Li–Ni–Mn-oxide nanoparticle synthesis by induction thermal plasmas for lithium ion battery electrode

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Synthesis of lithium nickel manganese oxide (LNMO) nanoparticles was performed by induction thermal plasmas. The change in the crystal structure of the LNMO nanoparticles was confirmed with the substitution of a part of Mn of the lithium nickel oxide nanoparticles with Ni. The formation mechanism of the nanoparticle crystal structure was investigated based on nucleation theory and thermodynamic considerations. The synthesized LNMO nanoparticles formed two crystal structures of cubic rock salt type Li₃Ni₄Mn₁.5O₄ (space group Fm3m) of non-stoichiometry and cubic spinel type LiNi₀.₅Mn₁.₅O₄ (space group Fd3m). The cubic rock salt structure nanoparticles are easily formed when the molar ratio of Mn and (Ni + Mn) is taken as 0.25. The cubic spinel structure nanoparticles are easily formed when the Mn/(Ni + Mn) molar ratio is 0.875. The formation mechanism of the LNMO was generated by condensation of MnO and Li₂O after nucleation of NiO. This report investigated the effect of the crystal structure and formation mechanism of the LNMO nanoparticles by varying the molar ratio of Ni and Mn formed by induction thermal plasma.

Key-words: Nanoparticles, Thermal plasma, Crystal structure, Nucleation theory, Thermodynamics

1. Introduction

The cathode material LiMn₂O₄ has a high discharge potential, and a theoretical capacity of 148 mAh/g. It exhibits an effective capacity of about 120 mAh/g when the average discharge potential is 4.1 V. LiMn₂O₄ has a lower cost than LiCoO₂ as a global resource and is a promising substitute for LiCoO₂ as a cathode material. Recently, research on Ni substitution of Li–Mn oxide and substituting with Mn in Li–Ni oxide has been reported as an improvement of LiCoO₂. The spinel type nickel manganese oxide (LNMO) compounds with Ni and Mn substitutions are the extensively researched materials suitable for high voltage cathodes. The spinel type LiNi₀.₅Mn₁.₅O₄ offers a high working potential of 4.7 V and an excellent theoretical specific capacity of 147 mAh/g. In this regard, they are previously synthesized by numerous routes such as co-precipitation method, sol-gel method and solid state method have been reported.

In the co-precipitation method, LNMO particles are prepared with various precursors such as the sulfates, carbonates, and chlorides of the corresponding starting metals. After washing and filtration of precursor, the sample is dried in a vacuum oven at 50–120 °C for 8–12 h. Required amount of LiOH is gradually added to the dried precursor which is subsequently heated in a furnace between 600–900 °C to prepare LiNi₀.₅Mn₁.₅O₄ particles. The wet-chemical routes of synthesis are adopted by many researchers due to the numerous advantages they offer such as low calcination/sintering temperatures, uniform chemical composition, better control on the size of the particles and their microstructure. The prepared LNMO gel is dried at 80 °C for 24 h. The obtained LNMO precursors are uniformly ground and heat treated at 450 °C in O₂ atmosphere to yield LNMO particles.

Solid state methods are the most common methods in which a stoichiometric composite materials of the raw materials is finely ground in a mortar and pestle, ball-milled, or jet-milled, and the green composite material thus obtained is heat treated in a furnace. The composite materials consisting of LNMO was heated in a furnace between 700–900 °C.

One of the main advantages of the synthetic methods with co-precipitation method, wet-chemical method and solid state method is the ease of control they offer on the chemical composition. However, they offer disadvantages such as elaborate manufacturing process and high chances of contamination.

Compared to these synthetic methods, Synthesis of compounds using the induction thermal plasma (ITP) technology offers many advantages for the production of highly crystalline and high purity materials, including choosing atmosphere control and synthesizing compounds of different elements. Rapid quenching of 10⁴–10⁶ K/sec is...
possible with the plasma flame tail. However, ITP synthesis has disadvantages such as stable supply of raw material powder, continuous recovery of synthetic material, and low production rate. ITP synthesis excels in producing composite nanomaterials with crystalline structures, morphologies, and desired composition of the constituents that are usually challenging to acquire. This report investigates the crystal structure and synthesis mechanism of nanoscale LNMO cathode material by ITP synthesis by varying the composition ratios of Ni and Mn.

2. Experimental

2.1 Experimental procedure

Figure 1 shows the schematic representation of the experimental setup utilized for the ITP process. The key components of the system include an induction plasma torch for plasma generation, a reaction chamber wherein the nanoparticles are synthesized, and a filter unit for the recovery of nanoparticles. The ITP process is described in the following segment of the section. The powdered starting material is provided along with the carrier gas and is evaporated using a plasma torch. In the reaction chamber homogeneous nucleation occurs and subsequently, through heterogeneous condensation, nanoparticles are synthesized.

The sheath gases were Ar and O₂. The inner and carrier gases were Ar. The flow rate of O₂ and the mixed Ar–O₂ sheath gas was 2.5 L/min and 60 L/min respectively.

The raw material consisted of a mixture of 99.9% pure 10 μm Mn (Kojundo Chemical Laboratory), 99.9% pure 3–5 μm Ni (Kojundo Chemical Laboratory), and 99.6%, 3.5 μm Li₂CO₃ (Honjo Chemical). The raw powder was duly mixed and added into the thermal plasma at a feed rate of 300 mg/min.

2.2 Characterization

The structural parameters of LMNO nanoparticles were analyzed by X-ray diffraction (XRD; Rigaku Multiflex) with Cu Kα radiation (λ = 0.1541 nm), in the 2θ range of 10–90°. The particle morphology was observed with a scanning electron microscope (SEM; Zeiss ULTRA55) at an accelerating voltage of 6 keV. The particle size distribution and its shape were analyzed with a transmission electron microscope (TEM; JEOL JEM-2100HCKM) based on about 200 particles. The elemental composition of the nanoparticles was analyzed at 200 keV using energy dispersive X-ray spectroscopy (TEM-EDS; JEOL JEM-ARM200F). The nanoparticles were dispersed on a molybdenum-coated copper mesh and were utilized as samples for TEM and scanning TEM (STEM) studies.

3. Results

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

The molar ratio of Li/(Ni + Mn) was chosen as 0.5 to study the effect of Mn/(Ni + Mn) on the crystal structure of the synthesized LNMO nanoparticles. LNMO nanoparticles were prepared using Li/(Ni + Mn) molar ratio of 0.5 at an O₂ level of 2.5 L/min.

3.1.1 Structural studies

The XRD patterns of the synthesized LNMO nanoparticles at various Mn/(Ni + Mn) molar ratios of 0.25, 0.5, 0.75, and 0.875 are presented in Fig. 2. It is evident from the XRD pattern that the LNMO nanoparticles possessed the chemical compositions corresponding to LiNi₀.₃Mn₁.₇O₄ (space group Fd3m) showing a spinel structure and Li₀.₂Ni₁.₆O₂ (space group Fm3m) showing a cubic rock salt structure. The LNMO nanoparticles which exhibited cubic rock salt structure were prepared when the Mn/(Ni + Mn) molar ratios were 0.25 and 0.5. The multi-phased nanoparticles with spinel structure and cubic rock salt structure were formed when the Mn/(Ni + Mn) molar ratio was 0.75. The LiMn₁.₅Ni₀.₅O₄ nanoparticles of spinel structure for single phase were synthesized when the Mn/(Ni + Mn) molar ratio was 0.875. The peaks for the [111] planes near 19° and the [311] planes near 36° became stronger when the Mn/(Ni + Mn) molar ratio was 0.875.
The XRD results of the synthesized nanoparticles shows that the reduction of Ni and increase of the Mn molar ratios improves the feasibility of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ formation. The XRD pattern also suggests that, with the increase and decrease of the molar ratio of Mn and Ni, respectively, the crystal structure shows a change from cubic salt structure to spinel structure.

The analysis of the XRD pattern confirms a correlation between the fraction of spinel structured nanoparticles synthesized and the Mn/(Ni + Mn) molar ratio. During nanoparticle synthesis, with increment in Mn content, the proportion of spinel structured phase also increased. Similarly, the concentration of cubic rock salt structured nanoparticles increased with increasing Ni content.

### 3.1.2 Particle size and morphology

The TEM images and particle size distributions of the prepared LNMO nanoparticles with varying Mn/(Ni + Mn) molar ratios of 0.875, 0.75, 0.5, and 0.25 are shown in Figs. 3 and 4. Comparison of TEM observations and the XRD results revealed that the synthesized LNMO compound including spinel structure formed polygonal particles when Mn/(Ni + Mn) was 0.875 [Figs. 3(a) and 4(a)] and 0.75 [Figs. 3(b) and 4(b)]. The LNMO nanoparticles prepared with increasing Ni content reduced polygonal particles and formed spherical particles when Mn/(Ni + Mn) was 0.5 [Figs. 3(c) and 4(c)] and 0.25 [Figs. 3(d) and 4(d)]. The mean diameters of the synthesized LNMO nanoparticles were 43, 66, 66, and 74 nm, pertaining to Figs. 4(a)–4(d), respectively.

**Figure 5** shows the field emission SEM images of the prepared LNMO nanoparticles at the Mn/(Ni + Mn) molar ratios of 0.875 and 0.5 respectively. The observed facet structure of the spinel type nanoparticles synthesized with the Mn/(Ni + Mn) molar ratio of 0.875 were confirmed a truncated octahedron structure. The structure of the observed spherical morphological nanoparticles were confirmed a truncated hexahedron structure when Mn/(Ni + Mn) molar ratio of 0.5 in cubic rock salt type nanoparticles.
The LNMO nanoparticles prepared by ITP process revealed a pruned structure which was significantly different from the structure conventionally obtained from other methods of synthesis. The truncated crystal structure was in the nanoscale and showed excellent crystallinity. The results confirmed that the prepared nanoparticles exhibited truncated structure due to their low surface energy values.

### 3.1.3 TEM-EDS analysis

The TEM-EDS elemental compositional analysis for elements such as O [Figs. 6(b)], Mn [Figs. 6(c)], and Ni [Figs. 6(d)] in LNMO nanoparticles prepared with the Mn/(Ni + Mn) molar ratios of 0.75, 0.5, and 0.25 are shown in Fig. 6. The red, blue and green-colored zones in Fig. 6 represent richness in O, Mn and Ni respectively. The TEM-EDS images reveal that O, Mn, and Ni are distributed in a uniform fashion in the prepared LNMO nanoparticles. The Mn and Ni concentration of the LNMO nanoparticles for the Mn/(Ni + Mn) molar ratio of 0.75 was 76.1 and 23.9 at.%, respectively. The Mn and Ni content for the Mn/(Ni + Mn) molar ratio of 0.5 was 51.9 and 48.1 at.%, respectively, and for the Mn/(Ni + Mn) molar ratio of 0.25 was 23.0 and 77.0 at.%, respectively. There is a reasonable match between the results obtained from the quantitative analysis and the stoichiometric values of the raw material powder calculated for each planned Mn/(Ni + Mn) ratio. Therefore, the results of the TEM-EDS analyses indicate that LNMO nanoparticles were prepared with a consistent composition.

The inferences of TEM-EDS and XRD studies confirmed that the chemical composition of the Li0.4Ni1.6O2 system was Li0.4Ni1.2Mn0.4O2 when the Mn/(Ni + Mn) molar ratio was 0.25.

## 4. Discussion

The mechanism of formation of LMNO nanoparticles fabricated by ITP process was studied. In this discussion, the nucleation temperature and nucleation species in the LNMO nanoparticles are clarified, and the thermodynamic stability is quantitatively investigated.

### 4.1 Determination of the homogeneous nucleation temperature

The synthesis mechanism of LMNO nanoparticles in Ar-O2 ITP process were discussed with respect to the nucleation temperature. The homogeneous nucleation temperatures of Ni, Mn, Li, and their oxides were computed with respect to the rate of homogeneous nucleation. This led to the estimation of the formation process of LNMO nanoparticles in ITP process. Among the numerous equa-
tions that exist in literature for the calculation of the homogeneous nucleation rate, the following equations based on classical nucleation theory\textsuperscript{14,15} have been used in this study.

The generated vapor in the ITP process is rapidly cooled in the bottom portion of the reaction chamber. With the rapid reduction in the saturated vapor pressure, homogeneous nucleation takes place as supersaturation increase. The nucleation rate \( J (m^{-3}s^{-1}) \) is expressed by Eq. (1), and the saturation ratio \( S \) and dimensionless surface tension \( \theta \) are given by Eqs. (2) and (3), respectively:

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

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

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

where \( n_i (1/m^3) \) is the monomer saturation concentration at temperature \( T \), \( \beta \) is the collision frequency function, \( i \) and \( j \) are the number of particles configured as molecules \((i = j = 1)\), \( \sigma \) (N/m) is the surface tension, \( S_i \) (m\(^2\)) is the monomer surface area, and \( k \) (J/K) is Boltzmann’s constant, \( P \) is the vapor pressure, and \( P_s \) is the saturation vapor pressure. It is observed that when the nucleation rate is \( \geq 1 \text{cm}^{-3} \text{s}^{-1} \), homogeneous nucleation is initiated.\textsuperscript{16}

**Figure 7** shows the computed nucleation temperature, melting point and boiling points of Ni, Mn, and Li along with their oxides. It is observed from the plot that the melting temperatures of NiO, MnO, and Li\(_2\)O are more than the nucleation temperatures of their respective metals, namely, Ni, Mn, and Li. The NiO melting temperature is more than that of MnO and Li\(_2\)O. The nucleation temperature reveals that NiO nucleation is the first to occur followed by the condensation of MnO and Li\(_2\)O on the NiO nuclei. In general, the nucleation temperature and its melting points of a transition metal are in the same range. This effect is also applicable for the metal oxide.

### 4.2 Thermodynamics of LNMO nanoparticles

The thermodynamics behind the synthesis of LNMO nanoparticles by Ar–O\(_2\) ITP process are discussed in this section. In this thermodynamic study, the upper limiting temperature was considered at 4000 K since Mn, Ni, and Li oxides dissociate into atoms above 4000 K.

The Gibbs free energy change of LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\), Li\(_{4}\)Ni\(_{1.2}\)Mn\(_{0.4}\)O\(_2\), NiO, MnO, and LiO with temperature are shown in **Figure 8**. The LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) was produced preferentially over MnO, NiO, and Li\(_{4}\)Ni\(_{1.2}\)Mn\(_{0.4}\)O\(_2\), and LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) with a cubic spinel structure showed better stability than MnO at a synthetic temperature of less than 3069 K. The LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) easily generated cubic spinel structure as the Mn molar ratio increased. The Gibbs free energy confirmed that LNMO change from cubic rock salt structure to spinel structure by the Mn molar ratio increased. The stability of LNMO at various temperatures are consolidated as follows. The NiO dominated in the range of 4000 to 2355 K and LNMO cubic rock salt structure dominated from below 2355 K when the Mn/ (Ni + Mn) molar ratio is 0.25. The MnO dominated in the range of 4000 to 3069 K, and LNMO of spinel structure dominated from below 3069 K when the Mn/(Ni + Mn) molar ratio was 0.875. Therefore, LNMO with a cubic rock salt and spinel structure were formed.

**Figure 9** depicts formation mechanism of LNMO nanoparticles. The thermodynamic study thus confirms that nucleation of NiO was the first to occur followed by the condensation of MnO and Li\(_2\)O vapors on the NiO nuclei. This results in the formation of LNMO oxides with a cubic rock salt and spinel structure.

### 5. Conclusions

The preparation and formation mechanisms of the LNMO nanoparticles obtained by ITP process were verified. The formation mechanism of the LNMO nanoparticles were theoretically revealed by using experimentally obtained results, nucleation temperature, and the change in the Gibbs free energy. Consequently, the change in the Gibbs free energy indicated that the LNMO having a spinel structure were the most stable among the products.

The result of the change in the Gibbs free energy for LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) suggested that LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) was pro-
duced more preferentially than the MnO, NiO, and Li_{0.4}Ni_{1.2}Mn_{0.4}O_2 at a synthesis temperature of below 3069 K. The stability of Li–Ni oxide could be explained as follows. The NiO dominated in the range of 4000 to 2355 K, and LNMO of cubic rock salt structure dominated below 2355 K when the Mn/(Ni + Mn) molar ratio was 0.25. The MnO dominated in the range of 4000 to 3069 K, and LNMO of spinel structure dominated from below 3069 K when the Mn/(Ni + Mn) molar ratio was 0.875. LNMO indicated that LNMO change from cubic rock salt structure to spinel structure by increasing Mn substitution. Thus, LNMO with a cubic rock salt structure and spinel structure were produced.

References
1) M. Shigeta and A. B. Murphy, *J. Phys. D Appl. Phys.*, 44, 174025 (2011).
2) G. Gabrielli, M. Marinaro, M. Mancini, P. Axmann and M. Wohlfahrt-Mehrens, *J. Power Sources*, 351, 35–44 (2017).
3) Y. Fan, J. Wang, X. Ye and J. Zhang, *Mater. Chem. Phys.*, 103, 19–23 (2007).
4) Y. K. Sun, S. W. Oh, C. S. Yoon, H. J. Bang and J. Prakash, *J. Power Sources*, 161, 19–26 (2006).
5) X. Fang, N. Ding, X. Y. Feng, Y. Lu and C. H. Chen, *Electrochim. Acta*, 54, 7471–7475 (2009).
6) B. J. Hwang, Y. W. Wu, M. Venkateswarlu, M. Y. Cheng and R. Santhanam, *J. Power Sources*, 193, 828–833 (2009).
7) G. Du, Y. NuLi, J. Yang and J. Wang, *Mater. Res. Bull.*, 43, 3607–3613 (2008).
8) T. F. Yi, C. Y. Li, Y. R. Zhu, J. Shu and R. S. Zhu, *J. Solid State Electr.*, 13, 913–919 (2009).
9) X. X. Xu, J. Yang, Y. Q. Wang, Y. N. NuLi and J. L. Wang, *J. Power Sources*, 174, 1113–1116 (2007).
10) Y. S. Lee, Y. K. Sun, S. Ota, T. Miyashita and M. Yoshio, *Electrochem. Commun.*, 4, 989–994 (2002).
11) S. U. N. Qiang, X. H. Li, Z. X. Wang and J. I. Yong, *T. Nonferr. Metal. Soc.*, 19, 176–181 (2009).
12) H. Sone, S. Yoshida, T. Kageyama, M. Tanaka and T. Watanabe, *J. Chem. Eng. Jpn.*, 53, 78–83 (2020).
13) A. Karim, S. Fosse and K. A. Persson, *Phys. Rev. B*, 87, 075322 (2013).
14) S. L. Girshick and C. P. Chiu, *J. Chem. Phys.*, 93, 1273–1277 (1990).
15) S. L. Girshick, C. P. Chiu and P. H. McMurry, *Aerosol Sci. Tech.*, 13, 465–477 (1990).
16) S. K. Friedlander, “Smoke D Haze Fundamentals of Aerosol Dynamics”, 2nd ed., Oxford University Press, New York, N.Y. (2000).