Spinel LiNi_{0.5}Mn_{1.5}O_4 cathode for rechargeable lithium-ion batteries: Nano vs micro, ordered phase (\textit{P}4_{3}32) vs disordered phase (\textit{Fd}\overline{3}m)

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ABSTRACT

Since the high-voltage spinel LiNi_{0.5}Mn_{1.5}O_4 (LNMO) is one of the most attractive cathode materials for lithium-ion batteries, how to improve the cycling and rate performance simultaneously has become a critical question. Nanosizing is a typical strategy to achieve high rate capability due to drastically shortened Li-ion diffusion distances. However, the high surface area of nanosized particles increases the side reaction with the electrolyte, which leads to poor cycling performance. Spinels with disordered structures could also lead to improved rate capability, but the cyclability is low due to the presence of Mn^{3+} ions. Herein, we systematically investigated the synergic interaction between particle size and cation ordering. Our results indicated that a microsized disordered phase and a nanosized ordered phase of LNMO materials exhibited the best combination of high rate capability and cycling performance.

1 Introduction

There is increasing interest in developing new cathode materials with high energy and power density for rechargeable lithium-ion batteries that have potential applications in large-scale energy storage and electric vehicles (EV) [1, 2]. Spinel LiNi_{0.5}Mn_{1.5}O_4 (LNMO) is particularly attractive because of its moderate capacity and high-voltage plateau (~4.7 V vs. Li+/Li) offering theoretically 20% higher energy density relative to conventional LiCoO_2 cathode materials [3–5]. In addition, LNMO has advantages including low cost, less environmental impact, and inherent high Li^{+} diffusivity within the three-dimensional channels of the spinel structure [6]. However, it remains challenging to achieve simultaneously satisfactory capacity, cyclability and rate performance, since the electrochemical properties of LNMO-based materials intimately depend on interrelated physicochemical parameters such as structure, composition, particle shape and size, and surface area [7–17].

LNMO spinels have two types of crystal structure,
namely the ordered $P4_{3}32$ phase and the disordered $Fd3m$ phase, depending on the ordering of Ni/Mn in the octahedral sites [8]. In the $P4_{3}32$ space group, Ni and Mn are located in an ordered fashion in the octahedral $4b$ and $12d$ sites, respectively, with the Li ions occupying the $8c$ sites and O ions in $8c$ and $24e$ sites. For the $Fd3m$ phase, Ni and Mn are randomly distributed in the $16d$ sites, with the Li and O ions occupying the $8a$ and $32e$ sites, respectively [9]. Previous investigations indicate that the cycling and rate performances of the disordered LNMO are superior to that of the ordered one due to higher Li$^+$ diffusion coefficients [5, 7], whereas experimental and computational studies have also shown that the ordered spinel exhibits excellent cyclability and high-rate capability [11]. In addition, an order–disorder phase transition of LNMO usually occurs on material annealing, being associated with a loss/gain of oxygen and generation/evanescence of Mn$^{3+}$ due to charge neutrality constraints [9]. The presence and content of Mn$^{3+}$ have been demonstrated to intricately affect the electrode performance [5]. On the one hand, the larger ionic radius of Mn$^{3+}$ relative to Mn$^{4+}$ results in an expanded lattice, which benefits fast Li$^+$ diffusion [15]. On the other hand, Mn$^{3+}$ can induce a Jahn–Teller structural distortion and dissolve into the electrolyte via a disproportionation reaction, which has an adverse effect on the capacity retention [18]. Furthermore, particle shapes and sizes of electrode materials are known to play a critical role in determining their electrochemical properties [18–25]. Creating nanostructures is a popular strategy to increase the rate capability due to the drastic reduction of Li$^+$ diffusion lengths [26, 27]. High rate capability and excellent cyclability have been attained for LNMO nanoparticles [16]. However, the occurrence of side reactions with the electrolyte due to the increased surface areas of nanoparticles has attracted increasing attention [28–30].

Therefore, the factors influencing the electrochemical performance should be synergistically taken into consideration for the development of advanced spinel cathodes. With this in mind, we have systematically investigated a series of LNMO materials. Herein, we focus on two dominating factors, the phase (structure and composition) and the particle morphology (size, shape and surface area). Four representative LNMO samples with similar particulate morphology have been synthesized without treatment such as cation doping or surface coating: a micro-sized $P4_{3}32$ phase (LNMO-MP), a micro-sized $Fd3m$ phase (LNMO-MF), a nanosized $P4_{3}32$ phase (LNMO-NP), and a nanosized $Fd3m$ phase (LNMO-NF) (Fig. 1). We attempt to identify the parameters that are critical in achieving optimal electrochemical performance including capacity, rate capability, and cyclability.

![Figure 1](image URL) A schematic illustration of the preparation of LNMO-NP, LNMO-NF, LNMO-MF, and LNMO-MP.

## 2 Experimental

### 2.1 Materials synthesis

The LNMO series were synthesized by a polyethylene glycol (PEG)-assisted co-precipitation method as shown in Fig. 1. In a typical synthesis, analytical reagent grade LiCH$_3$COO·2H$_2$O, Ni(CH$_3$COO)$_2$·4H$_2$O, and Mn(CH$_3$COO)$_2$·4H$_2$O in the molar ratio of 1.04:0.5:1.5 and in quantities corresponding to 0.9 g of LNMO were dissolved in 20 mL of water. The solution was heated to 50 °C and then 3 mL of PEG 400 was added. Under constant magnetic stirring, 4.5 g of tartaric acid was added to the solution. Then the solution was heated to 85 °C to afford a green viscous precursor.

The precursor was calcined at 700 °C or 900 °C in air for 10 h to obtain the nano-ordered (LNMO-NP) or micro-disordered (LNMO-MF) products, respectively. The as-prepared nano-ordered material was further