Supporting Information

Identifying Surface Structural Changes in Layered Li-excess Nickel Manganese Oxides in High Voltage Lithium Ion Batteries: A Joint Study of Electron Microscopy, Electron Energy Loss Spectroscopy, X-ray Diffraction and First-Principles Computation

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Figure S1 Rietveld refinement of the high resolution synchrotron X-ray diffraction pattern (λ = 0.4122) of pristine $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$. The superlattice peaks at 20-30° 2Θ are distinct, indicating long range cation ordering in the transition metal layer. The Rietveld refinement results listed in the inset table indicates a well-layered structure with little Li/Ni mixing.

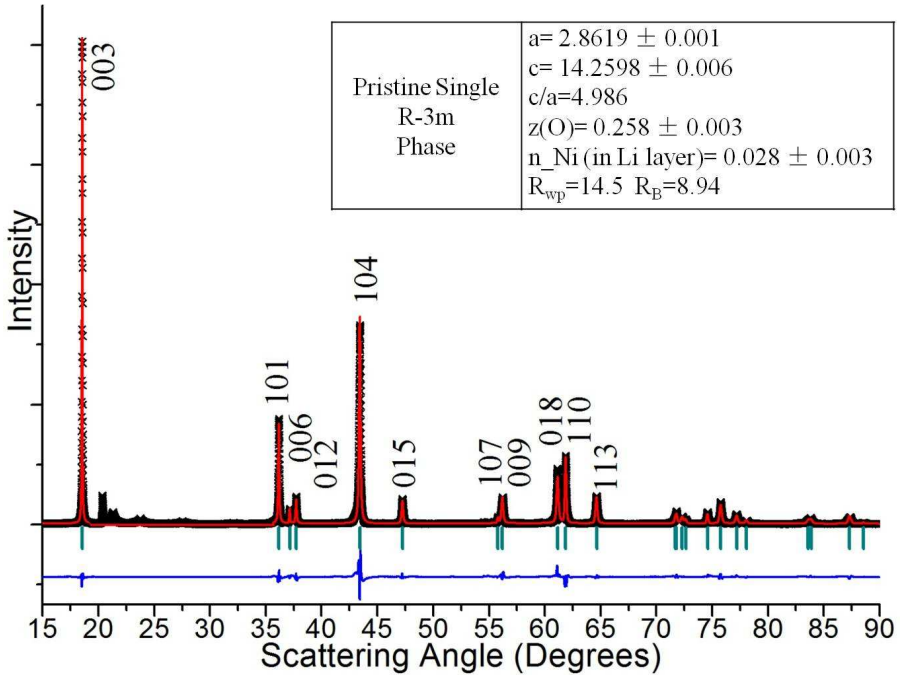


Figure S2-S4 Cation arrangements and energies of all the calculated models of $Li[Ni_{1/4}Li_{1/6}Mn_{7/12}]O_2$

Previous research[1] showed that, the excess Li ions in TM layer are preferred to be surrounded by Mn ions. Therefore in all the models, this principle is applied after the specific requirements are fulfilled.

Three sets of models are created. In each sets, two different models are calculated and their energies are compared in Table 1. The total energy of **model_1 is the lowest** and is set as the reference state.

Table S1 Calculated energy of different models (mode_1 is set as the reference state)

	Energy (eV per formula)
Model_1	0
Model_2	109
Model_3	32
Model_4	98
Model_5	105
Model_6	133

Figure S2 shows the first set of models.

In this set of models, Li layer is composed of Li ions only.

In model_1, excess Li ions in TM layer are surrounded by 6 Mn ions or 5 Mn ions. Li ions are 2^{nd} nearest neighbors.

In model_2, excess Li ions in TM layer are surrounded by 6 Mn ions or 4 Mn ions. Li ions are 3^{rd} nearest neighbors.

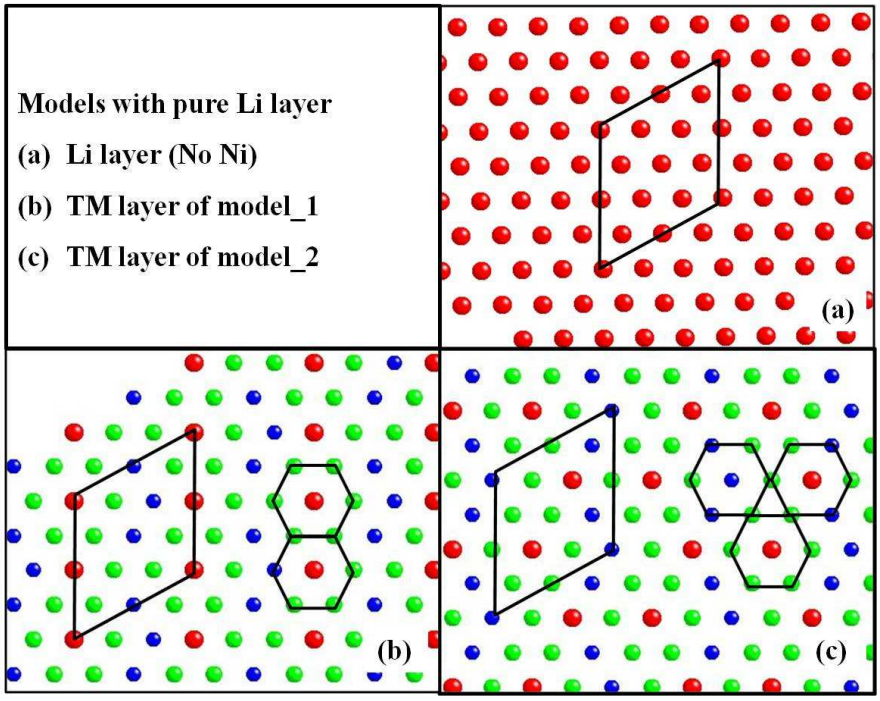


Figure S3 shows the second set of models.

In this set of models, Li-Ni interlayer mixing is introduced. The Li layer supercell is composed of 11 Li and 1 Ni. The TM layer supercell is composed of 3 Li, 2 Ni and 7 Mn .

In both models, Li ions in TM layer are 2nd nearest neighbors with each other. The TM ion arrangements in TM layer are slightly different.

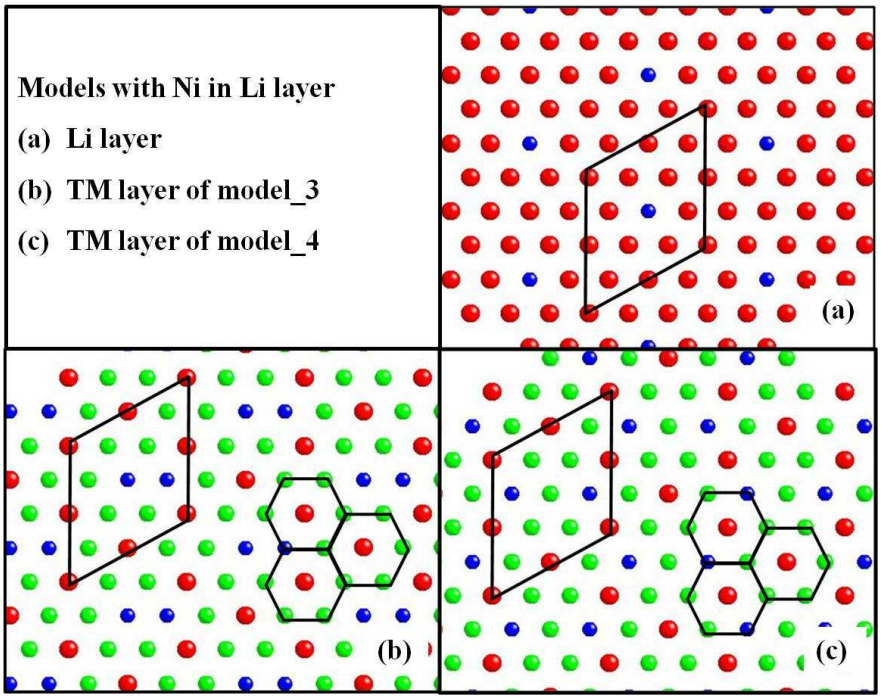


Figure S4 shows the third set of models.

In this set of models, the Li layer is similar to the second set of models, but the TM layers are different.

In both models, Li ions in TM layer are 3rd nearest neighbors with each other. This specific arrangements ensure that, the TM ions in TM layer are following the Mn lattice in [111] plane of $LiMn_2O_4$ spinel.

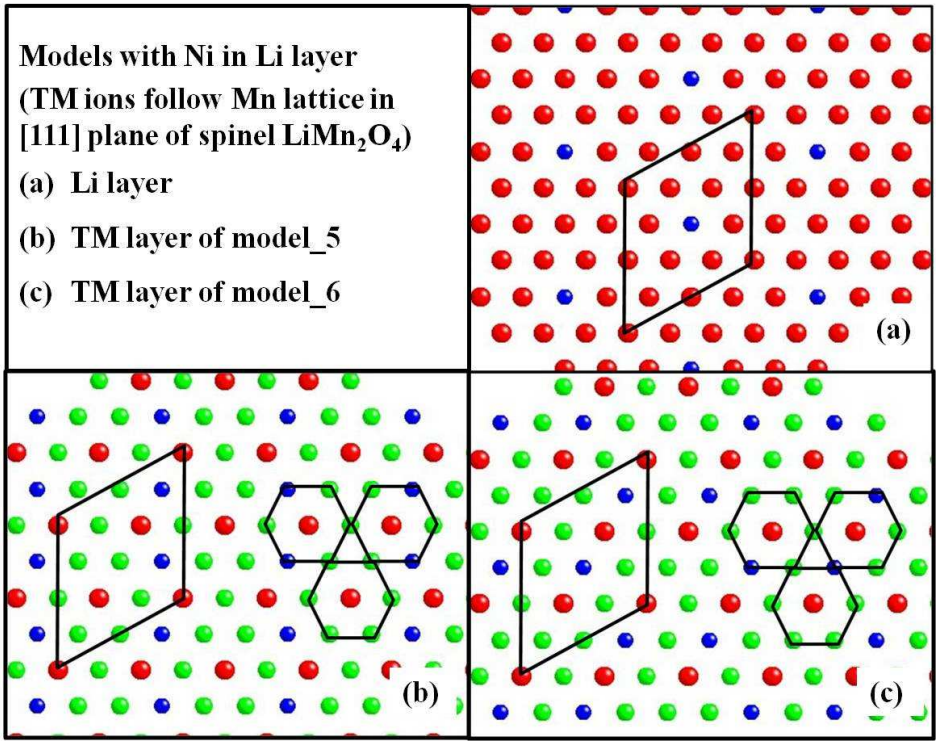
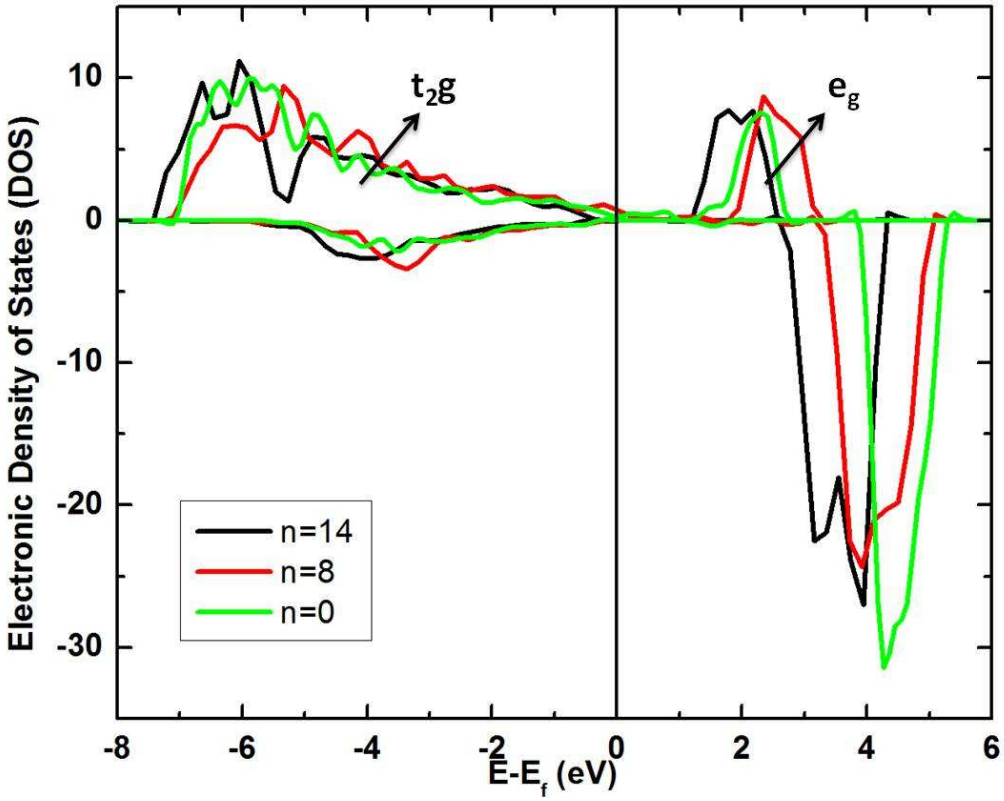


Figure S5 The projected density of states (DOS) of Mn ions in $Li_{n/12}Ni_{1/4}Mn_{7/12}O_2$ (n=14, 8, 0)

This figure shows the calculated projected DOS of Mn ions in $Li_{n/12}Ni_{1/4}Mn_{7/12}O_2$ with three different charging state, n=14 (black), n=8 (red) and n=0 (green).

In all three plots, the electron spin-up states of t_{2g} orbitals and are fully occupied, while the none spin-up states of e_g orbitals is occupied. The spin-down states of both orbitals are completely empty. The DOS plots are consistent with the t_{2g}^3 electron configuration of Mn^{4+} ion in previous research[2]. The trial shape differences may be caused by the change of local environments of Mn ions in different charging states.



Reference

(1) Breger, J.; Jiang, M.; Dupre, N.; Meng, Y. S.; Shao-Horn, Y.; Ceder, G.; Grey, C. P. *Journal of Solid State Chemistry* **2005**, *178*, 2575-2585.

(2) Xu, B.; Meng, S. *Journal of Power Sources* **2010**, *195*, 4971-4976.