Synthesis, crystal structure, and electrochemical hydrogenation of the La$_{2}$Mg$_{17-x}$M$_{x}$ (M = Ni, Sn, Sb) solid solutions

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**ABSTRACT**

The crystal structure of La$_{2}$Mg$_{17-x}$Sn$_{x}$ solid solution was determined by single crystal X-ray diffraction for the first time. This phase crystallizes in hexagonal symmetry with space group $P6_3/mmc$ ($a = 10.3911(3)$ Å, $c = 10.2702(3)$ Å, $V = 960.36(6)$ Å$^3$, $R_I = 0.0180$, $wR_2 = 0.0443$ for the composition La$_{2.35}$Mg$_{30}$Sn$_{1.10}$) and is related to the structure of Ge$_{17}$ and Th$_2$Ni$_{17-}$-types which are derivative from the CaCu$_5$-type. A series of isotypical solid solutions La$_{2}$Mg$_{17-}$$x$M$_{x}$ (M = Ni, Sn, Sb, x = 0-6) was synthesized and studied by X-ray powder diffraction, energy dispersive X-ray spectroscopy and fluorescent X-ray spectroscopy. All solid solutions crystallize with the structure related to the Th$_2$Ni$_{17}$-type. The electrochemical hydrogenation confirmed the similar electrochemical behavior of all studied alloys. The amount of deintercalated hydrogen depends on the physical and chemical characteristics of doping elements and increases in the sequence Sn < Mg < Sb < Ni. The most geometrically advantageous sites are octahedral voids 6h of the initial structure, thus a coordination polyhedron for H-atom is an octahedron [HLa$_2$(Mg,M)$_x$].

1. Introduction

Nowadays, materials related to the production, storage and conversion of energy are in great demand in different fields of technology and industry. The most profitable energy storage is possible during the accumulation of charge in various batteries or storage stations. Most of the batteries use intermetallic phases or composites with metallic matrix as electrodes [1]. Phases with large voids, such as R$_5$M$_3$ (Mn$_5$Si$_3$-type structure), are suitable for Li or Mg intercalation and for doping of La$_2$Mg$_{17}$ by Al and Sn for corrosion resistance [6,7]. Doping of Th$_2$Ni$_{17}$ by Mg, Al, Ge, Sn, Sb and Bi also enhances corrosion resistance and discharge time of the battery [8]. The alloys containing Mg became popular for the development of light and safe for the environment materials. As a basis are the phases that crystallize in the structure type GdCu$_5$ or its derivatives [9-15]. Gas hydrogenation and optimization of the synthesis procedure of the composite based on the mixture of La$_2$Mg$_{17}$ and LaNi$_5$ is presented in Ref. [16]. In this case, LaNi$_5$ accelerates the hydrogen sorption and desorption processes. The solubility of Sn in the La$_2$Mg$_{17}$ phase does not exceed 2 at. % at 500 °C according to Ref. [17], while in our research the solubility reaches 4 at. % at 400 °C that is confirmed by X-ray powder diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). The purpose of this research is to study the crystal structure of La$_2$Mg$_{17-}$$x$M$_{x}$, solid solutions and find the correlation between composition of the electrodes and their electrochemical characterization during hydrogenation/dehydrogenation processes.
2. Experimental

2.1. Synthesis of samples

Lanthanum, tin, antimony, nickel (commercial, small pieces), and magnesium (commercial powder) with nominal purity > 99.9 wt. % were used as starting materials. Similar method of synthesis is described in [5]. Alloys with the composition La$_{10.5}$Mg$_{85.5}$Sn$_{4}$ (M = Ni, Sn, Sb) were prepared by induction melting (re-melted two times) of pressed pellets of pure components (excess of Mg was 5 wt. % and Sn was 2 wt. %) under the purified argon atmosphere. To reach homogeneity the samples were sealed in evacuated silica tubes, annealed at 400 °C for 2 months and finally quenched in cold water. During the synthesis, the loss of weight did not exceed 2 wt. %. Higher annealing temperature, for example 600 °C causes the interaction of magnesium with surface of silica tube and further component loss.

2.2. Phase analysis

The phase analysis of the alloys before electrochemical processes was mainly carried out by powder X-ray diffraction using a diffractometer DRON-2.0M (FeKα-radiation, λ = 1.93608 Å, 20° ≤ 2θ ≤ 100°). The refinement of lattice parameters (least squares refinement method) was performed using LATCON [18] and PowderCell [19] programs. Qualitative and quantitative composition of the observed phases was studied using scanning electron microscope TESCAN Vega3 LMU (Oxford Instruments energy dispersive X-ray analyzer, Aztec ONE system) and REMMA-102-02. X-ray fluorescent spectroscopy (spectrometer ElvoX Pro) was used for investigation of the integral composition of electrodes before and after hydrogenation.

2.3. Electrochemical measurements

Electrochemical hydrogenation of a binary La$_2$Mg$_{17}$ and three ternaries (doped by 4 at. % of Ni, Sn, and Sb) alloys was carried out in 2-electrode Swagelok-type cells. The battery prototype consisted of a negative electrode containing 0.3 g of the studied alloy and a positive electrode containing a mixture of dried Ni(OH)$_2$ (mixture of α- and β-modifications) with 10 wt. % of graphite. A separator soaked in 6M KOH electrolyte (prepared from KOH with 99 wt. % purity, commercial) was placed between the electrodes to avoid contact. Chronopotentiograms of the Ni-MH battery prototypes were obtained in galvanostatic regime over 50 cycles using galvanostat MTech G410-2 [20]. The amount of deintercalated H-atoms per formula unit (H/f.u.) was determined for studied electrodes using Faraday’s formula, where H-content is directly proportional to the discharge time and inversely proportional to the amount of electrode material. The electrochemical reactions that occur on the electrodes can be presented by Scheme 1.

2.4. Single crystal determination

The crystal structure of the La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ solid solution was studied by single crystal X-ray diffraction (diffractometer Xcalibur Oxford Diffraction, CCD-detector, Mo Kα-radiation, ω-scan mode). A single crystal for investigation was selected from the alloy with the composition La$_{10.5}$Mg$_{85.5}$Sn$_{4}$. Absorption correction was performed by an empirical method using SADABS [21]. The analysis of the crystal structure was carried out by direct method using SHELXS [22] and full matrix least squares refinement on F$^2$ was performed using SHELXL [23].

3. Results and discussion

3.1. Crystal structure of the La$_{3.65}$Mg$_{30}$Sn$_{1.10}$

During the systematic investigation of the interaction between metallic components in the systems La–Mg–{Sn, Sb}, we observed the formation of the solid solutions of substitution on the basis of the binary phase La$_2$Mg$_{17}$ (ordered model with structure type Th$_2$Ni$_{17}$, space group P6$_3$/mmc, Pearson’s code hP38, Z = 2) with the homogeneity range up to 4 at.% of Sn or Sb. This structure is suitable for hydrogen storage and the phases with the same or relative crystal structure can serve as a negative electrode material in Ni-MH batteries. Detailed study of the crystal structure of this solid solution was carried out by single crystal X-ray powder diffraction on the sample La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ from which an irregularly shaped single crystal was selected. Solution the structure by direct methods indicated a significant disorder of the structure and the presence of split positions for La$_{2}$Sn$_{2}$ and Sn$_{1}$Sn$_{3}$. The refined composition from X-ray data is La$_{3.65}$Mg$_{30}$Sn$_{1.10}$. The crystal data and details of the structure refinement for La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ are given in Table 1. The standardized atomic positions and thermal displacement parameters are given in Table 2.

The results of structural refinement show that the formation of a La$_2$Mg$_{17}$-Sn$_{4}$ solid solution takes place by a complex mechanism. If the binary phase La$_2$Mg$_{17}$ dissolves tin, the Mg-atoms are replaced by Sn-atoms in a site 4 and additional Sn-atoms are inserted in the positions 4 and 2d, which are empty in the initial binary structure. The insertion of Sn atoms in the site 2b causes the subtraction of La atoms from 2b site because La$_{2}$Sn$_{2}$ are in the split position. It proves that La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ is more closely related to CeMg$_{10.3}$-type [24], however, it also differs from it due to the redistribution of atoms at some sites. (Table 3). The La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ structure is strongly disordered, as evidenced by the presence of adjacent atomic sites, which can not be occupied simultaneously, and by the existence of split positions. Therefore, in the average structure, two subcells (A and B) can be selected, with the fraction ratio of subcell A to subcell B as 4:1 (Figure 1). The A subcell has a composition La$_{3}$Mg$_{18}$Sn$_{10}$ and B subcell has a composition La$_{2}$Mg$_{17}$Sn$_{10}$. Detailed crystal chemical analysis shows that La$_{1}$ and La$_{2}$ atoms are enclosed in a pseudo-Frank-Kasper polyhedra [La$_{1}$Mg$_{12}$Sn$_{30}$] and [La$_{2}$Mg$_{8}$] respectively. For all Mg and Sn$_{3}$ atoms typical is kossahedral coordination. The Sn$_{1}$ and Sn$_{2}$ atoms are enclosed in 14-vertex polyhedra [Sn$_{1}$Mg$_{12}$Sn$_{30}$] and [Sn$_{2}$Mg$_{8}$], which can be treated as bicapped hexagonal antiprisms. The unit cell and coordination polyhedra of atoms are shown in Figure 2.
Table 1. Crystal data and details of the structure refinement for La$_{3.65}$Mg$_{30}$Sn$_{1.10}$.

| Parameters | Compound | La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ |
|------------|----------|-------------------------------|
| Empirical formula | | La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ |
| Formula weight (g/mol) | | 1366.7 |
| Temperature (K) | | 298 |
| Crystal system | | Hexagonal |
| Space group | | P6$_3$/mmc |
| α (Å) | | 10.3911(3) |
| β (Å) | | 10.3911(3) |
| γ (Å) | | 10.2702(3) |
| Volume (Å$^3$) | | 960.36(6) |
| Z | | 1 |
| ρcalc (g/cm$^3$) | | 2.363 |
| μ (mm$^{-1}$) | | 5.17 |
| F(000) | | 623 |
| Crystal size (mm$^3$) | | 0.06 × 0.06 × 0.02 |
| Radiation | | MoKα (λ = 0.71073) |
| 2Θ range for data collection (°) | | 2.3 to 26.3 |
| Index ranges | | -12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12 |
| Reflections collected | | 8711 |
| Independent reflections | | 408 [R(int) = 0.0261] |
| No. of reflections with I > 2σ(I) | | 339 |
| Data/parameters | | 408/28 |
| Goodness-of-fit on F$^2$ | | 1.27 |
| Final R indexes [I≥2σ(I)] | | R$_1$ = 0.0180, wR$_2$ = 0.0443 |
| Final R indexes [all data] | | R$_1$ = 0.0241, wR$_2$ = 0.0498 |
| Largest diff. peak/hole (e Å$^-3$) | | 0.34/ -0.86 |

Table 2. Fractional atomic coordinates and thermal displacement parameters (Å$^2$) for for La$_{3.65}$Mg$_{30}$Sn$_{1.10}$.

| Atoms | Wyckoff sites | x | y | z | U$^{11}$ | U$^{22}$ | U$^{33}$ | U$^{12}$ | U$^{13}$ | U$^{23}$ | Occ. (<1) |
|-------|---------------|---|---|---|---------|---------|---------|---------|---------|---------|-----------|
| La1   | 2c            | 1/3| 2/3| 1/4| 0.01499(18) | 0.0151(2) | 0.0151(2) | 0.00757(11) | 0.00000(10) | 0.00000(10) | |
| La2   | 2b            | 0 | 0 | 1/4| 0.0183(2) | 0.0220(4) | 0.0220(4) | 0.00264(12) | 0.00000(10) | 0.00000(10) | |
| Mg1   | 12k           | 0.36045(16) | 0.03294(16) | 1/4| 0.0246(3) | 0.0246(3) | 0.0246(3) | 0.0195(4) | 0.00000(10) | 0.00000(10) | |
| Mg2   | 12j           | 0.16402(7) | 0.32803(14) | 0.02035(13) | 0.0221(3) | 0.0221(3) | 0.0221(3) | 0.00000(10) | 0.00000(10) | 0.00000(10) | |
| Mg3   | 6g            | 1/2| 0 | 0 | 0.0195(4) | 0.0195(4) | 0.0195(4) | 0.00000(10) | 0.00000(10) | 0.00000(10) | |
| Sn1   | 4f            | 1/3| 2/3| 0.6018(2) | 0.025(2) | 0.2174(15) | 0.025(2) | 0.0195(4) | 0.00000(10) | 0.00000(10) | |
| Sn2   | 4e            | 0 | 0 | 0.1015(12) | 0.027 | 0.0404(12) | 0.027 | 0.0195(4) | 0.00000(10) | 0.00000(10) | |
| Sn3   | 2d            | 1/3| 2/3| 3/4| 0.027 | 0.032(2) | 0.027 | 0.0195(4) | 0.00000(10) | 0.00000(10) | |

The La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ (own type), La$_3$Mg$_{17}$ (Th$_2$Ni$_{17}$-type), and CeMg$_{10.3}$ (own type) structures are related to the parental CaCu$_5$-type structure (space group P6$_3$/mmc). As a result of tripling of the unit cell (1:5 stoichiometry) and replacing of a large atom (rare-earth element) with a pair of smaller atoms (transition element or other), we turn to the stoichiometry 2:17. By similar replacing, we can obtain other stoichiometry such as 2:7, 5:19, 3:22, 3:29, etc. Insertion of additional atoms causes the formation of CeMg$_{10.3}$ and La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ structures. The differences between these types of structures can be observed during the analysis of atomic networks that form magnesium atoms (Figure 3).
Table 3. Distribution of atoms in the Wyckoff sites for the La$_{2}$Mg$_{17}$, La$_{3.65}$Mg$_{30}$Sn$_{1.10}$, and Ce$_{1.71}$Mg$_{17.58}$ structures.

| Wyckoff sites | La$_{2}$Mg$_{17}$ | La$_{3.65}$Mg$_{30}$Sn$_{1.10}$ | Ce$_{1.71}$Mg$_{17.58}$ |
|---------------|-----------------|-----------------|-----------------|
| 12            | Mg 1.000        | Mg 1.000        | Mg 1.000        |
| 12j           | Mg 1.000        | Mg 1.000        | Mg 1.000        |
| 6g            | Mg 1.000        | Mg 1.000        | Mg 1.000        |
| 4f            | Mg 1.000        | Sn 0.217        | Mg 0.905        |
| 4e            | -               | Sn 0.040        | Mg 0.305        |
| 2d            | -               | Sn 0.032        | Ce 0.015        |
| 2c            | La 1.000        | La 1.000        | Ce 1.000        |
| 2b            | La 1.000        | La 0.826        | Ce 0.695        |

Figure 2. Unit cell and coordination polyhedra of atoms for La$_{3.65}$Mg$_{30}$Sn$_{1.10}$.

Figure 3. Magnesium atomic nets in the La$_{3.65}$Mg$_{30}$Sn$_{1.10}$, La$_{2}$Mg$_{17}$, and CeMg$_{10.3}$ related structures.

3.2. Powder XRD and EDX studies of La$_{2}$Mg$_{17-x}$M$_{x}$ alloy

The synthesized samples with the compositions La$_{10.5}$Mg$_{89.5}$, La$_{10.5}$Mg$_{85.5}$Sn$_{4}$, La$_{10.5}$Mg$_{85.5}$Sb$_{4}$ and La$_{10.5}$Mg$_{85.5}$Ni$_{4}$ were ingots of silver color and metallic luster and stable in air at room temperature. X-ray analysis showed the formation 2:17-phase (binary or ternary phases, ordered model) and small amounts of the other phases. The composition of this phase from EDX-analysis is La$_{11.2(5)}$Mg$_{88.8(9)}$ (Figure 4a). In binary alloy, the trace amount of LaMg$_{3}$ (structure type BiF$_{3}$, space group Fm-3m, $a = 7.4807(5)$ Å, $V = 418.63(8)$ Å$^3$) was observed. The cubic phase (LaMg$_{3}$) did not show the corrosion stability in the electrolyte and after hydrogenation we observed traces of La$_{2}$O$_{3}$.

Ni-contained alloys (from EDX-analysis La$_{10.3(4)}$Mg$_{85.3(7)}$Ni$_{4.4(7)}$) besides the main solid solution phase with nominal composition La$_{2}$Mg$_{16.2}$Ni$_{0.8}$ (Figure 4b) contained also the phase with high content of Mg (LaMg$_{12}$, composition from EDX-analysis is La$_{8.2(5)}$Mg$_{90.6(9)}$Ni$_{1.2(9)}$).
Authors [25] also confirmed that the solubility of Ni in the 2:17-phase does not exceed 4-5 at. %. Authors [26] also were interested in electrochemical hydrogenation alloys of La-Mg-Ni system.

Tin-contained alloy contained the main phase La$_{2}$Mg$_{16.2}$Sn$_{0.8}$ (main phase, from EDX-analysis La$_{10.6(5)}$Mg$_{85.7(8)}$Sn$_{3.7(9)}$) and trace amount of ~Mg (dark phase, see Figure 4c, La$_{24.3(5)}$Mg$_{73.4(6)}$Sn$_{2.3(7)}$). Similar content of phases is presented for Sb-contained alloy. Predicted solid solution La$_{2}$Mg$_{16.2}$Sb$_{0.8}$ (main phase, see Figure 4d) was with the composition La$_{11.1(5)}$Mg$_{84.2(8)}$Sb$_{4.7(6)}$. Trace amounts of Mg (La$_{2.2(6)}$Mg$_{95.9(8)}$Sb$_{1.9(8)}$) and cubic LaMg$_{3-x}$Sb$_{x}$ (La$_{24.8(5)}$Mg$_{72.2(7)}$Sb$_{3.0(7)}$, $a$ = 7.4639(8) Å, $V$ = 415.8(1) Å$^3$) phase were observed.

3.3. Electrochemical hydrogenation of La$_{2}$Mg$_{17-x}$M$_{x}$

All samples before and after electrochemical processes were examined by X-ray powder diffraction (diffractometer DRON-2.0M, Fe $K\alpha$-radiation), X-ray fluorescent spectroscopy and EDX-analysis. Spectral analysis (Figure 5) confirmed the changes in electrode composition occurred as a result of hydrogenation. The main reason for it was the etching of surface and the forming of oxides of La and Sn on the surface, and this reaction affects the discharge capacity. The grain size decreased by hydrogenation, the surface of electrode grains became more porous and the morphology of the grain surface was changed. Also, the composition of the grains was shifted in the direction of reducing the lanthanum content.

Electrochemical hydrogenation was carried out in two-electrode Swagelok-type cells at galvanostatic mode (2 mA/cm$^2$) to 3 H/f.u. For the binary and Sn-containing electrodes, we observed the formation and evolution of molecular hydrogen that correlates well with the discharge curves. In our opinion by gas hydrogenation we can obtain the hydrides with high H-content because high temperature and high pressure activates more grains. At the beginning of hydrogenation H-atoms occupy the octahedral voids with the position 6$h$ forming the coordination polyhedra from two large and four small atoms (La,Mg). Similar octahedral coordination of hydrogen atoms can be observed in the CaCu$_5$-type structure. When the H-content is larger than 3 H/f.u., the tetrahedral composition 12$i$ are occupied by hydrogen [27]. We think that H-atoms can occupy the tetrahedral positions of La$_{2}$Mg$_{17-x}$M$_{x}$ only by at high pressure or other extreme conditions. At experimental conditions we did not observe any evidences of structure decomposition after dehydrogenation.

Smaller amount of hydrogen (rectilinearly depends on the discharge time) was observed during dehydrogenation for La$_2$Mg$_{17}$ (1.36 H/f.u.) and La$_2$Mg$_{16.2}$Sn$_{0.8}$ (1.01 H/f.u.); in this case gas evolution took place as a side effect. Reversible content of hydrogen for the electrode on the basis of La$_2$Mg$_{16.2}$Sb$_{0.8}$ is 1.70 H/f.u. and for La$_2$Mg$_{16.2}$Ni$_{0.8}$ is 1.73 H/f.u. (Figure 6). After 50 cycles of electrochemical hydrogenation/dehydrogenation, the capacity of the battery prototype somewhat declined. It depends on the partial amorphization of the material and etching of the surface. While the electrochemical properties of the electrode materials depend on the corrosion stability of the alloys in the electrolyte solution (6 M KOH). In our previous works [5-7], doping Tb$_2$Ni$_{17}$-based electrodes by $s$-elements (Li, Mg) and Sb led to the increasing of the corrosion stability and hydrogen sorption ability.

Nominal discharge voltage for the batteries with La$_2$Mg$_{17-x}$M$_{x}$ electrodes is bigger than in commercial batteries with $AB_5$ or $AB_2$ electrodes and is ~1.25-1.30 V. For example, the batteries based on $AB_5$ and $AB_2$-electrodes with high Ni-content demonstrated the nominal discharge voltage in the range of 1.10-1.20 V.
Table 4. Unit cell parameters for 2:17 phases before hydrogenation (initial) and after hydrogenation (hydride of inclusion).

| Phase / hydride | a, Å  | c, Å  | V, Å³ | ΔV/V, % |
|-----------------|-------|-------|-------|---------|
| La₂Mg₁₇         | 10.339(1) | 10.259(1) | 949.7(2)  | 0.96    |
| La₂Mg₁₂Hₓ      | 10.365(1) | 10.303(2) | 958.0(2)  |          |
| La₂Mg₁₂Sn₀.₈ₓ  | 10.347(8) | 10.272(7) | 952.6(1)  | 0.45    |
| La₂Mg₁₂Sb₀.₈ₓ  | 10.362(6) | 10.288(8) | 956.9(1)  | 1.18    |
| La₂Mg₁₂Ni₀.₈ₓ  | 10.392(4) | 10.245(4) | 945.8(3)  | 1.43    |

(a) Integral composition – La₁₀.₅Mg₈₉.₅;
(b) Light phase – La₉.₉Mg₈ₐ.₁; dark phase – ~La₂₅.₉Mg₃₃.₂O₃ (oxides);
(c) Integral composition – La₁₀.₅Mg₈₅.₄Sn₄;
(d) Light phase – La₉.₂Mg₈₅.₈Sn₄; dark phase – oxides based on La, Sn

Figure 5. SEM-images of electrodes on the basis of La₁₀.₅Mg₈₉.₅ and La₁₀.₅Mg₈₅.₄Sn₄ before (a), (c), and after (b), (d) 50 cycles of electrochemical hydrogenation.

Changes in unit cell parameters of the solid solutions after electrochemical hydrogenation are presented in Table 4. For all samples after hydrogenation, we observed the increasing of the unit cell volume. As one can see, the unit cell parameters of the studied phases correlate well with the atomic radius of the alloying components (rMg = 1.60 Å, rNi = 1.24 Å, rSn = 1.62 Å, rSb = 1.59 Å).

4. Conclusion

Crystal structure of the solid solution La₂Mg₁₇–Snₓ was determined by single crystal X-ray diffraction on the sample with the stoichiometry La₃.₅Mg₉₀Sn₁₀₆. The phase crystallizes in the hexagonal symmetry with the space group P6₃/mmc and is related to the structure of Th₈Ni₁₇ (ordered) and CeMg₁₀.₃ (disordered). The structure of La₃.₅Mg₉₀Sn₁₀₆ is strongly disordered and characterized by the split of some positions. Therefore, in the average structure, two subcells (A and B) can be selected, with the fraction ratio of subcell A to subcell B as 4:1. The A subcell has a composition La₃.₅Mg₉₀Sn₁₀₆ and B subcell has a composition La₃.₅Mg₉₀Sn₁₀₆. The solubility of tin in the binary La₂Mg₁₇ intermetallic compound, studied by powder XRD and EDX-analysis, reaches 4 at. %. Solubility of Ni and Sb in the La₂Mg₁₇ compound is similar. The unit cell parameters of the solid solution La₂Mg₁₇–Mₓ (M = Ni, Sb, Sn) correlate well with the atomic radii of doping components. As the electrode...
materials studied, the alloys demonstrate the increasing of capacity in the line La$_2$Mg$_{16.2}$Sb$_{0.8}$ (1.01 H/f.u.) < La$_2$Mg$_{16.2}$Sn$_{0.8}$ (1.70 H/f.u.) < La$_2$Mg$_{16.2}$Ni$_{0.8}$ (1.73 H/f.u.) at 30-th cycle of charge/discharge. After 50 cycles of electrochemical measurements, the small shifting of electrode composition, changing of the morphology and grain size were observed.

**Supporting information**

CCDC-2059085 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [https://www.ccdc.cam.ac.uk/structures/](https://www.ccdc.cam.ac.uk/structures/), or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223 336033 and may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247 -808-666; e-mail: crysdata@fiz-karlsruhe.de).

**Disclosure statement**

Conflict of interests: The authors declare that they have no conflict of interest.

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Sample availability: Samples of the compounds are available from the author.

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