Journal of Power Sources 333 (2016) 37–42

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Facile design and synthesis of Li-rich nanoplates cathodes with habit-tuned crystal for lithium ion batteries

Jili Li [a, *], Tiekun Jia [a], Kai Liu [a], Junwei Zhao [a], Jian Chen [a], Chuanbao Cao [b]

[a] *Department of Material Science and Engineering, Luoyang Institute of Science and Technology, Luoyang 471023, China*
[b] *Research Centre of Materials Science, Beijing Institute of Technology, Beijing 100081, China*

HIGHLIGHTS

- $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ nanoplates with {010} planes are synthesized by a facile method.
- In this strategy, ethylene glycol plays a crucial role in {010} planes exposure.
- The growth of {010} planes are in favor of Li^+ intercalation/deintercalation.
- LNMO-NP cathode demonstrates high discharge capacity and excellent rate capability.

ARTICLE INFO

Article history:
Received 3 August 2016
Received in revised form
3 September 2016
Accepted 26 September 2016

Keywords:
Li-rich transition-metal oxide
Habit-tuned crystal
Nanoplates
Cathodes
Li-ion batteries

ABSTRACT

Li-ion batteries with high-energy and high-power density are pursued to apply in the electronic vehicles and renewable energy storage systems. In this work, layered Li-rich transition-metal oxide cathode $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ nanoplates with enhanced growth of {010} planes (LNMO-NP) is successfully synthesized through a facile and versatile strategy. Ethylene glycol plays an important role in the formation of LNMO-NP nanoplates with {010} electrochemically active surface planes exposure. As cathode for Li-ion batteries, LNMO-NP demonstrates a high specific discharge capacity of 270.2 mAh g^{-1} at 0.1 C (1 C = 300 mA g^{-1}) and an excellent rate capability. The good electrochemical performance can be attributed to the nanoplates with the growth of {010} electrochemically active planes which is in favor of Li^+ intercalation/deintercalation.

1. Introduction

Nowadays, layered Li-rich transition-metal oxide cathode materials $xLi_2MnO_3-(1-x)LiMO_2$ ($0 < x < 1$, M = Mn, Ni, Co) have attracted great attentions as the next generation cathode materials for lithium ion batteries (LIBs), which is due to their high specific capacity (ca. 250 mAh g^{-1}), low cost and environmental benignity [1–3]. They can be charged to a higher voltage (>4.5 V) than the conventional cathode materials leading to the drastically improved electrode capacity. However, there are numerous serious issues with this class of cathode materials in their practical application, such as intrinsic poor rate capability, severe capacity and voltage fading during cycling, etc. [4–10] The voltage decay was caused by the rearrangement of surface structure resulted from the activation of Li_2MnO_3 component above 4.5 V, the erosion from the electrolytes, and the structural transformation during cycling process [6,8].

It is well known that the morphology and surface microstructures are critical to the Li^+ transportation of electrode materials. Layered Li-rich transition-metal oxide cathode crystallized with α-$NaFeO_2$ structure in which Li^+ can only intercalate/deintercalate into/from the crystal along the direction parallel to the Li^+ layers. In the layered structure, the planes parallel to the *a*- (or *b*-) axis are indexed as {010} planes including (010), $(\bar{1}10)$), $(\bar{1}00)$, $(0\bar{1}0)$, $(1\bar{1}0)$ and (100) facets and the planes perpendicular to the {010} planes are (001) and $(00\bar{1})$ facets [4,5]. Among these planes, (001) and $(00\bar{1})$ facets are composed of the MO_6 octahedra which can hinder Li^+ insertion. The {010} planes are open structures with a wide window affording unimpeded paths for Li^+ diffusion. Our research group has recently demonstrated that the rate performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (layered cathode materials) can be enhanced by increasing the percentage of exposed {010} active planes

---

* Corresponding author.
E-mail address: lijili328@126.com (J. Li).

http://dx.doi.org/10.1016/j.jpowsour.2016.09.150
0378-7753/

through a facile strategy [11].

Sun's group has successfully prepared layered Li-rich cathode $Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ nanoplates with {010} planes exposure by using hydrothermal method [4]. L. Chen has shown the hierarchical $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ nanoplates with exposed {010} planes by a solid-state reaction of Li_2CO_3 and nickel-manganese hydroxide precursor [5]. The precursor was prepared through PVP-assisted co-precipitation process under nitrogen atmosphere. $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$ cathode materials with hierarchical spheres assembled by nanoplates with enhanced growth of {010} planes have been reported using a precipitation and followed an ionic interfusion strategy [8]. In the precipitation procedure of $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$, concentrated sulfuric acid and $AgNO_3$ were applied as catalyst. These methods are too complicated to undoubtedly increase the cost of LIBs. Therefore, it is still a huge challenge to prepare layered Li-rich transition-metal oxide cathode materials with enhanced growth of {010} planes which are easy to be vanished during synthesis.

Herein, we report a facile and versatile strategy to obtain $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ nanoplates (LNMO-NP) with enhanced growth of {010} planes in favor of Li^+ insertion/extraction. In our synthesis route, ethylene glycol is used not only as a solvent but also as a chelating reagent during the formation of LNMO-NP with {010} planes growing. LNMO-NP contains the {010} electrochemically active surface planes at the sided facets and the {001} planes at top and bottom planes. In addition, there are large amount of gaps between the nanoplates, which can facilitate electrolyte penetration in the batteries. It is demonstrated that LNMO-NP exhibits an excellent electrochemical performance as a cathode in LIBs.

2. Experimental

2.1. Preparation of LNMO-NP

$Ni(NO_3)_2 \cdot 6H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and $LiNO_3$ with 1:3:6.2 in the molar ratio were dissolved into ethylene glycol with a total metal ions concentration of 0.05 M. Continue stirring the solution under 85 °C for 12 h. Then, put it in an air dry oven and keep for overnight at 120 °C obtaining a gel-like solid. Grind the dried gel-like solid to fine powder. Finally, the mixture was pre-heated at 450 °C for 5 h and calcined at 850 °C for 12 h in air to gain the LNMO nanoplates.

2.2. Characterization of LNMO-NP

The structure of LNMO-NP was performed on a PANalytical X-pert diffractometer (PANalytical, Netherlands) with Cu Kα radiation to measure the powder X-ray diffraction (XRD) pattern from 10° to 80° at room temperature at 40 kV and 40 mA. Hitachi field-emission scanning electron microscopy (FE-SEM S-4800) and transmission electron microscopy (TEM) (Tecnai G2 F20) were applied to explore the size, morphology and microstructure of the sample. Inductive Coupled Plasma Atomic Emission Spectrometry (ICP-AES, ICAP-6300) was carried out to ensure the exact ratio of Li:Ni:Mn in the sample.

2.3. Electrochemical measurements of LNMO-NP cathode

CR2025 coin cells were fabricated to analyze the electrochemical performances of LNMO-NP cathode. Firstly, LNMO-NP sample, carbon black and poly(vinylidene fluoride) (PVDF) binder were mixed with 80:10:10 wt% in *N*-methyl-2-pyrrolidone (NMP) to form a slurry. Secondly, the slurry was uniformly cast onto aluminum foil. Thirdly, dry it in a vacuum oven at 120 °C for 12 h. Finally, the cells were assembled in an argon-filled glove box (with $O_2 < 1$ ppm and $H_2O < 1$ ppm). Li metal, Celgard 2400 films and a solution of 1 M $LiPF_6$ dissolved in ethyl carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC) (1:1:1 v/v/v) were used as the counter and reference electrodes, separators and the electrolyte, respectively. The loading mass of the active material in one electrode is 1.6–1.8 mg cm^{-2}. The galvanostatically charge-discharge testing was performed at different C rates between 2.0 and 4.8 V on a LAND CT-2001A cell test instrument at around 30 °C. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a CHI660E electrochemical workstation over the frequency range between 100 kHz and 0.01 Hz and applying an AC signal of 5 mV at room temperature.

3. Results and discussion

Ethylene glycol is an important solvent for $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ nanoplates growing simultaneously in both the [010] (or [100]) and [001] directions, which increases the yield of {010} nanoplates. There are bi-functional groups in ethylene glycol molecule, which can react with metal ions generating a plate-like structure through the hydrogen bond and chelating effects [11,12]. In the formation process, plate-like structural precursor can be first formed through ethylene glycol molecules capped on the surface of the crystal [13]. Once the plate-like structure is formed, ethylene glycol molecules can be immediately adsorbed on {001} surfaces via the bi-functional groups. After heat treatment at 450 °C, the ethylene glycol molecules are decomposed and the plate-like structure is obtained (shown in Fig. S1). Therefore, the crystal growth along [001] and the [010] (or [100]) is impeded. In addition, the nucleation of the precursor can be slowed down because of the larger viscosity of ethylene glycol [13].

The structure of LNMO-NP material has been characterized with X-Ray powder diffraction (XRD). All the sharp peaks in the XRD pattern of the LNMO-NP sample (Fig. 1a) are well indexed with α-$NaFeO_2$ layered structure (space group: R−3m) except for some weak superlattices reflections between 20 and 25° (red region in Fig. 1a) which are caused by Li^+/Mn^{4+} cation ordering in the transition metal layers [5,10]. The clear separations of the (006)/(102) and (108)/(110) peaks can be indicated to the highly ordered hexagonal layered structure [5,10]. Besides, the lattice parameters were calculated from the experimental XRD pattern with an assumption of R−3 m structure. The unit cell parameters are found to be $a = 2.869$ Å, $c = 14.247$ Å, in which the c/a of the sample is greater than 4.899 implying an explicit layer structure [14,15]. The exact molar ratio of Li:Ni:Mn in LNMO-NP material shows 1.21:0.21:0.58 ensured by ICP-AES in consistent with the expected stoichiometry within experimental errors.

The morphology and microstructure of the as-prepared LNMO-NP are characterized by the SEM, TEM and HRTEM and shown in Fig. 1b–f. As shown in the SEM images of the sample (Fig. 1b–c), LNMO-NP material is composed of nanoplates with a thickness of 50–160 nm. In addition, there are large amounts of pores between the nanoplates because of the presence of ethylene glycol molecules transformed to volatile products during the heating procedure [11]. The porous structure can offer an ample electrode/electrolyte interface for ion or charge accumulation and effectively facilitate LNMO-NP to be soaked into electrolyte. Detailed microstructure of LNMO-NP material can be clearly observed under the transmission electron microscope (TEM) and high resolution TEM (HRTEM) shown in Fig. 1d–f. The morphology and size of the nanoplates are in good agreement with the SEM results. Fig. 1e and f shows the HR-TEM images of the frontal plane and the lateral plane, respectively. There are three sets of clear fringes in the HR-TEM image of the frontal plane (Fig. 1e). One set has a *d* spacing of 1.43 Å assigned to (110) planes and the other two sets have the same *d* spacing of 2.46 Å assigned to the $(0\bar{1}0)$ and (100) planes,