

Supplementary information

# **Impacts of Mg doping on the Structural Properties and Degradation Mechanisms of a Li and Mn Rich Layered Oxide Cathode Material for Lithium-ion Batteries**

**Songyoot Kaewmala<sup>a</sup>, Natthapong Kamma<sup>2</sup>, Sunisa Buakeaw<sup>3</sup>, Wanwisa Limphirat<sup>4</sup>, Jeffrey Nash<sup>1</sup>, Sutham Srilomsak<sup>1,2</sup>, Pimpa Limthongkul<sup>3</sup>, and Nonglak Meethong<sup>1,2,\*</sup>**

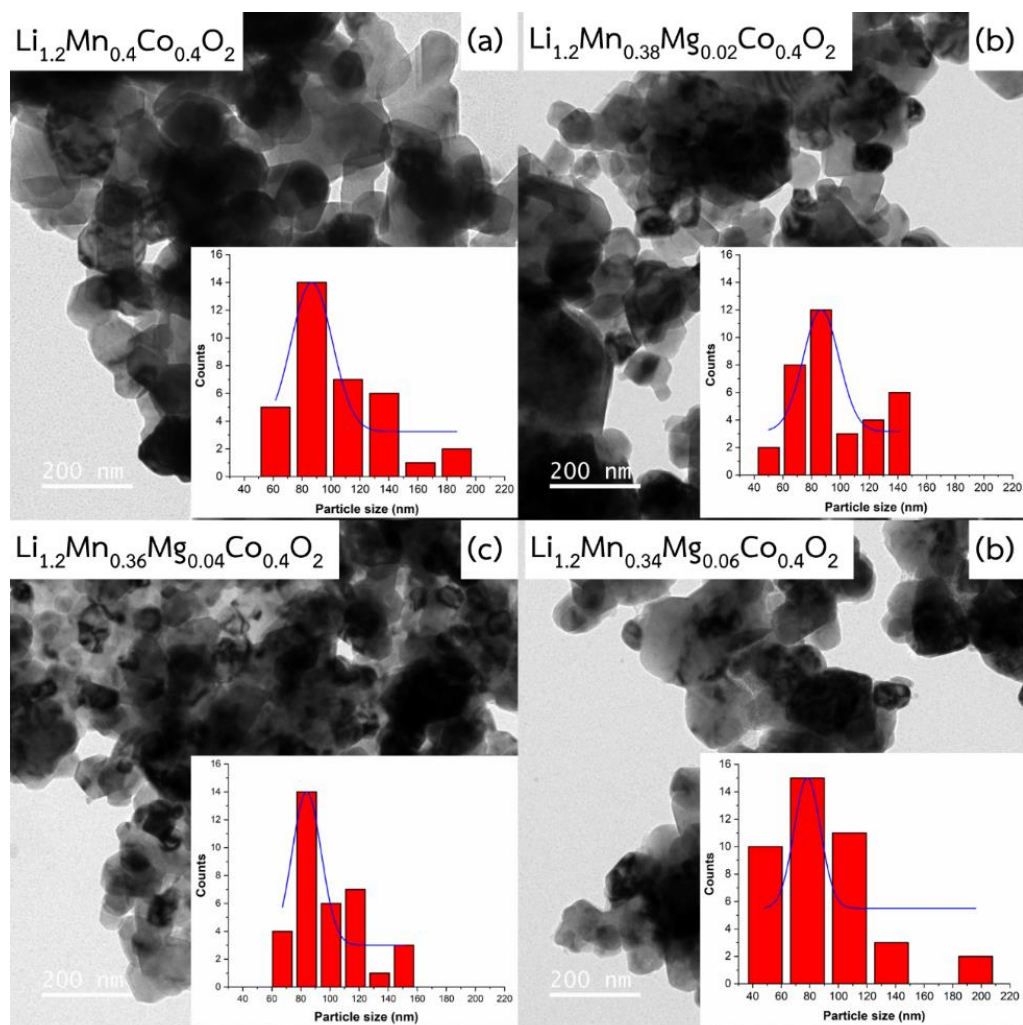
<sup>1</sup>Institute of Nanomaterials Research and Innovation for Energy (IN-RIE), Research Network of NANOTEC-KKU (RNN), Khon Kaen University, Khon Kaen 40002, Thailand

<sup>2</sup>Materials Science and Nanotechnology Program, Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

<sup>3</sup>National Energy Technology Center (ENTEC), National Science and Technology Development Agency, Pathumthani, 12120, Thailand

<sup>4</sup>Synchrotron Light Research Institute, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima 30000, Thailand

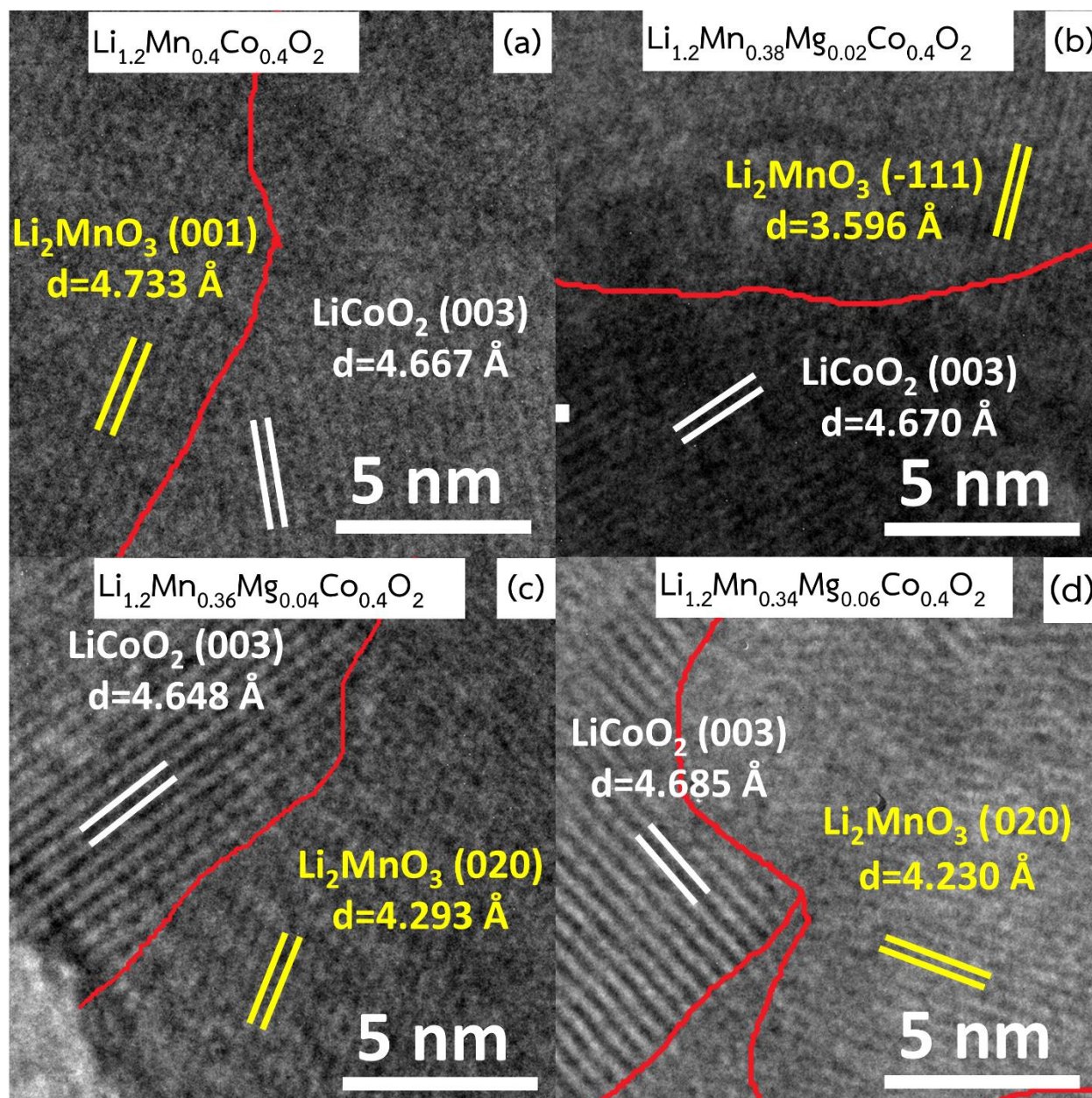
\* nonmee@kku.ac.th (N.M.)



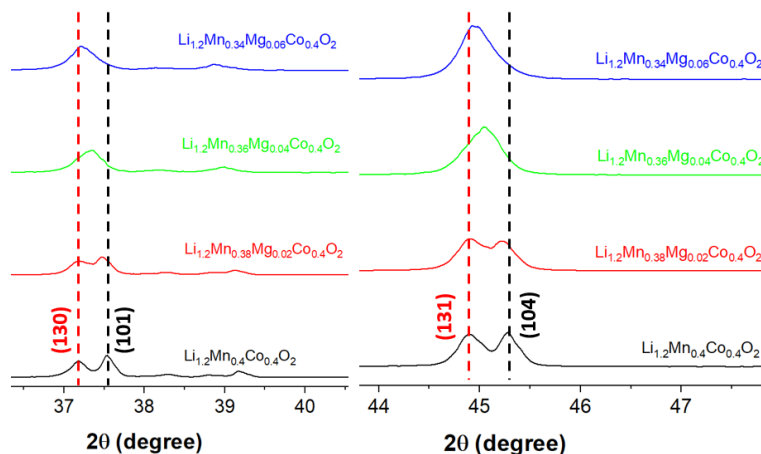
**Figure S1.** TEM images of the  $\text{Li}_{1.2}\text{Mn}_{0.4-x}\text{Mg}_x\text{Co}_{0.4}\text{O}_2$  ( $x=0.00, 0.02, 0.04, \text{ and } 0.06$ ) materials.

**Table S1.** The averages  $\text{Li}_2\text{MnO}_3$ -like and  $\text{LiCoO}_2$ -like domain sizes of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  and Mg-doped  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  materials

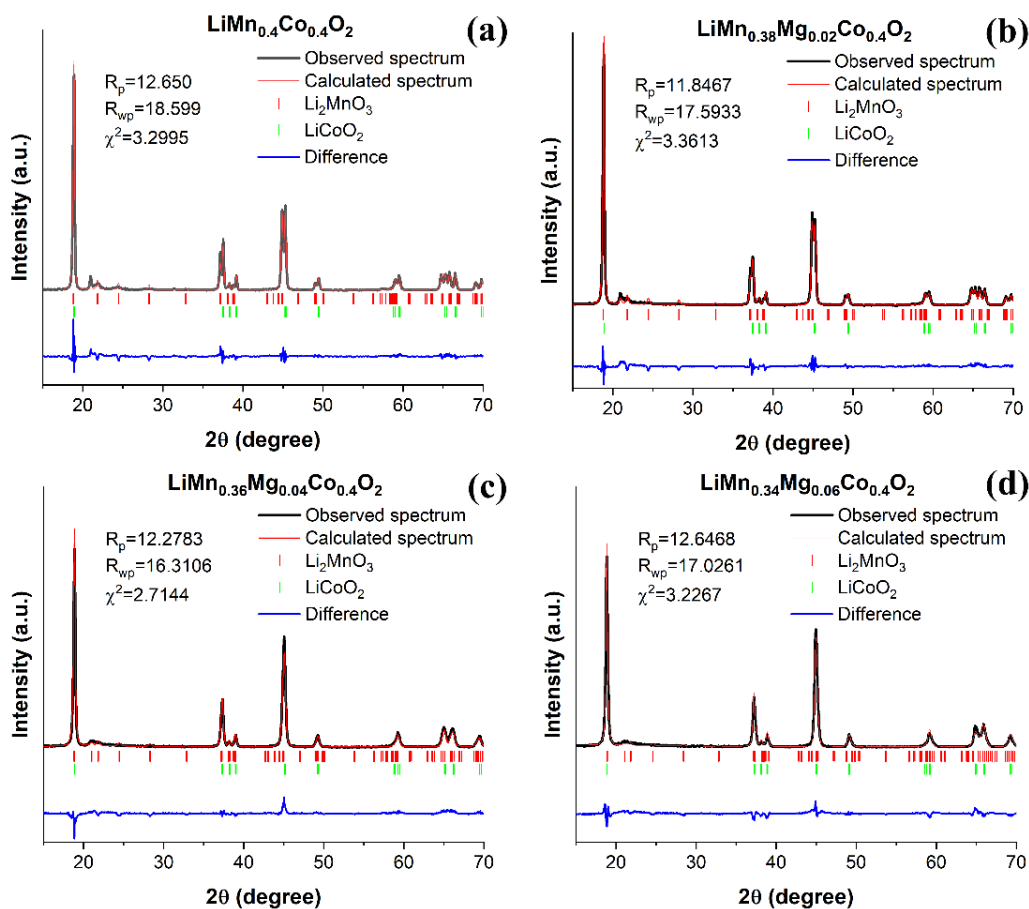
| Sample                                                                     | Average $\text{Li}_2\text{MnO}_3$ -like domain size (nm <sup>2</sup> ) | Average $\text{LiCoO}_2$ -like domain size (nm <sup>2</sup> ) |
|----------------------------------------------------------------------------|------------------------------------------------------------------------|---------------------------------------------------------------|
| $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$                  | 1000                                                                   | 1300                                                          |
| $\text{Li}_{1.2}\text{Mn}_{0.38}\text{Mg}_{0.02}\text{Co}_{0.4}\text{O}_2$ | 600                                                                    | 600                                                           |
| $\text{Li}_{1.2}\text{Mn}_{0.36}\text{Mg}_{0.04}\text{Co}_{0.4}\text{O}_2$ | 400                                                                    | 500                                                           |
| $\text{Li}_{1.2}\text{Mn}_{0.34}\text{Mg}_{0.06}\text{Co}_{0.4}\text{O}_2$ | 200                                                                    | 160                                                           |



**Figure S2.** Magnified images show the existence of  $\text{Li}_2\text{MnO}_3$  and  $\text{LiCoO}_2$  regions in individual particles of the prepared cathodes, corresponding to the dash green rectangles as demonstrated in Fig. 2.



**Figure S3.** Comparison of X-ray diffraction spectra of the  $\text{Li}_{1.2}\text{Mn}_{0.4-x}\text{Mg}_x\text{Co}_{0.4}\text{O}_2$  ( $x=0.00, 0.02, 0.04$ , and  $0.06$ ) materials at  $2\theta$  values of approximately  $37.5^\circ$  and  $45.0^\circ$ .



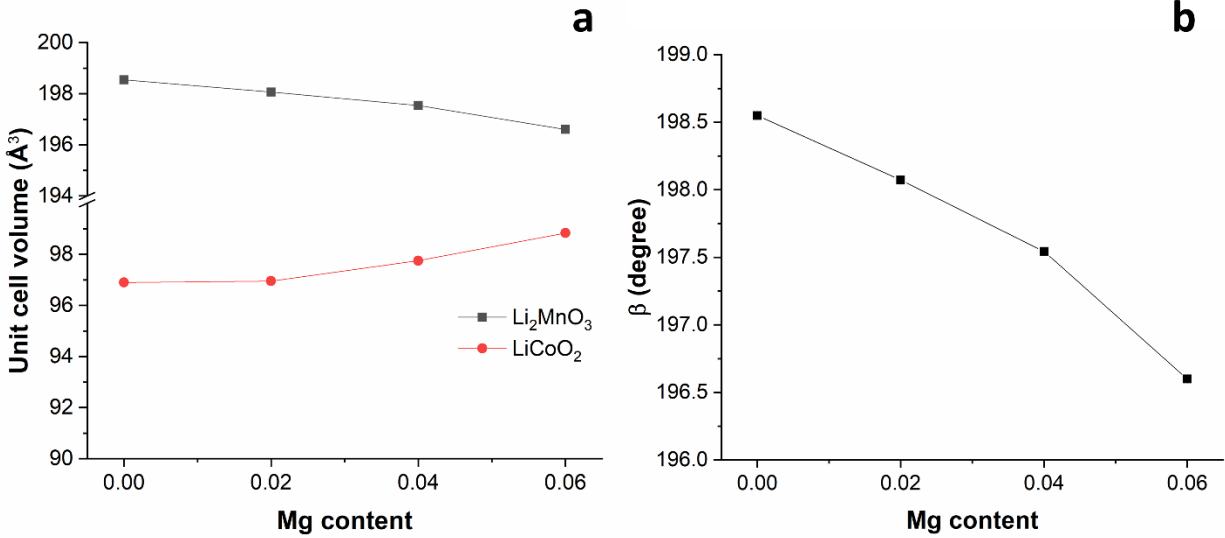
**Figure S4.** Rietveld refinement results of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  (a),  $\text{Li}_{1.2}\text{Mn}_{0.38}\text{Mg}_{0.02}\text{Co}_{0.4}\text{O}_2$  (b),  $\text{Li}_{1.2}\text{Mn}_{0.36}\text{Mg}_{0.04}\text{Co}_{0.4}\text{O}_2$  (c), and  $\text{Li}_{1.2}\text{Mn}_{0.34}\text{Mg}_{0.06}\text{Co}_{0.4}\text{O}_2$  (d) materials

**Table. S2** Atomic positions obtained from Rietveld refinement of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  and Mg-doped  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  materials

| Sample                                                                     | $\text{Li}_2\text{MnO}_3$ |                  |        |        |        |           | $\text{LiCoO}_2$ |                  |        |        |        |           |
|----------------------------------------------------------------------------|---------------------------|------------------|--------|--------|--------|-----------|------------------|------------------|--------|--------|--------|-----------|
|                                                                            | Element                   | Wyckoff position | X      | Y      | Z      | Occupancy | Element          | Wyckoff position | X      | Y      | Z      | Occupancy |
| $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$                  | Li1                       | 2a               | 0.0000 | 0.0000 | 0.0000 | 0.7300    | Co               | 3b               | 0.0000 | 0.0000 | 0.5000 | 1.0000    |
|                                                                            | Mn1                       | 2a               | 0.0000 | 0.0000 | 0.0000 | 0.2700    | Li               | 3a               | 0.0000 | 0.0000 | 0.0000 | 1.0000    |
|                                                                            | Li2                       | 2d               | 0.0000 | 0.5000 | 0.5000 | 1.0000    | O                | 6c               | 0.0000 | 0.0000 | 0.2395 | 1.0000    |
|                                                                            | Li3                       | 4h               | 0.0000 | 0.0159 | 0.5000 | 1.0000    |                  |                  |        |        |        |           |
|                                                                            | Mn2                       | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.8700    |                  |                  |        |        |        |           |
|                                                                            | Li4                       | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.1300    |                  |                  |        |        |        |           |
|                                                                            | O1                        | 4i               | 0.7197 | 0.0000 | 0.2251 | 1.0000    |                  |                  |        |        |        |           |
|                                                                            | O2                        | 8i               | 0.2524 | 0.1765 | 0.2234 | 1.0000    |                  |                  |        |        |        |           |
| $\text{Li}_{1.2}\text{Mn}_{0.38}\text{Mg}_{0.02}\text{Co}_{0.4}\text{O}_2$ | Li1                       | 2a               | 0.0000 | 0.0000 | 0.0000 | 0.7300    | Co               | 3b               | 0.0000 | 0.0000 | 0.5000 | 1.0000    |
|                                                                            | Mn1                       | 2a               | 0.0000 | 0.0000 | 0.0000 | 0.2700    | Li               | 3a               | 0.0000 | 0.0000 | 0.0000 | 1.0000    |
|                                                                            | Li2                       | 2d               | 0.0000 | 0.5000 | 0.5000 | 1.0000    | O                | 6c               | 0.0000 | 0.0000 | 0.2395 | 1.0000    |
|                                                                            | Li3                       | 4h               | 0.0000 | 0.0159 | 0.5000 | 1.0000    |                  |                  |        |        |        |           |
|                                                                            | Mn2                       | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.8300    |                  |                  |        |        |        |           |
|                                                                            | Li4                       | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.1300    |                  |                  |        |        |        |           |
|                                                                            | O1                        | 4i               | 0.7197 | 0.0000 | 0.2251 | 1.0000    |                  |                  |        |        |        |           |
|                                                                            | O2                        | 8i               | 0.2524 | 0.1765 | 0.2234 | 1.0000    |                  |                  |        |        |        |           |
| $\text{Li}_{1.2}\text{Mn}_{0.36}\text{Mg}_{0.04}\text{Co}_{0.4}\text{O}_2$ | Li1                       | 2a               | 0.0000 | 0.0000 | 0.0000 | 0.7300    | Co               | 3b               | 0.0000 | 0.0000 | 0.5000 | 1.0000    |
|                                                                            | Mn1                       | 2a               | 0.0000 | 0.0000 | 0.0000 | 0.2700    | Li               | 3a               | 0.0000 | 0.0000 | 0.0000 | 1.0000    |
|                                                                            | Li2                       | 2d               | 0.0000 | 0.5000 | 0.5000 | 1.0000    | O                | 6c               | 0.0000 | 0.0000 | 0.2395 | 1.0000    |
|                                                                            | Li3                       | 4h               | 0.0000 | 0.0159 | 0.5000 | 1.0000    |                  |                  |        |        |        |           |
|                                                                            | Mn2                       | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.7900    |                  |                  |        |        |        |           |
|                                                                            | Li4                       | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.1300    |                  |                  |        |        |        |           |
|                                                                            | O1                        | 4i               | 0.7197 | 0.0000 | 0.2251 | 1.0000    |                  |                  |        |        |        |           |
|                                                                            | O2                        | 8i               | 0.2524 | 0.1765 | 0.2234 | 1.0000    |                  |                  |        |        |        |           |
| $\text{Li}_{1.2}\text{Mn}_{0.34}\text{Mg}_{0.06}\text{Co}_{0.4}\text{O}_2$ | Li1                       | 2a               | 0.0000 | 0.0000 | 0.0000 | 0.7300    | Co               | 3b               | 0.0000 | 0.0000 | 0.5000 | 1.0000    |
|                                                                            | Mn1                       | 2a               | 0.0000 | 0.0000 | 0.0000 | 0.2700    | Li               | 3a               | 0.0000 | 0.0000 | 0.0000 | 1.0000    |
|                                                                            | Li2                       | 2d               | 0.0000 | 0.5000 | 0.5000 | 1.0000    | O                | 6c               | 0.0000 | 0.0000 | 0.2395 | 1.0000    |
|                                                                            | Li3                       | 4h               | 0.0000 | 0.0159 | 0.5000 | 1.0000    |                  |                  |        |        |        |           |
|                                                                            | Mn2                       | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.7500    |                  |                  |        |        |        |           |
|                                                                            | Li4                       | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.1300    |                  |                  |        |        |        |           |
|                                                                            | O1                        | 4i               | 0.7197 | 0.0000 | 0.2251 | 1.0000    |                  |                  |        |        |        |           |
|                                                                            | O2                        | 8i               | 0.2524 | 0.1765 | 0.2234 | 1.0000    |                  |                  |        |        |        |           |
| $\text{Li}_{1.2}\text{Mn}_{0.34}\text{Mg}_{0.06}\text{Co}_{0.4}\text{O}_2$ | Mg                        | 4g               | 0.0000 | 0.3308 | 0.0000 | 0.1200    |                  |                  |        |        |        |           |

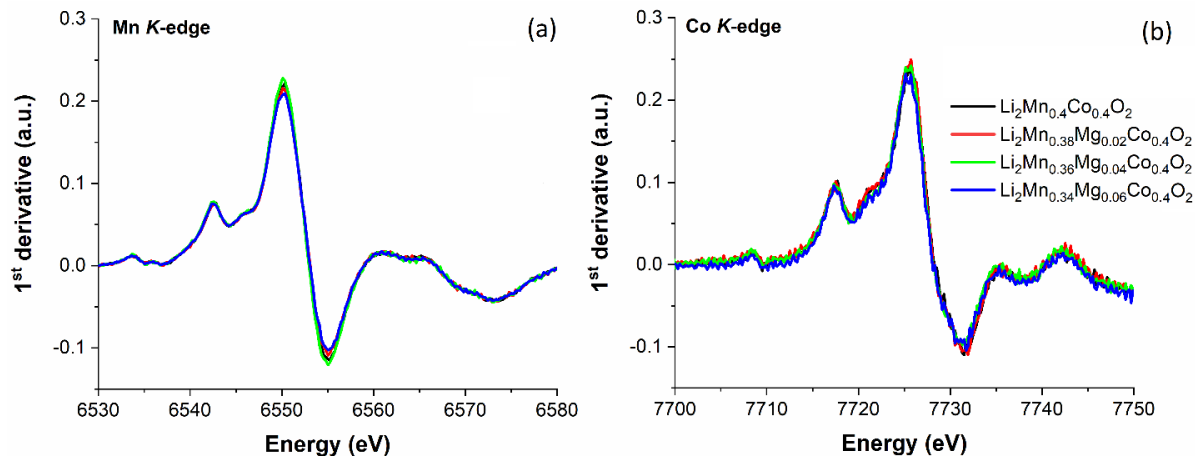
**Table. S3** Comparisons of the calculated lattice constants of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  and Mg-doped  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  materials

| Conditions                                                                 | Lattice parameters                                               |                        |                        |                       |                                    |                                                                                          |                      |                                    |
|----------------------------------------------------------------------------|------------------------------------------------------------------|------------------------|------------------------|-----------------------|------------------------------------|------------------------------------------------------------------------------------------|----------------------|------------------------------------|
|                                                                            | $\text{Li}_2\text{MnO}_3$ (C2/m)<br>$\alpha = \gamma = 90^\circ$ |                        |                        |                       |                                    | $\text{LiCoO}_2$ ( $R\bar{3}m$ )<br>$\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ |                      |                                    |
|                                                                            | a (Å)                                                            | b (Å)                  | c (Å)                  | $\beta$ (°)           | Unit cell volume (Å <sup>3</sup> ) | a and b (Å)                                                                              | c (Å)                | Unit cell volume (Å <sup>3</sup> ) |
| $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$                  | 4.9245<br>$\pm 0.0007$                                           | 8.5126<br>$\pm 0.0011$ | 5.0088<br>$\pm 0.0006$ | 108.9836 $\pm 0.0114$ | 198.5489                           | 2.8130 $\pm 0.0001$                                                                      | 14.1361 $\pm 0.0013$ | 96.8998                            |
| $\text{Li}_{1.2}\text{Mn}_{0.38}\text{Mg}_{0.02}\text{Co}_{0.4}\text{O}_2$ | 4.9210<br>$\pm 0.0007$                                           | 8.5028<br>$\pm 0.0013$ | 5.0061<br>$\pm 0.0007$ | 108.9851 $\pm 0.0133$ | 198.0718                           | 2.8149 $\pm 0.0001$                                                                      | 14.1290 $\pm 0.0017$ | 96.9527                            |
| $\text{Li}_{1.2}\text{Mn}_{0.36}\text{Mg}_{0.04}\text{Co}_{0.4}\text{O}_2$ | 4.9223<br>$\pm 0.0009$                                           | 8.4834<br>$\pm 0.0023$ | 5.0026<br>$\pm 0.0010$ | 108.9781 $\pm 0.0203$ | 197.5434                           | 2.8138 $\pm 0.0001$                                                                      | 14.1434 $\pm 0.0006$ | 97.7526                            |
| $\text{Li}_{1.2}\text{Mn}_{0.34}\text{Mg}_{0.06}\text{Co}_{0.4}\text{O}_2$ | 4.9262<br>$\pm 0.0009$                                           | 8.4594<br>$\pm 0.0013$ | 4.9766<br>$\pm 0.0008$ | 108.5603 $\pm 0.0136$ | 196.6003                           | 2.8361 $\pm 0.0002$                                                                      | 14.1883 $\pm 0.0008$ | 98.8321                            |

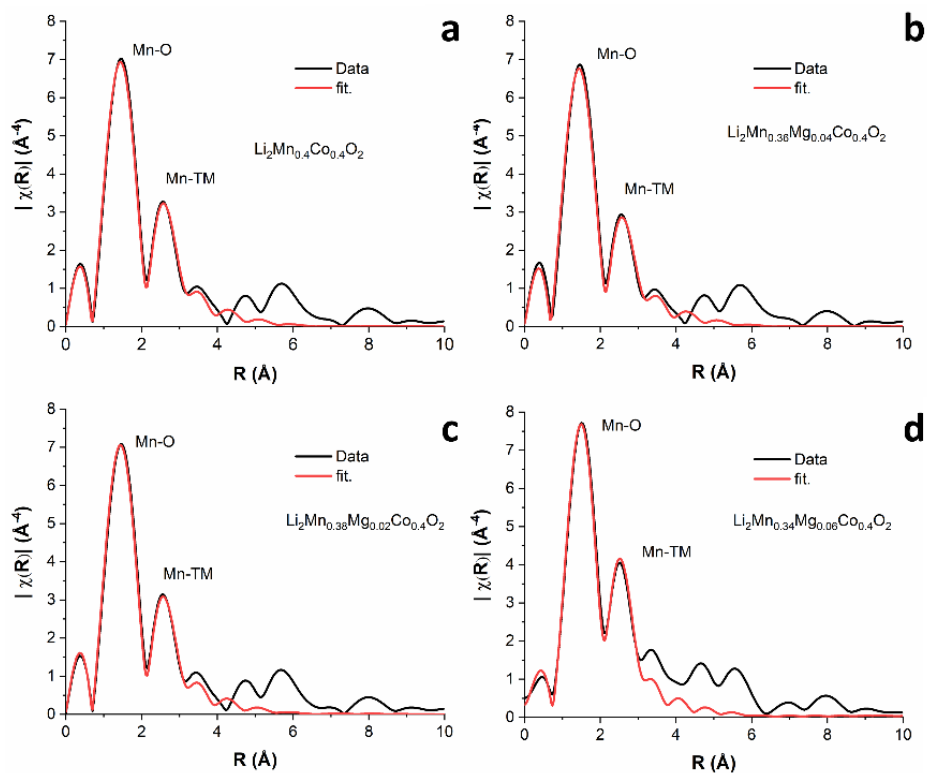


**Figure S5.** the calculated unite cell volume (a) and  $\beta$  (b) of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  and Mg-doped  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  materials

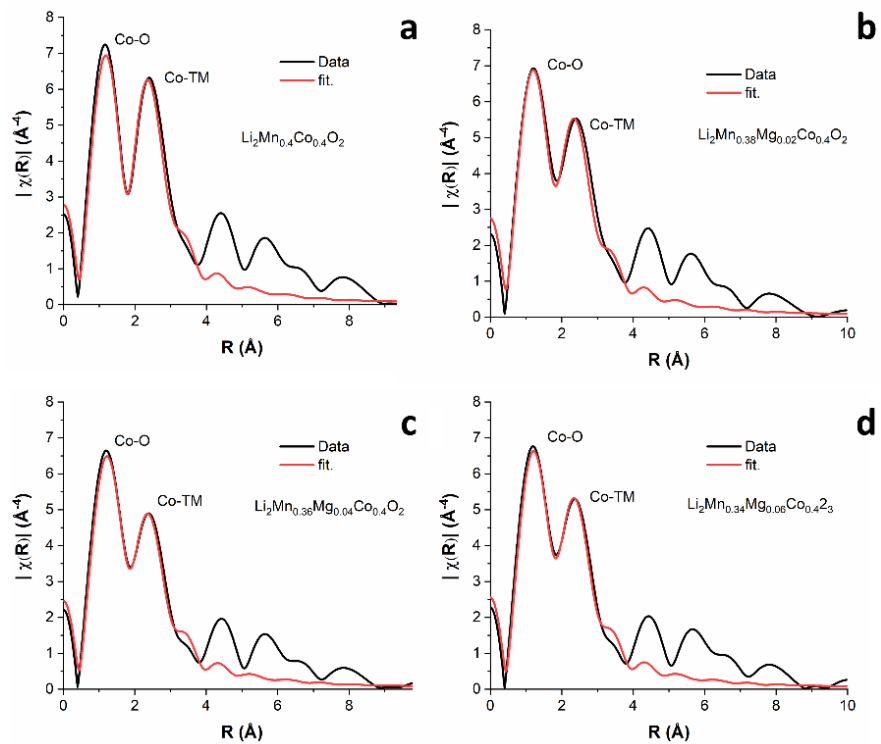




**Figure S6.** the 1<sup>st</sup> derivative spectra at the Mn (a) and Co (b) K-edges of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$ , Mg-doped  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$ ,  $\text{Li}_2\text{MnCoO}_3$ , and  $\text{LiCoO}_2$  materials



**Figure S7.** Mn K-edges EXAFS fitting results of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  (a),  $\text{Li}_{1.2}\text{Mn}_{0.38}\text{Mg}_{0.02}\text{Co}_{0.4}\text{O}_2$  (b),  $\text{Li}_{1.2}\text{Mn}_{0.36}\text{Mg}_{0.04}\text{Co}_{0.4}\text{O}_2$  (c), and  $\text{Li}_{1.2}\text{Mn}_{0.34}\text{Mg}_{0.06}\text{Co}_{0.4}\text{O}_2$  (d) materials

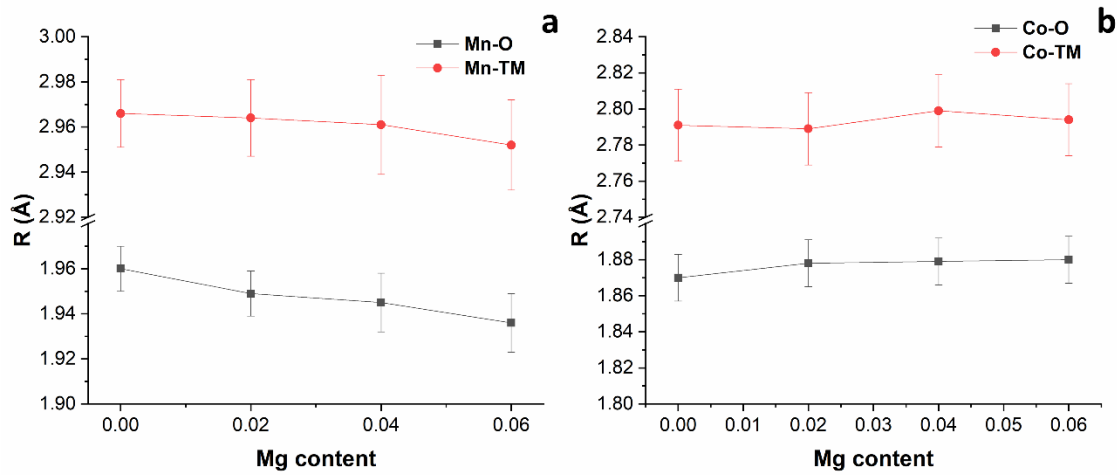


**Figure S8.** Co K-edges EXAFS fitting results of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  (a),  $\text{Li}_{1.2}\text{Mn}_{0.38}\text{Mg}_{0.02}\text{Co}_{0.4}\text{O}_2$  (b),  $\text{Li}_{1.2}\text{Mn}_{0.36}\text{Mg}_{0.04}\text{Co}_{0.4}\text{O}_2$  (c), and  $\text{Li}_{1.2}\text{Mn}_{0.34}\text{Mg}_{0.06}\text{Co}_{0.4}\text{O}_2$  (d) materials

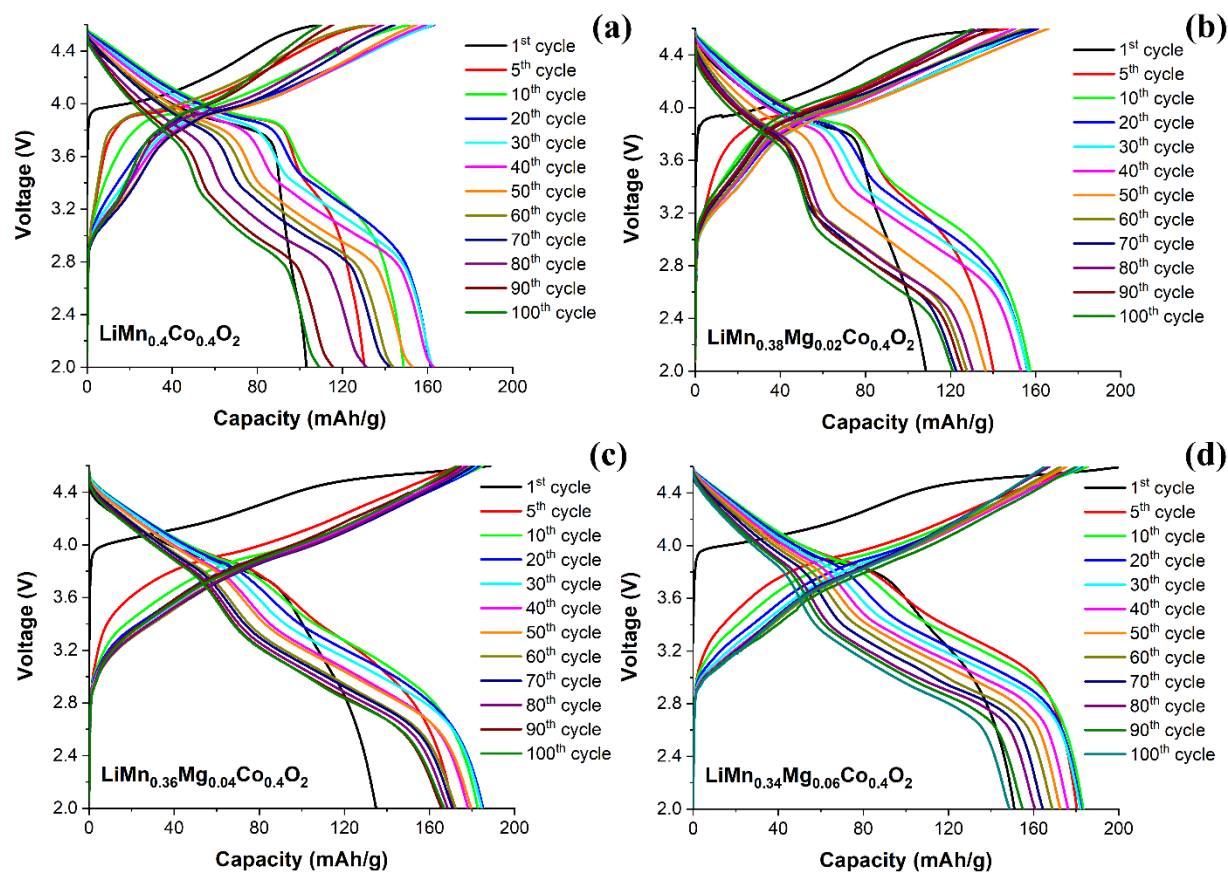


**Table S4.** The bond distances and agreement indices obtained from XAS spectra fitting of EXAFS spectra of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  and Mg-doped  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  materials

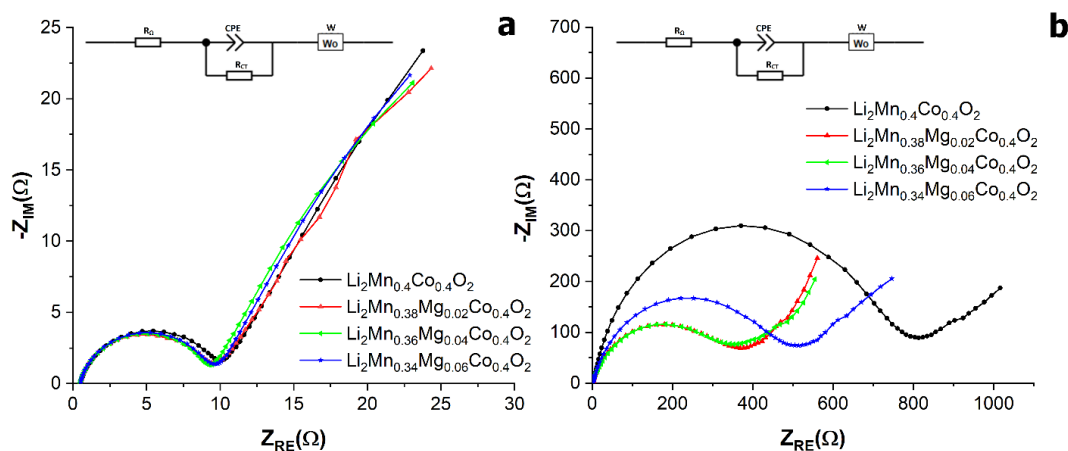
| Li <sub>2</sub> MnO <sub>3</sub> structure (Mn K-edge)                   |       |           |             |                                  |          |                     |
|--------------------------------------------------------------------------|-------|-----------|-------------|----------------------------------|----------|---------------------|
| Sample                                                                   | Shell | N (atoms) | R (Å)       | σ <sup>2</sup> (Å <sup>2</sup> ) | R-factor | E <sub>0</sub> (eV) |
| LiMn <sub>0.4</sub> Co <sub>0.4</sub> O <sub>2</sub>                     | O     | 6         | 1.961±0.010 | 0.001 (set)                      | 0.004    | 5.817               |
|                                                                          | Mn    | 3         | 2.966±0.015 | 0.003±0.002                      |          |                     |
| LiMn <sub>0.38</sub> Mg <sub>0.02</sub> Co <sub>0.4</sub> O <sub>2</sub> | O     | 6         | 1.949±0.010 | 0.001(set)                       | 0.004    | 5.817               |
|                                                                          | Mn    | 3         | 2.964±0.017 | 0.004±0.003                      |          |                     |
| LiMn <sub>0.36</sub> Mg <sub>0.04</sub> Co <sub>0.4</sub> O <sub>2</sub> | O     | 6         | 1.945±0.013 | 0.001(set)                       | 0.003    | 5.621               |
|                                                                          | Mn    | 3         | 2.961±0.022 | 0.005±0.003                      |          |                     |
| LiMn <sub>0.34</sub> Mg <sub>0.06</sub> Co <sub>0.4</sub> O <sub>2</sub> | O     | 6         | 1.936±0.013 | 0.001(set)                       | 0.012    | 5.803               |
|                                                                          | Mn    | 3         | 2.952±0.020 | 0.003±0.003                      |          |                     |
| LiCoO <sub>2</sub> structure (Co K-edge)                                 |       |           |             |                                  |          |                     |
| Sample                                                                   | Shell | N (atoms) | R (Å)       | σ <sup>2</sup> (Å <sup>2</sup> ) | R-factor | E <sub>0</sub> (eV) |
| LiMn <sub>0.4</sub> Co <sub>0.4</sub> O <sub>2</sub>                     | O     | 6         | 1.870±0.013 | 0.012±0.008                      | 0.010    | 9.500 (set)         |
|                                                                          | Co    | 6         | 2.791±0.020 | 0.004±0.006                      |          |                     |
| LiMn <sub>0.38</sub> Mg <sub>0.02</sub> Co <sub>0.4</sub> O <sub>2</sub> | O     | 6         | 1.878±0.013 | 0.008±0.009                      | 0.012    | 9.500 (set)         |
|                                                                          | Co    | 6         | 2.789±0.020 | 0.004±0.007                      |          |                     |
| LiMn <sub>0.36</sub> Mg <sub>0.04</sub> Co <sub>0.4</sub> O <sub>2</sub> | O     | 6         | 1.879±0.013 | 0.009±0.007                      | 0.007    | 9.500 (set)         |
|                                                                          | Co    | 6         | 2.799±0.020 | 0.006±0.006                      |          |                     |
| LiMn <sub>0.34</sub> Mg <sub>0.06</sub> Co <sub>0.4</sub> O <sub>2</sub> | O     | 6         | 1.880±0.013 | 0.011±0.008                      | 0.008    | 9.500 (set)         |
|                                                                          | Co    | 6         | 2.794±0.020 | 0.006±0.006                      |          |                     |



**Figure S9.** The calculated Mn-O, Mn-TM, Co-O, and Co-TM bond lengths of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  and Mg-doped  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  materials



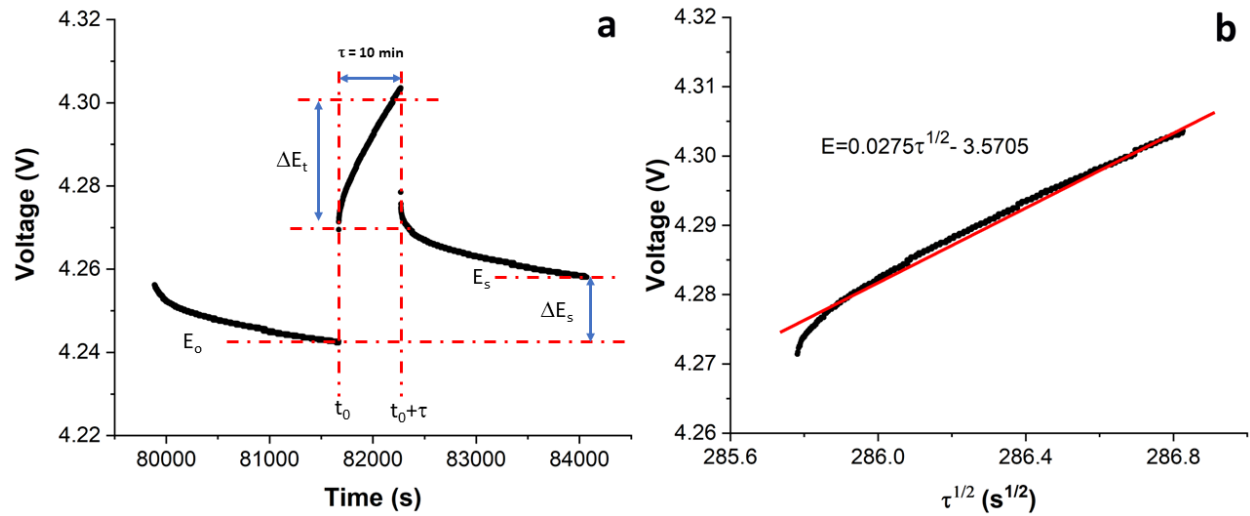
**Figure S10.** Voltage profiles of pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  and Mg-doped  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  materials cycled at C/3.



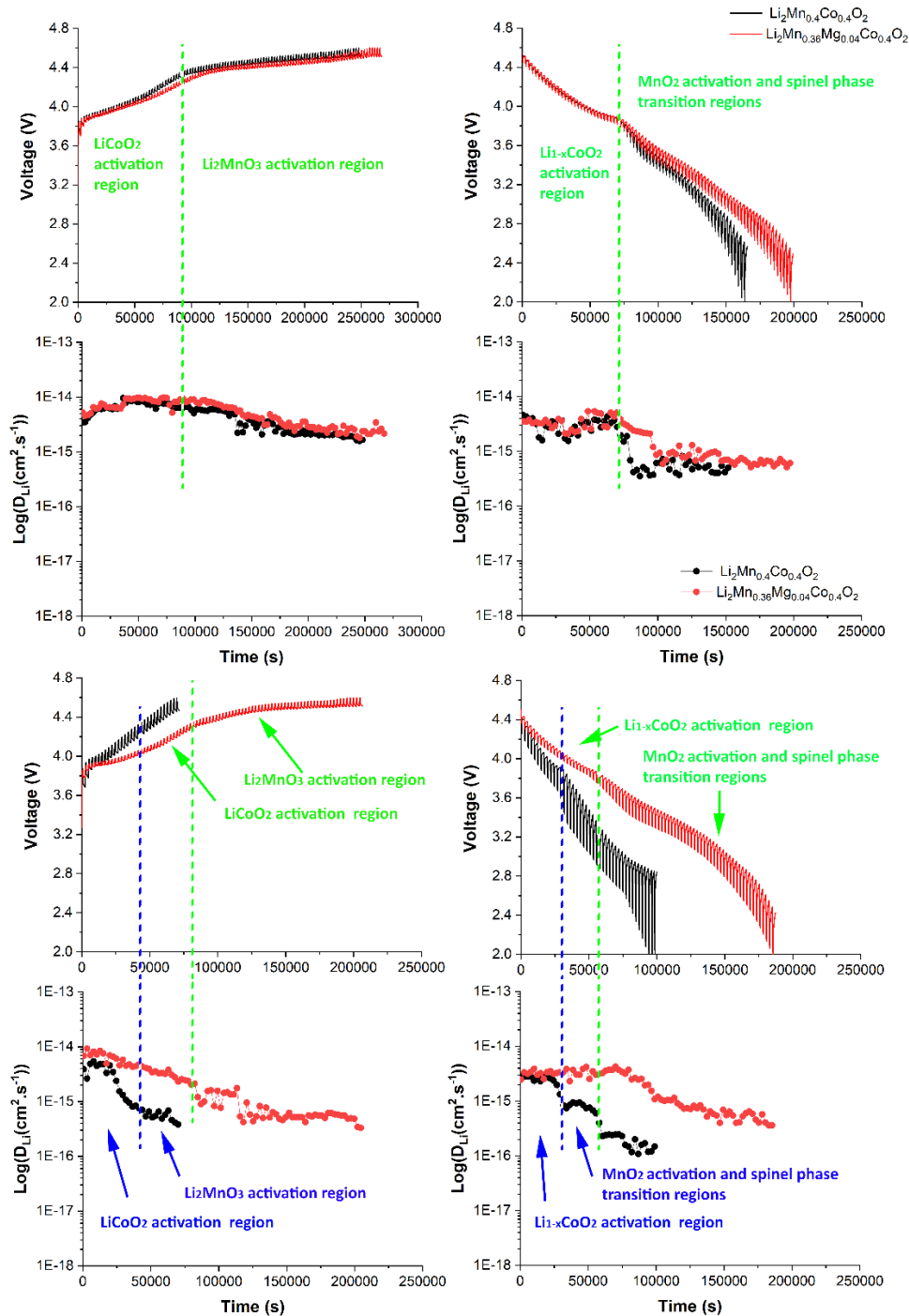
**Figure S11.** Nyquist plots of the fresh cell and the cells cycled at 0.3C after cycling for 100 cycles and the inset shows an equivalent circuit.  $R_\Omega$ ,  $R_{CT}$ , CPE, and W denote the ohmic resistance, the charge transfer resistance, constant phase element, and Warburg resistance, respectively.

**Table. S5** Comparison of calculated resistances obtained from fitting parameters using the equivalent circuit model illustrated in Fig. S7 of the fresh cell and the cells cycled at 0.3C after cycling for 100 cycles

| Sample                                                        | Fresh cell                |                       | After 100 cycles          |                       |
|---------------------------------------------------------------|---------------------------|-----------------------|---------------------------|-----------------------|
|                                                               | $R_{\Omega}$ ( $\Omega$ ) | $R_{CT}$ ( $\Omega$ ) | $R_{\Omega}$ ( $\Omega$ ) | $R_{CT}$ ( $\Omega$ ) |
| $\text{LiMn}_{0.4}\text{Co}_{0.4}\text{O}_2$                  | 0.432                     | 9.235                 | 0.575                     | 739.485               |
| $\text{LiMn}_{0.38}\text{Mg}_{0.02}\text{Co}_{0.4}\text{O}_2$ | 0.410                     | 8.452                 | 0.521                     | 345.214               |
| $\text{LiMn}_{0.36}\text{Mg}_{0.04}\text{Co}_{0.4}\text{O}_2$ | 0.472                     | 8.324                 | 0.554                     | 305.236               |
| $\text{LiMn}_{0.34}\text{Mg}_{0.06}\text{Co}_{0.4}\text{O}_2$ | 0.484                     | 8.624                 | 0.601                     | 479.258               |



**Figure S12.** Single titration at about 4.26 V during GITT measurement (a) and the cell voltage as a function of  $t^{1/2}$  (b)



**Figure S13.** GITT profiles and calculated lithium-ion diffusion coefficients as a function of time of a pristine  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$  and  $\text{Li}_{1.2}\text{Mn}_{0.36}\text{Mg}_{0.04}\text{Co}_{0.4}\text{O}_2$  materials at the 1<sup>st</sup> and 100<sup>th</sup> cycles for charging (a and c) and discharging (b and d) processes