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AB₅-type intermetallic compounds for biohydrogen purification and storage

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ABSTRACT

Intermetallic compounds (IMC) provide a promising solution for a biohydrogen purification problem due to their selective hydrogen absorption from gaseous mixtures produced during dark fermentation. A main IMC characteristic for use in biohydrogen purification is hydrogen equilibrium pressure, which has to be as low as possible during hydrogen sorption from a mixture. Intermetallic compounds LaNi_{5-x}M_x (M—Al, Sn, Fe; x = 0.1–0.3) were prepared and their PCT properties were investigated. Compositions LaNi_{4.6}Fe_{0.2}Al_{0.2} (0.049 MPa at 293 K) and LaNi_{4.6}Sn_{0.2}Fe_{0.2} (0.055 MPa at 293 K) are found to be the most promising for practical applications due to low equilibrium pressures.

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Introduction

Hydrogen production from biomass and organic wastes including wastewaters has become a subject of a great interest [1,2] and number of studies in this field has grown significantly. Hydrogen is recognized as a clean, low polluting energy carrier, which fits perfectly to variable renewable energy sources. It is considered to be a solution to replace the diminishing fossil fuels and beneficial in the protection of the global environment [3]. Development of pilot scale bioreactors for hydrogen production [4–11] and investigations of their economic feasibility [12–17] suggests a possibility of commercialization and practical implementation of biohydrogen production technologies in autonomous power supply systems.

The main technical barriers for practical use of biohydrogen are: low hydrogen content (generally not higher than 50%vol.), low partial pressure of hydrogen (less than 0.1 MPa) in a product gas and a necessity of bioreactor heating [18], because hydrogen has to be purified and compressed before usage for power production in fuel cells.

Common hydrogen purification methods are pressure swing adsorption, cryogenic distillation and metallic membranes. These technologies have been widely used in chemical and petrochemical industries. Regarding to biohydrogen purification, the common methods are inapplicable due to requirements for hydrogen content in feeding gas (up to 75–90% for PSA), operating pressures (1–3 MPa for both PSA and membranes) and temperatures (180–800 °C for metallic membranes) [19] They are energy-intensive, and the cost associated

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with the process operation is generally high. Different types of organic polymer membranes seem to be more suitable for biohydrogen separation [20,21]. Unfortunately, most investigations have been carried out under ideal conditions. Final H₂ concentration did not exceed 75–80%, which cannot be used directly in PEM fuel cells [22,23]. It is obvious that biohydrogen production methods cannot provide required conditions, so alternative purification methods are needed.

Metal hydrides (MH) provide a promising solution for the problem of biohydrogen purification. These materials have a remarkable combination of properties, including selective hydrogen absorption from gaseous mixtures, reversibility of interaction with hydrogen, mild operating conditions, high volumetric density of hydrogen in the solid state [24]. Mainly intermetallic compounds (IMC) of AB₅-type are used for hydrogen purification [25–31] due to their ease of activation, good tolerance to impurities, good cyclic stability. A great advantage of the AB₅ is a possibility of fine tuning of their operating conditions by shifting of pressure-concentration-temperature (PCT) diagram with alternation of a compound composition.

However, metal hydrides should meet requirements for effective biohydrogen purification. Biohydrogen produced from various organic substrates mostly consists of H₂ and CO₂, with hydrogen content about 30–50 vol% [32–35] and for overall gas pressure of 0.11–0.12 MPa hydrogen partial pressure do not exceed 0.04–0.06 MPa. Carbon dioxide do not affect AB₅-type alloys [30,36–38]. In the presence of poisonous gases (CO, H₂S, etc.) surface modification of metal hydrides [30,31,39,40] or removal of the impurities prior hydrogen sorption [28,37] are required. Thus, AB₅ IMC with low equilibrium pressures can be used for biohydrogen purification.

In this work we present a study of AB₅ intermetallic compounds to verify applicability of Ni-substituted LaNi₅ to purify biohydrogen. Intermetallic compounds LaNi_{5-x}M_x (M–Al, Sn, Fe; x = 0.1–0.3) were chosen due to their high impurity resistance and cyclic stability [36,41–45].

Experimental procedure

We have prepared LaNi_{5-x}M_x alloys by arc melting of pure La (99.9%), Ni (99.95%), Fe (99.99%), Al (99.9%) and Sn (99%) several times in a water cooled copper crucible under argon atmosphere [46]. In each case, we added 2% to calculated weight of Sn, Al in order to compensate evaporation during the melting process. At first the furnace chamber was vacuumed to a final pressure of 4·10⁻⁵ Pa and subsequently purged three times with argon at 41 kPa. Pure elements were joined together at a low voltage and were melt later 2 or 3 times at full power. Each melting step lasted about 1 min. After each step, alloy ingots were cooled and turned upside down. The resulting alloy ingots weighted 40–50 g each. Due to mild conditions and short time of melting steps the weight losses of samples did not exceed 0.5% of initial metals weight.

In order to determine structural parameters, powder samples were measured at room temperature by X-ray diffraction (XRD) using D8 Advance (Bruker) diffractometer with Cu K α radiation. Samples for X-ray analysis were

prepared by mechanical grinding to a powder. The step was 0.02 and the exposition time was 60.8 s by step. The 2 θ angles scanned were ranged from 10 to 120. Processing of diffraction patterns was performed using Jana2006 and Search-Match software.

A scheme of experimental setup for characterization of desorption isotherms is shown in Fig. 1, pressure range is 0.01–10 MPa at temperatures from 273 to 373 K. The installation consists of autoclaves, pressure gauges, valves, communications and calibrated glass tank with a vacuum gauge. Hydrogenation was conducted using hydrogen of high purity obtained from AB₅ metal hydride storage container.

Each ingot was mechanically broken into pieces of about 5–10 g, while exposed to air. Samples of about 5 g were cleaned from surface oxide film and placed in the autoclave, and the system was vacuumed to a residual pressure of 1 Pa. Hydrogen was supplied to the buffer tank and thereafter buffer tank was connected with autoclave. All samples readily reacted with hydrogen without any preliminary activation treatment. PCT-measurements were conducted with as-cast samples from the first absorption–desorption cycle. The reaction of IMC with hydrogen lasts for 15–30 min. Temperature and pressure were recorded after reaction completion. Calibrated hydrogen portions were evacuated from buffer tank or calibrated glass tank during desorption process. It was considered that balance in the system was achieved if the pressure changes did not occur within 20 min.

Results and discussion

The XRD measurements of IMC have shown high homogeneity of the samples, XRD diagrams confirm that the structure of the samples belong to CaCu₅ type. The resulting spectra are in a good agreement with theoretically predicted, positions of characteristic peaks coincide with the calculated values and no peaks of other phases are observed. Lattice parameters calculated from the XRD diagrams are given in Table 1. Replacement of Ni atoms by larger Al and Sn atoms leads to an increase in lattice size of the respective samples compared with the crystal structure of LaNi₅.

Prepared alloy samples start to absorb hydrogen after a period of 5–15 min. Any activation procedures of samples were not required. After hydrogenation, alloys fractured into fine powders inflammable in air.

In order to determine the enthalpy and the entropy of the hydride formation, PCT curves were measured at 20 °C, 40 °C and 60 °C for all samples (see Figs. 2–5). Enthalpies and entropies of reactions were calculated using Van't Hoff equation:

$$R \ln P = \frac{\Delta H}{T} + \Delta S \quad (1)$$

where, R is a universal gas constant, P is the equilibrium pressure, ΔH is the reaction enthalpy, T is the temperature and ΔS is the entropy change, plateau pressures as a function of the temperature are shown in Fig. 6. Results of the thermodynamic measurements are listed in Table 2.

The main IMC characteristic for use in biohydrogen purification is hydrogen equilibrium pressure, which has to be

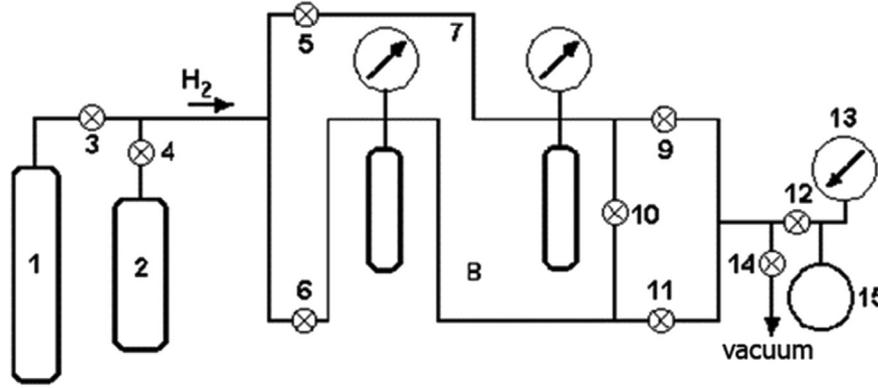


Fig. 1 – Experimental setup scheme: 1 – hydrogen cylinder, 2 – LaNi₅ hydrogen accumulator, 3–6, 9–11 – valves, 7 – manometers, 8 – autoclaves, 12,14 – vacuum valves, 13 – vacuum gauge, 15 – calibrated glass tank.

as low as possible during hydrogen sorption from a product gas. A slight plateau slope is also needed to increase operational capacity of alloy. All the samples were classified by equilibrium pressures, which vary in the range from 0.049 up to 0.071 MPa at 293 K. Tin and aluminium play important role in the decrease of equilibrium pressure. Equilibrium pressures for LaNi_{4.8}Sn_{0.2} are higher than reported in Ref. [43] due to PCT measurement without preliminary activation. Sample of LmNi_{4.8}Al_{0.2} (Lm is La-rich mischmetal) has similar

Table 1 – Crystal structure parameters of IMCs.

Intermetallic compound	Unit cell parameters		Unit cell volume Å ³
	a, Å	c, Å	
LaNi ₅ [42]	5.0137 (2)	3.8936 (3)	86.3 (3)
LaNi _{4.8} Sn _{0.2}	5.0332 (4)	3.9987 (5)	88.3 (3)
LaNi _{4.8} Sn _{0.1} Al _{0.1}	5.0295 (3)	3.9997 (4)	87.6 (2)
LaNi _{4.6} Sn _{0.2} Fe _{0.2}	5.0403 (5)	4.0107 (5)	88.2 (2)
LaNi _{4.6} Fe _{0.2} Al _{0.2}	5.0307 (2)	4.0052 (2)	87.8

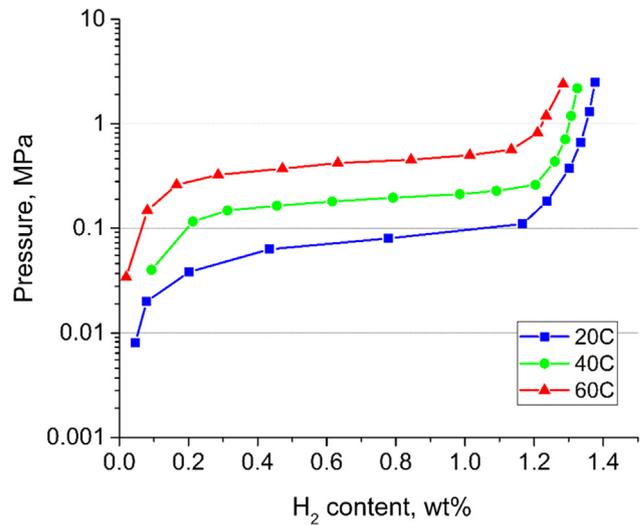


Fig. 3 – PCT diagram for LaNi_{4.8}Sn_{0.1}Al_{0.1} (desorption).

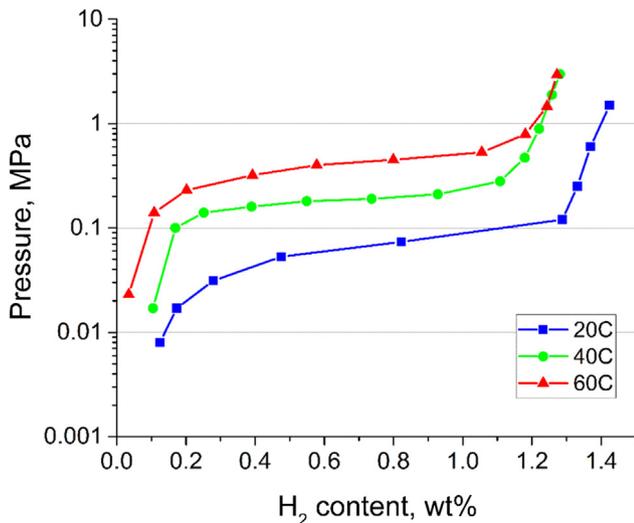


Fig. 2 – PCT diagram for LaNi_{4.8}Sn_{0.2} (desorption).

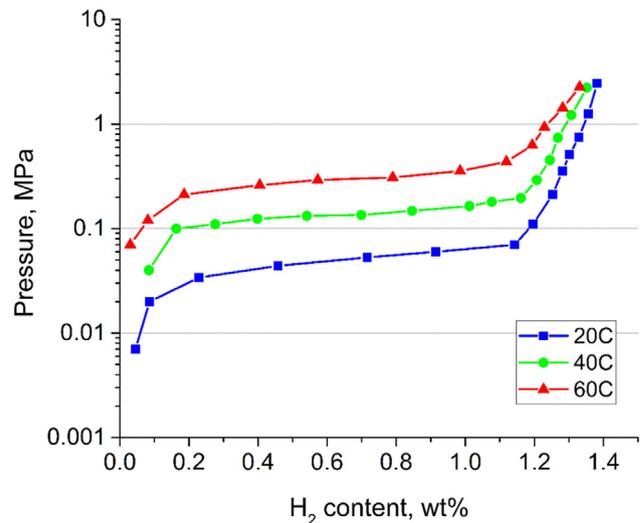


Fig. 4 – PCT diagram for LaNi_{4.6}Fe_{0.2}Al_{0.2} (desorption).

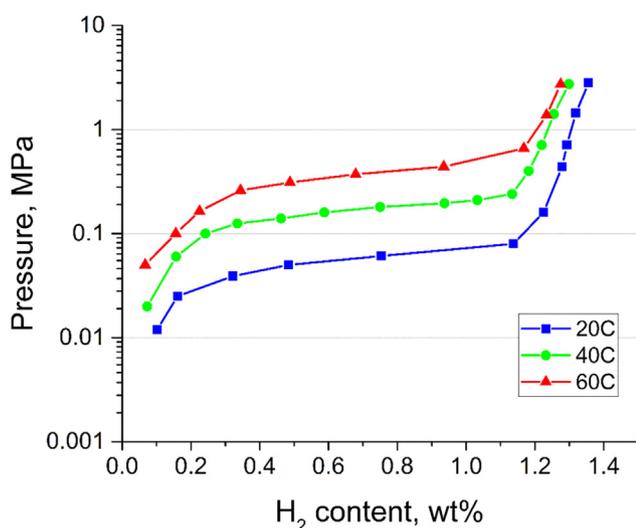


Fig. 5 – PCT diagram for $\text{LaNi}_{4.6}\text{Fe}_{0.2}\text{Sn}_{0.2}$ (desorption).

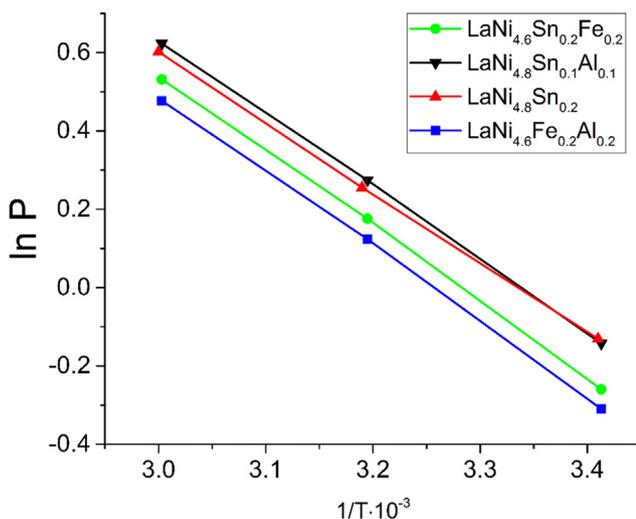


Fig. 6 – Van't Hoff plots of desorption plateau pressure for investigated samples.

equilibrium pressure and demonstrates high impurity resistance and good reactivation properties as reported in Ref. [47]. This indicates the possibility to use Al-substituted alloys for hydrogen purification from gas mixtures with traces of poisonous gases.

The reversible capacity C_{rev} depends on a plateau width, a maximum capacity C_{max} and on a shape of a PCT curve. Depending on the composition, the maximum capacity C_{max} varies between 1.36 and 1.42 wt%. The reversible capacity C_{rev} is calculated for lowest measured temperature and pressures. For practical purposes the reversible capacity C_{rev} can be estimated in the range from 1.0 to 1.1 wt%.

Two samples are recommended to meet requirements for biohydrogen purification: $\text{LaNi}_{4.6}\text{Fe}_{0.2}\text{Al}_{0.2}$ and $\text{LaNi}_{4.6}\text{Sn}_{0.2}\text{Fe}_{0.2}$. Low equilibrium pressures of these alloys at ambient temperatures (0.049 and 0.055 MPa, respectively) are favourable for absorption of hydrogen directly from a gas produced during dark fermentation. Desorption pressures at high temperatures allows to achieve hydrogen pressures suitable for a fuel cell without any compression.

Conclusions

Hydrogen partial pressure in a product gas from dark fermentation generally do not exceed 0.04–0.06 MPa. Selective hydrogen absorption by intermetallic compounds can be used for biohydrogen purification. The main IMC characteristic for use in biohydrogen purification is hydrogen equilibrium pressure, which has to be as low as possible during hydrogen sorption from a product gas.

Intermetallic compounds $\text{LaNi}_{5-x}\text{M}_x$ ($\text{M} = \text{Al}, \text{Sn}, \text{Fe}$; $x = 0.1\text{--}0.3$) were prepared by arc melting and characterized by X-ray diffraction. All samples readily reacted with hydrogen without any preliminary activation treatment. Equilibrium pressures for investigated IMCs satisfy the requirements for biohydrogen purification. Compositions $\text{LaNi}_{4.6}\text{Fe}_{0.2}\text{Al}_{0.2}$ and $\text{LaNi}_{4.6}\text{Sn}_{0.2}\text{Fe}_{0.2}$ are the most promising for practical use due to their low equilibrium pressures 0.049 MPa and 0.055 MPa, respectively, at 293 K.

Table 2 – PCT-properties of intermetallic compounds.

IMC	T, °C	P_{des} , MPa	C_{rev} , wt%	C_{max} , wt%	ΔH_{des} , kJ/mol	ΔS_{des} , kJ/mol K
$\text{LaNi}_{4.8}\text{Sn}_{0.2}$	20	0.063	1.12	1.42	−34.2	114.2
	40	0.185				
	60	0.4				
$\text{LaNi}_{4.6}\text{Sn}_{0.2}\text{Fe}_{0.2}$	20	0.055	1.00	1.36	−36.9	121.2
	40	0.17				
	60	0.372				
$\text{LaNi}_{4.8}\text{Sn}_{0.1}\text{Al}_{0.1}$	20	0.071	1.16	1.38	−35.8	119.4
	40	0.188				
	60	0.42				
$\text{LaNi}_{4.6}\text{Fe}_{0.2}\text{Al}_{0.2}$	20	0.049	1.11	1.38	−36.8	119.7
	40	0.135				
	60	0.3				

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