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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 refueled at reasonable H_2 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}.

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

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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.

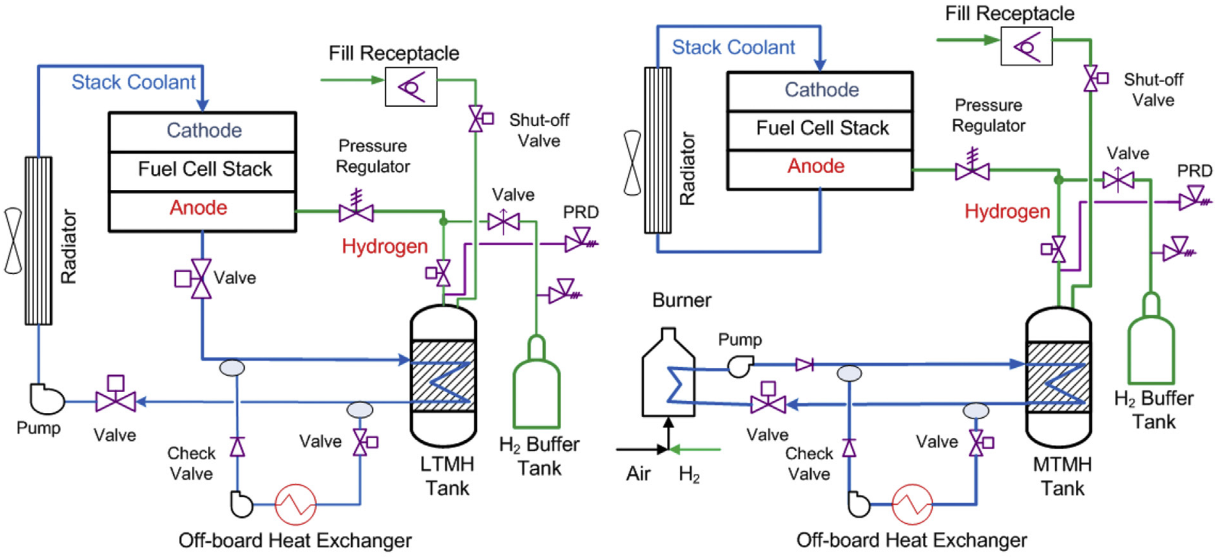
The scope of this work is limited to on-board reversible metal hydrides, i.e., to the first three classes of materials listed above. Off-board regenerable materials, such as alane [5–7] and ammonia borane [8–10], have also attracted considerable attention recently, but transporting these materials, maintaining 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 kWs (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.

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.



(a) LTMH (b) MTMH

Fig. 1 – Thermal integration of LTMH and MTMH storage systems with low-temperature fuel cell systems.