Electronic Supplementary Information

Nearly all-active-material cathodes free of nickel and cobalt for Li-ion batteries

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Methods

Synthesis

Partially ordered DRX $Li_{1.68}Mn_{1.60-x}Ti_{x}O_{3.70}F_{0.3}$ [x = 0 (LMOF), 0.30 (T30), and 0.45 (T45)] and full-DRX Li_{1.25}Mn_{0.17}(II)Mn_{0.58}(III)O_{1.33}F_{0.67} (LLF) powders were synthesized via a mechanical highenergy ball-mill process using a Retsch PM200 planetary ball-mill for 33 hrs at 450 rpm (LMOF, T30 and T45) and 40 hrs at 500 rpm (LLF). A stoichiometric amount of Li₂MnO₃ (obtained by calcination with Li₂CO₃ (Alfa Aesar, 99%, 5 wt% excess) and MnO₂ (Alfa Aesar, 99.9%) at 800 °C in air atmosphere for 16 hrs), MnO₂ (Alfa Aesar, 99.9%), Mn₂O₃ (Alfa Aesar, 98%), TiO₂ (Alfa Aesar, 99.6%) and MnF₂ (Alfa Aesar, 99%) for LMOF, T30, and T45, and Li₂O (Alfa Aesar, 99%, 5 wt% excess), MnO (Alfa Aesar, 99%), MnO₂ (Alfa Aesar, 99.9%) and LiF (Alfa Aesar, 99.99%, 5 wt% excess) for LLF were used as precursors. To synthesize Full-DRX Li_{1.1}Mn(III)_{0.7}Ti_{0.2}O₂, $Li_{1,2}Mn(III)_{0,4}Ti_{0,4}O_2$ (LMTO), $Li_{1,3}Mn(III)_{0,1}Ti_{0,6}O_2$, $Li_{1,1}Mn(III)_{0,8}Nb_{0,1}O_2$, $Li_{1,2}Mn(III)_{0,6}Nb_{0,2}O_2$ and Li_{1.3}Mn(III)_{0.4}Nb_{0.3}O₂, stoichiometric Mn₂O₃, Nb₂O₅, TiO₂ and Li₂CO₃ (with 5 wt% excess) precursors were dispersed into 20 ml ethanol and mixed via a planetary ball-mill (Retsch PM200) for 15 hrs at 300 rpm. The mixture was dried at 110 °C for a day and pelletized. The pelletized powder was calcinated at 950 °C in an Ar flow for 12 hrs (ramping rate 4 °C/min). After the calcination, the powder is pulverized for 2 hours using SPEX 8000D Mixer Mill with five 10 mm (diameter) and ten 5 mm (diameter) zirconia balls for 1g batch in 45 mL alumina jar. We used these pulverized DRX materials in most of our experiments, except for Fig. 1e. For all processes through a high-energy ball-mill using Retsch PM200, five 10 mm (diameter) and ten 5 mm (diameter) stainless-steel balls for 1g batch are introduced into a 50 ml stainless-steel jar. All sampling processes for ball-mill processes are performed in an Ar-filled glove box.

Electrochemistry

For fabrication of a cathode film, the powder of the cathode (LMOF, T30, T45, LLF, and (pulverized) LMTO) and conductive carbon (either carbon black (CB, IMERYS) or multiwalled CNT (MWCNT, Nanosolution, TMC 220-05 and TMC 220-10) were mixed using a Fritsch pulverisette 7 premium line planetary ball-mill with the various (weight) composition (70:20, 80:10, 90:5, 92:4, 94:3 and 96:2) at the rate of 300 rpm in the 50 ml stainless-steel jar except for LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NCM811, ROVS) cathode through hand mixing. TMC 220-10 with lower tap density (0.06 g/cc) was used for all experiments except for some experiments in which the other MWCNT (TMC 220-05, 0.09 g/cc) was introduced to explain the importance of the effects of MWCNT-type in Fig. S27 and the other evaluation in Fig. S42. The optimized mixing time of the cathode powder with the conductive carbon is 2 hrs for carbon black and 30 minutes for MWCNT, respectively. In all ballmill procedures for mixing the DRX cathode with carbon, five 10 mm and ten 5 mm zirconia balls were used for 1g batch powder. Then, binding material (BM, Polyvinylidene fluoride (PVDF), Solvay) dispersed in N-Methyl-2-pyrrolidone (NMP) was added to the mixed powder containing

active materials (AM) and conductive carbon to make AM:carbon:BM=70:20:10, 80:10:10, 90:5:5, 92:4:4, 94:3:3 and 96:2:2). Exceptionally, each PVDF9300 dispersed in NMP and styrenebutadiene rubber (SBR)/sodium salt of carboxymethyl cellulose (CMC) binder dispersed in water was used in 94:3:3 (PVDF9300) (Fig. S32a) and 96:2:1.33(SBR):0.67(CMC) cathode film (Fig. S32b) for the binder test. The compounds were mixed with a Thinky-mixer, and the mixed slurry was cast on the Al-foil to make a cathode film. In a high-rate test of half-cells, the loading level is more than 5 mg_{-cathode}/cm² to minimize the kinetic advantage of thin electrodes because low loading (thinner electrode) enables faster rate capability.

In full-cell evaluation, natural graphite (Bay carbon) was used as a counter electrode (N/P=1.2). At high-rate cycling tests, the N/P ratio was considered based on the discharge capacity of the cathode at the high rate in the half-cell test. The composition of anode for full-cell was graphite:SBR:CMC:CB=96:2:1:1 for a low-rate test (25 mA/g_{-AM}) and 94:2:1:3 for the high-rate tests (2 A/g_{-AM} and 4 A/g_{-AM}). The cathode film for all full-cell tests was composed of AM:carbon:BM = 92:4:4 except for the full-cell evaluation of 96:2:2 T30 cathode film in Fig. S39. The relative area of the electrodes (cathode/anode) is 0.80. Both electrodes include the formation step at the current of 25 mA/g_{-AM} (LMOF, T30, and T45), 20 mA/g_{-AM} (LLF), and 33 mA/g_{-AM} (Graphite) for 2 cycles. After two cycles, the half-cells for each cathode and anode electrode are disassembled and reassembled for the full-cell test. We note that 0.75 A/g_{-AM} is ~4C because of ~15 minutes of its actual discharging time (compared to 0.25 A/g_{-AM} , ~1C). The energy density and specific capacity of the LMOF, T30, and T45 in the full-cell tests were evaluated considering the weight change of the compounds after the pre-lithiation step.

For all electrochemical tests, each 1M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) solvents (volumetric 1:1, Enchem) and glass microfiber filter (Whatman) was used as the electrolyte, and the separator, respectively, except for the long-term cycling half-cell test at high-rate (in Figs. S39 and S40) and the loading test (in Fig. S25) including 5 wt% FEC in the baseline electrolyte. As a counter electrode, each Li metal foil (FMC) and natural graphite was selected as anode material for half-cells and full-cells, respectively. The loading level of the cathode film was ~ 5 mg_{-cathode}/cm².

All galvanostatic experiments were carried out using battery measurement system (WBCS 3000, WonATech) at room temperature. In galvanostatic charge and discharge, various experiments have their cut-off voltage and current density, which are written in each figure. Also, a constant voltage (CV) mode with a current cut-off value of C/20 was mostly included except for some conditions (Figs. 2g and S31-33) and the long-term cycling tests (more than 100 cycles, no CV step).

To evaluate the loading effect in highly concentrated Mn-DRX cathodes, we tested the electrochemical performance of 92(T45):4(MWCNT):4(PVDF) cathode/Li metal anode half-cell with a various cathode loading-level (3 mg_{-AM}/cm², 8 mg_{-AM}/cm² 12 mg_{-AM}/cm², and 16 mg_{-AM}/cm²). Rate-capability test includes a current of 25 mA/g_{-AM}, 250 mA/g_{-AM}, and 500 mA/g_{-AM}. In

cycling, the current was set to 250 mA/g_{-AM} after the pre-lithiation at the current of 25 mA/g_{-AM}. All galvanostatic charging steps include the CV step with a current cut-off value of C/20.

The charge-transfer resistance of half-cells was analyzed by electrochemical impedance spectroscopy measurement (SP-300, Biologic workstation). EIS measurements were performed under open-circuit conditions (0% SOC, Fig. 2d-f) and several states-of-charge (SOCs) [charging to 20, 50 (90:5:5), 100 mAh/g_{-AM} (70:20:10 and 80:10:10), and fully discharged state, Fig. S8] with an applied amplitude of 5 mV, and measurements were made in the frequency range of 1 MHz to 1 mHz. The fitting method is based on the randomize + simplex mode with 5000 iterations. The α value (the fitting parameter) is included in the EIS figure. The pristine samples had a resting time of 8 hours, and the cycled samples were measured within a few hours (~2 hours) after finishing the cycling. To identify the EIS data, we introduced distribution of relaxation times (DRT) analysis, the open-source MATLAB script-based software (DRT tools). The regularization derivative is 2nd-order, and the regularization parameter is 1E-3. The full width at half maximum (FWHM) in radial basis function (RBF) was 0.5, and the frequency range for fitting is commonly set to the range between 1 MHz to 5 mHz. In fitting EIS and DRT analyses, we did not consider the Warburg region for better fitting results.

For the galvanostatic intermittent titration technique (GITT) analysis, we charged various electrodes with differing LMOF:carbon:PVDF ratios (70:20(CB):10, 80:10(CB):10, 90:5(CB):5, and 90:5(MWCNT):5) at 20 mA/g, with a step size of 5 mAh/g, followed by a relaxation step for 2.5 hours. The charge capacity cut-off was 50 mAh/g due to the limited charge capacity of 90:5(CB):5 electrode.

Characterization

The X-ray diffraction patterns for all samples were obtained with Rigaku High Power XRD (D/8/MAX2500V/PC model) to analyze the crystal structure with Cu source in the 20 range of 10-90°. The scanning speed was 0.7°/min. The XRD fitting was performed by PANalytical X'pert HighScore Plus software. In the multi-phase refinement for LMOF, we considered the average volume of the standard unit-cell, which is based on the unit-cell of Fd-3m spinel phase (= 8 times the unit-cell of the Fm-3m DRX phase). To obtain the average volume in the multi-phase refinement, we first calculate the weight (g) of a unit-cell (= unit-cell volume (Å³) x unit-cell density (g/cm³) x 10⁻²⁴, which are obtained in XRD refinement). Then, the weight percentage of each phase obtained in XRD refinement is divided by the weight of each unit-cell to obtain the amount of each unit-cell per gram. It is noted that the total number of the standard unit-cell per gram is the sum of the number of Fd-3m spinel unit-cells and the number of Fm-3m DRX unit-cells divided by 8. Finally, the average volume of the standard cell is obtained by the overall volume of the phases per gram ((lattice parameter of spinel phase)³ x the number of spinel unit-cell per gram + (lattice parameter of DRX phase)³ x the number of DRX unit-cell per gram.

SEM images were obtained using Hitachi SU9000 microscope with HABSE detector & EDS for 40 to 60 min acquisition with a windowless detector with 1.2 kV accelerating voltage. To confirm the formation of the porosity after the subsequent cycling, a cross-section of each carbon film was produced by broad beam argon ion milling (ArIB) using the Hitachi IM4000 cross-section polisher with a beam energy of 6 keV.

The electrical conductivities of cathode materials are obtained by the DC polarization method. The powders of pulverized cathode materials are pelletized with a 13 mm diameter mold under 2 tons of pressure for 2 min. The resistance was measured with three steps where the constant voltage was introduced each step for 10 minutes (0.1 V, 0.2 V, and 0.3 V). The electrical conductivity (σ , S/cm) was obtained using the following equation: $\sigma = 1/R * L/A$, where R, L, and A are the resistance, length, and area of the conductor, respectively. We find that the conductivity values slightly increase with additional stack pressures or Au coating (G10 ion sputter coater, GSEM) on the powder pellets during the measurement (Fig. S9) but without changing the composition-electrical conductivity correlation. The values in Fig. 2h & 2i and Fig. 5a are obtained without stack pressure and Au coating.

Porosity and pore size distribution were measured by a mercury porosimeter of the Autopore V 9620 (Micromeritics). The analyzed pore range is between 3 nm and 150 nm based on the SEM results (Fig. 3d). To increase the accuracy of the analysis, twelve pieces of 1 cm x 2 cm electrode (cathode composite cast on Al foil) are used after a robust calendaring process (2.82, 2.98, 2.96, and 3.08 g_{-electrode}/cm³ for 80(LMOF):10(CB):10(PVDF), 90(LMOF):5(CB):5(PVDF), 90(LMOF):5(MWCNT):5(PVDF), and 96(LMOF):2(MWCNT):2(PVDF) electrode, respectively) along with the condition for electrochemical tests: Here, the g_{-electrode}/cm³ excludes the weight of the Al-current collector. We obtained a value of porosity (%) with this equation, (1 - the ratio of bulk density (with pore) to a skeletal density (without pore) of cathode composite) x 100%, after extracting the pure values of cathode composite from the obtained results having both cathode composite and Al foil. All values in the porosity calculation are included in Fig. S24.

For the peeling test of the electrode composite, High Tack Double Coated Tissue Tape (3M) was used as an adhesive tape. The tape attached to the electrode film was peeled off using AGX-100NX Universal Testing Machine (SHIMADZU).

To evaluate the soaking effect on the electrode, instead of cycling the cells, we rested the coin-cell for 4 days (corresponding to the time required to achieve 5 cycles at 25 mA/g_{-AM} between 1.5-4.8 V) and 11 days (\approx 20 cycles duration). Then, we disassembled the cells and observed the cross-section of the cathode films using SEM to see the electrolyte-soaking effects on the cathode microstructure.

Polaron conduction calculations

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP).¹ Spinpolarization was considered, and the projector-augmented wave (PAW) method was used with a plane-wave energy cut-off of 520 eV. For structural relaxation, the combined generalized gradient approximation (GGA) + U with the Perdew-Burke-Ernzerhof (PBE) functionals was implemented in VASP.² The Hubbard U correction was adopted for Mn (U=3.9) to address the self-interaction error of the d orbital states in GGA+U calculations.

For calculating the energy barrier of polaron conduction through the corner- and edgeshared Mn-Mn networks in LiMn³⁺O₂, cation-mixed LiMnO₂ with symmetric corner- and edgeshared Mn-Mn configuration was considered. Because the corner-sharing Mn-Mn configuration of ordered LiMnO₂ has not been reported elsewhere or deposited in the Materials Project,³ the cation-mixed LiMnO₂ was prepared using the 4 × 4 × 2 supercell of the cubic MnO (Space group = Fm-3m, mp-19006). The configurations were generated with all possible Li and Mn arrangements in the supercell and sorted by their electrostatic energies (the Ewald summation). The thirty lowest-energy configurations were evaluated by DFT calculations (GGA+U). For this evaluation, the structures were fully relaxed until stresses on the cell were smaller than 0.05 eV / Å. Based on their GGA+U energies, we select the most stable cation-mixed LiMnO₂ structure as a model structure among the structures containing symmetric corner- and edge-shared Mn-Mn configurations.

To study hole-polaron conduction in cation-mixed LiMnO₂, we evaluated the energy barriers for hole-polaron to migrate from a Mn-site to the nearest corner- or edge-shared Mnsite. The hole-polaron localization on Mn-site was carried out by removing one electron from the electron density of structures (we referred to the method in prior research⁴), and charge neutrality was ensured by compensation of the background charge. Contrary to the previous report, where the hole was easily localized in Fe-based phosphate cathode materials,⁴ the holepolaron was not easily localized in our case of cation-mixed LiMnO₂ by simply relaxing the structure with one fewer electron. Instead, we artificially prepared structures with a localized hole polaron, and then their atomic positions were relaxed via GGA+U calculations. We intentionally decreased the bond lengths of Mn-O bonds within the targeted localized MnO₆ octahedra to approximately 1.95 Å, which is close to the Mn⁴⁺-O bond length. For these calculations, the structures were moderately relaxed until stresses on the cell were less than 0.01 eV per formula unit. The hole localization was evaluated using magnetic moments of Mn ions. Additionally, Heyd-Scuseria-Ernzerhof hybrid functionals with the mixing parameter α of 0.25 (HSE06)^{4, 5} was employed to further localize the hole by electronically relaxing the obtained structure (by GGA+U) without an ionic relaxation. This approach led to obtaining a hole-localized energy state, as the hole on the target Mn-site was not fully localized by GGA+U calculation method alone.⁴ Then, the migration path for corner- or edge-shared Mn-Mn configuration is linearized between initial and final structures relaxed by GGA+U calculation. Concerning the possibility of other transition states not lying on the linear path, it is improbable that their energy state would be significantly lower than one on the linearized path.⁴ Five intermediate states along the linear path were generated and electronically relaxed by HSE06 functionals. Because the

intermediate states should not converge to either the initial or the final state and must lie along the migration path, the charge density was only relaxed, while atom positions remained fixed for this calculation.⁴

Electronic structure calculations

All electronic structure calculations were performed using VASP.¹ Li_{1.3}Mn_{0.1}Ti_{0.6}O₂, Li_{1.2}Mn_{0.4}Ti_{0.4}O₂, and Li_{1.1}Mn_{0.7}Ti_{0.2}O₂ DRX structures were implemented by using Li₁₄Mn₂Ti₈O₂₄, Li₂₀Mn₆Ti₆O₃₂, and Li₂₆Mn₁₂Ti₂O₄₀ supercells, which are spanned by the primitive cell of rocksalt MnO (mp-19006) from the Materials Projects.³ The electron wavefunctions were represented in the same manner as the polaron conduction calculations. Static range-separated HSE⁵ with the mixing parameter α (α = 0.15, 0.2, 0.25, and 0.3) were employed after structural relaxation using GGA+U calculations described in the polaron conduction calculations section. The KPOINTS files for density of states calculations were generated by pymatgen package⁶ with a grid density of at least 1500. The k-paths for band structure calculations were converged to 10⁻⁶ eV in total energy.

Cluster expansion

The energies of various DRX configurations were evaluated by the cluster expansion (CE) method implemented in the Statistical Mechanics on Lattices (smol) python package.⁷ The orthogonal sinusoidal basis sets were used to expand cluster function for sites on the lattice. The geometric clusters of the CE model were composed of pair interactions (<8 Å), triplet interactions (<6 Å), quadruplet interactions (<5 Å), and quintuplet interactions (<8 Å), triplet interactions (<6 Å), quadruplet interactions (<5 Å), and quintuplet interactions (<5 Å) about primitive rock-salt unit cells with a lattice constant of 2.94 Å, which is the average lattice constant of 300 energetically stable configurations. The CE models were fitted to DFT energies with PBE parametrized GGA+U (U_{Mn}=3.9) exchange-correlation functional through the L₁-regularized linear regression method. The accuracy of fitting was obtained by cross-validation. The CE models were trained by a total of 571, 631, and 774 DRX configurations with DFT energies, yielding 15.25 meV/cation, 11.03 meV/cation, and 9.15 meV/cation of root mean square deviation for each Li_{1.3}Mn_{0.1}Ti_{0.6}O₂, Li_{1.2}Mn_{0.4}Ti_{0.4}O₂, and Li_{1.1}Mn_{0.7}Ti_{0.2}O₂ composition, which are comparable with previous work.⁸

Monte Carlo Simulation

Short-range ordered DRX configurations were sampled from the canonical Markov Chain Monte Carlo (MCMC) simulations based on the CE models. All canonical MCMC simulations were run concerning $8 \times 8 \times 8$ supercells containing 512 cations based on the Metropolis-Hastings algorithm with 3273 K of the optimized temperature, reproducing previously reported short-range ordering (Fig. S48).⁹ Before the sampling, MCMC simulations were run during 1,000,000 steps to achieve equilibrium. After equilibrium, 1000 DRX configurations were sampled from the Markov Chain during 10,000,000 MCMC steps to ensure diversity of cation ordering. For Mn

percolation analysis, connected Mn atoms by edge-sharing and corner-sharing were obtained with pymatgen package.⁶ As the lithium-ion and d^0 metal ion (*e.g.*, Ti⁴⁺ or Nb⁵⁺) have extremely low electron affinities and high ionization energies, they were not considered as an electron/polaron hopping path.



Fig. S1. Morphology and size of MWCNT and CB. Scanning electron microscopy (SEM) images of (a) MWCNT and (b) CB conductive carbon: scale bars, 1µm. The morphology of MWCNT or CB is 1D vine-like or 3d spherical shape, respectively.



Fig. S2. The thickness of the electrode with the increasing AM content. The cross-sectional SEM images of LMOF cathode after calendering (a-c) with CB in (a) a 70:20:10 (AM:CB:PVDF, weight), (b) 80:10:10, and (c) 90:5:5 electrode film, and with (d) MWCNT in a 96:2:2 (AM:MWCNT:PVDF, weight) electrode film. It is observed that an electrode thickness decreases with less carbon (more AM) under a similar loading level of the electrode (mg_{-cathode}/cm²). AM particles are much denser than carbon or binder, occupying smaller volumes (thus thinner electrodes) per given electrode mass (or mass loading, mg_{-cathode}/cm²).



Fig. S3. The rate capability of CB-based LMOF electrode with different AM content. The first cycle voltage profiles of LMOF when cycled at 25 mA/g_{-AM} (black) or 250 mA/g_{-AM} (red) between 1.5–4.8 V in (a) a 70:20:10 (AM:CB:PVDF, by weight), (b) 80:10:10, and (c) 90:5:5 film.



Fig. S4. The calendering effect on the microstructure and electrochemical performances of CB- and MWCNT-based LMOF electrodes. (a-b) The voltage profiles and the capacity retention of LMOF when cycled at 25 mA/g_{-AM} between 1.5-4.8 V in (a) a 80:10:10 (LMOF:CB:PVDF, by weight), and (b) 90:5:5 (LMOF:MWCNT:PVDF, by weight) electrode film without calendering (0.80 (1.00) and 1.15 (1.28) g_{-AM}/cm³ (g_{-electrode}/cm³) for CB- and MWCNT-based electrode, respectively), with moderate (1.37 (1.71) and 1.62 (1.80) g-AM/cm³ (g-electrode/cm³) for CB- and MWCNT-based electrode, respectively) and high calendering (2.26 (2.82) and 2.66 (2.96) g-AM/cm³ (g-electrode/cm³) for CB- and MWCNT-based electrode, respectively) process. (c-e) The cross-sectional SEM images of the LMOF(80):CB(10):PVDF(10) electrode without calendering (c) before cycle and (d) after 20 cycles, and (e) with moderate calendering after 20 cycles. (f) The cross-sectional SEM images of MWCNT-based LMOF(90):MWCNT(5):PVDF(5) electrode without calendaring process before cycle. The white, gray, and black regions correspond to LMOF, CB/MWCNT/PVDF, and pores. The CB-based 80(LMOF):10(CB):10(PVDF) electrode has a poor electrochemical performance without a high calendering, whereas the electrochemical performance in 90(LMOF):5(MWCNT):5(PVDF) electrode is insensitive to the calendering process. A closer look at the noncalendered MWCNT-based electrode in (f) reveals that vine-like MWCNT forms a cross-linked network that introduces electrical connections through the pores, unlike CB.



Fig. S5. The impedance of CB-based LMOF half-cell. The Nyquist plots of LMOF (a-c, g) before cycle and (d-f) after 10 cycles at 25 mA/g_{-AM} between 1.5–4.8 V in (a, d) 70:20:10 (LMOF:CB:PVDF), (b, e) 80:10:10, (c, f) 90:5:5 and (g) 96:2:2 film. Equivalent circuit and parameters (R and α) obtained by Z-fitting (red) are included with experimental plots (black): electrolyte resistance (R_e) and another resistance in a high- and medium-frequency region between 1 Mhz and 1 mHz (R_{hmf}). In the fitting, we included three parts of resistance (R_{hmf1}, R_{hmf2}, and R_{hmf3}), assuming the R_{film}, R_{ct(cathode)}, and R_{ct(anode)} except for (d) having a clear semi-circle of R_{film} (37.6 Ω), supported by its high frequency (2300 Hz).^{10, 11} We note that the fitted numbers for the resistance of each component here serve as reference points to represent the sum of the resistance within the same high- and medium-frequency region instead of the most accurate values because the complicated contribution from various resistances hampers the accurate deconvolution into each single resistance.



Fig. S6. Distribution of relaxation times (DRT) analysis for pristine electrode. DRT analysis for (a-c) a cathode symmetry cell of (a) a 70:20:10 (AM:CB:PVDF, by weight), (b) 80:10:10, and (c) 90:5:5 pristine electrode, (d) Li symmetry pristine cell, and (e-g) pristine half-cell of (e) 70:20:10, (f) 80:10:10, and (g) 90:5:5 cathode with Li-metal anode.

With DRT analysis (on EIS results), we tried to distinguish contributions of resistances from different components in LMOF/Li half cells (Fig. 2). We first applied DRT analysis on the (1) symmetric "pristine/before cycle" LMOF/LMOF cells with different AM:CB:PVDF compositions to determine the frequency region where the cathode would show resistance (impedance) and the magnitudes of resistances in (a-c). Then, we performed the same analysis on a (2) symmetric "pristine/before cycle" Li/Li cell in (d). Before discussing the results, we point out that the electrode film (e.g., CEI for the cathode, SEI for the anode) contribution is widely associated with the higher frequency region (2 < 2 $\log(\text{frequency}) < 6)$ in the DRT analysis and that from the charge transfer resistances ($R_{ct(cathode)}$ or $R_{ct(anode)}$) with a lower frequency region (-3 < log(frequency) < 2).^{10, 11} The DRT results of "symmetric, pristine/before cycle" LMOF/LMOF cells in (a-c) and Li/Li cell in (d) show that $R_{ct(cathode)}$ is dominating over R_{film} (R_{CEI}) for the LMOF/LMOF cells, whereas the opposite is seen for the Li/Li cell. For the LMOF/LMOF cells with different electrode compositions in (a-c), we find that the R_{ct(cathode)} significantly increases with a higher LMOF content (a lower CB content), as evidenced by the increased total area within the lower frequency region (-3 < log(frequency) < 2). Note that regardless of the LMOF electrode composition, R_{ct} is notably greater for the LMOF/LMOF cells than the Li/Li cells. From the above information, we can understand the DRT signal from the LMOF/Li half-cells in (e-g), which is (i) the sum of signals from the LMOF/LMOF and Li/Li symmetric cells and (ii) constitutes the (depressed) semi-circle in Figs. 2d-f. In Fig. 2f, we showed that the half-cell made with the LMOF(90):CB(5):PVDF(5) electrode shows a much greater (depressed) semi-circle than that with the LMOF(70):CB(20):PVDF(10) electrode. The DRT analysis on the LMOF/Li half-cells in (e-g) confirms that the greater resistance in the non-cycled LMOF/Li half-cell with the LMOF(90):CB(5):PVDF(5) electrode (vs. LMOF(70):CB(20):PVDF(10) electrode) comes from the significantly larger R_{ct(cathode)}.



Fig. S7. Distribution of relaxation times (DRT) analysis for cycled electrode. DRT analysis for (a-c) a cathode symmetry cell of (a) a 70:20:10 (AM:CB:PVDF, by weight), (b) 80:10:10, and (c) 90:5:5 cycled electrode, (d-f) a cycled Li symmetry cell with (d) a 70:20:10, (e) 80:10:10, and (f) 90:5:5 cathode, and (g-i) cycled half-cell of (g) a 70:20:10, (h) 80:10:10, and (i) 90:5:5 cathode with Li-metal anode. All the half-cells undergo ten galvanostatic cycles at 25 mA g⁻¹ between 1.5-4.8 V (room temperature) and disassembled to fabricate each symmetry cell.

Comparing the area under the lower frequency region (-3 < log(frequency) < 2, representing R_{ct}) in the DRT results of "before cycle (Figs. S6a-c)" and "after 10 cycles (Figs. S7a-c)" LMOF/LMOF cells, the increase in $R_{ct(cathode)}$ of LMOF(80):CB(10):PVDF(10) and LMOF(90):CB(5):PVDF(5) symmetric cell is much more significant for the compared with the LMOF(70):CB(20):PVDF(10) case. However, the change of R_{CEI} (2 < log(frequency) < 6) is very small compared to the $R_{ct(cathode)}$ change. For the Li/Li symmetric cells made with 10-cycled Li-metal anodes in the LMOF/Li cell, the overall intensity in the DRT results is a bit smaller, most likely due to the activation of the Li-metal anode during cycling, decomposing the surface film on the Li-metal anode.¹² Meanwhile, the overall intensity in the DRT result from the (cycled) Li/Li cells show substantially smaller values than that from the cycled LMOF/LMOF cells, indicating that the degradation of the LMOF/Li cells upon cycling (leading to an increased overall depressed semi-circle in Figs. 2d-f) comes from the increased $R_{ct(cathode)}$ of the LMOF electrode instead of other resistance components (degradation of $R_{ct(anode)}$, R_{CEI} , R_{SEI}). This, in turn, makes the DRT signals in the cycled LMOF/Li cells in (g-i) notably similar to that of the (cycled) LMOF/LMOF cells (a-c).



Fig. S8 The influence of the state of charge (SOC) on the charge-transfer resistance. (a) The voltage profiles of LMOF when cycled at 25 mA/g_{-AM} between 1.5–4.8 V in the 70:20:10 (AM:CB:PVDF, by weight, black), 80:10:10 (red), and 90:5:5 electrode film (blue). The circles indicate different states-of-charge (SOCs) [before cycle, charging to 20 mAh/g_{-AM}, 50 mAh/g_{-AM} (90:5:5), and 100 mAh/g_{-AM} (70:20:10 and 80:10:10)] for EIS measurements in (b-e). (b–e) The Nyquist plots of LMOF/CB/PVDF half-cell before cycle (line), after charging to 20 (dash) and 100 mAh/g_{-AM} (or 50 mAh/g_{-AM} for d, dot) in the (b) 70:20:10, (c) 80:10:10, and (d) 90:5:5 film, and (e) after the first discharge in a 70:20:10 (black), 80:10:10 (red), and 90:5:5 film (blue).



Fig. S9. Additional methods for the electrical conductivity measurement of Mn-DRXs. Electrical conductivities (S/cm, log) of (a) pulverized Mn-DRXs (LMOF, Li_{1.25}Mn_{0.75}O_{1.33}F_{0.67} (LLF), and LMTO) as a function of the stack pressure and (b) pulverized Li⁺-Mn³⁺-Ti⁴⁺-O²⁻ (black) and Li⁺-Mn³⁺-Nb⁵⁺-O²⁻ (red) as a function of the Li-excess level (the Mn-content level) without the stack pressure (short dash) and under 3 ton of the stack pressure (line). (c) Electrical conductivities (S/cm, log) of Li⁺-Mn³⁺-Ti⁴⁺-O²⁻ (black) and Li⁺-Mn³⁺-Nb⁵⁺-O²⁻ (red) pellets, made of pulverized particles (short dash) and non-pulverized particles (just after the calcination, including Au sputtering process), as a function of the Li-excess level (the Mn-content level) without the stack pressure. The pellets consisting of pulverized particles under a high stack pressure and non-pulverized particles with the Au sputtering process can reduce interfacial resistances during the measurement.^{13, 14} In the Au sputtering process, each central surface of the pellet is coated three times, not the side, to prevent the current flow out of the cathode materials. The electrical conductivity of the sputtered pellet is measured using a coin cell.

Li_{1.68}Mn_{1.60}O_{3.7}F_{0.3} (LMOF)

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	5.34E-08	0.1	1,872,659	0.138	5.560E-08
1.3	1.3273	1.12E-07	0.2	1,785,714	0.138	5.831E-08
1.3	1.3273	1.70E-07	0.3	1,764,705	0.138	5.900E-08

Li_{1.2}Mn_{0.4}Ti_{0.4}O₂ (LMTO)

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	1.13E-10	0.1	887,311,446	0.162	1.379E-10
1.3	1.3273	2.47E-10	0.2	811,359,026	0.162	1.508E-10
1.3	1.3273	3.69E-10	0.3	812,567,714	0.162	1.628E-10

 $Li_{1.25}Mn_{0.75}O_{1.33}F_{0.67}$ (LLF)

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	2.80E-09	0.1	35,714,285	0.071	1.487E-09
1.3	1.3273	5.77E-09	0.2	34,662,045	0.071	1.532E-09
1.3	1.3273	8.69E-09	0.3	34,522,439	0.071	1.539E-09

LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811)

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	1.56E-03	0.1	64	0.092	1.081E-03
1.3	1.3273	3.23E-03	0.2	62	0.092	1.116E-03
1.3	1.3273	4.94E-03	0.3	61	0.092	1.134E-03

Fig. S10. Electrical conductivity of representative Mn-DRX materials (LMOF, LMTO and LLF) and commercialized Ni-rich LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) material. The direct current (DC) polarization method at room temperature. All samples were pelletized under 2 ton of pressure for 2 minutes. The calculated electrical conductivity was evaluated by the following formula: $\sigma = 1/R * L/A$, where σ , R, L and A are electrical conductivity (S/cm), resistance (ohm), the thickness of the pelletized sample (cm) and the cross-sectional area of the pelletized sample (cm²).



Fig. S11. Overpotentials in LMOF cathodes with different electrode compositions. (a) Charge profile of LMOF cathodes with CB in a 70:20(CB):10 (LMOF/CB/PVDF, wt%), 80:10(CB):10, and 90:5(CB):5 film, and with MWCNT in a 90:5(MWCNT):5 (LMOF/MWCNT/PVDF, wt%) film during the galvanostatic intermittent titration technique (GITT) test as a function of time. The inset shows a portion of GITT profiles in the 90:5(CB):5 film, demonstrating the dominant appearance of the voltage relaxation that instantly occurs after the current is off (non-Warburg term, *e.g.*, charge-transfer, IR drop, and etc.) relative to one that occurs slowly over time (Warburg term, *e.g.*, Li transport related (or mass-transfer)). The voltage relaxation upon the GITT charge of LMOF cathodes, coming from (b) non-Warburg resistance and from (c) Warburg resistance, showing the dominant contribution of non-Warburg resistance in the overpotential with increasing AM-loading.



Fig. S12. Electrode-fracturing test for two types of electrodes with different conductive carbons (MWCNT or CB) after cycling. (left) Folding test for electrode with (top) LMOF/MWCNT/PVDF = 92:4:4 and (bottom) LMOF/CB/PVDF = 80:10:10. The following cycling performance of the electrodes are included in the right side. Unlike 92:4:4 LMOF/MWCNT-based electrode, 80:10:10 LMOF/CB-based electrode, which delivers much poor cycling performance, shows a film detachment from an aluminum current collector after the repetitive folding test.



Fig. S13. Electrolyte soaking effect on the microstructures of CB-based electrode before and after cycling. The cross-sectional SEM images of the 80(LMOF):10(CB):10(PVDF) electrode (a) before cycling, (b) after 5 cycles, (c) after 20 cycles between 1.5-4.8 V at 25 mA/g_{-AM}, and (d) after electrolyte soaking of the electrode in a coin cell for 4 days (corresponding to the time required to achieve 5 cycles at 25 mA/g_{-AM} between 1.5-4.8 V) and (e) 11 days (\approx 20 cycles duration) without galvanostatic cycling. The white, gray, and black regions correspond to LMOF, CB/PVDF, and pores. No observation of a notable porosity increase or a crack development in the non-cycled electrolyte-soaked cathode films implies that the pore and crack generation after cycling mainly come from cycling-induced electrode degradation rather than the electrolyte soaking.



Fig. S14. Structural characterization of LMOF based on single-phase refinement during galvanostatic cycling. The XRD refinement and structural parameters of LMOF in a 90:5:5 (AM:MWCNT:PVDF, by weight) electrode film of (a) pristine, (b) 1st charge (1st CHG), (c) 1st discharge (1st DCHG), (d) 2nd charge (2nd CHG), and (e) 2nd discharge (2nd DCHG), based on the single-phase refinement. The galvanostatic charging and discharging are performed at a current of 25 mA/g_{-AM} between 1.5-4.8 V (room temperature). The space group is Fd-3m, based on the prior research.¹⁵



Fig. S15. Structural characterization of LMOF based on multi-phase refinement during galvanostatic cycling. The XRD refinement and structural parameters of LMOF in a 90:5:5 (AM:MWCNT:PVDF, by weight) electrode film of (a) pristine, (b) 1st charge (1st CHG), (c) 1st discharge (1st DCHG), (d) 2nd charge (2nd CHG), and (e) 2nd discharge (2nd DCHG), based on the multi-phase refinement. The galvanostatic charging and discharging are performed at a current of 25 mA/g_{-AM} between 1.5-4.8 V (room temperature). The space group of two phases are cubic Fd-3m and Fm-3m, based on the prior research.¹⁶ The details for the refinement are illustrated in the method part.

Fig. S16. The volume change of Mn-DRXs (LMOF, LLF, and LMTO). Ex-situ XRD patterns and cell volume (Å³) in an initial cycle for (a) LMOF (per $Li_xMn_{1.6}O_{3.7}F_{0.3}$ cell), (b) LLF (unit-cell) and (c) LMTO (unit-cell) in a 90:5:5 (AM:MWCNT:PVDF) electrode film. The cell volume is calculated with the lattice parameter of the cubic-type cell obtained from the XRD refinement. In LMOF sample, 2nd charge and 2nd discharge steps are included due to the pre-lithiation step (or a formation step) in the first cycle. The galvanostatic charging and discharging are performed at a current of 25 mA/g_{-AM} for LMOF, and 20 mA/g_{-AM} for LLF and LMTO, respectively, between 1.5-4.8 V (room temperature). For LMOF, we used both single-phase and multiphase models for the refinements as two different methods, whereas the single-phase XRD refinement was used for LLF and LMTO.

Fig. S17. The microstructure of the LMOF/CB/PVDF electrode before and after cycling. The SEM images on the surface of the (a,b) 80(LMOF):10(CB):10(PVDF) and (c,d) 70(LMOF):20(CB):10(PVDF) LMOF electrodes (a,c) before and (b,d) after 10 cycles in the range of 1.5–4.8 V at 25 mA/g_{-AM}. In the 80:10:10 electrode film, significant microcracks are clearly observed after 10 cycles unlike the 70:20:10 electrode film.

Fig. S18. Pores in CB-based pristine electrode. Scanning electron microscopy (SEM) images of the pristine electrode (LMOF:CB:PVDF, by weight) after calendering in an (a) 70:20:10, (b) 80:10:10, and (c) 90:5:5 electrode film. In electrodes with the higher AM contents, more amounts of considerable pores are observed.

Fig. S19. Microscale fractures of CB-based electrode after cycling. Scanning electron microscopy (SEM) images of the electrode (LMOF:CB:PVDF, by weight) after 10 cycles in (a) 70:20:10, (b) 80:10:10, and (c) 90:5:5 electrode film. For 80:10:10 and 90:5:5 films, evident micro-fractures are observed after cycling whereas the 70:20:10 electrode film is intactly preserved without any critical cracks after cycling.

Fig. S20. Pores in MWCNT-based pristine electrode. Scanning electron microscopy (SEM) images of the pristine electrode (LMOF:MWCNT:PVDF, by weight) in an (a) 70:20:10, (b) 80:10:10, (c) 90:5:5, and (d) 96:2:2 electrode film.

Fig. S21. Microscale fractures of MWCNT-based electrode after cycling. Scanning electron microscopy (SEM) images of the electrode (LMOF:MWCNT:PVDF, by weight) after 10 cycles in an (a) 70:20:10, (b) 80:10:10, (c) 90:5:5, and (d) 96:2:2 electrode film. In electrodes with the high AM content of AM/MWCNT/PVDF electrode (80:10:10, 90:5:5 and 96:2:2 films), significant micro-fracture is not observed at all after repetitive cycling in contrast to CB-based electrodes.

Fig. S22. The impedance of MWCNT-based LMOF half-cell. The Nyquist plots of LMOF (a-c, g) before cycle and (d-f) after 10 cycles at 25 mA/g_{-AM} between 1.5–4.8 V in (a, d) 70:20:10 (LMOF:MWCNT:PVDF), (b, e) 80:10:10, (c, f) 90:5:5 and (g) 96:2:2 film with MWCNT within the same frequency range. In contrast to the EIS results in the LMOF/CB/PVDF cathode-based half-cells (Fig. S5), LMOF/Li half-cells with MWCNT-based LMOF cathodes before cycle in (a-c, g) do not show any significant increase of a semi-circle size with the AM content, even in the 96 wt%_{-AM} LMOF cathode. Consequently, highly AM concentrated (>90 wt%_{-AM}) LMOF cathodes delivers a high discharge capacity (>360 mAh/g_{-AM}), which cannot be achieved in CB-based highly AM concentrated LMOF cathodes. Moreover, much-suppressed impedance growth in MWCNT-based LMOF cathode upon cycling in (d-f) enables the improved capacity retention (vs. CB).

Fig. S23. The high-rate capability of highly concentrated LMOF and LMTO cathodes. The first cycle voltage profiles of LMOF and LMTO half-cells at a low current of 20 mA/g_{-AM} (black) and high-currents of 2 A/g_{-AM} (red) and 4 A/g_{-AM} (blue) between 1.5–4.8 V in 80:10:10 (AM:MWCNT:PVDF, by weight, line) and 96:2:2 (short dash) electrode film. The constant voltage (CV) step at the end of the charge is included to compensate for the internal resistance of a cell.

Fig. S24. Mercury porosimeter measurements of CB- and MWCNT-based LMOF electrodes. (a) Log differential intrusion (mL/g) as a function of pore size diameter (nm) for CB-based a 80:10:10 (LMOF:CB:PVDF, by weight, 2.82 g_{electrode}/cm³) and 90:5:5 cathode (2.98 g_{electrode}/cm³), and MWCNT-based a 90:5:5 (LMOF:MWCNT:PVDF, by weight, 2.96 g_{electrode}/cm³) and 96:2:2 cathode (3.08 g_{electrode}/cm³): Here, the g_{electrode}/cm³ excludes the weight of the Alcurrent collector. (b) The tables of intrusion data obtained by the mercury porosimeter analysis. The calculated porosity (%) in a cathode film is highlighted as a red color. Mercury porosimeter measures the porosity (pore size of 3 nm to 150 nm) of 13.53% for 90:5(MWCNT):5, 16.65% for 96:2(MWCNT):2, 10.12% for 80:10(CB):10 and 13.41% for 90:5(CB):5 electrodes, showing an increase of porosity with higher AM content for both CB and MWCNT electrodes. Pore intrusion volume (mL/g) refers to an intrusion volume of mercury in a range of 3 nm and 150 nm. Other details for this analysis are in the Method part.

Fig. S25. AM loading effect on the electrochemical performance of MWCNT-based concentrated T45 cathodes (92 wt_{AM}%). The four types of loading levels [3 mg_{-AM}/cm² or 3.26 mg_{-cathode}/cm² (black), 8 mg_{-AM}/cm² or 8.7 mg_{-cathode}/cm² (red), 12 mg_{-AM}/cm² or 13 mg_{-cathode}/cm² (blue), and 16 mg_{-AM}/cm² or 17.4 mg_{-cathode}/cm² (green)] are prepared to evaluate the AM loading effect on the electrochemistry of T45 cathodes. (a) The first cycle voltage profiles of T45 in a 92:4:4 (AM:MWCNT:PVDF, by weight) electrode with a different loading level [1.5–4.8 V, 25 mA/g_{-AM}, room temperature, anode: Li metal]. (b) The first cycle discharge voltage profiles of T45 in a 92:4:4 electrode with each loading level at a different current density of 25 mA/g_{-AM} (line), 250 mA/g_{-AM} (dash), and 500 mA/g_{-AM} (short dash) [1.5–4.8 V, room temperature, anode: Li metal]. (c) Cycle retention of T45 in a 92:4:4 electrode with a different loading level at 250 mA/g_{-AM} after a pre-lithiation cycle at 25 mA/g_{-AM} [1.5–4.8 V, room temperature, anode: Li metal]. All charging processes include a constant voltage (CV) mode with a current cut-off value of C/20. By going from 3 mg_{-AM}/cm² to 16 mg_{-AM}/cm², we find that the capacity at a higher rate of 500 mA/g_{-AM} is decreased in (b), similar to what is commonly observed for various Li-ion cathodes due to increased Li⁺ and electron transport distance imposed by a thicker electrode associated with a higher AM-loading. Yet, even with 16 mg_{-AM}/cm², T45 with MWCNT can deliver a high capacity above 200 mAh/g_{-AM}, which is impossible with CB as a conductive carbon.

Fig. S26. The mechanical properties of LMOF electrode with different carbons/binders and air exposure. (a) The peeling test results (measured load (N/mm) to peel off the cathode film from the Al-foil as a function of displacement) LMOF(96):CB(2):PVDF(2), LMOF(96):MWCNT(2):PVDF(2), for and LMOF(96):MWCNT(2):SBR(1.33):CMC(0.67) electrodes, and (b-d) the photographs of the adhesive tapes (25 mm) after the tests. (e) The peeling test results for Ar-stored (in a glovebox) and air-exposed (for three weeks) LMOF(90):CB(5):PVDF(5) electrodes, and (f,g) the photographs of the adhesive tapes (14 mm) after the tests. The higher peeling strength of the LMOF(96):MWCNT(2):PVDF(2) (~0.4 N/mm) , compared to that of LMOF(96):CB(2):PVDF(2) (~0.2 N/mm) indicates the improved mechanical property of a highly AM-concentrated LMOF electrode with MWCNT conductive carbons forming a cross-linked entanglement network with LMOF and PVDF (Fig. S4f). Also, the LMOF(96):MWCNT(2):SBR(1.33):CMC(0.67) electrode shows about two times higher peeling strength (~0.8 N/mm) than the LMOF(96):MWCNT(2):PVDF(2) electrode (~0.4 N/mm), which proves that the SBR-CMC binder (vs. PVDF) improves the electrode's adhesive strength. Meanwhile, a decreased peeling strength after air exposure (from ~0.2 to ~0.1 N/mm, e-g) shows the deteriorating effect of surface Li species onto mechanical strength of cathode electrode.

Fig. S27. The effect of conductive carbon morphology (or type) on electrochemical performance. The voltage profiles of (a) LMOF, (b) LMTO, and (c) LLF with two different types of MWCNT [TMC220-10 (black) and TMC220-05 (red)] when cycled at 25 mA/g_{-AM} (LMOF) and 20 mA/g_{-AM} (LMTO and LLF) between 1.5–4.8 V in a 70:20:10 (AM:MWCNT:PVDF, wt%, line), 96:2:2 (dash) electrode film. Inset represents the capacity retention of (a) LMOF, (b) LMTO, and (c) LLF in a 70:20:10 (AM:MWCNT:PVDF, by weight, dense) and 96:2:2 (vacant) electrode film with a different type of MWCNT [TMC220-10 (black) and TMC220-05 (red)].

Fig. S28. The microstructures of highly concentrated (96 wt%_{-AM}) LMOF cathode before and after cycling. The crosssectional SEM images of the LMOF electrode in a 96:2(MWCNT):2 film (LMOF:MWCNT:PVDF, by weight) (a) before cycle and (b) after 20 cycles [1.5–4.8 V, 25 mA/g_{-AM}]. Unlike the CB-based LMOF 80(LMOF):10(CB):10(PVDF) electrode in Fig. 3f, the LMOF 96(LMOF):2(MWCNT):2(PVDF) electrode does not show a critical electrode fracture after 20 cycles.

Fig. S29. Morphologies and the structural characterization for other Mn-DRXs. (a,c,e) Scanning electron microscopy (SEM) images and (b,d,f) XRD measurement of (a,b) LLF, (c,d) T30 and (e,f) T45 powder.

Fig. S30. Materials properties in Mn-DRXs. The relative 1st discharge capacity and capacity retention of 96 wt%_{-AM} vs. 70 wt%_{-AM} MWCNT-based electrodes at 30th cycle as a function of the electrical conductivity and volume change of AM (LMOF, LLF, and LMTO). The volume change of Mn-DRXs in 90:5(MWCNT):5 electrode films was calculated by volumes of pristine and 1st charge state, except for LMOF in which the values in 1st discharge and 2nd charge are considered due to over-lithiation in the 1st discharge.

Fig. S31. The electrochemical properties of LLF cathode with the content of CB conductive carbon. The first cycle voltage profiles of LLF when cycled at 20 mA/g_{-AM} between 1.5–4.8 V in a 70:20:10 (AM:CB:PVDF, by weight, black), 80:10:10 (red), and 90:5:5 (blue) electrode film.

Fig. S32. Binder design for non-destructive electrode at high AM-level (>92%). The voltage profiles of LMOF electrode for (a) 94:3:3 (LMOF:MWCNT:binder, by weight) electrode film with PVDF5130 (black) and PVDF9300 (red) binder, and (b) 96:2:2 (LMOF:MWCNT:binder, by weight) electrode film with PVDF5130 (black) and SBR/CMC (SBR:CMC=2:1, purple) binder when cycled at 25 mA/g_{-AM} between 1.5–4.8 V.

Fig. S33. The electrochemical properties for a highly concentrated electrode of Ti-doped LMOF (T30 and T45) with MWCNT conductive carbon. The first cycle voltage profiles of (a) T30 and (b) T45 at a current of 25 mA/g_{-AM} between 1.5–4.8 V in a 70:20:10 (AM:MWCNT:PVDF, by weight, black), 92:4:4 (red), and 96:2:2 (blue) electrode film. T30 and T45 also show the superior 1st cycle discharge capacity in the highly AM concentrated cathodes. The CV step is not included for T30 and T45, which are designed to evaluate the full-cell.

Fig. S34. The high-rate capability of highly concentrated LLF cathodes. The first cycle voltage profiles of LLF halfcells at a low current of 20 mA/g_{-AM} (black) and a high-current of 2 A/g_{-AM} (red) between 1.5–4.8 V in (a) 80:10:10 (AM:MWCNT:PVDF, by weight) and (b) 96:2:2 electrode film. The constant voltage (CV) step at the end of the charge is included to compensate for the internal resistance of a cell. Based on the relationship between electrical conductivity and rate capability, LLF, which has 10 times higher electrical conductivity than LMTO, is supposed to exhibit better rate capability. However, concentrated LLF cathode shows a poorer rate capability in this figure. Although further investigation is required, we believe that the higher content of fluorination, which is known to be mostly formed in the surface region, might make the poorer electrical conductivity on the surface (relative to the bulk). Because most of the electrochemical reactions are believed to occur on the surface at a high current density (like 2 A/g_{-AM}), LLF might have a poor rate capability, in contrast with the expectation based on the electrical conductivity obtained by the DC polarization method in Fig. S10.

Fig. S35. The electrochemical properties of highly concentrated NCM811, partially ordered T30 and T45 cathodes at full-cell level with high cut-off voltages. The voltage profiles of commercialized (a,d) Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) cathode and partially ordered (b,e) T30 and (c,f) T45 Mn-DRX cathode with graphite anode at 25 mA/g_{-AM} in the operating voltage of (a) 2.0-4.55V, (b-c) 1.0-4.55V, (d) 2.0-4.75V, and (e-f) 1.0-4.75V.

Fig. S36. The full-cell performance for other Mn-DRX-MWCNT electrodes (LLF and LMOF). The voltage profiles of (a,b) LLF and (c) LMOF cathode with graphite anode when cycled at 20 mA/g_{-AM} (LLF, a-b) and 25 mA/g_{-AM} (LMOF, c) between (a,c) 1.8-4.35V and (b) 1.4-4.55V in a 92:4:4 (AM:MWCNT:PVDF, by weight) film. The N/P ratio is 1.2 with 5 mg_{-cathode}/cm² loading level.

Fig. S37. The electrochemical properties of highly concentrated partially ordered **T30** and **T45** cathodes at full-cell **level with a different cut-off voltage range.** The voltage profiles of partially ordered (a,b) T30 and (c,d) T45 cathode with graphite anode in the operating voltage of 1.8V-4.35V at (a,c) 25 mA/g_{-AM} and (b,d) 30 mA/g_{-AM} in a 92:4:4 (AM:MWCNT:PVDF, by weight) cathode film.

Fig. S38. The high-rate capability of highly concentrated T30 and T45 Mn-DRX half-cells. The first cycle voltage profiles of (a) T30 and (b) T45 half-cells at a high rate of 0.75 A/g_{-AM} (~4C-rate) after pre-lithiation at a current of 25 mA/g_{-AM} between 1.5–4.8 V in 92:4:4 (AM:MWCNT:PVDF, by weight) electrode film. The CV step is not included to determine the capacity of the cathode for full-cell design.

Fig. S39. The electrochemical properties of highly concentrated (96 wt%) Ti-doped LMOF (T30) half-cells and fullcells at high rates. The cycle performance of Ti-doped LMOF (T30) (a, b) half-cells and (c, d) full-cells (with graphite) at a high-current of (a, c) 0.25 A/g_{-AM} (~1 C-rate) and (b, d) 0.75 A/g_{-AM} (~4 C-rate) after pre-lithiation at a current of 25 mA/g_{-AM} in 96:2:2 (AM:MWCNT:PVDF, by weight) electrode film. The voltage window is set to (a) 2.0-4.6 V, (b) 1.5–4.8 V, (c) 1.5–4.55 V and (d) 1.0–4.75 V, respectively. The constant voltage (CV) step at the end of the charge is not included to minimize electrolyte decomposition at the high voltage. Despite the high reversible capacity, the 96 wt%-_{AM} T30 cathodes show poor capacity retention in long-term cycling.

Fig. S40. The electrochemical properties of highly concentrated (92 wt%) Ti-doped LMOF (T30) half-cells at highrates. The cycle performance of Ti-doped LMOF (T30) half-cells at a high current of (a) 0.25 A/g_{-AM} (~1 C-rate) between 2.0–4.6 V and (b) 0.75 A/g_{-AM} (~4 C-rate) between 1.5–4.8 V after pre-lithiation at a current of 25 mA/g_{-AM} between 1.5-4.8 V in 92:4:4 (AM:MWCNT:PVDF, by weight) electrode film. The constant voltage (CV) step at the end of the charge is not included to minimize electrolyte decomposition at the high voltage.

Fig. S41. The electrochemical properties of highly concentrated Ti-doped LMOF (T30)/Graphite full-cell at highrate. The cycle performance of Ti-doped LMOF (T30)/Graphite full-cells at 0.25 A/g_{-AM} (~1 C-rate) between 1.5–4.55 V in 92:4:4 (AM:MWCNT:PVDF, by weight) electrode film. The constant voltage (CV) step at the end of the charge is not included to minimize electrolyte decomposition at the high voltage.

Fig. S42. Determining a critical factor for severe degradation in a highly concentrated electrode. The capacity retentions of LMOF electrode (LMOF:MWCNT(TMC 220-05):PVDF) with different contents of conductive carbon and binder at a fixed content (94%) of active material [25 mA/g_{-AM}, 1.5–4.8 V, room temperature]. 94:04:02 (black), 94:03:03 (red) and 94:02:04 (blue). At the fixed AM composition (94%), the criticality of either conductive carbon (MWCNT, TMC 220-05) or binder (PVDF) is evaluated with the three different electrode compositions (94:04:02, 94:03:03, 94:02:04). In this figure, the electrode with the higher conductive carbon (MWCNT) content delivers a less capacity fading over cycling.

a. $Li_{1.1}Mn_{0.7}Ti_{0.2}O_2$

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	1.91E-08	0.1	5,235,602	0.146	2.105E-08
1.3	1.3273	5.13E-08	0.2	3,898,635	0.146	2.827E-08
1.3	1.3273	7.95E-08	0.3	3,773,585	0.146	2.921E-08

b. $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	1.13E-10	0.1	887,311,446	0.162	1.379E-10
1.3	1.3273	2.47E-10	0.2	811,359,026	0.162	1.508E-10
1.3	1.3273	3.69E-10	0.3	812,567,714	0.162	1.628E-10

c. $Li_{1.3}Mn_{0.1}Ti_{0.6}O_2$

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	2.77E-11	0.1	3,610,108,303	0.176	3.681E-11
1.3	1.3273	5.74E-11	0.2	3,484,320,557	0.176	3.814E-11
1.3	1.3273	7.44E-11	0.3	4,032,258,065	0.176	3.296E-11

Fig. S43. Electrical conductivity of Li-Mn³⁺-Ti⁴⁺-O Mn-DRX material as a function of Li-excess level (or Mn-content level). The direct current (DC) polarization method for (a) $Li_{1.1}Mn_{0.7}Ti_{0.2}O_2$, (b) $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ and (c) $Li_{1.3}Mn_{0.1}Ti_{0.6}O_2$ Mn-DRXs at room temperature. All samples were pelletized under 2 ton of pressure for 2 minutes. The calculated electrical conductivity is evaluated by the following formula: $\sigma = 1/R * L/A$, where σ , R, L and A are electrical conductivity (S/cm), resistance (ohm), the thickness of the pelletized sample (cm) and the cross-sectional area of the pelletized sample (cm²), respectively.

a. $Li_{1.1}Mn_{0.8}Nb_{0.1}O_2$

diar	Pellet meter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
	1.3	1.3273	2.90E-08	0.1	3,448,675	0.104	2.276E-08
	1.3	1.3273	5.84E-08	0.2	3,425,358	0.104	2.292E-08
	1.3	1.3273	8.80E-08	0.3	3,409,468	0.104	2.303E-08

b. Li_{1.2}Mn_{0.6}Nb_{0.2}O₂

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	7.92E-09	0.1	12,624,997	0.129	7.698E-09
1.3	1.3273	1.51E-08	0.2	13,287,095	0.129	7.310E-09
1.3	1.3273	2.18E-08	0.3	13,782,839	0.129	7.050E-09

c. $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$

Pellet diameter (cm)	Area (cm²)	Current (A)	Voltage (V)	Resistance (ohm)	Thickness (cm)	Electrical conductivity (S/cm)
1.3	1.3273	4.79E-10	0.1	208,827,512	0.123	4.448E-10
1.3	1.3273	8.69E-10	0.2	230,157,047	0.123	4.036E-10
1.3	1.3273	1.26E-09	0.3	238,958,277	0.123	3.888E-10

Fig. S44. Electrical conductivity of Li-Mn³⁺-Nb⁵⁺-O Mn-DRX material as a function of Li-excess level (or Mn-content level). The direct current (DC) polarization method for (a) $Li_{1.1}Mn_{0.8}Nb_{0.1}O_2$, (b) $Li_{1.2}Mn_{0.6}Nb_{0.2}O_2$ and (c) $Li_{1.3}Mn_{0.4}Nb_{0.3}O_2$ Mn-DRXs at room temperature. All samples were pelletized under 2 ton of pressure for 2 minutes. The calculated electrical conductivity is evaluated by the following formula: $\sigma = 1/R * L/A$, where σ , R, L and A are electrical conductivity (S/cm), resistance (ohm), the thickness of the pelletized sample (cm) and the cross-sectional area of the pelletized sample (cm²), respectively.

Fig. S45. Calculated electronic structures of Li-Mn³⁺-Ti⁴⁺-O Mn-DRX materials. The projected density of states (pDOS) of cation-disordered (a) $Li_{14}Mn_8Ti_2O_{24}$ (to model $Li_{1.1}Mn_{0.7}Ti_{0.2}O_2$), (b) $Li_{20}Mn_6Ti_6O_{32}$ (to model $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$), and (c) $Li_{26}Mn_2Ti_{12}O_{40}$ (to model $Li_{1.3}Mn_{0.1}Ti_{0.6}O_2$) structures. The Mn 3d, Ti 3d, and O 2p orbital projected band structures of (d) $Li_{14}Mn_8Ti_2O_{24}$, (e) $Li_{20}Mn_6Ti_6O_{32}$, and (f) $Li_{26}Mn_2Ti_{12}O_{40}$. The blue and red data represent up-spin and down-spin, respectively. The size of the circle represents the orbital character of the state, with larger circles indicating higher orbital character. The HSEO6 functional (mixing parameter = 0.25) was used in these calculations, as it is known to predict the band gap most accurately.¹⁷

Fig. S46. Calculated band gaps of Li-Mn³⁺-Ti⁴⁺-O Mn-DRX materials. Band gaps for $Li_{1.3}Mn_{0.1}Ti_{0.6}O_2$ (modeled by $Li_{26}Mn_2Ti_{12}O_{40}$), $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ (modeled by $Li_{20}Mn_6Ti_6O_{32}$), and $Li_{1.1}Mn_{0.7}Ti_{0.2}O_2$ (modeled by $Li_{14}Mn_8Ti_2O_{24}$) calculated by the HSE hybrid functional, varying mixing parameter. In general, the calculated band gap depends on the mixing parameter in the HSE functional, and the optimum mixing parameter for Li-TM oxide falls within the range of 0.15 and 0.3.¹⁸ Although the band gap, which influences the degree of thermally excited charge carrier generation, depends on the mixing parameter, it remains sufficiently large to render thermally excited conduction insignificant.

Fig. S47. The first-principles calculation for the polaron conduction in Mn-based symmetric cation-mixed structure. (a) Energy landscape upon polaron hoping through the edge-shared or the corner-shared Mn-Mn path. A change in magnetization of Mn ion during the polaron conduction for (b) the corner-shared Mn-Mn path and (c) the edge-shared Mn-Mn path. Note that the number of unpaired d-electron in Mn³⁺ (high-spin) and Mn⁴⁺ is four and three, ~3.9 of magnetization and ~3.3 of magnetization correspond to Mn³⁺ (high-spin) and Mn⁴⁺, respectively. The details are explained in Methods.

Fig. S48. Optimization of the setting temperature for Markov Chain Monte Carlo simulation. Occurrence of various tetrahedral clusters (0-TM, 1-TM, 2-TM) in LMTO as compared to the random limit with the various temperatures. The optimized temperature, which is the most well-matched with the previous literature⁹, is highlighted with a green box.

Fig. S49. Mn-Mn connectivity analysis based on random-based MC-structures for DRX Li⁺-Mn³⁺-O²⁻-F⁻ compounds. Mn percolation probability (~electron percolation probability) and average percolated Mn-content per X₂ (X= O and F) of DRX Li⁺-Mn³⁺-O²⁻-F⁻ compounds as a function of the fluorination level, considering (a) only the edge-sharing and (b) both the edge- and the corner-sharing Mn-Mn conduction path, obtained by Monte Carlo (MC) percolation simulation. Random cation distribution was assumed in the MC simulation.

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