## **Supplementary Information**

## Gradient-Morph LiCoO<sub>2</sub> Single Crystals with Stabilized Energy-density above 3400 Wh/L

Zhi Zhu<sup>1\*</sup>, Daiwei Yu<sup>1\*</sup>, Zhe Shi<sup>1</sup>, Rui Gao<sup>1</sup>, Xianghui Xiao<sup>2</sup>, Iradwikanari Waluyo<sup>2</sup>, Mingyuan Ge<sup>2</sup>, Yanhao Dong<sup>1</sup>, Weijiang Xue<sup>1</sup>, Guiyin Xu<sup>1</sup>, Wah-Keat Lee<sup>2</sup>, and Ju Li<sup>1†</sup>

<sup>1</sup>Department of Nuclear Science and Engineering, Department of Materials Science and Engineering & Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

<sup>2</sup> National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA. (\*Z.Z. and D.Y. contributed equally to this work. †Corresponding author. Email: liju@mit.edu (J.L.))



**Supplementary Fig. 1** SEM image of the prepared P-LCO particles, showing that most of their sizes were among 10-15 μm in diameter.



Supplementary Fig. 2 SEM image (a) with EDX mapping (b-d) of the G-LCO particles



**Supplementary Fig. 3** Quantitative analysis of the TEY sXAS Mn  $L_3$  edge for G-LCO particle with linear fitting of the standard references inserted, showing the valence of Mn at the particle surface was +3.4.



Supplementary Fig. 4 Cyclic voltammetry of P-LCO (a) and G-LCO (b) after 1 cycle and 20

cycles within 3.0-4.6 V, with 0.05 mV/s scanning rate.



**Supplementary Fig. 5** The XANES Co K-edge near site S at the surface of P-LCO particle (a) and site T at the surface of G-LCO particle (b) (marked in Fig. 4) when charged to 4.6V, indicating that, in the P-LCO particle, the Co ions in the core was able to be oxidized approaching +4, but those were gradually reduced to +2.7 near the surface, while all the Co ions in the CS-LCO were all oxidized to +4 from the bulk to surface.



**Supplementary Fig. 6** Oxygen sublattice matching of  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  (111) (lower left) and  $\text{Co}_3\text{O}_4$  (111) (lower right) against LCO (001). *d*'s are the distances between O atoms in the sublattices.



**Supplementary Fig. 7** The charge/discharge profiles of P-LCO (a) and G-LCO (b) in the initial 10 cycles when cycled within 3.0-4.7V in half-cells under 100m A/g, while charging, the cathodes were charged to 4.7V followed with a constant-voltage charging until the current decreased to 20 mA/g.

**Supplementary Table 1** The compressed densities of P-LCO and G-LCO electrodes. 8 electrode foils were measured for each sample.

Foil No.	1	2	3	4	5	6	7	8	Average	S.t. deviation
P-LCO g/cm <sup>3</sup>	4.23	4.19	4.09	3.99	4.16	4.01	4.13	4.07	4.11	0.08
G-LCO g/cm <sup>3</sup>	4.0	4.07	4.15	4.05	3.96	4.12	4.25	4.17	4.10	0.10

**Supplementary Table 2** Oxygen sublattice misfit strain ( $\delta$ ) and atomic pair distance ( $\delta$ ) of LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> against LCO.

	LCO	LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub>	Co <sub>3</sub> O <sub>4</sub>
$d_{01-02}$ (Å)	3.12426	3.18845	3.18999
Misfit strain ( $\delta_{01-02}$ )	-	0.0201	0.0206
$d_{02-03}$ (Å)	2.63575	2.58005	2.56471
Misfit strain ( $\delta_{02-03}$ )	-	-0.0216	-0.0277
$\delta_{01-02} + \delta_{01-02}$	-	-0.00146	-0.00709

## **Supplementary Discussion 1**

In order to reconcile the coherency between LCO and LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> found in our TEM micrograph (Fig. 5), we investigated the oxygen pair distance and translational invariant between different crystal surfaces and computed the oxygen sublattice misfit strain for coherent interfaces. It is known that, in a dual-phase crystal, if both materials across the boundary have an identical crystal lattice or sublattice with a small discrepancy in their lattice parameters, the interface between them often resumes high coherency. The oxygen sublattice structures of LCO (001), LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> (111) and Co<sub>3</sub>O<sub>4</sub> (111) are shown in Supplementary Fig. 5. There are two possible O atom pair distances, namely  $d_{O1-O2}$  and  $d_{O2-O3}$ , taking place

alternatively at the coherent interface for both LCO and LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> or Co<sub>3</sub>O<sub>4</sub>, giving rise to a slight sublattice misfit strain of ~ $\pm 2\%$  (Supplementary Table 2). This "Peierls-transition"-like atomic configuration leads to an overall mismatch of only -0.146% for LCO/ LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> interface and -0.709% for LCO/Co<sub>3</sub>O<sub>4</sub> interface, with each repeating unit having exactly one tensile region and one compressive region. This result indicates that the mismatch of LCO/LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> is even much less than that of the naturally formed LCO/Co<sub>3</sub>O<sub>4</sub> in P-LCO, implying a highly lattice-coherency between the LCO core and the LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> shell created in operando, in the cell formation process, and is in excellent agreement with our experimental observation.