



A mixed mechanochemical-ceramic solid-state synthesis as simple and cost effective route to high-performance $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinels.



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ABSTRACT

The implementation of high potential materials as positive electrodes in high energy Li-ion batteries requires to develop scalable and smart synthetic routes. In the case of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) spinel material, a successful preparation strategy must drive the phase formation in order to obtain structural, morphological and surface properties capable to boost performances in lithium cells and minimize the electrolyte degradation. Here we discuss a novel simple and easily scalable mechanochemical synthetic route, followed by a high temperature annealing in air, to prepare LMNO materials starting from oxides. A synergic doping with chromium and iron has been incorporated, resulting in the spontaneous segregation of a CrO_x -rich surface layer. The effect of the annealing temperature on the physico-chemical properties of the LMNO material has been investigated as well as the effect on the performances in Li-cells.

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1. Introduction

High potential positive electrode materials are in the spotlight of the current R&D efforts in the lithium-ion battery field [1–3]. Among the most promising materials, the lithium nickel manganese spinel (LNMO) deserves a special attention thanks to its environmental friendliness, low cost and interesting electrochemical performances [4,5]. It has the operating voltage at 4.7 V vs Li^+/Li , high good electronic and lithium ion conductivities, does not suffer of critical structural deformations upon cycling and has a good thermal stability [6]. The main weakness attributable to LNMO is related to its interaction with the electrolyte at high voltage, which can bring to corrosion reactions and electrolyte degradation, and finally to the progressive capacity fade [7].

LNMO can crystallize according to a cations ordered cubic structure, $\text{P4}_3\text{32}$, or a cations disordered one, Fd-3m [8,9]. Although both the ordered and disordered spinels have been demonstrated in lithium cells, the disordered one has been

reported to be more electron and Li^+ conductive, thanks to the presence of Mn^{3+} in its lattice, which is contemporary responsible of an electron hopping conduction mechanism and of the enlargement of the cell volume enabling faster lithium diffusion [6]. The crystallization according to the $\text{P4}_3\text{32}$ or Fd-3m space group is driven by the annealing temperature, being disorder favored by high temperature ($< 700^\circ\text{C}$) [10,11].

As recently reviewed by Yi [8], large efforts are spent worldwide to improve the performance and stability of LNMO. In particular structural tuning, morphological control, elemental doping and surface coating have been proposed as successful strategies to address the main limitation of LNMO electrodes [8,12–14].

A tailored synthesis is the key to control both structure and morphology [5,11,15]. Solid-state synthesis is the conventional and easier preparation route for LNMO spinels, but it does not allow any control on particle growth and aggregation [5]. Indeed, uniformly distributed small particles are highly desired in order to enhance electron conductivity and Li^+ diffusion. This goal has been achieved using co-precipitation or hydrothermal synthesis, which undoubtedly introduce complexity and costs at the large scale [8].

Doping is the most widely strategy adopted to improve electronic and ionic conductivity of LNMO [6,8,12]. One of the most promising dopant is iron, which besides being inexpensive

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and environmental friendly, is able [12,16,17] (i) to stabilize the cation disordered structure, (ii) to promote the Mn^{3+} formation, (iii) to suppress the accumulation of a thick solid-electrolyte interfacial (SEI) layer due to the spontaneous Fe-enrichment and Ni-deficiency on the surface, and finally (iv) to reduce the polarization loss arising from both fast charge transfer kinetics and lithium ion diffusion kinetics in the bulk [8]. Similar beneficial effects are also obtained by using chromium as doping element [18–21] with the additional results of limiting/suppressing the precipitation of the nickel oxide particles that is apparently unavoidable in the stoichiometric undoped LNMO spinel [5].

Particles surface coating is an effective strategy to mitigate the high voltage reactivity between the spinel and the electrolyte and limiting manganese and nickel dissolution [7,22]. Oxides, phosphates and fluorides are the materials most frequently proposed [6,8]. Indeed, the easy and low cost technique to produce a uniform and continuous particles coating has still to be developed.

The way to obtain a definitive improvement in LNMO performances would probably be a combination of all the above mentioned strategy, i.e. structure and morphology control, elemental doping and surface coating. However, this combined synthetic strategy may have a detrimental impact on the scalability and cost-feasibility.

In the present study, LNMO spinel has been synthesized from oxides, according to an easy mixed mechanochemical-ceramic solid-state route, also incorporating a synergic Cr- and Fe co-doping. In particular, High Energy Ball Milling (HEBM) has been used to mix and pretreat reagents, in order to improve powders reactivity and obtain the spinel phase with a finely tuned and very mild thermal treatment. High energy ball milling (HEBM) is a cost-effective and environmental friendly power processing technique, in which powder mixtures are subjected to repeated energy transfer phenomena carried out by hitting balls. The kinetic energy of the balls transferred to the powders induces several physico-chemical phenomena such as particles size reduction, formation of new active surfaces, induction of a high level of elastic shears and other stresses, increase of lattice defectivity. All these phenomena can turn into amorphization, crystallization, and even reaction to produce stable or metastable phases. Nevertheless, due to the impulsive nature of the energy transfer, HEBM is a “non equilibrium” process, giving rise to materials often characterized by enhanced reactivity [23–28]. This method allows an easy and reproducible synthesis with a quantitative final yield. The final optimized material is a disordered Fd–3m LNMO spinel doped with Fe(III) centers and coated with an amorphous CrO_x -rich layer. This synthetic route produces a final material with homogeneous morphology and exceptional electrochemical performance in terms of cycle life and rate capability.

2. Experimental

The Fe- and Cr-doped lithium nickel manganese spinel has been synthesized according to a mixed mechanochemical-ceramic solid-state route. Weighted amounts of metal oxides (i.e. Mn_2O_4 , NiO, Fe_2O_3 and Cr_2O_3) and $\text{LiOH}\cdot\text{H}_2\text{O}$ were introduced into a stainless steel vial in a 1.4:0.5:0.1:0.01:1.1 molar ratio for Mn, Ni, Fe, Cr and Li, respectively. Lithium reagent has been added with a 10% molar excess to supply eventual loss at high temperatures. Stainless steel balls with diameters of 10 mm were used in order to keep a powder to balls ratio 1:20. An overall milling of 5 hours has been carried on in a Spex Shaker M8000, alternating 30 minutes of milling with 15 minutes of rest in order to avoid massive overheating. In order to study the thermal annealing process at the end of the mechanochemical treatment the powder has been recovered and its thermal evolution to spinel phase has been studied by X-ray diffraction. This dynamic high temperature XRD

study was carried out by means of a simultaneous 120° angular dispersion Ital Structures X-ray diffraction apparatus ($\text{FeK}\alpha$) equipped with an Anton Paar reactive chamber and curved PSD INEL detector. A step heating procedure was programmed: the sample was heated at $10^\circ\text{C}/\text{min}$ for 5 minutes and left 10 min dwell before collecting isothermal 10 min XRD pattern.

Three samples obtained at different annealing temperatures (i.e. 600, 800 or 1000°C for 1 hour under air) were prepared by using controlled heating/cooling rates of $10^\circ\text{C}/\text{min}$. The obtained products were stored in close vials and characterized as prepared. No additional post-synthesis chemical or physical treatment was carried out. Samples have been labeled as LNMO_600, LNMO_800, and LNMO_1000, according to their annealing temperature. Stoichiometry has been checked dissolving few milligrams of each sample and analyzing diluted solution by Atomic Absorption Spectrophotometer (AAS) contraA[®] 300–Analytik Jena AG. Structure has been studied by XRD using a Rigaku Ultima+ Diffractometer ($\text{CuK}\alpha$). Morphology has been investigated by scanning electron microscopy (SEM – LEO 130 HRSEM) and transmission electron microscopy (TEM – FEI Tecnai cryo-HRTEM apparatus). Fourier Transformed Infra-Red Spectroscopy (FTIR) has been carried out thanks to a JascoFTIR-300. The X-ray photoelectron spectra (XPS) of the samples were recorded by a concentric hemispherical analyzer (CHA) and 9-channel detection in ultra-high vacuum (UHV) with a base pressure below 10^{-9} Torr by employing Al-K source (1486.7 eV) operating at 10 kV and a constant pass energy with an overall resolution of 0.7 eV. All binding energy values were charge-corrected to the adventitious C (1s) signal which was set at 285.1 eV [29]. Samples have been loaded into the XPS instrument spread onto a fluorinated polymeric tape on an aluminum stub.

Thin film electrodes were then prepared on Aluminum foils by casting a dispersion of the active materials, 10% of Super P carbon (conducting agent, Timcal) and 10% PVdF (binder, Solef, 6020) in N-methyl pyrrolidone (NMP, Aldrich). The resulting 40 μm thick films were cut into 10 mm diameter disks and dried at 50°C under vacuum to remove the residual solvent previous to lithium cell assembly. The average mass loading of the electrode film was $3.1 \pm 0.2 \text{ mg cm}^{-2}$. Half cells were prepared by coupling the electrode under study with a lithium foil (Chemetall, thickness 200 μm , counter and reference electrode) and a glass fiber separator (Whatman) imbibed by the LP30 electrolyte solution (1 M LiPF_6 in Ethylene Carbonate, Dimethyl Carbonate, 1:1 v:v, BASF). The galvanostatic cycling tests were carried out by using a Maccor series 4000 battery tester and R2032 coin-type cells, assembled in an argon-filled glovebox (H_2O and O_2 content less than 1 ppm). Cells were cycled at different current rates, increasing current from 100 mA g^{-1} (0.68C) to 1000 mA g^{-1} (6.8C). Bearing in mind that the theoretical capacity of the LNMO spinel is 146 mAhg^{-1} , the 1C current rate has been fixed to 146 mA g^{-1} .

3. Results and Discussion

3.1. Materials properties: structure and morphology

During our syntheses apparently no reaction occurs during HEBM: the powder is simply strongly pulverized and mixed to give a highly reactive mixture, capable to easily evolve into the desired spinel phase in very mild annealing conditions. Fig. 1 shows the XRD pattern evolution of the reagents mixture upon heating.

The starting material, after HEBM, is constituted by the original mixture of the reagents. Upon heating, under the adopted dynamic conditions, the conversion to spinel starts at 300°C and it is almost complete at 550°C . As temperature increases further, spinel peaks become more intense and no impurities can be detected. At 800°C , the grown of a new peak at about 55.8° highlights the reversible

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