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EFFECT OF LOW Al CONTENT ON THE ELECTRODE PERFORMANCE OF $LaNi_{5-x}Al_x$ HYDROGEN STORAGE ALLOYS

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ABSTRACT

The influence of low Al concentrations on the hydrogen capacity and cycling life of electrochemically hydrided $LaNi_{5-x}Al_x$ *(x < 0.1) is studied. Two alloys with well-defined composition (determined by EDX and ICP) are characterized microstructurally (XRD, SEM, TEM) and their electrochemical hydriding/dehydriding behavior are studied in a three-electrode electrochemical cell. It is found that small compositional differences do not result in noticeable changes in the* $LaNi_5$ *crystal lattice parameters. The opposite, however, is observed in the alloys' discharge capacity and cycling life. Particularly hydrogen capacity appeared to be very sensitive to small differences in the Al content. Higher capacity is detected for the alloys with lower Al concentration, which is in line with the already known influence of Al in* $LaNi_{5-x}Al_x$ *at higher Al concentrations (x > 0.1). During hydrogen charge/discharge cycling the higher capacity alloy decreases its capacity from 275 mAh* g^{-1}*, reaching 170 mAh* g^{-1} *after 50 cycles. The measured hydrogen diffusion coefficients* $1.2x10^{-11}$ cm^2 s^{-1} *and* $0.7x10^{-11}$ cm^2 s^{-1} *reveal higher value for the alloy with lower Al content.*

Keywords: $LaNi_{5-x}Al_x$, *hydrogen storage, discharge capacity, diffusivity.*

INTRODUCTION

For over thirty years the interest in $LaNi_5$ based materials for negative electrodes in Ni/MH batteries has not diminished. The mechanism of reversible hydrogenation is studied and one of the most successful ways to improve reversible hydrogenation is substituting partially La or Ni or both thus achieving extended battery life and better performance [1 - 4]. Aluminum is one of the elements proved to have such effect when partially substituting Ni. The maximum Al amount used in $LaNi_5$ alloys is 1.25 at. % and the optimal one in combination with other substitution elements, proved to be lower than 0.5 at. % [5]. In commercially used Ni/MH batteries usually, the content of Al in the alloys is 0.3 at. % [2, 6, 7].

Numerous studies have shown clearly that Al leads to larger unit cells and lower Vickers hardness of the alloy, thus stabilizing the crystal structure upon hydrogen absorption and desorption and preventing its degradation [8 - 10]. Thermodynamically there is a clear relationship between the Al content and hydrogenation properties. Higher aluminum content leads to lower plateau pressure even to several orders of magnitude, resulting in the formation of more stable hydrides and corresponding higher enthalpy of formation. However, the negative effect of the aluminum addition shown from gas-phase experiments (lower hydrogen capacity of the $LaNi_{5-x}Al_x$ alloys compared to $LaNi_5$) is still a result that can be neglected because of the positive influence of Al on the overall alloy performance [5, 8, 9, 11 - 13].

Electrochemical cycling experiments show a little bit different relationship between the electrode performance and the Al content. The substitution of Ni for Al was first shown to have a positive effect with the study of

$LaNi_{4.5}Al_{0.5}$, having 348 mAh g^{-1} discharge capacity calculated from the gas phase absorption at 20°C and 1 atm. and 278 mAh g^{-1} discharge capacity determined experimentally [14]. The following tendencies in the electrochemical performance with increasing of the Al content from 0.1 to 1 at. % are clarified: (1) the activation prolongs; (2) the discharge capacity increases up to 0.6 at. % Al then decreases; (3) cycle life becomes longer for all Al concentrations; (4) high-rate dischargeability also has a non-linear behavior being almost constant for Al content higher than 0.4 at. % [2, 14 - 20]. Better performance of the Al substituted alloys, especially better cycle life, is mainly attributed to the stabilized crystal structure which prevents the degradation of the electrodes. The high-rate discharge ability dependence on the exchange current density for the hydrogen evolution process has shown that the rate-determining reaction is the diffusion of hydrogen in the alloy for alloys with Al content higher than 0.4 at. % [14, 21].

$LaNi_{5-x}Al_x$ alloys with Al content lower than 0.1 atomic fraction have been shown to have a sloped pressure plateau for hydrogen sorption/desorption [2]. The pressure scanning calorimetry studies have shown that such effect is contributed to the formation of intermediate β phase - $LaNi_5H_3$ [22] in alloys with a content of Al lower than $x < 0.1$, which have two peaks hydrogen desorption behavior, similar to $LaNi_5$. The Al content higher than 0.1 atomic fraction leads to the disappearance of the peak split and one-step desorption [23 - 25].

Summarizing, the literature review shows some reliable results addressing the influence of Al on the hydrogen capacity, thermodynamics and kinetics of hydriding and cycling stability of $LaNi_{5-x}Al_x$. These data are obtained mainly from a hydrogen gas phase for $LaNi_{5-x}Al_x$ with $x > 0.1$. Therefore, in this work, we have focused on the electrochemical performance (discharge capacity, cycling stability and hydrogen diffusivity) of $LaNi_{5-x}Al_x$ alloys with lower Al content ($x < 0.1$) for which fragmentary information exists, mainly concerning some thermodynamic characteristics.

EXPERIMENTAL

$LaNi_{5-x}Al_x$ alloys were synthesized using induction melting of the pure metals (purity 99.99 % for nickel and aluminum, and min. 99 % for lanthanum), followed by re-melting for homogenization. Pulverization of the samples was performed under 50 bar H_2 pressure and temperature of 50°C. The composition of the alloys was verified using ICP - OES and STEM EDS mapping showing that the initial compositions were preserved during the synthesis procedures.

The phase composition of the alloys was defined by X-Ray diffraction analysis (XRD) using PHILIPS APD-15 diffractometer with Cu Kα radiation. Scanning electron microscopy (HITACHI TM 4000) was used to examine the microstructure and the particle size.

The electrochemical charge-discharge cyclic experiments were performed using a three-electrode cell with Ag/AgCl reference electrode and NiOOH/$Ni(OH)_2$ counter electrode in 6 mol/dm^3 KOH solution. The working electrode was prepared using a mixture of 100 mg active substance, 70 mg teflonized carbon black and 0.2 cm^3 heptane, cold pressed in air at about 155 kg cm^{-2} in a steel press form. The obtained electrode has a shape of a pellet with a diameter of about 16 mm and thickness of 1 mm. It is mounted in a teflon holder with nickel wire current collector. Charge rate of 100 mA g^{-1} and discharge rate of 100 mA g^{-1} were used in all experiments. The hydrogen diffusion coefficient was obtained using potentiostatic discharge experiments at 900 mV of fully charged under galvanostatic conditions electrodes after 16 charge/discharge cycles (ARSTAT 2273 electro-chemical system) [26].

RESULTS AND DISCUSSION

The as-prepared $LaNi_{5-x}Al_x$ alloys reveal a hexagonal $CaCu_5$ type structure with a minor variation in the crystal lattice parameters depending on the Al content, Fig. 1. As it could be expected adding very small amount of Al ($x < 0.1$) in the alloy results in negligible enlargement of the lattice parameters and crystal cell volume, Table 1.

The diffraction peaks in the XRD patterns are not narrow, which indicates a fine microstructure of the $LaNi_5$-based alloys. The latter is also confirmed by the TEM analysis of the alloys, composed by crystallites noticeably smaller than a micrometer. Fig. 2 shows a high-resolution TEM image of $LaNi_{4.92}Al_{0.08}$, which is typical for both alloys.

Similar to the structural identity of the two alloys studied, the particle size and morphology of the alloys' powders are also comparable - average particle size in

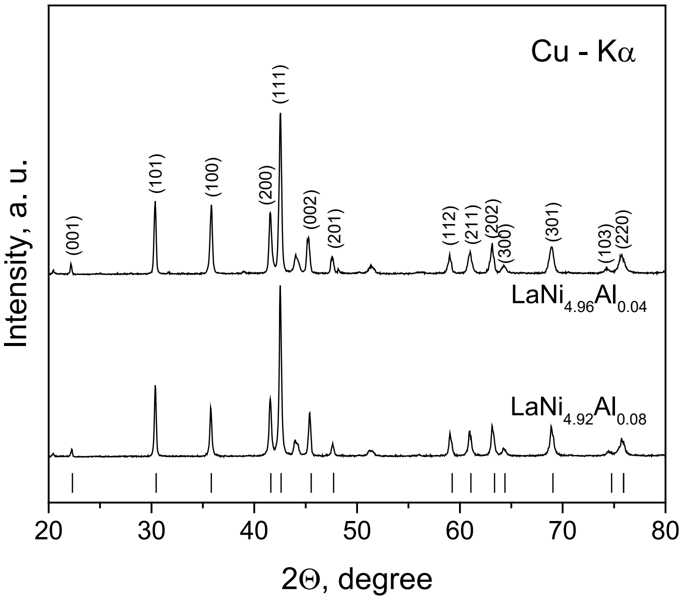

Fig. 1. XRD patterns of the two alloys (bars indicating pure $LaNi_5$ peaks positions).

Table 1. Lattice parameters and cell volume of the $LaNi_{5-x}Al_x$ alloys.

Alloy	Lattice Parameters, Å		Cell Volume, Å^3
	A	C	
$LaNi_5$ [5]	5.0170	3.9860	86.900
$LaNi_{4.96}Al_{0.04}$	5.0096	4.0083	87.112
$LaNi_{4.92}Al_{0.08}$	5.0190	4.0010	87.280

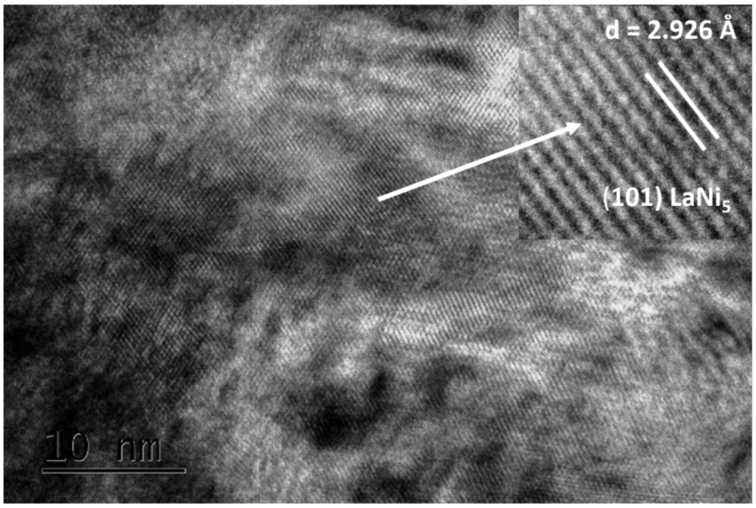

Fig. 2. High-resolution transmission electron microscopy (HRTEM) image for $LaNi_{4.92}Al_{0.08}$.

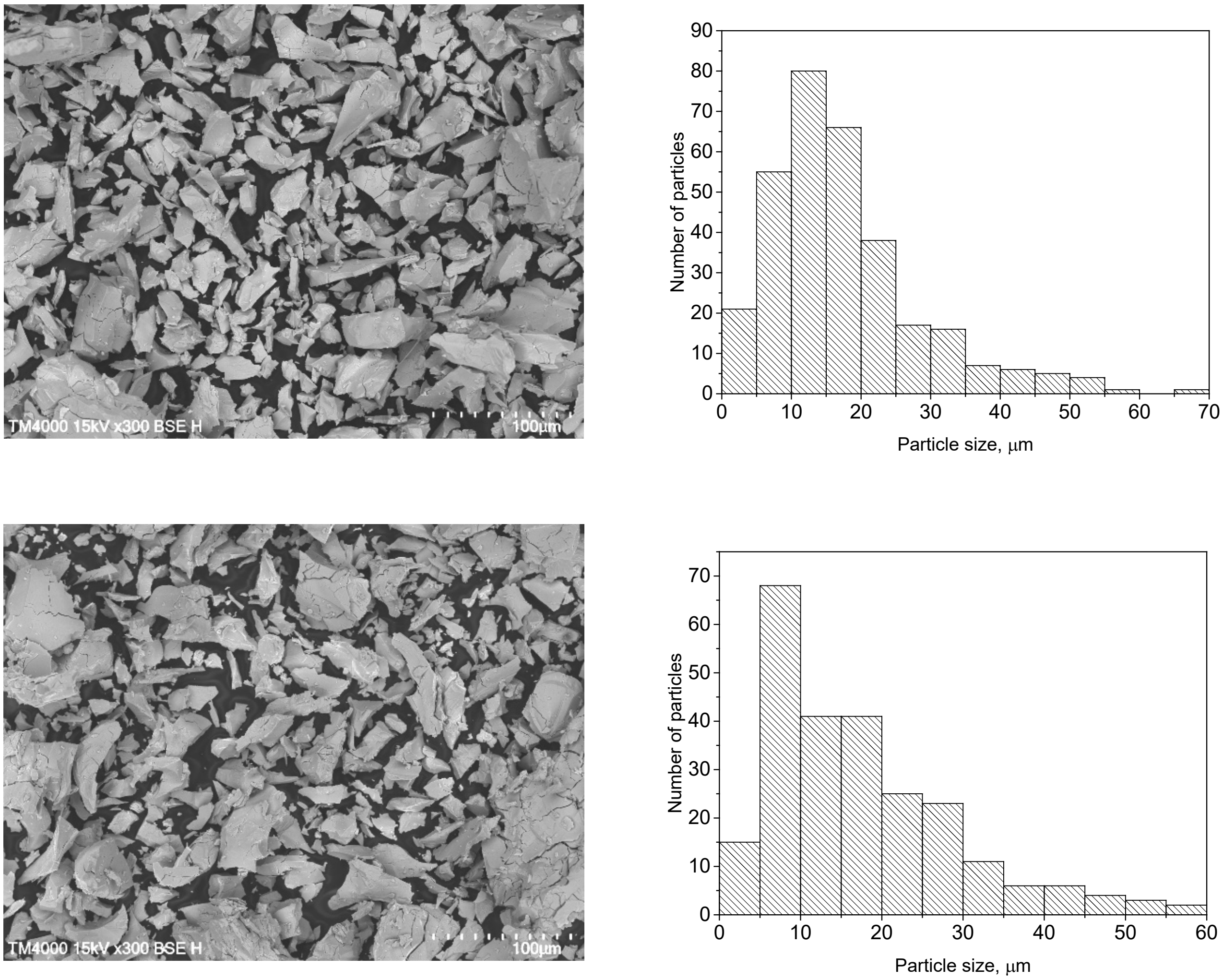

Fig. 3. SEM micrographs with particle size distribution of $LaNi_{4.96}Al_{0.04}$ (a) and $LaNi_{4.92}Al_{0.08}$ (b).

the range 10 - 15 μm, presence of surface microcracks, visible on the larger particles' surface, Fig.3. The cracks, result of decrepitation process during alloy synthesis, are considered to have a favorable effect on the hydriding and dehydriding kinetics.

STEM/EDX chemical microanalysis proved the Al content of the as-produced alloys and the average composition, obtained from 5 different sample sites, is shown in Table 2. Due to the low Al content it was necessary to verify its concentration by ICP-OES as well. Thus, the summary content of Al in the two $LaNi_{5-x}Al_x$ alloys were determined to be x = 0.04 and 0.08

Table 2. Data from STEM/EDS chemical microanalysis of $LaNi_{5-x}Al_x$ alloys composition.

	At. %	x
Al	0.6	0.04
	1.4	0.08
Ni	82.4	4.95
	82.0	4.92
La	17.0	1.02
	16.6	1.00

Electrochemical hydrogen charge/discharge experiments at a current density of 100 mA g^{-1} were carried out to determine the discharge capacity and cycling stability of the electrodes prepared form the two $LaNi_{5-x}Al_x$ (x = 0.04 and 0.08) alloys. Figs. 4(a) and 4(b) show typical discharge curves, obtained after the alloys activation and Fig. 4(c) presents the discharge capacities as a function of the cycle number. Maximum capacity of about 275 mAh g^{-1} is observed for the alloy with very small Al content, which decrease to 180 mAh g^{-1}after 50 cycles, whereas the electrode from the $LaNi_{4.92}Al_{0.08}$ alloy reveals maximum capacity of 200 mAh g^{-1} declining to 130 mAh g^{-1} after 20 cycles, then staying nearly constant up to 50 cycles. Comparable discharge capacity values for $LaNi_{5-x}Al_x$ in the range 200 - 300 mAh g^{-1} can be found in some earlier works as well [27, 28]. The available discharge capacity values for pure $LaNi_5$ vary, with some of the highest not exceeding 200 mAh g^{-1} [29 - 31]. Furthermore, a decrease of capacity is already demonstrated at higher Al content in this type of alloys, explained with the occupation of a larger space of the Al atoms in the $LaNi_5$ crystal lattice [31]. The new result in the present study reveals that even at very low Al content in the alloy its deteriorating effect on the discharge capacity is clearly manifested as well. At the same time, the positive effect on the cycling stability could not be noticeably observed at these low Al concentrations, although it was reliably proven at higher Al amount (x > 0.1) during gas phase hydrogenation of $LaNi_{5-x}Al_x$ [8 - 10].

The discharge electrodes potentials measured after alloys activation (Fig. 4) could be converted into hydrogen pressure, following the relationship between U and p(H_2) for the metal hydride electrode in 6 M KOH at 293 K and pressure 1 atm. [33, 34]:

$$E\ (V\ vs\ Hg/HgO) = -\ 0.932 - 0.0296.\log\ (p_{H_2})$$

The equilibrium discharge pressures (0.1 atm. for $LaNi_{4.96}Al_{0.04}$ and 1.4 for $LaNi_{4.92}Al_{0.08}$), obtained from the electrochemical experiments, agree well with those measured from the gas phase hydriding/dehydriding isotherms for $LaNi_5$ [35 - 37].

According to a method described in [28, 38], which is based on the jump in the potential (ΔE) during current switching between hydrogen charge and discharge (see Figs. 4(a,b), the exchange current density i_0 of the H_2O/H_2 system for the two alloys could be determined:

$$\log i^0_{H_2O/H_2} = \frac{1}{2}\log(i_a|i_c|) - \frac{\Delta E}{2b}$$

where i_c is charge current density, i_a - discharge current density and b - slope coefficient of Tafel lines (b=0.12 V in alkaline water solutions).

The two alloys revealed slightly different i_0 for the 50th charge/discharge cycle: 51 mA g^{-1} for $LaNi_{4.96}Al_{0.04}$ and 66 mA g^{-1} for $LaNi_{4.92}Al_{0.08}$. These values for i_0 are very similar to the exchange current density measured for pure $LaNi_5$, 63 mA g^{-1} [29]. As it could be expected the i_0 measured before alloys activation show lower values: 37 mA g^{-1} and 47 mA g^{-1} for $LaNi_{4.96}Al_{0.04}$ and $LaNi_{4.92}Al_{0.08}$, respectively. These results indicate the very similar performance of the two alloys regarding the charge transfer kinetics at the electrode/electrolyte interface in the course of charge/discharge cycling.

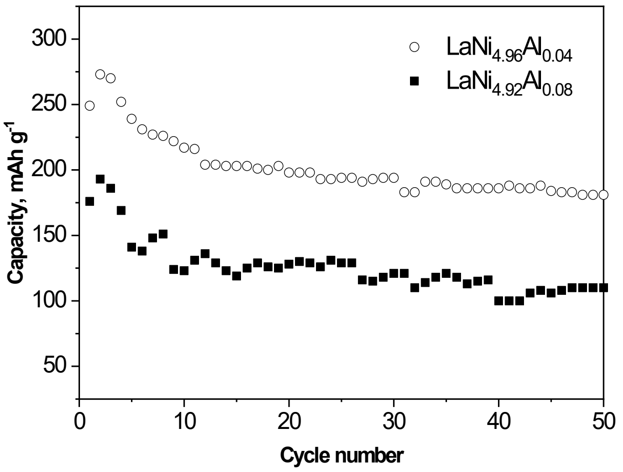

Fig. 4. Discharge capacities vs. cycle number for both alloys.

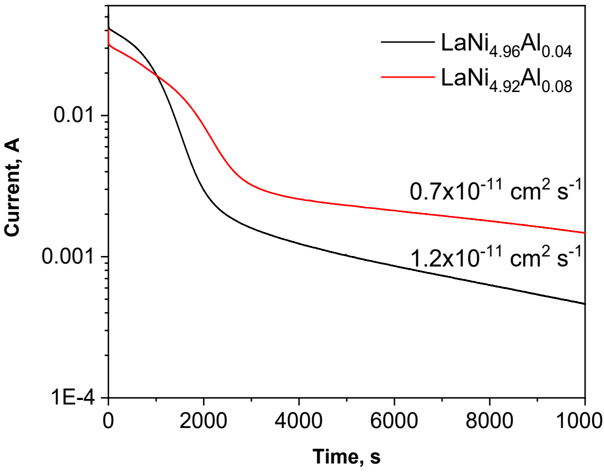

Fig. 5. Current vs. time during H discharge of $LaNi_{5-x}Al_x$ alloys.

The kinetics of $LaNi_5$ hydriding/dehydriding is another important issue, which is influenced by the partial replacement of Ni with Al. Gas phase experiments showed that Al leads to an increase in the activating energy and a decrease in the rate constant of hydrogenation, i.e. to deterioration of the $LaNi_{5-x}Al_x$

hydrogenation kinetics [8, 11, 12]. Therefore, in the present study we tried to prove if hydrogen transport difficulties could be the reason for the poorer hydriding kinetics when replacing Al for Ni in $LaNi_5$. Hence, the fully hydrided samples were potentiostatically discharged, Fig. 5, and the diffusion coefficients of hydrogen, D_H, are calculated according to a methodology described by Zheng et al., using mean particle size (diameter) of 15 μm for the both alloys (Fig. 3) [26].

The D_H values ($0.7x10^{-11}$ cm^2 s^{-1} and $1.2x10^{-11}$ cm^2 s^{-1}) are obtained at the later stage of discharge, in which hydrogen atoms diffuse from the depth of the electrode and correspond to the actual volume diffusion coefficients. Similar hydrogen diffusion coefficients were determined for pure $LaNi_5$ as well [31, 39]. Although the as-determined D_H values for the two alloys studied are not very different, still the diffusion coefficient for the alloy with higher Al content is about two times lower. Compared to the diffusion coefficients of hydrogen in $LaNi_{5-x}Al_x$ at higher Al content ($x > 0.1$) our D_H show quite similar values [39, 40].

Based on the available studies concerning the influence of Al on the thermodynamics and kinetics of hydrogen sorption and hydrogen capacity of $LaNi_{5-x}Al_x$, measured by gas phase and electrochemical methods, we can not reliably explain the fact that even small amounts of Al ($x < 0.1$) have noticeable influence on the alloy hydrogen capacity. However, the existing results suggest that the presence of Al may affect the sites that hydrogen atoms occupy in the crystal lattice of the alloy, both in terms of energy and number. A similar improvement of hydrogen storage capacity in $LaNi_5$ through substituting Ni by small amounts of Fe has also been reported previously [41].

CONCLUSIONS

$LaNi_{5-x}Al_x$ ($x = 0.04$ and 0.08) alloys were investigated as negative electrodes in Ni/MH batteries. The effect of very low Al content ($x < 0.1$) on the hydrogen discharge capacity, cycling life, and hydrogen diffusivity was especially considered. Generally, the already established tendency at higher Al concentrations ($0.1 < x < 1.0$) revealing a clear decrease of capacity with the Al addition increase, obtained from a hydrogen gas phase, was also followed during the electrochemical charge/discharge in the present study. It was shown that even a small increase in the Al content (from $x = 0.04$ to $x = 0.08$) results in noticeable reduction of the discharge capacity. The lower hydrogen diffusion coefficient, D_H, for the alloy with higher Al content was also evaluated. The D_H values ($0.7x10^{-11}$ cm^2 s^{-1} and $1.2x10^{-11}$ cm^2 s^{-1}) determined in the present study are comparable to those for $LaNi_{5-x}Al_x$ at higher Al content ($x > 0.1$) and about two orders of magnitude lower than D_H in pure $LaNi_5$.

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