Thermal plasma synthesis and electrochemical properties of high-voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$ nanoparticles

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Abstract

The synthesis of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ has been reported to change the crystal structure with the oxygen partial pressure and affect the battery characteristics. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ involves the formation of impurities, such as Li$_x$Ni$_{1-x}$O, Li$_x$Mn$_{3-x}$O$_4$, and Li$_2$CO$_3$, at a high temperature range exceeding 700 °C because oxygen loss occurs during synthesis. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrochemically contains Mn$^{3+}$, however, Mn$^{3+}$ is formed because of oxygen deficiency. The Li–Ni–Mn-oxide causes a disproportionation of Mn$^{3+}$ in an oxygen-deficient state. The synthesized Li–Ni–Mn-oxide nanoparticles at 10,000 K by induction thermal plasma formed spinel-type LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (space group Fd3m) of Mn$^{4+}$. The crystal structure of the cubic-spinel nanoparticles approached a LiNi$_{0.5}$Mn$_{1.5}$O$_4$ single phase as the flow rate of O$_2$ increased from 2.5 to 5 min$^{-1}$. The formation of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ was shown to be accelerated by increasing the O$_2$ gas flow rate. The measured current-voltage characteristics of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ nanoparticles appeared at around 4.7–4.8 V as the reaction peak of Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$. In contrast, the Mn of the Li–Ni–Mn-oxide nanoparticles synthesized in the oxygen-deficient state was less than trivalent, which caused disproportionation of Mn. The measured current-voltage characteristics showed peak of an oxygen desorption near 4.6 V. This study investigated the factors affecting the crystal structure formation and electrochemical properties of high-voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$ nanoparticles formed in thermal plasma.

1. Introduction

LiNiO$_2$ as a positive electrode material has a theoretical capacity of 274 mAh g$^{-1}$ with a high discharge voltage and high capacity. The effective capacity at an average discharge potential of 3.7 V is approximately 160 mAh g$^{-1}$. LiNiO$_2$ has a theoretical capacity of 148 mAh g$^{-1}$ and has attracted much attention due to advantages such as its low cost, the abundance of manganese in the earth’s crust, and its environmental harmlessness. Its effective capacity at an average discharge potential of 4.1 V is approximately 120 mAh g$^{-1}$.

Recently, studies on Mn-substitution in Li–Ni oxide and Ni-substitution in Li–Mn oxide have been conducted to improve Li–Ni oxide. Spinel-type Li–Ni–Mn-oxides substituted with Ni and Mn are the most studied high-voltage positive electrode materials. The spinel-type LiNi$_{0.5}$Mn$_{1.5}$O$_4$ presents features such as a high operating potential of 4.7 V and a good theoretical specific capacity of 147 mAh g$^{-1}$ [1]. Therefore, many methods for synthesizing Li–Ni–Mn-oxides have been reported, including co-precipitation, sol-gel, and solid state methods.

In the co-precipitation method, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles are synthesized from various precursors such as metal sulfates, metal carbonates, and metal chlorides [2–4]. The resulting precursor is mixed with the required amount of LiOH and calcined within the temperature range 600–900 °C to obtain LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles.

The sol-gel method is used by various research groups because of its low processing temperature, high chemical uniformity, and easy control of particle size and morphology [5–9]. The LiNi$_{0.5}$Mn$_{1.5}$O$_4$ precursor is synthesized similarly to the co-precipitation method. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles are obtained by grinding the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ precursor into fine particles and heating at 450 °C in an oxygen atmosphere.
The solid state method is the most common method by which a stoichiometric mixture of starting materials is ground or ball-milled together, and the resultant mixture is heat-treated in a furnace. After drying, the mixture is calcined at 400 °C to form a precursor. A stoichiometric amount of Li2CO3 is added to the Ni–Mn ratio. The mixture containing Li–Ni–Mn is calcined in the range 700 °C–900 °C [10].

These synthetic methods allow easy control of the composition. However, the manufacturing process is time-consuming, and the possibility of incorporating impurities is high.

Compared to these synthetic methods, induction thermal plasma processing offers many advantages for producing high-purity materials with high crystallinity, with a short synthesis time of milliseconds, and for synthesizing compounds of different elements. The nanoparticles synthesized using induction thermal plasma include oxide materials, boride materials, intermetallic compound materials, and lithium metal oxide. Accordingly, methods for controlling the particle size of nanoparticles have been reported [11–16]. Induction thermal plasma is better than conventional methods at producing morphologies, crystal structures, high-purity materials, and composite nanomaterials with chemical compositions that are normally difficult to obtain [17].

The synthesis of LiNi0.5Mn1.5O4 has been reported to change the crystal structure with the oxygen partial pressure and affect the battery characteristics. LiNi0.5Mn1.5O4 involves the formation of impurities, such as Li4Ni1−xO, Li2Mn3−xO4, and Li2CO3, at a high temperature range exceeding 700 °C because oxygen loss occurs during synthesis [18–21]. LiNi0.5Mn1.5O4 electrochemically contains Mn3+, however, Mn3+ is formed because of oxygen deficiency, and the charge neutrality is maintained [18, 22, 23]. The cubic-spinel structure causes a disproportionation of Mn3+ in an oxygen-deficient state and promotes Mn dissolution when the appropriate amount of Mn3+ is exceeded [23].

In this study, we investigated the synthesis, crystal structure, formation mechanism, valence change of Mn, and electrochemical properties of Li–Ni–Mn-oxide nanoparticles formed as a positive electrode material by induction thermal plasma, which completely evaporated the raw material powder to obtain a high-voltage synthetic material. The LiNi0.5Mn1.5O4 nanoparticle synthesis method was investigated by the effect of the Ni to Mn composition ratio at constant oxygen flow rate and the effect of different oxygen flow rate at fixed Ni to Mn composition ratio.

2. Materials and methods

2.1. Experimental configuration and procedure
A schematic of the experimental apparatus used for the induction thermal plasma process is shown in figure 1. The apparatus comprises an induction plasma torch for generating the plasma, a reaction chamber for synthesizing nanoparticles, and a filter unit for recovering the nanoparticles [16]. The induction thermal plasma process comprises the following steps: raw materials in powdered form are supplied together with a carrier gas and evaporated in the plasma torch; homogeneous nucleation occurs in the reaction chamber; and nanoparticles are formed via heterogeneous condensation.

Figure 1. Schematic of the experimental setup for the induction thermal plasma process.
The effect of the O2 flow rate in the sheath gas on the Li–Ni–Mn-oxide nanoparticles synthesis were conducted at atmospheric pressure with Ar as the carrier and inner gas and Ar and O2 as the sheath gas. The experimental frequency was 4 MHz, and the applied power was 20 kW. The flow rate of the O2 sheath gas was 0, 2.5, or 5 l min⁻¹. The flow rate of the Ar–O2 mixed sheath gas was adjusted to 60 l min⁻¹.

The raw material was a powder mixture of Li2CO3 (mean diameter: 3.5 μm, purity: 99.6%, Honjo Chemical), Ni (mean diameter: 3–5 μm, purity: 99.9%, Kojundo Chemical Laboratory), and Mn (mean diameter: 10 μm, purity: 99.9%, Kojundo Chemical Laboratory). The raw powder was fed into the thermal plasma at a feed rate of 300 mg min⁻¹.

2.2. Analysis

The crystal structures of the Li–Ni–Mn-oxide nanoparticles were evaluated by x-ray diffraction (XRD; Rigaku Multiflex) with CuKα radiation (λ = 0.1541 nm), a scanning rate of 2° min⁻¹, and a step of 0.02° in the range 10°–90°. The accelerating voltage was 40 kV, and the applied current was 50 mA. The particle shapes and size distributions were observed by transmission electron microscopy (TEM; JEOL JEM-2100HCKM) based on approximately 200 particles.

Elemental analysis was performed using TEM-energy-dispersive x-ray spectroscopy (TEM-EDS; JEOL JEM-ARM200F) at 200 keV. The electron diffraction patterns were observed by TEM (JEOL JEM-ARM200F) using a camera length of 0.8 m and an accelerating voltage of 200 keV. Samples for TEM and scanning TEM (STEM) were prepared by dispersing particles on molybdenum-coated copper meshes.

2.3. Examination of electrochemical properties

Electrochemical experiments were carried out using cyclic voltammetry (CV; Bio-Logic SAS VMP-300). After synthesis, the Li–Ni–Mn-oxide nanoparticles (LNMO) were mixed with a conducting reagent (AB) and polyvinylidene fluoride (PVDF) binder at weight ratio of 90:5:5 (LNMO:AB:PVDF) to form a slurry. After roll-pressing and vacuum-drying at 393 K for 6 h, a cathode with a diameter of 11 mm was prepared. A half-cell using lithium metal as a negative electrode was fabricated with the electrolyte of 1 mol LiPF6 dissolved in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) with EC/DEC = 3/7 (v/v). The current–voltage characteristics were measured with a constant temperature of 298 K under a fixed voltage of 0.1 mV s⁻¹.

3. Results

3.1. Effect of Ni/(Ni + Mn) molar ratio on the crystal structure

A Li/(Ni + Mn) molar ratio of 1/2 was used to investigate the effect of Ni/(Ni + Mn) on the crystal structure of the produced Li–Ni–Mn-oxide nanoparticles. Li–Ni–Mn-oxide nanoparticles were synthesized at an O2 flow rate of 2.5 l min⁻¹ with a Li/(Ni + Mn) molar ratio of 1/2.

3.1.1. XRD analysis

XRD patterns of the Li–Ni–Mn-oxide nanoparticles synthesized at Ni/(Ni + Mn) molar ratios of 0.75, 0.5, and 0.25 are shown in figure 2. The XRD results confirmed that the Li–Ni–Mn-oxide nanoparticles formed single and mixed phases of LiNi0.5Mn0.5O4 (space group Fd3m) with a cubic-spinel structure and Li0.8Ni1.2O2 (space group Fm3m) with a cubic-rock-salt structure. The Li–Ni–Mn-oxide nanoparticles with a cubic-rock-salt structure were synthesized at Ni/(Ni + Mn) molar ratios of 0.75 and 0.5. The mixed-phase nanoparticles with cubic-spinel and cubic-rock-salt structures were synthesized at a Ni/(Ni + Mn) molar ratio of 0.25. The crystal structure of the synthesized nanoparticles showed that reducing the Ni molar ratio and increasing the Mn molar ratio promoted the formation of Li–Ni–Mn-oxide with a cubic-spinel structure. The XRD pattern suggested that the crystal structure changed from a cubic-rock-salt structure to a cubic-spinel structure as the molar ratios of Mn and Ni were increased and decreased.

3.1.2. TEM-EDS analysis

The TEM-EDS elemental mapping Mn and Ni molar ratios of Li–Ni–Mn-oxide nanoparticles synthesized at Ni/(Ni + Mn) molar ratios of 0.25, 0.5, and 0.75 are shown in figure 3. The Mn and Ni molar ratios of the Li–Ni–Mn-oxide nanoparticles synthesized at a Ni/(Ni + Mn) molar ratio of 0.25 were 76.1 at% and 23.9 at%, respectively. At a Ni/(Ni + Mn) molar ratio of 0.5, these values were 51.9 at% and 48.1 at%, and at a Ni/(Ni + Mn) molar ratio of 0.75, they were 23.0 at% and 77.0 at%, respectively. The quantitative analysis results were approximately consistent with the Ni/(Ni + Mn) molar ratios in the raw material powder. Therefore, the TEM-EDS results indicated that the Li–Ni–Mn-oxide nanoparticles were synthesized with a uniform composition. The XRD and TEM-EDS results confirmed that the composition of the Li10.8Ni1.2O2 nanoparticles...
was Li_{0.4}Ni_{1.2}Mn_{0.4}O_{2} when the Ni/(Ni + Mn) molar ratio was 0.75. The Li_{0.4}Ni_{1.2}Mn_{0.4}O_{2} confirmed that the valence of Mn^{4+} was reduced to Mn^{3+} by charge compensation in the Ni^{2+} excess state.

3.2. Effect of oxygen partial pressure on the crystal structure

Section 3.1 investigated the effect of different composition ratio on the crystal structure. The O_{2} flow rate was changed to investigate the effect of the oxygen partial pressure on the crystal structure of the Li–Ni–Mn-oxide nanoparticles in section 3.2. The Li–Ni–Mn-oxide nanoparticles were synthesized at a Ni/(Ni + Mn) molar ratio of 0.25 and O_{2} flow rates of 0, 2.5, and 5 l min^{-1} with a Li/(Ni + Mn) molar ratio of 1/2.

3.2.1. XRD analysis

The XRD patterns of the Li–Ni–Mn-oxide nanoparticles synthesized at a Ni/(Ni + Mn) molar ratio of 0.25 and O_{2} gas flow rates of 0, 2.5, and 5 l min^{-1} are shown in figure 4. The Li–Ni–Mn-oxide nanoparticles had the same crystal structures as spinel-type LiNi_{0.5}Mn_{1.5}O_{4} at all O_{2} flow rates. Li_{0.4}Ni_{1.2}O_{2} nanoparticles with cubic-rock-salt structures were synthesized when Ar alone was used as the sheath gas. Conversely, LiNi_{0.3}Mn_{1.3}O_{4} was Li_{0.4}Ni_{1.2}Mn_{0.4}O_{2} when the Ni/(Ni + Mn) molar ratio was 0.75. The Li_{0.4}Ni_{1.2}Mn_{0.4}O_{2} confirmed that the valence of Mn^{4+} was reduced to Mn^{3+} by charge compensation in the Ni^{2+} excess state.

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nanoparticles with cubic-spinel structures were synthesized when O2 was added to the Ar sheath gas. The intensities of the Li0.4Ni1.6O2, Mn3O4, and Li2CO3 peaks decreased, and a peak corresponding to the (111) plane of LiNi0.5Mn1.5O4 appeared at around 19° when O2 was used as the sheath gas at a flow rate of 2.5 l min⁻¹. This peak became stronger and sharper when the flow rate of O2 as the sheath gas was increased to 5 l min⁻¹. This suggested that increasing the O2 gas flow rate increased the production of LiNi0.5Mn1.5O4. Thus, the crystalline structures of the particles changed from a Li0.4Ni1.6O2 structure to a LiNi0.5Mn1.5O4 structure as the flow rate of O2 increased. The XRD patterns suggested that the crystalline structure changed from a cubic-rock-salt structure to a cubic-spinel structure as the O2 flow rate increased.

3.2.2. Particle size and morphology
TEM images and particle size distributions of Li–Ni–Mn–O nanoparticles synthesized at a Ni/(Ni + Mn) molar ratio of 1/2 and different O2 flow rates: (a) 0, (b) 2.5, and (c) 5 l min⁻¹ and a Li/(Ni + Mn) molar ratio of 1/2. (☉: Li0.4Ni1.6O2, Δ: LiNi0.5Mn1.5O4, □: Mn3O4, and ●: Li2CO3).

Figure 4. XRD patterns of Li–Ni–Mn–O nanoparticles synthesized at different O2 flow rates: (a) 0, (b) 2.5, and (c) 5 l min⁻¹ and a Li/(Ni + Mn) molar ratio of 1/2. (☉: Li0.4Ni1.6O2, Δ: LiNi0.5Mn1.5O4, □: Mn3O4, and ●: Li2CO3).

Figure 5. Representative TEM images of the Li–Ni–Mn–oxide nanoparticles synthesized at a Ni/(Ni + Mn) molar ratio of 0.25 and O2 flow rates of (a) 0, (b) 2.5, and (c) 5 l min⁻¹.

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3.2.2. Particle size and morphology
TEM images and particle size distributions of Li–Ni–Mn–O nanoparticles synthesized at a Ni/(Ni + Mn) molar ratio of 0.25 and O2 flow rates of 0, 2.5, and 5 l min⁻¹ are shown in figures 5 and 6. The particle size distributions were determined from TEM observation of approximately 200 different particles. The average particle sizes for the Li–Mn–Ni–O nanoparticles were 50.9, 60.2, and 75.9 nm, corresponding to (a), (b), and (c), respectively. Multiple crystal structures were obtained when the oxygen partial pressure was low. A uniform crystal structure existed when the oxygen partial pressure was high. The synthesized nanoparticles had polygonal structures peculiar to the cubic-spinel structure at O2 gas flow rates of 2.5 and 5 l min⁻¹. The polygonal structure

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of the TEM image shows the transmission image of the truncated tetradecahedral structure of the cubic-spinel structure (LiNi_{0.5}Mn_{1.5}O_{4}). Meanwhile, the square structure of the TEM image illustrates the transmission images of the cubic-rock-salt (Li_{0.4}Ni_{1.6}O_{2}) and tetragonal-spinel (Mn_{3}O_{4}) structures.

FE-SEM images of Li–Ni–Mn-oxide nanoparticles synthesized at a Ni/(Ni + Mn) molar ratio of 0.25 and O_{2} gas flow rates of 0, 2.5, and 5 l min^{-1} are shown in figure 7. The synthesized LiNi_{0.5}Mn_{1.5}O_{4} nanoparticles had a hexahedral crystalline structure at O_{2} gas flow rates of 0 l min^{-1} and a tetradecahedral crystalline structure at O_{2} gas flow rates of 2.5 l min^{-1}. The Li–Ni–Mn-oxide nanoparticles synthesized by thermal plasma with oxygen formed a truncated structure that differed from that typically obtained using other synthesis
methods. The truncated tetradecahedral structure was a nanoparticle structure with high crystallinity. The crystal structure results indicate that the synthesized nanoparticles transformed into this truncated structure because of their lower surface energy.

3.2.3. TEM-EDS analysis

TEM-EDS elemental mapping images of dark field (a), O (b), Mn (c), and Ni (d) of Li–Ni–Mn-oxide nanoparticles synthesized at a Ni/(Ni + Mn) molar ratio of 0.25 and an O2 gas flow rate of 0 l min⁻¹ are shown in figures 8 and 9. The gray regions of the TEM-EDS maps denote O, the red regions represent Mn, and the green regions represent Ni. The TEM-EDS maps show that Mn, Ni, and O are uniformly distributed in the synthesized Li–Ni–Mn-oxide nanoparticles. The Mn and Ni contents of the Li–Ni–Mn-oxide nanoparticles synthesized at an O2 gas flow rate of 0 l/min were 65.0 at% and 35.0 at%, respectively. An O2 gas flow rate of 5 l min⁻¹ gave 80.1 at% and 19.9 at%, respectively. All the observed Li–Mn–Ni–O nanoparticles contained both Mn and Ni. Therefore, the TEM-EDS results indicated that the Li–Ni–Mn-oxide nanoparticles were synthesized with a uniform distribution. The results of XRD and TEM-EDS was concluded that the composition of the Li_{0.4}Ni_{1.6}O2 system was Li_{0.4}Ni_{1.6}MnO2 when the O2 gas flow rate of 0 l min⁻¹. The Li_{0.4}Ni_{1.6}MnO2 confirmed that the valence of Mn⁴⁺ was reduced until Mn²⁺ by charge compensation at the oxygen–deficient state.
3.2.4. Particle electron diffraction patterns

Changes in the atomic structure of the Li–Ni–Mn-oxide nanoparticles after thermal plasma synthesis were investigated using TEM. The TEM electron diffraction images of the nanoparticles synthesized at a Li/Ni molar ratio of 1/2 are shown in figure 10.

The scattered diffraction spot indices of the electron diffraction image for nanoparticles synthesized at an O₂ flow rate of 5 l min⁻¹ were \( d = 0.30 \) nm and \( a = 0.849 \) nm for the OA (220) plane; \( d = 0.21 \) nm and \( a = 0.84 \) nm for the OB (400) plane; and \( d = 0.30 \) nm and \( a = 0.849 \) nm for the OC (2–20) plane, with corresponding surface angles of \( \angle AOB: 44.6° \), \( \angle BOC: 43.6° \), and \( \angle AOC: 88.2° \). The plane indices of XRD for nanoparticles synthesized at an O₂ flow rate of 5 l min⁻¹ were \( d = 0.289 \) nm and \( a = 0.818 \) nm for the (220) plane at 30.9° and \( d = 0.205 \) nm and \( a = 0.819 \) nm for the (400) plane at 44.2°.

Therefore, these scattered diffraction spot indices, plane indices, and lattice spacings confirmed that the synthesized nanoparticles have a composition of LiNi₀.₅Mn₁.₅O₄ and a cubic-spinel structure (space group Fd3m) according to ICDD: 01-080-2984 (ICSD: 180032). The electron diffraction pattern of the Li–Ni–Mn–O nanoparticles synthesized by thermal plasma was consistent with the XRD pattern.

Electron diffraction analysis indicated that LiNi₀.₅Mn₁.₅O₄ was produced at an O₂ flow rate of 5 l min⁻¹. The electron diffraction results are consistent with the XRD patterns, which indicated that LiNi₀.₅Mn₁.₅O₄ could be synthesized.

3.3. Electrochemical properties of the synthesized Li–Ni–Mn-oxide nanoparticles

The current–voltage characteristics of half-coin cells fabricated using CV were measured to evaluate the redox reaction of Ni in the synthesized Li–Ni–Mn-oxide nanoparticles. The studied Li–Ni–Mn-oxide nanoparticles were synthesized at O₂ flow rates of 0 and 5 l min⁻¹ with a Ni/(Ni + Mn) molar ratio of 0.25.

The electrochemical properties of Li–Ni-oxide nanoparticles in the operating range 1.5 to 5.0 V are presented in figure 11. The open-circuit voltages of the Li–Ni–Mn-oxide nanoparticles when not energized were 3.20 and 3.26 V for those synthesized at O₂ flow rates of 0 and 5 l min⁻¹, respectively. The CV characteristics of the Li–Ni–Mn-oxide nanoparticles confirmed the reduction of Ni above 4.6 V during the first charging cycle. The Li–Ni–Mn-oxide nanoparticles caused oxygen desorption in the crystal structure when charged above 4.6 V. The Li–Ni–Mn–oxide nanoparticles suggested that the crystal structure has changed. A small peak derived from hopping conduction of Mn³⁺/Mn⁴⁺ of Mn was visible at around 4.0 V at the second cycle. However, no peaks of Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺ of Ni derived from LiNi₀.₅Mn₁.₅O₄ were confirmed at around 4.7 and 4.8 V. This suggested that the material had low electrical conductivity at an oxygen flow rate of 0 l/min. Furthermore, a strong Mn³⁺/Mn⁴⁺ peak of Mn was confirmed at a low potential near 3.2 V. This low-potential reaction indicated that the main reaction involved the cubic-rock-salt-type structure and the eventual Ni valence is Ni²⁺.

A strong peak derived from hopping conduction of Mn³⁺/Mn⁴⁺ of Mn derived from LiNi₀.₅Mn₁.₅O₄ synthesized at an O₂ flow rate of 5 l min⁻¹, was confirmed at around 4.0 V at the first cycle of charging. Strong peaks of Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺ of Ni derived from LiNi₀.₅Mn₁.₅O₄ were confirmed at around 4.7 and 4.8 V. The reaction from 4 to 5 V that was peculiar to Ni is expressed as

\[
\text{Li} \left[ \text{Ni}_{0.5}^{2+} \text{Mn}_{1.5}^{4+} \right] \text{O}_4 \rightarrow \text{Li}_{0.5} \left[ \text{Ni}_{0.5}^{4+} \text{Mn}_{1.5}^{2+} \right] \text{O}_4 + 0.5\text{Li}^+ + 0.5e^- \rightarrow \text{Li}_{0.5} \left[ \text{Ni}_{0.5}^{2+} \text{Mn}_{1.5}^{4+} \right] \text{O}_4 + 0.5\text{Li}^+ + 0.5e^-
\]

(1)
The same peak was confirmed after the second cycle, confirming that the material was potentially electrically conductive. These results indicated that the stable formation of LiNi0.5Mn1.5O4 was achieved by increasing the amount of oxygen. The observed electrochemical properties were confirmed to match those of LiNi0.5Mn1.5O4.

4. Discussion

The formation mechanism of Li–Ni–Mn-oxide nanoparticles fabricated by induction thermal plasma was investigated. This discussion clarifies the nucleation temperature and nucleation species in the Li–Ni–Mn–O nanoparticles, and the thermodynamic stability is quantitatively evaluated.

4.1. Estimation of the homogeneous nucleation temperature

The formation mechanisms of Li–Ni–Mn-oxide nanoparticles in Ar–O2 thermal plasma were considered based on the nucleation temperature. The homogeneous nucleation temperatures of Ni, Mn, Li, and their oxides were calculated based on the homogeneous nucleation rate, and the process of generating Li–Ni–Mn-oxide nanoparticles in induction thermal plasma was estimated. Many equations have been proposed for calculating the homogeneous nucleation rate. The following equations are based on classical nucleation theory and have been used for thermal plasma [24, 25].

The vapor generated in the thermal plasma is quenched at the bottom of the reaction chamber. Homogeneous nucleation occurs with supersaturation as the saturated vapor pressure rapidly decreases. The saturation ratio is expressed as

\[ S = \frac{P}{P_s}, \]

where \( S \) is the saturation ratio, \( P_s \) is the saturation pressure, and \( P \) is the partial pressure of the vapor elements. The nucleation rate is calculated as

\[ J = \frac{\beta_n n_s^2 S}{12} \left( \frac{\theta}{2\pi} \right) \exp \left[ \theta - \frac{4\theta^3}{27(\ln S)^2} \right], \]

where \( J \) (m\(^3\) s\(^{-1}\)) is the nucleation rate, and \( n_s \) (1 m\(^{-3}\)) is the number density at equilibrium vapor pressure. The dimensionless surface tension \( \theta \) is expressed as

\[ \theta = \frac{\sigma S_1}{kT}, \]

where \( \theta \) is the dimensionless surface tension, \( \sigma \) (N/m) is the surface tension, \( S_1 \) (m\(^2\)) is the surface area of a monomer particle, and \( k \) (J/K) is the Boltzmann constant. Homogeneous nucleation begins when the nucleation rate is \( \geq 1 \text{ cm}^{-3} \text{ s}^{-1} \) [26].

The calculated nucleation temperature and the melting and boiling points of Ni, Mn, Li, and their oxides are shown in figure 12. The melting point of NiO, MnO, and Li2O are 2,257 K, 2,113 K, and 1,705 K, respectively. The melting points of NiO, MnO, and Li2O are higher than the nucleation temperatures of Ni, Mn, and Li. The melting point of NiO is higher than those of MnO and Li2O. This indicates that NiO first forms nuclei, and MnO
and Li$_2$O then condense on the NiO nuclei. Generally, the nucleation temperature of a transition metal is close to its melting point, and this also applies to the metal oxides.

### 4.2. Thermodynamics of Li–Ni–Mn-oxides

The syntheses of Li–Ni–Mn-oxide nanoparticles using Ar–O$_2$ thermal plasma are considered thermodynamically in this section. The upper-limit temperature for this thermodynamic study was 4 000 K because Ni, Mn, and Li oxides dissociate into atoms above this temperature.

The changes in the Gibbs free energies of Li$_{0.5}$Ni$_{0.5}$Mn$_{1.5}$O$_4$, Li$_{0.4}$Ni$_{0.6}$MnO$_2$, NiO, and MnO with temperature at the saturated oxygen partial pressure are shown in figure 13. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with a cubic cubic-spinel structure was produced preferentially over MnO, NiO, and Li$_{0.4}$Ni$_{0.6}$MnO$_2$ at high oxygen partial pressures. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with a cubic cubic-spinel structure was more stable than MnO at a synthesis temperature below 3,069 K. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with a cubic cubic-spinel structure was easily generated as the oxygen partial pressure increased. The results of the nucleation temperature and the Gibbs free-energy change was concluded that the Gibbs free-energy change of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ is negative at around 2,257 K of NiO nucleation temperature, and the formation reaction of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ proceeds during NiO nucleation.

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**Figure 12.** Nucleation, boiling, and melting temperatures of Ni, Mn, Li, and their oxides. ( (): Nucleation point, ◇: boiling point, ◻: melting point).

**Figure 13.** Relationship between the Gibbs free-energy change and the temperature for Li$_{0.4}$Ni$_{0.6}$MnO$_2$, NiO, MnO, and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ at high oxygen partial pressures.
Changes in the Gibbs free energy of LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Li$_{0.4}$Ni$_{0.6}$MnO$_2$, MnO, NiO, and Mn$_3$O$_4$ with temperature with an oxygen partial pressure deficiency are shown in figure 14. LiNi$_{0.5}$Mn$_{1.5}$O$_4$ was not preferentially generated at low oxygen partial pressures. Reducing the oxygen partial pressure was shown to facilitate the formation of Li$_{0.4}$Ni$_{0.6}$MnO$_2$, MnO, NiO, and Mn$_3$O$_4$ at around 2,257 K of NiO nucleation temperature.

The Gibbs free-energy change indicated that Li–Ni–Mn-oxides changed to cubic rock salt and cubic spinel structure by the change of oxygen partial pressure. The stable Li–Ni–Mn-oxides at different oxygen partial pressures are summarized as follows. Li–Ni–Mn-oxide with a cubic-rock-salt structure and a cubic-spinel structure, MnO, NiO and Mn$_3$O$_4$ coexisted when the oxygen partial pressure was low. The cubic-spinel-structured Li–Ni–Mn-oxide dominated below 3,069 K when the oxygen partial pressure was high. The cubic-spinel-structured Li–Ni–Mn-oxide was stabilized by oxygen. Thus, Li–Ni–Mn-oxides with a cubic-rock-salt structure and cubic-spinel structure were produced.

A schematic of the formation mechanism of Li–Ni–Mn–O nanoparticles is shown in figure 15. The above the nucleation temperature and the Gibbs free-energy change discussions reveal that NiO initially nucleated, followed by the condensation of MnO and Li$_2$O vapors on the NiO nuclei, resulting in Li–Ni–Mn-oxides with cubic-rock-salt and cubic-spinel structures. The formation of Li$_2$O as the Li raw materials was not promoted, and Li-deficient Li–Ni–Mn-oxide with a cubic-rock-salt structure, Ni oxide, and Mn oxide were easily formed when the oxygen partial pressure was low. The formation of Li$_2$O was promoted and the formation of a Li–Ni–Mn-oxide with a cubic-spinel structure was facilitated when the oxygen partial pressure was high.
5. Conclusions

The electrochemical properties, synthesis, and formation mechanisms of the Li–Ni–Mn–O nanoparticles obtained by induction thermal plasma were verified. The synthesized LiNi0.3Mn1.5O4 (Mn4+) nanoparticles showed high voltage characteristics due to the reaction between Ni3+/Ni4+ and Ni3+/Ni4+ around 4.7–4.8 V, when the oxygen partial pressure was high. In contrast, the Li0.4Ni0.6MnO2 (Mn2+) nanoparticles synthesized in the oxygen-deficient state was shown peak of an oxygen desorption at near 4.6 V. The formation mechanism of the Li–Ni–Mn–O nanoparticles was theoretically revealed by experimentally obtained results, the nucleation temperature, and the Gibbs free-energy change. The Gibbs free-energy change suggested that the Li–Ni–Mn-oxide with a cubic-spinel structure was the most stable product when the oxygen partial pressure was high. Conversely, the Li–Ni–Mn-oxides with cubic-rock-salt and cubic-spinel structures, MnO, NiO, and Mn3O4 coexisted, when the oxygen partial pressure was low.

The Gibbs free-energy change of LiNi0.3Mn1.5O4 suggested that LiNi0.3Mn1.5O4 (Mn4+) was produced preferentially to MnO, NiO, and Li0.4Ni0.6MnO2 (Mn2+) at a synthesis temperature below 3,069 K, when the oxygen partial pressure was high. The cubic-spinel-structured Li–Ni–Mn-oxide was stabilized by oxygen. Li–Ni–Mn-oxides changed to cubic rock salt and cubic spinel structure by the change of oxygen partial pressure. Thus, Li–Ni–Mn-oxides with a cubic-rock-salt structure and cubic-spinel structure were produced.

Conflicts of interest

The authors declare no conflicts of interest.

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