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

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
I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable...

Jules Gabriel Verne, *The Mysterious Island*, 1874
I hereby declare that this thesis is my original work, which I have developed independently. All the literature and other resources to which I referred, quoted legally and declared in the list of references.

In Ostrava .......................... ...........................................

(signature)
ACKNOWLEDGMENT

I would like to thank all those who helped me to complete this thesis work.

First of all, 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. Special thanks go to those who directly participated on presented experiments: RNDr. Alexandr Martaus, Ph.D., Ing. Daniel Minařík Ph.D., Ing. Petr Moldřík Ph.D., and many others.

I also wanted to thank Ing. Lubomir Kral Ph.D. from Institute of Physics of Materials Czech Academy of Science, Brno, for his support, subsequent and next cooperation in metal alloys hydrogen storage field.

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. I am especially grateful to my spouse Jana who supports me in all my endeavors.

Thank you very much to all of you!
ANNOTATION

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. Because hydrogen is one of the prospective clean fuels of the future, it is very important to find sufficient materials for its storage and transportation. One of such 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 dissertation work describes the alternative way of hydrogen storage in compact solid form in low-temperature metal hydrides and their practical application and integration with fuel cells.

The first part of the work describes the present energetic situation in frames of fossil fuel limitation and serious environmental pollution and ways to use hydrogen as an alternative ecological fuel. However, the main disadvantage of hydrogen everyday practical use is its low storage density. In this part of the work, the main hydrogen storage techniques are described, with the main focus on hydrogen storing in the solid state in metal hydrides. Low-temperature La-Ni based metal hydrides allow storing hydrogen at ambient temperatures and relatively low working pressures in a compact form. Nevertheless, the price of the alloys and the metal hydrides working characteristics such as working temperature, pressure and hydrogen storage density are the issues of further study and modification.

The main aim of the work was an attempt to modify the well-known LaNi$_5$ metal hydride and find the optimal working temperature-pressures parameters of the alloy for reversible hydrogen sorption via fuel cells. In this part, steps have been taken to modify the LaNi$_5$ 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 LaNi$_5$ and (LaCe)Ni$_5$ 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 of 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)Ni₁₅-X-cast was traditionally cast into Cu mold and (LaCe)Ni₁₅-X-FC was remelted and cast on water-cooled Cu-plate. The structure of the (LaCe)Ni₁₅-X-FC sample contained fine grains and fine particles containing X (Ce) segregated on grain boundaries. The sample (LaCe)Ni₁₅-X-FC showed higher gravimetric capacity (up to 1.55 Wt.%) at lower sorption pressure in comparison with (LaCe)Ni₁₅-X-cast sample.

The preparation of materials with various structure states could be a completely novel way for influence of thermodynamic properties of hydrogen storage materials. 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 the low-temperature metal hydrides development.

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, what allows using more efficiently both components of the hydrogen system.

**Keywords:** hydrogen, hydrogen storage, metal hydrides, La-Ni based alloys modification, fuel cells, thermography.
Hledání bezpečného a nákladově efektivního způsobu skladování vodíku je jedním z hlavních cílů na cestě vývoje vodíkových technologií a jejich aplikace v každodenním životě. Protože vodík je jedním z perspektivních čistých paliv budoucnosti, je velmi důležité najít dostatečné materiály pro jeho skladování a přepravu. Jednou z takových možností je skladování vodíku ve formě hydridů, ale tento proces není zdáleka optimální vzhledem k nízkým sorpčním-desorpčním vlastnostem materiálu a pracovním parametřům teploty a tlaku.

Disertační práce popisuje alternativní způsob skladování vodíku v kompaktní pevné formě v nízkoteplotních hydridech kovů a jejich praktické využití a integraci s palivovými články.

První část práce popisuje současnou energetickou situaci v rámci omezení fosilních paliv a vážného znečištění životního prostředí a způsobů využití vodíku jako alternativního ekologického paliva. Hlavní nevýhodou každodenního praktického použití vodíku je však nízká hustota skladování. V této části práce jsou popsány hlavní techniky skladování vodíku s hlavním zaměřením na skladování vodíku v pevném stavu v hydridech kovů. Nízkoteplotní kovové hydridy na bázi La-Ni umožňují skladování vodíku při okolních teplotách a relativně nízkých pracovních tlacích v kompaktní formě. Nicméně cena těchto slitin a pracovních vlastností hydridů kovů, jako je pracovní teplota, tlak a hustota skladování vodíku, jsou otázkou dalšího studia a modifikace.

Hlavním cílem práce byl pokus o úpravu známého hydridu kovu LaNi₅ a nalezení optimálních parametrů pracovní teploty slitin pro reverzní sorpci vodíku přes palivové články. V této části byly podniknuty kroky k úpravě slitiny LaNi₅ částečnou náhradou La za Ce a Ni za Fe. Byly provedeny pokusy o optimalizaci časově-teplotních parametrů syntézy slitin a konečné hustoty skladování vodíku. Syntéza slitin byla prováděna dvěma různými způsoby: klasickým tepelným tavením čistých kovů a termochemickou reakcí chloridů kovů. Byla provedena srovnávací analýza získaných vzorků slitin La-Ni, La-Ce-Ni, La-Ce-Fe-Ni. Byla provedena podrobná fyzikálně-chemická analýza připravených slitin a odpovídajících hydridů. Data analýzy XRD a SEM ukazují, že zvýšení teploty syntézy slitiny a doby držení vzorku usnadňuje tvorbu požadovaných fází LaNi₅ a (LaCe)Ni₅. Bohužel problém oxidace vzorků připravených z chloridů kovů stále zůstává nevyřešen. Proto je zapotřebí dalšího výzkumu, který by zkoumal možnosti účinnějšího použití LiH nebo použití jiného redukčního činidla pro termochemickou syntézu slitin.

Předběžná studie slitiny LaNi₅, modifikovaná prvkem Fe ukázala významné změny tlaku sorpce vodíku. SPLITINA LaNi₅ modifikovaná prvkem Ce ukázala významné změny gravimetrické kapacity vodíku (až 1.55 Wt.%). Strukturovaný stav skladovacího materiálu může také ovlivnit termodynamické vlastnosti a hodnotu gravimetrické kapacity hydridů kovů. (LaCe)Ni₅-X-cast
byl tradičně odléván do Cu formy a (LaCe)Ni$_5$-X-FC byl přetaven a odlit na vodou chlazenou Cu desku. Struktura vzorku (LaCe)Ni$_5$-X-FC obsahovala jemná zrna a jemné částice obsahující X (Ce) oddělené na hranicích zrn. Vzorek (LaCe)Ni$_5$-X-FC vykazoval vyšší gravimetrickou kapacitu při nižším sorpčním tlaku ve srovnání se vzorkem (LaCe)Ni$_5$-X-cast.

Příprava materiálů s různými stavy struktury by mohla být zcela novým způsobem ovlivnění termodynamických vlastností materiálů pro skladování vodíku. Tyto materiály by mohly dosahovat dostatečných skladovacích vlastností při nízkých teplotách. Znalosti o vlivu stavu struktury na vlastnosti skladování vodíku mohou ukázat nové způsoby vývoje nízkoteplotních hydridů kovů.

Druhá část práce uvádí výsledky zkoušek hydridu kovů v reálných provozních podmínkách při reverzibilní sorpci vodíku. Byl studován komplexní vodíkový systém založený na výrobě, skladování a využití vodíku. Desorpce vodíku byla prováděna pomocí nízkoteplotních a vysokoteplotních palivových článků s následnou termografickou analýzou celého systému palivový článek - hydrid kovu. Další počítačová simulace přenosu tepla palivovým článkem pod zátěží umožnila určit odpadní teplo, které může být účinně využito k desorbování vodíku z nízkoteplotního hydridu kovu na bázi La-Ni, což umožňuje efektivněji využití obou složek vodíkového systému.

Klíčová slova: vodík, skladování vodíku, hydridy kovů, modifikace slitin na bázi La-Ni, palivové články, termografie.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Characteristic</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pre-exponential factor</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>Specific heat capacity of a substance</td>
<td>J kg(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>c(^*)</td>
<td>Equilibrium concentration, concentration at equilibrium point</td>
<td>%</td>
</tr>
<tr>
<td>C(_0)</td>
<td>The initial concentration of the component</td>
<td>%</td>
</tr>
<tr>
<td>Ca {A}</td>
<td>Concentration of the component (a) (A)</td>
<td>%</td>
</tr>
<tr>
<td>Cal</td>
<td>Calorific value</td>
<td>J kg(^{-1})</td>
</tr>
<tr>
<td>d</td>
<td>Particle size</td>
<td>μm</td>
</tr>
<tr>
<td>D</td>
<td>Coefficient of molecular diffusion (mass diffusivity)</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>E(_a)</td>
<td>Activation energy</td>
<td>J mol(^{-1})</td>
</tr>
<tr>
<td>F(_m)</td>
<td>Mass flow rate</td>
<td>kg s(^{-1})</td>
</tr>
<tr>
<td>F(_{sp})</td>
<td>Specific heat exchange surface</td>
<td>m(^2) m(^{-3})</td>
</tr>
<tr>
<td>F(_v)</td>
<td>Volumetric flow rate</td>
<td>m(^3) s(^{-1})</td>
</tr>
<tr>
<td>K (K(_{eq}))</td>
<td>Reaction rate constant (equilibrium reaction constant)</td>
<td>-</td>
</tr>
<tr>
<td>M</td>
<td>Molar mass</td>
<td>g mol(^{-1})</td>
</tr>
<tr>
<td>n</td>
<td>Amount of substance</td>
<td>mol</td>
</tr>
<tr>
<td>P (P(_{eq}))</td>
<td>Pressure (equilibrium pressure)</td>
<td>Pa</td>
</tr>
<tr>
<td>P(^{A-D})</td>
<td>Sorption-desorption pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>Q</td>
<td>Heat energy (energy value of chemical reaction)</td>
<td>J</td>
</tr>
<tr>
<td>r</td>
<td>Reaction rate</td>
<td>mol l(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>T(<em>C) (T(</em>{eq}))</td>
<td>Critical (equilibrium) temperature</td>
<td>K</td>
</tr>
<tr>
<td>U</td>
<td>Voltage</td>
<td>V</td>
</tr>
<tr>
<td>x (x(_{eq}))</td>
<td>Conversion rate or reactant conversion degree (at equilibrium point)</td>
<td>%</td>
</tr>
<tr>
<td>ΔG</td>
<td>Gibbs free energy change</td>
<td>J</td>
</tr>
<tr>
<td>ΔH</td>
<td>Enthalpy change</td>
<td>J mol(^{-1})</td>
</tr>
<tr>
<td>ΔS</td>
<td>Entropy change</td>
<td>J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>ΔT</td>
<td>Temperature difference</td>
<td>-</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Thermal conductivity coefficient</td>
<td>W m(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>ρ(_v)</td>
<td>Volumetric storage density (volumetric capacity)</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>ρ(_{wt})</td>
<td>Gravimetric storage density (gravimetric capacity)</td>
<td>Wt.%</td>
</tr>
<tr>
<td>Symbol</td>
<td>Acronyms</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
<td></td>
</tr>
<tr>
<td>CFD</td>
<td>Computer Fluid Dynamics</td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>Compressed hydrogen</td>
<td></td>
</tr>
<tr>
<td>CL</td>
<td>Catalyst layer</td>
<td></td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
<td></td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
<td></td>
</tr>
<tr>
<td>FC</td>
<td>Fuel cell</td>
<td></td>
</tr>
<tr>
<td>FLIR</td>
<td>Forward-looking infrared</td>
<td></td>
</tr>
<tr>
<td>FP</td>
<td>Flow plate</td>
<td></td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
<td></td>
</tr>
<tr>
<td>H/M</td>
<td>Hydrogen-metal ratio</td>
<td></td>
</tr>
<tr>
<td>HHS</td>
<td>Hydrogen hybrid system</td>
<td></td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
<td></td>
</tr>
<tr>
<td>HSM</td>
<td>Hydrogen storage materials</td>
<td></td>
</tr>
<tr>
<td>HT</td>
<td>High temperature</td>
<td></td>
</tr>
<tr>
<td>LCV</td>
<td>Lower calorific value</td>
<td></td>
</tr>
<tr>
<td>LH</td>
<td>Liquid hydrogen</td>
<td></td>
</tr>
<tr>
<td>LPG</td>
<td>Liquefied petroleum gas</td>
<td></td>
</tr>
<tr>
<td>LT</td>
<td>Low temperature</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Molar mass</td>
<td></td>
</tr>
<tr>
<td>MH</td>
<td>Metal hydride</td>
<td></td>
</tr>
<tr>
<td>MOFs</td>
<td>Metal-organic frameworks</td>
<td></td>
</tr>
<tr>
<td>NG</td>
<td>Natural gas</td>
<td></td>
</tr>
<tr>
<td>$P_{A-D}$</td>
<td>Sorption-desorption pressure</td>
<td></td>
</tr>
<tr>
<td>PCT</td>
<td>Pressure-Concentration-Temperature (diagram or analysis)</td>
<td></td>
</tr>
<tr>
<td>PEM</td>
<td>Proton-exchange membrane</td>
<td></td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton-exchange membrane fuel cell</td>
<td></td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure swing adsorption</td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
<td></td>
</tr>
<tr>
<td>SMR</td>
<td>Steam methane reforming</td>
<td></td>
</tr>
<tr>
<td>$T_{A-D}$</td>
<td>Sorption-desorption temperatures</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
<td></td>
</tr>
</tbody>
</table>
1. INTRODUCTION

Modern energetics is a system based on the widespread consumption of fossil sources; their production and consumption provide serious environmental pollution. 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 is the most widespread element, the basis for many compounds and it generally exists in the combination with other elements. It can be produced from a large number of different sources such as water, coal, natural gas, biomass, and others, through thermal, electrolytic or photolytic processes. 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. However, the main disadvantage of hydrogen everyday practical use is its low storage density. One of the possible safe and compact ways of hydrogen storage is solid-state storage in metal hydrides.

However, there are not ready materials with sufficient hydrogen storage properties at low temperatures. Therefore, decreasing the thermodynamic stability of these storage materials and sufficient hydrogen capacity are crucial for tuning their storage properties. One the way for influence of thermodynamic properties is changing of structure states and composition of MH materials. This work describes the possible ways of hydrogen storage in low-temperature La-Ni based metal hydrides (MH). This method of hydrogen energy storage can be applied to the increasingly widely used FC technologies.

The main goal of dissertation work is the development of alternative hydrogen storage ways in the form of low-temperature metal hydrides. This method allows for achieving a compact and safe way of hydrogen storage. As was mentioned before, an attempt was made to increase the sorption capacity of the LaNi$_5$ alloy by partial replacement of lanthanum (La) by cerium (Ce) and nickel (Ni) by iron (Fe), as well as to reduce the final product costs by using cheaper components for the alloy synthesis. The choice of these materials was not accidental, because this type of hydrides allows storing and desorbing hydrogen at low temperatures and pressures which enables their integrated use with the proton-exchange membrane fuel cells (PEMFC). Another task of the work was the optimization of the time-temperature regime of alloys synthesis with next detailed chemical analysis of prepared alloys. 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. The last but no less important goal of the work was. The last but no less important goal of the work was to study the possibility of practical use of low-temperature metal hydrides (LT MH) and their implementation to the hydrogen hybrid systems (HHS).
1.1. MOTIVATION

The effectiveness of the hydrogen storage system strongly depends on the development of novel materials so that a large amount of hydrogen can be stored and released at reasonable temperatures, pressures and speeds [Satyapal 2017, Zhang et al. 2016]. Many studies were aimed to hydrogen storage materials (HSM) development for the hydrogen storage volumetric densities increasing while reducing energy costs [Zuttel 2003, Godula-Jopek 2015, Basile et al. 2014].

The main goals for the all MH storage systems are the improvement of the hydrogen storage capacity and hydrogen reversible sorption characteristics (decreasing of the temperature-pressure working characteristics and sorption activation energy decreasing).

Generally, the hydrogen storage material thermodynamics properties significantly limit the utilization of most high capacity storage materials for industrial applications. In the case of metallic hydrides, the main limiting storage characteristic is a low gravimetric storage density or elevated working temperatures.

The reducing of the absorption-desorption temperatures (\(\Delta T\)) is 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 \(\Delta T\) [Lin et al. 2018, Sahlberg et al. 2016]. The thermodynamics of these storage alloys depends on resulted nanostructure after reversible hydrogen sorption cycles. These nanostructures of amorphous or ordered structures can significantly change the properties of the final HSM [Sadhasivam et al. 2017]. The thermodynamics of the MH formation is described, for example, in papers [Flanagan et al. 1988, Griessen et al. 1988, Fukai et al. 1993].

For the private sector and small production areas, elevated hydrogen storage pressure may cause problems due to safety regulations. La-Ni based MH, as an alternative hydrogen storage option at low pressure in a compact solid form, provides a possibility for the reversible hydrogen sorption. Where is a number of works described the LaNi\(_5\) alloy preparation by thermochemical synthesis with Mg reducing agent or LaNi\(_5\) modification by adding Co and Al to increase the lifetime of the alloy, and the optimization of the time-temperature parameters of the alloy synthesis [Giresan et al. 2016, Kamasaki et al. 1997]. Regarding the above-mentioned facts, further study of these hydrogen storage systems is promising.
1.2. THESIS WORK STRUCTURE DIAGRAM

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

2. Hydrogen storage
   Problematic of hydrogen storage and transportation.

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

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

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

6. 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.

7. 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 HSM properties. LT MH integration with FC. MH and FC thermography, computer simulation of the FC heat transfer for next FC waste heat utilization for MH discharging.
2. HYDROGEN TECHNOLOGIES DEVELOPMENT

2.1. HYDROGEN ENERGY

Currently, there is an urgent need to use alternative and non-fossil energy sources [Tsuchiya et al. 2014]. The global energy consumption is projected to double by 2050 cause of Earth population growth and the industrialization of developing countries [Hoffert et al. 1998]. One promising alternative to fossil fuels is hydrogen [Turner 1999].

In 1625, Johann Baptista van Helmont first described hydrogen as a gas. Later, Henry Cavendish determined hydrogen as a chemical element by reacting zinc with hydrochloric acid and found that water was made of hydrogen and oxygen. Electrolysis process was first introduced by Troostwijk and Diemann in 1789 [Trasatti 1999].

The idea of hydrogen use as an alternative fuel appeared in the 70s, due to the fuel crisis [Ikenberry 1986]. Decades before, in 1839, Christian Friedrich Schönbein detected that the electrolysis process also works the reverse way and can produce an electric current. It was the early version of the FC [Wengenmyr et al. 2012]. In the 90s, with the development of the FC technologies, transport companies have started to work on hydrogen vehicles. The hydrogen energetic started to gain interest because of its many advantages over fossil fuel economy [Dincer et al. 2015]. The most important energy process is the combustion of hydrogen, which releases large amounts of energy and water without any harmful emissions. Among the various types of fuels, hydrogen has the highest gravimetric calorific value of 33.33 kWh kg\(^{-1}\) that is a much higher value in comparison with many widely used hydrocarbons [Huot 2010]. Table 1 shows the lower calorific value (LCV) of different common fuels.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Calorific value, [MJ kg(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>120.0</td>
</tr>
<tr>
<td>Methane</td>
<td>50.0</td>
</tr>
<tr>
<td>LPG</td>
<td>50.18</td>
</tr>
<tr>
<td>Gasoline</td>
<td>43</td>
</tr>
<tr>
<td>Diesel</td>
<td>46</td>
</tr>
<tr>
<td>Petrol</td>
<td>43</td>
</tr>
<tr>
<td>Kerosine</td>
<td>47</td>
</tr>
<tr>
<td>Ethanol</td>
<td>26.9</td>
</tr>
</tbody>
</table>
2.2. HYDROGEN PRODUCTION

Speaking about hydrogen as an energy carrier, it must be said about its origin. Hydrogen production is a first step on the way of hydrogen energetics. Hydrogen practically does not occur in nature in the pure form. For this reason, the gas must be produced from other compounds through various physical and chemical reactions. There are few widely used technics for industrial hydrogen production: steam methane reforming (SMR), coal gasification, water electrolysis, biochemical production (from biomass), and pyrolysis. The most widely used industrial and cheapest method of hydrogen production is SMR. At temperatures up to 1000 °C in the presence of a Ni-based catalyst, water steam reacts with methane:

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad (\Delta H = 206 \text{ kJ mol}^{-1})
\]  (1)

The remaining carbon monoxide is then converted in the water steam-gas mixture to produce more hydrogen (water-gas shift reaction):

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (\Delta H = -41 \text{ kJ mol}^{-1})
\]  (2)

Figure 1 shows the basic SMR process flow sheet diagram. However, this production method is not environmentally friendly and releases a large amount of CO\textsubscript{2} into the atmosphere. Presence of carbon oxides impurities in the final product gas requires additional pressure swing adsorption unit (PSA), where the hydrogen is separated from other gases under elevated pressure using differences in adsorption properties [Ogden 1999].

![Figure 1 Basic process flow sheet – Steam-reforming plant [Mahler AGS]](image-url)
Electrolysis of water or the decomposition of water into oxygen and hydrogen gas by the action of an electric current is enabling the use of renewable energy sources and ensuring independence from the fossil sources. Hydrogen production via electrolysis from renewable energy sources was previously studied in the literature by various authors [Lodhi 2004, Lemus et al. 2010, Alstrum-Acevedo et al. 2015].

However, this method of hydrogen production is still little-used today. Only 5-8% of the hydrogen produced in a world comes from this process. Basically, the water electrolysis process could be described by followed reactions and Figure 2 below [Stolten et al. 2016]:

Reduction process (cathode): \[ 2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \]  
(3)

Oxidation process (anode): \[ 2OH^- \rightarrow \frac{1}{2} O_2 + H_2O + 2e^- \]  
(4)

Overall reaction: \[ 2H_2O \rightarrow 2H_2 + O_2 \]  
(5)

**Figure 2** Schematic view of the water electrolysis process [Saji et al. 2014]

In other words, hydrogen can be produced from a variety of fossil and renewable sources, such as NG and coal, biomass and water together with renewable energy sources and each technology brings benefits and complications [Wood et al. 2013]. Figure 3 shows an overview of available hydrogen production technologies.

**Figure 3** Possible ways of hydrogen production [Riis et al. 2006]
2.3. HYDROGEN APPLICATION

The hydrogen application field is very wide; it’s used as a raw material for the manufacture of many chemicals: ammonia, methanol, polymers. Hydrogen used as a reducing agent in the chemical industry, metallurgy, and microelectronics, as a hydrogenating agent to enhance saturation level of unsaturated oils and fats or use as gas for welding [Ramachandran et al. 1998]. Around 55 % of the hydrogen produced around the world is used for ammonia synthesis, 25 % in refineries, 10 % for methanol production [Fraile et al. 2015].

However, the problem of hydrogen storage is still open. One of the solutions is to produce hydrogen via electrolysis of water and to use that hydrogen as a fuel for the FC to produce electricity during times of low power production or peak demand. Figure 4 shows the block diagram of the hydrogen economy development.

![Figure 4: Ways of hydrogen and energy producing from renewables with subsequent use](Brandon et al. 2017)

2.4. HYDROGEN STORAGE

The main obstacle of the future hydrogen economy development is the lack of a safe and economically efficient way of hydrogen storage. Increasing the hydrogen storage pressure and applying storage temperatures that sharply differ from the ambient temperatures significantly increases the energy consumption for the gas storage. Nowadays, compression and liquefaction are the most common ways of hydrogen storage. None of these storage techniques is efficient enough and free of hazards:
- Storage of gaseous compressed hydrogen (CH) in cylinders and containers with pressure up to 70 MPa requires up to 20 % of the total stored hydrogen energy [Dagdougui et al. 2018]. CH storage requires following the pressure vessels safety regulations.

- The production and storage of liquid hydrogen (LH) at temperatures around 20 K gives a possibility to use just 1/700 volume of the hydrogen normal gaseous state. LH used as fuel for rockets and spacecraft, for which the low molecular weight and high specific energy content of hydrogen are very important. However, hydrogen liquefaction process at such low temperatures requires up to 40 % of the hydrogen stored energy [Riis et al. 2006]. In addition, direct contact with cryogenic liquids and gases can cause serious danger.

Furthermore, hydrogen can easily diffuse through different storage and transport materials, which can lead to gas leakages. Both of the above methods of hydrogen storage require significant costs for the installation of expensive equipment and the subsequent maintenance.

- Storage in solid state with the formation of chemical compounds (metal hydrides) with the possible reversible hydrogen sorption.

MH is one of the safe and economical reasonable ways of hydrogen storage in the solid compact form.

Figure 5 Hydrogen storage methods and schematic molecular structure of different hydrogen storage ways [U.S. DOE 2017, Sandrock 1999, Chesalkin et al. 2016]

Figure 5 shows the main hydrogen storage methods and their molecular structure. In comparison with classical gaseous and liquid hydrogen storage methods, the way of solid MH storage shows the potential advantages for future practical application. Metal hydrides and complex hydrides offer a very safe and efficient way to store hydrogen at lower storage pressure and physical volume, with high gas purity. La-based and Ti-based alloys are examples of low-
temperature materials for hydrogen storage. Figure 6 presents a comparative diagram of the hydrogen storage density in various materials.

![Figure 6](image)

**Figure 6** Hydrogen density of different storage materials and methods [Krishna et al. 2016]

2.4.1. HYDROGEN STORAGE IN METAL HYDRIDES

Hydrogen can be stored in solids by physical and chemical sorption. Due to the weak interaction between hydrogen molecules and the adsorbent during physical sorption, relatively high storage capacities are possible only at LT around 70-80 K. The advantages of the physical sorption mechanism are fast kinetics and full reversibility of hydrogen sorption-desorption processes with relatively small enthalpies of formation. Hydrogen storage capacities can reach up to 7 Wt.% at 70-80 K [Panella et al. 2010]. Palladium hydride was the first discovered MH which absorbed a large amount of hydrogen [Wisniak 2013].

The chemical reaction of hydrogen with the metals leads to the formation of qualitatively new chemical compounds – hydrides, with the new type of lattice. The study of reversible hydrogen sorption is of interest in a number of fields. Hydrogen accumulators were investigated for the maximum storage capacity [Zacharia et al. 2007]. Also, hydrogenation is studied in the nuclear power industry and other industries, where hydrogenation of various materials occurs: zirconium alloys, various steel grades, titanium alloys [McRae et al. 2010, Dong et al. 2009, Madina et al. 2009]. Lanthanum (La) and its compounds are widely used as components for the
hydrogen-containing compound detection [Fang et al. 2016]. As mentioned above, one of the best metals for hydrogen storage is palladium (Pd) and its alloys. These alloys have found their application as catalysts in many chemical processes, but their price prevents it from being used in hydrogen storage [Pikna et al. 2014, Zaluski et al. 1995, Sakintura et al. 2007].

Binary MHs can be separated into three groups regarding the metal-hydrogen interaction. The first group includes the MHs of alkali metals and alkaline-earth metals. In these hydrides, hydrogen exists as a negatively charged ion \( \text{H}^- \) [Libowitz 1965]. Typical binary ionic hydride NaH has a NaCl structure, and the alkaline-earth hydride such as a CaH\(_2\) has a BaCl\(_2\) structure. However, these types of MH are too stable for hydrogen storage application. The MgH\(_2\) is the intermediate hydride with partly ionic and partly covalent interaction between hydrogen and magnesium (Mg).

The second group of MHs is a covalent MHs, where hydrogen connected with non-metals via electron pairs sharing. Most of these MHs are gases or liquids: hydrocarbons, water, Al(BH\(_4\))\(_3\), SiH\(_4\), but most of them are difficult to synthesize [Ivey et al. 1983].

The third group is naturally metallic MHs and formed by connection of the transition rare earth or actinide metals with «metallic» hydrogen via metallic bond formation [Maeland 1977].

The MHs such as a TiH\(_2\), could be formed by direct reaction of hydrogen with the metal or by electrochemical reaction [Schlapbach et al. 2001]:

- direct interaction of hydride-forming metals (Me) with gaseous hydrogen (H\(_2\))

\[
\text{Me} + x\text{H}_2 \leftrightarrow \text{MeH}_x + Q \quad (6)
\]

- electrochemical reaction

\[
\text{Me} + x\text{H}_2\text{O} + e^- \leftrightarrow \text{MeH}_x + x\text{OH}^- \quad (7)
\]

A visual representation of the MH formation process is shown in Figure 7.

![Figure 7 The metal hydride formation process [Schlapbach et al. 2001]]
There are a number of compounds which provide hydrogen storage in a solid form: interstitial metal hydrides (AB₂, AB₃), complex hydrides (alanates, borohydrides), chemical hydrides (amides, aminoborates) or absorbents (nanocarbon, metal-organic frameworks (MOFs)). However, these compounds are able to satisfy only partially the different practical and economical requirements for the hydrogen storage systems.

One of the main disadvantages of the LT MH is the low gravimetric hydrogen capacity of 1-2 Wt.% at pressures around 1 MPa, however, the working absorption and desorption temperatures cover the technologically desired range of working temperature below 100 °C. Other groups of compounds can reach much higher hydrogen capacity up to 6 Wt.%, but the working temperatures are too low or high for wide application [Yartys et al. 2019].

The electropositive elements are the most reactive, i.e. scandium (Sc), yttrium (Yt), lanthanides, actinides, and members of the titan (Ti) and vanadium (V) groups. The microporous adsorbents and interstitial hydrides could have a similar hydrogen storage capacity, but the latter can operate at ambient temperatures [Zhang et al. 2015, Sandrock 1999]. Table 2 below shows the characteristics of different type of hydrides.

Table 2 Basic types of hydrides storage and their properties [Broom 2011, Riis et al. 2006]

<table>
<thead>
<tr>
<th>Hydrogen storage types</th>
<th>Gravimetric H₂ capacity, [Wt. %]</th>
<th>Working temperature, [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed hydrogen (CH)</td>
<td>up to 70 MPa</td>
<td>100</td>
</tr>
<tr>
<td>Liquid hydrogen (LH)</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Microporous adsorbents</td>
<td>Zeolite based</td>
<td>≤7.5</td>
</tr>
<tr>
<td>Interstitial hydrides</td>
<td>LaNi₅</td>
<td>1.49</td>
</tr>
<tr>
<td>Complex hydrides</td>
<td>Mg₂NiH₄</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The hydrogen storage materials (HSM) must have the necessary properties for a particular application. For example, the working adsorption-desorption pressure is a primary criterion for industrial Toyota trucks. It requires pressure of less than 1 MPa (P^d < 1 MPa). At the same time, additional requirements impose limitations to the hydrogen storage dimensions (30×60×50 cm) and hydrogen minimal releasing rate of 0.25 – 0.375 kg h⁻¹ [NineSigma 2019].

One example of prospective candidates with sufficient theoretical gravimetric and volumetric hydrogen capacity is magnesium hydrides or complex hydrides [Crivello et al. 2016]. Magnesium constitutes one of most studied material for hydrogen storage due to its Earth abundance, low cost, and reversibility of the adsorption-desorption reactions, but unfavorable thermodynamics and slow kinetics for industrial implementation. A number of articles were
focused on specific aspects of Mg-based HSM including rare-earth Mg-Ni based alloys for electrochemical applications, interrelations between composition, structure, morphology, and properties of the Mg-based hydrides [Webb 2015, Liu et al. 2018].

In the last decades, complex hydrides have been deeply investigated as potential hydrogen storage materials with high gravimetric and volumetric hydrogen capacity. Complex hydrides consist of an anionic complex where hydrogen is covalently bonded to a metal or non-metal, i.e. (BH₄), (AlH₄), (NH₂), (AlH₆), (NiH₄), combined to one or more alkali, alkali-earth, transition metal, or rare-earth metal cations [Orimo et al. 2007, Paskevicius et al. 2017]. However, the released hydrogen of magnesium or complex hydrides often occurs at relatively high temperatures (higher than 200 °C) and often take place at low hydrogen desorption pressures (P_d < 1 bar) [Milanese et al. 2019]. None of these systems are currently offering the required performances in terms of hydrogen storage capacity and adsorption/desorption processes [Tozzini et al. 2012].

2.4.2. LA-NI BASED MH FORMATION

Most of the metal hydrides are formed as a result of direct reaction with gaseous hydrogen. The formation of AB₅ type MHs occurs in accordance with the reaction presented below:

\[
AB_n + xH_2 \leftrightarrow AB_nH_{2x}
\]  

(8)

where: element (A) - rare earth or an alkaline earth metal and form a stable hydride (La); element (B) - transition metal and forms only unstable hydrides (Ni); n – the amount of substance [Huot 2010].

The hydrogen atoms will bond with an (A) atom (La) but they will also be in contact with element (B) (Ni) atoms. The atomic contact between elements (A) and (B) that was responsible for the heat of formation of the binary compound is lost. The contact surface is approximately the same for A–H and B_n–H thus implying that the ternary hydride AB_nH_{2x} is energetically equivalent to a mechanical mixture of AH_x and B_nH_m. Finally, the semi-empirical relation for the heat of formation of a hydride can be written as [Ivey et al. 1983]:

\[
\Delta H(AB_nH_{2x}) = \Delta H(AH_x) + \Delta H(B_nH_x) - \Delta H(AB_n)
\]  

(9)

The reaction of hydrogen gas with a La-Ni metal alloy can be described in terms of a simplified potential energy curve of MH formation and shown in Figure 8.

LaNi₅ + 3H₂ ↔ LaNi₅H₆

(10)
The hydrogen atoms contribute electrons to the metal structure. At a small hydrogen-metal ratio (H/M < 0.1), hydrogen exothermically dissolved in the metal and form the solid-solution (α-phase). During hydrogen sorption, the metal lattice expands proportional to the hydrogen concentration. At higher hydrogen-metal concentrations (H/M > 0.1), the H-H interaction becomes stronger due to the alloy lattice expansion, and the MH (β-phase) grows [Fukai 1989].

Figure 8 Energy curve of MH formation [Lennard-Jones 1932]

When α-phase and β-phase coexist, there is a plateau at the PCT isotherm. The length of the plateau corresponds to the MH hydrogen storage capacity. The two-phase region ends at a critical temperature point (T_C), above which the transition from α to β phase is continuous [Dornheim 2011]. Figure 9 below gives a visualization of MH formation process. This graph is called the Van't Hoff plot, where (ΔH/R) is the slope and (ΔS/R) is the intercept of the linear fit. The Van 't Hoff plot can be used to quickly determine the enthalpy of a chemical reaction [Choon Woo Lim et al. 2012, Hino et al. 2010].

Figure 9 Schematic PCT-diagram and Van’t Hoff plot of MH formation [Dornheim 2011]
The equilibrium pressure, \( P_{eq} \), is related to the changes in enthalpy \( \Delta H \) and entropy \( \Delta S \), respectively, as a function of temperature and could be described by the Van’t Hoff equation [Zuttel 2003]:

\[
\ln P_{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}
\] (11)

For a reversible reaction, the equilibrium constant \( K_{eq} \) can be measured at a variety of temperatures. Data can be plotted on a graph with \( \ln K_{eq} \) on the axis of ordinates and \( (T^{-1}) \) on the axis of abscissae. The data should have a linear relationship, and the process could be described by the linear form of the Van’t Hoff equation [Dickerson et al. 1976].

\[
\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\] (12)

The hydrogen sorption process is a spontaneous process, which goes with free energy and enthalpy decreasing \( (\Delta G \downarrow, \Delta H \downarrow) \). Hydrogen from the gaseous disorderly state goes to more ordered solid state in the MH lattice and process goes with entropy increasing \( (\Delta S \uparrow) \). Relationship between changes in the thermodynamic parameters described above could be expressed in the Gibbs-Helmholtz equation:

\[
\Delta G = \Delta H - T\Delta S
\] (13)

\[
\Delta G = RT \ln K_{eq}
\] (14)

For an exothermic reaction of \( \text{LaNi}_5\text{H}_6 \) hydride formation, heat is released, making the enthalpy change negative \( \Delta H < 0 \). The Van’t Hoff plot of this exothermic reaction, shown in Figure 10 (a) has a positive slope: \( -\Delta H/R > 0 \).

During the endothermic hydrogen desorption reaction from \( \text{LaNi}_5\text{H}_6 \), heat is absorbed, making the enthalpy change positive \( \Delta H > 0 \). The Van’t Hoff plot of this endothermic reaction, shown in Figure 10 (b) has a negative slope: \( -\Delta H/R < 0 \).

**Figure 10** The Van’t Hoff plot of: a) exothermic reaction of hydrogen sorption; b) endothermic reaction of hydrogen desorption
La-Ni based alloys are one of the possibility of hydrogen storage in MH at temperatures close to ambient, due to the relatively small MH formation enthalpy. As shown in Figure 11, none of the presented hydrides can fulfill the requirements of the desired properties combination for the mobility sector application. In this regard, the next development of the thermodynamic properties of MHs is needed.

![Figure 11](image-url) Common hydrides with their hydrogen capacities and reaction enthalpies [Dornheim 2011, Bogdanovic et al. 2009, Mauron et al. 2008, Li et al. 2008]

2.4.3. MH HEAT TRANSFER DURING H\textsubscript{2} REVERSIBLE SORPTION

Heat energy, which released in the course of the exothermic hydrogen sorption reaction, inside the alloy layer transferred to the MH storage tank walls. Heat removal occurs directly from the tank walls by coolant circulation (cold water) in the integrated internal or additional external heat exchanger. The emerging temperature and concentration gradients provide additional temperature and mass flow in the alloy layer [Kasatkin 1971]. According to the principle of Le Chatelier, for the exothermic reaction, the equilibrium could be shift to a product side by pressure increasing or temperature decreasing. Rate of reaction in a basic case described as the component concentration changing during a time [Laidler 1997]:

\[
r = \frac{\Delta c}{\Delta t}
\]

For the chemical reaction: aA + bB = cC + dD, the rate of the reaction described by followed equation:

\[
r = K\{A\}^a\{B\}^b
\]

where: \(K\) - reaction rate coefficient; \(\{A\}, \{B\}\) - component concentration
For the reaction of reversible hydrogen sorption in LaNi\textsubscript{5} alloy, the rate of the hydrogen sorption and desorption reactions described by equations below respectively:

\[
\begin{align*}
  r_s &= K_s C(\text{LaNi}_5) C^3(H_2) \\
  r_d &= K_d C(\text{LaNi}_5H_6)
\end{align*}
\]  

(17) (18)

where: \(K_s\) and \(K_d\) - hydrogen sorption and desorption reaction coefficients respectively

Each coefficient \(K\) has a temperature dependence, which is given by the Arrhenius equation [Laidler 1997]:

\[
K = A e^{-E_a/RT}
\]

(19)

where: \(A\) - the pre-exponential factor; \(E_a\) - the activation energy for the reaction; \(R\) - the universal gas constant

At the beginning of the hydrogen sorption process, reaction go fast with intensive rise of the temperature, and after some time temperature and reaction rate approaching the maximum point \((r_{\text{max}}, t_{\text{max}})\). After that, the temperature still increases, because of the exothermic reaction character. It finally leads to a rapid decreasing of reaction speed in accordance with Le Chatelier principle. At the temperature value equal to equilibrium temperature \(T_e\) (\(T_{eq}\)), conversion degree \((x)\) of hydrogen will be also close to equilibrium point \((x_{H2eq})\) and speed of reaction tends to zero \((r \to 0)\). The bigger conversion rate of hydrogen \((x_{H2})\) can be reached at a lower temperature of the reaction. For reaching bigger sorption efficiency of the MHS, reversible hydrogen sorption process should be done at optimal temperature conditions (close to isothermal). The heat balance of the closed ideal system in general form can be represented by the equation:

\[
Q_{\text{inlet}} = Q_{\text{outlet}}
\]

(20)

where: \(Q_{\text{inlet}}\) – the amount of heat entering the system per time; \(Q_{\text{outlet}}\) - the amount of heat consumed per time

For the exothermic reaction of MH formation the amount of income heat could be described by the next equation:

\[
Q_{\text{inlet}} = Q_{\text{chr}} + Q_{\text{reagents}}
\]

(21)

where: \(Q_{\text{chr}}\) – the amount of heat released due to the chemical transformation of substance, per time; \(Q_{\text{reagents}}\) – the amount of heat introduced by the initial reagents entering the reactor, per time
The heat consumption can be represented by the equation:

\[ Q_{\text{outlet}} = Q_{\text{product}} + Q_{\text{accum}} + Q_{\text{exch}} + Q_{\text{reagents}} \]  

(22)

where: \( Q_{\text{product}} \) – the amount of heat carried away from the system by the products of the reaction, per time; \( Q_{\text{accum}} \) – the amount of heat accumulated in the system per time; \( Q_{\text{exch}} \) – the amount of heat consumed per time due to the heat exchange with the environment.

The heat balance equation can take a different form, depending on the type of the system and the thermal regime of the process. In the general case, the process parameters like temperature, concentration change in the volume of the system or in time. For this purpose, the differential equation of convective heat transfer is used, in which additional terms are introduced, taking into account the heat removal as a result of heat exchange and the reaction heat [Kasatkin 1971]:

\[ \rho \ C_p \frac{\partial T}{\partial t} = -\rho \ C_p \left( W_x \frac{\partial T}{\partial x} + W_y \frac{\partial T}{\partial y} + W_z \frac{\partial T}{\partial z} \right) + \lambda \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) - F_{sp} K \Delta T + r Q_r \]  

(23)

where: \( \rho \) - density of reaction mass; \( C_p \) - heat capacity of reaction mass; \( \lambda \) - thermal conductivity coefficient; \( F_{sp} \) – specific heat exchange surface; \( Q_r \) - energy or heat of the reaction; \( \rho \ C_p \frac{\partial T}{\partial t} \) - accumulated energy in the system; \( F_{sp} K \Delta T \) - heat removal by heat exchange (for exothermic – \( F_{sp} K \Delta T \), for endothermic + \( F_{sp} K \Delta T \)); \( r Q_r \) - heat energy provided by chemical reaction (for exothermic + \( r Q_r \), for endothermic – \( r Q_r \)).

In ideal perfect mixing case, heat transfer along the axes is not presented. The group of terms on the left-hand side of equation (23) expresses the rate of heat accumulation in the elementary volume for which a heat balance is compiled. This term corresponds to the value of accumulated heat:

\[ Q_{\text{accum}} = \rho \ C_p \frac{\partial T}{\partial t} \]  

(24)

\[ Q_{\text{exch}} = F_{sp} K \Delta T \]  

(25)

\[ Q_{\text{chr}} = r Q_r \quad \text{or} \quad Q_{\text{chr}} = r \Delta H \]  

(26)
3. ANALYSIS TECHNIQUES DESCRIPTION

3.1. X-RAY DIFFRACTION

X-ray diffraction is a rapid analytical technique primarily used for phase identification of crystalline material. XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the X-rays with the sample produces the interference and could be described by Bragg’s law [Bish et al. 1989]:

\[ n\lambda = 2d \sin\theta \]  

(27)

where: \( n \) - "order" of reflection; \( \lambda \) - wavelength of the incident X-rays; \( d \) - interplanar spacing of the crystal; \( \Theta \) – the angle of incidence.

Bragg’s law calculates the angle where constructive interference from X-rays scattered by parallel planes of atoms will produce a diffraction peak. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

The scattering of X-rays from atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal. Amorphous materials do not have a periodic array with long-range order, so they do not produce a diffraction pattern. The position and intensity of peaks in a diffraction pattern are determined by the crystal structure [Rouquerol et al. 2013].

By scanning the sample through a range of 2\( \theta \) angle, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns [Cullity 1978, Klug et al. 1974]. Figure 12 below shows the XRD analysis of the La-Ni based alloy sample.

![Figure 12 La-Ni based alloy sample during X-ray scanning](image-url)
3.2. **SCANNING ELECTRON MICROSCOPY**

SEM analysis has many applications across a multitude of industry sectors. It can produce extremely high magnification images at high resolution up to 2nm [Goldstein et al. 2003]. After contact with the object, some of the electrons are scattered, depending on the order number of the element and its environment in the crystal structure, some excite the atoms of the object's matter, thereby causing emission of the characteristic radiation. The analysis of the energy spectrum of the emitted X-ray radiation produced by the interaction of the electron beam and the object atoms is carried out in an electron microscope with the help of a detector [Goldstein et al. 2003]. Figure 13 shows the basic view of the alloy SEM analysis.

Using an electron beam in electron microscopes or X-rays in X-ray fluorescence analyzers, the atoms of the sample are excited and emit radiation specific for each chemical element. The energy spectrum of such radiation can provide information about the qualitative and quantitative composition of the sample [McMullan 1995].

![Figure 13 SEM alloy sample analysis](image)

3.3. **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]. PCT stands for measurements and defines the technical reaction kinetics and the performance of metal hydride cooling systems [Paya et al. 2009, Gambini 1994].

This equipment enables safe and fully automated and repeated measurements in both sorption and desorption regimes. This ensures that the hydrogen pressure during sorption will be always above $P^{eq}$ and during desorption always below $P^{eq}$. These pressure values will be reached immediately after the start of the hydrogen reversible sorption experiment
The PCT Pro covers a temperature range from \(-260\, ^\circ\text{C}\) to \(500\, ^\circ\text{C}\) with different optional sample holders and pressure range between high and low-pressure transducers from \(0.0001\) to \(20\) MPa. Figure 14 below shows installation used for PCT sample measurement. The study was carried out at temperature range of \(273-318\) K and hydrogen pressure \(0.1-3\) MPa. The purity of both hydrogen and helium calibration gases was 6N.

**Figure 14** PCTPro installation and sample holder for PCT measurement

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 [PCTPro manual].

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 [PCTPro manual].

Figure 15 represents a PCT diagram of the alloy hydrogen reversible sorption. According to Gibb’s Law, the reaction will proceed at constant pressure (the plateau pressure) if the temperature is maintained at a constant level [Hosono et al. 2012].

**Figure 15** The diagram of the alloy PCT measurement at different temperatures [Hosono et al. 2012].
4. LA-NI BASED ALLOYS PREPARATION

4.1. DESCRIPTION OF THE ALLOYS PREPARATION TECHNIQUES

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 16 and Figure 17 below show the relevant La-Ni and La-Ce phase diagrams.

**Figure 16** Phase diagram of binary system La-Ni [Okamoto et al. 2016]

**Figure 17** 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 3 (the more detail information about used reagents is presented in the annex). 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 3** 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></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>8-60</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 relevant chemical reactions of La-Ni based alloys preparation are described below:

**LaNi₅**
- Preparation from pure metals:
  \[ \text{La} + 5\text{Ni} \rightarrow \text{LaNi}_5 \]
- Preparation from metal chlorides:
  \[ \text{LaCl}_3 + 5\text{NiCl}_2 + 13\text{LiH} \rightarrow \text{LaNi}_5 + 13\text{LiCl} + 6.5\text{H}_2 \uparrow \]

**{(LaCe)}Ni₅**
- Preparation from pure metals:
La + Ce + 5Ni → (LaCe)Ni$_5$

Preparation from metal chlorides:
LaCl$_3$ + CeCl$_3$ + 5NiCl$_2$ + 16LiH → (LaCe)Ni$_5$ + 16LiCl + 8H$_2$

**LaCe(NiFe)$_5$**

Preparation from pure metals:
La + Ce + 5Fe + 5Ni → LaCe(NiFe)$_5$

Preparation from metal chlorides:
LaCl$_3$ + CeCl$_3$ + 5NiCl$_2$ + 5FeCl$_2$ + 26LiH → LaCe(NiFe)$_5$ + 26LiCl + 13H$_2$

The initial components were mixed in a glow-box to prevent the oxidation of the reagents and moisture saturation. The time-temperature parameters of the alloy synthesis and information about the used reagents are shown in Table 3 above. Lithium hydride was used as a reducing agent during sample synthesis via a thermochemical reaction. Figure 18 shows the alloys prepared with the present of LiH (left side) and without LiH (right side).

![Figure 18](image)

**Figure 18** 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.

XRD measurement conditions: diffractometer Rigaku SmartLab; goniometer geometry – Bragg-Brentano theta-2theta; lamp – CoKα ($\lambda_1 = 0.178892$ nm, $\lambda_2 = 0.179278$ 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.

The scanning electron microscope Quanta FEG 450 (FEI) with EDS microprobe analysis was used for 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.
4.2. 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$_2$(NiO$_4$)$_{1.44}$ in the sample “2”.

Sample “3.2” prepared without LiH, had a brown-orange colour and looked amorphous (see Figure 18 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 19 above.

![X-ray diffraction patterns](image)

**Figure 19** X-Ray diffraction patterns of the prepared alloy samples: (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. The additional analysis of the alloy structure was carried out with the aid of the scanning electron microscopy (SEM). Table 4 shows the results of the SEM sample analysis.

Table 4 Chemical composition of the prepared alloy samples

<table>
<thead>
<tr>
<th>Sample “3.1” LaNi₅ metal chloride</th>
<th>Sample “4” (LaCe)Ni₄ metal chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.% 19.2 Ni 57.2 O 16.2 Other 7.4</td>
<td>Wt.% 34.8 Ni 35.4 Ce 12.7 O 17.1</td>
</tr>
<tr>
<td>At.% 8.1 Ni 44.3 O 35.7 Other 11.9</td>
<td>At.% 11.1 Ni 32.5 Ce 8.8 O 47.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample “5” (LaCe)Ni₃ powder metal</th>
<th>Sample “6” LaCe(FeNi)₃ powder metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.% 27.23 Ni 69.19 Ce 4.22</td>
<td>Wt.% 31.48 Ni 53.04 Ce 5.81 Fe 9.67</td>
</tr>
<tr>
<td>At.% 14.00 Ni 83.92 Ce 2.16</td>
<td>At.% 16.86 Ni 67.19 Ce 3.08 Fe 12.87</td>
</tr>
</tbody>
</table>

The structure photos of prepared non-oxidized (LaCe)Ni and LaCe(FeNi) alloys are shown in Figure 20.

Figure 20 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
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 5-8 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 make dominant the La$_1$Fe$_1$Ni$_4$ phase (Table 6 and Table 8). Lower iron content (Fe approx 1 Wt.%) make dominant the La$_{0.5}$Ce$_{0.5}$Ni$_5$ phase (Table 7). The present of H$_3$La$_1$O$_3$ in alloys composition (Table 6-8) associated with incomplete hydrogen desorption from the alloy, and was not observed after complete desorption.

Table 5 (LaCe)Ni$_5$ sample XRD pattern (La$_1$Ni$_5$ 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>98-042-6960</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$<em>{0.94}$Ni$</em>{5.116}$</td>
</tr>
</tbody>
</table>

Table 5 (LaCe)Ni$_5$ sample XRD pattern (La$_1$Ni$_5$ phase)

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

![Graph showing XRD pattern and table data](chart.png)
**Table 6** LaCe(FeNi)$_5$ sample XRD pattern (La$_{1}$Fe$_{1}$Ni$_{4}$ phase)

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

<table>
<thead>
<tr>
<th>Ref.Code</th>
<th>Score</th>
<th>Compound Name</th>
<th>Displ.[$\theta$]</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$<em>{1}$ Fe$</em>{1}$ 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 7** 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.[$\theta$]</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>
Sample “5” and “6” prepared from the pure metals were observed by next PCT analysis. Figure 21 shows the PCT diagrams of the prepared (LaCe)Ni₅ alloy sample. The maximum hydrogen capacity of the prepared modified (LaCe)Ni₅ alloy reached 1.21 Wt.%.

**Figure 21** Hydrogen weight content in (LaCe)Ni₅ alloy at different temperatures

These results were approved by PCTPro measurement of the alloy sample and shown in Figure 22. The biggest hydrogen weight content was reached at lowest testing temperature 300 K
and pressure around 2.0 MPa (red line on the diagram). The structure photos of (LaCe)Ni$_5$ alloy after hydrogen desorption are attached in Figure 23 below.

**Figure 22** PCT diagram for hydrogen reversible sorption in (LaCe)Ni$_5$ alloy

**Figure 23** SEM images of (LaCe)Ni$_5$ alloy after hydrogen desorption: (a) at 200 x; (b) at 1 kx; (c) at 2 kx; (d) at 10 kx
4.3. **INFLUENCE OF THE STRUCTURE STATE**

The structure state of HSM can also influence the thermodynamic properties and value gravimetric capacity of metallic hydrides. The preliminary study of (LaCe)Ni$_5$ alloy modified with transitional element X showed the significant changes of reversible sorption pressure ($P^{A-D}$) and hydrogen gravimetric capacity. Two (LaCe)Ni$_5$-X and two LaCe(FeNi)-X samples were compared. (LaCe)Ni$_5$-X-cast and LaCe(FeNi)-X-cast were traditionally cast into Cu mold and (LaCe)Ni$_5$-X-FC and LaCe(FeNi)-X-FC were remelted and cast on water-cooled Cu-plate. FC materials were cast in a compact MAM-1 arc furnace [Edmund Buhler]. 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 9 below.

**Table 9** SEM/EDS chemical composition analysis results of the cast and fact cooled samples

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Elements, [Wt.%]</th>
<th>Ni</th>
<th>La</th>
<th>Ce</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCeNi$_5$</td>
<td></td>
<td>51.1</td>
<td>44.2</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>LaCeNi$_5$ FC</td>
<td></td>
<td>51.1</td>
<td>44.9</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>LaCeNiFe 1</td>
<td></td>
<td>54.2</td>
<td>42.2</td>
<td>2.9</td>
<td>0.7</td>
</tr>
<tr>
<td>LaCeNiFe FC1</td>
<td></td>
<td>48.9</td>
<td>40.8</td>
<td>4.1</td>
<td>6.2</td>
</tr>
<tr>
<td>LaCeNiFe 2</td>
<td></td>
<td>56.4</td>
<td>28.1</td>
<td>2.4</td>
<td>13.1</td>
</tr>
<tr>
<td>LaCeNiFe FC2</td>
<td></td>
<td>49.6</td>
<td>36.5</td>
<td>2.1</td>
<td>11.8</td>
</tr>
</tbody>
</table>

The following comparative PCT analysis of the samples with different structure state shows that the sample (LaCe)Ni$_5$-X-FC and LaCe(FeNi)-X-FC showed higher gravimetric capacity at lower sorption pressure in comparison with corresponding X-cast samples. The hydrogen reversible sorption curves for both (LaCe)Ni$_5$ and LaCe(FeNi) structured samples are shown in Figure 24. 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 from 1Mpa to 0.3-0.5MPa.
Figure 24 Hydrogen reversible sorption: (a) in the (LaCe)Ni$_5$-X-cast and LaCeFeNi-X-cast alloys; (b) in the (LaCe)Ni$_5$-X-FC and LaCeFeNi-X-FC alloys.

In summary, the preparation of materials with various structure states could be a completely novel way for influence of thermodynamic properties of HSM. 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 LT. The knowledge about the influence of the structure state on hydrogen storage properties can show new ways for LT MHs development.
5. **MH INTEGRATION IN HYDROGEN HYBRID SYSTEMS**

MHs belong among functional materials characteristic of compact and safe hydrogen storage. The use of such storage systems in conjunction with FC makes hydrogen available as an alternative energy carrier. Private houses and industrial facilities, which are independent of any external energy sources always attracted people. The main task is an integration of all presented technologies into a single system. Hydrogen technologies currently find their use in mobile and stationary applications, combined with unstable renewable sources, such as solar and wind power plants and eliminate fluctuations of their power output. Such kinds of hybrid power systems were examined and tested by the authors in different studies [Ursua et al. 2013, Barbir 2005, Yilanci et al. 2009].

Joint use of the FC technologies with hydrogen storage systems based on MHs allows to use more effectively both of the HHS components and utilize FC excess heat energy for hydrogen desorption from the LT MH.

During the oxidation-reduction reaction in the FC chemical energy transformed into electrical energy. FC allows the direct conversion of the fuel chemical energy into the electrical energy without additional heat or mechanical work or transformations. The function of the FC can be thought of as the inverse process of electrolysis [Chesalkin et al. 2016]:

Anode (−): \[ 2H_2 - 4e^- \rightarrow 4H^+ \] (22)

Cathode (+): \[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \] (23)

Total current-forming reaction: \[ 2H_2 + O_2 = 2H_2O \] (24)

Electrons flowing spontaneously from the electrically negative pole to the positive pole of power. The electrolyte is the basis for the distribution of the FC for individual species. The principle of FC is illustrated in Figure 25.

![Figure 25 Principle functioning of the FC](image)

**Figure 25** Principle functioning of the FC [Chesalkin et al. 2016]
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].

The PEM membrane is formed by the thick perfluorinated polymer of sulphonic acid film covered with a layer of platinum (Pt) catalyzer. This membrane is a solid electrolyte that increases operational safety and the FC life-time. Cathodes and anodes are porous and allow to transmit hydrogen and oxidant. The flow field graphite plates provide minimum contact of gas with the membrane assembly. The end plates with electrodes are made from steel. Figure 26 below shows the construction of the hydrogen PEMFC.

![Figure 26 PEMFC construction](Open Modelica)

where: PEM (Proton Exchange Membrane) – the membrane is only permeable to H\(^+\) protons;  
FP (Flow Plates) - Fluid enters and exits the FC through channels in these plates;  
GDL (Gas Diffusion Layers) - Fluid spreads through these layers;  
CL (Catalyst Layers) - Fluid reacts in these layers.

PEMFCs are often combined in series (FC stack) to generate high voltages and power from the combined cells [Hwang et al. 2008, Metha et al. 2003]. Table 10 shows the main working characteristic of the LT and HT PEMFC.

<table>
<thead>
<tr>
<th>FC type</th>
<th>Fuel</th>
<th>Oxidant</th>
<th>Anode Reaction</th>
<th>Cathode reaction</th>
<th>Working temp., [°C]</th>
<th>Unit power range, [kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTPEM</td>
<td>H(_2)</td>
<td>Air</td>
<td>H(_2)→2H(^+) + 2e(^-)</td>
<td>(\frac{1}{2} O_2 + 2H^+ + 2e^-)→H(_2)O</td>
<td>60-80</td>
<td>0.05-100</td>
</tr>
<tr>
<td>HTPEM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>150-180</td>
<td>≤ 200</td>
</tr>
</tbody>
</table>
Both LT and HT PEMFC technologies can achieve up to 50% electrical efficiency. HT PEMFC provides better kinetics and easier heat regulation in comparison with LT PEMFC due to the higher working temperatures up to 180 °C. Variation of MHs composition and properties provides flexibility in working temperature and pressure for exact application [Dantzer 1997, Sandrock 1999, Sandrock et al. 2003].

As mentioned before, the La-Ni based alloys allow storing hydrogen at ambient temperatures and low pressures 1.0-1.5 MPa, which makes the application of these alloys quite attractive. 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.

![Diagram](image.png)

**Figure 27** Hydrogen-drive vehicle system diagram [NineSigma 2019]

Figure 27 above describes the concept of using hydrogen storage systems for Toyota industrial trucks. Such kind of storage system should be able to release up to 70 Nl min⁻¹ of hydrogen with a relatively low amount of heat during hydrogen sorption-desorption processes at working pressure up to 1.0 MPa.

Another example of joint MHs and FC integration to one HHS described below. 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 28 below, basically consists of the solar panels, power inverters, accumulator batteries, hydrogen production, and storage units. Hydrogen produced via a number of 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 units with a total input power of 17 kW and 4 m$^3$ h$^{-1}$ total hydrogen production. 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 regeneration of electrical power and heat. The working parameters of the FC and MH storage system are shown in Table 11.

![Figure 28 Block diagram and basic view of the HHS with integrated FC and MH hydrogen storage modules](image)

**Table 11** The main working parameters of fuel cells and hydrogen storage system

<table>
<thead>
<tr>
<th>Nexa FC</th>
<th>MH storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic</td>
<td>Value</td>
</tr>
<tr>
<td>Temperature</td>
<td>&lt; 65 °C</td>
</tr>
<tr>
<td>Rated power</td>
<td>1200 W</td>
</tr>
<tr>
<td>Maximum current</td>
<td>230 A</td>
</tr>
<tr>
<td>Operating voltage</td>
<td>22–50 V</td>
</tr>
<tr>
<td>Max H$_2$ consumption</td>
<td>20 Nl min$^{-1}$</td>
</tr>
</tbody>
</table>
5.1. **MH THERMOGRAPHY DURING H2 REVERSIBLE SORPTION VIA FC**

The surface temperature of any FC under load, also like the surface of the MH storage tank during charging-discharging processes can be determined by infrared (IR) thermography [Yamada et al. 2004]. IR thermography has been used for studying properties in different industrial and research fields: in medical research, metal production, building diagnostics, and for PEMFC parameters characterization [Shada et al. 2013, An et al. 2012, Cerdeira et al. 2011, Das et al. 2014].

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 29 shows the block-diagram of MH storage testing.

![Figure 29](image)

**Figure 29** La-Ni based MH storage system testing scheme

Hydrogen produced from the PEM electrolyzer with a purity of 99.99 % under 3 MPa pressure before entering the MH storage system passes through the pressure reducer where the pressure decreases to 1-1.5 MPa. This pressure required for the hydrogen sorption in La-Ni based MH. For the MH temperature stabilization during charging-discharging cycle’s external water cooling-heating system was used. The temperature of the storage system tank was measured by two thermostsensors, 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 30 shows the rising of MH tank surface temperature during hydrogen sorption reaction. Figure 30 (a) shows the MH storage tank temperature before hydrogen sorption process, and Figure 30 (b) represents the thermogram of the storage tank surface during charging.
Figure 30 Thermography of La-Ni based storage tank surface: (a) before charging, (b) during charging

Figure 30 could be compared with the corresponding temperature curves and charging parameters shown in Figure 31.

Figure 31 Temperature and charging parameters of storage system cooling by: (a) tap water, (b) chilled water

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 more 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 (∆ 6 °C) provides the significant change of hydrogen sorption speed and fully filling of the storage tank by hydrogen. As shown in Figure 31 the difference in hydrogen capacity between two chargings was around 233 Nl.

The same Nexa LT FC have 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 32 represent thermography of the MH storage tank discharging. Due to the endothermic reaction of hydrogen desorption, MH storage tank had been heated up to 35 °C. Discharging parameters of the storage system shown in Figure 33.

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

**Figure 32** MH storage surface thermography: (a) before discharging, (b) during discharging

![MH storage discharging parameters](image)

**Figure 33** MH storage discharging parameters

This part of thesis work has addressed the optional employment of thermal diagnostics in the practical operation of La-Ni based MH and LT FC and their integration into a more complex HHS. 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 and complicated process that requires careful study and control in practice. The maximal hydrogen capacity (923
Ni) that was reached in this experimental work during discharging cycle could provide energy amount of 2.765 kWh which was used by FC for direct transformation hydrogen to the 1 kWh of DC (direct current) electrical energy. Measurements and analyses helped identify the problematic spots, characteristics with an increased heating of the FC stack.

The enthalpy of the La-Ni based MHs formation is in the range of $\Delta H = - (28-34) \text{ kJ mol}^{-1}$. The calculation of the heat release during hydrogen sorption in $(\text{LaCe})\text{Ni}_3\text{H}_6$ metal hydride presented in annex. Due to the almost similar molar mass of La (138.91 g mol$^{-1}$), Ce (140.12 g mol$^{-1}$) elements, the calculation could be applicable also for different alloys composition in the variation of 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: $\Delta H(\text{LaCe})\text{Ni}_3\text{H}_6 = -30.8 \text{ kJ mol}^{-1}$; $(\text{LaCe})\text{Ni}_3\text{H}_6$ metal hydride hydrogen weight content (storage density) 1.386 Wt.%

Figure 34 below shows the results of calculation of the MH hydrogen storage capacity and corresponding heat release during hydrogen sorption in $(\text{LaCe})\text{Ni}_3\text{H}_6$ metal hydride depending on the total alloy weight.

![Figure 34](image)

**Figure 34** Diagram of $(\text{LaCe})\text{Ni}_3\text{H}_6$: (a) energy released during MH formation; (b) MH hydrogen storage density

5.2. **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. Thermography of the MH storage system during reversible sorption allows controlling temperature more accurate during charging-discharging processes and use MH storage system in a more efficient way. The FC overheating bring the risk of electrolyte drying (the PEM polymer membrane), with next membrane degradation. The FC stack thermography and computer simulation allowed to determine the regions of the stack local overheating 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, the crossover of reaction. The typical losses proportion gives the picture of the polarization curve, shown in Figure 35.

![Figure 35 FC polarization curve with voltage losses at working condition [Sammes 2006]](image)

Hydrogen could be produced directly from renewables via water electrolysis process and used as a fuel for FC. At the same time, hydrogen could be stored in LT MH which can serve the HHS as a backup storage buffer. 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 at 65 °C and 160 °C respectively. Table 12 and Table 13 below show working characteristic of tested HT and LT FC 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, and also methanol could be used in existing distribution systems. 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 36 below shows La-Ni based LT MH integration for the flexible hydrogen production, storage, and utilization via PEMFC.

**Figure 36** LTMH integration for the flexible hydrogen storage and utilization via PEMFC

**Table 12** 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 ºC</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 13** Working parameters of HT FC

<table>
<thead>
<tr>
<th>Type</th>
<th>HT FC 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 ºC</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>
5.2.1. **LT PEMFC THERMOGRAPHY**

The cooling fan draws air from the ambient surroundings in order to cool the LT FC module and regulate the operating temperature. For the LT FC thermography during metal hydride discharging measurements was taken during four different loads of the Nexa LT FC module: 100 W, 300 W, 500 W, 1000 W set on the linked electronic DC load. 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 this stack heats up significantly more, as it is closer to the entry of the cooling air supply channel. Figure 37 (a) shows a surface temperature for the FC module measured at the load of 500 W and Figure 37 (b) at the load 1000 W.

The heating curves based on the measurement results report that the system cooling will not be activated when the FC module is connected to a load of 100 W. The core temperature of the stack of 60 °C was reached with such load 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 when connected to higher loads (300 W, 500 W, and 1000 W). Those results in the lower operating temperature reached in this module. When linked to the top loads (above 1000 W), it’s highest operating inside temperature will reach 65 °C. Based on the obtained data, it can be argued that there is no dependence between hydrogen consumption and FC temperature increasing and temperature depends only on the applied load.

![Thermographic picture showing the surface of the stack of hydrogen fuel cells](image)

**Figure 37** Thermographic picture showing the surface of the stack of hydrogen fuel cells: (a) on the load of 500 W, (b) after 2 hours of operation with the constant load of 1000 W

Figure 38 and Figure 39 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.
5.2.2. 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 the heat dissipation. The controlled
radial fan ensures the air supply to the cooling channels via the plastic distributing channel, situated below the whole 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 40 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 ºC, while the temperature of the upper part was about 55-75 ºC. That is associated with heat transfer from fins into the cooling air which causes a rise in temperature of the upper fins.

Figure 40 CFD simulation of temperature distribution across the LT FC stack

The velocity of the cooling air flow inside the distribution channel across the longitudinal cross-section of the stack is shown in Figure 41. This air enters the distribution cooling channel from the right side at the velocity of 10 m/s 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 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 MH discharging process.
The first results of the simulation show that the heat could be distributed from the 0.036 m² 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.

5.2.3. HT PEMFC THERMOGRAPHY

Corresponding loads were used for the HT FC temperature measurements. Thermography of the FC surface was carried out using FLIR E 40 thermal IR camera and shown in Figure 42 below. Temperature measurement was also carried out by 2 thermosensors thermocouple (k-type) at coolant inlet and outlet of the stack.

Figure 41 CFD simulation of cooling air flow inside the LT FC stack

Figure 42 HTFC thermography at different load: (a) 500 W, (b) 1000 W

Figure 43 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 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 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 1-1.2 kW load.

![Temperature profiles of the HT FC stack coolant at different load](image)

**Figure 43** Temperature profiles of the HT FC stack coolant at different load

### 5.2.4. **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 a 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 (see the detail calculation in annex). 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 (LaCe)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 losses between FC stack and MH storage tank).
6. CONCLUSION

In the frames of that 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 H\textsubscript{2} storage in metal hydrides. Theoretical study all of the above aspects gave needed information for experimental study of LaNi\textsubscript{5} based alloys, like one of the more applicable type of the materials for daily hydrogen storage.

Steps were taken to investigate the possibility of modifying La-Ni based alloys for hydrogen storage and their next integration with FC technologies. 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 thermodynamic properties and value of gravimetric capacity of the hydrides. The fast cooled sample of the (LaCe)Ni\textsubscript{5} alloy showed higher gravimetric capacity (up to 1.55 Wt.\%) at lower sorption pressure in comparison with (LaCe)Ni\textsubscript{5} cast sample.

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 in order to investigate the possibilities of more effective use of LiH or using a different reduction agent for the alloy thermochemical synthesis. 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 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 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.
7. **FUTURE AIMS AND STEPS**

The main idea of the future work is to study the hydrogen storage properties of model 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 experimental storage materials containing transitional elements will be produced by various methods to reach chosen states of the structure. The alloys will be prepared by casting of a batch of pure materials. 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 also under hydrogen atmosphere. Rational modes of activation will be selected on the basis of studying the homogeneity of the chemical and phase composition of the resulting powder.

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.

As the last step will be the study of some very prospective experimental alloys in the consolidation form. The consolidation of the obtained powders will be carried out by methods of thermal appropriate deformation processing, in particular, such technologies as pressure sintering and extrusion at elevated temperature will be used for consolidation. Conducting a series of experiments will allow determining the rational technological conditions of the processes of thermal deformation (temperature, exposure time under pressure, etc.).

The identification of phases will be done 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 in the whole. Hydrogen kinetics and thermodynamics will be studied with the help of the SETARAM PCT-Evo and PCT-PRO devices. The PCT isotherms for both regimes will be measured for the experimental materials, which will enable to evaluate the hydrogen storage capacity, entropy, and enthalpy of storage and cycling stability.
REFERENCE LIST


Kasatkin A G (1971) Basic Processes and Apparatus in Chemical Technology (Основные процессы и аппараты химической технологии), Chemistry, Moscow


PUBLISHING ACTIVITY AND PROJECT PARTICIPATION

PUBLICATIONS AND CONFERENCES:


PROJECT PARTICIPATION:

LO1404 «Sustainable development of ENET Centre»

CZ02.2.69/0.0/0.0/16_027/0008463 «SCIENCE WITHOUT BORDERS»
Preparation and development of La-Ni based alloys for hydrogen storage, hydrogen-based power supply, fuel cells, hydrogen production, and storage systems development, hydrogen mobility with special focus on hydrogen technologies for CO and CO\textsubscript{2} utilization with next biofuel production.

CZ.01.1.02/0.0/0.0/15_019/0004771 «TORIFIKACE»

TK02010187 «Research of the potential use of hydrogen technologies for transformation of energy mix of Moravian-Silesian region, low-carbon energy, development of low-emission transport»
ANNEX

Calculation of the cooling water amount needed for the complete hydrogen sorption in the (LaCe)Ni₅ alloy (calculation of mass–energy transfer for the (La₀.₅Ce₀.₅)Ni₅H₆ formation)

\((LaCe)Ni₅ + 3H₂ → (LaCe)Ni₅H₆ + Q\)

Data for the calculation:

\(\Delta H(LaCe)Ni₅H₆ = -30.8 \text{ kJ mol}^{-1}\)

\(m(\text{LaCe})Ni₅H₆ = 9 \text{ kg}\)

where \(m\) – is a metal hydride mass

Alloy composition is: La₀.₅Ce₀.₅Ni₅

\(M(\text{La₀.₅Ce₀.₅})Ni₅ = 138.91 \times 0.50 + 140.12 \times 0.50 + 58.70 \times 5.00 = 433.01 \text{ g mol}^{-1}\)

\(M(\text{La₀.₅Ce₀.₅})Ni₅H₆ = 433.01 + 6.00 = 439.01 \text{ g mol}^{-1}\)

Calculation:

\[n(La₀.₅Ce₀.₅Ni₅) = \frac{m}{M}\]

where \(n\) – is a number of the metal hydride moles

\[n(La₀.₅Ce₀.₅Ni₅) = \frac{9000}{433.01} \text{ g mol}^{-1} = 20.78 \text{ mol}\]

\[n(H₂) = 20.78 \times 3.00 = 62.34 \text{ mol}\]

or \(m(H₂) = 62.34 \times 2 = 125 \text{ g} = 0.125 \text{ kg}\)

\[V(H₂) = \frac{0.125}{0.089} \frac{\text{kg}}{\text{kg m}^3} = 1.382 \text{ m}^3 \text{ (ideal case of full hydrogen sorption)}\]

Base of energy balance for ideal full hydrogen sorption in (LaCe)Ni₅ alloy

\[\Sigma Q_{\text{inlet}} = \Sigma Q_{\text{outlet}}\]

\[\Sigma Q_{\text{inlet}} = Q_{\text{form }}(LaCe)Ni₅H₆ = \Delta H(LaCe)Ni₅H₆ \cdot n(H₂)\]

\[\Sigma Q_{\text{inlet}} = -30800 \frac{J}{\text{mol}} \cdot 62.34 \text{ mol} = 1920.01 \text{ kJ}\]

\[\Sigma Q_{\text{outlet}} = Q_{\text{cooling water}} + Q_{\text{looses}}\]

Heat exchange losses with the exterior taken close to zero \((Q_{\text{losses}} \to 0)\), (ideal condition)

\[\Sigma Q_{\text{outlet}} = Q_{\text{cooling water}}\]

Coolant flow calculation:

\[Q_{\text{cooling water}} = Gw \cdot C_w \cdot \Delta T\]
where: \( G_w \) and \( C_w \) - mass flow rate and specific heat capacity of cooling water \((C_w = 4.187 \text{ kJ (kg K)}^{-1})\); \( \Delta T \) – cooling water temperature difference between \( T_{1\text{inlet}} \) and \( T_{2\text{outlet}} \).

Ideally, the cooling water should completely remove the heat of the exothermic hydride formation reaction:

\[
Q_{\text{cooling water}} = \sum Q_{\text{inlet}} = Q_{\text{form}} \ (\text{LaCe})N_i_5H_6 = 1920.01 \text{ kJ}
\]

\[
G_w = \frac{Q_{\text{form}} (\text{LaCe})N_i_5H_6}{C_w \Delta T}
\]

\[
G_w = \frac{1920.01 \text{ kJ kg K}}{4.2 \text{ kJ h} 4 \text{K}} = 114.29 \text{ kg h}^{-1}
\]

\( G_w = 1.9 \text{ l min}^{-1} \)

**Calculation of released heat during 1 kg of \((\text{La}_{0.5}\text{Ce}_{0.5})\text{Ni}_5\) alloy hydrogen sorption**

From previous calculation the ideal weight storage capacity for the \((\text{La}_{0.5}\text{Ce}_{0.5})\text{Ni}_5\) alloy is 1.386 Wt.% or 13.86 g H\(_2\) / 1000g of alloy or 156 l H\(_2\) / kg of alloy

The heat amount released during hydride formation reaction can be calculated as follow:

\[
Q_{\text{sorption}} = \Delta H (\text{LaCe})N_i_5H_6 \times nH_2
\]

\[\Delta H (\text{LaCe})N_i_5H_6 = -30.8 \text{ kJ per H}_2 \text{ mol.}\]

\[
n(H_2) = \frac{m}{M} = \frac{13.86 \text{ g}}{2 \text{ g mol}^{-1}} = 6.93 \text{ mol.}
\]

\[Q_{\text{sorption}} = -30.8 \text{ kJ mol}^{-1} \times 6.93 \text{ mol} = 213.44 \text{ kJ per 1 kg of alloy}\]

Diagram of \((\text{LaCe})N_i_5H_6\) energy released during MH formation
## Material parameters and load values for CFD simulation

<table>
<thead>
<tr>
<th>FC construction parts</th>
<th>Plates</th>
<th>Fins</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat conductivity, [W (m K)^{-1}]</td>
<td>318</td>
<td>140</td>
<td>0.25</td>
</tr>
<tr>
<td>Density, [kg m^{-3}]</td>
<td>19300</td>
<td>2300</td>
<td>2100</td>
</tr>
<tr>
<td>Specific heat capacity [kJ (kg·K)^{-1}]</td>
<td>0.129</td>
<td>0.837</td>
<td>1.1</td>
</tr>
<tr>
<td>Power losses [kW]</td>
<td>-</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Unit loses [kW m^{-3}]</td>
<td>-</td>
<td>733</td>
<td>2730</td>
</tr>
<tr>
<td>Volume of the component [dm^3]</td>
<td>-</td>
<td>1.087</td>
<td>0.433</td>
</tr>
</tbody>
</table>

## Reagents properties

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Molar mass, [g/mol]</th>
<th>Form/condition, Particle size [μm]</th>
<th>Density, [g cm^{-3}]</th>
<th>Melting / boiling temperature, [°C]</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCl₃</td>
<td>245.26</td>
<td></td>
<td>3.84</td>
<td>858 / 1000</td>
<td>h</td>
</tr>
<tr>
<td>CeCl₃</td>
<td>246.48</td>
<td></td>
<td>3.97</td>
<td>817 / 1727</td>
<td>UCl₃ type</td>
</tr>
<tr>
<td>Ni</td>
<td>58.70</td>
<td>Powder, anhydrous 8-60</td>
<td>8.9</td>
<td>1455 / 2730</td>
<td>fcc</td>
</tr>
<tr>
<td>La</td>
<td>138.91</td>
<td></td>
<td>6.19</td>
<td>920 / 3464</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>140.12</td>
<td>Powder, anhydrous 8-60</td>
<td>8.24</td>
<td>795 / 3443</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>55.845</td>
<td></td>
<td>7.85</td>
<td>1538 / 2861</td>
<td></td>
</tr>
<tr>
<td>LiH</td>
<td>7.95</td>
<td></td>
<td>0.82</td>
<td>688.7 / 900</td>
<td>fcc</td>
</tr>
</tbody>
</table>

- bcc – body-centered cubic
- fcc – face-centered cubic
- h - hexagonal
- dhcp – double hexagonal close-packed

Room t. – dhcp
≥ 310 °C – fcc
≥ 865 °C – bcc

≥ 726 °C – bcc
≤ 726 °C – fcc
≤ 1538 °C – bcc
≤ 1394 °C – fcc

NaCl type