



# Characterization of $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$ solid solution for secondary lithium ion batteries

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## ABSTRACT

A Co–Mn–Mg co-substituted  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  solid solution was synthesized and characterized by XRD, XPS, SEM and its electrochemical performance was investigated. Potato-like ( $\sim 15\ \mu\text{m}$ ) single phase  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  compound was obtained and its crystal structure was analyzed by Rietveld refinements. XPS results showed that Ni, Co, Mn and Mg at the surface of  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  powder exist at +4, +3, +3 and +2 oxidation states respectively. And Ni in the bulk was also determined to occur as electrochemical-active  $\text{Ni}^{3+}$  ion, which is beneficial for high capacity electrode. The synthesized  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  can deliver a high initial discharge capacity of  $191.5\ \text{mAhg}^{-1}$  at 0.2C rate and more than 93% of the initial specific discharge capacity was retained after 50 cycles.

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## 1. Introduction

Due to its relatively low cost and high reversible capacity,  $\text{LiNiO}_2$  has been recognized as an attractive cathode material for secondary lithium ion batteries [1–4]. However,  $\text{LiNiO}_2$  is also known for its poor cycling characteristics resulted from its two major material defects: its tendency to non-stoichiometry caused by Li/Ni cations displacement during the synthesis process and its structural instability during lithium intercalation/de-intercalation process [2,5–7]. An ideal layered structure for  $\text{LiNiO}_2$  is possible if all Ni elements are oxidized to +3 oxidation state. But  $\text{Ni}^{3+}$  ( $r = 0.56\ \text{\AA}$ ) is unstable, most lithium nickelates would contain some of the larger  $\text{Ni}^{2+}$  ions ( $r = 0.69\ \text{\AA}$ ) even if they are synthesized under oxidizing conditions. The similarity in size between  $\text{Ni}^{2+}$  and  $\text{Li}^+$  ( $r = 0.72\ \text{\AA}$ ) favors a three dimensional rock salt type of structure over a two dimensionally layered structure [8,9]. It is important to remove  $\text{Ni}^{2+}$  from the lithium sites that retard the diffusion of  $\text{Li}^+$  to achieve a stoichiometric  $\text{LiNiO}_2$ . One possible way to alleviate the occupancy of  $\text{Ni}^{2+}$  cations in lithium sites is to partly replace  $\text{Ni}^{3+}$  (in LNO) by  $\text{Co}^{3+}$  [10–12]. However, from several existing literature reports, it is clear that only when the amount of  $\text{Co}^{3+}$  substitution reach 30% of the total metal ions can the problem of cation disorder be grossly overcome [13,14]. Accordingly, its reversible capacity declines to less than  $190\ \text{mAhg}^{-1}$ , which has been identified by previous studies [11,12]. Furthermore, the replacement of Ni with Co is limited by the relatively

high price of Co and therefore, there have been efforts to replace some parts of Ni with cheaper metals.

Doping  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  solid solution with inert cation dopants has been a popular approach to improve its structural stability and cyclability. Several dopants such as  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Al}^{3+}$  have been studied intensively [12–16]. These inert cations doped in the  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  solid solutions, especially in the nickel-rich samples ( $x = 0.1\text{--}0.3$ ), have shown the improved cyclability and stability [17,18]. Among them, Mg has drawn our special attention. In literature, the introduction of divalent Mg into  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  is shown to improve safety, cycling stability, rate capacity and duration of overcharge [19–21]. It is commonly accepted [2,9,17] that low concentration of Mg dopant ions in the lithium plane can act as pillars that provide extra structural stability. Additionally, Mg occupancy in Ni sites helps retain more Li in the charged state and stabilizes the  $\text{NiO}_2$  slabs [21]. However, the partial substitution of divalent Mg to trivalent transition metal Co/Ni forces the  $\text{Co}^{3+}/\text{Ni}^{3+}$  ions to be pre-oxidized to  $\text{Co}^{4+}/\text{Ni}^{4+}$  [22]. If in the  $\text{LiNiO}_2$  system,  $\text{Ni}^{4+}$  will be formed to keep the charge balance, which is electrochemical inactive and structural unstable, will lead to capacity loss and structural decomposition of the compounds.

With the expectation to obtain a cathode material of high capacity as well as good cyclability, a strengthened layered structure with low cations mixing of Li/Ni is desired. In this work, an equivalent amount of Mn and Mg have been introduced into the  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  solid solution to suppress the Li/Ni cations displacement and strengthen the layered structure. Mn ions, which are supposed to be at their +4 oxidation states, are chosen to avoid the pre-oxidation of  $\text{Ni}^{3+}$  ions caused by substitution of  $\text{Mg}^{2+}$ . The introduction of  $\text{Mn}^{4+}$  ions can also bring about positive effect on suppressing the Li/Ni cations displacement and help

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the synthesis of stoichiometric solid solution as reported [23,24]. In this paper,  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  was synthesized and its metal oxidation states, structure, morphology and electrochemical performance were investigated.

## 2. Experimental

The precursor samples were prepared by the continuous co-precipitation method using its corresponding metal salts, NaOH and  $\text{NH}_3\cdot\text{H}_2\text{O}$  as starting materials. The concentration of  $\text{NH}_3\cdot\text{H}_2\text{O}$ , feed rate, temperature and pH of the mixture in the reactor were all well controlled. Then the co-precipitated hydroxides were removed continuously from the reactor followed by washing and drying. The hydroxides take the form of a powdered spherical particles with an average size around  $15\ \mu\text{m}$  observed from SEM. Then a mixing procedure of  $\text{Ni}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}(\text{OH})_2$  sample and excess  $\text{LiOH}\cdot\text{H}_2\text{O}$  ( $\text{Li}/[\text{Ni} + \text{Co} + \text{Mn} + \text{Mg}] = 1.04$ ) was carried out and the mixture was heated at  $750\ ^\circ\text{C}$  for 12 h under a stream of oxygen to form the  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  compound. For comparative purpose,  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ ,  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.025}\text{O}_2$  and  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mg}_{0.025}\text{O}_2$  were also synthesized by the exactly identical process.

The synthesized compounds were characterized for their structural information by using X-Ray diffraction (XRD) (Rigaku  $\theta/\theta$  diffractometer with  $\text{CuK}\alpha$  radiation ( $r = 1.54056\ \text{\AA}$ )). XRD data were obtained at  $2\theta = 10\text{--}110(80)^\circ$ , with a step size of  $0.02^\circ$  and a constant counting time of 10 s. The XRD patterns were also refined for their structural information by using the Rietveld refinement technique with the aid of the refinement program GSAS [25]. X-ray photoelectron spectroscopy (XPS) (PHI5600 ESCAN system using  $\text{Mg K}\alpha$  radiation) was adopted to investigate the oxidation states of Ni, Co, Mn and Mg on the surface of the powder. Curve fittings of slow scanned XPS spectra were carried out using a non-linear least square fitting program with a Gaussian function. Furthermore, the proportion of  $\text{Ni}^{3+}$  in all the nickel content ( $[\text{Ni}^{3+}]/([\text{Ni}^{2+}] + [\text{Ni}^{3+}])$ ) in the bulk of powder was determined by titration method described in reference [5]. Chemical analysis was conducted by atomic absorption spectroscope (Zhimadu 6650, AA spectrophotometer). The morphological features and particle sizes were observed by scanning electron microscope (Hitachi X-650).

The charge/discharge tests were carried out at room temperature by assembling 2025-type coin cells with a lithium metal anode, working cathode and Celgard 2400 microporous membrane. The working cathode used is consisted of 80 wt.%  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2/\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ , 10% acetylene black and 10% PVDF binder. A  $1\ \text{mol L}^{-1}$  solution of  $\text{LiPF}_6$  dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v) was employed as the electrolyte. The cells were assembled in an Argon-filled glove box. The charge–discharge tests were then examined on a Land cell test system controlled by computer, cells were set to be charged and discharged between 4.3 and 2.8 V vs. metallic lithium at certain constant current density. Cyclic voltammograms measurements were done by a Solartron 1287 electrochemical interface between 2.8 and 4.5 V at a scan rate of 0.1 mV/s. The cells for impedance measurements were performed on charged states (4.3 V) and relaxed for 24 h. The frequency range was 0.001 Hz–100 kHz at alternating current (AC) signal amplitude of 10 mV.

## 3. Results and discussion

The electrochemical properties of the compounds are greatly influenced by the morphologies of the powders as the electrodes are surface film controlled system, because they develop rich surface chemistry that determines their charge transfer behavior [26]. In the nickel rich region of the  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  systems, potato-shape submicron-size powders are preferred to maintaining excellent cyclability [27–29]. The powder morphologies of  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  and

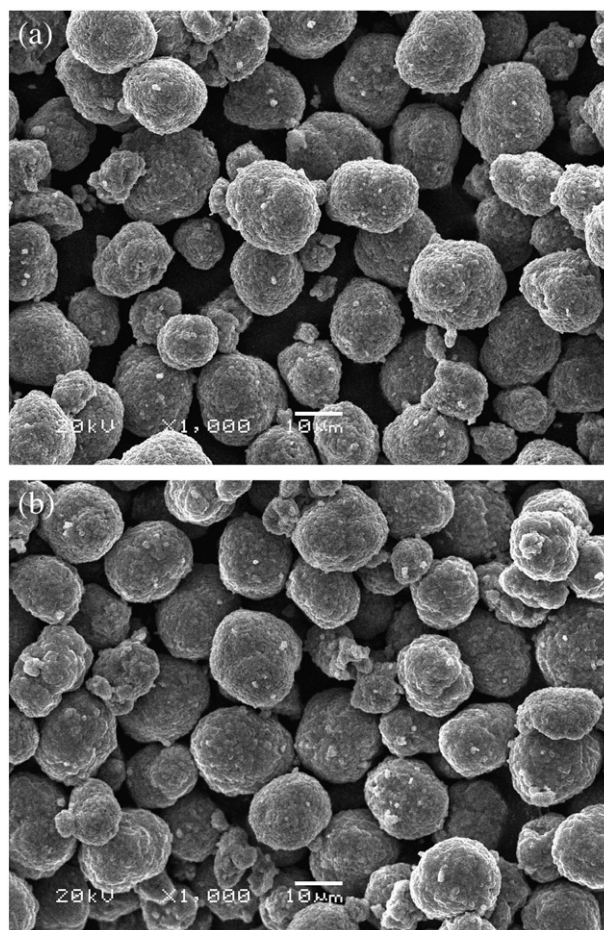


Fig. 1. SEM images of (a) –  $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.025}\text{Mg}_{0.025}\text{O}_2$  (b) –  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  powder.

$\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  synthesized here are shown in Fig. 1(a) and (b) respectively. It can be seen that the  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  powder consists of potato-shape secondary particles with an estimated average size of  $15\ \mu\text{m}$ . The  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  sample shares similar shape and size with  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$ , thus the impact of morphology on the electrochemical behavior can be roughly ruled out when comparing their electrochemical performances.

Table 1 shows the chemical compositions of the synthesized samples obtained from atomic absorption spectroscopy. The measured compositions of the materials are actually very close to the target compositions suggesting that the desired compounds have been successfully synthesized. And for this reason, the nominal compositions are used to describe the materials throughout this paper for simplicity.

Fig. 2 shows the XRD patterns of the as-prepared  $\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$  sample. In the X-ray diffraction spectra, all diffraction lines can be indexed to space group  $R\bar{3}m$ . No other diffraction lines, asymmetries or shoulders are detected in the spectra meaning that the synthesized sample is of single phase with homogeneous

Table 1

Designated and observed chemical formulas of the samples measured by atomic absorption spectroscopy.

Designated chemical formula	Analyzed chemical formula
$\text{LiNi}_{0.9}\text{Co}_{0.05}[\text{Mn}_{1/2}\text{Mg}_{1/2}]_{0.05}\text{O}_2$	$\text{Li}_{0.996}\text{Ni}_{0.899}\text{Co}_{0.051}\text{Mn}_{0.024}\text{Mg}_{0.026}\text{O}_2$
$\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$	$\text{Li}_{0.978}\text{Ni}_{0.898}\text{Co}_{0.12}\text{O}_2$
$\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.025}\text{O}_2$	$\text{Li}_{0.987}\text{Ni}_{0.9}\text{Co}_{0.051}\text{Mn}_{0.025}\text{O}_2$
$\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mg}_{0.025}\text{O}_2$	$\text{Li}_{0.989}\text{Ni}_{0.9}\text{Co}_{0.052}\text{Mg}_{0.026}\text{O}_2$

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