



Article Hydrogen Gas Phase and Electrochemical Hydriding of $LaNi_{5-x}M_x$ (M = Sn, Co, Al) Alloys

Stanislava Todorova¹, Borislav Abrashev², Vesselina Rangelova¹, Lyuben Mihaylov¹, Evelina Vassileva¹, Konstantin Petrov² and Tony Spassov^{1,*}

- ¹ Faculty of Chemistry and Pharmacy, Sofia University "St. Kl. Ohridski", 1 James Bourchier Blvd., 1164 Sofia, Bulgaria; nhtst@chem.uni-sofia.bg (S.T.); nhtvr@chem.uni-sofia.bg (V.R.); nhtlm@chem.uni-sofia.bg (L.M.); ejvasileva@uni-sofia.bg (E.V.)
- ² Institute of Electrochemistry and Energy Systems "Academician Evgeni Budevski", Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria; babrashev@iees.bas.bg (B.A.); k.petrov@iees.bas.bg (K.P.)
- * Correspondence: tspassov@chem.uni-sofia.bg

Abstract: Hydriding/dehydriding properties of a series of LaNi₅ based alloys were compared by applying both hydrogen gas phase and electrochemical hydrogen charge/discharge methods. The highest hydrogen absorption capacity of 1.4 wt.% H₂ was found for LaNi_{4.3}Co_{0.4}Al_{0.3}, although LaNi_{4.8}Sn_{0.2} also reveals comparable hydrogen capacity (>1.3%). A significant difference in the hydriding kinetics was observed for all studied alloys before and after activation. The activated alloys (5 cycles at 65 °C, 40 atm. H₂) reach their maximum capacities after less than a minute, whereas the pure LaNi₅ alloy needs several minutes for complete hydriding. The electrochemical hydriding/dehydriding behavior of the alloys reveals superior performance of LaNi_{4.8}Sn_{0.2} decreases by only 10% for 60 charge/discharge cycles at a current density of 100 mA/g. Good agreement between the hydrogen sorption kinetics of the alloys obtained electrochemically and from hydrogen gas phase has also been observed.

Keywords: LaNi5 alloys; hydrogen capacity; hydriding kinetics; cycle life; Ni-MH batteries

1. Introduction

Intermetallic compounds based on LaNi₅ are still a fundamental and applied research interest, as they can be used as materials for hydrogen storage both in gas storage tanks and as anodes in Ni-MH batteries [1–3]. The performance of such devices is strongly dependent on the reversible storage capacity of the material used as storage media. The main drawback of alloys based on LaNi₅ is their low hydrogen storage density, which is the reason why Li-ion batteries became dominant over the last years in portable electronic devices and rechargeable batteries for electric and hybrid vehicles. Despite this, researchers are still interested in anode material improvement because Ni–MH batteries have lower prices, high charge/discharge rates and are safer in regards to overheating [4,5].

A popular approach for improvement of LaNi₅ performance is a substitution of La by Mm and Ni by different metals like Al, Cr, Mn, Co, Fe, Sn, Cu, etc. The substitution of La by Mm contributes most to the price of the final product without compromising the electrochemical characteristics, while partial substitution of Ni in the crystal lattice was shown to significantly improve the performance of the alloy [5]. Co, Al and Mn are known to increase the cell volume, decrease the volume expansion upon hydriding and decrease the corrosion rate, thus leading to higher electrochemical capacity and improved cycle life [6,7]. These elements are the most commonly used ones for substitution of Ni in commercial alloys for Ni–MH batteries [8]. In gas storage, Co, Al and Mn have a positive effect as well—the increased unit cell volume leads to decreased plateau pressure and



Citation: Todorova, S.; Abrashev, B.; Rangelova, V.; Mihaylov, L.; Vassileva, E.; Petrov, K.; Spassov, T. Hydrogen Gas Phase and Electrochemical Hydriding of LaNi_{5-x} M_x (M = Sn, Co, Al) Alloys. *Materials* **2021**, *14*, 14. https://dx.doi.org/10.3390/ma1401 0014

Received: 20 November 2020 Accepted: 16 December 2020 Published: 22 December 2020

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Copyright: © 2020 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/). increased hydride stability [9–11]. Another element that is widely used as a substitute for Ni and has a very good effect of hydrogen storage properties of LaNi₅ is Sn. Typical alloys that have been studied are represented by the general formula LaNi_{4-x}Sn_x, where x varies in the range $0 \le x \le 0.5$ [12–15]. The effect of tin addition was first evaluated for gas storage, showing that the prepared alloys have a larger unit cell volume compared to LaNi₅ and a significant decrease of the plateau pressure which enhanced hydrogen storage properties [13–15]. It was also noted that improved stability upon an absorption—desorption cycling is proportional to the extent of Ni substitution up to $x \le 0.4$ [14,15]. Electrochemical cycling of Sn substituted alloys shows that the discharge capacity is significantly improved, reaching a maximum value of 300 mA/g in case of LaNi_{4.58}Sn_{0.42}. However, electrochemical discharge values do not show a linear correlation with the Sn content and the discharge capacity values strongly depend on the charge/discharge conditions [12,16].

In recent years, most relevant research studies have on one hand concentrated on the investigation of discharge capacity value performances at elevated temperatures or after thousands of cycles [17] and on the other on a thermodynamic characteristic like ternary or quaternary phase diagrams of the metals included in the alloy and hydrogen [18]. The hydrogen diffusion coefficient is another thermodynamic characteristic that is still of interest and has been studied through different techniques-nuclear magnetic resonance, various electrochemical techniques, neutron scattering or a combination of these [19,20]. Therefore in the present study, we concentrated on the complex characterization of hydrogen capacity and kinetics, both from a hydrogen gas phase as well as electrochemically, for the following alloys for comparison: LaNi_{4.3}Co_{0.4}Al_{0.3}, LaNi_{4.8}Sn_{0.2}, LaNi_{4.7}Sn_{0.3} and LaNi₅. The electrochemical performance of LaNi_{4 3}Co_{0.4}Al_{0.3} was previously studied by K. Giza [21] and showed a high capacity of 310 mA/g. However, there are no data about the electrochemical behavior that occurs during more than 10 cycles and there are no data for the gas phase hydrogenation. It is also of interest to compare the performance of LaNi_{4.3}Co_{0.4}Al_{0.3} to that of Sn substituted alloys, which are known for their very good resistance to cycling both from a gas phase and electrochemically [12,14,15,22–25]. It was shown that optimal content of Sn in LaNi_{5-x}Sn_x is in the range $0.2 \le x \le 0.3$ [24]. In that range, the hydrogenation properties of the alloys have significant differences [12,14]. Therefore, the aim of the present study was to compare them both electrochemically and from a gas phase; moreover, the aim was also to assess alloys with Sn content of exactly 0.3, which have been less commonly studied. The hydrogen diffusion coefficients for these compositions were also determined using potentiostatic discharge conditions and compared to the rather scattered existing values in the literature.

2. Materials and Methods

LaNi₅ based alloys (LaNi₅, LaNi_{4.3}Co_{0.4}Al_{0.3}, LaNi_{4.8}Sn_{0.2} and LaNi_{4.7}Sn_{0.3}) were synthesized by induction melting of the pure metals (purity 99.999%), followed by remelting to achieve chemical homogeneity of the alloys. The amount of the ingots was about 100 g and the melting was realized under vacuum by induction heating at a temperature of 1350–1400 °C. Then the alloys were pulverized by hydriding at 50 °C under 50 bar pure hydrogen atmosphere.

The structure and microstructure of the alloys were studied using X-ray diffraction (XRD) with Cu-K_{α} radiation and the morphology and size of the powders particles were characterized using scanning electron microscope JEOL 5510 (Jeol Ltd., Tokyo, Japan). ImageJ 1.53b software was applied to obtain the particles size distribution.

Hydrogen sorption kinetic curves of the samples were measured by a home-made Sieverts'-type apparatus at room temperature (20 °C maintained by thermostat and at a constant pressure of 10 and 40 atm H₂). The total volume of the device was 0.35 L and the sample weight was about 300 mg. The precision of the pressure sensor was 0.01%. The kinetic curves presented in the study were obtained after the five initial hydriding/dehydriding cycles (65 °C, 40 atm H₂) required for the alloys activation.

The electrochemical behavior of the alloys during charge/discharge cycling was studied using a three electrode cell. The working electrode was prepared using 100 mg of the synthesized materials, 70 mg of teflonized carbon and 0.5 mL of heptane. The mixture was pressed at about 150 atm. to form the electrode and then dried in air. NiOOH/Ni(OH)₂ was used as a counter electrode and Ag/AgCl was used as a reference. Each electrode was charged for 6 h at 5 mA and discharged to 500 mV at 2 mA in a water solution of 6 mol/dm³ KOH (Sigma Aldrich, Product number 30603). Additionally, a higher current density of 10 mA of charge and discharge was applied during the cycling stability test for all alloys.

To determine the hydrogen diffusion coefficient in the LaNi₅ alloys, first the samples were fully hydrided under galvanostatic conditions. Then, the hydrogen charged samples were discharged at potentiostatic conditions (900 mV) in the same electrolyte. The discharge potential was selected to correspond to the discharge potential plateau from the galvanostatic charge/discharge experiments.

3. Results and Discussion

3.1. Alloys Morphology and Microstructure

X-ray diffraction analysis revealed the same hexagonal CaCu₅ type structure of all LaNi₅ based alloys studied, as shown in Figure 1. The shift of the diffraction peaks maximums to lower diffraction angles was due to the alloying and was more pronounced when Ni was partially substituted for by Sn, due to the larger size of the tin atom compared to the nickel atom. Table 1 shows the XRD results for the alloys, including the lattice constants, cell volume and Atomic Radius Factor (calculated according to [26]). It was seen that the crystal lattice volume increases with the addition of all metals substituting for Ni in LaNi₅. Judging by the width and intensity of the diffraction peaks, the alloys that were assessed also have a similar microstructure (crystallite size, strain) except for LaNi_{4.7}Sn_{0.3}, which is characterized with noticeably finer crystallites that have an average size of about 35 nm (according to Scherrer's method).



Figure 1. X-ray diffraction (XRD) patterns of the studied LaNi₅ based alloys (Cu-Kα radiation).

Alloy	Lattice Parameters, Å		C. 11 M. L	Atomic Radius Factor
	a	с	Cell volume, A	(According to [18])
LaNi ₅	4.982	4.008	86.14	870
LaNi _{4.8} Sn _{0.2}	5.032	3.981	87.31	872
LaNi _{4.7} Sn _{0.3}	5.042	4.039	88.91	873
LaNi _{4.3} Co _{0.4} Al _{0.3}	5.018	4.019	87.65	867

Table 1. Experimentally determined lattice parameters, the crystal cell volume and the Atomic Radius Factor for LaNi₅ based alloys.

The alloys' powders did not show any major impacts on the particles' morphology and sizes as well, as shown in Figure 2. Particles with an average size of 18–20 μ m and an irregular shape occurred for all of the compositions that were assessed. The size distributions were relatively broad, including particles varying from several micrometers to 100 μ m, as shown in Figure 2 (insets). At higher magnifications, particle cracks were also clearly observed. The cracks could be better detected on the larger particles (>100 μ m), which obviously failed to fully fragment during the initial pulverization treatment (which is described in the experimental section). However, such particles were not commonly found in the powder samples and needed to be sought for this purpose.



(a)

Figure 2. Cont.



(b)



(c)

Figure 2. Cont.



Figure 2. Scanning electron microscopy micrographs of LaNi₅ based alloys and particle size distribution histograms, (**a**) LaNi₅; (**b**) LaNi_{4.3}Co_{0.4}Al_{0.3}; (**c**) LaNi_{4.8}Sn_{0.2}; (**d**) LaNi_{4.3}Sn_{0.3}.

3.2. Hydrogen Gas Phase Absorption

Initially, the hydrogen sorption properties of the alloys (LaNi_{4.3}Co_{0.4}Al_{0.3}, LaNi_{4.8}Sn_{0.2}, LaNi_{4.7}Sn_{0.3}) were studied during a hydrogen gas phase and were compared to pure LaNi₅. Figure 3 shows hydrogen absorption curves at a pressure of 10 atm. and at room temperature (20 °C) after initial activation of the alloys (5 absorption/desorption cycles at 65 °C). In practice under these conditions, all of the studied compositions, except for LaNi₅, reached their maximum capacity after less than a minute. The absorption kinetic curves were fully reproducible after the initial alloys activation. The maximum hydriding capacity of a given alloy measured in 3 consecutive absorption experiments differed in the range of only +/-5%. However, it is necessary to point out that the same alloys revealed much slower absorption kinetics prior to activation (see Figure 3b). It is commonly known that generally, the creation of a high density of defects such as planar defects (stacking faults), dislocations, point defects or compositional fluctuations [27], is the major mechanism for the activation of the hydriding process in hydrogen storage alloys. For LaNi₅, it was proven that after the initial activation cycles, the creation of planar defects in the alloy enhances hydrogen diffusion and assists with the subsequent transition of the α -phase to the hydride on later hydriding cycles.

It is obvious that compared to the binary LaNi₅, all alloys in the present study revealed substantial improvement of the hydrogen sorption kinetics and capacity. The LaNi_{4.3}Co_{0.4}Al_{0.3} alloy achieved maximum capacity (1.4 wt.% hydrogen) faster than the other alloys, followed by LaNi_{4.8}Sn_{0.2} and LaNi_{4.7}Sn_{0.3}. Similar hydrogen absorption capacities, decreasing from 1.35 wt.% to 0.95 wt.% with an increasing Sn content, were obtained by other authors for LaNi_{5-x}Sn_x ($0 \le x \le 0.5$) alloys [28]. The increased observed hydrogen storage capacity of the alloys compared to pure LaNi₅ was an expected consequence of the increased lattice volume as a result of the alloying elements [26]. Furthermore, when

using the dependence of the plateau pressure of hydrogen sorption on the atomic radius factor for LaNi₅ alloys [26], one could get an idea of the plateau pressure of the alloys in the present study, which is about 0.01 MPa for LaNi_{4.3}Co_{0.4}Al_{0.3}. The data available in the literature related to the hydriding kinetics of similar alloys vary in a large range, from a few minutes to half an hour, to reach a full capacity of the alloy [14,28,29]. These differences were mainly due to the variances in the microstructure (defects, grain size) of the materials. In our study, as a result of using a similar alloys composition and identical preparation method, these differences were small, which allowed for correct comparison of the alloy hydrogen sorption properties.



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Figure 3. Hydrogen absorption kinetic curves of the activated LaNi₅ based alloys (20 °C, 10 atm) (**a**); and before activation (**b**).

3.3. Electrochemical Hydriding

The electrochemical hydrogen charge/discharge behavior of the alloys studied was also compared. Figure 4 shows the first 10 cycles at a current density of 50 mA/g during the charge process and 20 mA/g during the discharge process. The potential of the working electrode (Uw) as a function of time dependences showed that during the charge process, the metal hydride electrode potential for LaNi4.3Co0.4Al0.3 changed from 1.17 V to 1.13 V (vs. Ag/AgCl), approaching that of pure LaNi₅. Similarly, the discharge curve of LaNi_{4.3}Co_{0.4}Al_{0.3} shifted to higher potential levels as a result of cycling. Both effects were due to the initial activation of the alloy. This was also clearly observed from the determined discharge capacities during cycling. For the Sn-containing alloys, both the charge and discharge potentials were close and correspond to those of LaNi₅. The most evident and important difference however was associated with the hydrogen discharge capacity of the electrodes prepared from the different alloys, as can be seen in Figure 5. Among the studied alloys, only LaNi₄ $_{3}Co_{0,4}Al_{0,3}$ needed an initial (3–5 cycles) activation before reaching its maximum capacity of about 260 mA/g, which could be explained by an increase in the surface area of the electrode and surface activation during the initial charge/discharge cycles. Similar behavior for this alloy was also observed by Giza [21], as his study was limited to 10 charge/discharge cycles only. As can be seen further in this article, the high capacity achieved for LaNi_{4.3}Co_{0.4}Al_{0.3} remained stable long after 10 hydriding/dehydriding cycles were completed. The alloys with Sn also showed clearly improved capacity compared to pure LaNi₅, as at this low discharge current density (20 mA/g), the sample with higher Sn content (LaNi_{4.7}Sn_{0.3}) slightly exceeded the capacity of LaNi_{4.8}Sn_{0.2}. The observed substantially higher discharge capacity of the Ni-substituted LaNi₅ based alloys compared to pure LaNi₅ could also be attributed to the increased crystal cell volume as a result of the alloying. It is worth noting that the electrochemical discharge capacities of the alloys corresponded as a trend (except for LaNi_{4.7}Sn_{0.3}) to the hydrogen absorption capacities measured in the hydrogen gas phase.

Figure 6 summarizes the maximum hydrogen capacities measured by the two techniques used: the hydrogen gas phase and electrochemical hydriding. The lines corresponded to the theoretical capacities with a different hydrogen content for the alloys. It is noteworthy that the capacities determined by the gas phase hydriding were slightly higher than those that were determined electrochemically. Obviously, the electrochemical method fails to fully charge the alloys, which is not surprising due to the complex structure of the electrode, including electrode components that could partially block the surface of the active material particles.

Due to the practical importance of the LaNi₅ based alloys used for the preparation of metal hydride electrodes in Ni–MH batteries, it was necessary to study their stability during multiple charge/discharge cycling. Figure 7 presents 60 charge/discharge cycles, measured at higher current densities (100 mA/g) of the charge and discharge process.

As can be seen from the cycling stability tests, all LaNi₅ based alloys in this study revealed stable capacities during 60 cycles. They remained in the range of 175–200 mA/g for the alloyed LaNi₅ based compounds. The alloys LaNi_{4.3}Co_{0.4}Al_{0.3} and LaNi_{4.8}Sn_{0.2} showed the best cycling performance, retaining a relatively high discharge capacity of above 170 mA/g after 60 cycles. It is important to note that at higher current densities of charge and discharge (100 mA/g), the alloy with lower Sn content revealed a higher discharge capacity and a better cycle life compared to LaNi_{4.7}Sn_{0.3} and the opposite was observed at a low current density (20 mA/g). This result, however, corresponds to a previous study on the electrochemical hydriding of LaNi_{5–x}Sn_x (0 ≤ x ≤0.5), where it was shown that the relationship between the electrochemical discharge capacity and Sn content is not linear and strongly depends on the charge/discharge conditions [12].



Figure 4. First 10 cycles for LaNi₅ based alloys at current density of 5 mA during charge and 2 mA during the discharge. LaNi_{4.3}Co_{0.4}Al_{0.3} (black) and LaNi₅ (gray) (**a**). LaNi_{4.8}Sn_{0.2} (black) and LaNi_{4.7}Sn_{0.3} (gray) (**b**).



Figure 5. Discharge capacities vs. the cycle number for the alloys studied at a current density of 50 mA/g during the charge period and 20 mA/g during the discharge period.



Figure 6. Hydrogen capacity as a function of the hydrogen content of the different alloys. The points correspond to the maximum alloys capacities measured by the two techniques—an electrochemical (\blacksquare in the corresponding color) and a hydrogen gas phase (\blacktriangle).



Figure 7. Discharge vs. cycle number curves for the alloys studied at a current density of 100 mA/g during charge and discharge.

These same (or very similar) discharge capacities measured at different current densities prove that a relatively high hydrogen diffusivity was present in the alloys studied, i.e., a clear indication of the lack of transport difficulties during hydrogen discharge. Independent measurements, based on a potentiostatic discharge of preliminary fully hydrogen-charged samples, were carried out to give additional evidence for the last observation and a quantitative assessment of hydrogen diffusivity.

Figure 8 compares hydrogen discharge curves of $\text{LaNi}_{5-x}M_x$ (M = Co, Al, Sn) alloys in coordinates "lg(J_H) vs. discharge time t". Thus, using the following approximation for the current density [30]:

$$\lg(J_H) = \lg[+\frac{6FD_H}{da^2}(C_o - C_s)] - \frac{\pi^2 D_H t}{2.303a^2}$$
(1)

the diffusion coefficients of hydrogen D_H into the LaNi₅ based alloys were determined. In this equation, J_H is the current density, t is the discharge time, a is the size of the particles (average particle size, which is in the range of 20–25 µm for the alloys studied), d is the density of the alloy, C_o is the initial hydrogen concentration and C_s is the hydrogen concentration after the electrode is anodically biased. From the slope of the plot "lg(J_H) vs. t", Figure 8, hydrogen diffusion coefficients for the LaNi₅ based alloys were determined, as seen in Table 2. The D_H values estimated for pure LaNi₅ and for the alloyed compounds were close to those obtained for similar alloys, which were usually in the range $10^{-8}-10^{-11}$ cm²·s⁻¹ [19,20,30–33]. It is worth mentioning that these values often significantly differed mainly due to the application of different methods for their assessment and because of the differences in the alloy microstructure (defects, grain size, etc.). In the present work, we compared the D_H values of alloys with a similar microstructure that were obtained at the same experimental conditions of potentiostatic discharge, therefore the comparison could be considered as being reliable. Thus, it can be concluded that the diffusion coefficients of all studied alloys were higher than that of the pure LaNi₅, as for LaNi_{4.3}Co_{0.4}Al_{0.3}, the diffusion coefficient D_H was one order of magnitude higher compared to LaNi₅. The higher hydrogen diffusion coefficients of the alloys compared to the pure LaNi₅ was in good agreement with the trend in the kinetic curves of hydrogen absorption as well.



Figure 8. " $lg(J_H)$ vs. discharge time t" during potentiostatic discharge of LaNi₅ type alloys.

Alloy	LaNi ₅	LaNi _{4.8} Sn _{0.2}	LaNi _{4.7} Sn _{0.3}	LaNi _{4.3} Co _{0.4} Al _{0.3}
$D_H \text{ (cm}^2/\text{s)}$	$2.8 imes10^{-11}$	$8.8 imes 10^{-11}$	$1.1 imes 10^{-10}$	$3.3 imes 10^{-10}$

 Table 2. Hydrogen diffusion coefficients for the LaNi₅ based alloys.

The experimental results obtained in the study allowed a rough estimation of the time for complete hydrogenation of the alloys. Applying the Einstein diffusion equation (diffusion distance (x) $x^2 = 2 \cdot D_H \cdot t$) and using the hydrogen diffusion coefficients D_H (Table 2) and the average particle size (Figure 2), for LaNi_{4.3}Co_{0.4}Al_{0.3}, this time was found to be about 5 min, while for LaNi₅ it was more than 30 min. These values are higher than those experimentally determined by the gas phase absorption but confirmed the significantly improved hydrogen sorption kinetics of the Ni-substituted LaNi₅.

4. Conclusions

Hydrogen storage capacity, hydriding kinetics, cycle stability and hydrogen diffusivity of three LaNi₅ based alloys (LaNi_{4.3}Co_{0.4}Al_{0.3}, LaNi_{4.8}Sn_{0.2}, LaNi_{4.7}Sn_{0.3}) were studied and compared to pure LaNi₅. Among the alloys that were studied, LaNi_{4.3}Co_{0.4}Al_{0.3} showed the highest hydrogen gas phase capacity (1.4 wt.%) and electrochemical discharge capacity of 260 mA/g, which remained above 180 mA/g after 60 charge/discharge cycles at a current density of 100 mA/g. A significantly improved discharge capacity of LaNi_{4.8}Sn_{0.2} was also observed, as this alloy revealed the highest cycling stability among the alloys

studied with a capacity decrease of only 10% for 60 charge/discharge cycles. The hydrogen absorption kinetics of the Ni-substituted compositions was also found to be significantly improved compared to pure LaNi₅. The determined hydrogen diffusion coefficients for all Ni-substituted alloys were higher than that of pure LaNi₅; as for LaNi_{4.3}Co_{0.4}Al_{0.3}, the hydrogen diffusion was an order of magnitude faster than in LaNi₅. Good agreement was obtained between the hydrogen sorption kinetics determined by the gas phase analysis and that attained by electrochemical methods. In summary, among the LaNi₅ based alloys in the present study, the best combination of hydrogen storage properties was found for LaNi_{4.8}Sn_{0.2}—high gas phase sorption capacity, electrochemical capacity and charge/discharge cycle life.

Author Contributions: T.S.: Conceptualization, Investigation, Validation, Formal analysis, Writing original draft, Supervision, Project administration. S.T.: Investigation, Formal analysis, Methodology, Writing—review & editing. B.A.: Investigation, Methodology, Visualization. V.R.: Investigation, Writing—review & editing. L.M.: Investigation, Methodology. E.V.: Investigation, Formal analysis, data curation. K.P.: Conceptualization, Supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Bulgarian Ministry of Education and Science under the National Research Program E+: Low Carbon Energy for the Transport and Households, grant agreement D01-2014/2018 and European Regional Development Fund within the Operational Programme "Science and Education for Smart Growth 2014–2020" under the Project CoE "National Center of Mechatronics and Clean Technologies" (BG05M2OP001-1.001-0008).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to the lack of such system within the university.

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

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