Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Toward a stabilized lattice framework and surface structure of layered lithium-rich cathode materials with Ti modification

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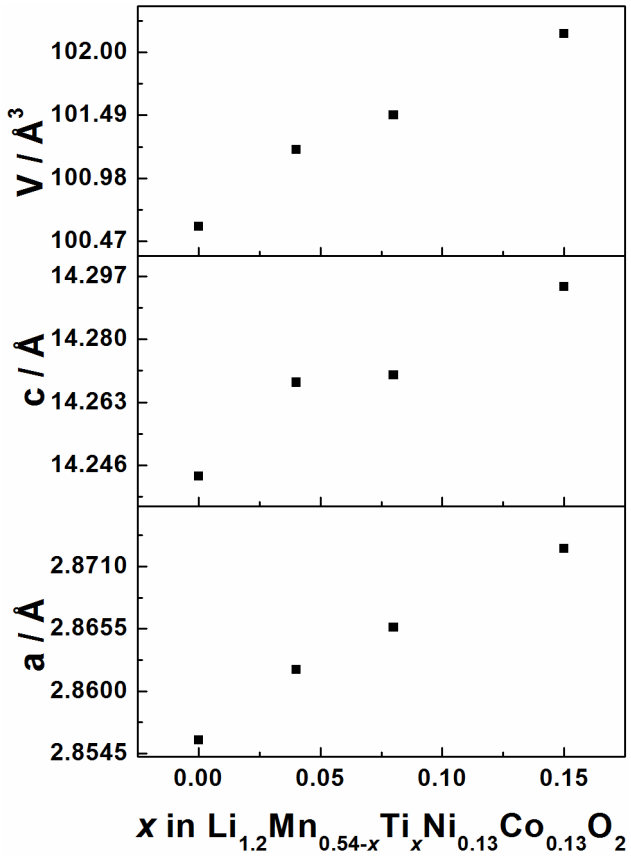

Figure. S1 Variations of lattice parameters and volume of $Li_{1.2}Mn_{0.54-x}Ti_xNi_{0.13}Co_{0.13}O_2$ (x =0, 0.04, 0.08, and 0.15) with respect to Ti content.

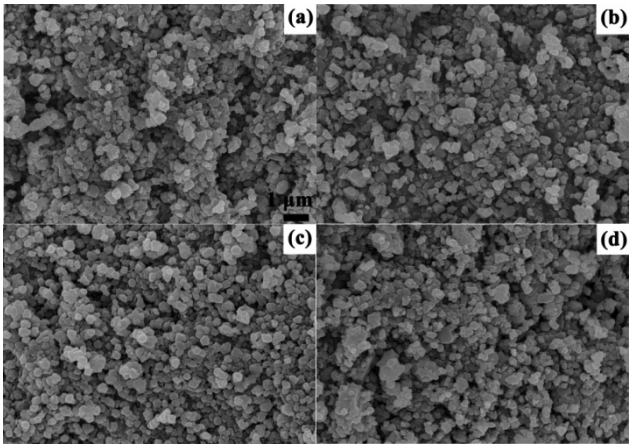

Figure. S2 SEM images of $Li_{1.2}Mn_{0.54-x}Ti_xNi_{0.13}Co_{0.13}O_2$. (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.08$, and (d) $x = 0.15$.

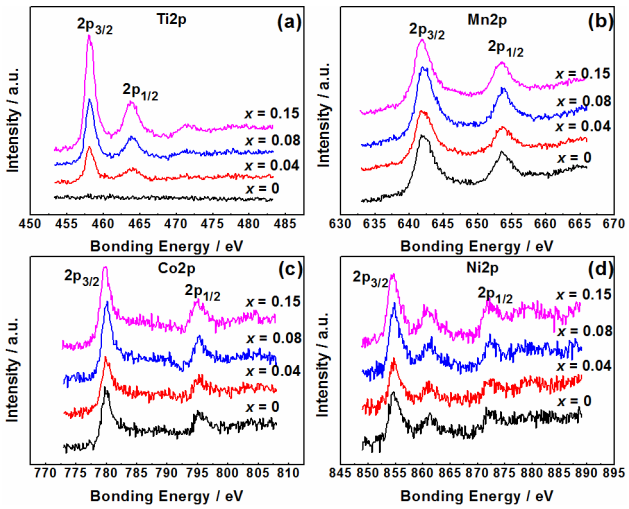

Figure. S3 XPS spectra of transition metals in $Li_{1.2}Mn_{0.54-x}Ti_xNi_{0.13}Co_{0.13}O_2$: (a) Ti 2p, (b) Mn 2p, (c) Co 2p, and (d) Ni 2p spectra.

In Fig. S3 (a), $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ does not show any peak in the Ti 2p spectrum. Peak intensity of the Ti 2p spectrum gradually increases with increasing Ti content. The bonding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ are 458.1 eV and 463.9 eV, respectively, suggesting that the valency of Ti in the Ti-substituted materials is +4. [1, 2] After Ti substitution, no obvious peak shifting of $2p_{3/2}$ and $2p_{1/2}$ peaks for Mn 2p, Co 2p and Ni 2p spectrum are observed (Fig. S3 (b)-(d)), and the bonding energies of Mn $2p_{3/2}$, Mn $2p_{1/2}$, Co $2p_{3/2}$, Co $2p_{1/2}$, Ni $2p_{3/2}$ and Ni $2p_{1/2}$ are 642.1 eV, 653.6 eV, 779.9 eV, 795.2 eV, 854.6 eV, and 872.5 eV, respectively. According to the literature, [3-5] the transition metal ions are in the state of Mn^{4+}, Co^{3+} and Ni^{2+} in all these materials, indicating that the equivalent Ti^{4+} substitution for partial Mn^{4+} does not affect the valencies of the other ions.

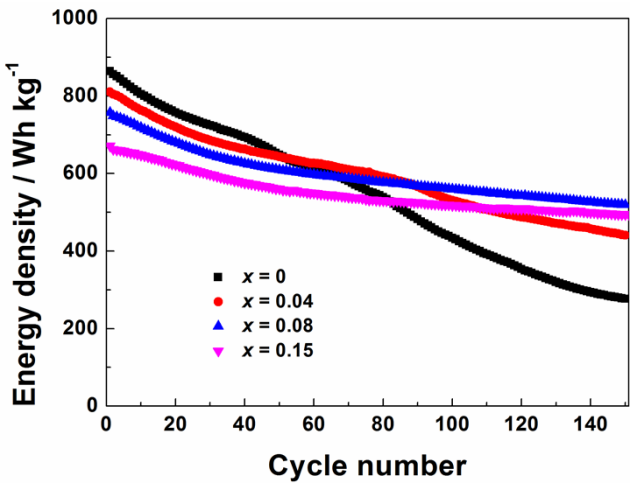

Figure. S4 Energy density of $Li_{1.2}Mn_{0.54-x}Ti_xNi_{0.13}Co_{0.13}O_2$ (x =0, 0.04, 0.08, and 0.15) materials cycled at a current density of 200 mA g^{-1}.

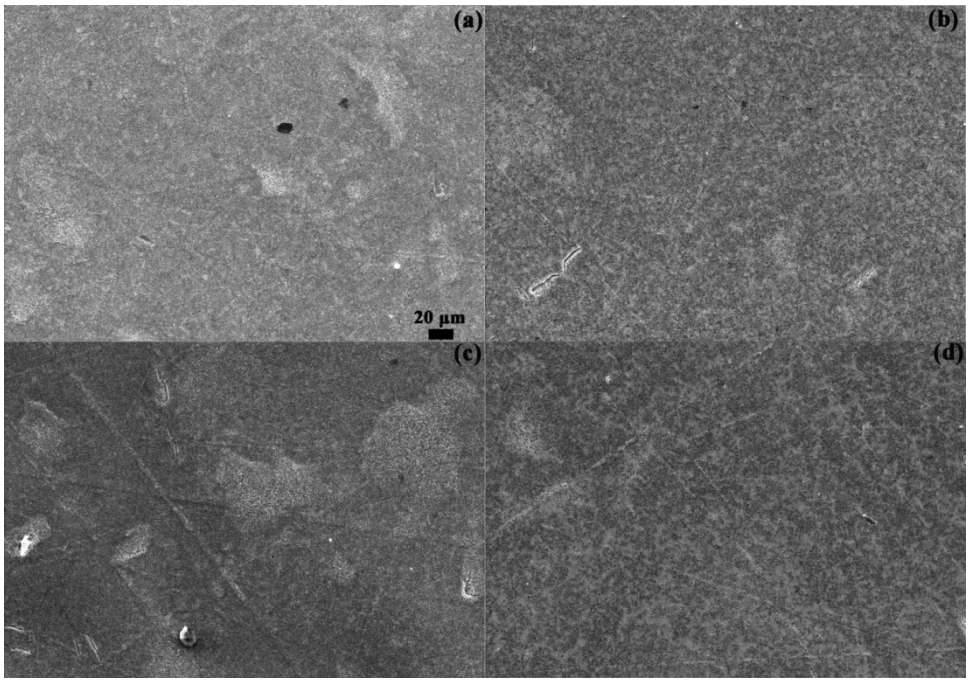

Figure. S5 SEM images of $Li_{1.2}Mn_{0.54-x}Ti_xNi_{0.13}Co_{0.13}O_2$ electrodes after 100 cycles at a current density of 200 mA g^{-1}. (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.08$, (d) $x = 0.15$.

Table S1. Chemical composition results of ICP-AES analysis for $Li_{1.2}Mn_{0.54-x}Ti_xNi_{0.13}Co_{0.13}O_2$ (x =0, 0.04, 0.08, and 0.15).

Theoretical stoichiometry	Measured stoichiometry from ICP-AES				
	Li	Ni	Co	Mn	Ti
x = 0	1.15	0.12	0.13	0.52	-
x = 0.04	1.23	0.13	0.14	0.50	0.04
x = 0.08	1.22	0.12	0.13	0.44	0.08
x = 0.15	1.15	0.12	0.13	0.39	0.16

Table S2. Fitting data of R_{sf} and R_{ct} for $Li_{1.2}Mn_{0.54-x}Ti_xNi_{0.13}Co_{0.13}O_2$.

	R_{sf} / Ω				R_{ct} / Ω			
	$x = 0$	$x =$ 0.04	$x =$ 0.08	$x =$ 0.15	$x = 0$	$x =$ 0.04	$x =$ 0.08	$x =$ 0.15
2nd	2.6	3.2	3.7	3.9	21.4	37.9	66.8	94.8
100th	11.4	0.4	1.0	1.2	373.2	264.1	413.9	985.7
150th	32.9	2.7	1.8	0.8	716.6	363.7	544.6	1047

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