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Electrochemical hydrogenation of $Tb_2Ni_{17-x}M_x$ (M = Mg, Sn) phases

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The electrochemical hydrogenation of $Tb_2Ni_{17-x}M_x$ phases (M = Mg, Sn) was studied for the first time. Both compounds have the hexagonal Th_2Ni_{17}-type structure and small homogeneity ranges, x = 0-1 for $TbNi_{17-x}Sn_x$ and x = 0-1.5 for $TbNi_{17-x}Mg_x$. Under the conditions of the experiment pure Tb_2Ni_{17} absorbed approximately 0.55 H/f.u. The Mg-containing phase absorbed approximately 1.14 H/f.u. and the Sn-containing phase ~0.63 H/f.u. In all cases intercalation of hydrogen occurred in octahedral voids 6*h* of the initial structures, so the coordination polyhedron of the H-atom is an octahedron [HTb_2M_4]. The $Tb_2Ni_{17-x}Mg_x$ phase absorbed the largest amount of hydrogen because magnesium, like rare-earth and transition metals, is able to absorb hydrogen and a combination of these elements leads to better hydrogen absorption. Electron microprobe analysis showed that the electrodes on the basis of $Tb_2Ni_{17-x}M_x$ were stable in the electrolyte during the electrochemical processes, *i.e.* the qualitative and quantitative composition of the observed phases remained unchanged.

Intermetallic compound / Ni-MH battery / Electrochemical hydrogenation

Introduction

Intermetallic compounds on the basis of rare-earth and transition metals show a variety of interesting physical properties. These compounds can also be used as electrode materials in Ni-MH batteries [1,2]. The best hydrogen absorption characteristics correspond to materials developed on the basis of intermetallic compounds with $CaCu_5$, $MgCu_2$, $MgZn_2$, $MgNi_2$, $CeNi_3$, $PuNi_3$, Th_2Ni_{17}, and U_3Si_2 structure types [3-6].

Many intermetallic compounds can form hydrides, but only some of them retain the original structure after the desorption process. Yartys and Denys [7] reported the formation of hydrides and deuterides $RE_2MgNi_9H_{12-13}$ (RE = La and Nd) on the basis of an ordered $PuNi_3$-type structure. The original matrix of these hydrides does not change during desorption. Shtender *et al.* [8,9] carried out gas hydrogenation of Tb–Mg–Co ternary phases and obtained a number of hydrides: $Tb_2MgCo_9H_{12}$, $Tb_4Mg_3Co_2H_4$, $Tb_4MgCoH_{12.5}$, $Tb_4MgCoH_{12.7}$, and $TbMgCo_4H_{5.3}$. Some of these hydrides contained more than 1 wt.% hydrogen.

Stetskiv *et al.* [10] carried out electrochemical hydrogenation and corrosion studies of $LaT_{5-x}M_x$ (T = Co, Ni and M = Al, Ge, Li) phases and confirmed that partial replacement of the transition metals Ni or Co by Al, Ge or Li increases the discharge capacity by 25 %. Doping of the $LaCo_5$ and $LaNi_5$ binary phases by Al, Ge and Li improves the corrosion resistance, thermal stability and absorption capacity during the electrochemical hydrogenation. These alloys are passivated in strong alkaline solutions such as 6 M KOH.

Similar alloys were investigated in [11]. *P-C* isotherms for hydrogen desorption of hydrogenated $LaNi_{4.8}Al_{0.2-x}Li_x$ alloys revealed that partial replacement of Ni by Al and Li causes a decrease of the equilibrium pressure and an increase of the hydrogen capacity. There exists information about other doping elements like Zn, Sb, Bi, and Mg, and their influence on absorption and desorption processes of this type of alloy [12-22]. Rozdzynska-Kielbik *et al.* [19] noticed that doping of $LaCo_5$-based alloys by small amounts of bismuth (3.3 at.%) increases the effectiveness of hydrogen absorption. Partial substitution of antimony, magnesium or bismuth for cobalt in $LaCo_5$ causes an increase of the hydrogen desorption rate.

Alloys with Th_2Ni_{17}-type structure were studied by Levytskyy *et al.* [23], who carried out gas hydrogenation of Dy_2M_{17} and $Dy_2M_{17}C_x$ (M = Co, Ni; $x < 0.5$) compounds. According to their results the Dy_2Co_{17} compound absorbs 3.4 H/f.u. and Dy_2Ni_{17}

3.5 H/f.u. at a hydrogen pressure of 5 MPa. The carbides $Dy_2Co_{17}C_x$ and $Dy_2Ni_{17}C_x$ absorbed less hydrogen – 2.7 H/f.u. and 2.8 H/f.u., respectively, because some octahedral voids (6*h*) were already occupied by carbon atoms.

The R_2Fe_{17} compounds studied in [24-26] absorb a considerable amount of hydrogen, forming stable hydrides $R_2Fe_{17}H_x$ that preserve the structure of the initial intermetallic compound. Isnard *et al.* [26] investigated several deuterides $R_2Fe_{17}D_x$ by neutron diffraction and found that the octahedral interstitial site 6*h* is favored for the hydrides (deuterides). Substantial occupation of the tetrahedral site 12*i* only occurs for higher H contents ($x > 3$).

The purpose of our research was to study the effect of doping components, namely Mg and Sn, on the amount of hydrogen absorbed by the Tb_2Ni_{17} intermetallic compound during electrochemical hydrogenation and the change of the surface morphology as a result of the electrochemical processes.

Experimental

Terbium, nickel, tin, and magnesium with a nominal purity of more than 99.9 wt.%, were used as starting materials. Alloys with the compositions $Tb_{10.5}Ni_{89.5}$, $Tb_{10.5}Ni_{84.2}Sn_{5.3}$ and $Tb_{10.5}Ni_{84.2}Mg_{5.3}$ were prepared by arc melting of the pure components under an argon atmosphere. To reach homogeneity the samples were sealed in silica ampoules, annealed at 600°C for two months and finally quenched in cold water. In the case of the alloy containing magnesium, this metal was added in an excess of about 20 wt.%, and the components of the sample were pressed into a pellet before melting to avoid mass losses due to the low boiling point of magnesium.

The phase analysis of the alloys before and after the electrochemical processes was carried out by powder X-ray diffraction using a DRON-2.0M diffractometer (Fe $K\alpha$-radiation). Refinement of the lattice parameters of the observed phases was performed using LATCON [27] and PowderCell [28] programs.

Electrochemical hydrogenation of the Tb_2Ni_{17} binary compound and its ternary derivatives $Ti_2Ni_{17-x}M_x$ (M = Mg, Sn) was carried out in Swagelok-type cells. The battery prototype consisted of a negative electrode containing 0.3 g of alloy and a positive electrode containing a mixture of $Ni(OH)_2$ with graphite for better electric conductivity.

A separator (pressed cellulose) soaked in electrolyte (6 M KOH) was placed between the electrodes. Testing of the batteries was carried out in galvanostatic regime (at 0.2, 0.5, 1.0, 1.5, 2.0 and 2.5 mA) over 30 cycles (galvanostat MTech G410-2 [29]). The qualitative and quantitative composition of the observed phases, and the morphology of the surface were examined using a scanning electron microscope REMMA 102-02.

Results and discussion

X-ray phase analysis of the alloys revealed that all the studied samples were single phase. The observed phases crystallize in the hexagonal Th_2Ni_{17}-type structure (space group $P6_3/mmc$, Pearson code *hP*38). A small homogeneity range (~1 at.%) was assumed for Tb_2Ni_{17} due to a slight change of lattice parameters for the samples $Tb_{11}Ni_{89}$ (a = 8.324(1) Å, c = 8.041(1) Å, V = 482.5(1) Å^3) and $Tb_{10.5}Ni_{89.5}$ (a = 8.318(2) Å, c = 8.040(1) Å, V = 481.8(1) Å^3).

A regular increase of the lattice parameters was also observed for the phases $Tb_2Ni_{17-x}M_x$ (M = Mg, Sn) as compared to the pure binary phase Tb_2Ni_{17} (Table 1). This occurs because nickel in the original structure of Tb_2Ni_{17} is partially replaced by tin or magnesium, the atomic radii of which (r_{Mg} = 1.6 Å, r_{Sn} = 1.62 Å) are larger than the atomic radius of nickel (r_{Ni} = 1.24 Å). The results of the EDX-analysis showed that the maximum homogeneity range for the $Tb_2Ni_{17-x}Mg_x$ phase reached 8 at.% Mg ($x \sim 1.5$), though Solokha [30] claimed that the binary compound Tb_2Ni_{17} does not dissolve any Mg. The maximum homogeneity range for $Tb_2Ni_{17-x}Sn_x$ reached 6 at.% Sn ($x \sim 1$).

The effectiveness of the electrochemical hydrogenation of the $Tb_2Ni_{17-x}M_x$ (M = Mg, Sn) phases, which served as negative electrode materials, was studied over 30 charge-discharge cycles. As a result of the hydrogen intercalation, we observed an increase of the unit cell volume (Table 1). Scanning electron microscopy also showed changes of the surface morphology and grain size of the materials (Fig. 1).

Table 1 Lattice parameters of $Tb_2Ni_{17-x}M_x$ (M = Mg, Sn) phases and their hydrides.

Composition	a, Å	c, Å	V, Å^3	$\Delta V/V$, %
Tb_2Ni_{17}	8.318(2)	8.040(1)	481.8(1)	1.52
$Tb_2Ni_{17}\mathbf{H}_{\mathbf{\sim 0.55}}$	8.367(1)	8.067(1)	489.1(1)	
$Tb_2Ni_{17-x}Sn_x$	8.356(2)	8.126(4)	491.4(3)	0.77
$Tb_2Ni_{17-x}Sn_x\mathbf{H}_{\mathbf{\sim 0.63}}$	8.380(2)	8.143(3)	495.2(2)	
$Tb_2Ni_{17-x}Mg_x$	8.335(1)	8.063(2)	485.2(1)	1.34
$Tb_2Ni_{17-x}Mg_x\mathbf{H}_{\mathbf{\sim 1.14}}$	8.380(1)	8.083(2)	491.7(1)	

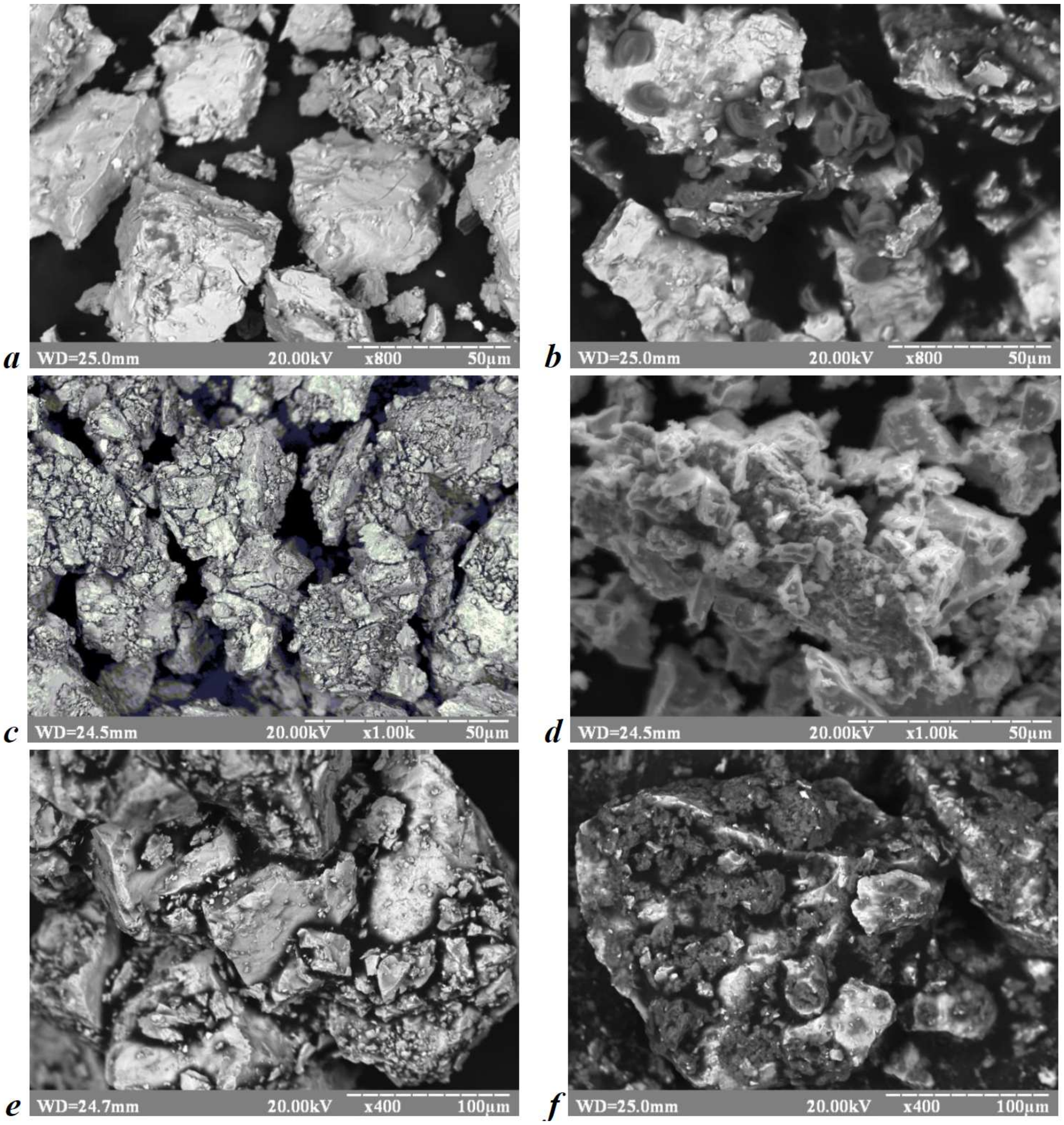

Fig. 1 SEM-images of the anode materials before and after 30 cycles of electrochemical hydrogenation: $Tb_{14.23}Ni_{79.26}Mg_{6.51}$ (*a*), $Tb_{12.29}Ni_{79.72}Mg_{7.99}$ (*b*), $Tb_{10.28}Ni_{87.81}Sn_{1.91}$ (*c*), $Tb_{13.78}Ni_{80.22}Sn_{6.00}$ (*d*), $Tb_{13.41}Ni_{86.56}$ (*e*), $Tb_{12.79}Ni_{87.21}$ (*f*).

The electrodes prepared from the studied materials were stable in the alkaline solution for more than 30 cycles of charge-discharge. No evidence of corrosion, proved by the absence of additional reflections (from oxides, hydroxides) in the powder patterns, was observed for the studied alloys after the electrochemical hydrogenation. The change of the qualitative and quantitative compositions of the phases was also insignificant after the hydrogenation.

The electrochemical reactions that occur on the electrodes can be represented by the following scheme:

$$Tb_2Ni_{17\text{-}x}M_x + zH_2O + z\bar{e} \xleftrightarrow{\text{charge–discharge}} Tb_2Ni_{17\text{-}x}M_xH_z + zOH^-;$$

$$Ni(OH)_2 + zOH^- - z\bar{e} \xleftrightarrow{\text{charge–discharge}} NiOOH + zH_2O.$$

Charging of the batteries with anode materials on the basis of Tb_2Ni_{17} or $Tb_2Ni_{17\text{-}x}M_x$ (M = Mg, Sn) was carried out in the galvanostatic regime at 2 mA, and discharging at 0.2, 0.5, 1.0, 1.5, 2.0, and 2.5 mA. During the first nine cycles surface and volume activation occurred. Charge and discharge curves for the studied Ni-MH prototype batteries are displayed in Fig. 2.

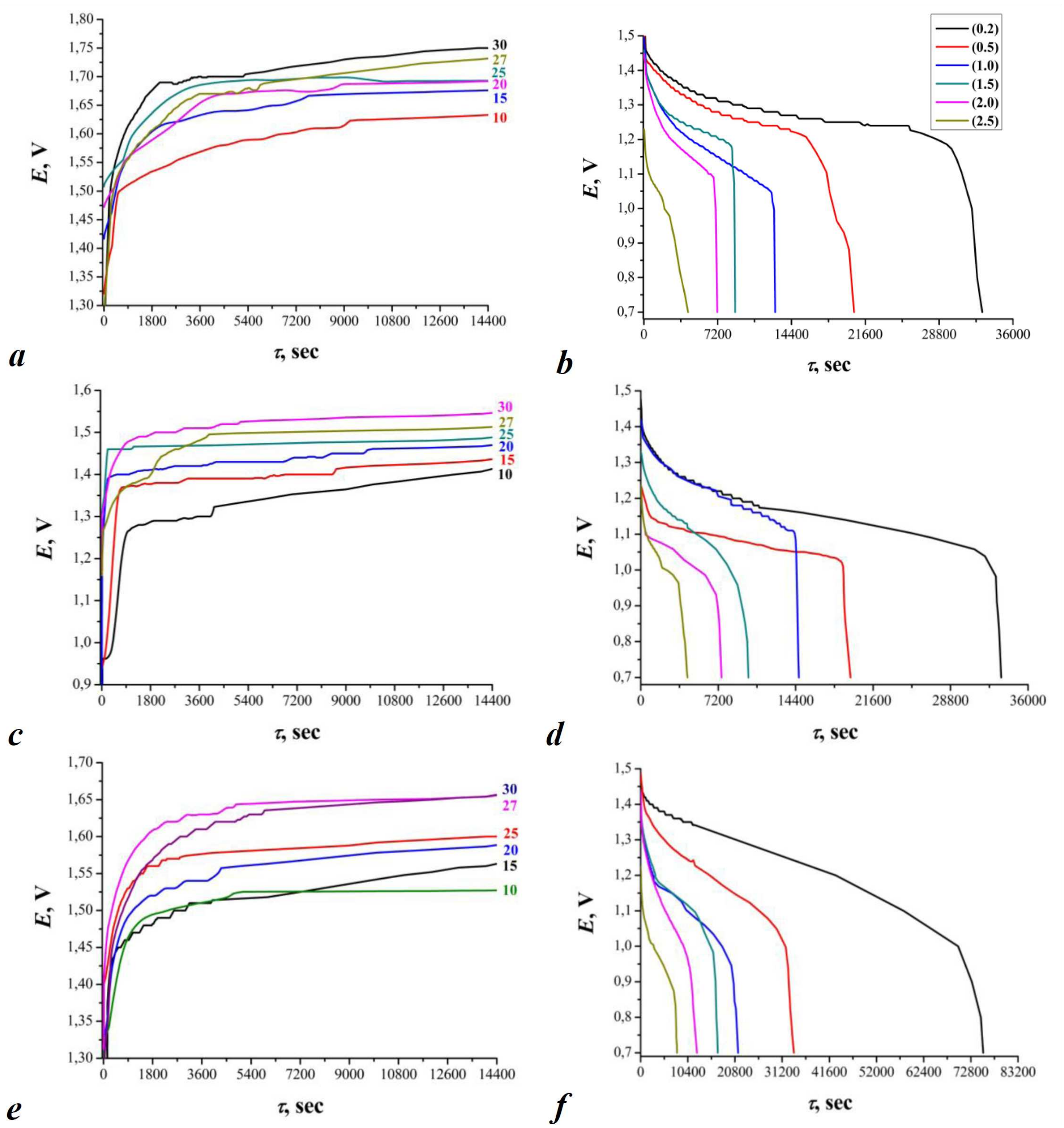

Fig. 2 Selected charge-discharge curves for the systems $Ni(OH)_2$ / Tb_2Ni_{17} (*a*, *b*), $Ni(OH)_2$ / $Tb_2Ni_{17-x}Sn_x$ (*c*, *d*) and $Ni(OH)_2$ / $Tb_2Ni_{17-x}Mg_x$ (*e*, *f*) (the number of cycles is indicated near the charge curves).

During the electrochemical hydrogenation the hydrogen atoms formed on the surface of the alloys, penetrate the bulk of the material. They occupy the octahedral interstitial site 6*h* of the structure. As a result the volume of the material matrix increases.

The increase of the unit cell volume does not only depend on the amount of intercalated atoms. For instance, the volume change of Tb_2Ni_{17} after hydrogenation is significant, but the amount of intercalated hydrogen is small. This fact can be explained by probable internal deformation of the structure (Table 1). The coordination polyhedron of the H-atom in the structure of $Tb_2Ni_{17-x}M_xH_y$ ($y < 3$) is an octahedron $[HTb_2M_4]$ (Fig. 3).

During of the charge process a charge of 8 mA·h was passed through the prototype battery. The highest efficiency of the electrochemical hydrogenation, about 76 %, was observed for the magnesium-containing electrode (~6.1 mA·h of electricity took during the discharge process). The Sn-containing electrode showed an efficiency of about 53 % (~4.2 mA·h). The binary phase Tb_2Ni_{17} absorbed the least amount of hydrogen and showed a hydrogenation efficiency of about 50 % (~4.0 mA·h).

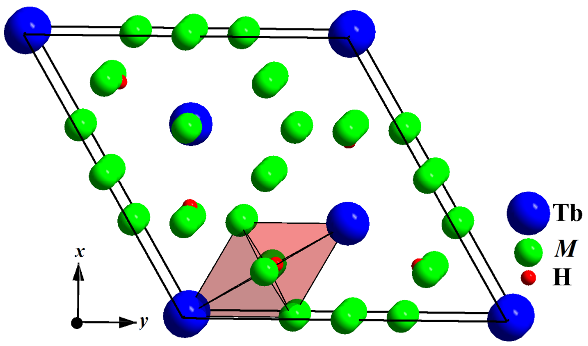

Fig. 3 Unit cell of $Tb_2Ni_{17-x}M_xH_y$ ($y < 3$) hydrides and coordination polyhedron of the H-atom.

The discharge capacity of the studied electrodes at the conditions of the experiment is low because of the low value of the charge passed through the electrodes. The discharge capacity for the batteries with $Tb_2Ni_{17-x}Mg_x$ electrodes reached 20.3 mA·h/g, 14.0 mA·h/g for the $Tb_2Ni_{17-x}Sn_x$ electrodes 13.3 mA·h/g for the Tb_2Ni_{17} electrode. If the amount of absorbed hydrogen reaches ~3.5 H/f.u. the discharge capacity of these electrodes can exceed 73 mA·h/g.

The maximal amount of intercalated hydrogen was not reached under the conditions of the experiment. The largest amount of hydrogen can be obtained by gas hydrogenation at high pressure. In the case of electrochemical hydrogenation, the H-atoms occupy the interstitial site 6*h* of the structure, while in the case of gas hydrogenation they occupy the same octahedral voids 6*h* and a tetrahedral site 12*i*.

Comparing the electrochemical behavior of the studied alloys with respect to the amount of absorbed hydrogen we can conclude that the $Tb_2Ni_{17-x}Mg_x$ phase is a more prospective material for negative electrodes of Ni-MH batteries.

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