



Communication **Tuning Hydrogen Storage Properties in La**_{1-x} $Y_xNi_{4.5}Cu_{0.5}$ (x = 0.1; 0.2; 0.3; 0.4, 0.5) Alloys

Mateusz Mańka ¹, Tomohiro Kinoshita ², Anita Nowak ³, Aleksandra Ludwik ³, Alicja Klimkowicz ^{2,4}, Akito Takasaki ² and Łukasz Gondek ^{3,*}

- ¹ Faculty of Energy and Fuels, AGH University of Krakow, Mickiewicza 30, 30-059 Krakow, Poland
- ² Department of Engineering Science and Mechanics, Shibaura Institute of Technology, Toyosu, Koto-ku, Tokyo 135-8548, Japan; alicja@shibaura-it.ac.jp (A.K.); takasaki@shibaura-it.ac.jp (A.T.)
- ³ Faculty of Physics and Applied Computer Science, AGH University of Krakow, Mickiewicza 30, 30-059 Krakow, Poland
- ⁴ Innovative Global Program, Faculty of Engineering, Shibaura Institute of Technology, Toyosu, Koto-ku, Tokyo 135-8548, Japan
- * Correspondence: lgondek@agh.edu.pl

Abstract: Metal hydrides of AB5 compositions have been investigated over the years as they offer extraordinary volumetric hydrogen densities with high cycling stability and purity of released hydrogen. Moreover, by doping with different elements, the sorption properties of alloys can be significantly changed according to their foreseen applications. In this contribution, we report the synthesis routes and hydrogenation characteristics of $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$. The synthesized alloys exhibit excellent structural purity with all reflections indexed by the hexagonal *P6/mmm* structure. It was found that the Y content can easily tune (raise) the equilibrium pressures of the pressure-composition isotherms, while overall gravimetric density remains at a level exceeding 1.5 wt.% up to x = 0.3 then strongly decreases. The pressure range for desorption can be tuned from 1.5 to 5 bars at room temperature. Some alloys (x = 0; 0.2) exhibit very good stability during 1000 cycles of hydrogen loading and unloading. Furthermore, activation of the alloys is prompt, making them good candidates for stationary hydrogen storage, non-mechanical hydrogen compressors, or soft actuators.

Keywords: hydrogen storage; AB5 alloys; metal hydrides

1. Introduction

Binary metal hydrides of AB5 stoichiometry, mainly derivatives of LaNi₅ crystallizing in the hexagonal CaCu₅ structure, are important chains in the hydrogen economy, being used in hydrogen storage and compression systems, fuel cells, purification devices, sensors, catalyst agents, and soft actuators, as well as in gas separators, which has recently attracted scientific interest [1–9]. Among the above-mentioned purposes, it seems that stationary storage, purification, compression and further uses for soft actuators, which will generate growing demand for new materials with a very different range of operating pressures [8,10,11].

The hydrogen sorption properties of the LaNi₅ alloy have been known since the 1970s. The alloy offers loading and unloading pressure below 2 bar, with relatively low hysteresis and a maximum concentration of around 1.4 wt.% [12]. The hydriding properties can be tuned according to the chemical composition of the alloy at a wide range of operating pressures [8]. However, the problem of alloy stability towards extended cycling is crucial, as the performance of some LaNi₅ derivatives deteriorates rapidly [13,14].

Although the LaNi₅ derivatives are quite well-exploited, the compositions tending toward high pressures are relatively rarely researched. The YNi₅ alloy has been shown to exhibit a two-plateaus pressure–concentration isotherm (PCI) curve with plateau pressures of about 300 and 1000 bar and a final concentration of hydrogen around 1 wt.% [15]. It was



Citation: Mańka, M.; Kinoshita, T.; Nowak, A.; Ludwik, A.; Klimkowicz, A.; Takasaki, A.; Gondek, Ł. Tuning Hydrogen Storage Properties in $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$ (x = 0.1; 0.2; 0.3; 0.4, 0.5) Alloys. *Energies* **2024**, 17, 71. https://doi.org/10.3390/en17010071

Academic Editors: Adam Revesz, Hai-Wen Li and Giovanni Esposito

Received: 30 July 2023 Revised: 25 October 2023 Accepted: 15 December 2023 Published: 22 December 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

2 of 11

concluded that the high pressure (above 100 bar) required for the formation of the YNi_5H_x hydrides originates in the rigidity of the compound, which is measured via estimation of the Debye temperature [16]. The last report on YNi_5 brought the PCI curve measurement to 2000 bar and the conclusion that the results are very different from those previously reported, as only one plateau was evidenced on the PCI curve above 600 bar [17]. On the other hand, the LaNi_{5-x}Cu_x system has been relatively more researched. The LaCu₅ alloy was reported to absorb hydrogen with PCI plateau pressures of 2–3 bar; however, similarly to the YNi₅ alloy, the hydrogen concentration was much lower than in the parent LaNi₅ alloy [18]. Recent studies revealed that LaNi_{5-x}Cu_x alloys exhibit decent electrochemical properties for storing hydrogen with ease of activation; however, their cycling stability is suppressed for mediocre Cu concentrations [19]. Interestingly, LaNi_{5-x}Cu_x alloys were tested for gas separation (harvesting hydrogen) from mixtures [20]. It was reported that YCu₅ does not undergo hydrogenation, while it is isostructural to the alloys discussed above. As a reason for this behavior, a too-small volume of the unit cell was given [21].

Surprisingly, only Co, Cu, Zn, Ir, and Pt can be introduced as M in LaNi_{5-x}M_x alloys in a wide concentration range up to x = 5 [22–26]. Other elements can be introduced with a limited upper range, usually lower than x = 1. However, such doping substantially improves hydrogenation properties. For example, introducing Al for Ni leads to a rapid drop of the equilibrium pressure of two orders of magnitude for x = 1 [27]. Another common substitution for Ni is Sn, which provides excellent stability during thousands of hydrogen loading/unloading without decreasing the maximum hydrogen capacity of the alloy [28]. On the other hand, La substitutions are restricted mainly to other rare earths such as Ce for raising the equilibrium pressures, as the CeNi₅ alloy exhibits equilibrium pressures in the range of 200 bars after activation [29]. To achieve cost efficiency of the storage beds, mischmetal (Mm) is often used in place of lanthanum. The mischmetal consists mainly of Ce (~50 wt.%), La(~35 wt.%), Nd, and Pr depending on the actual ore, which was used for production [30]. However, those alloys suffer from large hysteresis and rather high equilibrium pressures for hydrogen absorption/desorption because of the smaller lattice parameters, as La has the highest atomic radius compared to the other rare earths. Therefore, to tune the properties to be suitable for hydrogen reservoirs, compressors, or actuators, substitutions for Ni must be used. Apart from most 3d, 2p, and 3p elements, Al and Mn are the dopants which are commonly used [31]. For example, $MmNi_{5-x}Al_x$ alloys can be tuned to exhibit equilibrium pressures in the range of 0.1–20 bars [32]. The $LaNi_{5-x}Cu_x$ alloys exhibit lower equilibrium pressures than the $LaNi_{5}$, as well as hydrogen concentration [23,33]. However, the kinetics of Cu-doped LaNi₅ was significantly better than that of the parent alloy [23]. It was even suggested that the LaNi_{5-x}Cu_x alloys could be used for the extraction of hydrogen from gas mixtures [23].

For possible applications, the ease of the activation procedure is as important as other parameters. Usually, the activation procedure is related to the decrepitation of grains, which allows hydrogen to enter fresh surfaces. However, other mechanisms can be taken into account; that is, strains and defects can also play an important role in facilitating the activation process [34,35]. Neutron imaging studies revealed that the activation process is random within the entire hydrogen storage bed [34,35]. For the above reasons, rapidly cooled materials or materials as-synthesized, i.e., without thermal treatment, are particularly interesting in solid-state hydrogen storage. Another factor that limits the performance of the hydrogen storage bed is decrepitation followed by particle transport. In principle, decrepitation leads to an increase in the surface-to-volume ratio, which should speed up the reaction of hydrogenation. However, it decreases thermal transport, which is also crucial for strongly exothermic hydrogen sorption in metallic materials [34,35].

According to U.S. Department Of Energy, 2025, targets for "Onboard hydrogen storage for light-duty fuel cell vehicles" are as follows: total hydrogen gravimetric density— 5.5 wt.; total hydrogen volumetric density—0.04 kg/L; price of the system—300 USDfor 1 kg of stored H₂; cycle-life—1500 cycles [36]. Although AB5 metal hydrides do not meet the gravimetric density for vehicle applications, they are a good choice when it comes to stationary hydrogen storage, electrodes for Ni-MH batteries, soft actuators, and nonmechanical compressors [37]. For all the above-mentioned applications, the repeatability and consistency of metal hydride beds' behavior is considered crucial. Therefore, research on materials which possess those properties is still important.

In this contribution, we report the synthesis, structural, and hydrogen sorption properties of $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$ alloys, i.e., alloys that premise convenient operating pressure adjustment and stability and higher hydrogen concentrations in comparison to the parent alloys YNi_5 and $LaCu_5$. The alloys were not subjected to thermal treatment to accommodate structural imperfections.

2. Experimental Section

The alloys were synthesized via arc melting of the stoichiometric amounts of pure metals (La and Y—99.99%; Ni and Cu—99.999% by MaTecK GmbH (Jülich, Germany)) in protective Ar atmosphere. The products were remelted five times to achieve homogeneity. After synthesis, no annealing at elevated temperatures was applied, which is a typical procedure for obtaining alloys with excellent degree of atomic order. However, long annealing, even under high-vacuum conditions or in a high-purity Ar atmosphere, leads to contamination with oxygen in the form of simple oxides. According to our experience, alloys with stationary defects activate better (i.e., faster) and their performance is maintained for longer cycle life.

The materials were subjected to microstructural investigation by means of scanning electron microscopy (SEM) using JEOL JSM-7100F equipped with X-ray energy dispersive spectroscopy detector (EDS). The tests revealed a homogeneous distribution of elements without traces of spurious phases. The samples were powdered and examined via X-ray diffraction using a Panalytical Empyrean diffractometer, which was calibrated for the position of the lines and profiles widths using NIST 660 (LaB₆). Calibration was used for Rietveld refinements of the collected data, which were quantified by FullProf suite software (https://www.ill.eu/sites/fullprof/) [38].

TEM measurements were obtained using the JEOL JEM-2100 with an acceleration voltage of 200 kV. The samples were investigated using a bright field mode at various magnifications, high resolution at 400 kV, and diffraction with a camera length of 60 cm.

Hydrogen sorption studies were performed using a Setaram-automated PCT-PRO volumetric sorption analyzer. The sample of known mass, about 0.4 g for all alloys, was placed in Inconel steel container, then flushed 10 times with high purity He (99.9999%) and evacuated to remove residual gases from the powder. Subsequently, the residual volume of the container was estimated volumetrically by the expansion of the helium from the calibrated volume. The activation of the samples was carried out at a temperature of 30 °C via cycling at H₂ of 30 bar for 5 min, followed by evacuation for 5 min. When the sample showed stability for 5 subsequent cycles, PCI curves were measured on the same sample (without exposing it to the air). After the last desorption, the maximum concentration of hydrogen was checked at 25 °C. The pressure for that experiment was chosen on the basis of the PCI curve; the highest pressure of the plateau was doubled. Then, cycle life experiments were carried out for chosen samples to determine the deterioration of the specimens (1000 cycles at pressure set as described above).

3. Results

3.1. Structural Properties

The alloys turned out to be single-phased with good homogeneity, as evident from Figure 1. The high-resolution TEM images show atomic layers with distances, respectively, for the P6/mmm structure. In Figure 1a, some atomic layers (described by 111 and 002 Miller indices of the P6/mmm space group) with corresponding interplanar distances are revealed. The crystallite sizes show a distribution between 50–400 nm, which is typical for samples without annealing. TEM investigation also revealed the occurrence of various defects, as expected, via the synthesis route.



Figure 1. Electron microscopy results for the $La_{0.5}Y_{0.5}Ni_{4.5}Cu_{0.5}$ sample: transmission image (TEM) with layers of *P6/mmm* structure marked together with interplanar distances (**a**); scanning electron microscopy image (**b**) with elemental distribution—La (**c**); Cu (**d**); Y (**e**); Ni (**f**).

X-ray diffraction data were refined using the Rietveld method. For all investigated samples, the refined structural models showed reliability factors (R_{Bragg} and R_F) below 8%, which proves a proper choice of the structural model. To verify whether the substituting elements are located in the expected positions, different structural models were tested. Namely, the distribution of Y over the La 1a site, as well as the Ni 2c and 3g sites, was considered. The lowest reliability factors were obtained for Y solely occupying the 1a site. The possibility of Y occupation of the Ni 2c and 3g sites were excluded as it produced much higher R_{Bragg} and R_F factors, exceeding 13%. On the other hand, the Cu substitution was expected to occur solely for Ni atoms at 2c and 3g sites. Indeed, the models with Cu distributed over the 1a site increased the reliability factors above 12%. Therefore, the substitution of the copper atoms for the La/Y 1a site was excluded. There was an open question as to whether the Cu atoms are evenly distributed between both Ni sites (2c and 3g). As the difference in Cu and Ni atomic scattering factors for X-rays is very small, the X-ray diffraction is not a reliable tool for verifying this issue. The reliability factors for models with Cu evenly distributed over both Ni sites, or Cu located exclusively in the 2c or 3g sites, gave similar reliability factors. However, for the isostructural La_{0.75}Ce_{0.25}Ni_{4.8}Al_{0.2} alloy, the Al was reported to occupy only the 3g site, according to the neutron diffraction studies [39]. Hence, the positions of the atoms are as follows:

Y/La at the 1a site: 0; 0; 0,

Ni at the 2c site: $\frac{1}{3}$; $\frac{2}{3}$; 0,

Ni/Cu at the 3g site: $\frac{1}{2}$; 0; $\frac{1}{2}$.

Results of the X-ray diffraction of the synthesized alloys are presented in Figure 2. Usually, when mixing two elements over some crystallographic position, the 50:50 ratio has the highest possibility of disproportionation. As is apparent, this is not the case for the $La_{0.5}Y_{0.5}Ni_{4.5}Cu_{0.5}$ sample, which shows excellent phase homogeneity, without the occurrence of non-indexed reflections. Rietveld refinements revealed that all samples crystallize in the hexagonal P6/mmm structure. The results of the refinements are also collected in Table 1.

Sample	a (Å)	c (Å)	V (Å ³)	Strain (%)
LaNi _{4.5} Cu _{0.5}	5.0203(1)	3.9991(1)	87.29(1)	0.211(6)
La _{0.9} Y _{0.1} Ni _{4.5} Cu _{0.5}	5.0102(1)	3.9957(2)	86.86(1)	0.216(8)
La _{0.8} Y _{0.2} Ni _{4.5} Cu _{0.5}	5.0001(1)	3.9930(1)	86.45(1)	0.206(7)
La _{0.7} Y _{0.3} Ni _{4.5} Cu _{0.5}	4.9867(1)	3.9909(1)	85.94(1)	0.196(7)
La _{0.6} Y _{0.4} Ni _{4.5} Cu _{0.5}	4.9732(1)	3.9904(1)	85.47(1)	0.209(7)
La _{0.5} Y _{0.5} Ni _{4.5} Cu _{0.5}	4.9605(1)	3.9884(1)	84.99(1)	0.214(6)

Table 1. Rietveld refinement for $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$ alloys. The lattice parameters (a, c, V) as well as strains related to static defects are given. Uncertainty levels are given in parentheses.



Figure 2. Rietveld refinement for the X-ray diffraction pattern of the $La_{0.5}Y_{0.5}Ni_{4.5}Cu_{0.5}$ sample. The insert presents comparison of all collected patterns. Only the main reflections area is displayed, along with dependence of the unit cell volume on yttrium concentration.

It can be concluded that the lattice parameters change nearly linearly (i.e., decrease) with the concentration of Y, which could be expected since yttrium has a lower metallic radius than lanthanum (1.80 vs. 1.87). This is reflected in the unit cell volume drop with the increase in the yttrium concentration, as presented in the insert to Figure 2. The strains in the crystal are nearly at the same level, which means that their origin is purely due to the preparation procedure. However, the strains are surprisingly low for non-annealed materials.

3.2. Hydrogen Sorption Properties

The activation of the $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$ alloys with a low Y content is immediate, as shown in Table 2. Up to x = 0.3 activation is carried out in seven cycles of hydrogen loading and unloading according to the procedure described in Section 2. For higher yttrium concentrations, activation requires a much larger number of cycles. As the single

absorption and desorption (evacuation) cycle lasted 10 min (5 + 5 min) at 30 °C, it can be concluded that the activation of the samples with x < 0.4 took up to 70 min, while the highest concentrations were significantly longer. This is related to the rising of the equilibrium pressures of the specimens as the yttrium concentration increases. The PCI curves for the chosen samples are collected in Figure 3. When the yttrium content is rising, initially, only the equilibrium pressure in the middle of the plateau rises. However, the overall concentration is not affected, as can be inferred from Table 2. For x = 0.3 the maximum uptake was reduced. From that concentration, a higher amount of yttrium results in a gradual decrease in the maximum uptake. The decrease is strongly non-linear; therefore, the literature-based belief that purely geometric factors can be taken into account is obsolete in this case as the unit cell volume decreases linearly with the Y concentration. Also, the plateau pressures are rising with the Y concentration in a strongly non-linear (exponential) manner. In the insert to Figure 3c, this is presented as the equilibrium pressures rising linearly with x parameter on the semilog scale.



Figure 3. PCI curves for selected $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$ alloys with x = 0 (**a**), x = 0.1 (**b**), and x = 0.5 (**c**), collected at three different temperatures. The insert in part (**c**) shows the dependence of the equilibrium pressure at 25 °C on the yttrium concentration. The pressure scale is logarithmic.

The enthalpy (Δ H) of the formation changes consistently with the concentration of yttrium. The only exception is a sudden change between the reference LaNi_{4.5}Cu_{0.5} and La_{0.9}Y_{0.1}Ni_{4.5}Cu_{0.5}. After the measurements of PCI, the kinetics studies were performed according to the procedure described in the experimental section.

The results are presented in Figure 4a. It can be concluded that for samples from x = 0 to x = 0.3, the process of hydrogen uptake process is homogeneous. The curves look very similar; however, some changes in the speed of the reactions are apparent. The La_{0.8}Y_{0.2}Ni_{4.5}Cu_{0.5} sample, which shows the highest hydrogen concentration, exhibits the highest kinetic ratio, as evident from Figure 4a. All the above-mentioned samples have some upturn in kinetic curves around 20 s from the reaction start, then they reach saturation asymptotically. For a higher yttrium content, the curves apparently have a different character, with significantly lower kinetic. The above-mentioned upturn is not visible here, also yielding the result that the characteristic is significantly different in comparison to other samples. Similar conclusions can be drawn after inspection of cycle life measurements, which are presented in Figure 4b. Samples with x < 0.2 show better cycling stability, while for La_{0.5}Y_{0.5}Ni_{4.5}Cu_{0.5}, the deterioration of the maximum concentration proceeds much faster and the apparent shape of the curve is different from the other investigated samples.

Sample	#Cycles to Full Activation	ΔH _{ABS} ΔH _{DES} (kJ/moleH ₂)	ΔS _{ABS} ΔS _{DES} (kJ/moleH ₂ K)	Max. Uptake (wt.%)	P _{abs} (bar)	P _{des} (bar)
LaNi _{4.5} Cu _{0.5}	3	-30.1(1) 30.9(1)	-107.3(3) 106.8(2)	1.56(1)	2.1	1.4
La _{0.9} Y _{0.1} Ni _{4.5} Cu _{0.5}	7	-27.2(1) 27.5(1)	-99.8(4) 100.4(3)	1.56(1)	3.6	2.7
La _{0.8} Y _{0.2} Ni _{4.5} Cu _{0.5}	6	-26.9(1) 29.0(1)	-104.2(3) 107.7(3)	1.58(1)	4.5	3.5
La _{0.7} Y _{0.3} Ni _{4.5} Cu _{0.5}	6	-26.5(1) 28.7(1)	-105.9(3) 109.0(3)	1.46(1)	7.2	5.8
La _{0.6} Y _{0.4} Ni _{4.5} Cu _{0.5}	31	-26.0(1) 29.2(1)	-107.2(3) 116.2(4)	1.31(1)	11.1	11.7
La _{0.5} Y _{0.5} Ni _{4.5} Cu _{0.5}	46	-23.6(1) 26.5(1)	-105.1(2) 114.1(2)	1.01(1)	21.8	19.6

Table 2. Results of hydrogen sorption studies for alloys $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$: number of cycles for full activation, enthalpy, and entropy of hydride formation (Δ H and Δ S), maximum uptake, and plateau pressures absorption and desorption at 25 °C (P_{abs} and P_{des}).



Figure 4. Kinetics of hydrogen uptake for investigated alloys on a double logarithmic plot (**a**) and cycle life studies for chosen samples (**b**).

3.3. Structural Properties after Cycle Life Studies

An important issue of cycle-life stability can also be addressed via X-ray diffraction measurements performed after samples were removed from the sorption analyzer. Prior to exposing samples to air, the samples were desorbed for 6h at 50 °C under vacuum (10^{-5} mbar) . This procedure is essential, while hydrided AB5 and AB2 alloys often shows a tendency to self-ignite after exposure to air. The X-ray diffraction patterns of the desorbed samples exhibited a broadening of the reflections, while for the highest Y concentration, some amorphous contribution was noticed as well. The desorbed alloys exhibited somewhat higher lattice parameters in comparison to the parent ones, as apparent in Table 3.

However, for $x \ge 0.3$ desorbed samples showed a more expanded lattice in comparison to samples with smaller Y content. In general, the structure of the parent alloys was maintained. Only for the La_{0.5}Y_{0.5}Ni_{4.5}Cu_{0.5} compound was a small amorphous contribution noticed. Its abundance was estimated to be less than 2 wt.%. Analysis of the strains arising due to static defects in the crystal lattice revealed that for higher Y concentrations (x > 0.3), hydrogenation leads to a significant increase in strains with respect to the parent alloys. Interestingly, strains in the specimens with best cycle-life performance were found to be the smallest (x = 0.3).

Table 3. Rietveld refinement for cycled and desorbed $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$ alloys. The lattice parameters (a–v) and strains related to static defects are given. Uncertainty levels are given in parentheses.

Sample	a (Å)	c (Å)	V (Å ³)	Strain (%)
LaNi _{4.5} Cu _{0.5}	5.0211(1)	3.9998(1)	87.33(1)	0.523(9)
La _{0.9} Y _{0.1} Ni _{4.5} Cu _{0.5}	5.0110(1)	3.9963(1)	86.90(1)	0.482(9)
La _{0.8} Y _{0.2} Ni _{4.5} Cu _{0.5}	5.0021(1)	3.9941(1)	86.55(1)	0.412(8)
La _{0.7} Y _{0.3} Ni _{4.5} Cu _{0.5}	4.9892(1)	3.9982(1)	86.19(1)	0.487(8)
La _{0.6} Y _{0.4} Ni _{4.5} Cu _{0.5}	4.9796(1)	3.9978(1)	85.85(1)	0.591(8)
La _{0.5} Y _{0.5} Ni _{4.5} Cu _{0.5} + AMO	4.9674(1)	3.9899(1)	85.26(1)	0.638(8)

4. Concluding Remarks and Summary

The investigated $La_{1-x}Y_xNi_{4.5}Cu_{0.5}$ alloys crystallize in the hexagonal *P6/mmm* space group, similar to the parent LaNi₅ compound. The lattice parameter decreases linearly with the increase in the yttrium content, while the lattice strain is at a low level despite the lack of thermal treatment after arc melting.

The hydriding properties are not a simple (linear) function of the lattice parameters; the pressures of PCI plateaus follow the exponential growth with respect to decreasing the volume of the unit cell. The corresponding dependence is presented in Figure 5. One may conclude that a rise in the equilibrium pressure with the lowering of the unit cell volume originates from restricted volumes for the hydrogen sites and smaller potential H-H distances, which both require higher energies for hydrogen insertion.

Activation of alloys up to x = 0.3 is prompt and occurs in fewer than 10 cycles. For a higher yttrium content, activation requires at least 30 to 46 cycles for x = 0.4 and x = 0.5, respectively. The best kinetics, hydrogen concentration, and cycling stability parameters are evidenced for La_{0.8}Y_{0.2}Ni_{4.5}Cu_{0.5}. The alloy shows very good stability over 1000 cycles of hydrogen loading and unloading, with 88% of the highest H₂ capacity retained. The cycle-life performance seems to be correlated with residual stresses in the lattice arising due to hydriding; that is, the stresses may be an indicator of structural deterioration upon extended cycling. The desorption pressure of 3.5 bar at room temperature makes it a good candidate for stationary hydrogen storage, the first stage of compressor units, and H₂ supply for soft actuators.

It may be concluded that doping the LaNi₅ alloy with yttrium is a good option with which to tune desorption pressures in the range of 1.4 to 5 bar at room temperature. The pressure range is suitable for stationary storage systems and compressors; however, the alloys seem to be best-suited for soft actuators.



Figure 5. Dependence of the absorption equilibrium pressure on the unit cell volume of the $La_{1-x}Y_xN_{i4.5}Cu_{0.5}$ alloys.

Author Contributions: Conceptualization, Ł.G. and A.T.; methodology, Ł.G., A.T. and A.K.; formal analysis, M.M., A.T., Ł.G. and A.K.; investigation, M.M., A.K., Ł.G., A.L., T.K. and A.N.; resources, Ł.G. and A.T.; data curation, M.M., A.K., Ł.G., A.L., T.K. and A.N.; writing—original draft preparation, M.M. and Ł.G.; writing—review and editing, A.T., A.K. and M.M.; visualization, Ł.G. and M.M.; supervision, Ł.G. and A.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Polish National Agency for Academic Exchange (NAWA) within the Strategic Partnerships Programme, Project No. BPI/PST/2021/1/00023 (project title: Strategic cooperation with Japan in the field of Energy and Environmental Engineering).

Data Availability Statement: The data that support the findings of this study are available from the corresponding author [Ł.G.], upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Ivey, D.G.; Northwood, D.O. Storing energy in metal hydrides: A review of the physical metallurgy. *J. Mater. Sci.* **1983**, *18*, 321–347. [CrossRef]
- Tarasov, B.P.; Fursikov, P.V.; Volodin, A.A.; Bocharnikov, M.S.; Shimkus, Y.Y.; Kashin, A.M.; Yartys, V.A.; Chidziva, S.; Pasupathi, S.; Lototskyy, M.V. Metal hydride hydrogen storage and compression systems for energy storage technologies. *Int. J. Hydrogen Energy* 2021, 46, 13647–13657. [CrossRef]
- Ouyang, L.; Huang, J.; Wang, H.; Liu, J.; Zhu, M. Progress of hydrogen storage alloys for Ni-MH rechargeable power batteries in electric vehicles: A review. *Mater. Chem. Phys.* 2017, 200, 164–178. [CrossRef]
- 4. Notten, P.H.L.; Hokkeling, P. Double-Phase Hydride Forming Compounds: A New Class of Highly Electrocatalytic Materials. J. Electrochem. Soc. 1991, 138, 1877–1885. [CrossRef]
- Lototskyy, M.; Nyamsi, S.N.; Pasupathi, S.; Wærnhus, I.; Vik, A.; Ilea, C.; Yartys, V. A concept of combined cooling, heating and power system utilising solar power and based on reversible solid oxide fuel cell and metal hydrides. *Int. J. Hydrogen Energy* 2018, 43, 18650–18663. [CrossRef]
- Wang, X.; Chen, R.; Zhang, Y.; Chen, C.; Wang, Q. Hydrogen storage alloys for high-pressure suprapure hydrogen compressor. J. Alloys Compd. 2006, 420, 322–325. [CrossRef]

- Modibane, K.D.; Williams, M.; Lototskyy, M.; Davids, M.W.; Klochko, Y.; Pollet, B.G. Poisoning-tolerant metal hydride materials and their application for hydrogen separation from CO₂/CO containing gas mixtures. *Int. J. Hydrogen Energy* 2013, *38*, 9800–9810. [CrossRef]
- 8. Joubert, J.-M.; Paul-Boncour, V.; Cuevas, F.; Zhang, J.; Latroche, M. LaNi₅ related AB5 compounds: Structure, properties and applications. J. Alloys Compd. **2021**, 862, 158163. [CrossRef]
- Mishra, B.; Olson, D.L.; Termsuksawad, P. Sensing of hydrogen in advanced Ni-MH battery materials. Adv. Mater. Energy Convers. II 2004, II, 111–118.
- 10. Ino, S.; Sato, M.; Hosono, M.; Izumi, T. Development of a soft metal hydride actuator using a laminate bellows for rehabilitation systems. *Sens. Actuators B Chem.* 2009, 136, 86–91. [CrossRef]
- Li, K.; Nuchkrua, T.; Zhao, H.; Yuan, Y.; Boonto, S. Learning-based Adaptive Robust Control of Manipulated Pneumatic Artificial Muscle Driven by H₂-based Metal Hydride. In Proceedings of the 2018 IEEE 14th International Conference on Automation Science and Engineering (CASE), Munich, Germany, 20–24 August 2018; p. 8560584.
- Kuijpers, F.A.; van Mal, H.H. Sorption hysteresis in the LaNi₅-H and SmCo₅-H systems. J. Less Common Met. 1971, 23, 395–398. [CrossRef]
- 13. Sakai, T.; Oguro, K.; Miyamura, H.; Kuriyama, N.; Kato, A.; Ishikawa, H.; Iwakura, C. Some factors affecting the cycle lives of LaNi₅-based alloy electrodes of hydrogen batteries. *J. Less Common Met.* **1990**, *161*, 193–202. [CrossRef]
- 14. Liu, J.; Li, K.; Cheng, H.; Yan, K.; Wang, Y.; Liu, Y.; Jin, H.; Zheng, Z. New insights into the hydrogen storage performance degradation and Al functioning mechanism of LaNi_{5-x}Al_x alloys. *Int. J. Hydrogen Energy* **2017**, *42*, 24904–24914. [CrossRef]
- 15. Takeshita, T.; Gschneidner, K.A., Jr.; Lakner, J.F. High pressure hydrogen absorption study on YNi₅, LaPt₅ and ThNi₅. *J. Less Common Met.* **1981**, *78*, P43–P47. [CrossRef]
- 16. Takeshita, T.; Gschneidner, K.A., Jr.; Thome, D.K.; McMasters, O.D. Low-temperature heat-capacity study of Haucke compounds CaNi₅, YNi₅, LaNi₅, and ThNi₅. *Phys. Rev. B* **1980**, *21*, 5636–5641. [CrossRef]
- 17. Mitrokhin, S.; Zotov, T.; Movlaev, E.; Verbetsky, V. Synthesis and properties of AB5-type hydrides at elevated pressures. *J. Alloys Compd.* **2007**, 446–447, 603–605. [CrossRef]
- Spada, F.; Bowman, R.; Cantrell, J. Hydrogen absorption by LaCu₅ and nuclear magnetic resonance (NMR) studies of hydrogen diffusion in β-LaCu₅ hydride. J. Less Common Met. 1987, 129, 261–270. [CrossRef]
- Spodaryk, M.; Gasilova, N.; Züttel, A. Hydrogen storage and electrochemical properties of LaNi_{5-x}Cu_x hydride-forming alloys. J. Alloys Compd. 2019, 775, 175–180. [CrossRef]
- Endrzheevskaya, S.N.; Luk'Yanchikov, V.S.; Shablina, A.G.; Skorokhod, V.V.; Denbnovetskaya, E.N. Reactions of intermetallic compounds of the La-Ni-Cu system with hydrogen and hydrogen-containing gas mixtures. *Powder Metall. Met. Ceram.* 1984, 23, 710–713. [CrossRef]
- Kadir, K.; Sakai, T.; Uehara, I.; Eriksson, L. YCu₃Al₂, an example of an AB5 structure type. *Acta Crystallogr. C* 2001, *57*, 999–1000. [CrossRef]
- CColinet, C.; Pasturel, A.; Percheron-Guégan, A.; Achard, J. Enthalpies of formation and hydrogenation of La(Ni_(1-x)Co_x)₅ compounds. J. Less Common Met. 1987, 134, 109–122. [CrossRef]
- Pasturel, A.; Liautaud, F.; Colinet, C.; Allibert, C.; Percheron-Guégan, A.; Achard, J.C. Thermodynamic study of the LaNi_{5-x}Cu_x system. J. Less Common Met. 1984, 96, 93–97. [CrossRef]
- 24. De Negri, S.; Solokha, P.; Saccone, A.; Pavlyuk, V. Isothermal section of the La-Ni-Zn system from 16.7 to 100 at% La at 400 °C. *Intermetallics* **2008**, *16*, 168–178. [CrossRef]
- Joubert, J.-M.; Charton, J.; Percheron-Guégan, A. Investigation of structural and hydrogen absorption properties in the LaNi_{5-x}Pt_x-H2 system. J. Solid State Chem. 2003, 173, 379–386. [CrossRef]
- 26. Prigent, J.; Joubert, J.-M.; Gupta, M. The phase diagrams of the ternary systems La-Ni-M (M = Re, Ru, Os, Rh, Ir, Pd, Ag, Au) in the La-poor region. *Intermetallics* 2011, *19*, 295–301. [CrossRef]
- 27. Diaz, H.; Percheronguegan, A.; Achard, J.; Chatillon, C.; Mathieu, J. Thermodynamic and structural properties of LaNi_{5-y}Al_y compounds and their related hydrides. *Int. J. Hydrogen Energy* **1979**, *4*, 445–454. [CrossRef]
- Laurencelle, F.; Dehouche, Z.; Goyette, J. Hydrogen sorption cycling performance of LaNi_{4.8}Sn_{0.2}. J. Alloys Compd. 2006, 424, 266–271. [CrossRef]
- 29. Yartys, V.A.; Denys, R.V.; Webb, C.J.; Mæhlen, J.P.; Gray, E.M.; Blach, T.; Isnard, O.; Barnsley, L.C. High pressure in situ diffraction studies of metal–hydrogen systems. *J. Alloys Compd.* **2011**, *509S*, S817–S822. [CrossRef]
- 30. Sastri, M.V.C.; Viswanathan, B.; Murthy, S.S. *Metal hydrides*; Narosa Publishing House: New Delhi, India; Springer: Berlin, Germany, 1998.
- Kumar, E.A.; Maiya, M.P.; Murthy, S.S.; Viswanathan, B. Structural, hydrogen storage and thermodynamic properties of some mischmetal-nickel alloys with partial substitutions for nickel. J. Alloys Compd. 2009, 476, 92–97. [CrossRef]
- 32. Kumar, S.V.; Kumar, E.A.; Maiya, M.P.; Murthy, S.S. Experimental and theoretical studies on static and dynamic pressureconcentration isotherms of MmNi_{5-x}Al_x (x = 0, 0.3, 0.5 and 0.8) hydrides. *Int. J. Hydrogen Energy* **2014**, *39*, 18940–18951.
- Shinar, J.; Shaltiel, D.; Davidov, D.; Grayevsky, A. Hydrogen sorption properties of the La_{1-x}Ca_xNi₅ and La(Ni_{1-x}Cu_x)₅ systems. J. Less Common Met. **1978**, 60, 209–219. [CrossRef]

- Herbrig, K.; Pohlmann, C.; Gondek, Ł.; Figiel, H.; Kardjilov, N.; Hilger, A.; Manke, I.; Banhart, J.; Kieback, B.; Röntzsch, L. Investigations of the structural stability of metal hydride composites by in-situ neutron imaging. *J. Power Source* 2015, 293, 109–118. [CrossRef]
- Heubner, F.; Hilger, A.; Kardjilov, N.; Manke, I.; Kieback, B.; Gondek, Ł.; Banhart, J.; Röntzsch, L. In-operando stress measurement and neutron imaging of metal hydride composites for solid-state hydrogen storage. J. Power Source 2018, 397, 262–270. [CrossRef]
- 36. Available online: https://www.energy.gov/eere/vehicles/articles/us-drive-hydrogen-storage-technical-team-roadmap (accessed on 12 July 2023).
- von Colbe, J.B.; Ares, J.-R.; Barale, J.; Baricco, M.; Buckley, C.; Capurso, G.; Gallandat, N.; Grant, D.M.; Guzik, M.N.; Jacob, I.; et al. Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives. *Int. J. Hydrogen Energy* 2019, 44, 7780–7808. [CrossRef]
- Rodriguez-Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. *Phys. B* 1993, 192, 55–69. [CrossRef]
- Czub, J.; Jamka, W.; Przewoźnik, J.; Zarzecka, A.; Hoser, A.; Wallacher, D.; Grimm, N.; Gondek, Ł. Structural peculiarities in the β phase of the La_{0.75}Ce_{0.25}Ni_{4.8}Al_{0.2} deuterides. *J. Alloys Compd.* **2019**, *788*, 533–540. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.