Effect of cycling conditions on the electrochemical performance of high capacity Li and Mn-rich cathodes for Li-ion batteries

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HIGHLIGHTS

- A Co free Li and Mn-rich cathode $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ is synthesized.
- Galvanostatic cycling is tested with and without activation of this cathode material.
- A specific capacity ≥ 240 mAh g^{-1} is obtained in the potential range of 2.3–4.6 V.
- The discharge voltage decay is suppressed by controlling the upper potential limit to 4.3 V.
- An attractive low cost cathode material for Li-ion batteries is demonstrated.

ARTICLE INFO

ABSTRACT

Li and Mn-rich layered oxide cathodes although exhibit high specific capacities ≥ 240 mAh g^{-1}, suffer from capacity fading and discharge voltage decay during prolonged cycling to potential higher than 4.5 V. This study aimed at exploring an interesting Co-free Li and Mn rich cathode material and to understand how the upper potential applied affects its capacity and average discharge voltage upon prolonged cycling. $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ cathodes were explored in Li cells by galvanostatic charge-discharge cycling in several potential ranges. The specific capacity, capacity retention and average discharge voltage were compared with and without activation to 4.6–4.8 V when cycled to different upper potential limits. This cathode material exhibited a high discharge capacity of 242 mAh g^{-1} when cycled in the potential range of 2.3–4.6 V after activation to 4.8 V with gradual capacity fading and average discharge voltage decreasing from 3.62 V to 3.55 V during 100 cycles. When cycled in the potential range of 2.3–4.3 V after activation to 4.6 V, it exhibited a relatively stable capacity >160 mAh g^{-1} and stable average discharge voltage of 3.61 V, during 100 cycles. Thus, with optimized operating condition, the Li and Mn-rich cathode material $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ is promising for lithium-ion batteries.

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1. Introduction

Li-ion batteries are known as high energy density electrochemical devices, which are implemented as the major power sources for portable electronic devices. However, their energy density is limited by the low specific capacity (<170 mAh g^{-1}) of currently used cathode materials such as $LiCoO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$, $LiFePO_4$ etc. [1–3]. Recently, Li and Mn-rich cathode materials were found to exhibit high specific capacity ≥ 240 mAh g^{-1} depending on their compositions and cycling conditions such as the potential range and charge-discharge

currents used for cycling [4–19]. Of various compositions, several investigations included $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (containing Li-rich electrochemically inactive Li_2MnO_3 and active $LiNi_{0.5}Mn_{0.5}O_2$ phases) [13,14]. Using cobalt-free cathode materials in batteries is important because cobalt is a relative expensive element and its compounds are considered as toxic. Among other Co free compositions, $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ was rarely studied. For instance, Gao et al. tried to improve the electrochemical performance of this material by AlF_3 coating [15]. The high specific capacity of these cathodes results from the activation of Li_2MnO_3 upon charging to potential higher than 4.5 V in the 1st cycle and the consequent formation of an active Li_xMnO_2 phase, which can reversibly intercalate/deintercalate Li^+ ions upon cycling [13,16]. However, these cathode materials suffer from capacity fading as well as discharge voltage decay due to structural layered-to-spinel transformation upon

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prolonged cycling to potentials higher than 4.5 V [16–19]. The decrease in specific capacity as well as discharge voltage results in a decrease in specific energy, which is a major drawback of these cathode materials for being commercialized in Li-ion batteries. The decrease in specific capacity can be partially resulted from the interfacial reaction between the active material and liquid electrolyte solutions at high potentials. Surface coating with Al_2O_3, MgO, AlF_3, $AlPO_4$ etc. were found to be useful in preventing the capacity fading of these cathode materials upon cycling [20–24]. Additives such as LiBOB in standard electrolyte solutions were also found to be useful in suppressing the layered-to-spinel transformation in these materials and stabilizing their specific capacity upon cycling [25,26]. Doping by various cations like K^+, Mg^{2+} and Al^{3+} were also found to improve the cycling stability of these cathode materials [27–30]. Ito et al. reported the improved high voltage cycling performance of Li-rich cathode $Li_{1.2}Ni_{0.17}Co_{0.07}Mn_{0.56}O_2$ through a pre-cycling treatment, i.e., cycling in the potential range of 2.0–4.5 V (for about 5 cycles) before cycling to higher potentials of 4.6, 4.7 and 4.8 V [31]. Thus, cycling condition such as the potential range may have a significant effect in improving the cycling performance in terms of stability. The other drawback of these cathode materials is the decrease in the average discharge voltage upon cycling. We recently reported on the mitigation of the discharge voltage decay of Li and Mn-rich cathode materials by Al doping [30]. Although there are extensive studies on structural changes that occur upon activation and prolonged cycling to potential above 4.5 V, there are not enough detailed reports on the effect of cycling conditions in terms of potential ranges of operation.

In this study, we have tested the electrochemical performance of Li and Mn-rich $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ $(xLi[Li_{1/3}Mn_{2/3}]O_2.(1-x)LiNi_{0.5}Mn_{0.5}O_2$ $(x = 0.5))$ cathodes by galvanostatic charge-discharge cycling with various upper potential limits and examined the effect of cycling conditions on their stability.

2. Experimental

2.1. Synthesis and characterization of $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$

The Li and Mn-rich cathode material $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ was prepared by a self-combustion reaction (SCR) as reported earlier [18,19]. In a typical synthesis, stoichiometric amount of $LiNO_3$, $Mn(NO_3)_2$, $Ni(NO_3)_2$ (Ni:Mn:Li = 1:2.32:4.68) were dissolved in about 80 mL of DD water. 5 wt% of $LiNO_3$ was added in excess in order to compensate the Li loss during high temperature annealing. Then sucrose was added to this solution with continuous stirring for about 1 h. The water was then evaporated slowly followed by heating at 350 °C for the self-ignition of the reactants to give an amorphous mass. This product was finely ground and was annealed at 500 °C for 3 h in air. Finally, the sample was heated at 900 °C for 15 h with intermediate grinding. The elemental chemical analysis of the material was carried out using the inductive coupled plasma technique (ICP-AES, spectrometer Ultima-2 from JobinYvon Horiba). The structure of these materials was characterized by X-ray diffraction with a Bruker D8 Advance X-ray diffractometer using Cu K$_\alpha$ ($\lambda = 1.5418$ Å) as the source. Diffraction data for the Rietveld refinement were collected in the angular range of $10° < 2\theta < 90°$, step size 0.02°, step time 6 s/step. The data was analysed by the Rietveld structure refinement program, FULLPROF [32]. The structural data for the modelling were taken from previously reported articles for monoclinic phases [33]. The Thompson-Cox-Hastings pseudo-Voigt function was used for the peak-shape approximation. The morphology of the products was investigated by a scanning electron microscope Magellan XHR 400L FE-SEM-FEI. TEM characterization of $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ was carried out with a JEOL-

JEM 2100 electron microscope with LaB$_6$ emitter operating at 200 kV. Samples for the TEM studies were prepared by dispersing and sonicating the powdered samples in ethanol and adding a few drops of the resulting suspension to a TEM copper grid. Micro-Raman spectroscopy studies of pristine and cycled electrodes were performed using a micro-Raman spectrometer from Renishaw inVia (UK) equipped with a 514 nm laser, a CCD camera, and an optical Leica microscope. A 50× objective lens to focus the incident beam and an 1800 lines/mm grating were used. The spectra were recorded from 5 to 10 locations on each sample.

2.2. Electrodes preparation and electrochemical measurements

Slurries were prepared with 80 wt % active material $(Li_{1.17}Ni_{0.25}Mn_{0.58}O_2)$, 10 wt % of conductive super P carbon, and 10 wt % of PVDF binder in N-methyl-2-pyrrolidone (NMP) solvent in a vacuum mixture. The electrodes were made by casting slurries onto Al foils current collectors by using a doctor-blade. The electrodes were dried at 80 °C for 12 h in an oven, calendered uniformly and then punched into circular electrodes of 14 mm diameter. The electrodes were finally dried at 110 °C for 12 h under vacuum in order to remove the absorbed moisture and trace NMP before assembling in Li-ion cells. The electrochemical performance was tested using coin-type cells 2032 (NRC, Canada) assembled in an argon-filled dry glove box (MBraun). The cells consisted of a cathode and Li metal foil as the counter and reference electrodes separated by porous polypropylene separator from Celgard. The
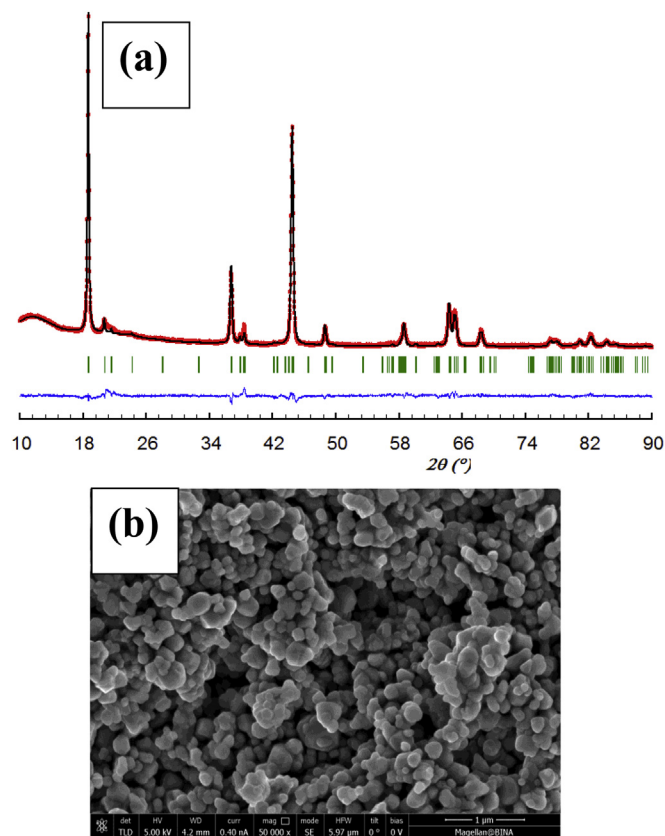
Fig. 1. (a) XRD Rietveld analysis of Li and Mn-rich $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ material. The calculated XRD pattern is shown by a solid curve and red dots show the observed intensities. The difference between the observed and calculated intensities is presented by the blue curve. (b) SEM image of the $Li_{1.17}Ni_{0.25}Mn_{0.58}O_2$ cathode material. The image includes a scale of 1 micron. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)