

Supplementary Information

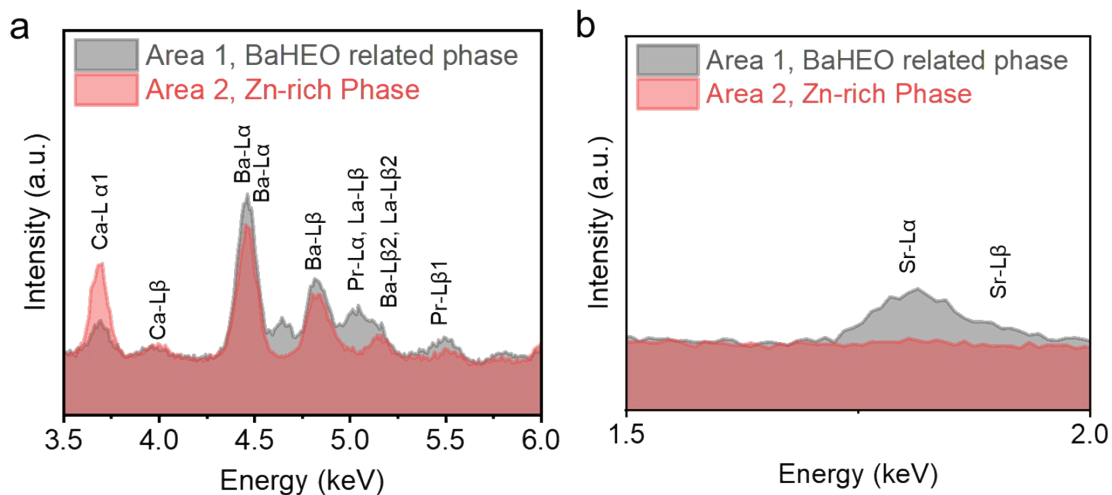


Fig S1. TEM-EDS survey scans of selected areas from the BaHEOZndefi nanocomposite: (a) from 3.5 to 6 keV (b) 1.5 to 2.0 keV.

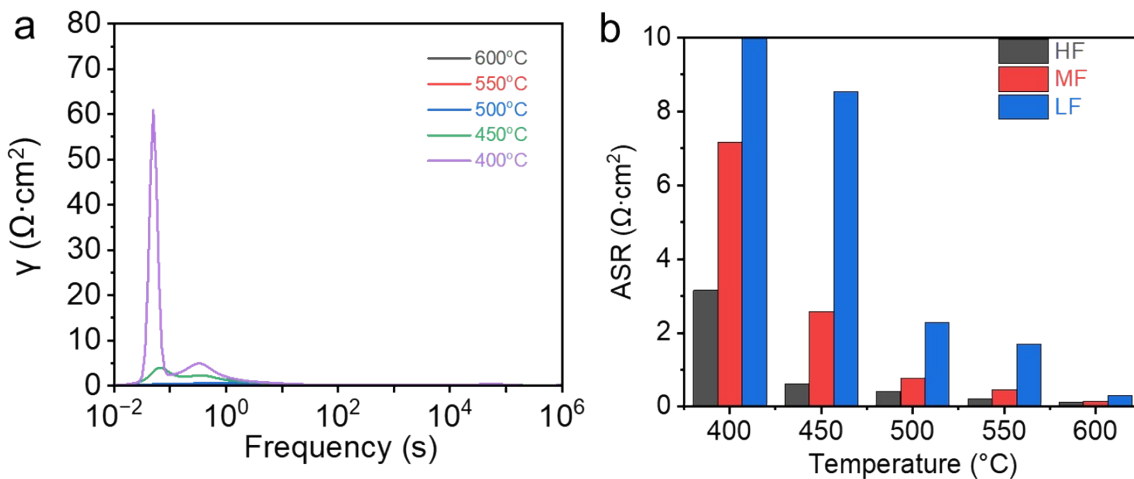


Fig S2. (a) DRT analysis of BaHEOZndefi symmetric cell from 400 to 600°C (b) ASR as function of temperature from 400 to 600°C for HF, MF and LF processes.

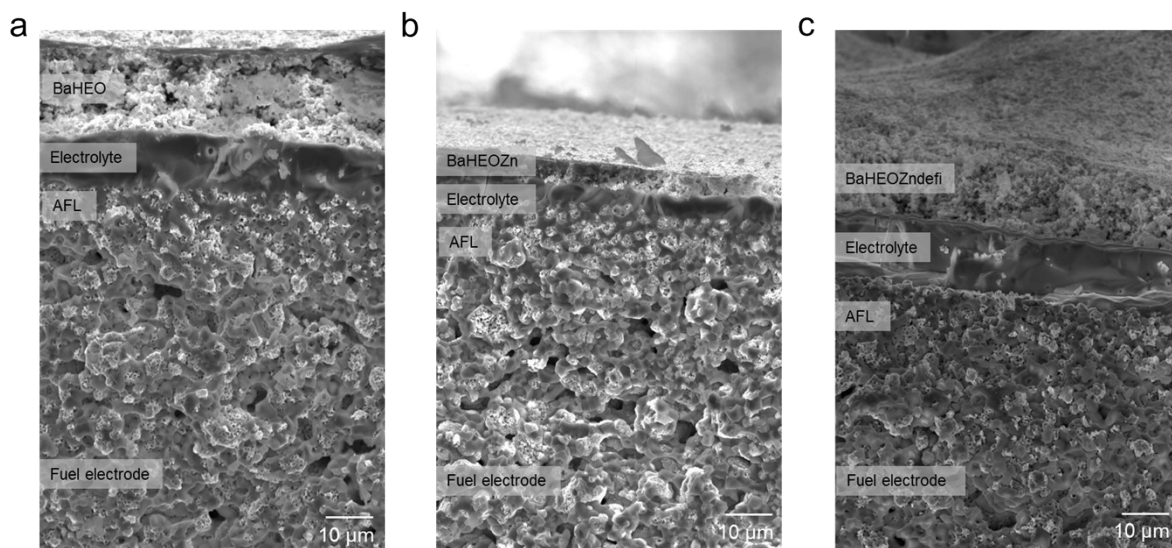


Fig S3. Cross-sectional image of PCC with (a) BaHfO₃ (b) BaHfO₃Zn (c) BaHfO₃Zn-deficient

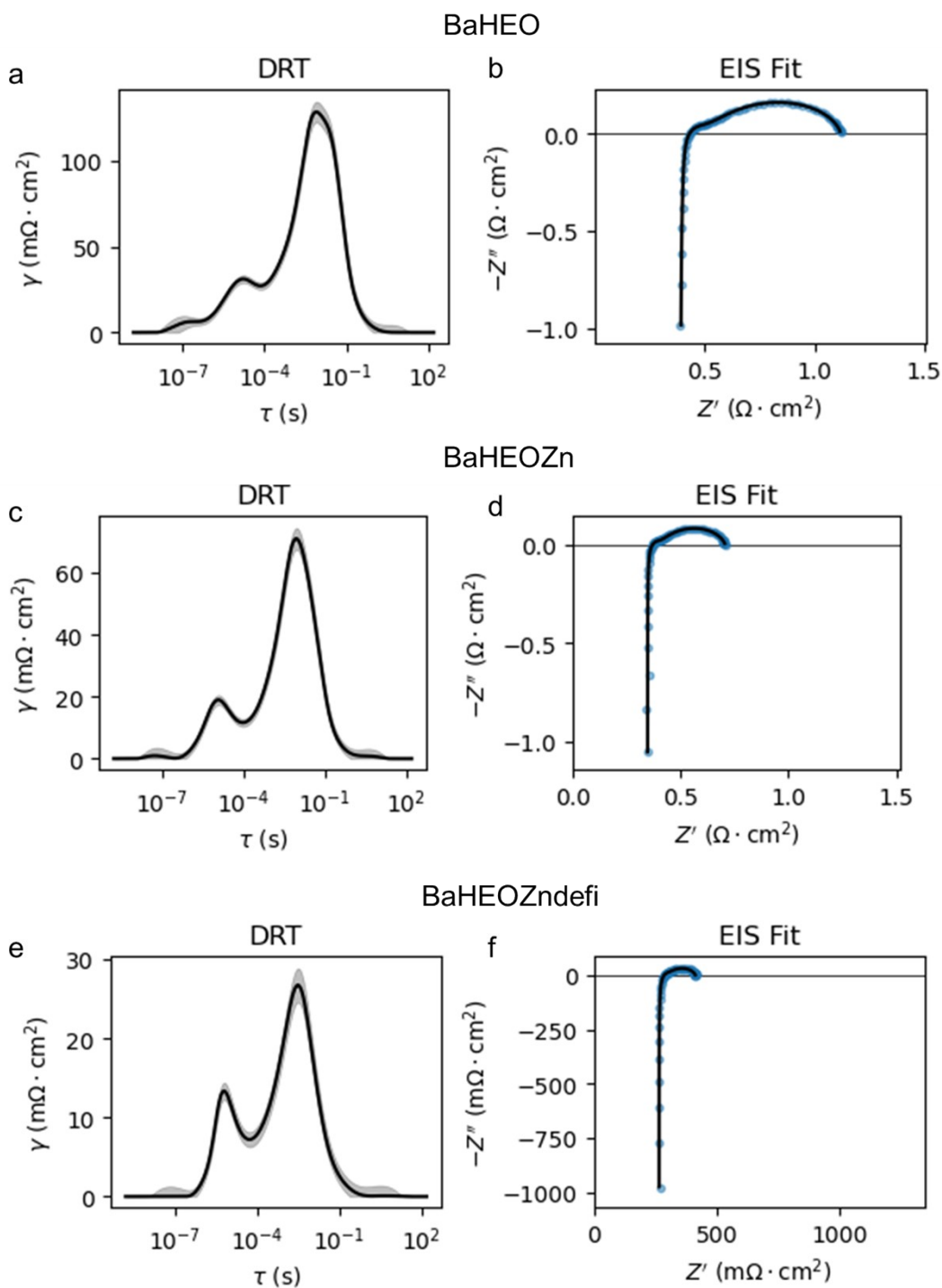


Fig S4. EIS analysis of PCC button cells with various air electrodes (BaHEO, BaHEOZn, and BaHEOZndefi) (a) DRT spectrum of BaHEO (b) equivalent circuit fitting results for BaHEO. Blue dots are experimental data and the black line is the model fit (c) DRT spectrum of BaHEOZn (d) EIS fitting results for BaHEOZn (e) DRT spectrum for BaHEOZndefi (f) EIS fitting results for BaHEOZndefi

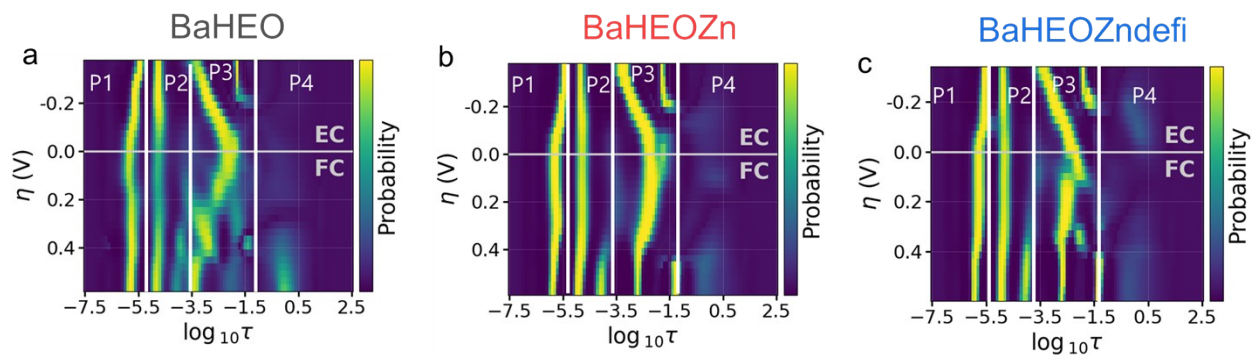


Fig S5. DRT peak probability plot as function of log time constant and overpotential. Yellow color indicates high likelihood of a “true” DRT peak. Based on the probability map, we divided the DRT distributions for each air electrode into 4 major peak regions or relaxation response regions: P1, P2, P3, and P4. (a) BaHEO (b) BaHEOZn (c) BaHEOZndefi

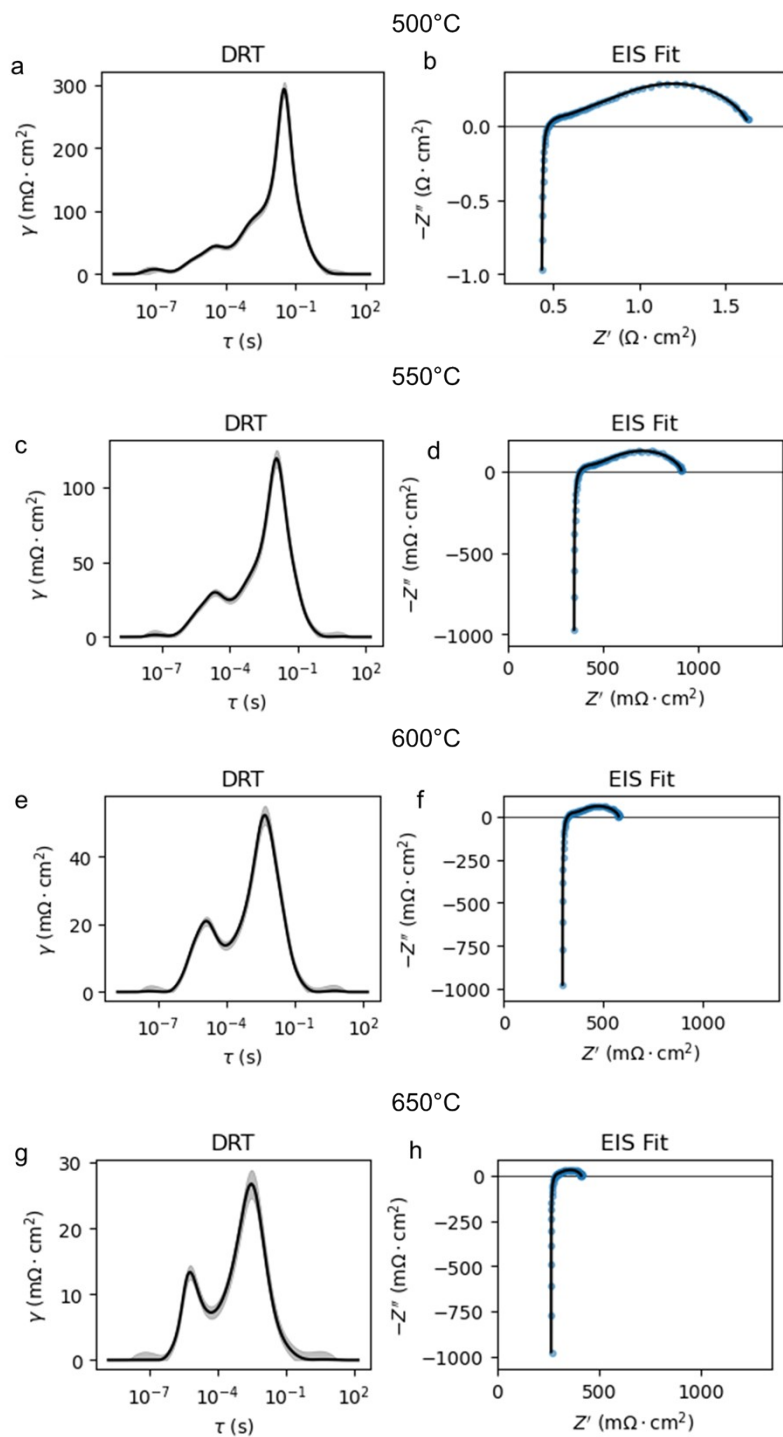


Fig S6. EIS analysis of PCC button cell with BaHEOZn_{defi} air electrode at 500, 550, 600 and 650°C (a) DRT spectrum at 500°C (b) corresponding EIS model fit at 500°C (c) DRT spectrum at 550°C (d) corresponding EIS model fit at 550°C (e) DRT spectrum at 600°C (f) corresponding EIS model fit at 600°C (g) DRT spectrum at 650°C (h) corresponding EIS model fit at 650°C

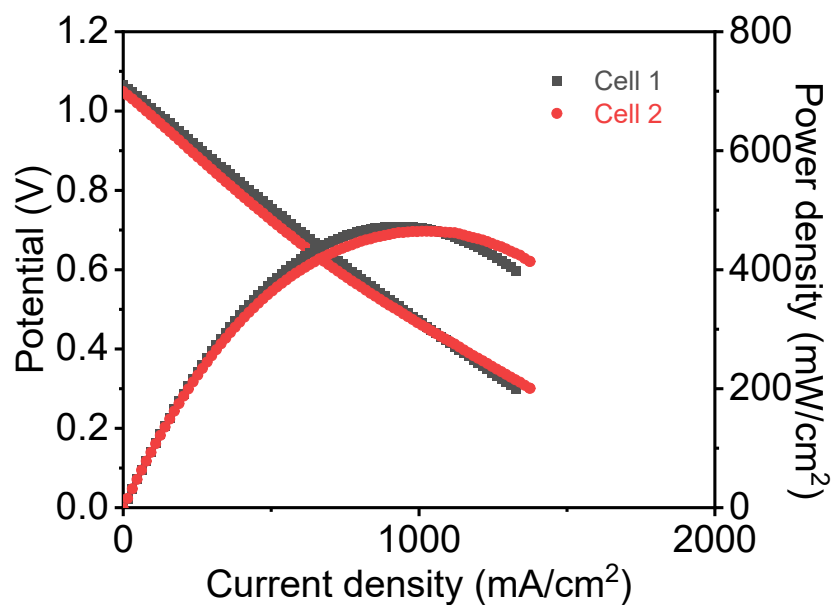


Fig S7. Reproducibility of duplicated BaHEOZndefi PCCs at 600°C. Cell 1 was used for performance measurement and durability testing under fuel cell mode. Cell 2 (~3X larger active area) was used for durability testing under electrolysis mode.

Table S1. EIS model fitting parameters for PCC button cells with various air electrodes (BaHEO, BaHEOZn, and BaHEOZndefi) at 600°C. R_0 = ohmic resistance, L_0 = inductance, $R_x_HN_x$ = resistance for each electrochemical process, $\text{Ln}(\tau)_HN_x$ = value of natural logarithm of time constant of specific electrochemical process, α = distribution skew, β = distribution width

	BaHEO	BaHEOZn	BaHEOZndefi
R_0	0.375	0.343	0.294
L_0	-15.657	-15.597	-15.675
$R_{1_HN_1}$	0.012	0.046	0.012
$\ln(\tau)_{HN_1}$	-15.693	-11.393	-12.881
α_{HN_1}	0.724	1	1
β_{HN_1}	0.773	0.759	0.946
$R_{2_HN_2}$	0.087	0.228	0.043
$\ln(\tau)_{HN_2}$	-11.181	-4.724	-11.188
α_{HN_2}	0.892	0.594	1
β_{HN_2}	0.675	0.795	0.825
$R_{3_HN_3}$	0.413	0.085	0.038
$\ln(\tau)_{HN_3}$	-4.88	-3.188	-8.088
α_{HN_3}	0.544	0.902	0.874
β_{HN_3}	0.789	0.845	0.695
$R_{4_HN_4}$	0.230		0.138
$\ln(\tau)_{HN_4}$	-3.41		-5.336
α_{HN_4}	0.976		0.727
β_{HN_4}	0.796		0.833
$R_{5_HN_5}$			0.050
$\ln(\tau)_{HN_5}$			-3.66
α_{HN_5}			0.936
β_{HN_5}			0.874

Table S2. EIS model fitting parameters for PCC button cell with BaHfO₃ZrO₂ air electrode at 500, 550, 600 and 650°C. R_0 = ohmic resistance, L_0 = inductance, $R_{x_HN_x}$ = resistance for each electrochemical process, $\ln(\tau)_{HN_x}$ = value of natural logarithm of time constant of specific electrochemical process, α = distribution skew, β = distribution width

	500°C	550°C	600°C	650°C
R_0	0.427	0.347	0.294	0.264
L_0	-15.679	-15.676	-15.657	-15.678
$R_{1_HN_1}$	0.159	0.021	0.013	0.025
$\ln(\tau)_{HN_1}$	-10.701	-12.665	-12.817	-11.843
α_{HN_1}	1	1	1	1
β_{HN_1}	0.586	0.85	0.946	0.837
$R_{2_HN_2}$	0.262	0.064	0.041	0.124
$\ln(\tau)_{HN_2}$	-6.274	-10.725	-11.185	-5.249
α_{HN_2}	0.816	1	1	0.605
β_{HN_2}	0.662	0.765	0.825	0.708
$R_{3_HN_3}$	0.794	0.162	0.039	
$\ln(\tau)_{HN_3}$	-3.336	-6.492	-8.082	
α_{HN_3}	0.972	0.682	0.875	
β_{HN_3}	0.735	0.716	0.697	
$R_{4_HN_4}$		0.232	0.132	
$\ln(\tau)_{HN_4}$		-4.561	-5.363	
α_{HN_4}		0.969	0.728	
β_{HN_4}		0.843	0.837	
$R_{5_HN_5}$		0.087	0.058	
$\ln(\tau)_{HN_5}$		-2.759	-3.66	
α_{HN_5}		0.888	0.936	
β_{HN_5}		0.871518	0.874726	