



Short communication

Synthesis and electrochemical performance of the high voltage cathode material $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ with improved rate capability

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ABSTRACT

The high voltage layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ cathode material, which is a solid solution between Li_2MnO_3 and $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$, has been synthesized by co-precipitation method followed by high temperature annealing at 900°C . XRD and SEM characterizations proved that the as prepared powder is constituted of small and homogenous particles (100–300 nm), which are seen to enhance the material rate capability. After the initial decay, no obvious capacity fading was observed when cycling the material at different rates. Steady-state reversible capacities of 220mAh g^{-1} at 0.2C, 190mAh g^{-1} at 1C, 155mAh g^{-1} at 5C and 110mAh g^{-1} at 20C were achieved in long-term cycle tests within the voltage cutoff limits of 2.5 and 4.8 V at 20°C .

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1. Introduction

Layered transition metal oxides have been investigated extensively as cathode materials for lithium-ion batteries. There into, LiCoO_2 is the most important commercial material because of its very good electrochemical performance. However, on the other hand, it also suffers some drawbacks, such as high cost, toxicity, and safety problems, which inhibit its further use in hybrid and pure electric vehicles [1–3]. The identification of a cheaper, higher capacity and safer layered cathode materials has been the focusing point in the study of cathode materials in the last decade. In this regard, the solid solutions of layered Li_2MnO_3 and LiMO_2 (M = Mn, Co, Ni, etc.) have been shown as promising candidates for cathode materials in lithium ion batteries since they exhibit a relatively high capacity, low cost and improved safety [2,4–11]. Two members of this family, $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.6}\text{Ni}_{0.2}]\text{O}_2$, which can be indicated as $0.6\text{Li}_2\text{MnO}_3 \cdot 0.4\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, and $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ (also indicated as $0.6\text{Li}_2\text{MnO}_3 \cdot 0.4\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$), are widely investigated already. Usually, these materials deliver an initial capacity of about 250mAh g^{-1} within the potential range extending from 2.0 to 4.8 V [8–12]. Between them, $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ always shows better performance because of the presence of cobalt that significantly reduce the

electrode polarization and improve the activation of the Li_2MnO_3 component, even if present in a small amount [13,14]. Nevertheless, the long-term cycling performance of this latter material is still not very satisfactory. In addition, it still contains 13 mol% of Co, which certainly represents an issue with regard to cost. Finally, most of the works on these materials report the electrochemical performance at very low current rates (such as C/20), which is of no help to ascertain their capability of matching with the requirement of today's lithium ion batteries.

In this work, we report on the synthesis and characterization of a novel cathode material with a substantially lower Co content. The material has a general formula of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$, which can also be seen as the solid solution of Li_2MnO_3 and $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ in 6:4 molar ratio. The structure, physical properties and electrochemical performance are reported in the following, with a special attention to the rate capabilities at high current rates.

2. Experimental

$\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ was synthesized by a solid-state reaction method from lithium hydroxide hydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$, Aldrich >98%) and manganese–nickel–cobalt hydroxide precursor [15]. This precursor was prepared by co-precipitating the aqueous solution of the three metal acetate salts (Mn, Ni, and Co; Aldrich >98%) in a stoichiometric ratio of 56:16:8, with lithium hydroxide. After extensive rinsing with distilled water, the precipitate

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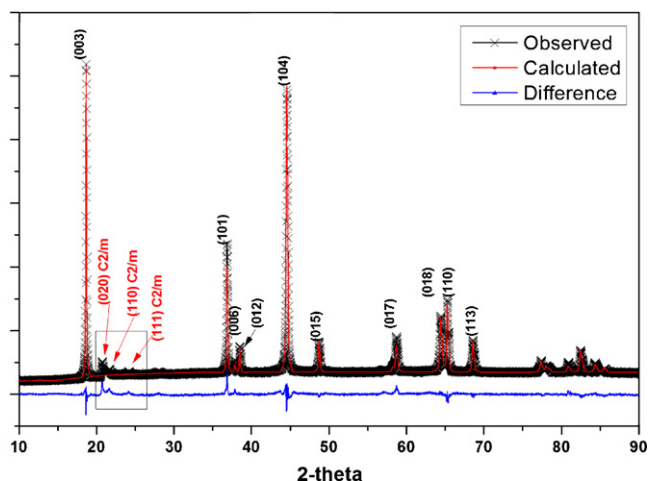


Fig. 1. Rietveld refinement results for the XRD pattern of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ material by GSAS.

was dried under vacuum at 120°C overnight. The dried material was then mixed with a stoichiometric amount of $\text{LiOH}\cdot\text{H}_2\text{O}$ by ball milling for 5 h in the zirconia jar. After suitable grinding, the mixture was annealed in air at 480°C for 5 h, and then, as a pellet, at 900°C for 24 h. The final material was obtained by quenching the pellet in liquid nitrogen in order to “freeze” the layered solid-solution phase.

The composition in terms of lithium and transition metal contents in the active material was determined by the inductively coupled plasma optical emission spectrometry (ICP-OES, SPECTRO ARCOS, Ametek, Germany). The crystalline structure was characterized by X-ray diffraction (XRD) using the $\text{Cu K}\alpha$ radiation on the Bruker D8 Advance (Germany) in the 2θ range from 10° to 90° . Lattice parameters were determined by Rietveld refinement with GSAS software. The particle size distribution was evaluated with the help of a high resolution Scanning Electron Microscopy (SEM, EVO[®] MA 10 microscope, Zeiss). The BET surface area and solid phase density were measured by using the ASAP 2020 and the AccuPyc II 1340 from Micromeritics Instrument Corporation (USA).

Electrodes were prepared by casting the slurry, with the composition of 80 wt% active material (by weight), 10 wt% Super P (TIMCAL), and 10 wt% PVDF (Kynar[®] FLEX 2801, Arkema Group), onto Al foil. The electrode active material mass loading was about 2 mg cm^{-2} while the thickness (after pressing at $3\text{--}4\text{ tons cm}^{-2}$ for 30 s) was $10\text{ }\mu\text{m}$. With metal lithium foil as the counter and reference electrodes, the cathode electrodes were assembled into swagelok cells with the 1 M LiPF_6 in 1:1 EC:DMC solution as the electrolyte. Cells were cycled galvanostatically at different constant current rates (nominal capacity = 200 mAh g^{-1} , $1\text{C} = 200\text{ mA g}^{-1}$) between 4.8 V and 2.5 V at 20°C using Maccor series 4000 battery tester (USA). All potential reported in this work refer to the Li/Li^+ couple.

All experiments, including synthesis, were duplicated to check reproducibility.

3. Results and discussion

Fig. 1 shows the XRD pattern and the Rietveld refinement results of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$. The values of χ^2 (4.926) and Rwp (9.9%) demonstrate a satisfactory refinement. With the exclusion of the low intensity reflections, in particular those within 20° and 25° , the crystal lattice was approximated as signed to the layered structure with space group of $R\bar{3}m$ [3], the intensity ratio of the (003) and (104) peaks (equal to 1.11), and the clear splitting of the (108) and (110) peaks suggest an ordering structure of $R\bar{3}m$ single phase.

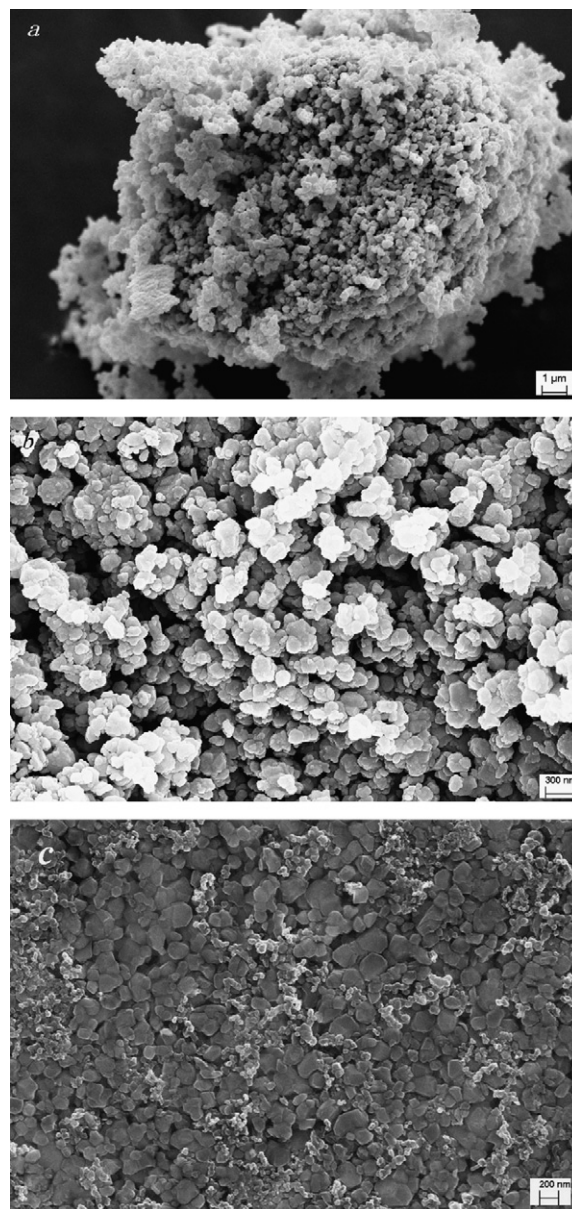


Fig. 2. SEM pictures of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ material at different magnifications. (a) $\times 5\text{k}$; (b and c) $\times 50\text{k}$.

The hexagonal lattice parameters were refined to be $a = 2.8560(1)\text{ \AA}$, $c = 14.283(2)\text{ \AA}$, and volume = $100.65(2)\text{ \AA}^3$, with a c/a ratio of 4.99. The weak reflections are known to originate from the monoclinic Li_2MnO_3 -like (C2/m) super lattice [16], which correspond to the ordering of the Li^+ , Ni^{2+} , and Mn^{4+} ions in the transition metal layer [17].

The ICP-OES analysis indicated the molar ratio of Li and the transition metal ions to be $\text{Li}:\text{Mn}:\text{Ni}:\text{Co} = 1.21:0.53:0.17:0.09$, i.e., in good agreement with the composition of the starting reactants. The crystallite size was calculated from XRD by using the Scherrer's formula [1] for the three main reflection peaks, e.g. (003), (101) and (104). The average result is 89 nm which is smaller than that of the pure $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ prepared with the same annealing conditions [18].

The morphology of the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ particles and pressed electrode, investigated by scanning electron microscopy, is shown in Fig. 2. The SEM image in Fig. 2a shows that the powder contains aggregates of primary, round sharp particles. These primary particles, which are better observed in

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