.

O 2p band center (in units of eV)	LSC-PrCa	LSC64
Spin-Up	-2.08	-2.48
Spin-down	-2.00	-2.37
Average	-2.04	-2.43

Table S6. Polarization contributions of LSC air electrode in FC mode at 850 °C determined from bode plots.

Processes	Frequency	Processes	Gas dependence
P1	<1 Hz	Gas conversion; air electrode reaction	Air electrode P _{O2} & minor gas flow rate
P2	1~10 Hz	Ion conductivity	Minor gas flow rate & P _{O2}
P3	10~100 Hz	Gas diffusion	Gas flow rate & minor P _{O2}

Table S7. Polarization contributions of LSC air electrode in EC mode at 850 °C determined from bode plots.

Processes	Frequency	Processes	Gas dependence
P1	<1 Hz	Gas diffusion/conversion	Gas flow rate & minor P _{O2}
P2	1~10 Hz	Ion conductivity	Minor gas flow rate & P _{O2}
P3	10~100 Hz	Oxygen surface exchange	Air electrode P _{O2} & minor gas flow rate

Table S8. Buckingham interionic potential parameters [1-6].

Interaction	A_{ij}/eV	$\rho_{ij}/\text{\AA}$	$C_{ij}/\text{eV \AA}^6$
O ²⁻ -O ²⁻	9547.96	0.2192	32.00
La ³⁺ -O ²⁻	2119.79	0.3459	23.25
Nd ³⁺ -O ²⁻	1995.20	0.3430	22.59
Pr ³⁺ -O ²⁻	2025.54	0.3427	13.85
Ca ²⁺ -O ²⁻	2036.07	2036.07	0.00

Table S8 Continued.

$\text{Sr}^{2+}\text{-O}^{2-}$	682.17	0.3945	0.00
$\text{Co}^{3+}\text{-O}^{2-}$	1226.32	0.3087	0.00

Reference

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