SUPPORTING MATERIALS

In operando monitoring reaction-diffusion streamlines and uncovering electrochemo-structural interactions in electrode

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Contents:

- Theoretical derivation;
- Fabrication of the LSCF/SDC/LSCF symmetric cells;
- Electrochemical testing and EIS analysis;
- 3D reconstruction and electrochemical simulations.

• Theoretical derivation

The following derivation is based on reaction-diffusion process in the oxygen electrode of solid oxide cells. In order to facilitate the derivation, the reaction-diffusion streamline (RDS) in Fig. 1 is redrawn as Sketch S1.



Sketch S1. Sketch for a reaction-diffusion streamline (RDS) to facilitate derivation of equations.

(1) Diffusion equation:

The transport of O²⁻ in electrode can be described by the flux equation [1],

$$\mathbf{J}_{\mathrm{O}^{2-}} = -\frac{\sigma_{\mathrm{O}^{2-}}}{4F^2} \nabla \left[\mu_{\mathrm{O}} - 2F\varphi \right]$$
(S1)

where $\mathbf{J}_{0^{2}}$ denotes the flux density of O²⁻ [mol.cm⁻².s⁻¹], μ_0 denotes the chemical potential of lattice O [J.mol⁻¹], φ denotes the electric potential [V], $\sigma_{0^{2}}$ denotes the ionic conductivity [S.cm⁻¹], and *F* denotes the Faraday constant 96485 [C.mol⁻¹]. In the oxygen electrode, the electric potential can be safely treated as a constant due to the high electronic conductivity. Therefore, Eq. S1 is rewritten as,

$$\mathbf{J}_{\mathrm{O}^{2-}} = -\frac{\sigma_{\mathrm{O}^{2-}}}{4F^2} \nabla \mu_{\mathrm{O}}$$
(S2)

Since μ_0 relates directly to the concentration of lattice O { δ , [mol.cm⁻³]}, Eq. S2 can be further linearized as Fick's diffusion law,

$$\mathbf{J}_{\mathbf{Q}^{2-}} = -D\nabla\delta \tag{S3}$$

where D is the chemical diffusion coefficient $[cm^2.s^{-1}]$.

Refocusing on the RDS (Sketch S1), the flux $\{N_{0^{2-}}, [mol.s^{-1}]\}$ of O²⁻ through the section area *A* at coordinate *l* can be given by,

$$\mathbf{N}_{0^{2*}} = \mathbf{J}_{0^{2*}} A = -D \frac{\partial \delta}{\partial l} A$$
(S4)

According to Fick's Second Law, the conservation of O2- in the RDS leads to,

$$A\frac{\partial\delta}{\partial t} = -\frac{\partial\mathbf{N}_{0^{2}}}{\partial l} = D\frac{\partial}{\partial l} \left(\frac{\partial\delta}{\partial l}A\right)$$
(S5)

and can be further written as,

$$\frac{\partial \delta}{\partial t} = D \frac{\partial^2 \delta}{\partial l^2} + \frac{1}{A} \frac{\partial A}{\partial l} D \frac{\partial \delta}{\partial l}$$
(S6)

which is the Eq. 2 in the manuscript.

(2) Boundary conditions:

The boundary conditions for the diffusion equation S6 must be defined to obtain the analytic steady-state solution of δ with respect to *l* and *t*. Following Adler's work [2], an small alternating current density (i_1e^{jwt}) will cause a proportional faradic modulation of O²⁻ flux density across the electrode/electrolyte interface (l = 0),

$$\mathbf{J}_{\mathbf{O}^{2-}}\Big|_{l=0} = -D\frac{\partial\delta}{\partial l}\Big|_{l=0} = \frac{i_1 e^{j\omega t}}{2F}$$
(S7)

where *j* denotes the imaginary unit, ω denotes the angular frequency. At the internal surface of electrode (l = L), oxygen reduction reaction (ORR) takes place drive by the

difference between δ in the electrode material and the equilibrium δ_0 corresponding to the atmosphere. Following the theory of electric conductivity relaxation [3-5], the rate of ORR can be given by the following equation via the surface exchange coefficient $(k, \text{cm.s}^{-1})$,

$$\mathbf{J}_{O^{2-}}\Big|_{l=L} = -D\frac{\partial\delta}{\partial l}\Big|_{l=L} = k\left(\delta - \delta_0\right)$$
(S8)

(3) Analytic steady-state solution:

At steady-state, the solution of δ subjects to a general form $\delta = \delta_0 + \hat{\delta_1} e^{j\omega t}$. Inserting this general solution into Eq. S6, we obtain,

$$j\omega\hat{\delta}_{1} = D\frac{\partial^{2}\hat{\delta}_{1}}{\partial l^{2}} + \frac{1}{A}\frac{\partial A}{\partial l}D\frac{\partial\hat{\delta}_{1}}{\partial l}$$
(S9)

Here we treat the term $\frac{1}{A} \frac{\partial A}{\partial l}$ as a constant, and introduce the shape factor defined by $s = \frac{L}{2A} \frac{\partial A}{\partial l}$. Therefore, Eq. S9 is rewritten as,

$$j\omega\hat{\delta}_{1} = D\frac{\partial^{2}\hat{\delta}_{1}}{\partial l^{2}} + \frac{2s}{L}D\frac{\partial\hat{\delta}_{1}}{\partial l}$$
(S10)

which has a general solution,

$$\hat{\delta}_{1} = C_{1} \exp\left[\left(-s + \sqrt{j\omega\tau + s^{2}}\right)^{l}_{L}\right] + C_{2} \exp\left[\left(-s - \sqrt{j\omega\tau + s^{2}}\right)^{l}_{L}\right]$$
(S11)

where $\tau = L^2/D$, denoting the characteristic diffusion time. C_1 and C_2 are coefficients to be determined by the boundary conditions,

$$-D\frac{\partial\hat{\delta}_{1}}{\partial l}\Big|_{l=0} = \frac{i_{1}}{2F}$$
(S12)

$$-D\frac{\partial\hat{\delta}_{1}}{\partial l}\Big|_{l=L} = k\hat{\delta}_{1}$$
(S13)

Inserting Eq. S11 into Eqs. S12 and S13, we obtain,

$$C_1\left(-s + \sqrt{j\omega\tau + s^2}\right) + C_2\left(-s - \sqrt{j\omega\tau + s^2}\right) = -\frac{Li_1}{2FD}$$
(S14)

$$C_{1} = -C_{2} \frac{\sqrt{\tau\gamma} - s - \sqrt{j\omega\tau + s^{2}}}{\sqrt{\tau\gamma} - s + \sqrt{j\omega\tau + s^{2}}} \exp\left(-2\sqrt{j\omega\tau + s^{2}}\right)$$
(S15)

where $\gamma = k^2/D$. Therefore, we have,

$$C_{1} = -\frac{Li_{1}}{2FD} \frac{\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(-\sqrt{j\omega\tau + s^{2}}\right)}{\left(\sqrt{j\omega\tau + s^{2}} + s\right)\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right)}$$
(S16)

$$C_{2} = \frac{Li_{1}}{2FD} \frac{\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right)}{\left(\sqrt{j\omega\tau + s^{2}} + s\right)\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right)}$$
(S17)

$$C_{2} = \frac{Li_{1}}{2FD} \frac{\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right)}{\left(\sqrt{j\omega\tau + s^{2}} + s\right)\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right)}$$
(S17)

(4) The normalized impedance of RDS:

The impedance of a RDS is given by the ratio between the overpotential (η) and the current perturbation (i_1e^{jwt}). According to Adler's work [2], the overpotential can be given by the Nernst equation,

$$\eta = \frac{1}{2F} \left(\mu_{\rm O} \big|_{l=0} - \mu_{\rm O}^0 \right) \tag{S18}$$

where μ_0^0 denotes the equilibrium chemical potential of lattice O corresponding to the atmosphere. Under small perturbations $(\mu_0|_{l=0} \approx \mu_0^0)$, the Nernst equation can be linearized as,

$$\eta = \frac{1}{2F} \frac{\partial \mu_{\rm O}}{\partial \delta} \left(\delta \Big|_{l=0} - \delta_0 \right) \equiv \frac{RT}{4F} f V_{\rm m} \left(\delta \Big|_{l=0} - \delta_0 \right) \tag{S19}$$

where f denotes the thermodynamic factor, and V_m is the molar volume of lattice O. Inserting the solution of into Eq. S19, we obtain,

$$\eta = \frac{RT}{4F} f V_{\rm m} \,\hat{\delta}_1 \Big|_{l=0} e^{j\omega\tau} = \frac{RT}{4F} f V_{\rm m} \left(C_1 + C_2\right) e^{j\omega\tau} \tag{S20}$$

Therefore, the impedance of a RDS $[\Omega.cm^2]$ is given by,

$$Z(\omega;\gamma,\tau,s) = \frac{\eta}{i_1 e^{j\omega\tau}} = \frac{RT}{4F} f V_{\rm m} \frac{C_1 + C_2}{i_1}$$
(S21)

Inserting Eq. S16 and S17 into Eq. S21, we obtain,

$$\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right) - \left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(-\sqrt{j\omega\tau + s^{2}}\right) - \left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(-\sqrt{j\omega\tau + s^{2}}\right) - \left(\sqrt{j\omega\tau + s^{2}} + s\right)\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right) + \left(\sqrt{j\omega\tau + s^{2}} - s\right)\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(-\sqrt{j\omega\tau + s^{2}}\right) - \left(\sqrt{j\omega\tau + s^{2}}\right) - \left(\sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(-\sqrt{j\omega\tau + s^{2}}\right)$$

Thus, the polarization resistance of the RDS $[\Omega.cm^2]$ is,

$$R_{\rm p}(\gamma,\tau,s) = Z(\omega=0) = \frac{RTfV_{\rm m}}{8F^2\sqrt{D}} \frac{\exp(-2s)}{\sqrt{\gamma}} + \frac{RTfV_{\rm m}}{8F^2\sqrt{D}}\sqrt{\tau} \frac{1-\exp(-2s)}{2s}$$
(S23)

The first term on the right of Eq. S23 is the resistance of reaction, and the second term corresponds to the resistance of diffusion. It is interesting to note that if there is no current constriction effect (s = 0), the polarization resistance is,

$$R_{\rm p}\left(s=0\right) = \frac{RTfV_{\rm m}}{8F^2k} + \frac{RTfV_{\rm m}L}{8F^2D}$$
(S24)

which is the same with the results for dense thin film electrodes by Adler [2]. The normalized impedance of RDS is defined by,

$$z_{\rm RD}(\omega;\gamma,\tau,s) = \frac{Z(\omega;\gamma,\tau,s)}{R_{\rm P}(\gamma,\tau,s)}$$
(S25)

that is,

$$\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right) - \frac{\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right)}{\left(\sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(-\sqrt{j\omega\tau + s^{2}}\right)} + \frac{\exp\left(-2s\right)}{\left(\sqrt{j\omega\tau + s^{2}} + s\right)\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(\sqrt{j\omega\tau + s^{2}}\right)} + \frac{\exp\left(-2s\right)}{\left(\sqrt{j\omega\tau + s^{2}} - s\right)\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^{2}} - s\right)\exp\left(-\sqrt{j\omega\tau + s^{2}}\right)}$$
(S26)

(5) The asymptotic limits of z_{RD} :

Physically, γ and *s* should be finite so that the reaction-diffusion process and the shape of RDS can be properly defined. But it is necessary to discuss the asymptotic behaviors of the kernel impedance when γ and *s* tend to extreme values. For convenience, we rearrange Eq. S26 as,

$$z_{\rm RD} = \frac{2s}{1 - \exp(-2s) + \frac{2s}{\sqrt{\gamma\tau} \exp(2s)}} \frac{1 - \frac{\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^2} - s}{\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^2} - s} \exp\left(-2\sqrt{j\omega\tau + s^2}\right)}{\left(\sqrt{j\omega\tau + s^2} + s\right) + \left(\sqrt{j\omega\tau + s^2} - s\right)}$$
(S27)
$$\frac{\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^2} - s}{\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^2} - s} \exp\left(-2\sqrt{j\omega\tau + s^2}\right)$$

For $s \to +\infty$, $1 - \exp\left(-2s\right) + \frac{2s}{\sqrt{\gamma\tau} \exp(2s)} \to 1$, $\frac{\sqrt{\tau\gamma} - \sqrt{j\omega\tau + s^2} - s}{\sqrt{\tau\gamma} + \sqrt{j\omega\tau + s^2} - s} \to 1 - \frac{2s}{\sqrt{\tau\gamma}}$, that

is,

$$z_{\rm RD} = 2s \frac{1 - \left(1 - \frac{2s}{\sqrt{\tau\gamma}}\right) \exp\left(-2\sqrt{j\omega\tau + s^2}\right)}{\left(\sqrt{j\omega\tau + s^2} + s\right) + \left(\sqrt{j\omega\tau + s^2} - s\right)}$$
(S28)
$$\left(1 - \frac{2s}{\sqrt{\tau\gamma}}\right) \exp\left(-2\sqrt{j\omega\tau + s^2}\right)$$

Since $s \exp\left(-2\sqrt{j\omega\tau + s^2}\right) \rightarrow 0$ for a certain value of γ (can be extremely small or

large, $\gamma \rightarrow 0$ or $+\infty$), Eq. S28 can be further simplified as,

$$z_{\rm RD} = \frac{2s}{\sqrt{j\omega\tau + s^2} + s} \tag{S29}$$

which is the Eq. 8 in the manuscript under the condition of $s \to +\infty$ and $\gamma \to 0$ or $+\infty$,

$$z_{\rm RD} = \frac{2}{1 + \sqrt{1 + j\omega \frac{\tau}{s^2}}}$$
(S30)

For s = 0, Eq. S26 becomes,

$$z_{\rm RD} = \frac{1}{1 + \frac{1}{\sqrt{\gamma\tau}}} \frac{\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau}\right) \exp\left(\sqrt{j\omega\tau}\right)}{\sqrt{j\omega\tau}\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau}\right) \exp\left(\sqrt{j\omega\tau}\right)}$$
(S31)
$$\frac{1}{\sqrt{j\omega\tau}} \frac{\sqrt{j\omega\tau}\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau}\right) \exp\left(\sqrt{j\omega\tau}\right)}{\sqrt{j\omega\tau}\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau}\right) \exp\left(-\sqrt{j\omega\tau}\right)}$$

Eq. S31 can be further simplified when $\gamma \rightarrow +\infty$,

$$z_{\rm RD} = \frac{\exp\left(\sqrt{j\omega\tau}\right) - \exp\left(-\sqrt{j\omega\tau}\right)}{\sqrt{j\omega\tau}\exp\left(\sqrt{j\omega\tau}\right) + \sqrt{j\omega\tau}\exp\left(-\sqrt{j\omega\tau}\right)}$$
(S32)

which is the Eq. 7 in the manuscript under the condition of s = 0 and $\gamma \rightarrow +\infty$,

$$z_{\rm RD} = \frac{\tanh\left(\sqrt{j\omega\tau}\right)}{\sqrt{j\omega\tau}} \tag{S33}$$

When $\gamma \to 0$, the diffusion process is relatively facial, indicating $\tau \to 0$, and thus $\exp(\pm \sqrt{j\omega\tau}) \rightarrow 1 \pm \sqrt{j\omega\tau}$. Therefore Eq. S31 can be simplified as,

$$z_{\rm RD} = \frac{\sqrt{\gamma\tau}}{1+\sqrt{\gamma\tau}} \frac{\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau}\right)\left(1+\sqrt{j\omega\tau}\right) - \left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau}\right)\left(1-\sqrt{j\omega\tau}\right)}{\sqrt{j\omega\tau}\left(\sqrt{\tau\gamma} + \sqrt{j\omega\tau}\right)\left(1+\sqrt{j\omega\tau}\right) + \sqrt{j\omega\tau}\left(\sqrt{\tau\gamma} - \sqrt{j\omega\tau}\right)\left(1-\sqrt{j\omega\tau}\right)}$$
(S34)

By some rearrangements, we obtain,

$$z_{\rm RD} = \frac{\sqrt{\gamma\tau}}{1 + \sqrt{\gamma\tau}} \frac{1 + \sqrt{\tau\gamma}}{\sqrt{\tau\gamma} + j\omega\tau}$$
(S35)

or,

$$z_{\rm RD} = \frac{1}{1 + j\omega\sqrt{\frac{\tau}{\gamma}}}$$
(S36)

Eq. S36 is the special case of the Eq. 6 in the manuscript under the condition of $\gamma \rightarrow 0$ and s = 0.

For $\gamma \to 0$ and s < 0, the diffusion process is relatively facial, indicating $\tau \to 0$, and 8/16

thus
$$\exp\left(\pm\sqrt{j\omega\tau+s^2}\right) \rightarrow \left(1\,\mathrm{m}\frac{j\omega\tau}{2s}\right)\exp(\mathrm{m}s), \ \sqrt{j\omega\tau+s^2} \rightarrow -s - \frac{1}{2s}\,j\omega\tau$$
. Eq. S26

becomes,

$$z_{\rm RD} = \frac{1}{\frac{1-\exp(-2s)}{2s} + \frac{\exp(-2s)}{\sqrt{\gamma\tau}}} - \frac{1-\frac{\left(\sqrt{\tau\gamma} + \frac{1}{2s}j\omega\tau\right)(2s+j\omega\tau)}{\left(\sqrt{\tau\gamma} - 2s - \frac{1}{2s}j\omega\tau\right)(2s-j\omega\tau)}} \exp(2s)}{\left(\sqrt{\tau\gamma} + \frac{1}{2s}j\omega\tau\right)(2s+j\omega\tau)} \exp(2s)$$
(S37)

Note
$$\left(\sqrt{\tau\gamma} - 2s - \frac{1}{2s}j\omega\tau\right)(2s - j\omega\tau) \rightarrow -4s^2$$
, $2s + j\omega\tau \rightarrow 2s$, Eq. S37 can be

further simplified as,

$$z_{\rm RD} = \frac{1}{\frac{1 - \exp(-2s)}{2s} + \frac{\exp(-2s)}{\sqrt{\gamma\tau}}} - \frac{1 - \left(\sqrt{\tau\gamma} + \frac{1}{2s}j\omega\tau\right) \frac{1}{2s} \exp(2s)}{-\frac{1}{2s}j\omega\tau + \left(2s + \frac{1}{2s}j\omega\tau\right) \left(\sqrt{\tau\gamma} + \frac{1}{2s}j\omega\tau\right) \frac{1}{2s} \exp(2s)}$$
(S38)

or,

$$z_{\rm RD} = \frac{1}{\frac{1 - \exp(-2s)}{2s} + \frac{\exp(-2s)}{\sqrt{\gamma\tau}}} \frac{2s \exp(-2s) + \sqrt{\tau\gamma} + \frac{1}{2s} j\omega\tau}{\left(2s + \frac{1}{2s} j\omega\tau\right) \left(\sqrt{\tau\gamma} + \frac{1}{2s} j\omega\tau\right) - j\omega\tau \exp(-2s)}$$
(S39)

Note that $2s \exp(-2s) + \sqrt{\tau\gamma} + \frac{1}{2s} j\omega\tau \rightarrow 2s \exp(-2s), \quad 2s + \frac{1}{2s} j\omega\tau \rightarrow 2s$, and $\frac{1 - \exp(-2s)}{2s} + \frac{\exp(-2s)}{\sqrt{\gamma\tau}} \rightarrow \frac{\exp(-2s)}{\sqrt{\gamma\tau}}$, we have, $z_{\rm RD} = \frac{1}{\frac{\exp(-2s)}{\sqrt{\gamma\tau}}} \frac{2s \exp(-2s)}{2s\sqrt{\tau\gamma} + j\omega\tau[1 - \exp(-2s)]}$ (S40)

Therefore, we obtain the Eq. 6 in the manuscript under the condition of $\gamma \rightarrow 0$ and s < 0

0,

$$z_{\rm RD} = \frac{1}{1 + j\omega\sqrt{\frac{\tau}{\gamma}}\frac{1 - \exp(-2s)}{2s}}$$
(S41)

For $s \to -\infty$ and $\gamma \to +\infty$, the reaction process is facial, however, due to the extremely large value of s, we can still obtain the following limitations as used in the derivation of Eq. S41 in case $\gamma \to 0$ and s < 0: $\exp\left(\pm\sqrt{j\omega\tau+s^2}\right) \to \left(1\,\mathrm{m}\frac{j\omega\tau}{2s}\right)\exp(\mathrm{m}s)$, $\sqrt{j\omega\tau+s^2} \to -s - \frac{1}{2s}\,j\omega\tau$, $\left(\sqrt{\tau\gamma}-2s-\frac{1}{2s}\,j\omega\tau\right)(2s-j\omega\tau) \to -4s^2$, $2s+j\omega\tau \to 2s$,

$$2s \exp(-2s) + \sqrt{\tau\gamma} + \frac{1}{2s} j\omega\tau \to 2s \exp(-2s), \qquad 2s + \frac{1}{2s} j\omega\tau \to 2s, \qquad \text{and}$$

$$\frac{1 - \exp(-2s)}{2s} + \frac{\exp(-2s)}{\sqrt{\gamma\tau}} \to \frac{\exp(-2s)}{\sqrt{\gamma\tau}}.$$
 Therefore, Eq. S41 can also be obtained

under the condition of $s \to -\infty$ and $\gamma \to +\infty$.

The roots for $z_{RD}(\omega;\gamma,\tau,s)=0$ can be obtained by setting the term associated with the imaginary unit 'j' being infinity. That is $\omega \sqrt{\frac{\tau}{\gamma}} \frac{1-\exp(-2s)}{2s} = +\infty$ from Eq. 6, $\omega \tau = +\infty$ from Eqs. 5 and 7, and $\omega \frac{\tau}{s^2} = +\infty$ from Eq. 8, as shown in Table S1.

Table S1. The roots for $z_{RD}(\omega; \gamma, \tau, s) = 0$.

	$\log_{10} \gamma \to -\infty$	$\log_{10}\gamma \to +\infty$
$s \rightarrow -\infty$	$\omega_{\sqrt{\frac{\tau}{\gamma}}} \frac{1 - \exp(-2s)}{2s} = +\infty$	$\omega_{\sqrt{\frac{\tau}{\gamma}}} \frac{1 - \exp(-2s)}{2s} = +\infty$
<i>s</i> = 0	$\omega \sqrt{\frac{\tau}{\gamma}} = +\infty$	$\omega au = +\infty$
$s \rightarrow +\infty$	$\omega \frac{\tau}{s^2} = +\infty$	$\omega \frac{\tau}{s^2} = +\infty$

• Fabrication of the LSCF/SDC/LSCF symmetric cells

SDC powders and LSCF powders were fabricated using a carbonate co-precipitation method [6] and a glycine-nitrate combustion method [7], respectively. Dense SDC pellets with a diameter of about 10.0 mm and thickness of about 0.5 mm were fabricated by uniaxially pressing the SDC powders followed by sintering at 1450 °C for 5 h in air. Then, both sides of the SDC pellets were symmetrically screen-printed using a LSCF slurry (LSCF powders mixed with a-terpineol and ethyl cellulose), and co-fired at 1200 °C for 2 h to form symmetric cells.

• Electrochemical testing and EIS analysis

The electrochemical spectra of the symmetric cells at 650 - 800 °C in air were measured using a Zennium E workstation with an AC amplitude of 10 mA in the frequency range typically from 1 MHz to 0.01 Hz with 10 points per decade. Silver pastes (Sina-Platinum Metals Co. Ltd.) were used as the current collector. Distribution of relaxation times (DRT) were calculated from the spectra using our prior method [8]. The results are shown in Fig. S1, showing clearly that the spectra can be attributed to a high-frequency (HF) process and a low-frequency (LF) process (Fig. S1a). The resistance of the LF process exhibits a negative activation energy of -0.27 eV (Fig. S1b), which is a strong evidence that the LF process represents the gas diffusion in electrode [9]. Therefore, the coupling of oxygen surface exchange and ionic diffusion, that is, the reaction-diffusion in electrode is attributed to the HF process. The spectra converted back from the DRT fit nicely to the experimental spectra (Fig. S1c), showing a high accuracy of the DRT analysis.



Figure S1. (a) The DRT spectra of the LSCF/SDC/LSCF symmetrical cell at different temperatures. (b) The temperature dependence of the resistances of the reactiondiffusion process at high frequency (HF) and the gas diffusion process at low frequency (LF), as marked in (a). (c) The comparision between the experimental EIS and the EIS converted from the DRT spectra at different temperatures.



Figure S2. (a) The EIS of a Gerischer circuit model $Z = R/(1+j\omega t)^{1/2}$ with R = 0.0633 Ωcm^2 , t = 0.016 sec [3], $k^2/D = 10^{-4}$ sec⁻¹, and the impedance Z_{cal} from the *DRDS* resolved from Z. (b) Inverse of impedance as a function of frequency for Z and Z_{cal} and the absolute error. (c) The *DRDS* calculated from Z.

• 3D reconstruction and electrochemical simulations

The 3D microstructure of the LSCF electrode is reconstructed from a single 2D micrograph of the electrode, based on the distance correlation function (DCF) method [10]. To prepare the 2D cross-section of electrode, the internal pores in electrode were filled by epoxy resin (EpoFix, Electron Microscopy Sciences, Hatfield, PA). Then the cell were manually fractured and ground using SiC papers from 240 to 800 grit, and then polished using colloidal silica (W0.25). To collect the 2D micrograph of the polished cross-section, the SEM InLens signal (ZEISS SUPRA55) was used under a voltage of 5 kV. An anisotropic diffusion smoothing was applied on the raw SEM micrograph to eliminate noise. The phases of LSCF and resin (pores) were segmented using a watershed algorithm. Then, the DCFs were calculated from the phasesegmented 2D micrograph. The 3D microstructure was reconstructed using a twopoint exchanging process with an objective that its DCFs converge to those of the 2D micrograph. The 3D symmetric cell was simulated by the reconstructed LSCF electrode and its symmetric duplicate, with a layer of SDC electrolyte sandwiching them. The details are shown in Fig. S3. The electrochemical fields, such as chemical potential of O₂ (μ_{O_2}), and electric potential (ϕ) in the 3D symmetric cell are calculated by solving the equations of partial currents for O^{2-} diffusion, e⁻ transport, and O_{2-} surface exchange, given respectively by,

$$i_{0^{2-}} = -\frac{\sigma_{0^{2-}}}{4F^2} \nabla \left[\frac{1}{2}\mu_{0_2} - 2F\varphi\right]$$
 (Eq. S42)

$$i_{e^{-}} = \frac{\sigma_{e^{-}}}{F} \nabla \varphi$$
 (Eq. S43)

$$i_{O^{2-}} = \frac{\Re}{2RT} \left[\mu_{O_2}^{\text{pore}} - \mu_{O_2} \right]$$
 (Eq. S44)

where \Re is the equilibrium exchange rate of surface exchange, σ_{0^2} is the ionic conductivity, and σ_{e^*} is the electronic conductivity. Herein, we just simulated the responses of the symmetric cell under a small pertubation of voltage (0.01 V) under air condition ($\mu_{0_2}^{\text{pore}} = \mu_{0_2}^0 + RT \ln 0.21$). Therefore, the kinetic parameters are assumed to be constant, as listed in Table S2. The derivation of Eqs. S42-S44 and an efficient algorithm appear in our previous study [1].



Figure S3. (a) Original 2D micrograph of the LSCF electrode (gray = LSCF, black = epoxy resin). (b) Phase-segmented micrograph of the LSCF electrode (white = LSCF, black = Pore). (c) Distance correlation functions (DCFs) of the 2D micrograph and the 3D reconstructed microstructure of the LSCF electrode. (d) 3D reconstructed microstructure of the LSCF electrode. (d) 3D reconstructed microstructure of the LSCF electrode. (e) The 3D microstructure of the LSCF/SDC/LSCF symmetric cell by inserting a SDC electrolyte layer between the symmetric LSCF electrodes for use of electrochemical simulations.

SDC ^[11] /LSCF ^[12]	\Re , [mol.cm ⁻² s ⁻¹]	σ_{i} , [S.cm ⁻¹]	$\sigma_{\rm e}, [{\rm S.cm}^{-1}]$
650 °C	ε/8.34×10 ⁻⁷	3.3×10 ⁻² /4.0×10 ⁻⁴	$\mathbb{P}_{\infty \setminus 3}$
700 °C	ε/1.60×10 ⁻⁶	4.6×10 ⁻² /1.3×10 ⁻³	$\infty \backslash 3$
750 °C	ε/2.87×10 ⁻⁶	6.3×10 ⁻² /3.7×10 ⁻³	$\infty \backslash 3$
800 °C	ε/4.88×10 ⁻⁶	8.2×10 ⁻² /9.8×10 ⁻³	$\infty \backslash 3$

Table S2. Kinetic parameters for SDC and LSCF materials at different temperatures.

¶ ε/∞ denotes a small/big value so that it does not impact the calculation results.

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