

Supporting Information

Optimizing Particle Size of Disordered Rocksalt Cathodes based on electrochemical performances

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Materials and methods

Material synthesis

$\text{Li}_{1.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_{1.9}\text{F}_{0.1}$ (LMTOF) was synthesized via solid-state method. Lithium carbonate (Li_2CO_3 , 99.0 %, JUNSEI), manganese (III) oxide (Mn_2O_3 , 99.0 %, Sigma Aldrich), titanium (IV) dioxide (TiO_2 , 99.0 %, JUNSEI), and lithium fluoride (LiF, 300 mesh, Sigma Aldrich) were dispersed in ethanol and ultrasonicated for 30 min. An additional 10 mL of ethanol was added to the mixture, which was then transferred to a zirconia jar. Ball-milling process was performed at 300 rpm for 16 h via a planetary mill (PULVERISETTE 6, FRITSCH), conducted in cycles of 30 min followed by a 15 min rest. This mixed solution was dried and calcined at 900 °C for 2 h under an Ar atmosphere. Additional ball-milled samples were ground and further ball-milled at 300 rpm for various durations of 5, 8, and 12 h, denoted as BM5, BM8, and BM12 in a sealed jar under an ambient atmosphere.

Electrochemical analysis

To prepare the cathode composite, 0.1 g of the active material and 0.0125 g of multi-walled carbon nanotubes (MWCNTs) were ball-milled in a zirconia jar at 300 rpm for 2 h using a planetary mill. A homogeneous slurry was prepared by blending 90% composite material and 10 wt% Poly(vinylidene fluoride) (PVDF) binder in N-methyl-2-pyrrolidone (NMP) solvent using a Thinky mixer at 2000 rpm for 30 min. The slurry was cast onto aluminum foil using the doctor blade technique, dried in a convection oven at a 60 °C, and further dried in a vacuum oven at 110 °C overnight. 2032-type coin cells were assembled using Li foil as the counter electrode and a Celgard 2400 separator. The electrolyte was 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7, v/v). Galvanostatic cycle test was conducted using a battery cycler (WBCS3000L, Won-A tech) in the voltage range of 1.5 and 4.8 V at 25 °C. The rate capability tests were performed at currents of 20, 50, 100, 200, 500, and 20 mA g^{-1} for 5 cycles at each within the same voltage range. Electrochemical impedance spectroscopy (EIS) was conducted in a frequency range of 1 MHz to 0.01 Hz, using a voltage amplitude of 5 mV s^{-1} .

Characterization

Powder X-ray diffraction (XRD) patterns of the synthesized pristine LMTOF0.1 and ball-milled samples were collected using diffractometer (D6 Phaser, Bruker AXS GmbH) equipped with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at room temperature. The data were recorded at 40 kV and 30 mA in the 2θ range of 10° to 80° with a step size of 0.02. The XRD refinements were conducted via FullProf program based on the XRD data. Surface morphology of the samples was investigated using field-emission scanning electron microscope (FE-SEM, S-4500, Hitachi). Dynamic light scattering (DLS) analysis was conducted using a Zetasizer system (Zetasizer Advance, Malvern Panalytical) with ethanol as the dispersant. To obtain the particle size distribution, measurements were performed at 25°C following an equilibration time of 120 seconds, with data acquired in backscattering detection mode. X-ray photoelectron

spectroscopy (XPS) was conducted using a scanning X-ray Microprobe (PHI GENESIS). Calibration of binding energies was performed using the C 1s peak at 284.8 eV for all samples.

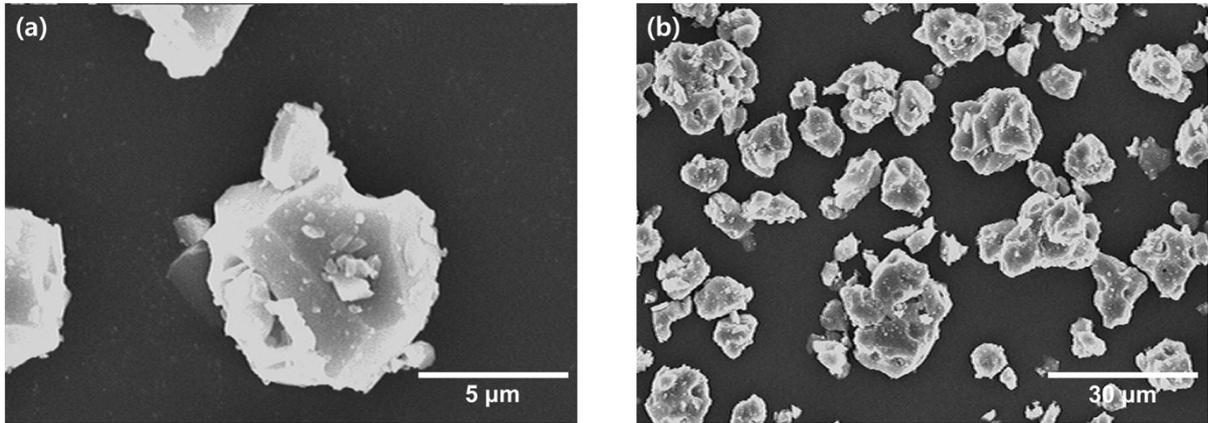


Fig. S1 SEM images of as prepared $\text{Li}_{1.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_{1.9}\text{F}_{0.1}$ with different scale of (a) 5 μm and (b) 30 μm .

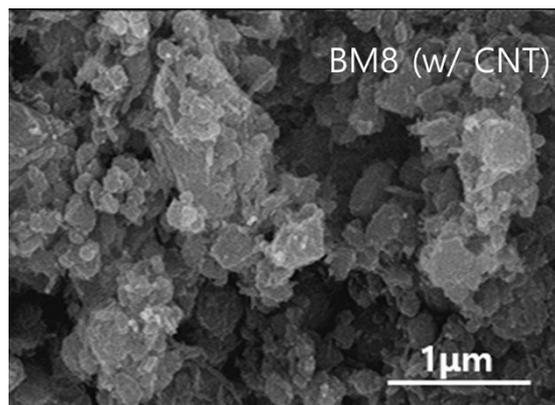


Fig. S2 SEM image of BM8 additionally ball-milled with multi-wall CNTs (MWCNTs).

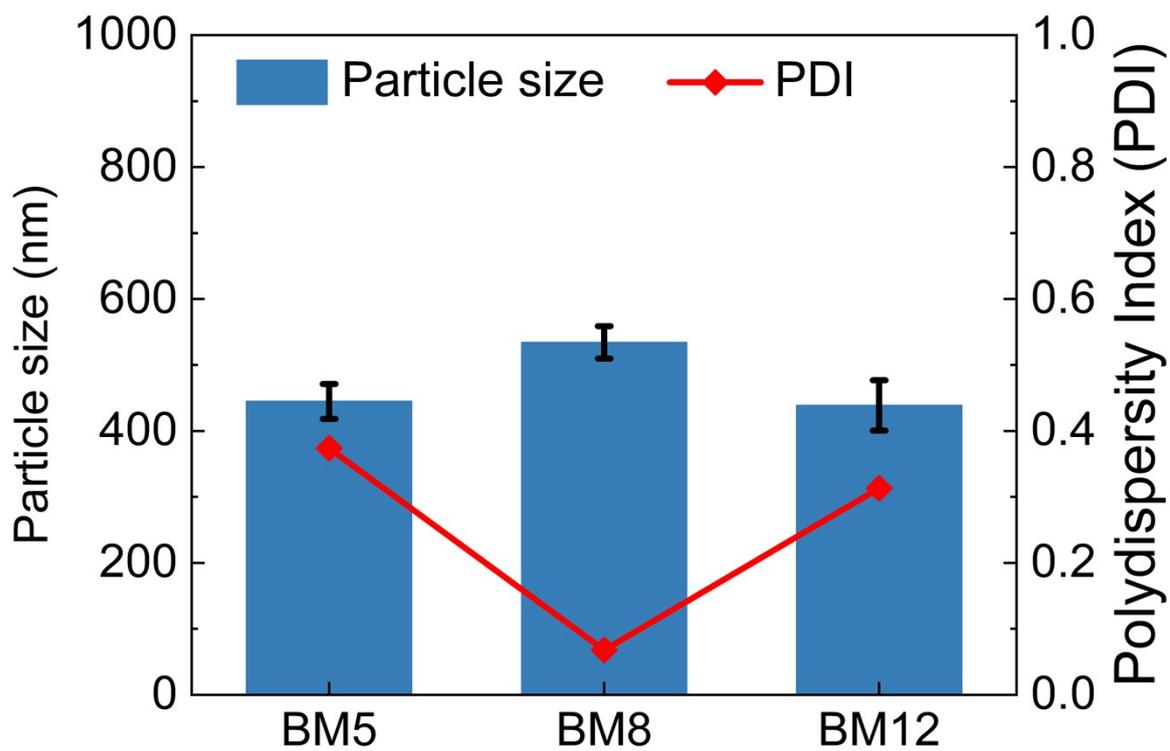


Fig. S3 Zetasizer analysis of particle size and polydispersity index (PDI). Bar graph representing the particle size (blue) with standard deviation error bars, and line plot showing the corresponding PDI (red).

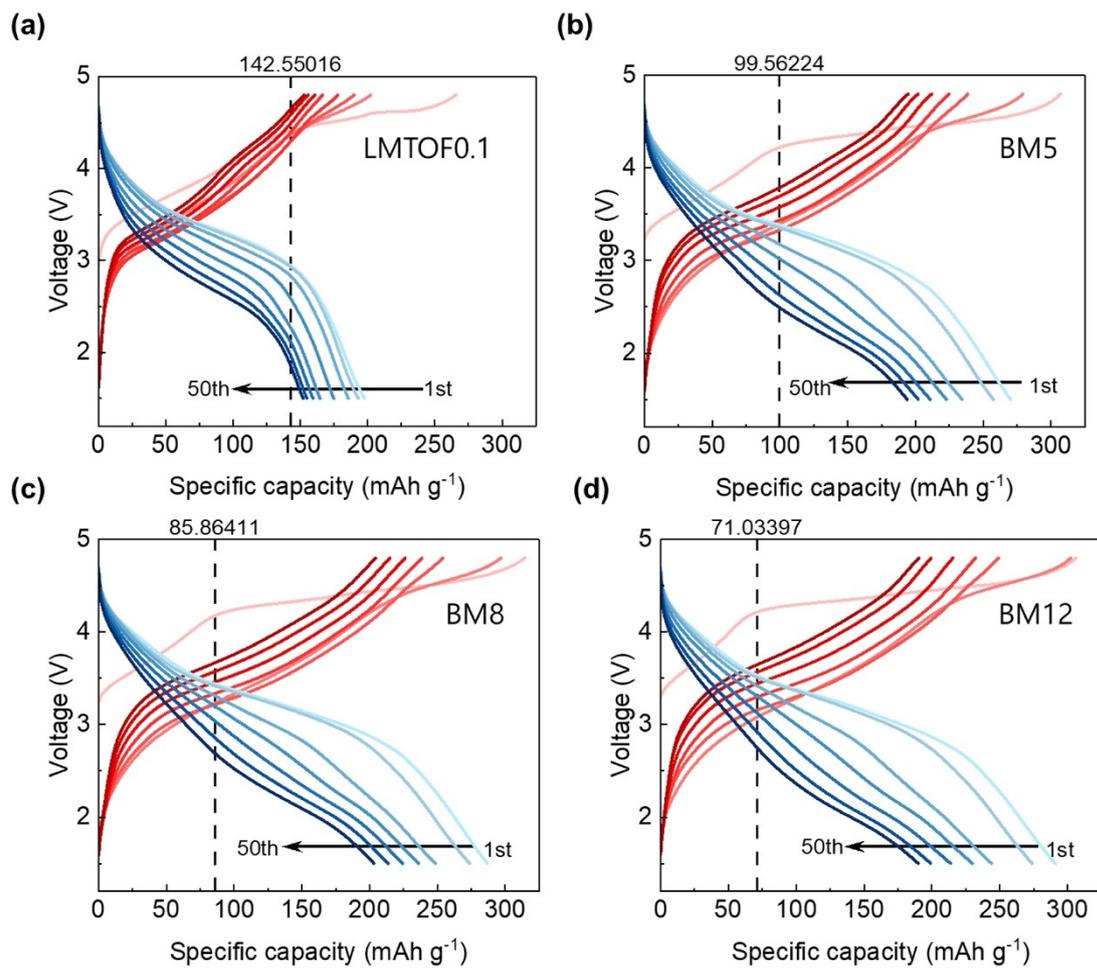


Fig. S4 Charge-discharge profiles for 50 cycles in the voltage range of 1.5 and 4.8 V at 50 mA g⁻¹. (a) LMTOF0.1, (b) BM5, (c) BM8, and (d) BM12.

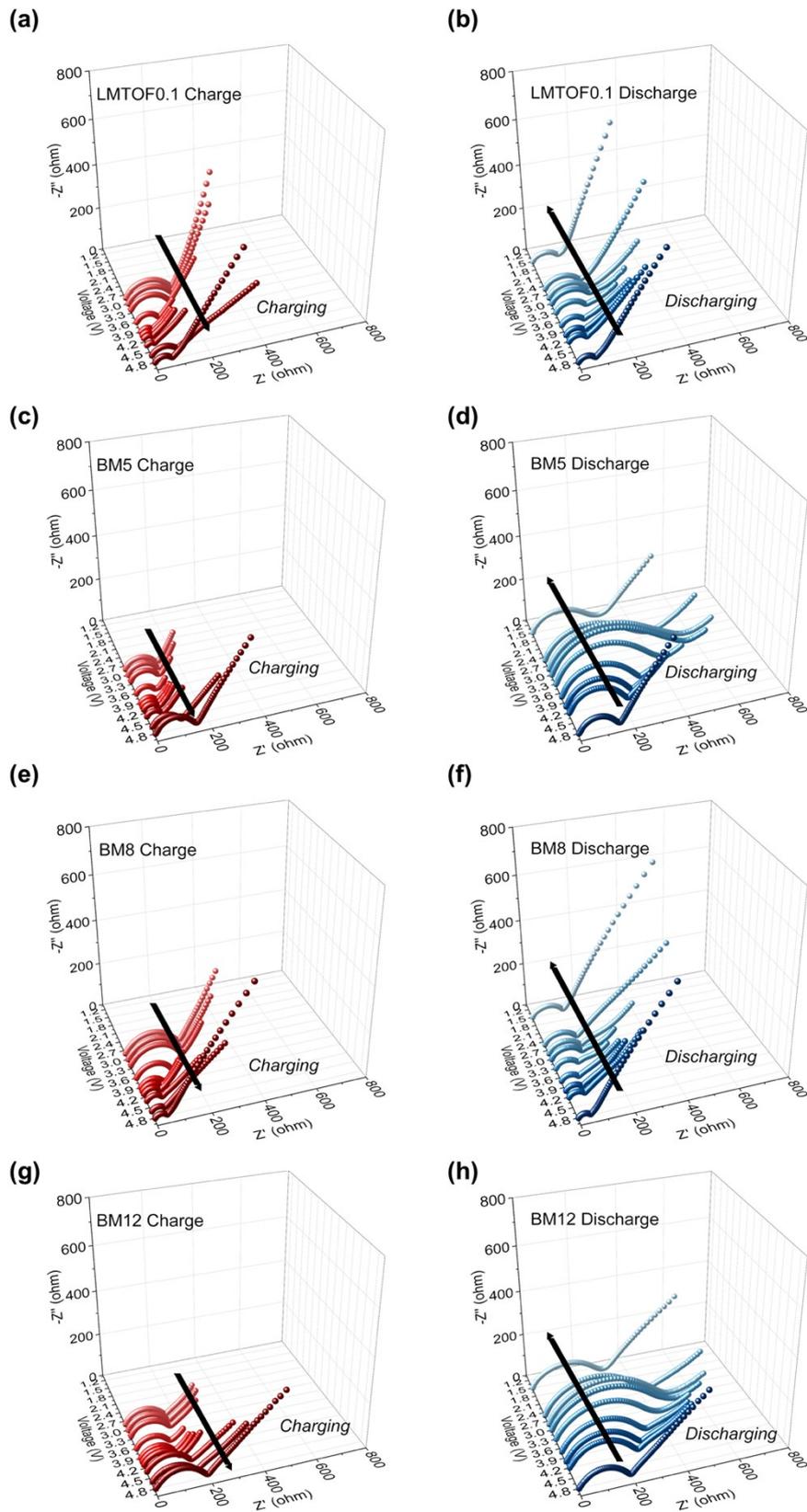


Fig. S5 In-situ EIS Nyquist plots of LMTOF0.1, BM5, BM8, and BM12 obtained during (a, c, e, g) charge and (b, d, f, h) discharge processes, respectively.

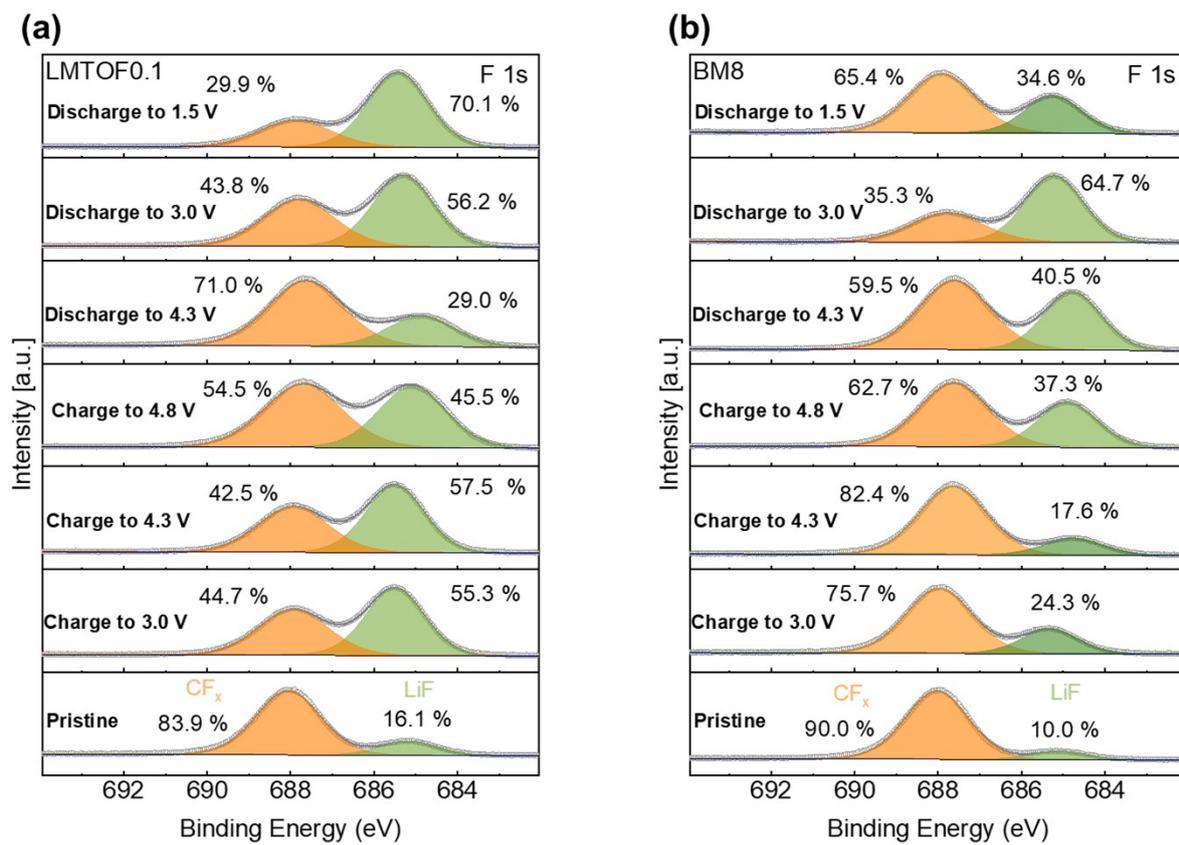


Fig. S6 Ex-situ XPS spectra of F 1s for (a) LMTOF0.1 and (b) BM8, acquired at various potential during the first charge-discharge cycle.

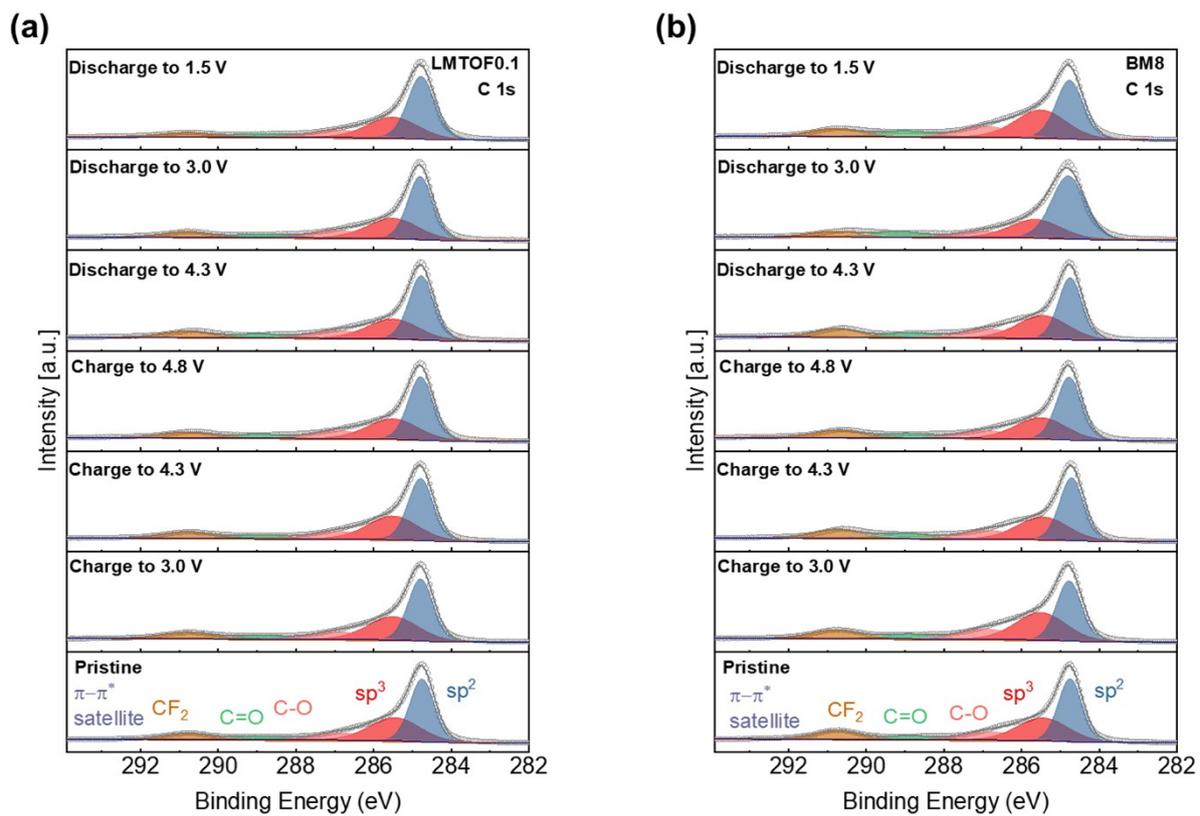


Fig. S7 Ex-situ XPS spectra of C 1s for (a) LMTOF0.1 and (b) BM8, acquired at various potential during the first charge-discharge cycle.

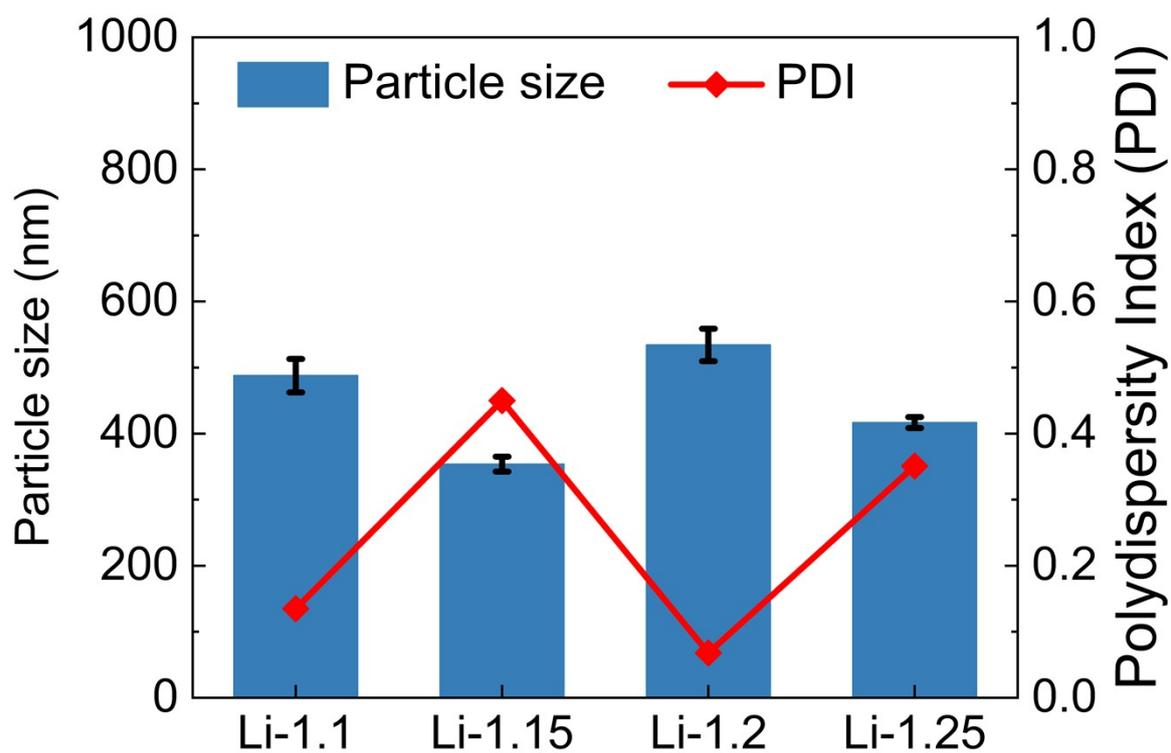


Fig. S8 Zetasizer analysis of particle size and polydispersity index (PDI). Bar graph representing the particle size (blue) with standard deviation error bars, and line plot showing the corresponding PDI (red) for Li-1.1, Li-1.15, Li-1.2, and Li-1.25.

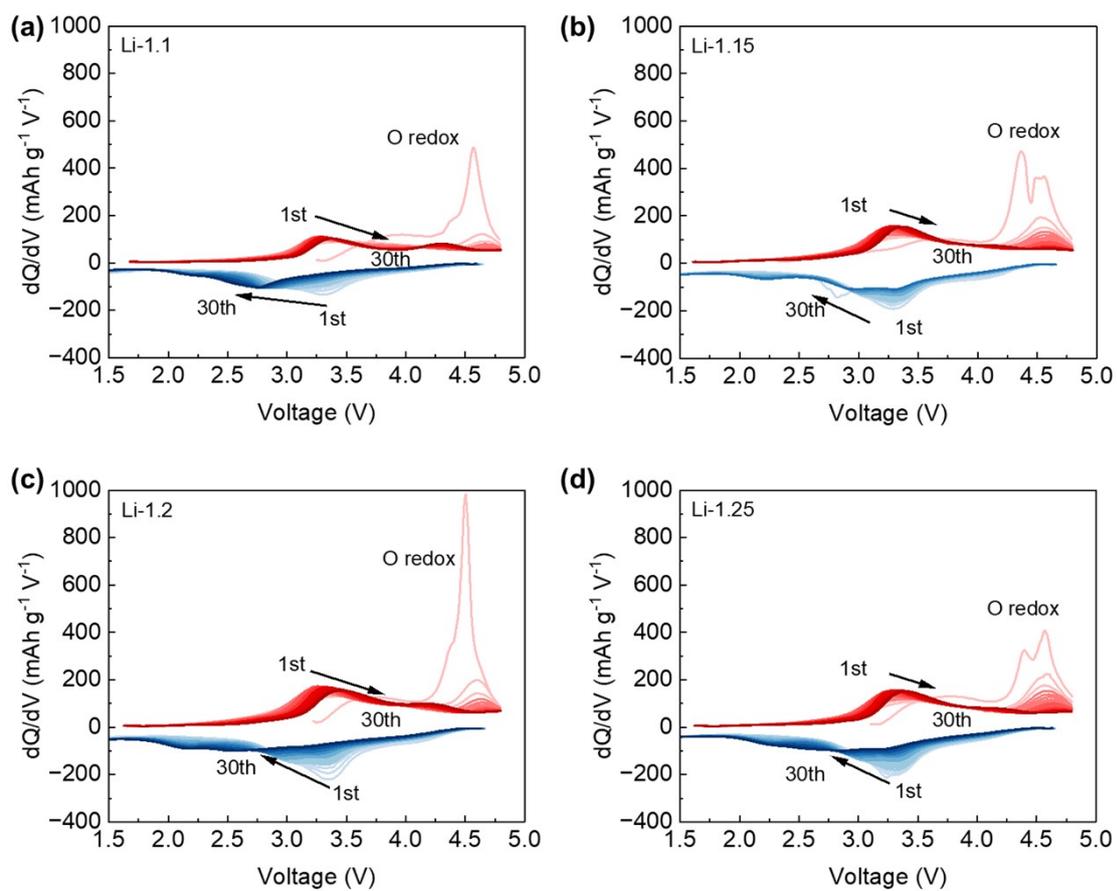


Fig. S9 The overlapped dQ/dV plots for (a) Li-1.1, (b) Li-1.15, (c) Li-1.2 and (d) Li-1.25 conducted in the voltage range of 1.5 – 4.8 V at 50 mA g^{-1} over 30 cycles.

Table S1. Rietveld refinement parameters for X-ray diffraction pattern collected from $\text{Li}_{1.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_{1.9}\text{F}_{0.1}$.

Compound: $\text{Li}_{1.2}\text{Mn}_{0.5}\text{Ti}_{0.3}\text{O}_{1.9}\text{F}_{0.1}$		Space group: $Fm-3m$ (225)			
R_{wp} : 6.15 %		R_{exp} : 2.49 %		R_{I} : 1.21 %	
a (Å): 4.15293		$Z=2$			
Site	Atom	x	y	z	Occ
Li	Li^+	0	0	0	0.6
Mn	Mn^{3+}	0	0	0	0.25
Ti	Ti^{4+}	0	0	0	0.15
O	O^{2-}	0.5	0.5	0.5	0.95
F	F^-	0.5	0.5	0.5	0.05

Table S2. Rietveld refinement parameters for X-ray diffraction pattern collected from BM5

Compound: BM5		Space group: <i>Fm-3m</i> (225)			
R_{wp} : 10.9 %		R_{exp} : 3.29 %		R_I : 4.88 %	
a (Å):	4.15107	$Z=2$			
Site	Atom	x	y	z	Occ
Li	Li ⁺	0	0	0	0.6
Mn	Mn ³⁺	0	0	0	0.25
Ti	Ti ⁴⁺	0	0	0	0.15
O	O ²⁻	0.5	0.5	0.5	0.95
F	F ⁻	0.5	0.5	0.5	0.05

Table S3. Rietveld refinement parameters for X-ray diffraction pattern collected from BM8

Compound: BM8		Space group: <i>Fm-3m</i> (225)			
R_{wp} : 13.3 %		R_{exp} : 5.80 %		R_I : 5.18 %	
a (Å): 4.15048		$Z = 2$			
Site	Atom	x	y	z	Occ
Li	Li ⁺	0	0	0	0.6
Mn	Mn ³⁺	0	0	0	0.25
Ti	Ti ⁴⁺	0	0	0	0.15
O	O ²⁻	0.5	0.5	0.5	0.95
F	F ⁻	0.5	0.5	0.5	0.05

Table S4. Rietveld refinement parameters for X-ray diffraction pattern collected from BM12

Compound: BM12		Space group: <i>Fm-3m</i> (225)			
R_{wp} : 17.1 %		R_{exp} : 6.15 %		R_I : 11.4 %	
a (Å):	4.15158	$Z=2$			
Site	Atom	x	y	z	Occ
Li	Li ⁺	0	0	0	0.6
Mn	Mn ³⁺	0	0	0	0.25
Ti	Ti ⁴⁺	0	0	0	0.15
O	O ²⁻	0.5	0.5	0.5	0.95
F	F ⁻	0.5	0.5	0.5	0.05