Supporting Information

Synergistic Ti/F Co-doping for Enhanced Electrochemical Performance of $LiNi_{0.5}Mn_{1.5}O_4$ Cathodes via Ti^{3+}/Ti^{4+} Redox and Structural Stabilization

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1.Results and Discussion

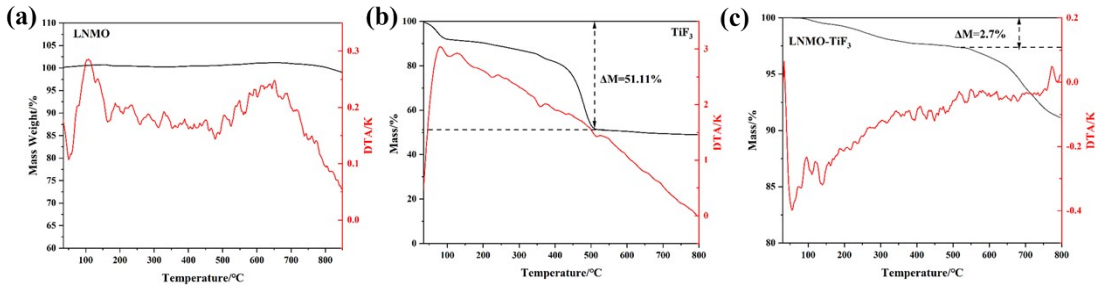
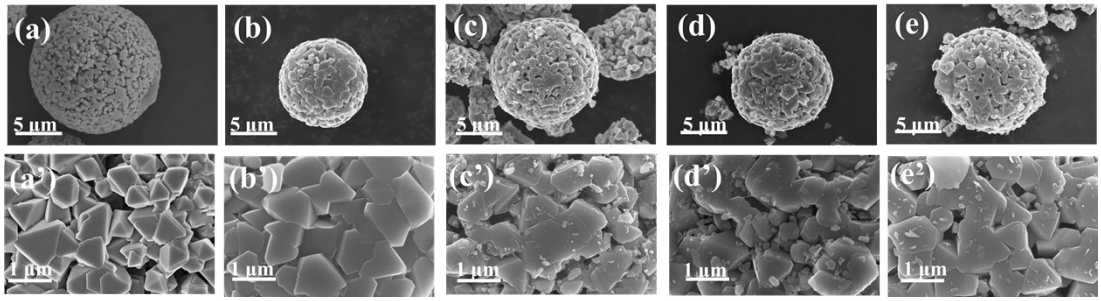


Figure S1 TG and DTA curves of (a) LNMO, (b) TiF_3, (c) LNMO-TiF_3



FigureS2 SEM images of all samples. (a)(a')LNMO, (b)(b')LNMO-550 °C, (c)(c') LNMO-TiF_3-2, (d)(d') LNMO-TiF_3-4, (e)(e') LNMO-TiF_3-6

The preparation process of LNMO and LNMO-550℃ samples is consistent with our previous work,[19] so we directly used the SEM image. *Copyright © 2023, American Chemical Society.*

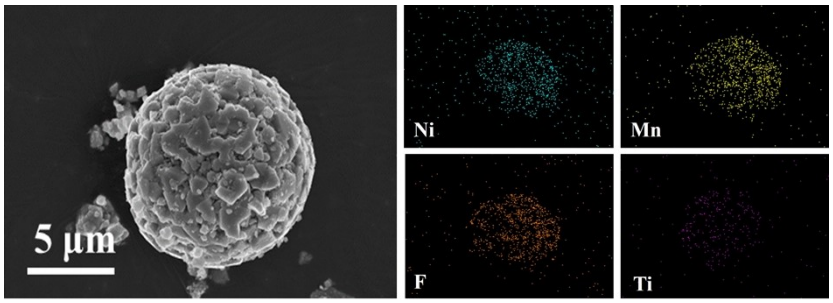


Figure S3 The SEM images and of EDX mapping of LNMO-TiF_3-4

Table S1. ICP-MS results for the all as-prepared samples

Samples	Molar ratio			
	Li	Ni	Mn	Ti
LNMO	1.08	0.50	1.51	/
LNMO-550 ℃	1.07	0.51	1.52	/
LNMO-TiF_3-2	1.06	0.49	1.49	0.02
LNMO-TiF_3-4	1.03	0.48	1.48	0.04
LNMO-TiF_3-6	1.06	0.48	1.46	0.06

Table S2 Table of refinement parameters for all samples

Samples	Phase	Parameter (Å)	Cell Volume (Å^3)	Occupancy		R_{wp}(%)	χ^2(%)
				TM	Ti		
LNMO	*Fd-3m*	8.1657(15)	544.530(17)	1.0000	0.0000	3.71	6.54
LNMO-550 ℃	*Fd-3m*	8.1675(12)	544.838(34)	1.0000	0.0000	1.82	2.08
LNMO-TiF_3-2	*Fd-3m*	8.1702(06)	545.378(32)	0.9914	0.0086	3.04	4.54
LNMO-TiF_3-4	*Fd-3m*	8.1736(88)	546.059(18)	0.9780	0.0220	2.82	4.22
LNMO-TiF_3-6	*Fd-3m*	8.1782(14)	546.567(18)	0.9688	0.0312	3.01	3.21

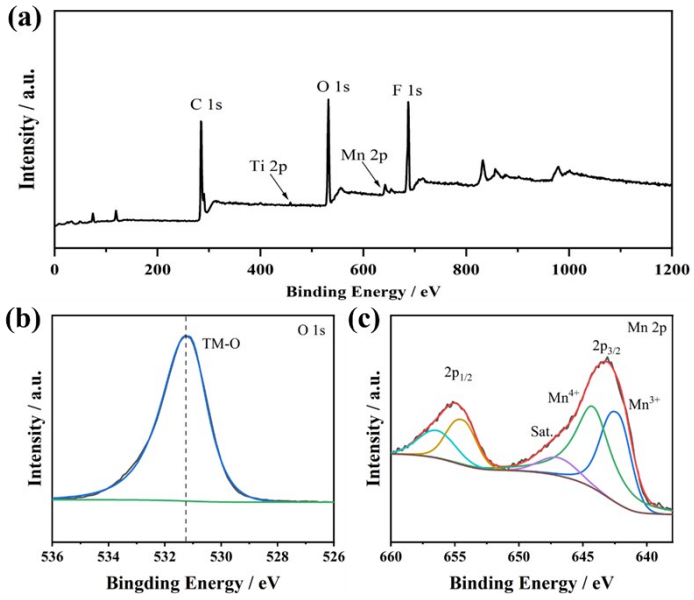


Figure S4 The XPS patterns of the LNMO-TiF_3-4 samples (a) survey spectrum (b) Mn 2p and (c)

O 1s

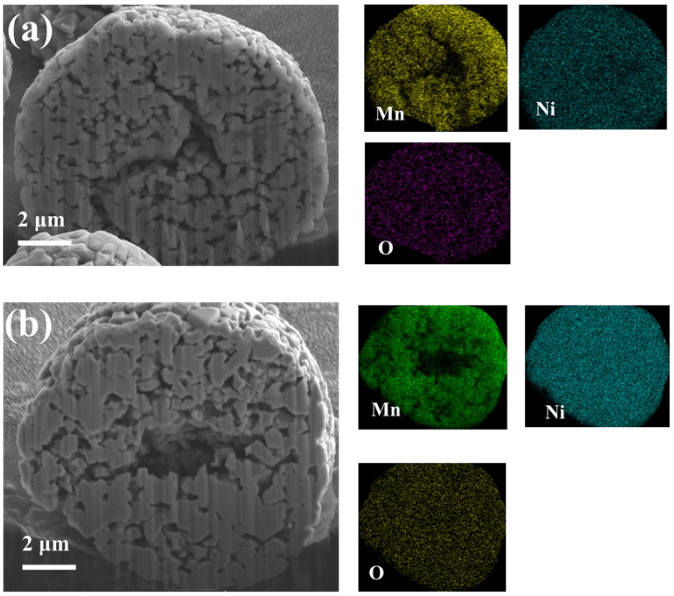


Figure S5 FIB-SEM images and of EDX mapping of (a) LNMO, (b) LNMO-550℃

The preparation process of LNMO and LNMO-550℃ samples is consistent with our previous work,[19] so we directly used the FIB-SEM image. *Copyright © 2023, American Chemical Society.*

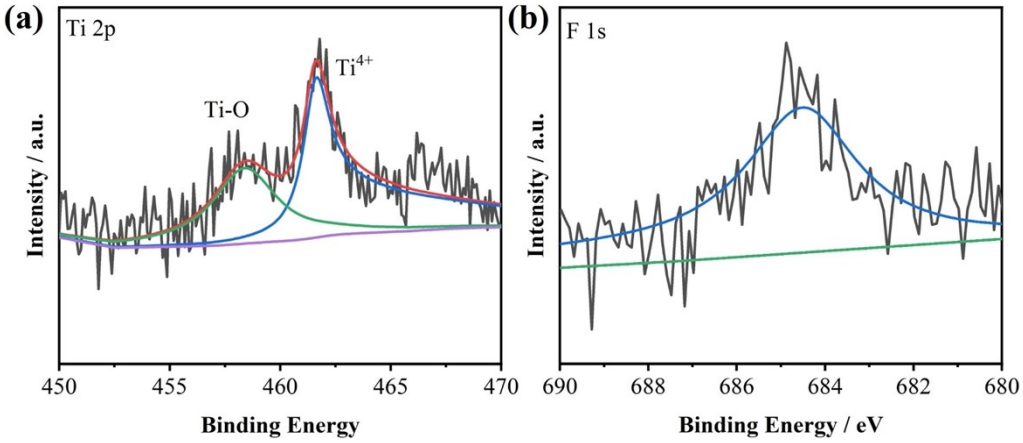


Figure S6 The XPS patterns of the LNMO-TiF_3-4 samples 100 nm of Ar^+ etching (a) Ti 2p, (b)F 1s.

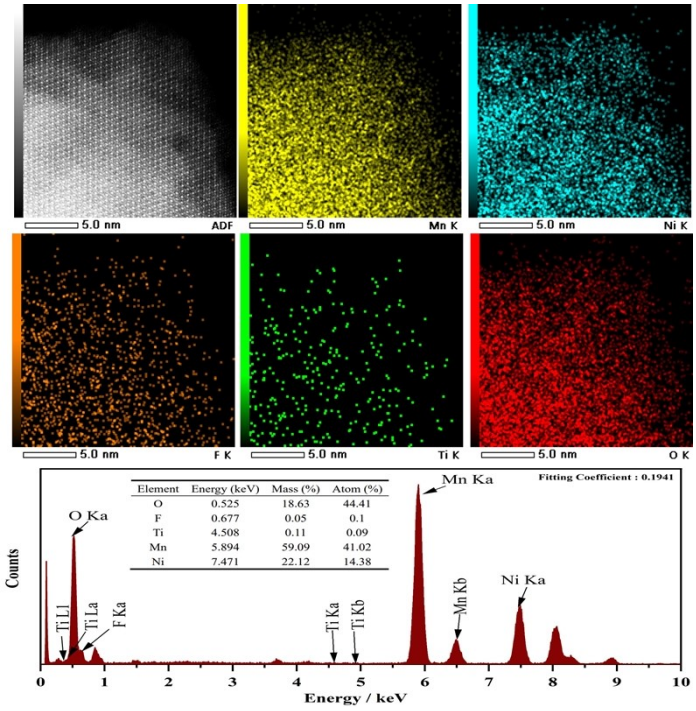


Figure S7 The STEM with EDS of LNMO-TiF_3-4.

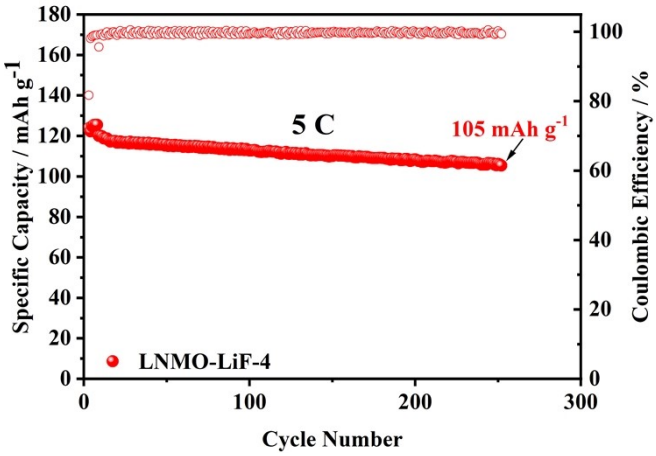


Figure S8 5 C cycling performance of LNMO-LiF-4.

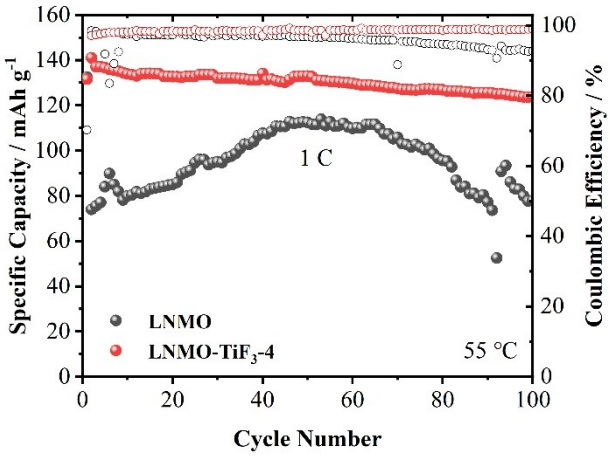


Figure S9 1 C cycling performance at 55 °C.

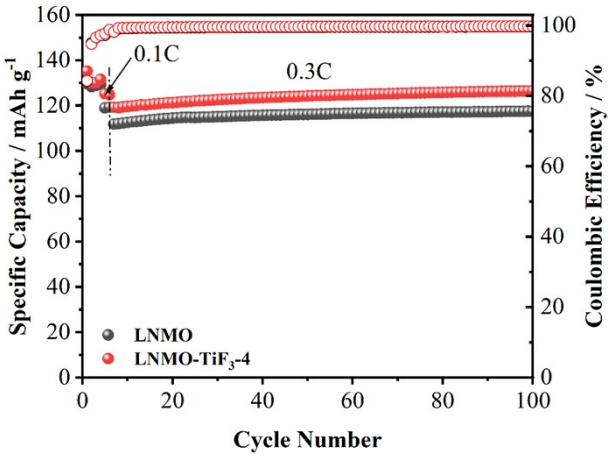


Figure S10 The cycle performance of LNMO//graphite and LNMO-TiF_3-4// graphite full cells at 0.3C rate.

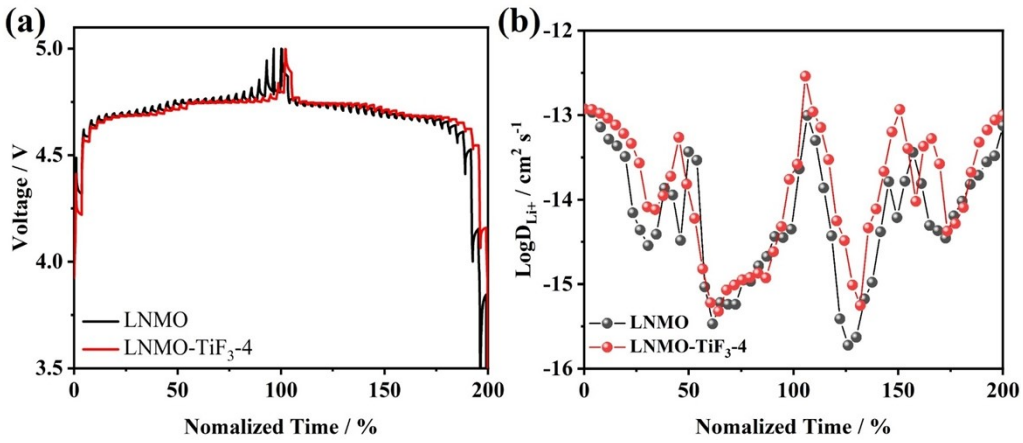


Figure S11 (a) The GITT curves of LNMO and LNMO-TiF_3-4, (b) Li^+ diffusion coefficients calculated from the GITT profiles during the charge-discharge process.

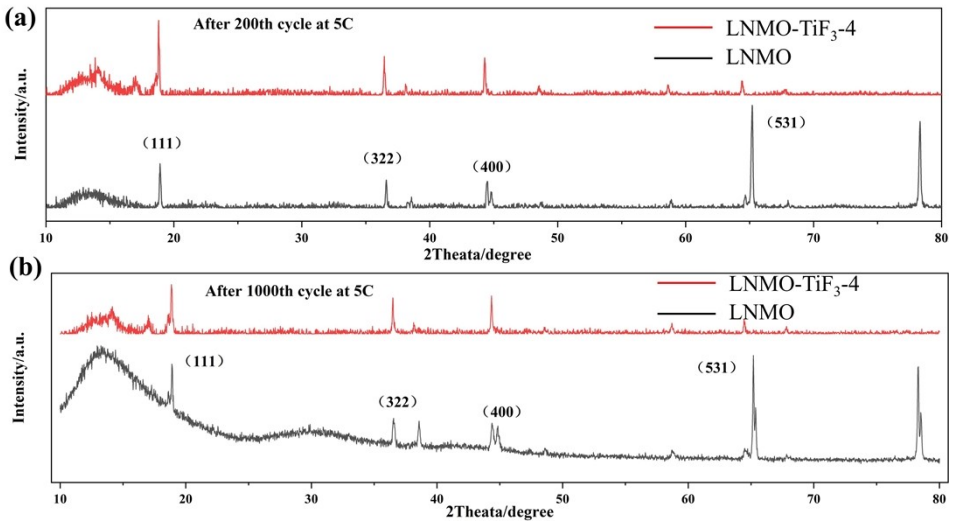


Figure S12 XRD patterns of LNMO and LNMO-TiF_3-4 samples. (a) XRD pattern after 200 cycles at 5 C, (b) XRD pattern after 1000 cycles.

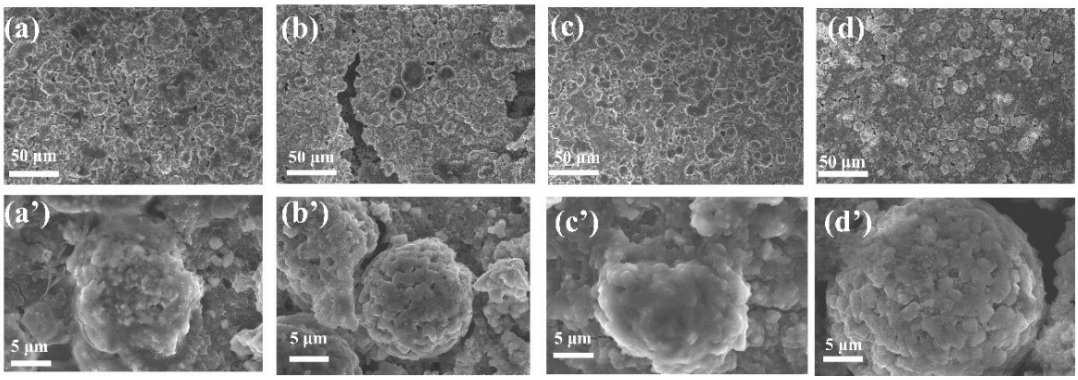


Figure S13 SEM images of (a)(a') LNMO, (b) (b') LNMO-TiF_3-4 after 200 cycles at 5 C, (c)(c') LNMO and (d)(d') LNMO-TiF_3-4 after 1000 cycles at 5 C, respectively.

Table S3. ICP-MS results for lithium after cycling

Sample	Element	Elemental concentration in digestion solution/original sample solution C_1（μg/L)	Elemental content W（%)
LNMO	Mn	2320.850	0.368
	Ni	715.900	0.114
LNMO-TiF_3-4	Mn	427.950	0.078
	Ni	165.600	0.030

The calculation process for the additional theoretical capacity increment is as follows:

Faraday's law:

$$C=(nF)/M$$

where, C represents theoretical specific capacity (C = 147 mAh g^{-1}). N is the number of Li^+ per molecule, representing the number of lithium ions that can be deintercalated per molecule in the positive electrode material. M is the molecular weight of the material, and the actual molecular weight of the active material of the positive electrode material is required for calculation. F is Faraday's constant, approximately 96485 C/mol.

The relative molecular weight values are as follows:

Li: 6.94; Ni: 58.69; Mn: 54.94; O: 16.00; Ti: 47.87

M_{LNMO}=6.94+58.69×0.5+54.94×1.5+16.00×4=182.695

At this moment, C = 147 mAh g^{-1}

Taking LNMO-TiF_3-2 as an example:

When Ti completely replaces the position of Ni 16d, the molecular formula is $LiNi_{0.48}Mn_{1.5}Ti_{0.02}O_4$,

M_1=6.94+58.69×0.48+54.94×1.5+47.87×0.02+16.00×4=182.4786.

Therefore, C_1=147.17 mAh g^{-1}, $\triangle C_1$=0.17 mAh g^{-1}.

When Ti completely replaces the position of Mn 16d, the molecular formula is $LiNi_{0.5}Mn_{1.48}Ti_{0.02}O_4$,

M_2=6.94+58.69×0.5+54.94×1.48+47.87×0.02+16.00×4=182.5536.

Therefore, C_2=147.11 mAh g^{-1}, $\triangle C_2$=0.11 mAh g^{-1}.

Due to the disorderly distribution of Mn and Ni, the theoretical increased capacity should be somewhere in between. 0.11 mAh g^{-1}<$\triangle$C< 0.17 mAh g^{-1}

Similarly, in LNMO-TiF_3-4, 0.22 mAh g^{-1}<$\triangle$C< 0.35 mAh g^{-1};

In LNMO-TiF_3-6, 0.34 mAh g^{-1}<$\triangle$C< 0.52 mAh g^{-1}.

Note: During the calculation, it was assumed that all doped Ti were doped and had electrochemical activity, but the true direct capacity contribution from Ti oxidation and reduction was less than the theoretical estimate.