Synthesis of Lithium Oxide Composite with Refractory Metal by Induction Thermal Plasmas

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Abstract: Lithium oxide composite nanoparticles with refractory metal were successfully synthesized by induction thermal plasmas. The composition ratio of Nb to Mo or Ni was changed to reveal the formation mechanism of Li oxide composite with refractory metal. Effect of Ni or Mo addition on the Li-Nb oxide with cubic rock-salt structure as one of the promising cathode material was investigated. The formation mechanism of nanoparticles was discussed based on the nucleation temperature with experimentally obtained results.

Keywords: Thermal plasma, refractory metal, Lithium ion batteries.

1. Introduction

Lithium metal oxides have attracted many researchers because of their unique properties as materials for lithium-ion batteries (LiB). Control of crystal structure for the lithium metal oxide is essential to enhance the battery characteristics. Layered rock-salt type, spinel type, and olivine type materials are considered as suitable structure of cathode material due to its high mobility of lithium ion. Therefore, these three structures have been commonly used in cathode materials.

Cubic rock-salt type Li_3NbO_4 was examined as the host structure of a new series of high-capacity cathode materials for rechargeable LiB [1]. In addition, cubic rock-salt type such as Li-Nb and Li-Ni composite oxide has attracted attention due to its high-stability and high-capacity cathode materials [1, 2]. Furthermore, lithium composite oxide with refractory metals (Nb and Mo) are also expected as candidate of cathode material due to its good cyclic stability and battery characteristics [3, 4].

The solid phase method and the liquid phase method have been used in the synthesis of cathode materials. However, productivity in those methods are insufficient for industrial application. Therefore, the synthesis method of lithium oxide with high productivity is strongly demanded.

Thermal plasmas are expected to be promising energy sources to fabricate nanoparticles at high productivity. Because thermal plasmas offer unique advantages: high enthalpy to enhance reaction kinetics, high chemical reactivity, rapid quenching rate in the range of 10^{3-6} K/s, and selectivity of atmosphere in accordance with the required chemical reactions. Thermal plasmas are capable of evaporating large amount of raw materials, even with high melting and boiling temperatures [5]. Furthermore, high-purity nanoparticles can be synthesized in an induction thermal plasma because thermal plasma can be generated in a plasma torch without internal electrodes [6].

The purpose of the present study is to synthesized lithium oxide composite with refractory metal by induction thermal plasmas. For Li-Nb-Ni system, Ni is added to improve the battery capacity without changing the cubic rock-salt structure. For Li-Nb-Mo system, Mo is added to enhance cyclic stability and battery characteristics. The formation mechanisms of Li oxide composite with different melting point metal nanoparticles will be investigated in this study.

2. Materials and method

2-1. Experimental setup and conditions

Figure 1 shows the synthesis apparatus, which includes plasma torch, a reaction chamber, and raw material evaporated in the plasma torch. Homogenous nucleation undergoes in the reaction chamber and condenses to form nanoparticles. The formed nanoparticles are carried to the recovery unit along with the gas, and collected after being accumulated in a filter.

Table 1. Experimental conditions for the induction thermal plasma system.

Input power [kW]	20
RF frequency [MHz]	4
Pressure [kPa]	101.3
Sheath gas rate [L/min]	57.5 (Ar)
Sheath gas rate [L/min]	2.5 (O_2)
Inner gas rate [L/min]	5 (Ar)
Carrier gas rate [L/min]	3 (Ar)
Discharge time [min]	6
Mean diameter [μm]	3 - 20
Powder feed rate [g/min]	0.3
Powder mole fraction	Li:Me = 1:1 (Me: Nb & Mo, Nb & Ni)

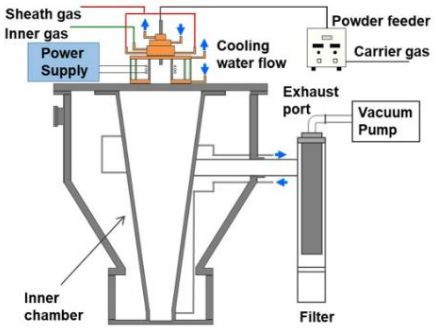

Fig. 1. Experimental configuration for nanoparticle synthesis by induction thermal plasma.

Table 1 shows the experimental conditions for nanoparticle synthesis under atmospheric pressure. Ar was used as the carrier and inner gases; Ar and O_2 were used as the sheath gases at 60 L/min. The plasma torch was 127 mm long, with an inner diameter of 48 mm, and it consists of a water-cooled quartz tube and a three-turn induction coil. The reaction chamber was placed below the torch. A powder mixture of Li_2CO_3 (3.5 μm, 99.6%, Honjo Chemical), Nb (20 μm, 99.0%, Kojundo Chemical Laboratory), Ni (3-5 μm, 99.9%, Kojundo Chemical Laboratory) and Mo (1.5 μm, 99.9 up%, Kojundo Chemical Laboratory) was used as the raw material and introduced into the plasma at a feed rate of 0.3 g/min. Powder mole fraction was set to Li:(Nb+(Ni or Mo)) = 1:1 to produce Li oxide composite with refractory metal Li-Nb-(Ni or Mo) system with different composition ratios of 1:1:0, 2:1.5:0.5, 2:1:1, 2:0.5:1.5, and 1:0:1 were compared to clarify the effect of the fraction of Ni or Mo on the crystal structure of the products.

2-2. Analysis

The crystal structure of the synthesized nanoparticles was determined through powders X-ray diffraction (XRD, Rigaku Multiflex), operating with a Cu Kα source (λ = 0.1541 nm). The diffraction data was collected using the continuous scan mode at a speed of 2° min^{-1} in the region of 10–90° with a step of 0.04°. The accelerating voltage and applied current were 40 kV and 50 mA, respectively. The particle morphology was observed by transmission electron microscopy (TEM, JEOL JEM-2100HCKM) and size distributions were measured by counting approximately 200 different particles. Element mapping of nanoparticles was analysed by scanning TEM-energy dispersive X-ray spectrometry (STEM-EDS, JEOL JEM-ARM 200F).

3. Results

3-1. Li-Nb-Ni system

The XRD patterns of nanoparticles synthesized at Li:(Nb+Ni) = 1:1 in raw material are presented in **Fig. 2**. Square symbols (Fm-3m) indicate cubic rock salt type. triangle and circle symbols indicate by-products, Li_3NbO_4 (I23) and Li_2CO_3. Cubic-rock salt type as target product was successfully synthesized in all conditions. By-products were not synthesized at Li:Nb:Ni = 2:1.5:0.5, 2:1:1, and 2:0.5:1.5.

Relative integrated intensity of nanoparticles with different Nb/(Nb+Ni) is presented in **Fig. 3**. Relative integrated intensity is the ratio of the integrated intensity of the highest peak from each product to the summation of the highest peaks from all products. Particularly Fm-3m was synthesized without by-products at Li:Nb:Ni = 2:1.5:0.5, 2:1:1, and 2:0.5:1.5.

The TEM images and particle size distributions for different Nb/(Nb+Ni) in raw materials are shown in **Fig. 4**. Mean diameter of nanoparticles were 53 nm and 63 nm, respectively. Spherical particles were mainly observed at Li:Nb:Ni = 2:1:1 and 2:0.5:1.5.

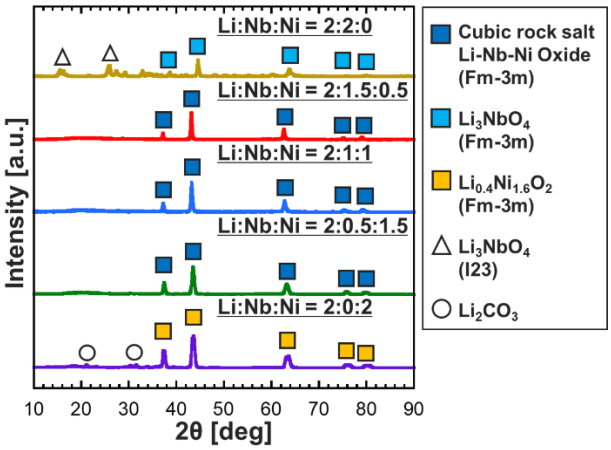

Fig. 2. XRD spectra of nanoparticles for Li-Nb-Ni system with different composition ratios: Li:Nb:Ni = 1:1:0, 2:1.5:0.5, 2:1:1, 2:0.5:1.5, and 1:0:1.

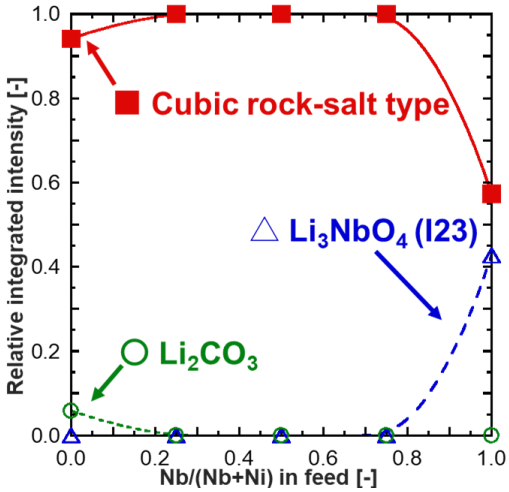

Fig. 3. Relative integrated intensity of nanoparticles with different Nb/(Nb+Ni); composition ratio of Li to (Nb+Ni) = 1:1.

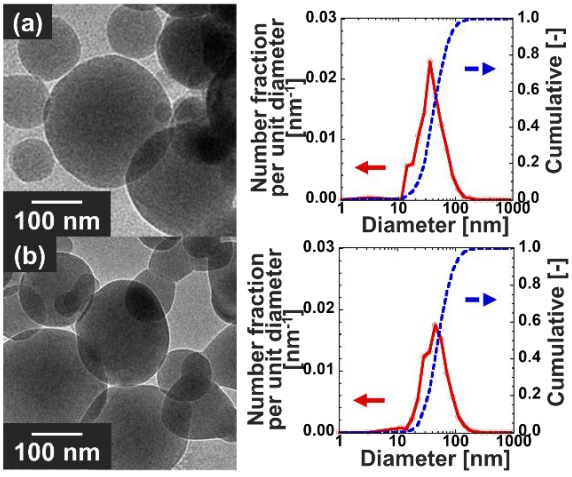

Fig. 4. Representative TEM images and particle size distribution of nanoparticles for Li-Nb-Ni system with different composition ratios: Li:Nb:Ni = 2:1:1 and 2:0.5:1.5.

Element mapping images and corresponding dark-field image by STME-EDS for nanoparticles synthesized at Li:Nb:Ni = 2:1:1 are presented in **Fig. 5**. Mappings of Nb, Ni, and O overlapped in all particles, and both Nb and Ni co-existed in the same particles. In other words, Li-Nb-Ni oxide nanoparticles were successfully formed. However, the element mapping of Nb and Ni have deviation, which indicates Nb and Ni have different composition in the same nanoparticles.

3-2. Li-Nb-Mo system

The XRD patterns of nanoparticles synthesized at Li:(Nb+Mo) = 1:1 in raw material are presented in **Fig. 6**. Diffraction peaks from Li-Mo composite oxides were indicated by inverted triangle, hexagon, and star symbols. Li-Nb composite oxides were indicated by square, circle, triangle, and diamond symbols. The other symbols indicated by-products MoO_2, MoO_3, and Li_2CO_3. Various compounds were synthesized in Li-Nb-Mo system.

Relative integrated intensity of Li-Mo composite oxide and Li-Nb composite oxide nanoparticles with different Nb/(Nb+Mo) is emphasized in **Fig.7**. Li-Mo composite oxide were mainly synthesized at Li:Nb:Mo = 2:1.5:0.5, 2:1:1, 2:0.5:1.5, and 1:0:1. Li-Nb composite oxide was synthesized at Li:Nb:Mo = 1:1:0, 2:1.5:0.5, and 2:1:1. No Li-Nb composite oxide was synthesized at Mo rich condition. In contrast, Li-Mo composite oxide can be synthesized in all the condition when Mo and Nb were mixed together as raw material. These crystal structures analysis cannot confirm the existence of Li-Nb-Mo composite oxide by XRD.

The TEM images for different Nb/(Nb+Mo) in raw materials are shown in **Fig. 8**. Mean diameter of nanoparticles were 45 nm and 69 nm, respectively. Spherical particles were mainly observed at Li:Nb:Mo = 2:1:1. Both spherical particles and polyhedron particles were observed at Li:Nb:Mo = 2:0.5:1.5.

Element mapping images and corresponding dark-field image by STME-EDS for nanoparticles synthesized at Li:Nb:Mo = 2:1:1 are presented in **Fig. 9**. Mappings of Nb, Mo, and O overlapped in all particles, and both Nb and Mo co-existed in the same particles. Each particle has similar

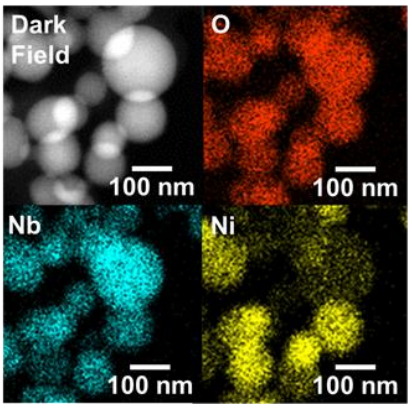

Fig. 5. Element mapping of nanoparticles at Li:Nb:Ni = 2:1:1.

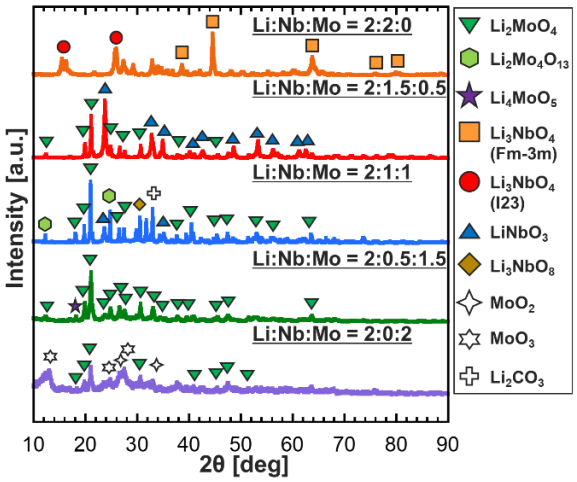

Fig. 6. XRD spectra of nanoparticles for Li-Nb-Mo system with different composition ratios: Li:Nb:Mo = 1:1:0, 2:1.5:0.5, 2:1:1, 2:0.5:1.5 and 1:0:1.

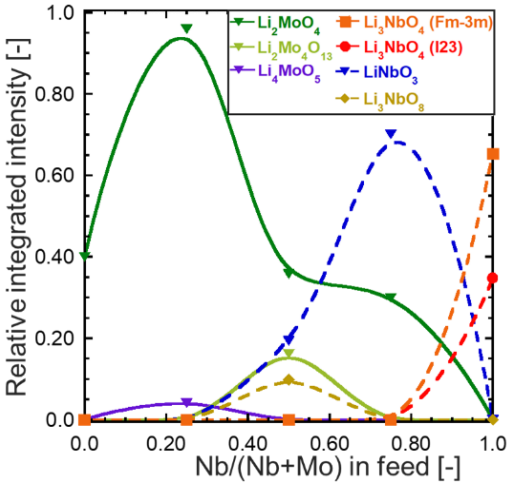

Fig. 7. Relative integrated intensity of nanoparticles with different Nb/(Nb+Mo); composition ratio of Li to (Nb+Mo) = 1:1.

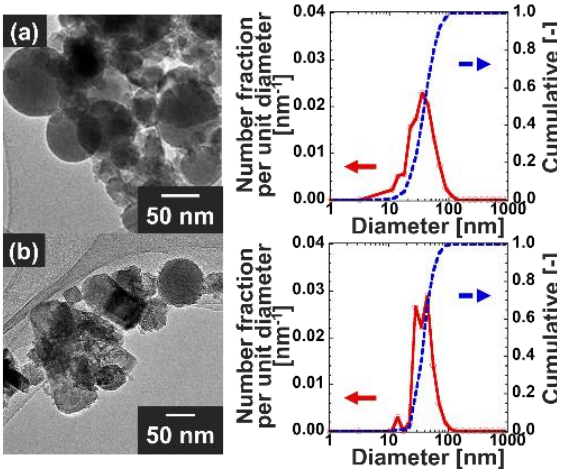

Fig. 8. Relative integrated intensity of nanoparticles with different Nb/(Nb+Mo); composition ratio of Li to (Nb+Mo) = 1:1

colour, therefore Li-Nb-Mo oxide nanoparticles were successfully formed.

4.Discussion

Formation mechanism is discussed from the perspective of nucleation. Homogeneous nucleation temperatures of metals considered in the present study were estimated based on nucleation theory considering non-dimensional surface tension [7]. The homogeneous nucleation rate J can be expressed as

$$J = \frac{\beta_{ij} {n_s}^2 S}{12}\sqrt{\frac{\Theta}{2\pi}}\exp\left[\Theta - \frac{4\Theta^3}{27(\ln S)^2}\right] \quad (1)$$

where S is the saturation ratio and n_s is the equilibrium saturation monomer concentration at temperature T. β is the collision frequency function. The dimensionless surface tension is given by the following equation:

$$\Theta = \frac{\sigma s_1}{kT} \quad (2)$$

where σ is the surface tension and s_1 is the monomer surface area. The surface tension and the saturation ratio have a dominant influence on determining the nucleation rate. The relationship between the calculated nucleation temperature and the boiling and melting points is summarized in **Fig. 10**. Only melting point are plotted for metal oxides, because of the unknown properties of metal oxides. The elements having the highest nucleation temperature nucleates in the system. Nucleation temperature of Nb is the highest in both Li-Nb-Ni and Li-Nb-Mo system. Therefore, Nb nucleates first.

Formation mechanism is examined in **Fig. 11** based on the above results. In Li-Nb-Ni system, Nb nucleated, then Li oxide and Ni oxide vapour condense and react on the Nb nuclei. The condensation continues until melting temperature of Ni. In contrast to the Li-Nb-Mo system, the melting temperature of Mo is near to the nucleation temperature of Nb. The condensation time of Li-Nb-Mo system is shorter than that of Li-Nb-Ni system. Therefore, different composition of nanoparticles was formed in Li-Nb-Ni system. Consequently, Li-Nb-Ni system has large deviation in the elements mapping.

5.Counclusion

Nanoparticles of Li oxide composite with refractory metal were synthesized by induction thermal plasma. In Li-Nb-Ni system, Cubic rock-salt type was successfully synthesized at almost single phase by changing composition ratio of Nb and Ni in raw materials. In Li-Nb-Mo system, Li-Nb-Mo composite oxide nanoparticles were successfully synthesized with same element concentration. Formation mechanism was investigated on the basis of the homogenous nucleation temperature. Nanomaterial fabrication with induction thermal plasma enables the production of high-purity Li oxide composite with refractory metal at high productivity.

References

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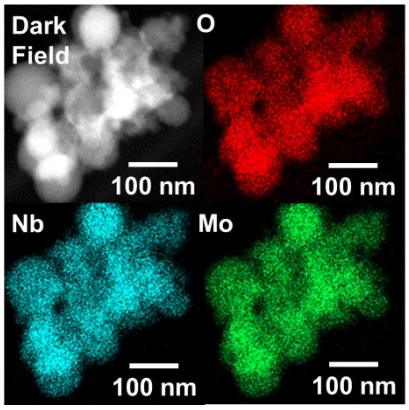

Fig. 9. Element mapping of nanoparticles at Li:Nb:Mo = 2:1:1.

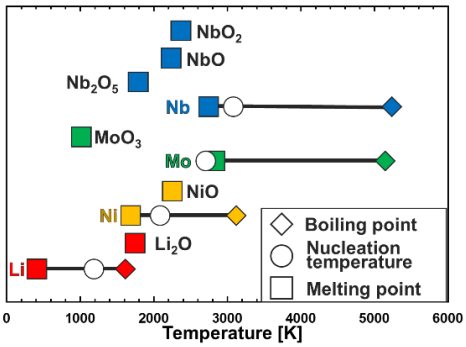

Fig. 10. Relationship between Melting point, Boiling point, and Nucleation temperature.

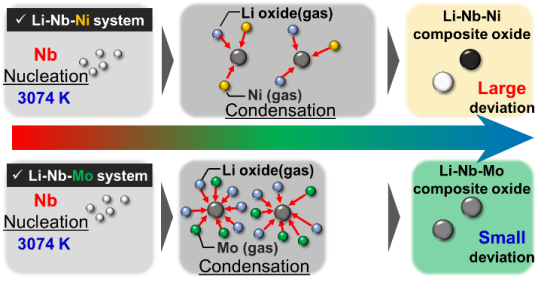

Fig. 11. Formation mechanism in each system.