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Effects of Metal Hydride Properties on the Performance of Hydrogen Storage Systems

T. Johnson, D. Dedrick
Sandia National Laboratories, Livermore, CA USA

S. Jorgensen
General Motors R&D, Warren, MI USA

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Abstract

Volumetric and gravimetric energy density are the primary performance metrics for the evaluation of hydrogen storage systems. The purpose of this study was to determine the effects of material properties such as thermal conductivity, and thermodynamic properties such as enthalpy of formation on these energy densities. This was accomplished by first defining volumetric and gravimetric energy density in terms of global system parameters, followed by defining relationships between these upper level parameters and the more tangible hydride properties; these. These relationships were built using a generalized hydrogen storage system design and included structural and heat transfer calculations. The end result was a complex set of equations relating hydrogen storage system energy densities to the properties of the hydride contained in the system.

These equations were solved for a range of metal hydride properties including effective capacity (amount of hydrogen per unit weight the metal hydride can absorb in a defined time period), material density, hydriding pressure, operating temperature, enthalpy of formation, thermal conductivity, and specific heat. The results show the relationship of these parameters to hydrogen storage system energy density. The combined effects of all variables in this multi-dimensional parameter space are presented as well as the isolated effect of each property on system volumetric and gravimetric energy density.

The results indicate that while effective hydrogen capacity is the most influential metal hydride property, several other properties are nearly as important. Specifically, metal hydride enthalpy and density are revealed as key contributors to a viable hydrogen storage system. Also, the combination of specific heat and operating temperature is shown to be important when desorption heating is considered as a parasitic loss. Other metal hydride properties such as thermal conductivity are shown to be less significant.

Introduction

Much has been written about the coming hydrogen economy. The world energy supply is controlled by a complex interconnection of geology, politics, technology, economics, research, ecology, and now climate. It is at best a daunting task to accurately predict the complex interplay of these forces; many factors will yet play a role in deciding our energy future. The transportation sector is an important component of the hydrogen economy since it accounts for one of the largest fractions of world-wide energy consumption

Research and development efforts in transportation fuel cells have enabled this alternative powerplant technology to compete with the ICE in both performance and cost. Although much effort remains, especially in the areas of cost and durability, there is sufficient reason to believe success is possible to drive billions of dollars in business investments in this technology, in addition to the billions in government spending. In addition, there is a need for appropriate infrastructure, standards, consumer education, and a plan for the transition from demonstration scale to mass market. Each of these vital topics has commanded multiple studies and will continue to do so.

In this paper we focus on the final major piece of the hydrogen economy, hydrogen storage, and specifically storage for use in vehicles. Current demonstration vehicles are fueled by either compressed gas or liquid hydrogen. It seems reasonably likely that one of these two options will be used to fuel the first production vehicles as well. These physical containment storage tanks will be sufficient for the initial launch of hydrogen fueled vehicles, but are insufficient to satisfy the USDOE and auto industry requirements for more compact, flexible and less expensive methods [1].

A number of solid-phase-storage methods are being pursued in order to improve on the performance of gas and liquid tanks. This work often focuses on new materials because no current hydrogen sorption material fits the needs of the consumer for driving range and performance. While it is too early to rationally select which of the many approaches is best, and we do not imply such a selection by this paper, we have chosen to look at complex hydride storage in this paper. Complex hydrides targeted for automotive applications are characterized generally by high capacity, moderate material density and relatively good hydrogen density, relatively high enthalpy of hydrogen release, low thermal conductivity in at least one phase, elevated hydrogen release temperatures, and slow kinetics at lower temperatures. Active research is underway to improve enthalpy, release temperature, and kinetics, but they are unlikely to become negligible.

Accordingly, we have performed a sensitivity study on the effects of hydride physical and chemical properties on the overall system performance. Specifically we include not just the material used in storing hydrogen, but also how the material properties affect engineering requirements. In order to increase applicability, no specific material is used and no detailed design is postulated, but instead the properties are varied in ranges conceivable for complex hydrides. This approach will allow us to identify material properties that most influence system performance. Further work on the engineering and materials aspects with the highest sensitivity will have the largest influence on improving hydrogen storage.

Metal Hydride Properties Important to System Design

From an engineering perspective, the properties of a metal hydride that are important to design a hydrogen storage system are those that effect either the thermal management or the structural requirements. Thermal material properties such as heat capacity and thermal conductivity are thus important. Density is important since it determines the storage volume of the system for a required mass of hydride. However, since most metal hydrides are finely divided powders, the achievable packing density is more important than the crystal/X-ray density. Achievable packing densities of metal hydrides are often significantly lower than the theoretical crystal density.

Since metal hydrides appropriate for automotive applications absorb gaseous hydrogen at elevated pressures, they must be contained within a suitable pressure vessel. Thus, there are no structural requirements of the hydride itself and properties such as yield strength and ductility are not important.

The thermodynamic properties of the metal hydride are also key properties to system design. These are the properties which define the sorption kinetics of the hydride. Material scientists often define hydrogen absorption and desorption rates in terms of an Arrhenius temperature dependence with a pre-exponential constant and an activation energy. This is often coupled with an expression for pressure dependence that includes the thermodynamic equilibrium pressure and empirically determined constants. While useful from a materials research standpoint, these rate constants are not that useful for a generalized engineering analysis like what is presented here. More tangible engineering properties can be extracted from these characteristic equations and related directly to design calculations. These properties are the hydrogen capacity, maximum operating pressure, and maximum operating temperature.

Hydrogen capacity can be described as the absorption rate integrated over the time of absorption. Thus, the refueling time must be specified. For this analysis, a time period of five minutes was used. Because absorption rate is dependant on hydride temperature and hydrogen pressure, these absorption conditions must be chosen to be consistent with the capacity. The system maximum operating pressure will be defined by the absorption pressure since desorption takes place at lower pressure. In contrast, the desorption temperature required to release hydrogen at a sufficient rate defines the maximum operational temperature. Here a sufficient release rate might be the DOE target of 0.02 g/sec/kW [1]. The last thermodynamic property key to design is the reversible enthalpy or heat of formation/release, ΔH.

Table 1 lists the ranges of these properties that were considered for this analysis. The ranges were defined to include known metal hydride properties as well as potential materials with higher capacity. Lower capacities typical of most classic metal hydrides were not included since these materials are not generally considered for automotive applications.

Table 1: Ranges of metal hydride properties

Property	Symbol	Units	Range
Effective capacity	ω	kg H_2/kg hydride	0.02 – 0.10
Packing density	ρ_p	kg/L	0.5 – 2.0
Specific heat	c	J/kg*K	500 – 2750
Thermal conductivity	k	W/m*K	0.5 – 5.0
Pressure	P	bar	20 - 140
Temperature	T	ºC	100 – 300
Enthalpy	ΔH	kJ/mol H_2	20 - 80

Thermal conductivities for these materials are generally low due to either low particle thermal conductivities or high inter-particle thermal resistances [2]. Extending the range to 5 W/m*K is optimistic for complex metal hydrides, but possible in the case of high thermal conductivity particles. Models and measurements indicate that the effective thermal conductivity of particles loaded in a packed bed is generally limited to values below ~5 W/m-K, even with significant increases in the particle thermal conductivity [3] [4].

Significant effort is ongoing to reduce the pressure required for hydrogen uptake in metal hydrides. However, a number of current materials require pressures above 100 bar for rapid absorption. Material researchers are at the same time trying to reduce the hydrogen release temperatures of these materials. Yet, as with pressure, significant temperatures up to 300 ºC are required for some complex metal hydrides. Note that the low end of the temperature range stops at 100 ºC. This is because release temperatures below this would allow for heating with the waste heat from the fuel cell. This possibility is considered separately in the conclusions section.

Experimental data for specific heat of metal hydrides is limited. The range of specific heats was selected based on typical values for interstitial metal hydrides (~500 J/kg-k) and complex hydrides (~1500 J/kg-K) [5].

Reversible hydrogen storage materials are characterized by endothermic decomposition and exothermic recombination. The enthalpy of the reversible reaction, ΔH, defines the quantity of heat that will be moved in and out of the system during one complete fueling cycle. The pressure and temperature operating regime of an on-board automotive hydrogen storage system limits the possible variation of the enthalpy of reaction regardless of the material chosen. The plateau pressure expression for any of these materials is described as follows;

$$\ln(P_{h2}) = -\frac{1}{RT}\cdot\left(\Delta \mathrm{H} - T\Delta S\right) = -\frac{\Delta \mathrm{H}}{RT} + \frac{\Delta S}{R} \quad (1)$$

where, P_{h2} is the plateau pressure, R is the gas constant, T is the temperature, and ΔS is the change in entropy. The change in entropy is approximately equivalent for any hydride solid as the hydrogen gas has lost nearly all its translational degrees of freedom when bonding to the metal species. Since the intercept of the plateau pressure expression is $\Delta S/R$, hydride solids that operate within a limited pressure and temperature regime have similar enthalpies of reaction. For this study, enthalpy was varied over the range 20 – 80 kJ/mol H_2. Lower enthalpy materials are unlikely to recharge at reasonable pressures and higher enthalpy materials will likely have desorption temperature outside the reasonable range.

Material Properties Link to System Energy Density

While cost, durability, and performance are all important aspects of a hydrogen storage system, system weight and volume are the primary metrics by which such systems are judged and are the focus of this study. In the following sections, we will establish a set of equations that link system weight and volume to the properties of the metal hydride contained in the system. The individual effect of metal hydride properties on these metrics will then be derived through a sensitivity analysis.

Definition of Energy Densities

Rather than absolute system weight and volume, the system metrics are normally given as a ratio of the amount of hydrogen that can be delivered to the vehicle power plant to the total storage system weight and volume. We chose to express this gravimetric storage efficiency in terms of energy density, using the lower heating value (LHV) for hydrogen of 120 MJ/kg H_2 as a conversion factor. For this study, gravimetric energy density will be depicted by the symbol ρ_{E_G}, with units of MJ/kg. Similarly, the ratio of hydrogen to system volume is termed volumetric energy density and is defined as the hydrogen energy divided by the total storage system volume; it will be depicted by ρ_{E_V} with the units MJ/L.

Goals for these two metrics have been developed by the USDOE and are used to rate potential hydrogen storage system solutions [1]. The 2010 USDOE targets are 5.4 MJ/L for volumetric energy density and 7.2 MJ/kg for gravimetric energy density. This is equivalent to a 6 wt % storage system. The 2015 targets are 9.72 MJ/L for volumetric energy density and 10.8 MJ/kg for gravimetric energy density. This is equivalent to a 9 wt% storage system. The primary reason that there are many different options being pursued for hydrogen storage is that no current solution meets the 2010 goals, much less the 2015 goals.

Definition of Upper Level Parameters

For the purpose of studying the effects of hydride properties on these two energy density terms, it is convenient to define them in terms of parameters that can then be related to hydride properties. Hydride storage system energy densities can be defined as a function of seven upper level parameters.

Gravimetric energy density was defined above as hydrogen energy that can be delivered to the fuel cell divided by the total storage system mass. Using the definition for effective capacity, *w* and introducing a new term, E_G, this definition can be written as:

$$\rho_{E_G} = \frac{w * E_G * LHV * H_d}{H_{st}} \quad (2)$$

Here H_d is the hydrogen delivered to the fuel cell, H_{st} is the mass of hydrogen stored in the hydride and E_G is the mass efficiency of the storage system design. In other words, E_G is the ratio of hydride mass that is stored in the system to the total system mass. For example, a design where the hydride makes up 60% of the total mass would have an E_G of 0.6. This term provides a basis for comparing different storage system designs irrespective of metal hydride.

In order to further separate Equation 2 into independent parameters related to hydride properties, consider H_d - the hydrogen available to be delivered to the fuel cell. This hydrogen can be defined as the total amount of hydrogen stored in the system minus the hydrogen used for overcoming the heat of formation of the hydride, H_1 and the hydrogen used for heating the system up to and maintaining the operating temperature of the hydride, H_2. Also, the total amount of hydrogen stored in the system includes the hydrogen stored in the hydride, H_{st} as well as the gaseous hydrogen that occupies the void space in the system, H_G. Combining these definitions leads to Equation 3 below.

$$H_d = H_{st} - H_1 - H_2 + H_G \quad (3)$$

Combining Equations 2 and 3 leads to the final definition of gravimetric energy density shown in Equation 4. Here we have introduced the three final upper level parameters, L_1, L_2, and G which are the ratios of H_1, H_2, and H_G to H_{st}.

$$\rho_{E\_G} = w*E_G *LHV *(1-L_1-L_2+G) \quad (4)$$

Volumetric energy density was defined above as hydrogen energy that can be delivered to the fuel cell divided by the total storage system volume. Total storage system volume, like mass, can be defined using a volume efficiency term, E_V which is the ratio of the volume of hydride stored in the system to the total system volume. This definition involves the hydride effective capacity as well as the packing density, ρ_P and is shown in Equation 5.

$$V_{tot} = \frac{H_{st}}{w * \rho_p * E_V} \quad (5)$$

Combining Equations 3 and 5 and using the definitions of L_1, L_2, and G results in the complete definition for volumetric energy density given in Equation 6.

$$\rho_{E\_V} = w*\rho_P*E_V *LHV *(1-L_1-L_2+G) \quad (6)$$

The upper level parameters are thus w, ρ_P, E_G, E_V, L_1, L_2, and G. In addition to effective capacity, w and packing density, ρ_P which have been previously defined we introduce five new parameters. E_G and E_V are efficiency values which depend on the system geometry. L_1 and L_2 are terms which depend on the extra hydrogen that must be stored in order to deliver hydrogen to the fuel cell. L_1 is the loss term for energy required to overcome ΔH and release hydrogen from the hydride. L_2 is the loss term for energy required to heat the system up to and maintain the operating temperature of the hydride. Additionally, the gaseous hydrogen that can be stored in the void volume of the system is accounted for via the term G.

The next step to link storage system energy densities to hydride material properties is to develop relationships for these upper level parameters. However, it is instructive to first consider the energy density goals in terms of the upper level parameters alone. This analysis requires no further development and no system design information. Yet, it may reveal important limitations to metal hydride storage systems.

In order to examine the entire range of mass and volume energy densities that could be achieved by combinations of these variables, a graphical approach was used. Both metrics were plotted as a function of hydride capacity, system efficiency, and system loss terms. Several of these variables were combined so that energy density could be displayed as a function of three parameters in a four-dimensional plot. For gravimetric energy density, the terms inside the parentheses in Equation 4 were combined. For volumetric energy density, volumetric efficiency and packing density were combined in addition. Figure 1 shows the results.

In both plots, hydride effective capacity varies from 2 to 10 wt%. The combination of heating loss terms and gaseous hydrogen is varied over a reasonable range from 0 to 1. E_G and E_V were also limited to realistic ranges. Note that high gravimetric energy density is more difficult to achieve than high volumetric energy density. Also note that since E_G and E_V depend on hydride capacity, not all combinations of these parameters are achievable.

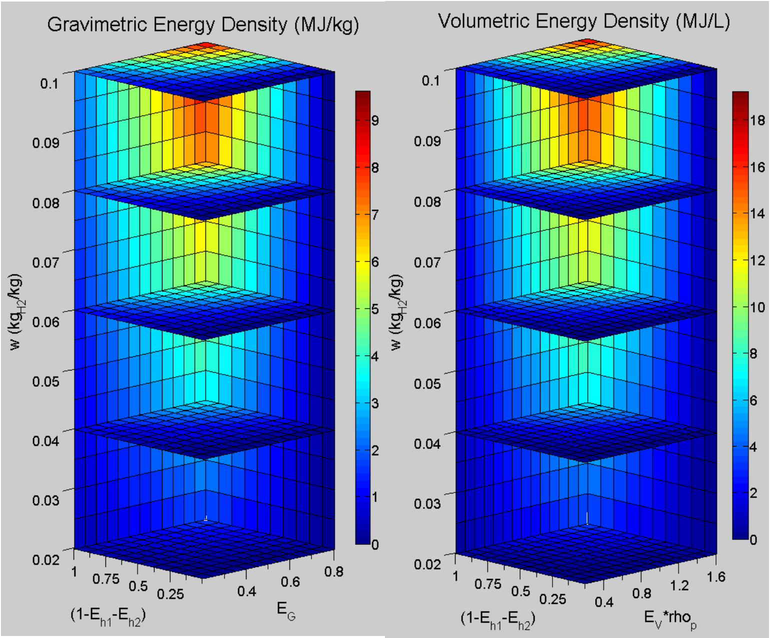


Figure 1 Effect of upper level parameters on gravimetric and volumetric energy density

Link between Upper Level Parameters and Metal Hydride Properties

Of the seven upper level parameters, five must be further defined in terms of hydride physical or chemical properties. Given some assumptions about the hydrogen storage system design and operation, E_G, E_V, L_1, L_2, and G will all be related to one or more of these properties.

System efficiencies, E_V and E_G

As defined above, E_G and E_V are gravimetric and volumetric efficiencies. They are design-specific values which depend on the system geometry. For the purpose of the analysis, a general storage system geometry was defined based on a few simple assumptions and is shown in Figure 2. The design consists of cylindrical pressure vessels in which the hydride is stored. Since most higher capacity metal hydrides require hydrogen absorption pressures greater than a few atmospheres there are few choices for vessel shape that will limit vessel mass other than cylinders or spheres. Cylinders are the more practical choice when it comes to loading the vessels with hydride. These vessels are cooled by external fluid flow during absorption to remove the heat of reaction and maintain a quasi-steady operating temperature. To provide the heat necessary for desorption, the hydride vessels contain heaters along the vessel axis. The efficiency of these heaters is a parameter included in the analysis.

Figure 2 shows all of the variables necessary to describe the system geometry: the inner and outer radius of the hydride, the wall thickness of the vessel and the heater tube, vessel length, and end plate thickness. The vessel length, L, was fixed at 36” for this study. To complete the description, a vessel material must also be chosen. This material must have a high tensile strength and be insensitive to hydrogen effects. These requirements limit the number of obvious choices to just a few. The nickel-based alloy A286 was chosen as the vessel material for this analysis based on its high strength and ductility and ability to maintain both in the presence of high pressure hydrogen at elevated temperatures.

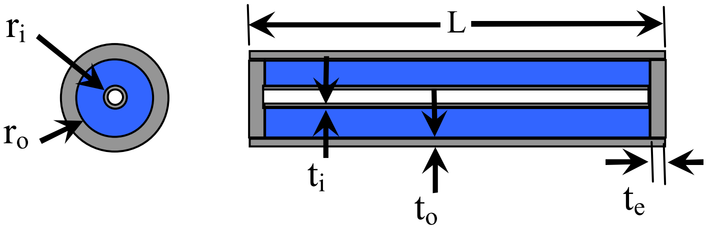


Figure 2 General system geometry

To account for as much detail as possible, the system was broken down into the components shown in Table 2.

Table 2 Breakdown of system components

System Components	Designator
hydride	m
heater	h
vessel	v
cooling	c
other	o

The 'heater' includes the heater tubing and whatever other components are needed for the heating system. The 'vessel' refers to the cylinders and end plates that contain the hydride and must be pressure rated. 'Cooling' covers a shell and the rest of the components needed for the cooling system, but does not include the heat transfer fluid since that is assumed to be left at the hydrogen refilling station. The 'other' category is a catch-all meant to account for system components or details not covered by the previous categories.

Using these designators, the gravimetric and volumetric efficiencies can be defined as follows:

$$E_G = \frac{m_m}{m_m + m_h + m_v + m_c + m_o} \quad (7)$$

$$E_V = \frac{v_m}{v_m + v_h + v_v + v_c + v_o} \quad (8)$$

Equation 7 shows that E_G is defined as the hydride mass divided by the sum of the masses of all of the system components. Equation 8 shows that E_V is defined as the hydride volume divided by the sum of the volumes of all of the system components. The volume of each component is calculated based on the system geometry. Then, the mass of each component can be calculated based on the component volumes and material densities.

In order to calculate specific values for system geometry, thermal and structural analysis is required. The thermal analysis determines the outer radius of the hydride assuming a fixed heater diameter of 3/8". Since a smaller heater takes up less mass and volume, this value was chosen as a reasonable minimum. The thermal analysis consists of a 1-D, steady-state, radial heat transfer calculation based on an average hydrogen absorption rate. Absorption is assumed to be the limiting case due to the much faster rate associated with filling the hydrogen storage system than with emptying it. The calculation assumes constant and uniform volumetric heat generation due to the reaction. This heat generation term, *Q*, is a function of *w*, ρ_p, ΔH, and absorption time, *t* as shown below in Equation 9. For this analysis the absorption time was assumed to be 5 minutes or 300 seconds.

$$Q(\tfrac{W}{m^3}) = \frac{w(\frac{gH_2}{g}) * \rho_P(\frac{g}{cc}) * 10^6(\frac{cc}{m^3}) * dH(\frac{kJ}{molH_2}) * 10^3(\frac{J}{kJ})}{2.017(\frac{gH_2}{molH_2}) * t(\sec)} \qquad (9)$$

Once *Q* is calculated, the outer radius of the hydride can be determined from an analytic solution to the differential heat transfer equation. The thermal conductivity of the hydride, *k*, is the other key variable in this calculation as shown below in Equation 10. Only one final assumption must be made to solve this equation for the outer hydride radius. The temperature gradient from the inner to outer radius must be fixed. As discussed in [6], a gradient in temperature can affect the kinetics of the absorption reaction and thus the effective capacity. A maximum reduction in effective capacity could be defined that would require a certain temperature gradient for each hydride. The temperature gradient would be centered on the absorption temperature that produces the highest hydrogen uptake. The size of the gradient would depend on the sensitivity of hydride kinetics to temperature. For the present study, a fixed 20 ºC temperature gradient was chosen. Alternatively, temperature gradient could have been added as a hydride property and varied over a range, but it was felt that the seven other parameters had greater potential impact on energy density. With all of the variables in the equation defined except for r_o, an iterative solver is used to find the solution.

$$T_i - T_o = \frac{Q}{4k} * (r_o^2 - r_i^2) + \frac{Q * r_i^2}{2k} * (\ln(r_i) - \ln(r_o)) \qquad (10)$$

After the outer hydride radius is found, a structural analysis is required to determine the wall thicknesses of the pressure vessels. This includes the cylinder wall thickness, *t_o*, the end plate thickness, *t_e*, and the heater tube wall thickness, *t_i*. This structural analysis is simply an analytic, thin-walled pressure vessel calculation which depends on the applied hydrogen pressure, *P*, the vessel material yield strength, σ_y, and Poisson's ratio, *v*, and a factor of safety, *FS* chosen as 3.5. The equations are shown below.

$$t_o = \frac{2P * r_o * FS}{(2\sigma_y - 1.2P * FS)} \qquad (11)$$

$$t_e = \sqrt{\frac{3FS * P * r_0^2 * \sqrt{v^2 - v + 1}}{4\sigma_y}} \qquad (12)$$

$$t_i = \frac{2P * r_i * FS}{(2\sigma_y - 1.2P * FS)} \quad (13)$$

With the thickness values calculated, the last value needed to perform the volume calculations is spacing around the vessels for fluid flow. This value is determined assuming that it is proportional to the cylinder outside diameter. The proportionality constant is based on a best guess without doing the detailed design work that would be required to find an exact value.

Now all of the system volumes can be calculated. Volumes are calculated on a unit cell basis assuming that a single cylinder, inner heater, and exterior coolant volume will be repeated to form a system. The hydride volume is then just the annulus defined by the inner and outer radii and the length. The vessel volume includes the outer cylinder and end plates while the heater volume is just the inner cylinder. The coolant volume is based on the space around each vessel. Additional volume associated with the coolant shell, insulation, manifolds, valves etc. is lumped into the other category. For this study it was assumed that these items added another 20% to the system volume.

The hydride and vessel masses are calculated directly from the volumes and the material densities of each. Because the coolant is assumed to remain at the hydrogen refilling station, the coolant mass is set to zero. Because a specific heater was not chosen, the heater mass is only based on the tube dimensions and A286 density. Lastly, the catch-all ‘other’ category is assumed to add 10% to the total system mass. Using Equations 7 and 8 above, the system efficiencies E_V and E_G can now be calculated

System loss terms, L_1 and L_2

As previously described, the stored hydrogen considered in calculating system energy density is that which can be delivered to the fuel cell. However, the system must actually store more hydrogen than this. This is due to energy required to deliver the desired amount of hydrogen to the fuel cell. This energy is assumed to come from stored hydrogen and is considered a system loss which can be accounted for by two loss terms: one for energy required to release hydrogen from the physical or chemical hydride bonds and the second for heat required to both elevate and maintain the hydride at an operating temperature at which the desorption kinetics are fast enough to supply a required hydrogen flow rate. The first of these loss terms was designated L_1 and the second L_2.

L_1 was previously defined (see development of Equation 4) as the ratio of H_1 heat of formation to H_{st}. The energy available from H_1 can be expressed using the LHV for hydrogen and a simple efficiency value for the heating system. This energy must balance the energy needed to desorb the stored hydrogen. Equation 14 shows this energy balance with heater efficiency shown as h_{eff} and the molecular weight of hydrogen shown as Mw.

$$\frac{H_1}{mw} * LHV * h_{eff} = \frac{H_{st}}{mw} * H \quad (14)$$

Using Equation 14 and the previous definition, L_1 can be redefined as shown in Equation 15.

$$L_1 = \frac{H}{LHV * h_{eff}} \quad (15)$$

Thus, L_1 is only a function of the hydride reaction enthalpy and the system heater efficiency which will be a design dependant value. Although not a metal hydride property, h_{eff} is included in this study over a range from 0.45 to 0.9.

Like L_1, L_2 has been defined as the ratio of H_2 to H_{st}, and can be defined in terms of hydride properties by defining an energy balance as in Equation 14. However, this energy balance is much more complicated to define because it is as much a function of the system design and operation as it is a function of the metal hydride thermal properties. So, a number of assumptions must be made.

The energy needed to heat the system up to the hydride operating temperature for desorption depends on a number of factors: the mass and heat capacity of each type of material that make up the system, the initial system temperature, the hydride operating temperature, and the number of times the system must be heated between refueling. A complete system design would be required to list all of the materials used in the system. For our generalized system design shown in Figure 2, a single material was chosen to represent all of the non-hydride components of the system. This assumption simplifies the analysis. Furthermore, the initial system temperature, after an overnight cool down for instance, will depend on how well the system is insulated. An overly optimistic assumption would be that the system is perfectly insulated and between refills would only require heating once to a higher desorption temperature. However, since perfect insulation can not be achieved this might be quite misleading. What is required then is to assume that a well insulated system is desired, but that some cooling takes place between driving periods.

As for the number of times the system is heated between hydrogen refills, that could vary as much as the driving styles of fuel cell vehicle operators. For this analysis, average driving statistics were applied to a simple driving pattern. It was assumed that the system was heated once each day for driving after having cooled from an overnight period. This cooling was defined by scaling the difference between the operating temperature and an assumed ambient temperature of 20 ºC. Cooling during the day was neglected assuming that the overnight cool down was the dominant term. Then, based on transportation statistics, a ten day refueling cycle was used.

The second part of the L_2 term is maintaining the system at the elevated operating temperature. This energy would depend on the difference between the operating temperature and the ambient temperature of the environment as well as the system insulation and total driving time between refills. However, since it has been assumed that the system is well insulated, this maintenance energy was assumed to be negligible compared to the heating energy and thus neglected.

The final definition for L_2 is shown in Equation 16. Note that L_2 depends directly on w, T, c, and E_G, which means it depends indirectly on every other hydride property. As will be seen in the results section, this makes it difficult to visualize hydride property effects and sensitivities.

$$L_2 = \frac{N * F * (T - T_{env}) * mw}{w * LHV * h_{eff}} * \left(c + \left(\tfrac{1}{E_G} - 1\right) * c_{ave}\right) \quad (16)$$

In this equation, N represents the number of heating cycles and is set to ten, F is the scale factor to account for insulation preventing the system from cooling completely to the ambient temperature T_{env}, and c_{ave} represents the average heat capacity of the non-hydride elements of the system. Here that term is just equal to the heat capacity of A286.

Lastly, to be complete, we must consider the gaseous hydrogen stored in the system. The mass of gaseous hydrogen will depend on the pressure at which the system is refueled and the volume available. Assuming that any metal hydride that starts in powder form will not be packed to its full crystal density, there will be void space that gaseous hydrogen can occupy.

The term G used in Equations 4 and 6 is actually the ratio of this gaseous hydrogen to the hydrogen stored in the metal hydride. Using a void volume defined by the difference between the hydride packing density and the hydride crystal density along with the ideal gas law, the mass of gaseous hydrogen can be calculated. However, this requires defining a range of hydride crystal densities to go along with the range of packing densities. As an alternative, a void fraction was defined as the fraction of the total hydride volume that is actually void volume. A range of void fractions could have been used in the analysis, but for simplicity a single value of 0.25 was chosen. Equation 17 shows the final definition for G where vf is the void fraction and R is the gas constant.

$$G = \frac{P * vf}{\rho_p * w * R * T} \quad (17)$$

Note that G is included in this analysis primarily for completeness. Since we are concerned in this study with solid storage materials, gaseous hydrogen is not necessarily desired even though in Equations 4 and 6 it is a positive term. In fact, minimizing pressure and maximizing packing density will minimize G but improve the system gravimetric and volumetric energy densities as will be seen in the results section.

Analysis Method

The goal of this analysis was to gain an understanding of the relationship between metal hydride material properties and the two main storage system performance metrics, gravimetric and volumetric energy density. The analysis was not focused on a single metal hydride but, by looking at these properties over a broad range, meant to encompass metal hydrides as a group. So, the first part of the analysis was to show the effects of combinations of different properties on the system metrics. The second part of the analysis was to identify properties that have the most significant effect on system mass and volume in order to steer material research in the most important directions. This was performed by isolating the effect of each metal hydride property.

To achieve both analysis goals, gravimetric and volumetric energy densities were first calculated for all combinations of the metal hydride properties. This was performed with the following methodology:

1. Define parameter ranges as shown in Table 1
2. Define all other variables involved in Equations 2- 17 as constants
3. Calculate Q as a function of w, ρ_p, and ΔH using Equation 9
4. Calculate vessel diameter based on the thermal analysis described previously using Equation 10

5. Calculate the heater and vessel wall thicknesses and the vessel end cap thickness based on the structural analysis described previously using Equations 11 - 13
6. Calculate spacing between vessels for cooling fluid flow
7. Calculate system masses and volumes using the results of steps 1 - 6
8. Calculate E_V and E_G using Equations 7 and 8
9. Calculate L_1 from Equation 15
10. Calculate L_2 from Equation 16
11. Calculate G from Equation 17
12. Finally, calculate system energy densities from Equations 4 and 6

The result is a seven dimensional array of values for both system metrics. Due to the ease of working with large arrays and the graphics capabilities, Matlab was used to perform this analysis. Even though Matlab is designed to work with large arrays, the property ranges were limited to 4 or 5 values each since the total number of calculations performed is the number of range values to the seventh power.

The resulting arrays can be post-processed in a number of ways. If a specific set of properties are known then the predicted energy densities can be found by interpolation within the arrays. To satisfy the first analysis goal and visualize the effect of the entire seven dimensional property space, a graphical method was developed. Since seven dimensions cannot be captured easily in a single visual, the results are displayed in a series of three and four dimensional plots. Figure 1 already showed how the energy densities vary with the upper level parameters. What remains is to display how the upper level parameters vary with metal hydride properties.

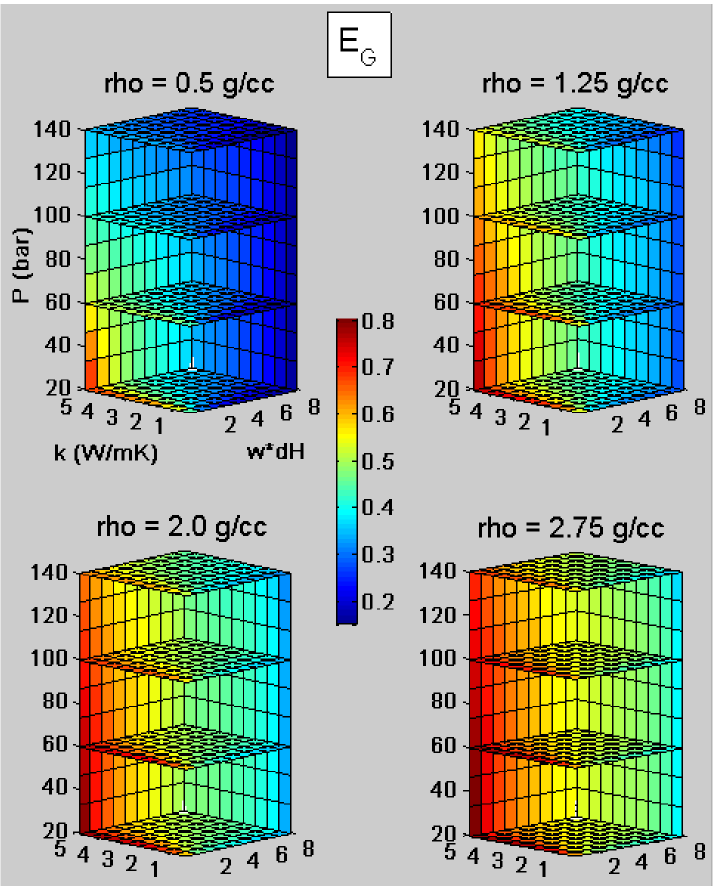
A separate method was used to assess the sensitivity of the metrics to each property individually. In this case, for each range value of a property the energy density results in the arrays were averaged to remove the effect of all other properties. The result was a vector of both gravimetric and volumetric energy density as a function of each property over its defined range. Larger deviations of the energy density values over a property range indicate a higher sensitivity to that property. This will be shown graphically in the following results section.

Results

Variation of Upper Level Parameters with Hydride Properties

The first upper level parameter to consider is gravimetric efficiency, E_G. Recall that this is a parameter specific to the storage system design and is defined as the ratio of hydride mass to total system mass. Figure 3 shows how E_G varies with hydride thermal conductivity, absorption pressure, packing density, and the combination of effective capacity and reaction enthalpy. These last two properties are combined since E_G only varies with their product and it reduces the required number of plots. Also shown in Figure 3 are example combinations of w and ΔH using the ranges from Table 1. E_G is represented by color in each plot and ranges from 0.1 up to 0.8. Packing density is varied linearly by 0.75 g/cc increments from plot to plot.

Several notable trends can be found upon inspection of these plots. High mass efficiency is achieved with low pressure, but only when thermal loads are low enough that vessel diameter and wall thickness are not at the minimum limits. Conversely, higher thermal conductivity, which allows for larger diameter vessels, only improves mass efficiency if vessel wall thicknesses are constrained by the minimum thickness. The product of effective capacity and reaction enthalpy has a similar but opposite effect as conductivity in that lower is better for mass efficiency. However, both capacity and enthalpy, unlike conductivity, affect system energy densities through other upper level parameters. Finally, packing density has a large effect on the mass efficiency of the design as might be expected.

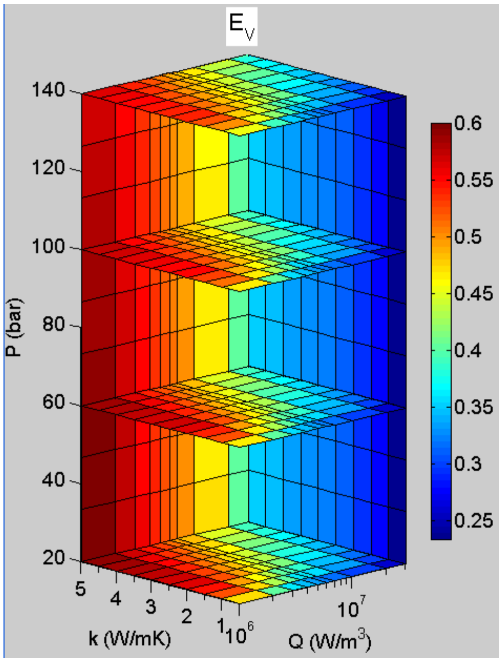


dH w	20	40	60	80
.02	.4	.8	1.2	1.6
.04	.8	1.6	2.4	3.2
.06	1.2	2.4	3.6	4.8
.08	1.6	3.2	4.8	6.4
.10	2	4	6	8

Figure 3 Variation of E_G *with hydride properties*

Only a single plot as shown in Figure 4 is required to show the effect of hydride properties on volume efficiency. This is because packing density, effective capacity and reaction enthalpy have only a combined effect on volume efficiency through the heat generation term Q. Like the previous figure, E_V is depicted in a color volume plot as a function of hydride operating pressure, thermal conductivity, and heat generation. Also like Figure 3, a table is used to show how Q varies with the product of w, ΔH, and ρ_p. Note that Q varies by two orders of magnitude over the range of these variables, thus the log scale in the figure. Over the range of hydride properties considered, the analysis resulted in volume efficiencies ranging from 0.2 up to 0.6.

Figure 4 shows that hydride operating pressure has little effect on volume. That is because pressure only determines the vessel wall thicknesses which have negligible volumetric impact. Volume efficiency is affected mainly by the heat transfer terms in Equation 10, Q and k, which determine the outer hydride diameter. Lower Q and higher k allow for a larger diameter. With a fixed internal heater diameter and limits set on minimum vessel wall thickness, this results in more hydride volume per system volume.



ΔH w	20	40	60	80	ρ_p
.02	.33	.66	.99	1.3	.5
.04	1.3	2.6	4.0	5.2	1.0
.06	3.0	5.9	8.9	11.9	1.5
.08	5.3	10.6	15.9	21.1	2.0
.10	8.3	16.5	24.8	33	2.5

Example combinations of w, H, and ρ_p give Q (W/m3 x10^6)

Figure 4 Variation of E_V with hydride properties

Figure 5 shows how L_1 varies with hydride reaction enthalpy and heater efficiency. Although it is not a property of a metal hydride, the affect of heater efficiency is shown here because it has important implications for system design. In the plot, L_1 is shown both on the vertical axis and by the color bar. Recall from Equations 4 and 6 that the loss terms L_1 and L_2 reduce the system gravimetric and volumetric energy densities, so lower values for these terms are desired. Thus the reason for the opposite color bar so that red still represents desired values. High heater efficiency and low enthalpy are required to minimize L_1. Loss terms can be viewed as fractional decreases in energy density so that an L_1 value of 0.2 results in a 20% decrease in energy density values. As the sensitivity analysis will show, this dependence makes reaction enthalpy a key hydride property for system design.

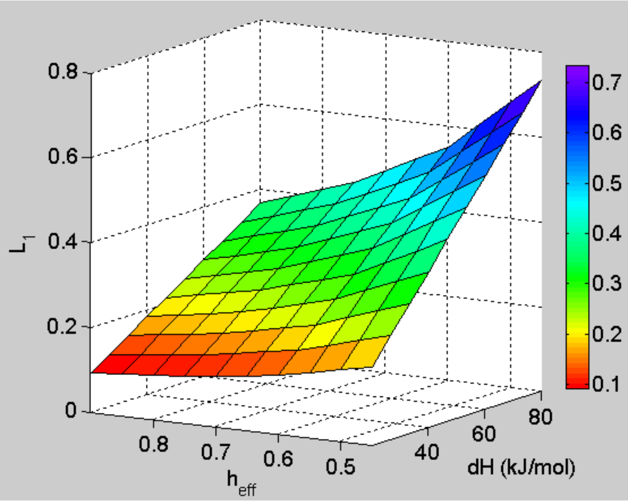


Figure 5 Variation of L_1 with ΔH and h_{eff}

While simple to define in words, it was shown above that L_2 has the most complicated dependency on hydride properties of all of the upper level parameters. This is due to the fact that this loss term involves heating of the entire storage system and so involves every hydride property. Still an attempt was made through Equation 16 and with Figure 6 to capture the variation of L_2 with metal hydride properties. However, it was not possible to decouple this term from the mass efficiency term E_G.

Figure 6 shows a range of L_2 values depicted, as with L_1, from low to high in color from red to blue. Two plots are shown, one for a low value of mass efficiency and one for a high value. Values in between would be linearly interpolated between the two plots. Hydride heat capacity is shown on the vertical axis while effective hydrogen capacity and a term involving hydride desorption temperature and heater efficiency are shown on the horizontal axes. As with the L_1 plot, a heater efficiency range was included to capture the effect of this system design variable.

Because of all of the assumptions involved in this loss term, the exact values depicted may not be truly accurate. However, the trends that may be inferred are of interest. Firstly, note that large values for this loss term occur within the property ranges chosen. Large here means values greater than perhaps 0.2 which would result in a 20% reduction in system energy density. In fact, values greater than 1.0 were calculated although the color bar saturates at this value. At that point the system uses all of the stored hydrogen to heat up to the operating temperature and has none left to deliver to the fuel cell. This can be the case for systems with low mass efficiency, high operating temperature, high heat capacity, low hydrogen capacity and poor heater efficiency.

The main message taken from this figure is that heating up to operating temperature can use a significant amount of energy. This can result from two causes: a large percentage of the system mass is non-hydride material or the hydride has low capacity. These are additional effects of E_G and w on system energy density.

Another message is that a well insulated system is important. As pointed out earlier, the constant F in Equation 16 is based on an assumption of insulation performance and set to a value of 0.33. Perfect insulation would drive this value to zero and L_2 along with it.

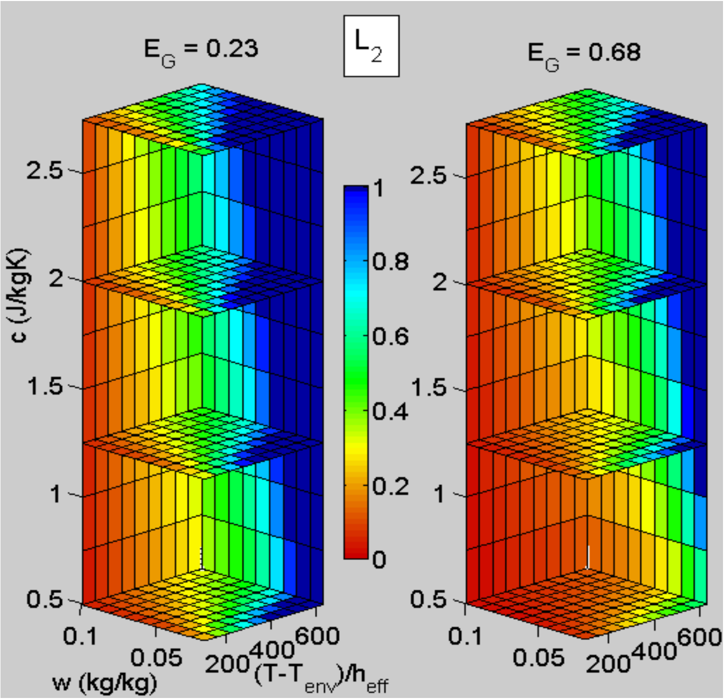


Figure 6 Variation of L_2 with hydride properties

Figures 3 through 6 coupled with Figure 1 present a graphical picture of how the performance metrics of system gravimetric and volumetric energy density vary with metal hydride thermal and thermodynamic properties. With a specific set of metal hydride properties, these five figures and Equation 17 could be used to estimate the performance of a hydrogen storage system based on that hydride. Furthermore, the combined plots indicate the potential bounds of the weight and volume of a metal hydride storage system within the property ranges and assumptions listed. The following section will show which properties have the greatest effect on these system performance metrics.

Sensitivity Analysis

The second goal of this engineering study was to identify those metal hydride properties that system mass and volume might be most sensitive to. Certainly effective capacity, which couples both absolute hydrogen capacity and reaction kinetics, must be important for both system weight and volume. It is this term that represents how much hydrogen can be contained in the hydride. But which properties determine the amount of hydride that can be contained within the system? Clearly packing density is important in that respect, but what other properties are key contributors? And how do other metal hydride properties, especially those that affect the system thermal and structural design, compare to these more obvious drivers?

To answer these questions, a technique was employed to isolate the effects of each property considered here. The technique was fairly simple and, as with the previous results, was graphical in nature. As described in the Analysis Method section, a set of seven dimensional arrays were created so that a value of ρ_{E_G} and ρ_{E_V} was calculated for every combination of every value of each of the seven metal hydride properties. To examine the sensitivity of ρ_{E_G} and ρ_{E_V} to a single property, the energy density values were averaged over all other properties.

The result was a vector of gravimetric and volumetric energy density for each metal hydride property range. Then, to visualize the effects together on the same plot, each property range was normalized by its largest value. The vectors are plotted in Figure 8.

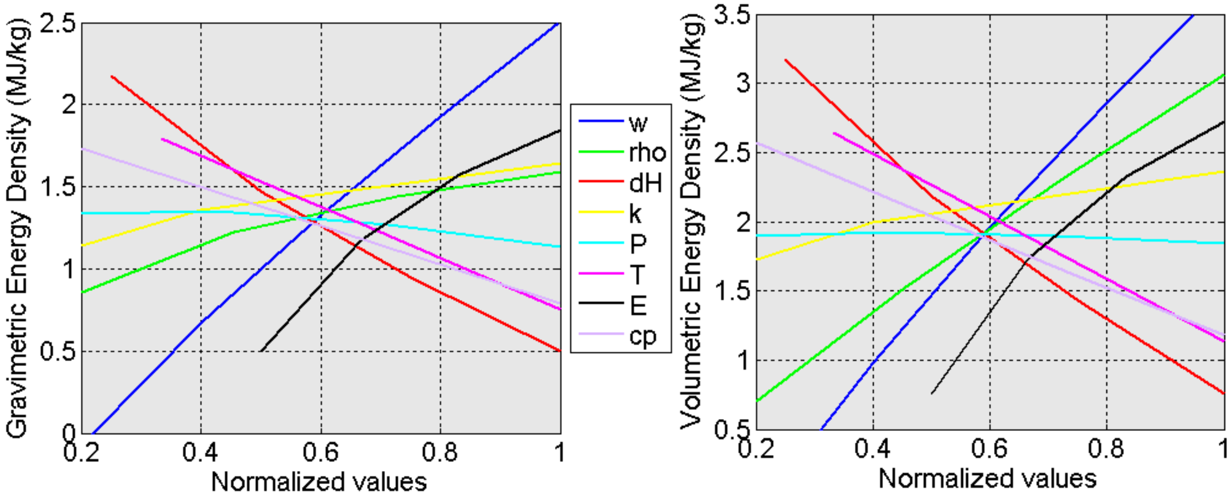


Figure 8 Sensitivity plots for gravimetric and volumetric energy density

Figure 8 shows a plot for gravimetric energy density on the left and volumetric energy density on the right. The important aspect of each plot is the slope of the lines for each normalized property range. A steeper slope, whether positive or negative, indicates a greater effect on system weight or volume. A quick glance confirms the most obvious result that effective capacity is the most influential metal hydride property. However, as suggested by Mosher and Anton [6], there is more to consider beyond weight percent of a metal hydride. Several other critical properties stand out in these plots. Reaction enthalpy emerges as the second most significant property for both weight and volume through its dominant role in the heating loss term L_1. Hydride packing density is more important for system volume than for mass, although not negligible in that respect. Hydride operating temperature and specific heat can have a substantial impact on energy density through the heating loss term L_2. However, as previously discussed, the validity of this loss term is somewhat tenuous. For instance, advanced insulation like that used in the design of liquid hydrogen storage systems might nearly nullify the impact of this term. In that case, T and c would have little effect on gravimetric and volumetric energy density.

Perhaps surprisingly to some, hydride thermal conductivity has a lesser effect on the system than other properties. That is because, although it has some effect on the upper level parameters of system mass and volume efficiency, these effects are secondary at the system energy density level. Hydride absorption pressure is also found to have little effect on either performance metric. Figure 8 shows only a minor change in system gravimetric energy density over the range of pressures considered and virtually no change in system volumetric energy density. However, pressure would have a greater mass impact if a different vessel material had been chosen for the analysis. For instance, if a more common stainless steel such as 316 had been used which has a much lower strength than A286, vessel mass would have been a larger fraction of the system mass. Variations in vessel mass due to pressure would then have had a greater impact on system mass.

Lastly, the black line in the plot represents the effect of heater efficiency which has been included to illustrate that design factors other than metal hydride properties can be a large influence on the system. The slope of the line is nearly as steep as that for hydride effective capacity due to the impact of heater efficiency on both loss terms. This suggests that an efficient heater can be very important for a high energy density storage system.

Summary and Conclusions

An engineering study has been performed to develop an understanding of how metal hydride properties influence hydrogen system performance. This analysis will enable the development of viable systems by identifying highly influential materials and systems research focus areas.

A generalized storage system design was used as a framework for relating metal hydride properties to system energy density values through thermal and structural calculations. Losses to the system storage density were included for energy required to desorb hydrogen and reach and maintain operating temperature. For completeness, gaseous hydrogen stored at the refueling pressure was also included.

The results of this study indicate that while required, high capacity is not sufficient to make a good hydrogen storage material. Other influential metal hydride properties can cause the system mass and volume to be excessive. For example, a hydride with high capacity but low packing density and high reaction enthalpy may result in a comparatively unfavorable storage system design.

Enthalpy of reaction is the second most effective factor in the overall system. This effect is embodied in the loss term associated with providing energy for desorption which, it is assumed, must come from stored hydrogen. Regardless of the energy source, this term is an unequivocal system loss that must be accounted for.

The loss term associated with heating the system up after a period of inactivity was defined with a number of assumptions about insulation efficiency, refueling cycle, and driving characteristics. Nevertheless, this is a term that must be accounted for as well. A system that operates at 300 ºC will lose heat to the ambient environment no matter how well it is insulated. This heat loss term can be minimized if the system is mass efficient and the hydride has high hydrogen capacity and low heat capacity.

Reducing the maximum operating temperature to a value within the operating range of the fuel cell could have the greatest potential impact on the system**.** The ability to use waste heat from the fuel cell for hydrogen desorption greatly reduces the effect of enthalpy and heat capacity. If waste heat can be used to reach and maintain the storage system operating temperature and drive hydrogen desorption then a number of benefits can be realized. Firstly, both L_1 and L_2 become zero since no extra hydrogen is used to fulfill these energy requirements. Secondly, an internal heater is no longer required which increases both mass and volume efficiency of the system and reduces the system complexity. The combination of these benefits could result in a significant increase in system energy density. Thus, research focused on reducing the operating temperature of advanced hydrides could have a large payoff. Of course, the other alternative is to increase the operating temperature of the fuel cell system. Research in this area is currently being pursued for increased fuel cell efficiency.

Finally, while heating system efficiency is purely a design factor rather than related to metal hydride properties, it has been included because of the large effect on system energy densities. Energy needed to supply hydrogen to the fuel cell from the metal hydride can not be neglected and the method for providing that energy must be efficient to minimize the impact on system efficiency and performance. This implies that heating by electrical resistance is not favorable as due to the low hydrogen, electron, heat conversion efficiency. Assuming that the electric current is fed off of the fuel cell output, the heater efficiency will be at best equal to the fuel cell efficiency and production PEM fuel cells are unlikely to have better than 50% efficiency in the near future.

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