Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

In Operando Synchrotron X-ray Studies of a Novel Spinel $(Ni_{0.2}Co_{0.2}Mn_{0.2}Fe_{0.2}Ti_{0.2})_3O_4$ High-Entropy Oxide for Energy Storage Applications

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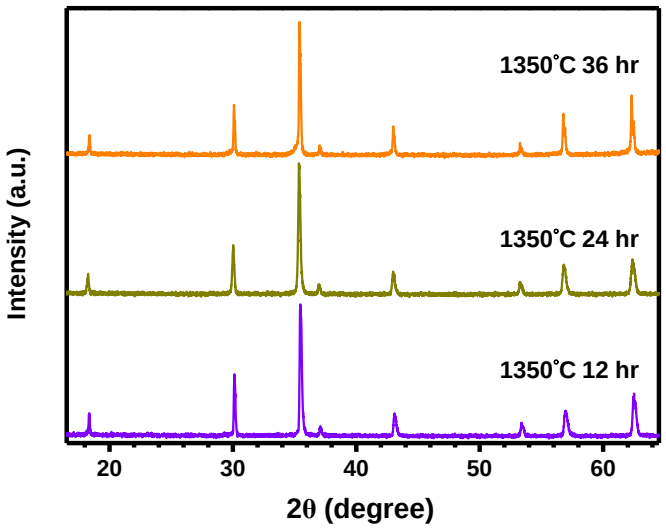

Figure S1. Enlarged XRD patterns of NCMFT at different sintering times.

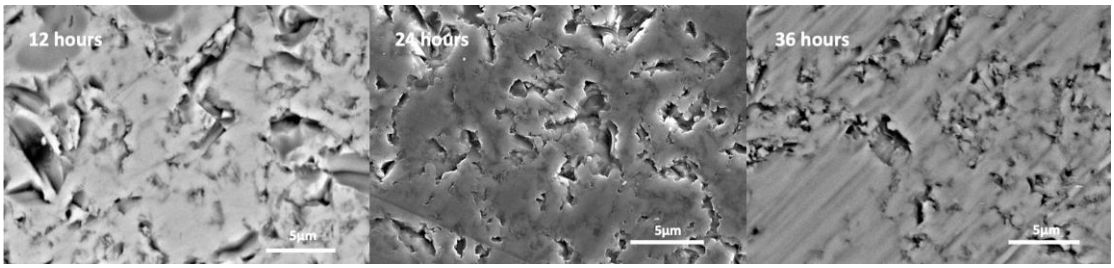

Figure S2. Backscattered Electron Image of NCMFT at different holding temperature time. From left to right, increasing holding time result in increasing homogeneity.

Table S1. Rietveld refinement parameters of NCMFT

	$(Ni_{0.2}Co_{0.2}Mn_{0.2}Fe_{0.2}Ti_{0.2})_3O_4$
Lattice	**Cubic**
Space group	**Fd-3m**
a (A°)	**8.440**
Rwp	**9.9**
GOF	**1.12**

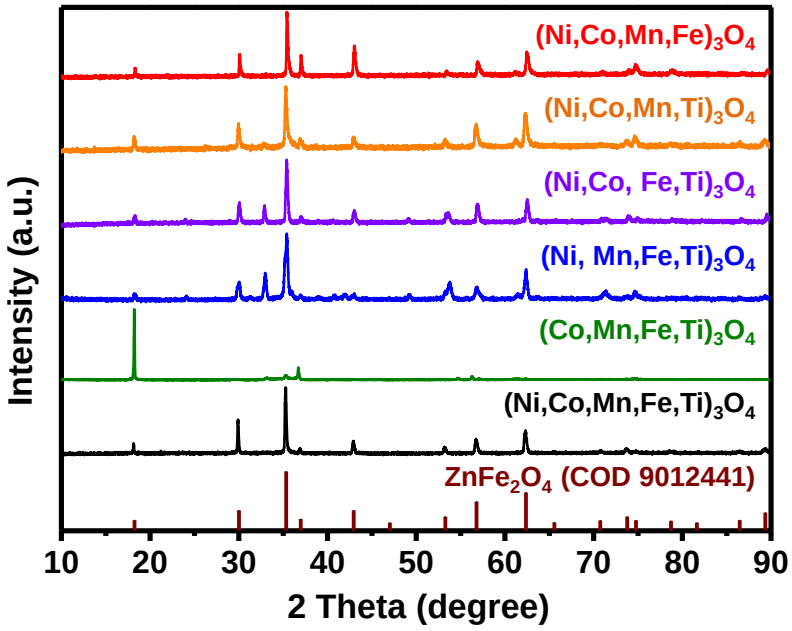

Figure S3. XRD patterns of NCMFT and quaternary oxides

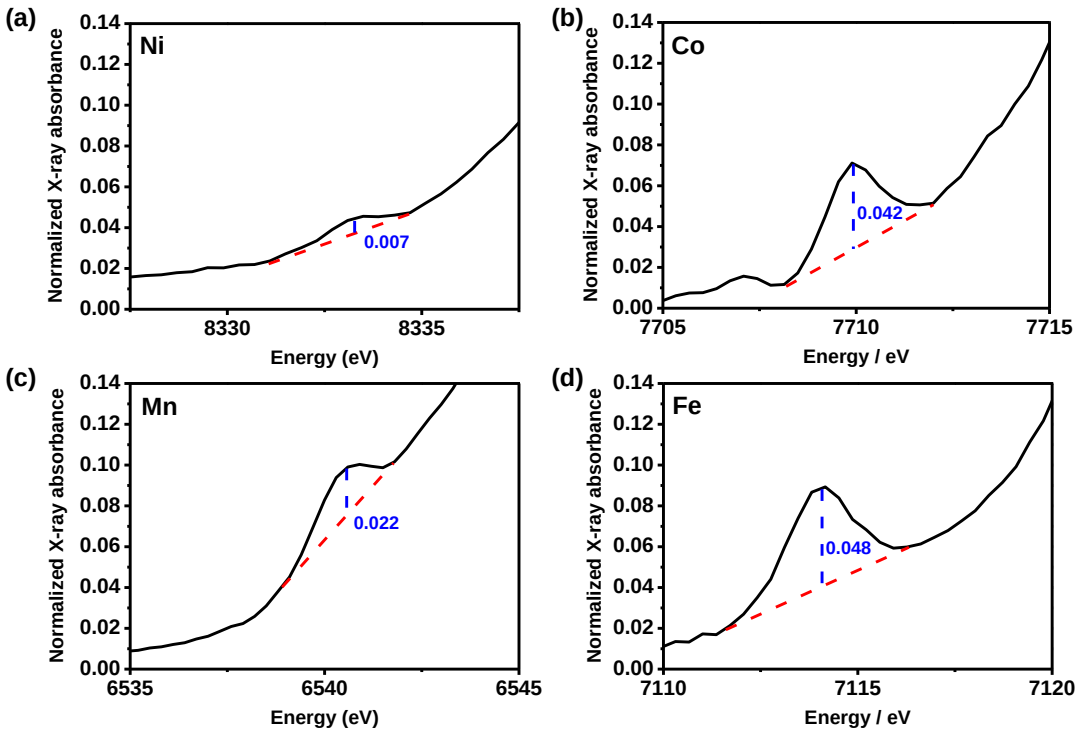

Figure S4. Enlarged XANES of NCMFT in the pre-edge part: (a) Ni K-edge; (b) Co K-edge; (c) Mn K-edge; (d) Fe K-edge.

Table S2. Comparison of the LIB anode performance of NCMFT with other conversion-type spinel anodes in the literature

Electrodes	Current density	1st / 2nd discharge capacity (mA h g^{-1})	Cycle No. (retention)	Rate performance	Ref.
Mn_3O_4	40 mA g^{-1}	1350/300	10th (~33%)	-	1
Co_3O_4	50 mA g^{-1}	1105/817	30th (~23%)	50 mA h g^{-1} @ 0.5 A g^{-1}	2
$MnFe_2O_4$	0.1C	1405/1050	10th (~48%)	200 mA h g^{-1} @ 0.5C	3
$NiFe_2O_4$	100 mA g^{-1}	1100/800	100th (~25%)	-	4
$NiFeMnO_4$	91.8 mA g^{-1}	1427/1100	50th (~73%)	500 mA h g^{-1} @ 0.46 A g^{-1}	5
$CoMnFeO_4$	91.7 mA g^{-1}	1448/1026	50th (~68%)	600 mA h g^{-1} @ 0.46 A g^{-1}	6
$(Ni_{0.2}Co_{0.2}Mn_{0.2}Fe_{0.2}Ti_{0.2})_3O_4$	100 mA g^{-1}	900/560	100th (~100%)	435 mA h g^{-1} @ 0.5 A g^{-1}	This work

Table S3. Lithiation/delithiation characteristics of conversion reaction spinel-structured transition metal oxide anodes.

Material	**Lithiation products**	**Reduction potential (vs. Li^+/Li)**	**Delithiation products**	**Oxidation potential (vs. Li^+/Li)**	**Ref.**
Mn_3O_4	Mn	0.2-0.4 V	Mn_3O_4	1.2-1.4 V	7 8
Fe_3O_4	Fe	0.8-1.0 V	FeO, Fe_3O_4	1.6-1.9 V	9 10
Co_3O_4	Co	0.9-1.4 V	CoO	2.0-2.3 V	11 12
$CoMn_2O_4$	Mn, Co	0.47 V, 1.25 V	MnO, CoO	1.44 V, 2.03 V	13 14
$NiMn_2O_4$	Mn, Ni	0.42 V, 1.13 V	Mn_3O_4, NiO	1.25 V, 1.96 V	15
$MnFe_2O_4$	Mn, Fe	0.76 V	MnO, Fe_3O_4	1.7 V	16 17
$CoFe_2O_4$	Co, Fe	0.75 V	CoO, Fe_2O_3	1.6-1.9 V	18
$NiFe_2O_4$	Fe, Ni	0.84 V, 0.98 V	NiO, Fe_2O_3	1.73 V, 2.12 V	16 19
$MnCo_2O_4$	Mn, Co	0.85 V	MnO, CoO	1.55 V, 2.05 V	20
$FeCo_2O_4$	Fe, Co	0.72 V, 1.57 V	FeO, Co_3O_4	1.69 V, 2.2 V	21 22
$NiCo_2O_4$	Ni, Co	0.81-1.25 V	NiO, Co_3O_4	1.5 V, 2.27 V	23 24

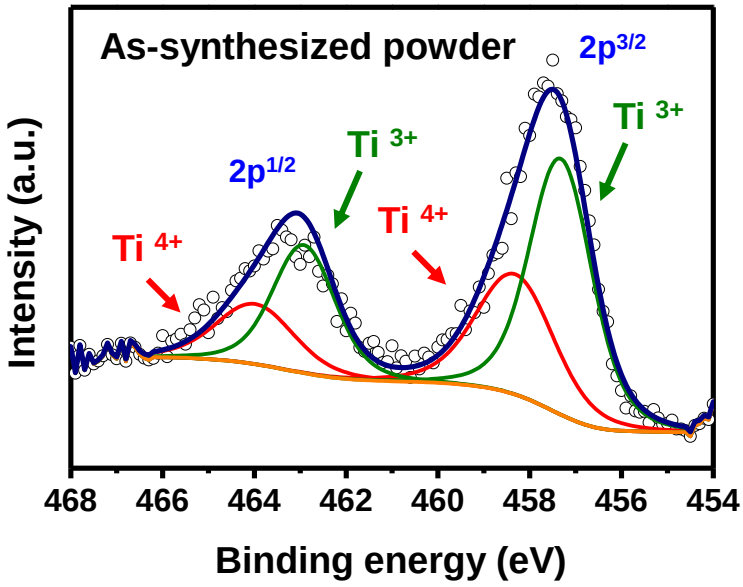

Figure S5. Ti 2p XPS spectrum of as-synthesized NCMFT powder

Table S4. The estimated positive charges of as-synthesized NCMFT powder and NCMFT electrode at OCV.

	as-synthesized Powder	Electrode at OCV
Ni	2.4+	2.8+ (measured in a coin cell)
Co	2.4+	2.4+ (measured in a coin cell)
Mn	2.6+	2.6+ (measured in a coin cell)
Fe	2.9+	2.4+ (measured in a coin cell)
Ti	3.4+	3.9+ (as-prepared electrode)
Total positive charges	8.2+	8.5+

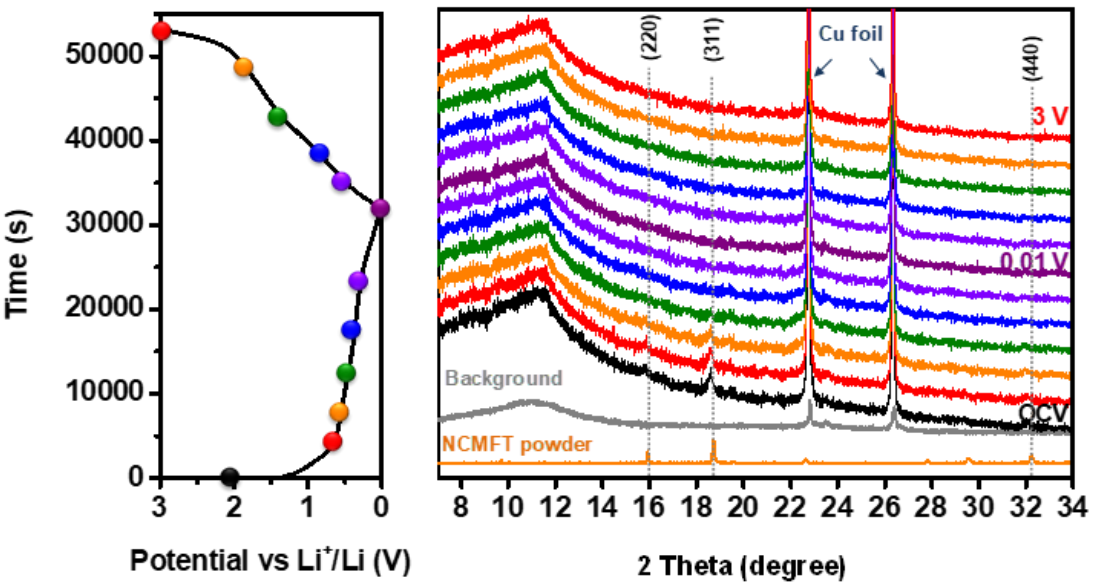

Figure S6. In operando synchrotron XRD patterns of the NCMFT anode.

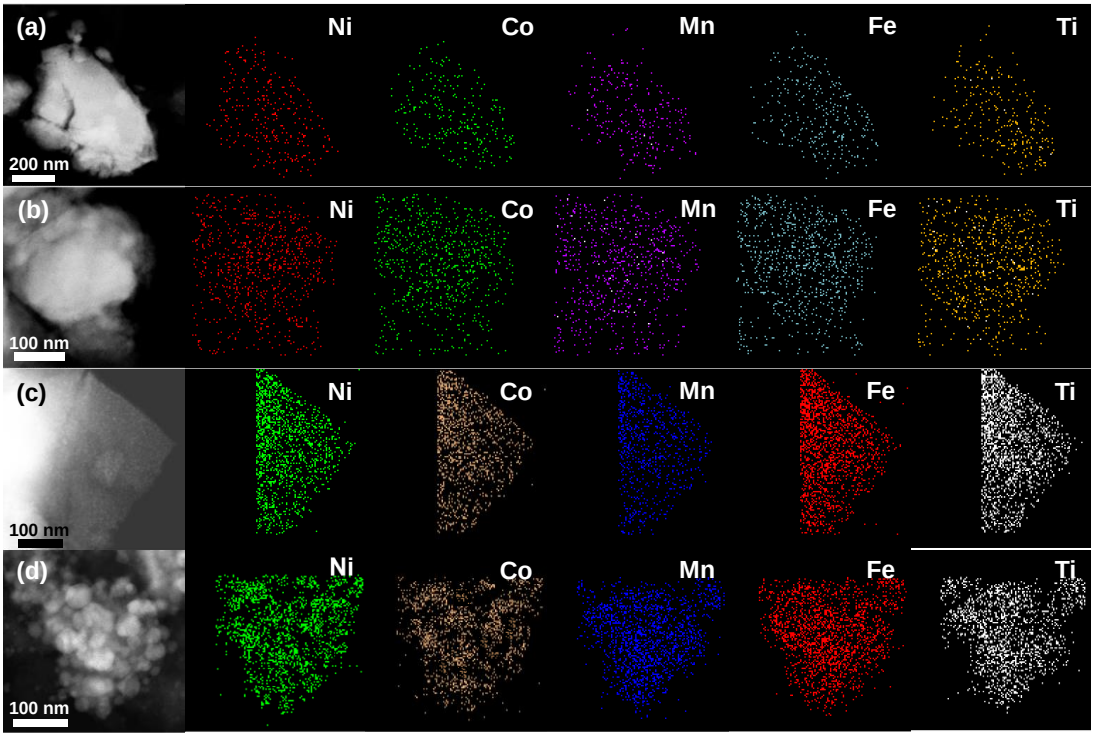

Figure S7. STEM-EDS analysis of NCMFT: (a) the 1st lithiation; (b) the 1st delithiation; (c) the 10th lithiation; (d) the 10th delithiation. Images labeled as Ni, Co, Mn, Fe, and Ti are intensity maps for characteristic X-rays.

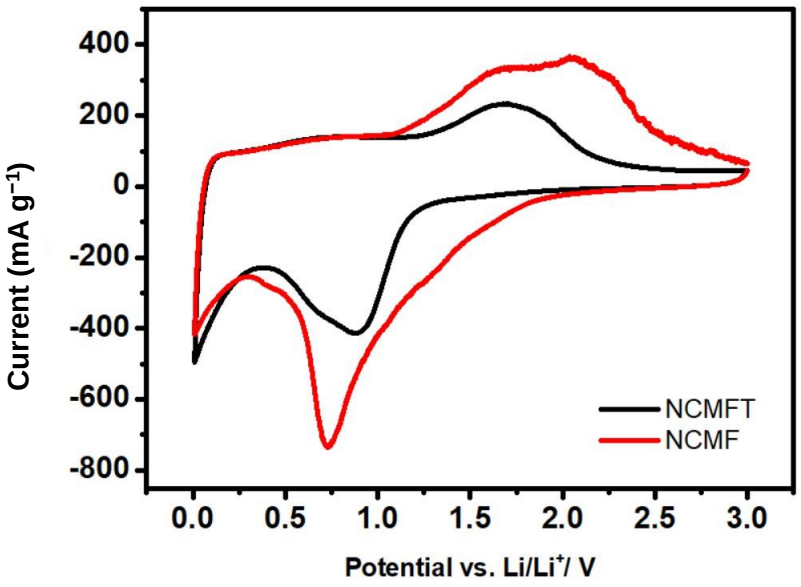

Figure S8. The CV curves of NCMFT and NCMF anodes in the 2nd cycle between 0.01 and 3.0 V vs. Li/Li$^+$ at a scan rate of 0.1 mV s^{-1}

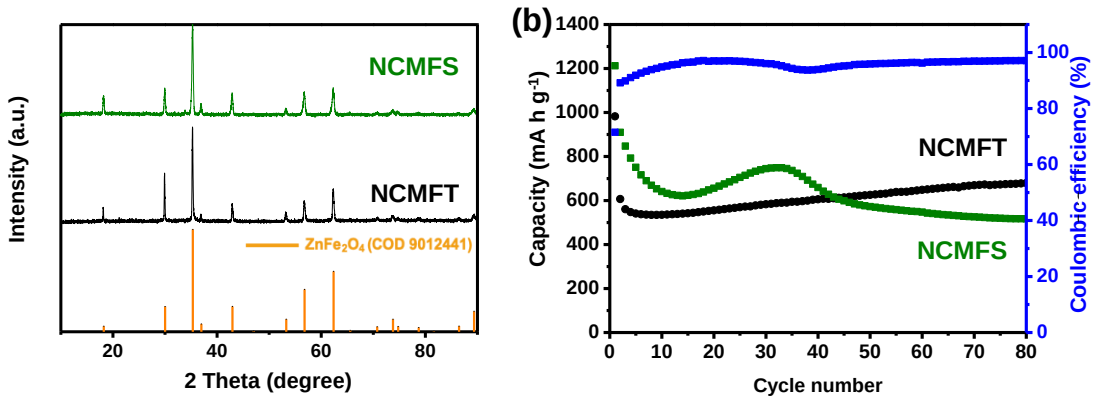

Figure S9. (a) XRD patterns of NCMFS and NCMFT. (b) The cycling performance of NCMFS and NCMFT anodes and the coulombic efficiency of NCMFS anode at current density of 50 mA g^{-1}.

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