UNIVERSITY OF LATVIA

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RESEARCH OF NEW COMPOSITE MATERIALS FOR HYDROGEN STORAGE

Summary of the Doctoral thesis

Department of Physics
Subsection of Material Science

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The work was performed in the Institute of Solid State Physics of University of Latvia, in cooperation with RISØ National Laboratory.

Implementation time years 2003 - 2006.

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/Līga Grīnberga/

Actuality of work

The amount of fossil fuel resources is decreasing rapidly due to the combined increase of population and energy consumption. Hydrogen used as an energy carrier offers a promising replacement; many countries around the world consider the development of a hydrogen economy as very important. It is the most abundant element on the Earth; moreover, the chemical energy per weight of hydrogen is at least three times larger than that of other chemical fuels – 39,4 kWh/kg to 13,1kWh/kg, respectively. The water vapour is the only exhaust gas in the hydrogen burning process if hydrogen is burned in low temperature fuel cells. Furthermore, if the hydrogen is produced using alternative sources as solar, wind, water and other renewable resources then the process is environmentally friendly and the system overall isn't dependent from fossil fuels. Hydrogen as fuel can be used in the same place where the fossil fuels are used – internal combustion and jet engines, stokeholds, turbines, etc. Hydrogen can be converted directly into electrical energy via fuel cells and this system can be exploited whenever electricity is used [1].

Research in every step of production, storage and usage in the hydrogen cycle is necessary, as we need to decrease the cost of using a hydrogen fuel to a competitive cost to that of fossils fuel [2]. A safe and non-expensive way of hydrogen storage is very important as it is a medium part in the hydrogen economics.

Hydrogen can be stored as a gas in a high pressure tanks, although for practical usage the pressure more than 500 bar is needed. The hydrogen can be liquefied at temperatures down to 4,2K, however it is very expensive and the infrastructure is complicated. One of the safest ways how to store hydrogen is solid state storage.

Hydrogen is capable to interact with some of metals and metal alloys and absorb into the bulk of the lattice where the amount of absorbed hydrogen in the volume exceeds gaseous and liquid storage significantly. Unfortunately the high desorption temperatures, slow absorption/desorption rates and small cycling capacity limit the widespread application of current metal hydrides [3]. Therefore any investigation and development that can compete with gas and liquid hydrogen tanks not only with amount but also with weight % of absorbed hydrogen can be a crucial point for new era of hydrogen economy.

Nanostructuring of materials and enhancement of surface absorption capability are two main factors to increase the amount of sorbed hydrogen. One way to combine the effectiveness of hydrogen absorption in metal hydrides and the desirable weight/volume proportion is to make composite material from alloy forming hydride and appropriate support material that isn't interacting with hydrogen by itself.

Aims of work

- To create a new composite material that consists of a AB_5 type metal alloy and borosilicate glass;
- To establish a composite material preparation methodology
- To develop an optional method for an electrochemical, volumetric and thermogravimetric measurements of the sample
- To investigate the influence of the particle size and the borosilicate glass phase on the physical and chemical properties of the composite material

Methods of investigations

For preparation of samples the following equipment were used:

- Retsch® MM200 energetic ball mill, tungsten carbide crucibles and balls (Institute of Solid State Physics (ISSP), Latvia);
- Mechanical press and stainless steel press forms for electrochemical experiments of prepared pellets (Western cape University, Republic of South Africa (WCU), RISØ National Laboratory, Denmark);
- Electrochemical cell, electroplating device (ISSP);

A surface, structure and composition were investigated by:

- Optical Microscope KKK (Carl-Zeiss) (ISSP);
- EVO 50 XVP scanning electron microscope (ISSP);
- LS™ 13 320 Series laser diffraction particle size analyzer (RISØ);
- Active surface determination device (BET) Kelvin 1024 (Latvian State Institute Of Wood Chemistry, Latvia);
- X-ray Diffractometer System X-STOE Theta/theta, STOE software and data base (RISØ).

Amount of absorbed hydrogen was determined by:

- Sartorius High Pressure Balance (RISØ);
- Self-constructed hydrogen reactor for detection of absorbed amount of hydrogen by Sievert methodology (ISSP);
- Shimadzu differential thermogravimeter DTG-60 (ISSP).

Equipment for electrochemical investigations:

- VoltaLab PGZ301 (ISSP);
- ECOCHEMIE AutoLab PGSTAT30 (WCU).

Scientific novelty

The new composite material is created that consists of AB_5 type metal alloy and borosilicate glass. Absorbed amount of hydrogen in the bulk of new material exceeds absorbed amount for a raw alloy due to the hydrogen spill-over effect.

It was found that a presence of silica activates a hydrogenation level of the AB_5 alloy by forming not only α and β hydride phase but also γ hydride phase.

There was developed a new method for. Modification of electrodes is performed by co-deposition of different powders of metal/alloys and electroplating.

Thesis of defence

There is created a new composite material by combining AB_5 type lanthanum nickel alloy and borosilicate glass that absorbs more hydrogen than raw materials separately.

A presence of silica activates a hydrogenation level of the AB_5 alloy by providing of hydrogen atoms on the boundary surface of alloy/glass.

Hydrogen absorption in the new composite material occurs due to the spill-over process from catalyst AB_5 to an inert material – borosilicate glass where the hydrogen atoms have higher bond energy than that to form hydrogen molecule.

The new methodology of co-deposition of different powders of metal/alloys and electroplated nickel is increasing catalytic activity and active surface of negative electrodes. New electrodes produce higher work current for electrolysis and electrode charging process.

Practical significance

Obtained results of investigations can be used to produce a hydrogen storage device that is economically suitable and safe to operate in hydrogen engine cars.

An established methodology of electroplating is suitable for a preparation of electrodes that can be applied for fuel cells or metalhydride accumulators to increase their work capability and stored energy.

The doctoral thesis, publications and elaborated laboratory work ‘Materials for hydrogen energetic’ can be employed to create study aids about hydrogen energy for schools and colleges and informative brochures for any interested person in Latvian.

Approbation of work

There is prepared 22 conference abstracts and published 9 papers in journals and conference proceedings during an elaboration of the doctoral work. Furthermore, there are attended 17 conferences in total, where 7 oral reports and 2 posters are presented in the international conferences and workshops as well as 4 oral reports and 2 posters in the local ones.

There was taken part in the seminars and schools according to the theme of doctoral studies that are listed bellow:

1) The 1st Nordic Energy Research (NORFA) summer school "New materials and technologies for low temperature fuel cells", Göteborg, Sweden, September 5-8, 2002;
2) NORFA Workshop organised by Nordic Energy Research – Electrochemical Energy Conversion ”Generalmønstring 2002”, Reval Hotel Latvija, Riga, November 27-28, 2002;
3) NORFA summer school “Infrastructure for the Hydrogen Society”, Reykjavik, Iceland, June 10-14, 2003;
4) Joint Research Centre (JRC) seminar “Advanced Technologies for Hydrogen Storage”, Petten, The Netherlands, October 9-10, 2003
5) Early Market Introduction of New Energy Technologies seminar/workshop “The Organisations for the Promotion of Energy Technologies”, Riga, Latvia, March 8-9, 2004;
6) JRC seminar "Experimental aspects of R&D on Hydrogen Storage Technologies", Petten, The Netherlands, October 17-18, 2005.

Reports in scientific seminars:

1) “Hydrogen energy and nanomaterials” ISSP scientific seminar, April 7, 2004, Riga, Latvia;
2) “Hydrogen energetics” seminar for pupils of Drustu primary school, January 29, 2005, Riga, Latvia;
3) “Hydrogen energetics” seminar for winners of Physics olympiad of Latvia, February 10, 2005, Riga, Latvia;
4) “Hydrogen energy” lecture for students od Social sciences of University of Latvia, February 28, 2005, Riga, Latvia;
5) “Possibilities and reality for hydrogen development in Latvia, Iceland and Republic of South Africa” November 16, 2005, Riga, Latvia;
6) “Investigations of the Influence of Glass Phase to the Lanthanum Rich Mischmetal” seminar in the RISØ National laboratory, December 7, 2005, RISØ, Denmark.

Together with supervisor Dr. Phys. J. Kleperis there was elaborated a laboratory work “Materials for hydrogen storage” for bachelor and masters degree students of University of Latvia during July – December 2006.

Structure of work

The dissertation work contains abstract, introduction part, experimental part, conclusions, references, list of publication s and conferences and acknowledgements. The thesis is represented in the following chapters:

- Chapter 1, “Literature overview”, where a short review about hydrogen energy, hydrogen society is illustrated. In addition there is described methods of hydrogen production from fossils and alternative sources, and explained the most common ways of hydrogen storage;
- Chapter 2, “Experimental ”, gives a brief description about chosen materials, methods and instruments;
- Chapter 3, “Results”, summarizes gained results and the explains the observation of experiments;
- Chapter 4, “Conclusions” revises the accomplished work and marks the future possibilities;
- Chapter 5, “Acknowledgements”;
- Chapter 6, “References”, where the literature sources are numerated
- Chapter 7, “Supplement”, consists of a list of publications and conference abstracts.

There are 125 literature sources, 79 figures and 31 tables used to complete a thesis. 9 copies of papers where the results are published are supplemented to this work.

Motivation of investigations

As hydrogen absorber, $LaNi_5$ has been one of the most investigated intermetallic compounds during the last decades. Despite of its high hydrogen capacity - one hydrogen atom to each metal atom - and easy activation, the binary compound is not suitable for applications due to its high plateau pressure and short lifecycle [4]. However, modification of the physical and chemical properties of $LaNi_5$ can be achieved by substituting lanthanum atom with a rare earth metal (e.g. Ce, Pr, Nd) or nickel with a transition metal (e.g. Al, Mn, Co, Cr). Specific sample preparation methods, such as melt–spinning, sputtering and mechanical milling have been used to improve the hydrogenation kinetics of intermetallic compounds. The resulting alloys exhibit particular structural characteristics as nano-crystalline grain size with a high density of grain boundaries and lack a long-range order (similar to an amorphous state). These microstructures currently provide fast hydrogenation kinetics and better lifecycle behaviour. Mechanical milling has become a popular technique because of its simplicity, relative inexpensive equipment and applicability to most intermetallic compounds. The mechanical milling has been used for several hydrogen storage alloys; a good improvement in hydrogen activation and kinetics was observed [5, 6].

The diffusion of active species on the surface may play an important role in reactions on multifunctional catalyst transport phenomena. Especially, migration of hydrogen atoms from a metal, to an oxide or carbon surface that by itself has no activity for dissociate hydrogen adsorption, is important. It is in fact well known, that noble metals like Pt and Pd can adsorb and diffuse hydrogen in reactive forms over relatively large distances. This property named as spill-over effect, is widely exploited in catalysis [7].

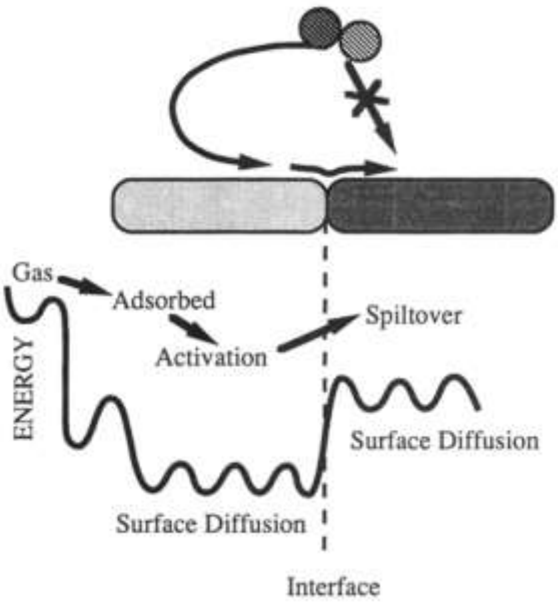


Figure 1: Schematic representation of spill-over of a gaseous diatomic from and energy level diagram for the processes. Dark oval - non-adsorbing surface, light oval – catalyst, small circles – hydrogen molecule [8].

Figure 1 represents a simplified hydrogen spill-over scheme. Oxide isn't absorbing hydrogen molecules, although if the molecule is adsorbed and dissociated on the catalyst, the formed hydrogen atoms are interacting with oxide phase.

The spill-over of hydrogen involves a transfer of electrons to acceptors within the support; this process modifies the chemical nature of the support and can also activate a previously inactive material and/or induce subsequent hydrogen physisorption. Dissociation of hydrogen molecule on a metal and subsequent spill-over of atomic hydrogen to its support is highly dependent upon the chemical bridges formed at the interface. Hydrogen spill-over can be assessed in a number of ways, but perhaps the most common is simple calculation of the hydrogen to metal ratio, either the surface metal or total metal content. When spill-over occurs, the relation Hydrogen/Metal surface will typically exceed unity. In the case of materials that form hydrides, this relation will exceed the stoichiometric ratio of the hydride [9].

In this work the possibility to use the spill-over effect to enhance catalytic activity and, in that way, the kinetics and the amount of absorbed hydrogen are explored.

Choice of objects

The lanthanum rich mischmetal (LaMm) with a trade name 7-10 produced by the company Metal Rare Earth Limited of China was used as catalyst and bulk material for hydrogen storage. This alloy is AB_5 type alloy where lanthanum is partly replaced with other rear earth elements and nickel is replaced by other transition metals. These substitutions are changing thermodynamic properties of an alloy and allow using it close to normal conditions. A silica based Pyrex glass was applied as material with developed surface for adsorption of spilled atomic hydrogen from AB_5 grain surfaces. Investigations of such kind of composite materials weren't found in observed literature.

Methodology of investigations

To study a surface morphology the Scanning Electron Microscope of Carl Zeiss brand, model EVO 50 XVP was used. The SEM images were taken in secondary electrons (SE); the acceleration voltage was equal to 30 kV, and the emission current was between 0,5pA and 500nA. The sample was studied in powdered form, "as delivered", i.e. without additional grinding and any other treatment. The powder was put onto the conductive carbon-containing adhesive paper which was glued to the aluminium sample holder. The energy dispersive detector for X-rays (EDX) was used for composite determination in the alloy 7-10.

The particle size distribution was determined in an emulsion of ethanol and powder. A powdered sample was degassed 2160 min at 150°C for active surface investigations with nitrogen.

Structural properties of the samples were studied by X-ray Diffractometer System X-STOE Theta/theta, using Kα Cu radiation λ=1,5406 Å; generation voltage 40kV, current 30mA. Powdered samples was placed on rotating stainless steel holder, smoothed and pressed with a glass plate. The starting x-Ray diffraction angle Θ was 20^0, finishing 90^0, step size $0,05^0$/sec. Desorption measurements were performed in special camera with nitrogen atmosphere, scanning angles from 27^0 to 37^0.

Initially were prepared composite material with different inert phases as WO_3, zeolite, glass, carbon and in variety of weight ratio of alloy/inert phase. Finally, the weight ratio 3,7 parts of alloy and 1 part of borosilicate glass milled for 30 min at 25Hz in a ball mill was taken for experiments.

A thermogravimetric technique has been used to study the hydrogen sorption on prepared samples. The measurements were performed by equipment based on the Sartorius high pressure balance (HPB). The sample was placed in the steel container that can be sealed to provide a vacuum or gas atmosphere and the pressure and temperature ranges of $1 \cdot 10^{-3}$ – 30 bar and from room temperature to 300°C, respectively.

The studied sample about 340 mg was initially degassed under vacuum down to 10^{-3} bars at the ambient temperature and flushed with helium gas. The further steps were heating the system until 260°C with followed vacuuming, activating at 10 bar hydrogen pressure and cooling down. Subsequently the previous actions were repeated two more times finishing with the vacuuming of system. Afterwards, stepwise changes of the pressure inside the measuring device were applied. For each pressure at constant temperature the increase of the sample weight, was measured as a function of time due to hydrogen sorption.

During the PhD studies in the Institute of Solid State Physics was constructed autoclave type device that could be used for volumetric investigations of the hydride alloys (figure 2).

It is equipped with pressure sensors ECO-1 from Greisinger Electronic GmbH in a range 0 – 10 and 0- 40 bar, a stainless steal container with an internal volume of 36 cm^3, vacuum pump, oven and thermocouple. The changes of pressure during hydrogenation of alloys and composites were observed due to the absorption/adsorption and desorption of hydrogen in the sample.

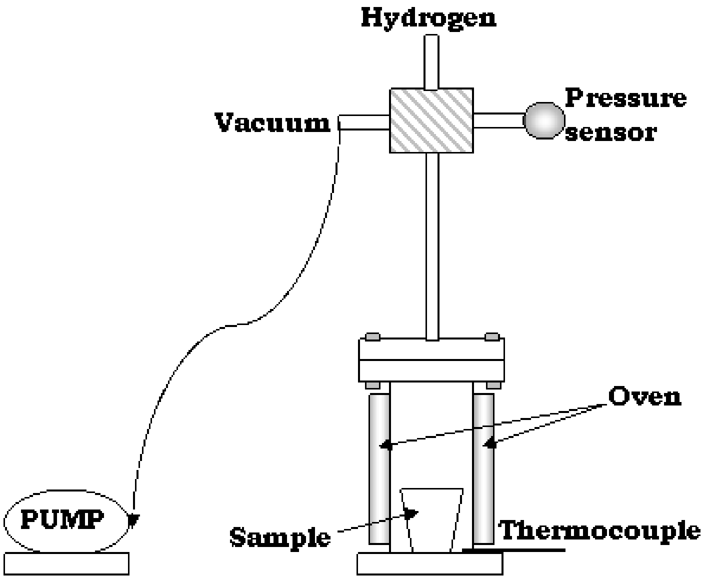


Figure 2: Self-made equipment for volumetric investigations.

Pre-treatment of samples was performed in the same way as for high pressure balance. The hydrogenation of samples was performed as follows: weighting the sample on a high precision balance, putting it into Volumetric device, vacuuming, performing alloy activation in hydrogen as heating up in vacuum to 170 °C and cooling down to room temperature, rising hydrogen pressure up to 3 bars and vacuuming the system at the temperature 200 °C. The next a phase is step rising of the hydrogen pressure and waiting until the pressure stabilizes to follow with other pressure increases. In the volumetric method the final step in the hydrogenation procedure was the heating of sample in a hydrogen atmosphere 2 bars up to 190°C, waiting for pressure stabilization, and next a cooling 30 degrees per minute down to room temperature.

A method was developed to determine the amount of permanently stored hydrogen in the samples, using an automatic differential thermogravimeter (TG) DTG-60 by Shimadzu Corporation. A sample was placed in the aluminium crucible and heated up to 300-500°C in an argon flow 75 ml/min in the same time the changes of the weight and temperature were registered.

Three different nickel substrates were used for electrochemical preparation: 0,2 mm bulk nickel, 0,1 mm electroplated Ni foil and 1mm porous bulk nickel.

All nickel samples were pre-treated by etching 5 minutes in 2 M H_2SO_4. Electroplating was performed at 58-60^{0}C using modified Watt-type bath (figure 3) and pH 5±0,2 electrolyte solution consisting of $NiSO_4.6H_2O$ (300 g/l), $NiCl_2.6H_2O$ (45 g/l), H_3BO_4 (30 g/l). Combined coating method was used to obtain co-deposited nickel and metal hydride alloy: during nickel plating the particles of alloy 7-10 (40 g/l) were co-deposited on the cathode together with a nickel metal from electrolyte. The current density was kept 10-30 mA/cm^2 that corresponds to the growth rate of nickel layer 0,3 - 0,4 µm per minute. Deposition time equal to 5 minutes was chosen for all substrates, which corresponded 1,5-2 µm thick deposited layers.

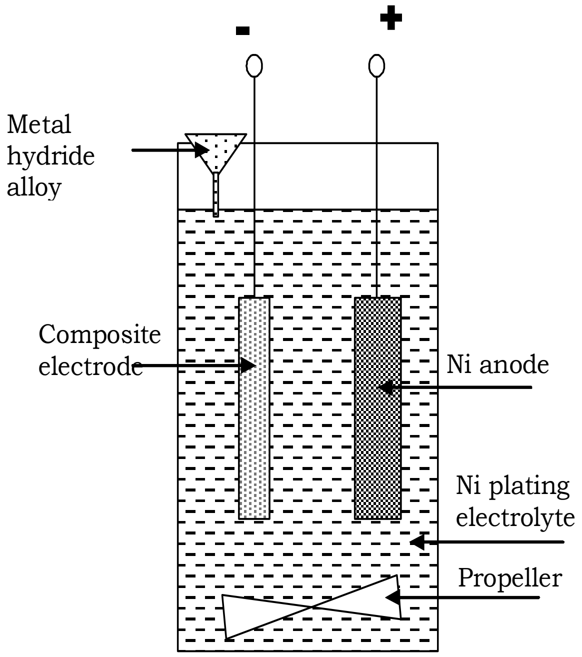


Figure 3: Electrochemical cell to obtain composite nickel electrode for hydrogen adsorption/absorption researches.

For charge/discharge studies the samples were charged with 1 mA/cm^2 current for 1 minute and discharged with 0,1 mA/cm^2 for 5 minutes.

For working electrode 1 cm^2 was left free and the rest of the sample was isolated with epoxy resin. The simple immersion method was used in all electrochemical measurements using PTFE sample holder. 0,1 M H_2SO_4 water solution was used as an electrolyte in an electrochemical cell supplied with calomel reference electrode and large surface Pd counter electrode. A Potentiostat/Galvanostat VoltaLab of “Radiometer Analytical Ltd” was used to record the voltamperic characteristics and polarization curves.

Only cathodic polarisation from +0,1 V to -1,2 V was used in order to prevent the formation of oxides during anodic polarisation.

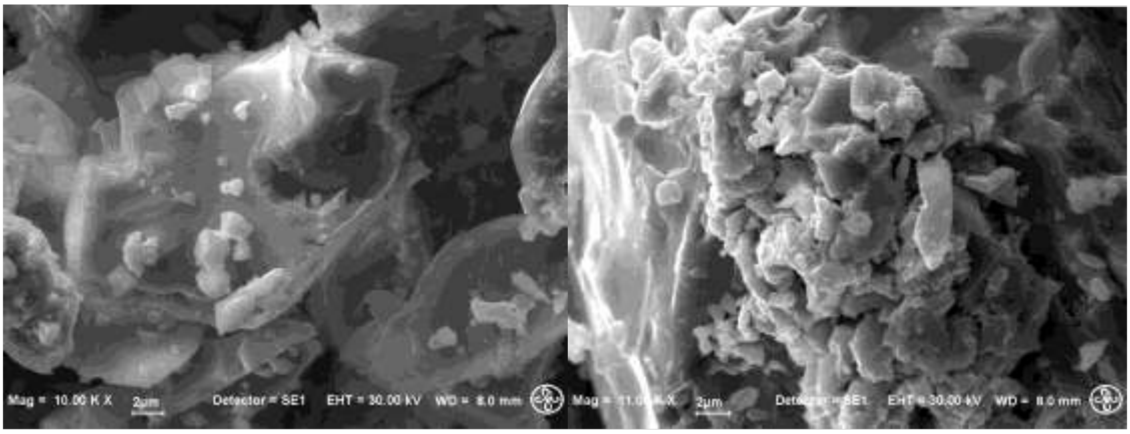
Skills of a sample preparation for metalhydride accumulator electrodes and investigations of electrochemical characteristics were obtained in the Western Cape University, Republic of South Africa. Pellets of 100mg alloy, 300mg of Cu and in some cases of 5% PVA, PTFR and zeolite in size of 1cm for electrochemical experiments were created under 500MPa pressure. Measurements were made in an open type three electrode electrochemical cell, 6M KOH, using calomel reference and Pt counter electrodes.

Voltamperic curves were taken by EcoChemie AutoLab PGSTAT30 in different range of voltage between -2 and +2V to get information about processes in material. Impedance spectra were taken by applying different polarisation voltages in a range from 0V to 1,8V and cut off potential at -0,6V according to reference electrode.

Investigations were prolonged in the ISSP with a potentiometer VoltaLab PGZ 301 using the same configuration of a cell and electrodes. There the samples were charged and discharged applying 2mA current for 20min, an open circuit potential was measured after a break for 5 min.

Results

The energy dispersive detector for X-rays (EDX) for component determination in the sample 7-10 shows that the composition of the sample corresponds to formula $A_{0,96}B_{5,04}$ where A=La, Ce, Nd, Pr and B=Ni, Co, Mn, Al, Cr. That is close to AB_5 stoichiometry and the molecular mass of this sample becomes 435,74 g/mol (Figure 4-5, Table 1). For determination of the molecular mass of the LaMm and further calculations was assumed that after the treatment a metalhydride material contains a diminutive amount of oxygen.



(a) (b)

Figure 4: SEM images of alloy 7-10 before (a) and (b) after hydrogenation, magnification 11 000

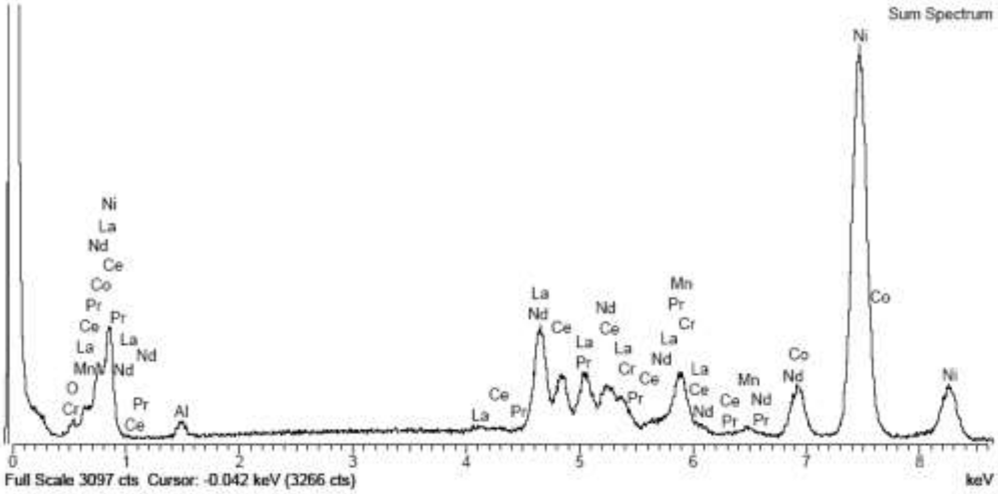


Figure 5: Energy spectra of secondary X rays collected from the total surface of the sample 7-10

Table 1: Quantitative EDX data for the total surface of the metal alloy 7-10

Element	Weight%	Atomic%
La	17.51	8.24
Ce	9.88	4.61
Nd	3.07	1.39
Pr	0.98	0.45
Ni	52.89	58.89
Co	6.23	6.91
Mn	5.08	6.05
Al	1.93	4.67
Cr	0.39	0.49
O	2,03	8,30

XRD pattern shows that they belong to single phase $LaNi_5$ hexagonal $CaCu_5$-type structure in the space group P6/mmm (Figure 6), [10].

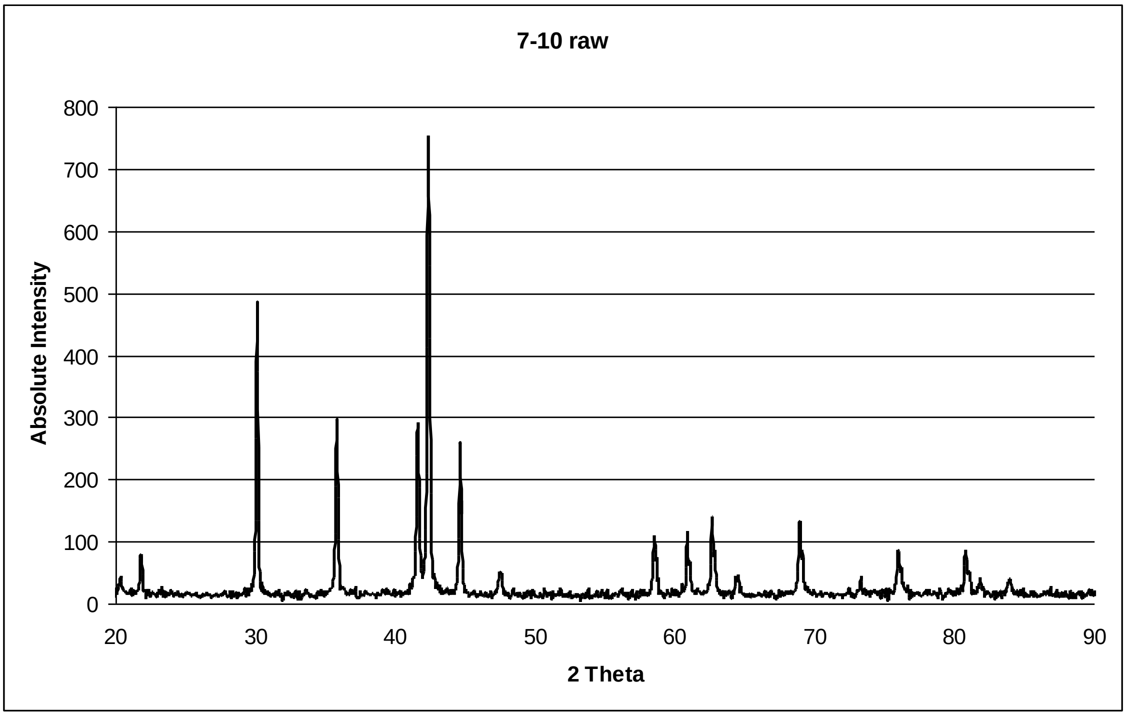


Figure 6: XRD patterns for the raw alloy 7-10, as received.

The HPB data analysis showed that, after treatment described above, the mass change reaches 1,28 mg of the raw alloy 7-10 that gives just 0,372 weight percent of the absorbed hydrogen. Composites that were prepared my mechanical mixing of alloy and glass, WO_3, zeolite was even worth [11]. Further experiments were performed by using composite with borosilicate glass only according to the previous spill-over related experiments in ISSP [12] and due to the absence of similar experiments in literature.

Investigations of composite alloy and borosilicate glass mechanically mixed together in weight ratio 3,7: 1, respectively, showed that hydrogen uptake is dramatically slow. Even after 100 hours the plateau wasn't reached and absorbed hydrogen amount reached 0,14 weight percents in total.

The sample preparation technique was revised and according to different articles published in press [e.g. 13-15] further a high energetic ball mill was used to improve hydrogen absorbing/desorbing properties of samples.

The SEM image illustrates (Figure 7) the raw sample after milling. The grain size do not exceeds 1-3 micrometers nevertheless, particles are agglomerated together [16].

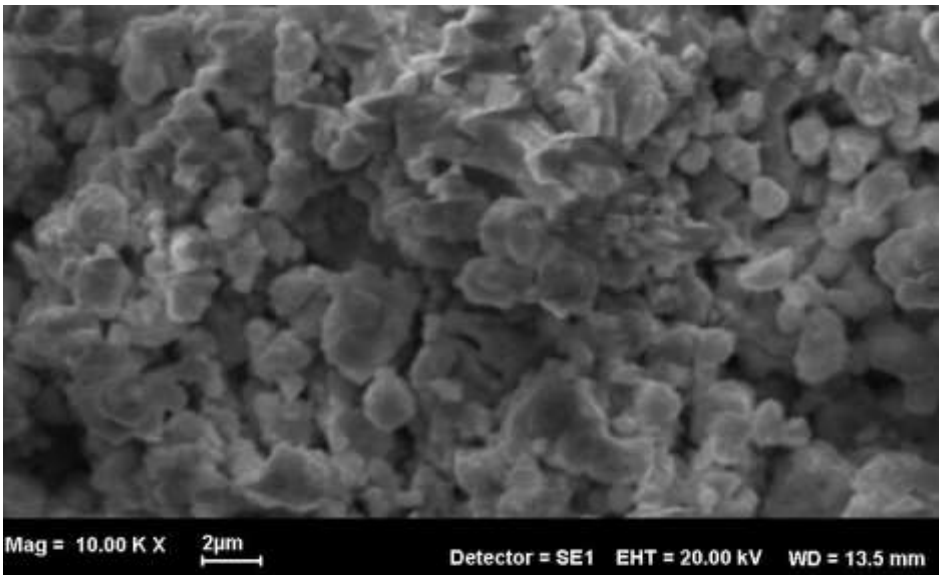


Figure 7: SEM image of 7-10 after milling for 30 min at 25Hz per min.

An active surface measurement analysis there was concluded that a surface area for composite alloy 7-10 and borosilicate glass is at least 3 times larger and a volume of pores exceeds even 5,5 times the parameters of a raw alloy 7-10 (table 2).

Table 2: The data of active surface area and pore volume of composite and raw alloy

Sample	7-10	7-10 + glass
BET surface area, m^2/g	0,27	0,84
Langmuir surface area, m^2/g	0,38	1,31
Total volume of pores, mm^3/g	0,50	2,73

Further experiments in the high pressure balance at RNL were carried out following the treatment procedure described previously. Analysing treated data it was figured out that raw hydride material 7-10 absorbing more hydrogen than classical $LaNi_5$ by itself. The HPB plots clearly shows that pure $LaNi_5$ absorbing and desorbing hydrogen when the pressure is changed. There just 0.26 w% of hydrogen is remaining in the pure $LaNi_5$ sample at the one atmosphere. Though, the data plot of LaMm sample 7-10 displays opposite tendency – the absorbed hydrogen amount just slightly decreasing after lowering the pressure to the one atmosphere but desorption occurs at 80°C (figure 8-9).

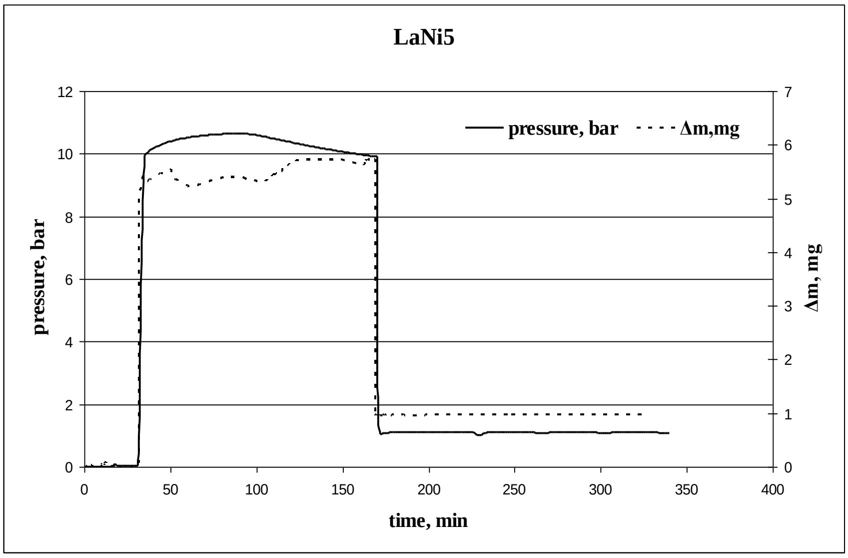


Figure 8: HPB data plot of the pure $LaNi_5$ at the room temperature.

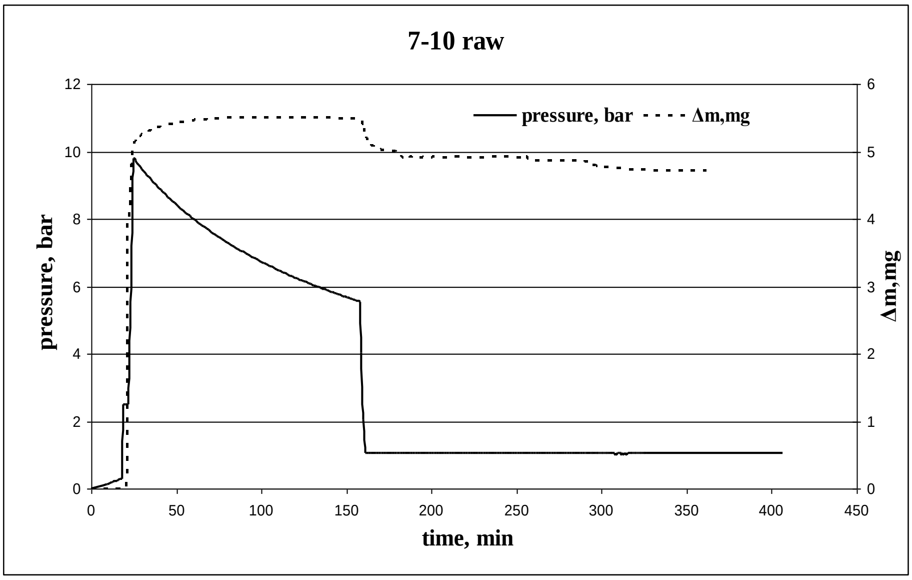


Figure 9: HPB data plot of the raw sample 7-10, at the room temperature.

Comparison of HPB plots of composite of both materials with the glass phase confirmed the same tendency – sample 7-10 and glass absorbed more hydrogen than $LaNi_5$ with glass.

The calculations of amount of absorbed hydrogen x and weight % in the raw material and composite, shows that it is more than for pure alloy sample 7-10 (Table 3). That could be explained with hydrogen spill-over and absorption in alloy-glass mixture.

Table 3: Calculations of HPB data for raw alloy (7-10) and composite (7-10+glass)

Δm	Δm, mg	w%	x
7-10			
Δm_{total}	5,507E-03	1,582	6,966
Δm_{av}	5,138E-03	1,477	6,499
Δm(1atm)	4,883E-03	1,405	6,177
7-10+glass			
Δm_{total}	5,048E-03	1,643	7,242
Δm_{av}	4,616E-03	1,504	6,621
Δm(1atm)	4,393E-03	1,433	6,302

The XRD results showed that the diffraction peaks of hydrogenated alloy 7-10 were largely shifted to the smaller angles than that of the starting alloy, indicating that the α-phase of hydride is changed into the β-phase and the lattice parameters and cell volume of the hydride is larger than that of the starting alloy. For the composite the observed shift of XRD peaks after hydrogenation was even larger than that for pure 7-10 alloy. Also corresponding lattice parameters and cell volume for hexagonal P6/mmm symmetry was larger of hydrogenated composite sample as for fully hydrogenated alloy 7-10 (Figure 10, table 4), [10].

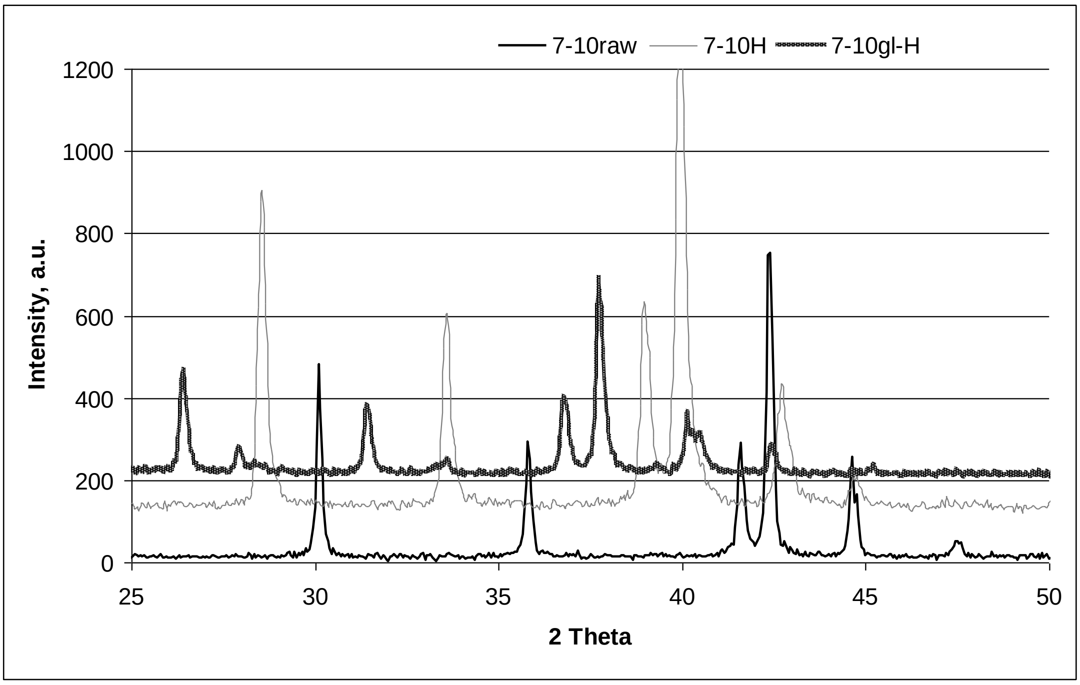


Figure 10: XRD plot of raw (7-10raw), hydrogenated pure 7-10 (7-10H) and hydrogenated alloy 7-10 with glass phase (7-10gl-H), for better recognition intensity is increased by 100 units for 7-10H and by 200 units for 7-10glH

Table 4: Structural parameters of raw and hydrogenated samples

Cell size / Sample	a, Å	c, Å	V, Å3
7-10	5,0083	4,0567	88,12
7-10hydrogenated	5,326	4,234	104,0
7-10+glass hydrogenated	5,369	4,2754	106,78

Investigations in a self made hydrogen reactor were used to define an absorption enthalpy for synthesized composite materials and for measurements of hydrogen desorption kinetics. A calculated value of enthalpy (41,28kJ/gmolH2) determined from a constructed Van't Hoff plot approved that material is suitable for electrode material of metalhydride batteries according to the literature [17].

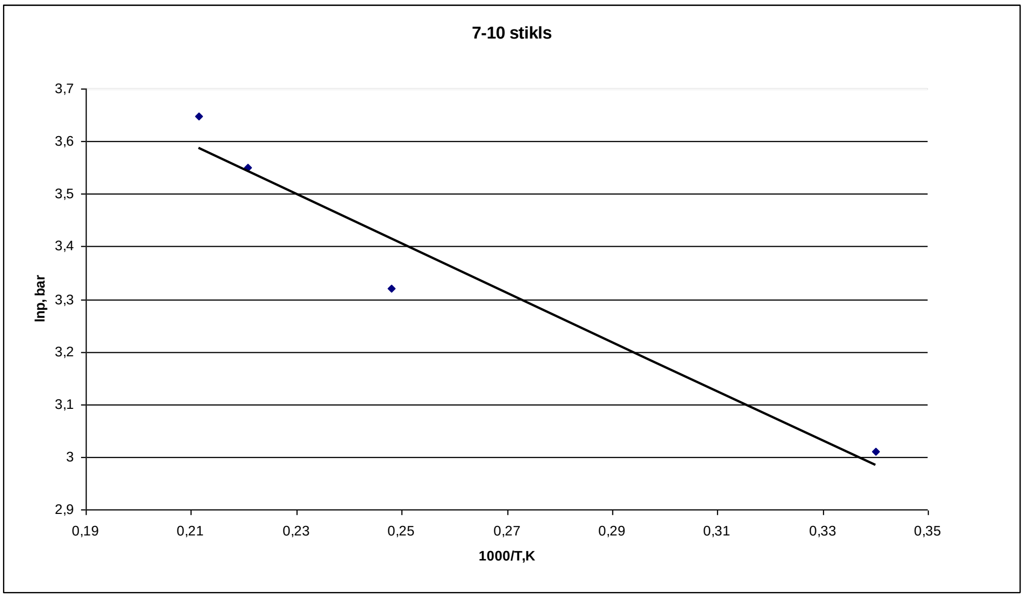


Figure 11: Van't Hoff plot for determination of hydrogen absorption enthalpy

Electrochemical investigations

Measurements of volt-ampere characteristics of alloy with different binders (PVA, PTFE, zeolite) were performed in the Western Cape University. Results showed that these binders aren't changing the characteristics a lot.

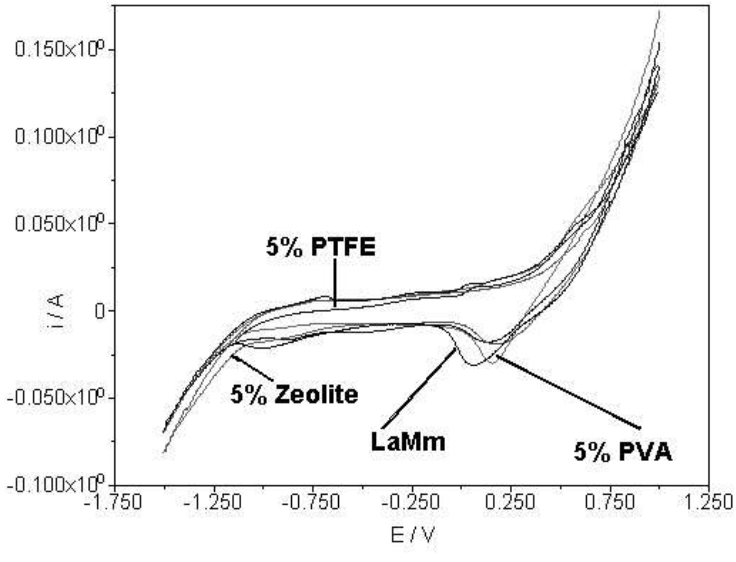


Figure 12: Volt-ampere characteristics for alloy 7-10 (LaMm) with different binders

Pellets for measurements in the ISSP were prepared by pressing 100mg of an alloy 7-10 and 300mg Cu, to provide a higher conductivity and durability in charging and discharging cycles (Figure 13), [18].

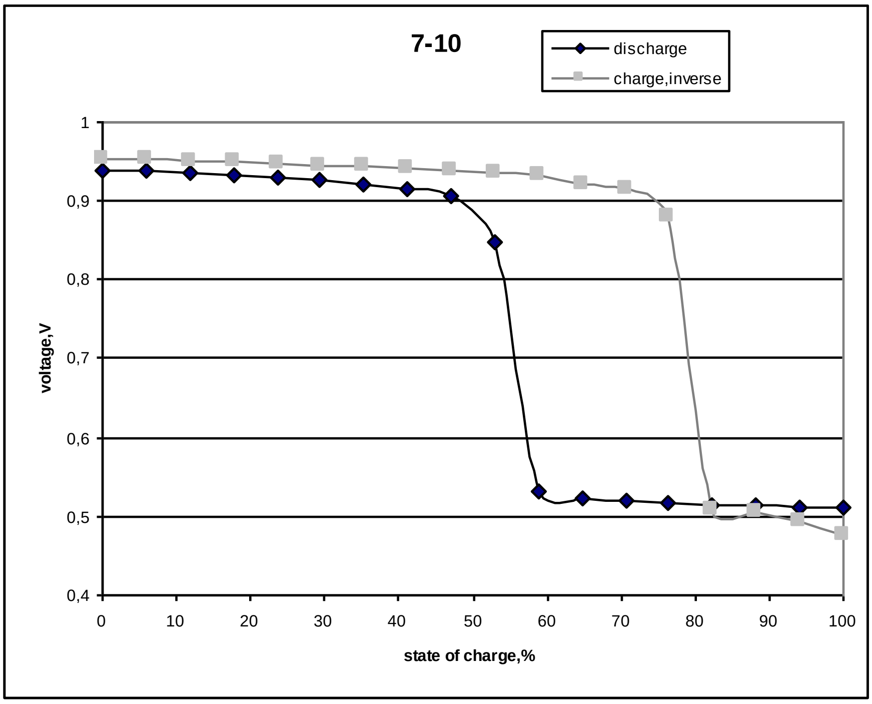


Figure 13: Voltage dependence from applied current, for easier comparison, charge cycle is inversed (x=state of charge,%, y=voltage,V).

Measurements proved that both charging and discharging of an electrode happens rapidly, though to some certain limit. At a 20% of maximum state of charge a rapid enlargement of voltage occurs that slowly continuously increasing until reaches a saturation level. A process of discharge is very similar - voltage changing slightly down to 50% of state of discharge, wherefrom voltage is decreasing rapidly.

Characteristic hydrogen adsorption/absorption and desorption maxima is observed on palladium electrode at -1,04 V and -0,28 V, respectively. It is less distinctive for porous nickel and decreases going from and electroplated samples to nickel substrate (Figure 14).

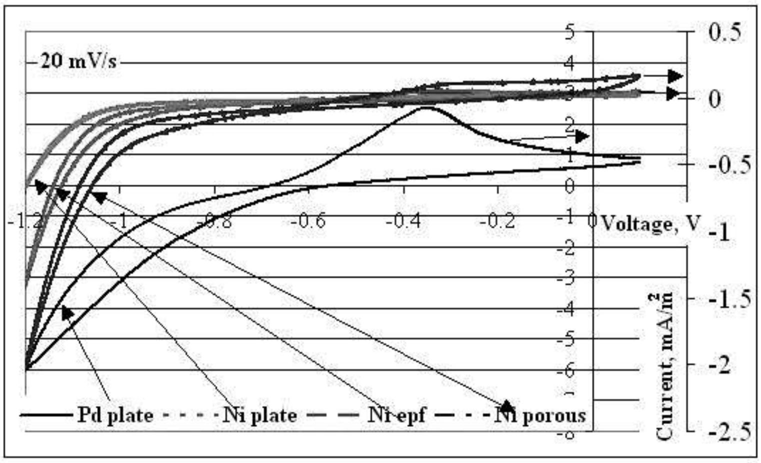


Figure 14: Volt-ampere curves of blank Ni(Ni plate), electroplated Ni foil (Ni epf), porous Ni (Ni porous) and Pd (Pd plate) samples. Two different current scales are used to indicate structures of curves from nickel samples.

The discharge curves (Figure 15) testify that the amount of accumulated hydrogen is increased about 2-3 times thought that is less as in the case of Pd is coating.

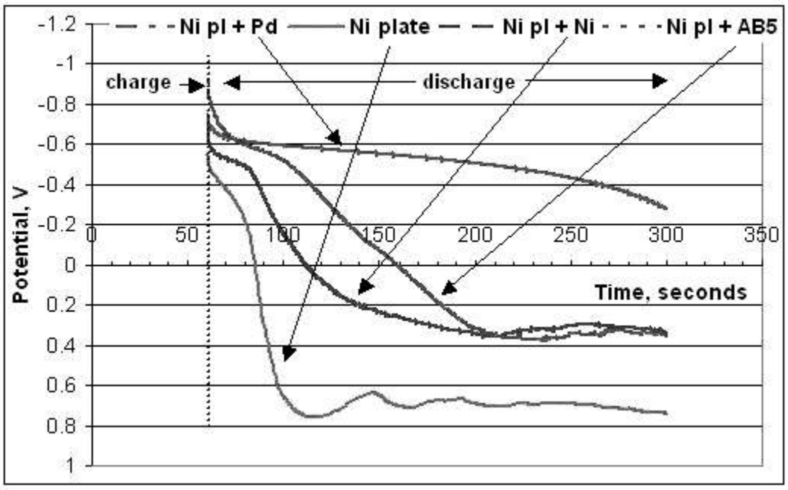


Figure 15: Discharge kinetics of Ni plate substrate coated with thin Pd, Ni and alloy AB_5

The addition of metal hydride powder to nickel during electroplating increased the electrochemical activity of coating and stored charge is also increased (Figure 16). The impact of the Ni coating on different nickel substrates is the same – the current values are higher for Ni/Ni samples (19).

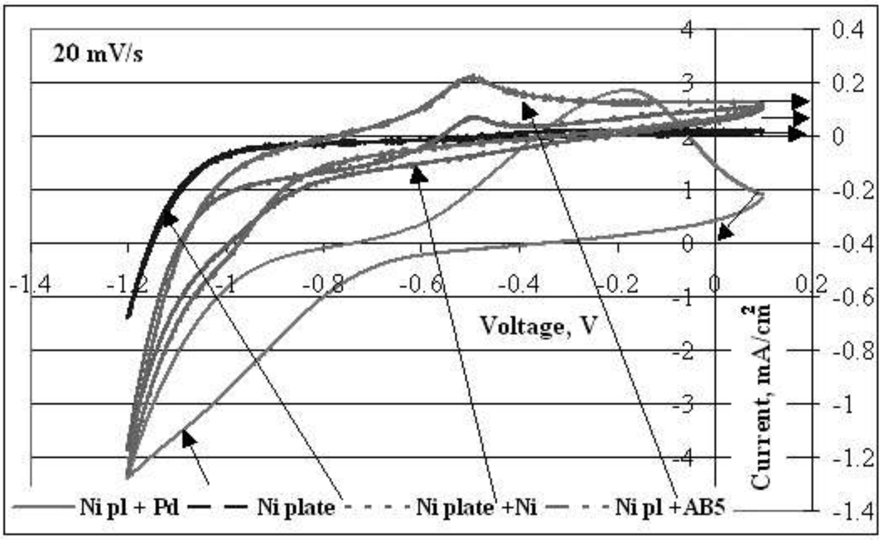


Figure 16: Volt-ampere curves of Ni plate substrate coated with thin films of Pd, Ni and alloy AB_5+Ni film

Conclusions

Thermogravimetric and pressure change measurements in HPB proved that the created composite material of alloy 7-10 and borosilicate glass absorbs more hydrogen per weigh unit than both components separately.

It is confirmed, that a β phase of ball milled composite material occurs earlier than for raw alloy. The X-ray diffraction patterns show that the gamma phase (γ) of composite material hydride is forming, that isn't observable for pure alloy 7-10. The γ phase contains more hydrogen atoms per unit cell than the β phase and hydrogen atoms prefer the interstitial sites closer to Ni atoms in an elementary cell, producing inhomogeneous distribution and large lattice distortions.

Enrichment with hydrogen of the created composite is explained basing on the hydrogen spill-over phenomena. The hydrogen molecule is dissociated and adsorbing at the surface sites found on the alloy. Interaction is proceeded by migration of an active hydrogen atoms to the bulk of LaMm and spilling over the surface of a borosilicate glass that depends form a good contact of surface boundaries of an alloy and a glass.

Investigations using self made hydrogen reactor verified that a new composite material is suitable for metal hydride electrode and hydrogen storage applications.

Surface modification of nickel materials by electroplated nickel and AB_5 additions provides not only surface activation of electrode materials but also enhancement of accumulated hydrogen amount in the electrodes.

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