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Operation of a PEM fuel cell with $LaNi_{4.8}Sn_{0.2}$ hydride beds

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Abstract

A series of measurements were performed using metal hydride sorbent beds to operate a 1.0 kW capacity proton electrolyte membrane (PEM) fuel cell hybrid power system. Two sorbent beds were filled with $LaNi_{4.78}Sn_{0.22}$ alloy and each unit had a maximum storage capacity of ~280 sL hydrogen. A single sorbent bed was able to supply hydrogen gas for ~20–25 min operation at 30 A net current and ~900 W output power. These hydride beds were also capable of supplying sufficient hydrogen flows and pressures to produce up to ~1.1 kW output power from the fuel cell for shorter durations. Good correlations for hydrogen consumption rates and power outputs were obtained and boundaries parameters for continual operation were identified. Various input and output parameters were recorded and analyzed to relate hydride bed, fuel cell, and battery behavior and assess their dynamic interactions.

Keywords: Intermetallics; Hydrogen storage materials; Fuel cells; Gas–solid reactions

1. Introduction

The reversible chemical reaction between hydrogen gas (H_2) and a generic metal alloy (AB_n) is represented by the following equation:

$$AB_n + (x/2)H_2 \leftrightarrow AB_nH_x + \Delta Q \quad (1)$$

In Eq. (1), ΔQ is the exothermic heat of reaction for hydride phase (AB_nH_x) formation, which generates heat release during hydrogen absorption and cooling during hydrogen desorption. Efficient operation of a metal hydride bed requires [1] that this heat be effectively managed (i.e., dissipated during absorption and provided during desorption, respectively). Although there are numerous metals and alloys that can react with hydrogen, only a relatively few have the combination of chemical and physical properties that will allow reversible hydrogen storage [2,3] in practical applications. The list becomes even shorter if the hydride uses the waste heat from a proton electrolyte membrane fuel cell (PEMFC) during H_2 desorption from the hydride bed to operate this fuel cell. Examples of these practical metal hydrides are VH_2, $TiFeH_2$, and substituted alloys of $LaNi_5H_x$ [3]. Candidate hydrides must also satisfy a number of criteria for successful utilization with PEMFC power systems. These include:

- H-storage capacity >1 wt.% (nominal—depends on the specific application).
- Low cost (both materials and processing).
- Desorption pressure (P_{des}) ~1–10 bar.
- Use waste heat for desorption (i.e., <90 °C for PEMFC).
- Fast kinetics (especially, H_2 absorption during refueling process).
- Durability during absorption/desorption and temperature cycling.
- Safety and low toxicity.
- Resistance to contamination and common impurities.
- Minimal demands for hydride sorbent bed activation.

For a PEMFC power system where minimal weight of the hydrogen storage vessel is *not* the pre-emptive requirement (i.e., flood light sets, utility vehicles, tow tractors, stationary electrical generation, etc.), tin (Sn) submitted AB_5 alloys offer

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excellent combinations of all these properties [4–6]. Consequently, it is proposed that a lanthanum (La)-rich mischmetal AB_5 alloy of nominal composition $LmNi_{4.8}Sn_{0.2}$ be used in near term metal hydride storage vessels for demonstrations with PEMFC power systems. Here, Lm is a lanthanum-rich mischmetal (i.e., a mixture of rare earth metals with approximate composition $La_{0.90}Ce_{0.05}Nd_{0.04}Pr_{0.01}$). This alloy composition should give desorption pressures above 1.0 bar for temperatures greater ~273 K to ensure meeting PEMFC supply pressure requirements.

2. Description of a hydride storage vessel for PEMFC applications

Beyond the metal hydride sorbent material itself, the design of the containment vessel is critical to overall performance and safety of the hydrogen storage vessel. The metal hydride powder must be securely retained in the sorbent bed while allowing for both minimal impediment of gas flow within the bed as well as permitting efficient heat transfer from the reactive, but low thermally conductive, hydride particles so that appropriate heating or cooling will occur.

Various bed design configurations have been proposed and tested over the last 40 years or so including the metal hydride beds developed for sorption cryocoolers [7–9]. These sorption cryocooler beds incorporate features that yield reliable, robust, and safe operation for this application [8,9] and a conceptual design configuration for 1–2 kg hydrogen capacity metal hydride storage vessels could be based upon adaptations of the Planck sorption cryocooler (PSC) low-pressure storage bed (LPSB) shown in Fig. 1. This PSC-LPSB bed uses $LaNi_{4.78}Sn_{0.22}$ alloy to store reversibly approximately 25 g or 280 standard-liters (sL) of hydrogen gas at ambient temperature. The mechanically crushed $LaNi_{4.78}Sn_{0.22}$ alloy powder is contained in porous Al metal foam to facilitate internal heat transfer within the hydride bed.

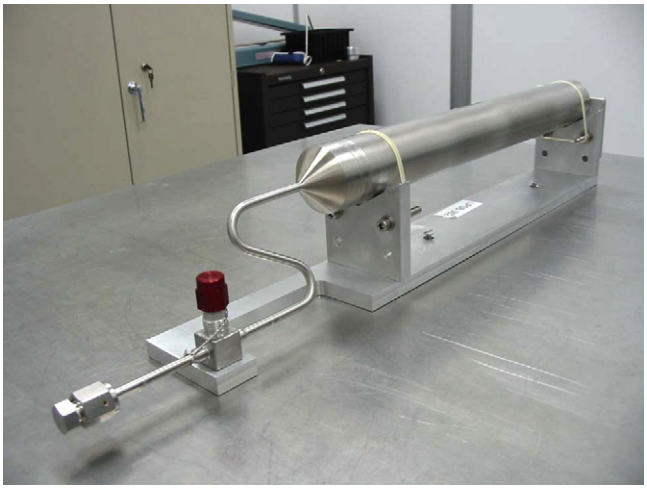

Fig. 1. Photograph of a low-pressure storage bed (LPSB) from the JPL Planck sorption cryocooler project that can be modified (i.e., greatly enlarged) to store sufficient quantities hydrogen to operate 1–5 kW size PEM fuel cell power systems.

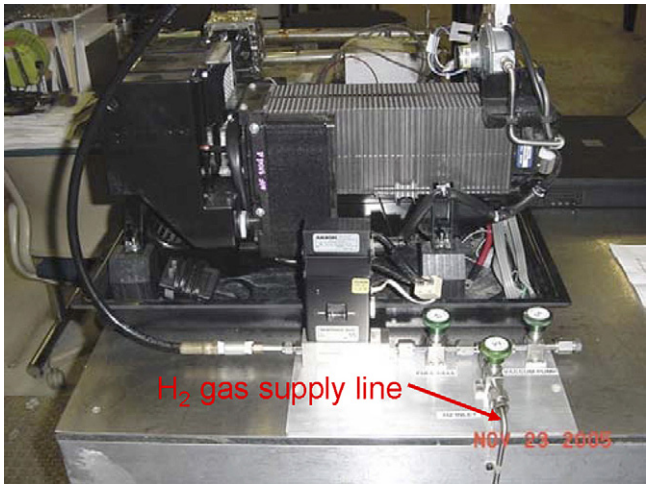

Fig. 2. Nexa™ power module uses a Ballard PEM fuel cell provides ≤1.2 kW by reacting H_2 gas with oxygen from ambient air and is air cooled.

3. Laboratory testing of PSC hydride beds with a hybrid fuel cell power system

In order to demonstrate the performance potential by existing JPL-built metal hydride sorbent beds to operate a 1.0 kW capacity PEMFC, a series of experiments were performed. Descriptions of the facilities are given in this section along with a brief summary of tests performed and key results obtained.

The Nexa™ power module shown in Fig. 2 can produce up to 1200 W of unregulated dc power at a nominal output voltage of 26 V dc via a Ballard PEMFC. According to the manufacturer's manual [10], the fuel cell consumes hydrogen at a flow rate ≤18.5 slpm (standard liters per minute) at maximum power. Hydrogen needs to be supplied to the fuel cell inlet at pressures ranging from 1.7 to 18.2 bar. Air from ambient surroundings is used in the fuel cell power reaction. The fuel cell is air cooled during operation and uses external lead-acid batteries to start and shut down.

The hydride beds that were for testing with the Nexa™ fuel cell module were the two LPSB units from the PSC engineering bread board (EBB) cooler described in Ref. [9]. These sorbent beds are filled with $LaNi_{4.78}Sn_{0.22}$ hydride and are similar to the unit shown in Fig. 1. Each EBB-LPSB had a maximum storage capacity of ~280 sL. A single LPSB should be able to supply hydrogen gas for ~20–25 min operation at 30 A net current and ~900 W output power. The pressure from the $LaNi_{4.78}Sn_{0.22}$ hydride is strongly dependent upon the bed temperature, as is the case for all metal hydrides [2,3]. The equilibrium absorption and desorption pressures for the $LaNi_{4.78}Sn_{0.22}H_x$ material have been measured previously [5] over the range from 273 to 473 K. In order for the desorption pressures across the plateau region of $x \sim 0.5$–5.0 to exceed the minimum fuel cell input pressure of 1.7 bar, the $LaNi_{4.78}Sn_{0.22}H_x$ must be heated above ~333 K. Since the LPSB units have no internal means of heating and the fuel cell is air cooled, the beds must be placed in external containers to provide the necessary heating. The glass vessels necessary for circulating either hot or cold liquids over the LPSB surface are shown in Fig. 3.

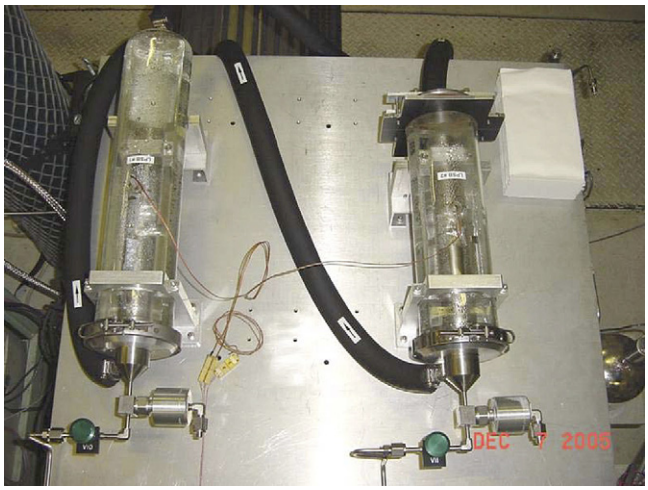

Fig. 3. Two low-pressure storage beds (LPSB) are each filled with $LaNi_{4.78}Sn_{0.22}$ alloy. Each LPSB unit is mounted in a glass housing allowing alternate circulation of heated or cooled water/glycol liquid to allow desorption or absorption of hydrogen from the hydride beds, respectively. Note the thermocouples mounted on the top surface of each LPSB to monitor external bed temperature during testing.

A schematic layout of the LPSB hydride beds, Nexa™ PEMFC, power management unit, and data acquisition/control system is shown in Fig. 4. Two refrigerator/heater baths were separately operated at about 15 and 75 °C to provide cooling and heating, respectively, to the individual LPSB units via a liquid manifold system. A mixture of water and ethylene glycol was circulated through these lines. The photograph in Fig. 3 shows the units in their glass jackets with liquid circulating to provide the temperature control during testing.

One computer system was used to collect various parameters including pressure, bed temperatures, hydrogen flow rates, electrical constants from the batteries and fuel cell power management systems via Lab View software. While another computer was used to control operating parameters for the fuel cell and battery subsystems, only manual procedures were used to regulate the temperatures and the hydrogen gas absorption and desorption flows and pressures. An Aalborg Model GFM37 flow meter (Cole-Parmer Instruments, Vernon Hills, IL) was installed at the hydrogen gas inlet to the fuel cell power system for monitoring H_2 flow rates and also estimating total gas consumed during these tests. Since this flow meter was not calibrated for hydrogen flows, it gave total hydrogen contents that were systematically ~20–25% too large compared to volumetric measurements (which are accurate to within ±2%) of the gas needed to refill the LPSB hydride beds after supplying gas to the fuel cell during testing. A summary of combined two-bed hydride/fuel cell tests is given in Table 1.

These experiments focused on three particular areas of interest: simultaneous refueling, hot-switching, and battery loading with a focus on achieving "hot-switch" (i.e., allowing the PEMFC to continue providing uninterrupted output power while the hydrogen supply beds were manually switched). This manual switching was a limitation of the mixed-mode control system.

A typical single-bed sequence is shown in Fig. 5. Here, the thermodynamic behavior of the EBB hydride is clearly seen, wherein the "fully charged" hydride bed builds pressure in response to increasing bath temperature. The operational methodology used in this and all cases called for a "hot-start" of the PEMFC; that is, the fuel cell began operation by reacting hydrogen coming directly from the supply lines exiting the hydride bed. In this way, it was shown that the integrated system did not require the separate gaseous hydrogen storage tank shown in Fig. 4 for startup. After continued operation, it can be seen in Fig. 5 that hydrogen pressure decreased from an initial peak pressure from the dynamic isotherm during bed heat up and entered "pseudo" steady-state behavior near ~30 Psia (~2 bar) as hydrogen desorbs across the hydride plateau region. It should be noted; however, that the fuel consumption of the PEMFC is independent of these variations in the supply pressure, which is regulated at the inlet to the fuel cell device. The Ballard/Nexa™ system showed that it would maintain normal operation over the hydrogen supply pressure range 21 Psia (1.4 bar) < P < 300 Psia (20.4 bar).

Fig. 5 also shows the particular behavior of the PEMFC's integrated hydrogen flow controller. Due to the need to maintain a moist hydrogen-rich environment in the vicinity of the fuel cell "stack" and heat exchanger, the PEMFCs control system commands a purge of the stack every 5 min in steady-state operation. This behavior appears as a punctuated flow rate in

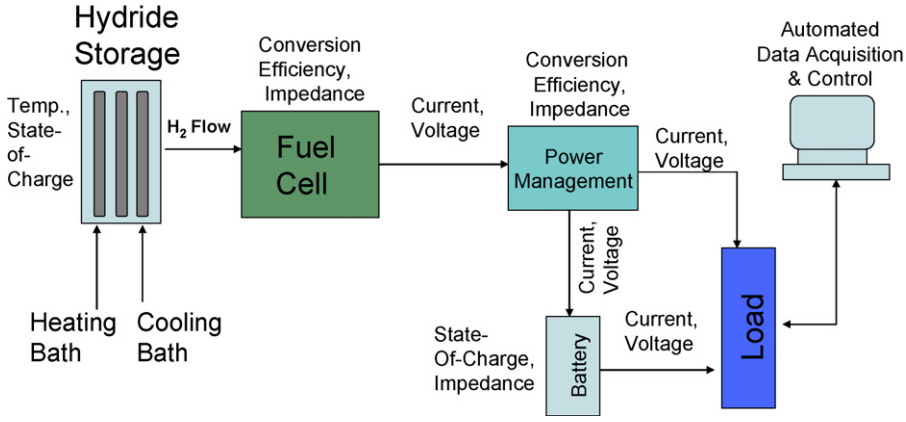

Fig. 4. Schematic representation of the metal hydride beds and PEMFC testing system.

Table 1
Summary of operational tests of LPSB hydride beds and fuel cell

Test modes	Duration (min)	Max power (W)	Notes and comments
Two-bed shakedown	75	900	Test; beds switched at zero output/zero load
System test	75	700	Test; beds switched at zero output/zero load
Refill-while-running	180	700	Proof-of-concept for hot-refueling procedure; bed refill took too long and fuel cell shut off
Hot-switch demo	70	1100	Proof-of-concept; beds "hot-switched" at 160 W output
"Full-up" system	60	1100	Hot-switching, battery charging/discharging

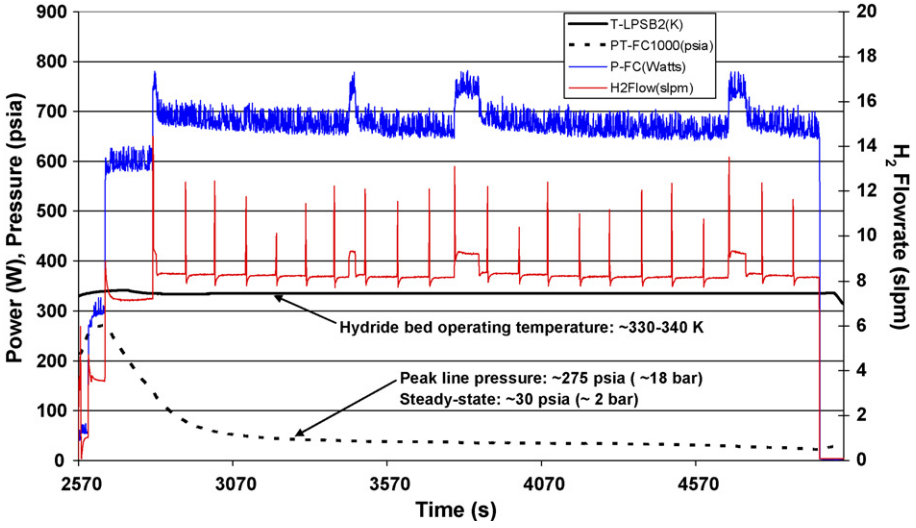

Fig. 5. Selected data from a typical system test shows hydrogen flow parameters where the peak-pressure curve and bed temperature are dynamically relating to the isotherm behavior of the $LaNi_{4.78}Sn_{0.22}$ hydride during desorption to supply H_2 gas to the fuel cell.

the recorded data. The total effect on overall consumption was found to be small. For example, the data in Fig. 5 show an average flow rate of approximately 8 standard liters/min (slpm) at ~30 Psia (2 bar) supply pressure, with a PEMFC output of approximately 700–750 W. This translates, in this case, to approximately 88 W/slpm H_2, or in terms of energy conversion, ~5 kJ/sL H_2 at the fuel cell stack.

In the "hot-switch" operation of the hybrid system, as one bed (i.e., LPSB #1) is depleted of hydrogen, the other (LPSB #2) is quickly brought up to operating temperature and switched into the supply loop. To achieve this without loss of continuous power, the switch must be performed quickly. The PEMFC output could be maintained in this mode only if the total power output is sufficiently low. This is expected; as the total latency

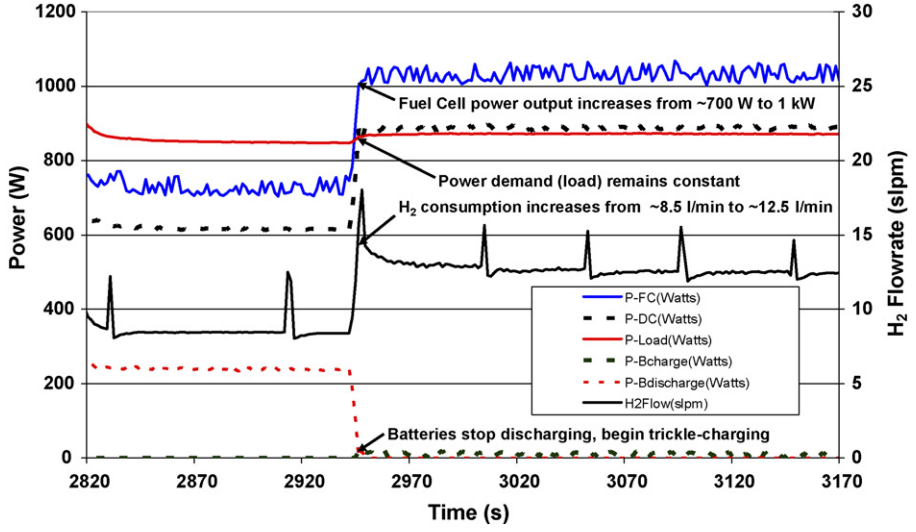

Fig. 6. A portion of an operational run demonstrating changes in hydrogen flow rate and battery discharging when the output power from the fuel cell is increased from ~700 to ~1000 W to maintain a nearly constant load.

of the switchover cannot exceed the time it takes the PEMFC to consume most of the available hydrogen in the supply lines between the hydride beds and fuel cell. Hot-switch operation was successfully tested to a PEMFC output level of approximately 175 W.

The last behavior to be evaluated was the impact of increasing the output power from the fuel cell on the quantity of hydrogen gas required while also ending the discharge from the batteries to keep the output load stable near ∼900 W. These results are shown in Fig. 6 where the transition from a battery discharge mode to charging mode occurs at the nominal 2950 s point along with increased H_2 flow and larger fuel cell output power. The ability of the hydride bed to supply sufficient H_2 gas to increase or maintain fuel cell power ≥1.0 kW is critically dependent on both the bed temperature (i.e., raising the intrinsic desorption pressure) and transfer of the heat from the hot circulating fluid on the bed's external walls into the hydride particles within the bed itself. This latter property is dominated by the effective thermal conductance of the Al foam in the bed and intrinsic conductivities for the gas and hydride powders. The maximum output power achievable from these LPSB hydrides was 1050 ± 50 W for durations shorter than ∼10 min before the hydrogen flow rates decreased sufficiently to cause power loss or shutdown from the PEMFC system. Probably, slightly highly hydrogen flows could be obtained if the LPSB hydrides were operated at temperatures greater than ∼80 °C.

4. Summary and conclusions

A conceptual configuration for H_2-capacity metal hydride storage devices based upon use of $LmNi_{4.8}Sn_{0.2}$ alloy has been developed. The modular sorbent beds should allow straightforward adaptations to larger size vessels up to about 5 kg of reversible hydrogen gas capacities. Various laboratory tests were performed using existing JPL-built $LaNi_{4.78}Sn_{0.22}$ hydride sorbent beds to operate a 1.0 kW capacity PEMFC. The laboratory tests verified these units were completely capable of supplying sufficient hydrogen flows and pressures to produce up to ∼1.1 kW output power from the PEMFC as well as undergo simultaneous hydrogen absorption and desorption from separate LPSB units and during switching between these bed modes while the fuel cell was running. Good correlations for hydrogen consumption rates and power outputs were obtained and parameters for continual operation were identified.

Acknowledgments

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References

[1] G. Sandrock, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.), Handbook of Fuel Cells—Fundamentals, Technology and Applications, vol. 3, Part 2, Wiley, Chichester, UK, 2003, pp. 101–112.
[2] G. Sandrock, J. Alloys Compd. 293–295 (1999) 877–888.
[3] R.C. Bowman Jr., B. Fultz, MRS Bull. 27 (2002) 668–693.
[4] R.C. Bowman Jr., C.H. Luo, C.C. Ahn, C.K. Witham, B. Fultz, J. Alloys Compd. 217 (1995) 185–192.
[5] R.C. Bowman Jr., C.A. Lindensmith, S. Luo, T.B. Flanagan, T. Vogt, J. Alloys Compd. 330–332 (2002) 271–275.
[6] V. Iosub, M. Latroche, J.-M. Joubert, A. Percheron-Guégan, Int. J. Hydrogen Energy 31 (2006) 101–108.
[7] L.A. Wade, R.C. Bowman Jr., D.R. Gilkinson, P.H. Sywulka, Adv. Cryogenic Eng. 39 (1994) 1491–1498.
[8] R.C. Bowman Jr., J. Alloys Compd. 356/357 (2003) 789–793.
[9] P. Bhandari, M. Prina, R.C. Bowman Jr., C. Paine, D. Pearson, A. Nash, Cryogenics 44 (2004) 395–401.
[10] Nexa™ (310-0027) Power Module Installation Manual and Integration Guide, Ballard Power Systems, Document Number: MAN5000054, Part Number: 5000508, Version: September 12, 2002.