Electrochimica Acta 281 (2018) 48–59

Contents lists available at ScienceDirect

Electrochimica Acta

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

High-voltage electrochemical performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material via the synergetic modification of the Zr/Ti elements

Yongxiang Chen [a, c], Yunjiao Li [a, c, *], Wei Li [a, c], Guolin Cao [a], Shuyun Tang [b], Qianye Su [a], Shiyi Deng [a, c], Jia Guo [a, c]

[a] School of Metallurgy and Environment, Central South University, Changsha 410083, PR China
[b] School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China
[c] Citic Dameng Mining Industries Limited, Nanning 530028, PR China

ARTICLE INFO

Article history:
Received 12 March 2018
Received in revised form
19 May 2018
Accepted 23 May 2018
Available online 26 May 2018

Keywords:
Lithium ion battery
$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$
High voltage
Zr/Ti synergetic modification

ABSTRACT

The stabilities of the host and interfacial structure for layered $LiNi_xCo_yMn_{1-x-y}O_2$ cathode materials are critical for their electrochemical properties, especially at high voltage. This study reports the synergetic effect of the Zr and Ti elements on the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material (NCM523). The as-obtained Zr/Ti modified $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material shows the excellent electrochemical performance at high voltage. It delivers 167.3 $mAh \cdot g^{-1}$ at 1 C over 3.0–4.4 V corresponding 94.20% capacity retention after 200 cycles. Moreover, the rate capability of Zr/Ti co-modified NCM523 at 16 C (3.0–4.4 V) rises to 139.4 $mAh \cdot g^{-1}$ and corresponding capacity retention (vs. 0.5 C) is 79.57%. In addition, its capacity retention reaches to 91.71% after 100 cycles at 1 C rate even at 3.0–4.6 V. Such superior electrochemical performances are ascribed to the Zr doping and Ti modification. The synergetic modifications of the Zr/Ti elements not only stabilize the crystal structure, but also absorb the lithium residues to form mixed $Li_4Ti_5O_{12}/Li_2TiO_3$ coating layers, which strengthen the stability of the interfacial structure and the kinetic characteristics of the cathode materials.

1. Introduction

Driven by the growing demands for clean efficient energy storage media ranging from portable electronics, electric vehicles to mass energy storage systems, Li-ion batteries (LIB) have attracted extensive worldwide studies from the academic communities to the enterprises [1–5]. Among various candidates of cathode materials, layered $LiNi_xCo_yMn_{1-x-y}O_2$ cathode materials have been considered as the most promising competitors in the coming years due to the low costs, high capacities and superior thermal stabilities [6–9]. However, a number of inherent defects for this cathode materials still need to be overcome, such as Li/Ni mixing in the bulk material and the residual lithium components (Li_2CO_3/LiOH) on the surface occurred during synthesis, structure degradation and side-reactions upon cycling etc. [10–13] Although this, the demand of higher energy density drives researchers to expand the cut-off voltage. As previously reported, the rise in highly reactive Ni^{4+} in cathode at high voltage and the existence of the residual lithium components (Li_2CO_3/LiOH) accelerate the side-reactions during cycling [11,14–16]. Additionally, the generations of the microstrain accompanied with secondary particle breakdown and phase transformation also lead to the capacity fading, especially at a relative high voltage (≥4.4 V) [9,17–19].

A series of strategies have been proposed by the researchers to solve the aforementioned drawbacks, such as surface coating, structural design, cation doping and additives into the electrolytes [16,20]. Among them, cation doping has been proved to be an effective strategy to improve the electrochemical properties. The cation substitution can balance the valence states of both oxygen and transition metals through charge compensation mechanisms and modify the interlayer/layer space of lithium ion and transition metals layers, further elevates the electronic and lithium ion conductivities as well as the stability of the bulk materials [21]. Zhang et al. studied on the Mo doped $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials and demonstrated that the Mo can help to improve the electrochemical performance and structural stability [22]. Schipper et al. reported that the structural transformation has been suppressed upon cycling and the electrochemical kinetics has been enhanced remarkably after Zr substitution in $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ [23]. Of course, some other doping elements such as Nd [8], F

---

* Corresponding author. School of Metallurgy and Environment, Central South University, Changsha 410083, PR China.
E-mail address: yunjiao_li@csu.edu.cn (Y. Li).

https://doi.org/10.1016/j.electacta.2018.05.154
0013-4686/

[24,25] and Si [26] etc. are conductive to improve the electrochemical performance. As another available way, surface coating also exhibits great advantages in improving the interfacial properties of the cathode materials. The coating layers can avoid the corrosion of the electrodes from the electrolytes [16]. Meanwhile, some of them assist to improve the electronic and lithium ion transportation on the surface of the electrodes to some degree [16,25,27]. Accordingly, various coating materials, including metal oxides (MoO_3 [22], Li_2O-B_2O_3 [28],Y_2O_3 [29]), phosphates ($FePO_4$ [30], $AlPO_4$ [31]) and fluorides (AlF_3 [32], $LiAlF_4$ [33]), have been applied to improve the interfacial properties of the cathode materials. Moreover, some coating layers (i.e. V [34] and PO2- 4 [35]) formed on the NCM surface can absorbed the residual lithium components (Li_2CO_3/LiOH), which is another effective routine to improve the interfacial stability of the cathode materials.

Above all, both the structural and interfacial stabilities of the cathodes are equally important. However, the individual modification can only solve parts of the issues. Hence, the combination of elemental doping and coating has come to the attention of researchers. Wang et al. declared that the electrochemical properties of the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material at high voltage have been significantly enhanced after the Zr doping and polypyrrole (PPy) coating [9]. Schipper et al. pointed out that the Zr from coating to doping by controlling the annealing temperature can improve the electrochemical performance of the $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode material [36]. Liu et al. also reported that the F^- doped and Al_2O_3 coated $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ cathode material delivered excellent electrochemical performance [25]. Therefore, the synergetic modification of doping and surface coating is an effective and potential way to promote the electrochemical stability of the cathode material.

In recent years, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material has gradually dominated the clean energy market, especially in electric vehicle (EV) and hybrid electrical vehicle (HEV) market, but its sustainable development in the future would be restricted by the fast capacity fading, especially in the high voltage ($\geq$4.4 V). For this reason, it is imperative to enhance its long-life cyclability in the high voltage. According to previous reports, the Zr^{4+} doped layered $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ [37], $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ [23] and $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ [38] cathode materials exhibit excellent electrochemical performance. This is attributed to the suppressed Li/Ni mixing after high-valent Zr^{4+} doping and enhanced structural stability resulted from the stronger Zr-O bond than that of the Ni, Co, Mn metal-Oxygen. As for the coating materials, a particularly promising coating of NCM is titanium (Ti). As well known, a series of Li-Ti-O compounds such as TiO_2 [39], Li_2TiO_3 [40], $Li_4Ti_5O_{12}$/$Li_7Ti_5O_{12}$ [41] and $LiTiO_2$ [42] etc. have been used as coating layers in lithium cathode materials. These Li-Ti-O compounds exhibit electrochemical inertness in a wide voltage range and structural stability in the organic electrolyte, and some of them also show high electronic/ionic conductivity.

In this paper, Zr-doped $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material was synthesized by traditional solid state method. And the Ti elements are coated on the Zr-doped $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material. Partial Ti atoms both diffuse into the crystal structure and absorb the lithium residues to form the mixed $Li_4Ti_5O_{12}$/Li_2TiO_3 coating layers on the surface. This strategy greatly improves the electrochemical performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material at high voltages (3.0–4.4 V and 3.0–4.6 V).

2. Experiments

2.1. Material synthesis

The pristine $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (P-NCM) and zirconium doped $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})_{0.9926}Zr_{0.0074}O_2$ (Zr-NCM) cathode materials were prepared by solid-state reaction method. The commercial $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ precursors (Hunan Brunep Recycling Corp., China) were mixed with excess Li_2CO_3 (Analytical grade, Tianqi Lithium co., LTD, China) and $Zr(OH)_4$ (Analytical grade, Aladdin, Shanghai) with nominal cation composition (mol ratio) of Li: Zr: (Ni + Co + Mn) = 1.06: x: (1-x) [$x = 0$ and 0.0074]. Redundant lithium (6%) was added to compensate for the lithium loss during the high temperature heat treatment process. The mixtures were preheated at 500 °C for 4 h and then further heat-treated at 750 °C for 4 h and 920 °C for 8 h in air. The Zr/Ti co-modified sample (Zr/Ti-NCM) was synthesized as follows: Zr-NCM sample was grounded with the 2000 ppm nano TiO_2 (mass ratio of TiO_2/Zr-NCM), and then heat-treated at 750 °C for 4 h in air.

2.2. Material characterization

Scanning electron microscope equipped with an energy dispersive spectrometer (SEM/EDS, JEOL JSM-6360LV, Japan) and transmission electron microscopy (TEM, Tecnai G12, 200 kV) were employed to observe the particle morphology and the status of the coating layer. X-ray powder diffraction (XRD, Rigaku D/max-2500) with Cu K_α radiation was collected in the 2θ range of 10–80° at a scan rate of $2^\circ \cdot min^{-1}$ and the Rietveld refinement was performed with the GSAS/EXPGUI program [9]. X-ray photoelectron spectroscopy (XPS, VG Multilab, 2000) was applied to investigate the elements composition on the surface of the samples. The electrodes after 200 cycles over 3.0–4.4 V were disassembled in the high-purity argon glove box (LS800S, DELLIS, Chengdu, China) and washed with the high purity dimethyl carbonate (DMC) to remove the residual electrolyte, and then were dried at 90 °C for 10 h prior to XRD analysis (scan rate: $10^\circ \cdot min^{-1}$), as a comparison, the electrodes without cycling were measured under the same conditions. The pH characterization was measured by the following steps: first, 5.000 g of the sample was added into 50 mL of the ultrapure water with vigorously stirring for 30 min, and then standing for 30 min to make it solid-liquid separation. Finally, the PHS-3C (Shanghai Precision & Scientific Instrument Co. Ltd) was employed to measure the pH value of the solution. The total lithium residue amounts, including LiOH and Li_2CO_3, were measured by titration method using Automatic Potentiometric Titrator (Schott TitroLine easy, Germany).

2.3. Electrochemical testing

The positive electrodes were prepared by mixing the active material, polyvinylidene fluoride (PVDF) and acetylene black with 80:10:10 mass ratios with N-methyl-2-pyrrolidone (NMP) as the solvent. The slurry was pasted on to aluminum foil and dried at 120 °C overnight, then pouched the discs of 14 mm in a diameter as the cathode electrode. 1 M $LiPF_6$ was dissolved in EC: DMC: EMC (1:1:1 vol ratio) as the electrolyte, Celgard 2400 was used as separator and metallic lithium as anode electrodes. CR2016 type coin cells were fabricated in the Ar-filled glove box (LS800S, DELLIS, Chengdu, China). The electrochemical performance were tested at various rates ($1\ C = 155\ mAh \cdot g^{-1}$, corresponding a current of ~0.5 mA) using Land Test System (CT2001A, Wuhan Jinnuo Electronic Co., Ltd., Wuhan China) at high cut-off voltages ranging from 3.0 to 4.4/4.6 V at 25 °C. Cyclic voltammetry (CV) tests were carried out over 3.0–4.6 V at a scan rate of $0.1\ mV\,s^{-1}$. The electrochemical impedance spectroscopy (EIS) measurements were conducted by charging to 4.4 V with a frequency range from 0.01 Hz to 100 kHz and an AC signal of ±5 mV amplitude after initial cycle.