



# Effect of pristine nanostructure on first cycle electrochemical characteristics of lithium-rich lithium–nickel–cobalt–manganese-oxide cathode ceramics for lithium ion batteries



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## H I G H L I G H T S

- TEM nano structure analysis of pristine Li-rich NCM composite structures.
- HRTEM analysis suggests  $[\sqrt{3}x\sqrt{3}]R30^\circ$  superstructure for NCM component.
- DIFFaX simulations are used to estimate  $\text{Li}_2\text{MnO}_3$  domain size in nano composite.
- First cycle voltage profiles are used to estimate anomalous capacity.
- Results show impact of nano structure on electrochemical performance.

## A R T I C L E I N F O

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## A B S T R A C T

Structural and electrochemical (EC) data of five different  $x\text{Li}_2\text{MnO}_3:(1-x)\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  cathode ceramics are presented. The aim of this work is to highlight the nano structure of this material class, next to the choice of right composition, as the key to anomalously high discharge capacities  $> 250 \text{ mAhg}^{-1}$ . Therefore, the pristine nano composite structure of five different samples has been analyzed extensively by transition electron microscopy with respect to  $\text{Li}_2\text{MnO}_3$  domain size, shape and dispersion. DIFFaX simulations and Rietveld refinements to synchrotron X-Ray diffraction patterns are used to confirm the TEM results with a statistically reliable bulk method.

The EC characteristics of the first cycle have been evaluated with respect to an EC active  $\text{Li}_2\text{MnO}_3$  component. By comparing the EC features of materials with  $x = 0.3$ ,  $x = 0.5$  and  $x = 0.7$ , it is evident that a composition of  $x = 0.5$  is the most promising. To point out the impact of the pristine nano structure on the EC performance, three samples with  $x = 0.5$  but considerable different nano domain arrangement, are compared. A strong influence has been found, with the highest discharge capacities for nano composites with small and evenly dispersed  $\text{Li}_2\text{MnO}_3$  domains.

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## 1. Introduction

Li-rich layered cathode materials (positive electrode) are a further development of the classic layered oxides  $\text{LiCoO}_2$  (LCO) and

its derivatives, such as  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  (NCM) and  $\text{Li}(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$  (NCA). The classic layered structures practically offer capacities between  $140 \text{ mAhg}^{-1}$  (LCO) and  $200 \text{ mAhg}^{-1}$  (NCA and NCM) due to their limited stability range for Li extraction [1,2]. The material class of Li-rich layered electrodes is in focus of research since they potentially provide an attractive specific capacity  $> 250 \text{ mAhg}^{-1}$  [3–5].

The classic layered structures are described by the R3m symmetry in which the 3a and the 3b sites of a cubic close packed (ccp) oxygen lattice are filled alternately with transition metal- (TM) and Li-ions [1,6].

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$\text{Li}_2\text{MnO}_3$  exhibits common structural features but with additional lithium sites on the TM-layer. The Li on the TM layer forms a honeycomb like superstructure with Mn reducing the symmetry to C2/m, resulting in loss of the three fold symmetry [7]. However, in single particles, domains of three different TM layer stacking sequences, equivalent to crystal rotations of  $120^\circ$  around the  $[103]_m$  axis (index m for monoclinic setting), are observed frequently. In case such rotational defect is limited to a single TM-layer, it can be described as stacking fault [4,8–10].

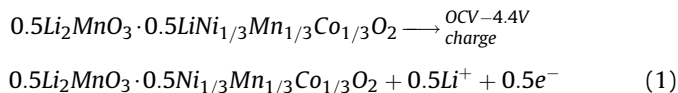
In Li-rich materials, the R3m and C2/m structures form a nano composite based on a coherent ccp-O-lattice with TM layer sequences of  $\text{Li}_2\text{MnO}_3$  and  $\text{Li(TM)O}_2$  character [3,11]. The structure of such materials is highly complex and depends on average composition and synthesis conditions. Several approaches can be found in literature to specify its pristine configuration, including the ongoing debate if the system should be regarded as solid solution or as composite structure [4,12–18].

The prevalent model for charge compensation during electrochemical delithiation (charging) is parallel oxidation of the TM and their reduction during lithiation (discharging) [19]. When used as cathode active ceramic in a lithium-ion battery (LIB), the EC-activity of NCM during charging is assigned to delithiation parallel to oxidation of  $\text{Ni}^{2+}$  and  $\text{Co}^{3+}$  to  $\text{Ni}^{4+}$  and  $\text{Co}^{4+}$ , respectively, while  $\text{Mn}^{4+}$  remains inactive. During discharge, the transition metals are reduced to their initial state ( $\text{Ni}^{2+}$  and  $\text{Co}^{3+}$ ) while the structure is lithiated [19–21].

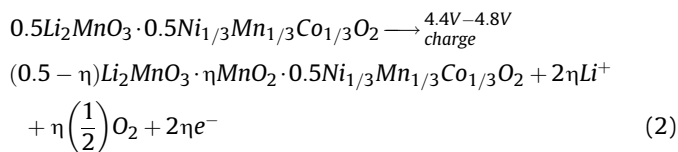
At moderate potentials  $\text{Li}_2\text{MnO}_3$  is EC-inactive, since  $\text{Mn}^{4+}$  cannot be oxidized to higher states in this system. By raising the potential to values higher than 4.5 V, lithium can be extracted, accompanied with an irreversible removal of oxygen from the system [5,22]. During this process, EC-active layered-like manganese dioxide is formed [23]. This structural transformation seems to be facilitated by planar crystal defects [24].

The charge-profile of Li-rich nano composites during the activation cycle can be divided into two parts: Firstly, by raising the potential to 4.5 V, the TM of the layered component are oxidized to 4+ and Li is extracted. In the second stage, the profile shows an extended plateau at approximately 4.5 V, similar to pure  $\text{Li}_2\text{MnO}_3$ , which is connected to oxygen loss and  $\text{MnO}_2$  formation [25–27]. According to Tran et al., the Li-sites on the TM-layer are filled by migrating TM cations from the particle surface, leading to a densification of the structure and the formation of layered-like  $\text{LiMnO}_2$  in the bulk [27]. The discharge profile exhibits similar features as for layered structures, while a high irreversible capacity loss is detected. Yu et al. proposed a reaction mechanism describing irreversible capacity loss and  $\text{LiMnO}_2$  formation [28]:

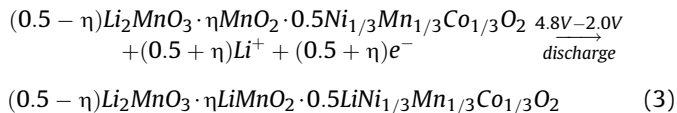
Oxidation of transition metals:



Activation of  $\text{Li}_2\text{MnO}_3$  phase and oxygen loss:



Lithiation and  $\text{LiMnO}_2$  formation:



According to this reaction mechanism, the maximum amount of formed  $\text{LiMnO}_2$  can be estimated by the irreversible capacity loss.

Most important, Li-rich nano composites show anomalously high discharge capacities in the first cycle that exceed the contributions of redox active TM. This surplus in capacity can be estimated by using Equation (1)–(3) to calculate the capacity provided by redox active TM and subtracting it from the overall discharge capacity. To explain the anomalous capacity, an EC-active  $\text{Li}_2\text{MnO}_3$  component needs to be considered with the oxygen lattice as anionic redox partner during EC-cycling [29–33].

The scope of this publication is to investigate the impact of pristine nano composite arrangement and composition of Li-rich NCM on first cycle EC-characteristic when used in a LIB.

A similar approach has been published before by McCalla and Li et al. [34,35]. By analyzing XRD patterns, they classified their material as single phase or layered-layered nano composite, with the outcome that a nano composite configuration negatively influences the EC performance. For the results presented in this publication, only  $\text{Li}_2\text{MnO}_3$ -NCM layered-layered nano composites have been investigated.

Therefore, three Li-rich NCM with the same nominal composition of  $0.5\text{Li}_2\text{MnO}_3:0.5\text{NCM}$  and two samples with  $0.3\text{Li}_2\text{MnO}_3:0.7\text{NCM}$  and  $0.7\text{Li}_2\text{MnO}_3:0.3\text{NCM}$  composition have been fabricated and first cycle characteristics of the active materials were measured in coin cells. Depending on synthesis route and composition, hereafter the samples will be called MS55, CP55-1, CP55-2, CP37 and CP73, where MS and CP stands for molten salt and coprecipitation synthesis route, respectively, and the first and second number indicate the ratio of  $\text{Li}_2\text{MnO}_3$  to NCM of the nominal composition. The nano composite structure of the pristine particles has been analyzed by transition electron microscopy (TEM). Complementary structural data of the pristine bulk material were recorded by synchrotron X-ray diffraction (XRD). The structural features are then correlated with features of the voltage profiles.

## 2. Experimental

### 2.1. Synthesis

MS55: The MS55 ( $0.5\text{Li}_2\text{MnO}_3:0.5\text{NCM}$ ) material was prepared via the molten-salt method using stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  (5% excess of lithium to compensate for any evaporative lithium losses during the calcinations) and the Ni–Co–Mn oxide (Ni: Co: Mn molar ratio of 0.13: 0.13: 0.54) in a KCl molten-salt flux (melting point,  $780^\circ\text{C}$ ) based on the previous work [36,37]. The mole ratio between the eutectic mixture and the Ni–Co–Mn oxide was fixed at 4:1. After well mixing, the mixture was placed in an alumina crucible, heated to  $800^\circ\text{C}$  for 10 h in air in a box furnace at a heating rate of  $5^\circ\text{C min}^{-1}$ , and was then allowed to cool to room temperature naturally. Finally, the product was washed with distilled water several times and filtered, and the powder was dried in air in an oven at  $120^\circ\text{C}$  for 24 h. The (Ni–Co–Mn) $\text{CO}_3$  precursor was prepared via a coprecipitation method. A 2 M aqueous solution of  $\text{NiSO}_4$ ,  $\text{CoSO}_4$ , and  $\text{MnSO}_4$  (Ni: Co: Mn molar ratio of 0.13: 0.13: 0.54) was pumped into a 2 M aqueous solution of  $\text{Na}_2\text{CO}_3$  that contained

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