



# Preparation of lithium-rich layered oxide micro-spheres using a slurry spray-drying process



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## HIGHLIGHTS

- Li-rich layered oxide microspheres composed of nano-size primary particles are prepared by a slurry spray-drying method.
- Spray-drying sample show relieved voltage fade compared to the co-precipitated counterpart during the cycling process.
- The relieved voltage fade is attributed to a more homogenous TM distribution in spray-drying sample.

## ARTICLE INFO

### Article history:

Received 12 February 2015

Received in revised form

10 April 2015

Accepted 14 April 2015

Available online

### Keywords:

Li-rich layered oxides

Spray-drying

Voltage fade

Cathode materials

Lithium-ion batteries

## ABSTRACT

0.5Li<sub>2</sub>MnO<sub>3</sub>·0.5LiMn<sub>1/3</sub>Ni<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> microspheres are prepared by a slurry spray-drying process (SD-LLO) with subsequent heat treatment. SEM images show that the SD-LLO microspheres are composed of nano-size primary particles. These particles are quite different from conventional LLO microspheres, which are composed of micron-scale plate-like primary particles prepared by a co-precipitation method (CP-LLO). The SD-LLO material experiences a smaller voltage drop during cycling than CP-LLO when used as cathode material in lithium-ion batteries. High-resolution transmission electron microscopy (HR-TEM) and energy dispersive spectroscopy (EDS) indicate that the smaller voltage drop of SD-LLO can be attributed to a more homogeneous distribution of transition metals.

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## 1. Introduction

In the past years, lithium-rich layered oxides (LLO) xLi<sub>2</sub>MnO<sub>3</sub>·(1-x)LiMO<sub>2</sub> (M = Mn, Ni, Co) have received much attention on account of their excellent properties, including low cost, environmental benignity and an exceptionally high reversible capacity of over 250 mAh g<sup>-1</sup> [1–4]. Despite having a higher capacity than the currently available commercialized cathode materials, LLO materials suffer from several intrinsic problems that need to be solved before their practical application, such as voltage decay and cycling instability during the charge/discharge process.

It has been well accepted that the electrochemical performance of cathode materials is strongly correlated to the preparation

method and synthesis conditions used [5–7]. Recently, Zheng et al. found that the voltage fade and energy degradation of LLO cathode materials can be significantly mitigated by improving the uniformity of chemical species on the atomic level [8]. Hydroxide co-precipitation is generally used to produce transition metal hydroxide precursors with a secondary microsphere morphology for layered oxide cathode materials [9]. However, with this method, a very long ageing time is required for the nano-size primary particles to grow into micron-scale secondary spheres. In addition, when this method is adopted in the preparation of hydroxide precursor microspheres with high manganese content, it results in micron-scale irregular primary particles during the ageing process owing to the inherent plate-shaped morphology of Mn(OH)<sub>2</sub> [10–13], which will affect the homogeneity of the transition metal distribution in the final product.

In this present work, we report on the preparation of LLO microspheres with different primary particles using the co-

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precipitation method (CP-LLO) and the slurry spray-drying method (SD-LLO). As an extension of the spray-drying method, the slurry spray-drying method has been successfully applied to prepare various electrode materials [14,15]. Unlike the traditional solution spray-drying method, the slurry spray-drying process does not need expensive initial or intermediate reagents, such as acetates and nitrates. The morphology, structure and electrochemical performance, especially the voltage fade, of CP-LLO and SD-LLO are carefully compared.

## 2. Experimental

### 2.1. Synthesis of SD-LLO and CP-LLO

SD-LLO was synthesized using a new method comprising co-precipitation, spray-drying and calcination in air, as illustrated in Scheme 1. First, the mixed metal hydroxide was obtained by a co-precipitation method, which involved the dropwise addition of the required amounts of the aqueous metal sulphate (Ni:Co:Mn = 0.13:0.13:0.54) solution into a 2 M NaOH solution under continuous stirring. After 4 h, the as-prepared precipitate was washed with distilled water several times before being dried at 100 °C for 12 h. The resulted hydroxide was then mixed with  $\text{Li}_2\text{CO}_3$  as a lithium salt with 5% Li salt excess in a wet-milling process to form a highly stable slurry, which was then spray-dried for sphere-making. The solvent used in the wet-milling process is water. The as-prepared precursors were first burned at 650 °C for 5 h and then subjected to a post-treatment at 900 °C for 10 h in air to produce SD-LLO microspheres.

For comparison, we prepared the same  $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  microspheres by the traditional co-precipitation method. An aqueous solution of transition metal sulfates was slowly pumped into a continuous stirred tank reactor under nitrogen atmosphere at 60 °C. At the same time, a 2 M NaOH solution (aq) and an appropriate amount of  $\text{NH}_4\text{OH}$  solution (aq) as a chelating agent were separately pumped into the reactor. The concentration of the solution, pH, amount of  $\text{NH}_4\text{OH}$ , stirring speed and temperature in the reactor were carefully controlled. After reaction, the sediment was filtered with deionized water several times to remove the residual ions before drying at 100 °C for 12 h. The obtained precursor powder and 5% excess  $\text{Li}_2\text{CO}_3$  were mixed thoroughly. The mixture was first burned at 650 °C for 5 h in air and then heated at 900 °C for 10 h to obtain the CP-LLO sample.

### 2.2. Compound confirmation

For the structural analysis of SD-LLO, the crystal structure of the as-prepared cathode material was characterized using X-ray diffraction (XRD) on a Bruker D8 diffractometer equipped with a Cu anticathode (Cu  $K\alpha$  radiation,  $\lambda = 0.154056$  nm) at room temperature. XRD patterns were collected at  $2\theta$  with a step size of  $0.02^\circ$  in the range  $10\text{--}80^\circ$  with a step time of 1 s. The collected XRD intensity data were analysed by the Rietveld method using the TOPAS 4-2 package. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6390 scanning microscope. Transmission electron microscopy (TEM) experiments were conducted using a JEOL 2100F microscope (Japan) operated at 200 kV. The TEM samples were suspended in ethanol and dropped onto holey carbon films supported on Cu grids.

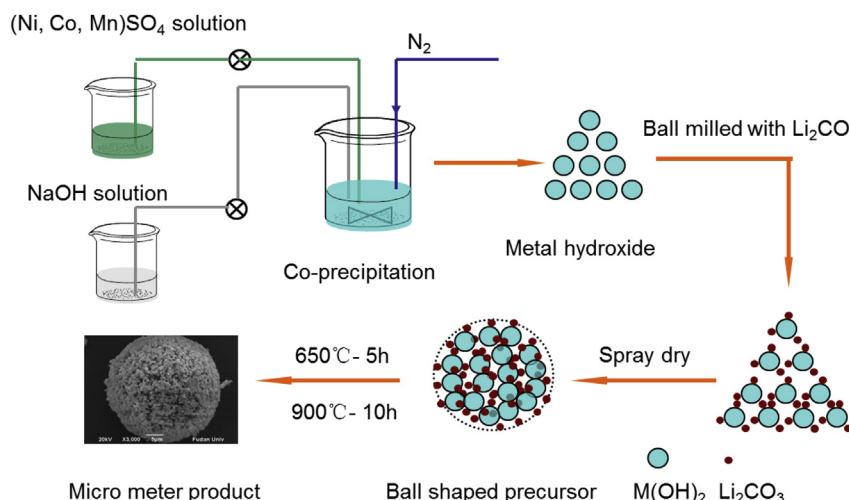
### 2.3. Electrochemical measurements

A black viscous slurry consisting of 80 wt% sample, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone (NMP) was cast onto aluminium foil with a blade to prepare positive electrodes. After coating, the electrode films were dried at 80 °C for 2 h to remove the solvent before pressing. The electrodes were cut into sheets with a diameter of 12 mm, vacuum-dried at 80 °C for 12 h and then weighed before assembly. The typical active material mass loading was approximately  $5\text{--}6$  mg/cm<sup>2</sup>. Electrochemical testing was conducted with CR2016-type coin cells assembled in an argon-filled glove box using Li metal as the negative electrode. The electrolyte solution used was 1 M  $\text{LiPF}_6$  dissolved in a 1:1:1 volume ratio mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). The other sets of experimental conditions are given in the Results and Discussion section. All the specific capacities mentioned in this paper were calculated from the weight of the active materials.

## 3. Results and discussion

### 3.1. X-ray diffraction and morphology

The XRD patterns of SD-LLO and CP-LLO are compared in Fig. 1. Most of the peaks in Fig. 1 can be indexed well to a hexagonal  $\alpha$ - $\text{NaFeO}_2$  structure with an  $R\bar{3}m$  space group. The low-intensity



**Scheme 1.** Schematic representation of the synthesis pathway used for the preparation of SD-LLO micro-spheres.

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