Electrochimica Acta 268 (2018) 41–48

Contents lists available at ScienceDirect

Electrochimica Acta

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

Improved stability of Ni-rich cathode by the substitutive cations with stronger bonds

Yang Jiang [a, b], Yujing Bi [b], Meng Liu [b, **], Zhe Peng [b], Liyuan Huai [b], Peng Dong [c], Jianguo Duan [c], Zhenlian Chen [b], Xing Li [a, ***], Deyu Wang [b, *], Yingjie Zhang [c]

[a] Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China
[b] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China
[c] National and Local Joint Engineering Laboratory for Lithium-ion Batteries and Materials Preparation Technology, Key Laboratory of Advanced Battery Materials of Yunnan Province, Kunming University of Science and Technology, Kunming 650093, PR China

ARTICLE INFO

Article history:
Received 2 December 2017
Received in revised form
18 January 2018
Accepted 19 January 2018
Available online 20 February 2018

Keywords:
Cation substitution
Ni–O bond energy
Ni-rich cathode
Lithium ion battery

ABSTRACT

In this work, we select four types of substitute cations, Ti^{4+}, Al^{3+}, Mg^{2+} and Zn^{2+}, to compare their influence on $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. After modification, the average lengths of Ni–O bonds are elongated with the turn of the Ti–, Al–, Mg–, pristine and Zn-substituted, namely the bond energies are diminished with this sequence, according to their roughly inverse square relation. This tendency is also obeyed by oxygen defects, which induces the Ni–Li exchanging and surface decomposition, and then exert the effect on electrochemical behavior of Ni-rich cathodes. Among the investigated samples, the Ti-modified sample, which possesses the highest Ni–O bond energy, presents the best cyclic stability and rate capability, retaining 93.8% in the 200th cycle and 155.1 mAh g^{-1} under 5C, which is ~12% higher than the pristine sample. Our approaches illustrate the importance of Ni–O network and provide a novel thought to further improve these promising cathodes.

1. Introduction

Rechargeable lithium-ion battery (LIB) is successfully employed in extensive applications, such as portable electronics, transportation and grids [1–4]. The layered ternary oxides, $LiNi_{1-x-y}Co_xMn_yO_2$ ($0 < x + y < 1$), are the most widely utilized cathode materials due to their advantages of cost effectiveness, adjustable performances by varying the ratio of transitional metal elements. Since firstly proposed by Dahn et al., the nickel contents in commercial products are gradually enhanced from 1/3, 0.4, 0.5 to 0.6 to achieve the higher energy density [5–7]. Currently, the Ni-rich cathode materials ($Ni \geq 0.8$) become the new focus due to its higher reversible capacity and relative mature chemistry [8].

The Ni-rich materials are still suffering in the structural incompleteness, which is manifested by the Ni/Li cation disorder and the decomposed surface layer [9–11]. Cation disorder between Li^+ ($r_{Li^+} = 0.74$ Å) and Ni^{2+} ($r_{Ni^{2+}} = 0.69$ Å), firstly observed in the $LiNiO_2$, is regarded as the indicator of cathodes' quality. Ni^{2+} occupied Li^+ layers would block the Li^+ ions' transportation and deteriorate the cathodes' kinetics [12]. The surface layer is the accumulation of the decomposed species, which obviously accelerated under heavy moisture, especially at high temperature [13,14]. As the main component in this layer, Li_2CO_3 could be chemically decomposed to LiF as the solid product, CO_2 and POF_3 as gaseous species. The gas evolution could destroy the interface of electrolyte and electrode, and seriously deteriorates the cyclic stability [15].

In Ni-rich cathodes, the amount of the oxygen defects should be the inherent reason for their structural incompleteness [16]. They facilitate the Ni–Li disorder and accelerate the surface decomposition due to less steric hindering and moisture adsorption. Their generation should be induced by the auto-reduction of the unstable Ni^{3+} ($t_{2g}^6 e_{2g}^1$) cations [17,18]. Simultaneously with the reaction of $Ni^{3+} \rightarrow Ni^{2+}$ cations, O^{2-} anions should be oxidized and released as oxygen gas to remain the defects [19,20]. Therefore to stabilize the Ni–O network should be helpful for the material's performance. The Ni–O bond strengths could be tailored by the cation's substitution, which does not attract the deserved attention.

In this work, we select four types of cations, Mg^{2+}, Zn^{2+}, Al^{3+}

---

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: liumeng@nimte.ac.cn (M. Liu), lixing@nbu.edu.cn (X. Li), wangdy@nimte.ac.cn (D. Wang).

https://doi.org/10.1016/j.electacta.2018.01.119
0013-4686/

Table 1
The parameters of substituted elements.

M^{n+}	Zn^{2+}	Mg^{2+}	Al^{3+}	Ti^{4+}	Ni^{3+}
M—O Bond Energy (kJ/mol)	284	394	512	662	391
Ionic radius (nm)	0.0740	0.0720	0.0535	0.0605	0.0560

and Ti^{4+} to investigate their influence on the characteristics of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$. Although their substitutions were reported by many researchers, it is the first time to discuss the influence of cation substitutions on the stability of Ni—O network [10,21,22]. After modification, the average lengths of Ni—O bonds are elongated with the turn of the Ti—, Al—, Mg—, pristine and Zn-substituted, namely the bond energies are diminished with this sequence, as shown in Table 1. This tendency is also obeyed by oxygen defects, which induces the Ni—Li exchanging and surface decomposition, and then exert the effect on electrochemical behavior of Ni-rich cathodes. Owing to the highest bond energy, the Ti-modified sample presents the best structural completeness and comprehensive electrochemical capability.

2. Experimental section

2.1. Material preparations

The pristine $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ precursor powders were synthesized by the co-precipitation method as described previously [23]. Various coated layer of 0.98 $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ •0.02 M $(OH)_n$ (M = Al, Mg, Zn and Ti) were prepared using a hydroxide precursor method. The required quantities of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), magnesium acetate ($(CHCOO)_2Mg \cdot 4H_2O$), or zinc acetate ($(CHCOO)_2Zn \cdot 2H_2O$) (corresponding to subsequent Al, Mg or Zn) were respectively dissolved in deionized water, and tetra-n-butyltitanate ($C_{16}H_{36}O_4Ti$, corresponding to subsequent Ti) dissolved in hydrous ethanol. And then, the above solution and LiOH solution was pumped into precursor suspension. After stirring at 65 °C for 4 h, the mixture was heated to 60 °C to vaporize the solvent with stirring to yield the $M(OH)_n$-coated $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ samples (M = Al, Mg, Zn and Ti).

Table 2
Parameters of structural analysis obtained from X-ray Rietveld refinement.

	Zn-811	811	Mg-811	Al-811	Ti-811
a/Å	2.8717	2.8660	2.8694	2.8678	2.8661
c/Å	14.2049	14.1820	14.1943	14.2028	14.1947
c/a	4.946	4.948	4.9520	4.9525	4.9526
$v/Å^3$	101.448	100.886	101.213	100.962	100.983
Ni^{2+} in Li^+ site/%	4.27	2.90	2.67	1.97	1.60
6c O occ	0.9361	0.9516	0.9612	0.9676	0.9749
Ni—O Length	1.9696	1.9672	1.9634	1.9608	1.9586
Rwp/%	2.29	2.68	2.22	2.69	2.19
Rp/%	1.75	1.98	1.73	2.01	1.70
CHI^2	1.040	1.553	1.019	1.407	0.989

$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ samples and $Li(Ni_{0.8}Co_{0.1}Mn_{0.1})_{0.98}M_{0.02}O_2$ (M = Al, Mg, Zn and Ti) were prepared using a high temperature solid-state method. The prepared precursor was mixed with $LiOH \cdot H_2O$ at a molar ratio of 1:1.05 and sintered at 800 °C in pure oxygen atmosphere for 10 h with a heating rate of 5 °C/min and cooling to room temperature automatically.

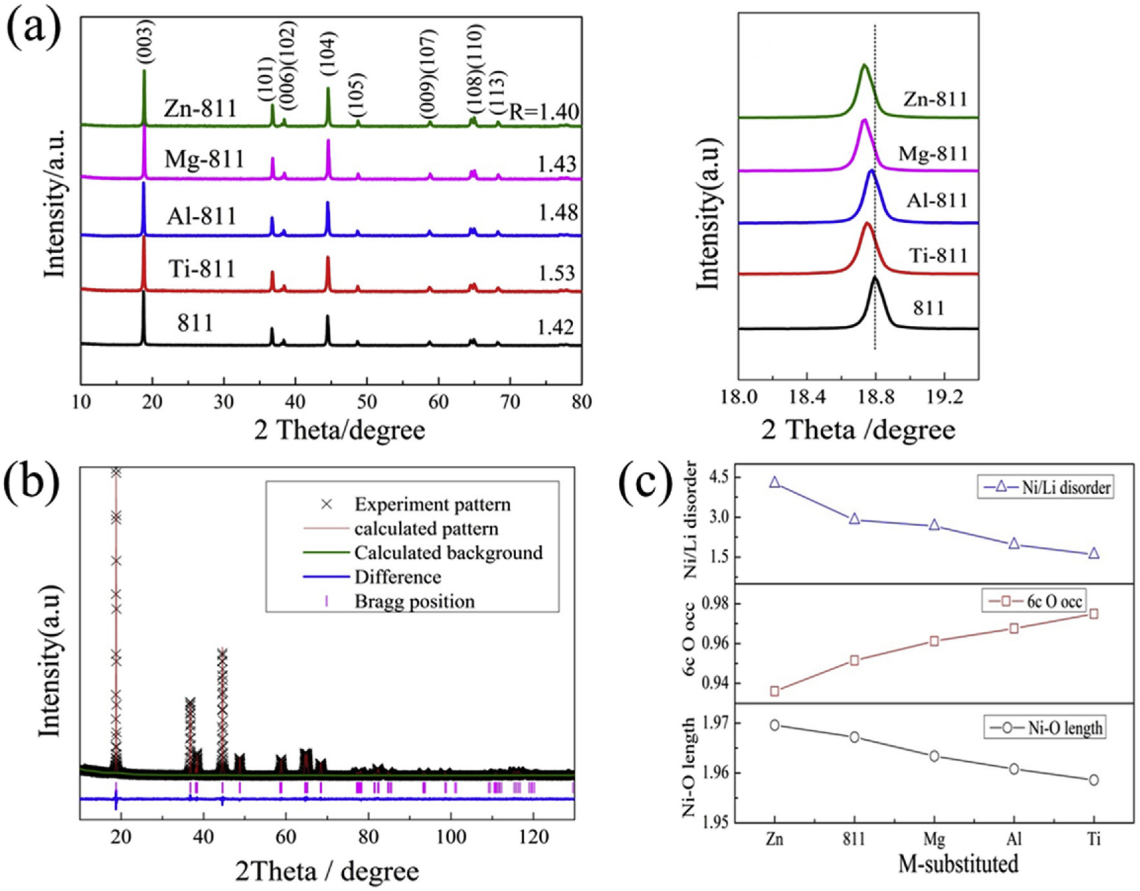

Fig. 1. (a) XRD patterns of the 811 and M-811 (M = Al, Mg, Zn and Ti) samples; (b) pattern of 811 sample and (c) results obtained from X-ray Rietveld refinement.