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PREPARATION OF NICKEL POWDERS BY REDUCTION OF NICKEL HYDROXIDE USING THE TAYLOR FLUID FLOW

In this study, $Ni(OH)_2$ was synthesized by the continuous reaction by the Taylor fluid flow and compared with those prepared from the conventional batch type reaction. The nickel powders were synthesized by reduction of $Ni(OH)_2$ in an aqueous solution with hydrazine hydrate acting as the reductant. And then the characteristics of the nickel powder according to the synthesis method were compared. The average particle size of the synthesized $Ni(OH)_2$ using Taylor reactor was generally decreased about 1.5~2.5 times more than the batch reaction. The nickel powders prepared by the batch reaction highly agglomerated with non-uniform particles. In the Taylor reaction, the agglomeration of particles was broken and uniform nickel powder was produced.

Keywords: $Ni(OH)_2$, Nickel, Taylor fluid flow, Fine powder

1. Introduction

Nickel hydroxide ($Ni(OH)_2$) is used as a cathode active material for nickel-based batteries such as NiCd and NiMH batteries [1,2]. In general, $Ni(OH)_2$ is prepared by the neutralization method in which nickel salts and alkali salts are mixed. However, the particle size of $Ni(OH)_2$ produced by general neutralization method is rather irregular ranging from one to several hundreds of micrometers. Moreover, the density of the particles is low, which makes difficult to use the $Ni(OH)_2$ for the battery applications. Since the electrochemical performance of $Ni(OH)_2$ is directly affected by shape and size of particles, various types of $Ni(OH)_2$ have been utilized [3,4].

In addition, Ni is used as an electrode material in MLCCs. For the downsizing of MLCCs and achieving a high capacitance, the thickness of Ni-based electrode layer reduces to the sub-micron scale, and it is required that Ni powder have a small size and narrow size distribution. Generally, the nickel powder is manufactured by the reduction of metal ions in aqueous or organic solution. The chemical reduction method has been studied intensively, which relates to superior capabilities and simple procedure for controlling the composition, size, and shape of nickel powders [5,6]. However, this preparing method of Ni and $Ni(OH)_2$ referred to as a tank-type batch reaction is not ideal to obtain uniform particles especially when the reactor capacity increases because the stirring is not properly performed.

The Taylor reactor of the two cylinder forms has a unique flow feature that is called the Taylor fluid flow because the outer cylinder is fixed and only the inner cylinder rotates. When the inner cylinder rotates, the fluid flows in the direction of rotation. The centrifugal force and the Coriolis force cause the fluids in the inner cylinder side to move in the direction of the outer cylinder. As the rotation speed increases, a vortex of ring pair array rotating in the opposite direction is formed [7].

The Taylor reactor exhibits excellent mass transfer rate and agitation strength compared to conventional batch reactors, and it has excellent performance in producing a homogeneous product by forming uniform donut-shaped loops by the Taylor fluid flow. In addition, it is possible to synthesize continuously uniform product without stagnant region by reducing the residence time of the reactant because of the simultaneous injection of the raw material and discharge of the reactant. For this reason, it can be applied to material industries including electric/electronic materials, fine chemicals, pharmaceuticals and etc. [8,9].

In this study, $Ni(OH)_2$ was synthesized by batch type reaction and continuous reaction in the Taylor flow. And the nickel powders were synthesized by reduction of $Ni(OH)_2$ in an aqueous solution. The size and size distribution of particles were analyzed based on the reaction processes. The characteristics of $Ni(OH)_2$ powders obtained under the different stirring speeds, a major factor in the Taylor reaction, were also investigated.

2. Experimental

2.1. Mater,ials

The nickel sulfate ($NiSO_4 \cdot 6H_2O$, ≥98.5%, DAEJUNG) and sodium hydroxide (NaOH, ≥97%, DAEJUNG) were used as the starting material. And the hydrazine hydrate ($N_2H_4 \cdot H_2O$, ≥80%, DAEJUNG) was used as the reductant.

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2.2. Synthesis of nickel hydroxide

First, we prepared $NiSO_4$ solution with [Ni] = 0.47M concentration, added 10% NaOH solution to synthesize $Ni(OH)_2$. In case of the batch reaction, 10% NaOH solution was added to 100 ml of 0.47M $NiSO_4$ solution to make the pH 12 to synthesize $Ni(OH)_2$. The experimental conditions for the batch reaction are shown in Table 1. $Ni(OH)_2$ was manufactured using the Taylor fluid flow reactor (Laminar, LCTR-Lab II-H) which can continuously react, and also synthesized using the conventional batch reactor for comparison (Fig. 1). In case of the Taylor reactor, $Ni(OH)_2$ was synthesized by injecting the solution of $NiSO_4$ and NaOH through the quantitative pump by calculating the amounts of the solution obtained from the batch reaction. Table 2 shows the experimental conditions of the Taylor reaction.

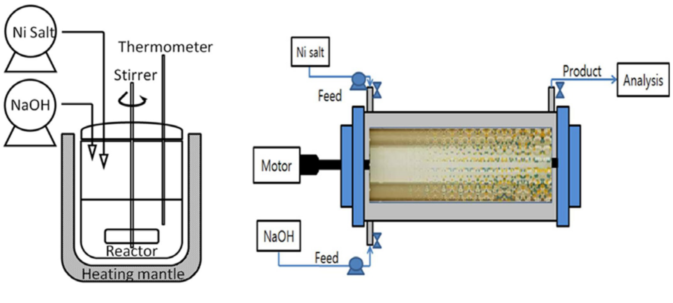

Fig. 1. Schematic diagram for the synthesis of $Ni(OH)_2$: (a) Batch type reactor and (b) Continuous type Taylor reactor

TABLE 1

Experimental conditions for batch reaction

Items	Conditions
Reactor Volume	100 ml
Concentration of Ni salt solution	0.47 M
Concentration of alkali solution	10%
Reaction temperature	25°C
Reaction time	30 min
Agitation speed	250 rpm

TABLE 2

Experimental conditions for continuous reaction using Taylor fluid flow

Items	Conditions
Flow rate of Ni salt solution (0.47M)	20 ml/min
Flow rate of alkali solution (10%)	6~13 ml/min
Reaction temperature	25°C
Mean residence time	6~8 min
Agitation speed	600~1200 rpm

2.3. Preparation of nickel powders from $Ni(OH)_2$

The nickel powders were synthesized by reduction of $Ni(OH)_2$ in an aqueous solution with N_2H_4 acting as the reductant. An appropriate amount of N_2H_4 was slowly added to the solution with continuous stirring at 70°C. During the addition, blue, violet, or gray precipitates depending on reaction molar ratio of $[N_2H_4]/[Ni^{2+}]$ were formed, and then precipitated out to the bottom as a black powder. At the end, the solution was centrifuged and washed with de-ionized water and absolute ethanol, and then dried in an oven at 80°C for 12 h. Table 3 shows the experimental conditions of the reduction reaction.

TABLE 3

Experimental conditions for chemical reduction reaction

Items	Conditions
$[N_2H_4]$ / [Ni]	4
Reaction temperature	70°C
Reaction time	30 min
Agitation speed	250 rpm

2.4. Characterization

The crystal structure of the $Ni(OH)_2$ and nickel powder was analyzed by X-ray diffractometer (SHIMADZU, XRD-6100). Particle size analyzer (Microtrac, S3500) and scanning electron microscope (FEI, Nova NanoSEM 200) was used to analyze the size and morphology of the powders.

3. Results and discussion

The X-ray diffraction patterns of the synthesized $Ni(OH)_2$ powder are shown in Fig. 2. The three characteristic peaks (100), (101) and (110), were observed, indicating that the resulting powders are hexagonal $Ni(OH)_2$. In Taylor reaction, the crystal structure was better developed than the $Ni(OH)_2$ synthesized in the batch reaction, and this is likely attributed to the homogeneous mixing since both the mixing strength and mass transfer rate increased by the Taylor fluid flow. The energy dissipation was estimated in terms of the rotation speed and reactor geometry. With

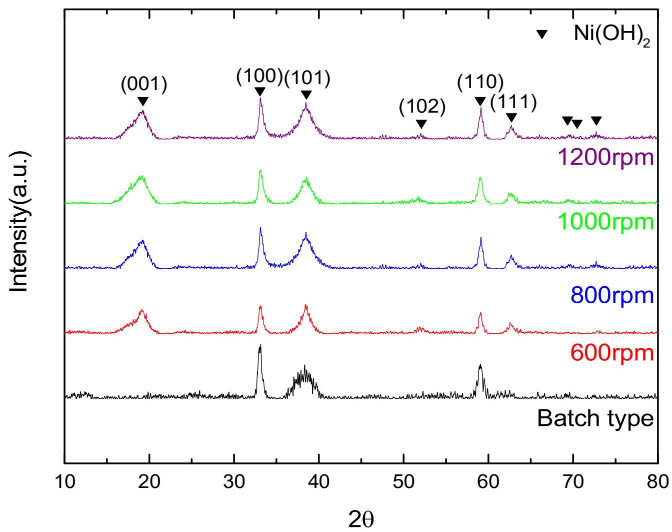

Fig. 2. XRD patterns of $Ni(OH)_2$ powders

a fixed rotation speed, the Continuous Taylor reactor was more effective in terms of dissipating the turbulent motion than the batch reaction, as the large contact surface of the inner cylinder in the Continuous Taylor reactor was more efficient for viscous dissipation than the inertia-driven turbulence from the impeller. Furthermore, when correlating the mass transfers in the turbulent flows, it was found that even with the same energy dissipation the mass transfer coefficient in the Continuous Taylor reactor was higher than that in the batch reaction, representing the primary reason why the Continuous Taylor reactor was so effective [10].

Table 4 and Fig. 3 show the PSA results of $Ni(OH)_2$. The average particle size of $Ni(OH)_2$ synthesized by batch reaction was about 15 μm and the size distribution was 5.2 to 57.3 μm. When the $Ni(OH)_2$ was synthesized by the Taylor reaction, the average particle size tended to decrease compared to the batch reaction. As the agitation speed in the Taylor reaction increased from 600 rpm to 1200 rpm, the particle size was reduced about 1.6 times. The reason for this is that at low agitation speed, the force of the fluid applied to the particles is weak so that even if the particles are weakly attached, particles are rather aggregated. At higher agitation speeds, turbulence created by the strong Taylor fluid flow caused the particles to collide strongly, resulting that the aggregated particles tend to fall off.

Fig. 4 shows the morphology of $Ni(OH)_2$ prepared by batch and Taylor reaction. It was found that these particles agglomerate easily with the irregular shape.

Fig. 5 shows the XRD results of the nickel powder according to the synthesis method of $Ni(OH)_2$. The three characteristic peaks for nickel $2\theta = 44.45$, 51.71 and 76.41°, corresponding to (111), (200) and (220), respectively, were observed, indicating that the resulting powders are face-centered cubic nickel.

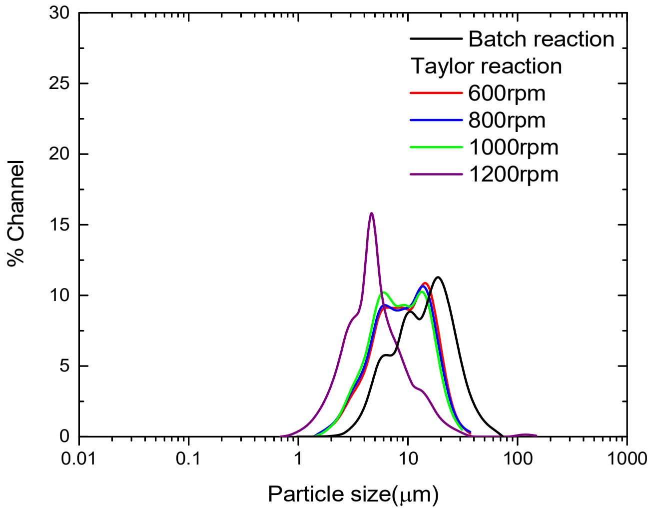

Fig. 3. Particle size distribution of $Ni(OH)_2$ powders

TABLE 4

Particle size of synthesized $Ni(OH)_2$

$Ni(OH)_2$		PSA	
		Mean diameter (μm)	**SPAN**
Batch reaction		14.98	1.62
Taylor reaction	600 rpm	9.68	1.59
	800 rpm	9.42	1.61
	1000 rpm	8.88	1.61
	1200 rpm	5.88	2.00

Table 5 and Fig. 6 show the PSA results of nickel. The average particle size of nickel synthesized by batch reaction was about 2 μm and the size distribution was 1 to 37 μm.

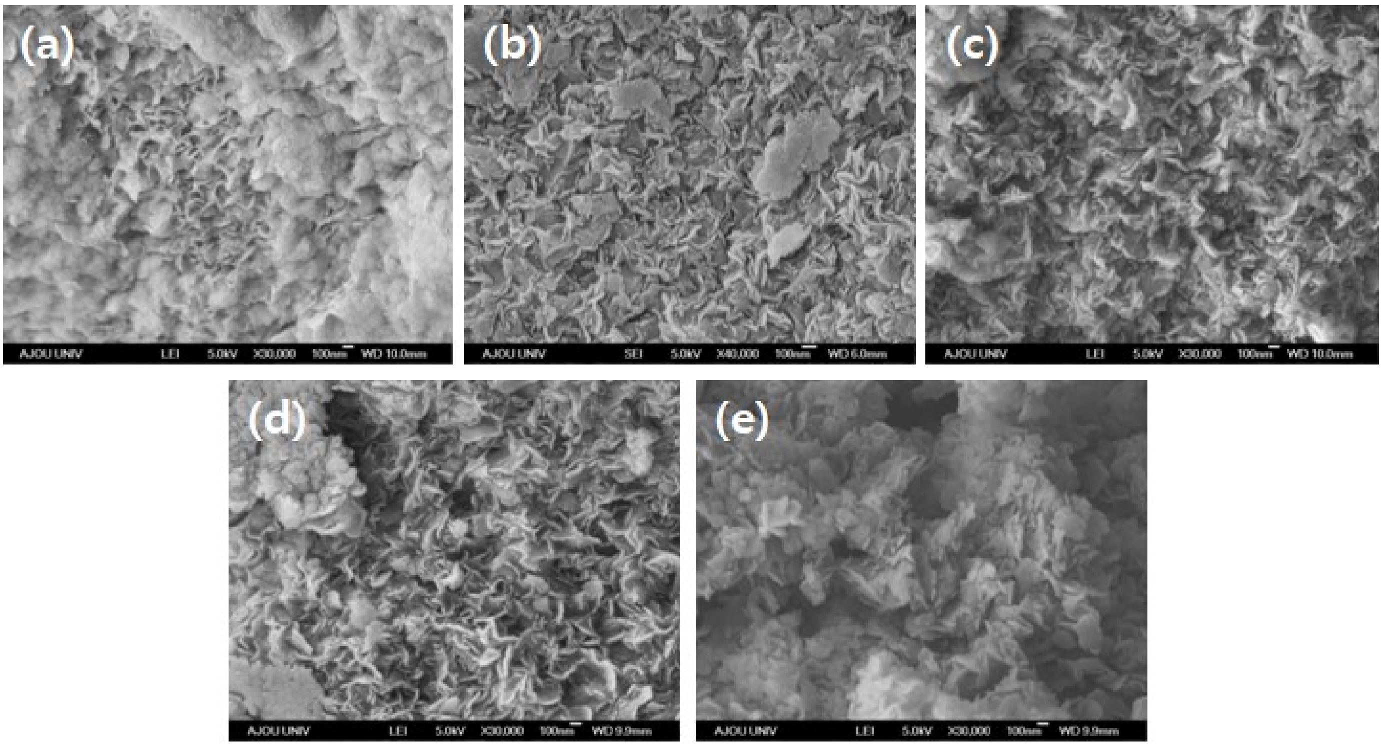

Fig. 4. SEM images of $Ni(OH)_2$ powders: (a) Batch reaction, Taylor reaction at (b) 600rpm, (c) 800rpm, (d) 1000rpm and (e) 1200rpm

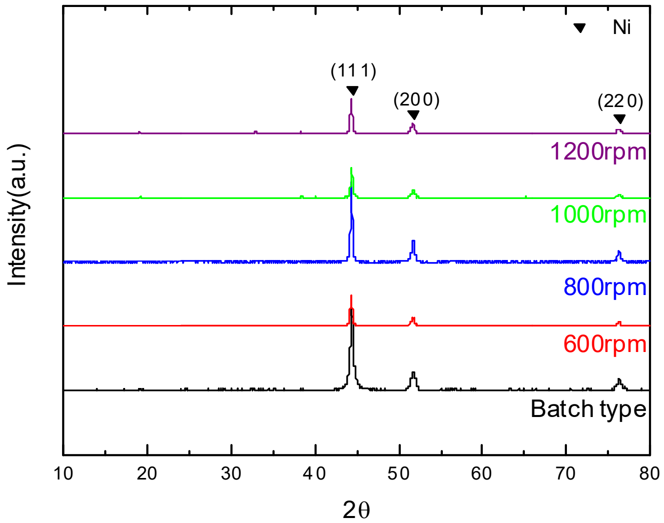

Fig. 5. XRD patterns of Ni powders prepared with different $Ni(OH)_2$ synthesis method

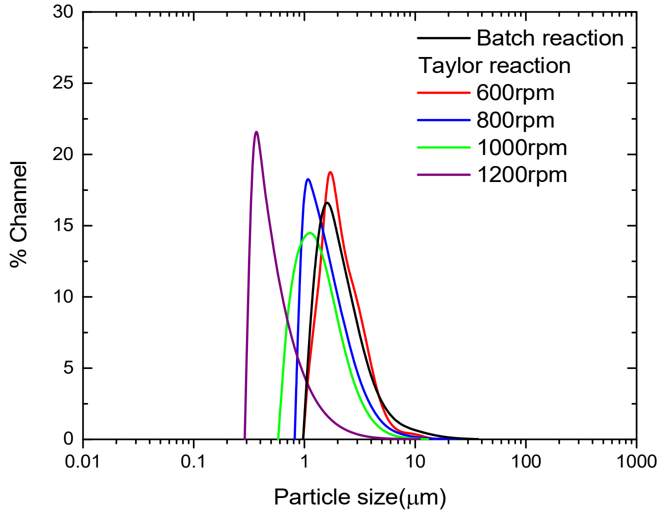

Fig. 6. Particle size distribution of Ni powders prepared with different $Ni(OH)_2$ synthesis method

TABLE 5

Particle size of synthesized Ni

Nickel		PSA	
		Mean diameter (μm)	SPAN
Batch reaction		2.36	1.52
Taylor reaction	600rpm	2.20	1.23
	800rpm	1.68	1.39
	1000rpm	1.40	1.39
	1200rpm	0.58	1.50

When the nickel was synthesized by the Taylor reaction, the average particle size tended to decrease compared to the batch reaction. Also, the average particle size of nickel decreased to 0.58 μm at higher agitation speed. When the agitation speed is 1200 rpm, it is considered that the generation of fine particles and the particle size distribution is increased by agglomeration between particles.

Fig. 7 shows the morphology of nickel powders produced by the chemical reduction method. $Ni(OH)_2$ prepared by batch

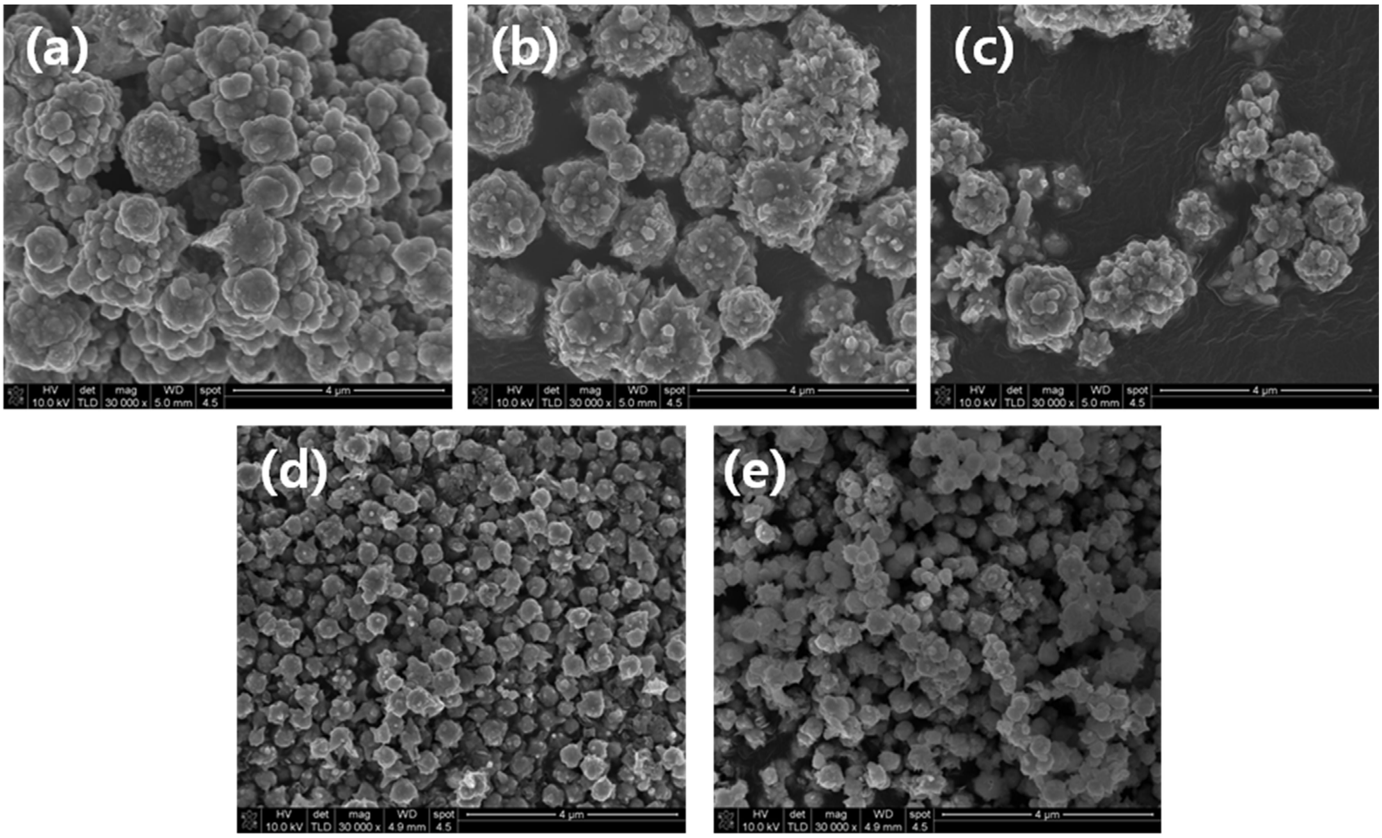

Fig. 7. SEM images of Ni powders prepared with different $Ni(OH)_2$ synthesis method: (a) Batch reaction, Taylor reaction at (b) 600 rpm, (c) 800 rpm, (d) 1000 rpm and (e) 1200 rpm

reaction or agitation speed of Taylor reaction less than 800 rpm, it was found that these particles agglomerate easily with the irregular shape. As the agitation speed in the Taylor reaction increased, the agglomeration of particles was broken and uniform nickel powders were produced.

4. Conclusions

In this study, we have synthesized $Ni(OH)_2$ and nickel powders by continuous Taylor reactor and compared with that synthesized in the batch reactor. The average particle sizes of the synthesized $Ni(OH)_2$ using the Taylor reactor were generally reduced than the batch reaction as the stirring speed increased. Also, the Ni particles produced by $Ni(OH)_2$ using Taylor reactor show less agglomeration and better-spherical. Moreover, the average particle size is decreased to 0.6 μm with narrow size distribution. The particle size and morphology of nickel are changed by the difference in the synthesis method of nickel hydroxide used in the reduction, and this result suggests that the continuous reaction using the Taylor fluid flow provide better methods to control particle size and morphology.

Acknowledgments

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