<Supplementary Materials>

Nanocrystalline $La_{0.6}Sr_{0.4}Co_{0.4}Fe_{0.6}O_{3-\delta}$ Interlayer for Enhanced Oxygen Electrode-Electrolyte Interface in Solid Oxide Cell

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Fig. S1: Schematic description of the solid oxide cell (SOC) fabrication with radio-frequency (RF)-sputtering assisted process for interlayered oxygen electrode.



Fig. S2: SEM images of (a) the bare SDC electrolyte and the as-deposited LSCF nanolayers on the SDC electrolyte, with thickness variation of (b) 50 nm, (c) 100 nm, (d) 150 nm, (e) 300 nm.



Fig. S3: Surface coverage estimation images, including (a) the original SEM image and (b, c) reproduced SEM images, illustrate that a 50 nm LSCF nanolayer covered approximately 70% of the SDC electrolyte after annealing at 900 °C for 2 h.



Fig. S4: Nanocrystalline LSCF interlayer with the formation of numerous grains and grain boundaries.



Fig. S5: I-V-P curves and Nyquist plots obtained at (a, b) 600 °C, (c, d) 650 °C, and (e, f) 700 °C.



Fig. S6: Comparison of current density at (a) 1.3 V and (b) 1.6 V of SOCs with thickness variation of LSCF nanolayer in EC operation.



Fig. S7: R_o values of the reference and modified full cells measured at 650 °C and a current density of 250 mA cm⁻² in EC operation for about 100 h.



Fig. S8: Cross-sectional SEM images of the microstructure of SOCs before and after 100 h EC operation.



Fig. S9: SEM-EDS line profiles at the interfacial region of SDC electrolyte showing the bulk to interface region. The profiles present the intensity ratios of each cation relative to sum of cations obtained by EDS. (a, b) reference samples before EC operation, (c, d) reference samples after 100 h EC operation, (e, f) modified samples before EC operation, (g, h) modified samples after 100 h EC operation.

The SOC system operates based on the difference in oxygen partial pressure between the cathode and anode. The voltage of the SOEC system was calculated as an open-circuit voltage from $P(O_2)$ difference.

$$E_{ocv} = \frac{RT}{4F} \ln \frac{P_{O_2}^{Air}}{P_{O_2}^{Fuel}}$$
(1)

 E_{ocv} is open circuit voltage (OCV), R is gas constant, T is temperature, F is faraday constant, $P_{0_2}^{Air}$ is oxygen pressure at oxygen electrode, and $P_{0_2}^{Fuel}$ is oxygen pressure at fuel electrode. By applying this equation, we can use the voltage difference to calculate the oxygen pressure difference. This suggests that the voltage loss in the electrode region can be represented as the difference in oxygen pressure between the electrode/electrolyte interface and the electrode itself.

$$\eta_{anode} = \frac{RT}{4F} \ln \frac{P^{Interface}}{P^{Air}_{O_2}}$$
(2)

 $E_{cell} = E_{ocv} + \eta_{ohmic} + \eta_{electrode}$ (3)

$$\eta_{anode} = \eta_{electrode} \times 0.85 \tag{4}$$

As outlined in equation (2), $P_{0_2}^{Interface}$ indicates oxygen pressure at the LSCF electrode/SDC electrolyte, while $P_{0_2}^{Air}$ is the oxygen pressure at the oxygen electrode with ambient air (0.21 atm). Voltage loss (η_{anode}) occurring in the anode region due to the oxygen concentration can be related to the oxygen pressure difference between the oxygen electrode and oxygen electrode/electrolyte interface. (This η is due to the oxygen concentration difference, and it is notable that activation loss was neglected.) Here, η_{anode} can be extracted from $\eta_{electrode}$ which

includes both cathodic and anodic losses. Determining η_{anode} from electrochemical data during full cell operation is quite complex. However, drawing from earlier studies [1, 2], we can make a helpful assumption that simplifies the loss to equation (4). This equation is expressed as the ratio of the simple resistances of the anode and cathode. To determine $\eta_{electrode}$, equation (3) is used, where E_{cell} , E_{ocv} and η_{ohmic} can be easily measured during electrochemical operation. For clarity, the cathode side has not been subjected to any engineering modifications; therefore, the cathode values have been standardized based on those obtained from the reference sample. Finally, recalling equation (2), the oxygen pressure at LSCF electrode/SDC buffer layer interface of the sample can be obtained, as shown in Table S4.

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Sample	La3d	Sr3d	Co2p	Fe2p	Ols	C1s	
As deposited	11.4	6.8	7.2	12.60	61.4	1.2	
(Cation ratio)	30	19	19	32			
Annealed	10.9	5.7	6.7	12.2	62.8	1.7	
(Cation ratio)	31	16	19	34			

Atomic composition, XPS (at. %)

Table S1: Atomic composition calculated from XPS spectra of LSCF nanolayer.

Resistance	Ref (0nm)	50nm	100nm	150nm	300nm
$R_p \ (\Omega \ cm^2)$	7.78	3.63	2.43	1.17	1.26
$R_{LF}~(\Omega~cm^2)$	0.20	0.10	0.10	0.03	0.04
$R_{MF} \left(\Omega \ cm^2 ight)$	4.67	2.86	2.02	1.02	1.08
$R_{\rm HF}(\Omega~cm^2)$	2.91	0.67	0.32	0.12	0.14

Table S2: The polarization resistance values (R_p) , including R_{LF} , R_{MF} , and R_{HF} , which are derived from the resistance proportions in the DRT plots, are analyzed as a function of thickness of the LSCF nanolayer during FC operation for all developed cells.

Resistance	0nm (Ref)	50nm	100nm	150nm	300nm
$R_p(\Omega \ cm^2)$	7.16	2.05	1.11	0.73	0.73
$R_{LF}\left(\Omega\;cm^2\right)$	0.29	0.04	0.03	0.02	0.03
$R_{MF} \left(\Omega \ cm^2 ight)$	4.30	1.89	0.97	0.61	0.57
$R_{\rm HF}(\Omega~cm^2)$	2.57	0.12	0.10	0.10	0.13

Table S3: The polarization resistance values (R_p) , including R_{LF} , R_{MF} , and R_{HF} , which are derived from the resistance proportions in the DRT plots, are analyzed as a function of thickness of the LSCF nanolayer during EC operation for all developed cells.

Current density (250 mA cm ⁻²)	0nm (Ref)	100nm (Modified)	
E _{ocv} (V)	0.97	0.98	
E _{cell} (V)	1.49	1.19	
$\eta_{ m ohmic}$ (V)	0.20	0.05	
$\eta_{ m electrode}$ (V)	0.32	0.16	
$\eta_{ ext{cathode}}$ (V)	(0.05	
$\eta_{ m anode}\left({ m V} ight)$	0.27	0.11	

Table S4: Parameters determined for the calculation of $P(O_2)_{interface}$.

Supplementary References

- 1. S. M. Shin, B. Y. Yoon, J. H. Kim and J. M. Bae, *Int. J. Hydrogen Energy.*, 2013, **38**, 8954-8964.
- 2. C. Su, Z. Lü, C. Wang, J. Li, P. Li, X. Yue and H. Li, *Int. J. Hydrogen Energy.*, 2019, **44**, 14493-14499.