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Effect of Dissolution Temperature on Purity of $LaNi_5$ Powder Synthesized with the Combustion-Reduction Method

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Highlights:

- A simpler process for producing $LaNi_5$ was designed by modifying the combustion-reduction process.
- The combustion process was prepared by synthesizing La nitrate and Ni nitrate at various temperatures to ensure that the La nitrate and Ni nitrate react perfectly and obtain higher La_2NiO_4 content.
- The reduction of rare earth metal oxide was carried out using CO gas because it is safer compared to H_2 gas and does not require special equipment.

Abstract. The $LaNi_5$ intermetallic phase has been extensively investigated because of its excellent properties, such as attractive hydrogen storage, medium plateau pressure, and easy activation. $LaNi_5$ phase is generally produced by a complicated method, which involves several steps, i.e. melting, alloying, casting, softening and making them into powder. This study aimed to develop a new $LaNi_5$ synthesis process by modifying the combustion-reduction method. In this method it is very important to produce La_2NiO_4, because $LaNi_5$ is formed from the process of reducing this phase. The precursor powders $La(NO_3)_3.6H_2O$ and $Ni(NO_3)_2.6H_2O$ were reacted with distilled water as a solvent medium and mixed using magnetic stirring. The synthesis process was carried out at room temperature, 60 °C, 70 °C, and 80 °C for 10 minutes until the solution became transparent green. The solution was then dried for 2 hours at 100 °C to form a transparent green gel. The gel was calcined at a temperature of 500 °C for 2 hours, producing a black powder. The optimal black powder was then reduced using CO gas at 600 °C for 2 hours. The powder samples were characterized using XRD, FTIR, and SEM-EDX. The analysis revealed that synthesis at room temperature was the most optimal method for the reduction process because it produced the most La_2NiO_4, at 12.135 wt%.

Keywords: *characterization; combustion-reduction; dilanthanum nickel oxide (La_2NiO_4); lanthanum pentanickel ($LaNi_5$); synthesis temperature.*

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1 Introduction

The usage of hydrogen storage alloys for the anode of batteries is an interesting topic that has been developed by several researchers. Hydrogen storage alloy research has become a very important subject because basically NiMH batteries utilize hydrogen storage alloys in the process of charging and discharging reactions to produce electrical energy. The role of hydrogen storage alloys in this case greatly affects the NiMH battery power density and besides that it is very important in the process of absorption/adsorption of H_2 at negative electrodes [1].

A good hydrogen storage alloy must have the following properties: (1) catalyst for hydrogen atoms; (2) good corrosion resistance; (3) reversible hydrogen storage capacity; (4) good operation at various temperatures; and (5) corresponding hydrogen pressure balance [2]. At present, many negative electrodes of NiMH batteries use AB_5 intermetallic phase-based alloys such as $LaNi_5$. Due to its structure this alloy is able to absorb H_2 atoms, which leads to the formation of metal hydride. $LaNi_5$ is one of the most studied intermetallic materials because it has a reversible storage capability of 1.4 wt% hydrogen at room temperature through electrochemical processes or hydrogen pressure [2]. In addition, the advantages of this intermetallic alloy can also be used in the application of solid-state hydrogen storage for hydrogen fuel applications [3]. One of the disadvantages of these materials is that their manufacture comprises difficult multilevel chemical reactions and is not cheap. Synthesis of $LaNi_5$ has been done through the combustion-reduction method in previous studies, using precursors of lanthanum/nickel oxide and H_2 gas as reducing agents [4]. The process consists of two stages, namely: (1) reduction or ignition, and (2) combustion. In the combustion stage, the metallic oxide precursor is synthesized using nitrate as starting material and glycin as complexing agent. The combustion process itself is ignited by the increasing temperature during calcination, until a black powder is obtained. After that, in the reduction stage, the product is reduced using an appropriate reducing agent to form the $LaNi_5$ intermetallic phase [4].

This research aimed to design a simpler process for producing $LaNi_5$ by modifying the combustion-reduction method by using CO gas as a reductor agent. CO gas was chosen because it is relatively safe and easier to obtain compared to H_2 gas, which requires special equipment. It is expected that 20% La_2NiO_4 oxide can be reduced to form $LaNi_5$.

2 Materials and Methods

The precursor powders used were: 1 mmol lanthanum nitrate hexahydrate ($La(NO_3)_3.6H_2O$), 5 mmol nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), and 7.2 mmol glycine ($C_2H_5NO_2$) were reacted. The synthesis process was carried out at room temperature, 60 °C, 70 °C, and 80 °C for 10 minutes, producing a transparent gel. The gel was calcined using a muffle furnace (LHT 04/17, Nabertherm, Germany) at a temperature of 500 °C for 2 hours to produce a black powder as an intermediate product. The black powder was characterized using X-ray diffraction (XRD) (SmartLab, Rigaku), carried out under test conditions with a voltage of 40 kV, a current of 30 mA and a 2θ angle range of 10° to 90° to see the phase formed. Fourier transform infra red (FTIR) (Thermo Scientific Nicolet iS50) spectography was performed in the range of wave numbers 4000 to 500 cm^{-1} to determine the reactions that occurred through the analysis of functional groups of the formed spectrum. From the results of the analysis, the optimal black powder was then reduced using CO gas at 600 °C for 2 hours. The optimal black powder used in the reduction process was the one that contained the most La_2NiO_4 phase. The reduced powder was then characterized by XRD to see the compounds formed and scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to see the morphology and shape of the particles due to the reduction process.

3 Results and Discussion

X-ray diffraction pattern analysis of the black powder samples was carried out using the Rietveld method with the PANalytical High Score Plus software. The identification of the phases formed in the samples is based on the similarity of the diffraction patterns found in the sample diffractograms with the Inorganic Crystal Structure Database (ICSD) database. The phase composition was determined by quantitative method using the same XRD analysis software.

The diffraction patterns of the black powder samples synthesized at temperatures of 60 °C, 70 °C, and 80 °C are shown in Figure 1. It is known that there are identical diffraction peak patterns in the range of angles from 10° to 90°. For the four black powder samples, the identical peak patterns were around 2θ angles of 37°, 43°, 62°, 75° and 79°, which were identified as the nickel oxide (NiO) phase. In the room temperature sample, using magnification with an angular range, peaks were identified at 2θ angles of 26°, 29°, 30° and 31°, which are peaks of the lanthanum oxide (La_2O_3) phase, whereas the peaks at 2θ angles of 23° and 31° are peaks of the lanthanum nickel tetraoxide (La_2NiO_4) phase. In addition, it was also observed that there were identical peaks at 2θ angles of 25° and 30°, which are peaks of the lanthanum oxide phase. Meanwhile, the peak at a 2θ angle of 28° experienced shrinkage as the temperature of the synthesis increased, which indicates that this angle represents the lanthanum oxide Ht (x-form) phase. This phase arises because there is a change in the shape of hexagonal P63/mmc crystals into cubic form of Im3m at high temperatures, caused by partial oxygen disturbance [5]. The peaks in the range of 50° to 60° at angles of 39° and 44°

show formation of the lanthanum oxide phase. As the temperature increased, the appearance of these peaks clearly showed that the lanthanum oxide phase was formed. Similarly, around 2θ angles of 40° and 45° also a peak formed, which indicates the development of the phase of lanthanum nickel trioxide at room temperature, but along with the increase in temperature, the lanthanum oxide phase appeared at the corners of 53° and 55°.

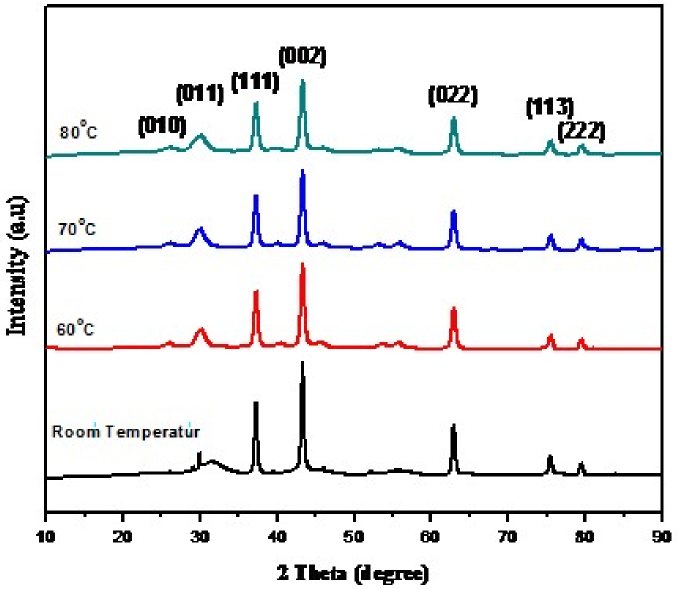

Figure 1 X-ray diffraction patterns of the four black powder (intermediate product) samples.

The results of the analysis of the phase composition of each black powder (intermediate product) sample are listed in Table 1. The table shows that the black powder synthesized at room temperature contained 12.135% La_2NiO_4 phase. In the black powder samples synthesized at 60 °C to 80 °C, the La_2NiO_4 phase did not form; the very dominant NiO phase tended to increase. In this work, dissolution was performed at room temperature, 60 °C, 70 °C and 80 °C. However, the La_2NiO_4 phase was only detected in the sample produced at room temperature. This is related to the low precursor melting point, where the melting point of lanthanum nitrate hexahydrate ($La(NO_3)_3.6H_2O$) is about 65 °C to 68°C, while for nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) it is about 56°C, according to the materials data sheet from the supplier. Nitrate phase is not very stable at high temperature, so if dissolution is performed at 60 °C, which is higher than the melting point of one of the precursors, the chemical reaction occurs imperfectly.

This results in the La_2NiO_4 phase not being formed evenly, even though the calcination temperature is the same. As the synthesis temperature increases, the La_2O_3 phase content tends to increase. Lanthanum oxide (La_2O_3) phase is formed due to the calcination temperature not yet reaching its optimal temperature [6].

Table 1 Phase composition of black powder samples.

Phase	**% Composition**			
	Room temperature (RT)	**60 °C**	**70 °C**	**80 °C**
La_2NiO_4	12.135%	-	-	-
NiO	79.942%	84.6%	82.0%	80.7%
La_2O_3	7.9238%	15.3%	17.8%	19.3%
La_2O_3 – Ht (x-form)	-	0.1%	0.2%	-

FTIR characterization was carried out to observe the function groups formed in the black powders. The IR spectra of the raw material and black powders for different process temperatures (room temperature (RT), 60 °C, 70 °C, and 80 °C) are shown in Figure 2, with the wavenumber ranging from 4000-500 cm^{-1}. The results of FTIR characterization of the raw material are shown in Figure 2.

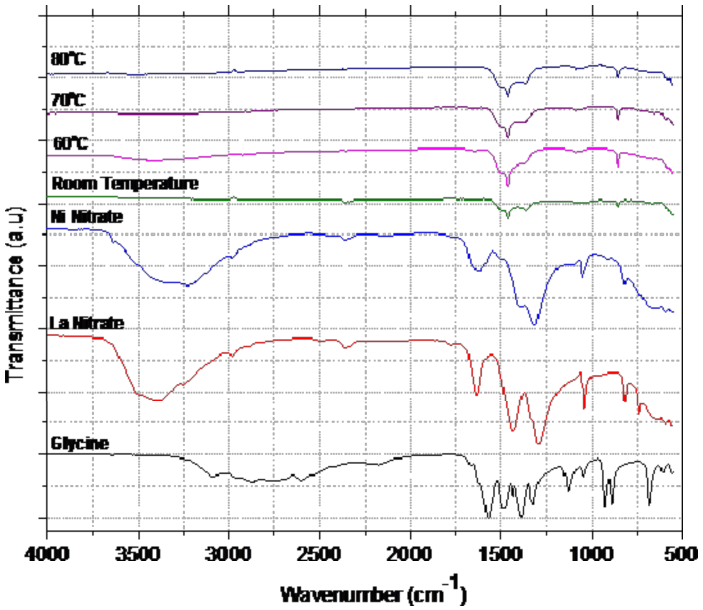

Figure 2 IR spectra of the raw material and the black powders synthesized at various temperatures.

Lanthanum nitrate hexahydrate and nickle (II) nitrate hexahydrate obtained fingerprints in the area of 3500-3000 cm^{-1}, showing OH groups in the area of 1750-1250 cm^{-1} and NO^{3+} groups. Meanwhile, the glycine FTIR results showed fingerprints in the area of 3100-2600 cm^{-1} showing NH^{3+} groups [6].

In Figure 2 there are no glycine spectra and a broad absorption band related to O-H stretching can be seen at 3600 to 3200 cm^{-1} in the IR spectra of the black powders synthesized at RT, 60 °C, 70 °C, and 80 °C, which indicates that the O-H was evaporated because of the calcination process [7]. Overall, the black powders' IR spectra were the same in all wavenumber regions. The difference in the spectra was in the intensity of the fingerprint area observed at 1600-800 cm^{-1}. Here, the different spectra around 1500, 1300, 1100, and 850 cm^{-1} indicate NH_3^+ from glycine, N-O from nitrate raw material (lanthanum nitrate hexahydrate and nickel (II) nitrate hexahydrate), NH_3^+ from glycine, and N-O from nitrate raw material, respectively. For lanthanum it is possible to have a wavenumber below 500 cm^{-1} because for anorganic materials this is difficult to observe with FTIR [8].

The intermediate products (black powders) that were considered optimal were reduced with CO gas at a temperature of 600 °C for 2 hours. The samples that were considered optimal for the reduction process were those containing La_2NiO_4 phase. This is the initial phase of the formation of the $LaNi_5$ phase during the reduction process [4]. The X-ray diffraction patterns before and after reduction using CO gas are shown in Figure 3. The results of the analysis of the composition of the phases contained in each powder sample (before and after reduction) are listed in Table 2. The table shows that the reduction with CO gas was successful and produced as much as 8.5% $LaNi_5$.

The EDS results in Figure 4 and Table 3 show that there was a reduction in oxygen, which indicates that the La_2NiO_4 and NiO reduction processes were already underway.

The morphological structure of the intermediate products (black powders) that were considered optimal were analyzed using SEM with 10,000x magnification using back scatter electron (BSE) mode, as shown in Figures 5 and 6. Observations were made to compare the morphology before and after the reduction process with CO gas.

In Figure 5(a) it can be seen that the La_2NiO_4 oxide powder was in the form of chunks. The size of the La_2NiO_4oxide powder was not uniform, with large lumps and small lumps/particles. The lump looks hollow or porous, with varying cavity sizes. In Figure 5(b) it can be seen that the powder after reduction also had a hollow structure. However, observed in greater detail and at a higher magnification using a secondary electron (SE) detector, morphological changes become visible in the powder sample after reduction (Figure 6). The results of SEM observation with secondary electron mode show that the structure was in the form of long fine threads/nano wire/nets that are connected to each other.

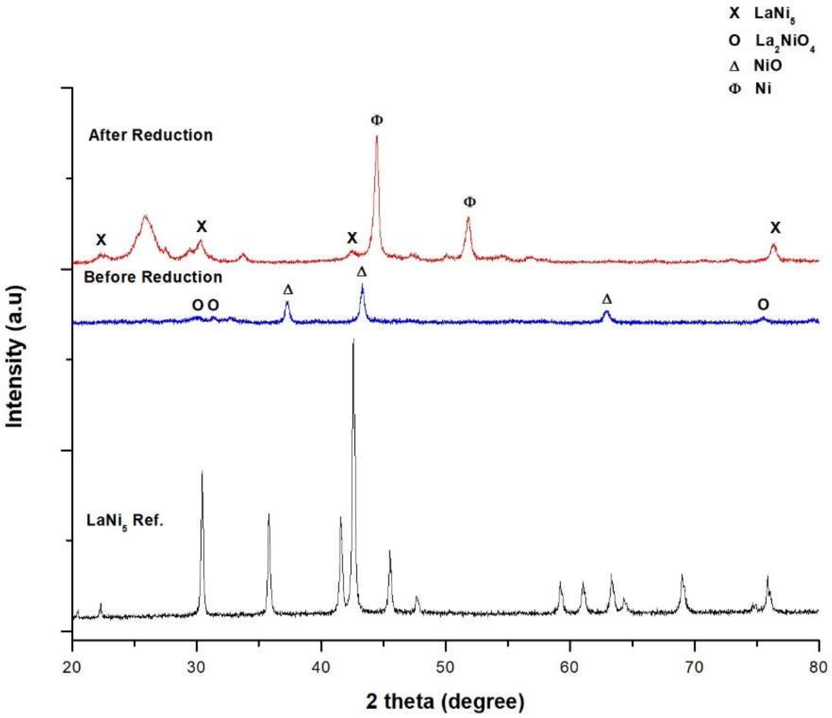

Figure 3 X-ray diffraction patterns before and after reduction using CO gas.

Table 2 Phase composition of the black powders before and after reduction.

Phase	**% Composition**	
	Before Reduction	**After Reduction**
La_2NiO_4	12.135	-
NiO	79.942	-
La_2O_3	7.9238	-
Ni	-	52.6
$LaNi_5$	-	8.5
La_7Ni_3	-	38.9

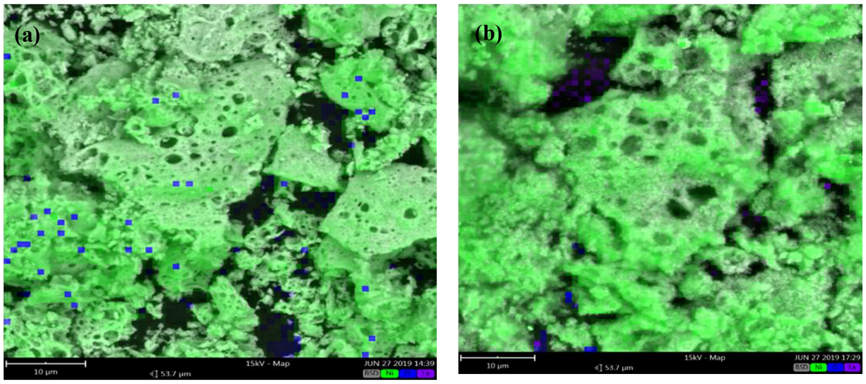

Figure 4 Mapping area for EDS (a) before reduction (left) and (b) after reduction (right).

Table 3 Composition of atom in black powder before and after reduction.

	Before reduction (At%)	After reduction (At%)
O	**44.63**	**26.06**
Ni	**43.28**	**56.94**
La	**12.09**	**17.01**

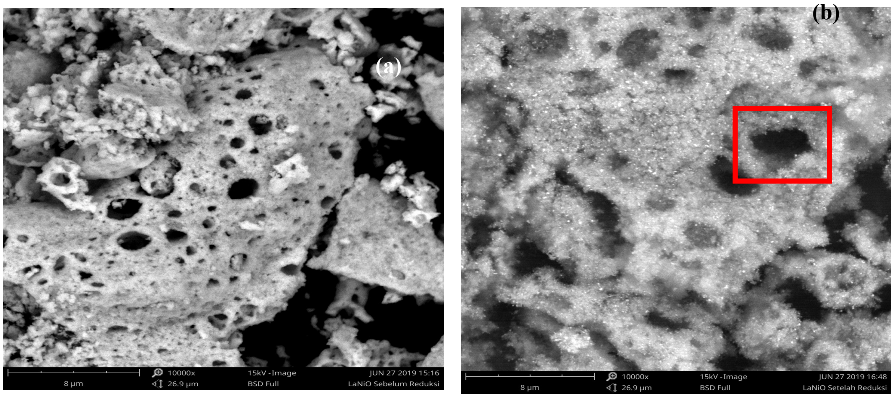

Figure 5 Powder morphology (a) before reduction (left) and (b) after reduction (right) at 10.000x magnification with BSE mode.

Reduction with CO gas was successfully carried out and produced as much as 8.5% $LaNi_5$, about 52.6% nickel, and another type La_7Ni_3. Reduction with CO gas in stages was successfully carried out in this study. If oxide still exists after the reduction process, this oxide will stimulate the oxidation process, which can be one of the factors causing storage capacity decay. In the initial stage of oxidation, the oxide layer on the surface of $LaNi_5$ exposed to air consists of La_2O_3, La $(OH)_3$ and metal nickel, thus serving as a barrier against further oxidation. However, at the level of further oxidation, the presence of these oxides causes $LaNi_5$ storage capacity loss [11].

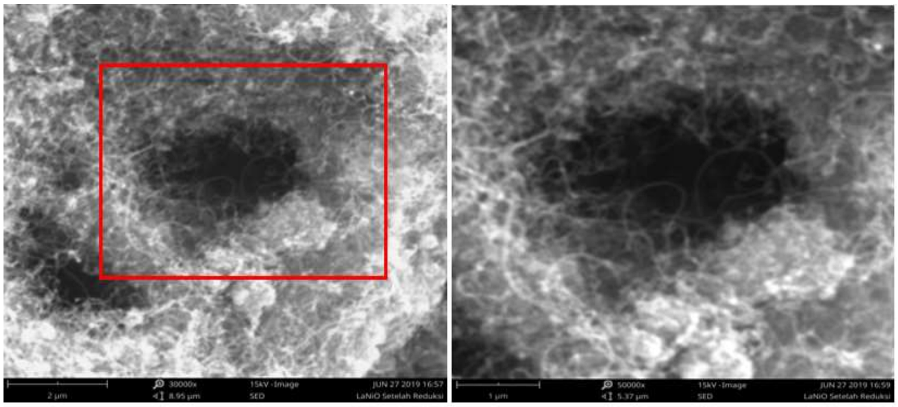

Figure 6 Image of the powder after reduction at 15,000x magnification with secondary electron (SE) mode.

4 Conclusion

Variation of temperature during synthesis causes La_2NiO_4 phase to disappear, creating two dominant phases, namely nickel oxide (NiO) and lanthanum oxide (La_2O_3). Besides that, there are still C-O and C-H bonds, which are bonds of glycine surfactants, indicating that the process of phase formation in comparison with the reference reaction is not optimal. Synthesis at room temperature was the most optimal for feeding the reduction process because it formed La_2NiO_4 at 12.135 wt%. The reduction process formed long fine threads/nano wire/nets that were connected to each other. The results of EDS after reduction showed that the concentration of O decreased from 44.63 at% to 26.06 at%. On the other hand, the concentration of Ni increased from 43.28% to 56.94%. Likewise the concentration of La rose from 12.09 at% to 17.01 at%. This is indicates that the reaction proceeded well and succeeded in reducing the amount of oxygen. Thus, reduction with CO gas was carried out successfully, producing as much as 8.5% $LaNi_5$.

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