

## SSH2S Report Summary

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### Final Report Summary - SSH2S (Fuel Cell Coupled Solid State Hydrogen Storage Tank)

#### Executive Summary:

The main results obtained in the frame of SSH2S project can be summarized as follow:

- Design and the synthesis, as well as the physico-chemical characterization, of existing and novel materials for solid state hydrogen storage has been undertaken. Ab-initio and thermodynamic/kinetic calculations helped to determine the selection of materials. The synthesis of materials has been performed by ball milling, firstly in a laboratory scale and then scaled-up. The characterisation has been currently performed by a combination of structural and spectroscopic experimental techniques.
- A new two-materials concept has been developed for the tank, combining hydrogen sorption properties of complex hydrides and metal hydrides. In particular, thanks to a careful control of thermal exchanges, synergic effects have been obtained, promoting fast hydrogen sorption reactions.
- The fluid-dynamic modelling of different tank concepts, as well as the experimental validation of the models in a lab-scale tank, drove the design of a prototype tank, optimized for use with the selected materials. The project and the development of the prototype tank have been undertaken by industrial partners.
- The results have been used to integrate the materials/tank systems with a HT-PEM Fuel Cell (1 kWel) to be used as APU in a light vehicle. A final "on road" testing on the developed APU has been performed.
- LCA and techno-economic evaluations have been defined at the end of the project. The estimation about possible scale-up has been considered.

#### Project Context and Objectives:

The main objective of SSH2S is to develop a solid state hydrogen storage tank fully integrated with a fuel cell and to demonstrate its application on a real system. A well assessed hydrogen storage material (i.e. a mixed lithium amide/magnesium hydride system) has been considered as the active material for the tank. The application of the hydrogen tank on a real system has been experimentally investigated with a 1 kW prototype on High Temperature Polymer Electrolyte Membrane (HTPEM) fuel cells. A scale-up of the tank up to a 5 kW APU has been estimated.

The project was organised in Work Packages (WP). At the beginning of the project, the design and the synthesis (WP1), as well as the physico-chemical characterization (WP2), of existing and novel materials for solid state hydrogen storage have been carried out. Ab-initio and thermodynamic calculations drove the selection of materials. Synthesis of material has been performed by ball milling. The characterisation has been performed by a combination of structural and spectroscopic experimental techniques.

The material selection was a fundamental milestone (M1) of the project. In fact, the selected material should be characterized by improved capacity and efficiency, in terms of thermodynamic and kinetic properties, resistance to cycling and thermal behaviour.

Two WPs aimed at the fluid-dynamic modelling of different tank concepts, as well as the experimental validation of the models, in a lab-scale tank (WP3) and at the development of a prototype tank (WP4) optimized for the use with the selected materials. The design and the development of prototype tank have been driven by industrial partners.

The results of these WPs have been used for the integration of the materials/tank systems with a low power HT-PEM Fuel Cell (1 kWel) (WP5). To this aim, on the basis of the obtained properties and simulation results, a suitable material composition have been defined for the scale-up production.

The final goal of the project was the application of the integrated system as 1 kWel APU to be installed in a Light Transport Vehicle (WP6). The decision about possible scale up of APU production has been taken after a critical techno-economic evaluation and it represented a fundamental milestone of the project (M4).

WP7 was devoted to management of the project.

#### Project Results:

##### Work packages 1: Material Design and Synthesis

WP1 aimed at the synthesis of materials to be used for the project. Li amides/imides and mixed-metal borohydrides systems have been considered. In particular, activities performed in WP1 can be summarized as follow:

- The synthesis of lithium amide/magnesium hydride mixed materials have been widely investigated. A careful selection of additives has been performed.

• The synthesis of mixed borohydride materials with high hydrogen contents and suitable thermodynamic and kinetic properties has been investigated. Three different methods have been used for the synthesis: wet chemical synthesis, reactive ball-milling, and cryo-milling. The synthesis of new borohydrides has been driven by ab-initio and Calphad modelling of compounds.

The main results obtained in the frame of WP1 can be summarized as follow.

#### Task 1.1: Synthesis of Li amides/imides

2LiNH<sub>2</sub>-MgH<sub>2</sub>-0.1KH system and 2LiNH<sub>2</sub>-1.1MgH<sub>2</sub>-0.1LiBH<sub>4</sub>-3wt%ZrCoH<sub>3</sub> system have been synthesized by ball milling. The effect of additives has been investigated on both systems (Figure 2).

An optimal composition of amide-system has been identified, which exhibits good cycle stability and reversibility in the hydrogen sorption test (Figure 3).

Preparation conditions on an up-scaled equipment have been investigated, in order to provide large amount of materials needed for tank test.

#### Task 1.2: Synthesis of mixed borohydrides materials

Several metals have been investigated in order to form the corresponding mixed metal borohydride materials, either with two light cations like LiMg(BH<sub>4</sub>)<sub>3</sub> or with one light cation and one transition metal, i.e. NaTi(BH<sub>4</sub>)<sub>4</sub>, NaMn(BH<sub>4</sub>)<sub>4</sub>, NaFe(BH<sub>4</sub>)<sub>4</sub>, MgMn(BH<sub>4</sub>)<sub>5</sub>, MgFe(BH<sub>4</sub>)<sub>5</sub>, MgZn(BH<sub>4</sub>)<sub>4</sub>, MgY(BH<sub>4</sub>)<sub>5</sub> and CaY(BH<sub>4</sub>)<sub>5</sub>. The synthesis of the materials was performed by mechano-chemical reaction of the corresponding single borohydrides or a single borohydride with a transition metal halide. For instance, milling of LiBH<sub>4</sub> and Mg(BH<sub>4</sub>)<sub>2</sub> leads to the formation of a physical mixture of the components rather than a new compound, whereas in the case of Mg(BH<sub>4</sub>)<sub>2</sub> and Y(BH<sub>4</sub>)<sub>3</sub>, the results pointed out to the formation of a mixed metal borohydride. The milling of Mg(BH<sub>4</sub>)<sub>2</sub> or NaBH<sub>4</sub> together with some metal halides (i.e. ZnCl<sub>2</sub>, MnF<sub>3</sub>, FeF<sub>3</sub> and TiFe<sub>3</sub>) led in some cases to the appearance of new diffraction peaks on the XRD pattern, which suggested the formation of a dual cation borohydride.

The optimization of the milling conditions to achieve a mixed metal borohydride system has been performed. None of the investigated composites showed the required properties for technical applications.

#### Task 1.3: Modelling of the thermodynamics and kinetics of the hydrogenation/dehydrogenation process

Ab-initio calculations suggested a possible formation of cation exchanges in Mg(BH<sub>4</sub>)<sub>2</sub>-Zn(BH<sub>4</sub>)<sub>2</sub> system (Figure 4).

Two thermodynamic databases able to describe the behaviour of the Mg(BH<sub>4</sub>)<sub>2</sub>-Zn(BH<sub>4</sub>)<sub>2</sub> mixture and the 2Li(NH<sub>2</sub>) + MgH<sub>2</sub> system have been created. Thermodynamic functions (not yet reported in literature) have been assessed for several compounds of interest for hydrogen storage applications (LiNH<sub>2</sub> - Li<sub>2</sub>NH - MgNH - Mg(NH<sub>2</sub>)<sub>2</sub> - Zn(BH<sub>4</sub>)<sub>2</sub>) (Figure 5).

#### Work packages 2: Materials Characterization

The work performed in WP2 aimed at the characterization of the Li amides/imides and mixed-metal borohydrides synthesized in WP1. A routinely characterization of each sample synthesized in WP1 was essential upon the selection of the most suitable material for the tank integration. Most promising systems underwent a more thorough characterization of their thermodynamic and hydrogen sorption properties.

Generally, the materials characterization performed in WP2 are:

- Structural/chemical identification of synthesized compounds and solid solutions.
- Phase formation during hydrogen sorption.
- Hydrogen storage capacities and thermodynamic properties.
- Kinetics of hydrogen absorption and desorption and determination of activation energies.

Activities have been performed on the basis of following tasks:

Task 2.1: Chemical/Structural characterization

Task 2.2: Investigation of thermal properties

Task 2.3: Investigation of kinetics of hydrogen sorption

The main results obtained in the frame of WP2 can be summarized as follow.

#### Li-Mg amides system

##### 2LiNH<sub>2</sub>-MgH<sub>2</sub>-0.1KH – system.

The dehydrogenation kinetics at temperature as low as 140 °C are very slow (requires more than 40 h) but also at 180 °C it takes 5 h to completely discharge the hydride. At 136 °C the hydrogenation process is very fast and is almost completed in less than 5 min at any temperature.

The plateau pressures at 180 °C are found to be 33 bar for the absorption and 19 bar for the desorption (Figure 6). The calculated values of enthalpy and entropy are in fair agreement with those presented in the literature for similar systems: H<sub>des</sub> = 42 kJ/molH<sub>2</sub>-1.

##### 2LiNH<sub>2</sub>-1.1MgH<sub>2</sub>-0.1LiBH<sub>4</sub>-3wt%ZrCoH<sub>3</sub> – system.

After an activation pre-treatment, PCI measurements have been performed (Figure 7). The desorption enthalpy of the system was determined to be -35.8 kJ/ molH<sub>2</sub>-1, a suitable value for real conditions application.

The activation energy was calculated as 145 kJ/mol. The optimal temperature combining desirable kinetics, full reversibility and good storage capacity is 160 °C. TGA and TPD with RGA showed that the mass loss up to 220 °C can be attributed merely to hydrogen evolution. The diborane emissions can be considered negligible.

ATR and PXD demonstrated that the cycling of the material causes increase of β- Li<sub>2</sub>Mg(NH)<sub>2</sub>, Li<sub>3</sub>BN<sub>2</sub> or LiMgBN<sub>2</sub> that

can be at the basis of the partial irreversibility of the absorption process. The desorption kinetics of the 2 LiNH<sub>2</sub> – 1.1 MgH<sub>2</sub> – 0.1 LiBH<sub>4</sub> – 3wt% ZrCoH<sub>3</sub> system depends on the particle size, which is constant after 10 h of ball-milling. In overall, the material exhibits a considerable stability in cycling, consisting it a suitable system for the tank integration (Figure 8).

The density of the as-milled sample is 1.00 g/ml and the density of the system in the desorbed is 0.78 g/ml.

Compaction at 150 MPa is sufficient to obtain bulk density close to skeleton density without affecting significantly the desorption/absorption kinetics.

ZrCoH<sub>3</sub> favours pulverisation / LiBH<sub>4</sub> facilitates the metathesis, leading to a faster kinetics than single component. A sustained kinetics has been obtained by pulverizing and by forming Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub>. No changes in lattice parameters and edge positions of ZrCoH<sub>3</sub> caused by H<sub>2</sub> cycling was observed. A concerted effect from combined LiBH<sub>4</sub>-ZrCoH<sub>3</sub> has been established.

#### Mixed MeH+CxH Material

The use of a combination of metal hydrides (MeH) with complex hydrides (CxH) as active material is one of the main results of the project. For this reason, specific measurements have been carried out in order to investigate possible interaction between the two materials.

In situ PXD during dehydrogenation and hydrogenation revealed significant differences after hydrogen sorption in the mixed material (Figure 9).

The x-ray energy dispersion spectroscopy (EDS) identified a La-Ni-Mg containing phase, suggesting interaction between the complex hydride and the intermetallic material. After the activation, the mixed material exhibits 2.6 wt% capacity. Release of N-H species during thermal decomposition of both the as-received and the activated MeH+CxH mixture suggests interaction of the two materials upon thermal treatment. Desorption/absorption cycling may result to passivation of the mixed material surface. The direct mixture of CxH and MeH was then not suggested, so that a specific design of the tank was necessary, as described in WP3 and WP4.

#### Mixed-metal borohydrides

Several mixtures of pure borohydrides have been considered, in order to investigate the possible formation of double-cation compounds or solid solutions.

Mixed-metal borohydride containing two light cations, MM'(BH<sub>4</sub>)<sub>n</sub> with M = Li and M' = Mg. The thermal analysis suggests that: i) the alpha phase of Mg(BH<sub>4</sub>)<sub>2</sub> is stable and ii) the eutectic composition lies in the range of 0.33 < x < 0.66.

Mixed-metal borohydrides containing one light cation and one transition metal cation, MM'(BH<sub>4</sub>)<sub>n</sub> with M = Mg, Ca and M' = Y. The work pointed out the formation of a mixed borohydride material in the case of Mg(BH<sub>4</sub>)<sub>2</sub> and Y(BH<sub>4</sub>)<sub>3</sub>. The formed mixed material is amorphous or calcium borohydride becomes amorphous after milling with Y(BH<sub>4</sub>)<sub>3</sub>.

Mixed-metal borohydrides containing one light cation and one transition metal cation, MM'(BH<sub>4</sub>)<sub>n</sub> with M = Mg and M' = Zn. Rietveld refinement on the PXD patterns of the as-milled systems indicated a unit cell shrinking of the tetragonal alpha-Mg(BH<sub>4</sub>)<sub>2</sub> phase, suggesting substitution of Mg<sup>2+</sup> by Zn<sup>2+</sup> and formation of a Mg(1-x)Zn<sub>x</sub>(BH<sub>4</sub>)<sub>2</sub> solid solution. The Mg(BH<sub>4</sub>)<sub>2</sub> -ZnCl<sub>2</sub>, milled under 50 bar of H<sub>2</sub> system exhibited an unknown endothermic event at 475 °C that has not been observed before in Mg(BH<sub>4</sub>)<sub>2</sub> based systems. All the α-Mg(BH<sub>4</sub>)<sub>2</sub> + 0.7ZnCl<sub>2</sub> systems have H<sub>2</sub> release that begins below 100 °C (Figure 10), however the systems are not free of B-H species (B-H) release.

Results on cycling carried out on the cryo-milled α-Mg(BH<sub>4</sub>)<sub>2</sub> + 0.7ZnCl<sub>2</sub> system showed a reversible storage up to 2.5 wt% with very slow kinetics. The systems exhibit negligible emissions of diborane.

Mixed-metal borohydrides containing one light cation and one transition metal cation, MM'(BH<sub>4</sub>)<sub>n</sub> with M = Mg and M' = Mn, Fe. The Mg(BH<sub>4</sub>)<sub>2</sub>-MnF<sub>3</sub> shows negligible emissions of diborane species and shifts the temperature of H<sub>2</sub> release down by 80 degrees comparing to pure Mg(BH<sub>4</sub>)<sub>2</sub>.

Mixed-metal borohydrides containing one light cation and one transition metal cation, MM'(BH<sub>4</sub>)<sub>n</sub> with M = Na and M' = Ti, Mn, Fe. The mixture of 0.8NaBH<sub>4</sub> + 0.2MnF<sub>3</sub> lead to a formation of a ternary fluoride that appears to be of high importance on the destabilization of NaBH<sub>4</sub> and on emission of H<sub>2</sub> from temperatures as low as 100 °C. The presence of transition metal fluorides, like TiF<sub>3</sub>, MnF<sub>3</sub> and FeF<sub>3</sub> initiates the decomposition of the borohydride in mid-range temperature regions.

#### Work packages 3: Lab-scale Tank Development

WP3 dealt with the characterization and simulation of a modular lab-scale solid state hydrogen storage tank. In particular, the following activities have been carried out:

- A CFD simulation tool has been established, modelling the storage tank bed including heat and mass transfer, pressure drop as well as absorption and desorption reactions.
- The experimental scenarios have been defined by the specifications of the coupled system, as they are being considered as a baseline for the technical requirements of the storage tank.
- The feasibility of a tank with a combination of two different materials has been studied by means of simulation and lab-scale experiment. This included the evaluation of the basic concept with both materials in the same or in different tubes, as well as more detailed simulations of a final tank design.

The main results obtained in the frame of WP3 can be summarized as follow.

#### Task 3.1: Extension of existing model

In the extended model for the fluid-dynamic modelling, the intermetallic compound (MeH), LaNi<sub>4.3</sub>Al<sub>0.4</sub>Mn<sub>0.3</sub>, was coupled with the optimized 2LiNH<sub>2</sub> + 1.1MgH<sub>2</sub> + 0.1LiBH<sub>4</sub> + 3wt%ZrCoH<sub>3</sub> material (CxH). Thus, a model including the ability to combine two materials in one domain or in two adjacent domains has been developed. Regarding the material properties, the existing model parameters for LaNi<sub>5</sub> have been successfully adapted and extended. Furthermore, a table with physical and chemical properties of the Li-Mg-Amide has been generated, using e.g. kinetic measurements

performed in the reactor shown in Figure 11.

The parameters and equations used for both the MeH and the CxH material have been validated for absorption as well as desorption, and some of the results for the kinetic measurements are shown in Figure 12. Then, the validated model has been used for the simulation of different setups and geometries. Throughout the project, the model has been extended and improved based on new information from additional experiments in lab-scale.

#### Task 3.2: Sensitivity analysis and basic tank simulation

Two basic geometries for a cylindrical shaped tank have been implemented into the model. Furthermore, a set of initial and boundary conditions has been defined for absorption as well as desorption. Using these conditions, the simulation of the mixture of two materials (combination of MeH and CxH) showed an improved behaviour in comparison to a pure CxH reactor concerning absorption as well as desorption. Therefore, it has been decided to also study the combination of two materials experimentally. Using the results of these experiments, the model has been validated and the final tank geometry has been determined. As an example, Figure 13 shows the results of a simulation scenario for three different tank geometries, starting at 30 bar and releasing a constant amount of hydrogen that corresponds to a completely desorbed tank after 2h. From the results, it has been concluded that it is possible to use quite large diameters for tanks based on the combination of CxH and MeH, without losing overall performance. Finally, with the according experimental results of the prototype, the model has been validated again (see WP 4 and 5).

#### Task 3.3: Lab-scale testing of H<sub>2</sub> storage tank

Two different tanks in lab-scale have been built. The first tank enabled the direct mixture of the two materials in order to define the optimum ratio between CxH and MeH (see Figure 14). However, the experiment showed that this mixing lead to some solid state interactions of the materials destroying the fast rate of reaction of the intermetallic for absorption.

In order to avoid a direct powder contact, a second tank has been built with two separate compartments for the different powders (see Figure 14). The obtained results demonstrate the concept of this combination of materials since it is possible to reduce the loading time by at least 50 % and extend the duration of the desorption reaction at application relevant pressures (above 1.5 bar), see Figure 15.

#### Work packages 4: Fabrication and Testing of Prototype Tank

The main objective of this work package was to design and test a prototype tank having the capacity to supply hydrogen for a fuel cell system with a maximum power of 1 kWel:

- A study has been performed to identify suitable lightweight materials and production technologies for the operating range being envisaged for the storage tank.
- Based on results from WP3, a prototype tank has been designed and built.

The main results obtained in the frame of WP4 can be summarized as follow.

#### Task 4.1: Identification of Tank Materials and Production Technologies

A complete scenario of the existing standards for the tank's design has been obtained and a complete report on safety has been produced. For tank production, a detailed analysis of various materials to be used has been carried out.

#### Task 4.2: Large-scale production

An up-scaled amount of 3 kg material for the prototype tank was prepared on a Retsch PM400 planetary ball mill with 4 platforms for grinding milling vial (Figure 16).

The effect of milling conditions (e.g. milling time) has been carefully investigated. It turned out that, in order to obtain suitable properties, a milling time of 106 hours is necessary for large batches production. So, a total amount of about 3 kg of the selected mixture (see Figure 17) have been prepared accordingly and it was made available for the development of the tank to be used in the 1 kW system.

#### Task 4.3: Prototype Tank Design

For the tank design, some CFD simulations have been performed in order to verify the behaviour of the material inside of the tank. As an example, the results of simulation of transformed fraction as a function of time for different tank geometries are reported in Figure 18.

On the basis of the results of simulation, a detailed drawing of the tank has been prepared, as reported in Figure 19.

#### Task 4.4: Fabrication of Prototype Tank

A specific glove-box has been set-up for the fabrication of the tank. Special care was taken for welding technique under protected atmosphere (Figure 20).

Single tubes were firstly set-up and then assembled together, as shown in Figure 21.

The tank was successfully fabricated and the operative performances turned out in accordance with the calculations. So, the production procedure has been well settled and the operations done to keep the powder in inert atmosphere were suitable to maintain the required level of quality.

#### Task 4.5: Testing

A two-step testing has been performed using the prototype tank. First, a single tube of the 12 identical tubes has been integrated into the available testing setup (Figure 22).

The measurements showed that charging was possible in ~ 15 min and for the desorption, the fuel cell coupling relevant conditions could be reached. Then, the complete prototype including all 12 tubes has been tested in the testing setup. In this case, it was not possible to realize a fast fuelling due to limitations of the testing setup in the

laboratory. However, for the desorption conditions applied, a satisfying performance for desorption was proven. Furthermore, it was possible to show the fast charging for the complete prototype later in the integrated system.

#### Task 4.6: Validation of Simulation

The model developed in Task 3.1 has been validated using the different reactor scales. For absorption, the model validation has been mainly performed using the lab-scale reactor studied in Task 3.3. For desorption, the results of the single tube have been used, as in this case the accuracy of the measurements has been satisfactory. As an example, the results of experiments and simulations for hydrogen desorption at 170 °C are reported in Figure 23.

Concluding, it can be stated that the model was fully validated for absorption and desorption in lab-scale, as well as in the scale of a single prototype tube.

#### Work packages 5: Tank/FC integration (1 kWel)

The main goal of WP5 was the coupling of the prototype tank with a liquid cooled high temperature PEM fuel cell system. Activities have been performed according to the following:

- Analysis and specification of system and system components for a 1kW coupled system. Design and test of liquid cooled HT-PEM fuel cell.
- Development of a balance of plan (BoP) of system and system components for the 1kW system. Set-up of liquid cooled HT-PEM fuel cell and building of system for the 1kW APU. Development of control systems and softwares.
- Testing of the coupled system for APU application. Techno-economical evaluation of the coupled system.

The main results obtained in the frame of WP5 can be summarized as follow.

#### Task 5.1: Specification of System

A system analysis was carried out with the input from the various partners. Specifications of the SSH2S coupled system are reported below.

##### Specification of the 1kW demonstrator system

Operating time 2h

Total stored energy 5 kWh

FC efficiency 0.4

External dimensions of the tank about 6 l

Mass of material about 3 kg

H<sub>2</sub> storage capacity about 1400 NI

Maximum H<sub>2</sub> internal pressure about 70-100 bar

Maximum temperature about 150 – 200 °C

Maximum H<sub>2</sub> release pressure 1.5 bar

Minimum number of charge/discharge cycles about 20

H<sub>2</sub> volume exchanges for each cycle about 1120 NI

Supply of H<sub>2</sub> flow 20 NI/min

Minimum filling time (due to limitation of existing test setup) 2h

#### Task 5.2: System Layout and Adjustment of Fuel Cell System

The fuel cell stack for the system was designed and tested, as well as different components for the system were identified and tested (Figure 25). Both long term tests and performance test on stacks build were sufficient to integrate it in the final system and to deliver the required power and heat to the system.

#### Task 5.3: Build-up of FC and BoP Components

The demonstrator system on the basis of the specification was designed. Minor modifications were necessary, e.g. positioning of the liquid pump, a bypass for the hydride tank and additional inertization system using N<sub>2</sub> gas. Additional electric heaters at the end plates of the fuel cell stack were added. A heat exchanger that was included in the specification to preheat the cathode air was dropped to reduce size and heat capacity. The demonstrator system was mounted in a framework of standard aluminum profiles, so it can easily be transported (see Figure 26). The control unit and all the electrical content were located in a switching box, which was mounted in front of the system.

#### Task 5.4: Testing of Coupled Systems

Before the coupled system has been integrated into the LTV, the system has been tested. Different heating-up procedures have been studied, leading to the conclusion that for the prototype system, still a huge amount of heat was required for start-up. Therefore, for the final system, it has been suggested to integrate an additional pressure tank that can supply the fuel cell during start-up of the system. The hydride tank was then included only when the system was sufficiently heated. Furthermore, the tests showed that it was possible to couple the two components on the hydrogen as well as on the heat transfer fluid side and an operation for 2 h at 1 kW has been proven. For absorption, it was possible to modify the setup for faster charging and fuelling times of 15-20 min could be realized. A summary of properties of developed system is reported below.

##### Property Planned value Check

FC power: 1 kWel ok

Operating time: 2 h ok

Total stored energy: 5 kWh 150 g H<sub>2</sub>, ok

FC efficiency: 0.4 0.376

External dimensions of the tank (to be defined in details): about 6 l tubes only: 12 x Ø42mm x 700mm = 11.7l



outer dimension of tank: 480mm x 894mm x 210 = 118 l  
Mass of material: about 3 kg 3.4 kg MeH and 3.4 kg CxH  
H2 storage capacity: about 1400 NI ok  
Maximum H2 internal pressure: about 70-100 bar ok  
Maximum temperature: about 150-200 °C ok  
Maximum H2 release pressure: 1.5 bar ok  
Minimum number of charge/discharge cycles: about 20 (so far 10 cycles)  
H2 volume exchanges for each cycle: about 1120 NI ok  
Supply of H2 flow: 20 NI/min ok, but even more have been realized  
Minimum filling time (due to limitation of existing test setup): 2h ok, even 15 min

#### Task 5.5: Techno-economic Evaluation

Both a life cycle analysis (LCA) of the entire storage and an economic evaluation was performed. Both the LCA analysis and the collection of economic data for the entire system, showed that there is significant impact on the use of structural materials on the system costs and environmental impact. If the use of structural material would be reduced, this can have a big positive impact on the system.

A cost analysis was performed in order to provide an economic evaluation of the integrated system (1 kW), extending the results to a theoretical commercialization scenario of the developed system. The analysis results showed that storage tank's production is responsible of the major contribution to total cost, consisting of, approximately, half of it. The auxiliary system, FC and the hydrides materials contributes with decreasing shares (32%, 12% and 5% respectively). Summing all the contributions, for the 1 kW system a total cost of 9.239 € per APU was estimated. A scheme of cost distribution for 1 kW system is reported in Figure 28.

From the analysis of cost distribution, it turned out that there are two options to reduce the cost of the hydrogen storage system:

- 1) Reduce the pressure of the storage. This will reduce the steel needed for the pressurized container, and the welding efforts associated with the thick tubes.
- 2) Reduce the material cost of the hydride. The hydride cost is 806 Euro pr. Kg and 3,4 kg is needed for a 1 kW system. In total, more than 2400 Euro, compared to a total system cost of 9239 Euro, are necessary for the raw material for storage.

#### Work packages 6: Final User Test

The main objective of this work package was to demonstrate the application of the integrated system as Auxiliary Power Unit (APU) on a commercial truck. The APU powered auxiliary equipment on a special electric vehicle, acting as energy source when the engine is switched-off. Activities have been performed according to the following:

- Conceptual study and basic process design of APU. Design of the equipment and control system design.
- APU building and installation.
- APU testing and evaluation.

The main results obtained in the frame of WP6 can be summarized as follow.

#### Task 6.1 : Conceptual study and Basic process design package

This task allowed defining in detail the vehicle where the APU was installed, the required energy storage capacity and the operating and environmental parameters. The APU was installed on an IVECO Daily Electric, a commercial light-duty vehicle.

#### Task 6.2: Detailed design of the equipment

On the basis of the specifications defined in the previous task, the detailed design of the APU components was realized. In order to fulfil the safety aspects related to the use of flammable gas on a vehicle, a detailed analysis on the possible creation of "dangerous atmosphere" in the installation area was considered. All the components installed on the APU were selected taking into account the requirement to minimize the possibility of hydrogen leaks. Each component was designed and built or selected to fulfil the project specifications.

#### Task 6.3. Control system design

The APU is controlled and monitored by a rapid prototyping Electronic Central Unit (ECU) Compact RIO-NI. Moreover, the APU control unit reads the Refill logical signal when hydrogen tanks are connected to the refilling station and actuates the more appropriate logic functions to complete this task ensuring adequate safety conditions too. A scheme of control system is shown in Figure 29.

#### Task 6.4. APU building

The APU components were manufactured or procured. After the preliminary integration of components and functional tests performed in WP5, the APU was built. During the final integration of components, the consortium decided to add a compressed hydrogen buffer tank to improve the start-up procedure. Figure 30 shows the final APU before the installation on vehicle and the gaseous buffer tank.

#### Task 6.5. APU installation

The APU was installed on a Iveco Daily Electric, with two batteries module of 40Ah capacity, 278 Volt of total voltage and 60 kW of maximum power. Figure 31 shows the APU installed on load area of the vehicle. The APU was presented and a demonstration test was done at the SSH2S final event in Torino the 25th June 2014.

#### Task 6.6. Testing and techno-economical evaluation

The APU was tested on vehicle under realistic working conditions to check its compliance with requirements and its performances. The performance of the APU were measured on a real road scenario, which was coherently defined with the urban characteristics of the vehicle Iveco Daily used for the application's development. In order to test the APU on road missions a "Low power urban cycle" and a "High power urban cycle" have been defined. The main difference between two cycles was the average electrical power required. The main outcome of this analysis is that an important part of the electric power produced by the fuel cell is used by the auxiliary components, as shown in Figure 32. For this reason, considering an optimization of the system for a future commercialization, additional work is required to improve the electric balance of the APU. This drawback will be mitigated scaling the APU to 5 kW output power, since some auxiliary components would remain the same used on the 1 kW prototype and their relative parasitic power absorption would be less important.

Economic analysis showed that storage tank's production is responsible of the major contribution to total cost, consisting of, approximately, half of it. The auxiliary components, fuel cell stack and the hydrides materials contribute with decreasing shares (32%, 12% and 5% respectively).

On the basis of the data collected with the developed prototype, a simulation of a 5 kW system has been performed. The lay out of the system would be a little bit different from the prototype. The changing is due to the maximum pressure allowed on the stack of 5 kW, that is limited to 200 mbar; the new system has been considered to have the heating/cooling circuit of the fuel cell (primary circuit) separated from the heating/cooling circuit of the hydrogen tank (secondary circuit).

#### Potential Impact:

Conclusions and potential impacts, including the socio-economic impact and the wider societal implications of the project

- A material for a solid state hydrogen tank with capacities of up to 4.5 H<sub>2</sub> wt%, fully reversible at 160-180 °C and with high stability on cycling has never been developed in previous European Projects. New concepts on the design and the coupling of solid state hydrogen tank with HT-PEM fuel cells represent a significant achievement of the project.
- The development of a APU prototype 1 kW integrated system is real advances in the field of solid state hydrogen storage.
- The results of the project may be of significant economic impact for large industries, as well as for SMEs' industrial partners. The possibility of coupling the HTPEM with a compact and safe hydrogen storage system will possibly increase business opportunities for SER and TD partners.
- The availability of safe hydrogen tanks at low pressures is expected to contribute to the social acceptance of hydrogen technologies.

#### Exploitation of results

- A general advancement of knowledge has been reached by the project, which will allow possible exploitations of the results.
- The development of catalyzed reversible MgH<sub>2</sub>/LiNH<sub>2</sub> composite to be applied for H storage tank applications with HT-PEMFC will open new possibility for applications of materials for solid state hydrogen storage.
- The combination of complex hydride with metal hydride for H storage tank applications opened new strategies for solid state hydrogen storage.
- The development of liquid cooled HTPEM fuel cell will allow further development for this particular class of fuel cells.
- The coupling of liquid cooled HTPEM to hydride tank will allow to explore new applications for this system for hydrogen storage.
- The development of APU based on HT-PEM FC and solid state H storage tank will allow the introduction into the marked of new environmental friendly devices.

#### Main dissemination activities

##### Training and education

2 PhD student and 6 PostDocs involved in the project, plus other students

##### Safety, Regulations, codes and standards

Safety assessment for the integrated system performed

##### Dissemination

##### Conference presentations

##### Talks:

1. "Hydrogen Storage in Complex Hydrides – Experimental Results and Validation by a Lab-Scale Tank", Utz I., Schmidt N., Linder M. und Wörner A. 8th European Congress of Chemical Engineering, Sept 25-28, 2011, Berlin (Germany).
2. M.Baricco, Task 22 meetings of the IEA-HIA, Hidelberg (Germany), May 6th-10th, 2012.
3. B.C. Hauback, Task 22 meetings of the IEA-HIA, , Heidelberg (Germany), May 6th-10th, 2012.
4. M. Fichtner, Task 22 meetings of the IEA-HIA, , Heidelberg (Germany), May 6th-10th, 2012.
5. "Storage Tank Concept with improved Dynamics for Complex Hydrides", I.Utz, M.Linder, A.Wörner, WHEC 2012, Toronto, Jun. 2012.
6. "Synthesis, crystal structure and properties of novel borohydrides", B.C. Hauback, S. Deledda, J.E. Fonnelløp, C. Frommen, S. Hino, I. Llamas-Jansa, J.E. Olsen, M.H. Sørby, International Symposium on Metal-Hydrogen Systems, Kyoto,

Japan, October 2012. Invited talk.

7. "Influence of transition metal oxides on  $\text{Mg}(\text{BH}_4)_2$ ", Saldan, I. Jansa Llamas, G. Kalantzopoulos, S. Hino, C. Frommen, and B. C. Hauback, Materials for Hydrogen Storage – Future Perspectives?, Hurtigruten (Norway) June 14th-18th, 2012.
8. "CALPHAD for Hydrogen Storage Materials", E.Pinatel, M.Palumbo, M. Baricco, Materials for Hydrogen Storage: Future Perspectives?, Hurtigruten (Norway) June 14th-18th, 2012.
9. "Hydrogen storage in complex hydrides", M. Baricco, invited talk at ISMANAM 2012, Moscow, June 18th-22nd, 2012.
10. "Metastability in Hydrogen Storage Materials", M.Baricco, 5th Latin American Conference on Metastable and Nanostructured Materials, São Carlo (Brasil) Sept. 2012.
11. "Theoretical And Experimental Study On  $\text{Mg}(\text{BH}_4)_2\text{-Zn}(\text{BH}_4)_2$  Mixed Borohydrides", E.Albanese, G.N.Kalantzopoulos, J.G.Vitillo, E.Pinatel, B.Civalleri, S.Deledda, S.Bordiga, B.C.Hauback, M.Baricco, MH2012, Kyoto (Japan), Oct. 2012.
12. "New  $\text{H}_2$  storage tank concept for complex hydrides", I.Utz, M.Linder, A. Wörnder, 7th International Symposium Hydrogen & Energy, Stoos, Switzerland, January 21st-25th, 2013.
13. "From theory to experimental study and synthesis optimization of magnesium and zinc mixed borohydrides", G.Kalantzopoulos, E.Albanese, J.G.Vitillo, E.Pinatel, B.Civalleri, S.Deledda, R. H. Heyn, S.Bordiga, M.Baricco and B.C.Hauback, 7th International Symposium Hydrogen & Energy, Stoos, Switzerland, January 21st-25th, 2013.
14. "Experimental and Simulated Results for a New Tank Concept for Complex Hydrides" I.Bürger, M. Linder, L. Komogowski, A. Wörner, 2nd international Conference on Materials for Energy, 12.-16. May 2013, Karlsruhe, (Germany).
15. "Ab-Initio Modelling of Metal Borohydrides as Hydrogen Storage Materials", B. Civalleri, E. Albanese, M. Corno, P. Ugliengo, M. Baricco, EUROMAT2013, European Congress and Exhibition on Advanced Materials and Processes, 8-13 Sept. 2013, Sevilla, Spain.
16. "SSH2S presentation", M.Baricco, FCH JU projects on hydrogen storage Joint Workshop, October 2nd, 2013, Santa Cruz, Tenerife, Spain.
17. "Materials and "combo concept"", M. Linder, FCH JU projects on hydrogen storage Joint Workshop, October 2nd, 2013, Santa Cruz, Tenerife, Spain.
18. "Hydrogen tank and system applications", M. Sgroi, FCH JU projects on hydrogen storage Joint Workshop, October 2nd, 2013, Santa Cruz, Tenerife, Spain.
19. "Experimental and simulated results for the desorption process in a complex hydride hydrogen storage reactor with addition of metal hydride" I.Bürger, Ch. Brack, M. Linder European Hydrogen Energy Conference, 12.-14.Mar. 2014, Sevilla, (Spain).
20. "Materials for Hydrogen Storage", M.Baricco, Invited talk at University of Sofia "St. Kl. Ohridski", May 20th, 2014, Sofia (Bulgaria).
21. "SSH2S presentation", M.Baricco, Joint Workshop of FCH JU projects on Fuel Cell based Auxiliary Power Units June 25th-26th, 2014 Turin (Italy).
22. "Materials and "combo concept"", M.Linder, Joint Workshop of FCH JU projects on Fuel Cell based Auxiliary Power Units June 25th-26th, 2014 Turin (Italy).
23. "Hydrogen tank and system applications", M.Sgroi, Joint Workshop of FCH JU projects on Fuel Cell based Auxiliary Power Units June 25th-26th, 2014 Turin (Italy).
24. "Optimization of the hydrogen storage process in a combined complex/metal hydrides storage system "M.Bhourri, I. Bürger, M.Linder, 15.-20- Jun 2014, Gwangju, (South Korea).
25. "Hydrogen Storage in Metal Hydrides and Complex Hydrides: Differences, Challenges and Advantages" I.Bürger, Ch. Brack, M. Linder, Metal Hydrides, 20.-25. Jul. 2014, Manchester (Great Britain).
26. "Hydrogen Storage in Metal Hydrides and Complex Hydrides: Differences, Challenges and Advantages" I.Bürger, Ch. Brack, M. Linder, MH2014 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and applications, 20.-25. Jul. 2014, Manchester (Great Britain).
27. "Thermodynamics of Borohydrides-based Materials Coupling ab-initioand Calphad Methods", E.R.Pinatel, E.Albanese, B.Civalleri, M.Baricco, MH2014 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and applications, 20.-25. Jul. 2014, Manchester (Great Britain).
28. "Solid State Hydrogen Tank coupled with High Temperature PEM: from materials to APU application", M.Baricco, M.Fichtner, B.Hauback, M.Linder, C.Luetto, M.Bang, M.Sgroi, P.Moretto, Invited talk at MH2014 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and applications, 20.-25. Jul. 2014, Manchester (Great Britain).
29. "Integrated System Of Fuel Cell And Hydride Tank", P.Rizzi, E.Pinatel, C.Luetto, P.Florian, A.Graizzaro, S.Gagliano, M.Baricco, MH2014 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and applications, 20.-25. Jul. 2014, Manchester (Great Britain).
30. "Composti intermetallici per immagazzinamento di idrogeno", M.Baricco, P.Rizzi, E. Pinatel, E.Marano, N.Belmonte, 35° Italian Metallurgical Association, 5-7 Nov. 2014, Rome, Italy.
31. "Materiali metallici per l'immagazzinamento di idrogeno", M.Baricco, P.Rizzi, A.Castellero, E.Pinatel, E.Marano, N.Belmonte, XII National Meeting AIMAT, 21-24 Sept. 2014, Lecce, Italy.

#### Posters:

1. "Mg/Zn Mixed-Metal Borohydride for hydrogen storage: ab-initio periodic computational study of the phase stability and decomposition", E. Albanese, B. Civalleri, Divisione di chimica teorica e computazionale of Società Chimica Italiana (DCTC12) Pisa (Italy), February 22-23, 2012.
2. "Mg/Zn Mixed-Metal Borohydride for hydrogen storage: ab-initio periodic computational study of the phase stability and decomposition", B. Civalleri, E. Albanese, E. Pinatel, M. Baricco, 27th European Crystallographic Meeting, Bergen (Norway), August 6-11, 2012.
3. "Wasserstoffspeicherung in Hydriden: Simulationen für das Reaktordesign eines Speichers mit Kombination aus Metallhydrid und komplexem Hydrid", I.Utz, M.Linder, A. Wörner, Jahrestagung Reaktionstechnik, Würzburg (Germany), May 2012.
4. "Thermodynamics of hydrogen sorption in  $2\text{LiNH}_2+\text{MgH}_2$  system", E. R. Pinatel, D. Chandra, M. Baricco, Calphad XLI,



Berkley (USA), June 2012.

5. "Destabilization Effect of Transition Metal Fluorides on Sodium Borohydride", G.N.Kalantzopoulos, M.N.Guzik, H.R.Heyn, S.Deledda, B.C.Hauback, MH 2012, 21-26th October 2012, Kyoto, Japan.
  6. "New Reactor Concept for Complex Hydrides based on Addition of Conventional Metal Hydrides" Bürger, Inga und Komogowski, Lars und Linder, Marc und Wörner, Antje, Gordon Research Conference on Hydrogen - Metal Systems, 14.-19. Jul. 2013, Toscana, Italy.
  7. "Ab-Initio Modelling of Metal Borohydrides as Hydrogen Storage Materials", B. Civalieri, E. Albanese, M. Corno, P.Ugliengo, M. Baricco, XLI Congresso Nazionale di Chimica Fisica, June 23-27, 2013, Alessandria, Italy.
  8. "Ab-initio modelling of metal borohydrides as hydrogen storage materials", E. Albanese, B. Civalieri, M. Baricco, Gordon Research Conference on Hydrogen - Metal Systems, 14.-19. Jul. 2013, Toscana, Italy.
  9. "HT-PEM fuel cell pre-heater based on metal hydrides", C. Brack, I. Bürger, M. Linder, FCH JU projects on hydrogen storage Joint Workshop, October 2nd, 2013, Santa Cruz, Tenerife, Spain.
  10. "New Reactor Concept for Complex Hydrides", I. Bürger, L. Komogowski, M. Linder, A. Wörner, FCH JU projects on hydrogen storage Joint Workshop, October 2nd, 2013, Santa Cruz, Tenerife, Spain.
  11. "Quality and safety management for up-scaled amount of amide-based hydrogen storage materials", J. Hu, M. Fichtner, M. Baricco, FCH JU projects on hydrogen storage Joint Workshop, October 2nd, 2013, Santa Cruz, Tenerife, Spain.
  12. "Study of the direct mixtures of Amide-based composite material with LaNi<sub>5</sub>-type compound and graphite", G. N. Kalantzopoulos, M. N. Guzik, S. Deledda, B. C. Hauback, FCH JU projects on hydrogen storage Joint Workshop, October 2nd, 2013, Santa Cruz, Tenerife, Spain.
  13. "Role of additives in hydrogen sorption on LiNH<sub>2</sub>-MgH<sub>2</sub> system", J. G. Vitillo, J. Hu, F. Dolci, A. Masala, S. Bordiga, P. Moretto, M. Fichtner, M. Baricco, FCH JU projects on hydrogen storage Joint Workshop, October 2nd, 2013, Santa Cruz, Tenerife, Spain.
- Workshops organized by the project
1. Joint Workshop on Solid State Hydrogen Storage, October, 2nd, 2013, Tenerife, Spain.
  2. Joint Workshop on Fuel Cell based APU, June, 25th. 26th, 2014, Turin, Italy.

#### Publications

1. J. Hu, A. Pohl, S. Wang, J. Rothe, M. Fichtner "Additive Effects of LiBH<sub>4</sub> and ZrCoH<sub>3</sub> on the Hydrogen Sorption of the Li-Mg-N-H Hydrogen Storage System", J. Phys. Chem C 116 (2012) 20246
2. E. Albanese, G.N.Kalantzopoulos, J.G.Vitillo, E.Pinatel, B.Civalieri, S.Deledda, S.Bordiga, B.C.Hauback, M.Baricco, "Theoretical and experimental study on Mg(BH<sub>4</sub>)<sub>2</sub>-Zn(BH<sub>4</sub>)<sub>2</sub> mixed borohydrides", JALCOM 580 (SUPPL1) (2013), pp. S282-S286
3. U. Ulmer, J. Hu, M. Franzreb, M. Fichtner, "Preparation, scale-up and testing of nanoscale, doped amide systems for hydrogen storage" Int. J. Hydr. Energy 38 (2013) 1439-1449
4. G.N.Kalantzopoulos, J.G.Vitillo, E.Albanese, E.Pinatel, B.Civalieri, S.Deledda, S.Bordiga, M.Baricco and B.C.Hauback, "Hydrogen storage of Mg-Zn Mixed Metal Borohydrides", J. Alloys. Compd. 615 (2014) S702-S705
5. I.Bürger, J.J. Hu, J.G. Vitillo, G.N. Kalantzopoulos, S. Deledda, M. Fichtner, M. Baricco, M. Linder, "Material properties and empirical rate equations for hydrogen sorption reactions in 2 LiNH<sub>2</sub>-1.1 MgH<sub>2</sub>-0.1 LiBH<sub>4</sub>-3 wt.% ZrCoH<sub>3</sub>", Int. J. Hydr. Energy 39 (2014) 8283-8292
6. I.Bürger, C. Luetto, M. Linder, "Advanced reactor concept for complex hydrides: Hydrogen desorption at fuel cell relevant boundary conditions", Int. J. Hydr. Energy 39 (2014) 7346-7355
7. I.Bürger, L. Komogowski, M. Linder, "Advanced reactor concept for complex hydrides: Hydrogen absorption from room temperature", Int. J. Hydr. Energy 39 (2014) 7030-7041
8. J. Hu, R. Witter, H. Shao, M. Felderhoff, M. Fichtner, "Beneficial effects of stoichiometry and nanostructure for a LiBH<sub>4</sub>-MgH<sub>2</sub> hydrogen storage system", J. Mater. Chem. A (2014) 66-72.
9. I.Bürger I., M.Bhouri, M. Linder, "Considerations on the H<sub>2</sub> desorption process for a combination reactor based on metal and complex hydrides", Int. J. Hydrogen Energy 40 (2015) 7072-7082.
10. M.Bhouri, I.Bürger, M.Linder, "Numerical investigation of hydrogen charging performance for a combination reactor with embedded metal hydride and coolant tubes", Int. J. Hydrogen Energy 40 (2015) 6626-6638.
11. M.Bhouri, I.Bürger, M.Linder, "Optimization of hydrogen charging process parameters for an advanced complex hydride reactor concept", Int. J. Hydrogen Energy, 39 (2014) 17726-17739.
12. E.Albanese, B.Civalieri, S.Casassa, M.Baricco, "Investigation on the decomposition enthalpy of novel mixed Mg(1-x)Zn<sub>x</sub>(BH<sub>4</sub>)<sub>2</sub> borohydrides by means of periodic DFT calculations", Journal of Physical Chemistry C, 118 (2014) 23468-23475.
13. E.R. Pinatel, E. Albanese, B. Civalieri, M. Baricco, "Thermodynamic modelling of Mg(BH<sub>4</sub>)<sub>2</sub>" Journal of Alloys and Compounds, In Press.

#### Patents

1. Application from DLR. Patent DE102012100875A1: Verfahren zur Speicherung von Wasserstoff und Wasserstoffspeichervorrichtung, I.Utz, M. Linder

#### List of Websites:

General information, public website and relevant contact details

#### Full project title

Fuel Cell Coupled Solid State Hydrogen Storage Tank

#### Project acronym

SSH2S

Call topic

SP1-JTI-FCH.2009.2.4 Improved solid state hydrogen storage systems

FCH JU Grant agreement number

256653

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Project start-date

01/02/2011

Project end-date

31/03/2015

Partners

1. Università di Torino Research Italy
2. Institute for Energy Technology Research Norway
3. Karlsruhe Institute of Technology Research Germany
4. Deutsches Zentrum für Luft- und Raumfahrt e.V. Research Germany
5. Tecnodelta s.r.l. Industry, SME Italy
6. Serenergy A/S Industry, SME Denmark
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### Publications

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