Supporting information

Effects of structure and magnetism on the electrochemistry of the layered $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ cathode material

Xiaofei Bian,[1] Rongyu Zhang,[2] Xu Yang,[2,]*

[1]School of Materials Science and Engineering, Dongguan University of Technology, Dongguan, 523808, China.

[2]College of Science, Shenyang Aerospace University, Shenyang, 110135, China.

Experimental

Characterization: Synchrotron X-ray diffraction (XRD) was carried out in transmission mode at the powder diffraction beamline P02.1 at the storage ring PETRA-III of DESY. The diffraction data were collected for a 0.5 mm diameter capillary, using radiation with a wavelength of 0.2097 Å. Magnetic characterization was performed by a superconducting quantum interference device magnetometer (Quantum Design MPMS-XL). The Field-cooled (FC) susceptibility and zero-field-cooled (ZFC) susceptibility were measured from 300 K to 5 K in the magnetic field of 100 Oe. The magnetization curves were measured at 5 K in the magnetic field of -5 T to 5 T. The temperature dependences of the ac susceptibility were measured in the ac field at frequencies from 1 to 500 Hz.

Electrocehmical measurement: Electrochemical measurements were performed using 2032-type coin cells with metallic lithium foil as the counter electrode. Active material, Super P, and polyvinylidene fluoride (PVDF) were mixed in a mass ratio of 75: 15: 10 with N-methyl pyrrolidone (NMP) solvent. The composite slurry was coated on Al foil with a thickness of 60 μm by a coating machine (MSK-AFA-I, Hefei Kejing Materials Technology., Ltd). After being dried in a vacuum oven at 120 ^{o}C for 12 h, the electrode was then punched into disks (Φ = 1.2 cm), with active material loading density of 2 mg cm^{-2}. The cells were assembled in an argon-filled glove box, with an electrolyte of 1 M $LiPF_6$ in a mixture of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate with a mole ratio of 1: 1: 8 by v/v ratio. Galvanostatic charge-discharge tests were performed on Neware (CT-4008) automatic battery tester.

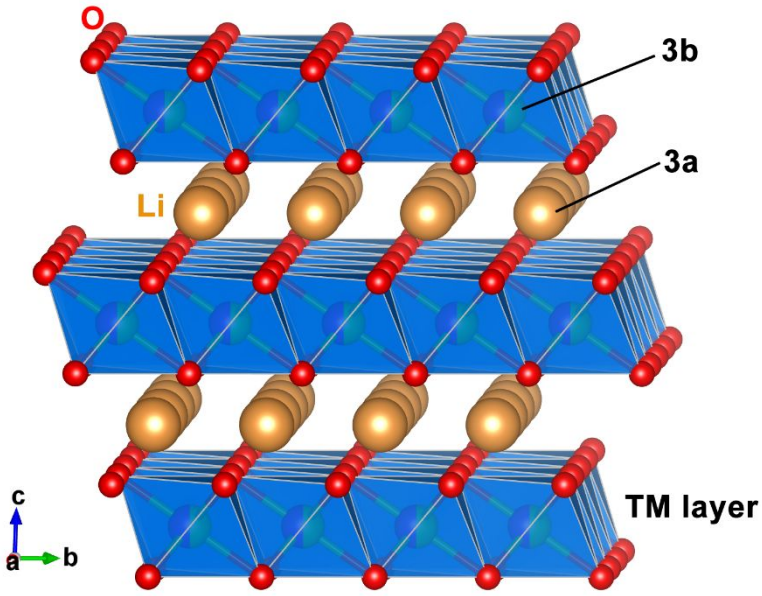

Figure S1 Crystal structure of $LiNi_{0.5}Mn_{0.5}O_2$ with a space group of *R-3m*.

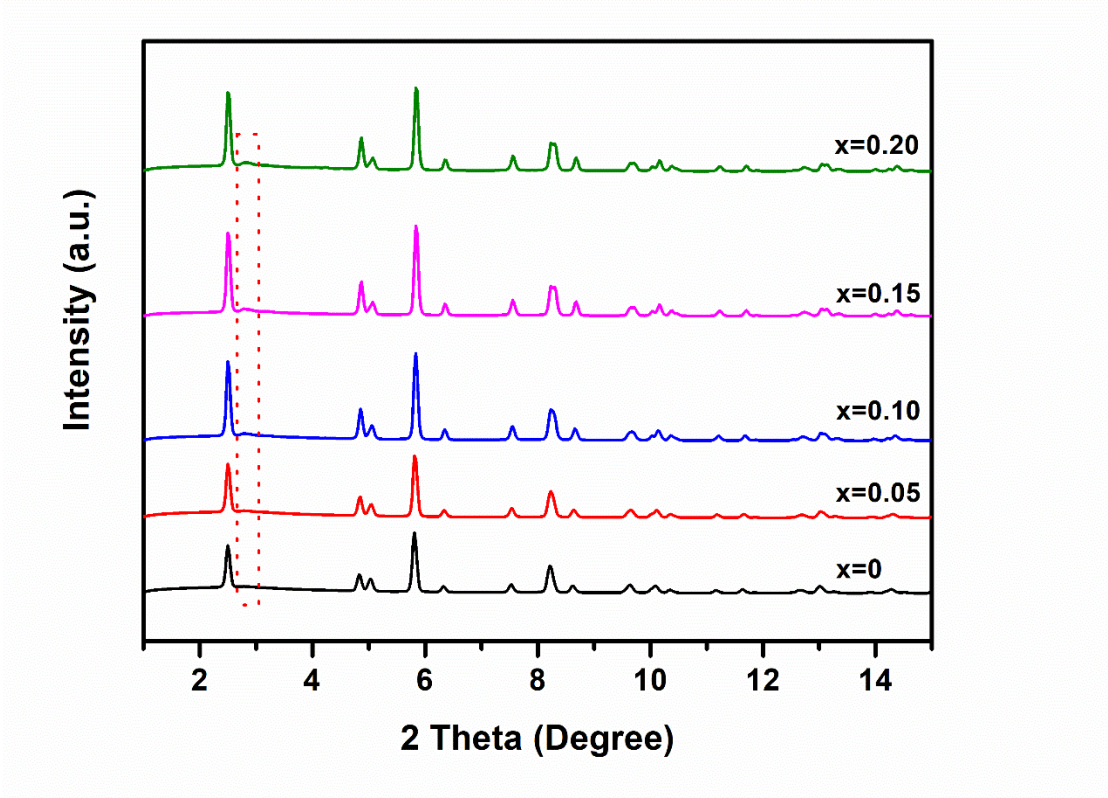

Figure S2 XRD patterns of $Li_{1+x}(Ni_{1/2}Mn_{1/2})_{1-x}O_2$.

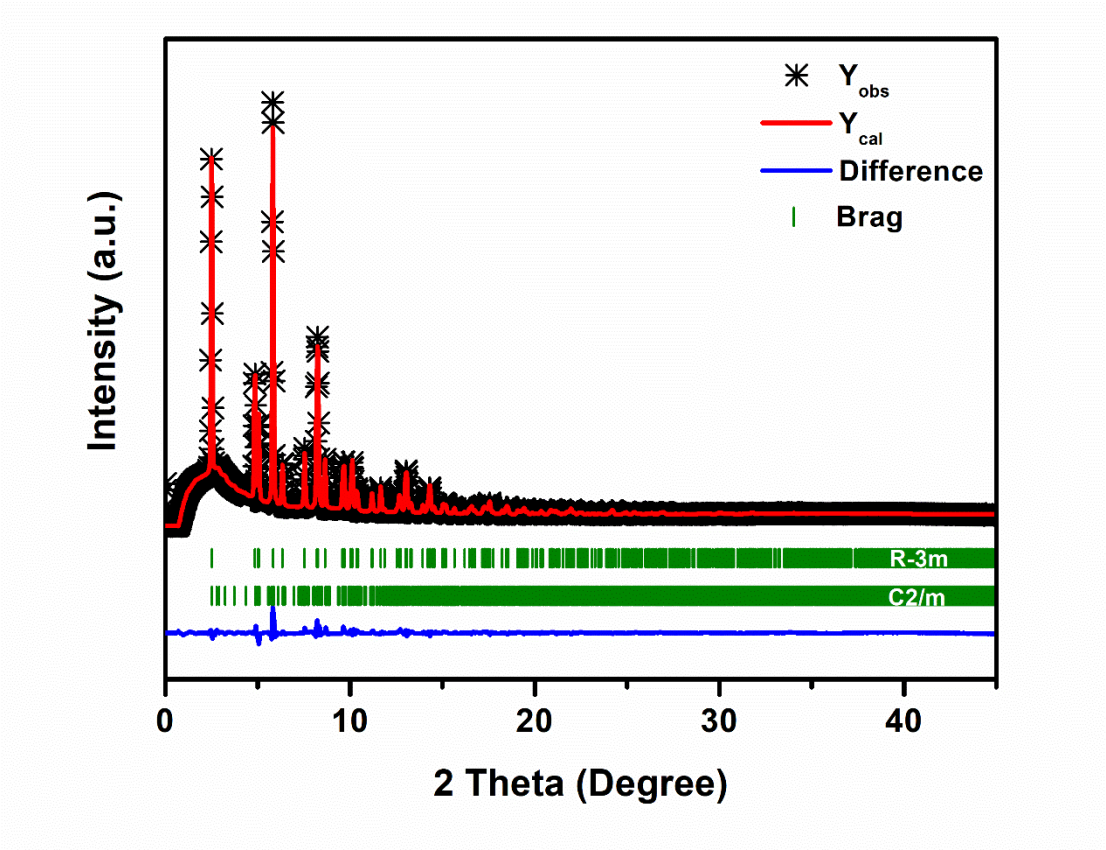

Figure S3 Rietveld refinement of $Li_{1.05}Ni_{0.475}Mn_{0.475}O_2$.

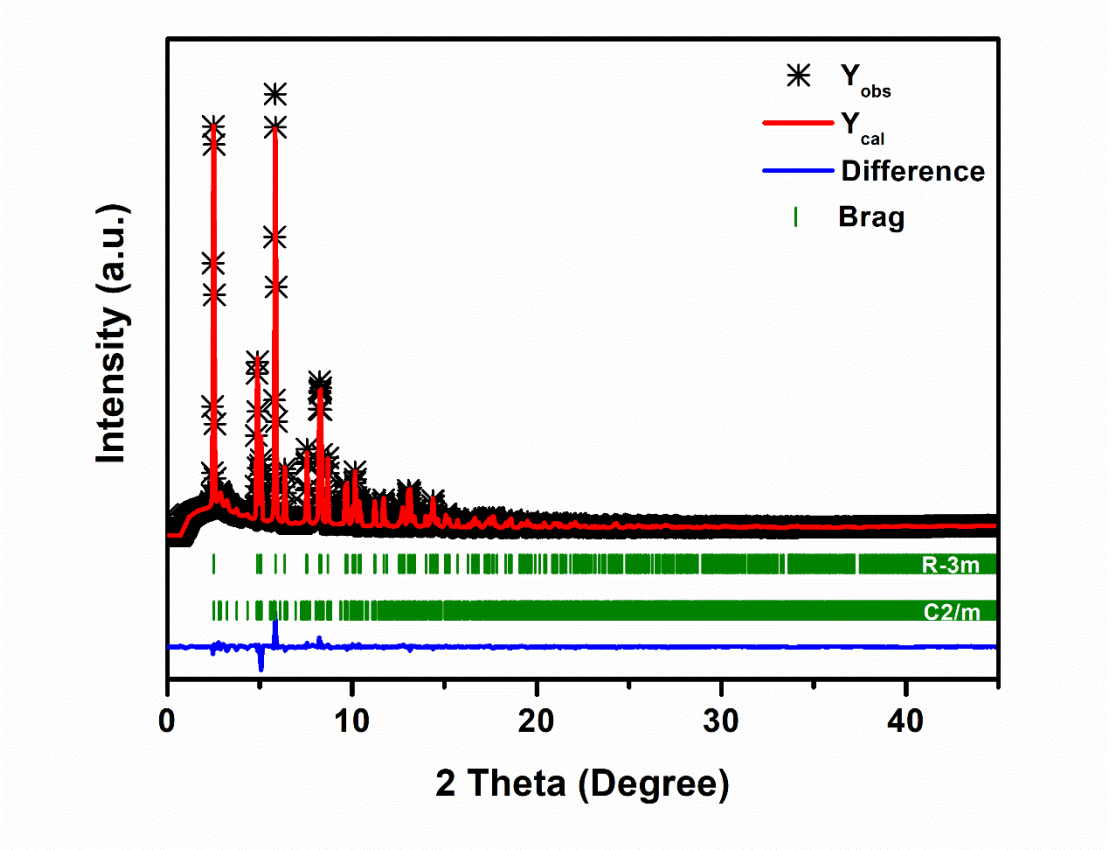

Figure S4 Rietveld refinement of $Li_{1.15}Ni_{0.425}Mn_{0.425}O_2$.

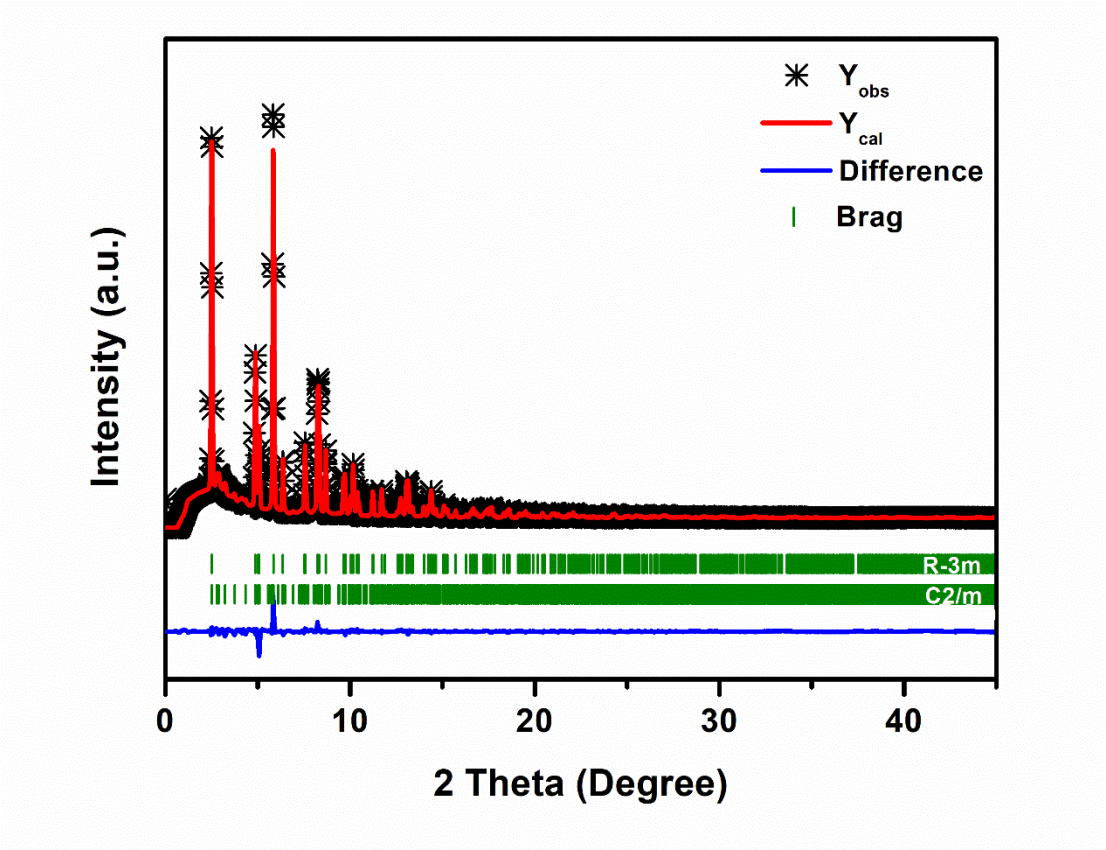

Figure S5 Rietveld refinement of $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$.

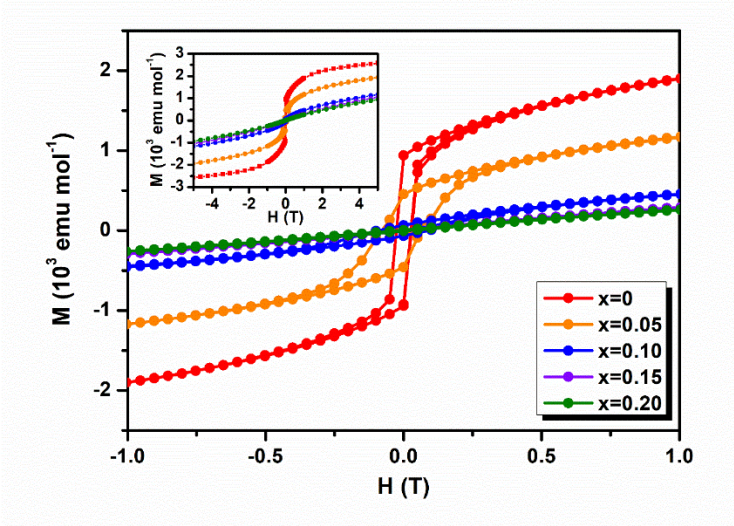

Figure S6 The magnetization curves of the $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ compounds.

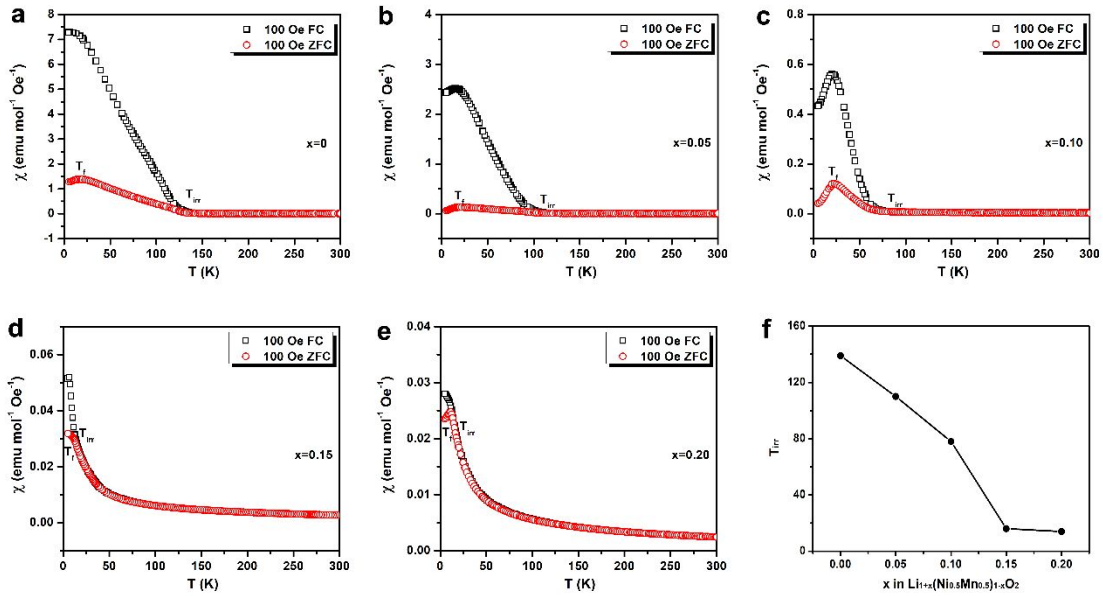

Figure S7 ZFC and FC curves of $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ (a) x=0, (b) x=0.05, (c) x=0.10, (d) x=0.15, (e) x=0.20. (f) The irreversible temperature (T_{irr}) of $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$.

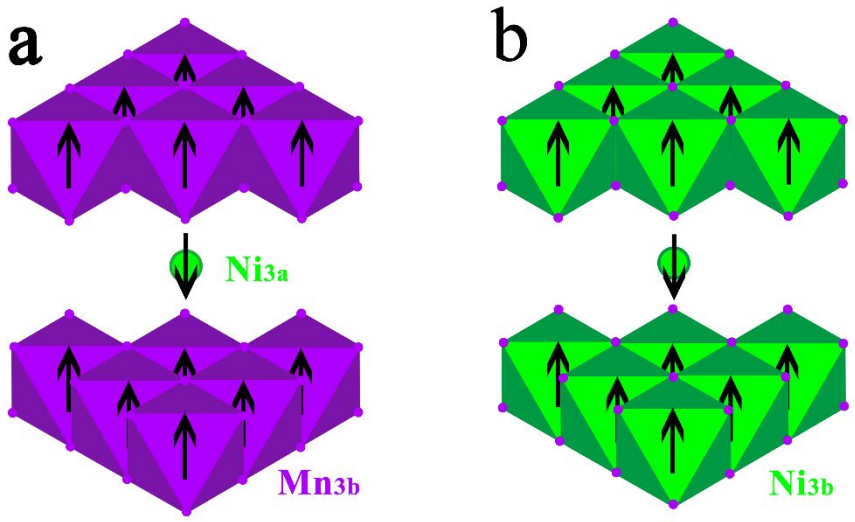

Figure S8 FM ordering of (a) Mn-rich region and (b) Ni-rich region with Ni^{2+} ions in the Li layer.

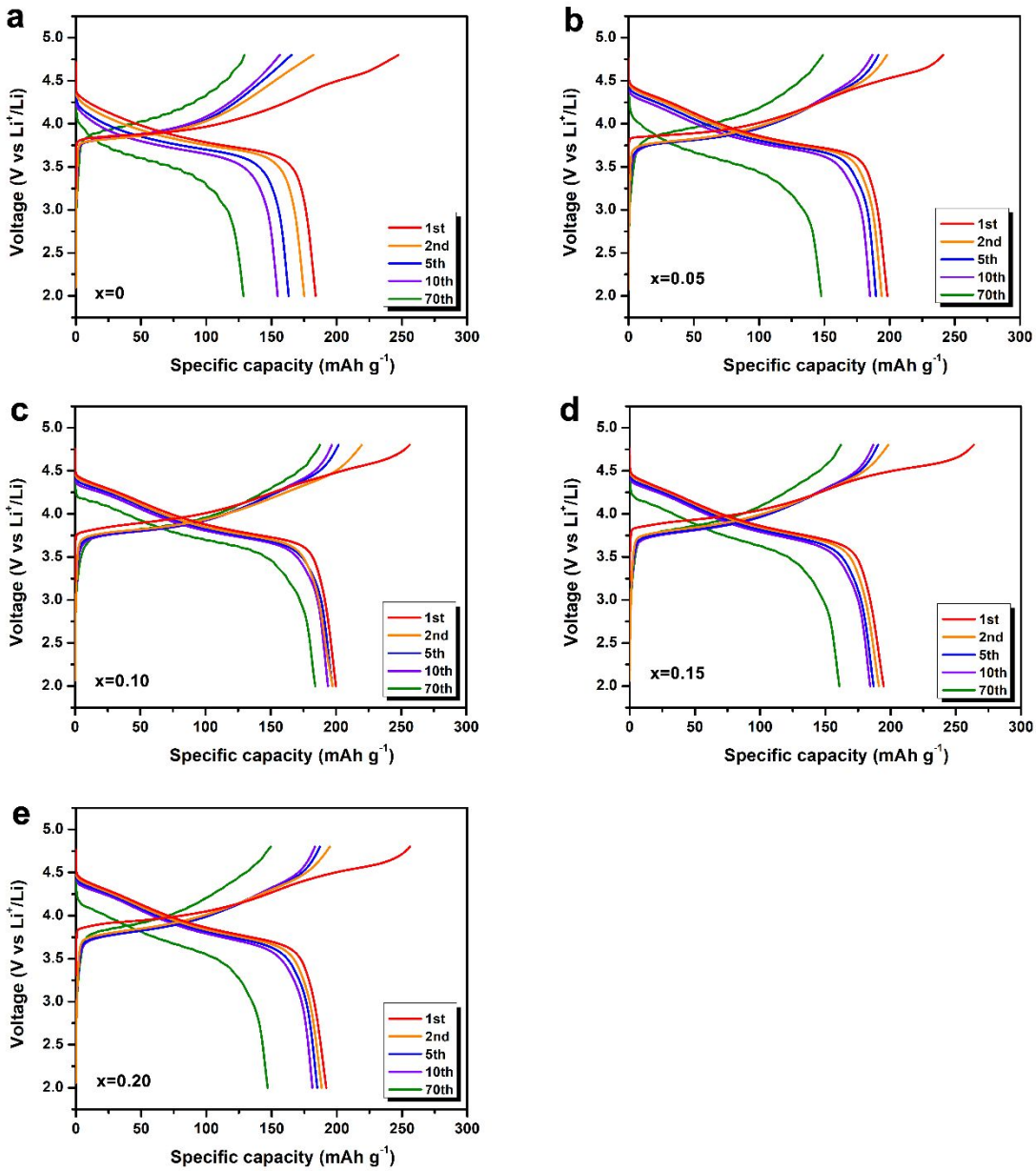

Figure S9 Charge/discharge curves of $Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$ when (a) x=0, (b) x=0.05, (c) x=0.10, (d) x=0.15, (e) x=0.20.

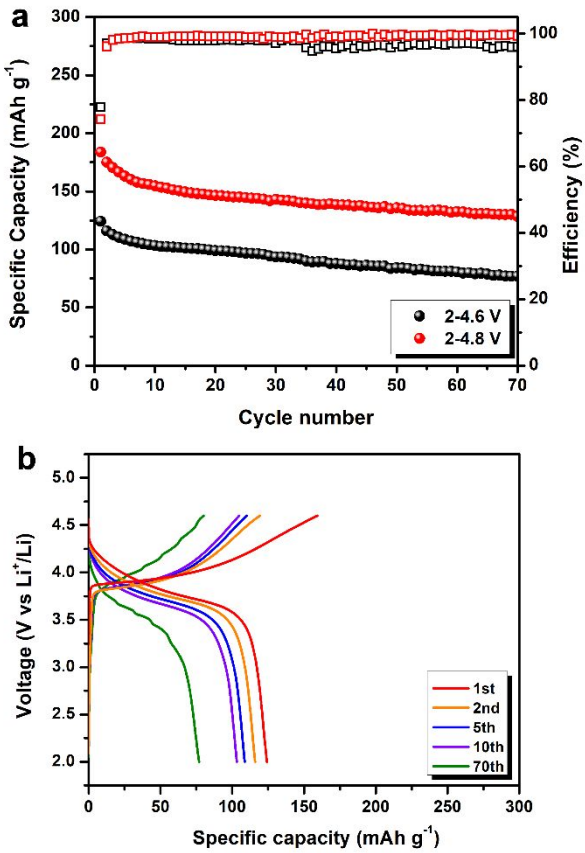

Figure S10 (a) Cycle performance and (b) Charge/discharge curves of $LiNi_{0.5}Mn_{0.5}O_2$ at a voltage range of 2-4.6 V.

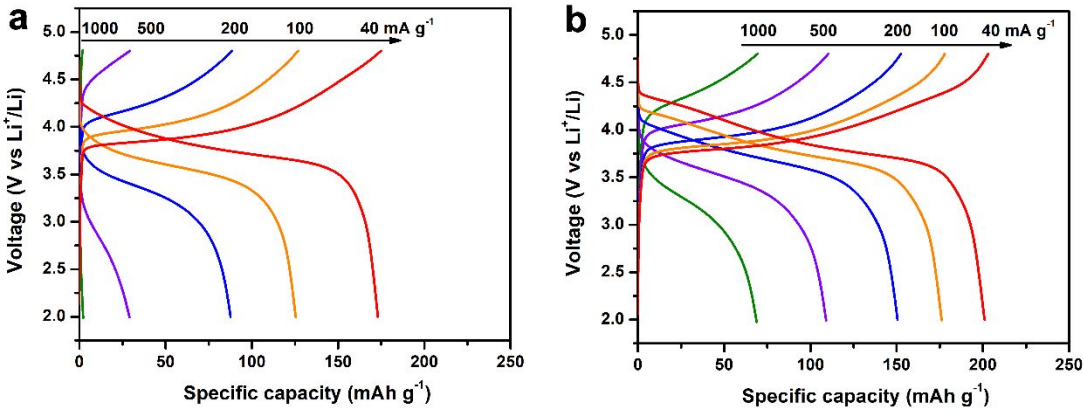

Figure S11 Charge/discharge profiles of (a) $LiNi_{0.5}Mn_{0.5}O_2$ and (b) $Li_{1.1}Ni_{0.45}Mn_{0.45}O_2$ at current densities from 40 to 1000 mA g^{-1}.

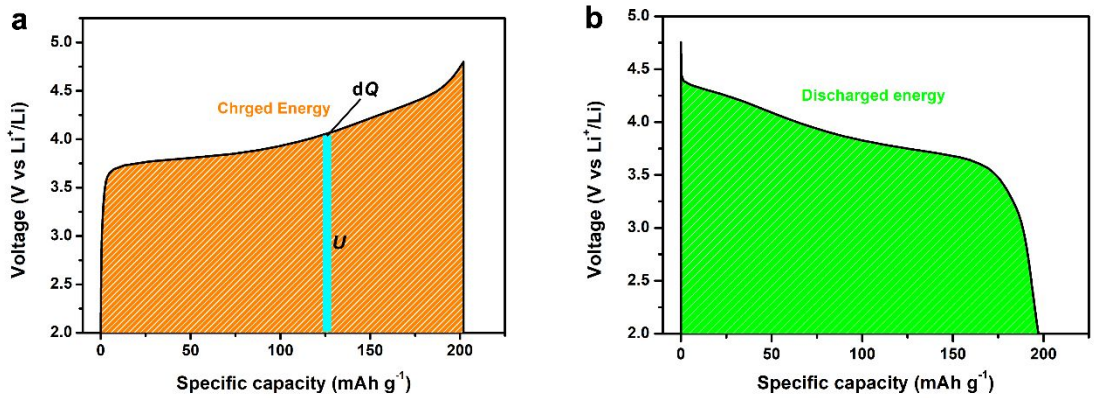

Figure S12 The calculation method of (a) charged and (b) discharge specific energy based on corresponding charge/discharge profiles.

The charge and discharge specific energy are calculated by:

$$\mathrm{E} = \int U i dt = \int U dQ \qquad \text{(S1)}$$

where E is the energy density, U is the voltage, i is the current density, and Q is the specific capacity. The energy density is based on the mass of cathode materials. As for power density (P), it could be calculated by:

$$P = E/\Delta T \qquad \text{(S2)}$$

where ΔT is the corresponding charge/discharge time.