Multiply depolarized composite cathode of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ embedded in a combinatory conductive network for lithium-ion battery with superior overall performances

Xichao Li [a], Lili Zheng [b], Zhao Zang [c], Tao Liu [a], Fengting Cao [a], Xiaolin Sun [a], Shimei Sun [a], Quanhai Niu [a], Yuxiang Lu [c], Takeo Ohsaka [d], Jianfei Wu [a, *]

[a] Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266042, China
[b] Power & Energy Storage System Research Center, and College of Mechanical & Electronic Engineering, Qingdao University, Qingdao, 266071, China
[c] College of Mechanical and Electrical Engineering, China University of Petroleum, Qingdao, 266580, China
[d] Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Midori-ku, Yokohama, 226 -8502, Japan

ARTICLE INFO

ABSTRACT

The multiply depolarized composite cathode consisted of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ (LMNCO) and a combinatory conductive network of graphene (GN) + carbon nanotubes (CNTs) in the active material and GN coating at the interface of current collector is synthesized via pasting LMNCO/GN/CNTs composite slurry on GN coated Al foil. The interlaced GN + CNTs conductive network improves both the electronic conductivity and Li ion transport and stabilizes the structure of composite. The GN coating at the interface of current/active materials interlaces with GN + CNTs in the active materials and improves the adhesion and reduces the resistance between the active material and current collector. Consequently, the LMNCO composite cathode exhibits superior rate capacities of 132 mAh g^{-1} at 5C and 97 mAh g^{-1} at 10C, high cycling capacity retentions of 86% at 1C and 85% at 2C after 100 cycles, respectively and lower voltage fading. This combinatory conductive network is much more efficient for reducing the resistance and polarization of electrode than any single conductive network of GN + CNTs, CNTs, GN or GN coating.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

In the past decades, global energy exhaustion and environment pollution make the development of electric vehicles (EVs) and hybrid electric vehicles (HEVs) an imperative trend. Lithium ion batteries (LIBs) have occupied a dominant position in energy storage devices to EVs and HEVs. However, most state-of-the-art LIBs use common commercial cathode materials with low specific capacity [1–5], such as LiFePO$_4$, LiMn$_2$O$_4$ and LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$, which severely limits the driving range of EVs and keeps them from widespread applications. Hence, novel high-capacity cathode materials are urgently needed to improve the energy density of LIB cell substantially. In the last several years, a series of Li-rich layered oxide materials with the general formula of xLi$_2$MnO$_3$·(1-x)LiMO$_2$ (M = Mn, Ni, Co), abbreviated as LMNCO, have attracted increasing interest owing to their high reversible capacities of 250−300 mAh/g in a wide voltage range of 2−4.8 V [6−10]. Recently, the high-capacity mechanism of LMNCO has been extensively investigated, and it is revealed that the high capacity is associated with the Li$_2$MnO$_3$ component. On one hand, Li$_2$MnO$_3$ can stabilize the structure of LiMO$_2$ during the delithiation process resulting in higher discharge capacity of LiMO$_2$ [11]; on the other hand, Li$_2$MnO$_3$ could be electrochemically activated above 4.4 V and supply reversible capacities by several possible mechanisms, such as oxygen anion reaction [12], oxygen ejection mechanism [13] and H$^+$ exchange mechanism [14,15]. However, the Li$_2$MnO$_3$ component is electronic insulated while the lithium ion diffusion coefficient in Li$_2$MnO$_3$ is much smaller than that in LMO$_2$ [16]. Therefore, the electrochemical reaction kinetics of Li-rich layered materials is controlled by the Li$_2$MnO$_3$ component, resulting in a relative poor rate performance. Some work also revealed [5] that the thicker solid/electrolyte interface film is formed on the surface of LMNCO electrode at high operating voltage, which could also slow down the lithium extraction/insertion in the surface region. During the

past years, in order to promote commercial application of Li-rich layered cathode material, many methods were proposed to enhance the rate performance and other electrochemical properties. Doping the Li-rich layered materials with elements such as Cr [17], Sn [18], Mg [19,20], Al [21] and Mo [22,23] could improve the electrical conductivity, structure stability and/or Li$^+$ diffusion coefficient, and consequently enhance the rate performance. In addition, surface coating such as Al_2O_3 [24], ZrO_2 [25], AlF_3 [26] are also employed to separate the Li-rich layered oxides from electrolyte. Then the side reaction can be largely avoided and the formation of SEI and surface phase could be reduced significantly, leading to promoted electrochemical properties.

Considering the large electronic resistance caused by the low electronic conductivity of Li-rich layered cathode material and its surface modified coating, conductive network should be employed in the electrode in order to bring into full play the high capacity and enhance the rate performance of active material. Recently, graphene (GN) and carbon nanotubes (CNTs) show significant potential as conductive medium for LIB electrodes owing to extraordinary electronic conductivity, high stability and high specific area. In the previous work, kinds of cathode-GN composites are synthesized by a simple mechanical mixing of $LiFePO_4$ [27], $LiMn_2O_4$ [28], $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [29], $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ [30] and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ [31] with GN, resulting in better electrochemical properties. Similarly, CNTs are generally employed as conductive additive and structural framework to form binder-free cathodes together with active materials [32,33]. The conductive networks constructed by GN or CNTs can act as the superhighway for the electron migration for the purpose of improving the inside electronic conductivity of these electrodes. Moreover, the cooperation of GN and CNTs is reported to be a more efficient method to improve the rate performance of $LiFePO_4$ due to both the merits of GN and CNTs [34].

Recently, the effects of contact resistance between the current collectors and electrode materials on the overall performances of the lithium ion batteries have also drawn much more attention. It is revealed that the surface modification of current collector by carbon-coating can improve the adhesion and reduce both the contact resistance between the collector and electrode materials, resulting in significant enhanced rate performance and cycle stability [35–38].

In this work, the multiple-structured combinatory conductive network consisted of GN + CNTs in the active material and GN coating at the interface of current collector has been designed. On one hand, GN sheets with large contact area are coated on the surface of LMNCO particles, may leading to improved electronic conductivity of LMNCO. CNTs interlace with GN sheets and connect to adjacent LMNCO particles, contributing to reinforced stability and integrality of three-dimensional network structure. Moreover, the cross-linked CNTs can supply fast pathways not only for electron but also for Li ion diffusion, avoiding the blocking effect of GN on the Li$^+$ transport. Hence, the GN + CNTs conductive network can enhance both the electronic conductivity and Li ion diffusion of LMNCO composite simultaneously and reduce the polarization. On the other hand, the GN + CNTs conductive network in active materials can also interlaced with the GN coating on the Al foil to form the overall combinatory three-dimensional conductive network, improving the adhesion between the active materials and current collector and reduce the resistance and polarization. Hence, the multiply depolarized LMNCO composite electrode with the combinatory three-dimensional conductive network exhibits superior electrochemical performance compared to that of LMNCO composite with single conductive network consisted of GN, CNTs, GN + CNTs or GN coating and pristine LMNCO. The effects of above different conductive networks on the electrochemical properties of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ cathode materials have also been investigated.

2. Experimental

2.1. Sample preparation and characterizations

The Li-rich cathode material $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ was prepared by of a co-precipitation method. $NiSO_4 \cdot 7H_2O$ (Aladdin, 99.9%), $CoSO_4 \cdot 7H_2O$ (Shanghai, 99.999%) and $MnSO_4 \cdot H_2O$ (Aladdin, 99%) were used as raw materials, and Na_2CO_3 and $NH_3 \cdot H_2O$ were used as precipitation agent and chelating agent, respectively. The preparation procedure was described briefly as follows: A 1 M mixed aqueous solution of stoichiometric $MnSO_4 \cdot H_2O$, $NiSO_4 \cdot 7H_2O$ and $CoSO_4 \cdot 7H_2O$ was added dropwise into a continuous stirred reactor. Meanwhile, a 1 M Na_2CO_3 solution and desired amount of $NH_3 \cdot H_2O$ was also fed into the reactor. The pH (7.8) and temperature (50 °C) were carefully controlled. Afterwards, the obtained precipitate was filtered, washed with de-ionized water for several times, and dried at 110 °C in vacuum oven for 12 h. Then the precursor was mixed with Li_2CO_3 (5% excess of the stoichiometric amount), pelleted and transferred to a muffle oven for calcination at 500 °C for 5 h and then at 900 °C for 12 h.

To prepare the cathode electrodes with different conductive networks, 1.9 g $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ and 0.1 g commercial GN (SUSN Sinotech New Materials Co.,Ltd), CNTs (SUSN Sinotech New Materials Co.,Ltd) or GN + CNTs (1:1 in wt.%) were dispersed in 50 ml and 30 ml ethanol, respectively and ultrasonicated for 1 h. Then the GN, CNTs or GN + CNTs suspension was added into $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ suspensions dropwise, respectively and magnetically stirred at 50 °C to form thick slurries. The obtained mixtures were dried in an vacuum oven at 80 °C overnight to obtain active materials with different conductive networks, named by LMNCO-GN, LMNCO-CNT, LMNCO-G + C, respectively. These active materials, polyvinylidene fluoride (PVDF), Super P at a weight ratio of 80: 10: 10 were blended in N-methyl-2-pyrrolidone (NMP) and spread uniformly on an Al foil and dried in vacuum at 120 °C for 12 h to obtain the LMNCO-GN, LMNCO-CNT or LMNCO-G + C electrode, respectively. For comparison, the mixed slurry of LMNCO, PVDF and Super P at a weight ratio of 80: 10: 10 was also prepared.

Graphene coated current collector was prepared by pasting the slurry of GN and PVDF in NMP on the Al foil and then drying the Al foil in an oven at 80 °C for 30 min. The mass loading of GN coating is determined to be about 0.1 mg cm^{-2}, with 50 wt% and 50 wt% PVDF. The electrodes made by pasting LMNCO and LMNCO-G + C on the GN coated Al foil are named by LMNCO/GN and LMNCO-G + C/GN, respectively. Thereinto, the final content of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$, GN, CNT, Super P, PVDF in the electrode is about 74.5 wt%, 2.9 wt%, 2.0 wt%, 9.8 wt% and 10.8 wt%, respectively in the LMNCO-G + C/GN electrode.

2.2. Characterizations

X-ray diffraction patterns of the LMNCO powder were obtained by an X-ray diffractometer (Bruker AXS D8) with a Cu Kα radiation. The microstructure of electrodes with different conductive networks was examined by using a scan electron microscope (SEM, Hitachi S-4800, Japan), equipped with an energy-dispersive spectroscopy (EDS, INCA, Oxford Instrument, Oxford, U.K.) system. The chemical composition of LMNCO sample was measured quantitatively by inductively coupled plasma emission spectrometry (ICP-AES, Thermo Fisher 7400, USA).