

Electronic Supplementary Material

A CO and CO₂ tolerating (La_{0.9}Ca_{0.1})₂(Ni_{0.75}Cu_{0.25})O_{4+δ} Ruddlesden–Popper membrane for oxygen separation

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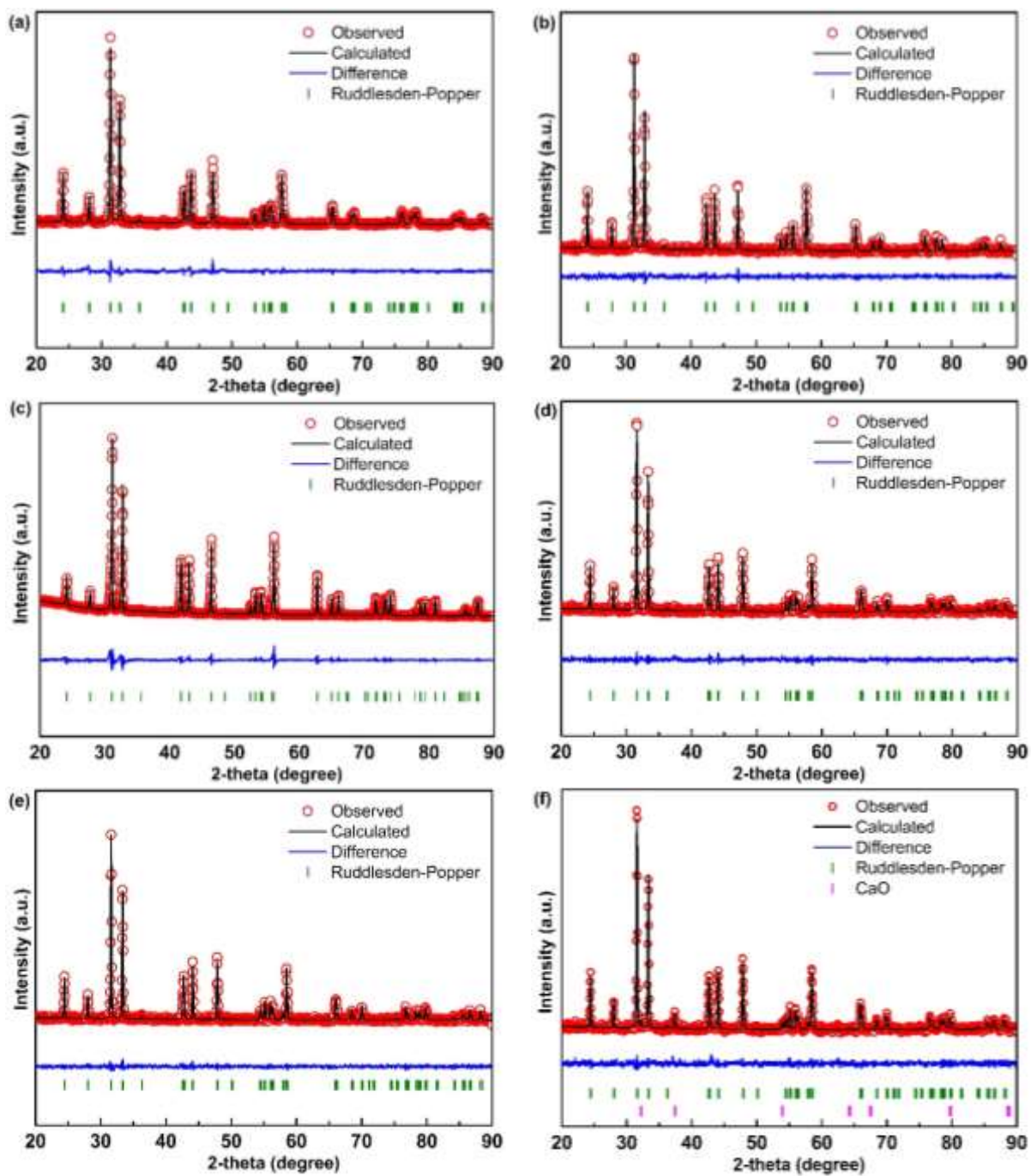


Figure S1. Rietveld refinements of PXRD patterns of $(\text{La}_{1-x}\text{Ca}_x)_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (a) $\text{La}_2\text{NiO}_{4+\delta}$. (b) $\text{La}_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (c) $(\text{La}_{0.9}\text{Ca}_{0.1})_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (d) $(\text{La}_{0.8}\text{Ca}_{0.2})_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (e) $(\text{La}_{0.7}\text{Ca}_{0.3})_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (f) $(\text{La}_{0.6}\text{Ca}_{0.4})_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$.

Table S1. Summarized refinements results of $(\text{La}_{1-x}\text{Ca}_x)_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. ((a) $\text{La}_2\text{NiO}_{4+\delta}$. (b) $\text{La}_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (c) $(\text{La}_{0.9}\text{Ca}_{0.1})_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (d) $(\text{La}_{0.8}\text{Ca}_{0.2})_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (e) $(\text{La}_{0.7}\text{Ca}_{0.3})_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$. (f) $(\text{La}_{0.6}\text{Ca}_{0.4})_2(\text{Ni}_{0.75}\text{Cu}_{0.25})\text{O}_{4+\delta}$.

Parameter	(a)	(b)	(c) [#]	(d)	(e)	(f)
Space group	<i>I4/mmm</i>					
a (Å)	5.4593(5)	5.4431(4)	5.4032(2)	5.3746(4)	5.3723(3)	5.3751(6)
c (Å)	12.689(1)	12.802(1)	12.7414(3)	12.729(1)	12.7311(9)	12.742(1)
V (Å ³)	378.17(6)	379.30(5)	371.98(1)	367.69(5)	367.44(4)	368.15(7)
$z(\text{La}/\text{Ca})$	0.3598(2)	0.3605(3)	0.3619(1)	0.3612(2)	0.3608(2)	0.3611(3)
$z(\text{O}(1))$	0.163(2)	0.175(3)	0.1702(9)	0.172(2)	0.172(3)	0.176(5)
$x(\text{O}(3))$	0.05*	0.07(2)	0.051(8)	0.05(2)	0.04(2)	0.07(2)
$z(\text{O}(3))$	0.202*	0.225(9)	0.202(4)	0.204(8)	0.19(2)	0.19(2)
$B_{iso}(\text{La}/\text{Ca})$ (Å ²)	2.3(1)	2.6(1)	0.24(2)	2.0(1)	2.1(1)	1.7(1)
$B_{iso}(\text{Ni}/\text{Cu})$ (Å ²)	2.6(2)	2.7(2)	0.21(5)	2.0(3)	2.2(3)	1.7(3)
$B_{iso}(\text{O}(1))$ (Å ²)	3.8(4)	2.7(5)	0.4(1)	2.0(5)	2.0(5)	1.7(6)
$B_{iso}(\text{O}(2))$ (Å ²)	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$
$B_{iso}(\text{O}(3))$ (Å ²)	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$	= $B_{iso}(\text{O}(1))$
$P(\text{La})$	1	1	0.888(8)	0.82(2)	0.84(2)	0.84(2)
$P(\text{Ca})$	--	--	0.112(8)	0.18(2)	0.16(2)	0.16(2)
w (wt.%)	100	100	100	100	100	89(4)
R_{Bragg} (%)	6.74	5.08	4.67	6.00	5.32	6.55
Space group ⁺	<i>Fm$\bar{3}m$</i>					
a (Å)	4.809(1)					
$B_{iso}(\text{Ca})$ (Å ²)	2.0*					
$B_{iso}(\text{O})$ (Å ²)	2.5*					
w (wt.%)	11(4)					
R_{Bragg} (%)	29.0					
R_p (%)	4.91	6.12	7.08	5.92	5.89	5.75
R_{wp} (%)	6.26	7.87	9.85	7.37	7.53	7.49
χ^2	1.95	1.20	2.90	1.21	1.29	1.28

* Fixed during refinements. # Mo- $K\alpha_1$ radiation. + CaO.

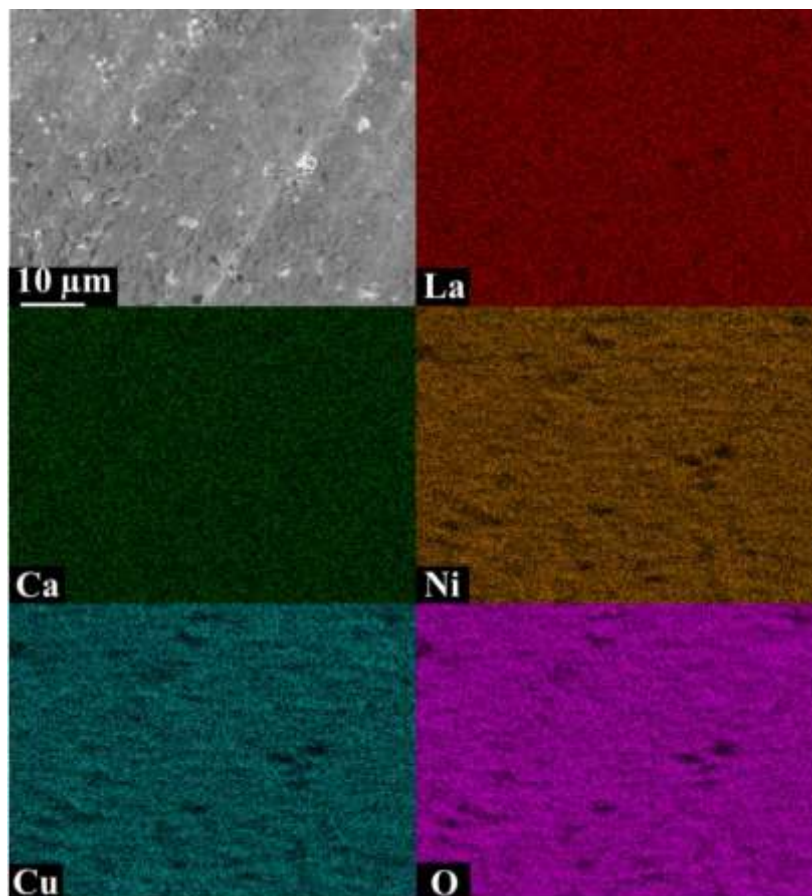


Figure S2. SEM images and EDXS elemental distributions of a fresh $(La_{0.9}Ca_{0.1})_2(Ni_{0.75}Cu_{0.25})O_{4+\delta}$ bulk sample.