



## Short communication

A new strategy to diminish the 4 V voltage plateau of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 

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## ABSTRACT

As for spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , there is 4 V voltage plateau in the charge–discharge profiles. This voltage plateau can be reduced by an annealing process, however it is hard to avoid it completely. In this study, a new strategy of partial substitution for Mn by Mg is applied. There is no 4 V voltage plateau in the charge–discharge profiles of Mg-doped compound  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$ . This compound exhibits good electrochemical properties which can be used as cathode material of lithium ion batteries. At 1 C rate, it can deliver a capacity of around 129 mAh  $\text{g}^{-1}$  and remain good cycle performance.

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## 1. Introduction

The spinel  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$  is considered a promising cathode material for a Li-ion battery owing to its high working voltage of ca. 4.7 V versus Li. The high working voltage can elevate power density of batteries. In fact, in the 4.7 V plateau, there are two distinct voltages which are attributed to the Ni(III)/Ni(II) and Ni(IV)/Ni(III) redox couples when Li ion is extracted from or inserted into crystal  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  [1,2].

In most cases, there is a 4 V shoulder originating from the oxidation and reduction of the Mn(IV)/Mn(III) couple. This 4 V voltage plateau will lower the power density of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . In synthesizing spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , oxygen deficiency usually takes place when the temperature increases above 700 °C. This process can be expressed by the following reaction [3–5]:



In order to keep the charge neutrality for the new product  $\text{LiNi}_{0.5-y}\text{Mn}_{1.5-y}\text{O}_{4-x}$ , there should be some amount of  $\text{Mn}^{3+}$  in the product  $\text{LiNi}_{0.5-y}\text{Mn}_{1.5-y}\text{O}_{4-x}$ .

In the past, many attempts have been made to diminish the 4 V plateau. Among these attempts, annealing process is the most effective one because it can compensate for the loss of oxygen in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-x}$ , and makes  $\text{Mn}^{3+}$  transfer into  $\text{Mn}^{4+}$ . However it is

hard to eliminate  $\text{Mn}^{3+}$  completely by means of a single annealing process [6].

In this study, we employ another strategy to eliminate  $\text{Mn}^{3+}$  in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-x}$ . Partial substitution of Mn by Mg is applied. Because  $\text{Mg}^{2+}$  is a stable oxide state, the chemical valence of Mn should be +4 in order to maintain the charge neutrality for  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . In the final product, the 4 V plateau is eliminated almost completely.

## 2. Experimental

Stoichiometric amounts of  $\text{LiNO}_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were used as starting materials and malic acid as chelating agent. The mole ratio of Li:Ni:Mn:Mg was 1:0.5:1.45:0.05. To compensate for the lithium loss at high temperature, small amount of the extra Li salt was added in this solution. At first, the starting materials were dissolved in distilled water and stirred for some time, and then malic acid was added into aqueous solution drop by drop. After stirring for 2 h, the mixed solution was evaporated at 100 °C to form a precursor. At last, the precursor was calcined at 900 °C for 8 h, and then annealed for 6 h before cooling to room temperature. In order to make a comparison, an undoped sample  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  was also prepared in the same way, only the annealing time was 20 h.

X-ray diffraction pattern was carried out on a Philips X-ray diffractometer equipped with Cu  $\text{K}\alpha$  radiation. The morphologies of the products were examined with a Hitachi scanning electron microscope (SEM).

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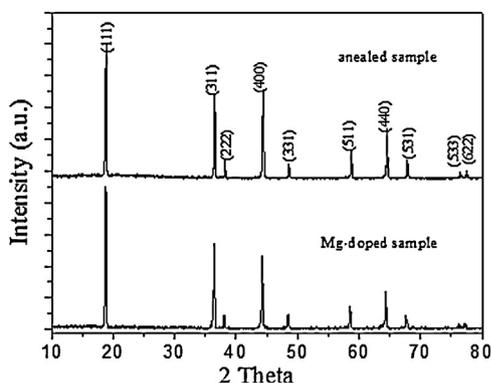


Fig. 1. XRD patterns of the as prepared samples.

Electrochemical performances were measured with coin half-cells composed of the nominal spinel cathode and metallic-lithium anode with  $1 \text{ mol L}^{-1}$   $\text{LiPF}_6$  in 1:1 diethyl carbonate/ethylene carbonate electrolyte and Celgard polypropylene separators. The cathodes were prepared by mixing 85 wt% active material with 10 wt% acetylene black and 5 wt% PVDF binder in NMP; the mixture was coated on aluminum foil, dried in an oven and punched out circular discs of 1.23 cm in diameter. All coin cells were assembled in an argon-filled glovebox. The cells were galvanostatically cycled at 1 C-charge/1 C-discharge rate between 3.50 V and 4.90 V.

### 3. Results and discussion

Fig. 1 shows the X-ray diffractions of the as prepared products  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . It can be seen that all peaks can be indexed as the cubic spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  phase. There are no apparent impurity peaks at  $37.5^\circ$ ,  $43.7^\circ$  and  $63.6^\circ$ , indicating no  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  phase in the samples [7–9]. The lattice constants are calculated to be 8.1726 Å and 8.1613 Å for  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  respectively by the least squares method. Because the ionic radius of  $\text{Mg}^{2+}$  is larger than that of  $\text{Mn}^{4+}$ , there is a difference in lattice constant between the two samples.

The morphological feature of the as-prepared sample is characterized by scanning electron microscopy, as displayed in Fig. 2. The sample is polyhedral shape and well crystallized. Most particles range from 1 to 3  $\mu\text{m}$  in size.

Fig. 3 shows the first charge and discharge curves of the as prepared samples at 1 C rate. For the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  sample, there

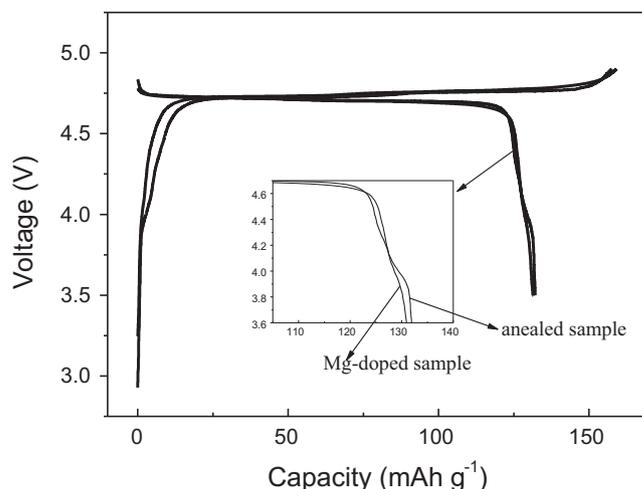


Fig. 3. Charge and discharge curves of the as prepared samples.

is still a small 4 V voltage plateau. It indicates that there are small amounts of  $\text{Mn}^{3+}$  in the sample. For the Mg-doped sample  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$ , there is no obvious 4 V voltage plateau. So the doped Mg element can make the chemical valence of Mn move to  $\text{Mn}^{4+}$  in order to keep the positive and negative charge balance in  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$ . It is worth mentioning that the annealing time for sample  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is longer than that for sample  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$ . It can be inferred that doping Mg is an effective method to eliminate the 4 V voltage plateau. We define that the 4-V region is the voltage range of 4.40–3.50 V, and the amount of  $\text{Mn}^{3+}$  in sample  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  can be calculated as 0.048 per formula unit. In order to keep the charge neutrality, the product should be  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.976}$ .

On the one hand, the larger lattice constant is propitious for the transportation of Li ions in the bulk of electrode materials. On the other hand, a portion of the  $\text{Mn}^{3+}$  ions on the surface of the sample may undergo the disproportionation reaction  $2\text{Mn}^{3+} = \text{Mn}^{2+} + \text{Mn}^{4+}$ , and the  $\text{Mn}^{2+}$  tends to dissolve in the electrolyte and migrate to the anode to degrade cell [6]. After doping Mg, the  $\text{Mn}^{3+}$  is transferred to  $\text{Mn}^{4+}$ . Therefore the cycle performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$  should be better than that of sample  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.976}$ . The testing results prove that doping Mg does improve the electrochemical properties, as shown in Fig. 4. At 1 C rate, the capacity retentions of the as prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.976}$  remain 92.2% and 81.3% after 100 cycles.

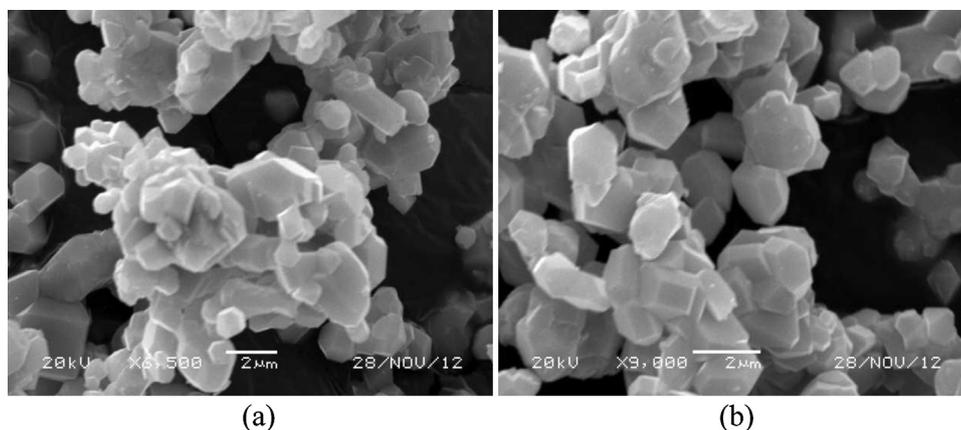


Fig. 2. SEM images of the as prepared samples (a)  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$  and (b)  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

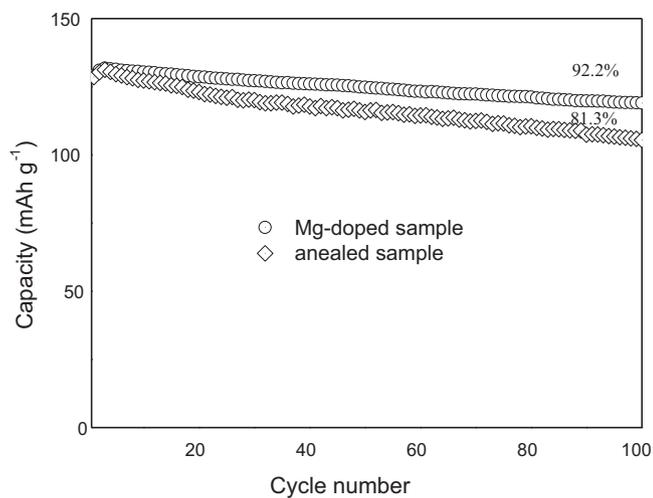


Fig. 4. Cycle performance of the as prepared samples.

#### 4. Conclusions

Doping Mg in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  can enlarge the lattice constant of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , and reduce the amount of  $\text{Mn}^{3+}$  in the crystal.

Therefore, doping Mg is an effective way to diminish the 4 V voltage plateau during charge and discharge process of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . The harmful effect of  $\text{Mn}^{3+}$  on the surface of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  can also be diminished. The Mg-doped compound  $\text{LiNi}_{0.5}\text{Mn}_{1.45}\text{Mg}_{0.05}\text{O}_4$  can deliver a capacity of  $129 \text{ mAh g}^{-1}$  at 1 C rate and the capacity retention is 92.2% after 100 cycles.

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