## Supplementary information

#### A method to determine oxygen reduction reaction kinetics via porous

## dual-phase composites based on electrical conductivity relaxation

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Fig. S1 Schematic diagram for the device designed for the experiment of determining ECR profiles for porous LSCF-SDC composite bar samples. V1-V4 denote valves. B1 and B2 denote buffer bottles. P1 and P2 denote vacuum meters. The unit differs from the actual size. The experimental details are described in our previous work.<sup>1</sup>



Fig. S2 Room temperature XRD patterns of porous LSCF-SDC composites after sintering at 1000 °C for 5 h in ambient air. The SDC volume content in LSCF-SDC is 0 % (pure LSCF), 10.10 %, 25.84 %, and 36.94 %.



Fig. S3 The BSE images for porous LSCF-SDC composites with various  $f_{V-SDC}$ , (a) 0 vol.%; (b) 10.10 vol.%; (c) 25.84 vol.%, and (d) 36.94 vol.%.



Fig. S4 Conductivity for porous bar samples of bare SDC, bare LSCF, and LSCF-SDC dual-phase composites determine in oxygen at 0.26 atm from 650 to 800 °C.



Fig. S5 The standard deviation for DCT fitting of the ECR profiles measured at 650 °C,700 °C,750 °C and 800 °C for porous LSCF-SDC composites with various SDC content.



Fig. S6 The comparison between fitting results using the single characteristic time  $(1-\exp(-t/\tau))$  fitting method and DCT fitting (Equ.11) used in this work. The experimental profile was obtained with porous bare LSCF at 800 °C.<sup>2</sup>



Fig. S7 Testing temperature dependence of the characteristic time of peak 1 ( $\tau_{P1}$ ) with  $f_{V-SDC} = 0$ , 25.84 %, and 36.94 %.

The resistance factor of gas diffusion in large pores,  $\lambda_1$ , is defined as:

$$\lambda_1 = \frac{R_1}{R_1 + R_p} \tag{S1}$$

$$\tau_{\rm P} = \frac{R_2 * R_3}{R_2 + R_3} = \frac{\tau_2 * \tau_3}{\tau_2 + \tau_3}$$
(S2)

$$\tau_3 = \tau_2 + \tau_{3g} \tag{S3}$$

where *R* is the resistance,  $\tau$  the characteristic time, 1, 2, 3, and p denote the parameters involved in processes 1, 2, 3, and parallel part, respectively. *R*<sub>3, g</sub> denotes the resistance of gas diffusion in tiny pores, and its resistance factor is defined as in Equ.S4,  $\lambda$  denotes the total resistance of gas diffusion.

$$\lambda_{3,g} = \frac{\tau_{3g}}{\tau_3} * \frac{\tau_2}{\tau_2 + \tau_3} * (1 - \lambda_1)$$
(S4)

$$\lambda = \lambda_1 + \lambda_{3,g} \tag{S5}$$



# Gas Diffusion in tiny pores + Surface Exchange

Fig. S8 Schematic diagram showing the routes for ORR in a porous LSCF-SDC composite. One route is the combination of P1 and P2 in series. The other is P1 and P3 in series. Meanwhile, P2 and P3 are in parallel.

$f_{ m V,LSCF}$ (%)	$f_{\rm S,I}$ (%)	A/V (cm <sup>2</sup> cm <sup>-3</sup> )	$\tau_{\rm p}({\rm s})$	ε(-)
0	1	1.06E+05	24.02	0.518
0.899	0.884	1.12E+05	9.33	0.508
0.7416	0.523	1.01E+05	18.03	0.514
0.6308	0.382	1.09E+05	25.10	0.513

Table S1 The parameters involved in Equ.16 at 800 °C.

#### References

- 1 Y. Zhang, F. Yan, B. Hu, C. Xia and M. Yan, Journal of Materials Chemistry A, 2020, 8, 17442-17448.
- 2 R. Ganeshananthan and A. V. Virkar, Journal of The Electrochemical Society, 2005, 152. A1620