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Fabrication of Nickel Nanosized Powder from $LiNiO_2$ from Spent Lithium-Ion Battery

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Abstract: In this study, a fabrication of nickel nanoparticles from LNO($LiNiO_2$), which is a cathode active material, was synthesized by the liquid reduction process of $NiSO_4$, obtained through a leaching and purification process. Hydrazine monohydrate ($N_2H_4 \cdot H_2O$) was used as a liquid reducing agent and it was added to $NiSO_4$ at a volume ratio of $NiSO_4$:$N_2H_4 \cdot H_2O$ = 10:3 and reacted for 10 min to synthesize the nickel hydrazine complex. Sodium hydroxide was added to the nickel hydrazine complex at the weight ratio of $NiSO_4$:NaOH = 10:1.25–1.5 and the reduction reaction was performed at 80 °C for 15 min to synthesize nickel particles. Synthesized nickel particles were agglomerated and had a mean size of 200 nm to 300 nm. Ultrasonic dispersion, which is a physical dispersion method, was conducted. The nickel had particles of 100 nm or less when dispersed for 2 h at an ultrasonic intensity of 40 kHz. In order to prevent the agglomeration of the dispersed particles again, polyvinylpyrrolidone (PVP), an interfacial stabilizer, was added to stabilize the dispersed particles. It was confirmed that the nanoparticles were stably retained when PVP was added in an amount of 1 to 2 wt % based on the weight of the nickel. The purity of nickel recovered was found to be 99.62 wt %.

Keywords: nickel; nanosized powder; hydrazine; liquid phase reduction; PVP

1. Introduction

Nano is a term derived from the Greek word 'nanos', which refers to an extremely fine atomic unit size of 1 nm corresponding to 10^{-9} m [1]. The nanoparticle in general refers to a particle with a size of 100 nm or less. It is an extremely fine particle with a wide surface area compared to its volume, so it has excellent strength, magnetic properties, electrical properties, absorbability, and catalytic activity [2].

There are two ways to fabricate these nanoparticles: the bottom-up method to assemble particles from atomic size to nanosize, and the top-down method to crush large particles into smaller particles. These can also be divided into chemical and physical methods according to the principle of synthesis [3,4]. The chemical method is a method of synthesizing nanoparticles using chemical reactions. It uses a small amount of energy, so the synthesis is fast and the reaction can be controlled uniformly. Typical examples are the sol-gel method, hydrothermal synthesis method, polyol process, and precipitation method. The physical method is a process of making micron-sized particles by applying high energy to micron-sized particles and pulverizing them. Therefore, it has the advantage of being able to fabricate nanoparticles continuously, thereby facilitating mass production. Typical methods include mechanical pulverization, ultrasonic methods, and vapor condensation.

Nanoparticles are extremely fine powders. When the concentration of nanoparticles is increased and the distance between the particles becomes extremely small in a solution, the agglomeration of each particle may take place [5]. Due to the agglomeration of powders, the particle size of the

micron unit becomes large, and the optical, electrical, magnetic, and chemical properties of nanosized particles can be lost. Therefore, agglomeration must be prevented through a treatment to generate a repulsive force greater than the van der Waals force acting between the particles. A surface stabilizer has been used as a typical method of dispersion to stabilize the nanoparticles. In general, the surface stabilizer is composed of hydrophobic and hydrophilic groups. The hydrophilic group is compatible with water and it is highly soluble in water. The hydrophobic group is not compatible with water and tends to escape from water. As a result, the surface stabilizer molecules migrate to the water surface and the hydrophobic groups are attached on the air. When the surface stabilizer is absorbed on the surface of the nanoparticles due to the intermolecular force, the surface energy of the particles changes, which in turn reduces the free energy so that the dispersed particles can be stabilized without re-agglomeration [6,7].

The nickel nanoparticle has small particle size, large surface area, and high activity, so it is applied to various industries. Typically, it is alloyed with iron and cobalt to be used as a magnetic fluid or used as a catalyst to treat exhaust gas from an organic hydrogenation reaction, and can be manufactured as an electrode with high discharge efficiency when used as a high-performance electrode material. It also has high plasticity even at low temperatures, and is used in various fields, such as lowering the firing temperature when used as a plastic additive in metal products or ceramic products.

There have been many studies to fabricate nickel nanoparticles using various methods, but there are only a few studies to extract and fabricate nickel nanoparticles from spent lithium ion batteries. In this study, nanosized nickel powder of 100 nm or less with excellent dispersion stability was fabricated through liquid phase reduction of $NiSO_4$ solution obtained by the leaching of LNO($LiNiO_2$), which is an anode material from waste lithium ion batteries. It was observed that change of particle size was affected according to the amount of reagent added. In addition, polyvinylpyrrolidone (PVP) was used as a surface stabilizer to prevent an agglomeration of particles and the effect of PVP addition on particle agglomeration was examined.

2. Materials

Nickel sulfate ($NiSO_4$) solution prepared by leaching and purifying LNO($LiNiO_2$), which is a cathode active material from waste lithium ion batteries, was used as a raw material in this study. The chemical composition of the solution was analyzed by inductively coupled plasma with mass spectrometer (ICP-MS), listed in Table 1.

Table 1. Chemical composition of $NiSO_4$ (wt %).

Element	Ni	Co	Cr	Ca	Cu	Fe	Li	Mg	Mn	Na	Al	Zn
Weight %	6.44	0.0009	N.D	N.D	N.D	N.D	N.D	0.0047	N.D	0.006	N.D	N.D

As a result of analyzing the raw sample, it was confirmed that the contents of nickel, cobalt and impurities of $NiSO_4$ solution were 6.44 wt %, 0.0009 wt % and 0.0107 wt %, respectively. Hydrazine monohydrate ($N_2H_4 \cdot H_2O$) was used as a reducing agent in the liquid reduction process and sodium hydroxide (NaOH) was added to prepare hydroxide.

The liquid reduction process is divided into three processes: the synthesis of nickel hydrazine complex through the addition of hydrazine, the formation of nickel hydroxide through the addition of sodium hydroxide (NaOH) to the nickel hydrazine complex, and the formation of nickel particles through the reaction of nickel hydroxide and hydrazine. The chemical equations used for each process are as follows:

$$NiSO_4 + nN_2H_4 \rightarrow [Ni(N_2H_4)_n]SO_4,\ n = 2, 3, \quad (1)$$

$$[Ni(N_2H_4)_n]SO_4 + 2NaOH \rightarrow Ni(OH)_2 + nN_2H_4 + Na_2SO_4, \quad (2)$$

$$Ni(OH)_2 + N_2H_4 + H_2O \rightarrow Ni + NH_3 + (NH_4OH) + O_2. \quad (3)$$

The Ni obtained through reduction process in liquid phase is dispersed into nanoparticles through ultrasonic dispersion in a solvent containing a surface stabilizer. PVP, the most commonly used surface stabilizer, was used and is an amorphous polymer that is molecular formula (C_6H_9NO). It has no toxicity to the human body and has very good surface film formation, so it is widely used in industries such as pharmaceuticals, dyestuffs, and adhesives [8,9]. The PVP used was the product of Aldrich, with a molecular weight of 10,000.

Ultrasonic dispersion was performed using Hwashin's Power Sonic 520 Ultrasonic Cleaner (GT Ultrasonic, Shenzhen, China). The range of temperature and time control for the device is 50–70 °C and 0–99 min, respectively, with 40 kHz of ultrasonic intensity. The effect of dispersion according to ultrasonic dispersion time was observed and the shape of particle size shape was analyzed by field emission transmission electron microscopy (FE-TEM) (HITACHI, Seoul, Korea), inductively coupled plasma with mass spectrometer (ICP-MS) (ThermoFisher, Waltham, MA, USA) and X-ray diffraction (XRD) (Rigaku, Tokyo, Japan).

3. Results and Discussion

The liquid reduction process takes place in three stages as described above, and in the hydrazine complex synthesis process corresponding to the first stage, the hydrazine complex can be synthesized by adding hydrazine solution to $NiSO_4$. The color of $NiSO_4$ solution was found to be changed from green to pink hydrazine complex after adding hydrazine, and the reaction was completed in 5 min to 10 min. The addition of sodium hydroxide to the synthesized hydrazine complex changed the phase from nickel hydrazine complex to nickel hydroxide, and in this process hydrazine was decomposed again in the nickel hydrazine complex. After a reduction reaction at 80 °C for 15 min the particle was recovered. To analyze the particle size and shape according to the amount of reagent added, a reduction reaction was conducted by varying the amount of sodium hydroxide (NaOH). The input ratios of reagent are listed in Table 2.

Table 2. Input ratio of reagent in reduction reaction.

Sample Name	$NiSO_4$ (mL)	NaOH (g)	$N_2H_4 \cdot H_2O$ (mL)
Amount of Input	100	10	30
	100	12.5	30
	100	15	30

After the reaction process was completed, the shape and size of obtained particles were analyzed by FE-SEM. It is shown in Figure 1 that when only NaOH was added to the nickel hydrazine complex ($[Ni(N_2H_4)_n]SO_4$), the powder of 100–500 nm was recovered after liquid reduction. When the weight ratio of NaOH to $NiSO_4$ was in the range of 12.5–15%, powders of less than 100 nm agglomerate to form 200–300 nm particles. This implies that the addition of NaOH to $NiSO_4$ at a weight ratio of 12.5–15% can prevent the agglomeration of powder after the reduction reaction, which makes it possible to recover nickel particles with a particle size of 100 nm or less.

To prevent the agglomeration of nickel particles, disintegration of agglomerated particles was attempted by ultrasonic dispersion. When a liquid sample is irradiated with ultrasonic waves, a vibrating plate is generated to bring strong energy, thereby dispersing the agglomerated fine particles [10]. In order to prevent the agglomeration of the dispersed particles, PVP was added to the solvent to coat the nanosized nickel powder to stabilize the dispersed particles to minimize agglomeration [11,12]. Ultrasonic intensity was fixed at 40 kHz, and ultrasonic dispersion was performed at 10 °C for 120 min. Alcohol was used as a dispersion solvent, and the amount of PVP, a dispersion stabilizer, was added at 1 and 2 times to induce stability in the dispersed particles. In order to confirm the dispersion stability according to the addition of PVP, ultrasonically dispersed particles were analyzed without adding PVP.

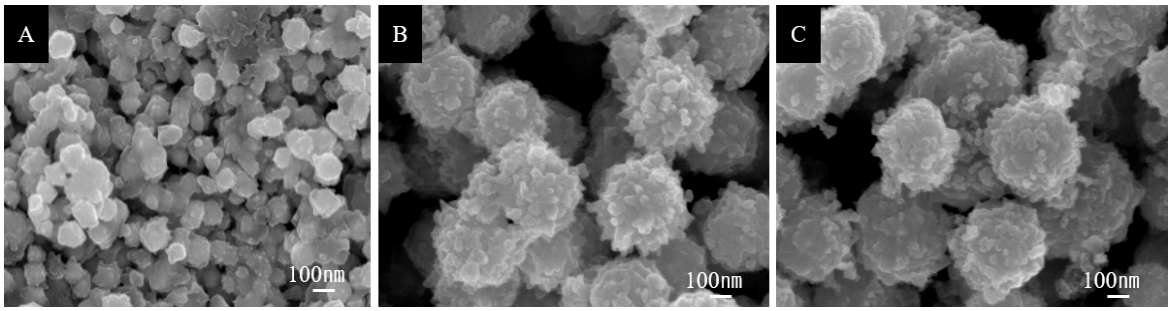

Figure 1. Field emission scanning electron microscopy (FE-SEM) images of reduced nickel particle: (**A**) NaOH of 10 g; (**B**) NaOH of 12.5 g; (**C**) NaOH of 15 g.

After 10 h of ultrasonic dispersion in the sample to which PVP was not added, the powders were found to be agglomerated and most of the powders precipitated as well. On the other hand, in PVP-added samples, it was observed that the precipitation did not occur through Brownian motion, because the dispersed particles were stable and did not aggregate [13,14]. The particle size and shape of the dispersed particles were examined by FE-TEM and its results are shown in Figure 2. FE-TEM analysis found that in the samples to which PVP was not added, most particles agglomerated to have a particle size of 100 nm to 150 nm. On the other hand, in the samples to which PVP was added, particles were dispersed stably without particle agglomeration to have particle sizes of 20–50 nm.

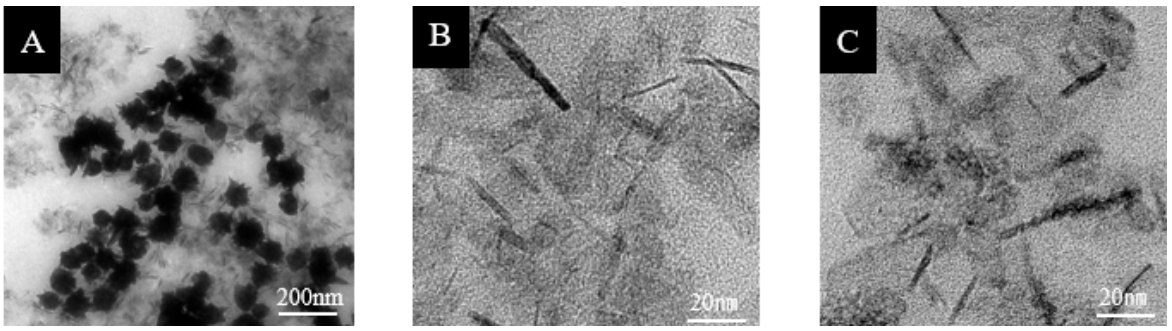

Figure 2. Field emission transmission electron microscopy (FE-TEM) images of synthesized nickel particle: (**A**) no addition of PVP; (**B**) PVP of 1 g; (**C**) PVP of 2 g.

In order to analyze the components of the recovered nanoparticles, the solid-liquid separation using a centrifuge was performed to remove the remaining PVP in the solution. Centrifugation was performed 3 times at 3000 rpm for 10 min each time. After centrifugation, ICP and XRD analysis were performed to examine components and phase. The analytical results obtained only for samples with a particle size of 20–50 nm by adding PVP of 1 g are listed in Table 3. In addition, Figure 3 shows that only Ni peaks were observed through XRD analysis. ICP analysis confirmed that nickel nanosized powder fabricated was found to have impurity of 0.38 wt % and its purity of 99.62 wt % was recovered.

Table 3. Chemical composition of synthesized nickel (wt %).

Element	Fe	Cu	Pb	Mn	C	S	Si	Co	Ni
Weight %	0.005	N.D	0.01	N.D.	0.31	0.025	0.01	0.02	Bal.

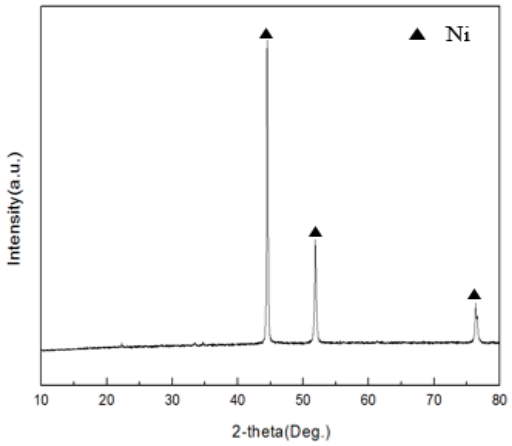

Figure 3. X-ray diffraction (XRD) pattern of synthesized nickel particle.

4. Conclusions

In this study, a synthesis of nickel nanoparticles from $NiSO_4$ obtained by leaching and purifying LNO($LiNiO_2$) has been conducted and the results are summarized as below.

1. When the NaOH input ratio is 12.5–15% (wt %) compared to $NiSO_4$, powders with less than 100 nm were agglomerated to become a size of 200–300 nm.
2. Agglomerated particles can be dispersed through ultrasonic dispersion for 2 h with 40 kHz ultrasonic intensity. Agglomerated nickel particles were dispersed into nanosized particles.
3. To prevent agglomeration after ultrasonic dispersion, PVP, a surface stabilizer, should be added. Particle size was found to be about 100–150 nm due to agglomeration of particles when PVP is not added. On the other hand, when PVP was added, particles of 20–50 nm were stably maintained.
4. The results of ICP and XRD analysis of the finally synthesized nickel powder confirmed that it is possible to synthesize nickel particles with a purity of 99.62 wt %.

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