Electronic Supplementary Information

Enhanced High-voltage Cycling Stability of Ni-rich Cathode Materials via Self-assembly of Mn-rich Shells

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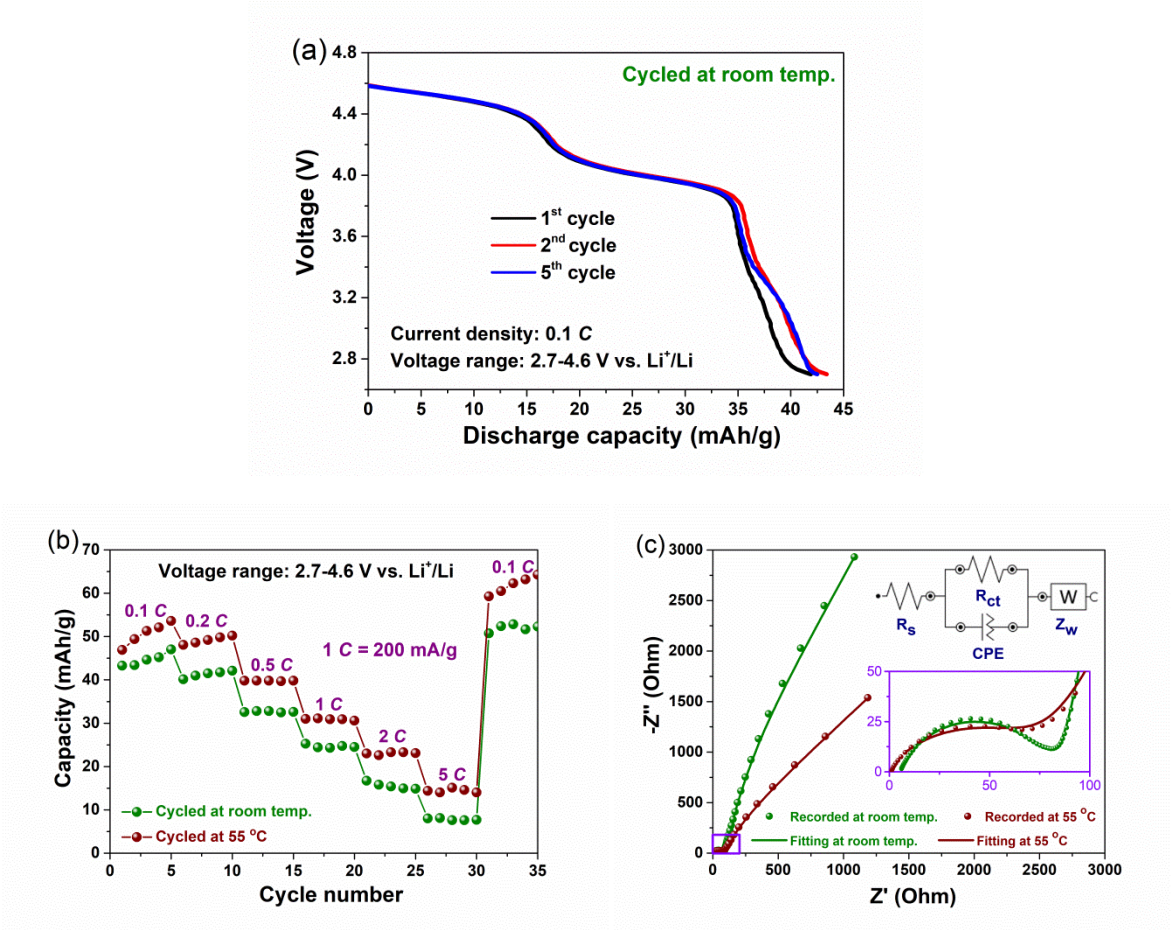

Figure S1. Electrochemical performance of the $Li_{0.65}Mn_{0.59}Ni_{0.12}Co_{0.13}O_{\delta}$ (mark as LMNCO) material as a cathode material in a voltage range of 2.7-4.6 V *vs.* Li^+/Li: (a) discharge curves in the 1st, 2nd, and 5th cycles at 0.1 *C*, and (b) high-rate performance up to 5 *C* and (c) EIS spectra with fitting profiles based on the equivalent circuit as the inset at room temperature and 55 °C.

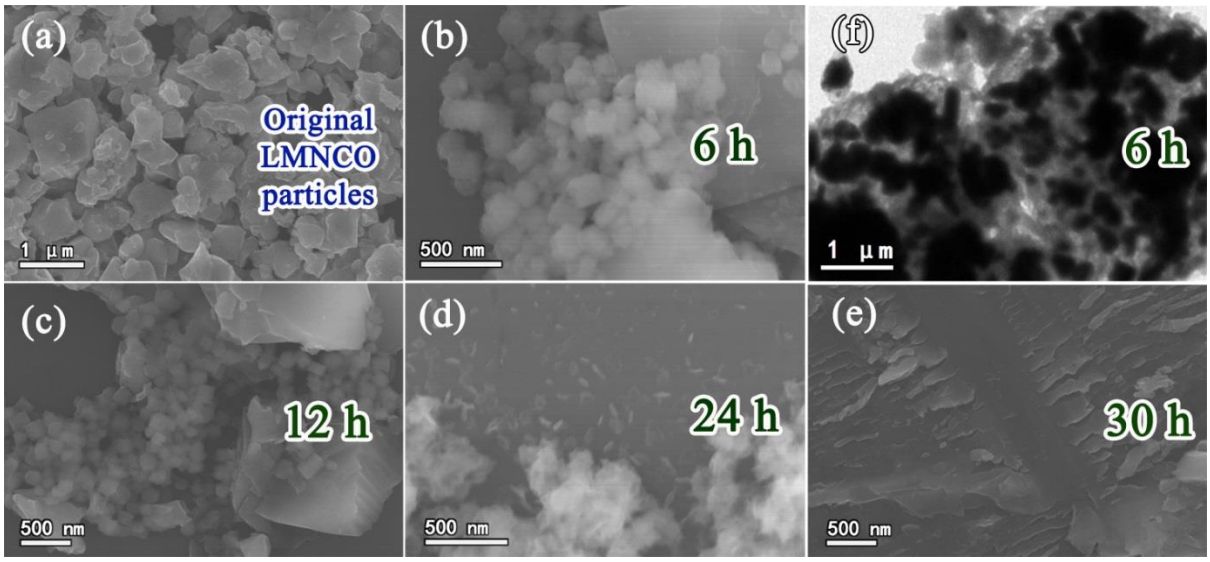

Figure S2. Time-resolved effects of the high-energy sonofragmentation on tailoring morphology and structure of the LMNCO material: SEM images showing distinct morphologic changes of the LMNCO material subjected to different sonication hours for (a) 0 h, *i.e.*, original LMNCO particles, (b) 6 h, (c) 12 h, (d) 24 h and (e) 30 h (marked as LMNCO-nh, respectively), and TEM image of (f) LMNCO-6h.

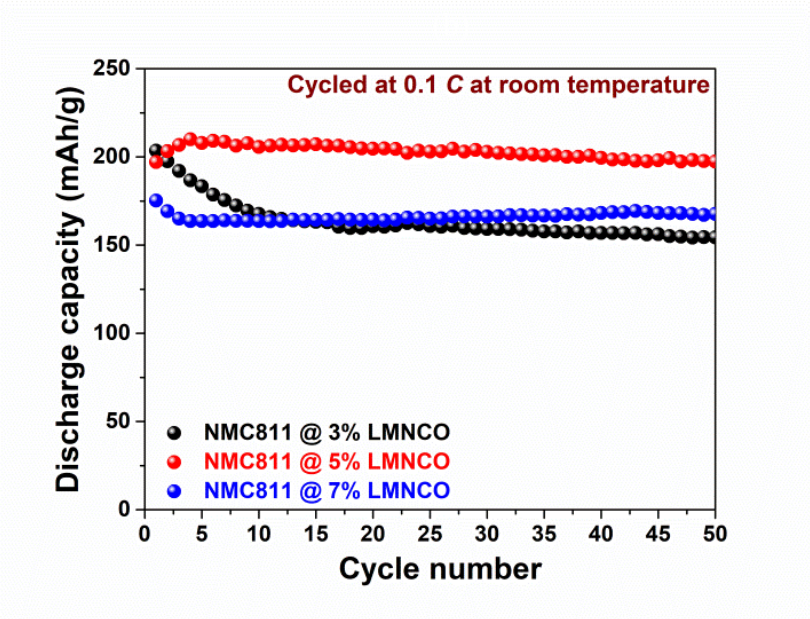

Figure S3. Comparative cycling performance of finalized NMC811@3% LMNCO, NMC811@5% LMNCO and NMC811@7% LMNCO cathode materials at 0.1 *C* in a voltage range of 2.7-4.6 V *vs.* Li^+/Li at room temperature.

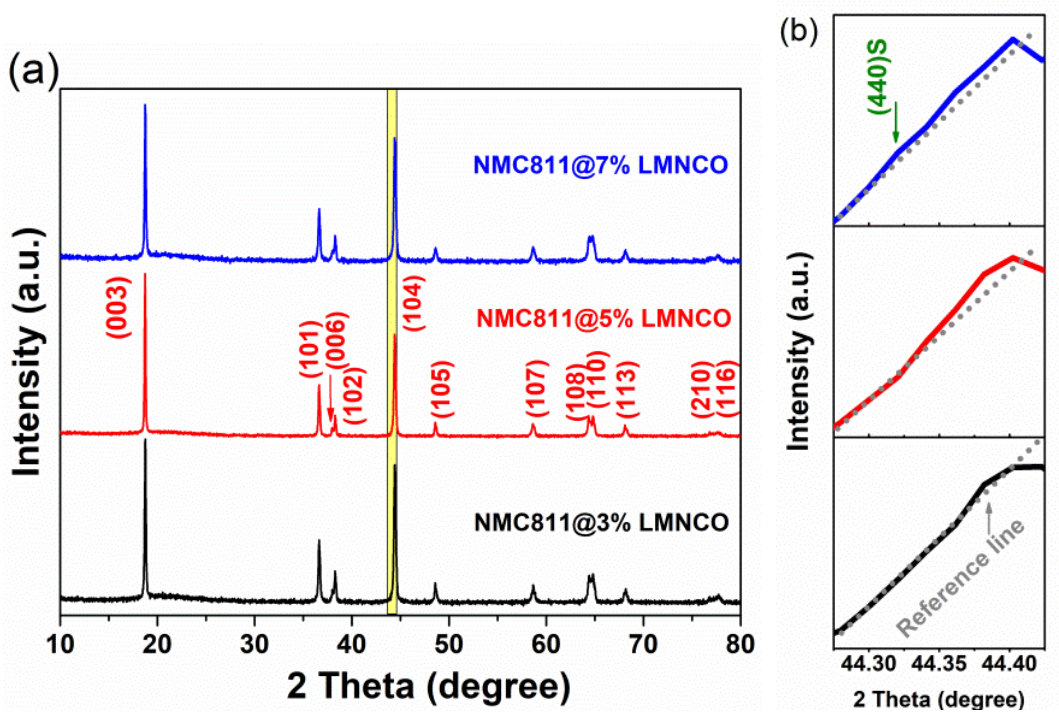

Figure S4. (a) XRD patterns of NMC811@3% LMNCO, NMC811@5% LMNCO and NMC811@7% LMNCO intermediates, and (b) an enlarged selected XRD portion at 2θ=44-45º highlighted in yellow in Figure S4a.

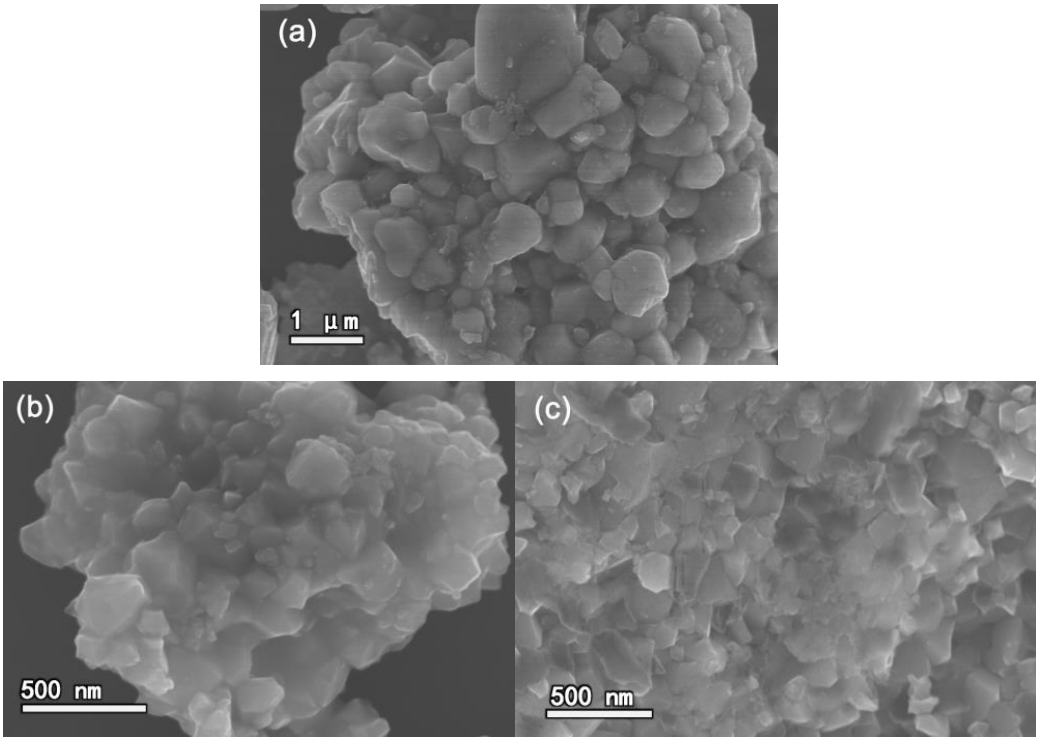

Figure S5. SEM images of (a) NMC811@3% LMNCO, (b) NMC811@5% LMNCO and (c) NMC811@7% LMNCO materials.

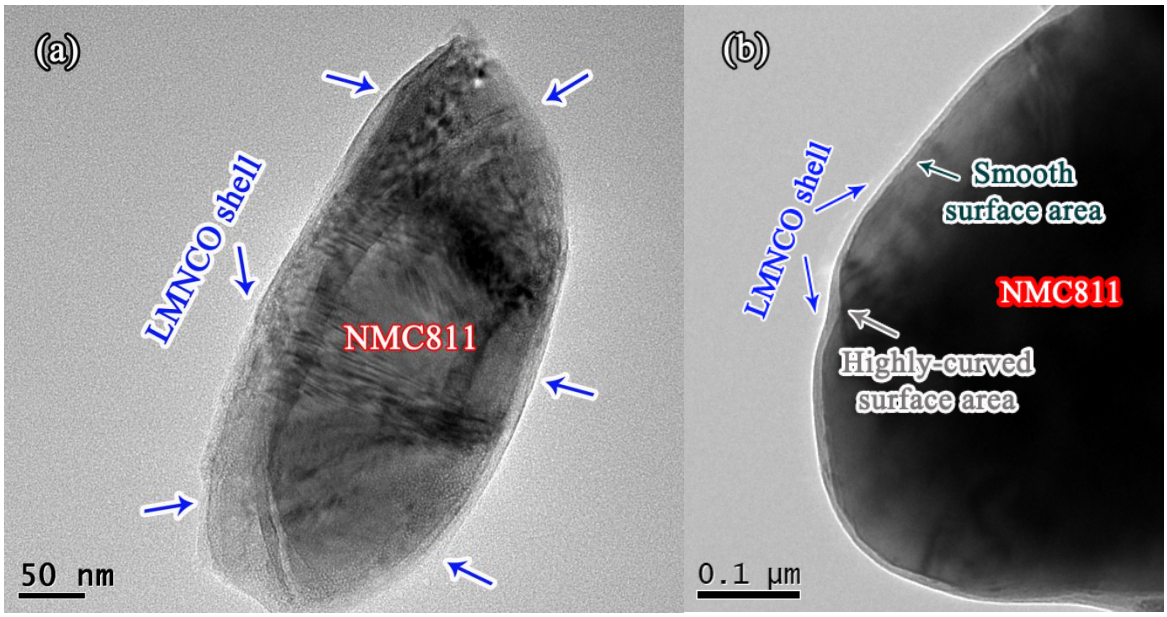

Figure S6. TEM images of the NMC811@5% LMNCO intermediate captured from different particles with (a) nano size and (b) micron size.

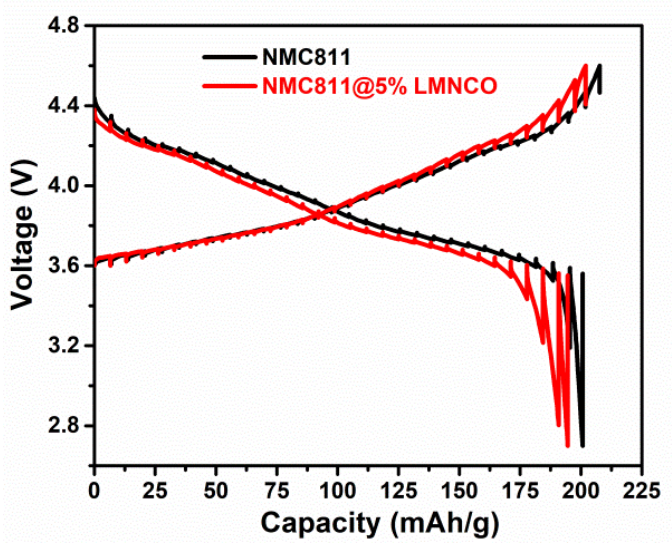

Figure S7. GITT curves of the bare NMC811 and core-shell-structured NMC811@5% LMNCO cathodes after the cells were first cycled at 0.1 *C* for 3 cycles in a voltage range of 2.7-4.6 V *vs.* Li^+/Li. For the GITT measurement, the cell was first charged from open circuit voltage (OCV) at a τ=20 min with current pulse of 0.1 *C*, followed by a relaxation time of 60 min to allow the system to reach electrochemical equilibrium.

Table S1. Cycling stabilities of various cathode materials cycled at elevated working temperatures.

Cathode materials (Operation conditions)	Initial Capacity (mAh g^{-1})	Capacity (retention) After 50 cycles	Capacity (retention) After 100 cycles	Capacity (retention) After 200 cycles	Reference
NMC811@5% LMNCO (2.7-4.6 V, 1*C*=200 mA g^{-1}, 55 ℃)	195.7	179.3 (91.6 %)	175.1 (89.5 %)	173.1 (88.5 %)	This work
NMC811 (2.7-4.6 V , 1*C*=200 mA g^{-1}, 55 ℃)	208.6	158.1 (75.8 %)	148.0 (70.95 %)	140.7 (67.5 %)	This work
NMC811 (2.7-4.4 V , 1*C*=200 mA g^{-1}, 55 ℃) [1]	209.0	140.03 (67 %)	--	--	Ref. S1
NMC811 (3.0-4.3 V, 1*C*=180 mA g^{-1}, 60 ℃)[2]	205.0	132.4 (64.6 %)	--	--	Ref. S2
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (2.8-4.3 V, 2*C*=360 mA g^{-1}, 55 ℃)[3]	196.8	--	132.0 (67.1 %)	--	Ref. S3
$LiNi_{0.62}Co_{0.14}Mn_{0.14}O_2$ (2.7-4.5 V, 1C=180 mA g^{-1}, 60 ℃)[4]	206.0	--	129 (62.6 %)	--	Ref. S4
$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (2.7-4.3 V, 1C=180 mA g^{-1}, 60 ℃)[5]	175.0	144.7 (82.6 %)	--	--	Ref. S5
$LiNi_{0.5}Mn_{1.5}O_4$ (2.7-4.9 V, 0.5C=60 mA g^{-1}, 55 ℃)[6]	120.0	--	18.0 (15 %)	--	Ref. S6
$LiMn_2O_4$ (3.5-4.3 V, 0.5C=74 mA g^{-1}, 50 ℃)[7]	131.0	--	--	108.7 (83.0 %)	Ref. S7
$LiMn_2O_4$ (3.0-4.3 V, 1C=148 mA g^{-1}, 55 ℃)[8]	130.0	74.0 (57.0 %)	--	--	Ref. S8

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