Synergic coating and doping effects of Ti-modified integrated layered-spinel Li$_{1.2}$Mn$_{0.75}$Ni$_{0.25}$O$_{2+\delta}$ as a high capacity and long lifetime cathode material for Li-ion batteries

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Figure S1. (a) EDX profiles of ST1 sample along with the elemental analysis as well as STEM image. Mapping shows Ti, Ni, and Mn atoms represented by dark green, green, and yellow colors, respectively. (b). EDX line scan signal counts across the particle shown in the STEM image.

From figure S1, it is clear that the ST1 sample has Ti-rich at surface. It is indicated that LMTO was located at outer part of particle.
Figure S2. XPS spectra of (a) Mn $2p_{3/2}$ and (b) Ni $2p_{3/2}$ with signal deconvolution and assignment to the indicated ions of ST0, ST1, and ST2.

Figure S3. XPS spectra for (a) Ni $3p$, (b) Ti $2p$ of ST0, ST1, and ST2.
To prepare Ti-doped $\text{Li}_{1.2}\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_{2+\delta}$ by sol-gel method, stoichiometry of Mn(CH$_3$COO)$_2$·4H$_2$O, Ni(CH$_3$COO)$_2$·4H$_2$O and LiCH$_3$COO·H$_2$O were dissolved in anhydrous ethanol. Ti(OiPr)$_4$ was added to above solution with ratio of Ti/TM equal to 7 % and 13 %. The solution was stirred for 1h and PVP was added for gelation. The solvent was evaporated and the obtained powder was fired in air at 450°C (heating rate: 2°C min$^{-1}$) for 5 h. The obtained powder was grinded and fired at 750°C in air (heating rate: 2°C min$^{-1}$) for 12 h. The sample was denoted as ST1-SG and ST2-SG for the ratio of Ti/TM equal to 7 % and 13 %, respectively.

![Cycling stability curves](image)

Figure S4. Cycling stability curves of ST1-SG and ST2-SG samples at C/10.
To test cycling stability of all samples at high C-rate, all samples were activated at C/10 in 8 cycles and then high current of 308 mA g$^{-1}$ (1C) were applied.

Figure S5. Cycling stability curves of ST0, ST1, and ST2 samples at 1C.
Figure S6. (a) X-ray patterns of ST0, ST1, and ST2 after 100 cycles. The standard marked with $C2/m$ (ICDD entry number 01-084-1634), $Fd\bar{3}m$ (ICDD entry number 01-080-2162), and $R\bar{3}m$ (PDF#09-0063) showed the peak positions correspond to Li$_2$MnO$_3$, LiMn$_{1.5}$Ni$_{0.5}$O$_4$ and LiMn$_{0.5}$Ni$_{0.5}$O$_2$ components, respectively. (b) Selected 2θ region of XRD patterns for the ST0, ST1, and ST2. The impurity phase of carbon and tetragonal phase were marked with “●” and “♦”, respectively. $M$, $S$, $R$, and $T$ represent for monoclinic, spinel, rhombohedral, and tetragonal, respectively.
The Li$^+$ diffusion coefficients of all samples were calculated using the following equation$^1$ and given in Table S1.

$$D = \frac{R^2 T^2}{2A n^4 F^4 C^2 \sigma^2} \quad (1)$$

where $R$ is the gas constant, $T$ is the absolute temperature, $A$ is the surface area of the cathode, $n$ is the number of electrons transferred in the half-reaction for the redox couple, $F$ is the Faraday constant, $C$ is the concentration of Li ion in solid, $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), and $\sigma$ is the Warburg factor, which is relative to $Z'$. $\sigma$ can be obtained from the slope of the lines in Figure S4.

$$Z' = R_D + R_L + \sigma \omega^{-1/2} \quad (2)$$

<table>
<thead>
<tr>
<th>sample</th>
<th>$\sigma$</th>
<th>$D_{Li^+}$ (cm$^2$ s$^{-1}$)</th>
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<tbody>
<tr>
<td>ST0</td>
<td>7.88</td>
<td>$1.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>ST1</td>
<td>7.5</td>
<td>$1.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>ST2</td>
<td>11.43</td>
<td>$4.7 \times 10^{-11}$</td>
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Figure S7. (a) EIS and (b) Real parts of the complex impedance versus $\omega^{-1/2}$ of the ST0, ST1, and ST2 before cycling.
References