The Electronic and Electrochemical Properties of the LaNi$_5$-Based Alloys

A. Szajek$^a$, A. Jezierski$^a$, M. Nowak$^b$ and M. Jurczyk$^b$

$^a$Institute of Molecular Physics, Polish Academy of Sciences
M. Smoluchowskiego 17, 60–179 Poznań, Poland.

$^b$Institute of Materials Science and Engineering, Poznań University of Technology
M. Sklodowska-Curie Sq. 5, 60-965 Poznań, Poland.

Mechanical alloying was used to synthesize LaNi$_5$-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 $^\circ$C for 0.5 h, X-ray diffraction confirmed the formation of the CaCu$_5$-type structures. The nanocrystalline materials were used as negative electrodes for a Ni–MH 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 LaNi$_5$ 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.

PACS numbers: 71.20.-b, 81.20.Ev

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 LaNi$_5$ alloy, which crystallizes in the hexagonal CaCu$_5$-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 LaNi$_5$ 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 pretreatment.

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-, ZrV$_2$- and LaNi$_5$-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: \( \leq 425 \mu m \); Ni: 3–7 \( \mu m \); Mn: \( \leq 45 \mu m \); Al: \( \leq 75 \mu m \); Co: 2 \( \mu m \)) 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 electronic 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 P\(6/mmm\) 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 (4d55sp) + 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 \( a = 5.010 \) \( \text{Å} \) and \( c = 3.972 \) \( \text{Å} \). 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 La(Ni,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 LaNi\(_{5.75}\)Mn\(_{0.75}\)Al\(_{0.25}\)Co\(_{0.25}\) discharge capacities up to 258 mA h g\(^{-1}\) (at 40 mA g\(^{-1}\) discharge current) were measured. The LaNi\(_5\)Mn and LaNi\(_{5.75}\)Mn\(_{0.75}\)Al\(_{0.25}\)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\(_5\)Mn 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

---

**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.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( a [\text{Å}] )</th>
<th>( c [\text{Å}] )</th>
<th>dc1 [mA h g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi(_5)</td>
<td>5.010</td>
<td>3.972</td>
<td>84</td>
</tr>
<tr>
<td>LaNi(_5)Al(_1)</td>
<td>5.058</td>
<td>4.008</td>
<td>223</td>
</tr>
<tr>
<td>LaNi(_5)Co(_1)</td>
<td>5.011</td>
<td>3.975</td>
<td>39</td>
</tr>
<tr>
<td>LaNi(_5)Mn(_1)</td>
<td>5.015</td>
<td>4.005</td>
<td>239</td>
</tr>
<tr>
<td>LaNi(_{5.75})Co(<em>1)Al(</em>{0.25})</td>
<td>5.016</td>
<td>3.997</td>
<td>212</td>
</tr>
<tr>
<td>LaNi(_{5.75})Co(<em>1)Al(</em>{0.5})</td>
<td>5.028</td>
<td>4.013</td>
<td>176</td>
</tr>
<tr>
<td>LaNi(_{5.75})Co(<em>1)Mn(</em>{0.25})</td>
<td>5.025</td>
<td>3.990</td>
<td>161</td>
</tr>
<tr>
<td>LaNi(_{5.75})Co(<em>1)Mn(</em>{0.5})</td>
<td>5.029</td>
<td>3.996</td>
<td>118</td>
</tr>
<tr>
<td>LaNi(<em>{5.75})Mn(</em>{0.75})Al(<em>{0.25})Co(</em>{0.25})</td>
<td>5.075</td>
<td>4.039</td>
<td>258</td>
</tr>
</tbody>
</table>
The Electronic and Electrochemical Properties . . .

For LaNi$_4$Al and LaNi$_3$AlCo, 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$75,Mn$_{0.25}$Co$_{0.25}$ the lowest energy was obtained for homogeneous distribution of impurities, which corresponds to the following situation La(Ni$_2$5,Mn$_{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$7,Mn$_{0.75}$Al$_{0.25}$Co$_{0.25}$)$_{(3g)}$(Ni$_2$5)$_{2c}$ and La(Ni$_1$3)$_{(3g)}$(Ni$_0$5,Mn$_{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 LaNi$_5$, 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 LaNi$_5$ 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 LaNi$_5$ alloy. In the nanocrystalline LaNi$_{3.75}$Mn$_{0.25}$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 LaNi$_5$ and adding Co and Al atoms, the impurities prefer 3g sites in the CaCu$_5$-type structure. For complicated stoichiometries like LaNi$_{3.75}$Mn$_{0.25}$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

This work was supported by the MNiSW grant No. 3 T10A 033 29.

References


