Low Temperature Synthesis of High Crystalline Spinel Oxides: $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$

Yasuaki MATSUDA,^{a,*} Masaki MATSUI,^{a,b} Takahiro SANDA,^a
Yusuke TAKASHI,^a and Nobuyuki IMANISHI^a

^a Department of Chemistry Mie University, 1577 Kurimamachiya Tsu, Mie 514-8507, Japan

^b Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

* Corresponding author: matsuda@chem.mie-u.ac.jp

ABSTRACT

The crystal growth process of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was investigated and the octahedral shaped $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was successfully synthesized by a low temperature synthesis. The morphology change was accelerated by the spinel-rocksalt phase transformation caused by the oxygen loss. After re-oxidation, high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with octahedral morphology was obtained. High crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with the particle size of 1–3 μm was obtained by the low temperature synthesis controlling the oxygen partial pressure. High crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ crystallized at 850°C exhibited an initial charge capacity of 145 mAh g^{-1} and an initial discharge capacity of 137 mAh g^{-1} with a plateau at 4.7 V, and 90% of cycle retention after 100 cycles at 60°C. Microparticulation of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ enhanced the discharge capacity.

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1. Introduction

Transition metal-substituted manganate spinel materials ($\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$, M : Ni, Cr, Co, Fe and Cu) have attracted much attentions as positive electrodes for rechargeable Li-ion batteries due to the high-voltage plateaus above 4.5 V vs. Li^+/Li .^{1–5} Among these materials, $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ is the most promising material because of its high discharge capacity and dominant plateau at approximately at 4.7 V coming from the redox process of $\text{Ni}^{2+}/\text{Ni}^{4+}$ together with lithiation and delithiation.^{4–10} However, the biggest problem of this material is the capacity degradation due to the decomposition of the electrolyte.

A significant improvement of the cycle stability was achieved by increasing crystallinity of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with the octahedral morphology.^{8,9} The facets of the (111) surface, which is the most stable surface, cover the largest area of the octahedron and might improve cycle stability.^{11–13} High crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with the octahedral morphology was synthesized by the two-step solid-state reaction and the morphology of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ changed with the pre-sintering temperature.^{8,9} We also confirmed that the cycle retention of the high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with octahedral shape was more than 90% after 100 cycles at 60°C. For the improvement of the power density, the decrease of the particle size of the octahedral $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ would be required. If low temperature synthesis is possible, it is favorable to obtain high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with small particle size. However, the formation mechanism of high crystalline spinel oxides has not been well understood yet.

Therefore, we investigated the crystal growth process of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ using high temperature X-ray diffraction (H.T.-XRD), scanning electron microscopy (SEM) and thermo gravimetric (TG) analysis and the octahedral shaped $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with small particle size was successfully synthesized at low temperature. In this study, the crystal growth mechanism and the electrochemical properties of the high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with different particle size were discussed.

2. Experimental

High crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was synthesized by the two-step solid-state method to study the crystal growth process of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.^{8,9} A nickel manganese double hydroxide ($\text{Ni}:\text{Mn} = 0.99:3.01$) synthesized by a coprecipitation method was annealed at 500°C for 8 h. The obtained complex oxide was mixed with stoichiometric amount of $\text{LiOH}\cdot\text{H}_2\text{O}$ (98%, Kanto Chemical, Japan) and calcined at 1000°C for 10 h in air and subsequently re-oxidized at 700°C for 24 h, 650°C for 24 h and 600°C for 48 h with a heating rate of 5 K min^{-1} and cooling rate of 1 K min^{-1} . To decrease the particle size of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$, low temperature synthesis was applied based on the hypothesis of the crystal growth process. Low temperature synthesis of the morphology controlled $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was performed using $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ synthesized at 800°C for 10 h as a starting material. $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was reduced in a N_2 gas flow at 850°C for 3 h and then re-oxidized at 850°C for 3 h, 700°C for 24 h, 650°C for 24 h and 600°C for 48 h in an O_2 gas flow with a heating rate of 5 K min^{-1} and cooling rate of 1 K min^{-1} .

A powder X-ray diffractometer (RINT 2500, Rigaku, with $\text{CuK}\alpha$ radiation) equipped with a high temperature furnace attachment was employed for the H.T.-XRD measurements to study the phase transformation of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ during the two-step solid-state reaction. Mixed powder of complex oxide and $\text{LiOH}\cdot\text{H}_2\text{O}$ was set at the equipment and H.T.-XRD data were taken in order to see the phase change during the heating and cooling processes between 25°C and 1000°C, time change of the phase at 1000°C and re-oxidation processes at 700°C. Morphology change of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ particles was observed by using scanning electron microscopy (SEM; S-4000, Hitachi). TG analysis (Thermo Plus TG 8120, Rigaku) was employed to measure the mass change in air and a N_2 gas flow. Elemental analysis for Li, Ni and Mn in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was conducted by using inductively coupled plasma spectroscopy (ICP-OES; Agilent Technologies ICP-OES 710). Surface area of morphology controlled $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was measured by the surface area and porosity analyzer (TriStar II, Micromeritics).

Figure 1. H.T.-XRD patterns for $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ during (a) heating process and (b) cooling process.

Figure 2. SEM images of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ during morphology changing process.

Galvanostatic charging–discharging tests were performed using a two-electrode cell (TJ-AC, Tomcell Japan). The cathode material consisted of the active material, acetylene black (AB) and polyvinylidene fluoride (PVDF) at a gravimetric ratio of 80:10:10. The anode was metallic lithium. The electrolyte was 1 M LiPF_6 dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 vol.%). Charge–discharge measurements were carried out in the range of 3.0–5.1 V vs. Li/Li at 60°C and at a charge/discharge rate of 1 C (1 C = 147 mAh g^{-1}).

3. Result and Discussion

Figure 1 shows H.T.-XRD patterns for $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ during (a) heating process and (b) cooling process. Diffraction peaks which could be indexed with the spinel structure were observed at 400°C and the formation of the spinel phase proceeded up to 800°C.^{4,8,14} The decrease of the peak intensity of the spinel phase and formation of the NiO like rocksalt phase began to occur above 900°C and the rocksalt phase became dominant at 1000°C. During the cooling step, the spinel phase was reformed and the rocksalt phase disappeared after sintering at 700°C for 20 h. Reversible phase transformation from the spinel to the NiO like rocksalt phase above 700°C in air was in good agreement with the previous reports.^{15,16}

Figure 2 shows SEM images of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ during morphology changing process. The morphology of the particle didn't show no significant change at 700°C and a slight growth of the

Figure 3. TG curves of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ measured in (a) air and (b) N_2 gas flows with a heating rate of 5 K min^{-1} and cooling rate of 1 K min^{-1} . The samples were kept at 1000°C for 5 h and 700°C for 3 h at cooling process.

primary particles was observed at 900°C. A drastic morphology change was observed at 1000°C and the octahedral-shaped particles were observed after 5 h. This indicates the spinel-rocksalt phase transformation enhanced the morphology change.

Figure 3 shows TG curves of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ measured in (a) air and (b) N_2 gas flows. Weight loss started at 750°C and reached about 8 wt% at 1000°C in air. The TG curve in air exhibited the good reversibility between cooling and heating process. On the other hand, TG curve under the N_2 gas flow showed that the weight loss

Figure 4. A schematic drawing of the morphology change process of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

Figure 5. XRD pattern for high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ synthesized at 850°C by changing synthesis atmosphere.

occurred at 650°C and poor reversibility was observed between heating and cooling processes. This suggests the existing of correlation between the reversible phase transitions and the oxygen content in the material process at high temperature.

Figure 4 shows a schematic drawing of the morphology change process of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. The morphology change was accelerated by the phase transformation to the rocksalt phase. The phase transformation to the rocksalt phase indicates that the diffusion process of Ni or Mn was accelerated resulting in the significant morphology change. And TG analysis proved the correlation between the reversible phase transformation and the oxygen loss process at high temperature. In addition, the surface energy of the particles should be minimized during the particle growth process. As a consequence, the morphology of the particle transformed to the octahedral shape, whose surface consists of the oxygen closed packed layer.

Since phase transformation of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ to rocksalt structure related to the oxygen loss, the temperature of the phase transition should be affected by oxygen partial pressure. We attempted the low temperature synthesis of octahedral shaped $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ by changing the synthesis atmosphere based on this hypothesis. $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ reduced under the N_2 gas flow at 850°C for 3 h, where the well-crystallized particles are expected to be obtained, and then re-oxidized by changing the atmosphere to an oxygen gas flow. Figure 5 shows XRD pattern for $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ crystallized at 850°C. All diffraction peaks were assigned to the spinel structure with a lattice constant of 8.17 Å, which is comparable to that of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ crystallized at 1000°C. The atomic ratio of Li/Ni/Mn in morphology controlled $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was 0.99/0.48/1.5 where the ratio was normalized according to Mn at 1.5, which showed no composition change of cations during the morphology change. No difference of the atomic ratio of Li/Ni/Mn was observed for high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ synthesized at different temperatures. Figure 6 shows SEM images of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ particles crystallized at 850°C. Octahedral-shaped particles

Figure 6. SEM image of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ crystallized at 850°C.

with the particle size of 1–3 μm were observed, which was smaller than those with the particle size of 5 μm crystallized at 1000°C in air. The surface area of the morphology controlled $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ increased from 4.648 to 5.428 m^2g^{-1} by the low temperature synthesis, which is in good agreement with the particle size change. By changing the synthesis atmosphere, we were able to successfully control the particle size of the high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

Figure 7 shows charge-discharge profiles of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ crystallized at 850°C (a), at 1000°C (b) and the comparison of cycle performance at a charge/discharge rate of 1 C with a voltage range 3.0–5.1 V at 60°C (c). The high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ synthesized at 850°C exhibited an initial charge capacity of 145 mAh g^{-1} and an initial discharge capacity of 137 mAh g^{-1} with a plateau at 4.7 V attributed to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple.^{8,10} Charge-discharge profiles were similar to those of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with Ni^{2+} and Mn^{4+} ordered structure.^{15–17} The discharge capacity of 122 mAh g^{-1} was maintained after 100 cycles. On the other hand, high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ synthesized at 1000°C showed the discharge capacity of 122 mAh g^{-1} at initial cycle and 118 mAh g^{-1} after 100 cycles. Both octahedral shaped $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ exhibit excellent capacity retention. The high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ synthesized at low temperature showed higher discharge capacity during 100 cycles. Coulombic efficiencies of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ samples were summarized in Table 1. Both high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ samples exhibited low coulombic efficiency at an initial charge/discharge cycle, which might be related to the electrolyte decomposition reaction at the initial charge process. High crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ synthesized at 1000°C exhibited 90% coulombic efficiency after 10 cycles. In contrast, $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ crystallized at 850°C showed 93% coulombic efficiency after 10 cycles. Micronization of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ might lead to an improvement of the kinetic performance by reducing the transport distance for lithium-ions, which decreases ohmic polarization loss due to lithium-ion migration. The decrease of the ohmic polarization loss should be affected for the enhancement of the coulombic efficiency of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. Our research confirmed the importance

Figure 7. Charge-discharge profiles of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ crystallized at 850°C (a), at 1000°C (b), and comparison of cycle performances of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ at a charge/discharge rate of 1 C with a voltage range 3.0–5.1 V at 60°C (c).

of the particle size control of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. Further investigation is needed for the understanding of the details of the relationship between the particle size and electrochemical properties of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

4. Conclusion

We investigated morphology change process of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. The morphology change was accelerated by the spinel/rocksalt phase transformation caused by the oxygen loss. We successfully

Table 1. Coulombic efficiencies of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

Cycle number	Coulombic efficiency (%)	
	Crystallized at 1000°C	Crystallized at 850°C
1	65.24	77.26
2	84.25	82.84
10	89.93	94.00
20	86.22	93.98
50	90.41	93.41
100	90.27	92.21

decreased particle size of the high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ with octahedral shape by the low temperature synthesis controlling the oxygen partial pressure. Particle size of the octahedral shaped $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ decreased from 5 μm to 1–3 μm . High crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ crystallized at 850°C exhibited an initial charge capacity of 145 mAh g^{-1} and an initial discharge capacity of 137 mAh g^{-1} with a plateau at 4.7 V, and 90% of cycle retention after 100 cycles at 60°C. Higher discharge capacity was observed by microparticulation of high crystalline $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

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