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Tailoring high-voltage and high-performance $LiNi_{0.5}Mn_{1.5}O_4$ cathode material for high energy lithium-ion batteries

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HIGHLIGHTS

- $LiNi_{0.5}Mn_{1.5}O_4$ is obtained via in continuous co-precipitation synthesis.
- The material shows high tap-density, controlled particle size and architecture.
- Additional thermal treatments allow controlled stoichiometry variations.
- Additional annealing allows controlled crystallites growth.
- Ordered material with small crystallites and particles give the best performance.

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ABSTRACT

Increased specific capacity and/or working potential are important prerequisites for high energy functional materials for lithium-ion batteries. Furthermore practical applications require materials with high tap density in order to maximize the loading of the electrodes, thereby optimizing the energy density on cell level.

Stoichiometric and phase pure $LiNi_{0.5}Mn_{1.5}O_4$ (LMNO) has been synthesised via a continuous co-precipitation and lithiation process, suited for large scale production. Powder properties have been controlled in order to obtain spherical particles consisting of a multitude of densely-packed primary crystallites. The obtained material exhibits a single plateau at 4.7 V vs. Li/Li^+ with high capacity, rate capability and cycling stability.

Morphological factors such as crystallite size, particle size and particle architecture, and additionally the variation of oxygen stoichiometry have been investigated. This study clearly illustrates the importance of these factors on the electrochemical performance of an optimized LMNO high-voltage material.

1. Introduction

Li-ion batteries are the most promising energy storage systems for electric vehicles (EV) and hybrid plug-in electric vehicles (HPEV) [1,2]. The first commercially available Li-ion battery system used $LiCoO_2$ as cathode material [3]. Nowadays, state of the art cathode materials are $LiMn_2O_4$ (LMS), $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC), $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA) and $LiFePO_4$ (LFP). Key issues for new generation cathode materials are cost reduction, availability of raw materials, environmental benignity, and increase in energy density and safety.

Increasing the energy density is one of the main targets for automotive applications. Improvements in this direction can be achieved by either optimizing cell architecture and/or exchanging the electrochemically active materials.

On cell level, optimising cell architecture means reducing the amount of inactive components which is mainly a task of engineering. Methods to achieve this include using thinner current collectors and lightweight cans, and increasing electrode loading. Powder density and processability are important factors in selecting the active materials for production.

On material level, the chemical composition and the structure of the active materials are key parameters in altering functional properties and increasing energy density. Two main concepts lead to higher energy density on material level. The first concept targets increasing the specific capacity. This is mainly applied to the class of layered oxides by increasing the nickel content or introducing

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Li_2MnO_3 domains into the crystal structure represented by the nickel-rich and the lithium-manganese-rich layered oxides respectively [4].

The second concept focuses on increasing the working potential by exchanging the electrochemically active transition metal in a given structure. This concept applies to the phospho-olivine-group (e.g. by exchange of Fe^{2+} in LFP with Mn^{2+} and Co^{2+}) and in the substituted spinel-type materials $LiM_xMn_{2-x}O_4$ (where M = Fe^{3+}, Ni^{2+}, Cr^{3+}, Co^{3+} …). Compared with the high-voltage phospho-olivines, the spinel materials show higher rate capability and stability [5–8]. Among these materials, the nickel-substituted spinel (LMNO) is the most promising candidate as high-voltage cathode material [9–12]. It follows the general formula $LiNi_xMn_{2-x}O_{4-\delta}$. The exchange of one lithium/electron per formula unit leads to a specific capacity of 147 mAh g^{-1}. Both nickel content "x" and oxygen stoichiometry "δ" can be varied within certain limits with significant impact on the electrochemical behaviour of the material. The formula $Li[Ni(II)_xMn(III)_{1-2x+2\delta}Mn(IV)_{1+x-2\delta}]O_{4-\delta}$ describes the distribution of the formal oxidation states in LMNO. Lithium extraction/insertion can occur at two different voltage plateaus, the length of which depends on the values of "x" and "δ": a) the plateau at 4.1 V vs. Li/Li^+ is assigned to the Mn^{3+}/Mn^{4+} redox pair, providing $(1-2x+\delta)$ electrons/lithium per formula unit; b) the plateau at 4.7 V vs. Li/Li^+ relates to the Ni^{2+}/Ni^{4+} redox pair contributing $(2x-2\delta)$ electrons/lithium per formula unit. The fully substituted stoichiometric phase is reached for a maximum nickel content of $x = 0.5$ which, in combination with ideal oxygen stoichiometry $\delta = 0$, leads to $Li[Ni(II)_{0.5}Mn(IV)_{1.5}]O_{4.0}$. In this case, one single high-voltage plateau at 4.7 V vs. Li/Li^+ is obtained. All manganese ions are formally present in the tetravalent state thereby avoiding ageing phenomena related to the presence of trivalent manganese in the structure. Typical effects are manganese dissolution and impact of lattice distortion due to the Jahn-Teller effect [13–16].

The aim of this work was to tailor an innovative LMNO to achieve maximum energy density in cell applications. This process involves the optimisation of stoichiometry, crystallite size and order, particle architecture and powder density. The synthesis is targeted to the stoichiometric composition $Li[Ni(II)_{0.5}Mn(IV)_{1.5}]O_{4.0}$, which leads to the highest energy density [Wh kg^{-1}] in the LMNO system: full lithium insertion/extraction takes place on a single high-voltage plateau related to the complete utilisation of the Ni(II)/Ni(IV) redox-step. A densified powder was engineered by optimisation of the synthesis route and parameters of a highly reproducible and scalable process. The particle size and shape were tailored in order to meet the same technical specifications of commercially available layered oxide materials.

On crystal level we explored the effects of size and oxygen stoichiometry on the electrochemical performance. This was done by applying additional thermal treatments on the pristine material. All the materials were characterized in depth.

In this paper the relationships between these parameters are shown for the pure material using half-cells. The behaviour in full cells and related ageing phenomena, as well as safety issues will be reported elsewhere.

2. Experimental

The LMNO materials were synthesised using a co-precipitation process followed by thermal treatment. The precursors are obtained by combining aqueous solutions of ammonia, nickel and manganese nitrates in alkaline environment. The relative amount of nickel and manganese in the solution was adjusted in order to obtain a ratio of 1:3 in the final precipitate. The precipitation step was performed in a continuous stirred tank reactor. A stoichiometric amount of lithium hydroxide was used to lithiate the precursors. The thermal treatment was performed under air with a final annealing step at 700 °C (sample LMNO-0).

Table 1
Results of the ICP analysis: metal content in LMNO-0, LMNO-T1, LMNO-T2, and LMNO-T3.

	Thermal treatment	Li [wt.%]	Mn [wt.%]	Ni [wt.%]
LMNO-0	Annealing 700 °C	4.03	47.31	16.86
LMNO-T1	800 °C – Annealing 700 °C	4.09	47.05	16.89
LMNO-T2	800° – slow cool down	4.11	47.63	16.85
LMNO-T3	800° – quenching	4.14	47.60	17.04

Three heat-treatments in air were applied in order to modify the oxygen stoichiometry and the crystallite size of the material:

i) Re-calcination of LMNO-0 at 800 °C for 5 h and cooling to 700 °C within 1 h, followed by annealing at 700 °C for 48 h; then passive cooling down to 100 °C in the oven (LMNO-T1). Target: to increase crystallite size and maintain ideal oxygen stoichiometry.
ii) Re-calcination of LMNO-0 at 800 °C for 1 h and cooling down at a rate of 1.6 °C min^{-1} (LMNO-T2). Target: to introduce a low number of oxygen vacancies.
iii) Re-calcination of LMNO-0 at 800 °C for 5 h with subsequent quenching to room temperature (LMNO-T3). Target: to introduce a high number of oxygen vacancies.

The chemical composition of these materials was determined by ICP-OES analysis using a Spectrometer-System Spectro Arcos SOP. Structural properties were investigated by X-ray powder diffraction XRD (Cu Kα radiation, 0.154 nm) with a Siemens D5000 diffractometer between $10° \leq 2\theta \leq 100°$ using a step size of 0.03° (2θ) and 16 s $step^{-1}$ counting time. The program TOPAS 2.1 from Bruker was used to analyse the obtained XRD patterns.

Scanning electron microscopy (SEM) images were taken using a LEO 1530 VP.

The particle size distribution was determined by laser diffraction on a Mastersizer MICRO analyser from Malvern Instruments.

Tap-densities were measured in a JEL Stampfvolumeter STAV 2003.

The electrodes for the electrochemical tests were prepared

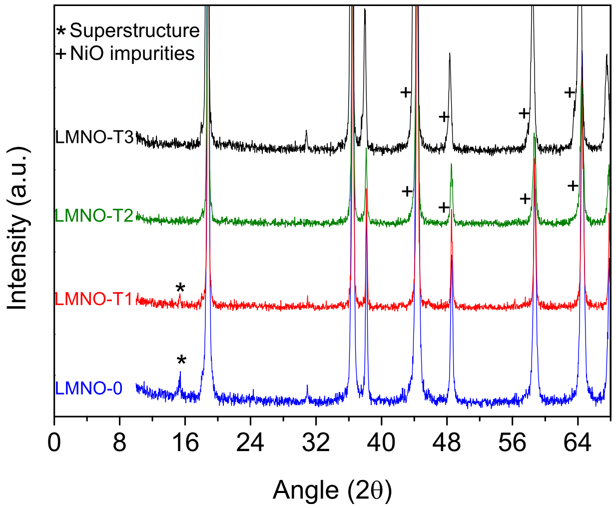

Fig. 1. XRD diffraction pattern: comparison between LMNO-0, LMNO-T1, LMNO-T2, LMNO-T3.