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Supplementary information

Oxygen diffusion behaviour of A-site deficient $(La_{0.8}Sr_{0.2})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ perovskites in humid conditions

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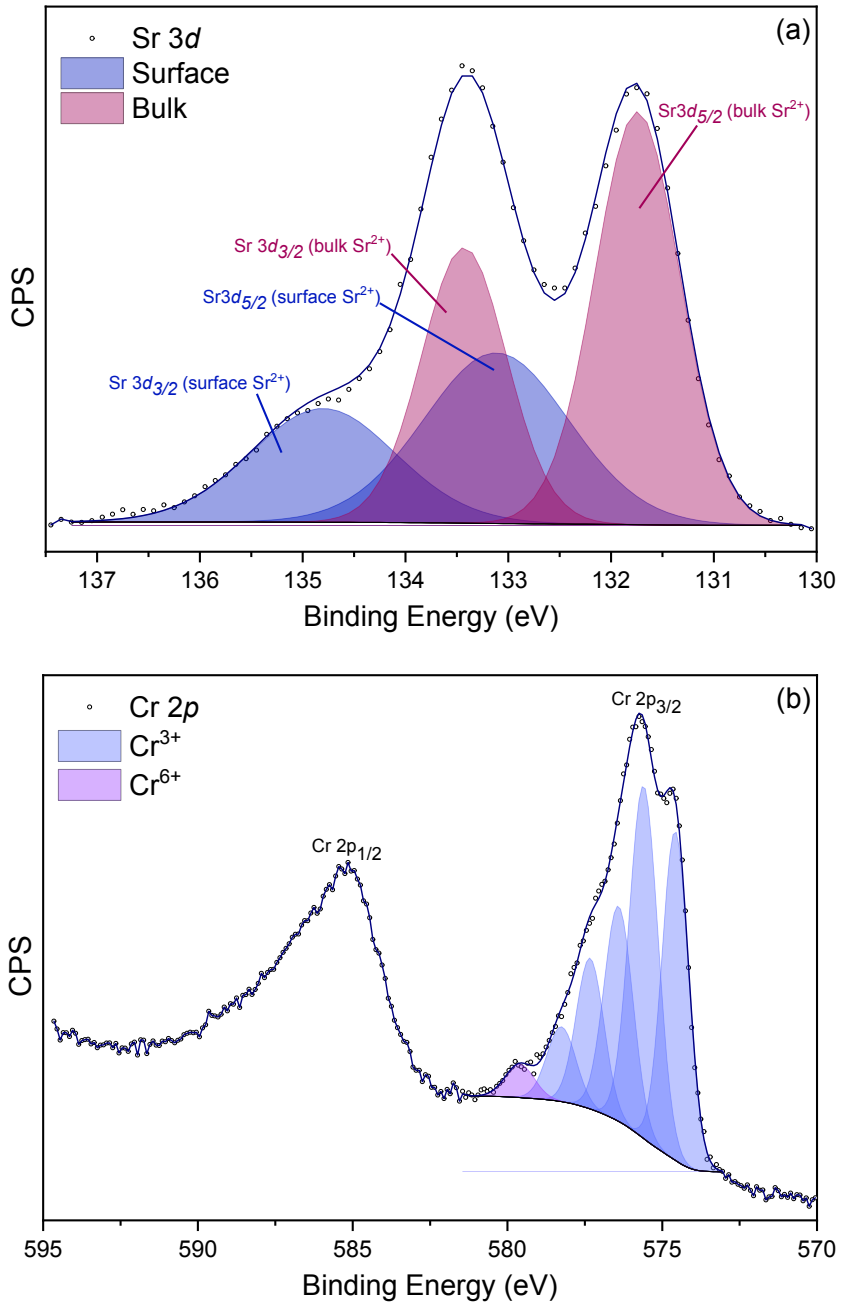

Figure S1. Fitted XPS spectra from the sintered pre-exchanged LSCrF8255 sample showing a) Sr 3*d* and b) Cr 2*p*

Table S1. The atomic ratio of each constituent ion of the sintered LSCrF8255 sample.

Surface Sr: Bulk Sr	La: Sr	Cr^{6+}: Cr^{3+}	Fe: Cr
37: 63	78: 22	3: 97	52: 48

Table S2. The atomic ratio of each constituent ion of LSCrF8255 after the wet oxygen exchange (pO_2 = 200 mbar, pH_2O = 30 mbar) and dry oxygen exchange (pO_2 = 200 mbar, pH_2O = 0 mbar) at 800 °C for 3 hours.

Anneal environment	**XPS spectra acquired at 0° tilt angle on the wet exchanged sample**				**ARXPS spectra acquired at 80° tilt angle on the wet exchanged sample**			
	Surface Sr: Bulk Sr	La:Sr	Cr^{6+}: Cr^{3+}	Fe:Cr	Surface Sr: Bulk Sr	La:Sr	Cr^{6+}: Cr^{3+}	Fe:Cr
Wet	53: 47	81: 19	3: 97	50: 50	80: 20	79: 21	5: 95	50: 50
Dry	63: 37	82: 18	6: 94	52: 48	78: 22	77: 23	9: 91	48: 52

Table S3. The atomic ratio of each constituent ion of LSCrF8255 after the wet oxygen exchange (pO_2 = 200 mbar, pH_2O = 30 mbar) and dry oxygen exchange (pO_2 = 200 mbar, pH_2O = 0 mbar) at 900 °C for 3 hours.

Anneal environment	**XPS spectra acquired at 0° tilt angle on the wet exchanged sample**				**ARXPS spectra acquired at 80° tilt angle on the wet exchanged sample**			
	Surface Sr: Bulk Sr	La:Sr	Cr^{6+}: Cr^{3+}	Fe:Cr	Surface Sr: Bulk Sr	La:Sr	Cr^{6+}: Cr^{3+}	Fe:Cr
Wet	66: 34	82: 18	3: 97	50: 50	83: 17	79: 21	5: 95	50: 50
Dry	68: 32	71: 29	4: 96	52: 48	96: 4	58: 42	7: 93	48: 52

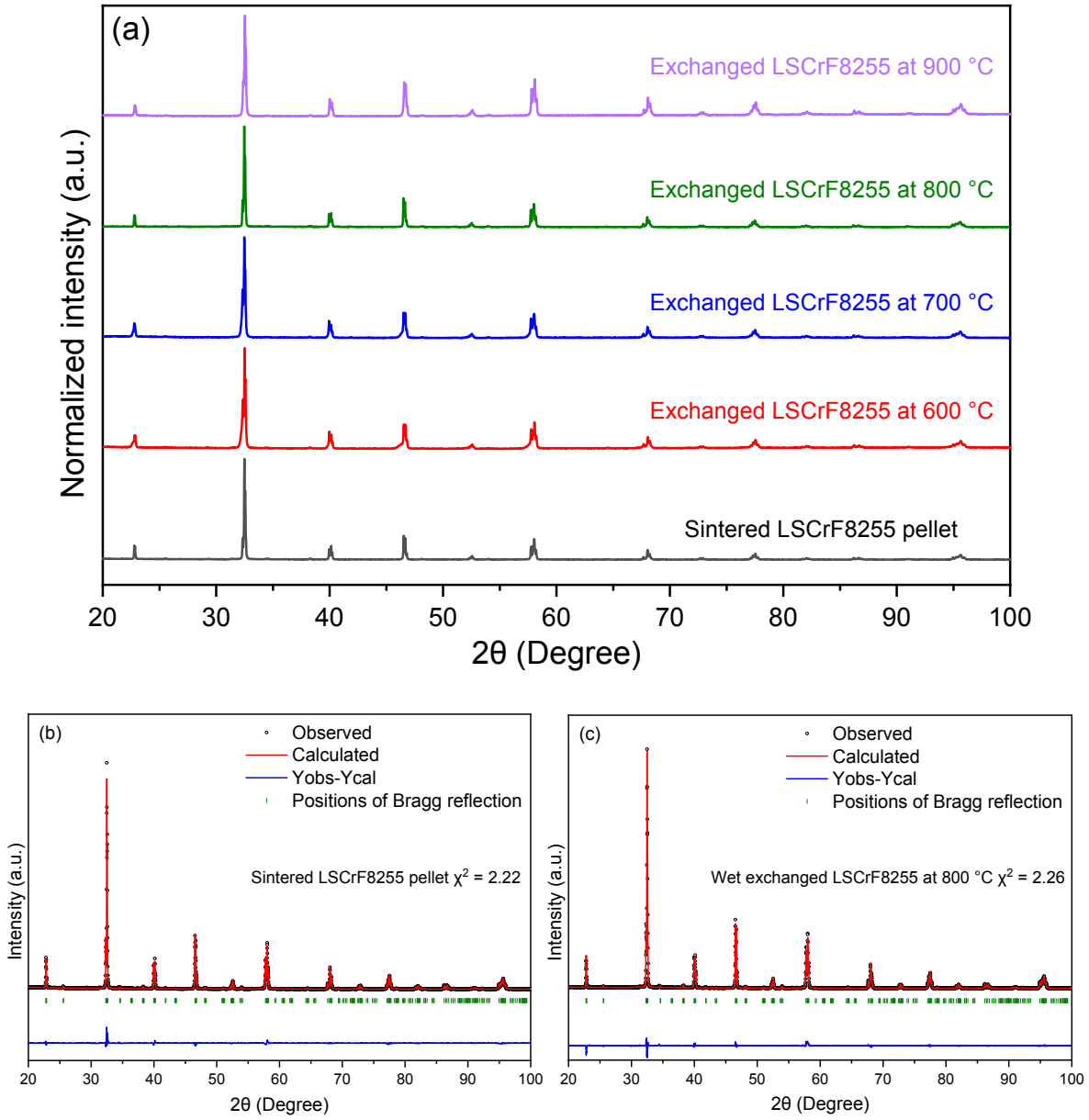

Figure S2. (a) XRD patterns of the sintered and wet exchanged LSCrF8255 pellets. (b and c) Rietveld refinement results of the sintered LSCrF8255 pellet and the wet exchanged LSCrF8255 at 800 °C where the black circles are the observed experimental data; the red solid line represents the calculated intensities; the blue solid line is the difference in intensity between the observed and calculated data (space group: *Pnma*); and the green vertical bars are the Bragg reflection positions.

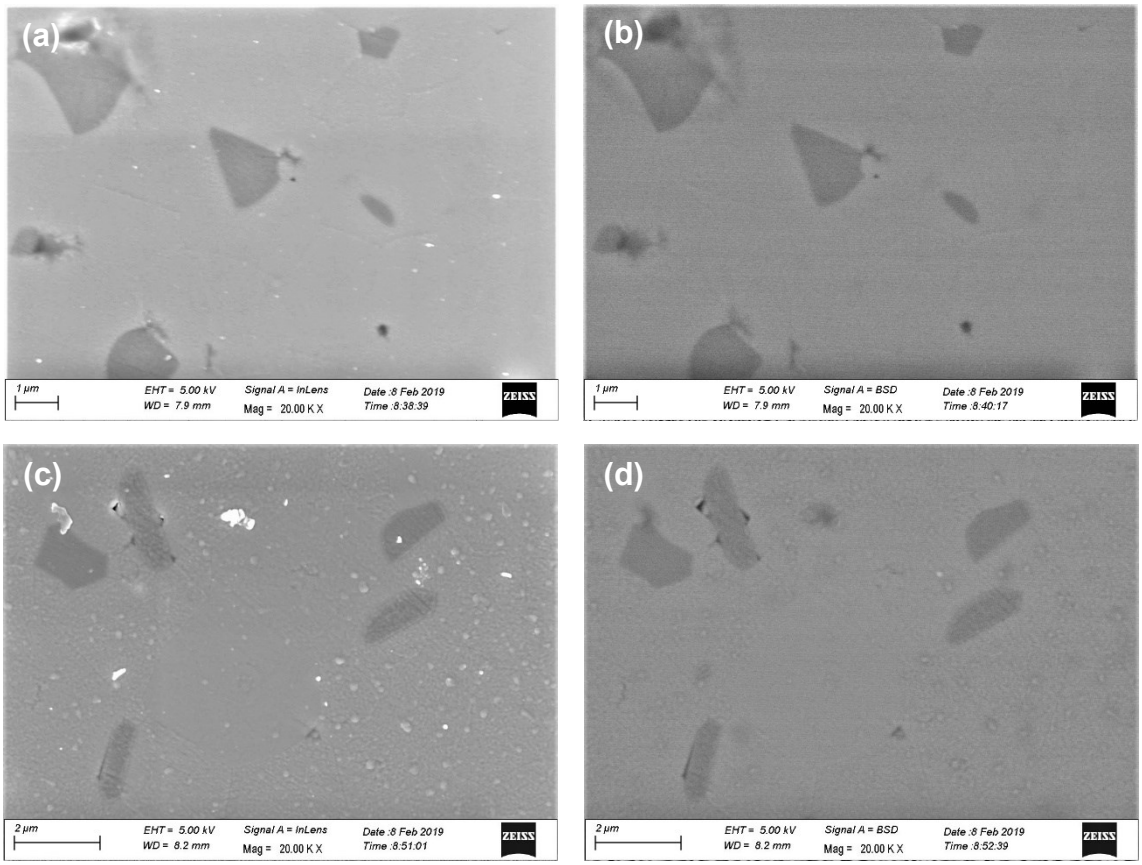

Figure S3. (a and b) SEM secondary electron (SE) and backscattered-electron (BSE) images of the LSCrF8255 sample wet exchanged at 600 °C; (c and d) SE and BSE images of the LSCrF8255 sample wet exchanged at 700 °C.

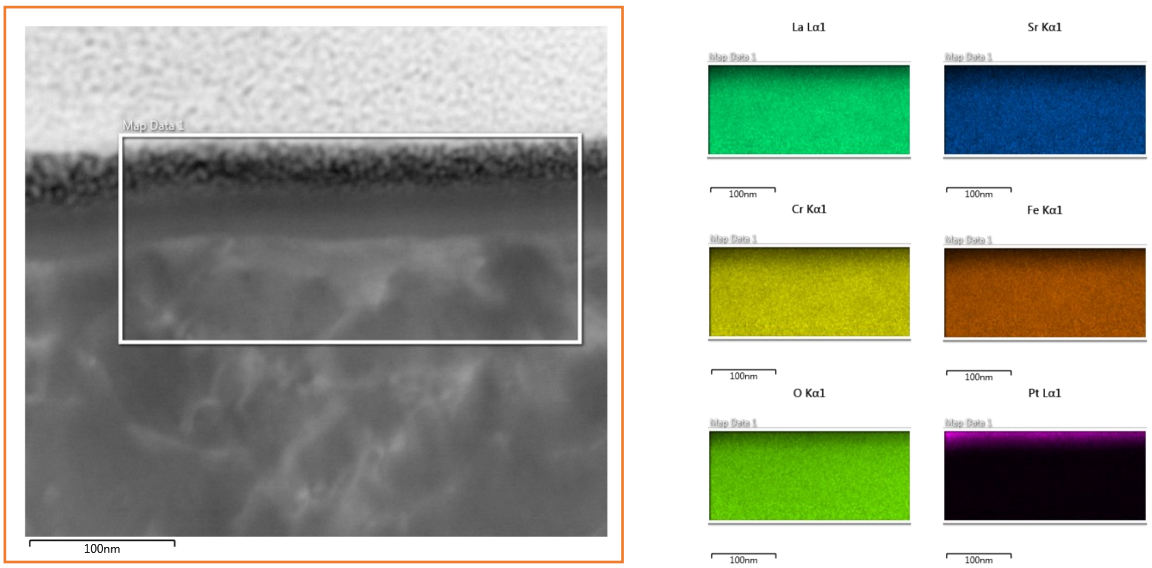

Figure S4. Representative STEM-EDX map showing an unsegregated grain. The sample surface was coated with Pt during TEM foil preparation.

Table S4. RGA data from the wet isotopic exchange environment (200 mbar $^{16}O_2$+30 mbar $H_2{}^{18}O$) at 600 and 700 °C. The abundance of each gas species is normalized to the abundance of oxygen gas O_2 mass 32.

Gas species abundance	**Wet oxygen exchange at 600 °C for 3 hours**		**Wet oxygen exchange at 700 °C for 3 hours**	
	At the start	At the end	At the start	At the end
Mass 16 ^{16}O: $^{16}O_2$	6.7%	6.6%	6.4%	6.0%
Mass 17 ^{16}OH: $^{16}O_2$	0.9%	0.9%	8.7%	1.1%
Mass 18 ^{18}O or H_2O: $^{16}O_2$	4.2%	4.0%	4.0%	5.1%
Mass 19 ^{18}OH: $^{16}O_2$	2.6%	2.2%	2.1%	2.1%
Mass 20 $H_2{}^{18}O$: $^{16}O_2$	9.9%	9.2%	8.8%	8.4%
Mass 34 $^{18}O^{16}O$: $^{16}O_2$	0.9%	1.6%	0.9%	2.0%
Mass 36 $^{18}O_2$: $^{16}O_2$	0.2%	0.2%	0.2%	0.5%