



Synthesis and characterization of a new layered cathode material for sodium ion batteries



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HIGHLIGHTS

- $\text{Na}_{2/3}\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$ by a sol gel method.
- This layered material adopts the P2-type structure as revealed by the Rietveld analysis.
- This cathode delivers a reversible discharge capacity of 110 mAh g^{-1} with an excellent capacity retention.
- Up to 140 mAh g^{-1} could be reached if cycled between 2.0 and 4.5 V.

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ABSTRACT

Owing to the high abundance of sodium and its low cost compared to lithium, sodium ion batteries have recently attracted a renewed interest as possible candidates for stationary and mobile energy storage devices. Herein, we present a new sodium ion intercalation material, $\text{Na}_x\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$, which has been synthesized by a sol–gel route in air followed by a heat treatment at 800°C for 12 h. Its structure has been studied by X-ray diffraction showing that the material crystallized in a P2-type structure (space group $\text{P6}_3/\text{mmc}$). As far as the electrochemical properties of $\text{Na}_x\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$ as positive electrode are concerned, this compound offers a specific capacity of 110 mAh g^{-1} when cycled between 2.0 and 4.2 V vs. Na^+/Na . The electrodes exhibited a good capacity retention and a coulombic efficiency exceeding 99.4%, as well as a reversible discharge capacity of 140 mAh g^{-1} when cycled between 2.0 and 4.5 V. These results represent a further step towards the realization of efficient sodium ion batteries, especially considering that the synthesis method proposed here is simple and cost effective and that all the electrochemical measurements were carried out without any use of additives or any optimization for both the materials and the cell components.

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1. Introduction

Sodium ion batteries were initially studied alongside with lithium ion (Li-ion) cells in the 80's [1–5]. However, the latter technology has been more investigated, due to the fact that lithium is the lightest metallic element and possesses the lowest redox potential ($E_{(\text{Li}^+/\text{Li})} = -3.04 \text{ V vs. SHE}$) among solids, which confers to Li-ion batteries a high voltage and an intrinsic high energy density. Besides, the small ionic radius of Li^+ typically enables a smooth

diffusion through most of the solids. Therefore, these favourable properties, coupled to the electrolyte–electrode interface problems in the case of sodium ion batteries, made the researchers focus exclusively on Li-ion cells.

Li-ion batteries are now the most common rechargeable technology in portable electronic devices and they are also regarded as possible candidates for powering future generations of hybrid and plug-in hybrid electric vehicles. In addition to the use of lithium in batteries, which represents 25–30% of its global consumption [6], this alkaline metal is also used in many other fields, thus increasing its demand each year. Therefore, the availability of lithium has attracted significant concerns lately, since it could become progressively more expensive and also because most of its natural sources are located in politically sensitive areas.

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The abundance and the low cost of sodium, as well as its suitable redox potential ($E_{(\text{Na}^+/\text{Na})} = -2.71$ V vs. SHE) have then made the electrochemical energy storage community to investigate once again Na-ion batteries as possible replacements for lithium ones. So far, a great number of compounds have been studied as positive electrode materials for sodium ion batteries, e.g. olivines, nasicon structures and also layered oxides, since their lithium counterparts are known for their commercial application as cathodes for Li-ion cells.

2D layered transition metal oxides NaMO_2 (with $M = \text{Co}, \text{Mn}, \text{Ni}, \text{Cr}, \text{Fe}$) have been studied as cathode materials for sodium ion batteries, even if their performance is not comparable to that of their lithium analogues. Nevertheless, they could still represent a further step towards the realization of sustainable sodium ion batteries, especially if combined in more cost-effective and simpler fabrications together with non-toxic and abundant materials for the remaining cell components [7]. Unlike LiMO_2 , NaMO_2 possess different crystal structures where Na is located either in octahedral or in prismatic sites between the layers of the transition metal octahedra MO_6 . These structures differ in the stacking of oxygen layers with ABCABC for O3, ABBA for P2 and ABBCA for P3 (O and P refer to the octahedral and prismatic sites of sodium, respectively) [3,8–15].

In particular, Na_xCoO_2 was investigated among these sodium oxides in 1980's demonstrating its feasibility as a cathode material for sodium ion batteries. Na_xCoO_2 crystallizes in different structures depending on the oxygen stoichiometry that depends on the oxygen pressure used during the synthesis and also on the Na amount which can vary depending on the synthesis conditions and the heat treatment temperature ($0.55 < x_{\text{Na}} < 0.60$ (P3); $0.64 < x_{\text{Na}} < 0.74$ (P2); $x_{\text{Na}} = 0.77$ (O3) and $x_{\text{Na}} = 1$ (O3)), where the P2-phase offers better cycle life and improved energy efficiency [2,5]. P2- Na_xCoO_2 has been reinvestigated [7,8] showing promising results with decent reversible capacity and cycleability. However, the intercalation/deintercalation of sodium ions in this material occurs by the existence of well defined steps in the voltage profile in the potential window 2.0–3.8 V vs. Na^+/Na . It has been reported in another work that the substitution of Co with Mn P2- $\text{NaCo}_{2/3}\text{Mn}_{1/3}\text{O}_2$ [13] stabilizes the structure, which exhibits only one voltage step at $x_{\text{Na}} = 0.5$ between 1.25 and 4.0 V, this being due to the coexistence of Co^{3+} and Mn^{4+} . However, neither the values of the capacity delivered by the material nor the coulombic efficiency were reported. The study of the structural and electrochemical properties of $\text{NaNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ was reported by Sathiya et al. [12]. This compound delivered 120 mAh g^{-1} at a current density of 12 mA g^{-1} between 2 and 3.75 V $\text{Na}_{0.63}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$, reported by Buchholz and al. [14] delivers a specific discharge capacity of 134 mAh g^{-1} at a current rate of 12 mA g^{-1} in the voltage range of 2–4.3 V. Similar compound with a slight difference in stoichiometry $\text{Na}_{0.67}\text{Mn}_{0.65}\text{Co}_{0.2}\text{Ni}_{0.15}\text{O}_2$ was reported by Yuan et al. [15]. A specific discharge capacity of 141 mAh g^{-1} was delivered by this electrode material when cycled between 2 and 4.4 V. These three compounds display high discharge capacities with good capacity retention and good rate capability. Thus, the coexistence of cobalt, manganese and nickel in the transition metal layers gives these materials their good electrochemical performances.

In this work, we have synthesized a new material, P2- $\text{Na}_x\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$, by a sol gel route, in order to improve the structural and electrochemical behaviour of NaCoO_2 where we assume the coexistence of Co^{3+} , Mn^{4+} and Ni^{2+} [16]. The choice of substituting Co with Mn and Ni actually comes from previous works done in our group on lithium analogues [16–19] which gave excellent specific discharge capacities, low polarization and extensive cycle life. Indeed, the electrochemical study of this material proves that the Na^+ intercalation/deintercalation process is reversible and

proceeds smoothly, thus demonstrating that the addition of both manganese and nickel with this stoichiometry stabilizes the structure. At the same time, this approach successfully improved the properties of the material leading to a good capacity retention during cycling and providing a high coulombic efficiency. Therefore, P2- $\text{Na}_x\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$ represents a new candidate for sodium ion batteries as a positive electrode material.

2. Experimental

$\text{Na}_x\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$ was synthesized by a sol gel route using sodium, cobalt, manganese, and nickel acetates in the molar ratio of 0.7:0.66:0.22:0.11 with 5% excess of sodium. The stoichiometric amounts of the precursors were mixed in distilled water and then stirred for 2 h before adding the chelating agent, which here was citric acid. The mixture was kept at 80°C under constant stirring until a homogeneous gel was obtained. The latter was dried over night at 110°C in order to obtain a powder. The resulting powder was ball milled and further heat-treated in a furnace at 800°C for 12 h under air. After this, the material was stored in an Ar-filled glove box ($\text{H}_2\text{O}, \text{O}_2 < 1 \text{ ppm}$).

The composition of the material $\text{Na}_x\text{Co}_{2/3}\text{Mn}_{2/9}\text{Ni}_{1/9}\text{O}_2$ was measured using Inductively Coupled Plasma (ICP) emission spectroscopy (Spectro Ciros ccd) in terms of sodium and transition metal contents. The crystalline structure of the synthesized material was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer equipped with $\text{Cu K}\alpha$ radiation. The XRD pattern was collected in the 2θ range of $10\text{--}90^\circ$ in a continuous scan mode with a step size of 0.01° and a constant counting time of 10 s. Lattice parameters were refined using a typical Rietveld method implemented in the FullProf program [20]. The powder morphology and the size distribution of the particles were observed by high resolution scanning electron microscopy (HR-SEM) using a Zeiss Leo 1550 scanning electron microscope equipped with a X-MAX EDX probe (Oxford Instruments) for elemental analysis. Infrared (IR) measurements were carried out via a Perkin–Elmer Spectrum One FT-IR spectrometer equipped with an attenuated total reflectance (ATR) probe. The resulting spectra were collected in the wavenumber range spanning from 650 to 3000 cm^{-1} .

For the electrochemical measurements, the positive composite electrodes were prepared by mixing 75 wt% of the active material with 15 wt% of carbon black (Super P) conductive additive and 10 wt% of polyvinylidene fluoride (PVDF) binder using *N*-methyl-2-pyrrolidone (NMP) as solvent. The slurry was then casted on an Al foil and dried at 60°C for 3 h in a convection oven. The electrodes were cut into 20 mm disks by a precision perforator (Hohsen) and dried over night at 120°C in a vacuum oven within the Ar-filled glove box (M-Braun). The active electrode materials have an average weight of 5 mg. Sodium metal was used as both reference and counter electrode by cutting, rolling and pressing sodium lumps into thin plates. A thin membrane (Solupore) was used as separator between the sodium plate and the working electrode. The electrodes were assembled and vacuum-sealed in the Ar-filled glove box into “coffee-bag” (polymer laminated aluminium pouch) cells [21] with 0.5 M NaPF_6 electrolyte dissolved in PC (polycarbonate). All the electrochemical measurements were carried out at room temperature (25°C) via a VMP2 (Bio-Logic) equipment. The charge/discharge studies were performed galvanostatically at a current rate of $C/20$ (i.e. 12.6 mA g^{-1}), where a period of 20 h is required to remove one sodium ion. In particular, two different cut-off voltages were used: the first one between 2.0 and 4.2 V and the second one between 2.0 and 4.5 V. The rate capability test with different constant current rates, C/n (with $n = 20, 10, 5, 2, 1, 0.5$), was performed as well. Cyclic voltammetry (CV) measurements were carried out at a typical scan rate of

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