HYDROGEN STORAGE IN LOW-TEMPERATURE La-Ni BASED METAL HYDRIDES AND THEIR INTEGRATION WITH FUEL CELLS

DOCTORAL DISSERTATION SUMMARY

Study program: Process engineering

Supervisor: Prof. Ing. Kamil Wichterle, DrSc.

Specialist supervisor: Prof. Ing. Stanislav Misak, Ph.D.

Ph.D. student: Ing. Artem Chesalkin

Ostrava, 2019
Acknowledgment

I would like to thank my supervisor Prof. Ing. Kamil Wichterle, DrSc., and supervisor specialist Prof. Ing. Stanislav Mišák, Ph.D. for their guidance and inspiration, which enabled writing of this thesis work. I would also like to express my gratitude to Prof. Ing. Lucie Obalová, Ph.D. and doc. Ing. Marek Večeř, Ph.D. whose counseling and support helped me throughout my doctoral study. Big thanks to all of my colleagues and friends from the Centre of Energy Utilization of Non-traditional Energy Sources (Centre ENET) VSB-TUO and Institute of Environmental Technology (IET) VSB-TUO for the great support in my lab research, pleasant working atmosphere and team spirit. I would like to thank colleagues from McPhy Energy, in particular, Ing. Cédric Dupuis Ph.D., the Chief Scientist Officer, McPhy France, for his inspiration and cooperation in metal hydride production and analysis. I want to express great gratitude to colleagues from the Department of Energy Technology, Aalborg University, Denmark, especially to Prof. Søren Knudsen Kær M.Sc., Ph.D., Asst. Prof. Xiaoti Cui Ph.D., and PostDoc. Sobi Thomas Ph.D. for my fruitful internship and a great experience. At last, I would like to thank my family and friends for their support and encouragement. Thank you very much to all of you!
CONTENT

1. Introduction 1

2. Dissertation work objectives and their realization 3
   2.1. Thesis work structure diagram 4

3. Alloys preparation procedures and analysis methods 5
   3.1. La-Ni based alloys preparation 5
   3.2. Alloys and metal hydrides analysis methods 7
      3.2.1. XRD measurement 7
      3.2.2. Scanning electron microscope (SEM) analysis 7
      3.2.3. PCT analysis 8

4. Results of the alloys synthesis 9
   4.1. Influence of the structure state 15

5. MH integration in hydrogen hybrid systems 17
   5.1. Experimental hydrogen hybrid system 17
   5.2. MH thermography during H₂ reversible sorption via FC 18
   5.3. FC thermography and waste heat utilization for the LT MH discharging 21
      5.3.1. LT PEMFC thermography 23
      5.3.2. LT PEMFC computer simulation 25
      5.3.3. HT PEMFC thermography 26
      5.3.4. HT PEMFC computer simulation 28

6. Conclusions 29
   6.1. Future aims and steps 29

7. References 31
1. INTRODUCTION

Due to the limited amount of oil and gas and related ecological problems in the last decade, development of the hydrogen energetics goes incredibly fast. Hydrogen can be used as a solution for the storage of excess solar, wind and hydropower. It can be also injected into existing natural gas (NG) pipelines, or be distributed to hydrogen refueling stations for fuel cell (FC) electric vehicles.

The search for a safe, efficient and cost-effective way of hydrogen storing is one of the main goals on the way of hydrogen technologies development and their application in daily life. One of these possibilities is hydrogen storage in the form of hydrides, but this process is far from optimal due to the material’s poor sorption-desorption characteristics and working temperature-pressure parameters. The effectiveness of the hydrogen storage system strongly depends on the development of novel materials so that hydrogen can be stored and released at reasonable temperatures and pressures.

The reducing of the absorption-desorption temperatures and pressures ($T_{A-D}$, $P_{A-D}$) are key characteristics for application of these types of materials. It was previously verified in a number of scientific papers that structure state of hydrogen storage alloys as amorphous, rapid-cooled or ordered-structure can significantly influence the hydrides working characteristics.

Another task was the optimization of the hydrogen storage capacity and the time-temperature regime of alloys synthesis. Practical study of alloys and hydrides formation with next thermodynamic testing of prepared (LaCe)Ni$_5$ and LaCe(FeNi)$_5$ alloys during isothermal reversible hydrogen sorption were carried out and described.

These types of hydrides allow reversible sorption and hydrogen purification at low temperatures and pressures, which makes it possible to integrate them with fuel cells with a proton exchange membrane (PEMFC) and implemented to the hydrogen hybrid systems (HHS).
2. DISSERTATION OBJECTIVES AND THEIR REALIZATION

The main aim of the work was an attempt to modify the well-known LaNi₅ metal hydride and find the optimal working temperature-pressures parameters of the alloy for reversible hydrogen sorption via FC. In this part of the work, steps have been taken to modify the LaNi₅ alloy by partial replacement of La by Ce and Ni by Fe. Attempts have been made to optimize the time-temperature parameters of the alloys synthesis, and final hydrogen storage density. Alloys synthesis was performed via two different methods: by classical thermal melting of pure metals, and by the thermochemical reaction of the metal chlorides. A comparative analysis of the obtained La-Ni, La-Ce-Ni, La-Ce-Fe-Ni alloy samples was carried out. The detailed physicochemical analysis of the prepared alloys and corresponding hydrides was conducted. XRD and SEM analysis data demonstrate that an increase in the alloy synthesis temperature and sample holding time facilitates the desired LaNi₅ and (LaCe)Ni₅ phases formation.

Unfortunately, the problem of oxidation of the samples prepared from metal chlorides still remains unsolved. Therefore, further research is needed in order to investigate the possibilities of more effective use of LiH or using a different reducing agent for the alloy thermochemical synthesis.

The preliminary study of LaNi₅ alloy, modified with element Fe shown the significant changes (reducing) of the working hydrogen sorption pressure. Modification of the LaNi₅ alloy by Ce and the structured state of the storage material can also influence the thermodynamic properties and value gravimetric capacity of the hydride. (LaCe)Ni₅-cast sample was traditionally cast into Cu mold and fast cooled (LaCe)Ni₅-FC sample was remelted and cast on water-cooled Cu-plate. The fast cooled (LaCe)Ni₅-FC sample showed higher gravimetric capacity (up to 1.55 Wt.%) at lower sorption pressure in comparison with (LaCe)Ni₅-cast sample.

The second part of the thesis declares the results of the metal hydride testing in real operation conditions during reversible hydrogen sorption. The complex hydrogen system based on hydrogen production, storage and utilization was studied. Hydrogen desorption was carried out via low and high-temperature fuel cells, with subsequent thermography analysis of the whole hydride-fuel cell system. The additional heat transfer computer simulation of the fuel cell under the load allowed to determine the waste heat which can be effectively used to desorb hydrogen from the La-Ni based low-temperature metal hydride, which allows to use more efficiently both of the HHS components.
2.1. Thesis work structure diagram

- **Hydrogen as an alternative energy source**
  - Problematic of fossil sources limitation. Hydrogen production and application.

- **Hydrogen storage**
  - Problematic of hydrogen storage and transportation.

- **Hydrogen storage in metal hydrides**
  - Metal hydrides, basic description and their characteristics, problematic of daily usage.

- **Low-temperature La-Ni based MH for H₂ storage**
  - LT MH and their characteristics, possible application. LaNi₅ alloy characteristics, possibilities for modification.

- **Modification of the LaNi₅ alloy by Ce and Fe for reversible H₂ storage**
  - Development of new La-Ni based alloys for H₂ storage.

- **La-Ni based MH storage system integration with PEMFC. MH thermography**
  - Laboratory experiments with La-Ni based alloy, a study of properties and operating parameters. Description of H₂ reversible sorption in (LaCe)Ni₅ alloy. MH thermography during H₂ reversible sorption.

- **FC thermography and computer simulation. LT MH application for the HHS**
  - PEMFC thermography, FC waste heat utilization for the H₂ desorption from LT MH (La-Ni based). Application of LT MH and FC for the hydrogen hybrid systems.

The theoretical part of the thesis work described in chapters “2-3” and deals with: problematic of energy and hydrogen storage; development of H₂ technologies and H₂ storage methods; hydrogen storage in metal hydrides, mechanism of MH formation and heat transfer during H₂ reversible sorption.

The practical part of the work described in chapters “4-5” and deals with: La-Ni based alloys preparation and modification, alloy samples analysis, the influence of the structure state the H₂ storage materials properties. LT MH integration with FC. MH and FC thermography, computer simulation of the FC heat transfer for next FC waste heat utilization for LT MH discharging.
3. **ALLOYS PREPARATION PROCEDURES AND ANALYSIS METHODS**

3.1. **La-Ni based alloys preparation**

Considering the synthesis temperature of different alloys, samples from pure metals were prepared in quartz crucibles. Graphite crucibles were used for the sample synthesis from metal chlorides. Alloy synthesis was carried out in an induction oven in an inert atmosphere of argon (Ar) with a constant Ar flow of 1.8-2 L min\(^{-1}\).

The initial components were mixed in a glow-box to prevent the oxidation of the reagents and moisture saturation. The preparation of alloys from pure metals required elevated temperatures and longer sample holding, compared to the corresponding parameters for the synthesis of alloys from metal chlorides. Figure 1 and Figure 2 below show the relevant La-Ni and La-Ce phase diagrams.

**Figure 1** Phase diagram of binary system La-Ni [Okamoto et al. 2016]

**Figure 2** Phase diagram of binary system La-Ce [Okamoto et al. 2016]
The time-temperature parameters of the alloy synthesis and information about the used reagents are shown in Table 1. The purity of the used reagents was 99.5 - 99.7 %, as declared by the manufacturer and the particle size of the powder metals was 8-60 μm.

**Table 1** Alloy synthesis parameters and properties of the reagents

<table>
<thead>
<tr>
<th>Metal chloride samples</th>
<th>Temperature, °C</th>
<th>Heating time, min</th>
<th>Holding time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample “1” La-Ni</td>
<td>750</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>Sample “2” La-Ni</td>
<td>900</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>Sample “3.1” La-Ni</td>
<td>1100</td>
<td>80</td>
<td>210</td>
</tr>
<tr>
<td>Sample “3.2” La-Ni</td>
<td>1100</td>
<td></td>
<td>210</td>
</tr>
<tr>
<td>Sample “4” (LaCe)Ni5</td>
<td>1100</td>
<td></td>
<td>210</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Powder metal samples</th>
<th>Temperature, °C</th>
<th>Heating time, min</th>
<th>Holding time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample “5” (LaCe)Ni5</td>
<td>1350-1450</td>
<td>90</td>
<td>300</td>
</tr>
<tr>
<td>Sample “6” LaCe(FeNi)5</td>
<td>1350-1450</td>
<td>90</td>
<td>300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Form</th>
<th>Density, [kg m⁻³]</th>
<th>Particle size, [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl₃</td>
<td>powder, anhydrous</td>
<td>3840</td>
<td>8-60</td>
</tr>
<tr>
<td>CeCl₃</td>
<td></td>
<td>3970</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>8900</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td></td>
<td>6190</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td></td>
<td>8240</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>7850</td>
<td></td>
</tr>
<tr>
<td>LiH</td>
<td></td>
<td>820</td>
<td></td>
</tr>
</tbody>
</table>

The ideal way of relevant chemical reactions of La-Ni based alloys preparation are described below:

**LaNi₅**

Preparation from pure metals:

La +5Ni → LaNi₅

Preparation from metal chlorides:

LaCl₃ + 5NiCl₂ + 13LiH → LaNi₅ + 13LiCl +6.5H₂↑

**(LaCe)Ni₅**

Preparation from pure metals:
La + Ce + 5Ni → (LaCe)Ni₅
Preparation from metal chlorides:
LaCl₃ + CeCl₃ + 5NiCl₂ + 16LiH → (LaCe)Ni₅ + 16LiCl + 8H₂↑

LaCe(NiFe)₅
Preparation from pure metals:
La + Ce + 5Fe + 5Ni → LaCe(NiFe)₅
Preparation from metal chlorides:
LaCl₃ + CeCl₃ + 5NiCl₂ + 5FeCl₂ + 26LiH → LaCe(NiFe)₅ + 26LiCl + 13H₂↑

Lithium hydride was used as a reducing agent during sample synthesis via a thermochemical reaction. Figure 3 shows the alloys prepared with the present of LiH (left side) and without LiH (right side).

**Figure 3** La-Ni based alloy samples, made with LiH and without LiH

After synthesis, all samples were cooled down to 200 °C and placed in the oven for complete drying under vacuum. The analysis of alloys structure and composition were conducted by X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis.

3.2. Alloys and metal hydrides analysis methods

3.2.1. XRD measurement

XRD measurement conditions: diffractometer Rigaku SmartLab; goniometer geometry – Bragg-Brentano theta-2theta; lamp – CoKα (λ₁ = 0.178892 nm, λ₂ = 0.179278 nm); detector – D/teX Ultra 250; range of the measurement 5 – 90° 2theta; sample holder – glass holder with cavity depth 0.5 mm. Data about the composition and structure of prepared alloys were obtained from XRD analysis of relevant samples. Measured patterns were evaluated using appropriate software and PDF-2 (ICDD) database was used as a phase standards library.

3.2.2. Scanning electron microscope (SEM) analysis

The scanning electron microscope Quanta FEG 450 (FEI) with EDS microprobe analysis was used for the characterization of the morphology of the studied samples. The measured
samples were not stable under ambient conditions. As a result, they were ground under the flow of nitrogen and covered with a 6 µm thick Mylar foil to avoid exposure to air humidity.

3.2.3. PCT analysis

The hydrogen sorption characteristics of prepared La-Ni based alloys were measured using Sieverts-type gas sorption analyzer PCT–Pro EVO (high accuracy option) Setaram Instrumentation. Pressure-Concentration-Temperature (PCT) measurement is a fully automated technique for measuring a sample’s gas sorption, thermodynamic properties and phase composition [Srinivas et al. 2008, Friedlmeier et al. 1977].

This equipment enables safe and fully automated and repeated measurements in both sorption and desorption regimes and ensures that the hydrogen pressure during sorption will be always above $P^{eq}$ and during desorption always below $P^{eq}$. The study was carried out at a temperature range of 273-318 K and hydrogen pressure 0.1-3 MPa. The purity of both hydrogen and helium calibration gases was 6N.

![PCTPro installation and sample holder for the PCT measurement](image)

The alloy sample at known pressure and volume is connected to a reservoir of known volume and pressure through an isolation valve. Opening the isolation valve allows a new equilibrium to be established. Gas sorption is determined by the difference in actual measured pressure against calculated pressure. These are isothermal measurements in which the alloy sample temperature is held constant and gas reversibly sorbed in the small aliquots. With each aliquot, the sample and gas are allowed to achieve an equilibrium energy state. This is defined by the pressure of the gas and temperature of the sample.
4. RESULTS OF THE ALLOYS SYNTHESIS

Four of the alloy samples (sample “1”, sample “2”, sample “3.1”, and sample “4”) prepared from metal chlorides had a grey-metallic color and looked monolithic. However, the sample “1” and sample “2” had visible oxidation on the surface. Subsequent XRD analysis of these samples (sample “1” and sample “2”), prepared at 750 °C and 900 °C, respectively, shows the presence of the separate phases of metal oxides: Li$_2$O, LaOCl, NiO, La$_2$(NiO$_4$) in the sample “1”, and Li$_2$O, LaOCl, NiO, La$_3$(NiO$_4$)$_{144}$ in the sample “2”.

Sample “3.2” prepared without LiH, had a brown-orange colour and looked amorphous (see Figure 3 above). Samples “3.1” and “4” prepared at elevated temperature and holding time represented the desired LaNi$_5$ and LaCeNi phases: Ni, LaO, NiO, LaNiO$_3$, LaNi$_5$ in the sample “3”, and Ni, CeO$_2$, LaNiO$_3$, (LaCe)Ni$_4$ in the sample “4” respectively. Sample “5” and sample “6” prepared from pure powder metals contained the (La$_{0.5}$Ce$_{0.5}$)Ni$_5$ and La(Fe$_{0.2}$Ni$_{0.8}$)$_5$ phases respectively. XRD patterns of the prepared samples are shown in Figure 6.

![Figure 6 XRD patterns of the prepared alloy samples](image)

(a) sample “3.1” with the LaNi$_5$ phase present; (b) sample “4” with the (LaCe)Ni$_4$ phase present; (c) sample “5” (La$_{0.5}$Ce$_{0.5}$)Ni$_5$ phase; (d) sample “6” La(Fe$_{0.2}$Ni$_{0.8}$)$_5$ phase
Broad diffraction at positions 16.0; 19.3; 30.0 °2theta corresponds to the Mylar foil (Figure 6a). The additional analysis of the alloy structure was carried out with the aid of the scanning electron microscopy (SEM). Table 2 shows the results of the SEM sample analysis.

**Table 2 Chemical composition of the prepared alloys sample**

<table>
<thead>
<tr>
<th>Sample “3.1” LaNi₅ metal chloride</th>
<th>Sample “4” (LaCe)Ni₄ metal chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>Ni</td>
</tr>
<tr>
<td>Wt.%</td>
<td>19.2</td>
</tr>
<tr>
<td>At.%</td>
<td>8.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample “5” (LaCe)Ni₅ powder metal</th>
<th>Sample “6” LaCe(FeNi)₅ powder metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>Ni</td>
</tr>
<tr>
<td>Wt.%</td>
<td>27.23</td>
</tr>
<tr>
<td>At.%</td>
<td>14.00</td>
</tr>
</tbody>
</table>

The structure photos of prepared non-oxidized (LaCe)Ni and LaCe(FeNi) alloys are shown in Figure 7.

**Figure 7** SEM images of prepared LaCeNi and and LaCeFeNi alloys: (a) (LaCe)Ni at 200 x; (b) LaCe(FeNi) at 200 x; (c) (LaCe)Ni at 1000 x; (d) LaCe(FeNi) at 1000 x
The next synthesis and study of LaCeNi and LaCeFeNi alloys made from pure powder metals were made in collaboration with the Institute of Physics of Materials Czech Academy of Science, Brno. Tables 3-6 below show the results of XRD patterns evaluation of the modified La-Ni based alloys with different La/Ce/Fe/Ni ratio in alloys composition after hydrogen absorption-desorption (A-D) cycles. 3 Wt.% content of iron (Fe) in the sample composition makes dominant the La$_1$Fe$_1$Ni$_4$ phase (Table 4 and Table 6). Lower iron content (Fe approx 1 Wt.%6) make dominant the La$_0.5$Ce$_0.5$Ni$_5$ phase (Table 5). The present of H$_3$La$_1$O$_3$ in alloys composition (Table 4-6) associated with incomplete hydrogen desorption from the alloy, and was not observed after complete desorption.

**Table 3 (LaCe)Ni$_5$ sample XRD pattern (La$_1$Ni$_5$ phase)**

(LaCeNi5 Abs, crushed, after A - D cycles, non-desorbed)

<table>
<thead>
<tr>
<th>Ref. code</th>
<th>Score</th>
<th>Compound name</th>
<th>Displ. [°2θ]</th>
<th>Scale fac.</th>
<th>Chem. formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>98-042-6960</td>
<td>28</td>
<td>Nickel</td>
<td>0.026</td>
<td>0.046</td>
<td>Ni$_1$</td>
</tr>
<tr>
<td>98-015-0200</td>
<td>90</td>
<td>Lanthanum Nickel (0.94/5.12)</td>
<td>0.058</td>
<td>0.987</td>
<td>La$_0.94$Ni$_5.12$</td>
</tr>
</tbody>
</table>

![XRD pattern of LaCeNi5 Abs](image-url)
Table 4 LaCe(FeNi)$_5$ sample XRD pattern (La$_1$Fe$_1$Ni$_4$ phase)

(LaCeNiFe$_5$, Fe approx. 3 Wt.%, crushed, after A - D cycles, non-desorbed)

<table>
<thead>
<tr>
<th>Ref. code</th>
<th>Score</th>
<th>Compound name</th>
<th>Displ. [°2θ]</th>
<th>Scale fac.</th>
<th>Chem. formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>98-005-3807</td>
<td>12</td>
<td>Nickel</td>
<td>0.045</td>
<td>0.007</td>
<td>Ni$_1$</td>
</tr>
<tr>
<td>98-029-1050</td>
<td>62</td>
<td>Lanthanum Nickel Iron (1/4/1)</td>
<td>-0.041</td>
<td>0.770</td>
<td>La$_1$Fe$_1$Ni$_4$</td>
</tr>
<tr>
<td>98-024-5670</td>
<td>56</td>
<td>Lanthanum Tris (hydroxide)</td>
<td>0.016</td>
<td>0.291</td>
<td>H$_3$La$_1$O$_3$</td>
</tr>
</tbody>
</table>

Table 5 LaCe(FeNi)$_5$ sample XRD pattern (La$_{0.5}$Ce$_{0.5}$Ni$_5$ phase)

(LaCeNiFe$_{0.95}$ Abs, Fe approx. 1 Wt.%, crushed, after A - D cycles, non-desorbed)

<table>
<thead>
<tr>
<th>Ref. code</th>
<th>Score</th>
<th>Compound name</th>
<th>Displ. [°2θ]</th>
<th>Scale fac.</th>
<th>Chem. formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>98-016-2279</td>
<td>24</td>
<td>Nickel</td>
<td>0.009</td>
<td>0.063</td>
<td>Ni$_1$</td>
</tr>
<tr>
<td>98-062-1452</td>
<td>49</td>
<td>Cerium Lanthanum Nickel (0.5/0.5/5)</td>
<td>-0.235</td>
<td>0.565</td>
<td>Ce$<em>{0.5}$La$</em>{0.5}$Ni$_5$</td>
</tr>
<tr>
<td>98-003-1584</td>
<td>50</td>
<td>Lanthanum Hydroxide</td>
<td>0.063</td>
<td>0.145</td>
<td>H$_3$La$_1$O$_3$</td>
</tr>
</tbody>
</table>

Artem Chesalkin. *Hydrogen storage in low-temperature La-Ni based metal hydrides and their integration with fuel cells* 
Table 6 LaCe(FeNi)₅ sample XRD pattern (La₁Fe₁Ni₄ phase)

<table>
<thead>
<tr>
<th>Ref. code</th>
<th>Score</th>
<th>Compound name</th>
<th>Displ. [°2θ]</th>
<th>Scale fac.</th>
<th>Chem. formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>98-005-3807</td>
<td>12</td>
<td>Nickel</td>
<td>0,045</td>
<td>0,007</td>
<td>Ni₁</td>
</tr>
<tr>
<td>98-029-1050</td>
<td>62</td>
<td>Lanthanum Nickel Iron (1/4/1)</td>
<td>-0,041</td>
<td>0,770</td>
<td>La₁Fe₁Ni₄</td>
</tr>
<tr>
<td>98-024-5670</td>
<td>56</td>
<td>Lanthanum Tris (hydroxide)</td>
<td>0,016</td>
<td>0,291</td>
<td>H₃La₁O₃</td>
</tr>
</tbody>
</table>

Sample “5” and “6” prepared from the pure metals were observed by next PCT analysis. Figure 8 shows the PCT diagram of the prepared (LaCe)Ni₅ alloy sample. The maximum hydrogen capacity of the prepared modified (LaCe)Ni₅ alloy reached 1.21 Wt.%.

Figure 8 Hydrogen weight content in (LaCe)Ni₅ alloy at different temperatures
These results were approved by the PCTPro measurement of the alloy sample and shown in Figure 9. The biggest hydrogen weight content was reached at the lowest testing temperature of 300 K and pressure around 2.0 MPa (red line on the diagram). The structure photos of (LaCe)Ni₅ alloy after hydrogen desorption are attached in Figure 10.

**Figure 9** PCT diagram for hydrogen reversible sorption in (LaCe)Ni₅ alloy

**Figure 10** SEM images of (LaCe)Ni₅ alloy after hydrogen desorption: (a) at 200 x; (b) at 1 kx; (c) at 2 kx; (d) at 10 kx
4.1. Influence of the structure state

The structure state of the hydrogen storage materials (HSM) can also influence the thermodynamic properties and value gravimetric capacity of metallic hydrides. Two (LaCe)Ni$_5$ and two LaCe(FeNi) samples were compared. (LaCe)Ni$_5$-cast and LaCe(FeNi)-cast samples were traditionally cast into Cu mold and fast cooled (LaCe)Ni$_5$-FC and LaCe(FeNi)-FC were remelted and cast on water-cooled Cu-plate. Fast cooled materials were cast in a compact MAM-1 arc furnace.

Experimental alloy samples were remelted in a protective atmosphere of Ar and suction molded (suction casting) into a water-cooled mold of 1.5 mm diameter. The cast material was crushed in a mortar and sieved through a 0.063 (mesh size 63µm) screen. Average chemical composition of the cast and fast cooled alloy samples after crushing and oversaturation presented in Table 7 below.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Elements, [Wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>LaCeNi$_5$</td>
<td>51.1</td>
</tr>
<tr>
<td>LaCeNi$_5$-FC</td>
<td>51.1</td>
</tr>
<tr>
<td>LaCeNiFe 1</td>
<td>54.2</td>
</tr>
<tr>
<td>LaCeNiFe-FC1</td>
<td>48.9</td>
</tr>
<tr>
<td>LaCeNiFe 2</td>
<td>56.4</td>
</tr>
<tr>
<td>LaCeNiFe-FC2</td>
<td>49.6</td>
</tr>
</tbody>
</table>

The following comparative PCT analysis of the samples with different structure states shows that the fast cooled samples of (LaCe)Ni$_5$-FC and LaCe(FeNi)-FC showed higher gravimetric capacity at lower sorption pressure in comparison with corresponding cast samples. The hydrogen reversible sorption curves for both (LaCe)Ni$_5$ and LaCe(FeNi) structured samples are shown in Figure 11. The presented results of the isothermal reversible hydrogen sorption for (LaCe)Ni and LaCe(FeNi) alloys show that it is possible to increase the hydrogen storage capacity of the well-known LaNi$_5$ alloy from 1.3-1.4 Wt. % to 1.55 Wt. % by partial replacement of La by Ce and via alloy structure changing. Partial replacement of Ni by Fe decreases the working pressure of hydrogen reversible sorption from 1MPa to 0.3-0.5 MPa.
In summary, the preparation of materials with various structure states could be a novel way for the influence of the HSM thermodynamic properties. The different state of the structure of hydrogen storage alloys can transform during reversible sorption cycles into nano-HSM with excellent hydrogen storage properties. These materials could reach sufficient storage properties at low temperatures. The knowledge about the influence of the structure state on hydrogen storage properties can show new ways for LT MHs development.

**Figure 11** Hydrogen reversible sorption: (a) in the LaCeNi$_5$-cast and LaCeFeNi-cast alloys; (b) in the fast cooled (LaCe)Ni$_5$-FC and LaCeFeNi-FC alloys.
5. MH INTEGRATION IN HYDROGEN HYBRID SYSTEMS

Joint use of the FC technologies with hydrogen storage systems based on MHs allows more effective exploitation of both HHS components via utilizing FC excess heat energy for hydrogen desorption from the LT MH. FC allows the direct conversion of the fuel chemical energy into electrical energy without additional heat or mechanical work. A proton exchange membrane fuel cell (PEMFC) is one of the most common and proven devices that could be operated in a range of low and high temperatures [Dell et al. 2001]. Among the fuel candidates for the PEMFC, hydrogen is the most probable from the present energy carriers [Thomas et al. 2000]. Such kind of hydrogen storage systems based on La-Ni based LT MH can find their applications in cases where the weight of the storage system is not a critical parameter, and low operating temperature and pressure are required. One of the ways of the practical application of hydrogen storage systems based on LT MH followed by direct conversion of hydrogen into electric power through FC is to use such kind of hybrid system in industrial trucks or forklifts.

5.1. Experimental hydrogen hybrid system

The experimental energetic system with implemented hydrogen technologies was developed in the Laboratory of Fuel Cells, Centre ENET, Technical University of Ostrava. This hydrogen hybrid energy system, shown in Figure 12 below, basically consists of the solar panels, power inverters, accumulator batteries, hydrogen production, and storage units. Hydrogen produced via several PEM water electrolyzers. Hydrogen could be stored in the solid-state in (LaCe)Ni5 LT MH or subsequently used for electricity generation via LT FC and stored in the battery bank.

The hydrogen accumulation system is designed to operate eight electrolyzer stacks with a total input power of 17 kW and 4 m³ h⁻¹ total hydrogen capacity. The photovoltaic (PV) plant with polycrystalline panels delivers 22.5 kWp output. The energy obtained from all the sources installed is mainly consumed internally, with potential surplus available to the local power grid supply. Combined electrical power technologies mainly for the accumulation of electrical power are connected to the processing technology to provide regular delivery and control of the distribution system. The accumulation block with lead batteries enable to store 550 kWh of power, and an additional 80 kWh can be stored in LiFePO batteries. These batteries accumulate energy for the PV power plant and stabilize energy for hydrogen production.

Five modules of LT PEMFC with an electric output power of 40 kW are used for the regeneration of electrical power and heat. The working parameters of the FC and MH storage system are shown in Table 8.
5.2. MH thermography during H₂ reversible sorption via FC

This part of the work has addressed the employment of thermal diagnostics in the practical operation of La-Ni based MH and FC and their integration into the HHS. The thermal field distribution over the LT FC and temperature of the MH based hydrogen storage system was measured by FLIR E45 thermal camera. Figure 13 shows the block diagram of the testing.

![Block diagram and basic view of the HHS with integrated FC and MH](image)

**Figure 12** Block diagram and basic view of the HHS with integrated FC and MH

**Table 8** The main working parameters of fuel cells and hydrogen storage system

<table>
<thead>
<tr>
<th>NHX FC Characteristic</th>
<th>Value</th>
<th>MH Storage Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>&lt; 65 °C</td>
<td>Charging pressure</td>
<td>1.5 MPa</td>
</tr>
<tr>
<td>Rated power</td>
<td>1200 W</td>
<td>Charging temperature</td>
<td>298 K</td>
</tr>
<tr>
<td>Maximum current</td>
<td>230 A</td>
<td>Discharging temperature</td>
<td>(298-318) K</td>
</tr>
<tr>
<td>Operating voltage</td>
<td>22–50 V</td>
<td>MH alloy type</td>
<td>(LaCe)Ni₅</td>
</tr>
<tr>
<td>Max H₂ consumption</td>
<td>20 Nl min⁻¹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The temperature of the storage system tank was also measured by two thermosensors, located at different zones of the storage tank. The first temperature sensor was situated close to the gas inlet; the second sensor was placed close to the water inlet (heat exchanger inlet). As
mentioned above the temperature of the storage tank surface was controlled by the thermal camera. Due to the exothermic reaction of hydride formation, the temperature of the MH storage system should be observed and maintained constantly. Figure 14 shows the rising of MH tank surface temperature during hydrogen sorption reaction. Figure 14 (a) shows the MH storage tank temperature before the hydrogen sorption process, and Figure 14 (b) represents the thermogram of the storage tank surface during charging. Figure 14 could be compared with the corresponding temperature curves and charging parameters shown in Figure 15.

**Figure 14** Thermography of La-Ni based storage tank surface: (a) before charging, (b) during charging

![Thermography of La-Ni based storage tank surface](image)

**Figure 15** Temperature and charging parameters of the tank cooled by: (a) tap water, (b) chilled water

![Temperature and charging parameters](image)
Time-temperature changes during the charging process depend also from inlet hydrogen flow. More intensive flow causes more intensive heating of MH due to the exothermic chemical reaction and respectively request a more intensive heat transfer.

The next charging was held at ambient temperature but the cooling system was feeding by chilled water with ice inside of the water tank. The temperature of the water was 10 °C. That not critical temperature change of cooling water (Δ 6 °C) provides a significant change of hydrogen sorption speed and fullness of the storage tank filling. As shown in Figure 15 the difference in hydrogen capacity between two chargings was around 233 NL.

The same Nexa LT FC has been used for the MH discharging. Thanks to FC integrated mass flow meter, it was possible to control and regulate precisely the hydrogen discharge flow. Figure 16 represents the thermography of the MH storage tank discharging. Due to the endothermic reaction of hydrogen desorption, the MH storage tank has been heated up to 35 °C.

Discharging parameters of the storage system shown in Figure 17.

![Figure 16 MH storage surface thermography: (a) before discharging, (b) during discharging](image)

![Figure 17 MH storage discharging parameters](image)

From the above, it follows that temperature controlling is a very important process for MH charging and approaching the maximum value of storage capacity is a complex process that requires careful study and control in practice. The maximal hydrogen capacity (923 NL) that was reached during the discharging cycle could provide an energy amount of 2.765 kWh that was
used by LT FC for the direct transformation hydrogen to the 1 kWh of DC (direct current) electrical energy.

The calculation of the heat release during hydrogen sorption in \((\text{LaCe})\text{Ni}_5\text{H}_6\) metal hydride presented in annex. Due to the almost similar molar mass of \(\text{La} (138.91 \text{ g mol}^{-1})\), \(\text{Ce} (140.12 \text{ g mol}^{-1})\) elements, the calculation could be applicable also for different alloys composition in the variation of \(\text{La/Ce} \) weight percentage in alloy composition from \(\text{La}_{0.9}\text{Ce}_{0.1}\) to \(\text{La}_{0.1}\text{Ce}_{0.9}\).

For calculation have been used next experimental data: \(\Delta H(\text{LaCe})\text{Ni}_5\text{H}_6 = -30.8 \text{ kJ mol}^{-1}\);

\((\text{LaCe})\text{Ni}_5\text{H}_6\) metal hydride hydrogen weight content (storage density) 1.386 Wt.%

Figure 18 below shows the results of the calculation of the MH hydrogen storage capacity and corresponding heat release during hydrogen sorption in \((\text{LaCe})\text{Ni}_5\text{H}_6\) metal hydride depending on the total alloy weight.

**Figure 18** Diagram of \((\text{LaCe})\text{Ni}_5\text{H}_6\): (a) energy released during MH formation; (b) MH hydrogen storage density

5.3. **FC thermography and waste heat utilization for the LT MH discharging**

The main purpose of this part of the study was to explore the possibilities of potential FC heat utilization for LT MH discharging. The thermography of the MH storage system during reversible sorption allows more accurate temperature controlling during the charging-discharging processes and more efficient MH storage system using. The FC overheating bring the risk of electrolyte drying (the PEM polymer membrane), with next membrane degradation. The FC stack thermography and computer simulation allow determination of the stack local overheating points and ensure more efficient and safe FC operation. In addition, these methods gave information about exhaust thermal energy available for the next useful utilization via LT MH discharging.

During load, FC loses a significant part of the heat and has smaller actual potential than a theoretical one. Voltage losses in operational FC could be caused by activation polarization (kinetics of chemical reaction), mass transport limitations of reactants, electrical and ionic internal
resistance. Common FC and LT MHs use in one HHS gives the advantage to avoid FC poisoning by unclean inlet hydrogen. Thermal energy released during the FC operation can be effectively used for the hydrogen desorption from the La-Ni based LT MHs. Cause the MH hydrogen desorption is an endothermic reaction, it requires external heating up to 40 °C. This heating could be provided by low and high-temperature FC working up to 65 °C and 160 °C respectively. Table 9 and Table 10 below show working characteristic of tested LT and HT PEMFC respectively.

It is also possible to use a methanol reformer together with a high-temperature FC (HT FC) and additional gas cleaning no needed. Methanol is an alternative energy carrier and is much easier to store liquid methanol fuel than gaseous hydrogen. For this reason, methanol production is one of the ways of hydrogen storage, which comes from renewables via water electrolysis process and the way of CO₂ utilization. Figure 19 below shows potential La-Ni based LT MH integration in HHS for the flexible hydrogen production, storage, and utilization via PEMFC.

**Table 9 Working parameters of LT FC**

<table>
<thead>
<tr>
<th>Type</th>
<th>LT PEMFC Nexa, Ballard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>1200 W</td>
</tr>
<tr>
<td>Number of cells</td>
<td>47</td>
</tr>
<tr>
<td>Working temperature</td>
<td>up to 65 °C</td>
</tr>
<tr>
<td>Cooling</td>
<td>Air</td>
</tr>
<tr>
<td>Active area</td>
<td>120 cm²</td>
</tr>
<tr>
<td>Membrane</td>
<td>Ion exchange with fluorinated sulfonic acid polymer</td>
</tr>
</tbody>
</table>

**Table 10 Working parameters of HT FC**

<table>
<thead>
<tr>
<th>Type</th>
<th>HT PEMFC SerEnergy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>2500 W</td>
</tr>
<tr>
<td>Number of cells</td>
<td>65</td>
</tr>
<tr>
<td>Working temperature</td>
<td>up to 180 °C</td>
</tr>
<tr>
<td>Cooling</td>
<td>triethylene glycol (TEG)</td>
</tr>
<tr>
<td>Active area</td>
<td>165 cm²</td>
</tr>
<tr>
<td>Membrane</td>
<td>Polybenzimidazole (PBI)</td>
</tr>
</tbody>
</table>
Figure 19  LT MH integration for the flexible hydrogen storage and utilization via PEMFC

5.3.1. LT PEMFC thermography

The cooling fan draws air from the ambient surroundings to cool the LT FC module and regulate the operating temperature. The thermography of the Nexa module during metal hydride discharging was done at four different DC loads: 100 W, 300 W, 500 W, 1000 W. The FC stack temperature is measured at the cathode air exhaust.

The obtained thermograms show evident temperature differences between individual parts of the FC stack surface. The left end of the stack heats up significantly more, as it is closer to the entry of the cooling air supply channel. Figure 20 (a) shows a surface temperature for the FC module measured at the load of 500 W and Figure 20 (b) at the load of 1000 W.

The heating curves based on the measurement results report that the system cooling will be not activated at 100 W load. The core temperature of the stack of 60 °C at such load was reached only 85 minutes after its starting. After the specified period, its average surface temperature dropped by more than 15 °C. The FC stack starts its active cooling system only at higher loads (300 W, 500 W, and 1000 W) and works at the lower-middle operating temperature range of the module. When linked to the top loads (above 1000 W), the stack will reach highest operating temperature of 65 °C.
Figure 20 Thermographic picture showing the surface of the stack of hydrogen fuel cells: (a) at 500 W load, (b) after 2 hours of operation with the constant 1000 W load.

Figure 21 and Figure 22 show the course of the temperature inside the stack in time obtained at various load levels and time paths by measurement at identical time intervals.

Figure 21 Time paths of temperature at various load: (a) inside the stack; (b) on the surface.

Figure 22 Time paths of the temperature inside the FC stack and on the FC surface at different load: (a) 100 W and 300 W; (b) 500 W and 1000 W.
5.3.2. *LT PEMFC computer simulation*

Unequal cooling of the hydrogen module, previously detected by thermography measurement was studied via numerical Computed Fluid Dynamics (CFD) model and its analysis using the ANSYS software.

The simulation determined the temperature distribution within the LT FC stack as well as the cooling air flow velocity inside the cooling channel and cooling fins. This simulation was performed for the stable working condition of the LT FC (1200 W load). Generated waste heat was simply exhausted through the cooling fins to the atmosphere.

The 3D model of the LT FC stack based on its actual dimensions was designed via SolidWorks software. The stack consists of 47 cells connected in series. The composed cells form a system of channels for cooling air circulation and heat dissipation. The controlled radial fan ensures the air supply to the cooling channels via the plastic distributing channel, situated below the complete module.

The heat transfer coefficient calculation for the CFD modeling of the system have been described in the previous study [Kacor et al. 2015]. The CFD modeling took into account also the energy losses incurred by the generation of heat within the FC stack due to the passage of the electric current. Material parameters and load values for CFD simulation presented in the annex.

Figure 23 shows the CFD model of the LT PEMFC temperature profile with uneven temperature distribution across the stack. The figure gives a clear image of the temperature difference between the lower and upper, right and left regions of the stack. The right part of the stack situated on the fan side reached the maximum temperature of 70-75 °C. At the same time, the left side was heated only up to 50-55 °C. The temperature at the bottom of the stack was only 30-35 °C, while the temperature of the upper part was about 55-75 °C. That is associated with heat transfer from fins into the cooling air which causes a rise in temperature of the upper fins.

![Figure 23 CFD simulation of temperature distribution across the LT FC stack](image-url)
The velocity of the cooling air flow inside the distribution channel across the longitudinal cross-section of the stack is shown in Figure 24. This air enters the distribution cooling channel from the right side at the velocity of 10 m s\(^{-1}\) and is further distributed into the individual vertical channels between the fins.

Cause of plastic cover plates at the inlet of distribution cooling channel of the stack, the cooling air flow is subject to extensive distortion and cooling air can not enter the right cooling fins effectively to remove the waste heat. It is the reason for the high temperature on the right side of the stack. The additional installation of the cooling system is needed. This cooling system will maximize the operational efficiency of the stack, eliminate the overheating of its right side and allow it to collect and use LT FC waste heat more efficiently. Currently, LT FC heat transfer simulations are underway directed to study the amount of FC waste heat which could be used for the MH discharging process.

**Figure 24** CFD simulation of cooling air flow inside the LT FC stack

The first results of the simulation show that the heat could be distributed from the 0.036 m\(^2\) stack upper surface, there a heat exchanger should be installed. The velocity of that heat flow could reach 3.06 m s\(^{-1}\) within 32-37 °C temperature. The total amount of the distributed heat from the stack upper surface to the LT MH depends on the construction, effective square of the heat exchange, and heat conductivity of the coolant. The detail calculation and information about LT PEMFC waste heat utilization for LT MH discharging will be added after ongoing CFD stack simulation.

5.3.3. *HT PEMFC thermography*

Corresponding loads were used for the HT FC temperature measurements. The thermography of the FC surface was carried out using a FLIR E 40 thermal IR camera and shown in Figure 25 below. Temperature measurement was also carried out by 2 thermocouple (k-type) at coolant inlet and outlet of the stack.
Figure 25 HTFC thermography at different load: (a) 500 W, (b) 1000 W

Figure 26 shows the temperature profiles of the HT FC stack at various loads. As can be seen from the graph the FC cooling system at 100W load activates periodically. The heat released during FC operation at such low load was used to maintain the operating temperature of the FC. As the load increases, the cooling system begins its regular operation. The flow of water for the external glycol cooling cycle depends on the actual temperature of the FC and can be changed by adjusting the cooling water supply valve. In connection with the use of a significant part of the HT FC released thermal energy to maintain the stack working temperature at low loads, further calculations of thermal energy that can be effectively used for hydrogen desorption from the LT MH is given for a higher 1000-1200 W load.

Figure 26 Temperature profiles of the HT FC stack at different load
5.3.4. **HT PEMFC computer simulation**

The detail calculation and information about HT PEMFC waste heat utilization for LT MH storage discharging will be added after completion of ongoing CFD stack simulation. The rough calculation presented below:

- From the experimental data, the 45 min of HT FC operation is equivalent to 12.206 kWh, which corresponds to 4391.6 kJ.
- The 1 h of operation correspond to 5855.47 kJ h\(^{-1}\) of HT PEMFC total electric output.
- Regarding the heat loses and around 50% efficiency of the FC, only half of the total FC electric output energy could be effectively utilized for MH discharging: 2927.735 kJ h\(^{-1}\).
- The required amount of energy for 1 kg MH hydrogen desorption is 213.44 kJ kg\(^{-1}\) of MH. Considering the heat losses (around 30%) during heat transfer from the FC to MH tank and inside the tank the required amount of energy is: 277.472 kJ kg\(^{-1}\).
- The total amount of \((\text{LaCe})\text{Ni}_5\) LT MH, which could be heated by HT PEMFC during 1h at 1 kW load is 21.10 kg (at 30% heat transfer loses between FC stack and MH storage tank).
6. CONCLUSIONS

In the frames of the thesis work was studied the actual problematic of fossil sources limitation and using hydrogen as an alternative source of energy. In that connection, the hydrogen storage methods were studied with the main accent in H₂ storage in metal hydrides. Theoretical study all of the above aspects gave needed information for experimental study of La-Ni based alloys, like one of the more applicable types of the materials for daily hydrogen storage.

Steps were taken to investigate the possibility of La-Ni based alloys modifying for the next hydrogen storage and their integration with fuel cells. It was experimentally shown the possibility of La-Ni based alloys hydrogen sorption capacity improving and the lowering of the working equilibrium pressure via alloys modification by Ce and Fe. Changing in the structured state of the La-Ni based alloys can influence the value of the gravimetric capacity of the hydrides. The fast cooled sample of the (LaCe)Ni₅-FC alloy shows higher gravimetric capacity (up to 1.55 Wt.%) at lower sorption pressure in comparison with (LaCe)Ni₅-cast sample. The knowledge about the influence of the structure state on hydrogen storage properties can show new ways for the low-temperature metal hydrides development.

The attempts of the alloys synthesis from cheaper reagents as a metal chlorides instead of the pure metals and using LiH as a reduction agent shows the existing problem of alloy samples oxidation. Therefore, further research is needed to investigate the possibilities of more effective use of the reduction agent for the alloy thermochemical synthesis.

The aspect of the practical application of such alloys/hydrides with fuel cells was also studied and described. It was shown that a significant part of the heat released during the operation of the HT and LT PEMFC can be effectively used for the hydrogen desorption from LT MHs. These results could be served for the further developing of new methodologies for hydrogen mass storage in the mobility and other application areas.

6.1. Future aims and steps

The main idea of the future work is to study the hydrogen storage properties of the LT MH in various states of structure from the critically cooled or amorphous state to ordered structure. This material could reach sufficient hydrogen storage properties at ambient temperatures, so the structure could not be influenced by experimental temperatures. The results could show new ways for the development of LT MH for hydrogen storage.

The main part of cast alloy will be crushed or ball-milled into the powder and sieved to separate big uncrushed particles. Some parts of experimental materials will be remelted and rapidly cooled for reaching the amorphous state of the structure and also long term annealed for...
reach equilibrated structure. These materials will be used for the study of the influence of structure state on storage properties. The fine powders of the experimental storage alloy will be obtained by the method of mechanical alloying in a high-energy planetary ball mill.

Preparation of bulk material alloys made from a batch of splinters (pure elements) for a study of the influence of bulk materials on storage properties will be done. All of these materials will be used for the study of the influence of structure state on hydrogen storage properties.

The identification of phases will be done by using the XRD, high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) analysis. These analyses will deliver a sufficiently complex picture that enables a better understanding of structure influence on hydrogen storage properties. Hydrogen kinetics and thermodynamics will be studied with the help of the SETARAM PCT-Evo and PCT-PRO devices. The PCT isotherms will be carefully measured for all experimental materials, so it will be enable to evaluate the hydrogen storage capacity, entropy, enthalpy and cycling stability.
7. REFERENCES

Chesalkin A, Minarik D (2016) Intermetallic compounds for energy storage. The 25th
Anniversary International Conference on Metallurgy and Materials, METAL 2016 -
Proceedings, pp. 1272-1279. EID: 2-s2.0-85010738777

Journal of Power Sources, vol. 100 (1-2), pp. 2-17. doi.org/10.1016/S0378-7753(01)00894-1

Friedlmeier G, Groll M (1997) Experimental analysis and modeling of the hydriding kinetics of
doi.org/10.1016/S0925-8388(96)03003-4

Kacor P, Minarik D, Moldrik P (2015) CFD Analysis of Temperature Distribution of PEM Type
EPE 2015, IEEE, 2015, pp. 507-12. doi.org/10.1109/EPE.2015.7161128


Srinivas G, Sankaranarayanan V, Ramaprabhu S (2008) Kinetics of hydrogen absorption in Ho1-
doi.org/10.1016/j.jallcom.2006.10.064

Thomas C E, James B D, Lomax F D, Kuhn, I F (2000) Fuel options for the fuel cell vehicle:
551-567. doi.org/10.1016/S0360-3199(99)00064-6