



# Synthesis, electrochemical investigation and structural analysis of doped Li $[\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2-x}\text{M}_x]\text{O}_2$ ( $x = 0, 0.05$ ; $M = \text{Al, Fe, Sn}$ ) cathode materials



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## HIGHLIGHTS

- Introducing of a new dopant (Sn) for Ni-rich NMC cathode materials.
- Lower lattice expansion during delithiation due to Sn-doping.
- Enhanced cycle life of Sn-doped cathode material.

## ARTICLE INFO

### Keywords:

Ni-rich Nickel Cobalt Manganese Oxide  
Cationic substitution  
Structural investigation

## ABSTRACT

Layered Ni-rich Li $[\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2-x}\text{M}_x]\text{O}_2$  cathode materials ( $x = 0, 0.05$ ;  $M = \text{Al, Fe, Sn}$ ) are synthesized via a co-precipitation synthesis route and the effect of dopants on the structure and electrochemical performance is investigated. All synthesized materials show a well-defined layered structure of the hexagonal  $\alpha\text{-NaFeO}_2$  phase investigated by X-ray diffraction (XRD). Undoped Li $\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  exhibits a discharge capacity of 170  $\text{mAh g}^{-1}$  in Li-metal 2032 coin-type cells. Doped materials reach lower capacities between 145  $\text{mAh g}^{-1}$  for Al and 160  $\text{mAh g}^{-1}$  for Sn. However, all doped materials prolong the cycle life by up to 20%. Changes of the lattice parameter before and after delithiation yield information about structural stability. A smaller repulsion of the transition metal layer during delithiation in the Sn-doped material leads to a smaller expansion of the unit cell, which results in enhanced structural stability of the material. The improved structural stability of Sn-doped NMC cathode active material is proven by thermal investigations with the help of Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

## 1. Introduction

The main objectives in the research and development of lithium ion batteries (LIBs) are to increase the energy density, cycle life and safety while reducing the costs. The characteristics of the LIB active materials play a major role for the electrochemical performance and intrinsic safety of the cell [1–5]. Well-known lithium-cobalt-oxide (LCO) cathode materials provide a theoretical capacity of 274  $\text{mAh g}^{-1}$  [6,7]. Nevertheless, it is so far impossible to fully exploit this high capacity due to a structural instability of the O3-type structure at lithium extraction degrees beyond  $x \approx 0.5$  in  $\text{Li}_{1-x}\text{CoO}_2$  resulting in a practical capacity of 140  $\text{mAh g}^{-1}$  vs.  $\text{Li/Li}^+$  [8]. Moreover, due to the high cobalt content, LCO is toxic and expensive. For these reasons, further developments of cathode active materials for (auto-) mobile and stationary energy storage applications are necessary.

Just like LCO, Lithium-Nickel-Manganese-Cobalt-Oxide (LNMC, or in short NMC) has a layered structure. The  $M$ - and the Li ions are occupying the octahedral coordinated positions in a cubic closed packed oxygen-grid, respectively. In [111]-direction of the cubic structure the lithium ions are located in between the  $\text{MO}_2$ -layers. In this layered structure, the diffusion of the lithium ions takes place two-dimensionally between the grid-space in  $a$ - and  $b$ -direction resulting in a high lithium ion mobility.

In the last years, NMC cathode materials are in the focus of research interest [9,10]. Compared to LCO, NMC can be charged to higher cut-off potentials, due to the presence of  $\text{Mn}^{4+}$ , which stabilizes the structure and supplies higher practical capacities ( $> 160 \text{mAh g}^{-1}$ ) than LCO at lower costs [11–14]. NMC is considered as a very promising material type to increase the energy density of LIBs. However, with higher energy densities challenges concerning cycle life, thermal

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stability and safety come along. An increase of the Ni content in NMC cathode materials provide a rise in energy densities. Nevertheless, due to side reactions at the surface during re-charge or storage under high temperature, the capacity fading accelerates [15–17]. Furthermore, materials with high Ni content have a lower thermal stability and release high amounts of heat in case of strong Li-depletion [18]. In addition, transition metal dissolution takes place, in particular at elevated charge cut-of potentials and voltages [19,20].

To counteract electrochemical degradation and to increase intrinsic cell safety, the structural integrity of cathode materials during repeated lithium ion insertion and extraction must be preserved. The structural instability of the electrode materials is a main reason for capacity loss of Ni-rich cathode materials [21–25]. The most promising approach to stabilize the cathode structure is “doping” of metal ions into the host structure; doping actually refers to cation substitution.

A common approach to select an appropriate doping metal is based on consideration of the bond dissociation energies between the metal and oxygen ions in the  $MO_6$  octahedron. A high bond dissociation energy provides a better structural stability and thus hinders oxygen release, which is an inevitable process during structural decomposition of NMCs [26]. Common doping elements are Al, [27–31] Mg, [32,33] Ti, [34,35] Cr, [36] Ga, [33,37] and Fe [30,31]. In general, the discharge capacity decreases with increased concentration of the doping element, while the structural stability grows [21,38]. The doping primary takes place through the substitution of Co by another element, due to several drawbacks of Co like the politically and economically unstable production countries, the high costs as well its toxicity [39]. Moreover, the substitution of Ni or Mn are not preferable because Ni provides high capacities and Mn maintains the structure stability [40].

In this study, the structural and electrochemical properties of a Ni-rich NMC-622 ( $LiNi_{0.6}Mn_{0.2}Co_{0.15}M_{0.05}O_2$ ) cathode material are analyzed for the dopants  $M = Al, Fe$  and  $Sn$ . Therein,  $Sn$  as a novel doping element for the NCM-622 is introduced.  $Sn$  is non-toxic and less expensive than  $Co$ , combines a high bond dissociation energy of  $548 \text{ kJ mol}^{-1}$  ( $368 \text{ kJ mol}^{-1}$  for  $Co-O$ ) [41] and a ionic radius of  $r = 69 \text{ pm}$  (similar to the transition metal ions  $Ni^{3+}$  ( $60 \text{ pm}$ ) and  $Co^{3+}$  ( $61 \text{ pm}$ )) [42]. It is investigated in comparison to  $Al$  ( $512 \text{ kJ mol}^{-1}$ ) [41], which is commonly used as doping element due to its stabilizing effects of the cathode material and  $Fe$  ( $409 \text{ kJ mol}^{-1}$ ) [41], which is a well-known doping element from the literature as well [31,43–45]. The content of substitution amounts 5%, which is considered as a good compromise between electrochemical performance and structural stability.

## 2. Experimental

### 2.1. Synthesis and chemical delithiation of the active materials

The active materials  $Li[Ni_{0.6}Mn_{0.2}Co_{0.2-x}M_x]O_2$  ( $x = 0, 0.05$ ;  $M = Al, Fe, Sn$ ) were synthesized via a co-precipitation method [46]. As starting compound  $NiSO_4 \cdot 6H_2O$ ,  $MnSO_4 \cdot H_2O$ ,  $SnSO_4 \cdot H_2O$  (all from Sigma Aldrich, USA; purity  $\geq 95\%$ ),  $CoSO_4 \cdot 7H_2O$ ,  $Al(NO_3)_3 \cdot 9H_2O$ ,  $Fe(NO_3)_3$  (all from Acros, USA; purity  $\geq 98\%$ ) and  $NaOH$  (Merck, Germany; purity  $\geq 97\%$ ) were used. A 100 mL aqueous solution of metal sulfates and metal nitrates in a stoichiometric ratio (total concentration equal to 2 M) and 100 mL of a 2 M solution of  $NaOH$  with a desired amount of  $NH_3$  (Sigma Aldrich, USA; 25%  $NH_3$  based  $NH_4OH$ ) were added continuously at a pH of 11 in a flask with 50 mL distilled water. After 18 h of stirring, the precipitate was washed several times and dried in air at  $80^\circ\text{C}$  overnight. The dried precipitate was ground in an agate mortar, then mixed with a stoichiometric amount of  $LiOH$  (Sigma Aldrich, USA; purity  $\geq 98\%$ ) and ground in an automatic ball mill (Fritsch, Germany; Pulverisette 4 ‘classic’). The mixed materials were calcinated in a muffle furnace from Nabertherm (Germany; P300) first at  $480^\circ\text{C}$  for 5h and finally at  $850^\circ\text{C}$  for 10h in air, yielding the desired products. For the delithiated phases  $Li[Ni_{0.6}Mn_{0.2}Co_{0.2-x}M_x]O_2$  ( $x = 0,$

$0.05$ ;  $M = Al, Fe, Sn$ ),  $Li$  was chemically extracted using a stoichiometric amount of  $Na_2S_2O_8$  (Acros, USA; purity  $\geq 98\%$ ) in  $H_2O$  at room temperature.

### 2.2. Electrode and cell preparation

The active materials were mixed with Super C65 carbon black (Imerys, Switzerland) and polyvinylidene fluoride binder (Solvay, Belgium; PVdF, Solef 6020) solved in N-Methyl-2-pyrrolidone (Carl Roth, Germany; NMP, purity  $\geq 99\%$ ) in a weight-to-weight ratio of 90:5:5% and coated on an Al foil (33 wt% solid content). After drying overnight in air at  $80^\circ\text{C}$ , electrodes were punched and dried again under vacuum at  $120^\circ\text{C}$  for 17h. Before assembling 2032-type (Hohsen, Japan; 2 spacers ( $0.5 \text{ mm} + 0.3 \text{ mm}$ ), 1 spring ( $0.7 \text{ mm}$ )) coin Li-metal/cathode cells (Lithium from Albemarle, battery-grade, USA) in a dry room (dew point:  $-65^\circ\text{C}$ ) the electrodes were pressed with 8.5 tones for 15 s. The used electrolyte was 1 M  $LiPF_6$ , in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC) [1:1] (BASF, Germany) and a six layer non-woven polypropylene fleece (Freudenberg, Germany; FS2226) was functioning as separator.

### 2.3. Powder X-Ray diffraction

Powder X-ray Diffraction (PXRD) studies were done with a D8 advanced device from Bruker (Germany) with a non-chromatic  $Cu-K\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) in the  $2\theta$  range of  $10^\circ$ – $90^\circ$  in Bragg-Brentano geometry to examine the synthesized materials for impurity phases and lattice constants which were calculated using the TOPAS software (Bruker AXS, Germany; Academic Version 4.2).

### 2.4. Electrochemical investigations

Constant current/constant voltage cycling was performed with a Series 4000 Battery Tester from Maccor (USA) at room temperature. The cell studies were performed by two different procedures in the voltage range of 2.5 and 4.3 V. The first one includes increasingly higher discharge current rates (C/10, C/2, 1C, 5C; each 5 cycles) with a constant current (CC) charge step of C/20 and subsequent cycling over 20 cycles with CC charge and a constant voltage discharge (CV) step until a rate of C/10 was reached. With the second cycling procedure, the cycling stability was investigated up to a state of health of 80% (SOH-80%). For cycling, CC charge and discharge were executed at a rate of 1C with a CV step during charge: the CV step was stopped when the rate decreased below C/100. The cycling experiment ended when the discharge capacity decreased to 80% of the initial capacity.

### 2.5. Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was performed using a TGA Q5000 device from TA Instruments (USA; V3.17 build 265). The helium (Westfalen AG, Germany; purity 6.0) flow rate at the sample was set to  $25 \text{ mL min}^{-1}$ . After equilibration at  $30^\circ\text{C}$ , the sample was heated to  $650^\circ\text{C}$  with a rate of  $10 \text{ K min}^{-1}$  in an alumina pan and the weight loss and the corresponding derivative weight under inert atmosphere were obtained. The weight after  $150^\circ\text{C}$  was used as an initial weight for calculation of the mass loss.

Exclusively samples in the delithiated state after charging to 4.3 V in coin-type Li-metal/cathode cells were investigated. Therefore, the cells were disassembled and the cathode electrodes were washed with 1.5 mL DMC to remove residuals from the electrolyte and the conducting salt and finally dried and punched in 4 mm pieces.

### 2.6. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measurements were realized using a DSC Q2000 device from TA Instruments (USA; V24.11

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