Electrochimica Acta 282 (2018) 311–316

Contents lists available at ScienceDirect

Electrochimica Acta

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

Amorphous Li-Zr-O layer coating on the surface of high-Ni cathode materials for lithium ion batteries

Young Jin Lim [a, 1], Sun-Me Lee [b, 1], Hayoung Lim [a], Bora Moon [b], Kyu-Sung Han [c], Jin-Ho Kim [c], Jun-Ho Song [b], Ji-Sang Yu [b], Woosuk Cho [b, **], Min-Sik Park [a, *]

[a] *Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin 17104, Republic of Korea*
[b] *Advanced Batteries Research Center, Korea Electronics Technology Institute, 25 Saenari-ro, Bundang-gu, Seongnam 13509, Republic of Korea*
[c] *Icheon Branch, Korea Institute of Ceramic Engineering and Technology, 3321 Gyeongchung-daero, Shindun-myeon, Icheon 17303, Republic of Korea*

ARTICLE INFO

Article history:
Received 17 December 2017
Received in revised form
29 May 2018
Accepted 8 June 2018
Available online 9 June 2018

Keywords:
Surface coating
Layered transition metal oxide
Cathode
Lithium ion batteries
Electrochemistry

ABSTRACT

Improving cycle performance and rate-capability of lithium ion batteries is necessary in moving toward their use in electric vehicles. Working towards this goal, we propose an amorphous Li-Zr-O coating on the surface of a high-Ni layered transition metal oxide ($LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$) *via* a simple wet process. By using residual Li on the surface of as-prepared $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ particles as a Li source, a non-stoichiometric Li-Zr-O compound can be successfully formed on the surface of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ particles at a low temperature of 400 °C. The formation of an amorphous Li-Zr-O layer is beneficial in minimizing undesirable side reactions associated with residual Li at the surface and, by extension, improving the cycle performance and rate-capability of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. The amorphous Li-Zr-O coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ exhibits a high reversible capacity of more than 190 mAh g^{-1} with improved cycle performance. This simple approach offers easy control of the surface characteristics of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, improving the surface stability and enhancing the thermal stability.

1. Introduction

Lithium ion batteries (LIB) are considered as promising power sources for electric vehicles (EVs) owing to their high-energy and high-power densities. In order to meet the rigorous standards of EV applications, commercial LIBs require higher energy densities than are currently available [1]. Much research has therefore been devoted to the development of advanced cathode materials with high reversible capacities and high operating voltages, key parameters in increasing the energy density of LIBs [2]. Layered transition metal oxides (e.g. $LiNi_xCo_yMn_zO_2$) are widely used as commercial cathode materials, coupled with carbonaceous anode materials (e.g. graphite) [1,2]. The crystal structures of layered transition metal oxides are generally composed of transition metals as redox centers, surrounded by oxygen frameworks. In principle, Li^+ can be reversibly intercalated and de-intercalated by electrochemical redox reactions of the transition metals in the structure [3,4]. Thus, the choice of transition metals is a key factor in determining the electrochemical characteristics of layered transition metal oxides [4]. Recent research has focused on the development of layered transition metal oxides with a high Ni content (≥80%) as this allows for double redox reactions of Ni^{2+}/Ni^{4+}, achieving a high reversible capacity of more than 190 mAh g^{-1} [5,6].

While increasing the Ni content effectively improves the reversible capacity of layered transition metal oxides, challenges remain regarding structural and thermal instabilities, particularly at the surface [7,8]. When the Ni content is increased, a large amount of residual Li remains at the surface due to the relatively low synthesis temperature (~800 °C). In addition, more highly reactive Ni is exposed to the surface, which makes it more vulnerable to moisture and more prone to the formation of impurity phases (e.g. rock-salt NiO) [1,9]. These high-Ni cathode materials therefore suffer from undesirable side reactions accompanied by a significant capacity loss during cycles. Moreover, the poor rate capabilities of high-Ni cathode materials still remains an open problem [10]. For these reasons, additional research is required to understand the surface nature of high-Ni cathode materials and to establish a reliable surface coating process to mitigate side reactions and improve structural stability before they can be

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: cho4153@keti.re.kr (W. Cho), mspark@khu.ac.kr (M.-S. Park).
[1] These authors equally contributed to this work.

https://doi.org/10.1016/j.electacta.2018.06.062
0013-4686/

deployed on a commercial scale.

To overcome these limitations, various surface modifications of the high-Ni cathode materials have been proposed [8,11–13]. Mohanty et al. proposed forming Al_2O_3 and TiO_2 coatings on the surface of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ *via* an atomic layer deposition (ALD) process, which showed stable cycle performance without rapid capacity fading [14]. While this approach is effective in improving the electrochemical performance of the high-Ni cathode materials, it would likely require additional production costs for mass production. More recently, Song et al. suggested using a crystalline Li_2ZrO_3 coating on $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2$ and claimed that this additional layer could suppress side reactions at the surface, improving the long-term stability during cycles. Unfortunately, controlling the uniformity of the coating layer is difficult because crystalline Li_2ZrO_3 tends to form islands on the surface [15].

Inspired by previous works, herein, we propose amorphous Li-Zr-O coatings on the surface of high-Ni $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (denoted as NCM811 hereafter) *via* a simple wet process combined with low temperature heating at 400 °C. During the coating process, residual Li can be used as a Li source to form an amorphous Li-Zr-O coating layer, which effectively improves the structural and thermal stabilities of NCM811 without a significant deterioration of the performance. This work would provide new insight to the development of reliable high-capacity cathode materials for advanced LIBs.

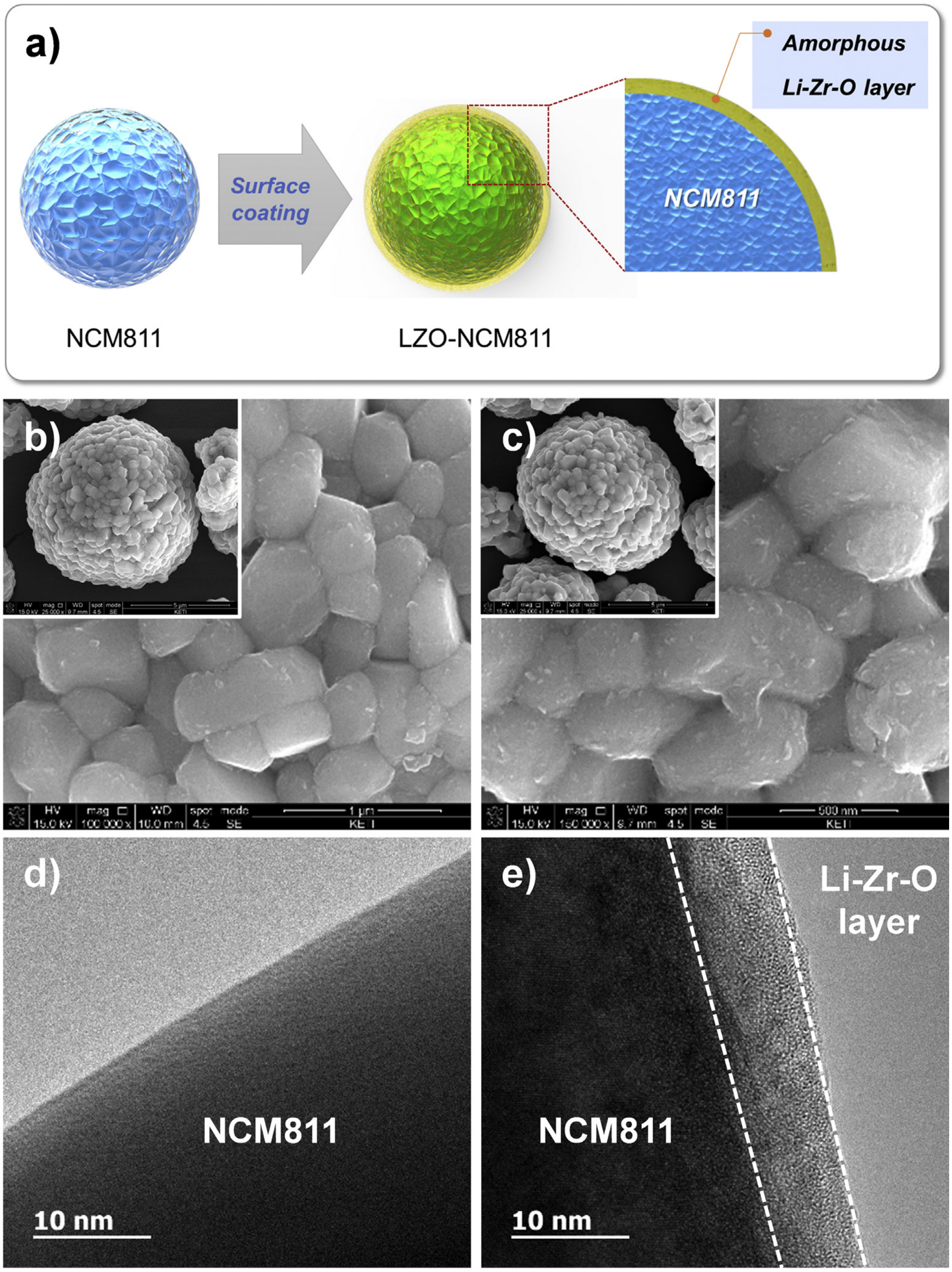

Fig. 1. (a) A schematic of LZO-NCM811 cathode material representing an amorphous Li-Zr-O layer coated on the surface of an NCM811 particle; FESEM images of (b) bare-NCM811 and (c) LZO-NCM811; TEM images of (d) bare-NCM811 and (e) LZO-NCM811 before and after the coating process, respectively.