Supplementary Information

Towards an atomic scale understanding on the early-stage deterioration mechanism of LSCF

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Note: this material contains Figures, Sections and Tables in the order of their appearance in the main manuscript.



Fig. S1 Schematics of electrolyte-supported button cell and electrochemical measurement setup.



Fig. S2 Electrochemical and transport properties of LSCF cathodes. (a) The kinetic curves of cathode degradation obtained by calculating the time derivatives of the fitted curves in (Fig.1(a)). (b) Variations of the oxygen bulk diffusion coefficient (D^*) and surface exchange coefficient (k^*) with time.



Fig. S3 Impedance spectra of LSCF cathode at 600 °C for Dry-OCV (a), Dry-bias (b), Wet-OCV (c) and Wet-bias (d). The spectra were collected at the beginning of test (0 h, black) and after operation for 5 h (red), 10 h (blue), 25 h (dark cyan), 50 h (magenta), 75 h (dark yellow) and 100 h (navy), respectively.

Section 1: Fitting of the galvanostatic curves.

The fitting of the galvanostatic curves (Fig. 1a) of Dry-bias and Wet-bias was performed using polynomial equations E1 and E2, respectively. For Dry-bias, the fitting is limited within 90 h because a steady state was observed after 90 h. The parameters and their errors are listed in Table. S1.

 $E_{\text{cathode}} = \text{Intercept} + B1^{*}t + B2^{*}t^{2}$ (*t* is time) (E1) $E_{\text{cathode}} = \text{Intercept} + B1^{*}t + B2^{*}t^{2} + B3^{*}t^{3} + B4^{*}t^{4}$ (E2)

Table. S1 Fitting parameters along with the errors for galvanostatic curves.

Sample	Intercept		B1		B2		B3		B4	
	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
Dry-bias	-0.219	7.79E-6	-1.99E-4	4.25E-7	9.70E-7	4.63E-9	-	-	-	-
Wet-bias	-0.215	1.46E-5	-6.49E-4	1.92E-6	8.82E-6	7.75E-8	6.34E-8	1.17E-9	1.68E-10	5.88E-12

Table. S2 Ohmic (R_o) and polarization (R_p) resistances for four cathodes at different time intervals evaluated from the impedance spectra.

Time (h)	Dry-OCV		Dry	-bias	Wet-	OCV	Wet-bias	
	Ro	R _p						
	$(\Omega \text{ cm}^2)$							
0	1.930	1.216	1.948	1.515	1.960	1.753	2.115	1.718
5	1.931	1.222	1.937	1.570	1.969	1.835	2.093	1.929
10	1.929	1.239	1.945	1.612	1.961	1.908	2.098	2.075
25	1.951	1.259	1.954	1.673	1.966	2.013	2.089	2.284
50	1.950	1.298	1.955	1.752	1.926	2.099	2.092	2.552
75	1.950	1.306	1.974	1.808	1.901	2.178	2.099	2.724
100	1.943	1.312	1.989	1.837	1.905	2.233	2.097	2.789



 R_{o} , ohmic resistance R_{HF} , high-frequency part of polarization resistance R_{LF} , low-frequency part of polarization resistance CPE, constant phase element GE, Gerischer element

Fig. S4 An equivalent circuit for the impedance fitting analysis. The polarization resistance was divided into two parts, namely high-frequency one ($R_{\rm HF}$) and low-frequency ($R_{\rm LF}$) one. The latter one is used to estimate the oxygen transport property.

Section 2: Evaluation of oxygen surface exchange coefficient (k^*) and diffusion coefficient (D^*) of porous LSCF electrode.

According to the equilibrium circuit in Fig. S3, the polarization resistance part of the impedance spectrum obtained in this study could be deconvoluted into high-frequency (R_{HF} and *CPE*) and low-frequency (R_{LF}) parts. And R_{LF} was fitted by a Gerischer element (Z_G) and used to estimate the activity of the oxygen reduction reaction (ORR), namely the transport properties of the LSCF electrode. The methodology involves the combination of Adler-Lane-Steele (ALS)^{1,2} and Transmission Line (TML)³ models. Although detailed description has been reported elsewhere,^{4,5} a brief explanation and summary is given as follows.

In the ALS model, Z_G is defined as:

$$Z_{\rm G} = R_{\rm G} \sqrt{\frac{1}{1 + j\omega t_{\rm G}}} \tag{1}$$

where R_G and t_G are the Gerischer resistance and a frequency parameter related to the thermodynamic, kinetic, and transport properties of MIEC cathode, while *j* and ω stand for the imaginary unit and perturbation frequency. Furthermore, R_G is expressed as

$$R_{\rm G} = \frac{RT}{4F^2} \sqrt{\frac{1}{4a \,\mathcal{R}_{\rm O} c_{\rm v} D_{\rm v,eff}}} \tag{2}$$

where R, T, F, a, \mathcal{R}_{O} , c_{v} and $D_{v,eff}$ are the ideal gas constant, temperature, Faraday constant, volumetric surface area, equilibrium molar exchange rate of O_2 between gas phase and the MIEC surface, oxygen vacancy concentration, and effective oxygen vacancy diffusivity of MIEC cathode, respectively. Among them, \mathcal{R}_{O} and $D_{v,eff}$ have the following relationships with the tracer transport parameters: the oxygen surface exchange coefficient (k^*) and diffusion coefficient (D^*) in equations (3) and (4), which were deduced from reported equations.^{1,4}

$$\Re_{O} = \frac{3k^{*}}{4V_{m}}$$
(3)
$$D_{v,eff} = \frac{3(1-\varepsilon)D^{*}}{\tau \delta f}$$
(4)

where $V_{\rm m}$, ε , τ , δ and f are the molar volume of MIEC, porosity, tortuosity, oxygen vacancy content of the MIEC cathode and the Bardeen-Herring correlation factor, respectively.

The TLM model was adopted by Kawada et al. to understand the equilibrium circuit by introducing three elements: volumetric surface reaction resistance ($^{R_{\rm F, eff}}$), effective ion resistivity ($^{\rho_{\rm i, eff}}$) and volumetric chemical capacitance ($^{C_{\rm chem}}$).³ Their corresponding equations are given as:

$$R_{\rm F, eff} = \frac{R_{\rm surf}}{a}$$
(5)

$$\rho_{\rm i, eff} = \frac{\tau}{\sigma_{\rm i}(1-\varepsilon)}$$
(6)

$$\frac{8(1-\varepsilon)\delta E^2}{c} = d\ln\delta$$

$$C_{\rm chem} = \frac{8(1-\varepsilon)\partial F^{-} - d\ln\partial}{RTV_{\rm m} \ d\ln p_{\rm O_2}}$$
(7)

where R_{surf} , σ_i and p_{O_2} stand for areal surface reaction resistance, intrinsic conductivity and oxygen partial pressure, respectively.

The relationship between TML and ALS can be established by equation (8) when $\omega=0.3$

$$R_{\rm G} = \sqrt{R_{\rm F, \, eff} \rho_{\rm i, \, eff}} \tag{8}$$

Thus, $R_{\rm F, eff}$ and $\rho_{\rm i, eff}$ can be separately expressed by comparing equations (2) and (8):

$$R_{\rm F, \, eff} = \frac{RT}{16F^2 a \,\mathcal{R}_{\rm O}} \tag{9}$$

$$\rho_{\rm i, \, eff} = \frac{RI}{4F^2 c_{\rm v} D_{\rm v, eff}} \tag{10},$$

where $R_{\rm F, eff}$ and $\rho_{\rm i, eff}$ are evaluated by equations (11) and (12) containing the Gerischer parameters, *GE-P* and *GE-T*, after fitting of the $R_{\rm LF}$ part in the impedance spectrum.

$$R_{\text{F, eff}} = \overline{C_{\text{chem}}(GE - P)}$$
(11)
$$\rho_{\text{i, eff}} = \overline{\frac{C_{\text{chem}}}{(GE - T)^2}}$$
(12)

Finally, the transport property parameters k^* and D^* are derived from the above equations.

$$k^{*} = \frac{RTV_{\rm m}C_{\rm chem}(GE - P)}{12aF^{2}}$$
(13)
$$D^{*} = \frac{f\tau RTV_{\rm m}(GE - T)^{2}}{12(1 - \varepsilon)C_{\rm chem}F^{2}}$$
(14)

In order to calculate k^* and D^* , the values of three microstructure parameters (ε , *a* and τ) need to be known. Thereafter, we conducted 3D reconstruction in the following steps. Firstly, the as-prepared cell was infiltrated with epoxy resin under vacuum. Secondly, the resininfiltrated cell was polished mechanically to get a smooth cross-section of LSCF/GDC cell. Thirdly, the polished cell was coated with gold to improve the conductivity. Fourthly, the slice and view operation was performed on the sample in a FIB-SEM (Helios 5 Hydra CX, Thermo Scientific) with a 60 nm slice depth and a through-the-lens detector (TLD) to collect the SEM images. Fifthly, the images were processed through alignment, denoising, cropping and phase segmentation by using AVIZO (Thermo Scientific) software. The images of one slice before and after processing are shown in Fig. S4a and b. The obtained 3D model (Fig. S4c) has a volume of 21.67 µm × 9.25 µm × 11.28 µm. Finally, the *TauFactor* application developed by Cooper et al.⁶ was adopted in MATLAB (MathWorks) to calculate the three parameters. The porosity (ε) is 46.2% while the volumetric surface area (*a*) is 24700 cm⁻¹. Regarding the LSCF tortuosity (τ), values of 1.58, 2.09 and 2.00 were obtained in three directions. Herein, we used their average value, 1.89, which is close to the values in literature.^{7–9} Based on these three parameters, we first calculated C_{chem} (equation (7)) to be 261.3 F cm⁻³ for LSCF6428 under conditions of 873 K and 0.21 bar O₂ after adopting 35.5 cm³ mol⁻¹ for

 $\frac{-\mathrm{dln}\delta}{\mathrm{dln}n}$

 $V_{m^{10}}$ and evaluating the values of $d^{1np}O_2$ and δ as 0.225 and 0.0075 from Hashimoto et al's paper.¹¹ Then k^* and D^* were estimated using equations (13) and (14), which contains a parameter *f* having a typical value of 0.69.¹²



Fig. S5 3D reconstruction of as-prepared LSCF cathode. (a) A raw SEM image used for reconstruction; bright: LSCF; black: resin. (b) The image after segmentation. (c) Reconstructed 3D model.



Fig. S6 XRD patterns of LSCF cathodes obtained from Bruker D2 PHASER. The samples are as-prepared (a), Dry-OCV (b), Dry-bias (c), Wet-OCV (d), and Wet-bias (e).



Fig. S7 An HRSEM image of the cross-section of as-prepared LSCF cathode.



Fig. S8 HRSEM images of the cross-sections of LSCF cathode at two locations: in the middle of cathode (left column) and near the LSCF/GDC interface (right column). The samples are: Dry-OCV (a, b), Dry-bias (c, d), and Wet-OCV (e, f), respectively.



Fig. S9 SEM-EDS maps of the polished cross-section of the cathode layer of Wet-bias. The sample was first infiltrated with resin. Then the cross-section was polished mechanically, during which process a delamination was created near the GDC. Finally, Ar ion milling was performed. The La signal in the region of GDC is caused by the overlap of the EDS peaks of La and Ce.



Fig. S10 SEM-EDS maps of the polished cross-section of Wet-bias near the cathode surface. The arrows point out some small particles like segregation. Enrichment and depletion appear in some regions on Sr map but not on other elements. However, no enrichment of any element on the grain surfaces can be seen.



Fig. S11 TEM analysis on Dry-bias. (a) STEM-EDS line scan profiles across the SrSO₄/LSCF interface. (b) An HRTEM image of the SrSO₄/LSCF interface.



Fig. S12 An HRSEM image of Dry-bias for the second TEM specimen. The dash line shows the ROI center.



Fig. S13 Profiles of the STEM-EDS line scan from LSCF surface to the bulk on Dry-bias.

Section 3: Preparation of Sr(OH)₂.

 $Sr(OH)_2$ was prepared by the reaction of SrO with water. $SrCO_3$ was used as a starting material and heated at 1068 °C for 2 h in a tubular furnace in dry air with a flow rate of 50 mL min⁻¹. Then the temperature was decreased to 515 °C and 1.2% H₂O was introduced into the furnace. After holding for 10 h, the furnace was cooled down to room temperature. The asprepared powder was subjected to XRD measurement. The pattern is shown in Fig. S13 and matches well with the data (JCPDS 27-847) in literature,¹³ indicating that we prepared pure Sr(OH)₂.



Fig. S14 XRD patterns of as-prepared Sr(OH)₂.

Section 4: <u>Attempts on observation of Co-rich oxide</u>.

We checked carefully all the TEM specimens presented in the main manuscript; no Co-rich oxide was detected. For example, all the areas near the cathode surface for the 1st TEM specimen of Dry-bias (Fig. 4) were scanned by STEM-EDS, however, no Co-rich oxide was detected while all the segregated nanoparticles are SrSO₄. Due to the limited area of the TEM specimen slice, we wondered whether we missed the Co-rich phase or not. Hence, more specimens were prepared and investigated. Two more specimens for Dry-bias and Wet-OCV were lifted out from the cathode surface. However, no Co-rich particle was detected.

In addition to all the specimens from the cathode surface, we also prepared specimens from cathode/electrolyte interface. One specimen was examined for Dry-bias and only the La-Co-rich phases were observed (Fig. S14a). As for the most degraded Wet-bias, three specimens were prepared, however, none was found to have Co-rich particle. The details of a small portion of one specimen are shown in Fig. S14b. The elemental maps of three ROIs labelled as 1, 2 and 3 are introduced. ROI 1 covers the LSCF/GDC interface. Although obvious heterogeneity inside LSCF grain was found, the element distribution at the LSCF/GDC interface is homogenous. ROIs 2 and 3 contain the GBs of LSCF and prove the formation of Sr(OH)₂ and SrSO₄ near the LSCF/GDC interface.



Fig. S15 STEM-EDS analysis near the LSCF/GDC interface. (a) Dry-bias. (b) Wet-bias. The elemental maps of three ROIs labelled as 1, 2 and 3 of Wet-bias are shown. It is noted that image rotations were conducted before mapping in cases of ROIs 2 and 3. The superimposed maps of elements La, Sr and Co were adopted instead of their individual ones.



Fig. S16 (a) Gibbs free energy changes (ΔG) of reactions (1)~(6) in their nominal molar ratios in the equations. (b) Equilibrium partial pressures of gas species. The partial pressure of O₂ in Equation (3) is fixed to be 0.21 atm. (c) A table illustration of the curves in (a) and (b). Each reaction is assigned a specific color.

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