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Short communication

Synthesis and electrochemical properties of $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ as a novel 5 V class positive electrode material for lithium-ion batteriesKazuki Chiba ^{a,b}, Masahiro Shikano ^{a,*}, Hikari Sakaebe ^a^a Research Institute of Electrochemical Energy, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan^b Office of Society-Academia Collaboration for Innovation, Kyoto University, Uji, Kyoto 611-0011, Japan

HIGHLIGHTS

- $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ is synthesized by thermal treatment at 500 °C.
- The initial discharge capacity of $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ with thermal treatment at 500 °C is 257 mA h g⁻¹.
- The charge/discharge profiles show a novel high-potential plateau region at 4.8 V.

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ABSTRACT

A lithium nickel manganese oxide, $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, is synthesized from the precursor, $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, by a Na^+/Li^+ ion exchange reaction using molten salt. Post-heating at 300, 400, 500, 600, and 700 °C is carried out for 5 h in air. The products are characterized by powder XRD, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), SEM, ⁶Li-magic-angle-spinning-NMR, and electrochemical measurements. The charge/discharge profiles of $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, thermally treated at 500 °C, show a high-potential plateau region at 4.8 V. Furthermore, sloping voltage profiles are observed at an average voltage of 3.21 V. An initial discharge capacity of 257 mA h g⁻¹ is obtained between 2.0 and 4.8 V with a current density of 15 mA g⁻¹ at 25 °C. This capacity corresponds to 0.90 electron transfers per formula unit. This study shows that Post-heating of $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ is effective to improve its electrochemical properties.

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1. Introduction

Lithium nickel manganese oxide, $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, with a layered structure has been extensively investigated as a positive electrode material for rechargeable Li-ion batteries [1–5]. Paulsen et al. revealed superior battery characteristics of O2-type $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, such as good cycle performance and a discharge capacity of about 170 mA h g⁻¹ between 4.6 and 2.5 V [1]. On the other hand, O3-type $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ shows a remarkable discharge capacity of about 200 mA h g⁻¹ between 4.7 and 2.5 V; however, it shows poor cycling [6]. The stacking of oxide ions in the O3-type structure is very similar to that of the spinel structure; therefore, the O3-type structure is unstable and easily converts to the spinel structure during electrochemical cycling. This is the main reason for the poor capacity retention in O3-type $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$.

$\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ exists as a metastable phase and has been prepared by the Li ion exchange reaction using the Na-based

layered compound, $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, in an anhydrous molten salt at about 300 °C. Similar chemical composition of $\text{O3-Li}_{0.9}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was reported to have a variation in the crystal structure, depending on the heat-treatment temperature [7]. Above 300 °C, the crystal structure of $\text{O3-Li}_{0.9}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ transform to the spinel structure; however, the electrochemical properties were not reported. It is well-known that the O3-type structures convert to the spinel structures during electrochemical cycling [2]. Therefore, the crystal structure is considered to be stabilized in the spinel-like form. Upon increasing the temperature, the $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ structure is expected to undergo phase transformation to the spinel-like form, which may improve the electrochemical properties.

In the present study, we have attempted the modification of the layered structure $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ using heat treatment. A 5 V class plateau was confirmed for the first time.

2. Experimental

The precursor, $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, was synthesized by a conventional solid-state reaction with stoichiometric amounts of

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CH_3COONa (98.5% pure), $\text{Ni}(\text{OH})_2$ (99.9% pure), and Mn_2O_3 (99.9% pure), with 3% excess Na [2,4,8]. The weighed powder was mixed by ball milling, and then pressed into pellets. The pellets were heated at 650 °C under O_2 flow for 10 h, and then pulverized. The $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ powder was mixed with LiNO_3 and LiCl (88:12 by weight, with $\text{Li/Na} = 7$) and heated at 260 °C for 1 h in air [2,4]. After the ion exchange reaction, the sample was washed with distilled water and then dried at 80 °C overnight. Finally, to control the crystal structure, the samples were heated at 300, 400, 500, 600, and 700 °C for 5 h in air. Hereafter, we denote $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ with thermal treatments at 300, 500, and 700 °C as O3_{300} -, O3_{500} -, and O3_{700} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, respectively.

The phase purity and crystal structure of the obtained samples were determined by powder X-ray diffraction (XRD) using an AXS D8 ADVANCE diffractometer (Bruker) with a $\text{Cu K}\alpha$ radiation source (operating conditions: 40 kV, 55 mA). The XRD intensity data were collected for 0.5 s at each 0.02° step over a 2θ range of 10° – 70° . TOPAS ver. 4.2 software package was used for Pawley analysis [9].

The solid-state ^6Li magic-angle-spinning nuclear-magnetic-resonance (^6Li -MAS-NMR) spectra of the samples were obtained at room temperature using an AVANCE300 spectrometer (Bruker) at 44 MHz with a spinning rate of 50 kHz for Li nuclei by a rotor-synchronized spin-echo pulse sequence. The pulse width was 3.6 μs ($\pi/2$ pulse). The chemical shift was recorded relative to 1.0 M $^6\text{LiCl}$ aqueous solution.

The particle morphology and qualitative chemical composition were verified by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis, respectively (Keyence, VE-8800). The cationic composition (e.g., Li, Na, Ni, and Mn contents) was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Shimadzu ICPS-8000).

Electrochemical cycling was performed using CR2032 coin-type cells. The working electrodes were prepared using 10 mg of active material, 10 mg of acetylene black as the conductive agent, and 2 mg of polyvinylidene difluoride as the binder. Al mesh was used as the current collector, and the electrode diameter was 14 mm. The counter electrode was a Li foil cut in a circle with 16 mm diameter and 0.2 mm thickness. A microporous polypropylene sheet was used as a separator. A solution of 1 mol dm^{-3} LiPF_6 in a 1:2 (v/v) mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. Cells were constructed in a dry room with a dew point below -50°C , and electrochemical measurements were carried out with a current density of 15 mA g^{-1} (19 mA cm^{-2}) at 25 °C after standing overnight under an open circuit condition.

3. Results and discussion

The XRD pattern of $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, the precursor for the ion exchange reaction, shows that it can be synthesized almost as a single-phase (Fig. 1). The lattice parameters, $a = 2.8865$ (1) and $c = 16.781$ (1) Å, are in good agreement with those of the previous report ($a = 2.8867$ and $c = 16.7812$ Å) [4]. The chemical formula of the precursor is $\text{Na}_{0.68}\text{Ni}_{0.33}\text{Mn}_{0.66}\text{O}_2$, which is very close to the ideal formula of $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$. The lattice parameters and the chemical compositions of all samples are listed in Table 1. After ion exchange with Li, some Na remains and the chemical formula of the sample can be written as $\text{Na}_{0.0018}\text{Li}_{0.66}\text{Ni}_{0.33}\text{Mn}_{0.66}\text{O}_2$, which corresponds to 0.05 wt% Na for $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$.

The XRD patterns of both O3- and O3_{500} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ are assigned an almost single phase of the layered rock salt-type structure (space group of $R\bar{3}m$), as shown in Fig. 1. The c -axis length of the samples after ion exchange is much shorter than that of the precursor because the ionic radius of Li^+ (0.76 Å) is smaller than that of Na^+ (1.02 Å) [10], which leads to a reduced distance between $\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ layers [11]. A comparison of O3- and O3_{500} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ XRD patterns shows a clear separation of Bragg

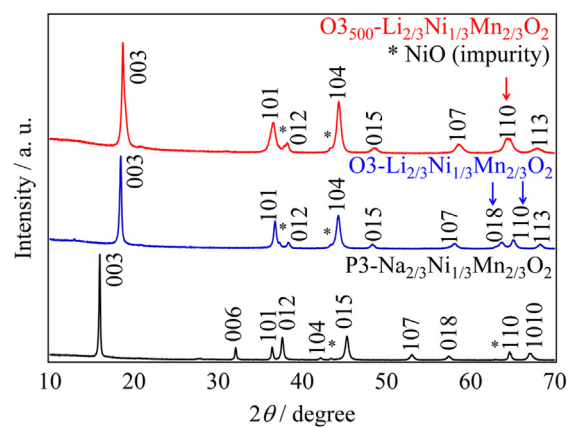


Fig. 1. XRD patterns for the precursor ($\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$), $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, and O3_{500} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$. The “*” marks indicate NiO (impurity).

diffraction lines for 018 and 110 in the as-prepared O3- phase. In the XRD pattern of O3_{500} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, however, both diffraction lines merge into a single broad line, indicating that the ratio of lattice parameters (c/a) is close to 4.90, which is lower than that of the as-prepared O3- phase (Table 1) [12,13]. The cubic close-packed oxygen array of the rhombohedral structure approaches cubic symmetry [7]. As mentioned earlier, the stacking of oxide ions in both the layered rock salt- and spinel-type structures is equivalent and the only difference between the structures is the transition metal site [14]. The c -axis is shortened by the heat treatment; therefore, the local structure of the transition metal ions is presumed to be similar to the spinel-type structure.

Fig. 2 shows the ^6Li -MAS-NMR spectra of O3- and O3_{500} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$. The $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ spectrum shows peaks at 1500 and 750 ppm, which suggests two types of Li sites in the structure [15]. A small and broad resonance at 1500 ppm is assigned to Li in a honeycomb-like arrangement of Mn ions (i.e., six Mn as the nearest neighbors) within the transition metal layer, as found in $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2]$ (Li_2MnO_3) [16,17]. The 750 ppm peak is assigned to Li in the alkali layer of the layered rock salt structure [15]. On the other hand, in the case of O3_{500} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, an additional peak at 925 ppm is observed, which should be related to the spinel-type structure [18]. It is believed that the spinel domains, which cannot be detected by XRD, are present.

Fig. S1 in the supplementary material shows the typical SEM images of $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, and O3_{500} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$. Although the particle morphology changes due to the ion exchange, the primary particle size remains unchanged. The ion exchange treatment temperature is estimated to be around the phase transition temperature. However, no significant difference is observed in O3- and O3_{500} - $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$.

Fig. 3a shows the charge/discharge curves of the $\text{O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ sample starting from Li extraction at 25 °C. Here, the voltage ranges between 2.0 and 4.8 V and the rate is 0.06 C. Two plateaus in the discharge curve are observed at around 4.2 and 3.0 V, as previously reported [2]. In the present $\text{Li/O3-Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ cell, the resultant average discharge voltage is 3.41 V and the initial discharge capacity is 194 mA h g^{-1} , which is a higher capacity than that previously reported (170 mAh g^{-1}) [2]. This observation can be explained by the expansion of the voltage range between 2.5 and 4.4 V. This value is equivalent to 0.67 electron transfers per formula unit. Even after 10 cycles of charge/discharge, the discharge capacity remains at 184 mA h g^{-1} and its efficiency is 94.8%. Meanwhile, Zhao et al. did not observe two plateaus and the discharge capacity was large in the voltage range between 4.2 and 4.7 V [6]. It was pre-

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