Supporting Information

The facilitated cathodic elementary reactions of solid oxide electrolysis cell for CO_2 conversion over Ce decorated $La_{0.43}Ca_{0.37}Ti_{0.94}Ni_{0.06}O_{3-\delta}$ electrocatalyst

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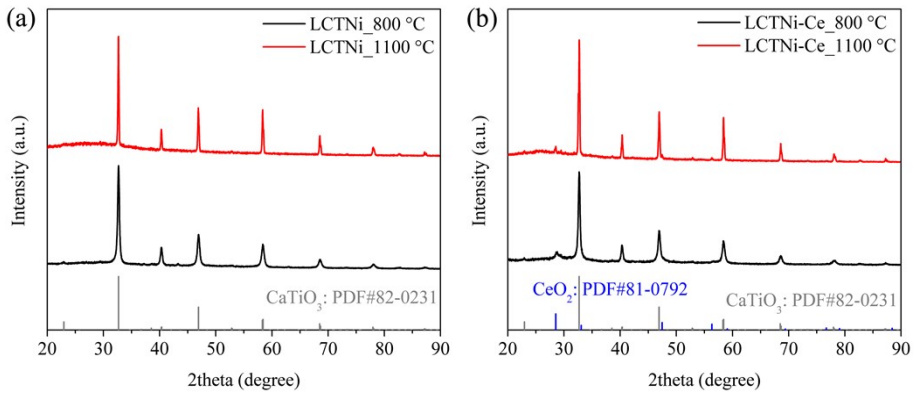

Figure S1. XRD patterns of (a) LCTNi calcined at 800 and 1100 °C for 5 h (denoted as LCTNi_800 °C and LCTNi_1100 °C), and (b) LCTNi-Ce calcined at 800 and 1100 °C for 5 h (denoted as LCTNi-Ce_800 °C and LCTNi-Ce_1100 °C).

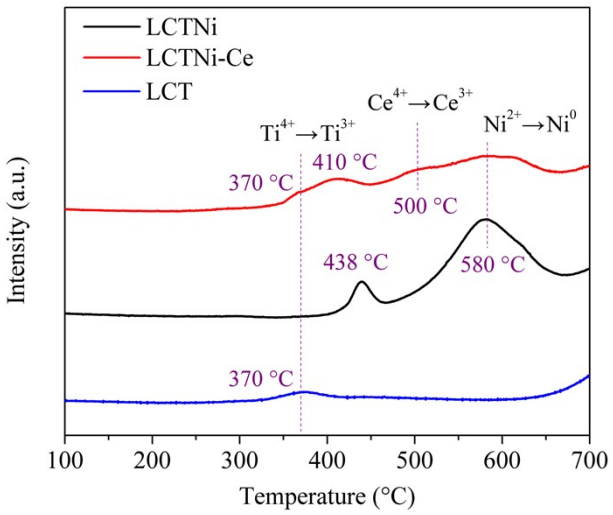

Figure S2. H_2-TPR curves of $La_{0.43}Ca_{0.37}TiO_{3-\delta}$ (LCT), LCTNi and LCTNi-Ce in 5% H_2/N_2 atmosphere ranging from 100 to 700 °C. Given that only Ti species can be reduced in LCT, the H_2 consumption peaks at ~370 °C for LCT, ~438 °C for LCTNi, and ~370 as well as ~410 °C for LCTNi-Ce, are related to the reduction of Ti^{4+} to Ti^{3+} in perovskite phase. The reduction peak at ~580 °C for both LCTNi and LCTNi-Ce is ascribed to the reduction of Ni^{2+} to Ni^0. The extra peak at 500 °C for LCTNi-Ce corresponds to the reduction of Ce^{4+} to Ce^{3+}, which is in agreement with the result of surface CeO_2 reported by Ni et al.[1]

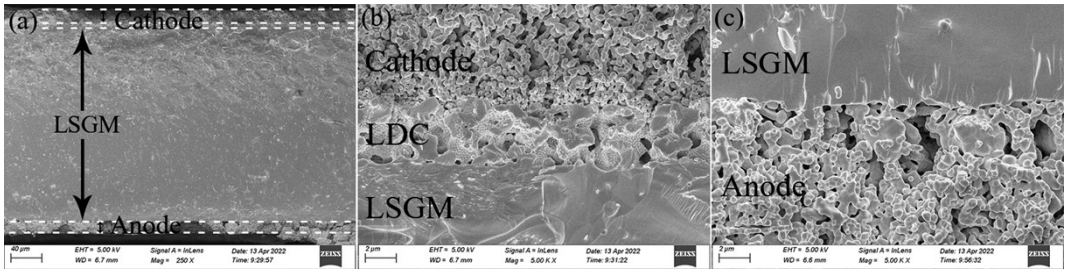

Figure S3. SEM images of the cross-sectional microstructure for (a) LCTNi-Ce||LDC|LSGM||LSCF-GDC|LSCF electrolysis cell, (b) cathode layer and (c) anode layer.

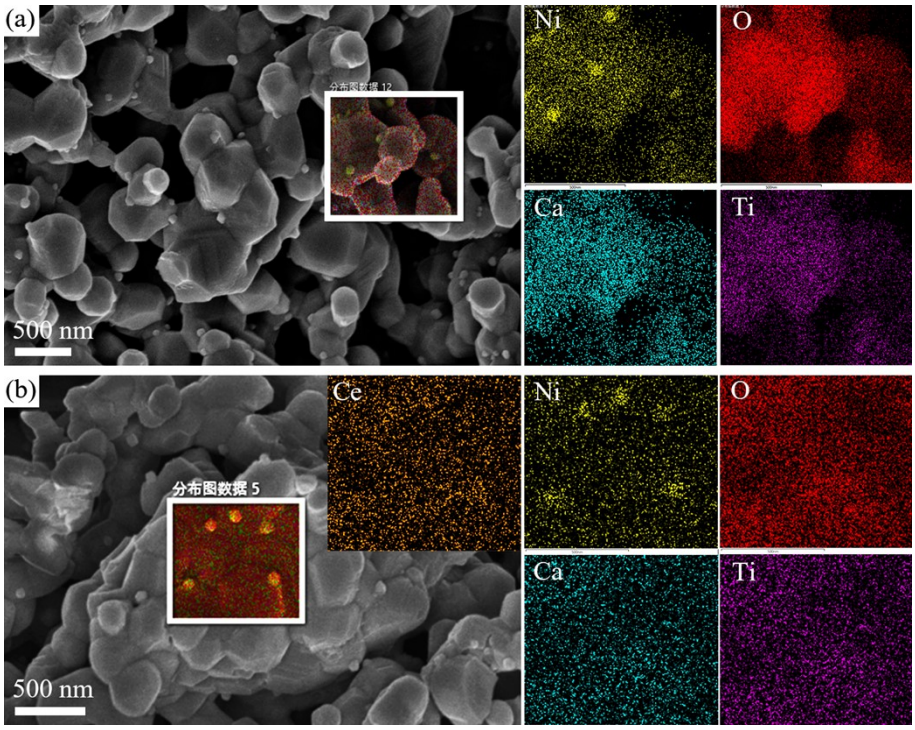

Figure S4. SEM images and EDS mappings (correspond to the selected area in left) of (a) LCTNi and (b) LCTNi-Ce after being reduced at 800 °C for 3 h in pure H_2. For LCTNi-Ce sample, the trumap analysis is applied because the energy window of Ce M_α is overlap with that of Ni L_α.

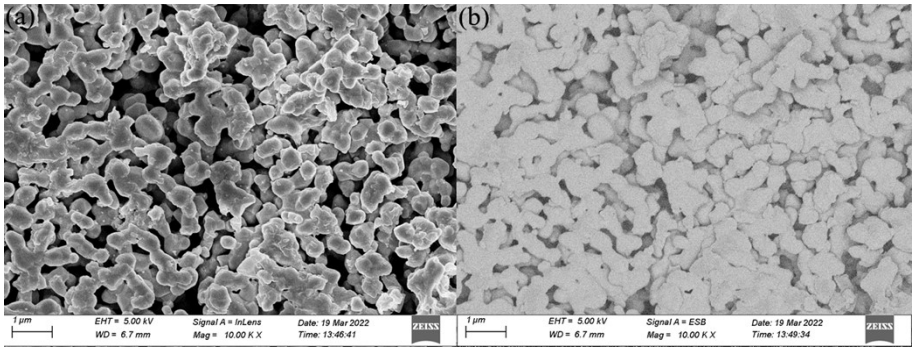

Figure S5. (a) SEM image and (b) BSE result of LCTNi-Ce after being reduced at 800 °C for 3 h in pure H_2.

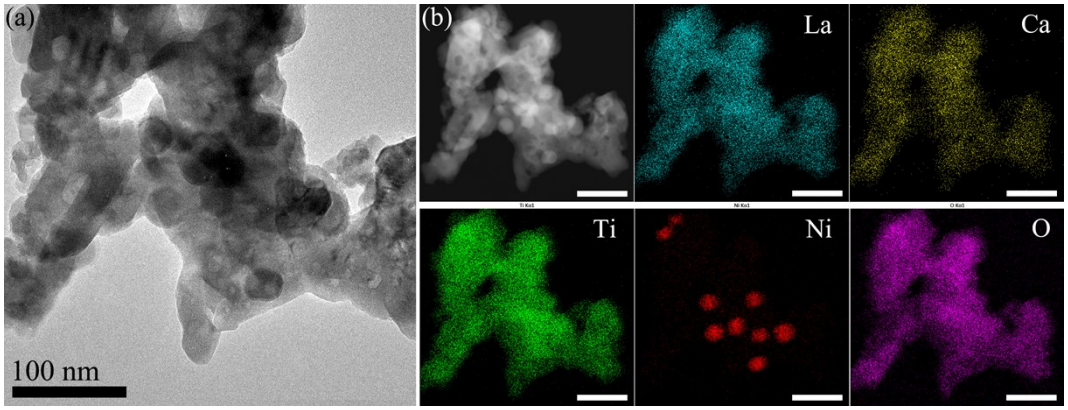

Figure S6. (a) TEM images and (b) HAADF-STEM and EDS mappings of reduced LCTNi powder, where scale bar refers to 100 nm.

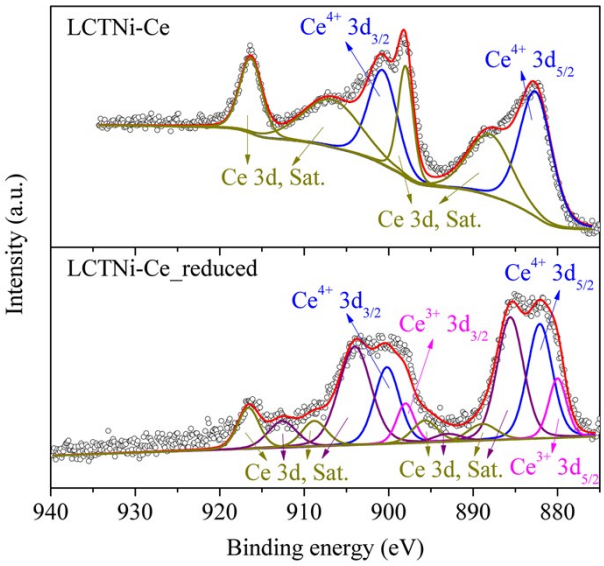

Figure S7. XPS spectra of Ce 3d in LCTNi-Ce before/ after reduction.

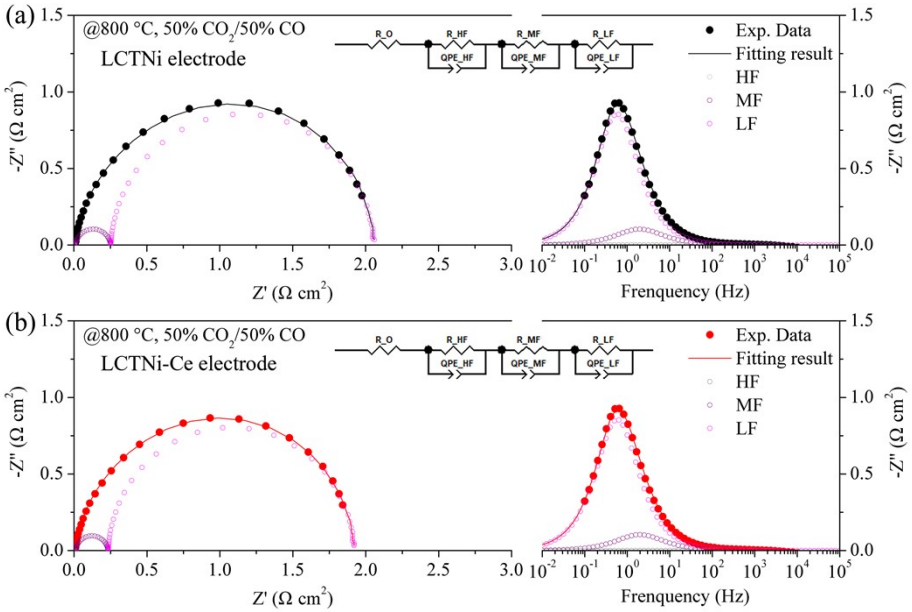

Figure S8. EIS fitting results using an equivalent circuit model of (a) LCTNi||LDC|LSGM|LDC||LCTNi and (b) LCTNi-Ce||LDC|LSGM|LDC||LCTNi-Ce half-cells tested at 800 °C in 50% CO_2/50% CO under OCV condition. All the ohmic resistances were subtracted for clear comparison.

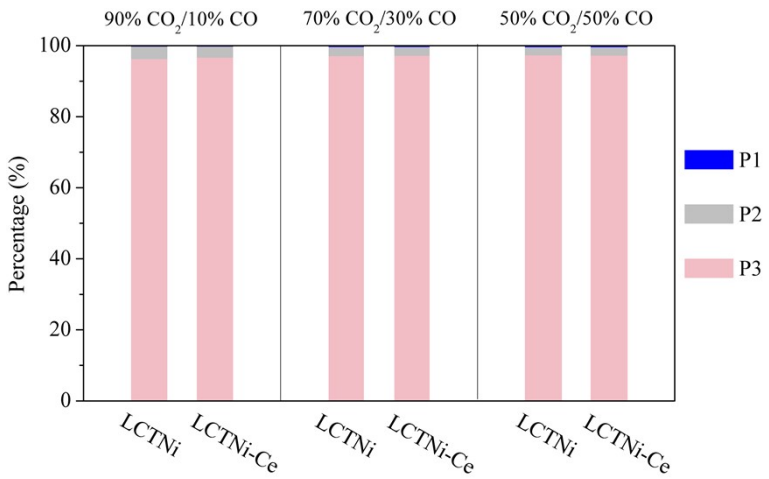

Figure S9. The calculated proportions of P1, P2 and P3 peaks based on the DRT analysis for LCTNi and LCTNi-Ce half-cells tested at 800 °C in the CO_2/CO atmosphere with different ratios under OCV condition.

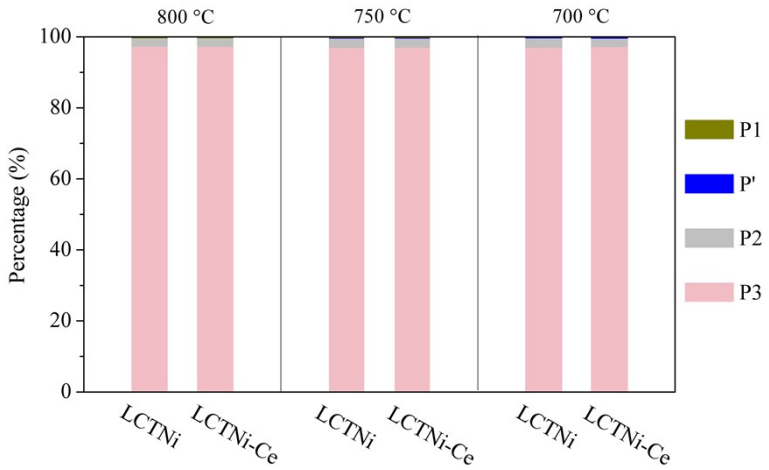

Figure S10. The calculated proportions of P1, P', P2 and P3 peaks based on the DRT analysis for LCTNi and LCTNi-Ce half-cells tested at 800, 750 and 700 °C in 50% CO_2/50% CO under OCV condition.

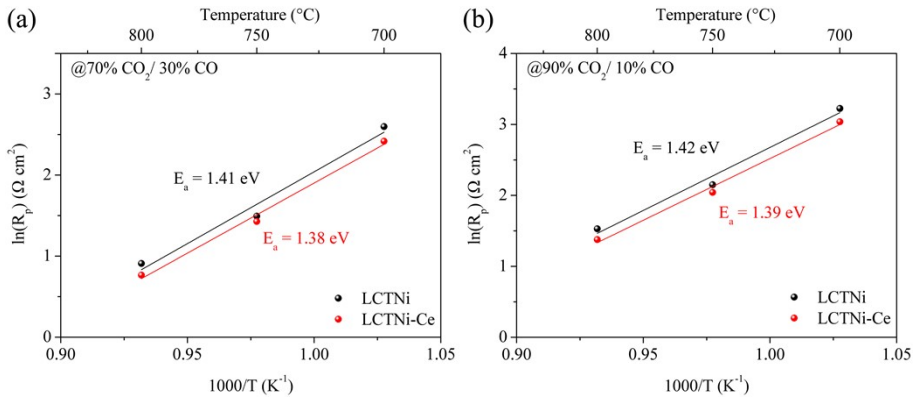

Figure S11. Arrhenius plots of R_p vs. reverse temperature for LCTNi and LCTNi-Ce half-cells tested in (a) 70% CO_2/30% CO and (b) 90% CO_2/10% CO.

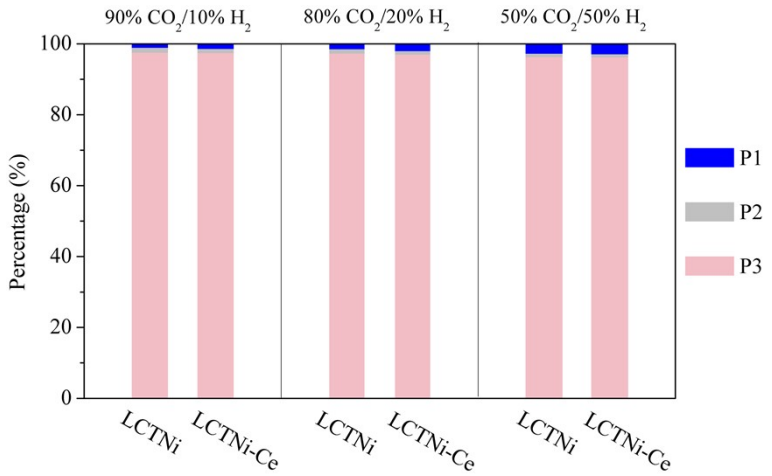

Figure S12. The calculated proportions of P1, P2 and P3 peaks based on the DRT analysis for LCTNi and LCTNi-Ce half-cells tested at 800 °C in the CO_2/H_2 atmosphere with different ratios under OCV condition.

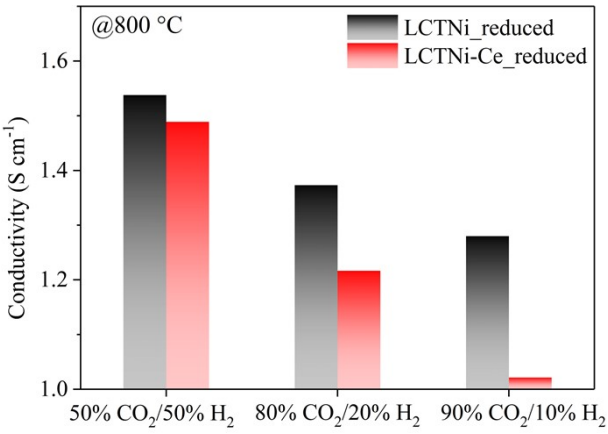

Figure S13. Total conductivities of the reduced LCTNi and LCTNi-Ce electrodes at 800 °C in the CO_2/H_2 atmosphere with different ratios.

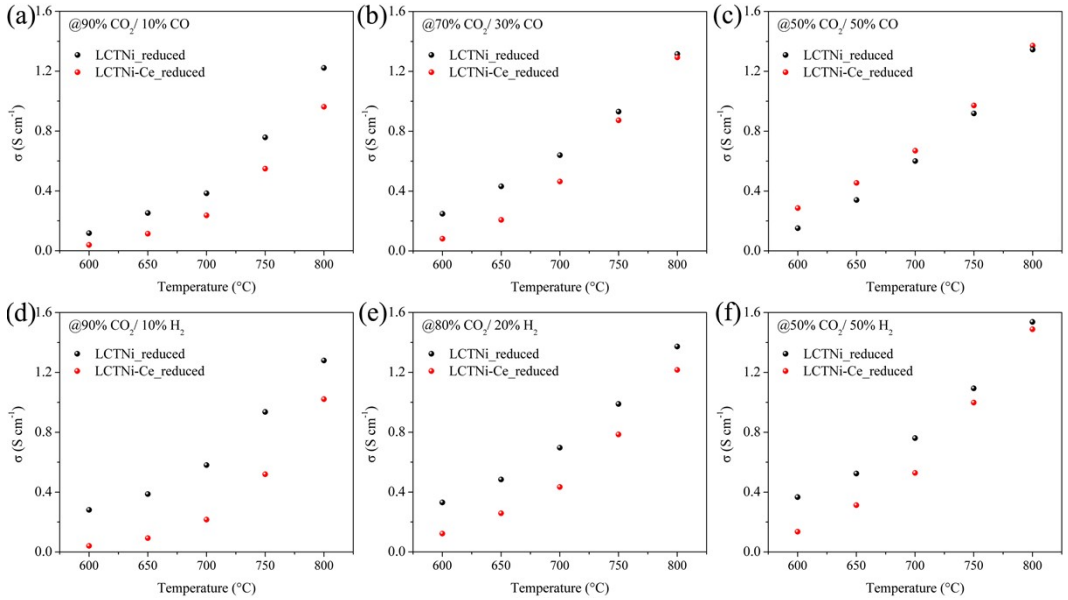

Figure S14. Total conductivities of the reduced LCTNi and LCTNi-Ce electrodes at 800 °C in (a) 90% CO_2/10% CO, (b) 70% CO_2/30% CO, (c) 50% CO_2/50% CO, (d) 90% CO_2/10% H_2, (e) 70% CO_2/30% H_2 and (f) 50% CO_2/50% H_2.

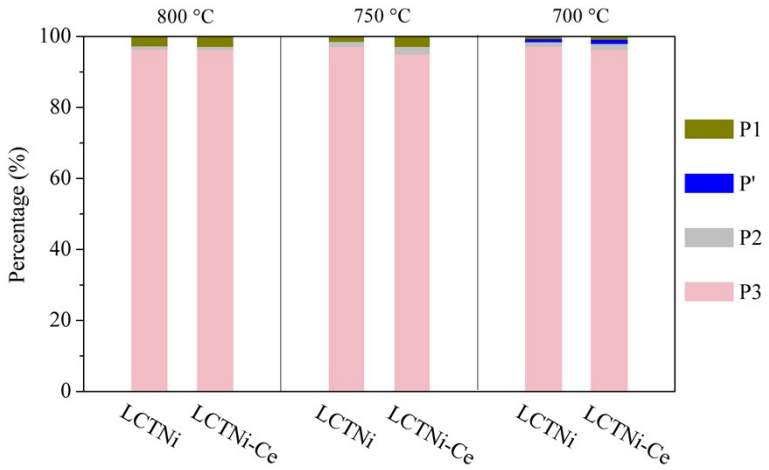

Figure S15. The calculated proportions of P1, P', P2 and P3 peaks based on the DRT analysis for LCTNi and LCTNi-Ce half-cells tested at 800, 750 and 700 °C in 50% CO_2/50% H_2 under OCV condition.

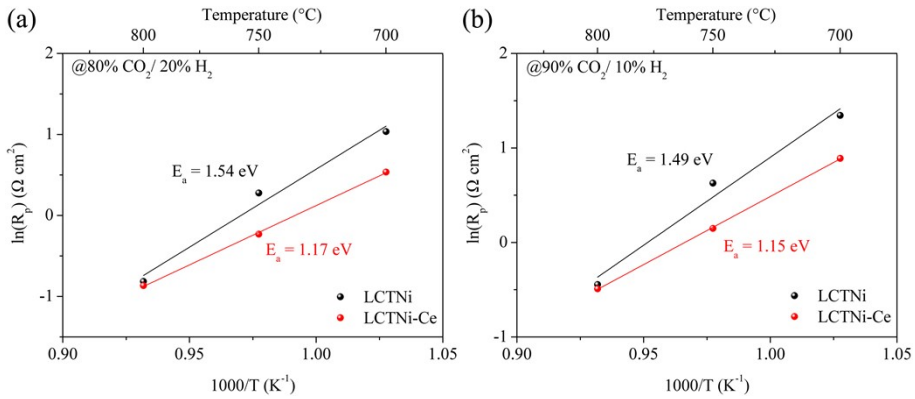

Figure S16. Arrhenius plots of R_p vs. reverse temperature for LCTNi and LCTNi-Ce half-cells tested in (a) 80% CO_2/20% H_2 and (b) 90% CO_2/10% H_2.

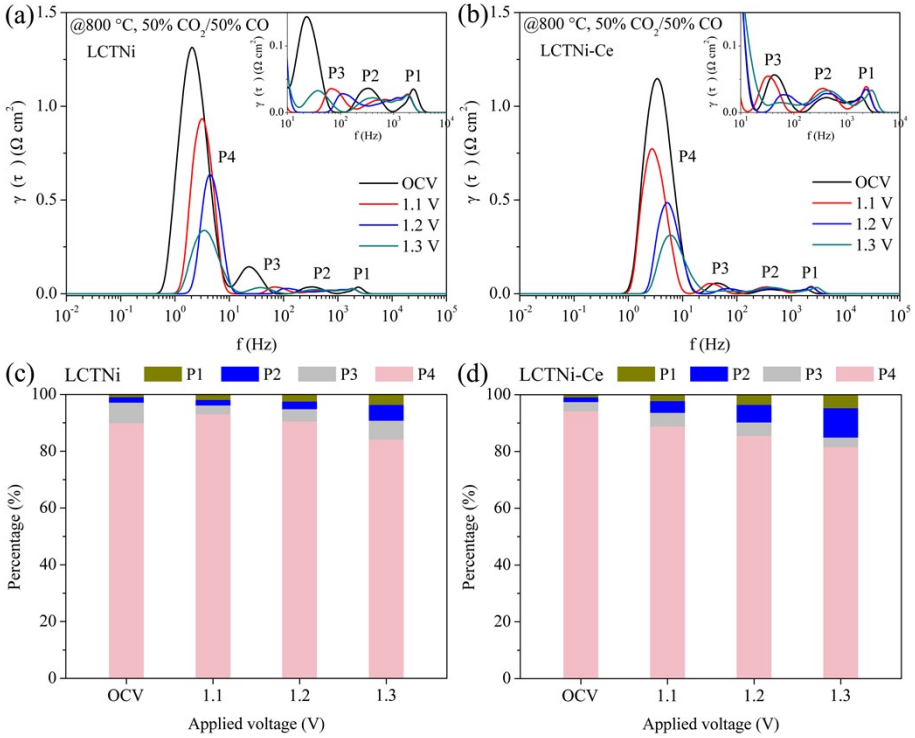

Figure S17. DRT analysis of (a) LCTNi||LDC|LSGM||LSCF-GDC|LSCF and (b) LCTNi-Ce||LDC|LSGM||LSCF-GDC|LSCF electrolysis cells in 50% CO_2/50% CO at 800 °C under OCV condition, as well as voltages of 1.1, 1.2, and 1.3 V. The calculated proportions of P1, P2, P3 and P4 peaks based on the DRT analysis for (c) LCTNi and (d) LCTNi-Ce electrolysis cells.

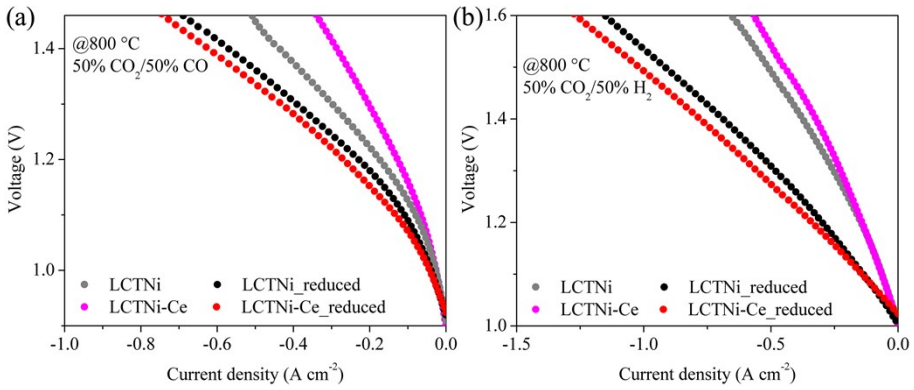

Figure S18. Electrolysis performances of LCTNi||LDC|LSGM||LSCF-GDC|LSCF and LCTNi-Ce||LDC|LSGM||LSCF-GDC|LSCF cells before/ after reduction in (a) 50% CO_2/50% CO and (b) 50% CO_2/50% H_2 at 800 °C.

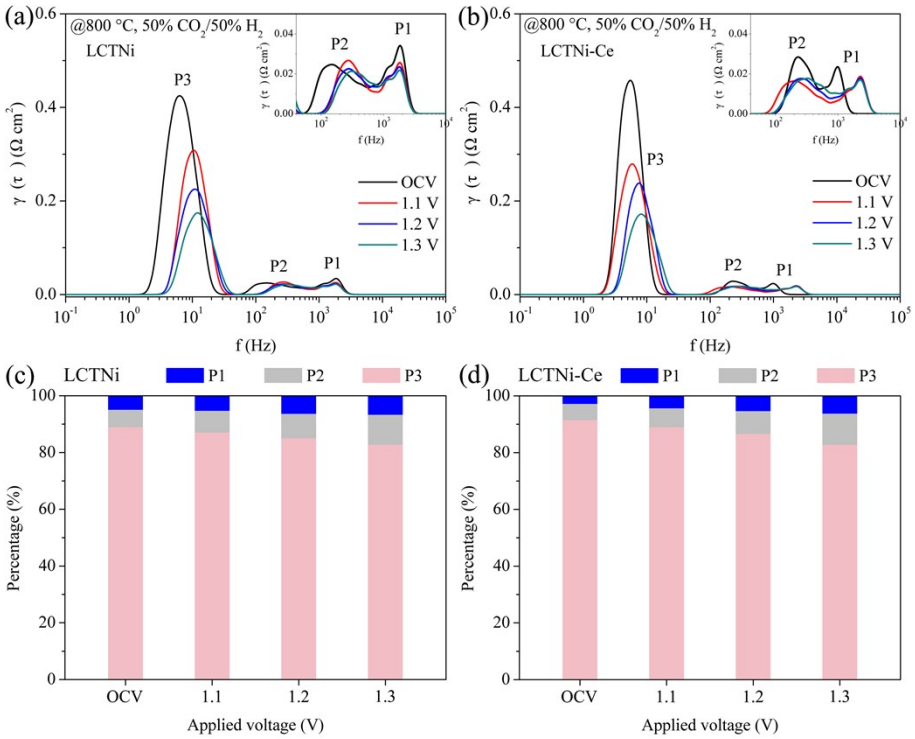

Figure S19. DRT analysis of (a) LCTNi||LDC|LSGM||LSCF-GDC|LSCF and (b) LCTNi-Ce||LDC|LSGM||LSCF-GDC|LSCF electrolysis cells in 50% CO_2/50% H_2 at 800 °C under OCV condition, as well as voltages of 1.1, 1.2, and 1.3 V. The calculated proportions of P1, P2, P3 and P4 peaks based on the DRT analysis for (c) LCTNi and (d) LCTNi-Ce electrolysis cells.

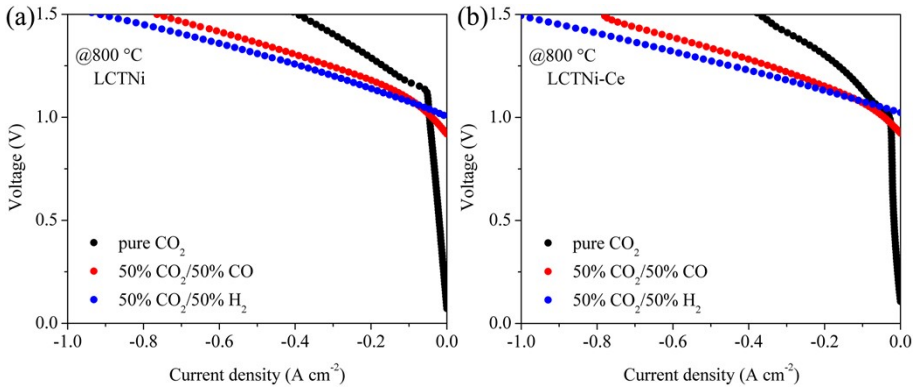

Figure S20. Electrolysis performances of (a) LCTNi||LDC|LSGM||LSCF-GDC|LSCF and (b) LCTNi-Ce||LDC|LSGM||LSCF-GDC|LSCF cells in pure CO_2, 50% CO_2/50% CO and 50% CO_2/50% H_2 at 800 °C.

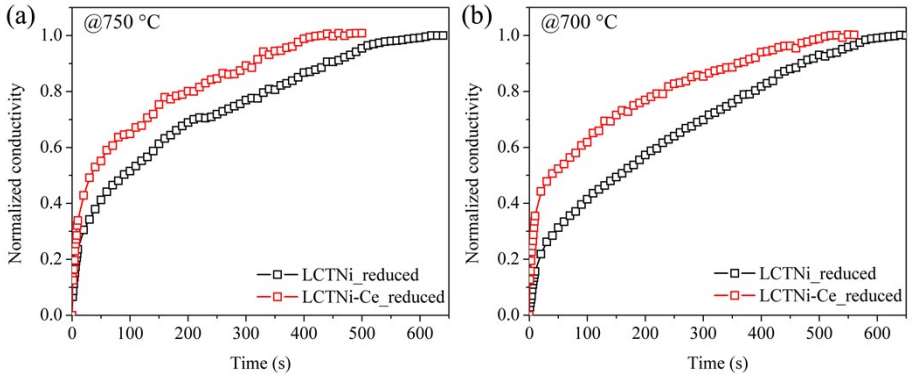

Figure S21. ECR results of reduced LCTNi and LCTNi-Ce porous electrodes at (a) 750 °C and (b) 700 °C with atmosphere quickly switching from 50% CO_2/50% CO to 70% CO_2/30% CO.

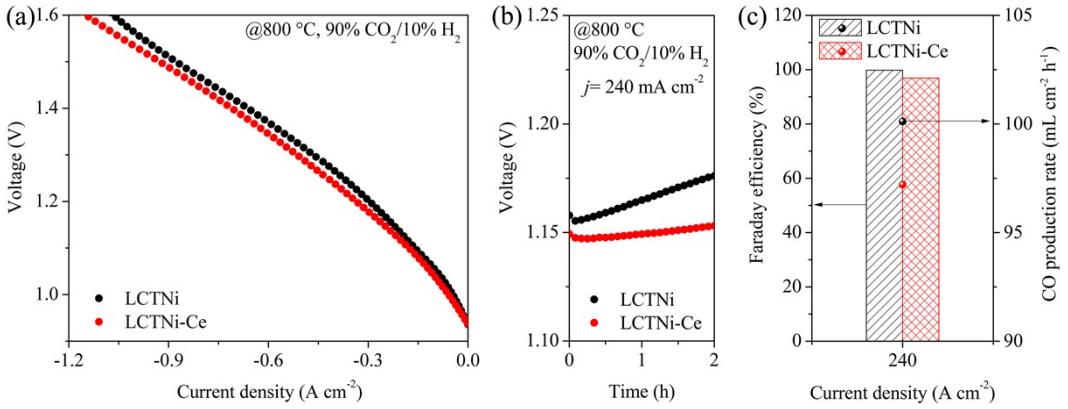

Figure S22. (a) Electrolysis performances of LCTNi||LDC|LSGM||LSCF-GDC|LSCF and LCTNi-Ce||LDC|LSGM||LSCF-GDC|LSCF cells in 90% CO_2/10% H_2 at 800 °C, (b) voltage vs. time of short term operation under constant current of 240 mA cm^{-2}, and (c) the corresponding Faradaic efficiency and CO production rate.

Table S1. Polarization resistances including R_{HF}, R_{MF}, R_{LF} and R_p values of LCTNi and LCTNi-Ce half-cells in the CO_2/CO atmosphere with different ratios at 800 °C under OCV condition.

CO_2/CO ratios	Samples	Resistances (Ω cm^{-2})			
		R_{HF}	R_{MF}	R_{LF}	R_p
90%/10%	LCTNi	0.015	0.605	3.995	4.615
	LCTNi-Ce	0.015	0.462	3.485	3.962
70%/30%	LCTNi	0.011	0.307	2.164	2.482
	LCTNi-Ce	0.011	0.233	1.905	2.149
50%/50%	LCTNi	0.010	0.243	1.805	2.059
	LCTNi-Ce	0.010	0.224	1.685	1.920

Table S2. Polarization resistances including R_{HF}, R_{MF}, R_{LF} and R_p values of LCTNi and LCTNi-Ce half-cells in 50% CO_2/50% CO at 800-700 °C under OCV condition.

Temperature (°C)	Samples	Resistances (Ω cm^{-2})				
		R_{HF}	R_{MF1}	R_{MF2}	R_{LF}	R_p
800	LCTNi	0.010	-	0.243	1.805	2.059
	LCTNi-Ce	0.010	-	0.224	1.685	1.920
750	LCTNi	0.017	0.008	0.328	3.199	3.552
	LCTNi-Ce	0.017	0.008	0.275	3.083	3.383
700	LCTNi	0.023	0.031	0.731	9.545	10.330
	LCTNi-Ce	0.023	0.031	0.408	8.843	9.305

Table S3. Polarization resistances including R_{HF}, R_{MF}, R_{LF} and R_p values of LCTNi and LCTNi-Ce half-cells in the CO_2/H_2 atmosphere with different ratios at 800 °C under OCV condition.

CO_2/H_2 ratios	Samples	Resistances (Ω cm^{-2})			
		R_{HF}	R_{MF}	R_{LF}	R_p
90%/10%	LCTNi	0.006	0.008	0.627	0.641
	LCTNi-Ce	0.008	0.007	0.598	0.613
80%/20%	LCTNi	0.006	0.006	0.431	0.443
	LCTNi-Ce	0.007	0.005	0.408	0.420
50%/50%	LCTNi	0.007	0.004	0.257	0.268
	LCTNi-Ce	0.007	0.003	0.249	0.259

Table S4. Polarization resistances including R_{HF}, R_{MF}, R_{LF} and R_p values of LCTNi and LCTNi-Ce half-cells in 50% CO_2/50% H_2 at 800-700 °C under OCV condition.

Temperature (°C)	Samples	Resistances (Ω cm^{-2})				
		R_{HF}	R_{MF1}	R_{MF2}	R_{LF}	R_p
800	LCTNi	0.007	-	0.004	0.257	0.268
	LCTNi-Ce	0.007	-	0.003	0.249	0.259
750	LCTNi	0.011	-	0.011	0.814	0.836
	LCTNi-Ce	0.018	-	0.010	0.445	0.473
700	LCTNi	0.014	0.014	0.018	1.763	1.809
	LCTNi-Ce	0.010	0.011	0.011	1.065	1.097

Reference

1. Z. Ni, X. Djitcheu, X. Gao, J. Wang, H. Liu and Q. Zhang, *Sci. Rep.*, 2022, **12**, 5344.