

Evaluation of Stability of Charged Lithium-rich Layer-structured Cathode Material at Elevated Temperature



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ARTICLE INFO

Article history:

Received 3 December 2014
Received in revised form 7 March 2015
Accepted 31 March 2015
Available online 11 April 2015

Keywords:

Lithium-ion battery
Lithium-rich layer-structured cathode
Thermal decomposition
Crystal structure
Oxidation state

ABSTRACT

The stability of charged $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ at elevated temperature was investigated by using thermal desorption spectrometry-mass spectrometry (TDS-MS), X-ray diffraction (XRD), and X-ray absorption fine structure (XAFS) measurements. The TDS-MS and XRD spectra indicated that the crystal structure of the delithiated $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ changed from layer to spinel, and oxygen was released at high temperature. However, the amount of oxygen released from $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ in a full-charge state was much less than that released from $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ in a full-charge state. The XAFS spectra indicated that the high oxidation state of manganese was more stable than that of nickel and cobalt. The high stability of charged $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ at high temperature was, therefore, attributed to the high manganese content of the transition metal.

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1. Introduction

Lithium-ion batteries have recently been applied to not only small devices such as cellular phones but also automotive products such as hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and electric vehicles (EVs). These applications require both high energy density and safety. These properties are closely related to those of materials used for the electrodes in batteries. Ni-based layer-structured cathode materials, $\text{LiNi}_{1-a}\text{M}_a\text{O}_2$ (M: metal), are promising in that regard due to their high capacity [1–4]. However, the stability of $\text{Li}_{1-y}\text{Ni}_{1-a}\text{M}_a\text{O}_2$ at elevated temperature is poor, especially in a highly delithiated state. The crystal structure of $\text{Li}_{1-y}\text{Ni}_{1-a}\text{M}_a\text{O}_2$ changes from layer to spinel, and then rocksalt, and oxygen is released at high temperature [5–15]. The oxygen-release from the cathode can lead to thermal runaway by reacting with electrolyte, and cause fire and explosion of lithium-ion battery. Therefore, the evaluation of thermal decomposition of the cathode is important.

We elucidated the stability of an Ni-based cathode, $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$, in a previous report, and its low stability due to heating was attributed to the instability of Ni^{3+} and Ni^{4+} in a high charge state [12,15]. Its poor stability has prevented it from being applied

to large-scale batteries; therefore, new cathode materials that satisfy both high capacity and high stability criteria are required.

It has been reported that lithium-rich layer-structured materials, $\text{Li}[\text{Li}_{1-a-b-c}\text{Ni}_a\text{Mn}_b\text{M}_c]\text{O}_2$ (M: metal), exhibit high capacity around 250 Ah kg^{-1} [16–20]. The crystal structure of $\text{Li}_{1.2-x}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ changed from layer to spinel at high temperature [21]. Therefore, the oxygen-release from charged Li-rich layer-structured cathode at high temperature might be lower than that from charged Ni-based layer-structured cathode. However, there are no results compared by the identical condition. Furthermore, the cause of the difference in structure change has yet to be clarified.

The stability of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ in a charge state at high temperature was evaluated in the present study, and compared with that of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ in a full-charge state. The oxygen release, crystal structure change, and oxidation state of each transition metal were investigated by using thermal desorption spectrometry-mass spectrometry (TDS-MS), X-ray diffraction (XRD), and X-ray absorption fine structure (XAFS) analyses.

2. Experimental

$\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ sample was synthesized by reacting stoichiometric mixtures of lithium acetate, nickel acetate, manganese acetate, and cobalt acetate. The mixture was stirred in distilled water for 1 h, and then dried. It was pre-heated at 500°C for 12 h in air, and then heated at 850°C for 12 h in air.

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$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ was synthesized by reacting lithium hydroxide, nickel oxide, manganese oxide, and cobalt oxide with 3% excess of lithium hydroxide. The mixture was pre-heated at 600 °C for 10 h in oxygen, and then heated at 850 °C for 10 h in oxygen.

The crystal structures of the $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ samples were evaluated by XRD (Rigaku, Rint-2200). The diffraction data were recorded at a 0.02° step width over a 2θ range from 10 to 70° using a Rigaku diffractometer with Cu Kα radiation ($\lambda = 1.54 \text{ \AA}$).

The electrochemical properties of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ samples were measured by using a three-electrode electrochemical cell containing $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ or $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrodes as a cathode, lithium foil as an anode, and a reference. The electrode was composed of the prepared sample, carbon, and binder (85: 10: 5 wt%). The electrolyte was a 1 M LiPF_6 solution containing a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) (1:2:2 vol%) solvents. The charge-discharge capacities of the samples were measured within a potential range of 2.5–4.6 V or 2.5–4.3 V (vs. Li/Li^+). The cells were charged at 0.05 C (1 C = 260 A kg^{-1}) to 4.6 or 4.3 V, and then held at 4.6 or 4.3 V until the current became less than 0.005 C. After that, the cells were discharged at 0.05 C to 2.5 V.

The lithium content after charging was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer, OPTIMA-3300XL).

The oxygen released from the cathode by heating was evaluated by using TDS-MS (ESCO Ltd. EMD-WA1000). The samples for TDS-MS were prepared with the following procedure. The $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrodes were charged to the prescribed composition, $\text{Li}_{1.2(1-x)}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ ($x = 0.6, 0.7, 0.8, 0.87$) and $\text{Li}_{1-y}\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ ($y = 0.8$), at a rate of 0.05 C. After that, the electrochemical cells were decomposed, and the electrodes were washed with DMC. The delithiated samples were placed in the TDS-MS chamber and heated to 400 °C in a vacuum at a rate of 5 °C/min.

The crystal structure of the $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ samples in a full-charge state at high temperature was evaluated by XRD. The samples for XRD were prepared with the following procedure. The $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrodes were charged up to a full-charge state, such as $\text{Li}_{1.2(1-x)}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ ($x = 0.87$) and $\text{Li}_{1-y}\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ ($y = 0.8$). After that, the electrochemical cells were decomposed, and the electrodes were washed with DMC. The charged electrodes were heated at 150–400 °C in an argon atmosphere for 1 h to expose them, and then cooled to room temperature (RT).

The oxidation state of each transition metal was investigated by XAFS at the BL-9C of the Photon Factory (PF) for High Energy Accelerator Research Organization (KEK) in Japan. The samples for XAFS were prepared with the same procedure as that used to prepare the XRD samples. The oxidation state of each transition metal was mainly evaluated by X-ray absorption near-edge structure (XANES) analysis. The Ni, Co, and Mn K-edge XANES spectra of the prepared samples were measured in transmission mode by using a Si(111) double-crystal monochromator. The XANES spectra were compared with those of the reference samples such as lithium transition metal oxide and transition metal oxide.

3. Results and discussion

3.1. Crystal structure of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$

Fig. 1 shows the XRD patterns of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ powder. Fig. 1(a) indicates that all the main

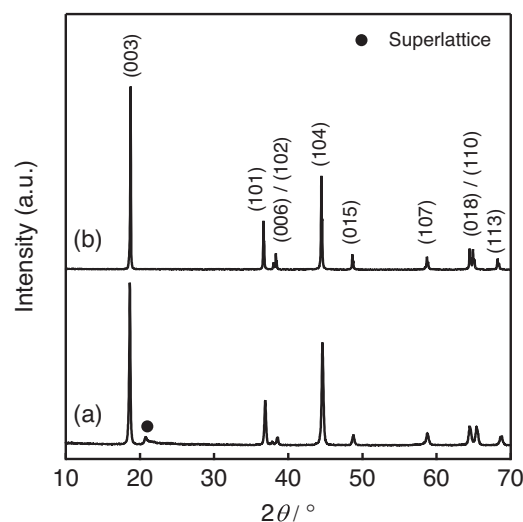


Fig. 1. XRD patterns of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ powder.

peaks of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ were assigned to a hexagonal $\alpha\text{-NaFeO}_2$ structure with space group R-3m. Small peaks also appeared between $2\theta = 20$ and 25° , indicating the presence of a superlattice structure such as LiMn_6 and LiMn_5Ni in the transition metal layer [17,20]. Fig. 1(b) indicates that all the peaks of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ were indexed to a hexagonal $\alpha\text{-NaFeO}_2$ structure.

3.2. Electrochemical properties of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$

The charge-discharge capacities of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ were measured within a potential range of 2.5–4.6 V for the former and 2.5–4.3 V for the latter (vs. Li/Li^+).

Fig. 2 shows the initial charge and discharge curves of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$. The initial charge and discharge capacities of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ were 327 and 251 Ah kg^{-1} , respectively. Even though 87% of lithium ions were de-intercalated in the charge process, only 67% of them were

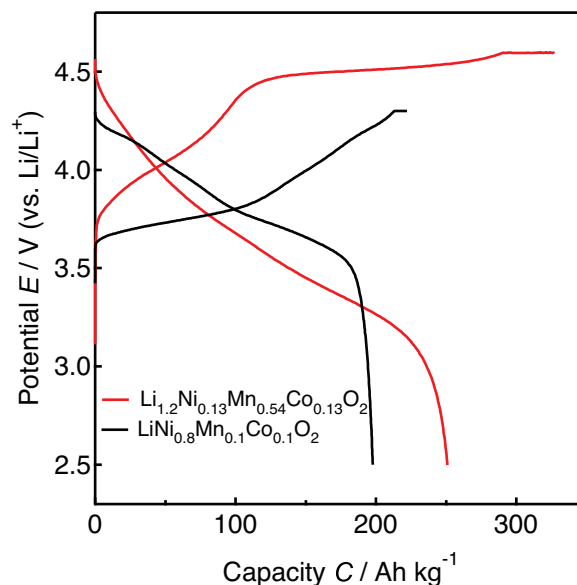


Fig. 2. Initial charge and discharge curves of $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ within potential range of 2.5–4.6 V, and 2.5–4.3 V vs. Li/Li^+ .

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