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A passive lithium hydride based hydrogen generator for low power fuel cells for long-duration sensor networks

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ABSTRACT

This paper focuses on developing an efficient fuel storage and release method for hydrogen using lithium hydride hydrolysis for use in PEM fuel cells for low power sensor network modules over long durations. Lithium hydride has high hydrogen storage density and achieves up to 95–100% yield. It is shown to extract water vapor freely from the air to generate hydrogen and has a theoretical fuel specific energy of up to 4900 Wh/kg. A critical challenge is how to package lithium hydride to achieve reaction completion. Experiments here show that thick layers of lithium hydride nearly chokes the reaction due to buildup of lithium hydroxide impeding water transport and preventing reaction completion. A model has been developed that describes this lithium hydride hydrolysis behavior. The model accurately predicts the performance of an experimental system than ran for 1400 h and consists of a passive lithium hydride hydrogen generator and PEM fuel cells. These results offer important design guidelines to enable reaction completion and build long-duration lithium hydride hydrogen generators for low power applications.

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Introduction

Long-life, low power sensor modules are a key component for many important sensor network applications. For example they could perform exploration and mapping of inaccessible environments, monitor disasters such as fires and earthquakes, monitor the environment including air quality in urban areas and soil conditions for agriculture (Fig. 1) [1]. In these applications several hundreds or thousands of modules might be deployed over large areas and wirelessly report their data to a base station. To be practical, once deployed, the modules need to operate unattended, ideally for years. A key

to making these sensor systems feasible is requiring them to have long-duration power supplies. Today's conventional battery technologies are limited by their chemistries and will not meet the needs of many of these systems due to their relatively low energy densities [2,3]. The low total energy of batteries will not be able to provide power for the multiple years required of many applications. A better solution is required.

Fuel cells can produce power continuously and have been suggested for long-duration, low power sensors because they typically have high energy densities and their low power is not an important constraint for low power sensor modules. Polymer Electrolyte Fuel (PEM) cells in particular operate at

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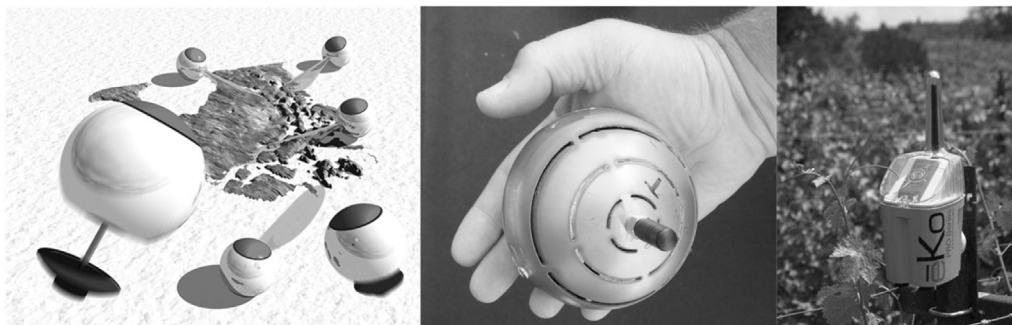


Fig. 1 – Low power mobile sensor network modules can be used in exploration and terrain mapping (left), for monitoring disasters using Intel’s sensor grenade concept (center) and environmental monitoring and agriculture (right).

room temperature, with high conversion efficiencies ranging from 50 to 65%, and are clean and quiet [4]. In cases with higher peak power but with low duty cycles, hybrid fuel cell/battery power supplies [5] can be effectively used.

However PEM fuel cells face several challenges. Unlike batteries, they are relatively less robust to operating conditions [6–8]. Wrong operating conditions can drastically shorten the life of a PEM fuel cell to a few hours or days due to degradation of its components [6,8]. Important work has been carried out to identify, model and control degradation of PEM fuel cells [6,7,9]. It has been recently shown that properly controlling a fuel cell’s operating conditions can avoid premature failures and, in theory, allow for long-lives of 3–5 years [8]. The second critical problem faced by PEM fuel cells is storing of the hydrogen fuel. Conventional storage and release of hydrogen can be prohibitively bulky and complex, making it unsuitable for small, low power applications like sensor networks. This includes storing hydrogen gas at high pressures, 300–700 bars [10]. Such technologies while proven for larger automobile sized applications face substantial challenges with miniaturization particularly low power sensor applications. A second approach is cryogenic storage of hydrogen in liquid form. This has been commonly demonstrated for applications in space exploration and is feasible for sensor network applications on the lunar surface [11]. However, for terrestrial applications, the systems can be complex, requiring substantial energy be expended to keeping the hydrogen at very low temperatures. This factor makes it inappropriate for low power, long-duration terrestrial sensor network module applications.

This paper addresses the fuel storage problem for the common Proton Exchange Membrane (PEM) fuel cell in a battery-hybrid power supply that would be appropriate for low power sensor modules with operational lives in the order of 3–5 years. The objective is to develop a fuel storage and release design that is pressure-controlled, small, light-weight, simple, compact, and is passive, not requiring active electronics, sensors, or actuators. Actively-controlled hydrogen generator concepts have been considered (see Fig. 5) [12] but is not the preferred option due to its increased complexity.

Feasibility studies of possible hydrogen storage mechanisms are performed and lithium hydride is selected as the storage medium because of its high weight density of

hydrogen, its simple chemistry, achieving up to 95–100% reaction completion rates at room temperature [12,13], and its hydrogen release can be controlled simply as will be shown later by exposing it to water vapor. The key challenge with lithium hydride is how to package lithium hydride to achieve reaction completion. Experiments here show that thick layers of lithium hydride substantially slow the reaction nearly choking it due to buildup of lithium hydroxide impeding water transport. A semi-empirical model has been developed that describes this lithium hydride hydrolysis behavior. In Section A [passive hydrogen generator](#), a prototype lithium hydride hydrogen generator is presented and experimentally tested with a PEM fuel cell power supply to validate the model. The lithium hydride model is shown to accurately predict the generator life and performance. The experimental fuel cell power supply consists of a lithium hydride generator that provides hydrogen and air breathing PEM fuel cells in a battery-hybrid system. In the hybrid system, fuel cell provide constant power trickle-charging a battery that meets the high and variable demands of the load. Based on the experimental results, guidelines to designing and operating long-duration lithium hydride hydrogen generators for low power applications are offered.

Background and literature review

Efficient hydrogen storage is a challenging problem and is one of the major factors preventing hydrogen from becoming a widespread energy source [14]. Here lithium hydride is explored for small, low power sensor network applications. Hydrogen stored as a liquid or compressed at very high pressures is not practical for this research because of the complexity and the difficulty integrating them into low power, long-life systems. Metal hydrides were then considered because of their high gravimetric hydrogen weight densities and the ease with which they could be stored on a low power system. Of the metal hydrides, lithium hydride was selected because of its high hydrogen weight density, its simple hydrolysis reaction, high yield, and the relative ease with which one can control the reaction. In this section, the first two advantages are reviewed, namely lithium hydride’s high hydrogen content and its high yield.

Table 1 – Table of various hydrides and their gravimetric hydrogen content, defined as the mass of the hydrogen divided by the total mass of the hydride.

Hydride	Hydrogen weight content
LiBH ₄	18.4%
NaBH ₄	10.6%
Be(BH ₂) ₄	20.8%
NaAlH ₄	7.4%
NaH	4.1%
CaH ₂	4.7%
LiH	12.5%

Lithium hydride's high hydrogen weight content

First, lithium hydride was selected for its high gravimetric density of hydrogen.

Table 1 shows lithium hydride compared with a variety of actively researched hydrides. Some borohydrides have higher weight densities, such as sodium borohydride, (NaBH₄) but require expensive catalysts for reaction completion and are prone to degradation [15]. Beryllium borohydride has very high hydrogen content but is too reactive and toxic to be considered [16]. Alkali metal hydrides, such as calcium hydride, sodium hydride, and lithium hydride all can produce hydrogen on contact with water. Of these hydrides, lithium hydride has the highest hydrogen weight content.

In spite of its high hydrogen content, lithium hydride is not always appropriate for fuel cell applications, particularly when the fuel needs to be recharged or be easily “reversible” at standard temperature and pressure. This means that it cannot be easily recharged with hydrogen after it has been released. This is not an important consideration for very long durations, low power applications such as a distributed field sensor network.

High hydrogen yield of lithium hydride and specific energy

The second reason for choosing lithium hydride is its simple hydrolysis reaction mechanism and high yields. To produce hydrogen, lithium hydride does not require an expensive catalyst and only needs liquid water or water vapor, which as will be presented later can be freely extracted from the air.

Lithium hydride (LiH) is composed of lithium metal bonded with hydrogen. It is typically gray or colorless solid and reacts with water to produce hydrogen gas and lithium hydroxide in the following hydrolysis reaction:



To test the yield of a lithium hydride hydrolysis reaction, 1.6 g of lithium hydride was placed in the reaction chamber and allowed to react with water vapor over the next several days. The volume of hydrogen output was measured in the collecting flask (Fig. 2). The results of this experiment are presented in Fig. 3. The plot shows that 1.6 g of lithium hydride produced the theoretical 4.5 L of hydrogen. These results agree with results from literature such as by Kong et al. that show 95–100% reaction completion rates [12,13]. For these small quantities of lithium hydride, it is found that the lithium hydroxide product does not block the hydrolysis reaction. This is a very promising result, because most chemical hydrides cannot produce the high yields reported for lithium hydride at room temperature and without catalysts [12,13,17].

With this high yield, lithium hydride fuel used in conjunction with a fuel cell can offer theoretically high specific energy. Consider a conventional lithium ion battery with a specific energy of 120 Wh/kg or a lithium thionyl chloride primary battery with specific energy of 450 Wh/kg (one of the highest specific energy for any battery). We also compare the net specific energy of methanol used in a Direct Methanol Fuel Cell (DMFC) [18]. State-of-the-art DMFC cells operate at 40% efficiency and consume a diluted (50%) methanol solution. They provide a net specific energy of 1000 Wh/kg, which is a substantial improvement compared to the best batteries. In comparison, consider a PEM fuel cell with lithium hydride as its hydrogen source, with a fuel cell chemical to electrical conversion efficiency of 65%, and where the exhaust water is recycled or extracted freely from the air as will be shown later in this paper. The net theoretical specific energy of the lithium hydride fuel in this scenario is 4900 Wh/kg, which is nearly 40-folds greater than the lithium ion batteries, nearly 11 folds greater than the lithium thionyl chloride primary battery and 5 folds greater than DMFC. For a conversion efficiency of 50%, the net theoretical specific energy for this system is 3800 Wh/kg which is nearly 4 folds greater than DMFC. However if the volumetric energy density were considered, then all the

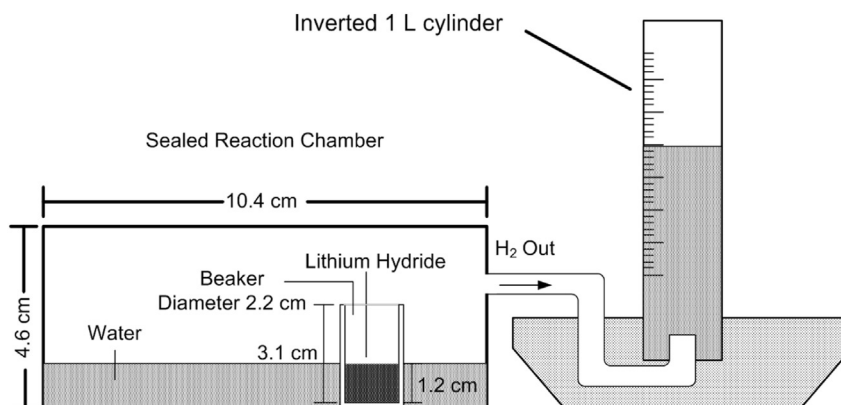


Fig. 2 – Experimental setup used to determine volume of hydrogen produced by lithium hydride.

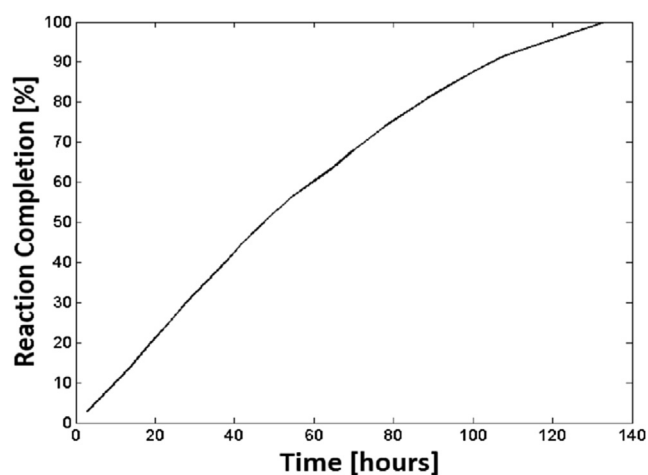


Fig. 3 – Lithium hydride reacted with water vapor.

options are nearly the same, with the best-case scenario for lithium hydride and DMFC showing a slight advantage over the other options. In this volumetric density calculation, lithium hydride expands 3 folds from its original volume as it's converted into lithium hydroxide and this will be discussed in the Section [Lithium hydride for long life, low-power PEM fuel cells](#).

Overall, the proposed lithium hydride technology can produce a system with much higher specific energy and operate for long duration with access to an excess supply of water; however this is at the price of increased complexity compared to DMFC. In these estimates, it should be noted that the mass of the fuel cell or balance of plant (BoP) are not included. Because these applications are for low power devices, the mass of the fuel cell and BoP is very low compared to the fuel carried. A typical 0.25 W PEM or DMFC fuel cell is estimated to weight 0.025 kg, with a well-designed BoP, that includes a hybrid battery and power electronics weighs about 0.10 kg. Additional mass required for fuel storage is accounted for in the specific energy. For long durations, i.e. 3–5 years, a PEM power supply operating 0.25 W would require 1.4–2.3 kg (respectively) of lithium hydride fuel. Thus in this comparison, it is the mass of fuel that dominates the total mass of the system. These results show that lithium hydride in theory is a very promising source of hydrogen for low power applications (see [Table 2](#)).

Lithium hydride for long-life, low power PEM fuel cells

Controlling hydrolysis

Another important reason for choosing lithium hydride is that its reaction is easily controlled. This can be done by controlling the lithium hydride surface area and exposure to an external source of water. Two series of experiments were done to obtain relationships between these variables and the rate of hydrogen production. For both experiments the same experimental setup is used as shown in [Fig. 2](#).

The first series of experiments investigated the effect of varying surface area on the hydrogen production rate. For these tests, the surface area was controlled by drilling 1 cm deep pocketed in a plastic base plate and then filling a certain number of pockets with packed lithium hydride. The diameter of each hole was 0.83 cm. Each run of the experiment varied the exposed lithium hydride surface area by changing the number of holes filled with hydride and the overall rate of reaction recorded. The rates of reaction for each are shown in [Fig. 4](#) (left) where it is evident that the hydrogen rate of production is roughly a linear function of surface area.

In a similar manner, the hydrogen rate of production as a function of relative humidity was experimentally studied. For each experiment the humidity was held constant at 55% through the use of a salt solution. Three holes were filled with lithium hydride on the plastic base plate to hold the surface area constant at 0.55 cm². The results of these experiments are shown in [Fig. 4](#) (right) and show the rate of hydrogen production increases roughly linearly with humidity.

From these tests, it is apparent that the rate of hydrogen production may be controlled by the relative humidity of water vapor in the chamber. To test this, a simple active feedback control system was built as shown in [Fig. 5](#) (left). Here, a pressure sensor provides feedback to a microcontroller, which controls an ultra-low-flow peristaltic water pump. When the reaction chamber pressure dropped below a certain threshold, the pump delivered a droplet of water into the system. The droplet does not touch the hydride; it evaporates on a wick. The raised reaction chamber humidity reacts with the hydride.

The results show it is possible to hold pressure at a given operating point within an error bound, which in this experiment was arbitrarily set to 1.1 bar \pm 0.01 bar ([Fig. 5](#) right). However, there is a time delay between the evaporation of the water vapor and the reaction of the water with the hydride. This is not a problem for the proposed hybrid fuel cell/battery system because the fuel cell produces constant power to charge the battery, while the battery handles the high and varying demand from the load.

While these results suggest that the generator could produce hydrogen at a flow required for low power sensor network module applications, the active control ([Fig. 5](#) left) is complex and consumes additional power. The objective of the work described below is to develop a totally passive control capable of maintaining the pressures of the hydrogen to ensure long-life.

Lithium hydride hydrolysis reaction in thick layers

Past work on lithium hydride has concentrated on the compound's chemistry and reaction kinetics as opposed to applications and control. A comprehensive literature review and discussions of the reaction and its kinetics can be found in Refs. [5–8]. The mechanisms and steps that control the rate of hydrogen production is complex and have been debated in literature [20]. Early work mentions that the rate of hydrogen production is not limited by diffusion of water vapor through the product layer of lithium hydroxide while some work claims that diffusion has a substantial effect [5,9]. In addition, it is found that in this hydrolysis reaction, either one of two

Table 2 – Comparison between LiH fuel energy content and batteries.

Energy storage	Specific energy	Volumetric density
Lithium ion battery	120 Wh/kg	620 Wh/L
Lithium thionyl chloride battery	450 Wh/kg	671 Wh/L
Methanol – direct methanol fuel cell	1000 Wh/kg	780 Wh/L
LiH fuel – PEM fuel cell (50% efficiency), water recycled or extracted from air [18,19]	3800 Wh/kg	610 Wh/L ^a
LiH Fuel – PEM fuel cell (65% efficiency), water recycled or extracted from air [18,19]	4900 Wh/kg	785 Wh/L ^a

^a Accounts for 3 fold increase in volumetric expansion of lithium hydride into lithium hydroxide.

products can form depending on the source humidity, including lithium hydroxide or lithium hydroxide monohydrate. Recently a “trilayer model” has been proposed for this process [21–24,20]. In this model, the product layer lithium hydroxide develops micro-cracks; the micro-cracks allow H₂O to penetrate through it. Sandwiched between the lithium hydroxide and unreacted lithium hydride is a layer of lithium hydroxide (Li₂O) that maintains constant thickness as the reaction proceeds. The thin layer of lithium oxide does not develop micro-cracks and is the rate-controlling mechanism in the reaction [11]. This model of the reaction has two effects on this study: because the thick lithium hydroxide layer develops micro-cracks, in theory water or water vapor is able to continuously permeate through and the reaction does not clog and the rate-controlling lithium oxide layer thickness remains constant, the rate of hydrogen production remains fairly constant. This would suggest it may be possible to design a hydrogen generator where the LiH area to volume ratio is relatively low, particularly for low power applications, such as sensor network module power supplies.

However, our experiments presented here shows a significantly different behavior from the lithium hydride hydrolysis reaction from what the trilayer model predicts and this has significant consequences on the design and control of a lithium hydride hydrogen generator.

In this section long-term behavior of lithium hydride hydrolysis reaction is characterized for suitability in the design and control of a lithium hydride hydrogen generator. In a series of experiments, lithium hydride is packed into 100 ml graduated cylinder (Fig. 6) to a volume of 55 ml. A chamber containing a source of water vapor is held at different humidity and is sealed to the top of the cylinder. The water evaporates

and diffuses into the cylinder until reacting with the hydride. A lithium hydroxide layer forms above the unreacted lithium hydride and a visible interface forms between the lithium hydroxide layer and lithium hydride. The hydrogen gas produced then collects at the top of a water column in an inverted 2 L cylinder. The volume of hydrogen gas produced is measured using a webcam (Microsoft LifeCam Cinema) that records the change in water level caused by hydrogen collected. Humidity sensors (Honeywell Model # HIH-4000-004) measure the relative humidity at critical points in the experimental setup and recorded using a microcontroller. These sensors allow measurement of the humidity gradient that forms between the water source and hydride surface.

Three sets of experiments are presented, Experiment A in which the water vapor source is at 100% humidity, a second experiment, Experiment B at 53% humidity and a third experiment, 100% relative humidity at 1.1 bar (Table 3). The water vapor source maintaining a 53% humidity contains a saturated salt solution of magnesium nitrate. Upon reaction of the lithium hydride with the water vapor, it converts into lithium hydroxide and expands in volume by up to a factor of 3.

The rate of hydrogen production versus time for Experiment A is shown in Fig. 7 (top). The source 100% relative humidity shows an initial ‘burst’ in hydrogen production followed by a gradual decline and slowing down of the reaction after nearly 50 days. This result is not predicted by the “Tri-Layer” Model, which predicts micro-cracks forming and letting water vapor permeate to unreacted lithium hydride. After nearly 50 days, a 1 cm layer of lithium hydride is converted into a lithium hydroxide layer reaching approximately 4 cm above the unreacted lithium hydride layer as shown in Fig. 7

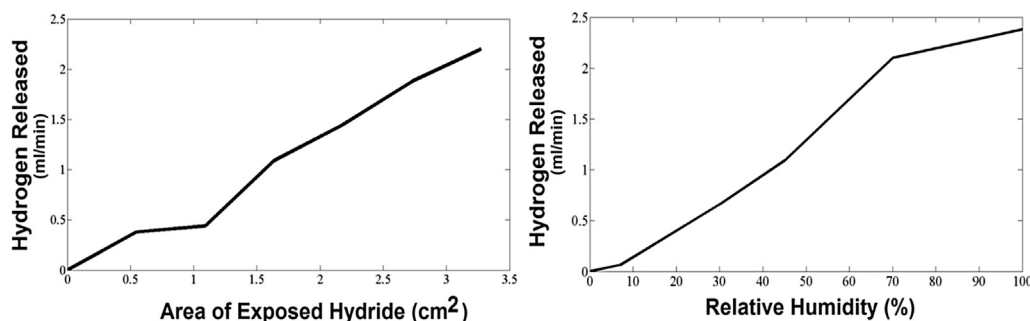


Fig. 4 – (Left) Rate of hydrogen production as a function of surface area. Humidity controlled at approximately 55%. (Right) Rate of hydrogen production as a function of chamber relative humidity. Surface area held constant at 0.55 cm².

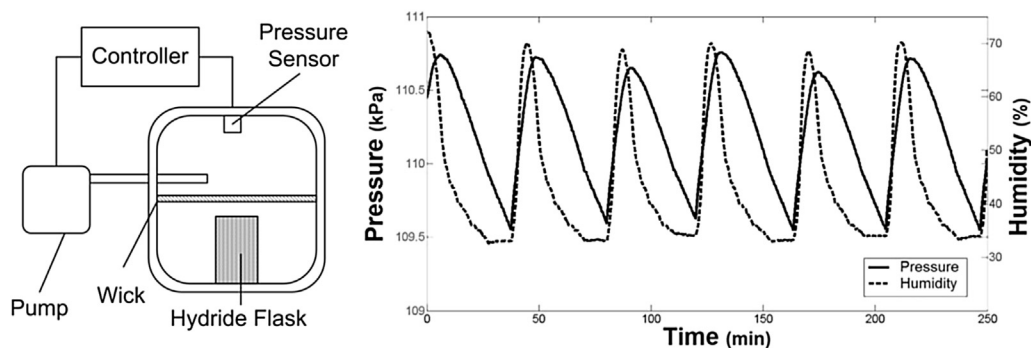


Fig. 5 – (Left) Feedback control system designed to control hydrogen pressure at 1.1 bar. (Right) Pressure and humidity results for controlled pressure experiment. Each peak in humidity and pressure accompanies the release of one droplet of water into the system.

(bottom). This is confirmed to be lithium hydroxide layer and not lithium hydroxide monohydrate as will be presented later. The volume of hydrogen produced from the experiment is shown in Fig. 7 (center). Once the hydroxide layer reaches 4 cm, it is evident that limited water vapor is transported to react with the remaining lithium hydride. Humidity readings above the lithium hydroxide layer shows the humidity starting from 20% reaching 100% by 50 days. This rise in relative humidity occurs because initially there is a humidity sink formed by the lithium hydride. Once the lithium hydroxide

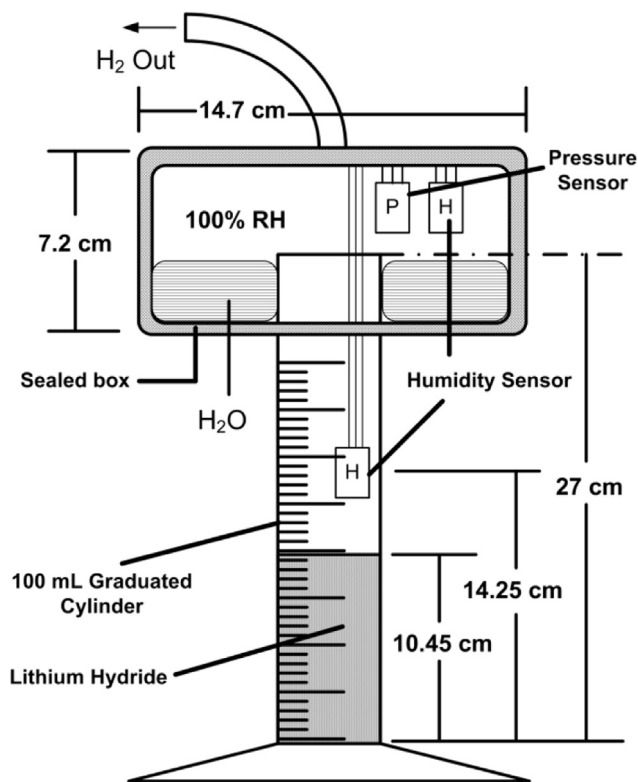


Fig. 6 – Experimental setup for long-duration lithium hydride hydrolysis reaction with source humidity of 100% and 53%. For 1.1 bar pressure experiments, a water column was connected to the hydrogen exit tube.

layer forms and thickens, it blocks off the humidity sink from the humidity source. This corresponds to a rise in humidity.

The experiment is repeated with a source humidity of 53%. Fig. 7 (top) shows the rate of hydrogen production. With the lower source humidity, the initial ‘burst’ in hydrogen production shows decreased amplitude, followed by a steady decline and slowing of the reaction. Fig. 7 (bottom) shows the thickness of the hydroxide layer over the span of the reaction and Fig. 7 (center) shows the total hydrogen volume produced.

In both experiments, the slowing down of the reaction occurs when the hydroxide layer reaches nearly 4 cm, irrespective of the source humidity. Based on these experiments it is evident that the lithium hydroxide layer forms a layer that substantially reduces water vapor transport to the unreacted lithium hydride. In a third scenario, Experiment C the source humidity is held at 100% and the pressure is maintained at 1.1 bar. This is to determine the effect of pressure on the lithium hydride hydrolysis reaction. Fig. 7 (top) shows the rate of hydrogen produced over time, while Fig. 7 (center) shows the volume of hydrogen generated. As expected, high pressure decreases the amount of hydrogen produced and results in choking of the reaction. This is because there is an additional resistance force due to higher pressure that needs to be overcome to release the hydrogen and this appears sufficient to block hydrogen production in combination with the low availability of water vapor.

To further test this observation that thick layers of lithium hydroxide slow down or prevent water transport and choke the hydrolysis reaction, an experiment was conducted to determine the water transport characteristics of lithium hydroxide and lithium hydroxide monohydrate, the two possible products of the lithium hydride hydrolysis reaction.

In this experiment, two chambers, with one, a humidity source targeted at RH 100% separated by a layer of lithium hydroxide or lithium hydroxide monohydrate (obtained from Sigma–Aldrich) and where the humidity is monitored in the second chamber. It is found that thick layers of lithium hydroxide substantially reduce water vapor transport (due to a large differential in humidity), see Fig. 8 (left). Lithium hydroxide monohydrate is permeable to water transport due to small differential in humidities between the chamber (Fig. 8 right).

Table 3 – Initial masses and densities of lithium hydride for long-duration experiments.

Experiment title	Mass of hydride (g)	Volume of hydride (cm ³)	Density of hydride (g/cm ³)	Surface area of exposed hydride (cm ²)
A – LiH – RH 100%	24.5	55	0.45	5.27
B – LiH – RH 53%	24.5	55.5	0.44	5.27
C – LiH – RH 100%, 1.1 bar	24.6	55	0.45	5.27

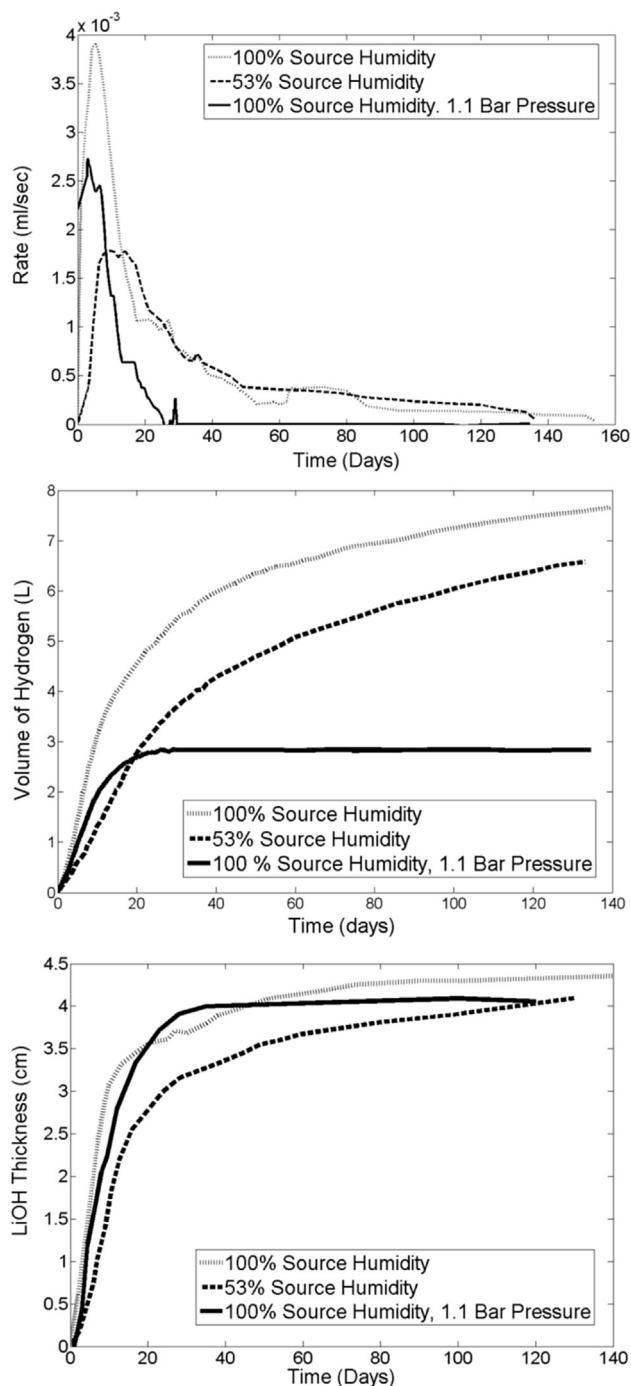


Fig. 7 – (Top) Volume of hydrogen produced. (Center) Rate of hydrogen production. (Bottom) Thickness of lithium hydroxide layer.

This confirms the earlier observation that it is the lithium hydroxide layer that chokes or slows down the reaction. While in our experiments, there is no evidence of lithium hydroxide monohydrate forming. This is a different scenario from what the “tri-layer” model predicts [21–24,20], where there exists a thin layer of lithium hydroxide and thicker layer of lithium hydroxide monohydrate. One reason for this difference could be that the partial pressure of water vapor just above the lithium hydride never reaches above 520 Pa, despite a source of humidity of 100%. This suggests that ratio of exposed lithium hydride area is too high compared to available water vapor in the air. However, the formation of lithium hydroxide monohydrate also presents a problem for applications in fuel cells, because it requires double the amount of water than would otherwise be required. This presents both a design and control trade-off in the application of lithium hydride as a source of hydrogen fuel, one provides excess water so that lithium hydride reacts to form lithium hydroxide monohydrate as product and permit reaction completion and other provides just enough water for hydrogen production, forming lithium hydroxide. This latter option requires careful design and packaging of the lithium hydride, by maintaining maximum thickness of 0.8 cm of lithium hydride from a water vapor source. The other option of removing the buildup of lithium hydroxide likely requires an active control system with a controller and actuators making the system complex.

Model of lithium hydride hydrolysis in thick layers

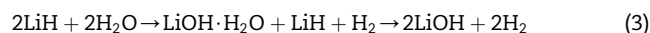
Based on the experiments performed, a semi-empirical model is developed of the hydrolysis of thick layers of lithium hydride for the purpose of design of lithium hydride hydrogen generator. The model predicts the total volume of hydrogen produced at given time, for a given humidity, volume, and exposed surface area of lithium hydride.

In this model, the lithium hydride hydrolysis reaction is sub-divided into a two stage reaction consisting of two consecutive, irreversible elementary steps as follows:



where the reactant [A] is converted to intermediary [B] at rate of k_1 and where the product [C] is formed from intermediary [B] at a rate of k_2 .

There is strong evidence to confirm that hydrolysis of lithium hydride occurs in at least two stages [20] and this is a critical assumption in the model. However it still remains debated as to what the two stages are. The reaction is assumed to take on the following steps proposed by Dinh et al. [25,20]:



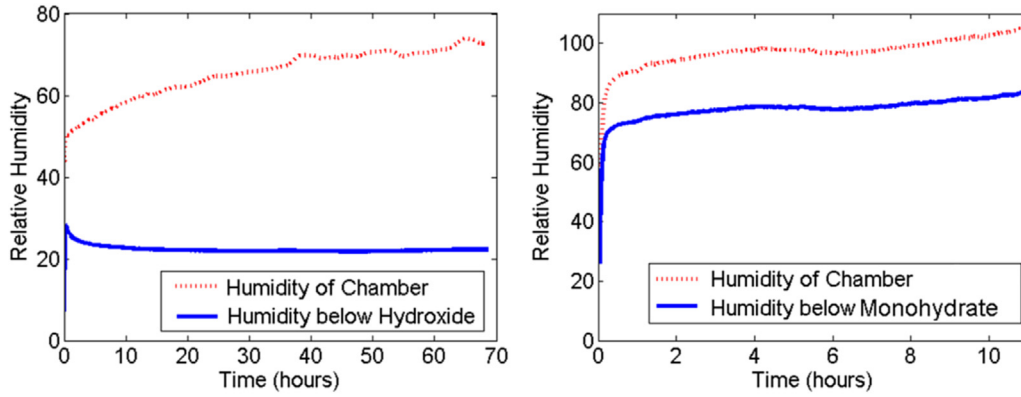


Fig. 8 – Results for permeability of lithium hydroxide monohydrate (left) and monohydrate (right).

Based on the assumption of a two stage reaction model and solving for the differential equations, one may obtain a relationship between the quantities of the reactant and product as follows:

$$[C] = \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right) [A] \quad (4)$$

Further we may assume the reactant is being supplied at a constant rate. Using this model, the volume of hydrogen (in liters) produced as a function of time, t , humidity, h , pressure p and area of lithium hydride, A_{LiH} :

$$V_{\text{H}_2}(t, h, p, A_{\text{LiH}}) = k_0 \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right) \quad (5)$$

where:

$$k_0 = A_{\text{LiH}} [0.84 + 0.30h - 5.9(p - p_0)] \cdot [1 + 0.021t] \quad (6)$$

and where

p is the pressure in bars

p_0 is the standard pressure in bars

This expression is related to the initial mass of lithium hydride and humidity, where

A_{LiH} is the area of exposed lithium hydride in cm^2
 h is the relative humidity.

The rates of reaction,

$$k_1 = 3.6 \left(\frac{h}{5} + (p - p_0) \right) \quad (7)$$

and

$$k_2 = \frac{k_1}{10} \quad (8)$$

where

h is the relative humidity.

From the volume of hydrogen produced, one can then calculate the depth at which lithium hydride has been converted to lithium hydroxide:

$$d_{\text{LiH}}(t) = \frac{M_{\text{LiH}} V_{\text{H}_2}(t)}{A \rho_{\text{LiH}} V_0} \quad (9)$$

where

t is time in days

M_{LiH} is the molar mass of lithium hydride

A_{LiH} is the exposed surface area of lithium hydride

ρ_{LiH} is the packing density of lithium hydride

V_0 is the molar volume of an ideal gas.

The comparison between the model and data are shown for the source relative humidity of 100% and 53% at 1 bar, and source relative humidity of 100% at 1.1 bar pressure in Fig. 9. The results show a good match between the presented model and the long-duration experiments. With this good match, it may be possible to use this model for longer term predictions of the behavior of the lithium hydride hydrolysis reaction.

A passive hydrogen generator

Past work has extensively studied lithium hydride's chemistry and has mentioned lithium hydride as a candidate fuel source for PEM fuel cells [12,13,14]. However, little work has been done to control its reaction rate or develop a lithium hydride hydrogen generator. This includes a high power reactor based on liquid water [13] and a concept of mixing lithium hydride into a slurry for use in automobiles [15]. Both of these focus on high power applications and are probably too complex for use in very low power applications, such as sensor modules. A set of papers presented in Refs. [13,12] analyze the effects of humidity and surface area on controlling the reaction of calcium hydride, which is similar to lithium hydride. A design for a lithium hydride generator developed by the U.S. Army that utilizes liquid water and a hydrophobic membrane is also presented in Ref. [12], although the generator is not the research's focus. Hence the design and development of a simple, effective, passive generator that can control the hydrogen pressure for long-life PEM fuel cell applications has yet to be addressed.

To experimentally validate lithium hydride for use in low power, long-life fuel cells, a hydrogen generator was designed

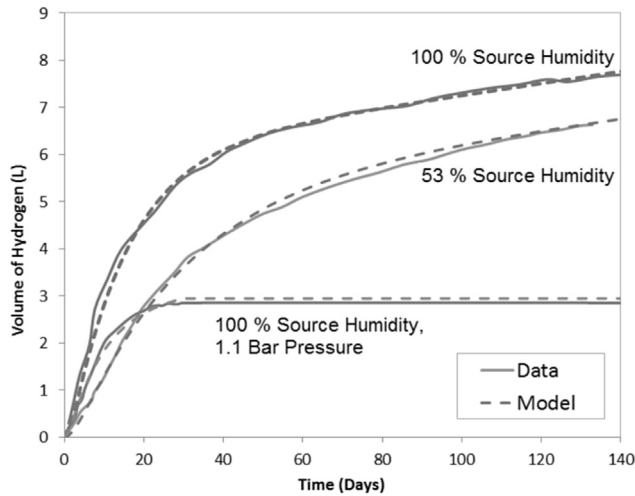


Fig. 9 – Comparison of model and data for volume of hydrogen produced from lithium hydride hydrolysis with a source relative humidity of 100%, 53% and 100% at 1.1 bar pressure.

and built as shown in Fig. 10. The generator was designed to not carry water onboard. While passive lithium hydride generators relying on liquid water have been mentioned in literature [12], this generator is unique in its ability to use water vapor from the atmosphere or fuel cell exhaust. Additionally, lithium hydride generators have not been experimentally validated for long periods of time or with a hybrid PEM fuel cell system. The features of this generator are discussed in the following section.

Water transport

In developing a passive hydrogen generator such as pictured in Fig. 10, it is necessary to have a membrane that allows for transport of water vapor into the system to react with the lithium hydride. The source of water vapor is the surrounding environment humidity or from a fuel cell cathode, although our experiments only use the environment humidity. At the same time, the membrane must prevent hydrogen leakage and channel the hydrogen to the fuel cell. Nafion™ has both of these properties. Commonly used as the proton transport membrane in PEM fuel cells, dry Nafion™ transports about an order of magnitude more water than hydrogen. The ability of Nafion™ to hold and transport water relates to its chemistry, specifically, the presence of sulfonic acid groups [26]. By extracting water vapor freely from the environment, operating the fuel cell at 61% conversion efficiency and accounting for the 5% loss of hydrogen due to leakage gives a fuel specific energy of 4370 Wh/kg.

Passive pressure control using compliant mechanism

To passively actuate the process, a compliant latex membrane is used. This membrane uses pressure feedback and works similarly to a valve. When the system pressure is higher than the set point, the membrane presses against the Nafion™ layer

and prevents water vapor from entering the system. When the pressure is low, the latex membrane pulls back and allows water to enter the system and activate the hydride. The entire process is illustrated in Fig. 10.

Latex was chosen as the complaint mechanism because of its resilience. Additionally, it is possible to alter the mechanism's compliance by selecting a thicker or thinner membrane (a latex sheet of thickness 0.3 mm was used in these experiments). Latex has the disadvantage of allowing a small percentage of the produced hydrogen to diffuse into the environment. Tests done on the generator described in this paper indicate that the leak rate was less than 5% of the hydrogen produced while running at 2.2 ml/min.

Model of hydrogen generator

A dynamic model for the pressure response of the hydrogen generator was developed considering mass flow rates, the effect of pressure on the compliant sheet, and the diffusion of water vapor through the lithium hydroxide layer covering the lithium hydride. The model assumes the relative humidity is uniform within the chamber.

To model the water entering the system, a model of water diffusion through Nafion™ developed in Ref. [27] is used. The molar flux of water through Nafion™ is given as follows

$$N_w = -\frac{\rho_M}{M_M \sigma_M} \int_{\lambda_1}^{\lambda_2} D_w d\lambda \quad (10)$$

where ρ_M is the Nafion's density, M_M is the molecular weight of the Nafion™, σ_M is the thickness of the Nafion™. D_w is the Fickian diffusion coefficient, presented as

$$D_w = 3.10 \times 10^{-3} \lambda (-1 + e^{0.28\lambda}) \exp\left[\frac{-2436}{T}\right] \quad (11)$$

and λ is the Nafion's water content, provided by

$$\lambda = 0.043 + 17.81a_w - 39.85a_w^2 + 36.0a_w^3 \quad (12)$$

where a_w is the activity of water.

The effect of pressure on the latex sheet was determined empirically. The amount of Nafion™ surface area covered by the latex membrane for a given pressure was empirically measured and a cubic polynomial was fit to these measurements given as follows:

$$x = -0.031P^2 + 7.19P - 409.24 \quad (13)$$

$$y = -0.0043P^2 - 0.76P + 32.20 \quad (14)$$

$$A_{\text{closed}} = \pi xy \quad (15)$$

where x and y run along and the length and width of generator respectively, P is the hydrogen pressure, and A_{closed} is the surface area of Nafion™ covered by the latex membrane, not available to diffusion. Therefore, the area allowed for water diffusion into the system is given by

$$A_{\text{open}} = A_{\text{total}} - A_{\text{closed}} \quad (16)$$

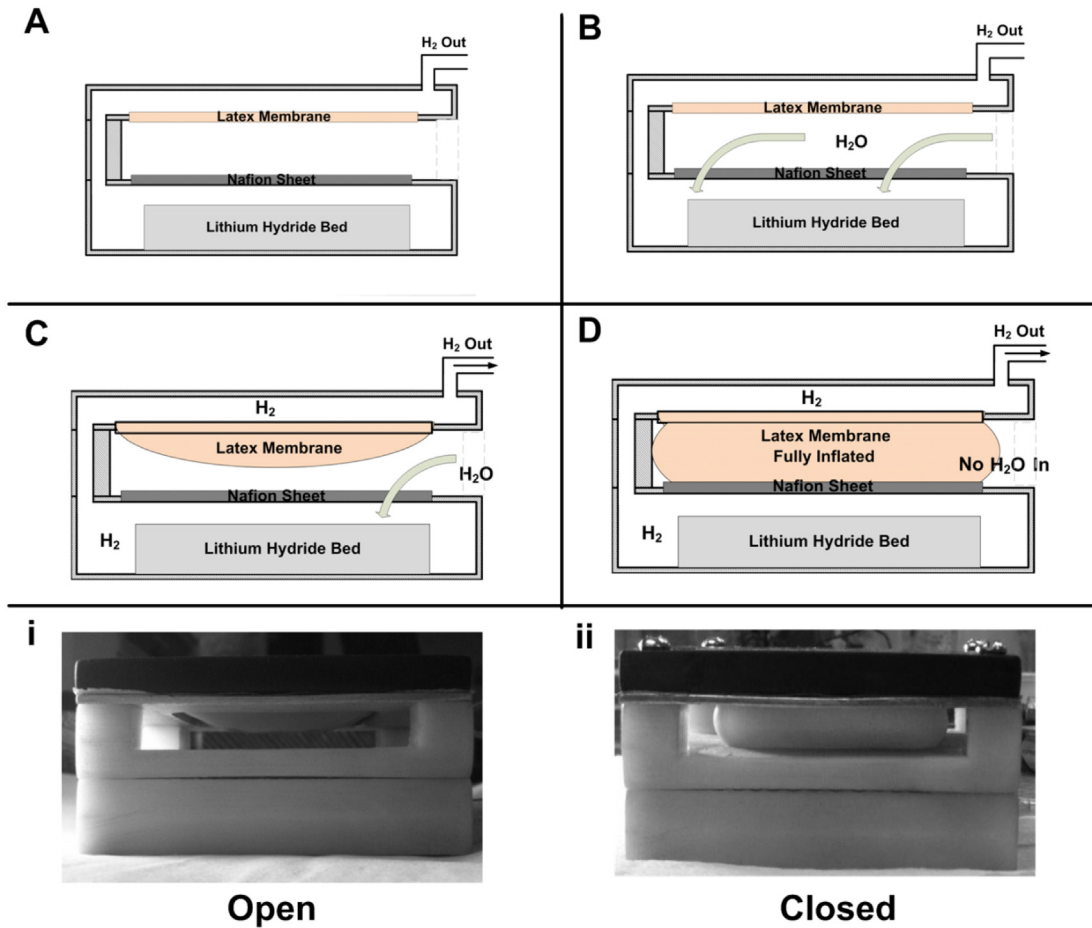


Fig. 10 – Cross-section view of passive lithium hydride generator. A) Generator consists of two opposing compartments that allow for pressure communication between them. B) Water vapor, either produced at the fuel cell’s cathode or from the environment, enters through the Nafion™ sheet. C) The water vapor reacts with the lithium hydride. The generated pressure travels to the upper chamber and inflates the latex membrane. D) The rate limiting mechanism occurs when the latex membrane presses against the Nafion™, greatly reducing the amount of water vapor entering the system. (i) Latex membrane fully contracted, allowing water vapor to enter the system. (ii) Latex membrane fully expanded at target pressure, not allowing water vapor to enter the system.

Finally, a simple molar balance on the generator provides

$$\dot{n}_{\text{H}_2\text{O}} = \dot{n}_{\text{H}_2\text{O},\text{Nafion}} - \dot{n}_{\text{H}_2\text{O},\text{absorbed}} \quad (17)$$

where the left hand side is the change in the number of moles of water within the generator, and the right hand side represents the water entering through the Nafion™ membrane minus the water vapor absorbed by the hydride bed. The amount of water consumed by the hydride reaction as a function of surface area and relative humidity was determined using the model from Section [Lithium hydride for long life, low-power PEM fuel cells](#):

$$\dot{n}_{\text{H}_2,\text{gen}} = \frac{d}{dt} \left(\frac{V_{\text{H}_2}(t, h, p, A_{\text{LiH}})}{V_0} \right) \quad (18)$$

where V_{H_2} is the total volume of hydrogen produced from (5) and is function of time, t , humidity, h and area of lithium hydride, A_{LiH} . Likewise, a rate equation for the molar balance of hydrogen can be written:

$$\dot{n}_{\text{H}_2} = \dot{n}_{\text{H}_2,\text{gen}} - \dot{n}_{\text{H}_2,\text{F.C.}} - \dot{n}_{\text{H}_2,\text{leak}} \quad (19)$$

where the three terms on the right hand side correspond to the generated hydrogen, the hydrogen consumed by the fuel cell, and the inherent leakage rate for the generator, which was measured to be about 5% of the total hydrogen produced. The results are presented in [Fig. 11](#), where the model is compared against the pressure response of the experimental hydrogen generator.

The system model describes generator performance. Because the generator is passively-controlled, its equilibrium pressure depends on both the power demanded by the fuel cell system and the ambient relative humidity. Because the fuel cell system should operate at a constant power, the model predicts that changes in environmental humidity will have a considerable impact on the generator’s pressure.

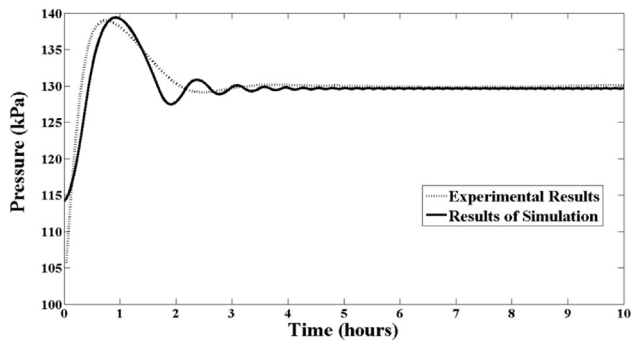


Fig. 11 – Pressure response of experimental hydrogen generator versus model.

Experimental system

The hydrogen generator concept presented in the previous section was tested using a bench top fuel cell system shown in Fig. 12. The system is nominally designed to produce 250 mW. The purpose of the experiment is to validate the hydrogen generator concept models.

The system was designed to simulate the power supply for a remote sensor. The sensor operates on a duty cycle, during which it switches on. To simulate this, the system is connected to a DC motor operating on a 10% duty cycle.

Hydrogen generator

The hydrogen generator concept discussed above is pictured in Fig. 10. As stated above, optimization of system volume was not an objective of the experiment. The generator's size was dictated by a two factors. First, the exposed surface area of Nafion™ was designed about twice as large as required to maintain the minimum flow rates. The reason for this was to ensure that the generator produced sufficient hydrogen in a wide range of relative humidity (the room in which this experiment took place experienced 25–75% relative humidity). Secondly, the hydrogen generator must be considerably taller than the height of the unreacted lithium hydride. This is

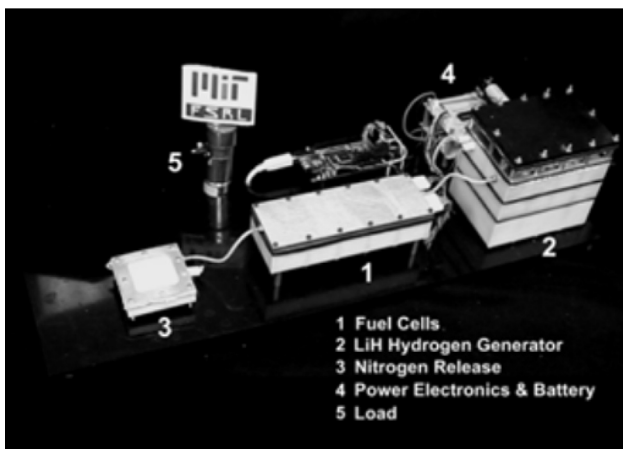


Fig. 12 – Bench top fuel cell experimental system.

because the lithium hydride tends to expand 3 times its original volume when converted to lithium hydroxide.

Fuel cells

Five fuel cells obtained from Horizon Fuel Cell Technologies, each with an MEA area of 5 cm² and max power output of 250 mW. The fuel cells are connected in series and total system voltage is maintained at 3.7–3.75 V, which is 0.74 V–0.75 V per cell and conversion efficiency of 60–61%. Maintaining the voltage below 0.8 V and keeping it constant, according to a fuel cell catalyst degradation research presented in Ref. [8] enables long fuel cell life.

Hybrid battery setup

Because the load in the experimental system operates on a duty cycle, there is a varying power demand on the system. A varying load connected directly with the fuel cell would cause voltage oscillations that reduce the life of the fuel cell [8]. For this reason, the fuel cell is connected in parallel with a battery. The fuel cell produces constant power to trickle charge the battery, while the battery handles the high and varying demands of the load.

Experimental results and discussion

The experimental system recorded several important environmental variables including the environment humidity and ambient pressure. The relative humidity experienced by the system is shown in Fig. 13 (top left). This corresponds with the humidity inside the hydrogen generator, though much lower, due to humidity sink from the lithium hydride. The outside humidity on average remained at 44%. Fig. 13 (top right) shows the hydrogen pressure generated by the hydrogen generator. The pressure on average remained at 1.03 bar. However, as observed the pressure was higher during early stages of the experiment and gradually decreases until crashing.

As expected from the system model, the pressure exhibits oscillations, which are connected to the varying ambient humidity. During the early part of the experiment, between days 5–10, the pressure and ambient relative humidity are closely correlated but after 10 days, the two starts to diverge. This is presumably due to the ever increasing phase lag between the absorption of water vapor into the generator and the production of hydrogen. In spite of the oscillations, the pressure remains above 1 bar and is able to provide a sufficient amount of hydrogen to prevent starvation of the fuel cell system until around 60 days.

Taking into the account the average pressure and average external humidity, the model presented in Section [Lithium hydride for long life, low-power PEM fuel cells](#) is used to predict the life of the hydrogen generator concept shown in Table 4. The predicted rate of hydrogen production is shown in Fig. 14. The model predicts that the generator will produce hydrogen for 67 days. After that hydrogen starvation is expected this is expected to cause a crash in fuel cell voltage. In this setup, rate of hydrogen consumed by the fuel cell is expected to go to zero, because of leakages in the system. Based on our tests, an average leakage of 5% is predicted. Further the model predicts 46.2 g of lithium hydride is consumed. This

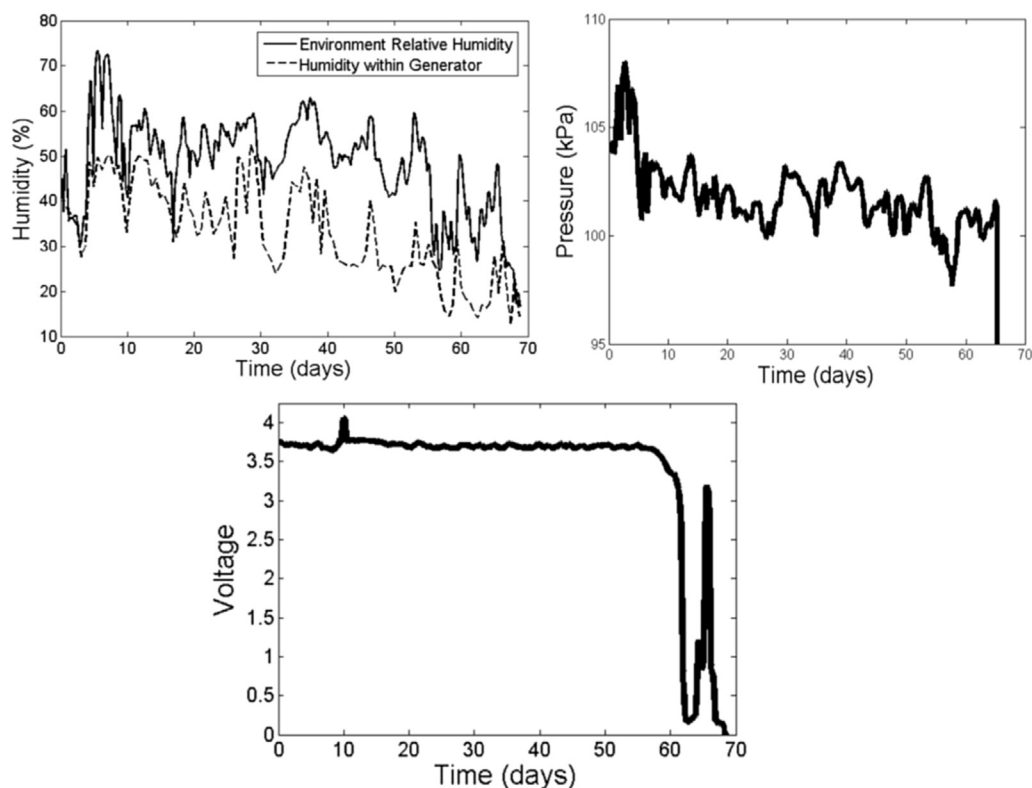


Fig. 13 – (Top left) Experimental system ambient relative humidity and humidity inside the hydrogen generator. (Top right) Pressure of hydrogen generator. (Bottom) Fuel cell system voltage over the course of the experiment. After 60 days, the voltage ‘crashes’ because the hydrogen generator stops producing hydrogen due to the choking phenomena from lithium hydroxide buildup.

result corresponds well with the estimate of lithium hydride consumed by the experimental system of 48.8 g. The voltage readings from the fuel cells are shown in Fig. 13 (bottom). The voltage readings remain steady due to the power control system that maintains the fuel cell at a fixed voltage, until there is hydrogen starvation, at which point the voltage crashes. This occurs after 62 days. The model predicts a burst in hydrogen production during early stages of the experiment (Fig. 14) followed by a gradual decline, until no hydrogen is produced due to the reaction slow down described earlier. This evidence is supported by the pressure readings from the hydrogen generator (Fig. 13 top right), which shows high pressure due to high hydrogen production rates at the beginning of the experiment followed by a gradual decline. However, in the experiment as opposed to the model, the ambient humidity oscillates, while in the model, the humidity is 44% (the average humidity). This difference accounts for the slight variation in results.

In this section, an experimental system that utilizes the hydrogen generator concept presented in Section A [passive hydrogen generator](#) is tested. The performance and life of the hydrogen generator is compared against a model developed in Section [Lithium hydride for long life, low-power PEM fuel cells](#) to predict thick layers of lithium hydride hydrolysis. In particular the model accounts for a choking or slow down behavior due to the buildup of lithium hydroxide over the lithium hydride. This physical phenomenon either reduces or blocks further water vapor transport to the lithium hydride significantly affecting hydrogen production. The predicted result from the model agrees with the behavior of the experimental system.

Based on these results, lithium hydride can only be packaged to a maximum depth of 0.8 cm to maximize utilization. Greater depths will result in the choking or slow down in hydrogen production. In addition, the ambient relative humidity needs to be 30% or higher for the hydrolysis reaction to

Table 4 – Model predicted and actual life of hydrogen generator.

	Environment conditions	Life	LiH consumed
Model	Pressure: 1.03 bar, RH: 44%	67 Days	46.2 g
Experiment	Pressure: 1.03 bar (Avg), RH: 44% (Avg)	62 Days	48.8 g

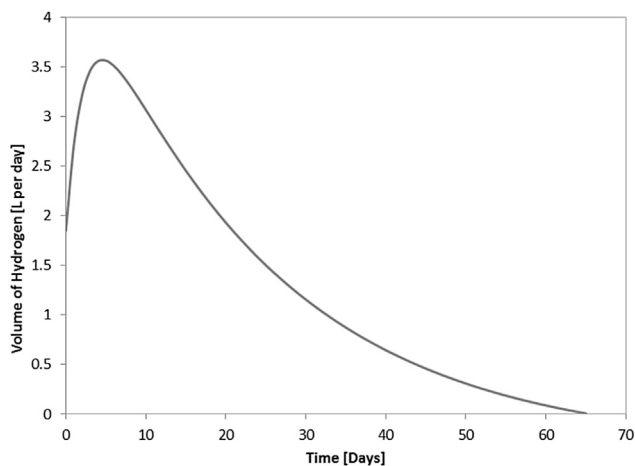


Fig. 14 – Predicted volume of hydrogen produced for an observed average humidity of 44% and average hydrogen pressure of 1.03 bars. The model predicts the generator stops producing hydrogen after 67 days. This corresponds well with the observed crash in voltage due to hydrogen starvation after 60 days.

proceed. Our models and experiments suggest that a system that can meet these constraints can supply hydrogen for 0.25 W systems for long durations of 3–5 years or more, with readily available, free supply of water. However to achieve long-life by minimizing water use requires advancement in packaging the lithium hydride (density 0.4 g/cm^3) with 0.8 cm depth into an area of $65 \text{ cm} \times 65 \text{ cm}$. For the intended field sensor applications, this would require packaging schemes such as spiral windings to maximize surface area, while minimizing the required volume. Alternately low power or passive methods to increase water capture from arid environments can also be used to overcome these limitations. Nominally, tropical and subtropical climates with excess rainfall and high atmospheric moisture are the ideal environments for the proposed passive lithium hydride hydrogen generator technology, in addition to mild coastal, oceanic and inland lake environments. Using this model that accurately describes the behavior of the lithium hydride hydrolysis reaction and design guidelines, it is now possible to optimize the design and control of a hydrogen generator so as to maximize life of a fuel cell power supply for applications in sensor networks modules.

Conclusion

Low power, long-life environmental sensor networks are limited by current power technology. This paper presents a solution based on a hybrid PEM fuel cell system that uses lithium hydride as a hydrogen source. Lithium hydride was selected for the study because of its high hydrogen weight density, its simple hydrolysis reaction, high reported conversion rates and the relative simplicity in controlling the reaction. Our work shows lithium hydride hydrolysis is faced by an

important challenge that can limit its utilization not reported in previous work. This is due to the buildup of the product, lithium hydroxide which can substantially reduce water vapor transport to unreacted lithium hydride. In this paper a semi-empirical model is developed to predict this lithium hydroxide buildup and slow down behavior obtained from a series of long-duration lithium hydrolysis experiments. The model is shown to accurately predict the life and performance of a fuel cell power supply experimental system containing a passive lithium hydride hydrogen generator. The passive generator works by exploiting the physical properties of materials to perform reaction control and without requiring electronics or powered sensors and actuators. Hydrogen is released at set point pressure and this is to prevent the fuel cells from failing due to fuel starvation or flooding. Based on the experimental results and model, a set of design guidelines is provided to build long-duration lithium hydride hydrogen generators for very low power applications, such as to power sensor networks modules.

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