

## Electrochemical performances discharged to lower potential for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material synthesized by PAA-assisted co-precipitation method

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**Keywords:** Lithium battery cathode material;  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ; Polyacrylic acid; Co-precipitation

**Abstract.** The cathode material  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  with cubic spinel structure was prepared by co-precipitation process using  $\text{LiCl}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  as raw materials, oxalate as a precipitant, polyacrylic acid(PAA) as a dispersant agent. The synthesized materials were analyzed and characterized by X-ray diffraction(XRD), scanning electron microscopy(SEM). It was found that all of the samples had cubic spinel structure without undesired impurities. According to the SEM, the powder had uniform particle size and its aggregations was reduced because of the assistance of polyacrylic acid. Moreover, on the basis of the electrochemical performances tests, it could be found that the initial discharge capacity discharged to lower potential for the samples with PAA addition were higher than the theoretical capacity of the spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . All the samples synthesized by PAA-assisted method possess good capacity retention and rate performance, compared to the sample without PAA addition. The discharge capacity for 3wt% sample was significantly enhanced about 87.5% at 1C, 39.4% at 2C and 43.5% at 5C with respect to the sample without PAA. The great enhancement could be attributed to an effectively shortened Li-ion diffusion path way.

### Introduction

Lithium ion battery has been widely used in the electronic devices such as cell phones, digital cameras and laptop.  $\text{LiCoO}_2$  has been the most widely used cathode material in commercial lithium-ion batteries [1]. Since  $\text{LiCoO}_2$  has economic and environmental issues [2], intensive research has been directed towards the development of alternative low cost, environmentally friendly cathode materials as possible replacement of  $\text{LiCoO}_2$ . Among them, spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  material is one of the promising and attractive cathode materials for next generation lithium-ion batteries because of its high voltage, acceptable stability, and good cycling performance [3,4].

Co-precipitation method has been widely used to synthesize  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  owing to the homogenous mixing of precursors to obtain well-crystallized spinel powders [5,6]. Besides, the method is relatively low cost. However, particle aggregations and the lack of size uniformity are observed in the resulting powder due to the un-dispersed mixture and the high temperature sintering process [7].

In this work, we proposed a facile method to synthesize  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , in which chemical homogeneity on an atomic scale was assured and smaller particles were obtained at 700°C with effect of PAA as dispersants. The performance of the resulting particles with PAA addition was compared with that of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particles synthesized without using PAA. Moreover, the

electrochemical performances discharged to a lower potential for  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  were studied.

## Experimental sections

Chloride-based transition metals ( $\text{LiCl}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) were used as the starting precursors with molar ratio of  $\text{Li}:\text{Ni}:\text{Mn}=1.05:0.5:1.5$ . The co-precipitation process was carried out by mixing the metal chlorides with 70% aqueous oxalic acid. The polyacrylic acid (M.W=1500) according to different weight ratio were mixed with the bare oxalate precursor. After thoroughly mixing at  $150^\circ\text{C}$  for 1h, the mixture was then put into a furnace to accomplish two-step calcinations (First step:  $400^\circ\text{C}$  for 3h, Second step:  $700^\circ\text{C}$  for 10h). The crystal structures of the treated powders were analyzed by X-ray diffractometry (X'Pert Pro MPD). The morphologies of the particles were characterized by scanning electron microscopy (SEM, FEI, XL 30S-FEG).

The electrode was prepared by mixing 80 wt% active material with 10 wt% acetylene black and 10 wt% polyvinylidene difluoride (PVDF) binder, coating the mixture on an aluminum sheet, and then cutting the sheet into pieces with  $1\text{ cm} \times 1\text{ cm}$ . The CR2032 coin cell was assembled in an Ar-filled Mikrouna glove box by using the prepared electrode as cathode, lithium film as anode, Celgard 2400 as separator and  $1\text{M LiPF}_6$  in EC:DMC (1:2 in volume) as electrolyte. And then, dried at  $120^\circ\text{C}$  for 12h to achieve the cathode. Land cell test system (Land CT2001A, China) was employed to test the cycling and rate performance of  $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  half cells in the voltage range of 1.5 and 4.8V at room temperature.

## Results and discussion

Figure 1 showed the XRD patterns of the samples with different PAA content. The X-Ray diffraction peaks for the samples with different PAA content was almost the same with the standard XRD patterns (PDF80-2162). All the diffraction peaks can be indexed based on a well-defined spinel cubic structure, along with minor traces of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  impurity phase close to the characteristic peaks of (311), (400) and (440). All the diffraction peaks belonged to the cubic spinel structure with an  $\text{Fd}3\text{m}$  space group [8,9]. Besides, the intense and well-defined diffraction peak indicates high-crystallinity of as-synthesized powders. The sharpness of the XRD peaks increased with the increasing PAA content.

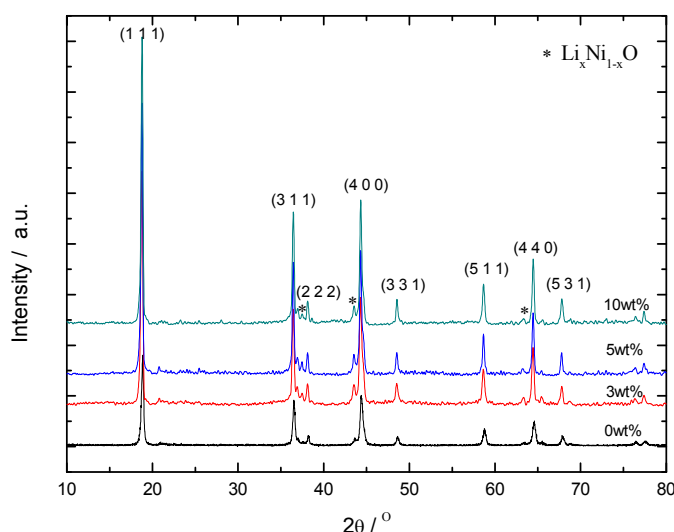


Fig.1 XRD patterns of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  with different PAA content

Figure 2 showed the FE-SEM images of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders synthesized with different PAA content. Except for the obvious particle size reduction, the uniformity was also successfully improved due to the addition of the PAA. The PAA chemical structure composes a long carbon

chain as the main body and a repeated organic function(–COOH) as the branch, which entangled with the precursor monomers and provided the homogeneous separation between the metal oxalates precursors during the chemical reaction process [6,10]. Therefore, the particle size and the particle aggregation were both reduced.

Moreover, the porous texture of as-synthesized powder was also found in the Figure 2. Oxalic acid formed a mixed precursor, which acted as substrate for the homogeneous distribution of the metal oxide phase. During calcination in air, the carbonaceous substrate was oxidized to CO<sub>2</sub>, a great amount of pores left in the powders.

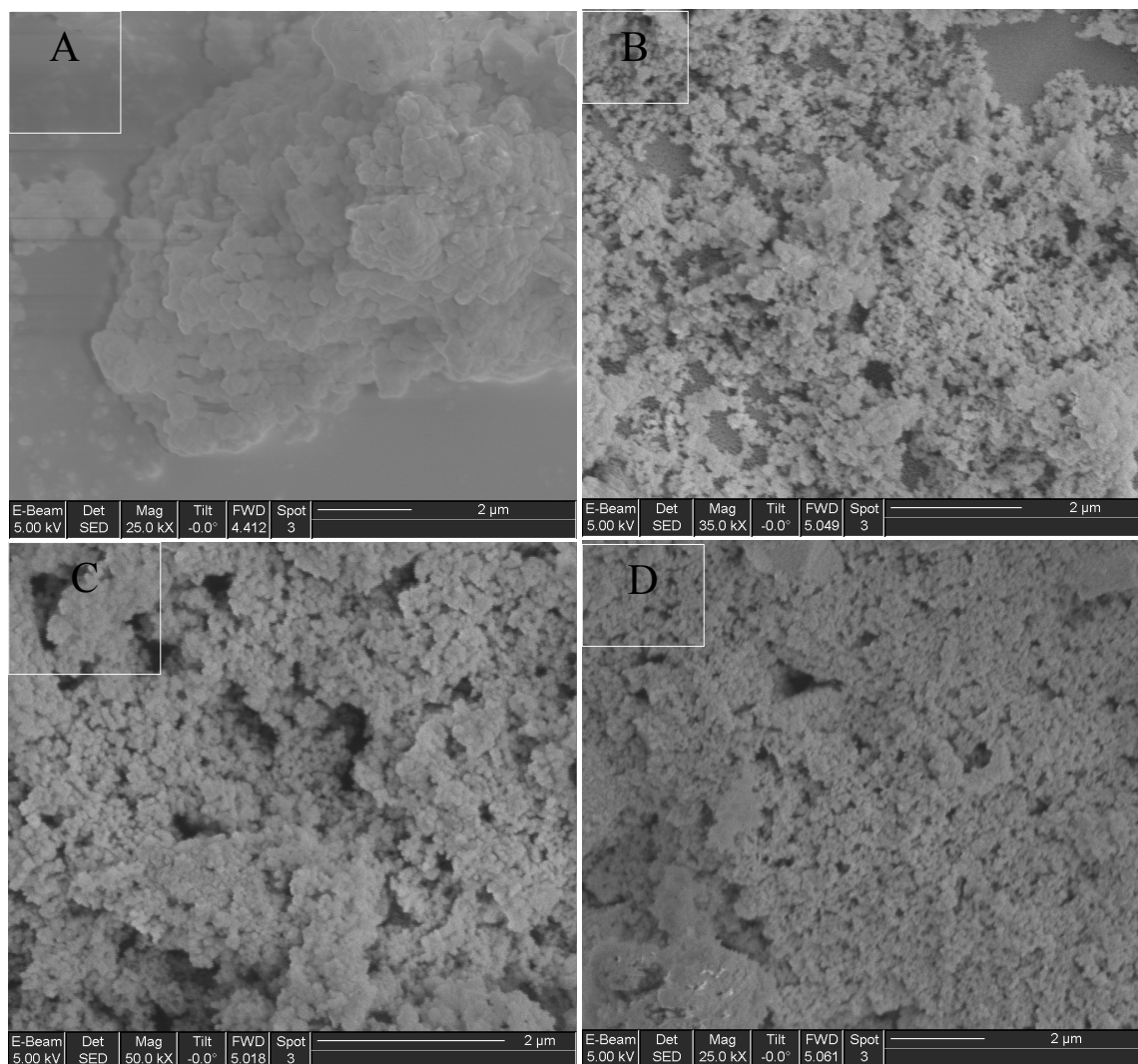


Fig.2 SEM images of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> with different PAA content: A.0wt%; B.3wt%; C.5wt%; D.10wt%

Figure 3 showed the discharge rate performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> with different PAA content. Comparing the electrochemical performance of the bare and the PAA-assisted sample, both the cycling and the c-rate performance were improved. An obvious capacity fading was occurred in LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> without PAA addition with the cycling rate increasing. However, compared to that, the good capacity retention was still maintained in the LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> with PAA addition at elevated cycling rate. For example, at 5C, the mean discharge capacity for the samples with 3wt%、5wt%、10wt% PAA addition was significantly enhanced about 43.5%、12.5%、31.2%, respectively.

The greater capacity of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> with the PAA addition compared to that of the sample without PAA could be attributed to the greater specific surface area of the former, which ensured a shorter lithium diffusion distance in the particles as well a greater surface area for the interfacial charge transfer [11]. On the other hand, the porous texture of the as-synthesized powder with the

PAA addition provided the space for the lattice stress caused by Jahn-Teller distortion [12,13] during cycles and thus enhanced the cyclic stability of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

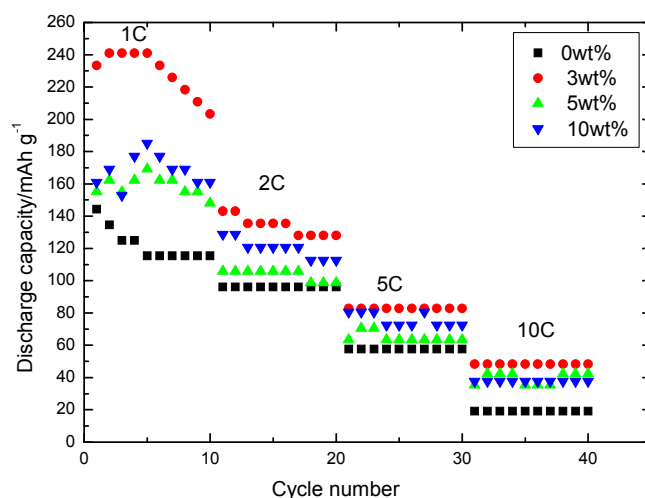


Fig.3 The discharge rate performance for the samples with different PAA content

Moreover, comparing that with the theoretical capacity of  $147\text{mAhg}^{-1}$  for the spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , it could be found that the capacity increased effectively [14,15,16] due to lower potential (1.5V). The initial discharge capacity at 1C for the samples with 3wt%、5wt%、10wt% PAA addition were  $233.4\text{mAhg}^{-1}$ 、 $155.1\text{mAhg}^{-1}$ 、 $161.1\text{mAhg}^{-1}$ , respectively.

## Conclusion

The pure spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode was synthesized by the PAA-assisted co-precipitation method. As a result of the addition of the PAA, the particle aggregation and the particle size of the sample were both reduced. The PAA chemical structure composes a long carbon chain as the main body and a repeated organic function( $-\text{COOH}$ ) as the branch, which entangled with the precursor monomers and provided the separation between metal precursors during the chemical reaction process. Comparing the electrochemical performance of the bare and the PAA-assisted sample, both the cycling and the c-rate performance were improved. Especially for 3wt% sample, the discharge capacity was significantly enhanced about 87.5% at 1C, 39.4% at 2C and 43.5% at 5C with respect to the sample without PAA. The great improvement could be attributed to an effectively shortened Li-ion diffusion path way due to the particle size decreasing. Moreover, the initial discharge capacity discharged to lower potential for the samples with PAA addition were higher than the theoretical capacity for the spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

## Acknowledgement

This work was supported by the Natural Science Foundation of Shandong Province (ZR2014EMQ005, ZR2010EQ001), the Project of Shandong Province Higher Educational Science and Technology Program (Grant No. J14LJ08), the Taishan Scholars Program of Shandong Province (ts20120528), China.

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