Supporting Information

An *in situ* hydrothermally self-crystallized dense ceria-based barrier layer for solid oxide fuel cells†

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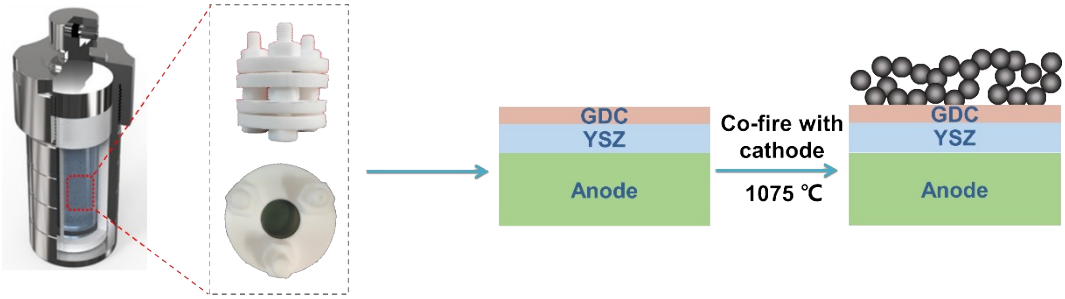

Figure S1 Flow chart of single cells preparation.

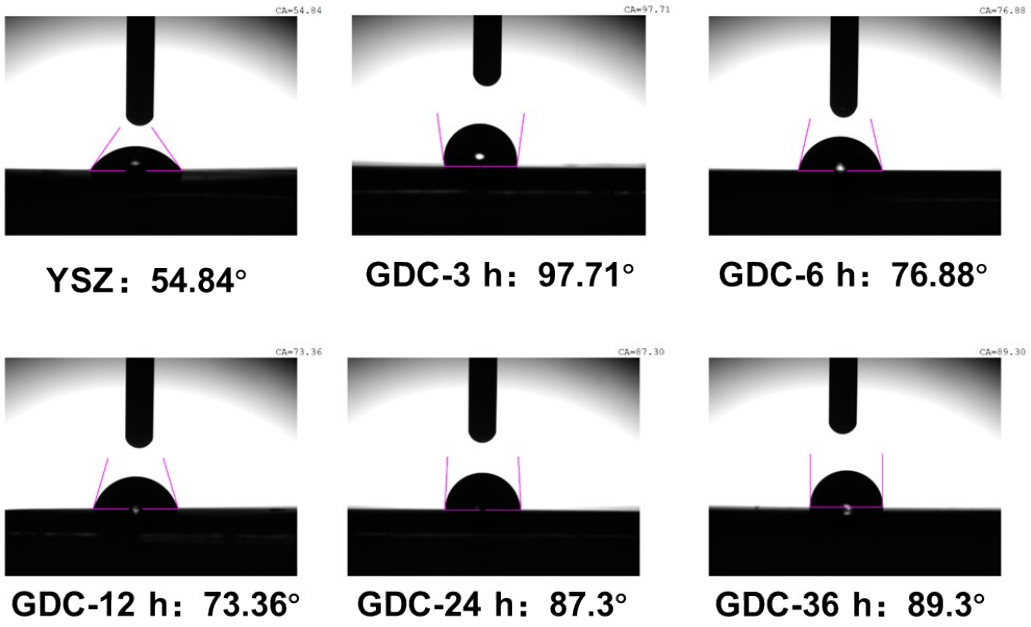

Figure S2 Hydrophilicity test on the surface of GDC barrier after different reaction times.

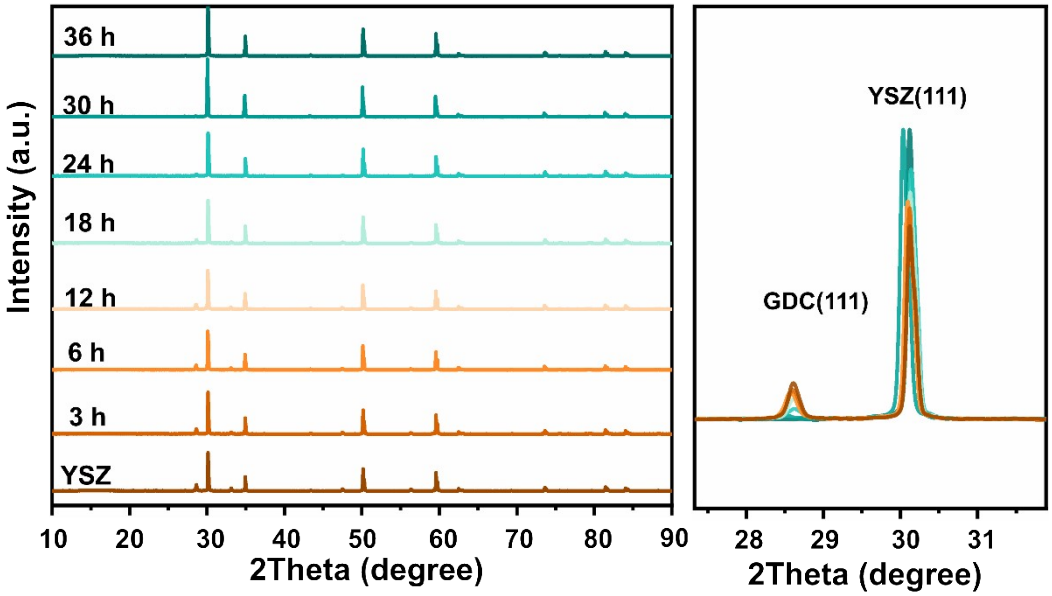

Figure S3 XRD patterns evolutions of GDC barrier layer as hydrothermal duration prolongs.

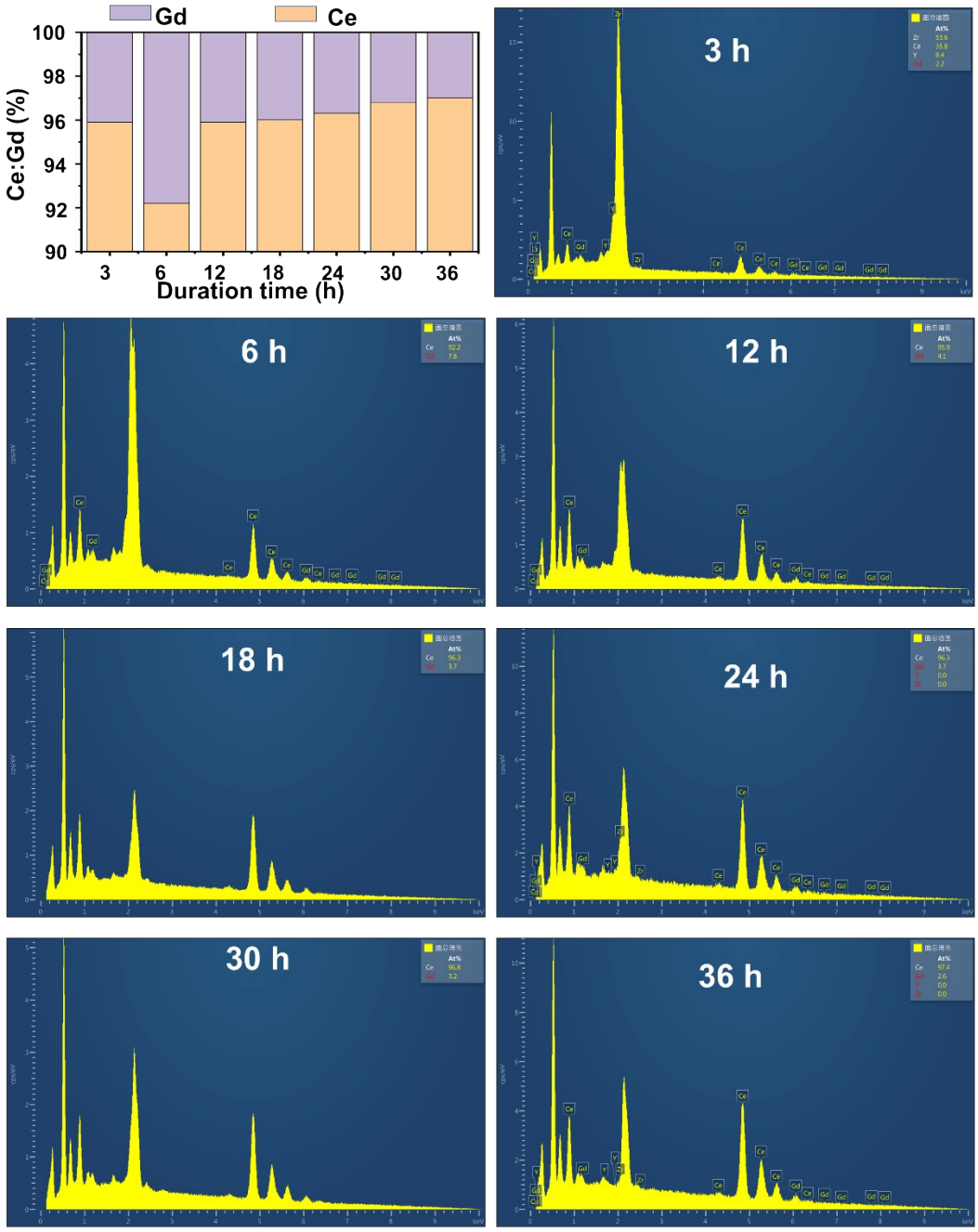

Figure S4 The atomic ratio of Ce to Gd in Figure 1b

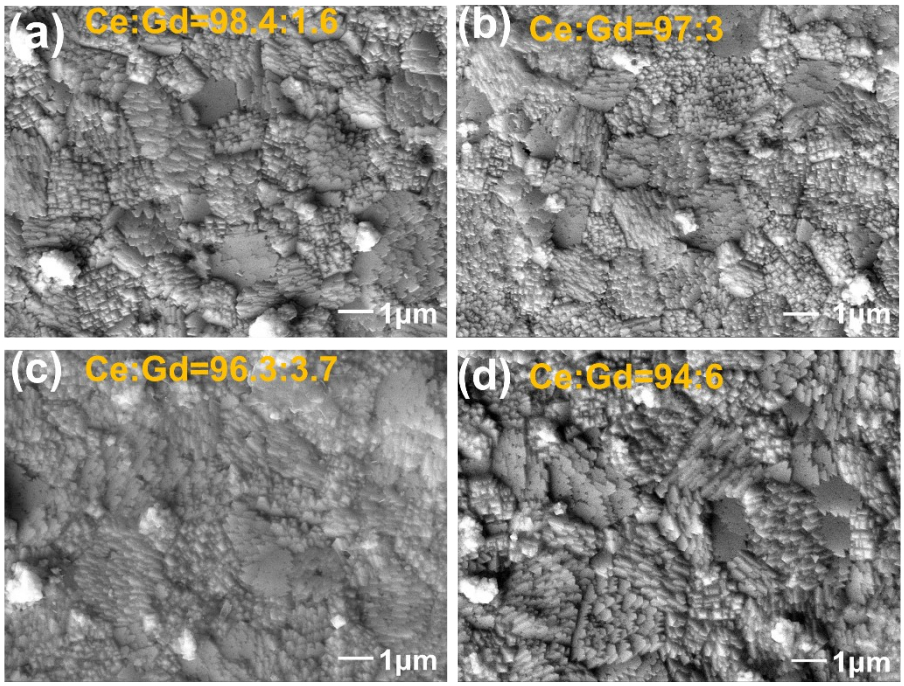

Figure S5 Surface morphology of GDCs grown in aqueous solutions with Ce:Gd ratios of 9:1, 8:2, 7:3, 6:4.

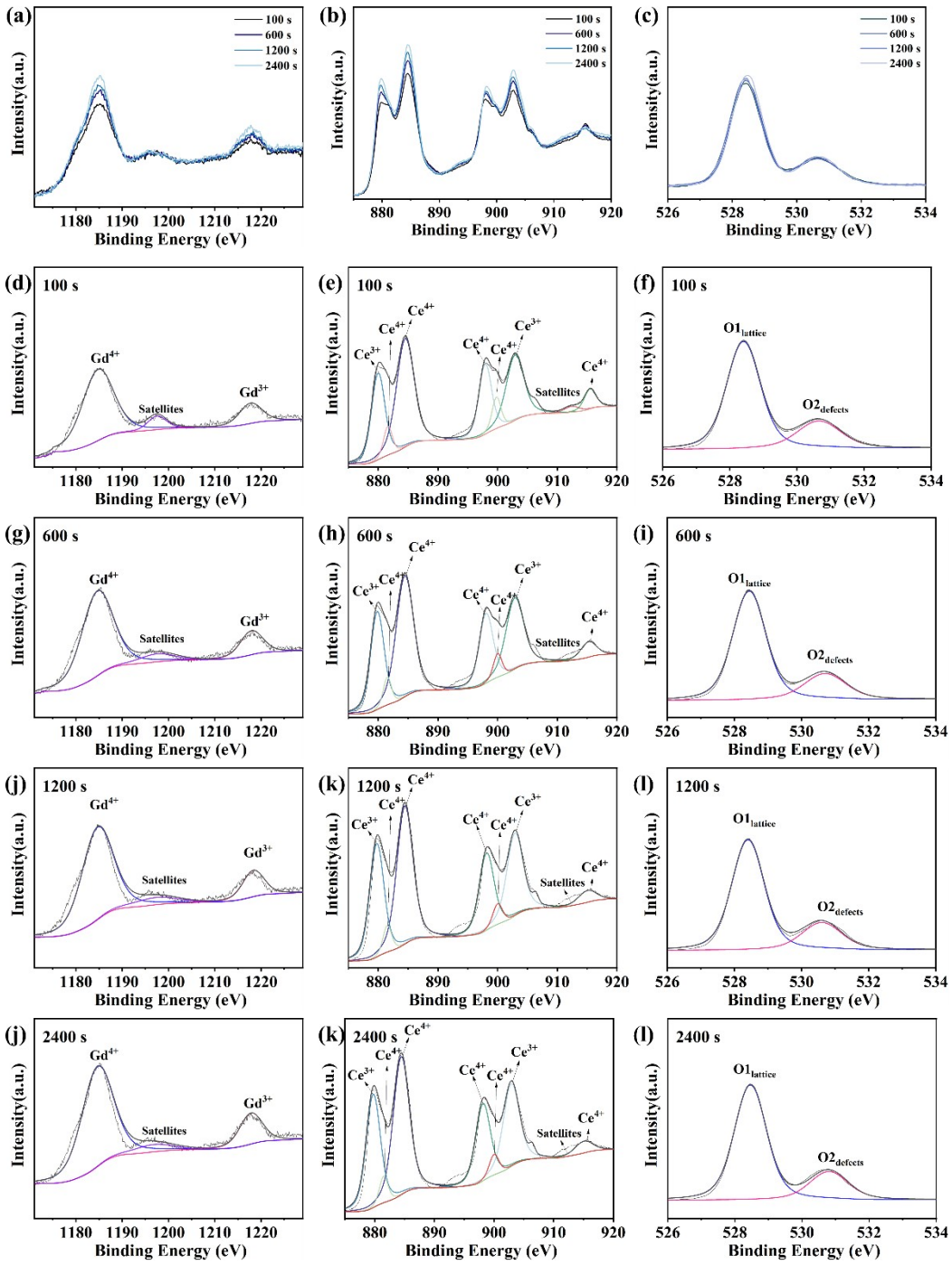

Figure S6. XPS spectra of Gd3d, Ce3d and O1s with different Ar+ etching times

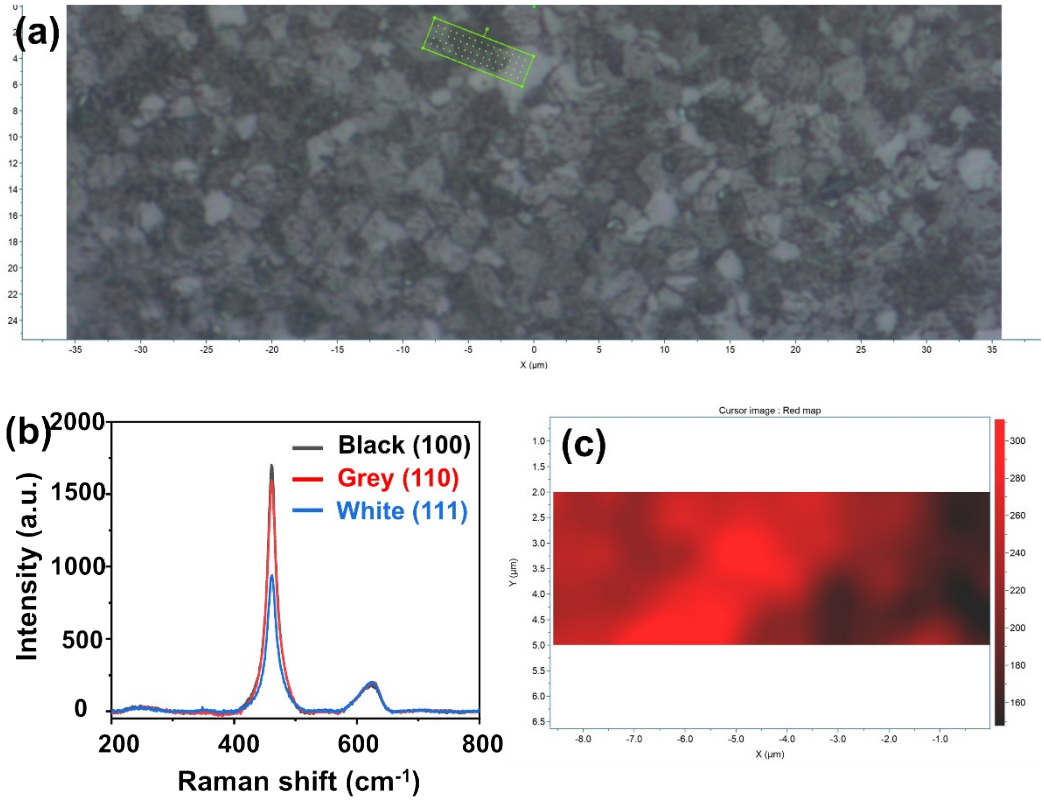

Figure S7 The image of Raman spectroscopy(a), point signals(b) and surface signals(c).

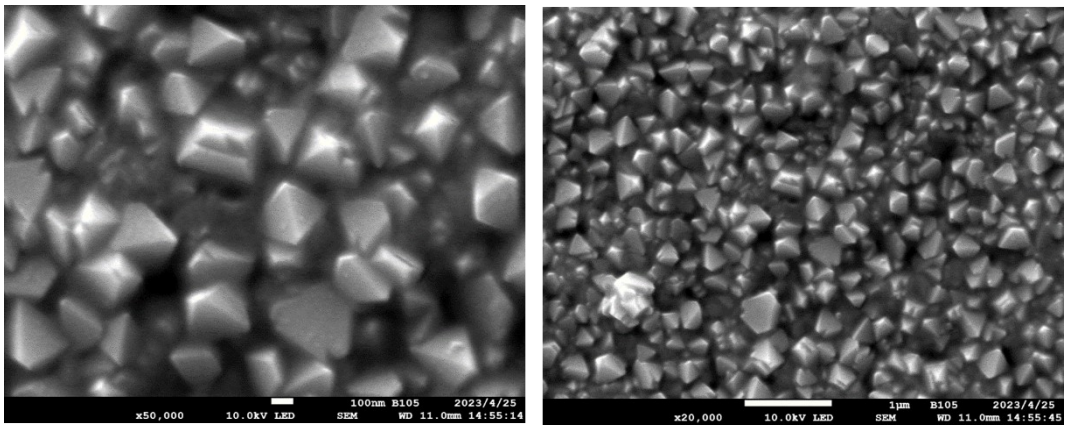

Figure S8 The surface morphology of GDC film grown on polished glass substrate.

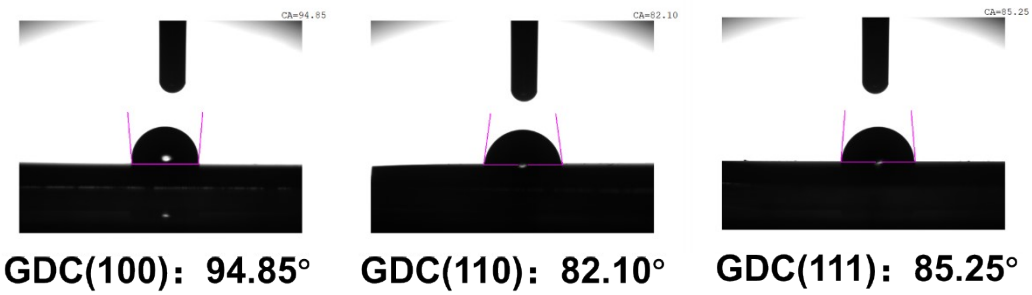

Figure S9 Hydrophilicity test on the surface of GDC barrier layer with three different crystal orientations.

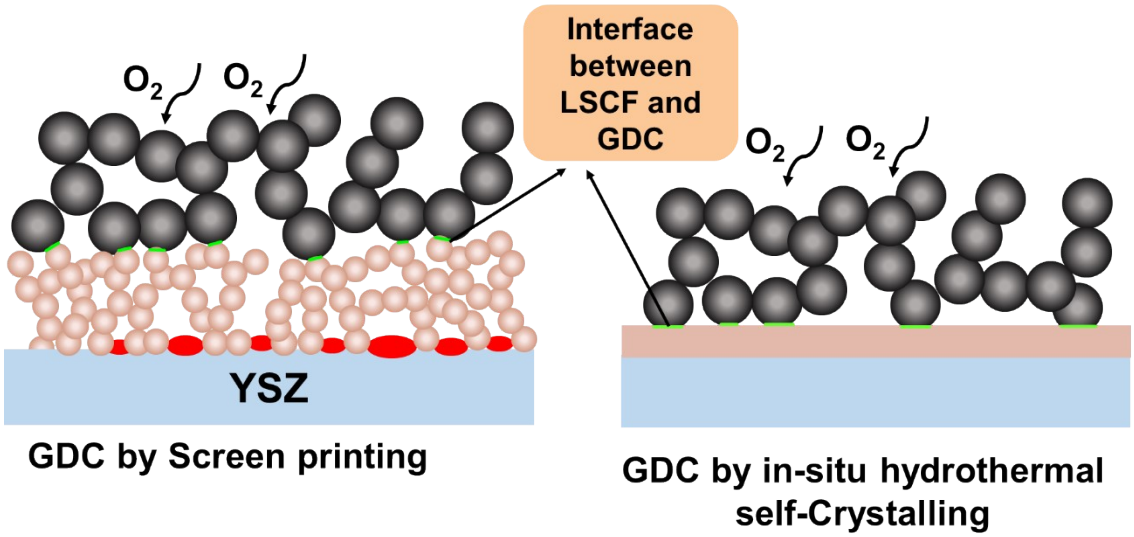

Figure S10 Schematic diagram illustrating the interface contact between the cathode and the GDC barrier layer in Cell-SP and Cell-HY.

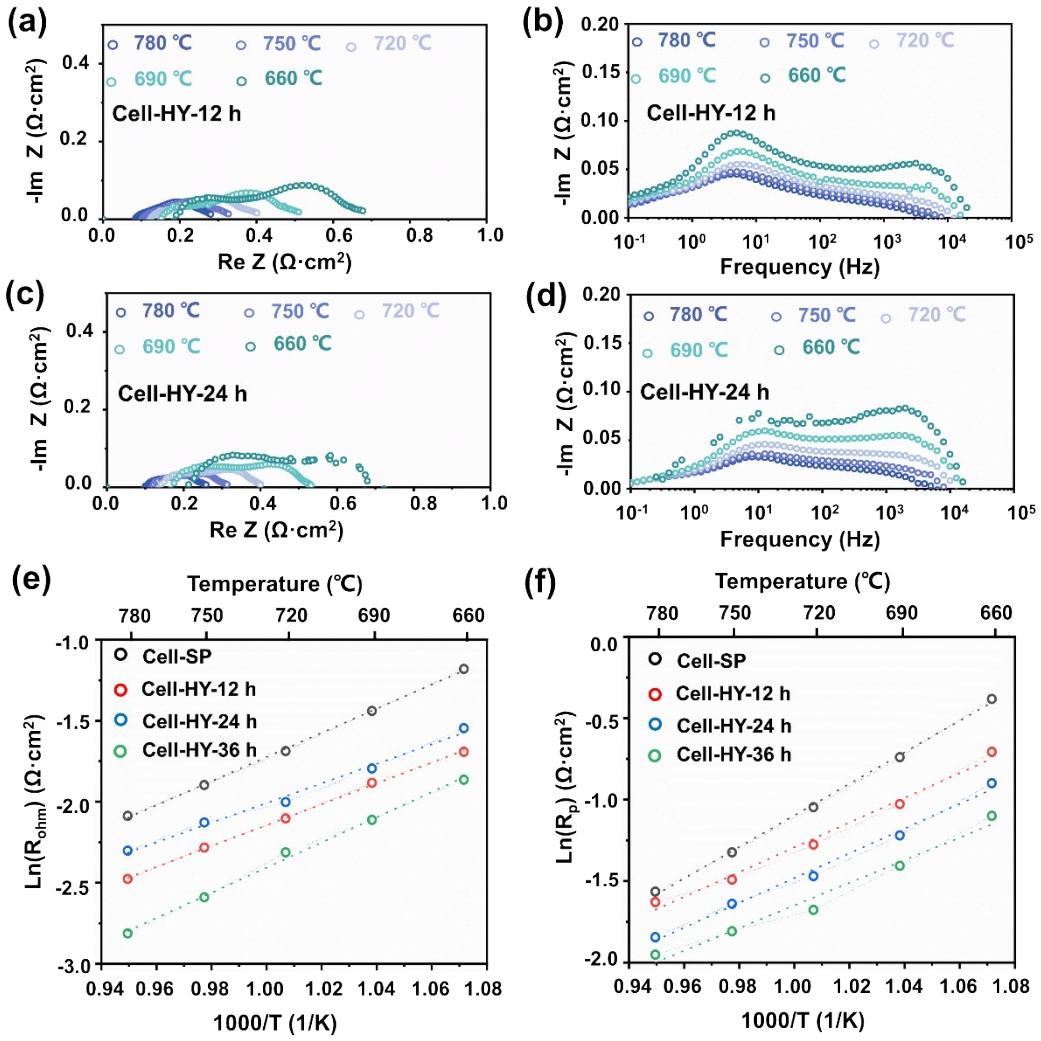

Figure S11 EIS spectra and Bode plot of Cell-HY-12 h (a, b) and Cell-HY-24 h (c, d);

Arrhenius plots of ohmic (e) and polarization (g) resistances of four cells.

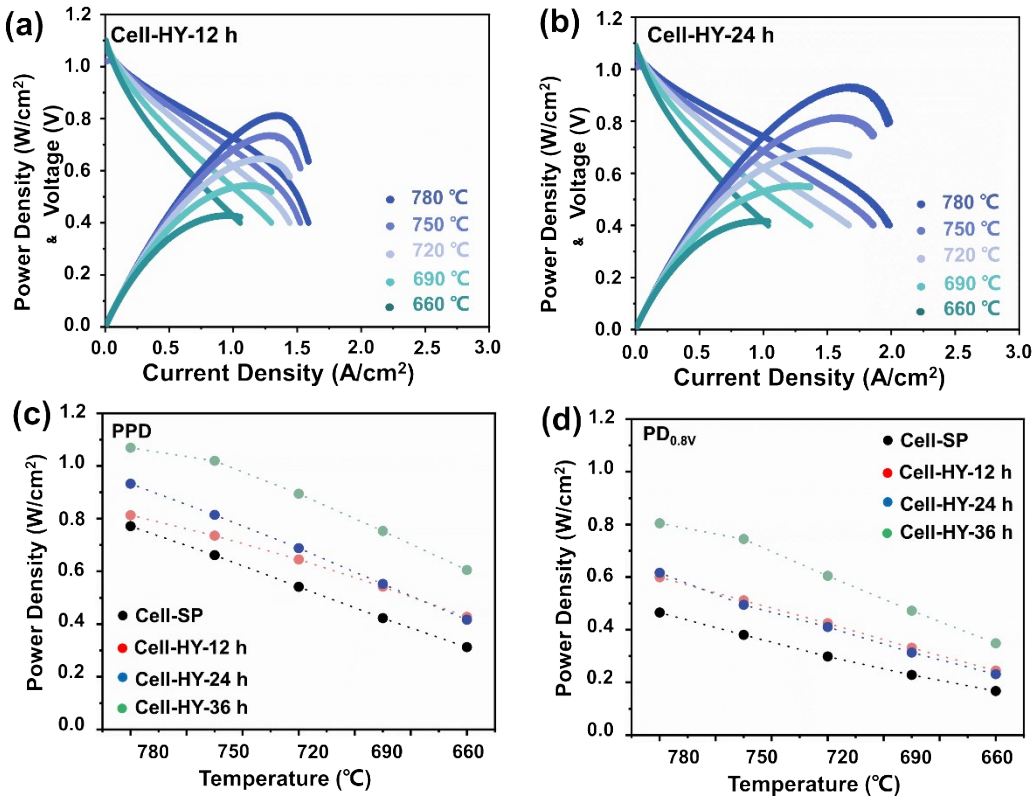

Figure S12 j-V-P curves of Cell-HY-12 h (a) and Cell-HY-24 h (b); the comparison of peak power densities (c) and power densities at 0.8 V (d) of four cells.

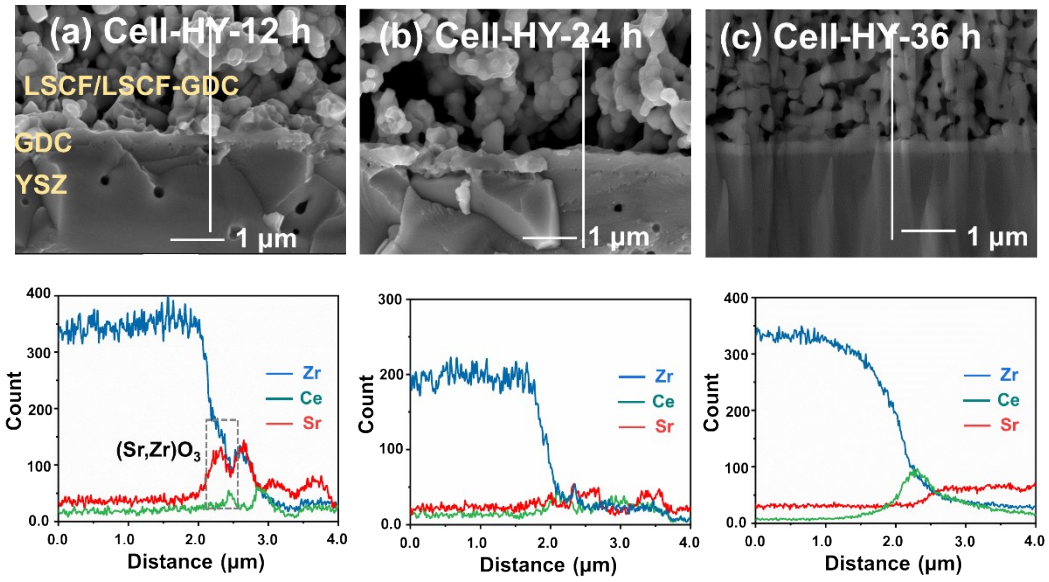

Figure S13 Cross-sectional images and Line scan results of Cell-HY-12 h, Cell-HY-24 h and Cell-HY-36 h after testing.

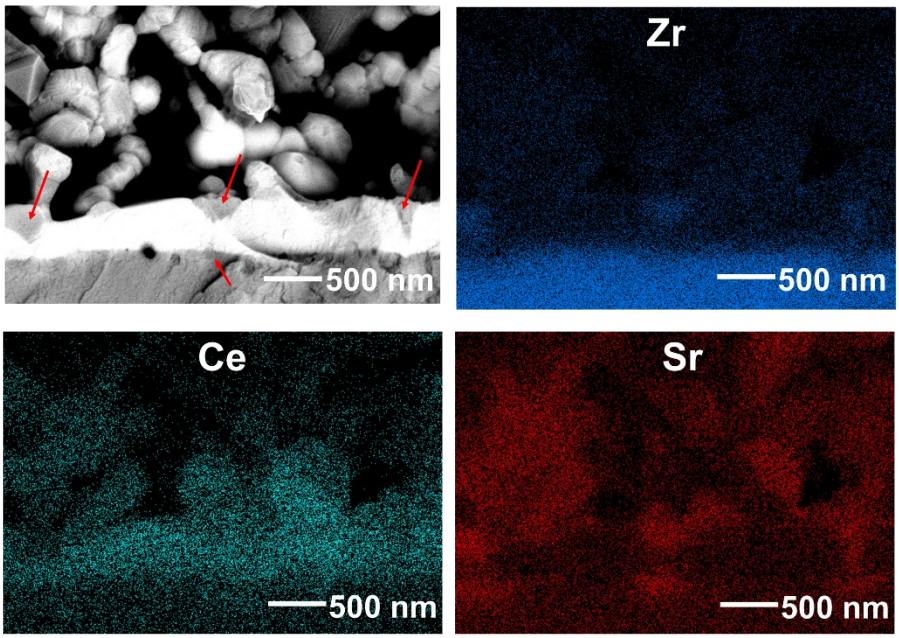

Figure S14 Cross-sectional SEM images and EDX mappings of Cell-HY after aging.

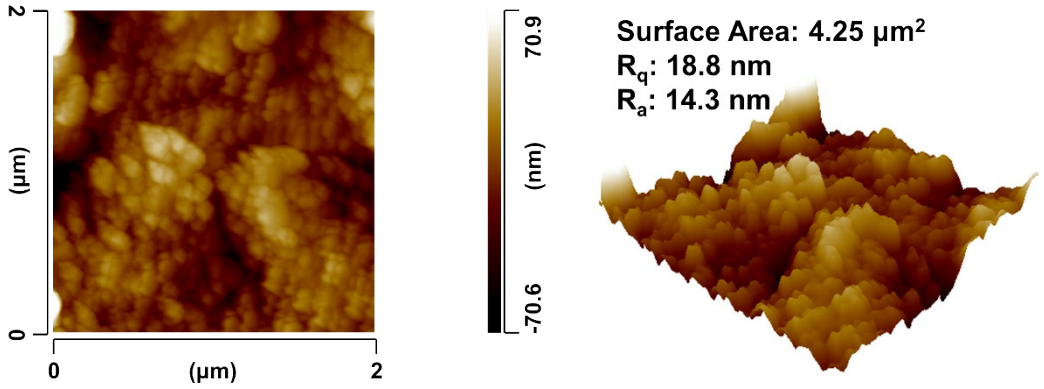

Figure S15 AFM image of GDC films surface,(a) 2D; (b) 3D.

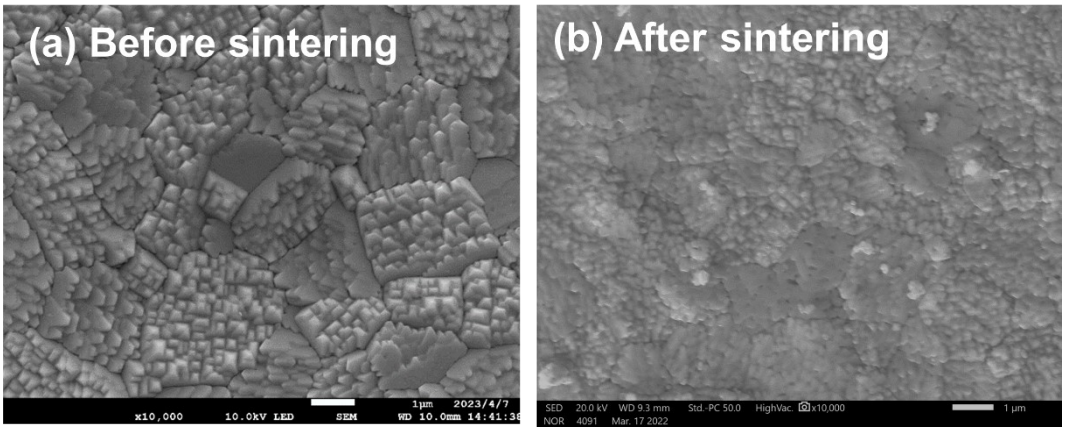

Figure S16 The surface SEM image of the GDC barrier layer by hydrothermal method (a) and after calcination at 1075 ℃ for 2 hours (b).

Table S1 The pH of solutions after different reaction times

	Before	**After**
3 h	5.0	3.5
6 h	5.0	3
12 h	5.0	3.5
18 h	5.0	2.5
24 h	5.0	2.0
30 h	5.0	1.5
36 h	5.0	1.0

Table S2 Aqueous solutions containing different Gd^{3+} contents

Solution composition	Gd^{3+} content	Ce:Gd in GDC films
$Gd(NO_3)_3 \cdot 6H_2O$: $Ce(NO_3)_3 \cdot 6H_2O$=0.1: 0.9	10%	98.5:1.5
$Gd(NO_3)_3 \cdot 6H_2O$: $Ce(NO_3)_3 \cdot 6H_2O$=0.2: 0.8	20%	97:3
$Gd(NO_3)_3 \cdot 6H_2O$: $Ce(NO_3)_3 \cdot 6H_2O$=0.3: 0.7	30%	96.3:3.7
$Gd(NO_3)_3 \cdot 6H_2O$: $Ce(NO_3)_3 \cdot 6H_2O$=0.4: 0.6	40%	94:6

Table S3 the peak area of Ce3d and Gd3d with different Ar+ etching times

Peak Area	100s	600s	1200s	2400s
Ce3d	982614.9	1031412.3	1113756	1143228
Gd3d	184725.1	217864.16	236575	259520.5
Gd3d:Ce3d	0.188	0.211	0.212	0.227

Table S4 The Gd^{3+}: Gd^{4+}, Ce^{3+}:Ce^{4+}, $O1_{lattice}$:$O1_{defects}$ with different Ar+ etching times

	100 s	**600 s**	**1200 s**	**2400 s**
Gd^{3+}: Gd^{4+}	0.220	0.217	0.209	0.239
Ce^{3+}:Ce^{4+}	0.648	0.692	0.634	0.738
$O1_{lattice}$:$O1_{defects}$	0.324	0.297	0.302	0.294

Table S5 Mismatch between YSZ single crystals and GDC crystals in Figure 2b.

Crystal face		2 Theta	Spacing (d_{hkl}, d(Å))	Mismatch
100	GDC	33.212	2.695	5.4%
	YSZ	35.057	2.558	
110	GDC	47.565	1.910	5.3%
	YSZ	50.240	1.814	
111	GDC	28.735	3.104	5.8%
	YSZ	30.449	2.933	

Table S6. $E_{a,ohm}$ and $E_{a,p}$ of four cells.

	Ea(Rohm)/(kJ/mol)	Ea(Rp)/ (kJ/mol)
Cell-SY	61.9	80.5
Cell-HY-12 h	53.5	63.2
Cell-HY-24 h	46.3	57.5
Cell-HY-36 h	64.7	57.7