Nanoparticle Formation Mechanism of Li-Ni-Ti Composite Oxide by Induction Thermal Plasmas

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Abstract: Lithium-nickel-titanium composite oxide nanoparticles regarded as the promising cathode material of lithium-ion battery have been successfully synthesized by induction thermal plasmas. The composition ratio of Ni to Ti was changed to investigate its effects on the products and formation mechanism of the nanoparticles. Cubic rock-salt type was mainly synthesized in Ni-containing systems. The formation mechanism was discussed based on the nucleation temperature and experimental results.

Keywords: thermal plasmas, lithium-ion battery, cathode material

1. Introduction

Thermal plasma has characteristics of high temperature, high chemical reactivity, rapid quenching rate and controllable atmosphere. In addition, electrodeless discharge, large plasma volume and low gas velocity are advantages in terms of induction thermal plasma. High purity nanoparticles can be synthesized at high production rate due to these advantages.

Lithium-ion battery has higher energy density than other rechargeable battery systems and is applied on the field of portable devices, electric vehicles, and energy storages. Lithium metal oxides are used as electrodes and electrolytes of lithium-ion battery. For cathode materials, they are classified in terms of the structure: layered rock-salt type, spinel type, olivine type and cubic rock-salt type [1-3]. Limited lithium-ion diffusion inhibits the further development of cubic rock-salt type. Increasing lithium content can deal with this problem by providing more fast migration channels for lithium ions [2, 3].

The purpose of this study is to synthesize Li-Ni-Ti composite nanoparticles and investigate the formation mechanism.

2. Experimental Section

The experimental setup of induction thermal plasma is shown in **Fig. 1**. The apparatus consists of a plasma torch, a reaction chamber, and a particle filter. Raw material was fed into the plasma torch followed by evaporation, nucleation, condensation, and coagulation. Synthesized nanoparticles are carried with the gas flow and collected by the filter. Argon was used as the carrier gas and inner gas. Gas mixture of Ar and O_2 was used as sheath gas at 60 L/min. A powder mixture of Li_2CO_3, Ni, Ti was used as raw material and introduced into the plasma at a feed rate of 0.2~0.4 g/min. Powder mole fraction was set to Li:(Ni+Ti) =1:1 to produce lithium metal oxide. Li-Ni-Ti system with different composition ratios of 1:1:0, 4:3:1, 4:2:2, 4:1:3, and 1:0:1 were compared to investigate the effect of the fraction of Ni and Ti on the crystal structure of the products.

The crystal structure of the synthesized nanoparticles was determined through X-ray diffraction (XRD, Rigaku Smartlab). Mass percentage of synthesized nanoparticles was calculated by Reference Intensity Ratio method (RIR method). The particle morphology was observed by transmission electron microscopy (TEM, JEOL JEM-2100HC) and size distribution were measured by counting more than 150 different particles. Elemental mapping of nanoparticles was analyzed by scanning TEM-energy dispersive X-ray spectrometry (STEM-EDS, JEOL JEM-ARM200F).

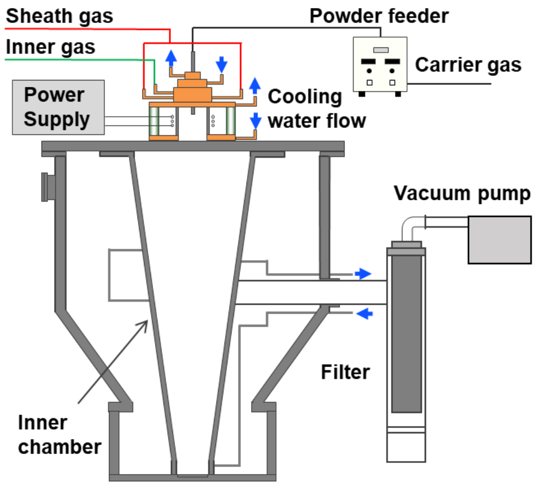

Fig. 1. Experimental setup of induction thermal plasma

Table 1. Experimental conditions

Power [kW]	20
Operation pressure [atm]	1
Current Frequency [MHz]	4
Sheath gas flow rate [L/min]	57.5 (Ar)
Sheath gas flow rate [L/min]	2.5 (O_2)
Inner gas flow rate [L/min]	5 (Ar)
Carrier gas flow rate [L/min]	3 (Ar)
Powder feed rate [g/min]	0.2~0.4

3. Result and Discussion

The mass percentage of the synthesized nanoparticles calculated from XRD spectrum by RIR method is shown in **Fig. 2**. Cubic rack-salt type structure was mainly observed in Ni-containing systems. Spinel type Fd-3m and C2/c space group peaks were observed in the Li-Ti system. Low-Li cubic and High-Li Cubic were classified based on the peak angle. There were peak shifts toward lower angle with increasing Ti amount and the spectrum intensity come from Li_2CO_3 became smaller by introducing Ti. These suggest the substitution of Ti into cation sites and larger amount of lithium oxide condensed into composite oxide with transition metals.

Spherical, rectangular, and hexagonal shaped nanoparticles were observed from TEM images of the synthesized nanoparticles. Most of them were spherical in shape. These spherical nanoparticles are assumed to have cubic rock-salt type structure. The mean diameters of the synthesized nanoparticles were 47 to 60 nm.

Elemental mapping of the synthesized nanoparticles in Li:Ni:Ti=4:3:1 condition is shown in **Fig. 3**. In this condition, each particle had a different composition, while the composition was almost uniform in Li:Ni:Ti=4:1:3 condition.

Formation mechanism is discussed from the perspective of nucleation. Homogeneous nucleation temperatures of metals were estimated based on nucleation theory considering non-dimensional surface tension [4]. The homogeneous nucleation rate J can be expressed as

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

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:

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

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. 4**. 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. Nucleating species were supposed to be NiO. There is a tendency that the nucleation temperature becomes higher when the raw material ratio is higher. Therefore, the difference of nucleation temperature of NiO and TiO_2 is supposed to be wider in Li:Ni:Ti=4:3:1 compared to that in Li:Ni:Ti=4:1:3. The difference causes the different composition of each particle.

4. Conclusion

Nanoparticles of Cubic rock-salt type Li-Ni-Ti composite oxide were synthesized by induction thermal plasma. Ti was assumed to encourage the condensation of lithium oxide in high temperature region. Formation mechanism was discussed based on the homogeneous nucleation temperature. The potential was shown of synthesizing cathode material of lithium-ion battery by induction thermal plasma.

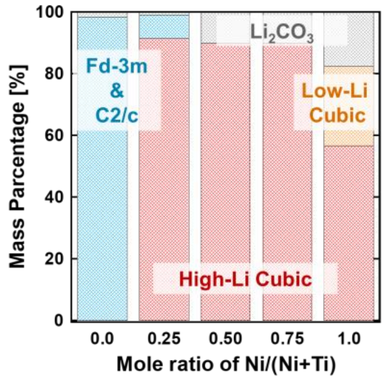

Fig. 2. Mass percentage of synthesized nanoparticles by RIR method under each condition.

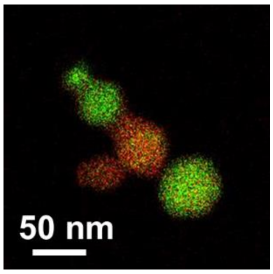

Fig. 3. Overlayed elemental mapping image in Li:Ni:Ti=4:3:1 condition. Green and red refer to Ni and Ti respectively.

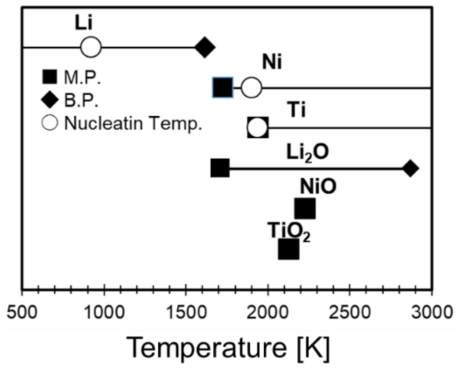

Fig. 4. Relationship between Melting point Boiling point, and Nucleation temperature in Li:Ni:Ti=4:3:1.

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