

# Physical and electrochemical properties of spherical $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$ cathode materials<sup>☆</sup>

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## Abstract

A  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{CO}_3$  precursor with a uniform, spherical morphology was prepared by coprecipitation using a continuously stirred tank reactor method. The as-prepared spherical  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{CO}_3$  precursor served to produce dense, spherical  $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$  ( $0 \leq x \leq 0.15$ ) cathode materials. These Li-rich cathodes were also prepared by a second synthesis route that involved the use of an  $\text{M}_3\text{O}_4$  ( $\text{M} = \text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}$ ) spinel compound, itself obtained from the carbonate  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{CO}_3$  precursor. In both cases, the final  $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$  products were highly uniform, having a narrow particle size distribution (10- $\mu\text{m}$  average particle size) as a result of the homogeneity and spherical morphology of the starting mixed-metal carbonate precursor. The rate capability of the  $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$  electrode materials, which was significantly improved with increased lithium content, was found to be better in the case of the denser materials made from the spinel precursor compound. This result suggests that spherical morphology, high density, and increased lithium content were key factors in enabling the high rate capabilities, and hence the power performances, of the Li-rich  $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{1-x}\text{O}_2$  cathodes.

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## 1. Introduction

$\text{LiCoO}_2$  is the most widely used cathode material in commercial lithium secondary batteries because of its easy mass production and reliable rechargeability with respect to the Li-ion cells that power consumer electronics. However, the toxicity and high cost of cobalt pose major obstacles that will limit its application in large-scale batteries, such as those

intended to power hybrid electric vehicles (HEVs). Recently,  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  material has been proposed as an alternative to  $\text{LiCoO}_2$  cathode material, mainly because of the former's higher reversible capacity and enhanced thermal stability [1–5].

The need for mass production of this promising cathode material has suggested adoption of the solid-state reaction method, which has advantages over other methods, especially from the standpoint of economics. However, in the case of the  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  material, the solid-state reaction method has led to impure phases, with none providing satisfactory cell performance [6]. Therefore, new preparation methods that allow for a better cationic distribution control are needed in order to eliminate secondary phases and improve the electrochemical behavior of the phases obtained. For this purpose, the coprecipitation method has been widely adopted as a preferred method to obtain mixed transition-metal hydroxide precursors with spherical morphologies. However, mixed transition-metal hydroxides containing Ni, Co, and Mn simultaneously have been found to be unstable, because during or after the coprecipitation process the  $\text{Mn}(\text{OH})_2$  hydroxide can be easily segregated from the mixed

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hydroxide and oxidized to  $\text{MnOOH}$  and/or  $\text{Mn}_3\text{O}_4$  phases. Here, we introduce a coprecipitation method for the preparation of a dense, spherical  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{CO}_3$  carbonate precursor using a continuously stirred tank reactor (CSTR) method. Unlike hydroxide coprecipitation, the carbonate coprecipitation method has the advantage of keeping the oxidation states of Ni, Co, and Mn constant (equal to 2) by the fixation of  $\text{CO}_3^{2-}$  anion groups. These carbonate precursors were used to obtain dense, spherical, lithium-rich  $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  materials with different Li contents. The physical and electrochemical properties of these advanced cathode materials are discussed in the light of their morphological, structural, and density characteristics.

## 2. Experimental approach

Spherical  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{CO}_3$  carbonate precursor was first synthesized by coprecipitation from a solution containing nickel, cobalt, and manganese sulfates by the addition of sodium carbonate solution and ammonia as a chelating agent solution. A 2.0 M aqueous solution of  $\text{NiSO}_4$ ,  $\text{CoSO}_4$ , and  $\text{MnSO}_4$  (Ni:Mn:Co = 1:1:1 molar ratio) was pumped into a CSTR Reac-

tor with a 4-L capacity. At the same time, a 2.0 M aqueous solution of  $\text{Na}_2\text{CO}_3$  and a 0.2 M  $\text{NH}_4\text{OH}$  solution were independently fed into the reactor. The pH of the solution inside the reactor, maintained at 7.5, was carefully controlled by the addition of the  $\text{Na}_2\text{CO}_3$  solution. A stirring speed of 1000 rpm was maintained throughout the coprecipitation process. The collected  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{CO}_3$  powder was washed, filtered, and then dried inside an oven at  $100^\circ\text{C}$  for several hours. Stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  were added to the as-prepared carbonate sample and thoroughly mixed, and then the mix was calcined at  $900^\circ\text{C}$  for 20 h to obtain  $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  ( $0 \leq x \leq 0.15$ ) powders. We also obtained these final samples, under the same thermal conditions, by reacting stoichiometric quantities of lithium carbonate and  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_3\text{O}_4$  oxide. The latter was obtained at  $600^\circ\text{C}$  after the thermal decomposition of the  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{CO}_3$  carbonate precursor.

Powder X-ray diffraction (XRD) patterns of the synthesized materials were collected using a Siemens D5000 diffractometer (Cu  $\text{K}\alpha$  radiation). The structural parameters were obtained by the Rietveld refinement method using the FullProf 2000 program [7]. The morphological features and particle size of the elec-

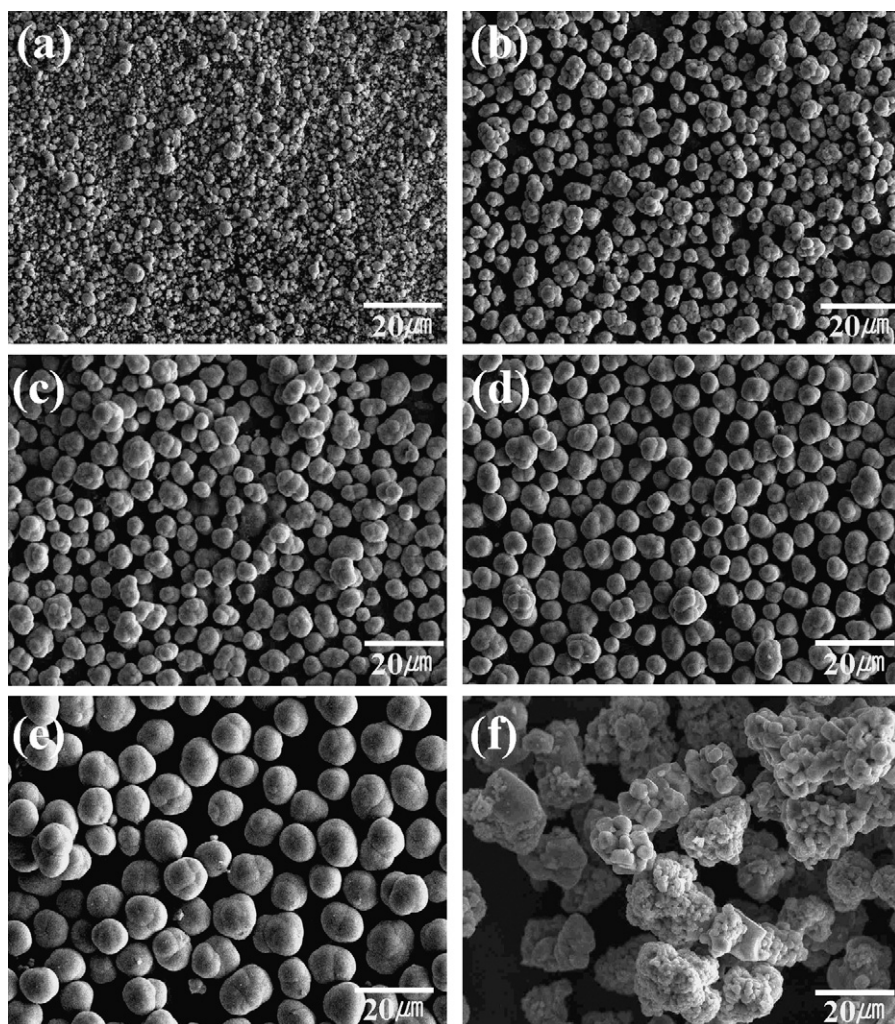


Fig. 1. Scanning electron micrographs of  $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{CO}_3$  powder collected at various reaction times: (a) 1 h, (b) 3 h, (c) 5 h, (d) 7 h, (e) 9 h, and (f) 9 h without  $\text{NH}_4\text{OH}$ .

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