



# Li<sub>1.15</sub>Mn<sub>0.49</sub>Ni<sub>0.18</sub>Co<sub>0.18</sub>O<sub>2</sub> nanoplates with exposed (012) plane as high energy and power cathode of Li-ion batteries



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## ABSTRACT

In this work, Li<sub>1.15</sub>Mn<sub>0.49</sub>Ni<sub>0.18</sub>Co<sub>0.18</sub>O<sub>2</sub> nanoplates with exposed (012) facet are prepared for the first time by co-precipitation method under the assistance of cetyltrimethyl ammonium bromide. As cathode materials of lithium-ion batteries, the Li<sub>1.15</sub>Mn<sub>0.49</sub>Ni<sub>0.18</sub>Co<sub>0.18</sub>O<sub>2</sub> nanoplates can deliver the initial discharge capacities of 219.8 and 192 mA h g<sup>-1</sup> at 300 and 700 mA g<sup>-1</sup>, respectively. It suggests the Li<sub>1.15</sub>Mn<sub>0.49</sub>Ni<sub>0.18</sub>Co<sub>0.18</sub>O<sub>2</sub> nanoplates possess an excellent rate capability. After 200 cycles, the capacity retention ratio at 700 mA g<sup>-1</sup> is still as large as 82.6%. The superior rate capability can be attributed to the shorter transport distance of lithium ions in these nanoplates with exposed (012) facet. The above results also indicate that the electrochemical performances of Li-rich layered oxides can be improved by allocating proper facets.

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## 1. Introduction

Cathode materials with high capacity and rate are crucially important for the next generation of lithium-ion batteries, especially for their application in electric and hybrid electric vehicles [1–3]. As a result, Li-rich transition-metal (TM) oxides (LROs) with general formula Li<sub>1+x</sub>M<sub>1-x</sub>O<sub>2</sub> (M = Co, Ni and Mn) have attracted much interest due to very high reversible capacity (>250 mA h g<sup>-1</sup>) [4–6]. These materials originate from layered rocksalt-type lithium-transition metal oxides, in which partial TMs are replaced by Li [7]. The staggering capacity of these materials is rooted in the cumulative reversibility of both cationic and anionic redox processes (2O<sup>2-</sup> → O<sub>2</sub><sup>n-</sup>, n = 1, 2, or 3) [8–10]. Nevertheless, these materials suffer from obvious voltage degradation and inferior rate capability, both of which are plaguing their implementation in practical batteries [11,12].

Recently, the design of stable channels for fast Li-ion diffusion in cathode materials has become a vital direction. For LRO cathodes, Li-ions can only transport along the plane groups which are parallel to the (001) facet [13,14]. The planes which can provide

unimpeded paths for Li-ions transportation are referred as active planes. Herein, high percentage of exposed active planes will help to optimize the rate capability of LROs greatly. For instance, both Sun's and Wu's groups have demonstrated that LROs with exposed {010} planes possess the outstanding rate performance [15,16]. However, it is still a challenge to prepare LROs with exposed active planes, because high-energy facets are easy to be vanished during preparation process.

In this work, Li<sub>1.15</sub>Mn<sub>0.49</sub>Ni<sub>0.18</sub>Co<sub>0.18</sub>O<sub>2</sub> samples are prepared by co-precipitation method under the assistance of cetyltrimethyl ammonium bromide. Through the characterizations of scanning electron microscopy and transmission electron microscopy, it is confirmed that the samples consist of abundant nanoplates with exposed (012) facet. Electrochemical performances as cathode materials of lithium-ion batteries are also evaluated. The initial discharge capacities of Li<sub>1.15</sub>Mn<sub>0.49</sub>Ni<sub>0.18</sub>Co<sub>0.18</sub>O<sub>2</sub> nanoplates with exposed (012) facet at 300 and 700 mA g<sup>-1</sup> can reach 219.8 and 192 mA h g<sup>-1</sup>, respectively. After 200 cycles, its capacity retention ratio at 700 mA g<sup>-1</sup> is still as large as 82.6%. The excellent rate capability of the nanoplates with exposed (012) facet can be attributed to short and unimpeded paths of Li-ions transportation in active materials. And our results also indicate that the rate capability of LROs can be improved by allocating appropriate facets.

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## 2. Experimental Section

### 2.1. Sample synthesis

To prepare  $\text{Li}_{1.15}\text{Mn}_{0.49}\text{Ni}_{0.18}\text{Co}_{0.18}\text{O}_2$  nanoplates, a CTAB-assisted co-precipitation method with a heat treatment process (CTAB: Cetyltrimethyl Ammonium Bromide) was designed. The starting materials were listed as follows: manganese sulfate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , AR), nickel sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , AR), cobalt sulfate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , AR), CTAB (AR), sodium hydroxide (NaOH, AR), and stronger ammonia water ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ). Firstly, 1825.4 mg  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , 1209.1 mg  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , 1293.1 mg  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , and 1 g CTAB were dissolved in 100 mL deionized water to obtain the aqueous solution. Then, 20 mL NaOH ( $2 \text{ mol L}^{-1}$ ) and 5 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  were added to the solution drop by drop under stirring. After stirring for 5 min, 25 mL NaOH ( $0.4 \text{ mol L}^{-1}$ ) was added slowly again. Finally, 15 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added slowly again after stirring for 20 h. The whole precipitation process was performed under  $\text{N}_2$  gas. The obtained hydroxide precipitates were filtrated, washed with distilled water, and then dried at  $160^\circ\text{C}$  for 12 h. These precipitates were respectively mixed with 1123.7 mg  $\text{LiOH} \cdot \text{H}_2\text{O}$  (5 mol% excess), calcined at 800, 850 or  $900^\circ\text{C}$  for 12 h, and then quenched to room temperature. The purpose of selecting different temperature to calcine the samples is to optimize the synthetical conditions and obtain the product with excellent electrochemical performance. The samples were named as S800 (calcined at  $800^\circ\text{C}$ ), S850 and S900. In addition, a comparative sample was obtained without CTAB. And the experimental process of the comparative sample was the same with that of the sample S850.

### 2.2. Sample characterization

The crystalline phases and particle morphologies of the synthesized materials were determined by X-ray diffraction measurement (XRD, Rigaku, D/max-Rbusing Cu K radiation) laser Raman spectroscopy (Renishaw in Via), field emission scanning electron microscopy (SEM) on a JEOL JSM-7401F instrument under an acceleration voltage of 5 kV and transmission electron microscopy (TEM) on a JEOL JEM-2010 apparatus with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were measured on an AXIS ULTRA DLD instrument using aluminum K X-ray radiation. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used to analyze the chemical composition of the synthesized materials.

### 2.3. Electrochemical test

Electrochemical performances of the synthesized materials were measured using the CR-2016-type coin cell. The cathode film was prepared as follows: 80 wt% of synthesized powders, 10 wt% of carbon black, and 10 wt% polyvinylidene fluoride (PVDF) were mixed using N-methyl pyrrolidinone (NMP) as a solvent. The slurry was coated on Al foil and dried under vacuum at  $110^\circ\text{C}$  for 12 h. The cells were assembled in an argon-filled glove box ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 1 \text{ ppm}$ ) using lithium foil as the anode, a polymer separator and 1 M  $\text{LiPF}_6$  in EC:DMC (1:1 in volume) as the electrolyte. The cell was charged and discharged galvanostatically on a CT2001a cell test instrument (LAND Electronic Co.) in a voltage range of 2.0–4.8 V at room temperature.

## 3. Results and Discussion

X-ray diffraction (XRD) is used to identify the crystal structure of the samples S900, S850 and S800. Fig. 1(a–c) shows the XRD patterns of the three as-prepared samples. Clearly, all the samples possess good crystallization and similar XRD pattern. All the strong

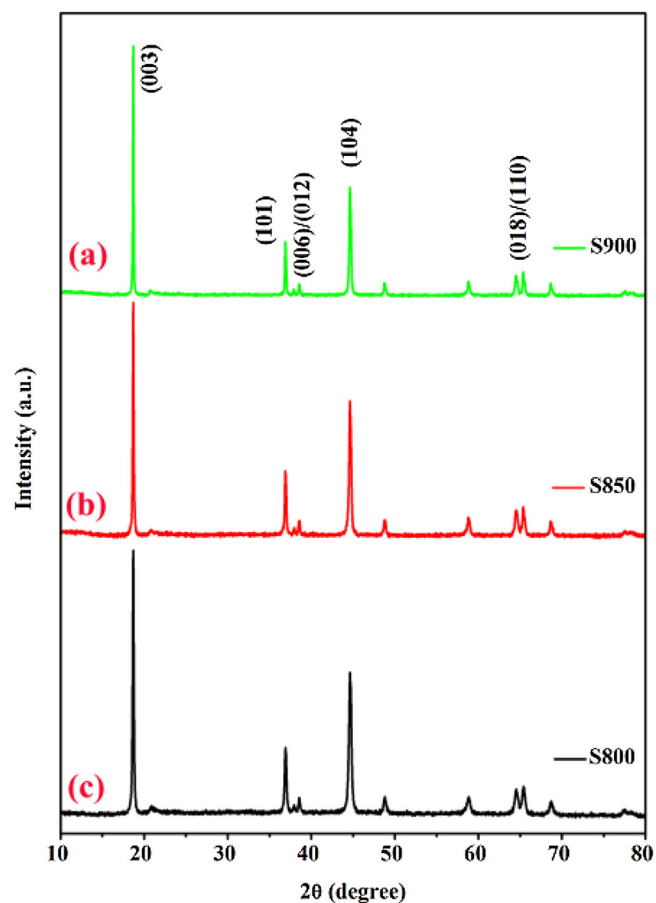


Fig. 1. XRD patterns of the as-prepared samples.

diffraction peaks in the three XRD patterns can be indexed on the basis of the hexagonal  $\alpha\text{-NaFeO}_2$ -type structure with a space group  $R\text{-}3m$  [17], except for the weak peaks in the  $2\theta$  range of  $20\text{--}25^\circ$ . These weak peaks are caused by lithium-cation ordering in the transition-metal (TM) layers [18], which is the feature of the integrated monoclinic  $\text{Li}_2\text{MnO}_3$  phase ( $C2/m$ ) [19]. Well splitting (006)/(012) and (018)/(110) peaks indicate that all the target products have well-formed layered structure [20]. Generally, the

Table 1  
Lattice parameters of the three samples.

Samples	<i>a</i>	<i>c</i>	<i>c/a</i>
S900	2.8552(2)	14.2408(5)	4.9877
S850	2.8548(4)	14.2395(3)	4.9879
S800	2.8531(2)	14.2320(6)	4.9883

Table 2  
Chemical composition analysis of the three samples by ICP.

Samples	Li	Mn	Ni	Co
S900	1.1467	0.4845	0.1829	0.1859
S850	1.1453	0.4910	0.1814	0.1823
S800	1.1455	0.4905	0.1808	0.1832

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