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**Supporting Information** 

## Design of nanofiber-based electrodes for solid oxide electrochemical cells

# with high performance and stability

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The structural characteristics of the LSC nanofibers at different sintering temperatures were compared. Figures S1(a) and S1(b) show the SEM images of the LSC nanofibers at different sintering temperatures, exhibiting a porous and hollow shape for LSC nanofibers sintered at 800 °C compared to a solid shape for those sintered at 900 °C. Figures S1(c) and S-d) show BET curves of the LSC powders and nanofibers with different sintering temperatures, exhibiting the specific surface areas of 2.34, 9.71, and 4.88 m<sup>2</sup> g<sup>-1</sup> for the LSC powders sintered at 900 °C, and LSC nanofibers sintered at 800 °C.



**Figure S1.** SEM images of the LSC nanofibers after sintering at (a) 800 °C and (b) 900 °C. BET curves of the (c) LSC powder after sintering at 900 °C, and LSC nanofibers (a) after sintering at 800 and 900 °C. (d) Specific surface areas based on the BET analysis.



Figure S2. Nyquist plots of the nanofiber cells sintered at 800 and 900 °C without the adhesion layer.



Figure S3. Electrochemical performance of the LSC nanofiber cells with and without LSC powder adhesion layer at 700 °C (a) I-V-P curves in FC mode, (b) Nyquist plots



Figure S4. Nyquist plots of the nanofiber cells with the adhesion layer sintered at 800 and 900 °C.



Figure S5. Nyquist plots of the nanofiber cells with the adhesion layer thickness of 2, 4, and 6 µm.



Figure S6. Electrochemical performance of the LSC nanofiber cells with different nanofiber thicknesses at 700 °C. (a) I-V-P curves in FC mode (b) Nyquist plot



Figure S7. (a, b) SEM images of the LSC nanofiber cell after a 300-h stability test. XPS O 1s spectra of the LSC nanofiber cell (c) before and (d) after the stability test.

We calculated the relative intensity ratios of  $O_{vacancy}/O_{lattice}$  as a quantitative index to compare the concentration of oxygen vacancies. Before the stability test, the LSC nanofibers exhibited an intensity ratio of 0.896, which is lower than 0.871 after the stability test, confirming the maintained stability of the concentration of oxygen vacancies in LSC nanofibers after the stability test.

	Reaction order (n)	Specific reaction	
P5	0.84	$O_{2(g)} \leftrightarrow O_{2,ad}$	
P4	0.39	$O_{2,ad} \leftrightarrow 2O_{ad}$	
Р3	0.2	$O_{ad} + 2e^- + V_o^{"} \leftrightarrow O_0^{\times}$	
P2	0.04	$H_2 + 0^2 \rightarrow H_2 0 + 2e^-$	
P1	0.12	$O_{TPB}^{2-} + V_{o}^{"} \leftrightarrow O_{o}^{\times}$	

Table S1. Reaction order value and definition of the corresponding reaction.

The reaction order was calculated using the following equation:

### $R_p \propto 1/p(O_2)^n$

In the high-frequency region, P1 is > 10<sup>4</sup> Hz at 700 °C and n is measured to be 0.12, which is close to 0.1, indicating that P1 is mostly associated with the oxygen ion transfer from the electrode/electrolyte to the electrolyte/electrode. In the intermediate-frequency region, including the P2–P4 peaks, P2 represents  $10^3-10^4$  Hz at 700 °C, and n is measured to be 0.04, which is close to 0, indicating that P2 is not affected by the oxygen partial pressure; thus, P2 is mostly associated with the hydrogen oxidation reaction and evolution reaction. P3 of  $10^2-10^3$  Hz at 700 °C with the slope n of 0.20, which is close to 0.25, is mostly associated with the oxygen charge-transfer reaction of ORR and OER. P4 of  $10-10^2$  Hz at 700 °C and slope n measured to be 0.39, which is close to 0.5, is mostly associated with oxygen dissociation and association. In the low-frequency region, P5 of <  $10^0$  Hz at 700 °C and n measured to be 0.84, which is close to 1, is mostly associated with gas-diffusion and oxygen adsorption and desorption. Similar peaks have also been established in previous studies.<sup>1,2</sup>

Table S2. Resistances and their proportion in the LSC powder cell associated with five frequencies to the total resistance at 550–700 °C in FC mode.

		Unit : Ωcm <sup>2</sup>		
Temperature (°C)	700	650	600	550
D5	0.013	0.016	0.028	0.039
F 3	(8.8%)	(6.8%)	(6.7%)	(4.3%)
D4	0.020	0.027	0.047	0.057
r4	(13.5%)	(11.4%)	(11.3%)	(6.3%)
D2	0.066	0.111	0.188	0.424
r3	(44.6%)	(46.8%)	(45.2%)	(46.8%)
Da	0.015	0.039	0.097	0.322
F2	(10.1%)	(16.5%)	(23.3%)	(35.5%)
D1	0.034	0.044	0.056	0.064
r i	(23.0%)	(18.6%)	(13.5%)	(7.1%)

Table S3. Resistances and their proportion of the LSC nanofiber cell associated with five frequencies to the total resistance measured at 550–700 °C under FC mode.

		Unit : Ωcm <sup>2</sup>		
Temperature (°C)	700	650	600	550
D <i>5</i>	0.013	0.018	0.023	0.033
P5	(9.5%)	(10.4%)	(8.5%)	(5.9%)
D.4	0.018	0.019	0.028	0.031
P4	(13.1%)	(11.0%)	(10.3%)	(5.6%)
D2	0.064	0.068	0.079	0.136
P3	(46.7%)	(39.3%)	(29.2%)	(24.4%)
Da	0.015	0.030	0.092	0.307
P2	(10.9%)	(17.3%)	(33.9%)	(55.0%)
DI	0.027	0.038	0.049	0.051
P1	(19.7%)	(22.0%)	(18.1%)	(9.1%)

Table S4. Activation energies of the LSC nanofiber and powder cells associated with the five frequencies to the total resistance measured at 550–700 °C under FC mode.

	LSC nanofiber	LSC powder	
P5	0.42	0.52	
P4	0.29	0.51	
Р3	0.34	0.84	
P2	1.41	1.40	
P1	0.29	0.30	

#### Unit: eV

Table S5. Resistances and their proportion in the LSC powder cell associated with the five frequencies to the total resistance measured at 550–700 °C under EC mode.

		Unit: Ωcm <sup>2</sup>		
Temperature (°C)	700	650	600	550
D5	0.004	0.011	0.015	0.018
r5	(5.6%)	(8.5%)	(4.7%)	(2.2%)
D.4	0.005	0.016	0.038	0.153
ľ4	(6.9%)	(12.4%)	(12.0%)	(18.6%)
<b>D</b> 2	0.004	0.020	0.124	0.487
P3	(5.6%)	(15.5%)	(39.1%)	(59.2%)
Da	0.024	0.025	0.081	0.100
P2	(33.3%)	(19.4%)	(25.6%)	(12.2%)
<b>D1</b>	0.035	0.057	0.059	0.064
r1	(48.6%)	(44.2%)	(18.6%)	(7.8%)

Table S6. Resistances and their proportion in the LSC nanofiber cell associated with five frequencies to the total resistance measured at 550–700 °C under EC mode.

		Unit: Ωcm <sup>2</sup>		
Temperature (°C)	700	650	600	550
D5	0.003	0.006	0.009	0.011
rð	(5.4%)	(6.4%)	(4.6%)	(2.4%)
D <i>4</i>	0.005	0.013	0.029	0.110
r4	(8.9%)	(13.8%)	(14.8%)	(23.8%)
D2	0.005	0.016	0.046	0.211
rə	(8.9%)	(17.0%)	(23.5%)	(45.6%)
Da	0.024	0.040	0.089	0.098
r 2	(42.9%)	(42.6%)	(45.4%)	(21.2%)
D1	0.019	0.019	0.023	0.033
F I	(33.9%)	(20.2%)	(11.7%)	(7.1%)

Table S7. Activation energies of the LSC nanofiber and powder cells associated with the five frequencies to the total resistance measured at 550–700 °C under EC mode.

	LSC nanofiber	LSC powder
Р5	0.60	0.67
P4	1.36	1.51
Р3	1.74	2.19
P2	0.69	0.76
P1	0.26	0.25

#### Unit: eV

#### References

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