

The Electronic and Electrochemical Properties of the LaNi₅-Based Alloys

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Mechanical alloying was used to synthesize LaNi₅-type hydrogen storage materials. X-ray diffraction analysis showed that, after 30 h milling, the starting mixture of the elements was decomposed into an amorphous phase. Following the annealing in high purity argon at 700°C for 0.5 h, X-ray diffraction confirmed the formation of the CaCu₅-type structures. The nanocrystalline materials were used as negative electrodes for a Ni-MH_x battery. A partial substitution of Ni by Al or Mn in LaNi_{5-x}M_x alloy leads to an increase in discharge capacity. On the other hand, the alloying elements such as Al, Mn and Co greatly improved the cycle life of LaNi₅ material. For example, in the nanocrystalline LaNi_{3.75}Mn_{0.75}Al_{0.25}Co_{0.25} powder, discharge capacities of up to 258 mA h g⁻¹ (at 40 mA g⁻¹ discharge current) were measured. The band structure *ab initio* calculations showed that 3g sites are preferred by Al, Co, and Mn atoms in the unit cell.

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1. Introduction

In recent years, polycrystalline hydrogen storage alloys based on lanthanum are commercially used as negative electrode materials for the nickel-metal hydride (Ni-MH_x) battery [1–3]. The LaNi₅ alloy, which crystallizes in the hexagonal CaCu₅-type structure can absorb up to 5.5 H/f.u. at room temperature. The merit of these compounds is that they exhibit low hysteresis, are tolerant to gaseous impurities and are easily hydrogenated in the initial cycle after manufacture. The properties of hydrogen host materials can be modified substantially by alloying, to obtain the desired storage characteristics e.g. proper capacity at a favorable hydrogen pressure. For example, it was found that the partial respective replacement of Ni in LaNi₅ by small amounts of Al resulted in a prominent increase in the cycle lifetime without causing much decrease in capacity [4]. Aluminum is believed to concentrate on grain boundaries and in connection with segregated La forms a porous oxide layer, which protects the material from further corrosion in KOH electrolyte. On the other hand, cobalt is added in the alloys to guarantee the long cycle life of the negative electrode [5]. These electrodes usually obtain their maximum capacity within a few charge-discharge cycles without any special pre-treatment.

Conventionally, the metal hydride materials have been prepared by arc melting and annealing. Substantial improvements in the hydriding-dehydriding properties could be possibly achieved by formation of nanocrystalline structures by non-equilibrium processing technique such as mechanical alloying [2, 3].

Recently, mechanical alloying has been used to make a nanocrystalline TiFe-, ZrV₂- and LaNi₅-type alloys [2]. As shown in our earlier work, nanocrystalline powder has bigger capacity than the amorphous parent alloy material. Annealing leads to grain growth, release of microstrain and to an increase in the storage capacity. This behavior is due to a well-established diffusion path for hydrogen atoms along the numerous grain boundaries [6].

In this work, as a continuation of previous research, the influence of chemical composition on the structural, electrochemical and electronic properties of nanocrystalline La(Ni,M)₅-type alloys, prepared by mechanical alloying and followed by annealing, was investigated (M = Al, Mn and Co). The nanocrystalline materials with 10 wt.% addition of Ni powder, were subjected to electrochemical measurements as working electrodes. Total energy *ab initio* calculations were used to verify site preference of Al, Mn and Co atoms in the unit cell.

2. Experimental and computational details

Mechanical alloying (MA) was performed under an argon atmosphere using a SPEX 8000 D Mixer Mill. The purity of the starting metallic elements La, Ni, Mn, Al and Co was 99.9, 99.9, 99+, 99.95, and 99.8 wt.%, respectively. The composition of the starting powder mixture corresponded to the stoichiometry of the "ideal" reactions with an extra 8 wt.% of La. The elemental powders

(La: $\leq 425 \mu\text{m}$; Ni: $3\text{--}7 \mu\text{m}$; Mn: $\leq 45 \mu\text{m}$; Al: $\leq 75 \mu\text{m}$; Co: $2 \mu\text{m}$) were mixed in the glove box (Labmaster 130) and poured into the vial. The mill was run up to 40 h for every powder preparation. The as-milled powders were heat treated at 700°C for 0.5 h under high purity argon to form hexagonal CaCu_5 -type phase. The MA process of the LaNi_5 -type mixtures has been studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Typical crystallite sizes were estimated from the half-width of lines using the Scherrer equation.

The mechanically alloyed and annealed (nanocrystalline) materials with 10 wt.% addition of Ni powder, were subjected to electrochemical measurements as working electrodes after pressing (under 80 kN cm^{-2}) to 0.5 g pellet form between nickel nets acting as current collector. A detailed description of the electrochemical measurements was given in Ref. [2]. In order to study elec-

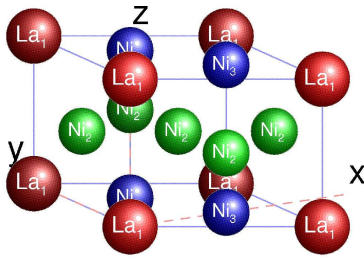


Fig. 1. The unit cell of the CaCu_5 -type structure for LaNi_5 compound: La_1 — 1a site (0,0,0); Ni_2 — 3g site ($1/2, 1/2, 1/2$); Ni_3 — 2a site ($1/3, 2/3, 0$).

TABLE

Structural parameters and discharge capacities for nanocrystalline LaNi_5 -type materials (current density of charging and discharging was 40 mA g^{-1}). dc1 — discharge capacity on 1st cycle.

Composition	a [Å]	c [Å]	dc1XXX [mA h g^{-1}]
LaNi_5	5.010	3.972	84
LaNi_4Al_1	5.058	4.008	223
LaNi_4Co_1	5.011	3.975	39
LaNi_4Mn_1	5.015	4.005	239
$\text{LaNi}_{3.75}\text{Co}_1\text{Al}_{0.25}$	5.016	3.997	212
$\text{LaNi}_{3.5}\text{Co}_1\text{Al}_{0.5}$	5.028	4.013	176
$\text{LaNi}_{3.75}\text{Co}_1\text{Mn}_{0.25}$	5.025	3.990	161
$\text{LaNi}_{3.5}\text{Co}_1\text{Mn}_{0.5}$	5.029	3.996	118
$\text{LaNi}_{3.75}\text{Mn}_{0.75}\text{Al}_{0.25}\text{Co}_{0.25}$	5.075	4.039	258

tronic structure of the LaNi_5 -type systems we used the full-potential local-orbital (FPLO) method [7, 8]. The scalar-relativistic mode was used in the calculations including coherent potential approximation (CPA) [9] to take into account chemical disorder introduced by Mn, Al, and Co impurities. The calculations were carried out

for the hexagonal CaCu_5 -type structure (see Fig. 1) with $P6/mmm$ space group and experimental values of the lattice constants (see Table). For the calculations we assumed the following configurations of atoms: La: core + semi core ($4d5s5p$) + valence electrons ($6s6p5d$); Ni: core + semi core ($3s3p$) + valence electrons ($4s4p3d$); Co: core + semi core ($3s3p$) + valence electrons ($4s4p3d$); Mn: core + semi core ($3s3p$) + valence electrons ($4s4p3d$); Al: core + semi core ($2s$) + valence electrons ($3s3p3d$). The calculations were performed for the reciprocal space mesh containing 133 points within the irreducible wedge ($1/24$) of the Brillouin zone using the tetrahedron method [10] for integrations. The exchange-correlation potential was assumed in the form proposed by Perdew and Wang [11]. The self-consistent criterion was equal to 10^{-8} Ry for the total energy.

3. Results and discussion

The behaviour of MA process has been studied by X-ray diffraction, microstructural investigations, atomic force microscopy (AFM) as well as by electrochemical measurements. Figure 2 (left part) shows a series of XRD spectra of mechanically alloyed La–Ni powder mixture (0.3212 wt.% La + 0.6788 wt.% Ni) subjected to milling for increasing time. The originally sharp diffraction lines of La and Ni (Fig. 2a, left part) gradually become broader and their intensity decreases with milling time. The powder mixture milled for more than 30 h has transformed completely to the amorphous phase, without formation of other phase (Fig. 2b, left part). Formation of the nanocrystalline alloy was achieved by annealing of the amorphous material in high purity argon atmosphere at 700°C for 0.5 h (Fig. 2c, left part). All diffraction peaks were assigned to those of the hexagonal crystal structure of CaCu_5 -type with cell parameters $a = 5.010 \text{ \AA}$ and $c = 3.972 \text{ \AA}$. Table reports the cell parameters of the studied materials.

The discharge capacity of electrode prepared by application of MA and annealed LaNi_5 alloy powder is low (Fig. 2 — right part, Table). It was found that the partial substitution of Ni by Al or Mn in $\text{La}(\text{Ni},\text{M})_5$ alloy leads to an increase in discharge capacity. On the other hand, alloying elements such as Al, Mn and Co substituting nickel greatly improved the cycle life of LaNi_5 -type material. In nanocrystalline $\text{LaNi}_{3.75}\text{Mn}_{0.75}\text{Al}_{0.25}\text{Co}_{0.25}$ discharge capacities up to 258 mA h g^{-1} (at 40 mA g^{-1} discharge current) were measured. The LaNi_4Mn and $\text{LaNi}_{3.75}\text{Mn}_{0.75}\text{Al}_{0.25}\text{Co}_{0.25}$ electrodes, mechanically alloyed and annealed from elemental powders, displayed the maximum capacities at the 1st cycle but the discharge capacity of LaNi_4Mn composition degraded strongly with cycling.

The calculations were performed for all possible localizations of the Mn, Al, and Co atoms in the unit cell to get the total energy of a given configuration and find the most stable one. Figure 3 presents the densities of electronic states (DOS) plots for distributions of

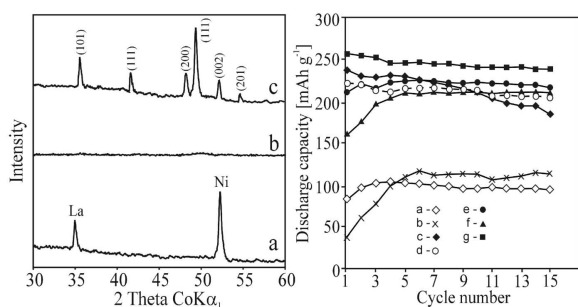


Fig. 2. (left) XRD spectra of a mixture of La and Ni powders mechanically alloyed for different times in an argon atmosphere: *a* initial state (elemental powder mixture), *b* after MA for 30 h and *c* — heat treated at 700°C for 0.5 h. (right) Discharge capacities as a function of cycle number of LaNi₅-type negative electrodes made from nanocrystalline powders prepared by MA followed by annealing: *a* — LaNi₅, *b* — LaNi₄Co, *c* — LaNi₄Mn, *d* — LaNi₄Al, *e* — LaNi_{3.75}CoMn_{0.25}, *f* — LaNi_{3.75}CoAl_{0.25}, *g* — LaNi_{3.75}Mn_{0.75}Al_{0.25}Co_{0.25} (solution, 6 M KOH; *T* = 20°C). The charge conditions were 40 mA/g. The cut-off potential vs. Hg/HgO/6 M KOH was -0.7 V. Lines are provided as a guide to the eye.

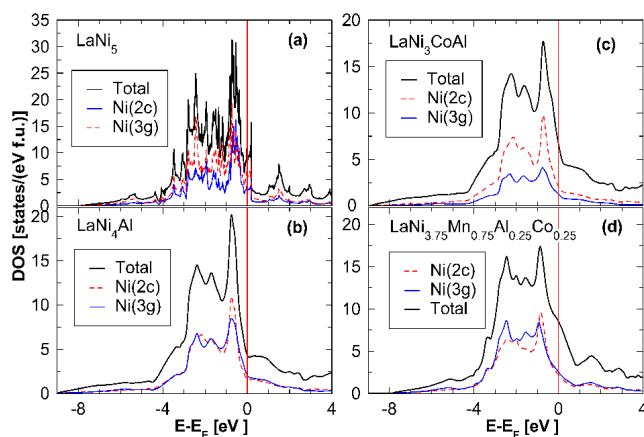


Fig. 3. Total DOS plots and Ni contributions in (a) LaNi₅-La(Ni₃)^{3g}(Ni₂)^{2c}, (b) LaNi₄Al-La(Ni₂Al)^{3g}(Ni₂)^{2c}, (c) LaNi₃CoAl-La(NiCoAl)^{3g}(Ni₂)^{2c}, (d) LaNi_{3.75}Mn_{0.75}Al_{0.25}Co_{0.25}-La(Ni_{2.25}Mn_{0.45}Al_{0.15}Co_{0.15})^{3g}(Ni_{1.5}Mn_{0.30}Al_{0.10}Co_{0.10})^{2c}.

atoms, which minimize energy for a given stoichiometry. The results for LaNi₅ are presented in Fig. 3a. It is an ordered system, the DOS peaks are sharp. Figures 3b–d present results with chemical disorder introduced by Mn, Al, and Co atoms. The DOS peaks are more broadened and the valence bands wider, especially when Al concentration in the formula unit is large. It is caused by Al(3*s*) electrons, which provide the main contribution to DOS near the bottom of valence band. Although the DOS curves of Al, Co, and Mn have low values, the impurities rebuild the total DOS's. Change of Ni concentrations is also observed on Ni DOS plots for 2c and 3g positions.

For LaNi₄Al and LaNi₃AlCo, the Al and Co atoms prefer 3g site. Distribution of atoms is the following: La(NiNiAl)^{3g}(NiNi)^{2c} and La(NiCoAl)^{3g}(NiNi)^{2c}. The DOS plots of Ni(3g) electrons are lower despite the fact that 3g site has one position more in the unit cell than the 2c one. This fact and lower energies show the site preference of Al and Co atoms in the unit cell. In the case of LaNi_{3.75}Mn_{0.75}Al_{0.25}Co_{0.25} the lowest energy was obtained for homogeneous distribution of impurities, which corresponds to the following situation La(Ni_{2.25}Mn_{0.45}Al_{0.15}Co_{0.15})^{3g}(Ni_{1.5}Mn_{0.30}Al_{0.10}Co_{0.10})^{2c}. It means that in complicated stoichiometry disorder is preferred, but comparing energies for La(Ni_{1.75}Mn_{0.75}Al_{0.25}Co_{0.25})^{3g}(Ni₂)^{2c} and La(Ni₃)^{3g}(Ni_{0.75}Mn_{0.75}Al_{0.25}Co_{0.25})^{2c} more stable is situation with Mn, Al, and Co atoms in 3g sites than in 2c ones. In real nanocrystalline samples, which are obtained by MA method, fraction of metastable states can be larger and the impurities prefer 3g sites than 2c ones. It is in agreement with experimental observations [12].

In the nickel sublattice of LaNi₅, substitution of Mn, Al and Co has been found to offer the best compromise between high discharge capacity and cycle life.

4. Conclusions

In conclusion, nanocrystalline LaNi_{5-x}M_x (M = Al, Co, Mn) alloys synthesized by mechanical alloying and annealing were used as negative electrode materials for Ni-MH_x battery. The discharge capacity of electrode prepared by application of MA and annealed LaNi₅ alloy powder displayed very low capacity. It was found that the alloying elements such as Al, Mn and Co substituting nickel greatly increase the discharge capacity of LaNi₅ alloy. In the nanocrystalline LaNi_{3.75}Mn_{0.75}Al_{0.25}Co_{0.25} powder, discharge capacity of up to 258 mA h g⁻¹ (at 40 mA g⁻¹ discharge current) was measured.

Starting from LaNi₅ and adding Co and Al atoms, the impurities prefer 3g sites in the CaCu₅-type structure. For complicated stoichiometries like LaNi_{3.75}Mn_{0.75}Al_{0.25}Co_{0.25} homogeneous distribution is more stable but in metastable states 3g sites are still more preferred than 2c ones.

The combination of nanocrystalline La(Ni,Mn,Al,Co)₅ hydride electrode and a nickel positive electrode to form a Ni-MH_x battery, has been successful.

Acknowledgments

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References

- [1] T. Sakai, M. Matsuoka, C. Iwakura, in: *Handbook on the Physics and Chemistry of Rare Earth*, Vol. 21, Ed. K.A. Gschneider, Jr., L. Eyring, Elsevier Sci. B.V., Amsterdam 1995, Ch. 142, p. 135.

- [2] M. Jurczyk, M. Nowak, in: *Nanostructured Materials in Electrochemistry*, Ed. Eftekhari Ali, Wiley, Weinheim 2008.
- [3] L. Smardz, M. Jurczyk, K. Smardz, M. Nowak, M. Makowiecka, I. Okonska, *Renewable Energy* **33**, 201 (2008).
- [4] Y. Nakamura, H. Nakamura, S. Fujitani, I. Yonezu, *J. Alloys Comp.* **210**, 299 (1994).
- [5] J.J.G. Willems, K.H.J. Buschow, *J. Less-Common Met.* **129**, 13 (1987).
- [6] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, *J. Alloys Comp.* **253-254**, 70 (1997).
- [7] K. Köpernik, H. Eschrig, *Phys. Rev. B* **59**, 1743 (1999).
- [8] I. Opahle, K. Köpernik, H. Eschrig, *Phys. Rev. B* **60**, 14035 (1999).
- [9] K. Köpernik, B. Velicky, R. Hayn, H. Eschrig, *Phys. Rev. B* **55**, 5717 (1997).
- [10] P. Blöchl, O. Jepsen, O.K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).
- [11] J.P. Perdew, Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- [12] J.-M. Joubert, R. Éryny, M. Latroche, A. Percheron-Guégan, K. Yvon, *J. Appl. Crystallogr.* **31**, 327 (1998).