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Supporting information

Sulfur-tolerant cathode catalyst fabricated with in situ exsolved CoNi alloy nanoparticles anchored on a Ruddlesden-Popper support for CO_2 electrolysis

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Table S1. Average oxidation states of the Co, Ni, and Mn in LSCNM, CoNi-R.P.LSCM and R.P.LSCM calculated by XANES analysis.

Catalysts	Elements		
	Co	Ni	Mn
LSCNM	3.002	2.716	3.523
CoNi-R.P.LSCM	2.458	0	2.918
R.P.LSCM	2.536	0	3.147

Table S2. Comparison of electrochemical performance of ceramic-based materials in which cobalt or nickel component exsolved for high temperature CO_2 electrolysis.

Catalyst	Exsolved element	Gas condition	Current density at 1.3 V (mA/cm^2)	Faraday efficiency (%)	Reaction time (hour)	Ref.
CoNi-R.P.LSCM	CoNi	30% CO/CO_2	703 (850°C) 423 (800°C)	97.8	90	This work
Co-R.P.LSCoMn	Co	30% CO/CO_2	ca. 630 (850°C)	97.4	12	[S1]
$Pr_{0.5}Ba_{0.5}Mn_{0.9}Co_{0.1}O_3$	Co	30% CO/CO_2	ca. 400 (800°C)	-	-	[S2]
$(La_{0.2}Sr_{0.8})_{0.95}Ti_{0.85}Mn_{0.1}Ni_{0.05}O_{3+\delta}$	Ni	100% CO_2	ca. 280 (800°C)	99.9	100	[S3]
$(La_{0.2}Sr_{0.8})_{0.95}Ti_{0.85}Cr_{0.1}Ni_{0.05}O_{3+\delta}$	Ni	100% CO_2	ca. 230 (800°C)	98.4	100	[S3]
$Ce_{0.85}Ni_{0.15}O_2$	Ni	100% CO_2	ca. 150 (800°C)	80	30	[S4]
$(La_{0.3}Sr_{0.7})_{0.9}Ti_{0.95}Ni_{0.05}O_{3-\delta}$	Ni	100% CO_2	ca. 120 (800°C)	89	48	[S5]
$(La_{0.75}Sr_{0.25})_{0.9}(Cr_{0.5}Mn_{0.5})_{0.9}Ni_{0.1}O_{3-\delta}$	Ni	100% CO_2	ca. 120 (800°C)	85	21	[S6]
$NbTi_{0.5}Ni_{0.5}O_4$	Ni	100% CO_2	ca. 100 (800°C)	65	1.5	[S7]
$(La_{0.2}Sr_{0.8})_{0.9}(Ti_{0.9}Mn_{0.1})_{0.9}Ni_{0.1}O_3$	Ni	100% CO_2	ca. 45 (800°C)	75	-	[S8]

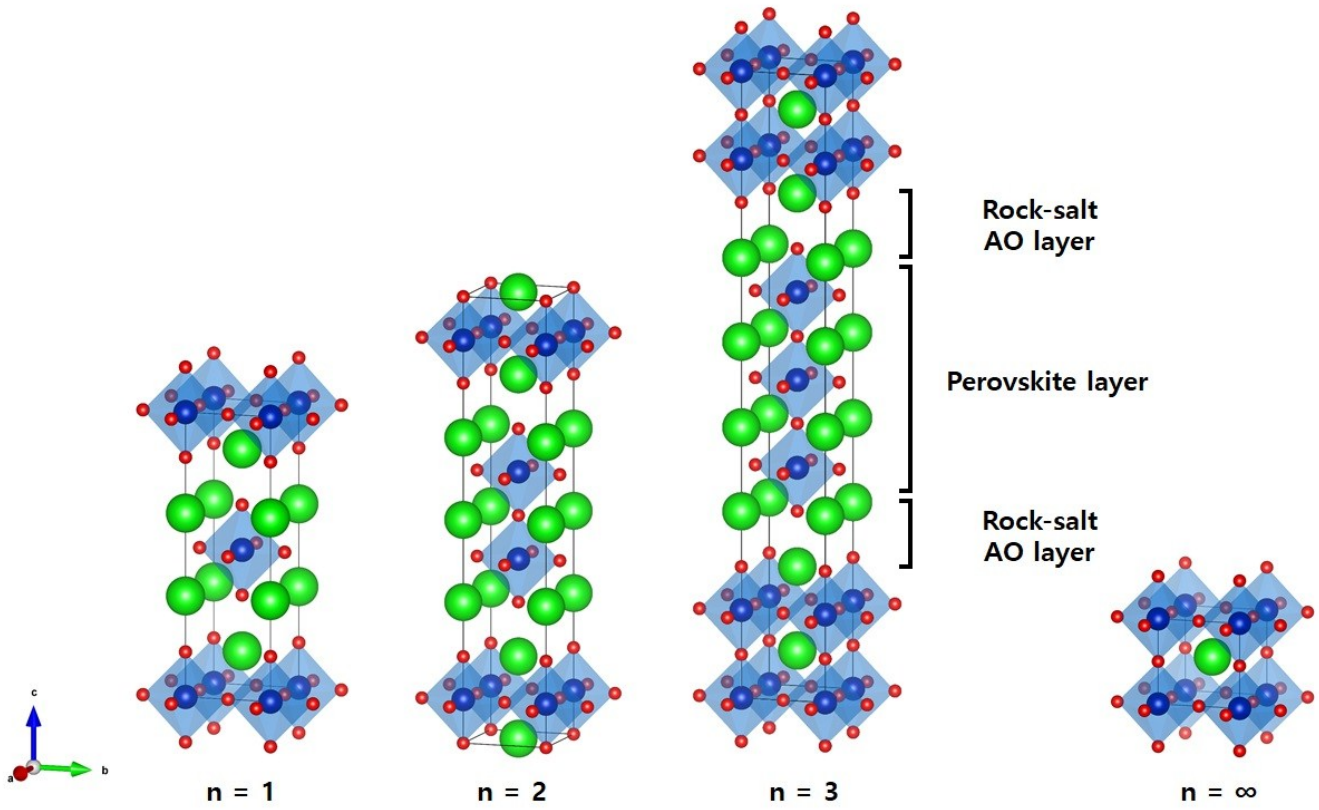

Fig. S1. Crystal structure image of a Ruddlesden-Popper phase ($A_{n+1}B_nO_{3n+1}$)

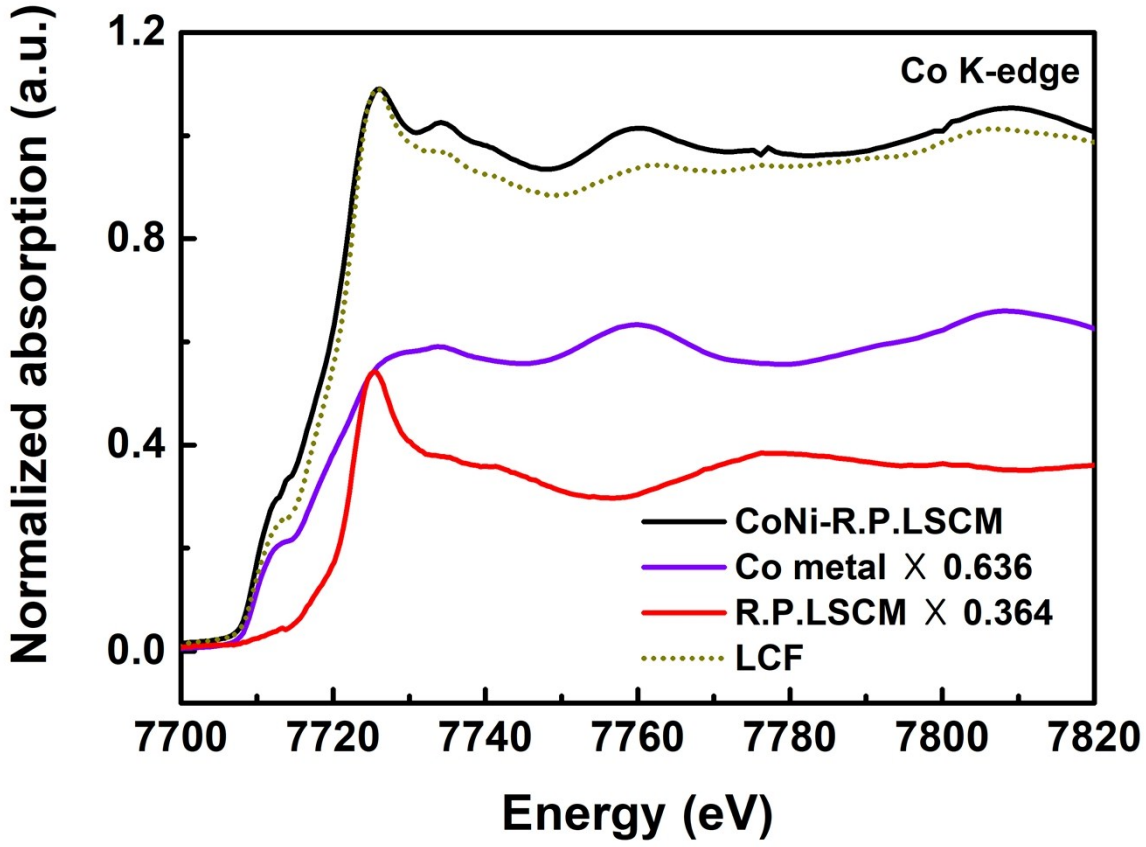

Fig. S2. Co K-edge XANES fittings for the CoNi-R.P.LSCM by linear combination fittings (LCF) of Co metal and R.P.LSCM. Dashed line is the fitted result.

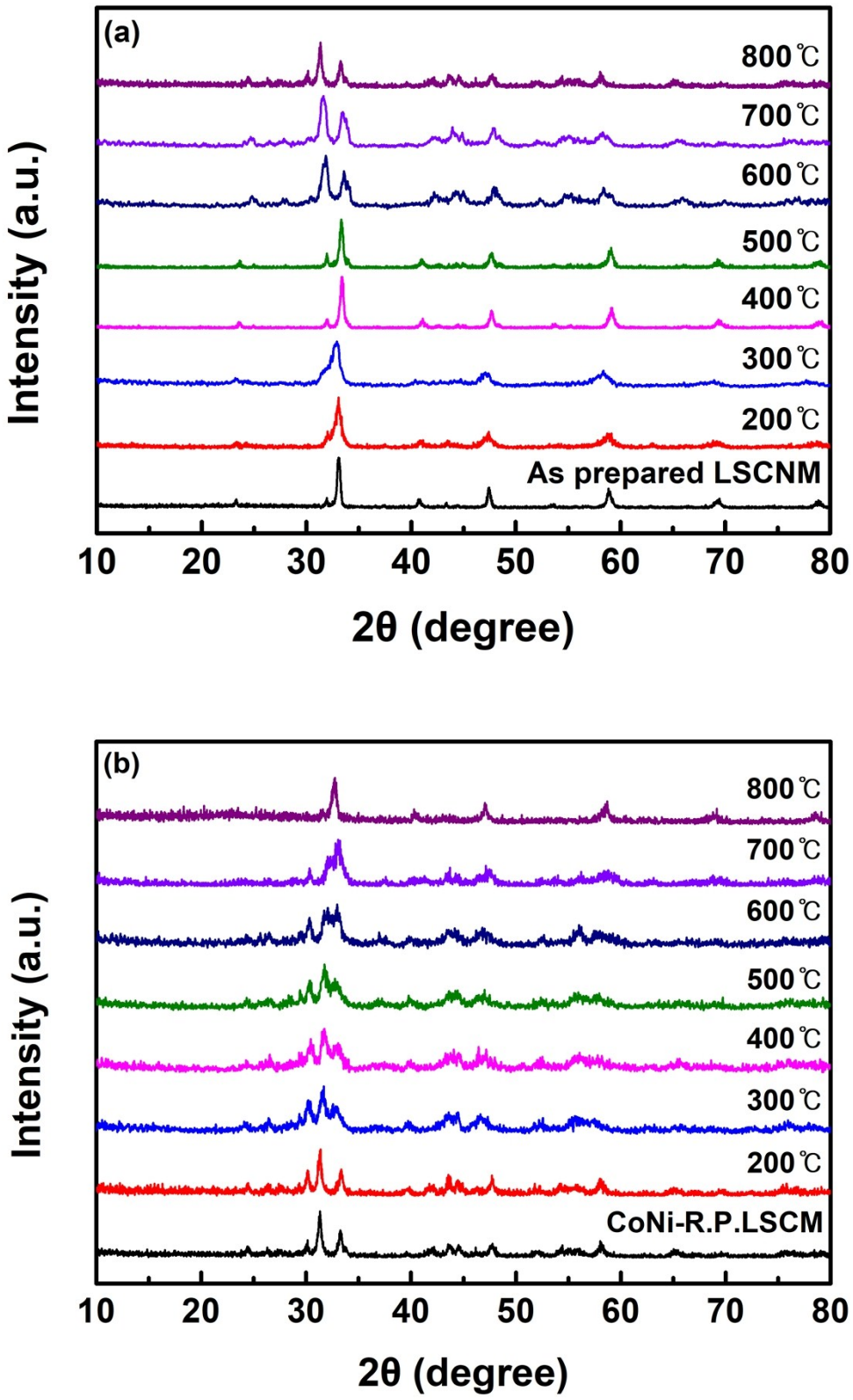

Fig. S3. XRD patterns of (a) LSCNM after heat treatment in the 20% H_2/N_2 and (b) CoNi-R.P.LSCM after heat treatment in the air, from room temperature to 800 °C.

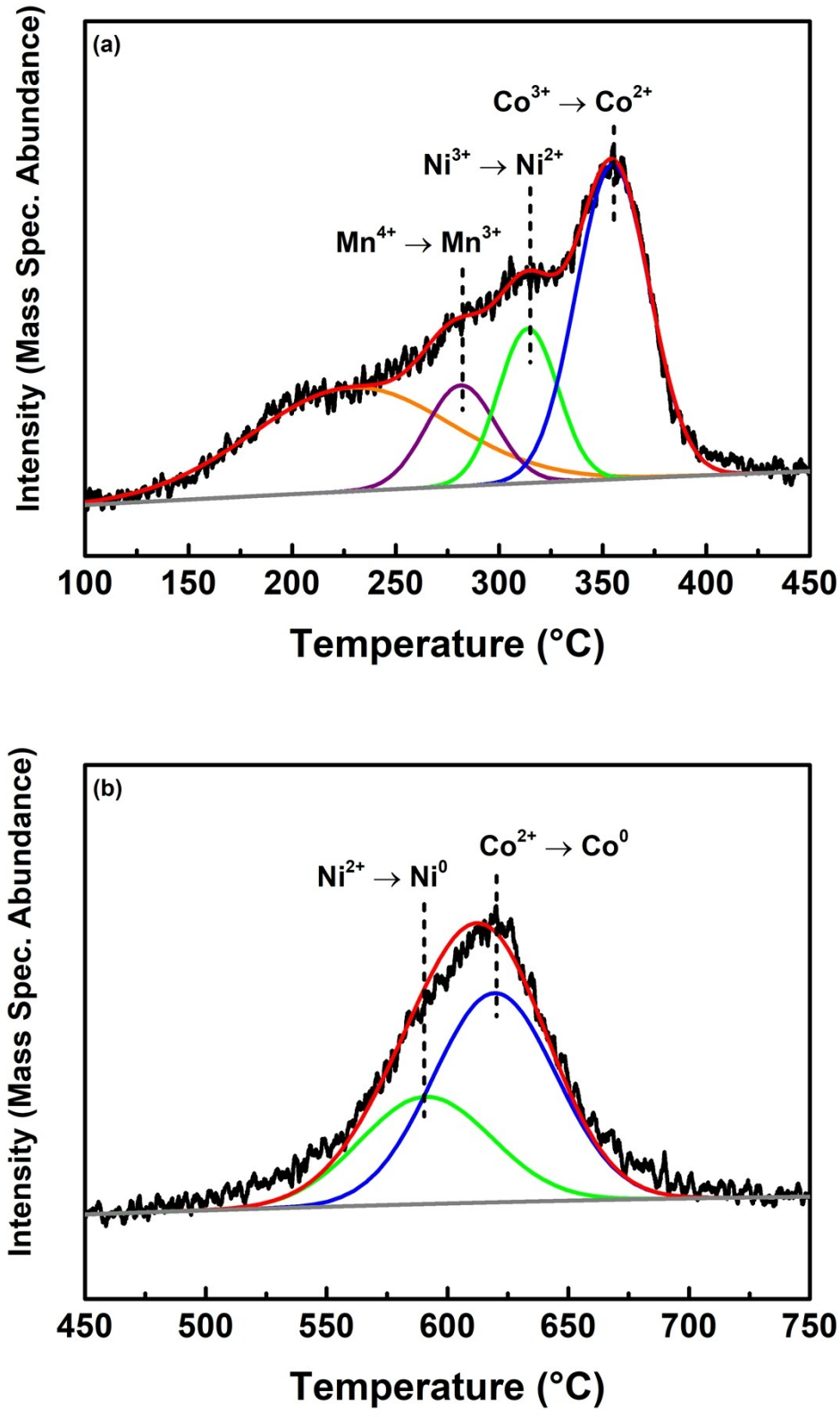

Fig. S4. H_2-TPR profile for the LSCNM. (a) The first peak located between 100 – 450 °C and (b) the second peak located between 500 – 700 °C.

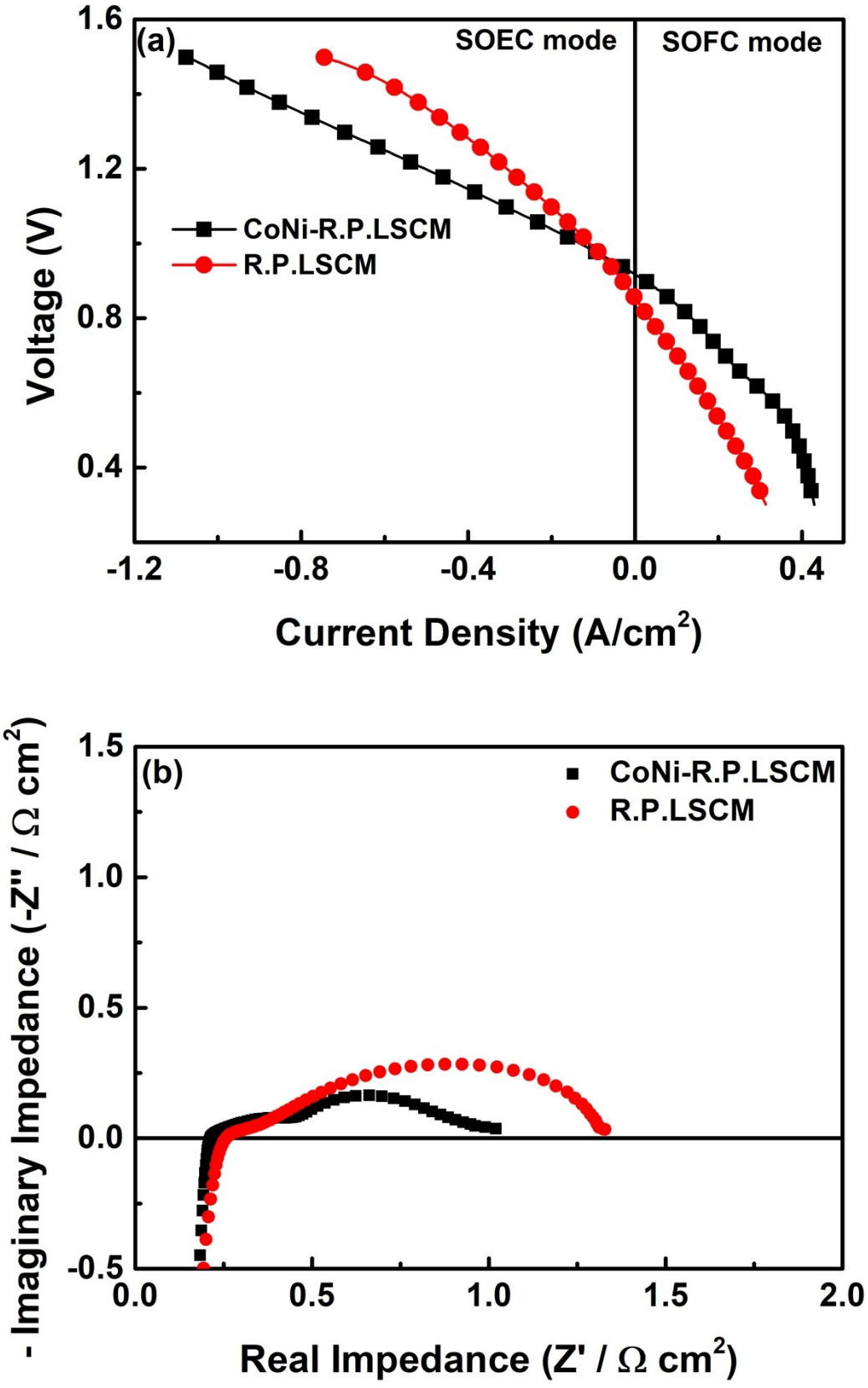

Fig. S5. (a) Current-voltage curves and (b) EIS curves of cell with the CoNi-R.P.LSCM and R.P.LSCM cathode in the gas mixture of 30% CO/CO_2 at 850 °C.

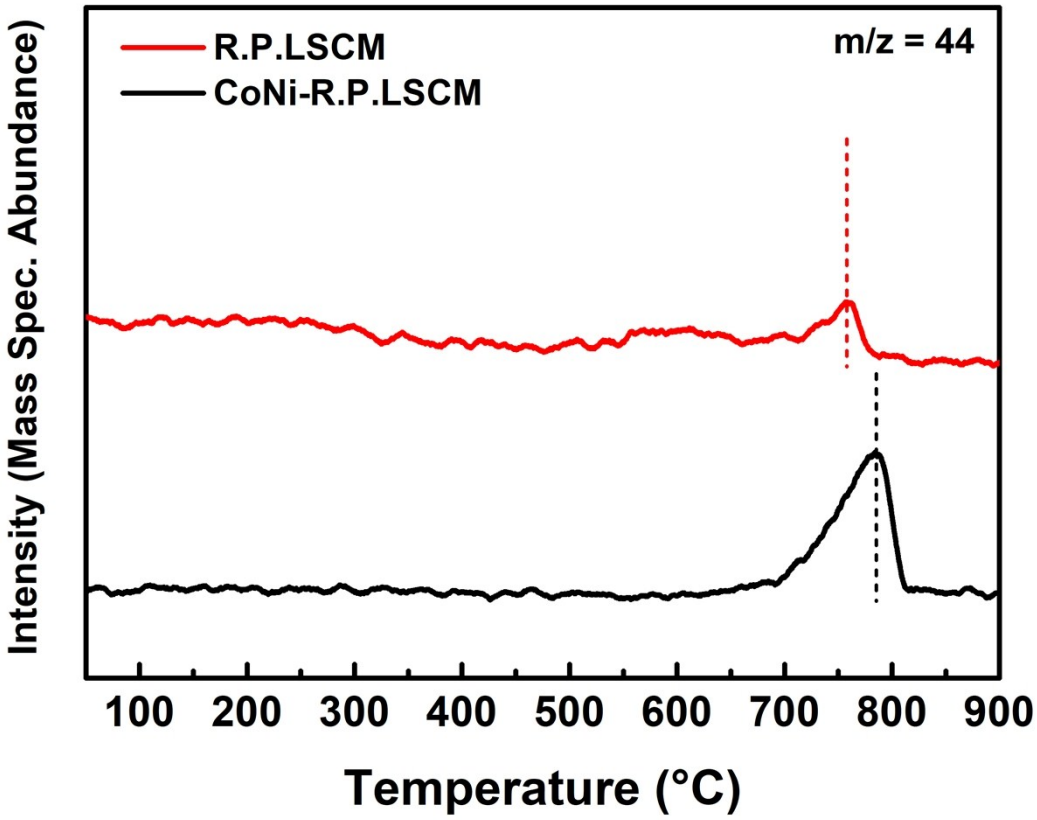

Fig. S6. CO_2-TPD profiles of the CoNi-R.P.LSCM and R.P.LSCM samples from 50 ℃ to 900 ℃.

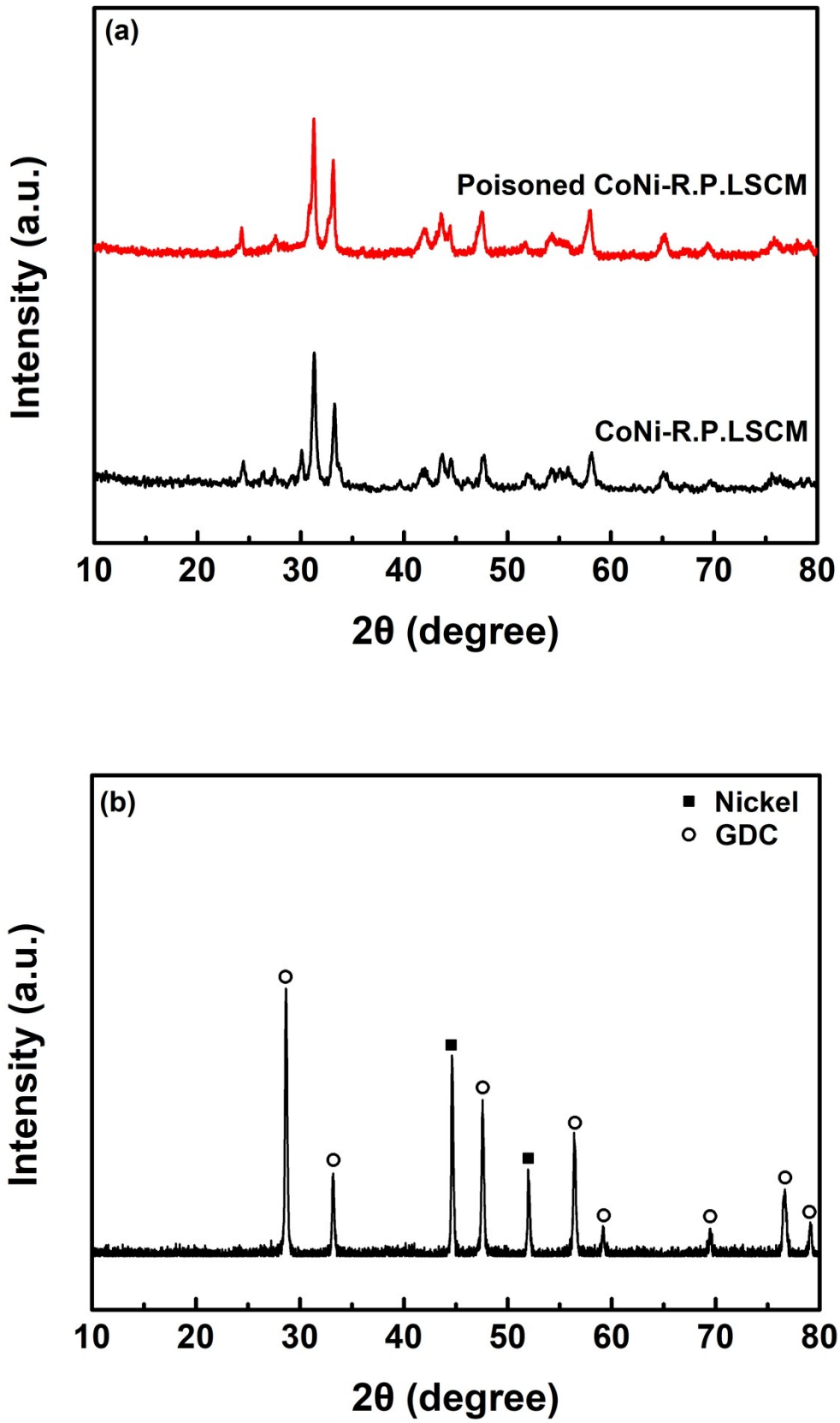

Fig. S7. XRD patterns of CoNi-R.P.LSCM, poisoned CoNi-R.P.LSCM, and (b) poisoned Ni/GDC.

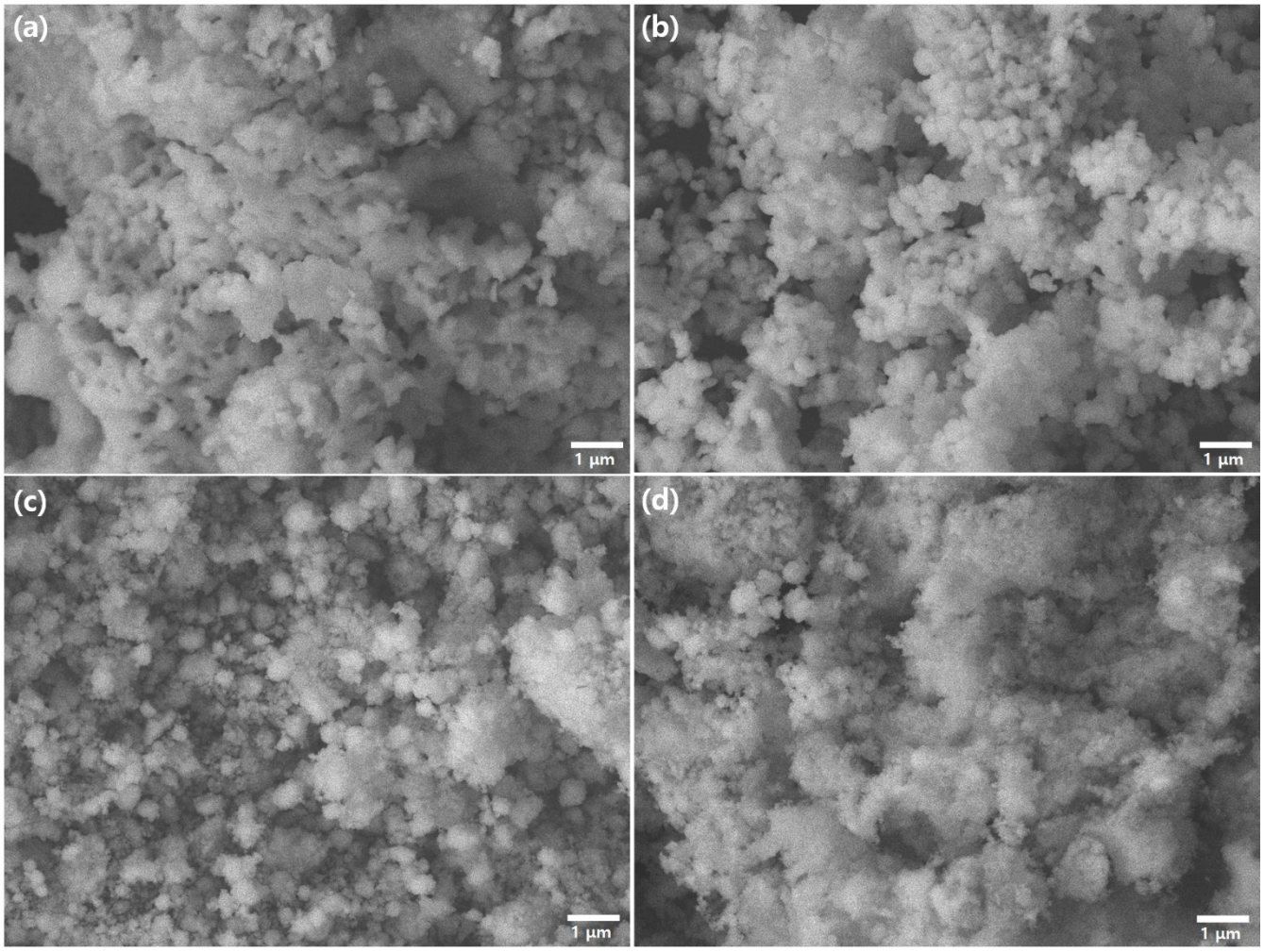

Fig. S8. SEM images of CoNi-R.P.LSCM (a) before and (b) after H_2S poisoning test, and Ni/GDC (c) before and (d) after H_2S poisoning test.

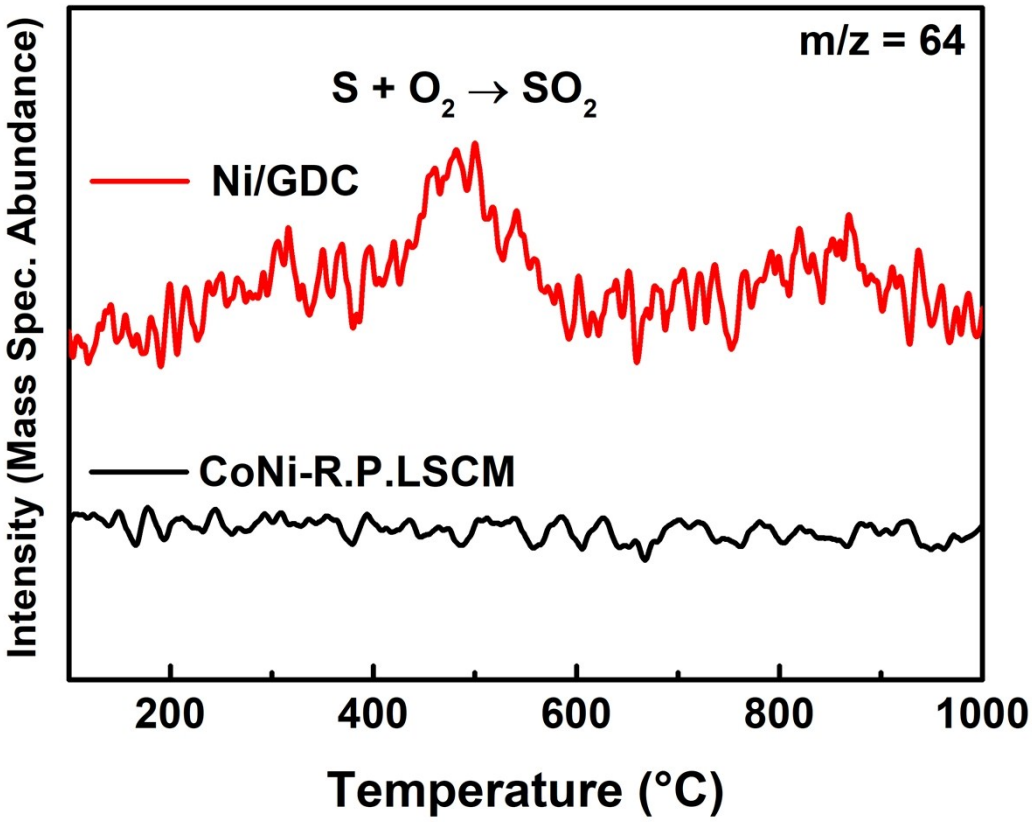

Fig. S9. TPO profiles for the Ni/GDC and CoNi-R.P.LSCM after the poisoning test.

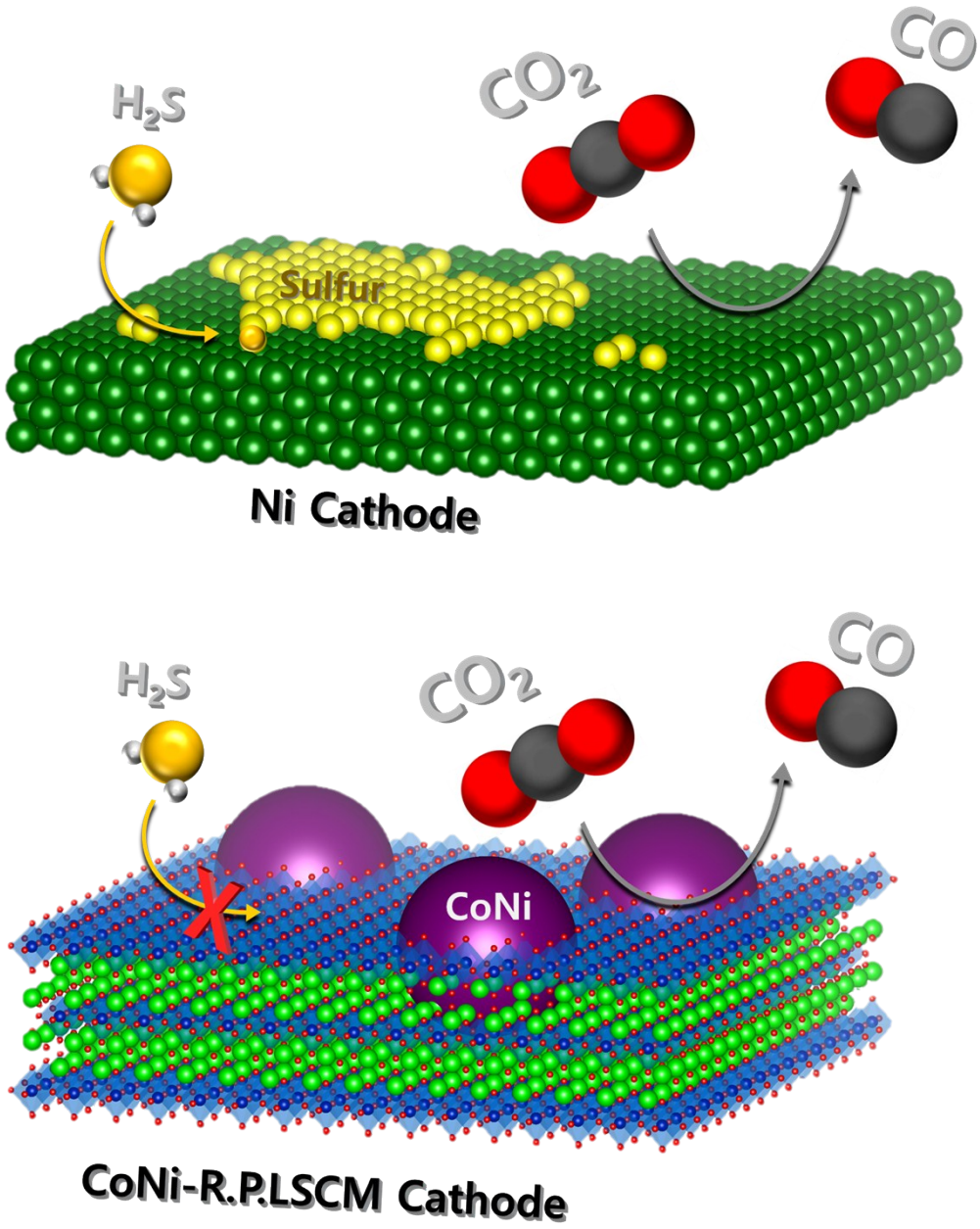

Fig. S10. The schematic of electrochemical CO_2 reduction process in the H_2S-contained CO_2 gas for Ni/GDC and CoNi-R.P.LSCM cathodes

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