



Short communication

A new approach to improve the high-voltage cyclic performance of Li-rich layered cathode material by electrochemical pre-treatment

Atsushi Ito^a, Decheng Li^a, Yasuhiko Ohsawa^b, Yuichi Sato^{a,*}

^a Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

^b Nissan Research Center, Nissan Motor Co., Ltd., 1 Natsushima-cho, Yokohama 237-8523, Japan

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ABSTRACT

Lithium-rich nickel–manganese–cobalt oxide, $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$, was prepared by a co-precipitation method, and its cyclic behavior at a high potential was investigated. The as-prepared material shows a rapid capacity fading in its initial several cycles when it was operated above 4.5 V, which could be significantly improved through a pre-cycling treatment. Its reversible capacity in the range of 4.8–2 V could be increased from 200 to 250 mAh g⁻¹ after 50 cycle through a stepped pre-cycling treatment.

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1. Introduction

Due to the relatively low practical capacities of current commercial cathode materials, it is necessary to develop new cathode materials with a high reversible capacity in order to meet the requirement for the electric vehicles (EVs) or hybrid electric vehicles (HEVs) in the near future. Recently, a solid solution system, $\text{Li}_2\text{MnO}_3\text{--LiNi}_{0.5-x}\text{Mn}_{0.5-x}\text{Co}_{2x}\text{O}_2$, which could be considered as a lithium-rich layered material, has drawn much attention due to its extraordinarily high capacity [1–3]. The origin of the anomalously high capacity of this system had been ascribed to the fact that the electrochemically inert Li_2MnO_3 would transform into the electrochemically active MnO_2 after both lithium and oxygen are simultaneously extracted from the lattice during the initial charge process when the electrode was charged above 4.5 V, and the resulting MnO_2 could participate not only the following discharge–charge process, but could also function as a structural unit to stabilize the structure over a wide composition range, and consequently, could exhibit a high capacity [3]. So far, the investigations have mainly focused on the preparation conditions [2], structural details and electrochemical behavior [3]. Only a few studies have been done on the cyclic performance, although it has been reported that the cyclic performance was not satisfactory [4,5].

In this study, we prepared $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$, which could be re-written as (6/15) Li_2MnO_3 (or (9/15) $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$)·(5/15) $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ·(1/15) LiCoO_2 , by a co-precipitation method and proposed a new approach to improve its high-voltage cyclic performance by an electrochemical pre-treatment, which is completely different from the traditional methods such as a surface modification by oxide coating [6] or fluorinating treatment [7].

2. Experimental

The preparation of the $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ was done by mixing the Ni–Mn–Co precursor with the $\text{LiOH}\cdot\text{H}_2\text{O}$. The Ni–Mn–Co precursor was prepared by co-precipitation using $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4\cdot 5\text{H}_2\text{O}$ as the starting materials, and 2 mol L⁻¹ Na_2CO_3 and 0.2 mol L⁻¹ NH_4OH solutions as the precipitation agents. The stoichiometric starting materials were initially dissolved in distilled water to form a 2-mol L⁻¹ solution, and then the precipitation agents as droplets were introduced to obtain the composited carbonate precursor. The obtained precursor was dried at 120 °C for 5 h, and then sintered at 500 °C for 5 h. After thoroughly mixing the pre-annealed precursor with the $\text{LiOH}\cdot\text{H}_2\text{O}$, the mixture was pressed into pellets. After the pellets were sintered at 900 °C in air for 12 h, they were dropped into liquid N_2 for quenching.

XRD measurements were carried out using a Rigaku Rint1000 diffractometer equipped with a monochromator and a Cu target tube.

* Corresponding author. Tel.: +81 45 481 5661x3885; fax: +81 45 413 9770.
E-mail address: satouy01@kanagawa-u.ac.jp (Y. Sato).

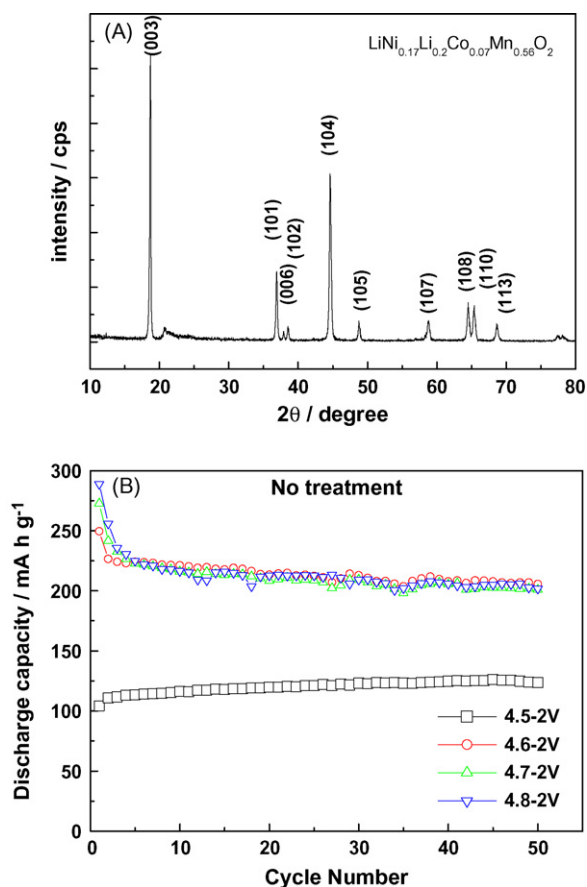


Fig. 1. XRD pattern of the $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ and its cyclic performances in the different voltage ranges.

The Li, Ni, Co and Mn contents in the samples were determined by Seiko SPS1500VR inductive-coupled plasma spectroscopy (I.C.P.).

The charge–discharge tests were carried out using a CR2032 coin-type cell, which consists of a cathode and a lithium metal anode separated by a Celgard 2400 porous polypropylene film. The cathode contains a mixture of 20 mg of accurately weighed active materials and 12 mg of Teflonized acetylene black (TAB-2) as the conducting binder. The mixture was pressed onto a stainless-steel mesh and dried at 130 °C for 4 h in a vacuum. The cells were assembled in a glove box filled with dried argon gas. The electrolyte was 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:2 by volume).

3. Results and discussion

The XRD pattern of the as-prepared $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ is shown in Fig. 1A. All peaks are sharp and well-defined and could be indexed on the basis of the α - NaFeO_2 structure, except for those broadened super lattice peaks around 22–25°. The lattice parameters for a and c , which were calculated by a least-squares method using 10 diffraction peaks, are 2.852 and 14.226 Å, respectively. The elemental analysis results for $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ showed that the as-prepared sample is slightly Li-deficient compared with its nominal formula, and its formula should be $\text{Li}_{1.17}\text{Ni}_{0.17}\text{Co}_{0.07}\text{Mn}_{0.57}\text{O}_2$. We will still use its nominal formula in the following discussion for convenience.

Fig. 1B illustrates the cyclic performance of the sample operated in the different voltage ranges. All cells were cycled at a constant

current density of 0.2 mA cm^{-2} (20 mA g^{-1}) at room temperature. When cell was operated in the range of 4.5–2 V, its initial discharge capacity was 110 mAh g^{-1} . In the following cycles, the cell showed a stable and gradual increase with respect to its discharge capacity and the discharge capacity increased to 125 mAh g^{-1} after 50 cycles. When the cells were operated at a voltage above 4.5 V, for instance, 4.6, 4.7 or 4.8 V, the initial discharge capacities would increase up to 250, 270, and 290 mAh g^{-1} , respectively. However, the discharge capacities at the high voltage would rapidly decrease in the following several cycles, and the retained discharged capacities after 50 cycles were about 200 mAh g^{-1} regardless of the cut-off voltages. The capacity retention ratios were 83, 74, and 69% for the cells charged to 4.6, 4.7, and 4.8 V, respectively.

If the cells were initially pre-cycled at 4.5 V at a current density of 0.2 mA cm^{-2} (20 mA g^{-1}) for several cycles (herein, 5 cycles), then increasing the cut-off voltage to 4.6, 4.7, or 4.8 V, the cells would exhibit a significantly improved cyclic performances compared for those without the pre-cycling treatment. As seen in Fig. 2A, the initial discharge capacities after 5 cycles at 4.5 V were 250, 270 and 290 mAh g^{-1} for the cells charged to 4.6, 4.7 and 4.8 V, respectively. These are the same as those without the pre-cycling treatment. However, after 50 cycles, the reversible discharge capacities were about 240 mAh g^{-1} for all cells, and the capacity retention ratios were 96, 88 and 83% for the cells charged to 4.6, 4.7 and 4.8 V, respectively. Both the reversible capacity and capacity retention are higher than those without the pre-cycling treatment.

Nevertheless, the rapid capacity fading in the initial several cycles was still observed for the cells operated in the range of 4.7–2 and 4.8–2 V. If cells were treated with a stepped pre-cycling mode,

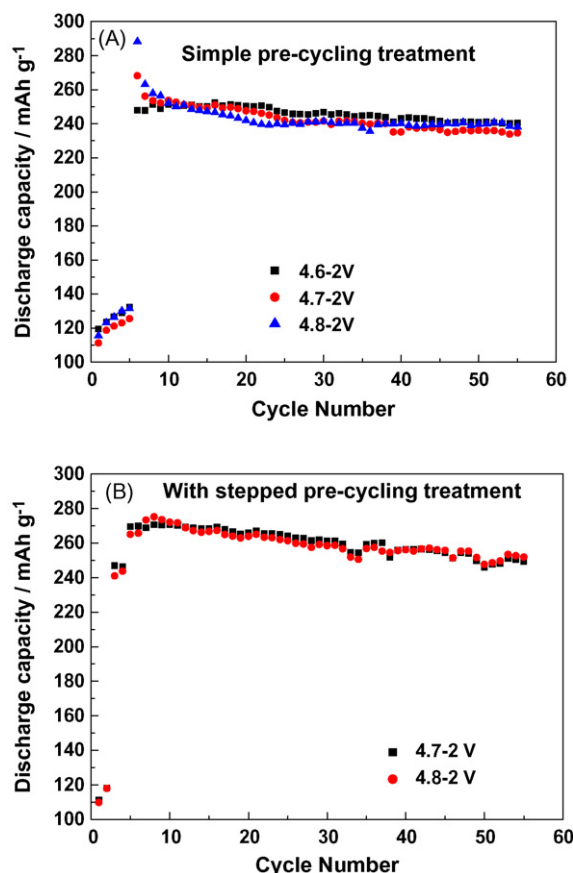


Fig. 2. Cyclic performances of the $\text{Li}[\text{Ni}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ with a pre-cycling treatment in the different voltage ranges.

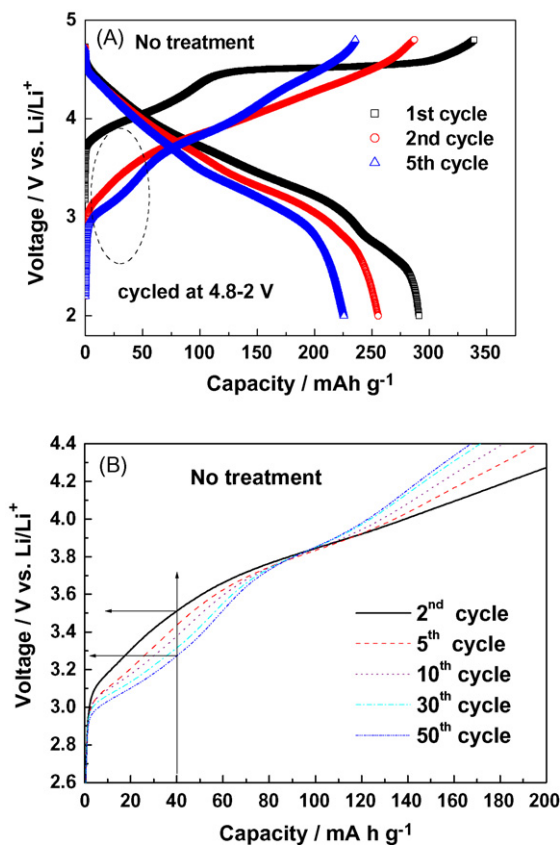


Fig. 3. Charge and discharge curves of the non-treated Li[Ni_{0.17}Li_{0.2}Co_{0.07}Mn_{0.56}]O₂ electrode with an increase in the cycle number.

for example, two cycles at 4.5–2 V and two cycles at 4.6–2 V, then starting the cycles at 4.7–2 V, the rapid capacity fading observed in the initial several cycles was successfully suppressed. This mode is also effective for the cells operated in the range of 4.8–2 V, as illustrated in Fig. 2B. Moreover, the reversible capacities are greater than 250 mAh g⁻¹ after 50 cycles for both cells operated in the range of 4.7–2 and 4.8–2 V. These results suggest that the stepped pre-cycling treatment is more effective for improving the high-voltage cycleability than the simple pre-cycling treatment in the range of 4.5–2 V.

However, the mechanism of the capacity fading when the electrodes were operated at the high voltages was not clarified. A closer inspection revealed that the change in shape was observed only in their charge curves with the increasing cycle number, as depicted by the dashed ellipse in Fig. 3A. Moreover, a remarkable voltage depression, for example, the potential corresponding to 40 mAh g⁻¹ decreases from 3.52 V for the 2nd cycle to 3.28 V for the 50th cycle, was observed in the charge curve in the region below 4 V, as demonstrated in Fig. 3B. Whether the voltage depression is related to the capacity degradation is not very clear. As a matter of fact, the voltage depression and the new plateau formation have been observed in 0.5Li₂MnO₃·0.5Li(Mn_{0.5-x}Ni_{0.5-x}Co_{2x})O₂ ($x \geq 0.25$) [5] and in Li[Co_{0.20}Li_{0.27}Mn_{0.53}]O₂ [4], both of which exhibited a rapid capacity fading in the initial several cycles. Much work is necessary to elucidate the origin of the capacity fading as well as the mechanism of the improved cyclic performances through the pre-cycling treatment.

4. Conclusions

Lithium-rich nickel–manganese–cobalt oxide, Li[Ni_{0.17}Li_{0.2}Co_{0.07}Mn_{0.56}]O₂, was prepared by a co-precipitation method. The as-prepared material shows a rapid capacity fading in its initial several cycles when it was operated at high voltages, which seems to be related to the voltage depression in their charge curves below 4 V. The poor cyclic performance at high voltages could be significantly improved through a pre-cycling treatment.

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