Electronic Supplementary Material (ESI) for Energy & Environmental Science.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Conditions for Stable Operation of Solid Oxide Electrolysis Cells: Oxygen Electrode Effects

Beom-Kyeong Park,[a] Qian Zhang,[a] Peter W. Voorhees[a] and Scott A. Barnett *[a]

[a] *Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA*

*** Corresponding author**

E-mail: s-barnett@northwestern.edu

This section of the supplemental materials provides additional electrochemical and microstructural data from various life tests performed in this work.

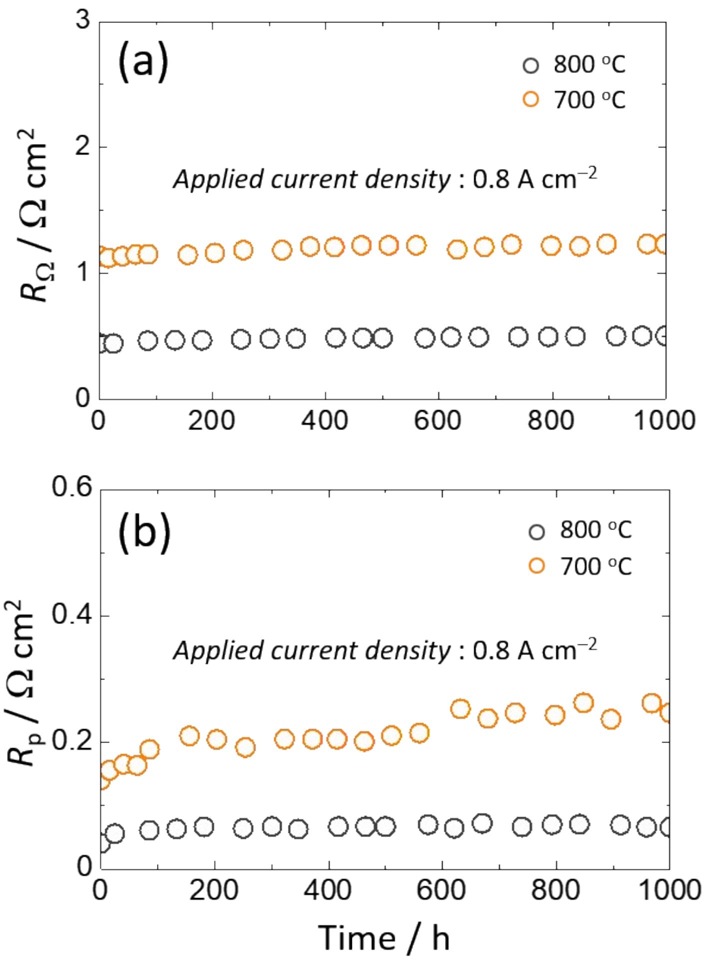


Fig. S1 Evolution of ohmic resistance (R_{Ω}) and polarization resistance (R_p) with time for STF-electrode symmetric cells tested with a constant current density $j = 0.8$ A cm^{-2} at temperature T = 700 (a) or 800 °C (b).

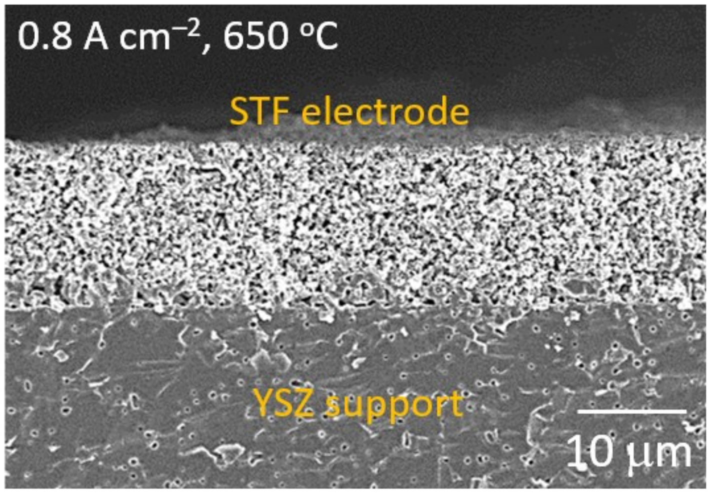


Fig. S2 Cross-sectional SEM images for an STF-electrode symmetric cells prior to testing.

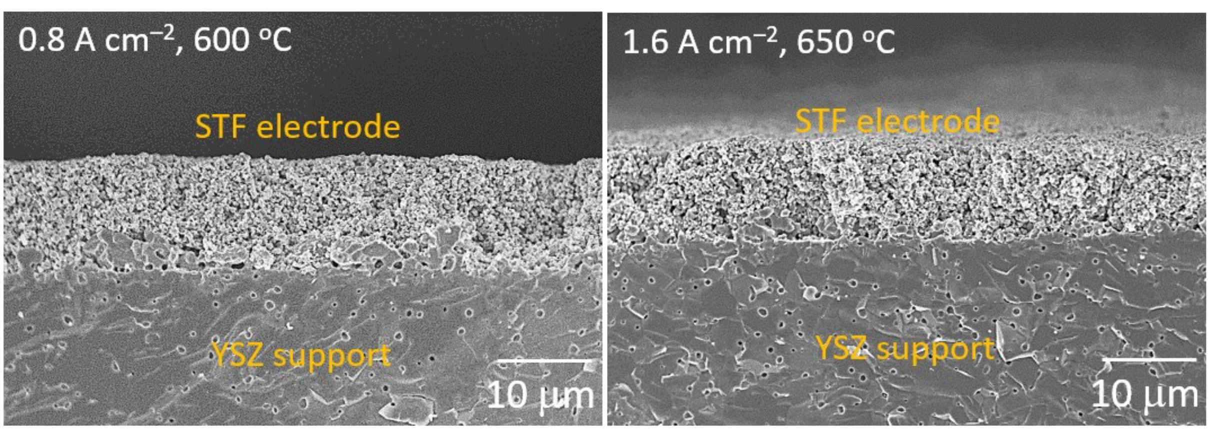


Fig. S3 Cross-sectional SEM images for the fuel-cell-sides of STF-electrode symmetric cells tested with 0.8 A cm^{-2} at 600 ^{o}C and 1.6 A cm^{-2} at 650 ^{o}C.

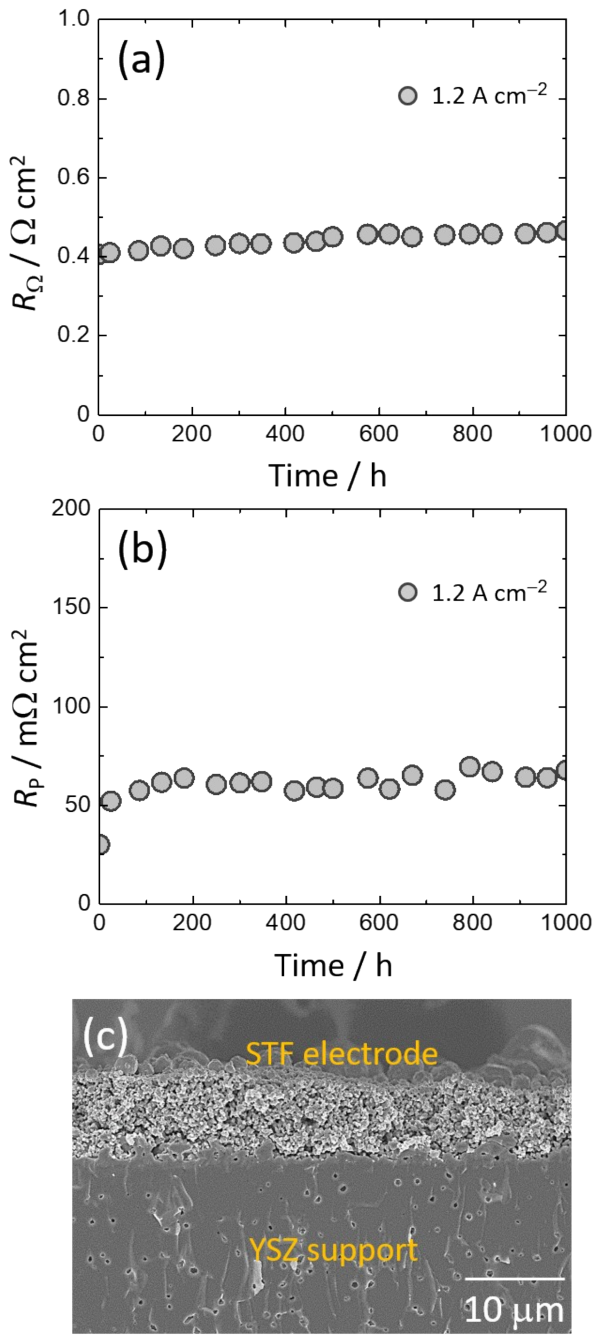


Fig. S4 Evolution of (a) ohmic resistance (R_Ω) and (b) polarization resistance (R_p) with time for STF-electrode symmetric cells tested with a constant current density of 1.2 A cm^{-2} at 800 ^oC. (c) Cross-sectional SEM images for an STF-electrode symmetric cells after the life test.

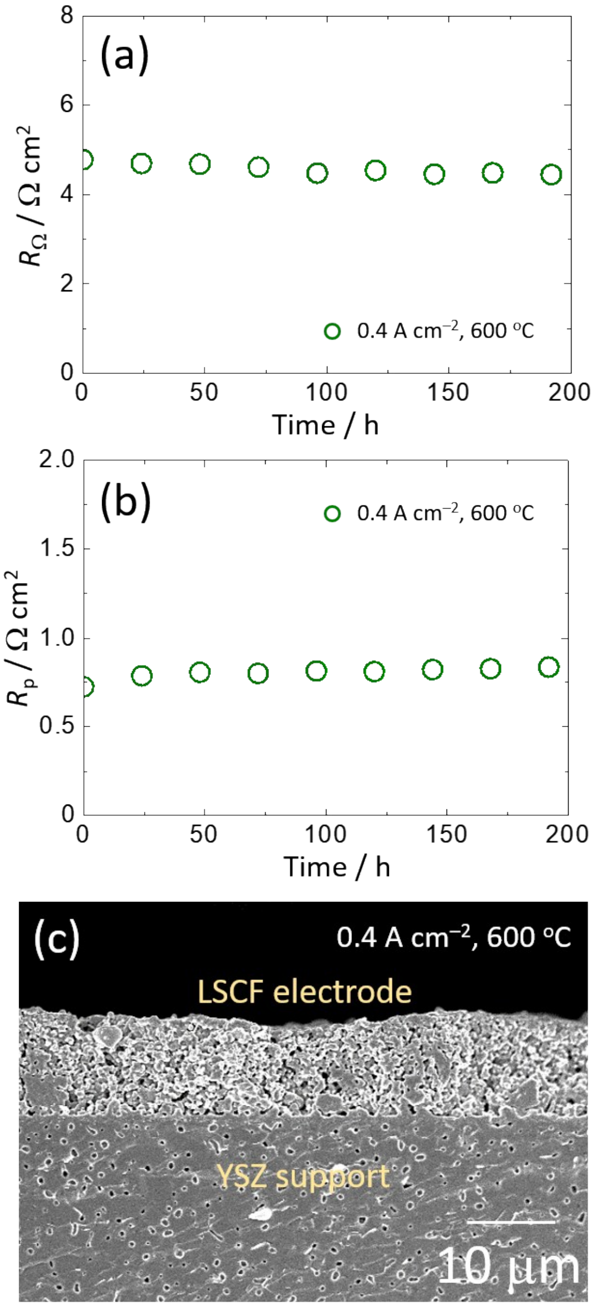
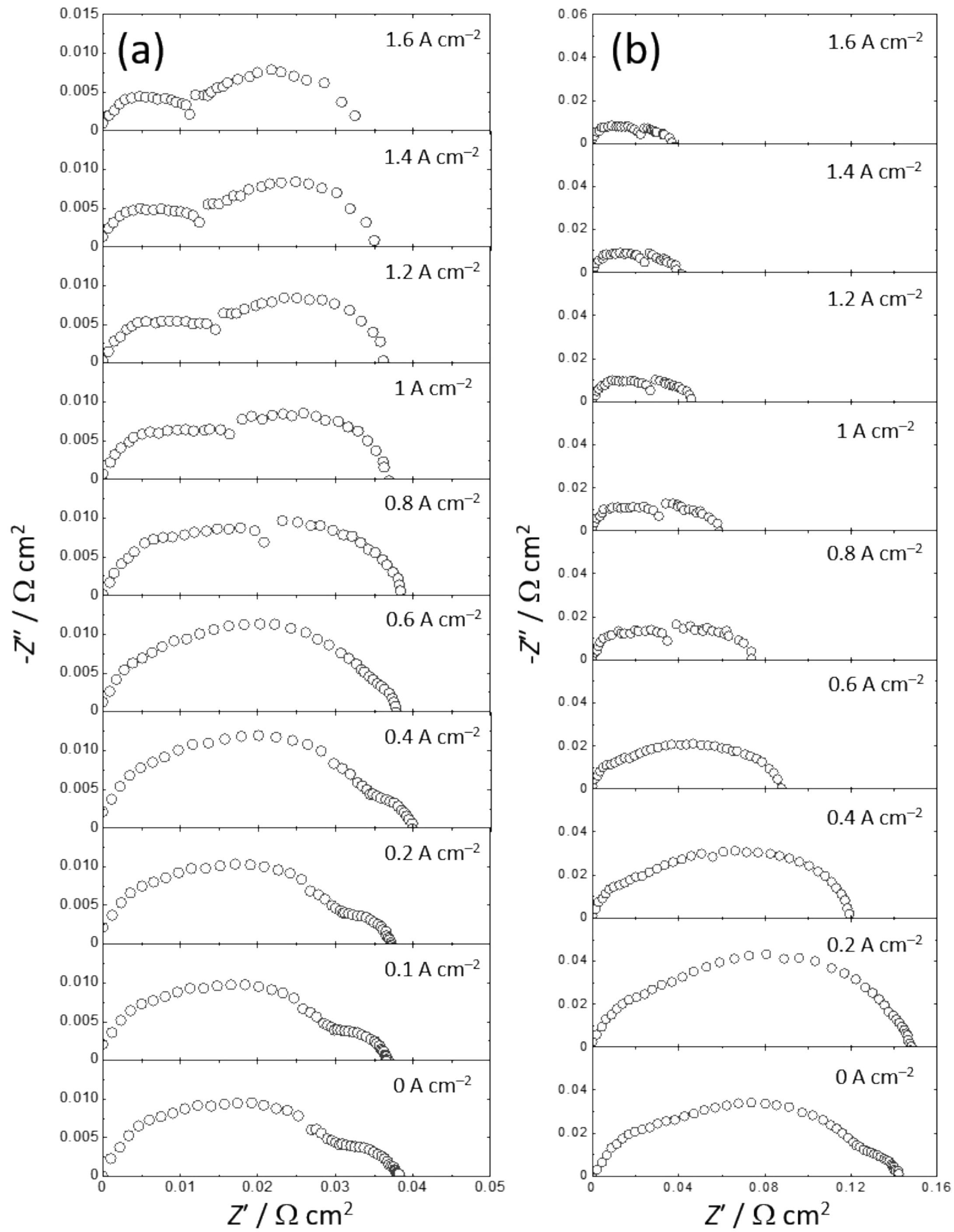


Fig. S5 Evolution of (a) ohmic resistance (R_Ω) and (b) polarization resistance (R_p) with time for STF-electrode symmetric cells tested with a constant current density of 0.4 A cm^{-2} at 600 ^{o}C. (c) Cross-sectional SEM images for an STF-electrode symmetric cells after the life test.

This section of the supplemental materials provides additional detail and data regarding the polarization resistance measurements on symmetric cells used to estimate electrode overpotential.



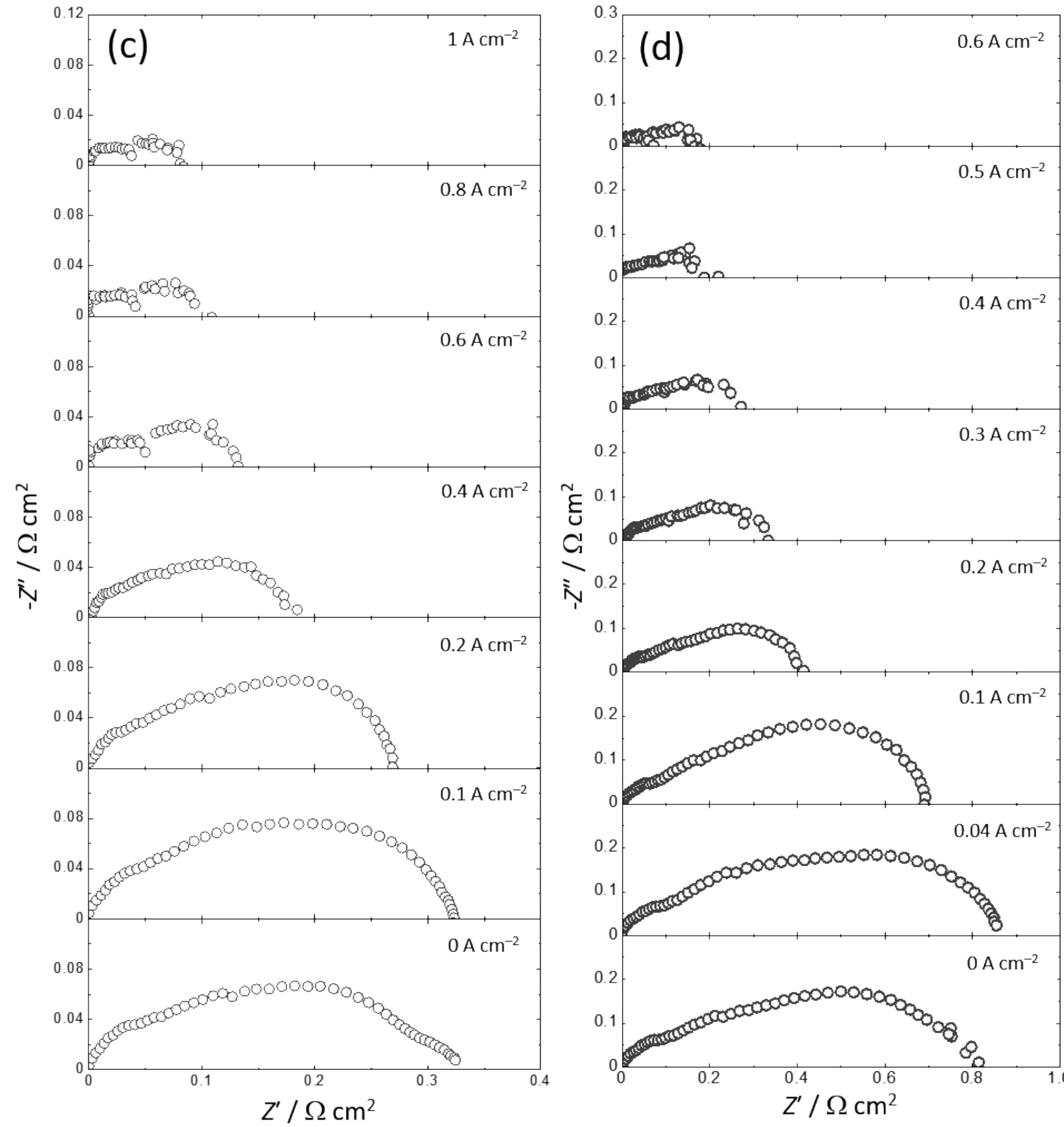


Fig. S6 Nyquist plots of EIS data taken from STF-electrode symmetric cells at different current densities at 800 (a), 700 (b), 650 (c), and 600 ^{o}C (d).

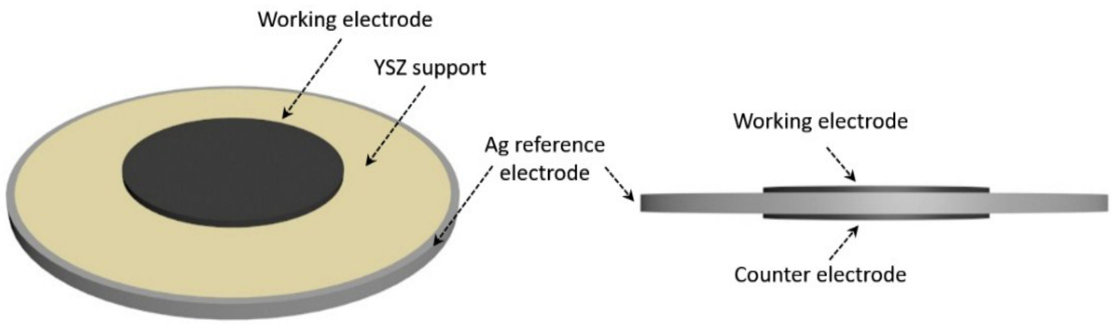


Fig. S7 A schematic diagram for a three-electrode cell used for electrochemical testing

Table S1. The averaged half-cell voltages in SOEC and SOFC modes at different temperatures and current densities.

Applied current density (A cm^{-2})	800 °C		700 °C		650 °C		600 °C	
	SOEC-side (mV)	SOFC-side (mV)	SOEC-side (mV)	SOFC-side (mV)	SOEC-side (mV)	SOFC-side (mV)	SOEC-side (mV)	SOFC-side (mV)
0.04	-	-	-	-	-	-	125	125
0.1	-	-	-	-	186	186	371	371
0.2	82	82	221	222	385	385	724	724
0.3	-	-	-	-	562	561	998	999
0.4	171	172	436	436	710	711	1204	1203
0.5	-	-	-	-	-	-	1357	1356
0.6	252	252	621	621	945	946	1455	1455
0.8	324	325	758	755	1105	1104	-	-
1	393	392	872	872	1204	1204	-	-
1.2	451	451	954	954	-	-	-	-
1.4	502	503	1017	1018	-	-	-	-
1.6	548	548	1071	1073	-	-	-	-

This section provides initial polarization resistance values versus temperature for the three different oxygen electrodes along with activation energy values derived from the data. These results were used as input in the calculations.

Table S2. The initial polarization resistance (R_p) at OCV for STF, STFC, and LSCF at different temperatures, along with activation energy values and pre-factors derived from the R_p values.

Temperature (^oC)	R_p (Ω cm^2)		
	STF	LSCF	STFC
600	0.6372	0.7375	0.3854
650	0.3751	0.4337	0.1831
700	0.1506	0.1798	0.0844
750	-	0.0720	0.0430
800	0.0405	0.0304	0.0238
-	STF	LSCF	STFC
Activation energy (eV)	3.13	3.7	3.1
Pre-factor (R_p^0)	1.85×10^{-7}	2.49×10^{-8}	1.13×10^{-7}

This section provides some background on the model used to get the oxygen partial pressure distribution in the electrolyte.

The chemical reactions within the electrolyte, during the electrolysis operation, can be described:

$$\frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-}, \qquad \text{(S1)}$$

$$e^- + h^+ \leftrightarrow nil. \qquad \text{(S2)}$$

For the mixed (electronic and ionic) conductor, the flux (j_x) of various species, such as electron (e), hole (h), and oxygen ion (O^{2-}), are determined by the following equation:

$$j_x = -\frac{D_x}{RT}C_x\nabla\bar{\mu}_x = -D_x\nabla C_x - \frac{z_xF}{RT}D_xC_x\nabla\phi, \quad x = e, h, O^{2-} \qquad \text{(S3)}$$

where *D*, *C*, $\bar{\mu}$, *z*, and ϕ are diffusivity, concentration, electrochemical potential, charge valance of corresponding species, and Galvani potential, respectively, and R, *T*, and F have their usual meanings. At steady state, total current density (*j*) is calculated:

$$j = F(j_h - j_e - 2j_{O^{2-}}). \qquad \text{(S4)}$$

Then, the mathematical model is obtained by combining the above equations (eqn (S3) and (S4)) with local equilibrium of reactions (eqn (S1) and (S2)) and charges neutrality. Here, the oxygen partial pressure (P_{O_2}) can be calculated using the definition of electrical potential (*E*), which is chemical potential of electron in volt, the local equilibrium conditions in reaction (4), and C_e derived *via* our model, as below:

$$E = E^0 - \frac{RT}{F}\ln\left(\frac{C_e}{C_e^0}\right) = E^0 + \frac{RT}{4F}\ln\left(\frac{P_{O_2}}{P_{O_2}^0}\right), \qquad \text{(S5)}$$

where the terms with superscript '0' in eqn (S5) are the corresponding quantities under standard state. The boundary conditions for the calculation are the oxygen-electrode and fuel-electrode overpotentials, which are calculated using eqn (2) and (3) based on measured polarization resistance values for the oxygen electrode $R_{p,O}(j = 0)$ and fuel electrode $R_{p,H}(j = 0)$. The latter values were estimated from fits of the full-cell EIS data using previously-developed Ni-YSZ electrode circuit models, as discussed in this supplement material. All the parameters in the numerical simulation are taken the same as that we obtained in the experimental measurement.