Materials Letters 217 (2018) 284–287

Contents lists available at ScienceDirect

Materials Letters

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

# Layered $Li[Li_{0.2}Ni_{0.133}Co_{0.133}Mn_{0.534}]O_2$ with porous sandwich structure as high-rate cathode materials for Li-ion batteries

Jian Chen *, Na Zhao *, Junwei Zhao

*Department of Materials Science and Engineering, Luoyang Institute of Science and Technology, Luoyang 471023, PR China*

ARTICLE INFO

*Article history:*
Received 13 December 2017
Received in revised form 11 January 2018
Accepted 17 January 2018

*Keywords:*
Li-rich layered oxides
Microstructure
Cathode material
Energy storage and conversion

ABSTRACT

$Li[Li_{0.2}Ni_{0.133}Co_{0.133}Mn_{0.534}]O_2$ sample with porous sandwich structure is prepared via a carbon gel–combustion synthesis process and a polypropylene membrane with microporous structure as hard template. As cathode materials, the discharge capacity of the sample is 230.2 mAh $g^{-1}$ in the first cycle at 0.2 C and 241.3 mAh $g^{-1}$ after 50 cycles, and the electrode still delivers average discharge capacity of 78.0 mAh $g^{-1}$ even at 30 C rate. The outstanding electrochemical properties for the 2-D porous structural features, high crystallinity and structural stability and low charge transfer resistance suggest the applications of Mn-based Li-rich layered oxides in high power lithium-ion batteries.

## 1. Introduction

As we know, the particle size and special topography of the electrode materials have an important effect on the physico–chemical kinetics and electrochemical properties [1]. In particular, two-dimensional (2-D) structured materials have been caused extensive studies as cathode materials for lithium ion batteries due to the high surface area, large surface–to–volume ratio, fast lithium ion transport and favorable structural stability. However, limited 2-D morphologies of electrode materials with porous structure have been reported for the difficultly grow in 2-D direction, especially for the multi–component electrode material [2,3].

The Li-rich layered metal oxides denoted as $xLi_2MnO_3{\cdot}(1-x)LiMO_2$ (M = Mn, Ni, Co, *etc.*) have attracted much attention for high specific capacity of 250–300 mAh $g^{-1}$, relatively low cost, and good safety performance comparing to cathode materials available on the market such as $LiCoO_2$ [4], $LiFePO_4$ [5], $LiMn_2O_4$ [6] and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ [7]. In this work, the porous $Li[Li_{0.2}Ni_{0.133}Co_{0.133}Mn_{0.534}]O_2$ ($0.5\ Li_2MnO_3{\cdot}0.5\ LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$) with 2-D sandwich structure was prepared via a simple carbon gel–combustion synthesis process using a monolayer polypropylene membrane with rich microporous structure as hard template. The electrochemical performance of $Li[Li_{0.2}Ni_{0.133}Co_{0.133}Mn_{0.534}]O_2$ with 2–D porous sandwich structure as cathode materials for lithium ion batteries was measured systematically, especially in high current rates.

## 2. Experimental

### 2.1. Powder preparation and treatment

Firstly, 1.303 g lithium nitrate ($LiNO_3$) (Lithium salt is added in excess of 5% to compensate volatilized Li), 0.580 g nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), 0.581 g cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and 1.963 g manganese acetate tetrahydrate ($C_4H_6MnO_4{\cdot}4H_2O$) were dissolved in 30 mL ethanol. Secondly, 2.2 g resorcinol ($C_6H_6O_2$) and 3.0 mL formaldehyde ($CH_2O$, 36.5 wt% in water) were added to the above solution and then stirred another 30 min. Thirdly, the above solution was poured into a Teflon–lined stainless steel autoclave, and the polypropylene microporous membrane (Celgard 2400) was added into the autoclave and immersed in the above solution. The autoclave was sealed and heated at 85 °C for 48 h. Finally, after naturally cooled to room temperature, the resulting membrane was taken out from the autoclave and then calcined at 850 °C for 10 h in air to obtain the electrode material.

### 2.2. Material characterization

The crystal structure, morphological features and elemental compositions of the as–synthesized sample were examined by X-ray diffraction (XRD, Rigaku D/Max 2550), field emission scanning electron microscopy (FESEM, JEOL JSM-6700F), transmission electron microscopy (TEM, Hitachi H-8100), X-ray photoelectron spectroscope (XPS, PHI5600), energy dispersive spectroscopy

---

* Corresponding authors.
*E-mail addresses:* chemcj@126.com (J. Chen), electro_zn@126.com (N. Zhao).

https://doi.org/10.1016/j.matlet.2018.01.108

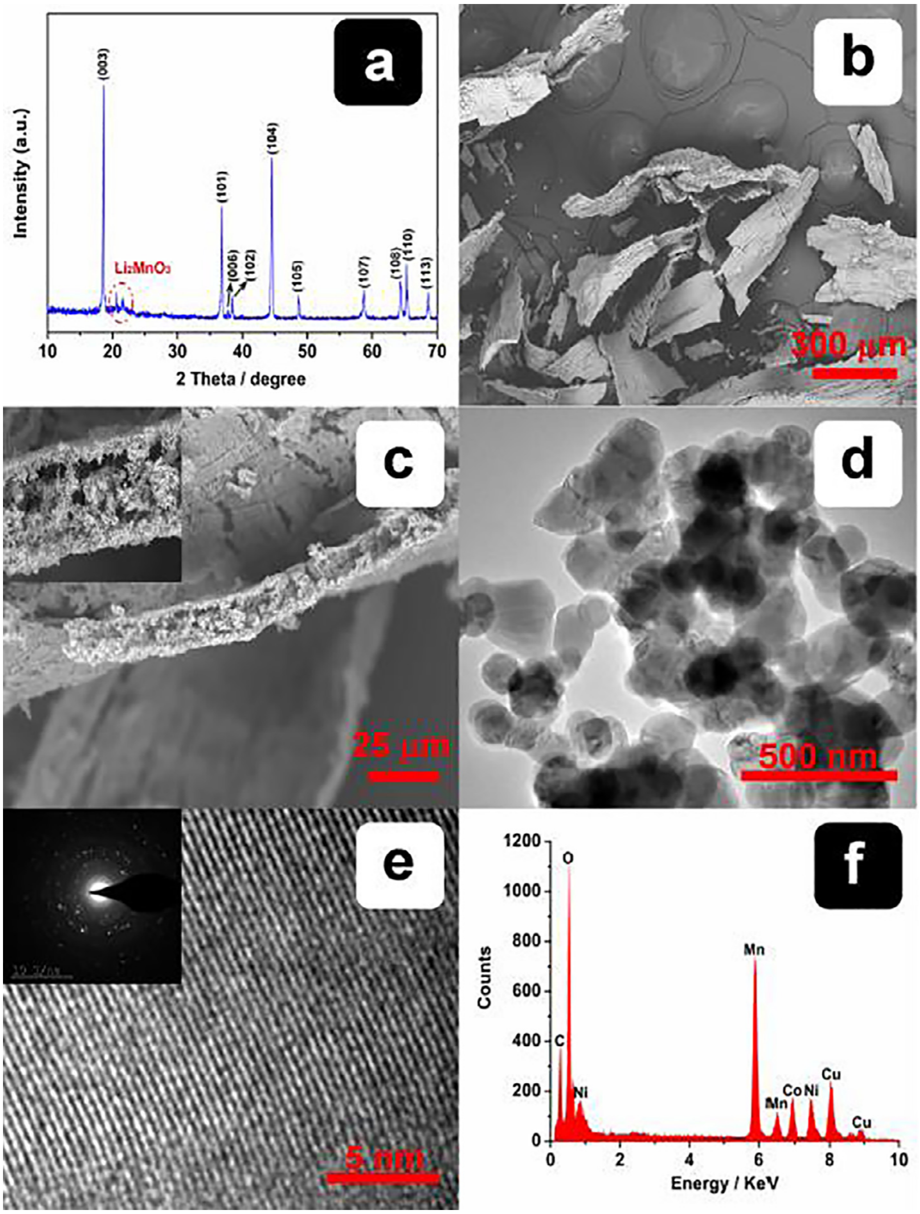

**Fig. 1.** XRD (a), SEM (b and c), TEM images (d and e) and EDS result (f) of the sample.

(EDS, Oxford INCA, Britain) and inductive coupled plasma atomic emission spectrometry (ICP-AES, ICAP-6300).

### 2.3. Electrochemical tests

The $Li[Li_{0.2}Ni_{0.133}Co_{0.133}Mn_{0.534}]O_2$, polyvinylidene fluoride and Super P carbon black were mixed together to prepare the working electrodes, and the weight ratio between them was 8:1:1. The electrolyte was 1 M $LiPF_6$ in a mixture of EC (ethylene carbonate), DMC (dimethyl carbonate) and EMC (ethylmethyl carbonate) (1:1:1 by weight). The batteries were assembled in an argon–filled gloved–box using the lithium metal as a counter and reference electrodes. Charge/discharge measurements at different C rates were conducted on a cell testing apparatus (LAND CT2001A) in the voltage range of 2.0–4.6 V. The electrochemical behavior of the electrode material was investigated by cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) on an electrochemical workstation (CHI 660E).

## 3. Results and discussion

Fig. 1a shows the XRD pattern of the $Li[Li_{0.2}Ni_{0.133}Co_{0.133}Mn_{0.534}]O_2$ sample. All of the diffraction peaks of the sample can be identified to the α-$NaFeO_2$ crystal structure with R-3 m space group excepting the superlattice peaks between 20° and 23°, and the weak peaks around 20°–23° can be indexed to monoclinic unit cell with space group symmetry of C2/m [8]. Simultaneously, the high intensity ratio of the (0 0 3) to (1 0 4) peaks (here is equal to 1.34) and the clear splitting of the 006/102 and 108/110 peaks of the $Li[Li_{0.2}Ni_{0.133}Co_{0.133}Mn_{0.534}]O_2$ sample indicate that the as–prepared sample has well-layered structure, improved crystallinity and low degree of cation mixing [8]. The molar ratio of Li:Ni:Co:Mn in the sample measured by ICP-AES analysis is 1.207:0.133:0.135:0.536 within the experimental error limits. As shown in Fig. 1(b and c), the sample shows a 2-D porous sandwich structure. Fig. 1d shows the TEM image of the electrode material, and the sample is composed of nanoscale particles. Fig. 1e shows the HRTEM image of the electrode material, and the clear light–dark lattice fringe