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Uncovering the role of Nb modification in improving the structure stability and electrochemical performance of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode charged at higher voltage of 4.5 V

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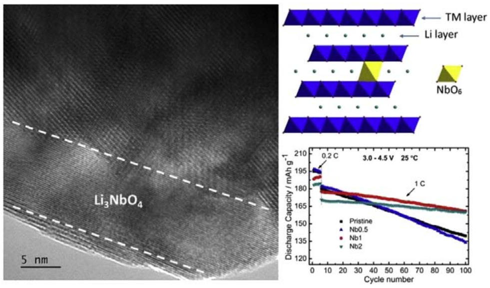
HIGHLIGHTS

- Nb^{5+} is incorporated into Li^+ site.
- Nb modification facilitates charge transfer kinetics.
- 1 mol% Nb modified $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ exhibits superior cycling stability.
- Nb modification alleviates surface structural degradation.

GRAPHICAL ABSTRACT



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ABSTRACT

Ni-rich cathode materials attract ongoing interest due to their high specific capacity (~200 mAh g^{-1}). However, these materials suffer rapid capacity fading when charged to a high voltage and cycled at elevated temperature. In this study, we propose a facile method to reconstruct the surface structure of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ via Nb modification, which integrates the merits of partial Nb^{5+} doping in the pristine structure and surface Li_3NbO_4 coating. The obtained results from Rietveld refinement and high resolution transmission electron microscopy confirm that Nb^{5+} is partially doped into Li^+ sites within the surface lattice. Further *ex-situ* powder X-ray diffraction and kinetic analysis using electrochemical impedance spectroscopy reveal that Nb modification stabilizes the layered structure and facilitates the charge transfer process. Owing to the robust surface structure, 1 mol% Nb modified $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ delivers a discharge capacity of 160.9 mAh g^{-1} with 91% capacity retention after 100 cycles at 3.0–4.5 V, whereas the discharge capacity of the pristine sample drops to 139.6 mAh g^{-1}, corresponding to 78% of its initial value. The presence of Nb^{5+} in the Li layer exhibits positive effects on stability of layered structure, and the surface Li_3NbO_4 coating layer increases interfacial stability, which results in superior electrochemical performance.

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1. Introduction

Although lithium-ion batteries (LIBs) have been widely adopted as energy storage systems in consumer electronics and electric vehicles, advanced LIBs with higher energy and power density are still imperative, which relies predominantly on the battery fabrication process and the development of electrode materials [1–3]. Considering that cathode materials are the critical component limiting the cell capacity and determining the battery cost, primary focus is therefore directed to the development of advanced cathode materials with high energy and power density. Among them, Ni-rich cathode materials are regarded as next-generation candidates for advanced LIBs due to their high specific capacity (~ 200 mAh g^{-1}) and reasonable price [4,5]. Despite these attractive advantages, great effort is still needed to optimize their electrochemical performance and some severe issues must be addressed [6]. One major problem of Ni-rich cathode materials is structural degradation during repeated cycling [4,7], originating primarily from metal ion rearrangement under highly delithiated states [8]. This rearrangement results in detrimental phase transformation from layered structure to disordered spinel structure and finally to rock salt structure, and brings about extra impedance for lithium ion transfer during Li^+ intercalation/deintercalation processes [9,10]. Another critical factor that precludes the large-scale application of Ni-rich cathode materials is the deleterious side reactions occurring at the electrode/electrolyte interface, followed by gas evolution (such as O_2 and CO_2) and increase of internal resistance [11,12]. Therefore, it is still a significant challenge to push forward the commercialization of Ni-rich cathode materials.

Extensive research has revealed that capacity fading of Ni-rich cathode materials results primarily from surface degradation rather than from bulk structural destruction, implying that surface modification is of paramount importance in electrochemical performance improvement [4,13]. Note that metal oxide and Li-ion conductors have been extensively investigated as coating materials to improve the electrochemical performance of cathode materials [14–16], in spite of the major obstacle of reversible capacity decrease. In addition, recent development of doping strategies that integrate extra metal ions (such as Al^{3+} [17], Mg^{2+} [18], Ti^{4+} [19] and Nb^{5+} [20].) into the layered structure demonstrates the positive effects of dopants on mitigating metal ion migration and on decreasing oxygen release at high potential.

Despite the fact that Nb has been accepted as a dopant to ameliorate the electrochemical capability of cathode materials [20–23], intrinsic mechanisms that are responsible for performance improvement are still ambiguous. This uncertainty arises mostly from whether the Nb^{5+} is doped into the bulk phase or just remains on the surface, along with major disputes regarding the doping position. Therefore, it is essential for researchers to find convincing evidence about the occupation sites of the dopants.

Herein, we propose a facile strategy that combines partial Nb^{5+} doping and coating to modify the surface structure of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$, and provide clear evidence of the Li site substitution by Nb^{5+}. Besides, the effects of the surface reconstruction layer on the electrochemical performance of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ under high voltage and elevated temperature are systematically investigated.

2. Experimental section

2.1. Material synthesis

$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ was synthesized through a solid state method. $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ (Jinchuan GROUP Co., Ltd., China) and Li_2CO_3 with a molar ratio of 1: 0.54 were thoroughly mixed using a ball-milling machine and then preheated at 600 °C for 7 h. The obtained powder was remixed and further annealed at 870 °C for 15 h under flowing oxygen. The Nb modified $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ materials [$Li(Ni_{0.6}Co_{0.2}Mn_{0.2})_{1-x}Nb_xO_2$, x = 0.005, 0.01 and 0.02] were synthesized following the same procedure. For the synthesis of $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})_{0.99}Nb_{0.01}O_2$ (Nb1), $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$, Nb_2O_5 and Li_2CO_3 with a molar ratio of 1:0.01:0.54 were thoroughly mixed (the molar ratio of $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ and lithium was fixed as 1:1.08 regardless of the Nb amount). The obtained powder was preheated at 600 °C for 7 h, and then remixed and further annealed at 870 °C for 15 h under flowing oxygen. The 0.5, 1, and 2 mol% Nb modified $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ samples are denoted as Nb0.5, Nb1 and Nb2 hereafter.

2.2. Material characterization

The crystalline phase was characterized by powder X-ray diffraction (XRD, Bruker D8 Discover, Cu Kα radiation, 1.5418 Å). For *ex-situ* powder XRD analysis, pristine $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ and Nb1 electrodes were first charged to the specific potential and held at this potential for 3 h to reach a steady state. The cells were then disassembled in an argon-filled glove box and rinsed with fresh dimethyl carbonate (DMC) to remove the electrolyte residues. Finally, the electrodes were naturally dried in the glove box before they were transferred to do XRD analysis. The morphology of the prepared powder was observed by scanning electron microscopy (FESEM, S-4800, Hitachi Co., Japan) coupled with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscopy (TEM, JEOL 2010F). The X-ray photoelectron spectroscopy (XPS) analysis was performed with a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer Co., USA) using monochromatic Al Kα radiation ($h\nu$ = 1486.6 eV), and the binding energy was calibrated with the C 1s peak at 284.8 eV.

2.3. Electrochemical measurements

To fabricate the cathode electrode, the active materials, Super P, and polyvinylidene fluoride (weight ratio 80:10:10) were thoroughly mixed in N-methylpyrrolidone (NMP) solution. The obtained slurry was cast onto aluminum foil and dried at 80 °C for 12 h in a vacuum oven. CR2016 coin-type cells were assembled in an argon-filled glove box using 1 M $LiPF_6$ in an ethylene carbonate (EC)-diethyl carbonate (DEC) mixture (1:1 vol ratio) as electrolyte, a polypropylene microporous film (Cellgard 2300) as the separator and lithium metal as the counter electrode. The galvanostatic charge-discharge characteristics (1 C = 180 mA g^{-1}) were measured between 3.0 and 4.5 V at room and elevated temperature using a battery test system (Land CT2001A, Wuhan Jinnuo Electronic Co. Ltd., China). Electrochemical impedance spectroscopy (EIS) measurements were tested on an electrochemical workstation (Zahner IM6e) within a frequency range of 100 kHz to 10 mHz.

3. Results and discussion

The powder XRD patterns of pristine and Nb modified $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ exhibit similar sharp diffraction lines correlating well with hexagonal $R\bar{3}m$ lattice, except for some extra peaks corresponding to Li_3NbO_4 phase [Fig. 1(a) and (b)] [23]. The distinguished split of (006)/(012) and (108)/(110) peaks indicates that a highly ordered layered structure is obtained. Further Rietveld refinement analysis of pristine $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ and Nb1 reveals that the lattice parameters increase slightly after Nb modification and partial Nb^{5+} (0.4%) prefers to occupy Li^+ site (Fig. S1). In addition, the degree of cation mixing decreases from 4.24% to 2.71% (Table 1). The expansion of lattice parameters and lower cation disordering are beneficial to Li^+ migration and are expected to bring about improved electrochemical performance.

Fig. 1(c) and (d) show the surface analysis results of elemental composition and valence states through X-ray photoelectron spectroscopy (XPS). The Ni 2p spectrum clearly reveals the fact that Ni^{3+} and Ni^{2+} coexist on the electrode surface, with resolved peaks located at