

ATTAINING DOE HYDROGEN STORAGE GOALS WITH CHEMICAL HYDRIDES

M. Klanchar¹, T. G. Hughes², and P. Gruber³

1. Introduction

The Applied Research Laboratory (ARL) of The Pennsylvania State University is developing an energy system concept that uses chemical hydride hydrogen storage to meet DOE's long-term storage goals in transportation applications. This concept draws on energy technologies that have been researched for the U.S. Navy as part of our mission to develop compact and energy dense underwater power sources. It includes application of our chemical hydrogen generator technology, which produces hydrogen gas through hydroreactive and decomposition reactions of chemical hydrides. [1-4] This energy system concept also incorporates the exchange of heat and mass byproducts between the energy convertor and hydrogen generator to increase system performance. Besides meeting DOE storage goals, this energy system aspires to allow a refueling process that is analogous to today's stop at a gasoline station in terms of convenience, cost and safety.

2. Energy System Concept

Our generic energy system concept that incorporates chemical hydride hydrogen storage is illustrated in Figure 1. The leading design consideration of this system is to meet or exceed the "Grand Challenge" goals [5] for hydrogen storage in DOE's Hydrogen Fuel Initiative and FreedomCAR programs. This technical approach results in the selection of base materials that have a high enough hydrogen storage potential to allow for the inclusion of necessary supporting hardware and auxiliaries in resulting systems. The concept intends to optimize the performance of the onboard hydride processor through the use of energy convertor byproducts and to develop efficient, economical off-board reprocessor and refueling concepts. This approach combines technology that has the potential to improve hydrogen yields, with first-order system analyses that identify critical technical issues for hydride processors, product reprocessors, and hydride feed systems for fuel cell and combustion engine convertors. Results of this analysis will provide valuable insights into the raw potential of chemical hydride systems to produce hydrogen and into the overall performance that can be achieved when these chemical hydride systems are coupled with candidate convertors in practical power systems.

There are four fundamental tenets associated with the generic technical concept illustrated in Figure 1.

¹ Research Associate,

² Head, ESPS Division

³ Senior Research Associate, all from the Applied Research Laboratory, The Pennsylvania State University, P.O. Box 30, State College, PA 16804

1. That the source chemical hydrides can be delivered to the on-board storage tank in their near-solid storage densities.
2. That water and other products of the convertor will be available to the hydride processor to maximize its efficiency.
3. That the products can be collected in a form that will permit easy transfer to the off-board reprocessor station at the time of refueling.
4. That the resulting products can be economically returned to source metal hydrides at the off-board station.

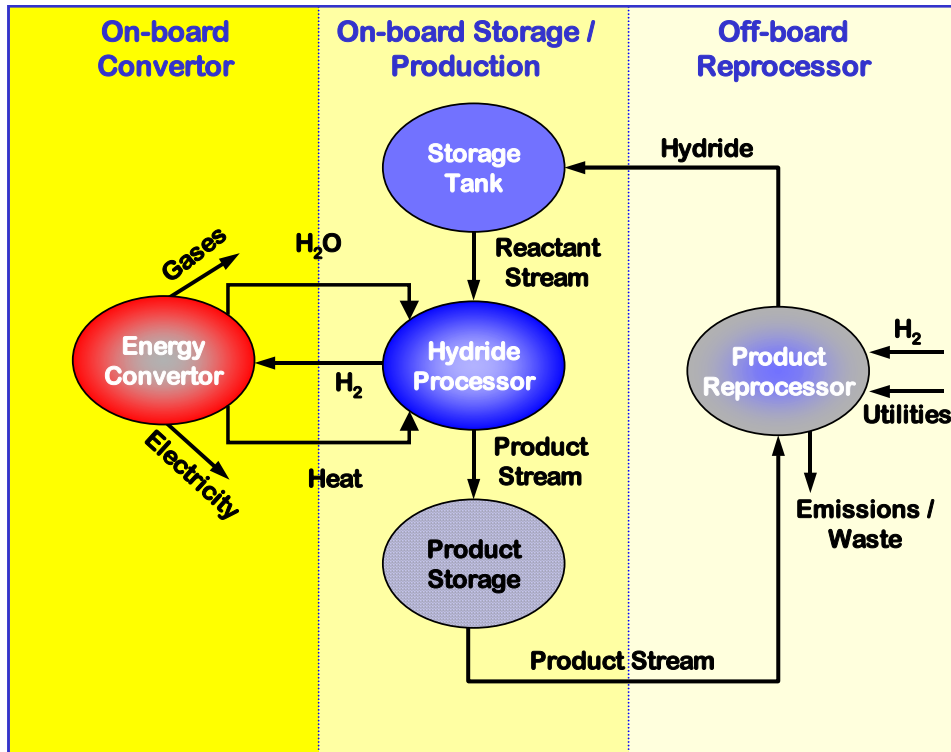


Figure 1. Energy System Concept Using Chemical Hydride Hydrogen Storage

2.1 Candidate Chemical Hydrides

Table 1 shows the primary reaction equation and associated hydrogen storage properties of some well-known chemical hydride materials, including lithium hydride, LiH; sodium hydride, NaH; calcium hydride, CaH₂; magnesium hydride, MgH₂; lithium aluminum hydride, LiAlH₄; titanium hydride, TiH₂; lithium borohydride, LiBH₄; and sodium borohydride, NaBH₄. The physical, chemical and safety properties of these reactants and products suggest that they could be used in a complete hydride-based storage system.

Typically, hydrogen can be generated from chemical hydrides via two mechanisms: through a direct reaction with water or through thermal decomposition. While both mechanisms are possible for most materials, only one

is likely to be practical for this system concept. Thus, LiH, NaH, CaH₂, LiAlH₄, LiBH₄, and NaBH₄ were assumed to react with water, while MgH₂ and TiH₂ were considered to undergo thermal decomposition. The water reactions also assumed low-to-moderate temperatures, which results in hydroxides being formed rather than oxides as predicted by standard chemical equilibrium analyses used at ARL. [6] As will be shown later, however, elevating the reaction temperature will produce metal oxide products rather than hydroxides in some cases (e.g., Li₂O rather than LiOH), which in turn could decrease reprocessor energy needs.

Table 1. Candidate Hydride Reactions and Hydrogen Storage Properties

Hydride and Reaction	Fraction H	H ₂ Specific Mass (kg H ₂ /kg)	H ₂ Density (kg H ₂ /liter)
$LiH + H_2O \rightarrow LiOH + H_2$	0.126	0.252	0.122
$NaH + H_2O \rightarrow NaOH + H_2$	0.042	0.083	0.106
$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$	0.048	0.095	0.121
$MgH_2 \rightarrow Mg + H_2$	0.076	0.076	0.110
$LiAlH_4 + H_2O \rightarrow LiOH + Al + 2.5 H_2$	0.105	0.132	0.121
$TiH_2 \rightarrow Ti + H_2$	0.040	0.040	0.152
$LiBH_4 + H_2O \rightarrow LiOH + HBO_2 + 4H_2$	0.184	0.367	0.235
$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$	0.105	0.211	0.226
Millennium Cell 35% Solution $NaBH_4 + 4H_2O \rightarrow NaBO_2 + 4H_2 + 2H_2O$		0.077	0.077

The hydrogen storage properties listed in Table 1 include:

- *Fraction H*, which is the number of hydrogen atoms in the hydride divided by the molecular weight of the hydride.
- *Hydrogen specific mass*, defined as the mass (kg) of H₂ produced per mass of original hydride material or solid product, whichever is larger (kg H₂/kg material).
- *Hydrogen density*, determined from the mass of hydrogen produced per volume of hydride or solid product, whichever is larger (kg H₂/liter).

Since the energy convertor will supply reactant water, almost all of the storage property listings (specific mass and density) exclude the volume of water. The only exception is the last reaction, which describes Millennium Cell's Hydrogen on Demand System™. [7] This process uses an aqueous solution containing 35 wt% NaBH₄ and liberates hydrogen when it comes into contact with a catalyst.

Figure 2 compares the hydrogen storage potential of the leading chemical hydride reactions and also includes data from more conventional storage systems such as 5000 psi gas, cryogenic liquid, and metal (reversible) hydrides. The lithium-containing hydrides of LiH, LiAlH₄, and LiBH₄ rate especially well and represent a class of materials that can exceed the 2015 DOE storage targets based on reaction chemistry. More importantly, these hydrides have sufficient hydrogen storage potential to allow for the inclusion of necessary supporting hardware, while still meeting DOE goals. Note that conventional storage methods are not capable of meeting 2015 goals, regardless of storage equipment or conditions. A key objective of this effort, therefore, will be to develop a compact hydride processor that maintains system storage density above DOE targets.

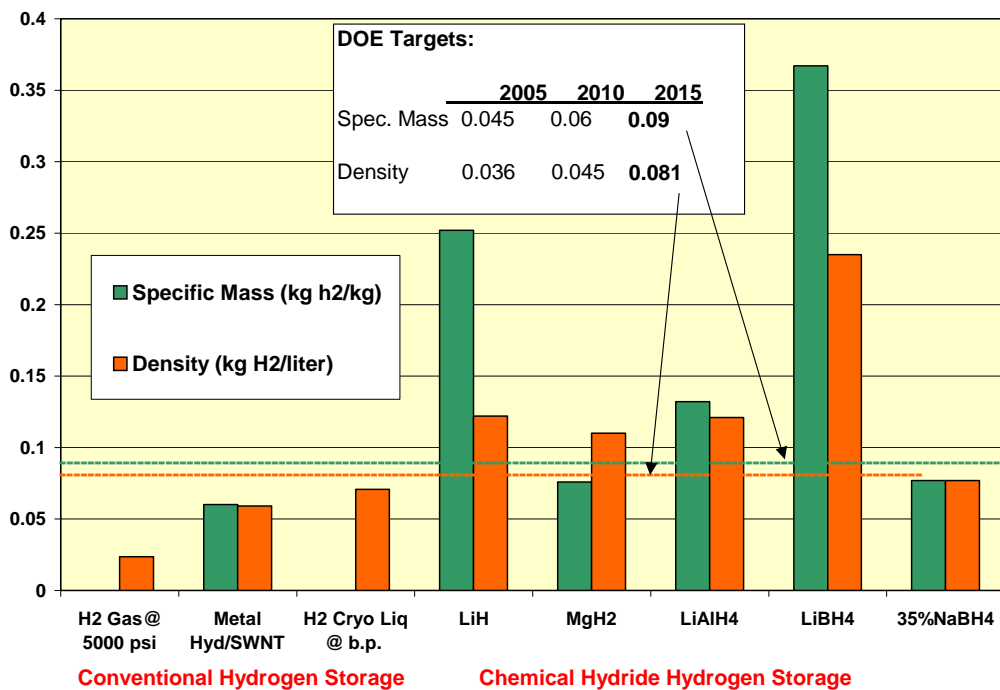


Figure 2. Comparison of Hydrogen Storage Properties

We have worked with LiH, LiAlH₄, and LiBH₄ in the past, and they represent our choice for hydride processor reactants. Other candidate chemical hydrides, including aqueous NaBH₄ and MgH₂, are also being pursued [8,9] and are perhaps better known, but we believe the lithium-based hydrides have the potential to perform as well if not better.

2.2 Hydride Processor Technology

Based on our work with underwater power systems, we envision that the chemical hydride could be transferred to the vehicle in particles or pellets in a fluidized stream or via a mechanical device such as an auger. Using mixed-size particles allows nearly solid storage densities to be achieved in the vehicle tank. Fluidization could be achieved with a carrier gas provided by the off-board

processor. The storage tank could be subsequently refilled from any depth of discharge. Alternately, solid hydride could be inserted into the storage tank in discrete, preformed solid blocks. This would allow for incremental partial refills of the storage tank. The two different hydride storage states, powder/pellets or solid blocks, would also affect the design of the hydride processor.

A representative powder feed system that we developed for delivering bulk quantities of aluminum and magnesium powders is shown in Figure 3. This piston-driven, dense phase fluidizer design [10,11] represents one example of powder-handling technology that could deliver pure chemical hydride powder to the hydride processor. It could also be applied to other parts of the concept that require transfer of solids.

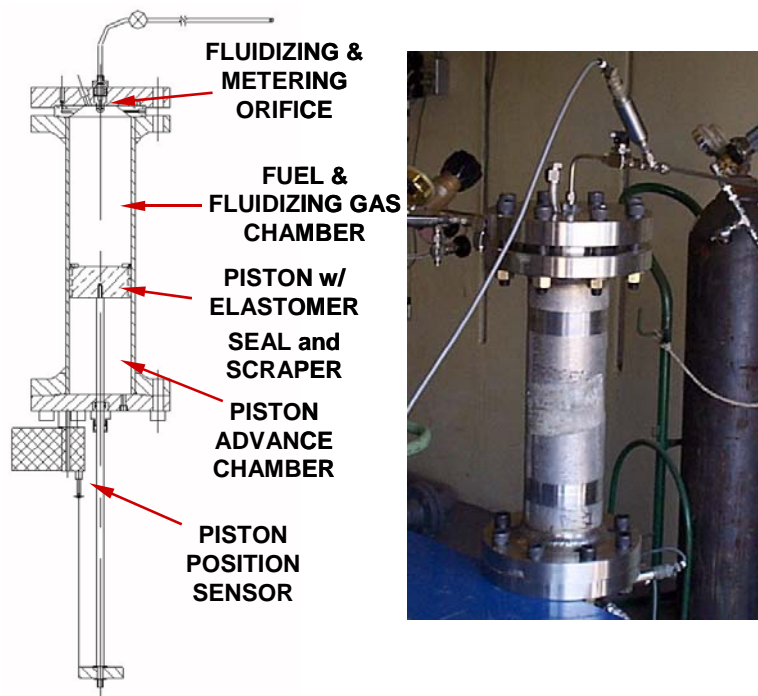


Figure 3. Example of a Powder Feed System

An important aspect of this energy concept is that it uses water and other products of the convertor to efficiently turn the hydride stream into hydrogen and reaction products. We have worked with both batch reactors and steady flow reactors, and both approaches are currently being considered. Steady flow reactors have been generally more efficient and controllable, while batch reactors have been simpler. There is the possibility that a batch reactor could be integrated with the storage tank. Incorporated into the hydride processor is a separation system, which separates hydrogen and other carrier gases from liquid or solid oxide/hydroxide products. Our experience suggests this can be accomplished with a continuous-operation cyclone separator [12], with perhaps a finer filtering element/membrane downstream.

Figure 4 outlines three generalized hydride processor designs for generating hydrogen. We have developed and tested prototype versions of the first two (batch and continuous flow reactors), as exhibited in Figures 5 and 6. These reactors have been tested with hydrosensitive materials that include pure lithium, magnesium and aluminum metals, and LiH, LiAlH₄, LiBH₄ and MgH₂ hydrides, in quantities ranging from 10g to 30kg.

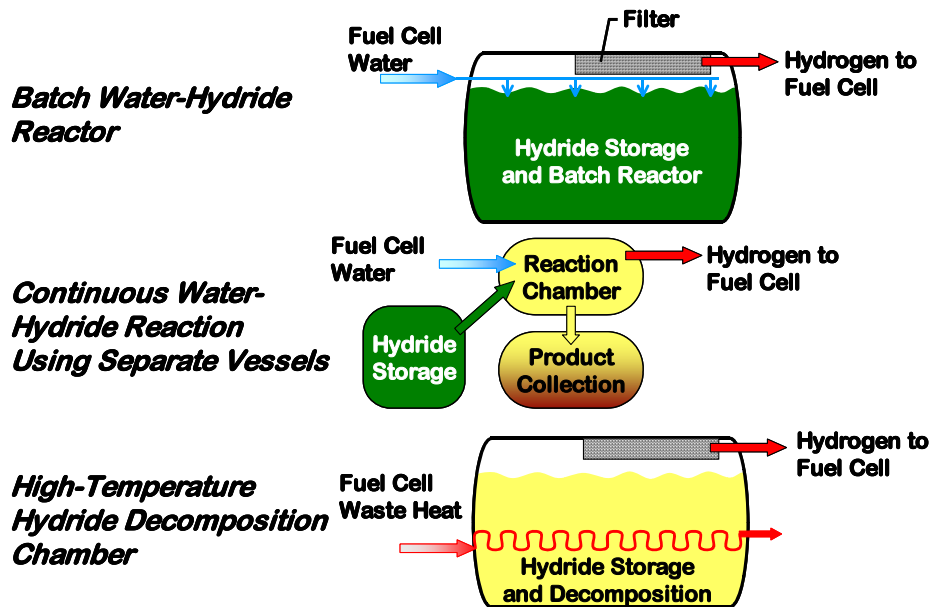


Figure 4. Hydride Processor Designs

2.3 Energy Convertor Integration

Key to our energy concept approach is the use of convertor byproducts to enhance system efficiency. The value of using product water is obvious. Less obvious are the potential advantages associated with using waste heat, product gases, and electricity to enhance the operation of the hydride processor. Different convertors produce different quantities of waste heat at different temperatures, just as different hydride processors will require different quantities of heat at different temperatures for optimum performance. Where these devices naturally complement each other, optimum systems will result, and this effort seeks to identify and analyze such systems. For instance, a convertor that discharged its waste heat as steam at elevated temperatures and flow rates (such as in a solid oxide fuel cell) might enhance certain hydrosensitive reaction processes to produce better hydrogen yield or power the decomposition reaction as depicted in the third processor of Figure 4.

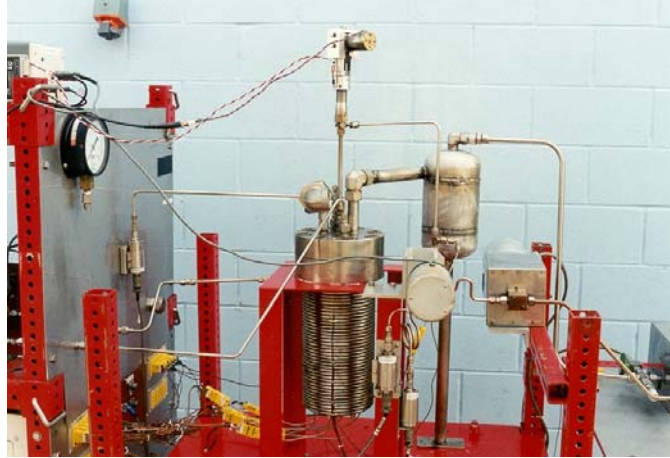


Figure 5. LiH-Steam Batch Reactor

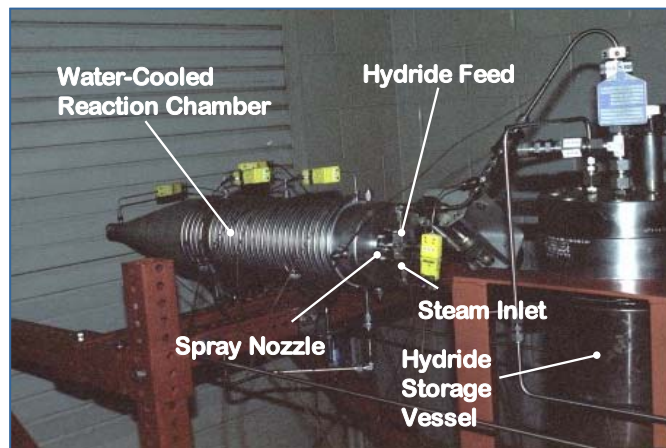


Figure 6. Continuous Flow Hydride Reactor

2.4 Reprocessor Technology

Our technical concept and experience suggest that the hydride processor can produce reaction products in a variety of states for product storage. The hydride processor might be configured to produce solid pellets from droplets or a water-based solution, depending on the hydride and process used. Ideally, however, the reaction products will be water-free. The presence of water in an oxide or hydroxide product will most likely represent greater energy use in reprocessing the material back to the original hydrides (product reprocessor). At the expense of some compressing power, atmospheric air could be used as both a coolant and fluidizing carrier for delivering those pellets to the storage tank in a manner similar to that of the powder feed system in Figure 3.

The concept envisions that the product stream will be off-loaded to the off-board reprocessor at the same time that hydride source material is on-loaded. The concept also envisions optimizing the product stream and reprocessor process together. Reprocessor designs are being investigated that use standard utilities

and hydrogen gas in minimum quantities and which produce a minimal or negligible stream of environmentally acceptable emissions and waste.

Reprocessing chemistries, that is, converting hydride processor products back to the original hydride, are certainly well known. But a critical issue associated with this component will be reprocessing cost. To be competitive with conventional hydrogen sources (methane steam reforming, electrolysis), it is estimated that product reprocessor costs must be on the order of \$1 to \$2/kg hydride. Minimizing reprocessor costs will take on greater importance as the system evolves.

As an example of the importance of this issue, Table 2 outlines a standard multi-step procedure for converting LiOH product back to LiH. Besides its complexity, this particular process requires 88% of the energy that can ultimately be generated from the stored hydrogen. This method obviously would not be cost-effective; thus, more efficient chemistries and processes need to be identified. Note that for this particular example, significant energy savings could be realized if dry Li₂O product was delivered to the reprocessor rather than hydrated LiOH.

3. Vision

Ultimately, our concept leads to hydrogen-powered vehicles that require an analogous refueling process to today's visit to the gas station. As envisioned in Figure 7, our vehicles would have an on-board hydride processor and energy convertor, and we would attach a nozzle to add chemical hydride material and remove accumulated hydride processor product. The "refueling station" would then reprocess the collected products or transfer them to a centralized reprocessing plant, designed to produce acceptable emissions and waste.

Table 2. An Energy Balance Example of Reprocessing Hydrides

Energy to Recycle LiH....	
$\text{LiOH}\cdot\text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2\text{O}$	+ 57 – 61 kJ
$\text{LiOH} \rightarrow \frac{1}{2} \text{Li}_2\text{O} + \frac{1}{2} \text{H}_2\text{O}$	+65 kJ
$\frac{1}{2} \text{Li}_2\text{O} + \frac{1}{2} \text{H}_2 \rightarrow \text{Li} + \frac{1}{2} \text{H}_2\text{O}$	+178 kJ*
$\text{Li} + \frac{1}{2} \text{H}_2 \rightarrow \text{LiH}$	-91 kJ
Net:	Net:
$\text{LiOH}\cdot\text{H}_2\text{O} + \text{H}_2 \rightarrow \text{LiH} + 2\text{H}_2\text{O}$	+ 213 kJ (Endothermic)
Theoretical Energy from Stored Hydrogen...	
$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	- 242 kJ

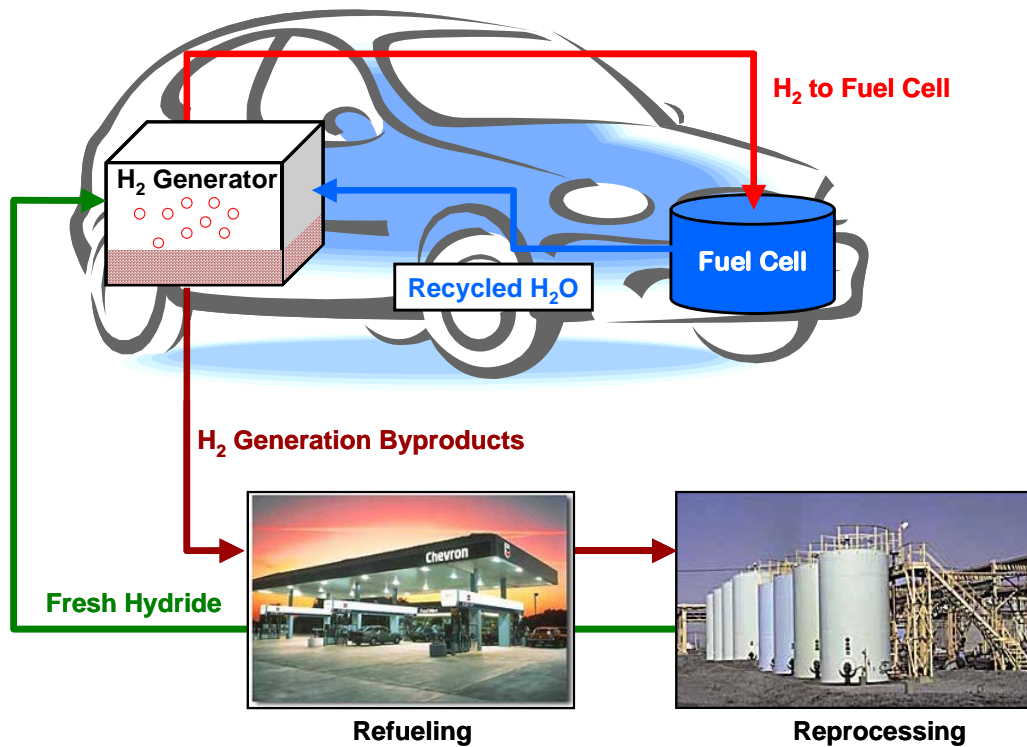


Figure 7. Vision of the Energy System Concept

4. Summary

The advantages of this energy system concept include:

- The potential to achieve high hydrogen storage density and attain DOE storage goals for 2015
- The ability of hydride processors to utilize products from an energy convertor (for example, water and waste heat from a fuel cell) to maintain high efficiency
- The use of hydride materials that are generally nontoxic and stable until combined with water or thermally decomposed
- The ability to produce a low pressure, non-venting source of hydrogen that can be regulated according to hydrogen demand
- The application of a system-level approach that attempts to integrate all components associated with chemical hydride-based storage in order to maximize efficiency

The primary technical issues associated with its development include:

- Achieving high hydrogen yield from a compact hydride processor
- Developing efficient and cost competitive hydride reprocessing technologies
- Developing effective and reliable methods of delivering hydride and removing products

- Matching operational characteristics of the hydride reprocessor with the energy convertor
- Developing compact, economical, reusable, and durable system hardware
- Ensuring a high level of safety in both the operational system and the refueling process

5. References

1. M. Klanchar and C. L. Lloyd, "Compact Hydrogen Generating Systems Based on Chemical Sources for Low and High Power Applications," *Proceedings of the 39th Power Sources Conference*, pp. 188-191, June 2000.
2. M. Klanchar and J. A. Peters, "Hydrogen Generation via a Molten Metal-Water Reaction in a Semi-Batch Reactor," *Proceedings of the 40th Power Sources Conference*, pp. 363-366, June 2002.
3. J. Phillips, M. C. Bradford, and M. Klanchar, "A Calorimetric Study of the Mechanism and Thermodynamics of the Lithium Hydride-Water Reaction at Elevated Temperatures," *Energy and Fuels*, Vol. 9, No. 4, pp. 569-573, July 1995.
4. M. Klanchar and T. G. Hughes, "System for Generating Hydrogen," U.S. Patent Nos. 5,634,341 (June 3, 1997) and 5,867,978 (February 9, 1999).
5. U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, "Grand Challenge for Basic and Applied Research in Hydrogen Storage," Solicitation No. DE-PS36-03G093013, July 24, 2003.
6. J. A. Peters, "Development of a Database of Thermochemical Parameters for Use with the SOLGASMIX computer program," Technical Report TR 88-08, The Applied Research Lab, The Penn State University, July 1988.
7. Millennium Cell, Inc., "Hydrogen on Demand™ Fact Sheet," <http://www.millenniumcell.com/news/hod.html>.
8. A. W. McClaine, "Chemical Hydride Slurry for Hydrogen Production and Storage (New FY 2004 Project)," U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, FY 2003 Progress Report for Hydrogen, Fuel Cells, and Infrastructure Technologies Program, October 2003.
9. Dr. Y. Wu, "Process for the Regeneration of Sodium Borate to Sodium Borohydride for Use as a Hydrogen Storage Source (New FY 2004 Project)," U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, FY 2003 Progress Report for Hydrogen, Fuel Cells, and Infrastructure Technologies Program, October 2003.
10. H. D. Fricke, J. W. Burr and M. G. Sobienick, "Fluidized Powders – A New Approach to Storable Missile Fuels," 12th JANNAF Liquid Propulsion Meeting, Vol. 201, CPIA, p. 393, 1970.
11. H. J. Loftus, L. N. Montannino and R. C. Bryndle, "Powder Rocket Feasibility Evaluation," AIAA Paper No. 72-1162, AIAA/SAE 8th Joint Propulsion Specialist Conference, 1972.
12. T. F. Miller, "A High-Pressure, Continuous-Operation Cyclone Separator Using a Water-Generated Flow Restriction," *Powder Technology*, Vol. 122, p. 61-68, 2002.

Curriculum Vitae of Authors

Dr. Martin Klanchar

Dr. Klanchar received a BS in chemical and petroleum engineering from the University of Pittsburgh in 1979 and a PhD in chemical engineering from The Pennsylvania State University in 1987. He has served as a research associate in the Energy Production Systems Department of ARL Penn State for the past 16 years. His expertise at ARL involves the development of systems that use chemical reactions to produce gaseous hydrogen and oxygen from compact vessels. He has extensive experience in characterizing and applying many of the mentioned reactant hydrides to experimental prototype systems. He also has investigated other high-energy chemical and combustion processes including liquid metal-water reactions. He is a registered professional engineer and a member of the graduate faculty in chemical engineering where he occasionally teaches and advises student research.

A few of Dr. Klanchar's publications relevant to this paper are cited in the References section.

Dr. Thomas G. Hughes

Dr. Hughes received his PhD in Mechanical Engineering from The Pennsylvania State University in 1974 with the support of an NDEA Title IV Fellowship for graduate study in two-phase heat transfer. He was initially responsible for the investigation of boiling and condensation processes in compact Rankine propulsion systems and was later responsible for system development and testing of the closed-cycle propulsion system used in the Navy's Mk 50 torpedo powerplant.

Dr. Hughes currently manages the Energy Science and Power Systems Division (ESPSD) of the Applied Research Laboratory, which develops power and energy systems under contracts with the U.S. Navy, other government agencies, and private companies. Since joining ARL in 1968, he has been instrumental in the development of a variety of advanced energy systems, has authored more than twenty papers on the subject, and holds patents on innovations associated with his work. He has worked on liquid metal and hydrocarbon combustion systems, Rankine, Stirling, and Brayton conversion systems, and batteries, fuel cells, thermophotovoltaics, and thermoelectrics. The Navy has selected him to review energy system designs, to analyze energy system failures, and to participate in international technical data exchange meetings. Dr. Hughes has received letters of commendation from Navy sponsors and he has taught undergraduate courses in thermodynamics and machine design. He has served as the thesis advisor or co-advisor for eight Master's candidates, three PhD candidates and two undergraduate honors students. In addition, he has served on five PhD committees and one Master's committee. He is a registered professional engineer in the Commonwealth of Pennsylvania and is a member and past chairman of the Propulsion Technical Committee of the ASME.

Dr. Patricia L. Gruber

Dr. Gruber received a BS in Meteorology from the Pennsylvania State University, a MS in Physical Oceanography from the University of Miami and a PhD in Applied Marine Physics from the University of Miami.

Dr. Gruber joined ARL in 2003, in Program Development, and works with ESPSD to develop concepts for hydrogen production and storage and power systems. Prior to joining ARL, Dr. Gruber was Director of Regional Marketing at Marconi, a global supplier of telecommunications equipment. She was responsible for developing market segment analyses, account strategies and targeted marketing programs for Marconi's major North American accounts. Dr. Gruber was a Solution Architect Manager at AT&T Solutions where she led teams that created business, technical and operational solutions for complex IT outsourcing contracts. She designed and implemented global network solutions for large financial firms, such as Merrill Lynch, Citicorp, and BancOne. As a distinguished member of the technical staff at AT&T Bell Laboratories, she served as Systems Engineer and Project Manager of telecommunications access products and was the Program Manager on several Navy contracts for the development of acoustic and electromagnetic system concepts for underwater surveillance. At the Naval Research Laboratory, she served as Principal Investigator for Navy research projects including acoustic transients, boundary scattering, system performance and ambient noise.