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# Al-Substituted $AB_5$-Type Intermetallics for Reversible Hydrogen Storage and Electrochemical Applications

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**Abstract**—The work summarizes research of La(Ni,Al) intermetallic compounds' hydrogen sorption and electrochemical properties. A number of analytic methods was applied. It is shown that the maximum capacity of electrodes with La(Ni,Al) composition reaches 321 mA h/g, straight correlation between gaseous and electrochemical capacity has been found. Accordance of compounds to Haucke-type structure has been verified by XRD and SEM methods.

**Keywords:** $LaNi_5$, hydrogen, intermetallic compounds, hydrogen sorption, electrochemical hydrogenation, Ni-MH power source, polymer electrolyte, intermetallic substitution

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## INTRODUCTION

The $LaNi_5$ compound is widely used as hydrogen storage material, as well as the negative electrode material in nickel-metal hydride power source systems [1]. This material shows a high storage capacity and fast electrochemical activation, high long-term cycling stability and high resistance to degradation in high rate discharge processes. $AB_5$-type intermetallic compounds form $CaCu_5$ hexagonal structures, known as Haucke phases. $LaNi_5$, the most researched and investigated one, forms $LaNi_5H_x$ hydrides (with x up to the value more than 6) with the highest known amount of hydrogen per lattice unit. However, it relates to comparatively low mass amount of hydrogen (around 1.5%), due to the high molar mass, and theoretical electrochemical capacity of 372 mA h/g which makes it a suitable material for Ni-MH power sources.

Main known disadvantages are the structure destructibility while cycling and limited capacity. Various properties can be modified by partial replacing atoms in the crystal lattice. According to the earlier reports, $LaNi_{4.1}Co_{0.3}Mn_{0.3}Al_{0.3}$ and $LaNi_{4.5}Co_{0.25}Al_{0.25}$ compounds [2, 3] show increased cycling stability (93.6 and 99.1%) alongside the reduced capacity by less than 20%. Some works describe the influence of nickel substitution by aluminum [3–6], however the electrochemical properties of those are insufficiently studied and most of the data is disorganized. In current research the hydrogen sorption properties and electrochemical characteristics of $LaNi_{5-x}Al_x$ ($x$ = 0...1) compound series have been studied.

## EXPERIMENTAL DETAILS

The samples were prepared by electric-arc melting and annealing at 1173°C. The purity of the initial components was at least 99.9 wt %. The compounds annealed were later milled to the 40–60 μm particle size for further investigations, apart from the bigger particles used for the scanning electron microscopy (SEM). SEM analysis was carried out with Tescan Vega II XMU microscope, registration parameters: 20 kV voltage, 0.2–1 nA electron consumption rate, registration time—70 s for quantitative analysis and 30 min for X-ray imaging. The powders were examined by X-Ray diffraction (XRD) analysis, with Cu Ka radiation (λ = 1.5418 Å). For hydrogen adsorption-desorption analysis the thermostated Sieverts apparatus was used, with hydrogen purity 99.999%. Electrochemical measurements were concluded with Elins P20X8 potentiostat-galvanostat in 3-electrode cell with the compound powder mixed with Ni particles of the same size in 1 : 4 ratio, pressed into a pellet, forming a working electrode; Hg/HgO electrode as reference electrode and 9M aqueous KOH electrolyte. All the measured and averaged data are correlating with

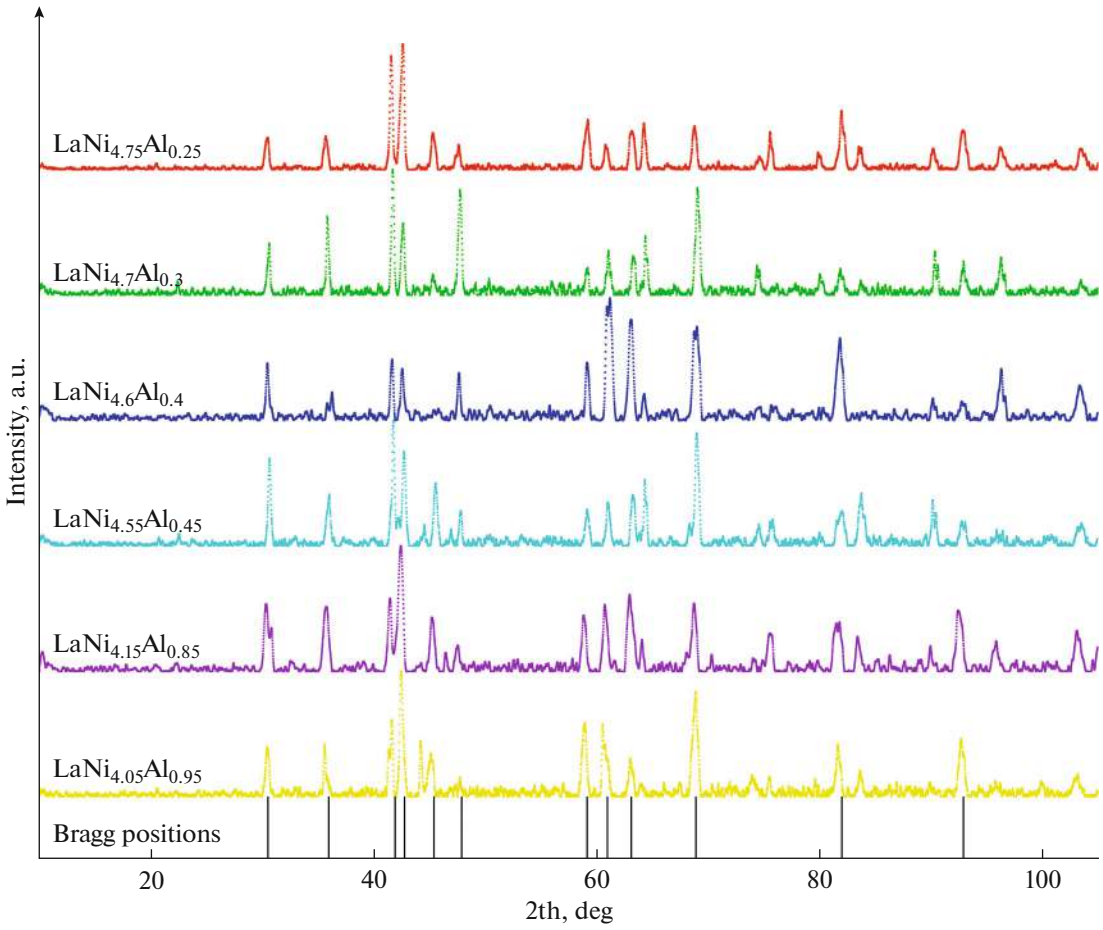


**Fig. 1.** Diffractograms of Al-substituted intermetallic compounds.

the corresponding approximation models ($R^2$ at least 0.95), unless stated otherwise.

## RESULTS AND DISCUSSION

According to the XRD results, the diffraction peak positions fully correspond to the $CaCu_5$ structure (Fig. 1). All the investigated compounds are of the hexagonal crystal lattice structure (*P6/mmm* group). Calculated lattice parameters indicate that Al-substitution increases cell volume—86.89, 87.35 and 88.19 Å$^3$ for $LaNi_{4.7}Al_{0.3}$, $LaNi_{4.6}Al_{0.4}$ and $LaNi_{4.45}Al_{0.55}$ accordingly.

Results of SEM analysis show the distribution of particles within the sample structure (Fig. 2). As shown in the figure below, homogeneity of compounds depends on the amount of Al. According to Energy-dispersive X-ray analysis the composition of samples correlates with the XRD data and elemental mapping shows components distributed uniformly. The darkened parts of SEM images relate to the zones enriched with Lanthanum (less than 1–3 wt % of sample); therefore, the overall compound structure is homogenous.

Also, the hydrogenation properties of $LaNi_{4.45}Al_{0.55}$ were studied. It was shown that as the amount of Al in compound composition (and lattice volume) increases, the equilibrium pressure of hydrogen decreases from approximately 0.2 ($LaNi_5$) to 0.01 ($LaNi_{4.45}Al_{0.55}$) MPa (Fig. 3A). At the same time, raising temperature increases the equilibrium pressure of hydrogen from 0.01 to 0.2 MPa ($LaNi_{4.45}Al_{0.55}$) in temperature range 20–90°C (Fig. 3B). Process of hydride formation alters the crystal lattice parameters, increasing cell volume by approximately 16.4%.

By processing and analyzing Vant-Hoff curves in Arrhenius coordinate system the enthalpy and entropy values for adsorption-desorption processes have been acquired (Table 1).

As it has been shown in earlier reports, in case of compounds of Al-substituted $LaNi_5$ series increasing the amount of aluminum in composition leads to lowering the equilibrium (plateau) pressure of hydrogen in wide range of temperatures, at the same time leading to decreasing maximum hydrogen capacity. Was stated

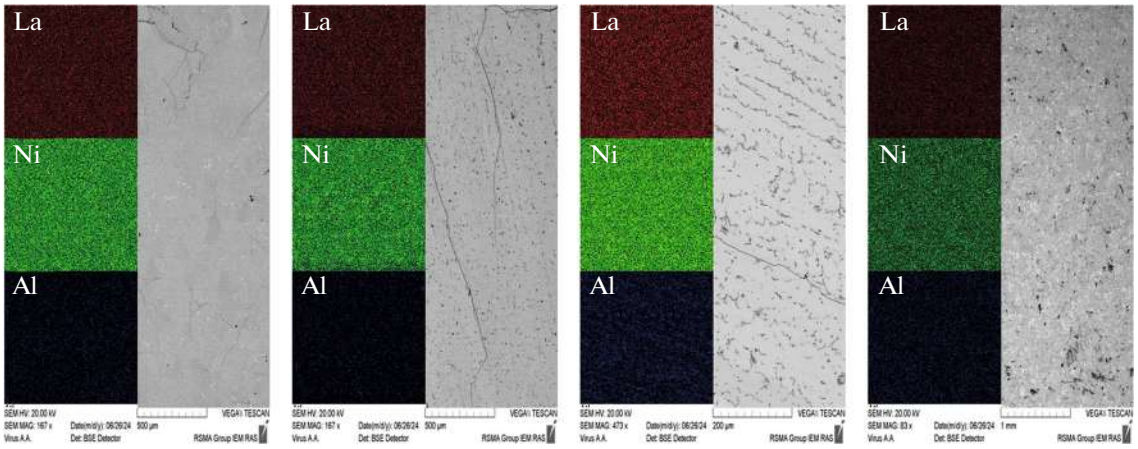


**Fig. 2.** SEM images of (left to right) $LaNi_{5-x}Al_x$ with $x = 0.25, 0.3, 0.55, 1$ respectively. Mapping (top to bottom)—La, Ni and Al distribution.

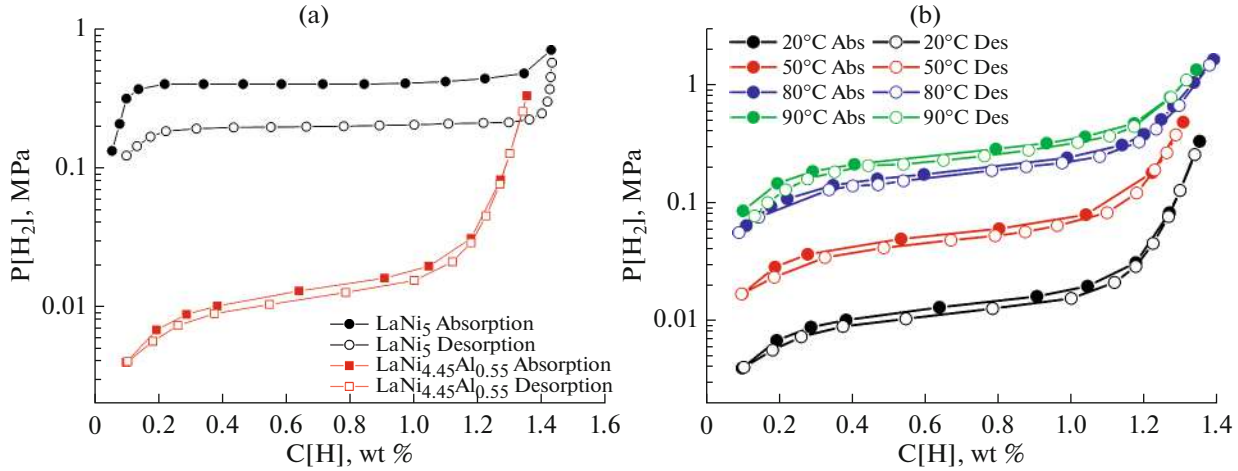


**Fig. 3.** (a) Pressure-composition diagram of $LaNi_{4.45}Al_{0.55}$ and $LaNi_5$. (b) Pressure-composition diagram of $LaNi_{4.45}Al_{0.55}$ at different temperatures.

the dependence of desorbed $H_2$ content at 40°C and pressure 0.1 MPa on Al content (Fig. 4) having bell-shaped distribution with peak values in $x = 0.5$–0.8 range.

Electrochemical measurements were conducted in several modes. The working electrode activation was performed with consistent charge-discharge cycles by applying 50 mA/g current rate. The high-rate discharge-ability was estimated by charging at 50 mA/g rate and full discharging with varying currents from 50 to 1000 mA/g with HRD standing for $C_{1000} \times 100\%/C_{100}$ ($C_n$—maximum capacity at the given current). Cycling stability was estimated by performing 100 charge-discharge cycles at 50 mA/g rate and calculated as $C^{100} \times 100\%/C^1$ ($C^n$—maximum capacity at the given cycle number).

The results show that Al-substituted intermetallic compounds possess high capacity and activation rate (2–7 cycles until reaching maximum capacity) (Fig. 5). Substitution of Ni for Al does not alter the charged state potential, which retains stability (0.85–0.95 V vs. Hg/HgO) during the measurements. The maximum capacity measured (321 mAh/g) relates to $LaNi_{4.55}Al_{0.45}$ compound. HRD value of all the samples is no less than 84% with maximum value of 94.6% reached at the composition mentioned above. Cycling stability is in poor relation with the compound composition ($R^2 < 0.6$ for linear, exponential, 2- , 3- and 4-degree polynomial approximation) and varies in range of 40–70%.

## CONCLUSIONS

The electric-arc melting and annealing compound preparation method allows to form a homogenous Haucke-type structure, as it was confirmed by XRD

**Table 1.** Thermodynamic properties of sorption and desorption processes in compound-$H_2$ systems

| ω($H$), wt % | $\Delta H_s^\circ$, kJ/mol | $\Delta S_s^\circ$, J mol$^{-1}$ K$^{-1}$ | $\Delta H_d^\circ$, kJ/mol | $\Delta S_d^\circ$, J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|
| | | **$LaNi_{4.7}Al_{0.3}$–$H_n$** | | |
| 0.6 | −32.40 ± 1.92 | −111.34 ± 5.79 | 34.56 ± 0.43 | 115.52 ± 1.29 |
| 0.8 | −31.97 ± 1.47 | −110.53 ± 4.42 | 34.01 ± 0.19 | 114.32 ± 0.59 |
| 1.0 | −31.42 ± 1.07 | −109.33 ± 3.23 | 33.95 ± 0.10 | 114.62 ± 0.30 |
| 1.2 | −31.75 ± 1.14 | −110.98 ± 3.44 | 33.77 ± 0.03 | 114.63 ± 0.09 |
| 1.4 | −30.80 ± 0.76 | −108.67 ± 2.31 | 33.76 ± 0.52 | 114.99 ± 1.58 |
| Av. | −31.67 ± 1.27 | −110.17 ± 3.84 | 34.01 ± 0.25 | 114.82 ± 0.77 |
| | | **$LaNi_{4.6}Al_{0.4}$–$H_n$** | | |
| 0.7 | −35.10 ± 0.57 | −113.13 ± 1.77 | 36.21 ± 0.29 | 115.22 ± 0.88 |
| 0.8 | −34.83 ± 0.39 | −112.84 ± 1.21 | 36.00 ± 0.26 | 115.07 ± 0.81 |
| 1.0 | −34.39 ± 0.29 | −112.77 ± 0.88 | 35.56 ± 0.30 | 114.91 ± 0.93 |
| 1.1 | −34.08 ± 0.30 | −112.60 ± 0.93 | 35.49 ± 0.12 | 115.39 ± 0.38 |
| 1.2 | −33.05 ± 0.25 | −110.42 ± 0.78 | 35.07 ± 0.17 | 114.90 ± 0.54 |
| Av. | −34.29 ± 0.36 | −112.35 ± 1.11 | 35.67 ± 0.23 | 115.10 ± 0.71 |
| | | **$LaNi_{4.45}Al_{0.55}$–$H_n$** | | |
| 0.6 | −38.28 ± 0.14 | −112.99 ± 0.42 | 39.15 ± 0.80 | 114.60 ± 2.33 |
| 0.7 | −38.22 ± 0.17 | −113.46 ± 0.51 | 38.86 ± 1.09 | 114.43 ± 3.16 |
| 0.8 | −37.66 ± 0.29 | −112.52 ± 0.87 | 38.31 ± 1.21 | 113.53 ± 3.51 |
| 0.9 | −37.54 ± 0.09 | −112.89 ± 0.26 | 38.31 ± 1.14 | 114.27 ± 3.30 |
| 1.0 | −37.24 ± 0.19 | −112.90 ± 0.59 | 37.59 ± 0.24 | 113.19 ± 0.69 |
| Av. | −37.79 ± 0.17 | −112.95 ± 0.53 | 38.44 ± 0.90 | 114.00 ± 2.60 |

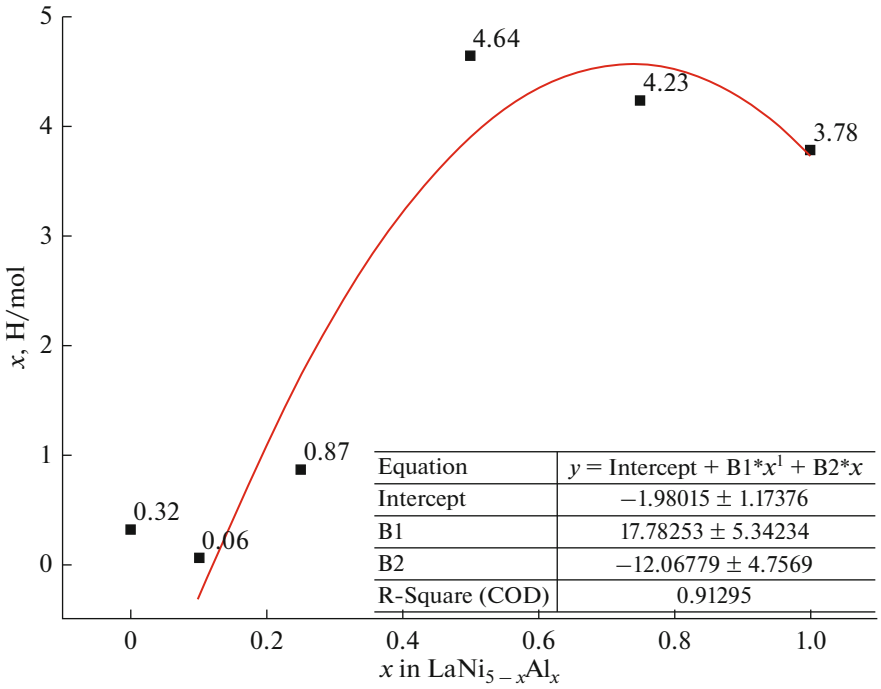


**Fig. 4.** Hydrogen desorption in aluminum-substituted $LaNi_5$ at $P(H_2) = 0.1$ MPa and $T = 40$°C [7, 8].

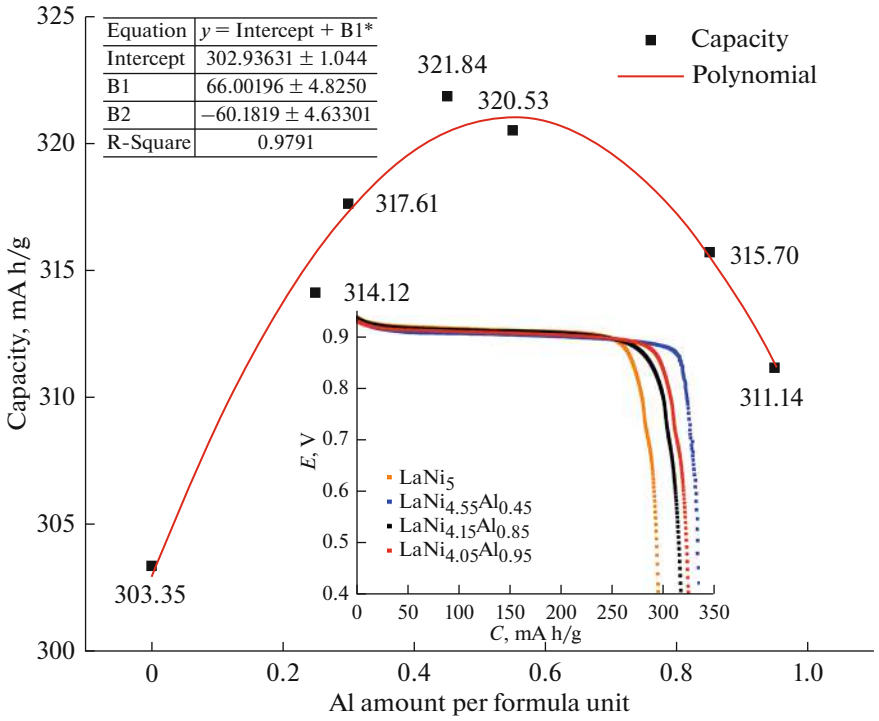


**Fig. 5.** Capacity vs. $x$ in $LaNi_{5-x}Al_x$. (lower) Smoothed discharge curves of $LaNi_{5-x}Al_x$.

and SEM methods. However, increasing the amount of Al in $LaNi_{5-x}Al_x$ alters the homogeneity of structure.

Samples with higher amount of Al exhibit lower equilibrium hydrogen pressure and lower mass capacity. Electrochemical capacity of Al-substituted compounds increases up to the value of 321 mA h/g and it makes compositions with $x$ = 0.4–0.6 perspective materials for Ni-MH rechargeable power sources. Gaseous and electrochemical capacity exhibit similar ball-shaped distribution.

## FUNDING

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## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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