A Facile Cathode Design Combining Ni-rich Layered Oxides with Li-rich Layered Oxides for Lithium-ion Batteries

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Abstract

A facile synthesis method has been developed to prepare $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07, 0.10, 0.20$, and 0.30) cathode materials, combining the advantages of the high specific capacity of the Ni-rich layered phase and the surface chemical stability of the Li-rich layered phase. X-ray diffraction (XRD), transmission electron microscopy (TEM), and electrochemical charge/discharge measurements confirm the formation of a Li-rich layered phase with $C2/m$ symmetry. The high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) reveals a spatial relationship that the Li-rich nano-domain islands are integrated into the conventional Ni-rich layered matrix ($R\bar{3}m$). Most importantly, this is the first time that Li-rich phase has been directly observed inside a particle at the nano-scale, when the overall composition of the layered oxide $\text{Li}_{1+\delta}\text{Ni}_{1-\gamma-\delta}\text{Mn}_\gamma\text{M}_z\text{O}_2$ ($M = \text{metal}$) is Ni-rich (> 0.5) rather than Mn-rich (> 0.5). Remarkably, the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathodes with optimized x value shows superior electrochemical performance at $C/3$ rate: an initial capacity of 190 mAh g^{-1} with 90 % capacity retention after 400 cycles in a half cell and **73.5 %** capacity retention after **900** cycles in a pouch-type full cell.

Keywords

Nickel-rich layered oxide, Lithium-rich layered oxide, surface chemical stability, pouch-type full cell

1. Introduction

The demand for high-energy-density power sources is rapidly increasing for applications ranging from small portable electronic devices to large systems such as electric vehicles and smart grids. Currently, the highest energy density provided by the state-of-the-art commercial lithium-ion batteries is $\sim 160 \text{ W}\cdot\text{h kg}^{-1}$. Therefore, new electrode materials capable of delivering higher energy densities with long cycle life and better thermal stability are necessary for next-generation batteries. Among the known cathode candidates, the layered structure generally offers high theoretical ($\sim 270 \text{ mA h g}^{-1}$) compared to the other competitors such as spinel (140 mA h g^{-1}) and olivine (170 mA h g^{-1}) systems.[1, 2] Unfortunately, only 50% of Li^+ ions could be reversibly extracted from the currently used layered $\text{Li}_{1-x}\text{CoO}_2$, resulting in a reduction in the energy density of the commercialized $\text{LiCoO}_2/\text{graphite}$ cells.

To explore an alternative, the co-substitution of Ni and Mn at the Co sites in LiCoO_2 produces a family of $\text{LiCo}_{1-y-z}\text{Ni}_y\text{Mn}_z\text{O}_2$ cathodes. The three ions play different roles in determination of the electrochemical properties of $\text{LiCo}_{1-y-z}\text{Ni}_y\text{Mn}_z\text{O}_2$: Ni as an electron supplier, Co for sustaining an ordering of layered structure, and Mn for good chemical stability.[3] In this regard, Ni-rich layered oxides $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ with Ni content $(1-y-z) > 0.5$ is drawing worldwide interest in recent years.[4-9] Sun's group[10] has summarized the different roles of Ni, Co, and Mn in the $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ system when Ni content exceeds $1/3$, in terms of specific capacity, cycle life, and thermal stability. It is important to note that although the Ni-rich cathodes are capable of delivering a $180 - 210 \text{ mA h g}^{-1}$ capacity when $0.6 < x < 0.9$, the capacity retention and thermal stability are sacrificed with increasing Ni content. Poor capacity retention is believed to be associated with undesirable side reactions between the tetravalent transition metal ions, in particular Ni^{4+} , and the electrolyte[11, 12] and phase transition from layered to rock-salt structure (NiO) at particle's surface,[13] both of which cause a substantial decline in the lithiation kinetics at the electrode-electrolyte interphase. On the other hand, poor thermal stability arises due to the release of oxygen from the crystal lattice at the highly delithiated state.[8, 14] Finding out the most suitable composition to meet the industry demands for overall performance remains a challenge to battery researchers.

As for another family of promising cathode candidates, the Li-rich layered oxides, denoted as $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_a\text{Co}_b\text{Mn}_c\text{O}_2$ ($a + b + c = 1$) have also gained extensive attention due to their even higher reversible capacities of more than 250 mA h g^{-1} . [15, 16] One of the signatures for these materials is that Li^+ ions partially reside at the transition-metal layer sites in the local lattice, where the Mn^{4+} -rich environment around the Li^+ ions form a superlattice arrangement with a special $C2/m$ symmetry. Upon charging, Li^+ ion extraction involves a release of oxygen from the lattice, leading to structural instability and inevitable rearrangement of residual Li^+ and transition-metal ions to form a thermodynamically-favorable spinel phase. [17-19] The layered to spinel transformation causes a voltage decay, resulting in a gradual loss of output energy density upon cycling. The voltage decay is recognized as the main issue hindering the practical application of the Li-rich layered oxide cathodes. Although spinel transformation is inevitable, the Li-rich layered oxide cathodes commonly show enhanced cyclability even though the charge cut-off voltage is relatively high ($\sim 4.6 \text{ V}$). Such enhanced cyclability is ascribed to the less reactivity of Mn^{4+} with the electrolyte that minimizes the decline of lithiation kinetics at the electrode-electrolyte interphase and the less formation of Jahn-Teller Mn^{3+} ions in the host lattice. [20, 21] In summary, the Ni-rich layered oxides deliver stable voltage profile with reasonable specific capacity but suffer from surface chemical instability, whereas the Li-rich layered oxides exhibit reasonably good surface chemical stability but suffer from voltage-decay upon cycling.

Inspired by the individual advantages and disadvantages of the Ni-rich and Li-rich layered oxide cathodes, here we report a novel $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07, 0.10, 0.20$, and 0.30 as molar ratio) layered oxide cathodes prepared by a facile method. The idea is to integrate a small amount of Li-rich phase into the Ni-rich phase to stabilize the Ni-rich phase from chemical corrosion, while avoiding the use of a large amount of Li-rich phase minimizes the voltage decay effect. As a result, the modified cathode materials show superior electrochemical performance compared to the conventional Ni-rich layered $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ oxide both at room and elevated temperatures. Li et al. [9] recently reported the synthesis of a core-shell structure with a Ni-rich composition as a core and a Li-rich composition as a shell to improve the performance. Choi et al. [22] also reported a smart compositional design of $(1-x)\text{Li}(\text{Ni}_{0.95}\text{Co}_{0.05})\text{O}_2 \cdot x\text{Li}_2\text{MnO}_3$ ($x = 0.05$ and 0.1) to achieve Li-rich features inside the Ni-rich

particles. Here in our case, for the first time, structural investigation with high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) shows a clear evidence of $C2/m$ nano-domains embedded in the $\sqrt{3}\sqrt{3}$ lattice for such high-Ni content layered oxides.

2. Experimental

2.1 Synthesis of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$

$\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}(\text{OH})_2$ precursor was prepared by a transition-metal hydroxide co-precipitation method with a continuous stirring tank reactor (CSTR). Prior to the precipitation reaction, a desired amount of saturated NH_4OH was added to the CSTR for the establishment of the initial condition. Subsequently, a metal solution containing $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ with a molar ratio of 70 : 15 : 15 at a combined concentration of 1.0 M was fed into the CSTR at a controlled rate. In the meantime, 2.0 – 4.0 M KOH aqueous solution with NH_4OH was pumped separately into the CSTR to maintain the pH value within the appropriate range (~ 11) during the reaction, along with N_2 as a protective gas. Throughout the co-precipitation process, the amount of NH_4OH added and the temperature (50°C) were also carefully monitored and controlled. After filtering, washing, and drying at around 100°C under vacuum overnight, the as-synthesized precursor particles were collected. To prepare the various $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07, 0.10, 0.20$, and 0.30 as molar ratios) samples, 2 g of the $\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}(\text{OH})_2$ precursor was mixed and ground with a certain amount of MnCO_3 (calculated based on the required amount of Li_2MnO_3) and corresponding amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ (with 3 % excess) for 10 min. Subsequently, the mixture was preheated at 500°C for 12 h before heating up to 800°C for 15 h, and then quenched in liquid nitrogen.

2.2 Structural Characterization

The chemical compositions were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 715 ES). Powder X-ray diffraction (XRD) analysis was carried out with a Rigaku Miniflex 600 in a 2θ range of $10^\circ - 80^\circ$ with a scan speed of 1° per min with $\text{Cu K}\alpha$ radiation. Lattice parameters and weight ratios of the two phases were further revealed by Rietveld refinement based on

the General Structure Analysis Software (GSAS).[23] Particle morphology and energy dispersive X-ray (EDX) elemental mapping were characterized by scanning electron microscopy (SEM, FEI Quanta 650). As-prepared cathode powders were dusted on carbon grids for transmission electron microscopy (TEM). A probe Cs-corrector scanning/TEM microscope (FEI TitanTM 80-300 operated at 300 kV) was used for high angle annular dark field (HAADF) imaging and EDX analysis. Under the STEM mode, the electron beam had a convergence angle of 17.8 mrad and HAADF signal was collected by the annular detector in the range of 55-220 mrad. Another FEI TitanTM 80-300 microscope with image Cs-corrector was used for selective area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM).

2.3 Electrochemical Measurements

Electrochemical charge-discharge measurements were carried out with CR2032 coin cells. First, the cathode slurry was prepared by mixing the active material, carbon black (Super P), and polyvinylidene fluoride (PVDF, Kureha KF 1120) in N-methyl-2-pyrrolidone (NMP) solution with a weight ratio of, respectively, 80: 10: 10. Then, the slurry was homogeneously deposited onto an aluminum foil current collector. After drying it at 120 °C under vacuum overnight, the typical loading of the electrode was 3.0 – 4.0 mg cm⁻². All coin cells were assembled in an Ar-filled glove-box with the as-prepared cathode, Li metal as an anode, one piece of polypropylene separator (Celgard 2500), and an electrolyte consisting of 1 M LiPF₆ in 1 : 1 ethylene carbonate (EC) and diethyl carbonate (DEC) mixture, unless otherwise specified in the text. An Arbin cycler was used to perform electrochemical charge/discharge tests, where 1C rate is equal to 180 mA g⁻¹. Electrochemical impedance spectroscopy (EIS) analysis was conducted with a Solartron 1260A impedance analyzer. For each cycling stage, all the cells (cycled at C/2 rate in a voltage window of 3.0 – 4.5 V) were charged to the same state of charge (SOC, 4.2 V) and held for another 3 h before the EIS measurement. Differential capacity plots (DCP) of dQ/dV vs. voltage were calculated based on the charge/discharge data of the corresponding cycle.

3. Results and Discussion

Table 1 summarizes the ICP results of the xLi₂MnO₃·(1-x)LiNi_{0.7}Co_{0.15}Mn_{0.15}O₂ (x = 0, 0.03, 0.07, and 0.10) samples. Comparing the calculated and experimentally observed chemical compositions, it is evident that

the amounts of all transition-metal ions are almost equal to the designed values. Figure S1 shows the XRD patterns of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07, 0.10, 0.20, \text{ and } 0.30$) samples. All strong peaks could be easily indexed to a rhombohedral phase with $\sqrt{3} \times \sqrt{3} \times 2$ symmetry, which clearly indicates a highly crystallized layered structure regardless of the chemical composition. Interestingly, the enlarged XRD patterns in the 2θ range of $20 - 30^\circ$, $44 - 45^\circ$, and $63 - 69^\circ$ imply a gradually increasing amount of Li_2MnO_3 -phase formation with $C2/m$ symmetry with increasing x value. Typically, as one of the strongest evidences of Li_2MnO_3 phase, a hump located at around 21° is a consequence of an ordering when $1/3$ of Li ions occupy the transition-metal layer leading to this superlattice peak apparent.[15] Meanwhile, shifting and broadening of the (104) peak toward the higher angle imply nucleation and growth of a new Li-rich layered phase which possesses very similar symmetry to the original phase. In order to investigate the evolution of lattice parameters and weight ratios, a two-phase Rietveld refinement was performed with GSAS and the results are shown in Table 2. It is necessary to point out that the two-phase refinement is hard when $x = 0.03$ since the formation and signal from Li_2MnO_3 phase is too small to be detected. Regarding the lattice parameters a and c of the $\sqrt{3} \times \sqrt{3} \times 2$ phase, it is apparent that both of them jump when x changes from 0.07 to 0.10, indicating a recognizable formation of $C2/m$ phase afterward. Before and after this separation point, the changes in both the a and c parameters of the $\sqrt{3} \times \sqrt{3} \times 2$ phase is relatively small, indicating less changes in the valence states of the transition-metal ions, occupancy of oxygen ions, *etc.* Another observation from the refinement is that the extent of $\text{Li}^+/\text{Ni}^{2+}$ cation mixing has barely changed with increasing amount of Li_2MnO_3 phase from 0 to 0.1, implying a negligible effect of Li_2MnO_3 -integration on the atomic ratio of $\text{Ni}^{2+}/\text{Ni}^{3+}$. However, the errors in the determination of the lattice parameters of the $C2/m$ phase are relatively large due to the low content of this phase. Nevertheless, R_p remains small throughout the series of refinement. Respective weight fractions of both $\sqrt{3} \times \sqrt{3} \times 2$ and $C2/m$ phases calculated based on the refinement are shown in Figure S2. Compared to the target amount of Li_2MnO_3 , the realistic values are clearly lower possibly due to a weak ordering of LiMn_6 in local lattice as a result of the co-existence of Ni and Co. It is also important to note that calculation of the weight fraction from a two-phase refinement is normally carried out for composite

Fig. 1 SEM images of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07$, and 0.10) powders.

materials, while in the case of Li-rich layered oxides, only a nano-domain composite structure has been reported, where whether composite structure exists is still debatable.[24, 25] This is another possible reason for the discrepancy between the observed and designed values.

Figure 1 shows the particle morphology of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07$, and 0.10) samples. As can be seen, all samples have a spherical or elliptical shape and a uniformly distributed particle size of around $9 \mu\text{m}$ in diameter, which are important to achieve high tap density and thus high volumetric energy density. The overall morphology of the secondary particles has barely changed after the modification with Li_2MnO_3 as the x value increases, except that a certain amount of small particles are

Fig. 2 SEM-EDX line scan of Ni, Co, and Mn at cross section of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ particles: (a) $x = 0$ and (b) $x = 0.10$.

present with less than 500 nm in size due to the addition of MnCO_3 as raw material during synthesis. It is easy to understand that decomposition of MnCO_3 leads to $\text{MnO}/\text{Mn}_3\text{O}_4/\text{MnO}_2$ formation at high temperatures, which hardly melts during the employed heating process. Images with higher magnification in Figure 1 also show the size distribution and shape of the primary particles. It could be seen that the primary particles are around 300 nm in size, which barely changes with increasing x from 0 to 0.1.

To investigate the distribution extent of Mn along the radial direction of one secondary particle, line-scan SEM-EDX on cross-sections of secondary particle was carried out for both the $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ and $0.1\text{Li}_2\text{MnO}_3 \cdot 0.9\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ samples, and the results are shown in Figure 2. As can be seen for the pristine particle, the atomic ratios of Ni, Co, and Mn typically fluctuate, respectively, at around 55, 20, and 25 % throughout the cross section, indicating a long-range homogeneous distribution of all transition-metal ions. Note that the relative increase in both Co and Mn at the expense of Ni originates from instrumental error as ICP results in Table 1 have already confirmed the chemical composition of the samples in a large scale. In comparison, in the case of the $0.1\text{Li}_2\text{MnO}_3 \cdot 0.9\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ particle, although the atomic ratios of all three ions again exhibit homogeneous distribution in the bulk, it is apparent that at the particle surface Mn increases to 30 % when Ni and Co decrease to 53 and 17 %.

Figures S3 and S4 in the supporting information show the cross section SEM-EDX elemental mappings of the pristine $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ and modified $0.1\text{Li}_2\text{MnO}_3 \cdot 0.9\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ samples, and further confirm the uniform distribution of the three transition-metal ions without any evidence of core-shell structure. According to the above observations, it is reasonable to conclude that Mn is able to diffuse from surface to bulk regions and being crystallized into local lattice even though the diffusion path is up to several micrometers. The high-temperature firing at 800 °C provides enough ionic mobility for diffusion. However, it is also important to note that although Mn shows a long-range homogeneous distribution, it is still possible that Mn could be locally enriched to form Li- and Mn-rich phases within a region of several nanometers given the EDX resolution. In fact, STEM results in a later section will provide direct evidence of a two-phase coexistence at the local region of one particle.

Fig. 3 Conventional TEM characterization of the (a-c) $x = 0$ sample and (d-f) the $x = 0.1$ sample; (a) and (d) are low-magnification bright field TEM images, and (b) and (e) are corresponding SAED patterns of the surface particles in (a) and (d), respectively; (c) and (f) are corresponding HRTEM images.

Figures 3a, 3b, and 3c present the conventional TEM images of the pristine ($x = 0$) sample. Selected area electron diffraction (SAED) image from the highlighted area of Figure 3a is shown in Figure 3b, where it could be easily indexed with the 110 rhombohedral zone axis. In addition, the HRTEM image shown in Figure 3c exhibits a typical layered structure with $\sqrt{3}\sqrt{3}$ symmetry. In comparison, Figures 3d, 3e, and 3f present TEM images of the modified ($x = 0.10$) sample. As shown by the SAED in Figure 3e, besides indexing with a typical layered structure with $\sqrt{3}\sqrt{3}$ symmetry, there is an additional set of streaks that is due to the formation of monoclinic structure domains with $C2/m$ symmetry, which is highlighted by a series of yellow arrows.[26] Again, the HRTEM image in Figure 3f from a small domain selected from the highlighted area of Figure 3d confirms a $C2/m$ -phase lattice.

Fig. 4 (a) Low-magnification STEM-HAADF image of one surface primary particle of the $x = 0.10$ sample. (b) Corresponding X-ray spectrum from the highlighted area in (a). (c) High-resolution STEM-HAADF image showing the lattice structure from the highlighted area in (a). The inset in (c) shows the corresponding FFT image.

To provide more information on the modified particle, STEM-HAADF imaging was conducted. As shown in Figure 4a, a surface primary particle was investigated. Figure 4c shows a high-resolution HAADF-STEM

image with identifiable lattice construction from the highlighted area of Figure 4a. Clearly, a $C2/m$ symmetry featured transition-metal in-plane ordering is verified and highlighted by yellow arrows, while the rest shows the $R\bar{3}m$ symmetry. The inset of Figure 4c is the corresponding Fast Fourier Transform (FFT) image, in which the extra diffraction spots highlighted by yellow arrows also confirmed the existence of $C2/m$ phase. Furthermore, it is interesting to point out that the EDX atomic ratio of Ni : Mn : Co from the selected area of the primary particle (Figure 4a) is 53 : 33 : 13. It agrees well with the SEM-EDX result of the cross section of a whole secondary particle. This implies that (i) this modification method induces a relatively uniform integration of additional Mn into the local lattice throughout the whole secondary particles, and (ii) an ordering of the Li-rich phase with $C2/m$ symmetry, prompted by the enrichment of Mn, only occurs in a small domain island within several nanometers, which is surrounded by the pristine layered phase with $R\bar{3}m$ symmetry. However, note that normally the Li-rich phase has been observed only when Mn is above 0.5 in $\text{Li}_{1+\delta}\text{Ni}_x\text{Mn}_y\text{M}_{1-x-y}\text{O}_2$. [15, 16, 27] Thus, a local separation in terms of phase and chemical composition (Ni-enriched and Mn-enriched) within a region of several nanometers probably occurs, giving rise to the overall atomic ratio of Ni : Mn : Co = 53 : 33 : 13. This is the first time to directly observe the formation of a Li-rich $C2/m$ phase within a Ni-rich layered particle at the nano-scale. It demonstrates that it is possible to form Li-rich $C2/m$ phase in a Ni-rich layered oxide by applying an proper chemical-compositional design and heating method.

Fig. 5 Schematic illustration of the synthesis strategy and the consequent effects on structural change.

Fig. 6 Charge-discharge curves and corresponding dQ/dV plots of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07, 0.10, 0.20$, and 0.30) cathodes cycled in a voltage window of $2.0 - 4.8$ V at C/20 rate.

Based on these observations from XRD, SEM-EDX, and STEM, Figure 5 summarizes the synthesis strategy and consequent structural changes for the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode materials. High-temperature heating of a mixture of $\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}(\text{OH})_2$ precursor, MnCO_3 , and $\text{LiOH} \cdot \text{H}_2\text{O}$ at 800°C for 15 h leads to a drastic diffusion of Li and Mn into the bulk particles of $\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}(\text{OH})_2$. During the heating process, they crystallize into two types of thermodynamically-stable phases, $\sqrt{3} \times \sqrt{3} \times 2$ and $C2/m$ phases, governed by the local composition. Therefore, we speculate that some regions with enriched Mn generate Li- and Mn- rich phases, while the other regions with low concentration of Mn only form the Ni-rich phase. Furthermore, Li- and Mn- rich phases ($C2/m$) exist in the form of nano-domain islands, surrounded by the bulk Ni-rich phase ($\sqrt{3} \times \sqrt{3} \times 2$). These nano-domain islands are too small for SEM-EDX to be identified in terms of the local variation of Mn between these two phases. According to two studies conducted by Sun's group [22] and Dahn's group [9], Li-rich phase has been observed in $\text{Li}_{1.033}\text{Ni}_{0.855}\text{Co}_{0.045}\text{Mn}_{0.067}\text{O}_2$ and in a core-shell structure with the chemical formula $0.67\text{Li}_{1.06}(\text{Ni}_{0.67}\text{Mn}_{0.33})_{0.94}\text{O}_2 \cdot 0.33\text{Li}_{1.2}(\text{Ni}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2})_{0.8}\text{O}_2$, which is also termed as $\text{Li}_{1.106}\text{Ni}_{0.473}\text{Mn}_{0.368}\text{Co}_{0.053}\text{O}_2$. In both cases, additional Li^+ ions at the transition-metal sites were purposely

designed and Mn has an oxidation state higher than 3+. Similarly, in our case, taking $0.1\text{Li}_2\text{MnO}_3 \cdot 0.9\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ as an example, a chemical composition of $\text{Li}_{1.064}\text{Ni}_{0.589}\text{Co}_{0.126}\text{Mn}_{0.221}\text{O}_2$ was confirmed by ICP, where two conditions, *i.e.*, some Li^+ ions at the transition-metal sites and an average valence state of $> 3+$ for Mn are satisfied. However, inter-diffusion among Ni, Co, and Mn can occur during high-temperature sintering ($> 700\text{ }^\circ\text{C}$). Dahn et al. [28] has shown that the inter-diffusion coefficient of $\text{Ni}^{3+}/\text{Mn}^{4+}$ couple is an order of magnitude lower than that of $\text{Ni}^{3+}/\text{Co}^{3+}$. This result suggests the possibility of forming a Mn-enriched region in the local structure, especially when excess Li is present. Based on the above considerations, we presume that if the chemical composition of Ni-rich oxide is carefully designed with two conditions (additional Li^+ ions at the transition-metal sites and partial Mn^{4+} formation to maintain charge neutrality), Li-rich phase could be formed in the presence of Ni-rich phase. As a consequence, the direct oxidation reaction between Ni^{4+} and electrolyte and thus the growth of solid-electrolyte interfacial (SEI) layer is suppressed due to the existence and the shielding effects from the Li-rich nano-domains at the surface region of the secondary particle. Meanwhile, the existence of Li-rich nano-domains also likely function as a pinning point to prohibit the phase transition in Ni-rich particles, which normally starts from the particle surface. These effects could benefit in enhancing the cyclability. In fact, the electrochemical cycling in a later section will show clear evidences of such enhancements.

Figure 6 shows the initial charge-discharge profiles of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07, 0.10, 0.20, \text{ and } 0.30$) cathodes cycled in a voltage window of $2.0 - 4.8\text{ V}$ at C/20 rate. The upper charge cut-off voltage of 4.8 V was chosen to fully activate the Li_2MnO_3 -like component in all samples to understand its effects on the reversible capacity.[29] As shown in Figure 6, in this voltage range, the discharge capacities are 220, 214, 211, 208, 196, and 175 mA h g^{-1} with coulombic efficiencies of 87.3, 81.1, 79.9, 81.1, 80.3, and 74.2 %, respectively, for the $x = 0, 0.03, 0.07, 0.10, 0.20, \text{ and } 0.30$ samples. It is clear that the discharge capacity gradually decreases with increasing x , even though the coulombic efficiency varies. This observation on the reduction of reversible capacity when integrating higher amount of Mn^{4+} from Li_2MnO_3 component is consistent with the results reported in the literature.²² It could be ascribed to the reduced amount of $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox. Plots of dQ/dV in Figure 6 indicate the evolutions of different redox peaks. Specifically, the intensity of the $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox peak located at around 3.75 V

decreases with increasing x value. Besides, this redox peak also shifts slightly, implying a reduced polarization effect in the presence of Mn^{4+} . [30]

In contrast, increasing intensity of the charging peak at 4.5 V with higher x values apparently indicates the formation of Li_2MnO_3 -like component, which agrees well with the XRD and TEM results. Johnson et al. reported a series of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials in the literature. [31] They found that the $0.1\text{Li}_2\text{MnO}_3 \cdot 0.9\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode delivers a discharge capacity lower than the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ when charging to 4.6 V, while increasing x to 0.3, 0.5, and 0.7 leads to much higher discharge capacities than the pristine one at the same charge-discharge condition. This observation implies that the overall molar ratio of Mn relative to Ni or Co must reach a critical point so that the additional reversible capacity at the lower part of 3.5 V could be triggered; otherwise, the overall reversible capacity decreases due to a loss of $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox. Similarly, since the highest Mn-content composition in our case is $\text{Li}_{1.13}\text{Ni}_{0.46}\text{Co}_{0.09}\text{Mn}_{0.35}\text{O}_2$ (x = 0.3), where Mn content is still lower than Ni, this material is a Ni-rich overall rather than Mn-rich layered oxide in terms of chemical composition. Therefore, it is understandable that the value of the initial discharge capacity decreases with increasing x from 0 to 0.3 as shown in Figure 6. We speculate that although both Li^+ and O^{2-} ions could be extracted from the local $C2/m$ domains, the non-activity of O^{2-}/O^- and/or $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox reactions is responsible for the reduced reversible capacity in our case, but it commonly contributes to the capacity in other “real” Li- Mn-rich layered oxides. [32-34] This is supported by an absent peak that is normally observed at the lower part of 3.5 V in Figure 6. Such an observation of reduced capacity in Ni-rich layered oxides in the presence of a Li-rich phase also implies a competing relationship between Ni and Mn in determining the active redox mechanisms. In this regard, we only focused on the electrochemical performance of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ oxides when x is smaller than 0.1 in order to strike a balance between the reduced capacity and the enhanced stability.

Fig. 7 Cycle performance of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07$, and 0.10) cathodes tested under various conditions: 25 °C and 3.0 – 4.5 V, 25 °C and 3.0 – 4.6 V, 55 °C and 3.0 – 4.5 V.

The cycle performances at C/3 rate of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07$, and 0.10) cathodes under various conditions are shown in Figure 7, *i.e.*, at 25 °C and 3.0 – 4.5 V, 25 °C and 3.0 – 4.6 V, 55 °C and 3.0 – 4.5 V. With the condition of 25 °C and 3.0 – 4.5 V, the initial discharge capacity is 185, 188, 189, and 173 mA h g^{-1} , respectively, for the $x = 0, 0.03, 0.07$, and 0.10 samples. It demonstrates that the reversible capacity is not affected notably when the integrated amount of Li_2MnO_3 is smaller than 7 mol%. Additionally, the capacity retention over 100 cycles is improved from 78.7 % for the pristine sample to 89.2, 92.4, and 94.6 %, respectively, for the $x = 0.03, 0.07$, and 0.10 samples, demonstrating that higher amount of Li_2MnO_3 results in better cyclability. As increasing the charge cut-off voltage from 4.5 to 4.6 V, the initial discharge capacity increases to 204, 195, 192, and 183 mA h g^{-1} , respectively, for the $x = 0, 0.03, 0.07$, and 0.10 samples. Again, the capacity retention after 80 cycles is improved from 77.7 % for the pristine sample to 80, 88, and 94.5 %, respectively, for the $x = 0.03, 0.07$, and 0.10 . Under this cycling condition, it is clear that the coulombic efficiency throughout all cycles of the modified samples is higher

than the pristine counterpart. It suggests the enhanced surface stability for the modified samples with suppressed surface side reactions with electrolyte especially when the voltage is higher than 4.5 V. Furthermore, the extent of surface stability is a function of Li_2MnO_3 content. As well-known, the poor cycle performance of the Ni-rich layered cathodes at elevated temperatures is its most considerable drawback. In our case, the capacity retention over 50 cycles is improved from 84.4 % for pristine sample to 88.9, 90, and 97.7 %, respectively, for the $x = 0.03, 0.07$, and 0.10 samples. It will be shown later that the cycling test at 55 °C with a modified electrolyte could provide even better cyclability. All the results in terms of initial discharge capacity, capacity retention, and average coulombic efficiency are summarized in Table 3. Figure S5 in the supporting information shows the electrochemical performance of the $0.1\text{MnO}_2 \cdot 0.9\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode. Notably, both the initial capacity and cyclability are not comparable to that of the $0.1\text{Li}_2\text{MnO}_3 \cdot 0.9\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode. The results indicate the advantage of Li_2MnO_3 -like component formation.

The charge-discharge curves and the corresponding dQ/dV plots with the cycle number of the $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ and $0.07\text{Li}_2\text{MnO}_3 \cdot 0.93\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathodes at 55 °C are shown in Figure S6. It is apparent that the polarization effects in terms of voltage increase upon charge and voltage drop upon discharge are both significantly reduced during 50 cycles because of the Li_2MnO_3 modification, as indicated by the arrows in Figure S6b and S6d. Figure S7 shows the rate capability of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07$, and 0.10) samples. All the samples before and after modification exhibit good rate capability, ca. 62 % of capacity retention at 10 C compared to the discharge capacity obtained at C/10 rate. Specifically, the rate capability is slightly improved as the x value increases from 0 to 0.10. This is possibly due to the suppressed side reactions between particles' surface and electrolyte. It consequently leads to the formation of less inert species having poor Li^+ ion and electronic conductivity. Although the rate capability of Li-rich $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ oxides is always considered to be poor due to the presence of the Li_2MnO_3 phase, here in our case, the amount of Li_2MnO_3 is relatively small. In essence, we presume that the transport of both Li^+ ions and electrons is dominantly controlled by the surface species rather than bulk structure.

Long-term cycling performances of the pristine $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ and modified $0.07\text{Li}_2\text{MnO}_3 \cdot 0.93\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathodes at 25 and 55 °C are shown in Figure 8a and 8b. Remarkably, 90.3 and 81.3 % of capacity retention, respectively, after 400 and 200 cycles cycled at C/3 rate have been achieved, taking advantage of both the stabilized structure and the modified electrolyte. Additionally, Figure 8c shows 73.5 % capacity retention after 900 cycles with laminated pouch full cell fabricated with $0.07\text{Li}_2\text{MnO}_3 \cdot 0.93\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode and graphite anode.

Fig. 8 Cycling performances of the pristine $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ and modified $0.07\text{Li}_2\text{MnO}_3 \cdot 0.93\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathodes in 1.2 M LiPF_6 in a 3 : 7 mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) electrolyte at (a) 25 °C (a) and (b) at 55 °C, and (c) laminated-type pouch cell with the $0.07\text{Li}_2\text{MnO}_3 \cdot 0.93\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode and graphite as anode. The pouch-type full cell was cycled at C/10 rate for first 2 cycles and at C/3 rate for the rest of the cycles.

AC impedance measurements were conducted to monitor the evolution of cell impedance with the pristine and modified cathode materials as a function of cycle number, i.e., 1st, 10th, 50th, and 100th cycles. The Nyquist plots are shown in Figure S8. The first semicircle at high frequency is correlated with the resistance of Li^+ -ion migration through the solid-electrolyte interfacial layer (R_s), while the second semicircle at middle-range frequency is associated with the charge-transfer resistance (R_{ct}) between the surface film and the bulk cathode.[35] As can be seen, the R_{ct} is significantly reduced with increasing integrated amount of Li_2MnO_3 from 0 to 0.03, 0.07, and 0.1. Most importantly, this tendency of reduced R_{ct} is quite consistent with each other from the initial cycle to the very end of 100th cycle. This conclusion is supported by the fitting results of the Nyquist plots with an equivalent circuit, and the values are shown in Table 4. Two possible mechanisms are assumed to be responsible for such a reduction in R_{ct} . First, the formation of a Li-rich layered phase as a nano-domain structure integrated into the outer surface region of the primary particles minimizes a direct oxidation reaction between Ni^{4+} and electrolyte.[36] Second, the Li-rich layered nano-domains (C2/m) formed inside the $\text{R}\bar{3}\text{m}$ layered matrix plays a role like pinning points to prohibit migration and reorganization of the transition-metal ions, which causes phase transition from $\text{R}\bar{3}\text{m}$ to $\text{R}\bar{3}\text{m}$ (rock-salt) that starts from the particle surface.

4. Conclusion

A facile, novel synthesis method, involving only the grinding of the coprecipitated $\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}(\text{OH})_2$ precursor with MnCO_3 and $\text{LiOH} \cdot \text{H}_2\text{O}$ and firing at a high temperature, has been developed to obtain high-performance $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode materials. It has been found that although the secondary particle size of the $\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}(\text{OH})_2$ precursor is large (9 μm in diameter on average), the addition of Mn and thus the

solid-state diffusion at high temperatures still induces a homogeneous increase in Mn content throughout a whole secondary particle. Furthermore, the additional Mn forms a Li-rich layered phase with $C2/m$ symmetry based on the observations of XRD, TEM, and electrochemical charge-discharge measurements. Most importantly, the HRTEM and STEM not only shows the evidence of $C2/m$ phase formation, but also reveals the spatial relationship between the conventional $2/3/2$ layered phase and the newly-formed $C2/m$ layered phase. Specifically, the $C2/m$ phase exists in relatively-small nano-domain islands embedded into the $2/3/2$ layered matrix. This is the first straightforward observation of the Li-rich phase formed inside a primary particle with Ni-rich composition. Notably, the resultant $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ cathode with optimized x value combines the advantages of the relatively high capacity from the Ni-rich phase and the high surface chemical stability from the Li-rich phase, leading to superior electrochemical performances with 90 and 81 % of capacity retention, respectively, after 400 cycles at 25 °C and 200 cycles at 55 °C in half cell, and 73.5 % of capacity retention after 900 cycles in pouch-type full cell. This facile synthesis method sheds light on a smart design of combining Ni-rich and Li-rich layered phases for advanced lithium-ion battery cathodes, which could be easily scaled up for practical, industrial applications.

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Tables

Table 1. ICP results of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07$, and 0.10).

Sample	Designed formula	Calculated composition	Experimental composition
$x = 0$	$0\text{Li}_2\text{MnO}_3 \cdot 1.0\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$	$\text{Li}_{1.0}\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$	$\text{Li}_{1.011}\text{Ni}_{0.694}\text{Co}_{0.150}\text{Mn}_{0.145}\text{O}_2$
$x = 0.03$	$0.03\text{Li}_2\text{MnO}_3 \cdot 0.97\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$	$\text{Li}_{1.015}\text{Ni}_{0.669}\text{Co}_{0.143}\text{Mn}_{0.173}\text{O}_2$	$\text{Li}_{1.026}\text{Ni}_{0.664}\text{Co}_{0.141}\text{Mn}_{0.169}\text{O}_2$
$x = 0.07$	$0.07\text{Li}_2\text{MnO}_3 \cdot 0.93\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$	$\text{Li}_{1.034}\text{Ni}_{0.629}\text{Co}_{0.135}\text{Mn}_{0.202}\text{O}_2$	$\text{Li}_{1.039}\text{Ni}_{0.626}\text{Co}_{0.134}\text{Mn}_{0.201}\text{O}_2$
$x = 0.10$	$0.1\text{Li}_2\text{MnO}_3 \cdot 0.9\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$	$\text{Li}_{1.048}\text{Ni}_{0.6}\text{Co}_{0.129}\text{Mn}_{0.224}\text{O}_2$	$\text{Li}_{1.064}\text{Ni}_{0.589}\text{Co}_{0.126}\text{Mn}_{0.221}\text{O}_2$

Table 2. Rietveld refinement results of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07, 0.10, 0.20$, and 0.30).

Sample	$\sqrt{3}\sqrt{2}$ -like component					$C2/m$ -like component					R_p
	a (nm)	c (nm)	Ni occupancy at Li site (%)	Vol (nm ³)	Weight fraction (%)	a (nm)	b (nm)	c (nm)	Vol (nm ³)	Weight fraction (%)	
$x=0$	0.28763(3)	1.4232(1)	2	0.10197(3)	100			— ^a			6.4
$x=0.03$	0.28765(4)	1.4234(2)	3.5	0.10199(3)	100			— ^b			7.6
$x=0.07$	0.28757(4)	1.4235(2)	2.5	0.10194(4)	96.3	0.48713(52)	0.87304(68)	0.50632(89)	0.20343(36)	3.7	7.9
$x=0.10$	0.28692(0)	1.4214(0)	2.5	0.10134(1)	91.8	0.49182(47)	0.86309(81)	0.50782(52)	0.20228(48)	8.2	7.8
$x=0.20$	0.28682(1)	1.4219(1)	2.5	0.10130(1)	88.6	0.49103(44)	0.85346(81)	0.50110(47)	0.19949(20)	11.4	9.6
$x=0.30$	0.28656(0)	1.4215(0)	2.5	0.10109(1)	80.8	0.49343(19)	0.85223(23)	0.50371(14)	0.20117(8)	19.2	9.9

^aNo $C2/m$ -like component was present. ^bWeak peak signal from $C2/m$ -like component.

Table 3. Summarized values of cycle performance of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ ($x = 0, 0.03, 0.07$, and 0.10) cathodes.

Sample	25 °C and 3.0 – 4.5 V			25 °C and 3.0 – 4.6 V			55 °C and 3.0 – 4.5 V		
	Initial capacity (mA h g ⁻¹)	Capacity retention (100s, %)	Average CE (%)	Initial capacity (mA h g ⁻¹)	Capacity retention (80s, %)	Average CE (%)	Initial capacity (mA h g ⁻¹)	Capacity retention (50s, %)	Average CE (%)
$x = 0$	185	78.7	98.6	204	77.7	97.3	207	84.4	94.8
$x = 0.03$	188	89.2	98.8	195	80.0	98.3	213	88.9	95.8
$x = 0.07$	189	92.4	98.9	192	88.0	98.1	203	90.0	95.5
$x = 0.10$	173	94.6	99.4	183	94.5	99.6	187	97.7	95.9

Table 4. R_s and R_{ct} values from a fitting of Nyquist plots using equivalent circuit.

Sample	1 st cycle		10 th cycle		50 th cycle		100 th cycle	
	R_s (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{ct} (Ω)
x=0	7.4	10.3	9.1	65.8	15.2	451.7	3.4	1115.0
x=0.03	7.9	8.7	9.1	53.2	10.1	324.0	2.0	774.9
x=0.07	5.5	7.9	9.1	47.4	7.3	277.3	2.4	579.1
x=0.10	10.5	7.6	19.0	33.5	26.9	172.8	32.5	376.1

Graphical Abstract

A facile method was developed to integrate a small amount of Li-rich material into Ni-rich material to improve its surface chemical stability. As a result, enhanced cyclability with 73.5 % of capacity retention after 900 cycles in pouch-type full cell at C/3 has been achieved.