

Facile synthesis of Li-rich layered  
 $\text{Li}_{1.23}\text{Ni}_{0.09}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$  and its structural transformation  
 at first cycle measured by in situ X-ray diffraction

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Recently, Li-rich layered cathode materials have been attracting a lot of attention due to their high capacity (> 230 mAh/g) [1]. However, several problems still hinder the practical application of the promising Li-rich layered cathode materials such as large irreversible capacity loss in the first cycle, poor rate capacity and voltage fade during charge-discharge process. Meanwhile, the charge mechanism at high voltage plateau above 4.5 V is not well clarified. It is well known that electrochemical performances of cathode materials effectively depend on their synthesis route. Currently, many methods have been used to synthesize Li-rich layered cathode materials, such as co-precipitation process, microwave heating process, sol-gel process, ion-exchange reaction, solid reaction process and combustion method. In this presentation, we will report a novel approach (aqueous solution-evaporation route) to prepare Li-rich layered composite cathode material and studied its charge-discharge mechanism at first cycle by in situ X-ray diffraction.

Figure 1 depicts the ex-XRD results of the  $\text{Li}_{1.23}\text{Ni}_{0.09}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$  material. The sharp splits in (006)/(102) and (108)/(110) peaks identify the layer structure of the as-prepared material. In addition, it is indicated that the material has a low level of  $\text{Li}^+$  and  $\text{Ni}^{2+}$  disordering because the  $I_{003}/I_{104}$  ratio of 1.52 is greater than 1.2. It is also confirmed that a well-ordered structure is obtained in the as-prepared layered cathode material, according to the low  $(I_{006}+I_{102})/I_{101}$  ratio of 0.235. Thus, the composite structure may benefit the reversible insertion/extraction of lithium ion through the two-dimension channel built by  $\text{MO}_6$ .

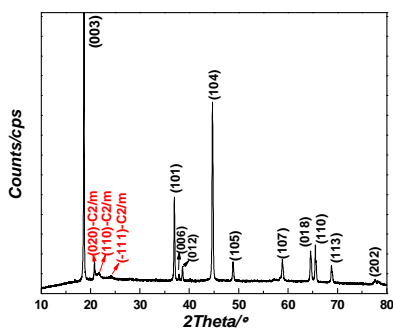


Fig.1 The ex-XRD pattern of the as-prepared  $\text{Li}_{1.23}\text{Ni}_{0.09}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$  material.

As shown in Fig.2, this cathode materials show a high voltage plateau at ~ 4.5 V vs.  $\text{Li}/\text{Li}^+$  during the first charge, which is attributed to the simultaneous removal of lithium and oxygen from the  $\text{Li}_2\text{MnO}_3$ . This charge plateau at ~ 4.5V disappears after the first charge, which confirms that irreversible structural changes occur during the first charge process. However, continuous voltage fade is observed in the charge/discharge profiles, indicating the cathode material undergoes gradual structural changes

after the first charge.

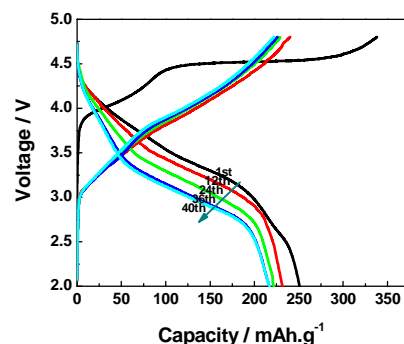


Fig.2. Charge / discharge curves of the as-prepared  $\text{Li}_{1.23}\text{Ni}_{0.09}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$  material in 1<sup>st</sup>, 12<sup>th</sup>, 24<sup>th</sup>, 36<sup>th</sup> and 40<sup>th</sup> cycles.

Fig.3 shows the in situ XRD patterns of the the as-prepared  $\text{Li}_{1.23}\text{Ni}_{0.09}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$  material at the first 1.5 cycles. From figure.3 we can see that (003) reflection shifts toward lower  $2\theta$  values obviously as depth of charging (DOC) deepens at the first cycle, which is the proof that the c-parameter is increasing. When the charging voltage reaches about 4.56V, the (003) peak begins to move to higher angle gradually. Meanwhile, the peak width starts to broaden and the c-parameter stops increasing. During the discharging process, this reflection starts moving back to the lower angle and makes c-parameter increase. The c-parameter decreases at the second cycle charging process due to the fact that the general trend of (003) Bragg reflection shifts backward. It is worth noting that in figure 3, during the first charging process, from  $40^\circ$  to  $40.5^\circ$  ( $2\theta$  angle value) we can see clearly a new peak came out, this is a new phase which was proved to be (200) reflection of MnO phase after standardizing. Therefore, we speculate that the reaction of  $\text{Li}_2\text{MnO}_3 \rightarrow \text{Li}_2\text{O}_2 + \text{MnO}$  may happen in the platform potential of nearly 4.5V, and this means the Mn dissolution phenomena also takes place.

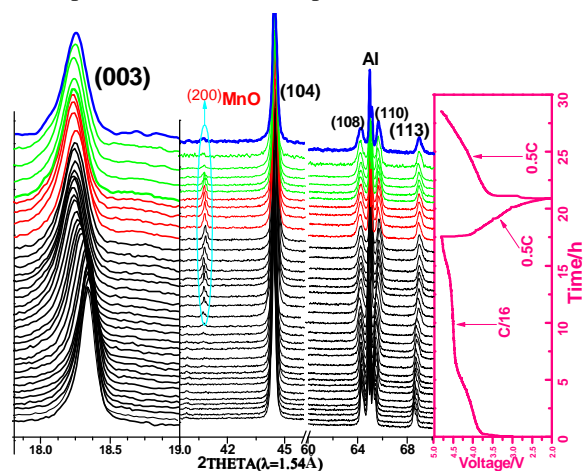


Fig.3. The in situ XRD pattern of the as-prepared  $\text{Li}_{1.23}\text{Ni}_{0.09}\text{Co}_{0.12}\text{Mn}_{0.56}\text{O}_2$  material during initial 1.5 cycles.

#### Reference

[1] M. M. Thackeray, C. S. Johnson, J. T. Vaughey, N. Li, and S. A. Hackney, *J. Mater. Chem.*, 15 (2005) 2257

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