Supplementary Information

The role of Al-doping with different sites on structure and electrochemical performance of spherical LiNi_{0.5}Mn_{1.5}O_4 cathode materials for lithium-ion battery

Anyong Chen,‡a Linglong Kong,‡b,c Yang Shu,c Wenchao Yan,b,c Wei Wu,b,c Yongji Xu,*a Hongtao Gao,**a and Yongcheng Jin*b,c

a State Key Laboratory Base of Eco-Chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science & Technology, Qingdao 266042, China.
b Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.
c Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China.

*corresponding authors
E-mail address: xuyj1960@126.com (Y. Xu), gaohtao@qust.edu.cn (H. Gao), jinyc@qibebt.ac.cn (Y. Jin)
‡ These authors contributed equally to this work.
Table S1 The ICP-AES results of the prepared LNMO samples.

| Sample                         | Li   | Ni   | Mn   | Al   |
|--------------------------------|------|------|------|------|
| LiNi0.5Mn1.5O4                 | 1.01 | 0.49 | 1.49 | 0.00 |
| Li0.98Ni0.45Al0.05Mn1.5O4      | 0.98 | 0.44 | 1.49 | 0.047|
| Li1.05Ni0.4Al0.05Mn1.45O       | 1.05 | 0.51 | 1.46 | 0.028|
| LiNi0.475Al0.05Mn1.475O4       | 1.02 | 0.468| 1.47 | 0.047|

Table S2 Lattice parameters of LNMO cathode materials with Al-doping at different sites and various contents.

| Sample                         | a/nn | V/nn³ | I_{111}/I_{111} |
|--------------------------------|------|-------|-----------------|
| LiNi0.5Mn1.5O4                 | 0.81715 | 0.54564 | 2.04            |
| Li0.99Ni0.49Al0.01Mn1.5O4      | 0.81697 | 0.54528 | 2.08            |
| Li0.97Ni0.47Al0.03Mn1.5O4      | 0.81693 | 0.54520 | 2.27            |
| Li0.95Ni0.45Al0.05Mn1.5O4      | 0.81684 | 0.54502 | 2.34            |
| Li0.97Ni0.43Al0.07Mn1.5O4      | 0.81675 | 0.54484 | 2.11            |
| Li1.00Ni0.4Al0.01Mn1.45O       | 0.81679 | 0.54492 | 2.09            |
| Li1.03Ni0.3Al0.03Mn1.45O4      | 0.81681 | 0.54496 | 2.54            |
| Li0.90Ni0.5Al0.05Mn1.45O4      | 0.81682 | 0.54498 | 2.20            |
| Li1.00Ni0.5Al0.07Mn1.45O4      | 0.81686 | 0.54506 | 2.41            |
| LiNi0.495Al0.01Mn1.495O4       | 0.81676 | 0.54486 | 2.04            |
| LiNi0.485Al0.03Mn1.485O4       | 0.81661 | 0.54456 | 2.28            |
| LiNi0.475Al0.05Mn1.475O4       | 0.81652 | 0.54438 | 2.28            |
| LiNi0.465Al0.07Mn1.465O4       | 0.81643 | 0.54420 | 2.18            |
| JCPDS (80-2162)                | 0.817 | 0.54534 | 2.66            |
Table S3 Structural parameters after Rietveld refinements.

Li\textsubscript{0.95}Ni\textsubscript{0.45}Al\textsubscript{0.05}Mn\textsubscript{1.5}O\textsubscript{4}

(Fd\textsuperscript{3}m, a = b = c = 8.1650 Å, α = β = γ = 90°, Rp=2.29, GOF=1.16, wRp=2.91.)

| Atom  | Wyckoff symbol | x     | y     | z     | Uiso  | Site occupancy |
|-------|----------------|-------|-------|-------|-------|----------------|
| Li1   | 8a             | 0.500 | 0.500 | 0.500 | 0.042 | 0.886          |
| Li2   | 16d            | 0.625 | 0.125 | 0.125 | 0.042 | 0.008          |
| Mn1   | 16d            | 0.625 | 0.125 | 0.125 | 0.003 | 0.750          |
| Al1   | 16d            | 0.625 | 0.125 | 0.125 | 0.012 | 0.025          |
| Ni1   | 16d            | 0.625 | 0.125 | 0.125 | 0.003 | 0.217          |
| Ni2   | 8a             | 0.500 | 0.500 | 0.500 | 0.003 | 0.017          |
| O1    | 32e            | 0.635 | 0.365 | 0.135 | 0.015 | 1.000          |
| Li2   | 16d            | 0.625 | 0.125 | 0.125 | 0.042 | 0.008          |
| Mn1   | 16d            | 0.625 | 0.125 | 0.125 | 0.003 | 0.750          |

Li\textsubscript{1.03}Ni\textsubscript{0.5}Al\textsubscript{0.03}Mn\textsubscript{1.47}O\textsubscript{4}

(Fd\textsuperscript{3}m, a = b = c = 8.1666 Å, α = β = γ = 90°, Rp=2.23, GOF=1.22, wRp=2.90)

| Atom  | Wyckoff symbol | x     | y     | z     | Uiso  | Site occupancy |
|-------|----------------|-------|-------|-------|-------|----------------|
| Li1   | 8a             | 0.250 | 0.250 | 0.250 | 0.053 | 1.000          |
| Mn1   | 16d            | 0.625 | 0.125 | 0.125 | 0.009 | 0.735          |
| Al1   | 16d            | 0.625 | 0.125 | 0.125 | 0.012 | 0.015          |
| Ni1   | 16d            | 0.625 | 0.125 | 0.125 | 0.009 | 0.250          |
| O1    | 32e            | 0.638 | 0.362 | 0.138 | 0.010 | 1.000          |

LiNi\textsubscript{0.475}Al\textsubscript{0.03}Mn\textsubscript{1.475}O\textsubscript{4}

(Fd\textsuperscript{3}m, a = b = c = 8.1653 Å, α = β = γ = 90°, Rp=2.75, GOF=1.11, wRp=3.51)

| Atom  | Wyckoff symbol | x     | y     | z     | Uiso  | Site occupancy |
|-------|----------------|-------|-------|-------|-------|----------------|
| Li1   | 8a             | 0.250 | 0.250 | 0.250 | 0.053 | 0.968          |
| Li2   | 16d            | 0.625 | 0.125 | 0.125 | 0.053 | 0.016          |
| Mn1   | 16d            | 0.625 | 0.125 | 0.125 | 0.007 | 0.738          |
| Al1   | 16d            | 0.625 | 0.125 | 0.125 | 0.012 | 0.025          |
| Ni1   | 16d            | 0.625 | 0.125 | 0.125 | 0.007 | 0.221          |
| Ni2   | 8a             | 0.250 | 0.250 | 0.250 | 0.007 | 0.032          |
| O1    | 32e            | 0.635 | 0.135 | 0.365 | 0.015 | 1.000          |
Fig. S1 SEM images of (a) LiNi$_{0.5}$Mn$_{1.5}$O$_4$, (b-e) Li$_{1-x}$Ni$_{0.5-x}$Al$_x$Mn$_{1.5}$O$_4$ (x=0.01, 0.03, 0.05 and 0.07), and (f-i) Li$_{1+x}$Ni$_{0.5}$Al$_x$Mn$_{1.5-x}$O$_4$ (x=0.01, 0.03, 0.05 and 0.07). The scale bar for the larger graphs is 20 μm, and the scale bar for the inserted graphs is 2μm.

Fig. S2 Cross-sectional images of (a) LiNi$_{0.495}$Al$_{0.01}$Mn$_{1.495}$O$_4$ (x=0.01), (b) LiNi$_{0.485}$Al$_{0.03}$Mn$_{1.485}$O$_4$ (x=0.03), (c) LiNi$_{0.475}$Al$_{0.05}$Mn$_{1.475}$O$_4$ (x=0.05), and (d) LiNi$_{0.465}$Al$_{0.05}$Mn$_{1.465}$O$_4$ (x=0.07)

Fig. S3 Elemental map of LiNi$_{0.475}$Al$_{0.05}$Mn$_{1.475}$O$_4$ (x=0.05).
Fig. S4 TEM images of (a) LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and (b) LiNi$_{0.475}$Al$_{0.05}$Mn$_{1.475}$O$_4$ combined with relevant elemental mappings of Ni, Mn, O, and Al.

Fig. S5 Cyclic voltammetry curves of Li$_{1-x}$Ni$_{0.5}$Al$_x$Mn$_{1.5}$O$_4$ (x=0, 0.01, 0.03, 0.05, and 0.07) (a) and Li$_{1+x}$Ni$_{0.5}$Al$_x$Mn$_{1.5-x}$O$_4$ (x=0, 0.01, 0.03, 0.05, and 0.07) (c) combined with the relevant enlarged area (b) and (d) in the potential intervals of 3.7~4.3 V (vs. Li/Li$^+$).
Fig. S6 Capacity ratios of (a) Li$_{1-x}$Ni$_{0.5-x}$Al$_x$Mn$_{1.5}$O$_4$ and (b) Li$_{1+x}$Ni$_{0.5}$Al$_x$Mn$_{1.5-x}$O$_4$ (x=0, 0.01, 0.03, 0.05, and 0.07) at various current densities (0.5 C, 1C, 2C, 5C, 10C and 20C).

Table S4 The specific capacities and capacity ratios of Li$_{1-x}$Ni$_{0.5-x}$Al$_x$Mn$_{1.5}$O$_4$, Li$_{1+x}$Ni$_{0.5}$Al$_x$Mn$_{1.5-x}$O$_4$, and LiNi$_{0.5-x/2}$Al$_x$Mn$_{1.5-x/2}$O$_4$ (x=0, 0.01, 0.03, 0.05 and 0.07) at 55 °C (0.5C).

| Sample                          | 1st cycle (mAh g$^{-1}$) | 50th cycle (mAh g$^{-1}$) | Capacity ratio (%) |
|---------------------------------|-------------------------|----------------------------|--------------------|
| LiNi$_{0.5}$Mn$_{1.5}$O$_4$     | 131                     | 57.7                       | 44.05              |
| Li$_{0.99}$Ni$_{0.01}$Mn$_{1.5}$O$_4$ | 127.9                 | 109.3                      | 85.46              |
| Li$_{0.97}$Ni$_{0.03}$Al$_{0.03}$Mn$_{1.5}$O$_4$ | 121.9                 | 103.2                      | 84.66              |
| Li$_{0.95}$Ni$_{0.05}$Al$_{0.05}$Mn$_{1.5}$O$_4$ | 127.8                 | 115.2                      | 90.14              |
| Li$_{0.93}$Ni$_{0.07}$Al$_{0.07}$Mn$_{1.5}$O$_4$ | 119.1                 | 103.9                      | 87.24              |
| Li$_{1.01}$Ni$_{0.02}$Al$_{0.02}$Mn$_{1.48}$O$_4$ | 125.3                 | 101.3                      | 80.85              |
| Li$_{1.03}$Ni$_{0.01}$Al$_{0.03}$Mn$_{1.47}$O$_4$ | 126.8                 | 112.6                      | 88.80              |
| Li$_{1.03}$Ni$_{0.03}$Al$_{0.05}$Mn$_{1.45}$O$_4$ | 129.3                 | 109                        | 84.30              |
| Li$_{1.07}$Ni$_{0.07}$Al$_{0.05}$Mn$_{1.44}$O$_4$ | 121                   | 102                        | 84.30              |
| LiNi$_{0.495}$Al$_{0.01}$Mn$_{1.495}$O$_4$    | 124.6                  | 96.3                       | 77.29              |
| LiNi$_{0.485}$Al$_{0.03}$Mn$_{1.485}$O$_4$    | 128.9                  | 106.8                      | 82.85              |
| LiNi$_{0.475}$Al$_{0.05}$Mn$_{1.475}$O$_4$    | 126                    | 111.7                      | 88.65              |
| LiNi$_{0.465}$Al$_{0.07}$Mn$_{1.465}$O$_4$    | 126.1                  | 84.7                       | 67.17              |
Fig. S7 EIS spectra of (a, b) Li$_{1-x}$Ni$_{0.5-x}$Al$_x$Mn$_{1.5}$O$_4$ and (c, d) Li$_{1+x}$Ni$_{0.5}$Al$_x$Mn$_{1.5-x}$O$_4$ (x=0, 0.01, 0.03, 0.05 and 0.07) before (a, c) and after 200 cycles (b, d) at 0.5C combining with the applied equivalent circuit (e). $R_1$ refers to the solution resistance, $R_2$ relates to the charge-transfer resistance, CPE$_1$ is the constant phase element, and $W_1$ donates the semi-infinite Warburg diffusion impedance.
Table S5 The stimulated values of $R_2$ before and after 200 cycles corresponding to the samples of $\text{Li}_{1-x}\text{Ni}_{0.5-x}\text{Al}_x\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Al}_x\text{Mn}_{1.5-x}\text{O}_4$, and $\text{LiNi}_{0.5-x/2}\text{Al}_x\text{Mn}_{1.5-x/2}\text{O}_4$ ($x=0, 0.01, 0.03, 0.05$ and $0.07$) utilizing the equivalent circuit.

| Sample                | $R_2$-$0^{th}$ cycle ($\Omega$) | $R_2$-$200^{th}$ cycle ($\Omega$) | $\Delta R_2$ ($\Omega$) |
|-----------------------|----------------------------------|----------------------------------|--------------------------|
| $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ | 232.6                            | 400                              | 167.4                    |
| $\text{Li}_{0.99}\text{Ni}_{0.49}\text{Al}_{0.01}\text{Mn}_{1.5}\text{O}_4$ | 218.7                            | 200.3                            | -18.4                    |
| $\text{Li}_{0.97}\text{Ni}_{0.47}\text{Al}_{0.03}\text{Mn}_{1.5}\text{O}_4$ | 170.8                            | 160.3                            | -10.5                    |
| $\text{Li}_{0.95}\text{Ni}_{0.45}\text{Al}_{0.05}\text{Mn}_{1.5}\text{O}_4$ | 175                              | 158.5                            | -16.5                    |
| $\text{Li}_{0.97}\text{Ni}_{0.43}\text{Al}_{0.07}\text{Mn}_{1.5}\text{O}_4$ | 105.6                            | 147.7                            | 42.1                     |
| $\text{Li}_{1.01}\text{Ni}_{0.32}\text{Al}_{0.01}\text{Mn}_{1.40}\text{O}_4$ | 175.4                            | 370.1                            | 194.7                    |
| $\text{Li}_{1.03}\text{Ni}_{0.32}\text{Al}_{0.03}\text{Mn}_{1.47}\text{O}_4$ | 172.4                            | 107.5                            | -64.9                    |
| $\text{Li}_{1.05}\text{Ni}_{0.32}\text{Al}_{0.05}\text{Mn}_{1.44}\text{O}_4$ | 250.9                            | 112.7                            | -138.2                   |
| $\text{Li}_{1.07}\text{Ni}_{0.32}\text{Al}_{0.07}\text{Mn}_{1.40}\text{O}_4$ | 256.4                            | 136.3                            | -120.1                   |
| $\text{Li}_{0.89}\text{Ni}_{0.49}\text{Al}_{0.01}\text{Mn}_{1.49}\text{O}_4$ | 210.8                            | 160.2                            | -50.6                    |
| $\text{Li}_{0.85}\text{Ni}_{0.49}\text{Al}_{0.03}\text{Mn}_{1.48}\text{O}_4$ | 160.6                            | 158.4                            | -2.2                     |
| $\text{Li}_{0.87}\text{Ni}_{0.47}\text{Al}_{0.05}\text{Mn}_{1.47}\text{O}_4$ | 155                              | 115.3                            | -39.7                    |
| $\text{Li}_{0.65}\text{Ni}_{0.46}\text{Al}_{0.07}\text{Mn}_{1.46}\text{O}_4$ | 135.1                            | 360.8                            | 225.7                    |

Fig. S8. SEM images of the cycled lithium anode in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (a) and (c) $\text{LiNi}_{0.475}\text{Al}_{0.05}\text{Mn}_{1.475}\text{O}_4$ batteries systems combining with the distribution of Mn in the Li anode surface (b, d). The scale bar for (a) and (c) is 200 μm.
Table S6 The specific content values of Mn on the Li anode referring to LiNi_{0.5}Mn_{1.5}O_4 and LiNi_{0.475}Al_{0.05}Mn_{1.475}O_4 batteries systems from the EDS.

| Sample                     | Mn dissolution content (%) |
|----------------------------|----------------------------|
| LiNi_{0.5}Mn_{1.5}O_4     | 0.52                       |
| LiNi_{0.475}Al_{0.05}Mn_{1.475}O_4 | 0.35              |