

Supplementary materials

High-temperature behavior, oxygen transport properties and electrochemical performance of Cu-substituted Nd_{1.6}Ca_{0.4}NiO_{4+δ} electrode materials

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Table S1. Characteristics of the as-prepared electrode materials of the Nd_{1.6}Ca_{0.4}Ni_{1-y}Cu_yO_{4+δ} series (y = 0.0 – 0.4) (denoted as NCNCO00 – NCNCO04) and materials of the electrode collector layers: structure and unit cell parameters, specific surface area of the powders used for the electrode preparation (*S_{BET}*)

y	0.0	0.1	0.2	0.3	0.4	LaNi _{0.6} Fe _{0.4} O _{3-δ}	La _{0.6} Sr _{0.4} MnO ₃
Notation	NCNCO00	NCNCO01	NCNCO02	NCNCO03	NCNCO04	LNF	LSM
Structure	O*	O	O	O	O	H**	H
Space group	Bmab	Bmab	Bmab	Bmab	Bmab	R-3c	R-3c
a, Å	5.3291(1)	5.3168(1)	5.3063(2)	5.2992(2)	5.2949(2)	5.5071(2)	5.4902(2)
b, Å	5.3775(1)	5.3825(1)	5.3795(2)	5.3743(1)	5.3717(2)	5.5071(2)	5.4902(2)
c, Å	12.2782(1)	12.3114(3)	12.3568(1)	12.3890(4)	12.4476(6)	13.2554(6)	13.3562(5)
V, Å ³	351.861(1)	352.323(2)	352.729(2)	353.089(3)	354.037(3)	402.012(5)	402.587(5)
<i>S_{BET}</i> , m ² /g	2.72(5)	2.62(3)	2.43(7)	3.00(10)	1.98(7)	2.01(3)	2.31(5)

* orthorhombic structure

** hexagonal structure

Table S2. Characteristics of the electrolyte materials: structure and unit cell parameters

Electrolyte	$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$	$\text{BaCe}_{0.8}\text{Sm}_{0.19}\text{Cu}_{0.1}\text{O}_{3-\delta}$	$\text{BaCe}_{0.8}\text{Gd}_{0.19}\text{Cu}_{0.1}\text{O}_{3-\delta}$	$\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Yb}_{0.1}\text{O}_{3-\delta}$
Notation	SDC	BCSCuO	BCGCuO	BCZYYbO
Structure	C*	O**	O	R***
Space group	Fm-3m	Pnma	Pm \bar{c} n	R-3c
a , Å	5.4304(4)	6.2305(9)	6.2521(2)	6.1330(3)
b , Å	-	8.8010(14)	8.7913(1)	6.1330(3)
c , Å	-	6.2268(11)	6.2184(4)	14.9910(1)
V , Å ³	160.138(3)	341.449(7)	341.789(3)	488.290(5)
S_{BET} , m ² /g	2.05(5)	2.77(5)	3.00(10)	2.40(3)

*cubic structure

**orthorhombic structure

*** rhombohedral structure

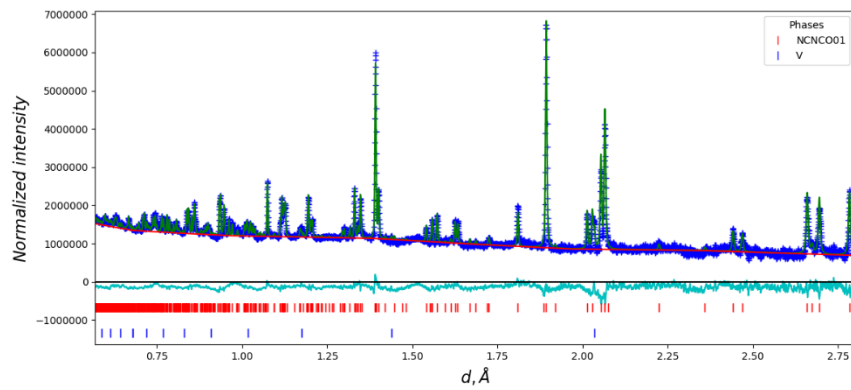


Figure S1. TOF NPD Rietveld refinement results for the NCNCO01 sample before the temperature treatment in air.

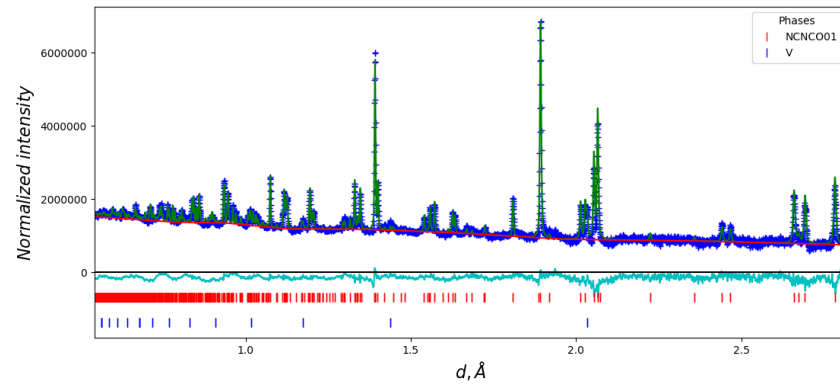


Figure S2. TOF NPD Rietveld refinement results for the NCNCO01 sample after the temperature treatment in air.

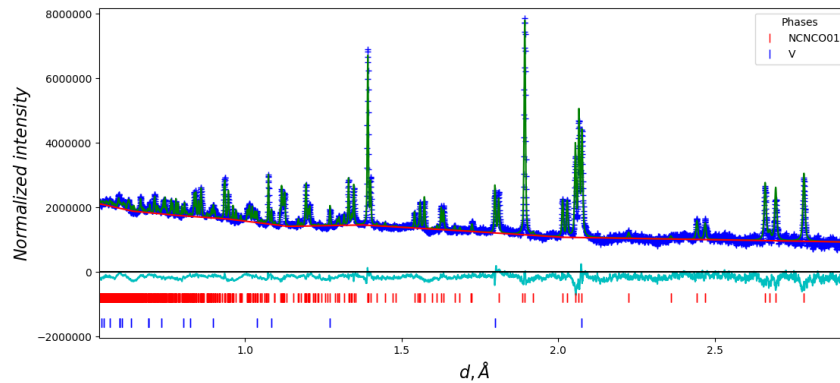


Figure S3. TOF NPD Rietveld refinement results for the NCNCO01 sample before the temperature treatment in a vacuum.

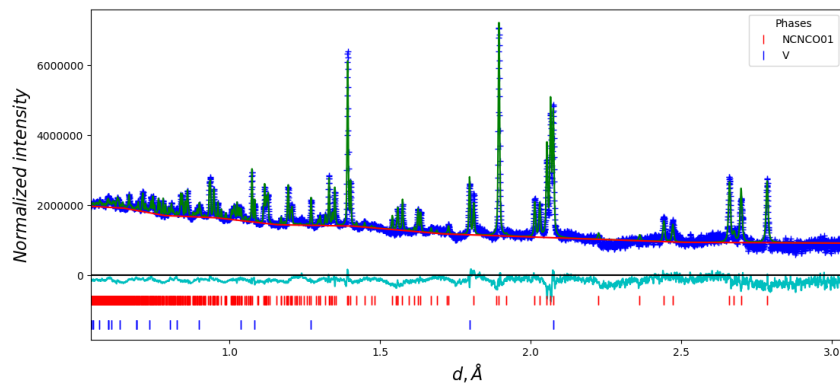


Figure S4. TOF NPD Rietveld refinement results for the NCNCO01 sample after the temperature treatment in a vacuum.

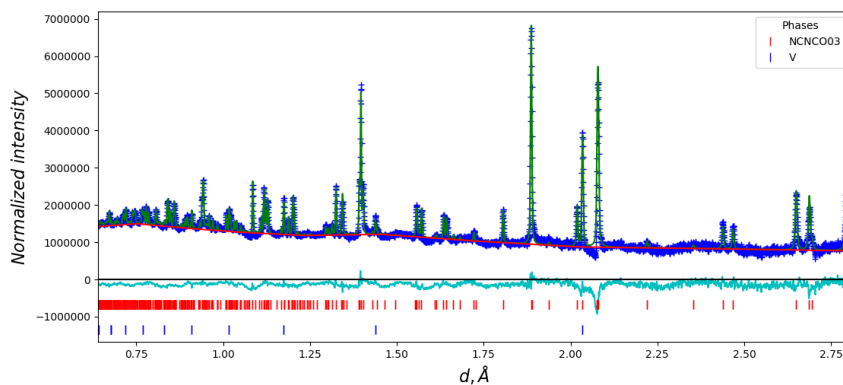


Figure S5. TOF NPD Rietveld refinement results for the NCNCO03 sample before the temperature treatment in air.

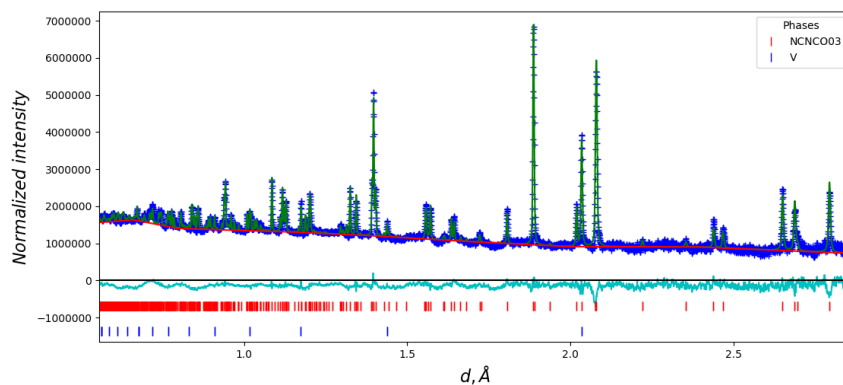


Figure S6. TOF NPD Rietveld refinement results for the NCNCO03 sample after the temperature treatment in air.

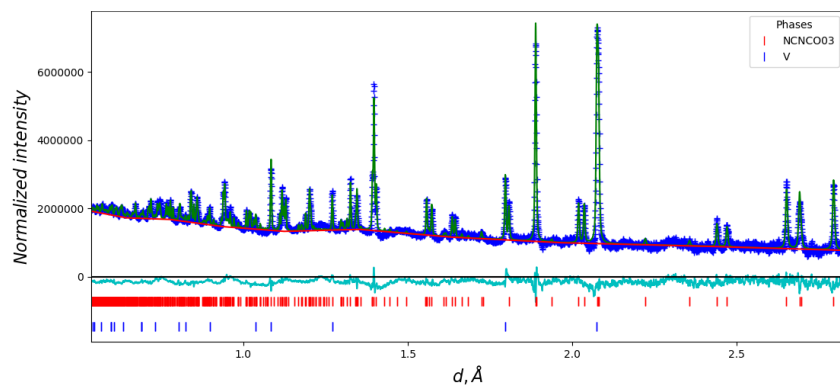


Figure S7. TOF NPD Rietveld refinement results for the NCNCO03 sample before the temperature treatment in a vacuum.

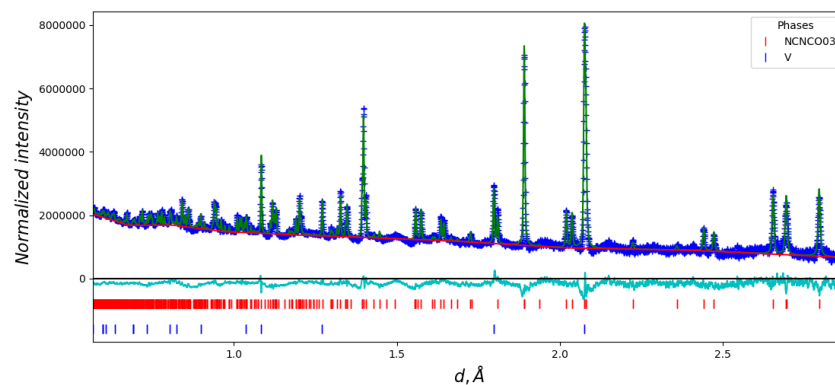


Figure S8. TOF NPD Rietveld refinement results for the NCNCO03 sample after the temperature treatment in a vacuum.

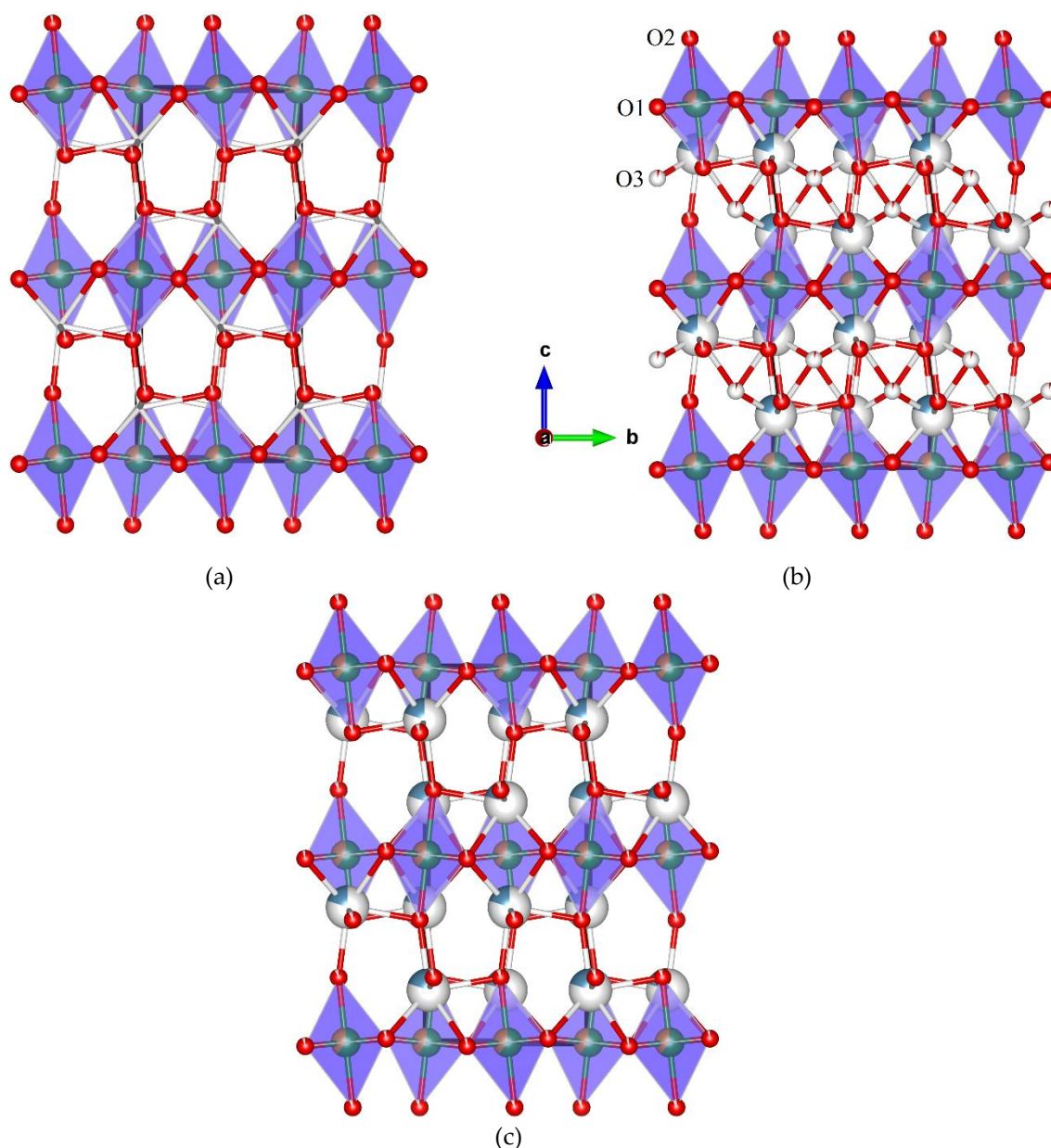


Fig. S9. Visualization of the structure (software package VESTA [70]) with structural parameters presented in Table 2, 3. The NCNCO03 sample after synthesis – (a), The NCNCO03 sample after high-temperature treatment in static air – (b), The NCNCO04 sample after high-temperature treatment in static air – (c). On the picture the oxygen atoms are presented in red color, Ni/Cu in green (with orange part), Nd/Ca in white (with blue part). Partial coloring of the atom represents occupancies of the site.

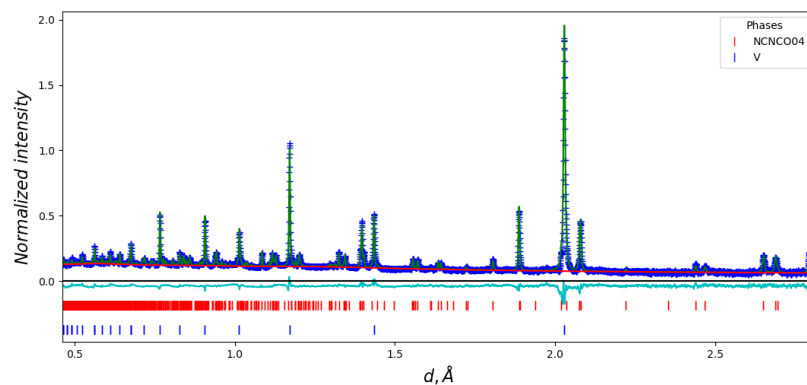


Figure S10. TOF NPD rietveld refinement results for the NCNCO04 sample before the temperature treatment in air.

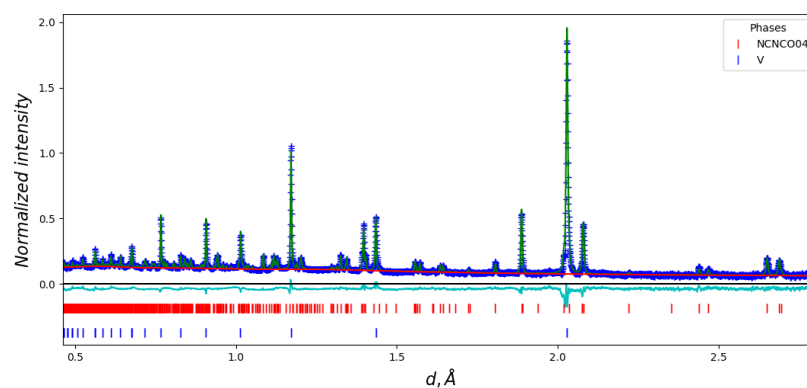
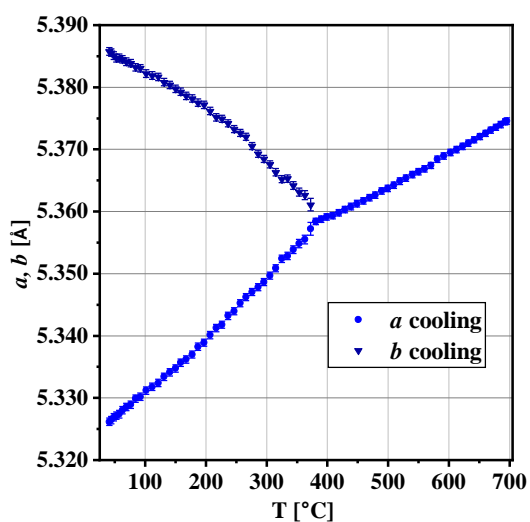
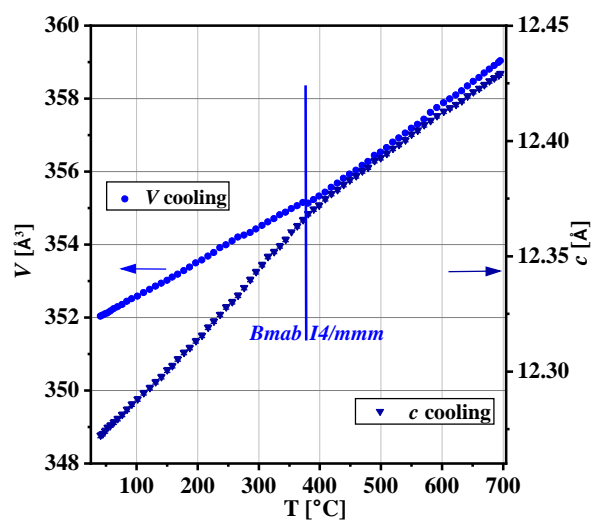


Figure S11. TOF NPD Rietveld refinement results for the NCNCO04 sample after the temperature treatment in air.

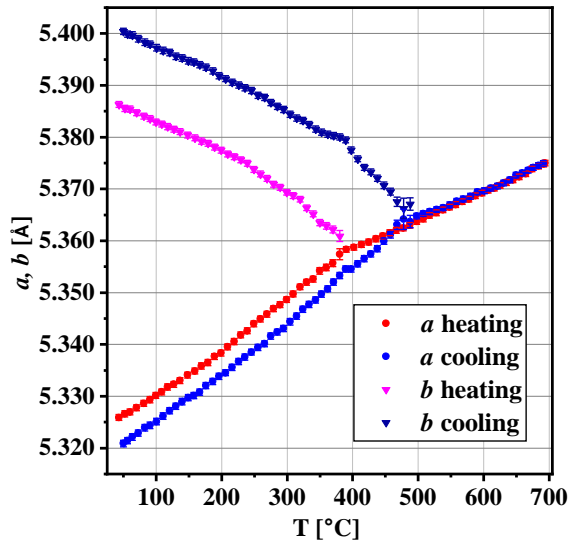


(a)

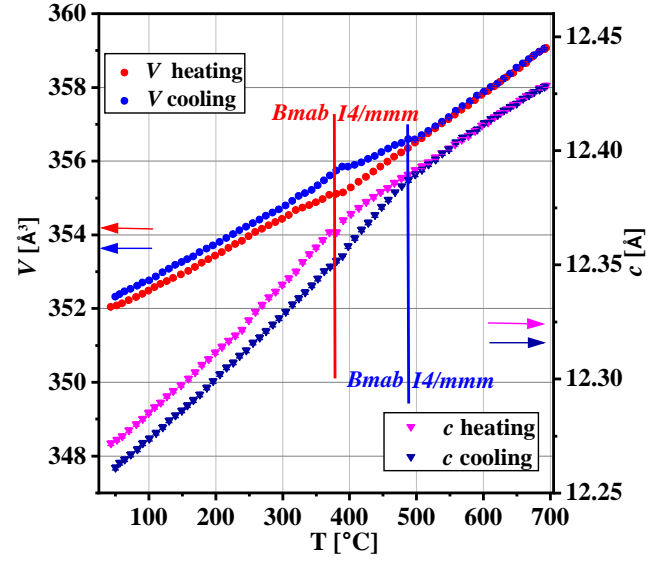


(b)

Figure S12. Changes in the a and b lattice parameters upon cooling in the air flow (a); the unit cell volume and the c parameter change (b) for the NCNCO00 sample.

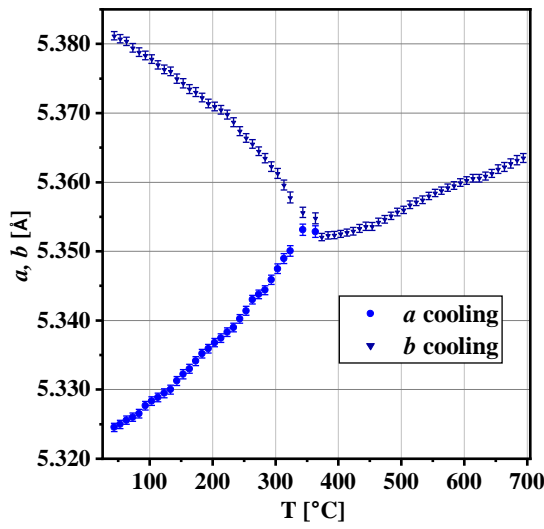


(a)

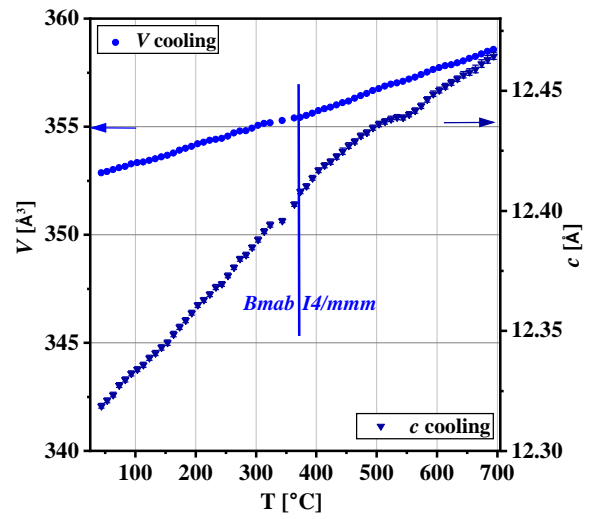


(b)

Figure S13. Changes in the a and b lattice parameters upon heating/cooling in the He flow (a); the unit cell volume and the c parameter change (b) for the NCNCO00 sample.



(a)



(b)

Figure S14. Changes in the a and b lattice parameters upon cooling in the air flow (a); the unit cell volume and the c parameter change (b) for the NCNCO01 sample.

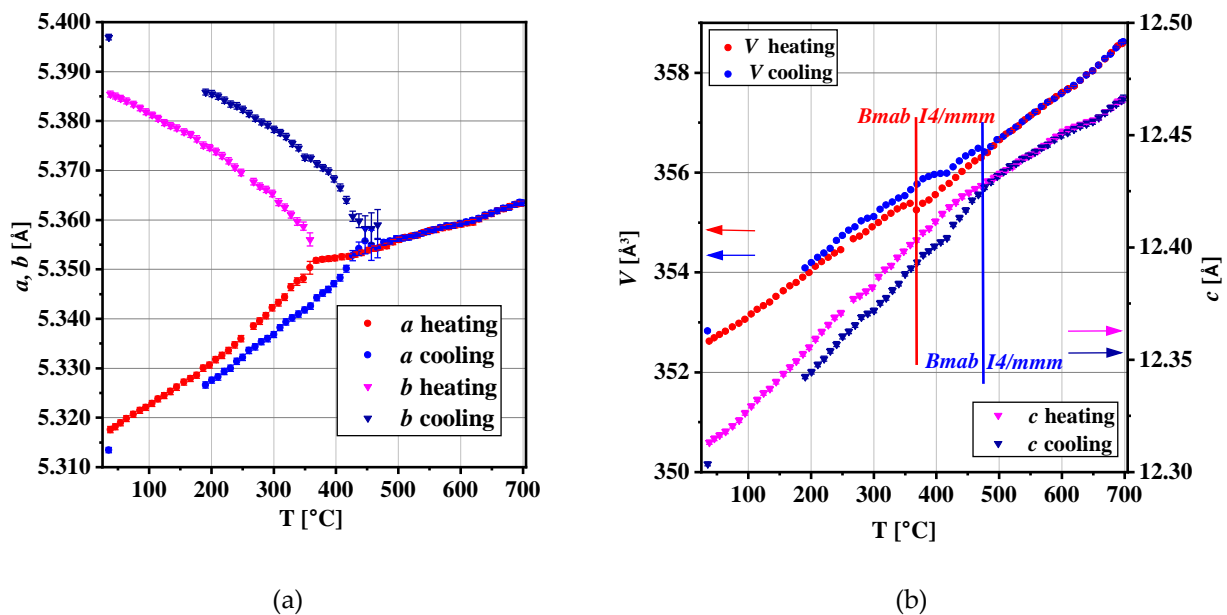


Figure S15. Changes in the a and b lattice parameters upon heating/cooling in the He flow (a); the unit cell volume and the c parameter change (b) for the NCNCO01 sample.

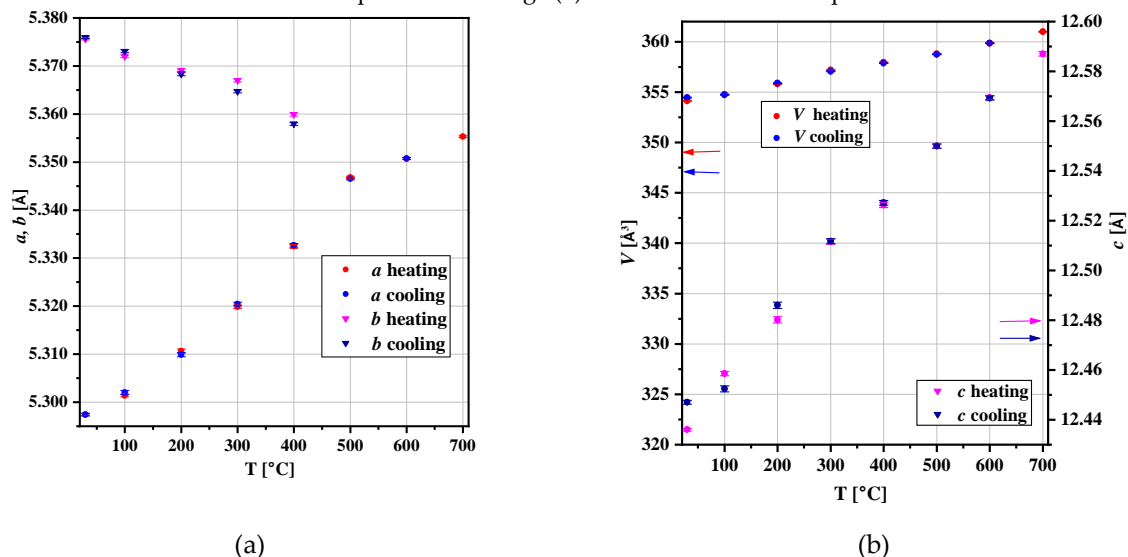


Figure S16. Changes in the a and b lattice parameters upon heating/cooling in the air flow (a); the unit cell volume and the c parameter change (b) for the NCNCO03 sample.

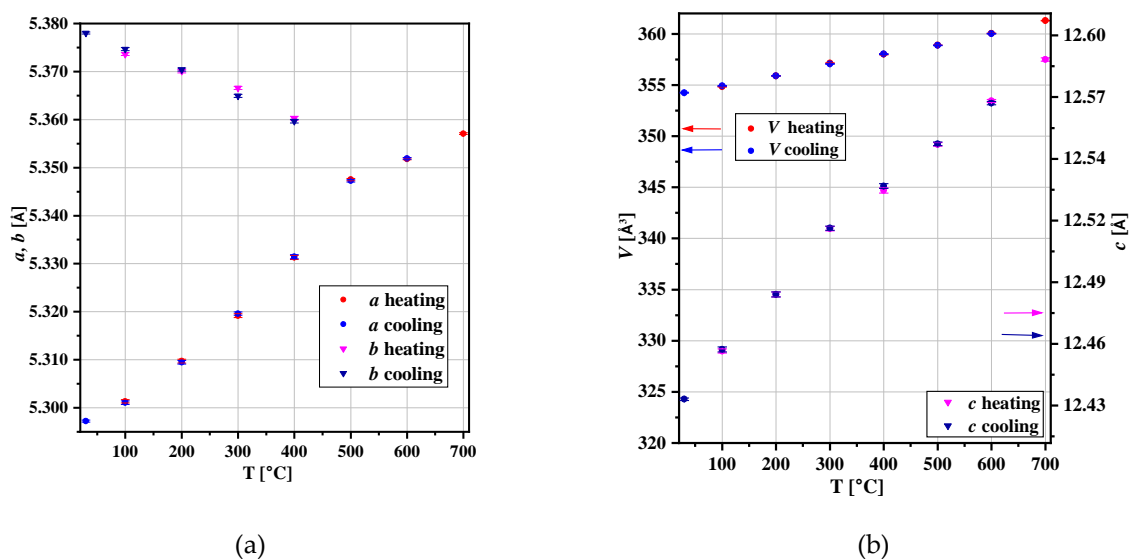


Figure S17. Changes in the a and b lattice parameters upon heating/cooling in the He flow (a); the unit cell volume and the c parameter change (b) for the NCNCO03 sample.

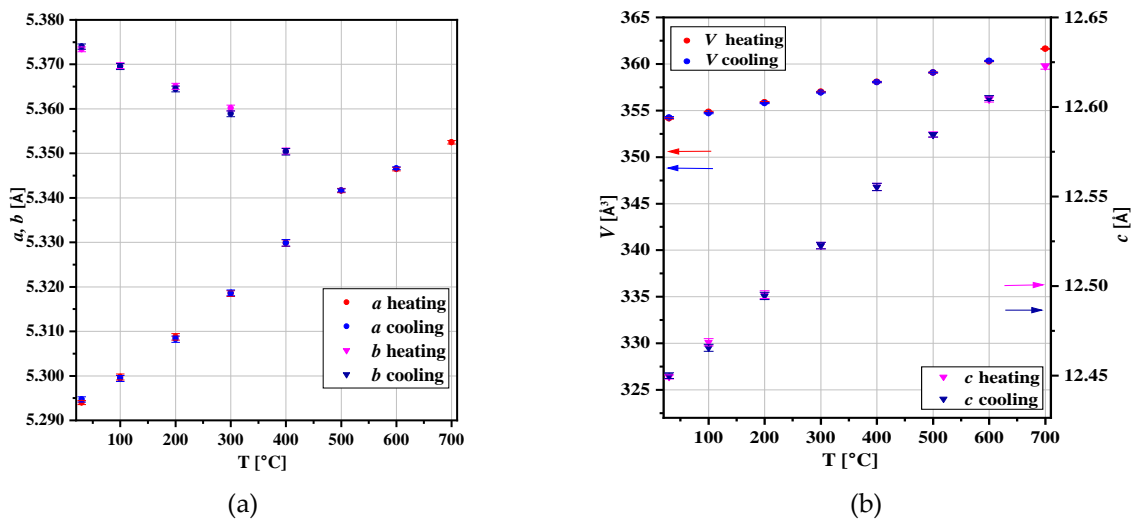


Figure S18. Changes in the a and b lattice parameters upon heating/cooling in the air flow (a); the unit cell volume and the c parameter change (b) for the NCNCO04 sample.

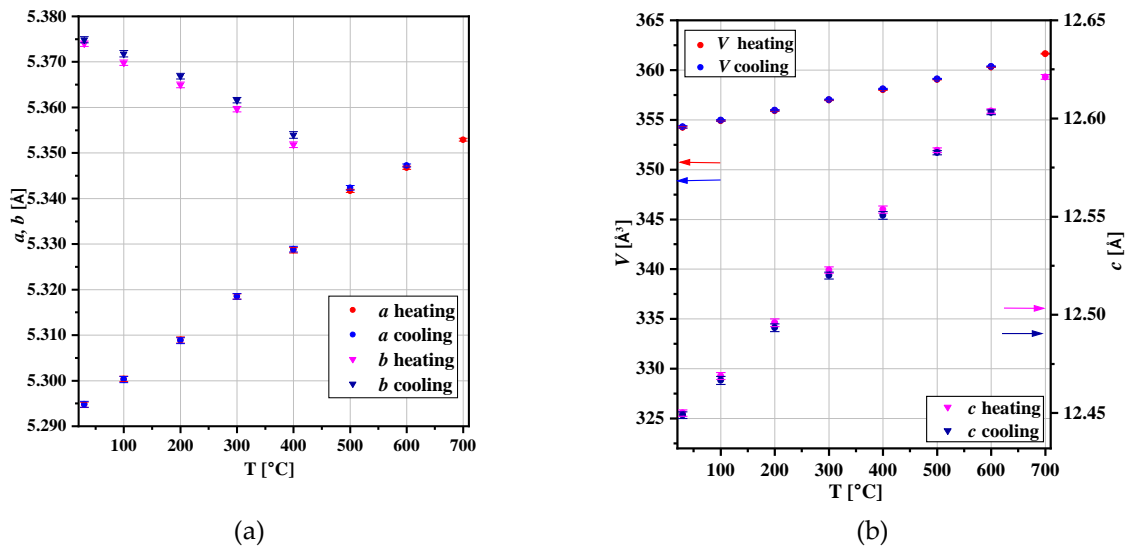


Figure S19. Changes in the a and b lattice parameters upon heating/cooling in the He flow (a); the unit cell volume and the c parameter change (b) for the NCNCO04 sample.

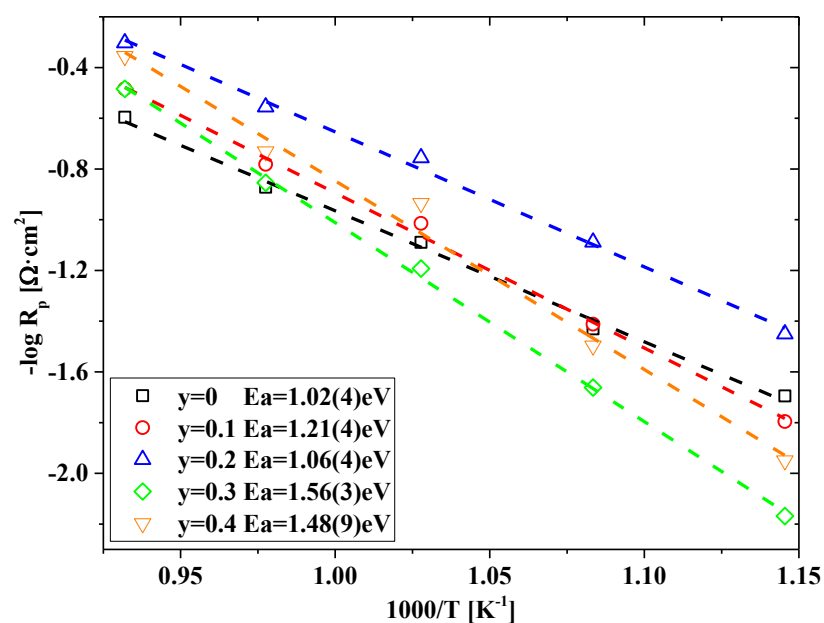


Figure S20. Temperature dependences of the polarization conductivity obtained by the impedance spectroscopy method for the $\text{Nd}_{1.6}\text{Ca}_{0.4}\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta}/\text{SDC}$ symmetrical cells with functional layers sintered at 1000 °C.

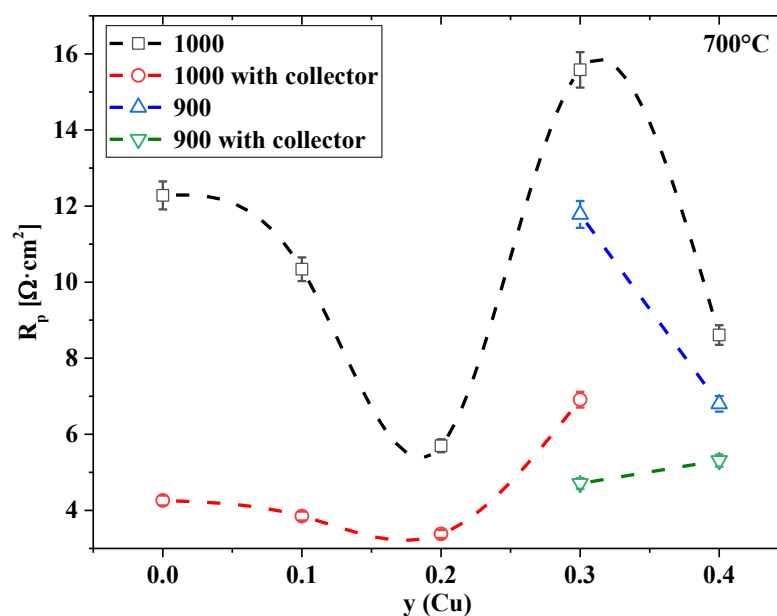
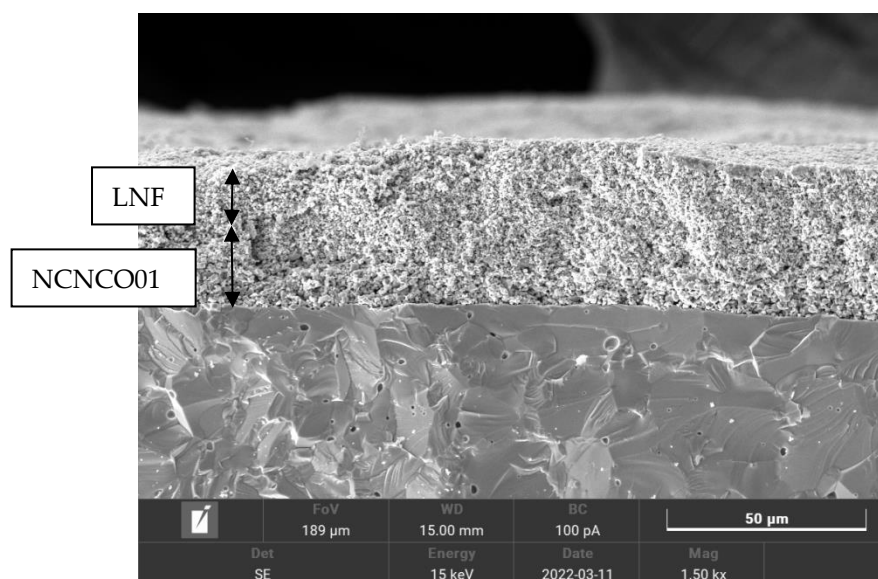
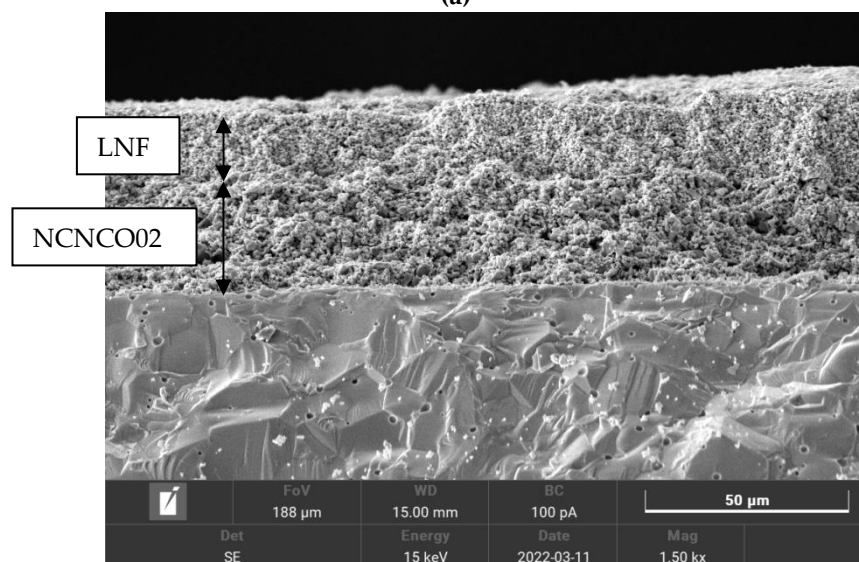


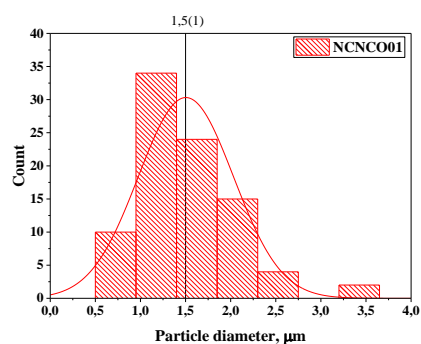
Figure S21. Concentration dependences of polarization resistance for the NCNCO electrodes without and with LNF+3 wt.% CuO collector. The sintering temperatures of the functional layers are shown in Legend (900 or 1000 °C), the sintering temperature of the collector layers – 900 °C.



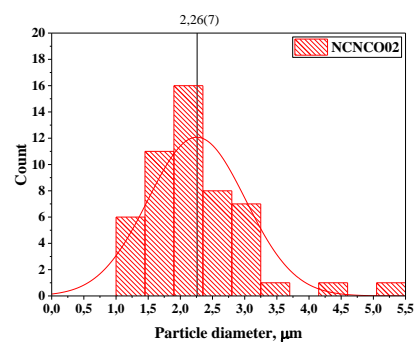
(a)



(b)

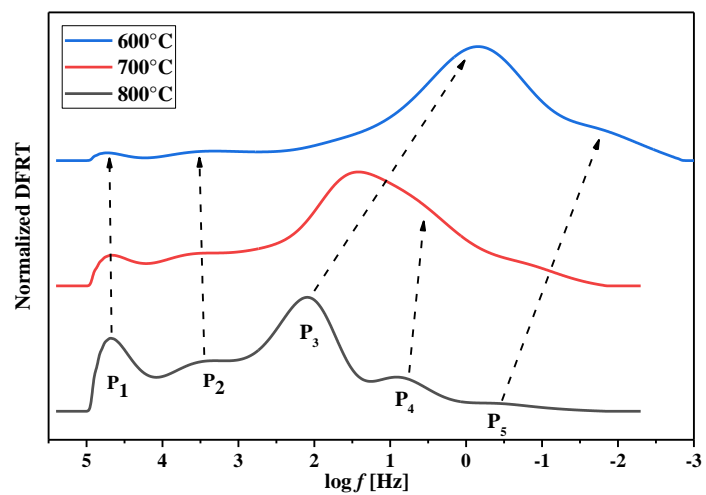


(c)

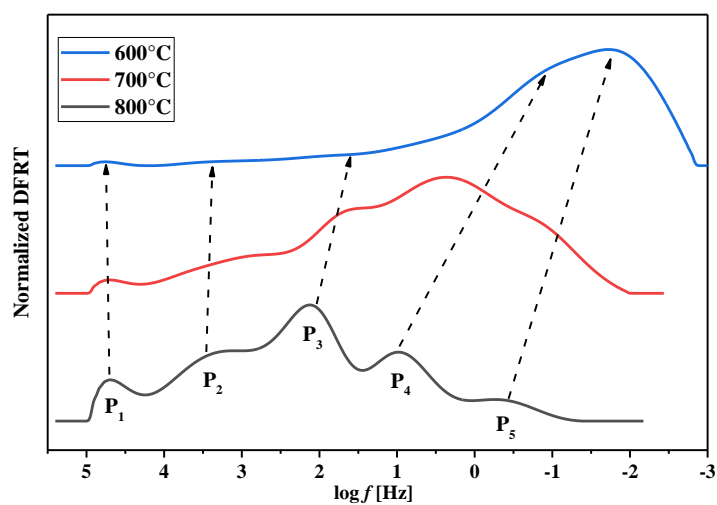


(d)

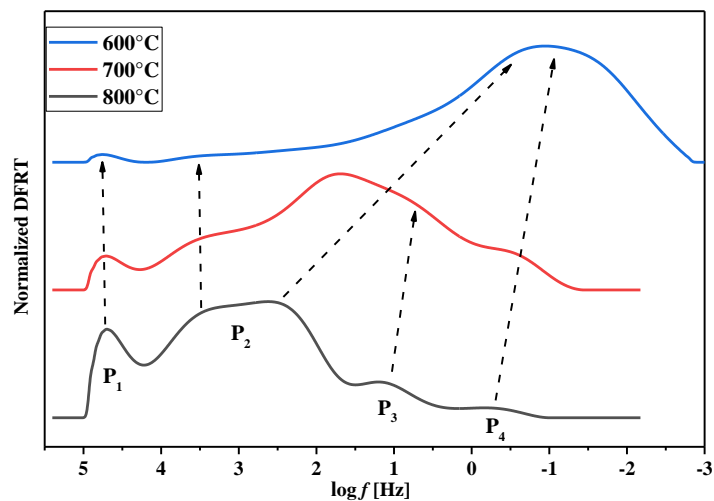
Figure S22. SEM images and calculation of the average particle sizes for NCNCO01 and NCNCO02-based electrodes with the LNF + 3wt.% CuO collector layer. The sintering temperatures of the functional layers is 1000 °C, the sintering temperature of the collector layers is 900 °C.



(a)

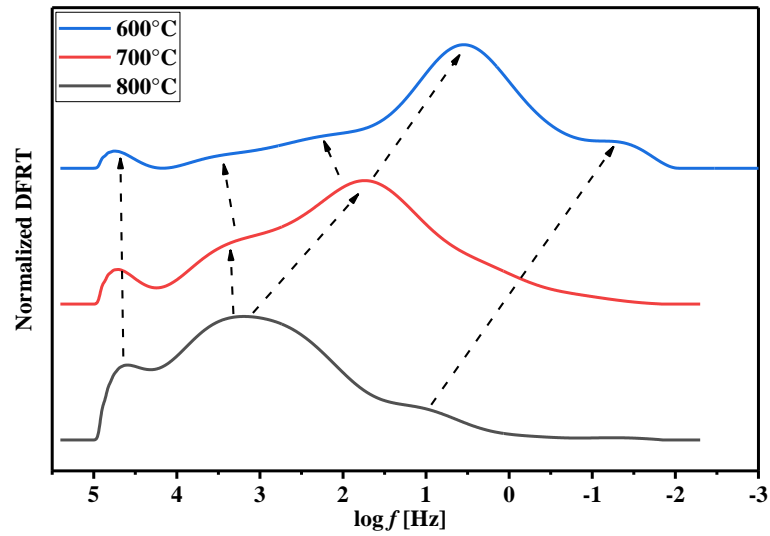


(b)

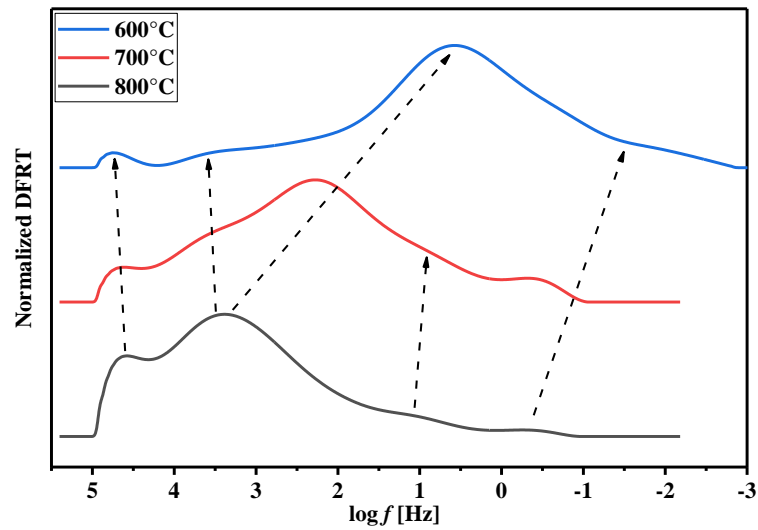


(c)

Figure S23. DFRTs obtained from the EIS data (at 600 – 800 °C) for the symmetrical cells with the functional layers sintered at 1000 °C: NCNCO01 (a); NCNCO03 (b); NCNCO04 (c)



(a)



(b)

Figure S24. Temperature evolution of the DFRTs obtained from the EIS data (at 600-800 °C) for the symmetrical cells with the functional layers sintered at 1000 °C and LNF-based collector, sintered at 900 °C: NCNCO00 (a); NCNCO02 (b)

Table S3. Chemical compatibility of the $\text{Nd}_{1.6}\text{Ca}_{0.4}\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ with different solid state electrolytes.

Electrolyte	900 °C	1000 °C	1100 °C
$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$	-	-	-
$\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$	-	-	-
$\text{BaCe}_{0.8}\text{Gd}_{0.19}\text{Cu}_{0.01}\text{O}_3$	-	-	-
$\text{BaCe}_{0.8}\text{Sm}_{0.19}\text{Cu}_{0.01}\text{O}_{2.9}$	-	-	BaCO_3 (3.7%), $\text{Ba}_2\text{CaCuO}_4$ (1.5%), Ca_2CuO_3 (0.7%)

Table S4 Polarization resistance of Nd₂NiO_{4+δ}-based electrodes

Electrode	Ref.	$R_p, \Omega \cdot \text{cm}^2$ /700, °C	Electrolyte
Nd _{1.8} Sr _{0.2} Ni _{0.6} Cu _{0.4} O _{4+δ}	[92]	0.20	Ce _{0.8} Gd _{0.2} O _{1.9}
Nd _{1.8} La _{0.2} Ni _{0.75} Cu _{0.25} O _{4-δ}	[93]	1.85	Ce _{0.8} Sm _{0.2} O _{1.9}
Nd _{1.8} Ce _{0.2} Cu _{0.5} Ni _{0.5} O _{4+δ}	[94]	0.44	Ce _{0.9} Gd _{0.1} O _{1.95}
Nd ₂ NiO _{4+δ} ¹	[95]	0.46	LSGM ⁴
Nd ₂ NiO _{4+δ} ²	[95]	0.98	
Nd ₂ NiO _{4+δ} ³	[95]	2.43	
Nd ₂ NiO _{4+δ} /LaNi _{0.6} Fe _{0.4} O _{3-δ}	[37]	0.71	Ce _{0.8} Sm _{0.2} O _{1.9}
Nd _{1.6} Ca _{0.4} NiO _{4+δ} /LaNi _{0.6} Fe _{0.4} O _{3-δ}	[37]	0.37	
Nd ₂ NiO _{4+δ}	[96]	1.27	Ce _{0.9} Gd _{0.1} O _{1.95}
Nd _{1.8} Sr _{0.2} NiO ₄	[96]	2.51	
Nd _{1.6} Sr _{0.4} NiO ₄	[96]	0.97	
Nd ₂ NiO _{4+δ}	[41]	1.02	
Nd ₂ Ni _{0.8} Cu _{0.2} O _{4+δ}	[41]	0.51	
Nd ₂ Ni _{0.6} Cu _{0.4} O _{4+δ}	[41]	4.28	Ce _{0.9} Gd _{0.1} O _{1.95}
Nd ₂ Ni _{0.4} Cu _{0.6} O _{4+δ}	[41]	7.80	
Nd ₂ NiO _{4+δ}	[97]	5.11	
Nd _{1.6} Ca _{0.4} NiO _{4+δ} /LaNi _{0.6} Fe _{0.4} O _{3-δ}	This study	4.26	Ce _{0.8} Sm _{0.2} O _{1.9}
Nd _{1.6} Ca _{0.4} Ni _{0.8} Cu _{0.2} O _{4+δ} /LaNi _{0.6} Fe _{0.4} O _{3-δ}	This study	3.37	
Nd ₂ NiO _{4+δ}	[98]	8.47	BCZYYbO ⁵
Nd _{1.8} Ba _{0.2} NiO ₄	[98]	3.20	
Nd _{1.9} Ba _{0.1} NiO ₄	[98]	1.78	
Nd ₂ NiO _{4+δ}	[99]	7.50	BaCe _{0.9} Y _{0.1} O _{3-δ}
Nd _{1.6} Ca _{0.4} Ni _{0.8} Cu _{0.2} O _{4+δ} /La _{0.6} Sr _{0.4} MnO ₃	This study	2.74	BCZYYbO
Nd _{1.6} Ca _{0.4} Ni _{0.8} Cu _{0.2} O _{4+δ} /La _{0.6} Sr _{0.4} MnO ₃	This study	3.23	BCGCuO

¹ obtained via a hexamethylenetetramine route² obtained via a citrate-nitrate route³ obtained via a solid-state reaction technique⁴ La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}⁵ BaCe_{0.5}Zr_{0.3}Y_{0.1}O_{3-δ}⁶ BaCe_{0.80}Gd_{0.19}Cu_{0.10}O_{3-δ}