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A study on the synthesis of fine nickel hydroxide crystalline powder using the taylor fluid flow

Il-Jeong Park, Dae-Weon Kim† and Hang-Chul Jung

Advanced Materials and Processing Center, Institute for Advanced Engineering (IAE), Yongin 17180, Korea

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Abstract In this study, nickel hydroxide crystalline powders were synthesized by continuous reaction in the taylor fluid flow using nickel chloride, nickel sulphate and sodium hydroxide as raw materials and compared with those prepared by a conventional batch type reaction. The crystallinity of nickel hydroxide prepared by the Taylor fluid flow reaction was higher than that of nickel hydroxide obtained by batch reaction. The particle size of nickel hydroxide decreased about 2.5 to 3.6 times, and the specific surface area was increased.

Key words Nickel hydroxide, Taylor fluid flow, Fine powder, Nickel-based battery

1. Introduction

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

In order to obtain high-density nickel hydroxide powders, Shin et al. [4] carried out series of experiments in which nickel salt, hydroxide salt and ammonia were continuously supplied to the reaction tank during nickel hydroxide synthesis. Recently, it is reported that the activity of nickel hydroxide electrode can be significantly improved when nano-sized nickel hydroxide is added to micro-sized nickel hydroxide [5, 6]. In particular, nano-sized nickel hydroxide with a mesoporous structure has been reported to greatly improve electrochemical performance [7].

In addition, nickel oxide (NiO) is used as a p-type semiconductor, catalyst, electrochemical capacitor, fuel cell electrode, and gas sensor material [8, 9]. Generally, the nickel oxide powder is manufactured in such a manner that the nickel hydroxide is fired in air conditions to induce the growth and crystallization of the particles [10]. Since the electrochemical performance of nickel hydroxide is directly affected by shape and size of particles, various types of nickel hydroxide have been utilized [11-13]. However, this preparing method of nickel hydroxide 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 a high-paired array rotating in the opposite direction is formed [14, 15].

The Taylor reactor exhibits excellent mass transfer rate and agitation strength compared to conventional tank type 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, foods, pharmaceuticals, etc. [16, 17].

†Corresponding author
E-mail: mdsimul@naver.com

In this study, nickel hydroxide crystalline powders were synthesized by batch type reaction and continuous reaction in the Taylor fluid flow. The size and particle size distribution of nickel hydroxide particles were analyzed based on the raw materials and reaction processes. The characteristics of nickel hydroxide powders obtained under the different stirring speeds, a major factor in the Taylor reaction, were also investigated.

2. Experimental Method

Nickel hydroxide powders were prepared using reagent grade nickel sulfate ($NiSO_4 \cdot 6H_2O$, ≥ 98.5 %, DAEJUNG), nickel chloride ($NiCl_2 \cdot 6H_2O$, ≥ 96 %, DAEJUNG), sodium hydroxide (NaOH, ≥ 97 %, DAEJUNG) and nickel chloride solution (Ni 0.47 M) supplied by the K Company as the starting material. Nickel hydroxide 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).

First, we prepared nickel sulfate and nickel chloride solution with [Ni] = 0.47 M concentration, added 10% NaOH solution to synthesize nickel hydroxide. In case of the batch reaction, 10 % sodium hydroxide solution was added to 100 ml of 0.47 M nickel sulfate and nickel chloride solution to make the pH 11 to 12 to synthesize nickel hydroxide. The precipitated powders were washed and dried, and nickel hydroxide powder was thus obtained. The experimental conditions for batch reaction are shown in Table 1.

In case of the continuous reaction using the Taylor fluid flow reactor, nickel hydroxides were synthesized by injecting the solution of nickel sulfate, nickel chloride and sodium hydroxide through the quantitative pump by calculating the amounts of solution obtained from the batch reaction. In order to examine the characteristics of nickel hydroxide powders according to the variation of agitation speed of the Taylor reactor, we experimented under the condition of 600 and 1200 rpm. Table 2 shows the experimental conditions of the continuous type Taylor fluid flow reaction.

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	Room temperature
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 (0.47 M)	20 ml/min
Flow rate of alkali solution (10 %)	6~13 ml/min
Reaction temperature	Room temperature
Mean residence time	6~8 min
Agitation speed	600, 1200 rpm

The properties of the synthesized nickel hydroxide powder were analyzed using a laser particle size analyzer (PSA, Microtrac, S3500) and a specific surface area analyzer (BET, Micromeritics, Tristar II 3020). The crystal structure of nickel hydroxide was analyzed by X-ray diffractometer (XRD, SHIMADZU, XRD-6100).

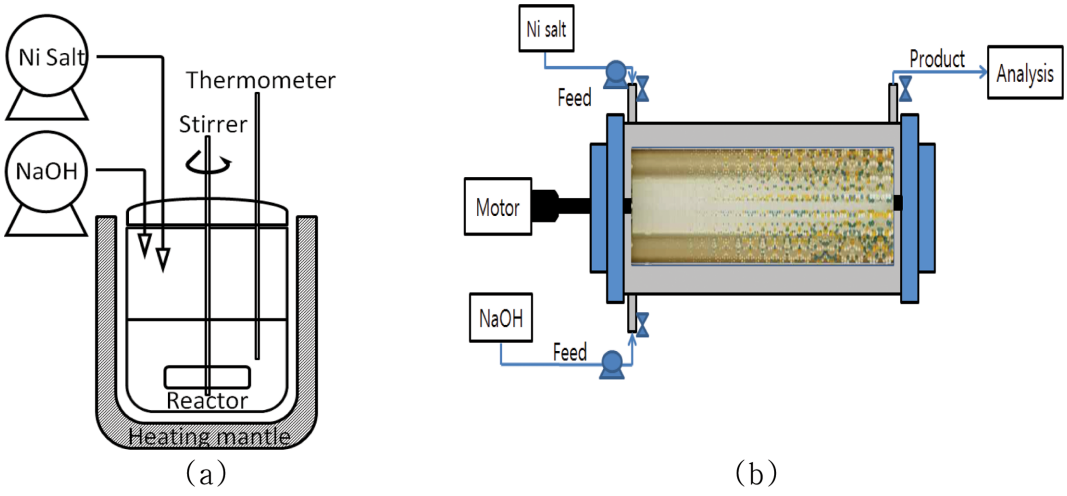

Fig. 1. Schematic diagram for the synthesis of nickel hydroxide: (a) Batch type reactor (b) Continuous type Taylor reactor.

3. Results and Discussion

The reactions are shown in equations (1) and (2) when sodium hydroxide is added to the nickel sulfate and nickel chloride precursors used in the batch type reactor and the continuous reactor using the Taylor fluid flow in this study. In both reactions, nickel hydroxide is produced by the reaction of nickel salt and sodium hydroxide. The difference between the two reactions is that sodium sulphate and sodium chloride are present as reactants in solution, but they can be removed by washing with water.

Case I. In the case of $NiSO_4$ solution

$$NiSO_4(aq) + 2NaOH(aq) \rightarrow Ni(OH)_2(s) + Na_2SO_4(aq) \quad (1)$$

Case II. In the case of $NiCl_2$ solution

$$NiCl_2(aq) + 2NaOH(aq) \rightarrow Ni(OH)_2(s) + 2NaCl(aq) \quad (2)$$

Table 1 shows the batch reaction conditions for the preparation of nickel hydroxide, and the X-ray diffraction patterns of the synthesized nickel hydroxide powder are shown in Fig. 2. The nickel hydroxide powders prepared by using the nickel sulfate and nickel chloride salts were all grown in the (100) and (101) directions and had a hexagonal structure which is a unique structure of nickel hydroxide. As shown in Fig. 2, the diffraction intensity of nickel hydroxide synthesized with nickel chloride salt was stronger than that of nickel sulfate.

Table 3 and Fig. 3 shows the results of analysis of particle size and particle size distribution by PSA and BET of nickel hydroxide powders synthesized through batch reaction. The average particle sizes of nickel hydroxide synthesized from nickel sulfate and nickel chloride were about 15 μm and 23 μm, respectively, and the size distribution was between 5.2 μm and 57.3 μm. These

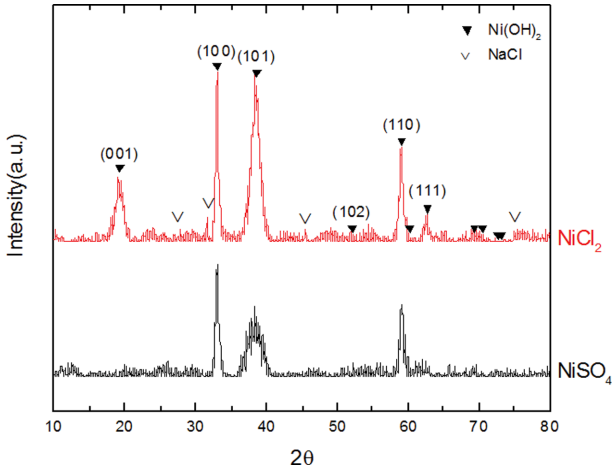

Fig. 2. The XRD patterns of synthesized $Ni(OH)_2$ powders by batch reaction.

Table 3
The mean diameter and surface area of synthesized $Ni(OH)_2$ powders by batch reaction

Batch reaction	PSA		BET
	Mean diameter (μm)	SPAN	Surface area (m^2/g)
$NiSO_4$	14.98	1.620	66.2
$NiCl_2$	23.11	2.271	72.7

results show that the average particle size of nickel hydroxide in Junsei Co., Ltd., which was reported in 1995 by Shin et al. [4], was less than 40 μm and the particle size distribution was less than 2.5~80 μm. The reason for such results is that the mixing effect was created because the amount of the solution used during the synthesis of the nickel hydroxide by the batch reaction was relatively small. On the other hand, the results obtained by the continuous reaction by Shin et al. were similar to the current results. These results show that the nickel ion precipitates rapidly as hydroxide according to the increasing pH, nonuniform particles are formed by the uneven of the nucleation rate and the growth rate

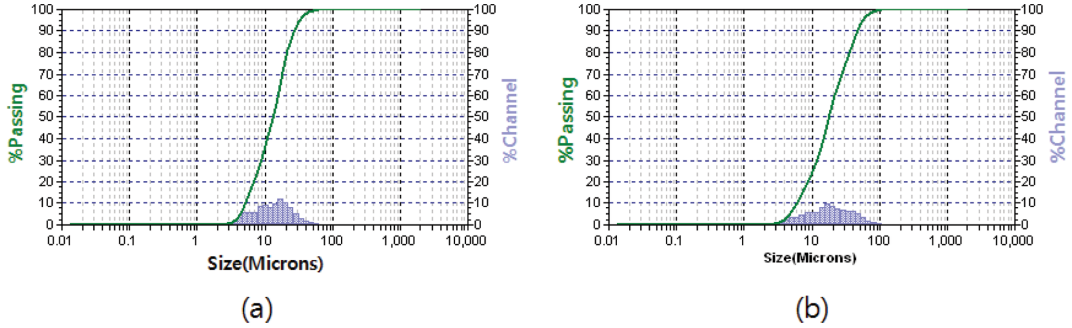

Fig. 3. The particle size distribution of synthesized $Ni(OH)_2$ powders by batch reaction: (a) $NiSO_4$ salt, (b) $NiCl_2$ salt.

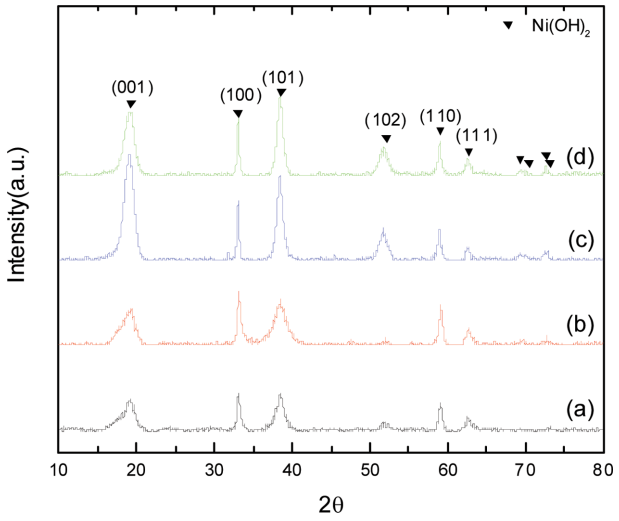

Fig. 4. The XRD patterns of synthesized $Ni(OH)_2$ powders by Taylor reaction: (a) $NiSO_4$ 600 rpm, (b) $NiSO_4$ 1200 rpm, (c) $NiCl_2$ 600 rpm, (d) $NiCl_2$ 1200 rpm.

when the rapid reaction progresses [4].

Continuous Taylor reactor was used to improve the particle size and particle size distribution characteristics of nickel hydroxide powders prepared by the typical batch reaction. As batch reaction, nickel hydroxide was synthesized using nickel sulfate and nickel chloride solution as raw materials. The X-ray diffraction patterns of synthesized nickel hydroxide powder is shown in Fig. 4.

The synthesized nickel hydroxide powders by the Taylor reaction were grown in the (100) and (101) directions similar to the results of the batch reaction, and showed crystal structure with hexagonal nickel hydroxide. As in the batch reaction, the diffraction intensity of nickel hydroxide synthesized with nickel chloride salt was stronger than that of nickel sulfate.

In addition, the crystal structure was better developed than the nickel hydroxide synthesized in the batch reaction, and this is likely attributed to the homogeneous

Table 4
The mean diameter and surface area of synthesized $Ni(OH)_2$ powders using $NiSO_4$ salt by Taylor reaction

$NiSO_4$ Taylor reaction	PSA		BET
	Mean diameter (μm)	SPAN	Surface area (m^2/g)
600 rpm	9.68	1.588	112.9
1200 rpm	5.88	2.001	151.8

mixing since both the mixing strength and mass transfer rate increased by the Taylor fluid flow. In general, the mixing strength can be quantitatively indicated by the energy dissipation. Accordingly, the energy dissipation in the Continuous Taylor reaction and batch reaction was estimated in terms of the rotation speed and geometry [18].

Table 4 and Fig.5 show the analysis results of particle size and particle size distribution of the nickel hydroxide powder synthesized using nickel sulfate salt in a continuous Taylor fluid flow reactor. When the nickel hydroxide was synthesized by the Taylor reaction, the average particle size tended to decrease compared to the batch reaction. Also, when nickel hydroxide was synthesized at 600 rpm and 1200 rpm in the Taylor reactor, the average particle size of nickel hydroxide synthesized in the batch reactor decreased from 14.98 μm to approximately 9.68 μm and 5.88 μm, respectively.

Also the specific surface area of the nickel hydroxide obtained from the Taylor reactor at a stirring speed of 1200 rpm was about 151.8 m^2/g, which was about 2.3 times greater than that obtained from the batch reactor. 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 do not fall but are rather aggregated. At higher agitation speeds, turbulence created by the strong Tay-

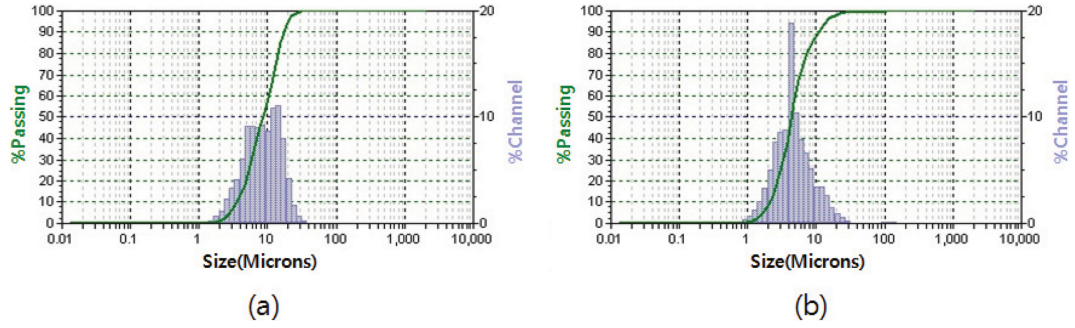

Fig. 5. The particle size distribution of synthesized $Ni(OH)_2$ powders using $NiSO_4$ salt by Taylor reaction: (a) 600 rpm, (b) 1200 rpm.

Table 5
The mean diameter and surface area of synthesized $Ni(OH)_2$ powders using $NiCl_2$ salt by Taylor reaction

$NiCl_2$ Taylor reaction	PSA		BET
	Mean diameter (μm)	SPAN	Surface area (m^2/g)
600 rpm	7.05	2.377	105.5
1200 rpm	6.45	1.171	142.5

lor fluid flow caused the particles to collide strongly, resulting that the aggregated particles tend to fall off.

Table 5 and Fig. 6 show the analysis results of particle size and particle size distribution of nickel hydroxide powders synthesized with nickel chloride salt solution in a continuous Taylor fluid flow reactor. The particle size of the nickel hydroxide synthesized at 1,200 rpm in the Taylor reactor was about 6.5 μm, which was about 3.6 times smaller than the average particle size of the nickel hydroxide synthesized in the batch reactor. The particle distribution of the nickel hydroxide synthesized at 1,200 rpm in the Taylor reactor was about 1.171, which was 2 times smaller than the average particle size of the nickel hydroxide synthesized in the batch reactor. Moreover, the specific surface area of the Taylor reactor was about 142.5 m^2/g, twice that of the batch reactor, 72.7 m^2/g.

In conclusion, the nickel hydroxide synthesized in the continuous Taylor reactor demonstrated a considerable decrease in particle size irrespective of the nickel sulfate and nickel chloride salts used as the raw materials in the nickel hydroxide synthesized in the batch reactor. This result indicated that the particle size was reduced more than twice as much as the particle size by continuous reaction proposed by shin et al. In 1995 and the reaction time was greatly reduced. This suggests that continuous reaction using the Taylor fluid flow may provide better methods to control particle size and reduce reaction time.

4. Conclusion

In this study, we have synthesized nickel hydroxide powders by continuous Taylor reactor and compared with that synthesized in batch reactor. The results are as follows.

1) The particle sizes of the nickel hydroxide synthesized in the batch reactor using reagent grade nickel sulfate and nickel sulfate salt were about 23 μm and 15 μm, respectively.

2) The crystallinity of nickel hydroxide synthesized with nickel chloride salt was higher than that of nickel hydroxide synthesized with nickel sulfate salt.

3) The average particle size of the synthesized nickel hydroxide using nickel sulfate in the Taylor reactor was generally decreased, and it further decreased by about 2.5 times at the stirring speed of 1200 rpm.

4) In addition, the average particle size of nickel hydroxide synthesized by using nickel chloride hydrochloride was also reduce, and it was also decreased by about 3.6 times at the stirring speed of 1200 rpm.

In this study, we obtained fine and uniform nickel hydroxide crystal powders. In order to produce high density nickel hydroxide in the future, advanced research with controlled particle shape will be necessary.

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References

[1] W.K. Hu and D. Noréus, “Alpha nickel hydroxides as

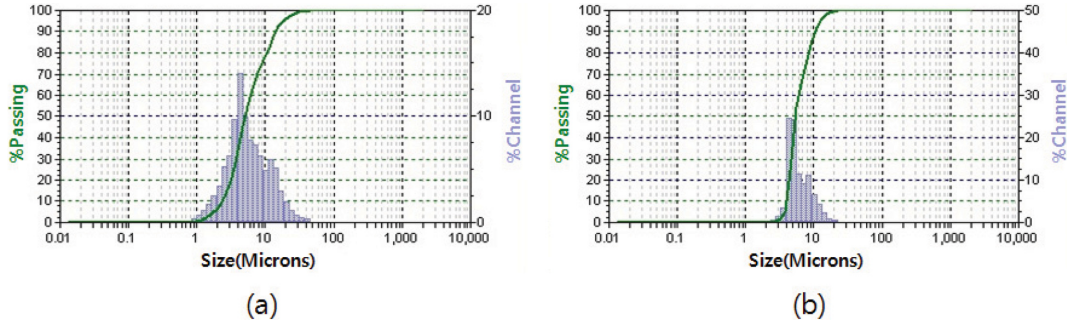

Fig. 6. The particle size distribution of synthesized $Ni(OH)_2$ powders using $NiCl_2$ salt by Taylor reaction: (a) 600 rpm, (b) 1200 rpm.

lightweight nickel electrode materials for alkaline rechargeable cells", Chem. Mater. 15 (2003) 974.
[2] X.M. He, J.J. Li, H.W. Cheng, C.Y. Jiang and C.R. Wan, "Controlled crystallization and granulation of nano-scale β-$Ni(OH)_2$ cathode materials for high power Ni-MH batteries", J. Power Sources 152 (2005) 285.
[3] W.G. Zhang, W.Q. Jiang, L.M. Yu, Z.Z. Fu, W. Xia and M.L. Yang, "Effect of nickel hydroxide composition on the electrochemical performance of spherical $Ni(OH)_2$ positive materials for Ni-MH batteries", Int. J. Hydrogen Energy 34 (2009) 473.
[4] D.Y. Shin, W.I. Cho, C.B. Shin and B.W. Yun, "Fabrication of high density nickel hydroxide powder I", J. the Kor. Institute of Surface Eng. 28 (1995) 92.
[5] X.H. Liu and L. Yu, "Influence of nanosized $Ni(OH)_2$ addition on the electrochemical performance of nickel hydroxide electrode", J. Power Sources 128 (2004) 326.
[6] X.J. Han, P. Xu, C.Q. Xu, L. Zhao, Z.B. Mo and T. Liu, "Study of the effects of nanometer β-$Ni(OH)_2$ in nickel hydroxide electrodes", Electrochim. Acta 50 (2005) 2763.
[7] B. Li, M. Ai and Z. Xu, "Mesoporous β-$Ni(OH)_2$: synthesis and enhanced electrochemical performance", Chemical Communications 46 (2010) 6267.
[8] M.S. Wu and H.H. Hsieh, "Nickel oxide/hydroxide nanoplatelets synthesized by chemical precipitation for electrochemical capacitors", Electrochim. Acta 53 (2008) 3427.
[9] X.F. Song and L. Gao, "Facile synthesis and hierarchical assembly of hollow nickel oxide architectures bearing enhanced photocatalytic properties", J. Phys. Chem. C 112 (2008) 15299.
[10] M.H. Cao, X.Y. He, J. Chen and C.W. Hu, "Self-assembled nickel hydroxide three-dimensional nanostructures: a nanomaterial for alkaline rechargeable batteries", Cryst. Growth. Des. 7 (2007) 170.
[11] X. Han, X. Xie, C. Xu, D. Zhou and Y. Ma, "Morphology and electrochemical performance of nano-scale nickel hydroxide prepared by supersonic coordination-precipitation method", Opt. Mater. 23 (2003) 465.
[12] X.Y. Guan and J.C. Deng, "Preparation and electrochemical performance of nano-scale nickel hydroxide with different shapes", Mater. Lett. 61 (2007) 621.
[13] T.N. Ramesh, "Crystallite size effects in stacking faulted nickel hydroxide and its electrochemical behaviour", Mater. Chem. Phys. 114 (2009) 618.
[14] J. Wang, W.B. White and J.H. Adair, "Synthesis of calcium carbonate particles in octylamine/water bilayer systems", KONA Powder and Particle Journal 31 (2014) 156.
[15] W.M. Jung, S.H. Kang, W.S. Kim and C.K. Choi, "Particle morphology of calcium carbonate precipitated by gas-liquid reaction in a Couette-Taylor reactor", Chem. Eng. Sci. 55 (2000) 733.
[16] W.S. Kim, "Application of taylor vortex to crystallization", J. Chem. Eng. Jpn. 47 (2014) 115.
[17] W.K. Park, H.K. Kim, T.Y. Kim, Y. Kim, S. Yoo, S.D. Kim, D.H. Yoon and W.S. Yang, "Facile synthesis of graphene oxide in a Couette-Taylor flow reactor", Carbon 83 (2015) 217.
[18] A.T. Nguyen, "Application of Couette-Taylor vortex to crystallization: Drowning-out crystallization of guanosine 5′-monophosphate and reaction crystallization of barium sulfate", Ph. D. Thesis (2011) 217.