Bounding Material Properties for Automotive Storage of Hydrogen in Metal Hydrides for Low-Temperature Fuel Cells

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Abstract

Metal hydride material properties required for on-board hydrogen storage for use with automotive polymer electrolyte fuel cell systems are discussed. Thermodynamic relationships between enthalpy and entropy of sorption are determined such that the storage system can be thermally integrated with the fuel cell system and be refuelled at reasonable H₂ supply pressures of 50-200 atm. Simple criteria are developed for specifying minimum discharge kinetic rates needed to satisfy hydrogen demand on automotive duty cycles. Simple criteria are also developed for specifying minimum charge kinetic rates needed to refuel metal hydride tanks in reasonable time. Accessible intrinsic capacity and bulk density of the metal hydride are determined for the storage system to achieve system level targets for gravimetric and volumetric capacities. Based on these analyses, it is recommended that the storage media properties be measured on samples prepared by mixing the metal hydride with a high thermal conductivity material, and compacted to 600 kg.m⁻³ bulk density. The compact should have a minimum effective thermal conductivity of 8.5 W.m⁻¹.K⁻¹.

Keywords: Metal hydrides; Hydrogen storage systems; Thermodynamics of sorption; Kinetics of sorption and desorption; Heat transfer

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1 Introduction

Hydrogen storage in metal hydrides (MH) continues to be regarded as a promising material-based solution [1, 2] that with continued development may replace gaseous hydrogen storage in high-pressure tanks for automotive fuel cell systems (FCS). Many types of hydriding alloys and complexes have been investigated, including solid solutions, intermetallic compounds (AB_5 , AB_2 , AB , A_2B , etc.), transition and non-transition-metal complexes of borohydrides and alanates, and metastable hydrides [3]. Some of these hydrides are more suitable for non-automotive applications such as mobile devices, stationary power sources, and aerospace technologies. To date, intensive efforts on an international scale have not identified a metal hydride suitable for automotive applications [1, 2, 4].

A recent multi-year, multi-organization study evaluated four classes of developmental metal hydrides [4]: (1) **destabilized hydrides** (especially borohydrides and lithium hydride), including nano-confinement in nano-porous scaffolds; (2) **complex anionic materials** that contain well-defined chemical moieties with particular emphasis on alanates and borohydrides; (3) **amide/imide materials**, including mixtures of amides and borohydrides, amides and alanates, and $LiMgN$; and (4) **off-board regenerable materials** (AlH_3 and $LiAlH_4$). The study concluded that a metal hydride suitable for automotive hydrogen storage does not as yet exist and recommended that future work should focus on $LiBH_4/MgH_2$, $LiBH_4/Mg_2NiH_4$, $Mg(BH_4)_2$, $2LiNH_2/MgH_2$, and $LiNH_2/MgH_2$. The purpose of this work is to establish specific targets for material properties to guide such future efforts.

The scope of this work is limited to on-board reversible metal hydrides, i.e., to the first three classes of materials listed above. Off-board regenerable materials, such as alane [5 - 7] and ammonia borane [8 - 10], have also attracted considerable attention recently, but transporting these materials, maintaining them in liquid form (liquid, slurry, or solution), loading and off-loading, and off-board regeneration cost and efficiencies remain as major

obstacles [11 - 14]. The requirements for the off-board regenerable materials are different as they are largely dictated by these off-board issues rather than the on-board issues, such as heat transfer and sorption kinetics during refueling, for the reversible materials.

The scope of this work is further limited to low-temperature metal hydride (LTMH) systems, shown in Fig.1a, in which hydrogen desorbs at a temperature below the temperature at which the FCS coolant leaves the fuel cell stack. In an LTMH system, the waste heat generated in the stack can be used to liberate hydrogen from the metal hydride medium. It is distinguished from a medium-temperature metal hydride (MTMH) system, shown in Fig. 1b, in which hydrogen desorbs at a temperature higher than the temperature at which the coolant leaves the stack. In an MTMH system, some hydrogen must be burned to heat an intermediate fluid that is circulated through the MH bed to supply the enthalpy of desorption (ΔH). System simulations indicate 18-25% penalty in net system efficiency if an MTMH configuration is used with catalyzed sodium alanates [15]. There is also an additional penalty since some H_2 must be burned to heat the MTMH bed to its operating temperature as the system starts up from cold.

In addition to a fill receptacle for H_2 , Fig. 1 includes flexible connections that must be made during refueling to an off-board cooling circuit that consists of a heat exchanger, valves, an off-board coolant and a coolant pump [15]. This circuit is needed since, depending on ΔH for absorption and H_2 refueling rate, the heat load can be several hundred kW (250 kW for ΔH of 20 kJ.mol^{-1} and 1.5 kg.min^{-1} H_2 refueling rate). The radiator on-board the vehicle can typically reject only a fraction of this heat load, and that too with the assist of ram air at cruising speeds [16, 17]. Cross-contamination of the on-board and off-board coolants is also a concern and may be mitigated if the two fluids are chemically compatible or preferably have the same composition.

2 Material Requirements

Table 1 lists some of the near-term and ultimate technical system targets for on-board hydrogen storage for light-duty fuel cell vehicles [18] that are relevant to the material covered in this work. Compared to stationary and material-handling applications, automotive duty cycles impose stringent requirements on H_2 refueling rates and short transient response times for varying H_2 flow rates from 10 to 90% and from 90 to 0% in order to accommodate fast dynamic changes in vehicular loads (sudden acceleration and braking). There are additional important targets for storage system cost, fuel cost, off-board efficiency (important for off-board regenerable materials), material stability (shelf life and durability over multiple charge-discharge cycles), fuel quality (i.e., purity of H_2 from storage system) and environmental health and safety, but they are not specifically addressed here. The purpose of this section is to lay the rationale and foundation for translating these system-level targets to material-level requirements for on-board reversible metal hydrides.

Reference [18] should be consulted for a complete discussion of the basis and assumptions underlying the automotive storage system targets. Whereas Table 1 lists the target for usable H_2 as 5 kg and Ref. [1] notes a large variability (5.2-9.3 kg) in the estimates of H_2 requirement for different vehicle platforms and fuel economies, this study uses a value of 5.6 kg usable H_2 to be consistent with earlier investigations [5, 15, 17]. Table 1 also lists 90% as the target for on-board efficiency, defined as the fraction of stored H_2 that is available to the fuel cell. The on-board efficiency is taken as 100% in this study since its scope is limited to LTMH systems.

2.1 Operating Temperatures

Figure 2a shows a conceptual 80-kW_e automotive polymer electrolyte fuel cell (PEFC) system with compressed hydrogen storage that has been extensively analysed for performance and cost in several of our earlier studies [16, 17]. In the present work, our

objective is to determine the boundary conditions for a prospective metal-hydride hydrogen storage system that may potentially replace the 700-bar hydrogen storage tank in this FCS. Figure 2b presents the FCS efficiency and the ethylene glycol coolant temperature at stack exit that vary between 47.5%/85°C at rated power and 59.3%/62°C under idling conditions. For a thermally integrated metal hydride system, in which the enthalpy of desorption (ΔH) comes from the waste heat produced in the stack and transferred to the stack coolant, the idling condition limits the maximum allowable ΔH to 100 kJ.mol⁻¹ and sets the minimum desorption temperature to about 60°C.

2.2 Material Thermodynamics

Maximum ΔH ($\Delta H_{\max}$) is further restricted by the requirement that, during discharge, the equilibrium pressure (P_{eq}) at the minimum FCS coolant temperature (60°C) should be higher than the target minimum delivery pressure (5 atm in Table 1 for 2017). Using the van't Hoff equation for plateau pressure [19],

$$\ln(P_{eq}) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}, \quad (1)$$

one can determine the relationship between $\Delta H_{\max}$ and ΔS such that P_{eq} equals 5 bar at 333 K; this relationship is shown in Fig. 3a.

There is also a lower limit on ΔH since, during refueling, the equilibrium pressure at the maximum allowable bed temperature should be lower than the H₂ supply pressure. Figure 3a includes the relationship between $\Delta H_{\min}$ and ΔS for 100°C maximum temperature and 50-200 atm refueling pressures, as determined from Eq. (1).

An acceptable material should have ΔH between $\Delta H_{\min}$ and $\Delta H_{\max}$, as defined in Fig. 3a. Figure 3b shows that some of the known materials in the MH database [20] have an enthalpy-entropy relationship that falls within this thermodynamic acceptability band [20], although they do not satisfy one or more other requirements as discussed below.

2.3 Containment Tank

Type 3 tanks are generally preferred for containing metal hydrides if temperatures above 80°C are encountered during refueling [21]. These consist of an inner aluminium liner that is impervious to H₂ and an outer layer of wound high strength carbon fiber-resin (CF) composite designed to withstand 225% of the nominal storage pressure. Table 2 summarizes the mechanical properties of the most-common in use high-strength and high-modulus T700S fiber and the fiber-resin composite with 60% T700S fiber by volume [22]. Prior to formal finite-element analysis using codes such as ABAQUS [23, 24], the tank geometry, optimal dome shape, winding angle, and preliminary helical- and hoop-layer thicknesses of the CF overwrap are generally determined by a netting analysis. A geodesic winding design for the dome, in which all fibers are uniformly stressed and display no shearing or bending stiffness, has a minimum mass of the CF composite for a given cylinder diameter and storage pressure [25 - 27]. Eqs. (2) and (3) can be used to determine the thicknesses of the helical and the hoop layers.

$$t_{\alpha} = pR / (2\sigma_{f,\alpha} \cos^2 \alpha) \quad (2)$$

$$t_{90} = pR(2 - \tan^2 \alpha) / (2\sigma_{f,90}) \quad (3)$$

where p is the storage pressure, R is the tank radius, α is the helical winding angle, $\sigma_{f,\alpha}$ and $\sigma_{f,90}$ are design allowable stress of fiber in the helical layer and the hoop layer, respectively. Typically, the helical thickness is about half the hoop thickness in the cylinder section, and increases in the dome. Type 3 pressure vessels that are subjected to fluctuating pressure are auto-frettagged to generate residual compressive stresses in the liner, shift tensile loads to the CF composite, and extend the fatigue life of the metal liners [28]. SAE J2579 requires a fatigue life of 5500 pressure cycles at 125% of the nominal working pressure [29].

Figure 4 shows the weight and volume of 97-L Type-3 containment tanks as a function of storage pressure for designs in which the CF overwrap bears 85-90% of the pressure load

with the balance being absorbed by the liner. The amount of CF needed is directly proportional to the storage pressure. For storage pressures under 100 atm, the liner thickness is held constant at a minimum value, but it increases with increasing pressures above 100 atm. At the highest analysed storage pressure of 200 atm, the containment tank accounts for ~23% of the weight of an on-board storage system that stores 5.6 kg usable H₂ and has 5.5% gravimetric capacity. For comparison, the containment tank for a 700-bar compressed hydrogen storage system accounts for ~70% of the total system weight [21].

2.4 Hydrogen Buffer Tank

While starting from cold (ambient temperature T_a), a buffer tank may be needed to provide H₂ for the duration of time that the bed takes to reach temperature (T_s) at which the equilibrium pressure exceeds the minimum delivery pressure and the discharge kinetics is sufficiently fast to provide H₂ at the target minimum full flow rate. The buffer capacity ($w_{H_2}^s$) is determined by the amount of H₂ consumed in the PEFC stack while the stack and the MH bed heat to reach the start-up temperature. Recognizing that in a storage system without a burner, the bed (subscript b) is heated indirectly by using the waste heat produced in the stack (subscript FC), the required buffer capacity may be estimated from the following equation.

$$w_{H_2}^s = \frac{(w_{FC} C_{FC} + w_b C_b)(T_s - T_a)}{\Delta H_{H_2} (1 - \eta_{FC})} - w_{H_2}^p \quad (4)$$

where w denotes the mass, C is the heat capacity, ΔH_{H_2} is the lower heating value of hydrogen, η_{FC} is the stack efficiency during start-up, and $w_{H_2}^p$ is the usable amount of gaseous H₂ in the void space of the MH bed (i.e., amount of H₂ available above 5 atm).

Figure 5a presents an illustrative method of coupling the buffer H₂ tank with the MH tank. The MH tank is charged with H₂ at 100 atm and may reach a peak temperature of 116°C during refueling if the material has ΔH of 28 kJ.mol⁻¹ and ΔS of 110 J.mol⁻¹.K⁻¹. The buffer is discharged and supplies H₂ to the PEFC stack during start-up while the bed temperature is

below 20°C (actually 16.8°C for this material). Between refuelings, the buffer is replenished with H₂ released from the MH bed during normal operation when the stack coolant is at near the peak temperature. The buffer pressure is limited to 40 atm, which is the equilibrium pressure at 80°C for this material.

Figure 5b presents the minimum total and usable (above 5 atm delivery pressure) amounts of buffer H₂ needed for a single start from the indicated ambient temperatures. These results were obtained using Eq. (2) with the following values for the heat capacities of the stack ($w_{FC}C_{FC}$) and the MH bed (w_bC_b) and other parameters: $w_{FC}C_{FC} = 20 \text{ kJ.K}^{-1}$, $w_bC_b = 70 \text{ kJ.K}^{-1}$, $\Delta H_{H_2} = 120 \text{ MJ.kg}^{-1}$, $\eta_{FC} = 35\%$, $T_s = 16.8^\circ\text{C}$, and $w_{H_2}^p = 0$. We estimate that ~80 g of buffer H₂ capacity is sufficient for FCS start from -40°C.

2.5 Desorption Kinetics

Not all the intrinsic H-capacity of a storage material may be accessible. For a simple material whose pressure-composition-temperature (PCT) isotherm can be represented by the van't Hoff equation, there is a lower limit of the state-of-charge (X) below which the equilibrium pressure declines rapidly with decrease in X . Hydrogen stored below this lower limit is not accessible for release at reasonable back pressures. Similarly, there is an upper limit of the state-of-charge (SOC) above which the equilibrium pressure rises rapidly with increase in X . The metal hydride cannot be charged above this upper limit at reasonable refueling pressures. The accessible lower and upper limits of SOC are functions of temperature, and the difference between the two limits for simple metal hydrides becomes smaller at higher temperatures [19].

Chemical kinetics may further limit the usable portion of the accessible intrinsic H-capacity (β). Let X_{min} and X_{max} denote the kinetically-limited usable minimum and maximum state of charge. The minimum SOC (also called the maximum state of discharge) is determined by the kinetic requirement that the MH bed should be able to supply the

minimum full flow of H_2 at the lowest operating temperature [15]. Consider a simple representation of the desorption kinetics in which the kinetic rate ($\dot{r}_d$) is first order in X and $(P_{eq} - P)$.

$$\beta \frac{dX}{dt} = -k_d X (P_{eq} - P) = -\dot{r}_d \quad (5)$$

For isothermal discharge at constant back pressure P , Eq. (5) can be integrated to obtain the following equation for discharge time (τ_d) between X_{max} and X_{min} .

$$\tau_d = \left[\frac{\beta}{k_d (P_{eq} - P)} \right] \ln \left(\frac{X_{max}}{X_{min}} \right) \quad (6)$$

Knowing τ_d , Eqs. (5) and (6) can be used to determine X_{min} at which the H_2 discharge rate ($\dot{w}_{H_2}$) from a bed containing w_{MH} amount of MH equals 1.6 g.s^{-1} (required minimum full flow rate for an 80-kW_e FCS) at the minimum coolant temperature.

$$X_{min} \ln \left(\frac{X_{max}}{X_{min}} \right) = \frac{\dot{w}_{H_2} \tau_d}{\beta w_{MH}} \quad (7)$$

Figure 6 shows the relationship between τ_d and X_{min} for a bed that contains 5.6 kg of usable H_2 (w_{H_2}).

$$\beta (X_{max} - X_{min}) w_{MH} = w_{H_2} \quad (8)$$

Naturally, for given X_{max} , the faster the desorption kinetics, the smaller is τ_d , and the lower is the allowable X_{min} .

2.6 Sorption Kinetics

Just as the desorption kinetics determines the minimum SOC, the sorption kinetics determines the maximum SOC [15]. The relationship between X_{max} and the target 3.7-min refueling time is best illustrated by considering, analogous to Eq. (5), a simple representation of the sorption kinetics in which the kinetic rate ($\dot{r}_c$) is first order in $(1 - X)$ and $(P - P_{eq})$, and the rate constant k_c has Arrhenius dependence on temperature.

$$\beta \frac{dX}{dt} = k_c (1 - X)(P - P_{eq}) = \dot{r}_c \quad (9)$$

$$k_c = k_{c0} e^{-E_c / RT} \quad (10)$$

Because k_c increases and $(P - P_{eq})$ decreases with increase in temperature, there is an optimum temperature at which $\dot{r}_c$ is the highest. At this optimum refueling temperature (T_{op}), the equilibrium pressure ($P_{eq}(T_{op})$) is related to the refueling pressure (P) by the following equation.

$$P_{eq}(T_{op}) = \left(\frac{E_c / \Delta H}{1 + E_c / \Delta H} \right) P \quad (11)$$

It follows that the off-board coolant that removes the heat of sorption from the MH tank should always be at a temperature below T_{op} . Figure 7a presents T_{op} and $P_{eq}(T_{op})$ as a function of refueling pressure for a set of ΔH , ΔS and E_c .

For isothermal refueling at constant pressure, Eq. (9) can be integrated to determine the kinetic refueling time (τ_r). The actual refueling time will be greater than τ_r due to heat transfer limitations.

$$\beta \ln \left(\frac{1 - X_{\min}}{1 - X_{\max}} \right) = k_c (P - P_{eq}) \tau_r \quad (12)$$

Taking τ_r as 50% of the target refueling time, Fig. 7b presents the relationship between k_c at T_{op} and refueling pressure for different $X_{\max}$. It quantifies the levels of $k_c(T_{op})$ needed to meet the refueling time target and the enhancement in kinetic rates needed to widen the operating SOC window.

2.7 Material Compaction and Heat Transfer

In powder form, metal hydrides and adsorbents have low bulk density and poor thermal conductivity. Meeting the stringent volumetric target requires that the powders be mechanically compacted and consolidated to form pellets and disks. Attention must be paid to allow for the volumetric changes that occur as the material expands upon hydriding and the

contact resistance between the compact and heat transfer surfaces. The compacts also must possess sufficient permeability for acceptably uniform hydrogen flow during rapid charging so that the MH sorption kinetics is not greatly impaired.

Many methods have been investigated to augment heat transfer in metal hydride beds, including the use of metal foams, wires and fins [30, 31]. Densified metal hydride compacts with high conductivity materials, such as aluminum powder and expanded natural graphite (EG), as additives appear particularly promising. Sanchez et al [31] have shown that the measured effective thermal conductivity (λ_{eff}) of these compacts can be correlated by a simple model with parallel thermal resistances of metal hydride and the enhanced heat transfer additive.

$$\lambda_{eff} = \varepsilon_{MH} \lambda_{MH} + \varepsilon_{EG} \lambda_{EG} \quad (13)$$

In the above equation, ε is the material fill factor and it can be represented in terms of the mass fractions (Y), material densities, and the bulk density (ρ_b) of the bed composed of these compacts.

$$\varepsilon_{MH} = Y_{MH} \left(\frac{\rho_b}{\rho_{MH}} \right) \quad (14)$$

$$\varepsilon_{EG} = Y_{EG} \left(\frac{\rho_b}{\rho_{EG}} \right) \quad (15)$$

$$\varepsilon = \varepsilon_{MH} + \varepsilon_{EG} \quad (16)$$

Figure 8 presents λ_{eff} of a compact with $\lambda_{MH}=1.74 \text{ W.m}^{-1}.\text{K}^{-1}$ and $\lambda_{EG}=150 \text{ W.m}^{-1}.\text{K}^{-1}$. It shows that the effective thermal conductivity can be improved considerably by increasing the fill factor, i.e., by densifying the powder. However, >10% of expanded natural graphite is needed if it is desired that the bed have thermal conductivity higher than $7.5 \text{ W.m}^{-1}.\text{K}^{-1}$ at a reasonable fill ratio of 0.75.

The existing data for metal hydrides suggest that there may be a correlation between the material density of metal hydrides (i.e., crystal structure) and their H-capacity [32 - 34]. The

data in Fig. 9 indicate that ρ_{MH} is smaller for metal hydrides with higher β ; as these are the materials that contain low molecular weight elements, lithium and boron. In the balance of this study, this relationship between ρ_{MH} and H-capacity, as represented by the solid line that is least-squares fit of the data in Fig. 9, is assumed to hold.

3 Reverse Engineering: A Case Study

The concepts presented in Section 2 can be employed to determine the envelope of material properties needed to satisfy the system level targets listed in Table 1. The case study discussed in this section pertains to a low-temperature metal-hydride hydrogen storage system that is thermally integrated with the FCS, as shown schematically in Fig. 1a. The storage system uses the FCS coolant to supply heat during discharge and an off-board coolant to remove heat liberated during refueling. There is no H_2 burner in the system so that the on-board storage system efficiency is 100%. Consistent with the discussion in the previous section, the scope of this study is limited to a Type 3 containment tank, buffer H_2 tank for FCS start-up from -40°C ambient and system temperature, and expanded natural graphite for thermal conductivity enhancement. Table 3 lists the reference values of coolant temperatures, $MH \Delta H$, ΔS and E_c , and Y_{EG} considered in this study. Table 3 also includes the specifications for minimum delivery pressure and refueling pressure, and the targets for system gravimetric and volumetric capacities.

3.1 MH Refueling: Temperature Profile and Conversion

An important aspect of designing metal hydride tanks is heat removal during fast refueling with compressed hydrogen. A dynamic model is needed to track the temperature profile and hydrogen uptake, both of which change continuously with time during refueling. Consider a unit annular cell of outer radius r_2 that consists of a representative heat transfer tube of radius r_1 surrounded by MH-EG compact. Assuming that the gas and solid are in local equilibrium,

the following equations describe the dynamic changes in temperature and conversion (state-of-charge).

$$\rho_b C_b \frac{\partial T}{\partial t} = \frac{\lambda_{eff}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \rho_b^{MH} \dot{r}_c \left(\frac{\Delta H}{M_{H_2}} \right) \quad (17)$$

$$\beta \frac{dX}{dt} = k_c (1 - X)(P - P_{eq}) = \dot{r}_c \quad (9)$$

$$-\lambda_{eff} \frac{\partial T}{\partial r} = h(T_1 - T) \text{ at } r = r_1 \quad (18)$$

$$\frac{\partial T}{\partial r} = 0 \text{ at } r = r_2 \quad (19)$$

where r is the radial coordinate, t is the time, ρ_b^{MH} is the bulk density of MH, M is the molecular weight, h is the coolant-side convective heat transfer coefficient, and T_1 is the temperature of the coolant. Equations (17) - (19) were solved numerically using an implicit finite difference scheme with the spatial derivative (heat conduction term) discretized by central differencing.

The finite-difference model was used to run a set of simulations designed to investigate the effect of off-board coolant temperature on refueling at constant pressure ($P = 100$ atm), starting from $T = T_1$ and $X = X_{min} = 0.1$, and using the values of ΔH , ΔS , E_c and Y_{EG} listed in Table 3 and the kinetic constant k_c for sorption estimated from Eq. (12). The size of the unit cell was determined iteratively to achieve complete refueling, defined as average $X = 0.9$, in 3.7 min (t_r). Figure 10 summarizes the results from these simulations. The results indicate that even with EG additive the λ_{eff} is low, and in the short refueling time (i.e., sorption kinetics is fast and the heat release rate is high), the unit cell periphery heats up rapidly, overshoots the optimum temperature well within $t/t_r = 0.2$, and then approaches the equilibrium temperature corresponding to 100 atm refueling pressure. At longer times, the unit cell actually cools because of the heat removed by the coolant and the slowing

exothermic absorption reaction. The bed temperature profile evolves continuously during the refueling process, i.e., a steady-state temperature profile is not established.

Figure 10 shows that the conversion (X_2) at cell periphery ($r = r_2$) is the slowest and that it is limited more by heat transfer rather than by sorption kinetics. At 60°C initial and coolant temperature, the maximum conversion occurs at a non-dimensional distance of 0.22 at $t/t_r = 0.2$; with time, the point of maximum conversion tracks the location of T_{op} ($\sim 87^\circ\text{C}$) and slowly moves farther out from the heat exchanger tube. At 90°C coolant temperature, the maximum conversion occurs at the surface of the heat exchanger tube and it does not move with time as the bed temperatures are higher than T_{op} .

3.2 System Analysis Methodology

In an earlier publication [15], we described a system model to analyse the performance of low-temperature metal hydride systems. In this work, we modified it to incorporate the unit-cell transient reaction and heat transfer model discussed in Section 3.1. The method of using this updated model to conduct reverse engineering analysis is discussed below.

As indicated in Tables 3 and 4, we assume that the following variables are specified: material thermodynamic properties (ΔH , ΔS , E_c); minimum and maximum limits of SOC (X_{min} , X_{max}); on-board and off-board coolant temperatures; refueling pressure; heat transfer tube parameters (aluminium, tube diameter, tube thickness); EG weight fraction (Y_{EG}); weight and volume of the balance-of-plant (BOP) components (pumps, valves, piping, etc.); and H₂ collection and distribution system (five stainless-steel sintered metal tubes).

The following are the target performance parameters to be determined from the reverse engineering analysis: charge kinetic rate; discharge kinetic rate; bulk density of MH/EG composites; number of heat transfer tubes; liner thickness; CF composite thickness; vessel diameter, vessel length; and the amount of buffer H₂ and weight/volume of buffer tank.

The reverse engineering analysis is conducted subject to the following constraints that must be satisfied: amount of usable H₂; system gravimetric capacity; system volumetric capacity; minimum full flow rate of H₂; refueling time; start-up from cold; SAE code for liner fatigue; SAE code for burst safety factor; and vessel aspect ratio (study parameter).

There is not a one-to-one correspondence between the performance parameters and the constraints. For example, bulk density affects both the volumetric capacity and the thermal conductivity and hence the refueling time. A multidimensional non-linear equation solver is needed and one based on steepest descent method with quasi-Newton update has been found to be particularly suitable. The challenge was to embed, within the iteration loop of the equation solver, the finite-difference algorithm discussed in Section 3.1 for determining the temperature profile, conversion and refueling time.

3.3 Reference Material Properties

Table 4 lists the reference material properties needed to satisfy the system targets as determined using the system model outlined in Section 3.2. The system model indicates that a prospective MH candidate should have greater than 13.5% accessible intrinsic H-capacity (β) for the system to have 5.5 wt% gravimetric capacity. When mixed with 10% expanded natural graphite, the metal hydride should be capable of being compacted to 589 kg.m⁻³ (ρ_b^{MH}) for the system to reach 40 g.L⁻¹ volumetric capacity. The resulting MH/EG compact in the fully-hydrated state has 24.7% bed porosity and 8.4 W.m⁻¹.K⁻¹ thermal conductivity. The 3.7-min refueling time target can be met if the rate constant for charge kinetics is greater than 4.2 g.(kg-MH)⁻¹.min⁻¹.atm⁻¹ for isothermal refueling at the optimum temperature corresponding to 100-atm back pressure. The 1.6 g.s⁻¹ full flow rate requirement can be met if the metal hydride can be discharged from an SOC of 0.9 to 0.1 in ≤ 16.8 min at 60°C and 5-atm back pressure.

As indicated in Table 4, 85 U tubes are needed for circulating the off-board coolant at 80°C and charging the MH tank at 1.5 kg.min⁻¹ refueling rate. The mean spacing between the tubes is 3.1 times the tube diameter. The tank needs to be loaded with 51.2 kg of MH (and 5.1 kg of EG) for 5.6 kg usable H₂ between X_{min} and X_{max} .

A 33.7-L buffer tank capable of storing 80 g of H₂ at 80°C and 40 atm is needed for a single start from -40°C. The tank weighs 11.1 kg if it is made of Al 6061-T6 alloy.

Figure 11 presents the weight and volume distribution of an MH storage system that meets all system requirements. It shows that the MH storage medium accounts for 50% of the overall weight and that 21% of the weight is due to the heat transfer subsystem that includes EG, the heat transfer fluid and the in-bed heat exchanger tubes. On a volume basis, MH and the buffer H₂ tank are the largest components accounting for 60% and 24% of the overall system volume, respectively.

3.4 Sensitivity Study

The reference material targets in the above section were based on certain assumptions regarding the off-board coolant temperature, refueling pressure, EG to MH weight ratio, and minimum and maximum states-of-charge. This section briefly discusses the effect of relaxing these assumptions.

Figure 12a summarizes the results from a sensitivity study on the effect of off-board coolant temperature on the target accessible H-capacity of the MH. It shows that for an MH with ΔH , ΔS and E_c listed in Table 4, target β is smaller if the coolant temperature is lowered to 60°C from 80°C. This is due to the higher heat rejection rate at 60°C and the resulting saving in weight as fewer heat exchanger tubes are needed. The simulation results clearly indicate that conversion is limited by heat transfer if the sorption kinetics is sufficiently fast to meet the 1.5 kg.min⁻¹ refueling rate target.

Figure 12b summarizes the results from a sensitivity study on the effect of refueling pressure on β . We find that β is lowest at 100-110 atm refueling pressure. At higher refueling pressures, β has to be larger to compensate for the heavier liner and CF composite. Also, at lower refueling pressures, T_{op} is lower (see Eq. (11)), and more heat transfer tubes are needed to maintain the bed at a lower temperature during refueling.

Figure 12c summarizes the results from a sensitivity study on the effect of EG to MH weight ratio on β . The study shows that an EG to MH weight ratio of 0.1 is about the optimum. The effective thermal conductivity increases at higher EG to MH ratio but the added weight of EG is greater than the resulting saving in the weight of the heat transfer tubes.

Figure 13a summarizes the results from a sensitivity study on the effect of desorption kinetics, k_d , on material targets. Doubling k_d (same as halving τ_d) from the reference value lowers X_{min} to 0.05 from 0.1 and results in a small decrease (beneficial) in the needed β ; this decrease is proportional to $(X_{max} - X_{min})$. However, a 50% reduction in k_d results in a larger increase (penalty) in the needed β .

Finally, Fig. 13b summarizes the results from a sensitivity study on the effect of sorption kinetics, $k_c(T_{op})$, on the material targets. Doubling k_c from the reference value raises X_{max} to ~ 1 from 0.9 while lowering X_{min} to 0.06 from 0.1, and results in an 11% decrease in β . However, a 50% decrease in k_c lowers X_{max} to 0.52 (with an accompanying small increase in X_{min}) and results in $>63\%$ increase (penalty) in the needed β .

4 Discussion of Results

We have developed an integrated model to determine the bounding thermodynamic, physical, kinetic and thermal requirements for on-board hydrogen storage in reversible, low-temperature metal hydrides.

The thermodynamic requirements have been defined as a relationship between ΔH and ΔS for simple metal hydrides for which the plateau pressure can be represented by a single van't Hoff equation. The acceptable ΔH for these simple materials should be between the upper and lower limits identified in Fig. 3a as a function of ΔS . This thermodynamic requirement also applies to all the absorption/desorption steps in more complex materials that store and release H_2 through multiple reaction pathways. The underlying requirement is that the equilibrium pressure should be greater than 5 atm at the minimum FCS coolant temperature (60°C in this study) for at least one desorption step and less than 100 atm at 100-150°C for all adsorption steps.

This study has determined that the intrinsic hydrogen capacity, i.e., the material gravimetric capacity, accessible between 5 and 100 atm at 60-150°C, should be higher than 13.5 wt%. The volumetric capacity (product of bulk density and gravimetric capacity), accessible between the same range of operating pressures and temperatures, should be higher than 80 kg- H_2 .m⁻³-sorbent.

The desorption kinetic requirement has been defined in terms of the time to discharge the metal hydride between a range of the state-of-charge at 60°C and 5-atm back pressure. Meeting this requirement ensures that the system can supply H_2 at 1.6 g/s minimum full flow rate over the complete range of operating pressures, temperatures and SOC (X). Although the discharge time was determined for a simple hydride with specified ΔH and ΔS and desorption kinetics that is first-order in X and $(P - P_{eq})$, the 17-min recommended value for τ_d may be used as an initial guide for more complex materials that may follow a different desorption kinetic pathway.

Our analysis indicates that a candidate material should be capable of being charged isothermally from 10% to 90% of the accessible intrinsic capacity within 1.85 min at constant 100-atm and any temperature between 60 and 150°C. The proposed kinetic time is half of the

system target for refueling time to allow for heat transfer limitations. A detailed transient model that considers reaction kinetics and temperature distribution supports the simpler methodology used in developing the criterion for sorption kinetics. As above, although the charging time was determined for a simple hydride with specified ΔH and ΔS and sorption kinetics that is first-order in $(1 - X)$ and $(P - P_{eq})$, the 1.85-min recommended value for τ_c may be used as an initial guide for more complex materials that may follow a different sorption kinetic pathway.

Since metal hydride powders have low thermal conductivity, they must be compacted and mixed with high conductivity materials, such as aluminium and expanded natural graphite, to augment heat transfer characteristics. This study suggests a minimum effective thermal conductivity of $8.4 \text{ W.m}^{-1}.\text{K}^{-1}$ as a reasonable target for the metal hydride compact. The heat transfer additive to metal hydride weight ratio preferably should be less than 0.1.

Whereas the foregoing material requirements are extremely stringent in isolation, the bigger challenge is to meet them simultaneously. In spite of several decades of intensive material research on an international scale, no metal hydride capable of meeting these requirements has been identified, let alone verified [1, 2, 4]. Fundamental research is urgently needed to identify and develop high capacity materials that can be thermodynamically destabilized and catalyzed to absorb and release hydrogen in the range of operating temperatures and pressures and at rates indicated in Table 4.

The results of this study compliment the earlier work by Pasini et al [33] who concluded that the low-temperature metal hydrides need to have 11 wt% gravimetric capacity, somewhat lower than 13.5 wt% suggested by us. There are two main reasons that may account for this difference. First, Ref. [33] assumes that Type 4 tanks with a polymer liner can be used for service at temperatures above 120°C. We follow the SAE J2579 guideline that limits high-density polyethylene (HDPE) plastic liner to excursions at temperatures

exceeding 80°C. Second, we include a hydrogen buffer tank for start-up from cold and provide sufficient capacity for a single start from -40°C. Ref. [33] does not specifically discuss the rationale for excluding the buffer tank in their analysis.

5 Summary and Conclusions

Automotive duty cycles impose some unique and stringent requirements on on-board hydrogen storage systems. These requirements can be used to derive certain minimum material properties that metal hydrides must have to be viable candidates for the automotive application. The following is a summary of the minimum thermodynamic, physical, kinetic and thermal requirements for prospective metal hydrides.

- a) The equilibrium pressure should be greater than 5 atm at the minimum FCS coolant temperature (60°C in this study) and less than 100 atm at 100-150°C.
- b) The intrinsic hydrogen capacity (β), accessible between 5 and 100 atm at 60-150°C, should be higher than 13.5 wt% (135 g-H₂ per kg).
- c) The material should discharge from 90% to 10% of the accessible intrinsic capacity in <17 min at the minimum FCS coolant temperature and 5-atm back pressure.
- d) The material should be capable of being charged isothermally from 10% to 90% of the accessible intrinsic capacity within 1.85 min at constant 100-atm. The charge temperature can be between 60 and 150°C.
- e) All properties should be measured on samples prepared by mixing the metal hydride with a high conductivity material (such as expanded natural graphite) and after compacting the sample to 600 kg.m⁻³ MH bulk density. The compact should have a minimum effective thermal conductivity of 8.4 W.m⁻¹.K⁻¹. The heat transfer additive to metal hydride weight ratio preferably should be less than 0.1.

6 Acknowledgements

This work was supported by the Fuel Cell Technologies Office of the U.S. Department of Energy's (DOE) Office of Energy Efficiency and Renewable Energy. Ms. Grace Ordaz was the DOE Technology Development Manager for this work. Argonne is a DOE, Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago, Argonne, LLC.

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Figure Captions

Figure 1: Thermal integration of LTMH and MTMH storage systems with low-temperature fuel cell systems

Figure 2: Conceptual automotive fuel cell system with compressed hydrogen storage tank. The symbols in 2(b) denote the range of possible FCS coolant exit temperatures.

Figure 3: Thermodynamic requirement of metal hydrides suitable for on-board hydrogen storage

Figure 4: Weight and volume of CF composite and liner in Type-3 containment tank with ~95 L internal volume

Figure 5: Integration of buffer H₂ tank and MH bed and buffer capacity needed for cold start

Figure 6: Desorption kinetics requirements defined in terms of time to discharge MH from X_{max} to X_{min} at 60°C, 5-atm back pressure

Figure 7: Sorption kinetics requirements defined by considering isothermal refueling at constant pressure

Figure 8: Effective thermal conductivity of compacts as function of fill factor and EG to MH weight ratio

Figure 9: Correlation between MH material density and intrinsic H-capacity, data from Van Hassel et al [27]

Figure 10: Temperature profile and conversion during refueling from X_{min} to X_{max} at constant pressure (100 atm)

Figure 11: Weight and volume distribution for a H₂ storage system using a metal hydride with material properties that combine to satisfy all the system-level requirements listed in Table 1

Figure 12: Single-parameter sensitivity study to examine the effect of off-board coolant temperature, refueling pressure and EG to MH weight ratio on intrinsic material capacity target

Figure 13: Single-parameter sensitivity study to examine the effect sorption and desorption kinetics on intrinsic material capacity target

Table Captions

Table 1: Technical System Targets for On-board Hydrogen Storage for Light-Duty Fuel Cell Vehicles

Table 2: Properties of T700S Carbon Fiber and Composite (60% fiber volume)

Table 3: Reverse Engineering Study Parameters

Table 4: Reference Metal Hydride Targets

(a) LTMH

(b) MTMH

Figure 1: Thermal integration of LTMH and MTMH storage systems with low-temperature fuel cell systems

(a) Fuel cell system (b) Operating temperatures and FCS efficiencies

Figure 2: Conceptual automotive fuel cell system with compressed hydrogen storage tank. The symbols in 2(b) denote the range of possible FCS coolant exit temperatures.

(a) Acceptable enthalpy-entropy relationship (b) ΔH - ΔS map of selected metal hydrides

Figure 3: Thermodynamic requirement of metal hydrides suitable for on-board hydrogen storage

Figure 4: Weight and volume of CF composite and liner in Type-3 containment tank with ~95 L internal volume

(a) Integration of H₂ buffer tank and MH bed (b) Buffer capacity for single start from cold

Figure 5: Integration of buffer H₂ tank and MH bed and buffer capacity needed for cold start.

Figure 6: Desorption kinetics requirements defined in term of time to discharge MH from X_{max} to X_{min} at 60°C, 5-atm back pressure.

(a) Optimum sorption temperature

(b) Sorption kinetic constant at T_{op}

Figure 7: Sorption kinetics requirements defined by considering isothermal refueling at constant pressure

Figure 8: Effective thermal conductivity of compacts as function of fill factor and EG to MH weight ratio

Figure 9: Correlation between MH material density and intrinsic H-capacity, data from Van Hassel et al [27]

Figure 10: Temperature profile and conversion during refueling from $X_{\min}$ to $X_{\max}$ at constant pressure (100 atm)

(a) Weight distribution

(b) Volume distribution

Figure 11: Weight and volume distribution for a H₂ storage system using a metal hydride with material properties that combine to satisfy all the system-level requirements listed in Table 1.

Figure 12: Single-parameter sensitivity study to examine the effect of off-board coolant temperature, refueling pressure and EG to MH weight ratio on intrinsic material capacity target

(a) Desorption kinetics

(b) Sorption kinetics

Figure 13: Single-parameter sensitivity study to examine the effect sorption and desorption kinetics on intrinsic material capacity target

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Table 1: Technical System Targets for On-board Hydrogen Storage for Light-Duty Fuel Cell Vehicles

Storage Parameter	Units	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H ₂ (net useful energy/max system mass)	kWh/kg (kg H ₂ /kg system)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H ₂ (net useful energy/max system volume)	kWh/L (kg H ₂ /L system)	1.3 (0.040)	2.3 (0.070)
Durability/Operability:			
Operating ambient temperature	°C	-40/60 (sun)	-40/60 (sun)
Min/max delivery temperature	°C	-40/85	-40/85
Operational cycle life (1/4 tank to full)	Cycles	1500	1500
Min delivery pressure from storage system	atm (abs)	5	3
Max delivery pressure from storage system	atm (abs)	12	12
On-board efficiency	%	90	90
Charging/Discharging Rates:			
System fill time (5 kg)	min (kg H ₂ /min)	3.3 (1.5)	2.5 (2.0)
Minimum full flow rate	(g/s)/kW	0.02	0.02
Start time to full flow (20°C)	s	5	5
Start time to full flow (-20°C)	s	15	15
Transient response at operating temperature 10%-90% and 90%-0%	s	0.75	0.75

Table 2: Properties of T700S Carbon Fiber and Composite (60% fiber volume)

Property	Unit	Fiber	Composite
Tensile Strength	MPa	4900	2550
Tensile Modulus	GPa	230	135
Tensile Strain	%	2.1	1.7
Density	kg/m ³	1800	1580
Compressive Strength	MPa		1470
Flexural Strength	MPa		1670
Flexural Modulus	GPa		120

Table 3: Reverse Engineering Study Parameters

Parameter	Units	Reference Values	Range of Values	Comments
FCS Coolant Temperature	°C	62 - 85		Reference FCS [12]
Off-Board Coolant Temperature	°C	80	60 - 100	
MH Thermodynamics	ΔS , J/mol.K	110	TBD	$\Delta H_{\min} = 26.8$ kJ/mol
	ΔH , kJ/mol	28	TBD	$\Delta H_{\max} = 32.2$ kJ/mol
Sorption Activation Energy	E_c , kJ/mol	45	TBD	NaAlH ₄ data
Minimum Delivery Pressure	atm	5		DOE target [1]
Minimum Full Flow Rate of H ₂	g/s	1.6		DOE target [1]
Refueling Pressure	atm	100	50 - 200	
EG/MH Weight Ratio		0.1	0.05 - 0.25	IJHE (2003) 515-527 [22]
System Gravimetric Capacity	%wt.	5.5		DOE target [1]
System Volumetric Capacity	g/L	40		DOE target [1]

Table 4: Reference Metal Hydride Targets

Variables	Related Variables	Reference Values	Constraints
MH Intrinsic Capacity		13.6% H capacity	5.5 wt% gravimetric
Fill Ratio	Bulk Density	24.7% bed porosity	40 g/L volumetric
	Thermal Conductivity	589 kg/m ³ MH bulk density 8.4 W/m.K bed conductivity	
Desorption Kinetics	$X_{\min} = 10\%$	$\tau_d = 16.8$ min	1.6 g/s min full flow
Sorption Kinetics	$X_{\max} = 90\%$	$k_c = 4.2$ g/kg _{MH} /min/atm	$X_{\min}$ to $X_{\max}$ in 1.85 min
HX Tube Spacing	Number of HX Tubes	$r_2/r_1 = 3.1$ 85 U tubes	1.5 kg/min refueling
Mass of MH	Mass of Expanded	51.2 kg MH	5.6 kg usable H ₂
	Natural Graphite	5.1 kg EG	
Buffer Tank Capacity	Weight of Al tank	11.1 kg buffer tank weight 33.7 L buffer tank volume	Startup from -40°C