Supplementary Information

Ti surface doping of LiNi_{0.5}Mn_{1.5}O_{4-δ} positive electrodes for lithium ion batteries

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Increasing the NH\textsubscript{3} catalyst concentration from 0.5 to 3 mL during synthesis results in increased agglomeration, globular cluster formation within the LNMO particles, with a 500°C anneal (Figure S1). This is an indication of free amorphous TiO\textsubscript{x} formation by homogenous nucleation, which crystallizes into TiO\textsubscript{2} during annealing as shown by XRD (Figure S2). The amount of the observable globular clusters reduces and the crystallite shapes change with 700°C annealing of this sample (Figure S1).

Figure S1. TEM images of surface modified LNMO synthesized using 3 g LNMO, 12 mL TBOT and 3 mL NH\textsubscript{3} (a) without annealing and with annealing at (b) 500°C and (c) 700°C.

Figure S2. XRD data for surface modified LNMO samples synthesized using 12 mL TBOT and 3 mL NH\textsubscript{3}; followed by annealing at 500 and 700°C. High NH\textsubscript{3} (25 wt.%) catalyst concentration caused an increase in the amorphous TiO\textsubscript{x} loading; resulting in anatase (JCPDS/ICDD 1-562) formation with 500°C anneal, anatase and rutile (JCPDS/ICDD 2-494) formation with 700°C anneal.
Figure S3. SEM image showing the different morphology of free TiO$_2$ formed inside LNMO powder during synthesis; using 3 g LNMO, 12 mL TBOT and 3 mL NH$_3$. Sample was annealed at 700°C temperature (sample dispersion in ethanol, dropping onto 200 mesh copper TEM grid).

Figure S4. Zeta potential measurements as a function of pH, made in 10 mM KNO$_3$ aqueous suspensions of 0.01 wt.% LNMO and amorphous TiO$_x$. Each data point was collected as an average of minimum 3 runs. An important observation is that the surface charge at basic pHs is negative, both for LNMO and amorphous TiO$_x$. Amorphous TiO$_x$ was synthesized using 12 mL TBOT and 0.5 mL NH$_3$.

Figure S5. HAADF-STEM images of the commercial LNMO powder composed of (a) loose 15-50 nm nanoparticles and (b) 200 nm - 2 μm agglomerates.
Table S1. The Mn/Ni ratios from commercial LNMO measured by STEM-EDX from regions indicated in Figure S5.

| Mn/Ni | Region | 15-50 nm particles | 200 nm – 2 µm particles |
|-------|--------|---------------------|-------------------------|
| 1     | 3.1    | -                   | -                       |
| 2     | 3.0    | -                   | -                       |
| 3     | 2.9    | -                   | -                       |
| 4     | 3.0    | -                   | -                       |
| 5     | 2.8    | -                   | -                       |
| 6     | 2.9    | -                   | -                       |
| 7     | 0.3    | -                   | -                       |
| 8     | -      | 3.5                 | -                       |
| 9     | -      | 1.3                 | -                       |
| 10    | -      | 1.8                 | -                       |

Figure S6. PXRD pattern of the commercial LNMO.

Table S2. Chemical composition analysis results by ICP-AES for bare (commercial) LNMO without any anneals and for bare and surface modified LNMO with anneals at different temperatures

| Sample          | Measurement | Li (mol) | Li (wt%) | Ni (mol) | Ni (wt%) | Mn (mol) | Mn (wt%) | Ti (mol) | Ti (wt%) | Stoichiometry (based on Ni standardization) | Li:Ni:Mn:Ti (average molar ratio) |
|-----------------|-------------|----------|----------|----------|----------|----------|----------|----------|----------|-------------------------------------------|-------------------------------|
| bare (comm.) LNMO | 1           | 3.35     | 4.81E-04 | 15.4     | 2.63E-04 | 44.2     | 8.05E-04 | -        | -        | Li_{0.91}Ni_{0.50}Mn_{1.45}O_{x}         | 0.91:0.5:1.51                 |
| bare LNMO-500°C | 1           | 3.50     | 5.03E-05 | 17.0     | 2.89E-05 | 46.0     | 8.37E-05 | -        | -        | Li_{0.87}Ni_{0.50}Mn_{1.45}O_{x}         | 0.87:0.5:1.45                 |
| bare LNMO-800°C | 1           | 3.55     | 5.10E-05 | 16.5     | 2.81E-05 | 45.2     | 8.23E-05 | -        | -        | Li_{0.91}Ni_{0.50}Mn_{1.46}O_{x}         | 0.92:0.5:1.49                 |
| surface mod. LNMO-500°C | 1       | 3.32     | 4.78E-05 | 15.2     | 2.58E-05 | 44.6     | 8.11E-05 | 1.44     | 3.01E-06 | Li_{0.92}Ni_{0.50}Mn_{1.57}T_{0.06}O_{x} | 0.92:0.5:1.54:0.06             |
| surface mod. LNMO-800°C | 1       | 3.26     | 9.37E-06 | 14.9     | 5.07E-06 | 42.9     | 1.56E-05 | 2.08     | 8.70E-07 | Li_{0.92}Ni_{0.50}Mn_{1.54}T_{0.09}O_{x} | 0.92:0.5:1.53:0.08             |
| bare LNMO-500°C | 1           | 3.32     | 4.86E-05 | 15.4     | 2.63E-05 | 43.3     | 7.89E-05 | 1.47     | 3.07E-06 | Li_{0.92}Ni_{0.50}Mn_{1.50}T_{0.08}O_{x} | 0.92:0.5:1.53:0.08             |
Table S3. Lattice parameter refinement results and crystallite size calculations obtained from XRD data of bare and surface modified LNMO annealed at different temperatures.

| Sample               | a (Å)          | %Rwp | %R_bragg | χ²   | I_ξ  | Average crystallite size (nm) |
|----------------------|----------------|------|----------|------|------|------------------------------|
| surface mod. LNMO-500°C | 8.18170(10)    | 3.19 | 1.96     | 1.449 | 14.98 | 53                           |
| surface mod. LNMO-600°C | 8.18269(21)    | 3.26 | 2.17     | 1.520 | 15.22 | 52                           |
| surface mod. LNMO-700°C | 8.18551(19)    | 3.51 | 2.18     | 1.753 | 7.36  | 108                          |
| surface mod. LNMO-750°C | 8.18594(7)     | 3.15 | 1.49     | 1.433 | 4.23  | 188                          |
| surface mod. LNMO-800°C | 8.18574(7)     | 3.64 | 3.57     | 1.876 | 3.67  | 216                          |
| surface mod. LNMO-850°C | 8.18547(7)     | 3.65 | 2.16     | 1.903 | 0.82  | 967                          |
| bare LNMO-500°C        | 8.17909(19)    | 3.04 | 1.61     | 1.331 | 13.33 | 60                           |
| bare LNMO-600°C        | 8.17913(19)    | 3.01 | 2.00     | 1.314 | 16.31 | 49                           |
| bare LNMO-700°C        | 8.17952(7)     | 2.87 | 1.51     | 1.180 | 10.24 | 78                           |
| bare LNMO-750°C        | 8.18100(6)     | 3.01 | 2.16     | 1.275 | 8.36  | 95                           |
| bare LNMO-800°C        | 8.18184(6)     | 3.46 | 2.20     | 1.691 | 3.86  | 206                          |
| bare LNMO-850°C        | 8.17976(12)    | 3.87 | 2.40     | 2.224 | 4.16  | 191                          |

Table S4. Atom sites used for both LiNi₀.₅Mn₁.₅O₄₋₄.₈ and LiNi₀.₅Mn₁.₅₋₁.₅Ti₁.₅O₄ lattice parameter refinements [1] (Ti was assumed to replace Mn at the 16d sites [2])

| atom | site | x     | y     | z     | site occupancy |
|------|------|-------|-------|-------|----------------|
| Li   | 8a   | 0.125 | 0.125 | 0.125 | 1              |
| Ni   | 16d  | 0.5   | 0.5   | 0.5   | 0.25           |
| Mn   | 16d  | 0.5   | 0.5   | 0.5   | 0.75           |
| O    | 32e  | 0.26314(6) | 0.26323(5) | 0.2632(7) | 1              |

[1] Branford, W., Green, M.A., Neumann, D.A., Structure and ferromagnetism in Mn(4+) spinels: A Mn₀.₅Mn₁.₅O₄ (A = Li, Cu; M = Ni, Mg). Chem. Mater., 2002. 14: p. 1649-1656.

[2] Le, M.-L.-P., Strobel, P., Colin, C., Pagnier, T. and Alloin, F. Spinel-type solid solutions involving Mn⁴⁺ and Ti⁴⁺: Crystal chemistry, magnetic and electrochemical properties. Journal of Physics and Chemistry of Solids, 2011. 72(2): p. 124-135.
Figure S7. Refinement profiles for surface modified LNMO samples prepared using 3 g LNMO, 12 mL TBOT and 0.5 mL NH3 (25 wt.%), followed by anneals at different temperatures. The Bragg positions of LiNi$_{0.5}$Mn$_{1.5}$O$_{4-δ}$ and LiNi$_{0.5}$Mn$_{1.5-y}$Ti$_{y}$O$_{4}$ phases are shown as tick marks located in upper and lower positions, respectively.

Table S5. Particle diameter measurements based on TEM images (30-2700 x magnifications)

| # | diameter (nm) | # | diameter (nm) | # | diameter (nm) | # | diameter (nm) |
|---|---|---|---|---|---|---|---|
| 1 | 15.944 | 1 | 21.809 | 1 | 62.618 | 1 | 242.249 |
| 2 | 16.582 | 2 | 22.989 | 2 | 67.08 | 2 | 338.151 |
| 3 | 18.005 | 3 | 24.866 | 3 | 70.562 | 3 | 357.693 |
| 4 | 19.133 | 4 | 26.809 | 4 | 72.593 | 4 | 366.788 |
| 5 | 21.287 | 5 | 26.907 | 5 | 74.031 | 5 | 379.958 |
| 6 | 21.429 | 6 | 27.682 | 6 | 78.002 | 6 | 425.512 |
| 7 | 22.395 | 7 | 29.078 | 7 | 78.186 | 7 | 436.651 |
| 8 | 22.862 | 8 | 29.895 | 8 | 84.876 | 8 | 443.005 |
| 9 | 24.766 | 9 | 30.67 | 9 | 88.403 | 9 | 478.273 |
| 10 | 26.156 | 10 | 33.154 | 10 | 90.203 | 10 | 499.664 |
| 11 | 26.427 | 11 | 34.559 | 11 | 91.472 | 11 | 593.319 |
| 12 | 26.634 | 12 | 36.348 | 12 | 96.42 | 12 | 630.629 |
| 13 | 26.907 | 13 | 37.068 | 13 | 97.923 | 13 | 647.912 |
| 14 | 27.298 | 14 | 38.26 | 14 | 100.921 | 14 | 659.789 |
| 15 | 27.807 | 15 | 40.148 | 15 | 106.983 | 15 | 677.489 |
| 16 | 28.321 | 16 | 42.264 | 16 | 109.327 | 16 | 680.846 |
| 17 | 31.671 | 17 | 42.389 | 17 | 111.799 | 17 | 712.422 |
| 18 | 32.986 | 18 | 42.732 | 18 | 113.58 | 18 | 721.63 |
| 19 | 33.072 | 19 | 43.618 | 19 | 118.264 | 19 | 737.223 |
| 20 | 33.808 | 20 | 43.919 | 20 | 118.485 | 20 | 754.125 |
| 21 | 34.587 | 21 | 43.919 | 21 | 119.724 | 21 | 806.878 |
| 22 | 34.868 | 22 | 44.159 | 22 | 121.962 | 22 | 823.101 |
|   |   |   |   |   |
|---|---|---|---|---|
| 23 | 36.996 | 23 | 44.636 | 23 | 125.387 | 23 | 891.579 |
| 24 | 37.86 | 24 | 45.977 | 24 | 126.568 | 24 | 1024.652 |
| 25 | 39.793 | 25 | 46.548 | 25 | 127.267 | 25 | 1240.571 |
| 26 | 42.458 | 26 | 46.888 | 26 | 127.896 | 26 | 1257.456 |
| 27 | 43.204 | 27 | 47.168 | 27 | 130.004 | 27 | Avg. 647 |
| 28 | 43.241 | 28 | 49.752 | 28 | 130.236 | 28 |   |
| 29 | 44.78 | 29 | 50.36 | 29 | 140.021 | 29 |   |
| 30 | 44.921 | 30 | 52.523 | 30 | 144.665 | 30 |   |
| 31 | 46.923 | 31 | 54.239 | 31 | 146.049 | 31 |   |
| 32 | 51.418 | 32 | 58.609 | 32 | 150.063 | 32 |   |
| 33 | 54.841 | 33 | 58.609 | 33 | 153.239 | 33 |   |
| 34 | 66.061 | 34 | 61.77 | 34 | 158.114 | 34 |   |
| 35 | 211 | 35 | 62.451 | 35 | 164.699 | 35 |   |
| 36 | 236 | 36 | 63.915 | 36 | 165.92 | 36 |   |
| 37 | 249 | 37 | 66.825 | 37 | 176.652 | 37 |   |
| 38 | 249 | 38 | 66.962 | 38 | 179.811 | 38 |   |
| 39 | 282 | 39 | 67.298 | 39 | 201.74 | 39 |   |
| 40 | 319 | 40 | 69.338 | 40 | 215.377 | 40 |   |
| 41 | 325 | 41 | 71.669 | 41 | 220.379 | 41 |   |
| 42 | 325 | 42 | 73.088 | 42 | 247.5 | 42 |   |
| 43 | 374 | 43 | 73.088 | 43 | 253.973 | 43 |   |
| 44 | 381 | 44 | 74.136 | 44 | 264.447 | 44 |   |
| 45 | 441 | 45 | 75.03 | 45 | 287.529 | 45 |   |
| 46 | 479 | 46 | 75.162 | 46 | 288.444 | 46 |   |
| 47 | 557 | 47 | 77.19 | 47 | 317.128 | 47 |   |
| 48 | 557 | 48 | 80.755 | 48 | 350.903 | 48 |   |
| 49 | 578 | 49 | 81.342 | 49 | 355.258 | 49 |   |
| 50 | 646 | 50 | 86.055 | 50 | 402.87 | 50 |   |
| 51 | 658 | 51 | 89.744 | 51 | 407.922 | 51 |   |
| 52 | 819 | 52 | 89.972 | 52 | 441.603 | 52 |   |
| 53 | 837 | 53 | 100.72 | 53 | 447.145 | 53 |   |
| 54 | 924 | 54 | 119.188 | 54 | 467.718 | 54 |   |
| 55 | 1047 | 55 | 187.155 | 55 | 479.383 | 55 |   |
| 56 | 1150 | 56 | 292.984 | 56 | 496.258 | 56 |   |
| 57 | 1577 | 57 | 332.498 | 57 | 508.652 | 57 |   |
| 58 | 1756.457 | 58 | 355.258 | 58 | 523.161 | 58 | Avg. 243 |
| 59 | 201.74 | 59 | 358.612 | 59 | 528.242 | 59 | Avg. 338 |
| 60 | 411.556 | 60 | 366.956 | 60 | 528.242 | 60 |   |
| 61 | 436.663 | 61 | 366.956 | 61 | 528.652 | 61 |   |
| 62 | 461.85 | 62 | 366.956 | 62 | 528.652 | 62 |   |
| 63 | 464.378 | 63 | 366.956 | 63 | 528.652 | 63 |   |
| 64 | 495.496 | 64 | 366.956 | 64 | 664.326 | 64 |   |
| 65 | 547.42 | 65 | 366.956 | 65 | 664.326 | 65 |   |
| 66 | 738.607 | 66 | 366.956 | 66 | 676.391 | 66 |   |
| 67 | 760.096 | 67 | 366.956 | 67 | 701.807 | 67 |   |
| 68 | 790.79 | 68 | 366.956 | 68 | 830.152 | 68 |   |
| 69 | 899.3 | 69 | 366.956 | 69 | 851.34 | 69 |   |
| 70 | 1064.97 | 70 | 366.956 | 70 | 876.737 | 70 |   |
| 71 | 1099.226 | 71 | 366.956 | 71 | 1023.05 | 71 |   |
| 72 | 1191.807 | 72 | 366.956 | 72 | 1088.128 | 72 |   |
| 73 | 1542.807 | 73 | 366.956 | 73 | 1371.248 | 73 |   |
| 74 | 1632.547 | 74 | 366.956 | 74 | 1462.358 | 74 |   |
| 75 | 1756.457 | 75 | 366.956 | 75 | 1476.835 | 75 |   |
Figure S8. (a) Particle size distribution diagram for bare (commercial) LNMO without any anneals and Ti surface modified LNMO annealed at different temperatures. (b)(c) Particle size distributions for the bare (commercial) LNMO with 500 or 800°C anneals; and Ti-surface modified LNMO samples, with 500 or 800°C anneals. Measurements were made using TEM images (30-2700 x magnifications).

Figure S9. HAADF-STEM image of surface modified LNMO annealed at 500°C (left). The green line marks the region used to plot the profiles of atomic content of Mn, Ni and Ti (right). At the surface layer (2-3 nm) Ti concentration is higher.
Figure S10. HAADF-STEM image of surface modified LNMO annealed at 800°C (left). The green line marks the region used to plot the profiles of atomic content of Mn, Ni and Ti (right). At the surface layer (2 nm) Ti concentration is higher.

Figure S11. HAADF-STEM image of surface modified LNMO annealed at 850°C (left). The green line marks the region used to plot the profiles of atomic content of Mn, Ni and Ti (right). At the surface layer Ti concentration is higher.
Figure S12. BET measurements for bare and Ti surface modified LNMO with 500°C anneals. Surface areas were determined to be 20 and 24 m²/g for bare and Ti surface modified LNMO samples, respectively.

Figure S13. High resolution HAADF-STEM image, mixed (Mn, Ni), (Mn, Ti) and O STEM-EDX maps of surface modified LNMO annealed at 800°C. Ti layer does not exceed the edges of the crystal, therefore it has spinel structure. The area marked by white arrow corresponds to another crystal.
Figure S14. Effect of 1.5wt.% Ti exclusion from the total active material mass on discharge capacity (mAh/g) of surface modified, 500°C annealed LNMO. Since the effect of 1.5wt.% Ti exclusion on discharge capacity (mAh/g) is very small, the Ti was included in the total active material mass for all samples.

Figure S15. Comparison of cycle life and Coulombic efficiency of the bare LNMO sample without any anneals (as received from Sigma Aldrich) to a surface modified LNMO with 700°C anneal (synthesis made using 3 g LNMO, 6 mL TBOT and 0.5 mL NH₃). Measurements were made using a EC/DEC electrolyte, at 0.1 C, in a potential window from 3.4 to 5 V, for 50 cycles.