

Synthesis and Performance of Fusiform and Sphere Hierarchical Layered Li-Rich Materials $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ for Lithium-Ion Batteries

Jinge Yang, Yujie Li^a, Chunman Zheng*

College of Aerospace Science and Engineering, National University of Defense Technology, Changsha 410073, China

*Corresponding author e-mail: Zhengchunman@nudt.edu.cn, ^apowerlyj@163.com

Abstract. Layered Li-rich cathode materials have a series of issues such as sharp voltage fading and bad cycling stability. To cure the problem, we developed a urea-based hydrothermal method followed a heat treatment to synthesize microscale fusiform and sphere hierarchical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ assembled with nanoparticle. The hierarchical fusiform $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ present high capacity of 259mAhg^{-1} at 0.1C and 270mAhg^{-1} at 0.05C and capacity retention of fusiform sample is up to 96% after 30 cycles at 0.1C, showing an excellent cycle performance.

1. Introduction

Lithium ion batteries have been widely applied to electronic devices and one of the most important energy-storage systems [1]. Lithium ion batteries have been commercialized since 1991 and nowadays lithium ion batteries are in sore need of improvement of the higher energy density. Lithium-rich manganese-based layered cathode materials have attracted much attention because of high specific capacity and have been considered as one of the most promising cathode materials [2] [3] [4] [5]. However, there is a series of issues of this kind of materials such as large first-cycle irreversible capability, limited rate capability and poor term performance due to the erosion from electrolytes and layered-to-spinel structural transformation during cycling process[6] [7].

Many works have been considered to solve the problems effectively such as coating metal oxides, substitution by other transition metal ions. In recent years to design hierarchical architecture morphology electrode materials has been demonstrated as an effectively approach to enhance electric performance.

In this study, we successfully developed a urea-based hydrothermal method followed a heat treatment. This method could synthesize microscale fusiform and sphere Li-rich manganese-based layered cathode materials $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ assembled with nanoparticles. Compared to sphere materials, the fusiform $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ showed an excellent cycling stability. This method is instructive for synthesizing other cathode materials in energy storage field.



2. Experimental

2.1. Synthesis of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$

A **Synthesis of fusiform $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$** : In a typical procedure, stoichiometric $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ were dissolved into 40ml of deionized water stirring for 1h to obtain homogeneous solution. The amount of transition metal ion was 0.01mol. Then 0.02mol urea and NH_4Ac (~1g) was add and the resultant mixture was continually stirred for another 1h and transferred into a Teflon lined stainless-steel autoclave. The autoclave was sealed and maintained at 180 °C for 15h in electron. The system was cooled to ambient temperature naturally. The products were collected by filtration, washed with deionized water and ethanol several times and dried for 12h. After washing, the precursors were mixed with 1.05 stoichiometric ratio of Li_2CO_3 and then calcined at 500 °C for 8h and thereafter at 900 °C for 15h in air to obtain fusiform $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$.

Synthesis of sphere $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$: In a typical procedure, stoichiometric $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ were dissolved into 40ml of homogeneous solution mixed of water and glycol(1:1 in volume) stirring for 1h. The amount of transition metal ion was 0.01mol. Then 0.02mol urea was add and the resultant mixture was continually stirred for another 1h and transferred into a Teflon lined stainless-steel autoclave. The autoclave was sealed and maintained at 180 °C for 15h in electron. The system was cooled to ambient temperature naturally. The products were collected by filtration, washed with deionized water and ethanol several times and dried for 12h. After centrifugal washing, the precursors were mixed with 1.05 stoichiometric ratio of $\text{LiOH} \cdot \text{H}_2\text{O}$ and then calcined at 500 °C for 8h and thereafter at 900 °C for 15h in air to obtain $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$.

2.2. Material characteristics

X-ray diffraction (Bruker D8 Advance) was conducted to determine the phase and crystal form of the product. The test conditions: Cu-K alpha, the tube voltage is 40 kV, the working current is 200 mA, the scanning speed is 6° min⁻¹, and the scanning range is 10°~90°. The morphology of the product were observed by HitachiS-4800 field emission scanning electron microscope.

2.3. Electrochemical measurements

The cathode material powder (80%), acetylene black (10%) as conductive additive, and Polyvinylidene fluoride (10%) as binder in N-methyl-pyrrolidinone were mixed, stirring for few hours to form a homogeneous slurry. After stirring, the slurry was coated on aluminum foil by a roll press to get a laminate. The laminate was dried in a vacuum oven at 110 °C for 12h, and then cut into discs of diameter 15 mm. 1.2 M LiPF_6 dissolved in EC and EMC (3:7 in volume) were used as the electrolyte, and Celgard 2400 was as the separator. The galvanostatic charge–discharge tests were performed on electrochemical workstation (LAND CT2001A) between 2.0 and 4.8V. EIS measurements were performed on electrochemical workstation (CHI660C).

3. Results and discussion

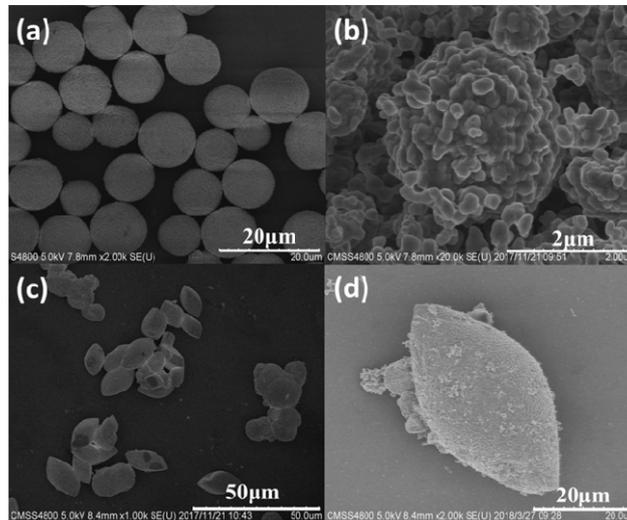


Figure 1. Scanning electron microscopy (SEM) images for precursors and $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, (a) precursors of sphere sample, (b) sphere $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ powder, (c) precursors of fusiform sample, (d) fusiform $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ powder

The SEM of the precursors and layered Li-rich materials are shown in Figure 1. As shown in Figure 1(a), the size of precursor of sphere sample is uniform and approximately 5-10 μm and shape can be seen into perfect sphere micro-particles. Sphere sample powders can maintain morphology of as-prepared precursors and size of one sphere powder is 10 μm . As shown in Figure 1(c), the size of precursors of fusiform sample can reach 20 μm . Fusiform powders can maintain the morphology of precursors, however, diameter of particles of fusiform became bigger after sintering.

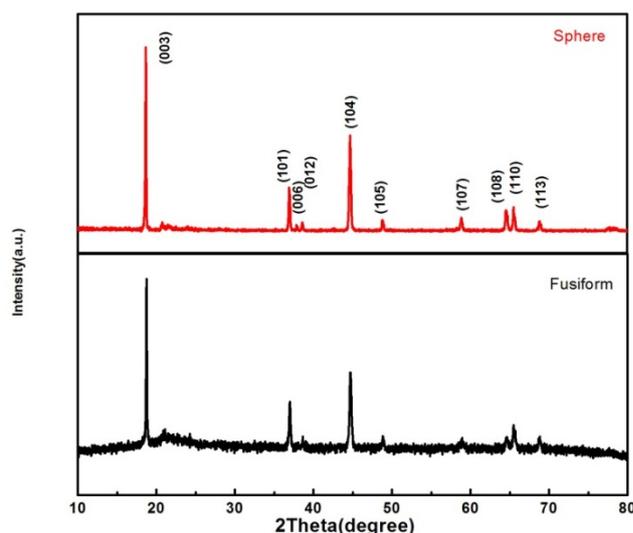


Figure2. X-ray diffraction pattern of fusiform and sphere powders

Figure2 shows the XRD patterns of sphere and fusiform samples. All the XRD patterns of the samples can be indexed to the layered rock-salt form with $\alpha\text{-NaFeO}_2$ -type structure with a space group of R3m. The low-intensity peak near $2\theta=20\text{-}25^\circ$ is the characteristic of Li-rich layered material close

to the Li_2MnO_3 composition with $C/2m$ space and the pattern can be demonstrated from superlattice ordering of Li and Mn [9] [10]. The clear splitting (006)/ (012) and (108)/ (110) peaks indicates a good crystallinity of layered structure [8]. The intensity ratio of I_{003}/I_{104} for fusiform and sphere samples are 1.85 and 1.91, which indicating a lower cation mixing for both two samples [11].

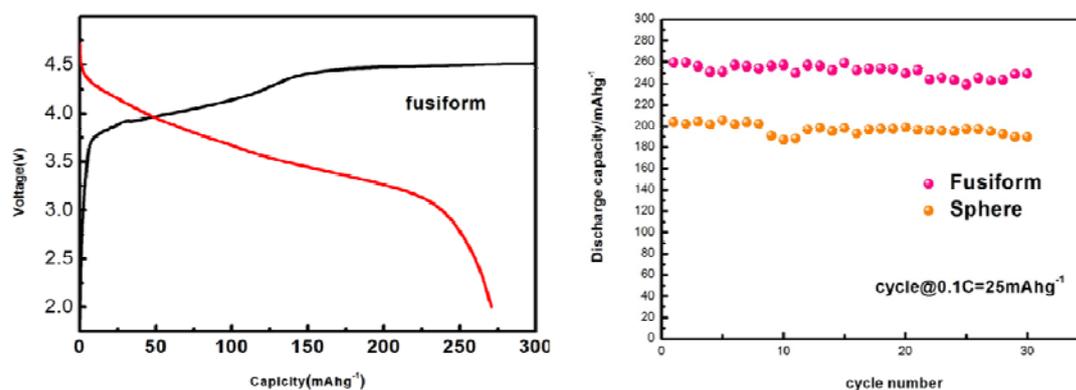


Figure 3. (a) Initial charge/discharge curves of fusiform sample (b) Cycling performance of fusiform and sphere samples at 0.1C rate

Fig. 3(a) shows the initial charge-discharge curves plot of fusiform sample at a current density of $C/20$ (12.5mAhg^{-1}). The discharge capacity of fusiform sample reached to 270.2mAhg^{-1} . The comparison of cycle performance at 0.1C (25mAhg^{-1}) between fusiform and sphere samples is exhibited in Fig.3 (b). To obtain a high discharge capacity, samples need some cycles at low rate before cycles of 0.1C. The initial discharge capacity of sphere sample is 203.6mAhg^{-1} and the capacity retention of sphere sample is up to 93% after 30 cycles. The initial discharge of fusiform sample is 259mAhg^{-1} and capacity retention of fusiform sample is up to 96% after 30 cycles, showing an excellent cycling performance.

4. Results and discussion

In this study, we successfully developed a urea-based hydrothermal method followed a heat treatment to synthesize microscale fusiform and sphere hierarchical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ assembled with nanoparticles. Fusiform hierarchical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ have a good crystallinity of layered structure, presenting high capacity of 259mAhg^{-1} at 0.1C and 270mAhg^{-1} at 0.05C and capacity retention is up to 96% after 30 cycles, showing an excellent cycle performance.

Acknowledgments

We acknowledge the funding support of the National Postdoctoral Program for Innovative Talents (BX201700103).

References

- [1] Armand M, Tarascon J M. Building better batteries [J]. *Nature*, 2008, 451 (7179): 652-657.
- [2] Thackeray M M, Johnson C S, Vaughey J T, Li N, Hackney S A. Advances in manganese-oxide 'composite' electrodes for lithium-ion batteries [J]. *J. Mater. Chem.*, 2005, 15 (23): 2257-2267.
- [3] Armstrong A R, Holzapfel M, Novák P, Johnson C S, Kang S-H, Thackeray M M, Bruce P G. Demonstrating Oxygen Loss and Associated Structural Reorganization in the Lithium Battery Cathode $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ [J]. *J. Am. Chem. Soc.*, 2006, 128 (26): 8694-8698.
- [4] Kang S-H, Johnson C S, Vaughey J T, Amine K, Thackeray M M. The Effects of Acid

- Treatment on the Electrochemical Properties of $0.5 \text{ Li}_2\text{MnO}_3 \cdot 0.5 \text{ LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$ Electrodes in Lithium Cells [J]. *J. Electrochem. Soc.*, 2006, 153(6): A1186-A1192.
- [5] Johnson C S, Kim J-S, Kropf A J, Kahaian A J, Vaughey J T, Thackeray M M. Structural and electrochemical evaluation of $(1-x)\text{Li}_2\text{TiO}_3 \cdot (x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes for lithium batteries[J]. *J. Power Sources*, 2003, 119–121(0): 139-144.
- [6] Zhou L, Zhao D, Lou X W (David). $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow structures as high-performance cathodes for lithium-ion batteries [J]. *Angew. Chem. Int. Ed.*, 2012,51: 239-241
- [7] Zhang L, Wu B, Li N, et al. Rod-like hierarchical nano/micro $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ as high performance cathode materials for lithium-ion batteries [J]. *J. Power Sources*, 2013, 240: 644-652
- [8] Zhang Bin, Chen Gang, Xu Ping, et al. Effect of equivalent and non-equivalent Al substitutions on the structure and electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [J]. *Journal of Power Sources*, 2008, 176 (1): 325-331
- [9] Lu Z, MacNeil D D, Dahn J R. Layered cathode materials $\text{Li} [\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]\text{O}_2$ for lithium-ion batteries [J]. *Electrochem. Solid-state Lett.*, 2001, 4: A191-A194
- [10] Lu Z, Beaulieu L Y, Donaberg R A, et al. Synthesis, structure, and electrochemical behavior of $\text{LiNi}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{O}_2$ [J]. *J. Electrochem. Soc.* 2002,149: A778-A791
- [11] Li J, Klopsch R, Stan M C, Nowak S, Kunze M, Winter M, Passerini S. Synthesis and electrochemical performance of the high voltage cathode material $\text{Li} [\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ with improved rate capability [J]. *J. Power Sources*, 2011, 196: 4821-4825