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Chemical and structural evolution during synthesis of layered Li(Ni,Co,Mn)O₂ oxides

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Abstract:

The discovery of Li-containing transition-metal (TM) oxides has attracted broad interest and triggered intensive studies on these oxides as cathodes for lithium-ion batteries over decades. Unfortunately, a clear picture of how Li/TM/O ions are transported and electrons are transferred during synthesis of these compounds is still missing, especially when cubic close-packed (ccp) anion sublattices are involved, as it is the case for spinel, layered, or rock-salt systems. In the present study, a series of layered $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$ oxides was chosen as target materials to elucidate the underlying formation mechanism of these compounds during high-temperature lithiation reaction. The consistent experimental results demonstrate that, as lithium ions are inserted from surface to bulk, some transition metal cations located within the bulk of crystallites are able to diffuse to the near-surface region. They create cation vacancies for the inserted lithium ions, the mass transport behavior of these elements is driven by chemical potential gradient. Concurrently, oxygen anions from lithium oxides and/or ambient oxygen are adsorbed and incorporated into the ccp oxygen lattice on the surface structure, connecting the relocated transition metal cations and the incorporated lithium ions by forming ionic bonds. This process is concomitant with crystal growth, surface reorganization caused by phase transformation, occurrence and disappearance of pores.

1. Introduction

The solid-state chemical reaction of alkali species and oxygen with transition metal (TM) oxides is of fundamental significance to various areas of science, ranging from solid-state physics to material science, synthetic chemistry and electrochemical energy storage.^{1–5} The core of these reactions is tied to the kinetic events associated with the cleavage and formation of the chemical bonds (e.g., Li-O and TM-O bonds). Usually, high temperature is required to overcome the energy barriers of surface reaction and/or ionic diffusion in solid-state reactions, thus resulting in the formation of low energy products.⁶ The solid-state reactions are complicated, as exemplified by the synthesis of lithium-containing 3d-transition-metal oxides (LTMOs), i.e. chemical reactions among lithium compounds, oxygen and transition-metal oxides.^{1,7,8} After decades of study, some LTMOs such as spinel LiMn_2O_4 , layered LiCoO_2 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ have been successfully used as positive electrode materials for lithium-ion batteries (LIBs),^{9–11} but the formation mechanism of these compounds during synthesis has remained elusive. Unravelling the structural evolution during synthesis of LTMOs, hence, has become essential for improving their quality and developing new types of active materials.

The routine process for preparing layered LTMOs involves two steps: (1) the preparation of their precursors such as $\text{TM}(\text{OH})_2$, TMCO_3 and TMC_2O_4 by co-precipitation method and (2) the high-temperature lithiation reaction.^{12–14} These precursors can be easily decomposed into the gases (e.g. CO_2 or H_2O) and the Li-free spinel TM_3O_4 ($Fd\bar{3}m$) / rock-salt-type TMO ($Fm\bar{3}m$) at temperatures below 500 °C. For the formation of Li-rich 3d transition-metal oxides from Li-poor oxides, oxygen is incorporated into the host spinel/rock-salt structure in most cases (i.e. oxygen uptake), e.g. $\frac{1}{3}\text{Co}_3\text{O}_4 + \frac{1}{2}\text{Li}_2\text{O} + \frac{1}{12}\text{O}_2 \rightarrow \text{LiCoO}_2$ (Δ indicates calcination). Nevertheless, there are only few studies on the effects of lithium/oxygen incorporation on the microstructure of crystallites during synthesis of layered LTMOs. The pressing open questions in the field of chemistry needed to be addressed are: (i) Since the spinel, rock-salt and layered structure

possess a common cubic close-packed (ccp) oxygen sub-lattice, how and where are oxygen anions inserted into the host matrix during high-temperature lithiation? (ii) Owing to the fact that some of the octahedral/tetrahedral interstices within the ccp oxygen array in the spinel/rock-salt structure are occupied by transition-metal cations, where do they move with incorporation of lithium ions into the interior structure of these Li-poor/free oxides?

Figure 1. Schematic diagram for the preparation of 3d transition-metal oxides via different synthetic routes.

In the present study, the formation of a series of layered $\text{Li}(\text{Ni}, \text{Co}, \text{Mn})\text{O}_2$ oxides during heating was monitored in real-time by *in situ* high-temperature synchrotron radiation diffraction. The results indicate that the generation of layered LTMOs is a consequence of Li/O incorporation into the Li-free precursor obtained by hydroxide precipitation reaction. Without offering a lithium source (e.g., $\text{LiOH} \cdot \text{H}_2\text{O}$), the precursor would convert into spinel and/or rock-salt-type oxides during annealing as a result of oxygen/hydrogen/water release (see route I in **Figure 1**). In contrast, when the precursor reacts with lithium species under air atmosphere at high temperature, a large amount of oxygen could be inserted into the host structure of the precursor forming layered LTMOs (route II). More interestingly, the oxides obtained by heating of the precursor alone can also react with $\text{LiOH} \cdot \text{H}_2\text{O}$ and oxygen to produce layered LTMOs (route III). Therefore, the experimental results unambiguously confirm that all these reactions are

thermodynamically favored, i.e. the driving force of Li/O-insertion-induced mass transport and charge transfer is a chemical potential (concentration) gradient.

2. Experimental section

2.1 Materials synthesis

The precursor for layered $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ was prepared by a hydroxide coprecipitation route. A 2 M aqueous solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and/or $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and/or $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was fed into a reactor. Simultaneously, 4 M sodium hydroxide and a desired amount of ammonia solution were pumped into the reactor. The whole process was performed at a pH value of 11.3 ± 0.3 , reaction temperature of 52 ± 2 °C, and agitation speed of 500 rpm under a nitrogen atmosphere. The precipitates were filtered, washed and dried at 100 °C overnight.

The as-synthesized precursor was heated at 850 °C for 12 hours to obtain the Li-free oxides (route I in **Figure 1**). The layered $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ oxides were synthesized by heating of a mixture of obtained precursor/Li-free oxides and 7 % excess of $\text{LiOH} \cdot \text{H}_2\text{O}$ at 850 °C for 12 hours in air (route II and III). The precursor, the Li-free oxide and the Li-containing layered oxide are marked as NCMOH, NCMO and LNCMO, respectively.

2.2 Materials Characterization

The phase composition and crystal structure of the prepared samples were measured by *ex situ* high-resolution synchrotron radiation diffraction (SRD), which was performed at the Material Science Powder Diffraction (MSPD) beamline at ALBA synchrotron, Barcelona, Spain, and X-ray powder diffractometer (XRD, $\lambda = 0.7093$ Å) using a STOE diffractometry with $\text{Mo K}\alpha_1$ radiation (40 kV, 40 mA) in the range 5-40°. *In situ* high-temperature synchrotron radiation diffraction experiments were carried out at the beamline P02.1, storage ring PETRA-III at DESY (Deutsches Elektronensynchrotron) in Hamburg, Germany. The reactants, i.e. precursor,

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3 mixture of precursor/Li-free oxides and $\text{LiOH}\cdot\text{H}_2\text{O}$, were sealed in a quartz capillary in air. The
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5 crystallographic parameters and phase fraction were obtained by the Rietveld method using the
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7 FULLPROF program. The shape and microstructure of the materials were observed by a
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9 scanning electron microscope (SEM, Zeiss Merlin). Thermogravimetric (TG) and differential
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11 scanning calorimetric (DSC) experiments were performed on a thermal gravimetric analysis
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13 (Netzsch STA 449) with a heating rate of 10 K min^{-1} up to 1000 or 1200 °C in air. The specific
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15 surface area of the samples was measured by the Nitrogen physical adsorption isotherms
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17 (Gemini VII 2390, Micromeritics GmbH), and calculated according to the Brunauer, Emmett
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19 and Teller (BET) theory. A mercury intrusion porosimetry (CEI Pascal 1.05, Thermo Electron)
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21 was used to evaluate the porosity of the materials. The structure and elementary distribution of
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23 the materials were investigated by high-resolution transmission electron microscopy (HRTEM)
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25 and high angle annular dark-field scanning transmission electron microscopy (HAADF-
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27 STEM)-energy dispersive X-ray (EDX) mapping measurements under 300 KV operation
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29 voltage performed using a FEI Titan 80–300 (FEI Compnay, Portland). Computed scanning
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31 micro X-ray fluorescence (μXRF) and absorption contrast data were collected at the microXAS
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33 beamline (X05LA), Swiss Light Source (SLS), Paul Scherrer Institute, Switzerland. The
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35 $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ powders in capillaries mounted on tomography pins were raster-scanned in
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37 projection mode with a step size of $0.5\text{ }\mu\text{m}$, and in scanning tomography mode with a lateral
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39 step size of $0.5\text{ }\mu\text{m}$ at several projections equally spaced by around 1° over 180° .
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49 **2.3 Electrochemical Characterization**

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51 The electrochemical properties of the prepared materials were carried out by galvanostatic
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53 cycling in a coin-type half-cell (CR2032). The positive electrode was composed of a mixture
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55 of active LNCMO material, super P conductive agent and polyvinylidene fluoride (PVdF) (80
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57 wt% : 13 wt% : 7 wt%). Lithium metal, Celgard 2325 film and LiPF_6 in ethylene carbonate (EC):
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59 dimethyl carbonate (DMC) 1:1 (w/w) (LP30) were employed as the negative electrode,
60

separator and electrolyte, respectively. The cells were fabricated in an MBraun glove box under argon atmosphere. The battery test was conducted at a Bio-logic VMP3 potentiostat with a current density of 28 mA g⁻¹ between 2.7 - 4.3 V (vs. Li⁺/Li) at 25 °C.

3 Results

3.1 Synthesis of layered LiCoO₂

In order to unravel the formation mechanism of layered Li(Ni,Co,Mn)O₂ oxides during synthesis, a typical sample of LiCoO₂ (LCO) was firstly used to investigate the phase transformation from a Li-free precursor to a final Li-containing layered product. A hydroxide precipitation method^{13,15,16} was applied to prepare the precursor for LCO (see experimental part in supporting information). The obtained precipitates were filtered, washed with deionized water to remove the impurity ions, and dried in air at 100 °C. The results of the Rietveld refinement method¹⁷ against synchrotron radiation diffraction (SRD) patterns (see **Figure 2(c)**) show that the synthesized LCO's precursor (COH) is composed of a mixture of two trigonal layered phases, i.e. layered Co(OH)₂ (space group $P\bar{3}m1$) and layered CoOOH ($R\bar{3}m$). The weight fraction of the layered Co(OH)₂ and the layered CoOOH is determined to be 44(2) and 56(2) %, respectively. Based on these data an oxidation reaction is proposed:

Figure 2. Thermal evolution of cobalt hydroxides. (a) *In situ* HTSRD patterns and (b) the corresponding phase fraction evolution of LCO's precursor (COH) as a function of heating temperature; Rietveld refinement against the *in situ* diffraction patterns of the COH at 25 °C and (d) heated at 850 °C. In Figure (d), the intensity of the 220_s reflection at around 4.1° is indicative of the cobalt occupancy on the tetrahedral positions in the spinel oxide.

To explore the thermodynamically stable phase of Li-free transition metal oxides, *in situ* high-temperature SRD (HTSRD) was carried out to monitor the structural evolution of the LCO's precursor (COH) without lithium source, as shown in **Figure 2(a)**. Each SRD pattern was analyzed using Rietveld refinement in this study. **Figure 2(b)** displays the relative phase fractions of the mixtures during heating. Clearly, with an increase of temperature up to 850 °C, both layered $\text{Co}(\text{OH})_2$ and CoOOH in the precursor are converted into a cubic spinel $\text{Co}[\text{Co}]_2\text{O}_4$ phase ($Fd\bar{3}m$) according to the following reactions

Reaction (3) might be oversimplified. There might be the intermediate phases like CoO or CoOOH.¹⁸ Anyhow, no hints for these intermediate phases were found in the SRD patterns. To evaluate the fractional occupancy of cobalt ions on tetrahedral and octahedral sites in the cubic spinel structure of COH heated at 850 °C, Rietveld refinement against SRD was performed by assuming a spinel model ($Fd\bar{3}m$) with the chemical formula $(\text{Co})_x[\text{Co}]_y\text{O}_4$, see **Figure 2(d)**. The refinement results yield lattice parameters of $a = b = c = 8.1425(2) \text{ \AA}$, unit cell volume = $539.8595(5) \text{ \AA}^3$. The resultant chemical composition is $(\text{Co})_{0.97}[\text{Co}]_{1.98}\text{O}_4$, very close to the nominal formula $\text{Co}[\text{Co}]_2\text{O}_4$. Importantly, around one-third of the total cobalt ions migrates to tetrahedral positions in the spinel structure from octahedral sites in the layered structure as a consequence of oxygen and hydrogen release during thermal treatment (**Figure 2(c & d)**). It was reported that half-filled octahedral positions within a ccp oxygen sublattice contain Co^{3+} (electronic configuration $3d^6: t_{2g}^6 e_g^0$), whereas one-eight of the tetrahedral positions contain Co^{2+} ($3d^7: e^4 t_2^3$)¹⁹, implying that trapping of cobalt cations in the tetrahedral sites could enhance the structural stability of Li-free/Li-poor cobalt oxides.

Figure 3. Observation of an unexpected Li-containing rock-salt-type ($\text{Li}_x\text{Co}_{1-x}\text{O}$) phase during high-temperature lithiation reaction. (a) *In situ* HTSRD patterns and (b) the corresponding phase fraction evolution of a mixture of the precursor COH and lithium source as a function of annealing temperature; Rietveld refinement against the *in situ* diffraction patterns of the mixture of COH and $\text{LiOH} \cdot \text{H}_2\text{O}$ sintered at (c) 550°C and (d) 850°C . In Figure (a), several weak reflections over a 2θ range of 3° to 6° indicate the impurity of Li_2SiO_3 , the red area shows the Li-containing rock-salt-type phase.

Table 1. Crystallographic parameters of the mixture of COH and $\text{LiOH} \cdot \text{H}_2\text{O}$ sintered at 550°C .

Cell parameters (layered phase, 79(2) wt%)					
Space group: $R\bar{3}m$, $a = b = 2.8298(2) \text{ \AA}$, $c = 14.1798(2) \text{ \AA}$, $V = 98.3357(5) \text{ \AA}^3$, $Z = 3$, formula:					
ABO ₂					
Atomic positions					
Name	site	x	y	z	occupancy

Li1	3a	0.000	0.000	0.000	0.995(5)
Co1	3b	0.000	0.000	0.500	0.995(5)
O1	6c	0.000	0.000	0.241(2)	1.000
Cell parameters (rock-salt-type phase, 21(2) wt%)					
Space group: $Fm\bar{3}m$, $a = b = c = 4.2810(2)$ Å, $V = 78.4594(5)$ Å ³ , $Z = 4$, formula: AB					
Atomic positions					
Name	site	x	y	z	occupancy
Co1	4a	0.000	0.000	0.000	0.924(5)
Li1	4a	0.000	0.000	0.000	0.076(5)
O1	4b	0.500	0.500	0.500	1.000
Refinement parameters					
$R_{wp} = 15.800$ %, $R_p = 12.500$ %, χ^2 : 6.424					

Since the layered structures cannot be formed by heating of COH alone, it is relevant to follow how the COH precursor maintains its layered structure during incorporation of lithium and oxygen. *In situ* HTSRD experiments were performed to uncover the lithiation mechanism of composite reactants of COH combined with LiOH·H₂O, see **Figure 3(a)**. At the beginning of the lithiation reaction, the precursor, both layered Co(OH)₂ and layered CoOOH, starts to become a Li-containing layered LiCoO₂ with $R\bar{3}m$ symmetry and Li-poor spinel oxides ($Fd\bar{3}m$) by a temperature increase to about 200 °C, see **Figure 3(b)**. With continuous increase in the temperature from room temperature to approximately 450 °C, the emergence and disappearance of the 220_s reflection corresponding to the cubic spinel structure ($Fd\bar{3}m$) suggests cobalt migration to the tetrahedral 8a sites accompanied by release of O/H and the substitution of Li for Co on the 8a site induced by Li/O insertion in the spinel matrix. The Li-containing layered LiCoO₂ is supposed to be generated at the surface of the COH in contact with the lithium species, whereas the Li-poor spinel phases are formed in the inner region of the crystallites as a

consequence of the water release. The non-isothermal mass-loss process of the mixture of COH and LiOH·H₂O was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The weight loss of the mixture during annealing takes place mainly at temperatures below 500 °C, this reflects the thermal decomposition/dehydration of reactants and oxidation reaction of layered Co(OH)₂ occurring at this stage¹⁸. As more lithium and oxygen ions are inserted into the spinel structure at higher temperature (500-700 °C), in addition to some reflections, e.g., 003_{T3} and 104_{T3}, belonging to the layered LiCoO₂ (*R* $\bar{3}$ *m*, **Figure 3(a)**), other reflections such as 111_R at 4.8° and 200_R at 5.6° can be unambiguously assigned to the rock-salt structure (space group *Fm* $\bar{3}$ *m*) with random arrangement of Li and Co on the 4*a* site. These data provide direct evidence for the formation of a fully disordered Li-containing rock-salt-type (Li_xCo_{1-x})O (0 < *x* ≤ 0.5) intermediate. **Figure 3(c)** and **Table 1** shows the results of the Rietveld refinement against the HTSRD of the compounds at 550 °C. The relative phase portion of the rock-salt-type (Li_xCo_{1-x})O and the layered LiCoO₂ is found to be 79(2) and 21(2) wt%, respectively. Around 8at.% lithium is inserted into the rock-salt structure at this point (**Table 1**). Finally, the thermodynamically stable layered LiCoO₂ (*R* $\bar{3}$ *m*) oxide is produced from disordered rock-salt structure as a continuous incorporation of Li/O at even higher temperature (750-850 °C), see the following reaction and **Figure 3(b-d)**

In general, the transformation from spinel Co₃O₄ to rock-salt-type CoO emerges at much higher temperature (> 900 °C) under air²⁰, while Li-containing rock-salt-type (Li_xCo_{1-x})O intermediate is formed at temperatures between 500 and 700 °C and thus it could be viewed as high-temperature metastable phase. Together, structural basis of the reaction coordinates for layered LiCoO₂ formation during synthesis is proposed, as shown in **Figure 4**.

Figure 4. Schematic diagram of the phase transition during high-temperature reaction between precursor COH and LiOH. The phase transformation from a Li-poor spinel $\text{Co[Co]}_2\text{O}_4$ ($Fd\bar{3}m$) to a Li-containing spinel $\text{Li[Co]}_2\text{O}_4$ ($Fd\bar{3}m$) corresponds to the appearance and disappearance of the 220_s reflection in *in situ* HTSRD patterns in Figure 3(a), and a set of reflections like 111_R , 200_R , 220_R and 311_R is associated with the fully disordered Li-containing rock-salt-type ($\text{Li}_x\text{Co}_{1-x}$)O phase.

Figure 5(a) displays the TG/DTG and DSC curves of a mixture of spinel Co_3O_4 (CO) together with $\text{LiOH}\cdot\text{H}_2\text{O}$ during calcination. An obvious weight loss (TG/DTG) is visible as an endothermic peak (DSC) at about 100°C because of the removal of water from lithium hydroxide monohydrate. The second weight loss between 500 and 650°C can be ascribed to the decomposition of LiOH (i.e. $2\text{LiOH} \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{H}_2\text{O}$). The peaks in the DSC curve at $\sim 471^\circ\text{C}$ and $\sim 579^\circ\text{C}$ are still endothermic, which is probably attributable to the lithium ion insertion into spinel Co_3O_4 and/or the oxidation of cobalt ions during transformation of Li-poor spinel/rock-salt-type phases to Li-containing layered phase. Interestingly, an increase in the mass of the mixture is clearly found in the TG curve with an increase in the lithiation

temperature from 650° to 800°C, thereby confirming the incorporation of ambient oxygen into the oxides (see the following)

Figure 5. Lithium/oxygen incorporation into the metastable rock-salt-type ($\text{Li}_x\text{Co}_{1-x}\text{O}$) phase. (a) TG/DTG/DSC plots of a mixture of Co_3O_4 (CO) and $\text{LiOH}\cdot\text{H}_2\text{O}$; Rietveld refinement against the *in situ* diffraction patterns of (b) the mixture of Co_3O_4 and $\text{LiOH}\cdot\text{H}_2\text{O}$ heated at 550 °C; (c) Schematic diagram of the phase transition during high-temperature reaction between Co_3O_4 and LiOH .

In situ HTSRD results reveal the reaction coordinates for this high-temperature lithiation reaction (Figure S2 and Figure 5(c)), i.e. from reactants of Li-free spinel Co_3O_4 and Li/O species to intermediate Li-containing disordered halite-type oxides (Figure 5(b)) and eventually to layered LiCoO_2 . This Li-containing rock-salt-type phase is particularly interesting

because it can be thought of as a kind of intermediate transition state from ‘Li-poor’ spinel ($n_{\text{Li}}:n_{\text{Co}}=0\sim0.5:1$) to ‘Li-rich’ layered phase ($n_{\text{Li}}:n_{\text{Co}}\sim1:1$). Obviously, both lithium and cobalt are fully disordered on the octahedral positions in the halite-structured ($\text{Li}_x\text{Co}_{1-x}\text{O}$). Thus, it is reasonable to assume that the rock-salt-type phase exists between ‘Li-rich’ layered phase at the surface in contact with Li sources and ‘Li-poor’ spinel phase in the inner part of the crystallites,¹ resulting from the insertion of Li ions from surface to bulk and the movement of Co ions in the reverse direction.

3.2 Synthesis of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

To clarify whether the discovered lithiation mechanism during synthesis of LiCoO_2 has broad implications for the design of a class of layered $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ oxides, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LNCM111O) was chosen as a final product. The precursor for LNCM111O (NCM111OH) is $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{OH}$ (NCM111OH) and was synthesized by the same preparation procedure described above in which the cobalt(II) sulfate solution was changed into a mixture of nickel(II)-cobalt(II)-manganese(II) sulfate solution (molar ratio of 1:1:1). After air-drying of obtained coprecipitates, the precursor was oxidized into a mixture of trigonal layered TMOOH phase ($R\bar{3}m$, 55(4) wt%) and monoclinic layered TMOOH phase ($C2/m$, 44(4) wt%). The possible reactions can be represented as follows

Figure 6. Formation of LNCM1110 through various synthetic procedures. *In situ* HTSRD patterns of (a) NCM1110H precursor, (c) a mixture of the NCM1110H and lithium source, and (e) a mixture of NCM1110 together with lithium source. The corresponding phase fraction evolution of (b) NCM1110H, (d) the mixture of NCM1110H and $\text{LiOH} \cdot \text{H}_2\text{O}$, and (f) the mixture of NCM1110 and $\text{LiOH} \cdot \text{H}_2\text{O}$, respectively, as a function of heating temperature.

In situ HTSRD results of NCM111OH (**Figure 6(a & b)**) reveal that layered transition-metal oxide hydroxides decompose into a cubic spinel TM_3O_4 oxide ($Fd\bar{3}m$) and a TMO oxide (halite-type, $Fm\bar{3}m$) with increasing temperature from 25 °C to 850 °C. When the NCM111OH is heated to the temperature of 850 °C. The weight fraction of spinel TM_3O_4 phase and rock-salt-type TMO phase are estimated to be 90(2) % and 10(1) % (**Figure S4**), respectively, manifesting that release of oxygen/hydrogen from layered NCM111OH results in an extensive migration of TM cations. It is notable that the cubic spinel TM_3O_4 phase and the rock-salt-type TMO phase do not have even distribution of three transition elements, as described below for the aberration-corrected high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) results of NCM111O.

Subsequently, a mixture of NCM111OH precursor together with $\text{LiOH}\cdot\text{H}_2\text{O}$ was used as reactants to obtain the layered LNCM111O after high-temperature lithiation reaction. As shown in **Figure 6(c & d)**, the mixture is converted to lithium-containing compounds with trigonal layered structure ($R\bar{3}m$) and rock-salt structure ($Fm\bar{3}m$) as annealing temperature increases up to around 550 °C. By further increasing the annealing temperature to 850 °C, the Li-containing cubic rock-salt-type phase is gradually transformed to the layered LNCM111O, as evidenced by the splitting of the two reflections of 006/012 and 018/110 (typical characteristics of layered $\alpha\text{-NaFeO}_2$ -type structure). Hence, the overall reaction during the heating process can be described as follows

As shown in reaction (10), both O/H release and Li/O incorporation are involved during the reaction between precursor and lithium sources under air environment at high temperature. Therefore, it is difficult to reveal the reason for lithium-insertion-induced oxygen uptake during phase transformation from spinel/rock-salt to layered structure, because all these structures have a common distorted ccp oxygen lattice framework.

To exclude the effects of O/H loss from the precursor in high-temperature solid-state reaction, we focus on the formation of layered LTMOs from Li-free spinel/halite-type oxides. Herein, an oxide (NCM111O) obtained by heating of NCM111OH to 850 °C for 12 hours was employed as a raw material to react with LiOH·H₂O for preparing a layered LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ oxide. At the early stage of this lithiation reaction (25-500 °C) (see **Figure 6(e & f)**), the decrease in intensity of the 220_s reflection provides compelling evidence for the replacement of TM by Li on the tetrahedral sites in the spinel structure (*Fd $\bar{3}m$*). Simultaneously, oxygen anions are supposed to be incorporated into the ccp oxygen surface-lattice to provide octahedral coordination sites for TM cations which are substituted by Li ions (see **Figure 6(e)**, inset) in the bulk of the particles. As chemical insertion of Li and O into the surface of particles during annealing at temperatures above 500 °C, the spinel (Li_xTM_{1-x})[TM]₂O₄ (0 < x ≤ 1) phase (*Fd $\bar{3}m$*) is successively transformed to a mixture of a rock-salt-type (Li_xTM_{1-x})O (*Fm $\bar{3}m$*) and a layered LiTMO₂ (*R $\bar{3}m$*), which is analogous to the formation of LiCoO₂ (**Figure 5**). When the temperature reaches 800 °C, the final product of LNCM111O is progressively formed. Note that a pure LNCM111O can be obtained from NCM111O and Li source by adding excess of LiOH·H₂O (~ 10 %) or increasing temperature (~ 900 °C) during synthesis. Previous studies have confirmed that nickel, cobalt and manganese in LNCM111O exist predominantly as Ni²⁺, Co³⁺, Mn⁴⁺, respectively.^{21,22} While the lithium source (i.e. LiOH·H₂O) would not be able to oxidize the TM cations of host oxides by its insertion alone, additional oxygen atoms from ambient oxygen, thus, are supposed to be adsorbed, reduced and incorporated into the anion sub-lattice on the crystal surface. Therefore, the adsorption and incorporation of oxygen anions with large ionic radius ($r_{O^{2-}} = \sim 1.4 \text{ \AA}$)²³ at the surface of crystallites result in a changing crystal shape, particle size and porosity during the high-temperature lithiation reaction, as described below.

3.3 Synthesis of layered $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (crystal growth)

It is worthwhile to synthesize layered Ni-rich oxides because their higher reactivity of the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple during electrochemical cycling could lead to an improvement in battery capacity.^{24–27} Herein, LNCM622O was selected as a synthetic product to gain new insights into the microstructural evolution of the oxides during high-temperature lithiation reaction. Considering that the phase transformation during synthesis of layered $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ is strongly dependent on the chemical composition, *in situ* HTSRD was used to trace the structural evolution of the mixture of NCM622OH precursor and lithium hydroxide during annealing, see **Figure 7(a)**. A quantitative estimate of the weight fraction of each phase is shown in **Figure 7(b)**. Unlike the phase transition process during synthesis of LiCoO_2 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ oxides, no 220_{S} reflection corresponding to the TM_3O_4 spinel intermediate phase is found during the formation process of layered $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$. Most interestingly, all the reactants convert to a Li-containing rock-salt-type intermediate between 550 and 650 °C, which is verified by the disappearance of $00l$ reflections in the HTSRD patterns of layered phases (**Figure 7(a)**). The Li content (x value) increases up to ~ 0.6 in the rock-salt structure $\text{Li}_x\text{NCM622}_{1-x}\text{O}$, see **Figure S5**, when the mixture is heated to 850 °C. Concomitantly, the layered LNCM622O is generated as a consequence of equally distributed TM and Li cations in the fully disordered rock-salt host structure migration into two different layers (i.e. Li layer and TM layer), see **Figure 7(c)**.

Figure 7. Phase transition mechanism during synthesis of layered Ni-rich oxides. (a) *In situ* HTSRD patterns and (b) the corresponding phase fraction evolution of a mixture of the NCM622OH and lithium source, (c) schematic diagram of the phase transition during synthesis of layered LNCM622O. In Figure (a), T1, T2, T3 and R represent the trigonal layered $\text{TM}(\text{OH})_2$ ($P\bar{3}m1$), the trigonal layered TMOOH ($R\bar{3}m$), the trigonal layered LiTMO_2 ($R\bar{3}m$) and the fully disordered Li-containing rock-salt-type $\text{Li}_x\text{TM}_{1-x}\text{O}$ ($Fm\bar{3}m$), respectively.

In order to unveil the correlation between Li/O incorporation and microstructural evolution, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$'s precursor (NCM622OH) was prepared by hydroxide coprecipitation method. Rietveld refinement against SRD patterns of NCM622OH indicates that the NCM622OH owns a single layered CdI_2 -type structure ($P\bar{3}m1$) with preferred orientation perpendicular to the (100) plane (**Figure 8(a)**). Li-free transition-metal oxide (NCM622O) and Li-containing $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (LNCM622O) were respectively prepared by heating of the

NCM622OH alone and the mixture of NCM622OH together with Li source at 850 °C for 12 hours, respectively. Compared to the pure layered LNCM622O ($R\bar{3}m$), the phase constitution of NCM622O is determined to be a composite of a cubic spinel TM_3O_4 phase and a cubic rock-salt-type TMO phase with a weight ratio of 55(2):45(2), see **Figure 8(b-c)**. The two phase nature of NCM622O is likely to result in a segregation of transition metal ions, i.e. the two phases contain different amounts of Ni, Co and Mn ions, see the HAADF-STEM-energy dispersive X-ray (EDX) mapping results of NCM622O below.

Figure 8. Lithium/Oxygen-incorporation-induced crystal growth. Rietveld refinement against the high-resolution synchrotron radiation diffraction patterns of (a) NCM622OH, (b) NCM622O and (c) LNCM622O, respectively. SEM images of (d) NCM622OH, (e) NCM622O and (f) LNCM622O, insets in (e) and (f) are cross section SEM images of NCM622O and

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3 LNCM622O, respectively; (g) the particle size distribution and (h) the pore size distribution of
4 the samples; (i) electrochemical performance of as-synthesized LNCM622O for galvanostatic
5 cycling at 28 mA g⁻¹ between 2.7 and 4.3 V at 25 °C.
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12 The morphologies of three specimens such as NCM622OH, NCM622O and LNCM622 are
13 shown in **Figure 8(d-f)**. All these samples consist of distinctive quasi-spherically shaped
14 secondary particles. During thermal treatment, the primary crystals with a platelet-like
15 morphology in the NCM622OH grow and their surface becomes smooth for both NCM622O
16 and LNCM622O. It can be observed in **Figure 8(e & f)** that LNCM622O has a denser
17 appearance and a larger secondary particle size than NCM622O, and voids between primary
18 particles are clearly found in NCM622O. The particle size distribution of the samples
19 determined by light scattering (**Figure 8(g)** and **Table 2**) suggests that the average size of
20 secondary particles of NCM622O has decreased to 4.55 μm, while the secondary particle size
21 of LNCM622O has increased to 6.86 μm, compared to that of NCM622OH precursor (4.96 μm).
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23 The main reason for a larger particle diameter and a wider size range in LNCM622O compared
24 to NCM622OH and NCM622O is the strong aggregation of the secondary particles (see SEM
25 images). **Figure 8(h)** and **Table 2** reveal that NCM622O has a larger internal porosity than both
26 NCM622OH and LNCM622O. In the first case, this can be attributed to the release of O/H from
27 the precursor during thermal treatment. The volumes per oxygen atom of NCM622OH,
28 NCM622O and LNCM622 obtained by Rietveld refinement results (**Figure 8(a-c)** and **Table**
29 **S1-3**) are listed in **Table 2**. These data reveal that Li/O insertion into the spinel/rock-salt-type
30 oxides (e.g., NCM622O) could induce contraction in crystal lattice during synthesis of LTMOs
31 (e.g., LNCM622O), which is probably due to the strong electronegativity of oxygen anions
32 and/or the small cationic radii of TMs at higher oxidation states.
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Compared with NCM622O, LNCM662O exhibits a reduction of porosity and surface area, an enhancement of secondary particle size and a shrinkage of the structural unit cell in the LNCM622O. Taken together, these results provide conclusive evidence for crystal growth by incorporation of Li and O (i.e. increasing the number of unit cells). Although SRD is not suitable to detect the light elements like lithium and the X-ray scattering factors of Ni, Co and Mn are similar, it is very powerful to determine the precise lattice parameters and symmetry of the structure. Thus, the chemical evolution and local rearrangement of TM ions during synthesis of layered LTMOs can be indirectly deduced from the corresponding reliable structure models. Since all involved structures, i.e. spinel/rock-salt-type/layered phases, share the same ccp oxygen anion lattice, the diffusion of oxygen is supposed to play a minor role here. As oxygen anions incorporate into the surface structure of crystallites, lithium ions from surface-attached lithium species have to move into the inner part of the Li-free/poor oxides, while some TM cations located within the interior region of these particles are supposed to be transported to the near-surface area driven by chemical reactions, and hence resulting in the formation of layered $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ with a uniform distribution of Li, Ni, Co and Mn, see the discussion below.

Table 2. The physicochemical properties of NCM622OH, NCM622O and LNCM622O.

Items	NCM622OH	NCM622O	LNCM622O
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	4.43 ± 0.80	1.34 ± 0.80	0.46 ± 0.80
Average size of secondary particles (D50, μm)	4.96 ± 0.20	4.55 ± 0.20	6.86 ± 0.20
Porosity (%)	49.10 ± 1.00	62.90 ± 1.00	58.70 ± 1.00
Volumetric mass density (g cm^{-3})	3.99 ± 0.10	6.08 ± 0.10	4.48 ± 0.10
Volume per oxygen atom ($\text{\AA}^3$)	19.30 ± 0.10	18.15 ± 0.10	16.84 ± 0.10

With respect to battery application, the as-synthesized LNCM622O was fabricated into a CR2032-type coin cell for the assessment of its electrochemical performance. The cell was

galvanostatically cycled at a current density of 28 mA g⁻¹ (0.1 C) between 2.7 and 4.3 V at room temperature. **Figure 8(f)** displays the cycling performance and the corresponding charge-discharge voltage profiles of the LNCM622O cathode. The LNCM622O electrode delivers a smooth and monotonous charge/discharge profile, which can be ascribed to the insertion/extraction mechanism in layered LTMOs during electrochemical cycling.^{28,29} After 100 cycles, the specific discharge capacity of LNCM622O is 167.2 mAh g⁻¹, which is about 94 % of the initial capacity (178.7 mAh g⁻¹), demonstrating the good cycling performance.

3.4 Thermodynamically driven element segregation in Li-free spinel/rock-salt oxides

According to the analysis of phase transformation during synthesis of LCO, LNCM111O and LNCM622O, whether the spinel TM₃O₄ intermediate is formed, i.e. TM cations migrating to the tetrahedral sites within the ccp oxygen lattice, is closely tied to the relative site preference of TM ions. To figure out the preference of TM ions for a particular site symmetry or coordination in the Ni-rich Ni-Co-Mn-O system between 25 and 850 °C, *in situ* HTSRD was used to probe the phase transitions of Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂ (NCM622OH), Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ (NCM811OH) and Ni(OH)₂ (NOH) (**Figure 9(a)**), which is the precursor for the preparation of LNCM622O, LNCM811O, LNO, respectively. All the reflections in SRD patterns of these three precursors can be indexed according to a layered CdI₂-type phase (*P* $\bar{3}$ *m**l*) with chemical composition TM(OH)₂. No reflection assigned to the NCM(OOH) phase is detected in the Ni-rich hydroxides at room temperature. With increasing the temperature to 850 °C, both NCM811OH and NOH transform to a single rock-salt-type TMO phase (*Fm* $\bar{3}$ *m*), whereas the NCM622OH converts to a mixture of a rock-salt-type phase (*Fm* $\bar{3}$ *m*) and a cubic spinel phase (*Fd* $\bar{3}$ *m*). These data illustrate that nickel ions have a strong preference to occupy the octahedral sites forming rock-salt structure at this temperature range, see **Figure 9(b)**. Such site preferences probably contribute to preclude the formation of spinel (Li_xTM_{1-x})[TM]₂O₄ intermediates during synthesis of Ni-rich LiNi_xCo_yMn_{1-x-y}O₂ ($x \geq 0.6$), see **Figure 7**.

Figure 9. Thermal-induced structural changes of Ni-rich hydroxides. (a) *In situ* HTSRD patterns of NCM622OH, NCM811OH and NOH, (b) schematic diagram of the phase transition during thermal treatment of these compounds. The blue and red area show the spinel and rock-salt-type phases, respectively.

A spinel/rock-salt-type heterostructured NCM111O, after annealing of NCM111OH at 850 °C for 12 h, was selected to study the elementary distribution in the crystallites. The fraction of spinel phase and rock-salt-type phase is approximately 93(2) and 7(2) %, evaluated by Rietveld refinement against SRD patterns of NCM111O, **Figure 10(a)**. The HAADF-STEM-EDX mapping results (**Figure 10(b, e-i)**) demonstrate that cobalt, manganese and oxygen are homogeneously distributed among the particles, while a strong Ni segregation on the near-surface region is obviously observed in **Figure 10(f)**. High-resolution transmission electron microscopy (HRTEM) image (**Figure 10(c)**) of a Ni-rich region shown in **Figure 10(b)** displays two sets of lattice fringes with a d -spacing of 0.24 and 0.21 nm at an angle of 125 °, which can be indexed to the $(\bar{1}11)$ and (200) planes of the $Fm\bar{3}m$ symmetry. The corresponding Fast Fourier Transform (FFT) patterns in **Figure 10(d)** exhibit an array of dots with a cubic rock-salt symmetry, proving the Ni-rich rock-salt phase at the surface of NCM111O.

Figure 10. Direct observation of Ni-rich rock-salt-type phase in multi-structured NCM111O. (a) Rietveld refinement against SRD patterns, (b) HAADF-STEM, (c) HRTEM and corresponding FFT patterns, (e-i) HAADF-STEM-EDX mapping images of NCM111O.

Since the oxygen can only be released from the ccp oxygen lattice on the surface, the oxygen-poor TMO rock-salt-type phase, compared to the spinel TM_3O_4 phase, is more likely to be formed at the near-surface region. Thermodynamically, the formation of rock-salt-type NiO is more favourable than that of CoO and MnO over a temperature range from 25 to 900 °C in air^{20,30}, as shown in **Figure 10(f)**. Such a surface segregation of Ni is often described in the literature^{1,31} and is strictly correlated to the oxygen content in the crystal structure. **Figure 11** presents the HAADF-STEM-EDX mapping images of NCM622O, obtained by heating of NCM622OH at 850 °C for 12 h. SRD patterns of NCM622O is shown in **Figure 8(b)**. The

internal void, polyhedral shape and primary particle size (~ 200 nm) of NCM622O observed by HAADF-STEM (**Figure 11(a)**) are in a good agreement with the SEM results (**Figure 8(e)**). Apparently, the Ni-rich crystallites are separated from the Co-Mn-rich particles. They are probably linked to the rock-salt-type phase and the spinel phase, respectively. These results also demonstrate that Co and Mn have a strong tendency to form a solid solution.

Figure 11. Severe segregation of Ni in Li-free Ni-rich oxide. (a) HAADF-STEM and (b-e) HAADF-STEM-EDX mapping images of NCM622O.

After high-temperature lithiation reaction, a Li-free oxide with spinel and rock-salt-type phases, i.e. NCM111O or NCM622O, can convert to a Li-containing oxide, i.e. LNCM111O or LNCM622O, with a single trigonal α -NaFeO₂ layered structure ($R\bar{3}m$). In contrast to NCM111O, STEM-EDX maps of LNCM111O (**Figure S7**) exhibit a uniform distribution of Ni, Co and Mn. The even distribution of three TM elements in the LNCM622O is also confirmed by spatially resolved scanning micro-X-ray fluorescence (μ -XRF) images (**Figure S8**). These intriguing findings could broadly help explain why the formation of nanopores and the migration of Ni ions are so commonly found in these layered LNCMO materials after long-

term cycling, i.e. thermodynamically driven formation of rock-salt/spinel phase triggered by Li/O release.

4. Discussion

The experimental results demonstrate that the synthetic reaction of layered LTMOs is limited by both surface chemical reaction and ionic diffusion in the solid state. This explains why the synthesis process has a pronounced influence on the phase composition, specific surface area, porosity, particle shape and size of final products. In this scenario, a representative synthesis reaction (11) of Li-free spinel oxide and lithium oxide together with oxygen is used to understand how mass is transported and charge is transferred during the process of Li/O incorporation, described as follows

Thermodynamically, the driving force for the chemical reaction between these reactants in air or oxygen-rich atmosphere is the difference in Gibbs free energy (ΔG) between all the reactants and the final layered LTMO product. Previous work suggested that ΔG is less than zero in the temperature range of 25 – 900 °C in air environment,^{32,33} so the reaction (11) proceeds from left to right, i.e. Li/O insertion into the spinel host architecture. Because the ccp oxygen sublattice is involved during this phase transition, the oxygen from both, the Li source and the ambient air, can only be incorporated into the surface of crystallites, resulting in the growth of oxides, see **Figure 8**.

Figure 12. (a) Rietveld refinement against XRD patterns of NCM622O-600-3 and LNCM622O-600-3, (b) schematic illustration of the thermally-induced phase transformation of the precursor without Li source (top) and with Li source (bottom); (c) TEM image and (d) the

corresponding SAED patterns of a secondary particle for LNCM622O-600-3; (e) HRTEM image and (f) the corresponding FFT patterns of LNCM622O-600-3 for the area shown in (c).

In order to elucidate the transport/redistribution of the Li, O, and TM species during synthesis of layered LTMOs, the precursor NCM622OH and a mixture of NCM622OH and LiOH·H₂O were heated at 600 °C for 3 hours in air. These samples are labelled in the following, NCM622O-600-3 and LNCM622O-600-3. As determined by XRD results (**Figure 12(a)**), NCM622O-600-3 is found to be a mixture of a spinel phase ($Fd\bar{3}m$) and a rock-salt-type phase ($Fm\bar{3}m$), and LNCM622O-600-3 is composed of a blend of a Li-containing rock-salt-type phase ($Fm\bar{3}m$) and a Li-containing layered phase ($R\bar{3}m$). A detailed microstructural analysis was performed on LNCM622O-600-3 using TEM, high resolution TEM (HRTEM) and electron diffraction (ED). Several nanograins with platelet-like morphology are attached to the surface of an agglomerate particle, as shown by the TEM image of LNCM622O-600-3. The corresponding selected area electron diffraction (SAED) pattern in **Figure 12(d)** presents bright circular rings, which correspond to the (003)_T, (101)_T, (006)_T, (012)_T and (104)_T planes of trigonal layered structure ($R\bar{3}m$) and the (111)_R and (220)_R planes of rock-salt structure ($Fm\bar{3}m$), in good agreement with the analysis of XRD results in **Figure 12(a)**. The HRTEM image (**Figure 12(e)**) of the region marked in **Figure 12(c)** exhibits clear lattice fringes with interplanar spacing of 0.47(1) nm that can only be indexed to the (003) plane of the layered structure. The FFT patterns in **Figure 12(f)** are indexed according to (003)_T, (101)_T, (006)_T, (012)_T and (104)_T reflections of the layered $R\bar{3}m$ symmetry, confirming that the nanograins on the surface have a layered structure. The Rietveld refinements results (**Figure 12(a)**) show that the weight fraction of layered phase and Li-containing rock-salt phase is approximately 53(2) and 47(3) %, thereby, the Li-containing rock-salt phase is supposed to remain in the interior area of the agglomerate, see **Figure 12(b)**. These data unambiguously prove that, with incorporation of Li/O species into the Li-free precursor during high-temperature solid-state

reaction, the 'Li-rich' layered $\text{Li}(\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2})\text{O}_2$ phase is grown on the surface of the 'Li-poor' spinel/rock-salt-type intermediate phase originally formed from the precursor.

Figure 13 shows a possible model for the growth of crystals in air atmosphere at high temperature. Firstly, lithium species and atomic oxygen are attached on the spinel oxide surface (stage 1). The nucleation occurs at favourable sites forming a 'Li-rich' nucleus on the surface of crystallites at stage 2. As the ultrafine 'Li-rich' particles grow (stage 3), Li ions are gradually inserted into the inner part of oxides while the TM cations continuously migrate to the near-surface region driven by concentration gradient. Synchronously, oxygen anions (O^{2-}) are successively incorporated into the ccp oxygen surface lattice to provide the indispensable nutrient for the recrystallization and growth of Li-containing oxide particles. When the atomic oxygen from air reacts with TM cations, the oxidation of TMs takes place, $\text{TM}^{n+} \rightarrow \text{TM}^{(n+1)+} + e^-$ ($n = 2$ or 3). Finally, a homogeneous distribution of Li, Ni, Co, Mn and O in the layered oxides is achieved driven by chemical potential (i.e. concentration) gradients (stage 4). It should be mentioned that the thermal stresses during crystal growth could cause defects, e.g., micro-cracks, porosity and cavities.^{34,35} This ideal mass transfer model for oxide growth requires that the positively charged Li ions move inward, while the TM cations and electrons move outward. The inward flux of oxygen anions can be basically ignored because of the already fully occupied ccp oxygen lattice. Cations and electrons diffuse together to keep electroneutrality. The solid-state reaction is limited by either the slowest diffusing species or the chemical reaction at the oxide surfaces. For instance, the slow oxidation of nickel from Ni^{2+} to Ni^{3+} increases the energy barrier for the synthesis of Ni-rich layered LTMOs.³⁶

Figure 13. A possible model for crystallite growth during formation of LiTMO_2 oxides from spinel TM_3O_4 oxides at high temperature.

Figure 14. Schematic illustration for a possible lithium/oxygen-incorporation-induced structural evolution during the synthesis of layered LiTMO_2 oxides starting from Li-free spinel oxides, showing the local arrangement of Li and TM atoms in spinel/rock-salt/layered structure.

From the oxygen lattice point of view, there is indeed no significant discrepancy between spinel and rock-salt/layered structure types. The differences between these phases are largely attributable to the different arrangements of cations within the ccp oxygen sub-lattice, i.e. all the Li/TM cations are located on the octahedral sites in the rock-salt/layered structure, while around one-eighth of the tetrahedral sites is also occupied in spinel structures. Instead, the key difference between these Li-containing oxides in the chemical composition (lithium/oxygen content) is obvious. On the basis of the experimental results and our previous work^{1,8}, a possible mechanism from Li-free spinel ($Fd\bar{3}m$) to Li-containing layered phase ($R\bar{3}m$) is proposed for visualizing the changes in the local atomic structure of the involved Li-containing spinel/rock-salt-type intermediates (**Figure 14**). As lithium species (e.g., Li_2O) continuously react with cubic spinel $(\text{TM})[\text{TM}]_2\text{O}_4$ particles, Li ions tend to occupy the tetrahedral $8a$ site in the spinel structure and push TM ions located on $8a$ positions to the near-surface region. Concurrently, the displaced TM is the electron donor to atomic oxygen, and interacts with oxygen anions forming TMO_6 octahedra (stage 1 & 2), or, in other words, the incorporated oxygen provides additional coordination sites for the displaced TM ions. Thus, the Li-containing spinel $(\text{Li})[\text{TM}]_2\text{O}_4$ ($Fd\bar{3}m$) is generated. It is important to keep in mind that the TM content is constant during synthesis, so oxygen anions are supposed to be incorporated into the oxides to keep charge neutrality as a consequence of Li-ion insertion and oxidation of TM cations. With incorporation of more Li ions and O anions, both Li and TM cations could migrate to the vacant $16c$ site in the cubic spinel structure, causing the formation of rock-salt-type $(\text{Li}_x\text{TM}_{1-x})\text{O}$ ($Fm\bar{3}m$) in which the Li/TM ions are randomly distributed on the octahedral sites, see stage (3 & 4). These cations in the disordered rock-salt structure have a tendency to separate into two different layers (i.e. Li layer and TM layer) caused by insertion of Li/O at high temperature, which contributes to the formation of a thermally stable layered $\text{Li}(\text{TM})\text{O}_2$ (stage 5 & 6). Therefore, the original ccp oxygen lattice is maintained but the total number of structural units is increased during phase transformation, this process involves Li insertion and TM migration, electron

transfer, surface reorganization, atomic rearrangement, crystal growth and reduced porosity. It is worth mentioning that different valence states, site preferences and chemical compositions of the TM ions can elicit various pathways of LNCMO formation and different diffusion paths of TM ions in the closed-packed crystals, but the formation mechanism of LNCMO uptaking Li and O from surface Li/O species is universal.

5. Conclusions

In summary, the structural evolution during synthesis of layered LiTMO_2 oxides ($R\bar{3}m$) from Li-free precursor/oxides occurs during high-temperature lithiation reaction in air/O-rich atmosphere, accompanied by the Li/TM transport, charge transfer, oxygen uptake and crystal growth. When an appropriate amount of lithium sources and Li-free compounds come together at high temperature, the mixture gradually transforms to a kind of activated complex with the spinel ($Fd\bar{3}m$) and/or rock-salt ($Fm\bar{3}m$) structure that decays into a Li-containing layered product ($R\bar{3}m$). The results unveil a specific origin of oxygen incorporation during synthesis of layered $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ cathode materials, which can help to prepare the layered LTMOs with good cyclability and to bridge the gap between fundamental studies and industrial requirements for the production of the Li–Ni–Co–Mn oxides on a large scale. Finally, these findings provide new insights into solid-state chemistry for developing high-energy transition-metal oxide electrodes and deeper understanding of the important degradation mechanism of these materials.

Supporting Information

Rietveld refinement results of SRD data, crystallographic parameters, TG/DTG/DSC curves, cross section SEM images, HAADF-STEM-EDX mapping and μ -XRF images of the samples.

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Author Contribution

W.H. conceived the idea and discussed with M.K., B.S., S.W., J.B., X.D., X.J., S.I., and H.E. W.H., H.L., J.L. and S.W. carried out the preparation experiments; W.H., K.W., A.S., A.M., D.F.S., and S.I. performed the synchrotron-based diffraction measurements and TEM experiments; the data was analyzed by W.H., B.S. and S.I., W.H., M.K., B.S. and S.I. wrote and revised the manuscript. All authors have given the approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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