Solid gas and electrochemical hydrogenation properties of the selected

R,R'MgNi_{4-x}M_x (R,R' = La, Pr, Nd; M = Fe, Mn; x = 0.5, 1) alloys

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Keywords: *alloys, intermetallics, hydrides, phase composition, hydrogenation.*

New R,R'MgNi_{4-x}M_x (R,R' = La, Pr, Nd; M = Fe, Mn; x = 0.5, 1) phases with cubic structure have been synthesized by powder sintering method. By the hydrogenation of the parent alloys seven hydrides with cubic (LaMgNi_{3.5}Fe_{0.5}H_{6.0}, PrMgNi_{3.5}Mn_{0.5}H_{~6} and NdMgNi_{3.5}Mn_{0.5}H_{~5}) and orthorhombic (PrMgNi_{3.5}Fe_{0.5}H_{4.5}, NdMgNi_{3.5}Fe_{0.5}H_{4.3}, La_{0.5}Pr_{0.5}MgNi_{3.5}Fe_{0.5}H_{4.6} and La_{0.5}Nd_{0.5}MgNi_{3.5}Fe_{0.5}H_{4.4}) structures were obtained. The relationship between the structure, hydrogen content and the relative increase of the lattice volume of the new and early known hydrides is shown. Electrochemical parameters of the electrodes based on new materials are compared with already known ones. Highest discharge capacity is observed for PrMgNi_{3.5}Mn_{0.5} (271 mAh/g) and NdMgNi_{3.5}Mn_{0.5} (263 mAh/g). The best cyclic stability was seen for the electrode based on NdMgNi_{3.5}Fe_{0.5} (S₅₀ = 74%).

Introduction

Intermetallic RMgM₄ phases (R - rare earth metal, M - transition d-metal) and their alloys have been intensively studied during the last ten years [1]. They are paid attention not only of their structural features and physical properties, but also of their hydrogen sorption properties [2]. Most of the RMgM₄ alloys reversibly absorb hydrogen from the gas phase and electrochemically. The amount of absorbed hydrogen can reach up to 6 H/f.u. Highest discharge capacity of the electrodes for these materials can reach 400 mAh/g [3]. Although there are many studies on the hydrogen

adsorption properties of the multi phase alloys which containing RMgM₄ intermetallics [4], a comprehensive study of single-phase RMgM₄ samples is limited to a few dozen works, most of which are devoted to the study of stoichiometric 1:1:4 composition [5-13]. In our recent studies we shown the effect of the rare earth and transition metals substitution on the hydrogen sorption properties based on the LaMgNi₄ compound [14-15]. We also turn our attention to the investigation alloys containing heavy rare earth metals and different multiple substitution of the transition metals [16-17]. In present work, we synthesized RMgNi₄ alloys (R = La, Pr, Nd), where the nickel atoms is partially replaced by Mn and Fe ones. The influence of such

substitution on hydrogen sorption properties and hydride structures is shown, and the obtained results are compared and briefly discussed.

Experimental part

Starting materials for the preparation of the $R,R'MgNi_{4-x}M_x$ alloys were ingots of La, Pr, Nd, Ni, Fe and Co (all with purity $\geq 99.9\%$) and Mg powder (325 mesh, 99.8%). In the first step, $R,R'Ni_{4-x}M_x$ ($x = 0.5$ and 1) precursors were prepared by arc melting in a purified argon atmosphere. The as-cast alloys were ground in an agate mortar and after obtained powders with size less than 0.04 mm then mixed with Mg powder in certain proportions. Mg was added with 3 wt. % excess to compensate for its evaporation loss at high temperatures. The powder mixtures were pressed into pellets with diameter of 10 mm at 10 ton, placed into stainless steel containers and sealed under an Ar atmosphere. Samples further heated up to 800°C and down to 500°C step by step within six days, and annealed at 500°C ten days. No reaction with the containers was observed. The composition of the samples was controlled by comparing the mass of the obtained alloys with the total mass of the initial load (~ 2 g). The mass losses during sintering did not exceed 1% . Structural analysis of the samples was carried out by X-ray powder diffraction (XRD) using a DRON 3M diffractometer (Cu $K\alpha$ radiation). The scans were taken in the $\theta/2\theta$ mode with the following

parameters: 2θ region $20\text{--}90^\circ$, step scan 0.04° , counting time per step 10 s. Crystal structures of the compounds were refined by Rietveld method from the diffraction data using Fullprof software [18]. A pseudo-Voigt profile shape function was assumed. The background was refined with a polynomial function. Determination of size and strain were performed with a help of PowderCell program [19].

Elemental composition of the alloys was examined by scanning electron microscopy (SEM) using an EVO 40XVP microscope equipped with Inca Energy 350 spectrometer for energy dispersive X-ray analysis (EDX).

Hydrogen absorption-desorption properties of the alloys were characterized using a Sieverts-type apparatus. The samples were activated by heating up to 200°C in dynamic vacuum by using turbomolecular pump, cooled to 20°C , and then hydrogenated with high-purity hydrogen gas (99.999%). Parent samples are stable in dry air. Special care was taken with the hydrides manipulation (store under argon atmosphere) due to their susceptibility to oxidation in contact with humid air.

The electrode materials made of the alloys were prepared by mixing of with carbonyl Ni powder with the $1:3$ wt. ratio. The pellet electrodes with a diameter of 12 mm were made by cold-pressing the powder mixture under a pressure of 10 ton/cm^2 and then sandwiched between two Ni foams with the fixed conductor.

Electrochemical properties were tested in a three-electrode system. Platinum auxiliary and metal hydride (MH) working electrodes were placed in a glass cell filled with KOH solution ($C_M=6$ M) electrolyte, while the Ag/AgCl reference electrode was connected to the system via an agar bridge. Cycling stability of the MH electrodes

was studied galvanostatically at the current densities of 50 mA/g at room temperature. The potential for the charge/discharge was measured between -0.6 V and -1.2 V versus the Ag/AgCl electrode.

Table 1. Lattice parameters of the parent intermetallics and their hydrides

Nº	Phase	a or a,b,c (Å)	V (Å ³)	$\Delta V/V$ (%)	$\Delta V/n_H$ (Å ³ /n)
1.	LaMgNi _{3.5} Fe _{0.5}	7.1872(5)	371.26(5)	-	-
2.	PrMgNi _{3.5} Fe _{0.5}	7.1356(4)	363.32(3)	-	-
3.	NdMgNi _{3.5} Fe _{0.5}	7.1216(4)	361.19(4)	-	-
4.	La _{0.5} Pr _{0.5} MgNi _{3.5} Fe _{0.5}	7.1530(2)	365.99(2)	-	-
5.	La _{0.5} Nd _{0.5} MgNi _{3.5} Fe _{0.5}	7.1523(2)	365.88(2)	-	-
6.	LaMgNi _{3.5} Mn _{0.5}	7.2278(4)	377.59(4)	-	-
7.	LaMgNi ₃ Mn	7.2505(7)	381.16(6)	-	-
8.	PrMgNi _{3.5} Mn _{0.5}	7.1601(2)	367.08(2)	-	-
9.	PrMgNi ₃ Mn	7.2175(7)	375.98(7)	-	-
10.	NdMgNi _{3.5} Mn _{0.5}	7.1458(3)	364.89(2)	-	-
11.	NdMgNi ₃ Mn	7.2042(6)	373.90(5)	-	-
12.	LaMgNi _{3.5} Fe _{0.5} H _{6.0}	7.659(3)	449.3(3)	21.0	3.25
12.	PrMgNi _{3.5} Fe _{0.5} H _{4.5}	5.0949(12) 5.5058(15) 7.4317(19)	208.47(9)	14.8	2.98
13.	NdMgNi _{3.5} Fe _{0.5} H _{4.3}	5.0837(11) 5.4898(13) 7.4149(18)	206.94(8)	14.6	3.06
14.	PrMgNi _{3.5} Mn _{0.5} H _{~6}	7.587(12)	436.7(12)	19.0	2.90
15.	NdMgNi _{3.5} Mn _{0.5} H _{~5}	7.484(14)	419.2(14)	14.9	2.71
16.	La _{0.5} Pr _{0.5} MgNi _{3.5} Fe _{0.5} H _{4.6}	5.116(1) 5.515(2) 7.463(2)	210.6(2)	15.1	3.00
17.	La _{0.5} Nd _{0.5} MgNi _{3.5} Fe _{0.5} H _{4.4}	5.1147(6) 5.5186(7) 7.460(1)	210.59(8)	15.1	3.14

a or a,b,c - Lattice parameters of cubic or orthorhombic structures; V - Cell volume;
 $\Delta V/V$ - Cell volume expansion; $\Delta V/n_H$ - Specific volume expansion for one hydrogen atom.

Figure 1. X-ray diffraction patterns of the selected parent alloys (a) and their hydried (b).

Results and discussion

Sample synthesis and crystal structure of parent alloys

By using powder sintering method a series of the doped RMgNi_4 alloys were prepared. Single phase was observed in the Fe-based $\text{RMgNi}_{3.5}\text{Fe}_{0.5}$ ($\text{R} = \text{La}, \text{Pr}, \text{Nd}$) and $\text{La}_{0.5}\text{R}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}$ ($\text{R} = \text{Pr}, \text{Nd}$) and Mn-based $\text{RMgNi}_{3.5}\text{Mn}_{0.5}$ and RMgNi_3Mn ($\text{R} = \text{La}, \text{Pr}, \text{Nd}$) alloys. These phases belong to the cubic SnMgCu_4 structure type (space group $F-43m$) and their lattice parameters are given in **Table 1**. In the SnMgCu_4 structure, the R atoms occupied the Mg ($4a, 0\ 0\ 0$) site, statistical mixture Ni with Fe or Mn are distributed over the Cu ($16e, 0.625\ 0.625\ 0.625$) site, and the Mg atoms are situated in the Sn ($4c, 1/4\ 1/4\ 1/4$) positions. XRD patterns of selected alloys are illustrated in **Figure 1**. Lattice constants for doped RMgNi_4 , as an expected, are increased compared to parent RMgNi_4 , where small nickel atoms ($r = 1.24\ \text{\AA}$) are partially substituted by bigger Fe ($r = 1.26\ \text{\AA}$) or Mn ($r = 1.30\ \text{\AA}$) ones.

All samples were analyzed by semiquantitative EDX analysis with internal standards. Surfaces of the selected alloys are shown in **Figure 2**. Measured compositions of the alloys are close to the nominal ones. The experimentally observed compositions were all within $\pm 0.1\text{--}0.5\ \text{at. \%}$. No impurities were observed.

Solid gas hydrogenation properties

At the beginning hydrogenation process was first performed for $\text{LaMgNi}_{3.5}\text{Fe}_{0.5}$, $\text{PrMgNi}_{3.5}\text{Fe}_{0.5}$ and $\text{NdMgNi}_{3.5}\text{Fe}_{0.5}$, further continued for alloys where half of lanthanum atoms are substituted by Pr and Nd ones ($\text{La}_{0.5}\text{Pr}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}$ and $\text{La}_{0.5}\text{Nd}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}$), and then obtained results were compared (**Figure 3**). The analysis of the obtained kinetic curves makes it possible to distinguish three separate stages of the process. The first section corresponds to the induction period, during which the hydrogen absorption was too small. In this area, the nucleation process probably takes place, i.e. the hydride phase begins to form. It can be seen from the curves the lanthanum containing alloys have a small induction time (up to 30 min). The second section corresponds to the active hydrogen absorption and it is traditionally associated with two- or three-dimensional growth of existing nuclei at the inter-phase boundary at a constant or decreasing rate. The third section on the kinetic curves is characterized by slow hydrogen absorption, which is characterized by the completion of active process. It takes place when the previously formed nuclei of hydride phases have already increased so much to the sizes which limit further growth in three-dimensional space.

Comparing the hydrogenation curves for $\text{PrMgNi}_{3.5}\text{Fe}_{0.5}$ and $\text{NdMgNi}_{3.5}\text{Fe}_{0.5}$ with $\text{La}_{0.5}\text{Pr}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}$ and

$\text{La}_{0.5}\text{Nd}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}$, we can note that lanthanum-substituted alloys rapidly absorb hydrogen and saturated hydrides are formed after 100 minutes, but the complete saturation by hydrogen of $\text{PrMgNi}_{3.5}\text{Fe}_{0.5}$ and $\text{NdMgNi}_{3.5}\text{Fe}_{0.5}$ is 10 times slower. It should be noted that the amount of absorbed hydrogen for above mentioned alloys was almost the same (~ 4.45 H/f.u). Experimental data were further analyzed by using the Johnson-Mehl-Avrami equation: $y = 1 - \exp[-(kx)^n]$, where y is the completeness of the reaction or the volume fraction of unreacted

material ($0 < y < 1$), x is the reaction time (min), k is the reaction rate constant (min^{-1}), n is the kinetic parameter (indicates the reaction mechanism). The kinetic characteristics obtained using this equation with a help of least squares method are shown in **Table 2**. The value of the exponent n can be used to judge the conditions of formation and growth of nuclei, and reaction mechanism. Here $n > 1$, thus the reaction rate depends weak on the rate of nucleation and it is determined mainly by the growth of existing nuclei.

Figure 2. Microphotographs of the surface of: (a) $\text{La}_{0.5}\text{Pr}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}$, (b) $\text{La}_{0.5}\text{Nd}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}$, (c) PrMgNi_3Mn and (d) NdMgNi_3Mn .

Figure 3. Curves of first hydrogenation of the Fe doped alloys.

Table 2. Values of the reaction rate constants for $R,R'MgNi_{3.5}Fe_{0.5}$.

No	Alloy	k	n	R^2
1.	LaMgNi _{3.5} Fe _{0.5}	0.01842(10)	3.83(10)	0.982
2.	PrMgNi _{3.5} Fe _{0.5}	0.003227(7)	2.354(16)	0.994
3.	NdMgNi _{3.5} Fe _{0.5}	0.002095(4)	1.838(8)	0.993
4.	La _{0.5} Pr _{0.5} MgNi _{3.5} Fe _{0.5}	0.02223(15)	2.19(5)	0.990
5.	La _{0.5} Nd _{0.5} MgNi _{3.5} Fe _{0.5}	0.02222(9)	3.74(7)	0.995

Table 3. Values of the calculated dimension of the crystallites and the lattice distortion.

No	Hydride	Symmetry	L (nm)	$e \cdot 10^3$
1.	LaMgNi _{3.5} Fe _{0.5} H _{6.0}	cubic	12	2.5
2.	PrMgNi _{3.5} Fe _{0.5} H _{4.5}	orthorhombic	20	1.5
3.	NdMgNi _{3.5} Fe _{0.5} H _{4.3}	orthorhombic	21	1.4
4.	PrMgNi _{3.5} Mn _{0.5} H _{~6}	cubic	8	3.6
5.	NdMgNi _{3.5} Mn _{0.5} H _{~5}	cubic	7	4.0
6.	La _{0.5} Pr _{0.5} MgNi _{3.5} Fe _{0.5} H _{4.6}	orthorhombic	18	1.6
7.	La _{0.5} Nd _{0.5} MgNi _{3.5} Fe _{0.5} H _{4.4}	orthorhombic	22	1.3

Crystal structure of the saturated hydrides

In the present work, seven saturated hydrides at a pressure of 10 bar were synthesized: PrMgNi_{3.5}Fe_{0.5}H_{4.5}, NdMgNi_{3.5}Fe_{0.5}H_{4.3}, La_{0.5}Pr_{0.5}MgNi_{3.5}Fe_{0.5}H_{4.6}, La_{0.5}Nd_{0.5}MgNi_{3.5}Fe_{0.5}H_{4.4}, LaMgNi_{3.5}Fe_{0.5}H_{6.0}, PrMgNi_{3.5}Mn_{0.5}H_{~6} and NdMgNi_{3.5}Mn_{0.5}H_{~5}. The first four hydrides are formed with an orthorhombic structure, the last three have a

cubic structure. It should be noted that iron doped alloys with the exception of LaMgNi_{3.5}Fe_{0.5} changed their structure during hydrogenation, while the samples with manganese retained the structure of the original matrix. For comparison hydrides of the cobalt-containing alloys with the same stoichiometry have an orthorhombic for NdMgNi_{3.5}Co_{0.5}H_{4.4} or cubic LaMgNi_{3.5}Co_{0.5}H_{6.3} structures. Synthesized hydrides with orthorhombic structure were obtained in

crystalline form, while the cubic ones exhibit the crystallinity of low level (see **Figure 1 (b)**). XRD of the hydrides were also analyzed to determine the dimension of the crystallites and the lattice distortion. Size (L) and strain (e) parameters (**Table 3**) were obtained from the equation [20]: $FMHW^2/\tan^2\theta = (K \cdot \lambda/L) \cdot (FMHW/(\tan\theta \sin\theta)) + 16e^2$, where K is the constant, λ is the wavelength, θ is the position of the peak maximum, $FMHW$ is the full width at half maximum. It can be noted, that hydrides with cubic structure are characterized by smaller grain size and bigger lattice distortion comparing with those ones with orthorhombic structures.

It is possible to obtain hydrides of different composition and structure by varying experimental conditions under hydrogenation. It is also known from the literature that the structure of hydrides depends on the stoichiometry of $R_{1-x}Mg_{1+x}Ni_4$ alloys, the nature of alloying additives and the amount of hydrogen absorbed. This can be seen in **Figure 4**. It is constructed in the coordinates of the hydrogen content (H/f.u.) vs. the relative increase in the volume of the original matrix (%). The diagram presents the data of 47 known hydrides from the literature [5-17] and obtained ones in the present work. Based on the literature data of the $RMgNi_4$ - $RMgCo_4$ hydride systems, the calculated line is obtained by the method of least squares which shows the approximate dependence of the relative increase in the volume of the original matrix on the amount of hydrogen absorbed.

Here we can clearly distinguish two areas of existence of cubic and orthorhombic hydrides, which is outlined in the diagram by dashed lines. Cubic hydrides $RMgNi_4$ and $RMgCo_4$ are shown by dark red squares, and substituted $RMgNi_{4-x}Co_x$ ($x \neq 0$) alloys is shown by light red ones. Interestingly, the last ones together with the synthesized in this work $RMgNi_{3.5}Mn_{0.5}H_{5-6}$ and $LaMgNi_{3.5}Fe_{0.5}H_{6.0}$ hydrides are usually located below calculated line. Here, the relative volume increase in the substituted $RMgNi_{4-x}Co_x$ hydrides ($x \neq 0$) is slightly smaller compared to $RMgNi_4$ and $RMgCo_4$, which may indicate on some enhancement of the interaction between hydrogen atoms and statistical mixtures of the transition metals in the hydride structure. The amount of absorbed hydrogen for this series of hydrides varies from 4.8 to 6.8 H/f.u. Cubic hydride $CeMgCo_4D_{4.2}$ ($dV/V = 20\%$) and the hydrides of nonstoichiometric composition of the type $R_{1-x}Mg_{1+x}Ni_4$ with $x > 0$ are the exceptions to this rule; they are marked by dark green squares on the diagram. Specific place on the diagram is occupied by orthorhombic hydrides with $H/f.u. = 3.6 - 4.4$; they are marked here by dark blue ($RMgNi_4$) and light blue ($RMgNi_{4-x}Co_x$) balls, respectively. Hydrides of this work $RMgNi_{3.5}Fe_{0.5}H_{4.3-4.6}$ with orthorhombic structure also fall into this region (crossed balls) and they are below the specified line. It should be noted that from the literature only one representative of the hydride ($TbMgCo_4H_{3.3}$) with a monoclinic structure is reported. Due to

the smallest value of $H/f.u = 3.3$ this hydride is much left shifted in the diagram and marked by light green triangle. The so-called α -phases, solid solutions of hydrogen inclusion based on $RMgM_4$ alloys, were not discussed here due to

the lack of sufficient information in the literature. Up to our best knowledge, the structure only for one representative, the $LaMgNi_4H_{0.75}$ hydride, has been studied.

Figure 4. Dependence of the hydrogen content vs. the relative increase in the volume of the original matrix (parent alloys).

Electrochemical properties

Electrochemical studies of all synthesized alloys were performed in the cycling manner at charge and discharge current densities of 50 mA/h. Discharge capacities as a function of discharge cycle are illustrated in **Figure 5**. Some electrochemical properties are listed in **Table 4**. The electrodes are characterized by rapid activation, and the maximum values of the discharge capacity do not exceed 300 mAh/g. It is highest in $PrMgNi_{3.5}Mn_{0.5}$ (271 mAh/g) and

$NdMgNi_{3.5}Mn_{0.5}$ (263 mAh/g). Electrodes of the iron containing alloys, with the exception of $LaMgNi_{3.5}Fe_{0.5}$, have better cyclic stability ($S_{50} = 62 - 74\%$), compared with manganese doped ones. It should also be noted that the cyclic stability of $RMgNi_{3.5}Mn_{0.5}$ alloys ($S_{50} = 43 - 58\%$) is higher than that of $RMgNi_3Mn$ ($S_{50} = 22 - 29\%$) for $R = Nd$ and Pr .

The discharge curves (capacity vs. potential) for some electrodes in 5, 25, and 50 cycles are shown in **Figure 6**. As can be seen

from the figure (for example on the curves in the fifth cycle) the electrochemical release of hydrogen is usually begins above -1.1 V, then there is a slight linear increase in potential, the slope and length of which depends on the composition of the electrode. The wide discharge plateau that further follows corresponds to the main discharge process, where most of the absorbed hydrogen by the intermetallic phase is oxidized. The sharp decrease of potential to -0.6 V corresponds to the completion of the discharge process, at this potential the value of capacity in each cycle was calculated.

Finally, we compared the maximum discharge capacity and cyclic stability of the investigated electrodes with RMgNi_4 and the cobalt-doped $\text{RMgNi}_{3.5}\text{Co}_{0.5}$, respectively. As can we see from **Figure 7**. for the praseodymium and neodymium based alloys the maximum capacity is usually close to 250 mAh/g, and only in alloys with lanthanum it is increased, which is explained by the size factor. For comparison, the atomic radius of lanthanum is equal to 1.87 Å, while for Pr and Nd is ~ 1.82 Å. The cyclic stability of lanthanum containing alloys is lowest due to its low corrosion resistance. Manganese-doped alloys were observed as less corrosion-resistant than RMgNi_4 alloys and the alloys with cobalt or iron.

Conclusions

The influence of partial substitutions of Ni for Fe and Mn on the structural characteristics of the parent alloys and their hydrides has been studied. Seven new hydrides were synthesized and their structure was studied. The hydrides $\text{LaMgNi}_{3.5}\text{Fe}_{0.5}\text{H}_6$, $\text{PrMgNi}_{3.5}\text{Mn}_{0.5}\text{H}_6$ and $\text{NdMgNi}_{3.5}\text{Mn}_{0.5}\text{H}_5$ preserved the cubic structure of the original matrix. The orthorhombically deformed structure is found for $\text{PrMgNi}_{3.5}\text{Fe}_{0.5}\text{H}_{4.5}$, $\text{NdMgNi}_{3.5}\text{Fe}_{0.5}\text{H}_{4.3}$, $\text{La}_{0.5}\text{Pr}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}\text{H}_{4.6}$ and $\text{La}_{0.5}\text{Nd}_{0.5}\text{MgNi}_{3.5}\text{Fe}_{0.5}\text{H}_{4.4}$. The linear relationship between the amount of absorbed hydrogen and the relative increase in lattice volume for a number of hydrides is observed. Hydrides with $\text{H/M} = 4 \pm 0.5$ are formed with orthorhombic structures, while the those ones with $\text{H/M} \geq 5$ preserved parent structures. The electrochemical properties of the electrodes based on new synthesized alloys have been studied. It was found that the doping of Fe and Mn slightly increases the discharge capacity of the electrodes. Highest discharge capacity of 271 mAh/g and 263 mAh/g is observed for $\text{PrMgNi}_{3.5}\text{Mn}_{0.5}$ and $\text{NdMgNi}_{3.5}\text{Mn}_{0.5}$, respectively. The best cyclic stability, however, was observed only for $\text{NdMgNi}_{3.5}\text{Fe}_{0.5}$ ($S_{50} = 74\%$).

Figure 5. Cyclic stability of the $R,R'MgNi_{4-x}M_x$ electrodes.

Table 4. Selected electrochemical properties of the electrodes

№	Electrode	C_{max} , mAh/g	C_{50} , mAh/g	S_{50} , %
1.	$LaMgNi_{3.5}Fe_{0.5}$	253	91	36
2.	$PrMgNi_{3.5}Fe_{0.5}$	247	163	66
3.	$NdMgNi_{3.5}Fe_{0.5}$	254	188	74
4.	$La_{0.5}Pr_{0.5}MgNi_{3.5}Fe_{0.5}$	240	152	63
5.	$La_{0.5}Nd_{0.5}MgNi_{3.5}Fe_{0.5}$	226	141	62
6.	$LaMgNi_{3.5}Mn_{0.5}$	236	77	33
7.	$LaMgNi_3Mn$	108	56	51
8.	$PrMgNi_{3.5}Mn_{0.5}$	271	117	43
9.	$PrMgNi_3Mn$	193	57	29
10.	$NdMgNi_{3.5}Mn_{0.5}$	263	151	58
11.	$NdMgNi_3Mn$	260	58	22

Figure 6. Discharge curves of the selected electrodes.
The numbers at curves correspond to the number of cycles.

Figure 7. Diagram for comparison of influence of rare-earth and transition metals on discharge capacity and cyclic stability of electrodes.

References

- [1] Villars P, Cenzual K, Pearson's Crystal Data - Crystal Structure Database for Inorganic Compounds, Release 2014/15, ASM International: Materials Park, OH; 2014.
- [2] Verbovytskyy YV, Zavaliy IY. New metal-hydride electrode materials based on $R_{2-x}Mg_xNi_4$ alloys for chemical current sources. *Mat. Sci.* 2017; 52(6): 747-759.
- [3] Wang ZM, Zhou HY, Cheng G, Gu ZF, Yu AB. Preparation and electrode properties of new ternary alloys: $REMgNi_4$ (RE = La, Ce, Pr, Nd). *J. Alloys Compd.* 2004; 384: 279-282.
- [4] Liu Y, Cao Y, Huang L, Gao M, Pan H. Rare earth-Mg-Ni-based hydrogen storage alloys as negative electrode materials for Ni/MH batteries, *J. Alloys Compd.* 2011; 509(3): 675-686.
- [5] Guéneé L, Favre-Nicolin V, Yvon K. Synthesis, crystal structure and hydrogenation properties of the ternary compounds $LaNi_4Mg$ and $NdNi_4Mg$. *J. Alloys Compd.* 2003; 348: 129-137.
- [6] Chotard J, Sheptyakov D, Yvon K. Hydrogen induced site depopulation in the $LaMgNi_4$ -hydrogen system. *Z. Kristallogr.* 2008; 223: 690-696.
- [7] Sakaki K, Terashita N, Tsunokake S, Nakamura Y, Akiba E. In situ X-ray diffraction study of phase transformation of $Mg_{2-x}Pr_xNi_4$ during hydrogenation and dehydrogenation ($x = 0.6$ and 1.0). *J. Phys. Chem. C.* 2012; 116: 1401-1407.
- [8] Sakaki K, Terashita N, Tsunokake S, Nakamura Y, Akiba E. Effect of rare earth elements and alloy composition on hydrogenation properties and crystal

- structures of hydrides in $\text{Mg}_{2-x}\text{RE}_x\text{Ni}_4$. J. Phys. Chem. C. 2012; 116: 19156-19163.
- [9] Terashita N, Sakaki K, Tsunokake S, Nakamura Y, Akiba E. Hydrogenation properties of ternary intermetallic compounds $\text{Mg}_{2-x}\text{Pr}_x\text{Ni}_4$. Mat. Trans. 2012; 53: 513-517.
- [10] Denys RV, Riabov AB, Černý R, Koval'chuk IV, Zavaliy IY. New CeMgCo_4 and Ce_2MgCo_9 compounds: Hydrogenation properties and crystal structure of hydrides. J. Solid St. Chem. 2012; 187: 1-6.
- [11] Sakaki K, Terashita N, Kim H, Proffen T, Majzoub EH, Tsunokake S, Nakamura Y, Akiba E. Crystal structure and local structure of $\text{Mg}_{2-x}\text{Pr}_x\text{Ni}_4$ ($x = 0.6$ and 1.0) deuteride using in situ neutron total scattering. Inorg. Chem. 2013; 52(12): 7010-7019.
- [12] Shtender VV, Denys RV, Paul-Boncour V, Riabov AB, Zavaliy IY. Hydrogenation properties and crystal structure of YMgT_4 ($T = \text{Co}, \text{Ni}, \text{Cu}$) compounds. J. Alloys Compd. 2014; 603: 7-13.
- [13] Czub J, Shtender VV, Przewoźnik J, Zarzeska A, Hoser A, Gondek Ł. On the properties of the novel $\text{CeMgNi}_2\text{T}_2$ ($T = \text{Co}, \text{Cu}$) alloys and their hydrides. J. Alloys Compd. 2020; 814: 152244 (1-7).
- [14] Verbovytskyy YV, Shtender VV, Lyutyy PY, Zavaliy IY. Electrode materials based on $\text{LaMgNi}_{4-x}\text{Co}_x$ ($0 < x < 1$) alloys. Powder Met. Met. Ceramics. 2017; 55(10-11): 559-566.
- [15] Verbovytskyy YV, Shtender VV, Hackemer A, Drulis H, Zavaliy IY, Lyutyy PY. Solid-gas and electrochemical hydrogenation properties of the $\text{La}_{1-x}\text{Nd}_x\text{MgNi}_{4-y}\text{Co}_y$ alloys. J. Alloys Compd. 2018; 741: 307-314.
- [16] Shtender VV, Denys RV, Paul-Boncour V, Verbovytskyy YV, Zavaliy IY. Effect of Co substitution on hydrogenation and magnetic properties of NdMgNi_4 alloy. J. Alloys Compd. 2015; 639: 526-532.
- [17] Shtender VV, Paul-Boncour V, Denys RV, Crivello JC, Zavaliy IY. $\text{TbMgNi}_{4-x}\text{Co}_x$ -(H,D)₂ system. I: Synthesis, hydrogenation properties, and crystal and electronic structures. J. Phys. Chem. C. 2020; 124(1): 196-204.
- [18] Rodriguez-Carvajal J, Roisnel T, FullProf.98 and WinPLOTR: New Windows 95/NT Applications for Diffraction Commission for Powder Diffraction. International Union for Crystallography, Newsletter N20; 1998.
- [19] Kraus W, Nolze G, PowderCell for Windows. Version 2.3, Federal Institute for Materials Research and Testing, Berlin, Germany, 1999.
- [20] Nolze G, PowderCell: a mixture between crystal structure visualizer, simulation and refinement tool. Powder diffraction: proceedings of the II International School on Powder Diffraction, Kolkata, India, 2002.