Electrochimica Acta 268 (2018) 358–365

Contents lists available at ScienceDirect

Electrochimica Acta

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

Improving cycling performance and rate capability of Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode materials by $Li_4Ti_5O_{12}$ coating

Ya-Di Xu [a], Wei Xiang [b, c, *], Zhen-Guo Wu [a], Chun-Liu Xu [a], Yong-Chun Li [a], Xiao-Dong Guo [a, **], Gen-Pin Lv [c], Xi Peng [a], Ben-He Zhong [a]

[a] College of Chemical Engineering, Sichuan University, Chengdu 610065, PR China
[b] College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, PR China
[c] Post-doctoral Mobile Research Center of Ruyuan Hec Technology Corporation, Guangdong, Ruyuan, 512000, PR China

ARTICLE INFO

Article history:
Received 2 January 2018
Received in revised form
8 February 2018
Accepted 8 February 2018
Available online 9 February 2018

Keywords:
$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$
Ni-rich
Coating
$Li_4Ti_5O_{12}$

ABSTRACT

A simple wet chemical process followed by high temperature calcination has been successfully used to coat Li-ion conductive $Li_4Ti_5O_{12}$ on the surface of Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. Physicochemical characterization results indicate that a $Li_4Ti_5O_{12}$ with a thickness of about 2–3 nm was uniformly distributed on the surface of microspheres, without inducing significant change of the structure and morphology. Electrochemical test results show that proper content of $Li_4Ti_5O_{12}$ coating layer can greatly improve the cycling performance and rate capability of Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ for the improved Li^+ ions diffusion rate and suppressed side reactions between electrode and electrolyte. Notably, the 1 *wt%* $Li_4Ti_5O_{12}$ coated sample exhibits excellent cycling stability with the capacity retention of 75.86% at 1 C after 170 cycles when cycled between 2.7 and 4.3 V at 25 °C, while that is only 39.40% for bare $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

From $LiCoO_2$ to layered lithium nickel cobalt manganese oxide $LiNi_{1\text{-}x\text{-}y}Co_xMn_yO_2$, rechargeable lithium batteries are still recognized as the attractive power sources for electric vehicles (EVs) and hybrid electric vehicles (HEVs) in the next decades [1,2]. During the past years, extensive research have focused on identifying and developing advanced cathode materials in terms of high energy density, long cycling life and high rate capability [3,4]. Among the existing cathodes for LIBs, nickel rich layered lithium transition metal oxides ($LiNi_{1\text{-}x\text{-}y}Co_xMn_yO_2$, where$1\text{-}x\text{-}y>0.6$) are the most practical candidates for EVs and have drawn worldwide interest mainly because of their high reversible capacity, good rate capacity and low cost of raw material [5,6].

However, the industry application of Ni-rich cathodes is impeded by the inherent chemical instability, which lead to insufficient cycle life and poor thermal stability, especially at elevated temperatures and in highly delithiated state [7]. One reason is that the distortion of the rhombohedral phase and the formation of spinel-like structures due to the migration of Ni^{2+} (0.069 nm) into Li^+ (0.076 nm) caused by similar radius [8–10]. In response, great efforts have been focused on alleviating the cation disorder and prohibiting the phase transitions. In this regard, element doping (Ti, Mg, Al, Cr, *etc.*) is effective for the bulk stabilization and has revived the Ni-rich materials [11–13]. Meanwhile, the particle surface chemistry is also vital to the electrochemical performance, especially the long term cycle stability. Because chemical instability Ni^{4+} formed during the delithation/lithation tends to react with electrolyte and form inacitve products (NiO), the inhibition of the direct contact between Ni^{4+} and electrolyte is essential to stabilize the surface of Ni rich layered oxides and achieve long term cyclability [14]. Surface coating, as a very effective strategy to protect the active materials from the serious side reactions, has been widely investigated. Different coating materials include mental oxides, metal fluorides, mental phosphates, metal carbonates and carbon have been reported as suitable coating materials to date [15–18]. However, some inert materials as coating layer are generally unfavorable for Li-ion conduction of cathode, which lead to weaken the electrochemical performance. In view of this point, material such as Li_3VO_4, $Li_2Si_2O_5$ and Li_2ZrO_3 with high Li-ion diffusivity is especially suitable for the surface modification of Ni-rich cathode to enhance the cycling performance and rate

---

* Corresponding author.College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, PR China.
** Corresponding author.
E-mail addresses: xiangwei@cdut.edu.cn (W. Xiang), xiaodong2009@163.com (X. Peng).

https://doi.org/10.1016/j.electacta.2018.02.049
0013-4686/© 2018 Elsevier Ltd. All rights reserved.

capability [19–21].

Li-ion conductor $Li_4Ti_5O_{12}$ (LTO) has been widely researched as the next generation of anode materials due to its intrinsic characteristics. The spinel structure notonly ensures rich channels for fast lithium ion transportation but also displays a good structural stability during repeated lithiation/delithiaton process (zero-strain insertion material). Moreover, LTO has high voltage platform of 1.55 V (*vs*. Li/Li^+) which can avoid the formation of solid electrolyte interface (usually occurring below 1.0 V *vs*. Li/Li^+) [22,23]. Based on these merits, it can be concluded that a thin and uniform LTO coating layer would have positive effects on the electrochemical performance enhancement of Ni rich cathode materials. Yunjian Liu et al. found that the electrochemical performance (especially rate performance) of $Li_{1.5}Ni_{0.25}Mn_{0.75}O_{2.5}$ was improved effectively after $Li_4Ti_5O_{12}$ coating [24]. Yan-Rong Zhu et al. reported that $Li_4Ti_5O_{12}$-coated $LiMn_{1.5}Ni_{0.5}O_4$ by sol-gel method exhibited increased cycling stability [25]. But to our knowledge, there is no any research about using LTO as coating layer to improve the electrochemical performance of $LiNi_{1\text{-}x\text{-}y}Co_xMn_yO_2$ ($1\text{-}x\text{-}y>0.6$).

In this work, LTO was coated on the surface of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ by a novel simple wet chemical route followed by high temperature calcination to improve the electrochemical performance of the material. The effects of LTO on the structure and electrochemical performance of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ were systematically investigated. With the inhibition of side reaction and facilitation of lithium diffusion, the 1 *wt%* LTO coated sample exhibits excellent rate performance and cycle stability.

2. Experiment

2.1. Sample preparation

Commercial $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powder was used as the uncoated material (denoted as LNCM). The LTO coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ was synthesized by a facile wet chemical method followed by high temperature calcination using $Ti(C_4H_9O)_4$, $LiOH\cdot H_2O$ and commercially supplied $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. The coating process is schematically illustrated in Fig. 1. First, required amounts of $Ti(C_4H_9O)_4$ (AR, 95%) were dissolved in pure ethanol. Then, the required $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ was added into the solution. After the solution was ultrasonic treated for 5 min, a mixed solution containing ethanol and distilled water (the volume ratio of ethanol/water was controlled at 3:1) was added dropwise into the above solution at room temperature under stirring to slowly hydrolyze $Ti(C_4H_9O)_4$ on the surface of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. The coated precursors were obtained through evaporating the solvent of ethanol and water with the addition of stoichiometric $LiOH\cdot H_2O$ (AR, 98%) in air at 80 °C for 6 h. Then the coated dry precursors particles were calcined at 600 °C for 12 h in air with a heating rate of 5.0 °C min^{-1} to get the final LTO coated samples. Various coating amounts of 1 and 3 *wt%* were applied, and the corresponding samples are denoted as LNCM-1 and LNCM-2.

2.2. Materials characterization

The crystal structure of the samples were identified by X-ray diffraction (Philip Company, Pw1730) with a Cu Kα radiation ($\lambda = 1.54178$ Å) in the 2θ range of 10–70° at a scanning rate of $0.06°s^{-1}$. Particle morphology and structure were measured by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, JEM-2100). The element mapping is performed by energy dispersive spectroscopy (EDS) using the same instrument with the SEM characterization. Surface element information was obtained by X-ray photoelectron spectrometer (XPS, VG Multilab 2000).

2.3. Electrochemical measurement

Electrochemical performances of the samples were tested in CR 2032 coin type cells. In preparation of positive electrode, the active material, carbon black (electronic conductor) and PVDF (binder) with a weight ratio of 80:13:7 were homogeneously mixed in N-methyl-2-pyrrolidone. Then, the slurry was spread uniformly onto an aluminum foil current collector, and the electrodes were dried under vacuum at 120 °C for 12 h (the loading of the active material for LNCM, LNCM-1 and LNCM-2 were 2.18 ± 0.05, 2.20 ± 0.05 and 2.16 ± 0.05 mg cm^{-2} respectively). After compressing at 20 Mpa between two stainless steel plates, the electrodes were assembled with metallic lithium anode, microporous polymer separator (Celgard 2300) and electrolyte (1 M lithium $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 by volume)) in a glove box under argon atmosphere (O_2 and H_2O lower than 0.5 ppm). All the electrochemical tests were characterized in the voltage range of 2.7–4.3 V using a constant-current protocol at room temperature (25 ± 2 °C) on a battery testing system (Neware BTS-610) at room temperature. The electrochemical impedance spectroscopy (EIS) was measured on electrochemical workstation (Zennium, IM6) in the frequency range from 100 kHz to 10 mHz with a voltage amplitude of 5 mV.

3. Results and discussion

To analyze the structure of all the samples, the phase of the pristine and coated samples with different coating contents were confirmed by XRD. As shown in Fig. 2, all the patterns are similar and can be indexed to a well-defined hexagonal α-$NaFeO_2$ structure with *R*3*m* space group without any impurity phase. And the obvious peak split of the adjacent peaks ((006)/(102) and (108)/(110)) in all XRD patterns indicates the well-ordered layered structures were formed for all samples. The absence of obvious peaks related to LTO for coated samples could be ascribed to the low coating content or small crystal size of coating material. All

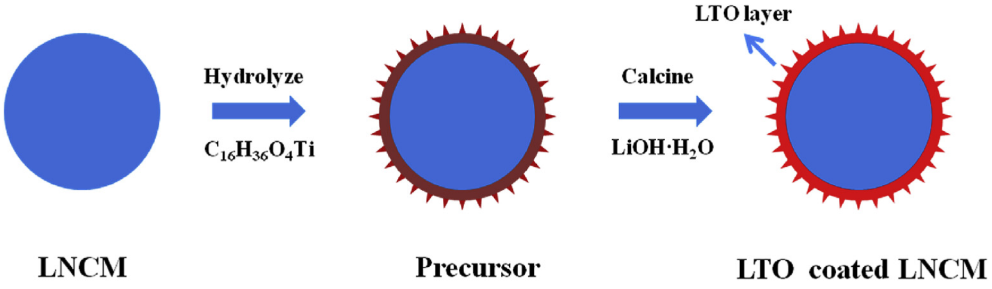

Fig. 1. Schematic illustration of the synthesis of LTO coated particles.

Download English Version:

https://daneshyari.com/en/article/6603822

Download Persian Version:

https://daneshyari.com/article/6603822

Daneshyari.com