Optimization of Absorption/Desorption Parameters of Brownmillerite $\text{SrCoO}_{2.5}$ for Oxygen Storage

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Supplementary Material

Figure S 1 Refined XRD patterns of the samples after absorption at different temperatures (a) 623 K (b) 648 K (c) 673 K (d) 693 K and (e) 723 K.

Figure S 2 Comparison of XRD patterns of (a) as synthesized BM $\text{SrCoO}_{2.5}$ and (b-f) samples after desorption.

Figure S 3 Schematic representation of reduction through (a) contracting sphere model (b) nucleation and growth model (adapted from ref 1). Comparison of (c) extent of conversion (α) vs time (d) $d\alpha/dt$ vs α for contracting sphere and nucleation and growth models (adapted from ref 1). (e-g) Desorption curves fitted with the equation given in table S3.

Figure S 4 (a) XPS wide spectra of BM $\text{SrCoO}_{2.5}$ and the sample absorbed at 673 K, (b) zoomed version of the spectra in (a) up to 80 eV and (c) C 1s region of BM and absorbed sample showing an increased contribution of carbonate carbon in absorbed sample.

Figure S 5 Plots of $\ln(\sigma T)$ vs inverse of temperature (From DC conductivity measurements) of (a) BM $\text{SrCoO}_{2.5}$ sample and (b) the sample absorbed at 673 K

Figure S 6 BM SrCoO_{2.5} (a) normalized impedance plots (b) variation of real part of impedance with frequency at different temperatures (c) Imaginary part of modulus versus frequency (d) variation of real part of modulus with frequency, Arrhenius plots of (e) conductivity and (f) frequency maximum

Table S1: Lattice parameter values obtained from Rietveld refinement for different absorbed samples

Absorption Temperature (K)	Space group	Lattice Parameters (Å)			Cell Volume (Å ³)	Cell formula units	Normalized Cell Volume (Å ³)
		a	b	c			
623	<i>Ima2</i>	15.707(8)	5.557(8)	5.456(9)	476.405	8	59.550
648	<i>P4/mmm</i>	3.385(5)	3.385(5)	7.696(9)	113.230	2	56.615
673	<i>P4/mmm</i>	3.830(8)	3.830(8)	7.691(6)	112.868	2	56.434
693	<i>P4/mmm</i>	3.833(1)	3.833(1)	7.693(8)	113.045	2	56.522
723	<i>P4/mmm</i>	3.833(3)	3.833(3)	7.692(2)	113.033	2	56.517

Table S2: Oxygen stored and delta value from desorption experiments and Iodometric titration

Absorption temperature (K)	From desorption experiment			From Iodometric titration		
	Pressure change (m bar)	O ₂ evolved cm ³ /g of SrCoO _{3-δ}	Delta	Composition after absorption	Composition after desorption	Delta
723	41.1	13.24	0.22	SrCoO _{2.65±0.02}	SrCoO _{2.41±0.02}	0.24
693	43.9	14.16	0.23	SrCoO _{2.65±0.01}	SrCoO _{2.38±0.01}	0.27
673	47.1	15.28	0.26	SrCoO _{2.67±0.02}	SrCoO _{2.40±0.01}	0.27
648	36.5	11.76	0.19	SrCoO _{2.68±0.01}	SrCoO _{2.43±0.01}	0.25
623	1	0.14	0	SrCoO _{2.43±0.01}	SrCoO _{2.43±0.01}	0

Table S3: Fitting results for desorption kinetics study

Temperature (K)	Equation used for fitting	A1	τ1 (s)	A2	τ2 (s)	Adj. R square
673	$\alpha = 1 - \exp(-t/\tau)$	-	444.2(3)	-		0.9989
693	$\alpha = A1 \cdot \exp(-t/\tau1) + A2 \cdot \exp(-t/\tau2) + 1$	-0.93(3)	53.8(3)	-0.06(3)	287(12)	0.9979
723		-0.85(3)	13.8(1)	-0.15(2)	165(2)	0.9936

References

1. N. W. Hurst, S. J. Gentry, A. Jones, B. D. McNicol, Temperature programmed reduction, Catalysis Reviews Science and Engineering 24 (2) (1982) 233-309