



High energy spinel-structured cathode stabilized by layered materials for advanced lithium-ion batteries



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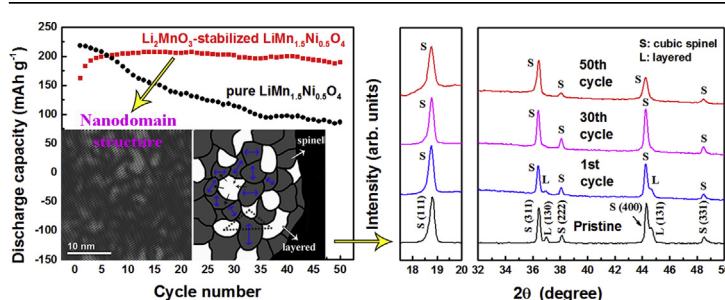
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HIGHLIGHTS

- Li_2MnO_3 nanodomains are embedded in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ matrix by co-precipitation method.
- $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ shows significantly improved cycling stability.
- Jahn–Teller distortion has been successfully suppressed with nanodomain structure.
- $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ shows promise for high energy density Li-ion batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to well-known Jahn–Teller distortion in spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, it can only be reversibly electrochemically cycled between 3 and 4.8 V with a limited reversible capacity of $\sim 147 \text{ mAh g}^{-1}$. This study intends to embed the layer-structured Li_2MnO_3 nanodomains into $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel matrix so that the Jahn–Teller distortion can be suppressed even when the average Mn oxidation state is below +3.5. A series of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1 are synthesized by co-precipitation method. The composites with intermediate values of $x = 0.1, 0.2, 0.3, 0.4$ and 0.5 exhibit both spinel and layered structural domains in the particles and show greatly improved cycle stability than that of the pure spinel. Among them, $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ delivers the highest and almost constant capacity after a few conditional cycles and shows superior cycle stability. Ex-situ X-ray diffraction results indicate that no Jahn–Teller distortion occurs during the cycling of the $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ composite. Additionally, $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ possesses a high energy density of $\sim 700 \text{ Wh kg}^{-1}$, showing great promise for advanced high energy density lithium-ion batteries.

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1. Introduction

Developing high energy and high power lithium-ion batteries for applications in electric vehicles (EVs) and hybrid-electric vehicles (HEVs) has attracted great attention [1,2]. However, current

cathode materials, such as LiCoO_2 , LiMn_2O_4 and LiFePO_4 , cannot meet the requirements of high energy density due to their limited specific capacities [3]. To achieve high energy and high power densities, it is highly important to develop new cathode materials with a large specific capacity and high operating voltage for the next generation of lithium-ion batteries. In recent years, spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ has attracted substantial interest as high energy and high power cathode material due to its high operating voltage of about 4.7 V, good cycle performance, and good rate capability as a

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result of three-dimensional Li^+ ion diffusion channels [4–10]. $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel is fundamentally different from LiMn_2O_4 as all redox activity takes place on Ni with Mn theoretically remaining in 4+ state when cycled between 3 and 5 V, suppressing both Jahn–Teller distortion and Mn dissolution. In theory, the framework of $\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ can accommodate two moles of Li^+ with a specific capacity of about 294 mAh g^{-1} when Li ions are inserted into both 8a tetrahedral and 16c octahedral sites of the spinel lattice at the voltage of $\sim 4.7 \text{ V}$ and $\sim 2.8 \text{ V}$, respectively [11–15]. However, for Jahn–Teller distortion at 2.8 V associated with a cubic to tetragonal phase transition, although the degree of distortion in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ($c/a = 1.07$) is smaller than that of LiMn_2O_4 ($c/a = 1.16$), there is still a big volume change of about 5% [16–19]. It is believed that the phase transition induced strain is too large for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ grains to maintain structural integrity, thus resulting in fast capacity fading upon cycling. By far, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ can only be reversibly charged and discharged between 3 and 5 V with limited capacity of 147 mAh g^{-1} , which hinders the use of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ for high energy applications. In order to practically use the theoretical capacity of 294 mAh g^{-1} , Jahn–Teller distortion in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ needs to be further suppressed to make this material can be reversibly charged and discharged between 2 and 5 V with 2 Li^+ extraction/reinsertion. To achieve this, cation and/or anion dopings in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ have been employed to suppress the Jahn–Teller distortion with improved cyclic performance between 2 and 5 V. Alcántara et al. [12] reported that Mg-doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ exhibits a net improvement in capacity retention as Mg content increases when cycled in the 3 V region. Similarly, Lin et al. [15] reported that the Ti-doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ exhibits improved capacity retention compared to the undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ in the wide voltage region of 4.95–2.0 V. However, it is worth noting that both Mg- and Ti-doping at either Ni or Mn site significantly decrease the reversible capacity of materials and cannot completely solve the problems associated with Jahn–Teller distortion. As a result, the obtained reversible capacity and cycle performance are still far from the requirements for practical applications.

Inspired by recent achievements in substitution of structural units rather than cations or anions, improved structural stability has been demonstrated by Li_2MnO_3 stabilized layered LiMO_2 (M refers to transition metals) in a wide voltage window between 2 and 5 V [20–23]. Since Li_2MnO_3 is electrochemically inactive below 3 V [24], if the nano dimension Li_2MnO_3 structural units can be embedded in the spinel structure, such nanostructure units may be able to help accommodate stress from the Jahn–Teller distortion, leading to improved structural stability of the spinel in a wide voltage window between 2 and 5 V. Moreover, Li_2MnO_3 phase could be activated by extracting Li_2O from Li_2MnO_3 to yield electrochemically active MnO_2 at high voltage region and it will further contribute to the capacity of the composites. Despite the variation in crystallographic space group symmetry, $R\bar{3}m$ (trigonal) for LiMO_2 and $Fd\bar{3}m$ (cubic) for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, the structural compatibility in view of (001)_{monoclinic} [20] and (111)_{cubic} [25] lattice fringes [26] allows the integration of the Li_2MnO_3 nanodomains in spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ with the success in the layered–layered composites. Unlike layered–layered composite structure in which the (001) and (003) lattice fringes of the Li_2MnO_3 and LiMO_2 are coincident in the HRTEM, it is more readily to differentiate two structurally compatible layered and spinel components with this technique [20].

In this work, a series of layered-spinel $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ($x = 0.1, 0.2, 0.3, 0.4$ and 0.5) are prepared by co-precipitation method. We demonstrate that the layered Li_2MnO_3 nanodomains are successfully embedded in the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel particles so that Li_2MnO_3 nanodomains are able to stabilize

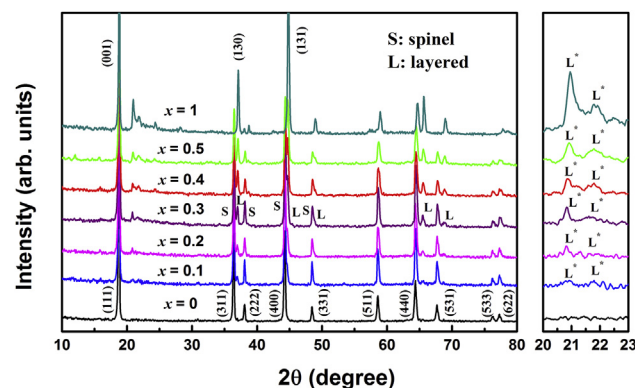


Fig. 1. Powder X-ray diffraction spectra of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1). S and L refer, respectively, to the cubic spinel and layered phase; L^* refers the superstructure reflections arising from an ordering among Li^+ and Mn^{4+} in the layered phase.

$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ providing a large reversible capacity of about 200 mAh g^{-1} where $x = 0.3$ and excellent cycle stability in the wide voltage window between 2 and 4.8 V. The greatly improved cyclability of the spinel between 2 and 4.8 V can be attributed to the improved structural stability as a result of the dispersed Li_2MnO_3 nanodomains in the spinel matrix, as ex-situ X-ray diffraction (XRD) confirms that no Jahn–Teller distortion takes place for this composite when discharged to 2 V.

2. Experimental

2.1. Materials synthesis

A series of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1) composites were prepared via co-precipitation followed by calcination. In a typical synthesis, stoichiometric amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in distilled water and then added dropwise into a mixed aqueous solution of Na_2CO_3 and NH_4HCO_3 with continuous stirring. The obtained co-precipitated carbonate powders were then filtered, washed, and dried in an air oven at $80 \text{ }^\circ\text{C}$. Thereafter, the dried carbonate powders were mechanically mixed with required amounts of lithium carbonate. The mixtures were first heated at $600 \text{ }^\circ\text{C}$ for 5 h and then calcined at $900 \text{ }^\circ\text{C}$ for 10 h in air to obtain the final products. A 5 wt% excess lithium carbonate was used in the mixtures to compensate for lithium loss during the high temperature calcination process.

2.2. Materials characterization

The crystal structure of the as-prepared powders was characterized by X-ray diffraction (Shimadzu XRD-6000 Cu-K α radiation) in a 2θ range of $10\text{--}80^\circ$ at a scan rate of 2° min^{-1} . Morphology and microstructure of different samples were investigated by a field emission scanning electron microscopy (S-4300 Shimadzu, 15 kV) and a high resolution transmission electron microscope (FEI Tecnai G2 F20), respectively.

Electrochemical properties of the synthesized materials were evaluated using 2016-type coin cells assembled in an Ar-filled glove box. The electrodes were prepared by mixing 80 wt% active material, 10 wt% Super P carbon conducting additive, and 10 wt% polyvinylidene fluoride (PVDF) binder in a *N*-methyl-2-pyrrolidone (NMP) solution and stirred overnight for uniform mixing. Then the slurry was casted on circular aluminium foils and dried at $120 \text{ }^\circ\text{C}$ for 24 h. Coin cells were assembled with the as-prepared cathode,

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