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EVALUATION OF VALUABLE METAL RECYCLING BEHAVIOR USING NICKEL SULFATE WASTE SOLUTION AND PRE-TREATMENT BY-PRODUCTS RECOVERED FROM WASTE LITHIUM-ION BATTERIES

In this study, high-crystallinity nickel metal powder was synthesized from a nickel sulfate solution recovered from Lithium-Ion Batteries(LIBs) waste via a continuous precipitation-liquid phase reduction process. The effects of hydroxide precipitation conditions and reducing agent concentration on phase formation, crystallinity, and particle morphology were systematically investigated. Nickel hydroxide was first prepared as an intermediate product by controlling the [OH]/[Ni] molar ratio using Sodium hydroxide as a precipitant, followed by liquid-phase reduction with hydrazine to produce metallic nickel powder. Single-phase nickel metal powder was obtained under [OH]/[Ni] = 7-14 conditions, with average particles sizes ranging from 4.05 to 4.35 μm.

Keywords: LIBs waste; Recycling; liquid-phase reduction process

1. Introduction

Lithium-Ion Batteries(LIBs) are currently the most advanced electrochemical energy storage technology due to a favorable balance of performance and cost properties. Demand for various types of LIBs is increasing, ranging from medium and large-sized to small LIBs applied to portable home appliances such as smartphones and tablet PCs. Along with the growth of LIBs, the amount of waste LIBs generated every year rapidly increasing [1-3]. Because of that in recent years, the battery recycling industry has focused extensively on developing high-efficiency recovery technologies for valuable and rare metals contained in the black mass of spent LIBs [4]. Recycling is essential for the efficient use of valuable metals included in waste LIBs. In previous studies, many reports on the recovery of valuable metals have been reported, but not much research has been conducted to recycle nickel from LIBs and use it as a raw material [5-7].

Accordingly, this study aims to produce highly crystalline nickel metal powder using nickel salts recovered from ESS(Energy Storage System) based on discarded LIBs technology as raw materials. Although there are many methods for producing nickel metal powder, a chemical reduction method through a wet chemical reaction process is particularly preferred because the composition, size, and shape of the nickel powder are easy to control [8-11]. In general, research on the production of nickel metal through a reduction process is conducted using a hydrazine(N_2H_4) reducing agent, and in this study, N_2H_4 was also used to reduce nickel metal [12]. In order to prepare the nickel metal powder, firstly, the ratio conditions with the precipitant and secondly, the variables of the ratio condition with the reducing agent were controlled. Finally, the nickel metal powder manufacturing behavior was confirmed according to the nickel metal powder manufacturing change according to the precipitant input condition variable control and the nickel metal powder manufacturing behavior according to the reducing agent input condition.

2. Experimental

To selectively recover valuable resources from ESS(Energy Storage System) lithium-ion battery waste, a two-stage process consisting of precipitation followed by liquid-phase reduction was conducted continuously. Nickel metal powder was produced through this sequential process, with a nickel sulfate($NiSO_4$) solution serving as the starting material for this metal recovery study. This is a high-purity Ni solution obtained after solvent extraction during the hydrometallurgical process, suitable for direct use as a precursor. Fig. 1 and TABLE 1. show the characteristics of each recovered precursor. Fig. 1 shows the XRD pattern of the powder obtained by drying the $NiSO_4$ solution recovered

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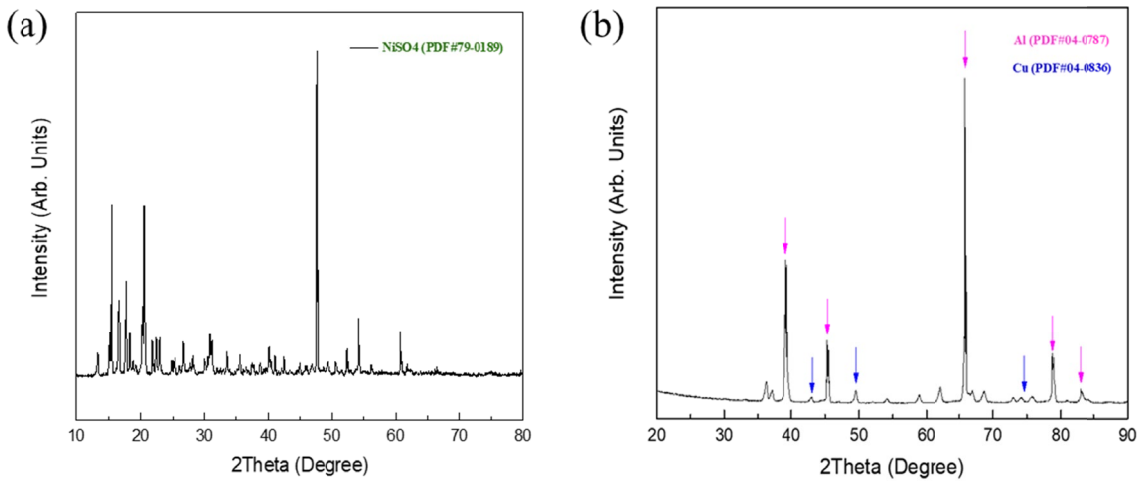

Fig. 1. XRD pattern of representative crystallization properties of (a) $NiSO_4$ precursors and (b) by-product

from ESS waste. XRD analysis confirmed that the recovered powder consisted of (a) single-phase $NiSO_4$(JCPDS 79-0189). In addition, the concentration of Ni in the solution was confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES). Furthermore, residual pre-treatment (b) by-product samples remaining after the recovery of high-value metals were also analyzed; further recovery from these by-products will be pursued through physical processing.

TABLE 1

Result of concentration analysis of $NiSO_4$ solution recovered from waste LIBs

	Co	Ni	Na	Ca	Mg	Li
$NiSO_4$ (ppm)	192	3114	268.4	156.7	127	16

In this study, $NiSO_4$ solution recovered from a waste LIBs containing a cathode material providing nickel ions, a valuable resource, was applied as a starting material, and nickel metal powder was finally obtained through continuous research of precipitation and reduction processes. It is a study to manufacture, and the overall schematic is shown in Fig. 2(a).

$$NiSO_4\ (aq) + NaOH\ (s) = \\ = Na_2SO_4\ (aq) + Ni(OH)_2\ (s) \downarrow \quad (1)$$

$$2\ Ni(OH)_2\ (s) + N_2H_4\ (l) = \\ = 4\ H_2O\ (l) + N_2\ (g) + 2\ Ni\ (s) \downarrow \quad (2)$$

Highly crystalline nickel metal powder, experiments were conducted on the hydroxide preparation conditions and nickel metal reduction conditions. To investigate the effect of sodium hydroxide (NaOH) concentration conditions ([OH]/[Ni] = 1~14) on the synthesis of intermediate $Ni(OH)_2$, 0.02 mol of recycled $NiSO_4$ solution precursor recovered from LIBs waste resources was prepared. The fixed experimental conditions for the synthesis of the intermediate $Ni(OH)_2$ were set at room temperature with a reaction time of 1 hour. Subsequently, N_2H_4 as a reducing agent was introduced at molar ratio conditions of 5, 10, and 14 relatives to the nickel content, and the resulting metallic powder was finally recovered for characterization analysis. To derive optimal conditions, experiments were conducted with the ratio of nickel precursor and precipitant ([OH]/[Ni]) = 1~14) and hydroxide and reducing agent (1:5, 10, 14).

3. Results and discussion

To investigate the synthesis behavior of the final nickel metal powder product, experiments were conducted by varying the NaOH concentration ratio, using the $NiSO_4$ solution recovered from ESS waste was used as the research raw material. Fig. 2 is the result of an experiment conducted under conditions of (b) NaOH input concentration ratio as an intermediate product and (c) reducing agent input concentration ratio to confirm the behavior of nickel metal powder according to the $Ni(OH)_2$ manufacturing concentration ratio. Precipitation time and reduction time, the metal reduction concentration ratio was fixed. To produce the metal hydroxide intermediate product, the synthesis of $Ni(OH)_2$ according to concentration conditions was preferentially performed by using recovered $NiSO_4$ as a starting material. For the production of $Ni(OH)_2$, an intermediate product, from $NiSO_4$, the reaction temperature was fixed at room temperature and the reaction time was 1 hour, and NaOH was used as a precipitant to prepare [OH]/[Ni] concentration ratio. As a result of confirming the crystallinity of the powder recovered through solid-liquid separation after completion of the precipitation process, it was confirmed that the hydroxide crystallinity was low in all conditions. It was determined that there was difficulty in producing only the intermediate product, and it was decided to proceed with the continuous liquid phase reduction process through the introduction of a reducing agent directly into the solution in which the intermediate product, hydroxide was prepared.

Fig. 2(b) is the result of confirming the crystal phase of the powder manufactured with the continuous liquid phase reduction process according to the concentration ratio of [OH]/[Ni] = 1~14, which is the NaOH input condition. N_2H_4 was used at a concentration ratio of 1:5 as a reducing agent in the manufacturing

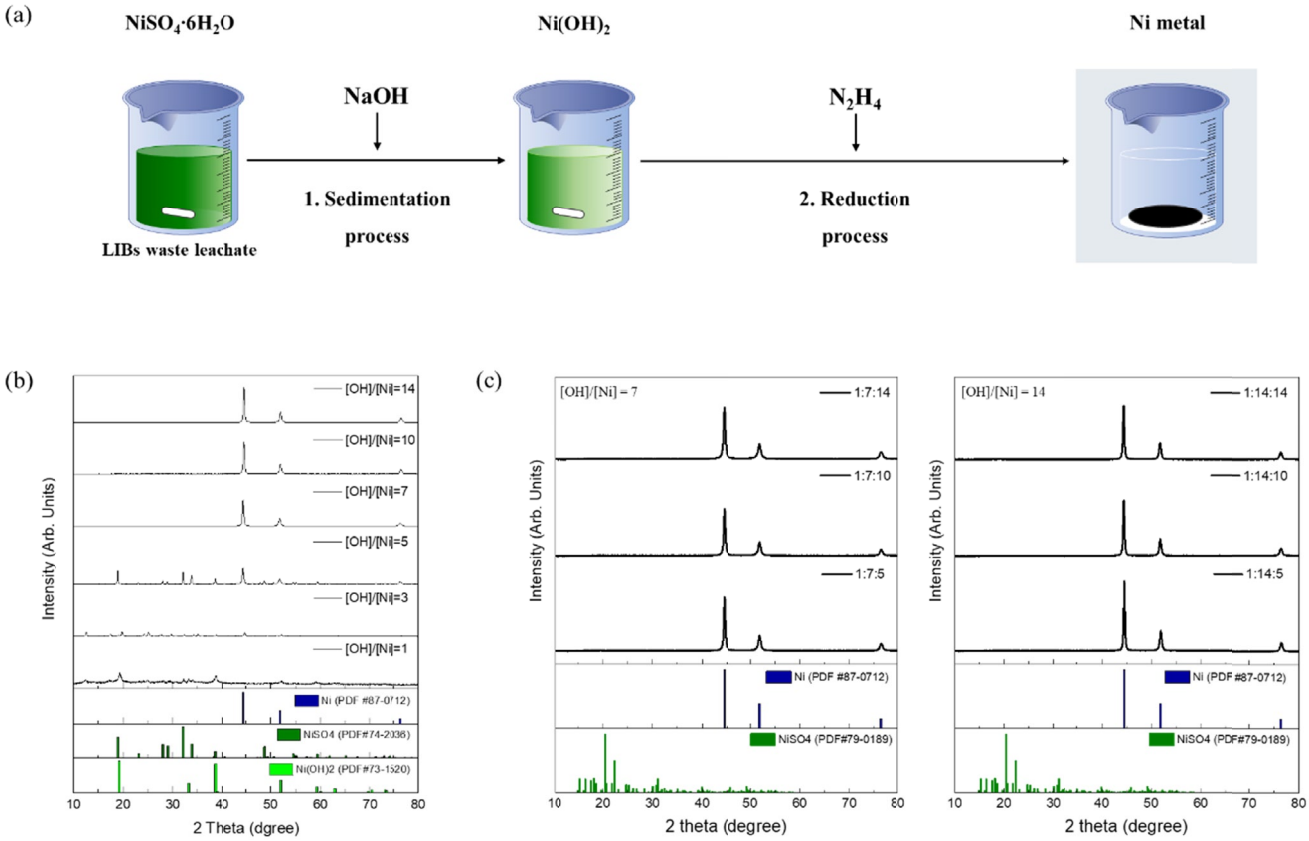

Fig. 2. (a) Schematic diagram of the metal powder synthesis process using a continuous liquid-phase route from recovered valuable resources, XRD pattern analysis of (b) hydroxide powders prepared under varying NaOH concentration ratios, and (c) metal powders prepared under varying N_2H_4 concentration ratios

process of nickel metal powder, the final product, and the reaction temperature was room temperature and the reaction time was fixed at 24 hours for maximum reaction. Under [OH]/[Ni] = 1~5, the raw material $NiSO_4$ and the intermediate product $Ni(OH)_2$ although a crystal peak is confirmed, it can be confirmed that a nickel single phase was produced in conditions [OH]/[Ni] = 7.

In addition, a study was conducted to confirm the crystallinity of nickel metal powder according to the reducing agent concentration ratio conditions, and $NiSO_4$: N_2H_4 = 1:5, 10, 14 was set as the hydrazine input condition. Fig. 2(c) shows the crystallinity results of the Ni metal powder prepared according to the reducing agent concentration ratio conditions, and the higher the concentration of $Ni(OH)_2$ used to prepare the intermediate product, the higher the crystallinity of the Ni powder. Fig. 3(a) is the result of a comparative experiment with a commercial reagent to confirm the Ni metal powder prepared from the LIBs

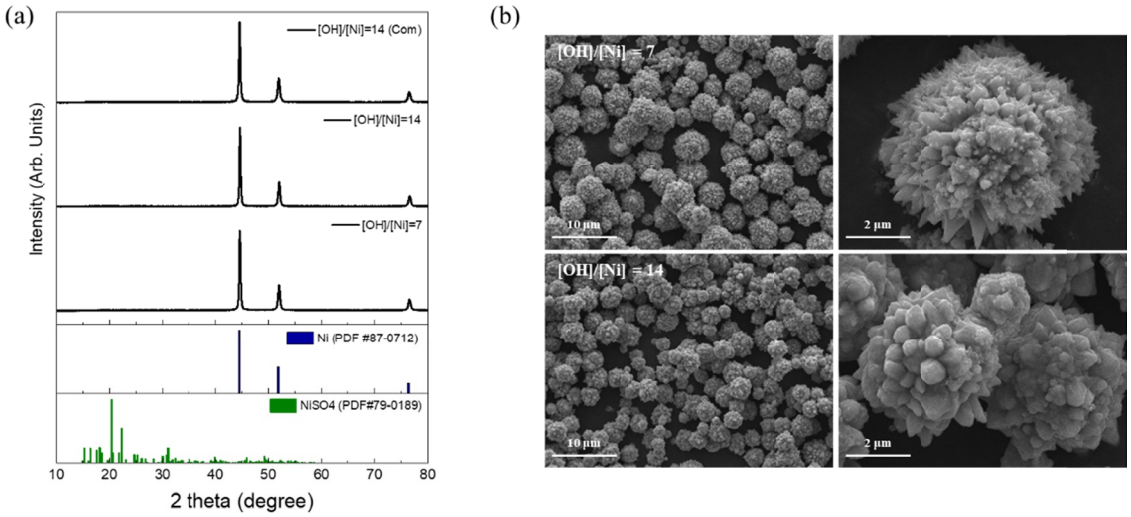

Fig. 3. Results for NaOH concentration ratios ([OH]/[Ni] = 7, 14) for $Ni(OH)_2$ synthesis and reduction ratio ($NiSO_4$:N_2H_4 = 1:5) for Ni powder reduction; (a) XRD patterns and (b) SEM images

recovery resource as a starting material. It was confirmed that the crystallinity of the metal powder manufactured through commercial reagents and recovered resources was the same as that of a single Ni metal powder, and that the intensity was similar.

Finally, SEM analysis was performed to confirm the particle size and microstructure of condition ([OH]/[Ni] = 7, 14), that produced the powder with the highest crystallinity, which can be seen in Fig. 3(b). The Nickel powder particle size was 1.1 to 7.0 μm in condition 1 ([OH]/[Ni] = 7) and 3.3 to 5.4 μm in condition 2 ([OH]/[Ni] = 14). It can be confirmed that nickel powder having a generally non-uniform particle size was synthesized which can be confirmed through SEM images in Fig. 3(b). Through this, it was found that the finally synthesized nickel powder crystallinity and the size of the powder particles were also affected according to the input OH concentration.

4. Conclusions

In this study, the manufacturing behavior of the finally synthesized metal powder was confirmed according to the production concentration ratio of hydroxide, an intermediate product, using nickel sulfate solution recovered from the ESS for the selective recovery of valuable resources from ESS waste. $Ni(OH)_2$, an intermediate product was prepared through NaOH concentration conditions, and Ni metal powder was prepared by continuously adding a N_2H_4 reducing agent. Finally, single-phase Ni metal powder was synthesized through crystallization analysis of the Ni metal powder synthesized under [OH]/[Ni] = 7 and 14 conditions, and it was confirmed that the average particle size was 4.05 to 4.35 μm.

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