Supporting information

A Novel Strategy of Entropy Engineering at the A-Site in Spinel Oxides for Developing High-Performance SOFC Cathodes

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Supplemented figures

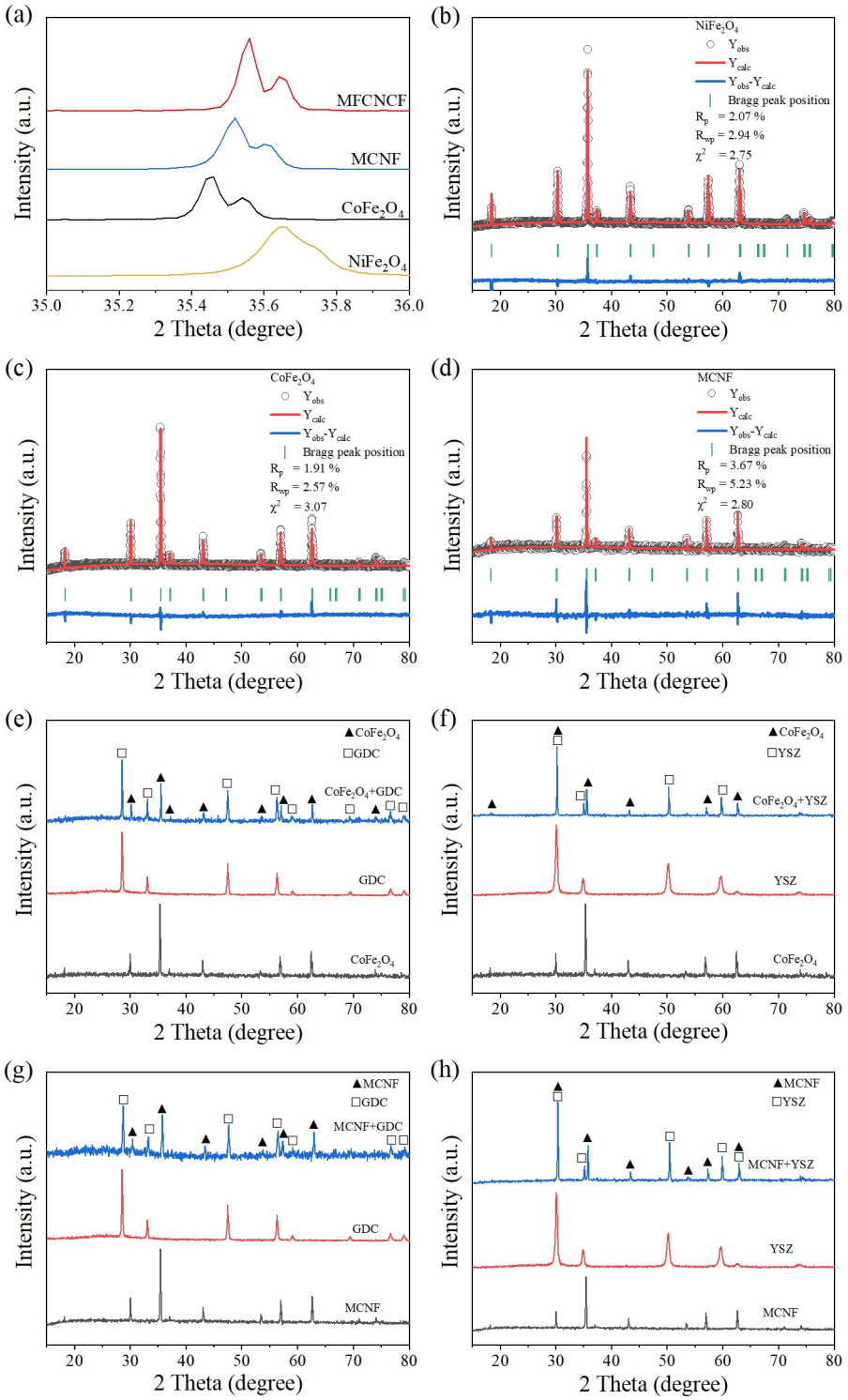
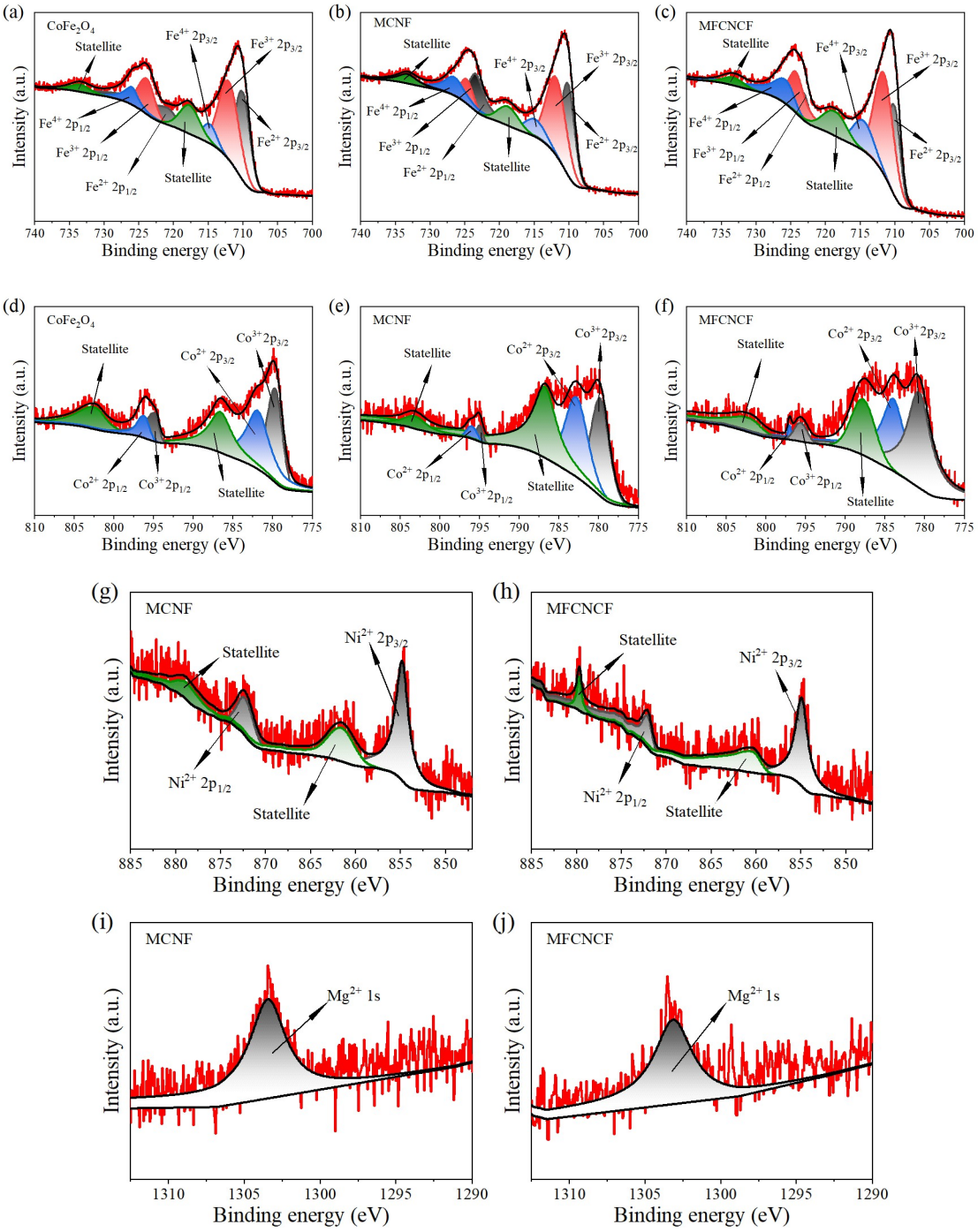


Fig. S1 (a) A magnification of the same XRD from 35.28° to 36.28° of 2θ; The Rietveld refinement patterns of pristine $NiFe_2O_4$ (b), $CoFe_2O_4$ (c) and MCNF (d); Chemical compatibility of $CoFe_2O_4$ (e-f) and MCNF (g-h).


(a)
CoFe2O4
Satellite
Fe4+ 2p3/2
Fe3+ 2p3/2
Fe4+ 2p1/2
Fe3+ 2p1/2
Fe2+ 2p3/2
Fe2+ 2p1/2
Satellite
Intensity (a.u.)
740 735 730 725 720 715 710 705 700
Binding energy (eV)
(b)
MCNF
Satellite
Fe4+ 2p3/2
Fe3+ 2p3/2
Fe4+ 2p1/2
Fe3+ 2p1/2
Fe2+ 2p3/2
Fe2+ 2p1/2
Satellite
Intensity (a.u.)
740 735 730 725 720 715 710 705 700
Binding energy (eV)
(c)
MFCNCF
Satellite
Fe4+ 2p3/2
Fe3+ 2p3/2
Fe4+ 2p1/2
Fe3+ 2p1/2
Fe2+ 2p3/2
Fe2+ 2p1/2
Satellite
Intensity (a.u.)
740 735 730 725 720 715 710 705 700
Binding energy (eV)
(d)
CoFe2O4
Satellite
Co2+ 2p3/2
Co3+ 2p3/2
Co2+ 2p1/2
Co3+ 2p1/2
Satellite
Intensity (a.u.)
810 805 800 795 790 785 780 775
Binding energy (eV)
(e)
MCNF
Satellite
Co2+ 2p3/2
Co3+ 2p3/2
Co2+ 2p1/2
Co3+ 2p1/2
Satellite
Intensity (a.u.)
810 805 800 795 790 785 780 775
Binding energy (eV)
(f)
MFCNCF
Satellite
Co2+ 2p3/2
Co3+ 2p3/2
Co2+ 2p1/2
Co3+ 2p1/2
Satellite
Intensity (a.u.)
810 805 800 795 790 785 780 775
Binding energy (eV)
(g)
MCNF
Satellite
Ni2+ 2p3/2
Ni2+ 2p1/2
Satellite
Intensity (a.u.)
885 880 875 870 865 860 855 850
Binding energy (eV)
(h)
MFCNCF
Satellite
Ni2+ 2p3/2
Ni2+ 2p1/2
Satellite
Intensity (a.u.)
885 880 875 870 865 860 855 850
Binding energy (eV)
(i)
MCNF
Mg2+ 1s
Intensity (a.u.)
1310 1305 1300 1295 1290
Binding energy (eV)
(j)
MFCNCF
Mg2+ 1s
Intensity (a.u.)
1310 1305 1300 1295 1290
Binding energy (eV)

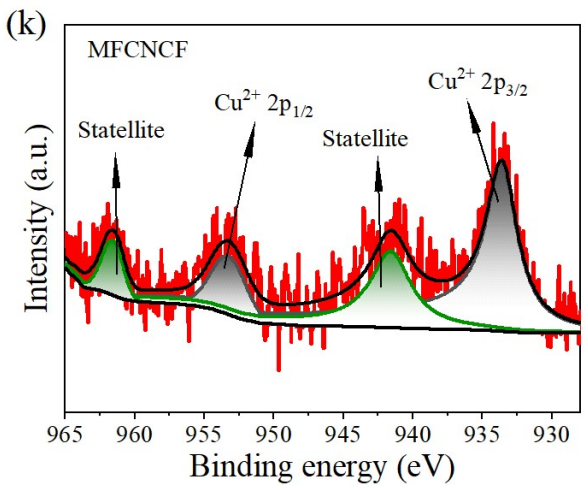


Fig. S2 XPS spectra of CoFe2O4, MCNF and MFCNCF: high resolution spectra of Fe 2p (a-c); Co 2p (d-f); Ni 2p (g-h); Mg 1s (i-j) and Cu 2p (k).

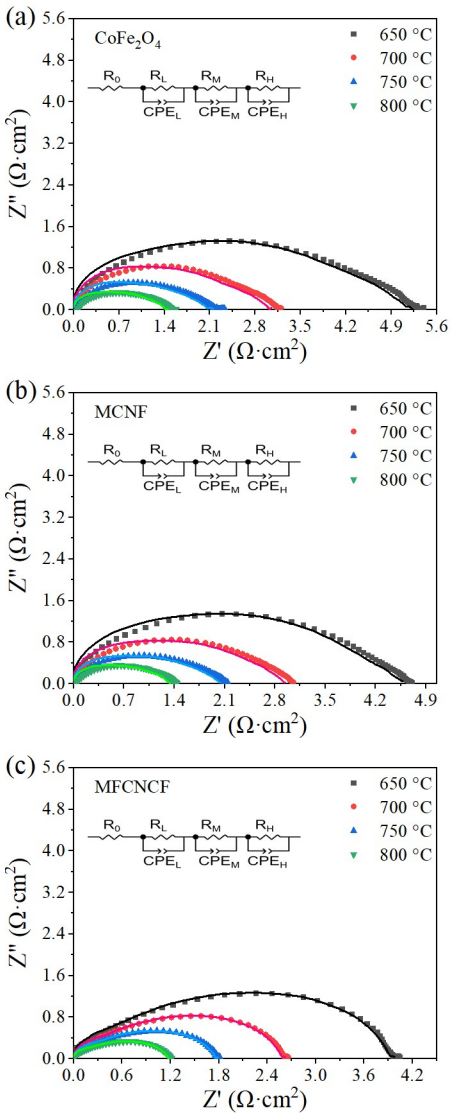


Fig. S3 Nyquist plots of $CoFe_2O_4$ (a), MCNF (b) and MFCNCF (c) from 650 to 800 °C.

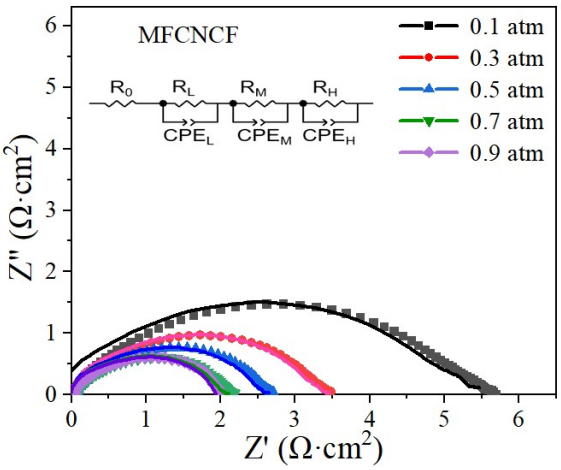


Fig. S4 EIS plot of MFCNCF symmetric cell under different oxygen partial pressures at 750°C.

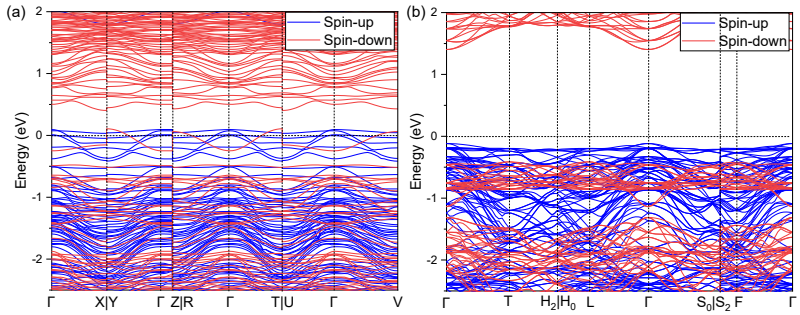


Fig. S5 The electronic band structures of MFCNCF (a) and $CoFe_2O_4$ (b)

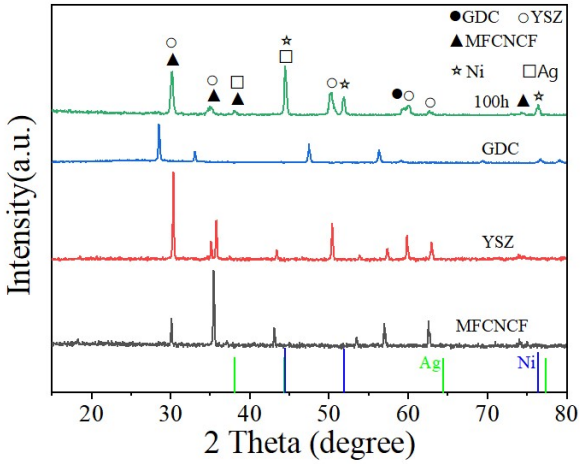


Fig. S6 XRD of cell cross-section of the single cell after 100 h long-term testing.

Table S1 Molar ratio between metal cations for $CoFe_2O_4$, MCNF, and MFCNCF

Ratio	$CoFe_2O_4$	MCNF	MFCNCF
$Fe^{2+} + Fe^{3+}/Fe^{4+}$	7.284	4.593	2.999
Co^{2+}/Co^{3+}	0.919	0.870	0.776

Table S2 Comparison of the K_{ex} and D_{chem} of different spinel-based cathode in this study and reported in literature at 800 ℃

Material	K_{ex} ($cm \cdot s^{-1}$)	D_{chem} ($cm^2 \cdot s^{-1}$)	reference
$CoFe_2O_4$	1.01×10^{-4}	1.05×10^{-5}	This work
MCNF	1.36×10^{-4}	3.10×10^{-5}	This work
MFCNCF	1.95×10^{-4}	8.82×10^{-5}	This work
$CuBi_2O_4$	5.93×10^{-3}	6.71×10^{-6}	[1]
$Ni_{0.2}Fe_{0.8}Co_2O_4$	4.8×10^{-5}	1.7×10^{-6}	[2]
$Mg_{0.4}Ni_{1.4}Mn_{1.2}O_4$	1.2×10^{-3}	6×10^{-5}	[3]

Table S3 Relationship between Reaction Order n Values from Theoretical Calculation and Experimental Testing for MFCNCF Cathode

Steps	Elemental reactions	Reaction order	Polarization	Experimental result
1	$O_2\,(g) \rightarrow 2O_{ad}$	n = 1	R_L	n = 0.93
2	$O_{ad} \leftrightarrow O_{TPB}$	n = 0.5	R_M	n = 0.45 (Rate-limiting)
3	$O_{TPB} + e^- \rightarrow O_{TBP}^-$	n = 0.375	R_M/R_H	/
4	$O_{TPB}^- + e^- \rightarrow O_{TPB}^{2-}$	n = 0.125	R_H	n = 0.27
5	$O_{TPB}^{2-} + V_{\ddot{O}} \leftrightarrow O_o^x$	n = 0	R_H	/

Reference:

1 N. Li, L. Sun, Q. Li, T. Xia, L. Huo and H. Zhao, *J. Power Sources*, 2021, **511**, 230447.

2 F. Zhong, *Chem. Eng. J.*, 2021, **425**, 131822.

3 F. Zhong, X. Wang, C. Han, H. Fang, Y. Huang, Y. Luo, C. Chen, L. Lin, C. Au and L. Jiang, *J. Alloys Compd.*, 2023, **939**, 168625.