Achieving high capacity and rate capability in layered lithium transition metal oxide cathodes for lithium-ion batteries

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HIGHLIGHTS

- Composition of layered oxides are tuned for high capacity and rate capability.
- $LiNi_{0.4}Co_{0.4}Mn_{0.2}O_2$ is proposed as one of the promising cathode materials.
- Lesser structural changes during charging lead to excellent cycling stability.
- $LiNi_{0.4}Co_{0.4}Mn_{0.2}O_2$ delivers a capacity over 200 mAh g^{-1} via single-phase reaction.

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ABSTRACT

In this study, we target to find a new composition for a layered mixed metal oxide, which has a high structural stability and a good electrochemical performance. Our strategy is to alter the transition metal composition focusing on the relative amounts of redox active Ni and Co to the inactive Mn, based on highly-stabilized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. X-ray absorption near-edge structure and X-ray diffraction analyses show that the degree of cation disorder decreases on increasing the ratio of Ni and Co to Mn, by the presence of Ni^{3+}, suggesting that slightly higher Ni and Co contents lead to improved structural stability. Electrochemical studies demonstrate that $LiNi_{0.4}Co_{0.4}Mn_{0.2}O_2$ cathodes exhibit considerable improvements in both the reversible capacity and the rate capabilities at a voltage range of 2.5–4.6 V. In situ XRD measurements reveal that $LiNi_{0.4}Co_{0.4}Mn_{0.2}O_2$ maintains a single-phase and undergoes lesser structural variations compared to controlled compositions during a delithiation process up to 4.6 V, while achieving a high reversible capacity over 200 mAh g^{-1}. As a result, $LiNi_{0.4}Co_{0.4}Mn_{0.2}O_2$ experiences fewer structural degradations during electrochemical cycling, which explains the excellent long-term cycling performance.

1. Introduction

The development of lithium ion batteries target to high energy, high power, and durability with the growing demand for large-scale applications to electric vehicles and energy storage systems [1–3]. Layered lithium transition metal oxide cathode materials have been extensively studied for optimizing electrochemical performances such as the specific capacity, rate capability, and cycling stability [4–7]. The electrochemical behaviors in $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM) rely considerably on the elemental composition of the transition metal that determines the crystal and electronic structures [8,9]. In NCM, the role of each transition metal component is vastly different. Nickel is responsible for the high capacity because most of the redox reaction is contributed by the reversible redox couples of Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} [9,10]. Cobalt also takes part in the redox reaction of Co^{3+}/Co^{4+} pair at high potential and contributes to the increase in the electronic conductivity, affecting the rate capability [10,11]. The electrochemically inactive Mn^{4+} ions can stabilize the crystal structure of the layered oxides during lithium-ion insertion and extraction [12].

In NCM cathodes, a high capacity and rate performance have not been easily achieved concurrently with the cycling stability to date.

One of the extensively studied compositions, $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, composed of Ni^{2+}, Co^{3+}, and Mn^{4+}, exhibits excellent capacity retention and a good rate capability, which is attributed to the highly-stabilized structure as a result of a low degree of cation disorder and a small change in the cell volume (about 3%) [13–17]. Unfortunately, this structural stability is maintained only in the moderate voltage ranges, thereby the reversible capacity is limited to ~150 mAh g^{-1}. However, at higher upper cutoff voltages than 4.3 V, the capacity retention rapidly deteriorates with the electrochemical cycling [10,17,18].

Another promising composition, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, exhibits a high reversible capacity of ~200 mAh g^{-1} [5]. However, it is prone to rapid capacity fade over cycling, owing to material degradation related to the phase transition to the spinel and rock-salt upon high-voltage operation of 4.5 V [7,19–21]. Accordingly, the capacity and the capacity retention during cycling in layered $LiNi_xCo_yMn_{1-x-y}O_2$ ($0.33 \leq x \leq 0.85$) is often in a trade-off relationship [22,23]. The effects of such transition metal compositions on the electrochemical behaviors have been focused on the nickel-rich NCM ($Ni > 0.5$) [11,23–25]. It has been reported that the addition of manganese enhances the capacity retention in $LiNi_{0.52}Co_{0.16+x}Mn_{0.32-x}O_2$ [25] and $LiNi_{0.85}Co_xMn_{0.15-x}O_2$ [11] compounds. In addition, it has demonstrated that the incorporation of cobalt in $LiNi_{0.85}Co_xMn_{0.15-x}O_2$ plays a role in enhancing the rate capability by lowering the structural disorder during charging.

In this study, we focus to achieve both high capacity and high rate capability with a good cycling stability, based on $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, overcoming the limited electrochemical properties. It was realized by the optimization of compositional variations as $Li[Ni_{(1-x)/2}Co_{(1-x)/2}Mn_x]O_2$ ($x = 0.10, 0.20$, and 0.33), which involves increases in the amounts of primary redox metals such as nickel and cobalt, and simultaneously decrease in the manganese content of $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$. The valence states of transition metals and the structural characteristics were obtained using advanced analytical measurements such as X-ray absorption near edge structure (XANES) and *in situ* X-ray diffraction (XRD) to reveal the relationship on electrochemical properties and structural stabilities. As a result, an in-depth understanding of the degree of cation mixing, the changes in the oxidation state of the redox active metal, and the structural changes during delithiation processes, are discussed to evaluate the improvement of the electrochemical performances in the layered ternary metal oxide cathode materials.

2. Experimental

2.1. Material synthesis

For the synthesis of $Li[Ni_{(1-x)/2}Co_{(1-x)/2}Mn_x]O_2$ ($x = 0.10, 0.20$, and 0.33) materials, stoichiometric amounts of $LiNO_3$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Mn(NO_3)_2 \cdot 4H_2O$ were added to a solution containing 0.5 wt.% zirconium (IV) acetate hydroxide ($(CH_3CO_2)_xZr(OH)_y$, $x + y \sim 4$) as a complexing agent [18,26]. The precursors were thoroughly dissolved under ultrasonic agitation for 90 min. Then, it was placed in an oven at 100 °C for 3 h for solvent evaporation. A gel-like substance was subsequently preheated at 600 °C for 5 h and heated at 950 °C for 10 h in air. After the heat treatment, the powders were gently ground using an agate mortar and pestle. For convenience, as-synthesized $LiNi_{0.45}Co_{0.45}Mn_{0.10}O_2$, $LiNi_{0.40}Co_{0.40}Mn_{0.20}O_2$, and $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ cathode materials are denoted as **NCM10**, **NCM20**, and **NCM33**, respectively, where the digits represent the molar percent of manganese among transition metals.

2.2. Material characterization

The chemical composition of as-prepared $Li[Ni_{(1-x)/2}Co_{(1-x)/2}Mn_x]O_2$ materials was estimated by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300 DV, Perkin-Elmer). The particle size distribution of the $Li[Ni_{(1-x)/2}Co_{(1-x)/2}Mn_x]O_2$ powders was determined by a particle size analyzer (PSA, ELS-2000ZS, Otsuka Electronics). The BET surface area was measured by analyzing the N_2 adsorption isotherm (Micromeritics ASAP 2010). The electrical conductivities of the NCM powders were measured after pelletized with the thickness of 400–700 μm using a Hall Effect measurement system (HMS-5000, Ecopia) at room temperature.

The powder morphology was observed by scanning electron microscopy (SEM, Inspect F, FEI) and the corresponding elemental analysis was carried out by energy dispersive X-ray spectroscopy (EDS) mapping. All the images were taken using an accelerating voltage of 15 kV. Fast EDS mapping with a high-angle annular dark-field (HAADF) - scanning transmission electron microscopy (STEM) detecting mode was conducted using an FEI Talos F200X with an accelerating voltage of 200 kV. High-resolution Transmission Electron Microscopy (HRTEM) were carried out using a Cs-corrected FEI Titan 80–300 microscope operated at an accelerating voltage of 300 kV. TEM samples were prepared by dropping a sonicated solution of NCM powders and anhydrous ethanol onto a lacey carbon 200-mesh copper grid (Electron Microscopy Sciences).

The crystallographic structure of the synthesized powers was examined by XRD using Cu-Kα radiation (D/MAX-2500 V, Rigaku) the range from 15° to 75° at a scan rate of 1° min^{-1}. The lattice parameters were calculated using the UnitCell program. The XANES measurements for the electrodes were performed on the 1D XAS beamline in the 2.5 GeV Pohang Light Source (PLS-II) with a ring current of 100–150 mA. The Ni, Co, and Mn K-edge spectra were measured in the transmission mode. Reference compounds were used from the standard samples of Mn_2O_3 (Mn^{3+}), MnO_2 (Mn^{4+}), $Co(C_2H_3O_2)_2$ (Co^{2+}), $Co(C_2H_3O_2)_3$ (Co^{3+}), and NiO (Ni^{2+}). The data was analyzed using the Athena program [27]. *In-situ* XRD was measured using the Rigaku MicroMax-007HF and the R-AXIS IV++ image plate detector. A coin-type cell with a central hole of window for X-ray beam passage was utilized for the measurement. The data was recorded with Mo Kα radiation ($\lambda = 0.71073$ Å) and later converted to Cu Kα radiation ($\lambda = 1.54$ Å) for easy comparison with literature data. The cells were charged to 4.6 V at a 0.1C rate using a battery cycler system (WBCS3000, WonA Tech).

2.3. Electrochemical measurement

A composite made of 90 wt.% as-prepared powder, 6 wt.% acetylene carbon black (Denka Black, Denki Kagaku), and 4 wt.% polyvinylidene fluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidone (NMP) was mixed in a planetary ball mill (Pulverisette 23 Mini-Mill, Frisch Gmbh) at 2400 oscillations min^{-1} for 30 min. The electrodes were prepared by casting the slurry onto an aluminum current collector. After drying at 80 °C, the electrodes were pressed to 70% of their original thicknesses. Then, they were dried at 80 °C in a vacuum oven for 24 h to remove the residual moisture. The half-cells were assembled along with a metallic lithium anode using 2032-type coin cells in a dry room (dew point as low as −100 °C). The average loading of the active material was approximately 2.0–2.2 mg cm^{-2}. Porous polypropylene (Celgard 2500) was used as a separator. The electrolyte used 1.0 M lithium hexafluorophosphate ($LiPF_6$) solution in a 1:1:1 (v/v %) mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) (PANAX ETEC). Electrochemical measurements of the cycling properties were performed in constant current modes