



# Improving rate performance of high-voltage spinel cathode by changing structural evolution from two-phase to solid-solution reactions



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## ARTICLE INFO

### Article history:

Received 17 January 2018

Received in revised form

13 May 2018

Accepted 23 May 2018

Available online 24 May 2018

### Keywords:

Cathode material

LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>

High voltage

Rate performance

Structural evolutions

## ABSTRACT

The Ni/Mn ratios are changed to improve rate performance of high-voltage spinel. LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and LiNi<sub>0.4</sub>Mn<sub>1.6</sub>O<sub>4</sub> with annealed treatment are prepared. The structural evolutions during delithiation/lithiation are studied by in-situ XRD technique. It is found that the decrease of Ni/Mn ratios can change the structural evolutions from two-phase transformations to solid-solution reaction. The variations of electronic conductivity and lithium diffusivity during discharge are calculated by the galvanostatic intermittent titration technique. LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and LiNi<sub>0.4</sub>Mn<sub>1.6</sub>O<sub>4</sub> have similar electronic conductivity and different lithium diffusivity. Lithium diffusion coefficients of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> with two-phase transformations are low due to limited lithium diffusion across the interface between two phases. For LiNi<sub>0.4</sub>Mn<sub>1.6</sub>O<sub>4</sub>, the single phase solid-solution reaction is beneficial to lithium diffusion. Attributed to higher lithium diffusivity, the rate performance of LiNi<sub>0.4</sub>Mn<sub>1.6</sub>O<sub>4</sub> is obviously improved.

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## 1. Introduction

Li-ion batteries have been the most promising energy storage systems for electric vehicles (EV) and hybrid electric vehicles (HEV) available in the market. The development of EV and intelligent electronic devices are in urgent need of rechargeable batteries with higher power, energy density and longer lifespan [1,2]. At present, the energy density of lithium ion batteries are limited by cathode materials. Among cathode materials, high voltage spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> has received great attention [3–6]. With high potential plateau (4.7 V) and high specific capacity (147 mAh g<sup>-1</sup>), LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> has a high theoretical energy density above 600 Wh kg<sup>-1</sup>.

As a cathode material, high power density is requisite for

LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> to meet application demands of EVs and HEVs. One way to improve the rate performance is the synthesis of nanosized LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> [7,8]. However, nanosized LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> has poor cycling stability due to its high contact area between the electrode and the electrolyte. Besides, it has been believed that LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> without annealed treatment shows better rate performance [9–11]. The reasons for difference of rate performance have been discussed. Attributed to the presence of Mn<sup>3+</sup>, samples without annealed treatment have two orders of magnitude higher electronic conductivity than samples with annealed treatment [10]. While, it's reported recently that Mn<sup>3+</sup> is not critical to enable high rate capability [12]. Because Mn<sup>3+</sup> is all oxidized to Mn<sup>4+</sup> and there is no Mn<sup>3+</sup> present in the material during most of the charge/discharge cycle. However, lithium diffusivity is not considered in their study [10,12].

The structural evolutions during delithiation/lithiation are of great importance to the electrode behavior. There are two structural evolutions: two-phase transformation (represented by LiFePO<sub>4</sub>) and solid-solution transformation (represented by LiCoO<sub>2</sub>). The influences of annealed treatment on structural

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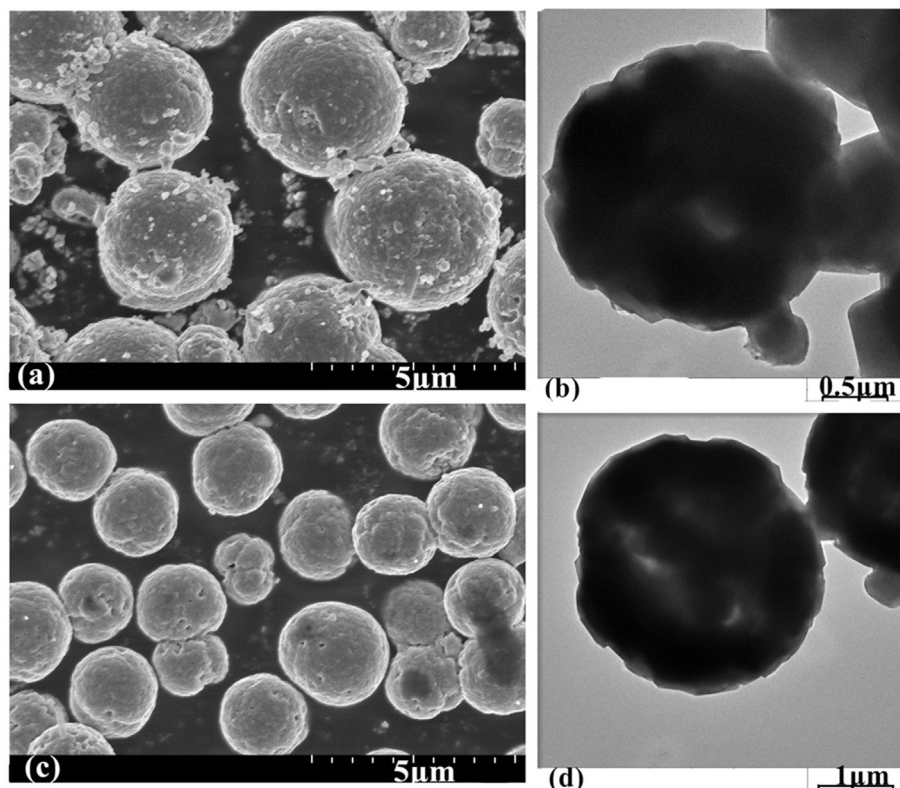


Fig. 1. SEM and TEM micrographs of (a,b)  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and (c,d)  $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ .

evolutions of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  were studied [9,13,14]. During high-temperature calcination above  $700^\circ\text{C}$ , loss of oxygen occurs, leading to the appearance of  $\text{Mn}^{3+}$  in the spinel. The  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  obtained by high-temperature calcination undergoes solid-solution transformation. The oxygen loss is reversible and can be recovered by annealing, which can also reduce  $\text{Mn}^{3+}$  content. After annealed treatment at  $700^\circ\text{C}$ , the reaction paths of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  are turned to two-phase transformation.

Here, rate performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  with annealed treatment is improved by changing Ni/Mn ratios in spinel.  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$  with annealed treatment are tested by in-situ XRD technique. It is found that the decrease of Ni/Mn ratios in spinel will change the reaction paths from two-phase transformations to solid-solution reaction. The better rate performances are mainly attributed to higher lithium diffusivity, rather than electronic conductivity. The single phase solid-solution reaction is beneficial to Lithium diffusion, leading to the better rate performance of  $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ .

## 2. Experimental

### 2.1. Preparation of LNMO

An aqueous solution of  $\text{NaHCO}_3$  with a concentration of  $0.4 \text{ mol L}^{-1}$  was poured rapidly to the aqueous solution of  $\text{NiSO}_4$  and  $\text{MnSO}_4$  with total concentration of  $0.04 \text{ mol L}^{-1}$ . After continuously stirring for 5 h at room temperature, the precipitates were filtered and washed several times with distilled water. The molar ratios of  $\text{NiSO}_4$  and  $\text{MnSO}_4$  are 0.5:1.5 and 0.4:1.6, respectively.

The precipitates were mixed with LiOH as lithium source at the designed stoichiometry, and then calcined at  $800^\circ\text{C}$  for 12 h and annealed at  $700^\circ\text{C}$  in air for 48 h to obtain  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$  powder, respectively.

### 2.2. Characterization

The as-prepared samples were analyzed by inductively coupled plasma (ICP, PerkinElmer, Optima 5300DV) tests. Electrochemical tests of the as-prepared samples were carried out by using coin-type cells (2025). The cathode material of the cell was made from a slurry containing 80 wt.% active material, 10 wt.% conductive acetylene black as conductive agent, and 10 wt.% polyvinylidene fluoride (PVDF) as binder dissolved in *n*-methyl pyrrolidinone. The slurry was evenly coated onto an aluminum foil and then dried in a vacuum oven at  $120^\circ\text{C}$  for overnight. Then the foil was punched

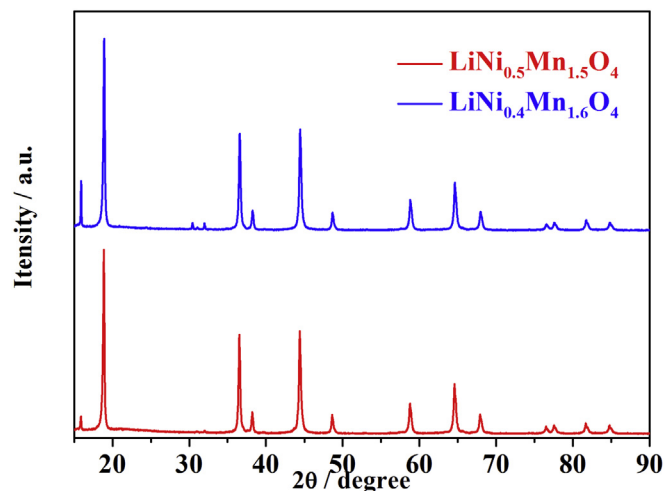


Fig. 2. XRD patterns of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  and  $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ .

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