# Supporting Information

# Unusual Spinel-to-Layered Transformation in $LiMn_2O_4$ Cathode Explained by Electrochemical & Thermal-Stability Investigation

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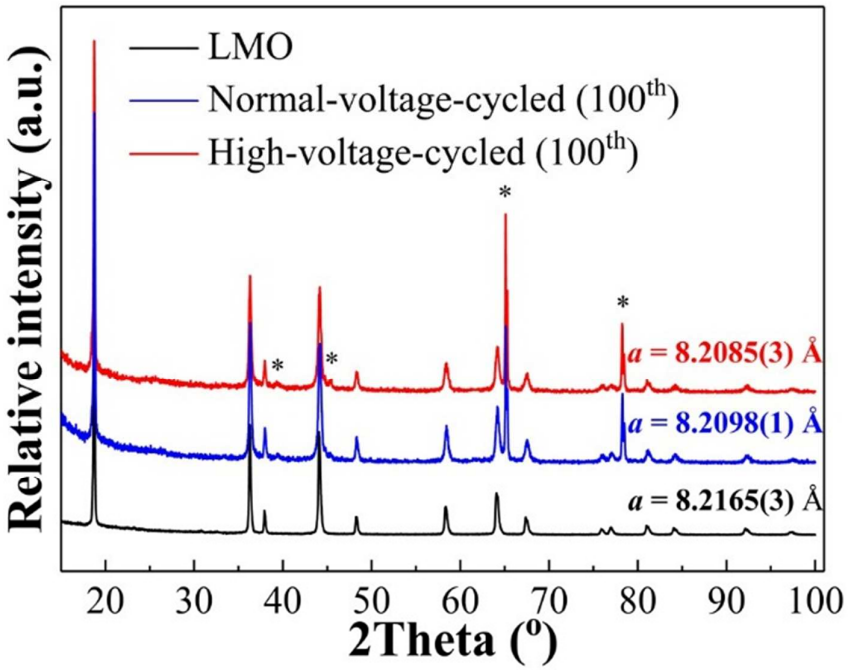


**Figure S1.** XRD patterns of pristine, normal-voltage-cycled (3-4.3 V, 100$^{th}$ cycle) and high-voltage-cycled (3-4.9 V, 100$^{th}$ cycle) LMO. Black asterisks indicate the reflections associated with the Al current collector.

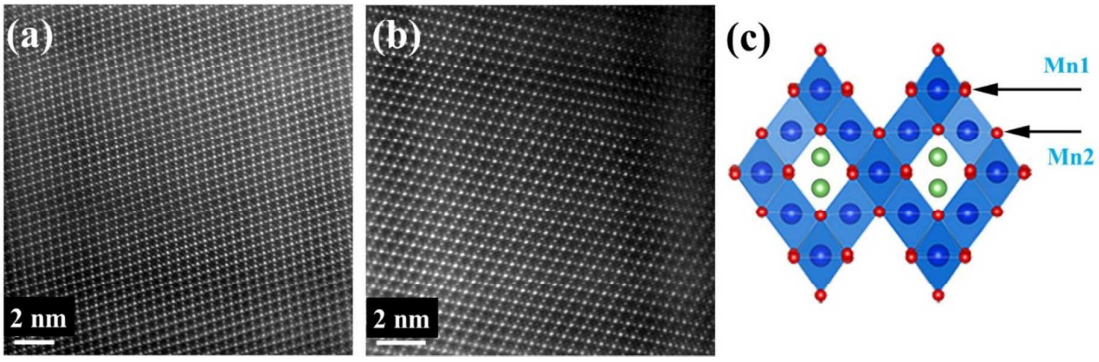


**Figure S2.** STEM-HAADF image of the bulk region of (a) normal-voltage-cycled (3-4.3 V, 16$^{th}$ cycle) and (b) high-voltage-cycled (3-4.9 V, 16$^{th}$ cycle) LMO. (c) Schematic of crystal structure of spinel LMO viewed along the [1 1 0] direction.

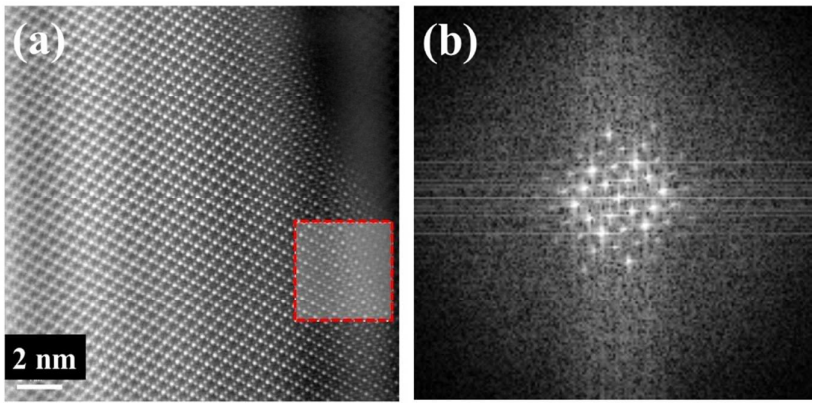


**Figure S3.** (a) STEM-HAADF of the surface and subsurface regions of normal-voltage-cycled (3-4.3 V, 16$^{th}$ cycle) LMO and (b) FFTs corresponding to the distorted $LiMn_3O_4$-like surface region marked by red box in (a).

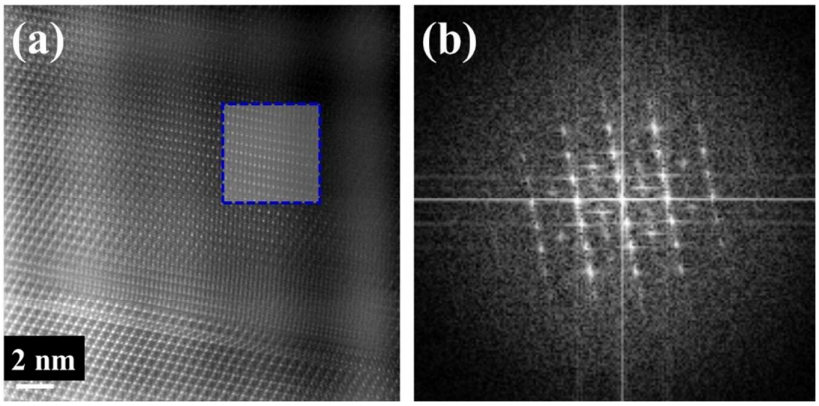


**Figure S4.** (a) STEM-HAADF image of the surface and subsurface regions of high-voltage-cycled (3-4.9 V, 16$^{th}$ cycle) LMO and (b) FFTs corresponding to the distorted layered-like surface region marked by red box in (a).

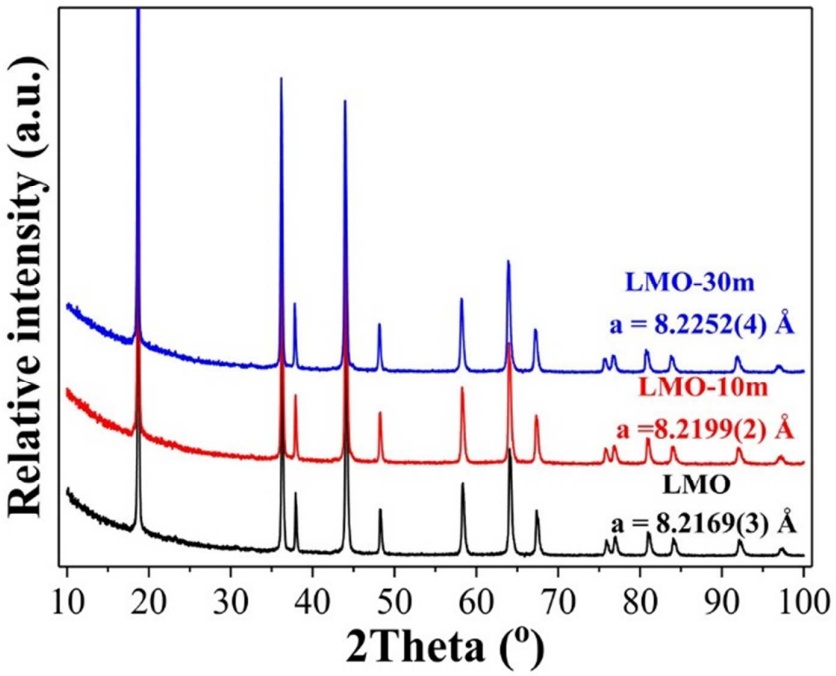


**Figure S5.** XRD patterns of pristine LMO and heat-treated LMO (600 $^{o}$C for 10 and 30 minutes).

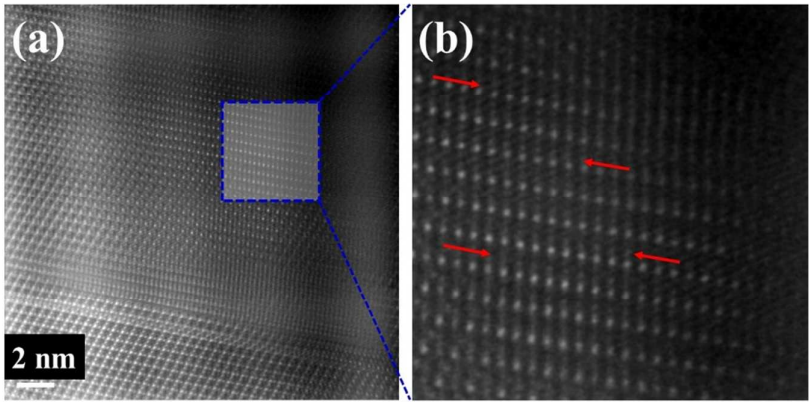


**Figure S6.** (a) STEM-HAADF image of the surface and subsurface regions of high-voltage-cycled (3-4.9 V, 16$^{th}$ cycle) LMO and (b) enlarged image corresponding to the layered-like surface region marked by blue box in (a). Red arrows in (b) indicate weak contrast associated with Mn ions between the layers.

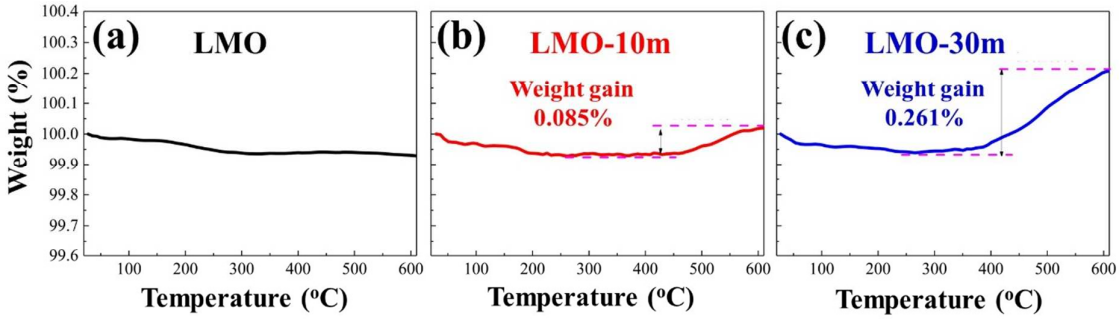


**Figure S7**. TGA curves of (a) pristine LMO, (b) LMO-10m and (c) LMO-30m. The heating rate is 10 °C/minute and the atmosphere during the experiments is 80% argon and 20% oxygen.

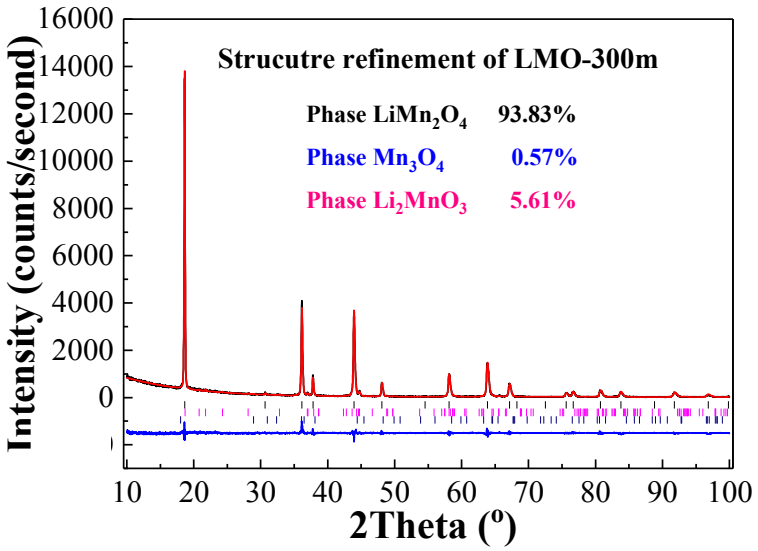


**Figure S8a.** Rietveld refinement profiles using room-temperature XRD data for LMO-300m refined in space group Fd-3m. The secondary phases are indexed as defect spinel $LiMn_3O_4$ and layered $Li_2MnO_3$, which are refined in space group of Fd-3m and C2/m, respectively. Observed, calculated and difference profiles are shown in blue, red and gray, respectively. Top tick marks show reflection positions for spinel $LiMn_2O_4$, middle tick marks show reflection positions for defect-spinel $LiMn_3O_4$ and bottom tick marks show reflection positions for layered $Li_2MnO_3$.

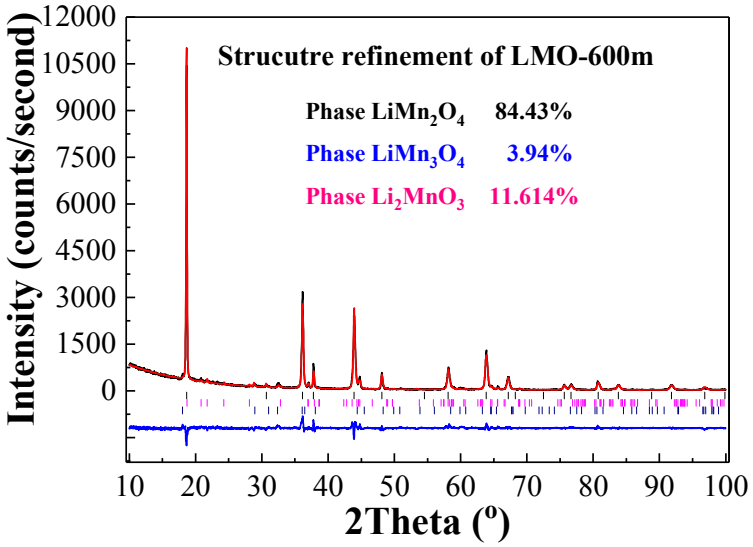


**Figure S8b.** Rietveld refinement profiles using room-temperature XRD data for LMO-600m refined in space group Fd-3m. The secondary phases are indexed as defect spinel $LiMn_3O_4$ and layered $Li_2MnO_3$, which are refined in space group of Fd-3m and C2/m, respectively. Observed, calculated and difference profiles are shown in blue, red and gray, respectively. Top tick marks show reflection positions for spinel $LiMn_2O_4$, middle tick marks show reflection positions for defect-spinel $LiMn_3O_4$ and bottom tick marks show reflection positions for layered $Li_2MnO_3$.

**Table S1.** Refined structural parameters for spinel LMO phase, defect spinel $LiMn_3O_4$ phase and layered $Li_2MnO_3$ phase in LMO-300m.

| **Refined structural parameters for spinel LMO phase in LMO-300m** | | | | | |
|---|---|---|---|---|---|
| **Space group Fd-3m, $a = b = c = 8.2398(3)$ Å, Phase fraction 93.83%** | | | | | |
| **Atom** | **Wyckoff site** | **x** | **y** | **z** | **Beq** |
| **Li** | 8a | 0 | 0 | 0 | 1.53 |
| **Mn** | 16d | 5/8 | 5/8 | 5/8 | 0.74 |
| **O** | 32e | 0.3875 | =x | = x | 1 |
| **Refined structural parameters for defect spinel $LiMn_3O_4$ phase in LMO-300m** | | | | | |
| **Space group $I4_1/amd$, $a = b = 5.8139(1)$ Å, $c = 9.3675(3)$ Å, Phase fraction 0.57%** | | | | | |
| **Atom** | **Wyckoff site** | **x** | **y** | **z** | **Beq** |
| **Mn1** | 4a | 0 | 1/4 | 0.8284 | 0.74 |
| **Mn2** | 8d | 0 | 1/2 | 1/2 | 0.74 |
| **O** | 16h | 0 | 0.3752 | 0.3402 | 1 |
| **Structural parameters obtained for layered $Li_2MnO_3$ phase in LMO-300m** | | | | | |
| **Space group C2/m, $a = 4.9272(4)$ Å, $b = 8.5361(3)$ Å, $c = 5.0234(1)$ Å, Phase fraction 5.60%** | | | | | |
| **Atom** | **Wyckoff site** | **x** | **y** | **z** | **Beq** |
| **Li1** | 2b | 0 | 1/2 | 0 | 1.53 |

| | | | | | |
|---|---|---|---|---|---|
| **Li2** | 2c | 0 | 0 | 1/2 | 1.53 |
| **Li3** | 4h | 0 | 0.7087 | 1/2 | 1.53 |
| **Mn** | 4g | 0 | 0.1713 | 0 | 0.74 |
| **O1** | 4i | 0.2805 | 0 | 0.2233 | 1 |
| **O2** | 8j | 0.2483 | 0.3529 | 0.2255 | 1 |

wRp = 9.182%, Rp = 6.564%, gof = 1.306. To avoid over-refinement of XRD data, site occupancy are fixed to 1, Beq for the same element is fixed to the same value and fraction occupancy of Li in $LiMn_3O_4$ is not refined.

**Table S2.** Refined structural parameters for spinel LMO phase, defect spinel $LiMn_3O_4$ phase and layered $Li_2MnO_3$ phase in LMO-600m.

| **Refined structural parameters for spinel LMO phase in LMO-600m** | | | | | |
|---|---|---|---|---|---|
| **Space group Fd-3m, *a* = *b* = *c* = 8.2412(4) Å, Phase fraction 84.43%** | | | | | |
| **Atom** | **Wyckoff site** | **x** | **y** | **z** | **Beq** |
| **Li** | 8a | 0 | 0 | 0 | 1.47 |
| **Mn** | 16d | 5/8 | 5/8 | 5/8 | 0.62 |
| **O** | 32e | 0.3849 | =x | = x | 1 |
| **Refined structural parameters for defect spinel $LiMn_3O_4$ phase in LMO-600m** | | | | | |
| **Space group $I4_1/amd$, *a* = *b* = 5.8139(2) Å, *c* = 9.3675(3) Å, Phase fraction 3.94%** | | | | | |
| **Atom** | **Wyckoff site** | **x** | **y** | **Z** | **Beq** |
| **Mn1** | 4a | 0 | 1/4 | 0.8284 | 0.62 |
| **Mn2** | 8d | 0 | 1/2 | 1/2 | 0.62 |
| **O** | 16h | 0 | 0.3752 | 0.3402 | 1 |
| **Structural parameters obtained for layered $Li_2MnO_3$ phase in LMO-600m** | | | | | |
| **Space group C2/m, *a* = 4.9272(3) Å, *b* = 8.5361(1) Å, *c* = 5.0234(2) Å, Phase fraction 11.63%** | | | | | |
| **Atom** | **Wyckoff site** | **x** | **y** | **z** | **Beq** |
| **Li1** | 2b | 0 | 1/2 | 0 | 1.47 |
| **Li2** | 2c | 0 | 0 | 1/2 | 1.47 |
| **Li3** | 4h | 0 | 0.7029 | 1/2 | 1.47 |
| **Mn** | 4g | 0 | 0.1736 | 0 | 0.62 |
| **O1** | 4i | 0.2605 | 0 | 0.2110 | 1 |
| **O2** | 8j | 0.2427 | 0.3628 | 0.2419 | 1 |

wRp = 9.883%, Rp = 6.984%, gof = 1.376. To avoid over-refinement of XRD data, site occupancy are fixed to 1, Beq for the same element is fixed to the same value and fraction occupancy of Li in $LiMn_3O_4$ is not refined.

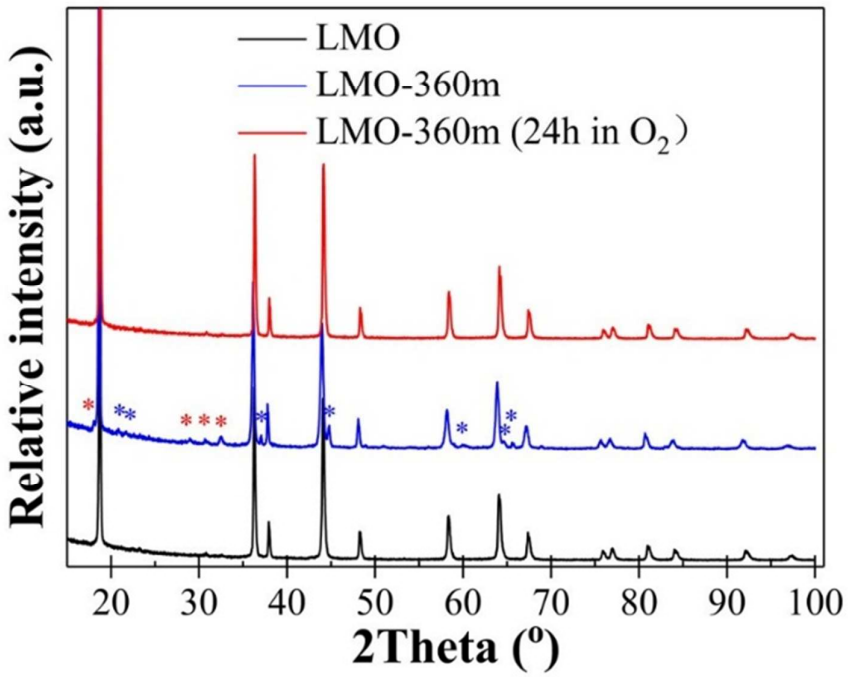


**Figure S9.** XRD patterns of LMO, heat-treated LMO-360m (argon atmosphere) and re-annealed LMO-360m ($O_2$). Red asterisks indicate the reflections associated with $LiMn_3O_4$ and blue asterisks indicate the reflections associated with $Li_2MnO_3$.