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Micropower Chemical Fuel-to-Electric Conversion: A “Regenerative Flip” Hydrogen Concentration Cell Promising Near Carnot Efficiency

Karl Wally

Prepared by Sandia National Laboratories
Livermore, California 94550

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Karl Wally

Sandia National Laboratories
P.O. Box 969
Livermore, CA 94551-0969

Abstract

Although battery technology is relatively mature, power sources continue to impose serious limitations for small, portable, mobile, or remote applications. A potentially attractive alternative to batteries is chemical fuel-to-electric conversion. Chemical fuels have volumetric energy densities 4 to 10 times those of batteries. However, realizing this advantage requires efficient chemical fuel-to-electric conversion. Direct electrochemical conversion would be the ideal, but, for most fuels, is generally not within the state-of-the-science. Next best, chemical-to-thermal-to-electric conversion can be attractive if efficiencies can be kept high. This small investigative project was an exploration into the feasibility of a novel hybrid (i.e., thermal-electrochemical) micropower converter of high theoretical performance whose demonstration was thought to be within near-term reach. The system is comprised of a hydrogen concentration electrochemical cell with physically identical hydrogen electrodes as anode and cathode, with each electrode connected to physically identical hydride beds each containing the same low-enthalpy-of-formation metal hydride. In operation, electrical power is generated by a hydrogen concentration differential across the electrochemical cell. This differential is established via coordinated heating and passive cooling of the corresponding hydride source and sink. Heating is provided by the exothermic combustion (i.e., either flame combustion or catalytic combustion) of a chemical fuel. Upon hydride source depletion, the role of source and sink are reversed, heating and cooling reversed, electrodes commutatively reversed, cell operation reversed, while power delivery continues unchanged. This “regenerative flip” of source and sink hydride beds can be cycled continuously until all available heating fuel is consumed. Electricity is efficiently generated electrochemically, but hydrogen is not consumed, rather the hydrogen is regeneratively cycled as an electrochemical “working fluid”.

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Micropower Chemical Fuel-to-Electric Conversion: A “Regenerative Flip” Hydrogen Concentration Cell Promising Near Carnot Efficiency

Overview of Problem and Proposed Solution

Although battery technology is relatively mature, power sources continue to impose serious limitations for small, portable, mobile, or remote applications. A potentially attractive alternative to batteries is chemical fuel-to-electric conversion. Chemical fuels have volumetric energy densities 4 to 10 times those of batteries. Realizing this volumetric advantage in small devices requires efficient conversion. Direct electrochemical conversion would be the ideal, but, for most fuels, direct conversion is generally not within the present state-of-the-science. Alternatively, chemical-to-thermal-to-electric conversion can also be attractive if efficiencies can be kept high. In this Laboratory Directed Research and Development (LDRD) work, we propose a novel hybrid thermal-electrochemical micropower converter of high theoretical performance whose demonstration is within near-term reach using existing technologies and materials. The system is comprised of a hydrogen concentration electrochemical cell with identical hydrogen electrodes as anode and cathode, each electrode in communication with an identical bed of low-heat-of-formation thermally reversible metal hydride. In operation, electric power is generated electrochemically by a hydrogen concentration differential across the cell; said differential is established by coordinated heating and passive cooling of the corresponding hydride source and sink. The hydride source is driven by heat obtained from exothermic reaction of a chemical liquid fuel source. Upon hydride source depletion, the roles of hydride source and sink are reversed, heating and cooling reversed, electrodes commutatively reversed, cell operation reversed, while power delivery continues unchanged. This "regenerative-flip" can be cycled indefinitely until all available fuel is consumed. Electricity is efficiently generated in an electrochemical converter, but hydrogen is not permanently consumed, rather, regeneratively cycled from one hydride bed to another. This is a Carnot cycle in the sense that it converts heat energy to electricity through a conversion process. But the converter is an electrochemical converter whose conversion efficiency can be relatively high since its performance limitations are free energy constraints. The proposed system is shown schematically in figure 1.

An underappreciated aspect of micropower generation is the severity of the constraints imposed by heat transfer and thermal conductivity, so that in small structures it is difficult to exploit fully the high temperatures of combustion of liquid fuels. Heat engines for power generation accept heat at high temperature and reject waste heat at a lower temperature. The greater the temperature differential between available source and sink, the greater the potential to perform work. Such heat engines are bounded in their performance by the Carnot cycle, which is an idealized heat engine operating between a heat source and sink. But in miniature structures, it is difficult, if not infeasible, to isolate heat on the high temperature side only. Heat conduction in solids ranges over only a relatively narrow band of conduction values, so that heat isolation over small distances becomes exceedingly difficult in miniature structures made of real materials. The result is that miniature structures tend to have relatively greater heat conduction losses resulting in reduced efficiency relative to larger structures operating between similar heat source and sink.

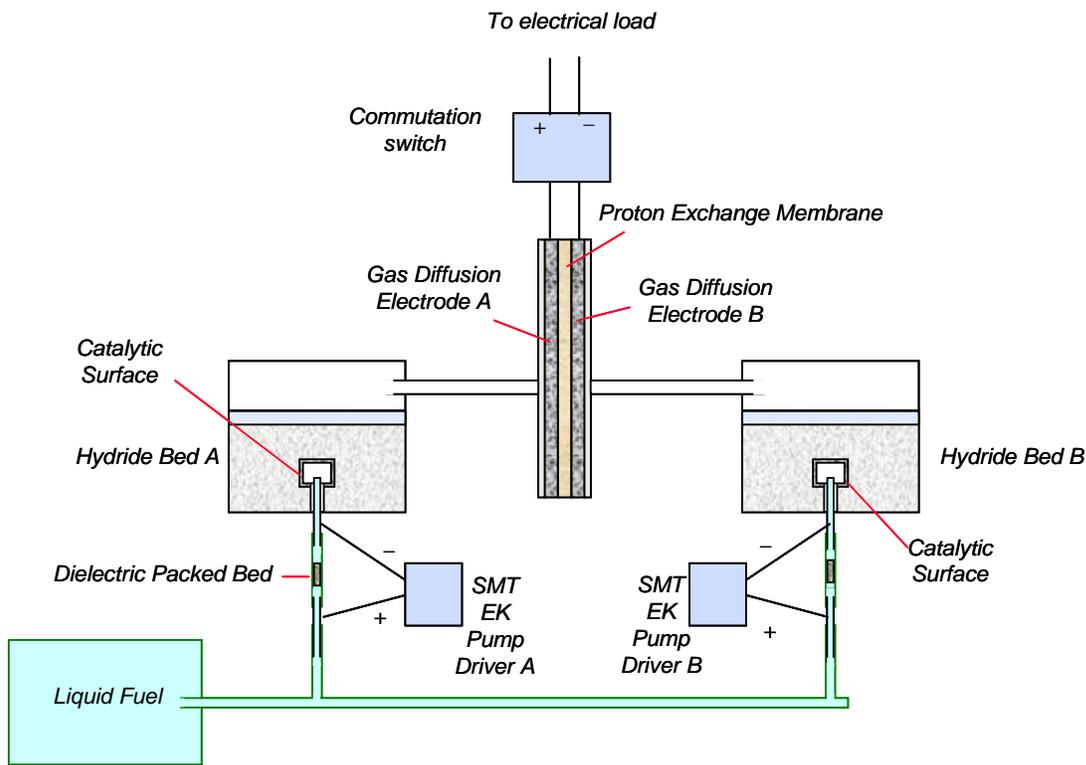


Figure 1. Schematic of Proposed Regenerative “Flip” Hydrogen Concentration Cell

An additional problem in miniature devices is that high temperatures can affect the function, even the survival, of nearby components. It is clear that for miniature devices isolation of high temperature hot spots is a paramount design driver, and temperature avoidance is a better strategy. The scheme we propose with this hybrid converter is a practical compromise highly suitable for micro and miniature devices. It calls for operation at modest temperatures to drive the thermally reversible hydride source, while employing a very highly efficient electrochemical converter to achieve maximum approach to the limits of performance.

Proposed Research and Development

As initially proposed, the project was to be a near-term effort aimed at demonstration of the proposed novel hybrid thermal-electrochemical power source. The technologies needed to complete the demonstration in a near-term timeframe are available from related fields and applications.

Demonstration of the hydrogen electrochemical concentration cell borrows technology from the present generation of Proton Exchange Membrane (PEM) hydrogen fuel cells, which have enjoyed significant success in recent years in a variety of transportation and portable power demonstrations. For the proposed research and development, the concentration cell would use as electrolyte a Nafion solid polymer electrolyte membrane, and electrodes of catalyst-coated carbon powder composite gas-diffusion electrodes as anode and cathode. In conventional state-of-the-art hydrogen fuel cells, polarization losses in the oxygen cathode predominate, but the hydrogen anode is generally considered to have relatively small polarization losses. In the proposed hydrogen concentration cell, both the anode and cathode would be a hydrogen electrode, producing a converter with relatively small polarization losses overall. Nafion electrolyte membranes generally operate below the boiling point of water to avoid dry-out and runaway increase of internal resistance. The proposed hydrogen concentration cell would also operate at this modest temperature. Internal resistances in the electrodes and in the electrolyte membrane, and contact conduction resistances between the electrodes and the electrolyte membrane are anticipated to be the main sources of losses.

Demonstration of the cyclic regenerative operation of thermally reversible hydride beds would use palladium hydride, a thermally reversible hydride system that has been much studied at Sandia/CA. Although palladium is an expensive material, palladium hydride is potentially an excellent hydride choice for a micropower source for several reasons. First, it is capable of producing the required operating pressures of hydrogen at modest operating temperatures. Other hydrides, e.g. iron-titanium hydride, could do the same. But second, palladium hydride has a relatively low heat of absorption, about half that of other practical hydrides, e.g. iron-titanium hydride. Therefore, the heat input required to desorb hydrogen from a palladium hydride is approximately half what is required for most other thermally reversible metal hydrides, yielding more than twice the efficiency of hydrogen generation than most other hydride systems. More importantly, this good performance can be achieved at relatively modest temperatures, important to the practical operation and survival of miniature devices. Hydride state-of-fill will be an important operating parameter if effective regenerative cycling is to be achieved, because it is needed to know when to “flip” the operation of the source and sink hydride beds. Measurement of hydride state-of-fill remains a problematic issue in hydride research and development. It will not be addressed in this work, although electrical conductivity of the metal hydride bed may hold promise as a state-of-fill indication.

To avoid problems with high temperatures in miniature structures, it is necessary to combust, or exothermically react or decompose the liquid fuel in a highly controlled manner. For practical micropower devices, three leading methods could be considered: 1) catalytic microcombustion of fuels using atmospheric oxygen, 2) catalytic exothermic decomposition of monergolic fuels, and 3) exothermic reaction of hypergolic fuels. The latter two options would allow the micropower device to be operated in environments where atmospheric oxygen is unavailable, for example in the vacuum of space, or underwater, or in inert atmospheres. Electrokinetic pumping provides a means for precision control of the fuel feed in miniature applications. Both electrokinetic pumping and catalytic microcombustion have been explored at Sandia/CA in previous LDRD projects. Either continuous flows or pulsed flows are equally possible. The importance of controlled heat generation should not be underestimated. It is one of the keys to limiting the operating temperatures incurred in a practical miniature device.

A fully funded one year effort would entail the separate demonstration of hydride bed performance, hydrogen concentration cell performance, and liquid fuel heat source development, to be subsequently followed by a integrated demonstration of the complete concept incorporating all of the separate elements into a functionally whole. Such a work plan might have the following goals and milestones:

R&D Goals and Project Milestones

<u>Goal/Milestone</u>	<u>Completion Date</u>
• Demonstrate Desorb/Absorb w/ miniature Pd Hydride Beds	Dec/04
• Demonstrate H ₂ Concentration Cell	Jan/05
• Demonstrate H ₂ Cell w/ Hydride Beds w/ “Regenerative flip”	Feb/05
• Demonstrate Heat Source w/liquid fuel	Mar/05
• Demonstrate EK-pumped Liquid Fuel Delivery	Apr/05
• Demonstrate Heat Source w/EK-pumped Delivery	May/05
• Demonstrate Hydride Beds w/ EK-pumped Heat Source	June/05
• Demonstrate Regenerative Flip H ₂ Cell as conceived	July/05

Revised Plan of Work for Reduced Funding

In the actual event, this project was selected for funding at a reduced level as a seniors LDRD project. A more modest plan of research and development was therefore laid out to explore the demonstration of key aspects the proposed micropower scheme. Performance of the hydrogen source and sink beds, and performance of the hydrogen concentration cell were the main focus of the reduced demonstration. An additional focus of the work was to confirm expected performances and identify any performance limitations. Development of the micro liquid chemical fuel heat sources was beyond the scope of the reduced funding. Fortunately, an avenue toward liquid chemical fuel heat sources remains available through a separately funded LDRD project that deals with electrokinetically-pumped liquid propellants for microthrusters. Hopefully, useful results from that work can find application in a later integrated demonstration of a regenerative “flip” hydrogen concentration cell power generation scheme. The goal of demonstrating the electrokinetically-pumped delivery of liquid chemical fuel heating must await future work, as must also the goal of an integrated demonstration combining hydride beds, concentration cell, and micro liquid chemical fuel heat sources into a functional regeneratively cycling micropower source.

The key issues to be investigated are two. First, the intrinsic performance of hydrogen concentration cells limits their output voltage to very modest levels (~ 57 mV, see the Theoretical Considerations) at the modest temperature and pressures we propose for operation of a PEM-based cell. Therefore, it is extremely important that internal losses be as small as possible to maximize performance. Internal losses in individual cells are of three types. One, the electrocatalytic anode and cathode are subject to polarization losses, including polarization losses particular to the triple conjunction (gas-electrolyte-conductor) nature of gas diffusion electrodes. Two, the electrolyte membrane exhibits some irreducible impedance or resistance that is a function of the electrochemical composition of the membrane (equivalent weight), and the membrane’s thickness. Three, the conductor in the gas diffusion electrodes (anode and cathode) exhibit an electrical resistance in transporting electrons during current collection. A fourth internal loss mechanisms is readily observed in bipolar stacks of unit cells, that of contact resistance at discontinuities in the structure, e.g. inter-cell, or, between plys.

The second key issue relates to the hydrated-nature of the PEM electrolyte. To be satisfactorily conductive, these membranes must retain a substantial fraction of liquid water (in the case of Nafion, a ratio of 0.25 water-to-sulfonic acid groups). Unlike hydrogen-air/oxygen PEM fuel cells where

cathodic product water is available to hydrate the PEM electrolyte, the proposed regenerative PEM hydrogen concentration cell system must maintain a partial pressure of water vapor available in the anode or cathode hydrogen to maintain equilibrium with the electrolyte membrane water content. That is, the metal hydride beds of our proposed regenerative hydrogen concentration cell scheme must operate with a not-insignificant partial pressure of water vapor. Some researchers have found that water vapor, in reduced concentration (ppms), can act as a retardant to hydride kinetics in metal hydride systems. The question of hydride performance in the presence of more significant water vapor content does not appear to have been studied. A side question requiring some consideration would be the question of reductive/oxidative interactions between the water vapor and the containment/conductive materials in the system.

The revised/reduced plan of work investigated these two issues through two sets of experiments. One set of experiments investigated the performance of palladium hydride in the presence of a not-insignificant partial pressure of water vapor. The second set of experiments investigated questions of PEM hydrogen concentration cell performance.

The question of hydride bed performance in the presence of water vapor was investigated using a custom fabricated palladium hydride bed using commercially available palladium powder pressed into a compact of intermediate density. Equilibrium stoichiometric performance (quantitative) and kinetic performance (qualitatively observed) were compared to baseline performance without water vapor. Because the Nafion membrane introduces a not-insignificant partial pressure of water vapor, attention must be paid to inertness of test apparatus and instrumentation surfaces. The principal investigator has significant experience preparing and conditioning metal hydride beds, and conducting experiments to determine pressure-composition-temperature performance of hydride beds. For purposes of the study, the key question to be answered was whether or not the partial pressure of water vapor will allow implementation of a practical hydride storage device with acceptable, reproducible kinetic and stoichiometric performance.

The concentration cell performance issues were investigated using a hydrogen cell membrane electrode assembly (MEA) procured commercially. Although electrochemical cells can be investigated using a variety of techniques (e.g. impedance spectroscopy, potentiostatic or galvanostatic measurements, cyclic voltametry, potential sweeps, etc.), the simplest and most direct method of testing is operation as a hydrogen concentration cell into a series of resistive loads. The principal investigator has significant experience performing such tests for hydrogen fuel cells. For purposes of the proposed study, the key question to be answered was whether or not the available performance using state-of-the-art fuel cell technologies can be seen to lead to a practical hydrogen concentration cell device.

Revised R&D Goals and Project Milestones for Reduced Funding

<u>Goal/Milestone</u>	<u>Completion Date</u>
• Demonstrate Desorb/Absorb w/ miniature Pd Hydride Beds	Jan/04
• Demonstrate H ₂ Concentration Cell	Mar/05
• Demonstrate H ₂ Cell w/ Hydride Beds w/ “Regen. flip”	July/05

Risk and Likelihood of Success

Various loss mechanisms could be difficult, or not possible, to suppress. As described in the theoretical considerations, the very low voltages entailed in concentration cell performance, combined

with an irreducible kernel of internal and contact resistances, poses the greatest risk to success. Nevertheless, building on previous experience with hydrogen fuel cells, we were hopeful that practical results could be achieved.

Relationship to Previous Work

Several previous Sandia/CA LDRDs have provided hands-on experience in solid polymer electrolyte membrane hydrogen fuel cells, electrokinetic pumping, and microcombustion. Experience from these projects is directly applicable to the current project, as are many of the results. Many of the results from the above projects may be considered direct antecedents contributing to the ideas and concepts synthesized into the regenerative “flip” hydrogen concentration cell concept that lies at the heart of this work.

Relationship to Other On-going Work

The Sandia/CA microChemLab and Chem/Bio Threat Detection activities make strong use of electrokinetic pumping on an on-going basis. Existing Sandia LDRD work is investigating electrochemically-pumped micro liquid chemical fuel reactions for nanosatellite microthruster application. Sandia/CA’s long involvement with palladium hydride is on-going also.

Appropriateness of Approach

We contend that the proposed approach is highly appropriate for miniature power sources. First, the approach recognizes electrochemical conversion as a key to high efficiency of conversion at low to moderate temperatures. Micro- and miniature heat engines suffer notoriously from problems of inadequate isolation between hot and cold sides, without which efficiency suffers greatly. Second, the approach recognizes heat transfer limitations in miniature structures, or more specifically, the inability to prevent heat transfer in small structures. Engineering materials have but a finite range of thermal conductivity available, so that similitude of heat transfer is generally not possible at reduced scale. We propose to overcome this limitation with controlled heat release through precise control of fuel feed. Third, the approach minimizes complexity by recognizing the great ability of metal hydrides to control the pressure of hydrogen gas by means of hydride temperature, without need of moving parts such as pistons, or compressor wheels, or regulator apparatus.

Importance and Relevance to Laboratory Mission

The Department of Energy and the Department of Homeland Security national security missions often seek to utilize portable, remote, unattended, or mobile systems for sensing, monitoring, and/or communications applications. Very often, available battery technology proves inadequate for the envisioned applications and missions. Electric power sources fueled by chemical liquid fuels, with volumetric energy densities 4 to 10 times those of batteries, could enable a broad range of applications and missions heretofore constrained by limited battery capacity. Power sources continue to pose crucial limitations to the deployment of a variety of small, portable, or mobile applications, including portable microChemLab systems, portable hybrid emergency radiation detectors (HERD), power for “cognitive arthropod” robot insect sensor platforms, etc. The ability to use liquid chemical fuel sources to power these various applications would broaden the range and types of missions that could be undertaken. A successful result could find immediate applications.

Theoretical Considerations

The thermodynamic work available from conversion of a chemical potential to electrical energy in an electrochemical concentration cell in a reversible constant temperature process can be characterized by the change in the free energy. The theoretical change in free energy is the maximum work available from such a system:

$$\Delta G = -nFV \quad \text{where } V \text{ is the electrical potential,}$$

n is the number of electrons transferred per mole of reactant
 F is the number of coulombs per mole of reactant, the Faraday constant

For an ideal gas, which hydrogen approximates so long as the pressures involved are not too great, the change in the free energy associated with a change in pressure at constant temperature can be expressed:

$$\Delta G = RT \ln (P_2/P_1) \quad \text{where } R \text{ is the gas constant,}$$

T is the absolute temperature,
 P_2 and P_1 are the final and initial gas pressures

The above expression, too, describes the maximum work available from the hydrogen concentration differential. Equating these expressions for the change in free energy results in an expression for the maximum electrical potential attainable in the concentration cell:

$$V = - (RT/nF) \ln (P_2/P_1)$$

Not surprisingly for a device referred to as a “concentration cell”, the electrical potential increases with the pressure (i.e. concentration) ratio. Perhaps less intuitively, the electrical potential also increases with the temperature.

For a system using heat to release hydrogen, the maximum efficiency is given by:

$$\eta = \Delta G/\Delta Q \quad \text{where } \Delta Q \text{ is the minimum heat to desorb a quantity of}$$

hydrogen having free energy ΔG .

For most thermally reversible metal hydrides, the heat of absorption (i.e., heat of formation) in the two-phase region is approximately constant, and not strongly a function of temperature. So for each thermally reversible metal hydride, the value of ΔQ is nominally fixed, though it does vary from metal hydride to metal hydride. To show this variation, some heats of absorption values for selected metal hydrides are tabulated below:

<u>Hydride</u>	<u>ΔQ, KJ/mole H₂</u>
Pd ₂ H	-40.0
VH ₂	-58.6
FeTiH	-84.1
UH ₃	-83.7

To maximize the efficiency of the proposed micropower “regenerative flip” hydrogen concentration cell, one would choose a metal hydride with a relatively low heat of absorption. Using this criterion, palladium hydride is a good choice.

Fortuitously, palladium hydride is a much-studied system, so a great deal of useful information is available to assist the estimation of performance. Researchers have derived equations for the dissociation pressure plateau of palladium hydride in the two-phase region of its phase diagram:

$$\log P_{\text{mm}} = 7.3278 - 1835.4/T \quad 0 \text{ to } 180 \text{ C}$$

$$\log P_{\text{mm}} = 7.483 - 1877.82/T \quad 200 \text{ to } 295 \text{ C}$$

The critical temperature for the palladium hydride system is 295C, at which point the two-phase region disappears altogether. To maintain approximately constant operating conditions during discharge of the source metal hydride bed, operation should be limited to temperatures in the two-phase region.

One can use these same relationships to describe the low-side absorption pressure plateau at the operating temperature of the cooled sink hydride bed. Of course, all real hydride beds exhibit some hysteresis in their pressure-composition isotherm -- the absorption pressure plateau is higher than the desorption pressure plateau. The extent of this hysteresis is very much a function of the past history of the metal material - its state of strain or anneal, its dislocations, impurities, etc. Nevertheless, with this simple mathematical model, one can estimate the maximum performance of a hydrogen concentration cell operating in conjunction with its source and sink palladium hydride beds.

For example, selecting 50 C for the temperature of the sink palladium hydride bed, 180 C for the temperature of the source palladium hydride bed, and 80 C for the operating temperature of the electrochemical cell itself, one can estimate the following limits of performance:

$$P_{180} = 1894.5 \text{ mm Hg} \quad P_{50} = 44.5 \text{ mm Hg}$$

$$\Delta G = RT \ln (P_2/P_1) = (8.314)(353) \ln (44.5/1894.5) = -11.0 \text{ KJ per mole H}_2$$

$$V = - (RT/nF) \ln (P_2/P_1) = (11,000)/[(2)*(96,500)] = 0.057$$

where V = 57 mV is the open cell voltage

$$\eta = \Delta G/\Delta Q = 11.0 / 40.0 = .275 \text{ or } 27.5\% \text{ (ignoring losses and inefficiencies)}$$

$$\eta_{\text{Carnot}} = 1 - T_{\text{low}}/T_{\text{high}} = 1 - (323.15)/(453.15) = .29 \text{ or } 29\%$$

Of course, for any heat engine, the limit of performance is the Carnot efficiency. The proposed scheme is indeed a heat engine since a heat source and sink are required for operation. But it is clear that the estimated limits of performance for the proposed scheme can approach the Carnot limit, which is an interesting result.

Practical Implications of Theoretical Results

A further observation is that the open cell voltage is quite low, only 57mV. This is generally characteristic of electrochemical concentration cells. Unfortunately, this is the key limitation to practical exploitation of electrochemical concentration cells. Series connection of cells to achieve a more practical working voltage will be required. But, due to unavoidable internal resistances and contact resistances, a series connected bipolar cell stack may entail greater losses than one would want. Therefore, a good strategy would conclude that once a minimum workable level of voltage is

achieved through bipolar stacking, say 0.3 – 0.8 volts, it may be more effective to avoid further bipolar stacking to increase voltage, and rather employ a DC-to-DC voltage step-up conversion circuit to bring the voltage to a final usable level. The trade-off will depend on comparative losses. Photovoltaic cells have similar issues in practice, and similar power conditioning schemes have found application. A scheme of DC-to-DC voltage step-up conversion in this range of input voltage can be expected to have a conversion efficiency of 75% to 80%. Accepting this level of loss to reach a practical voltage may prove a better choice than seeking to achieve the desired voltage through an excessively large bipolar stack of unit cells.

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Experimental Results

Verification of Palladium Hydride Performance

Palladium hydride performance was investigated using existing small palladium beds that the principal investigator had used several years previously in an unrelated palladium hydride study in a different field of endeavor. These palladium hydride beds proved to be suitable for use in the present experiments. The key technical issue requiring verification was to demonstrate the pressure-temperature-composition performance of palladium hydride is consistent and reproducible while directly connected to an electrochemical in which a water-containing Nafion solid electrolyte membrane is in continuous intimate communication with the hydrogen overpressure in the system.

A simple hydrogen manifold apparatus was assembled to investigate this question. The manifold was made up using Nupro valves, Whitey stainless steel vessels, and stainless steel tubing with Cajon fittings. The experimental arrangement is shown in figure 2.

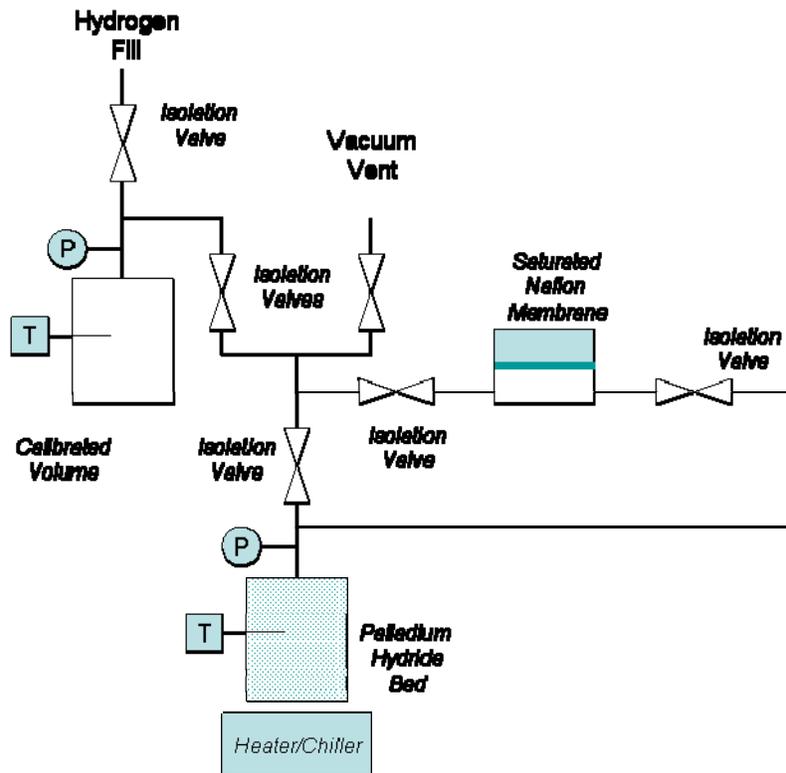


Figure 2. Schematic of Manifold for Hydride Experiments

Isolation valves allow the manifold to be configured with or without hydrogen gas contact with the water-containing nafion membrane. Pressure measurements were made using MKS baratron pressure transducers. Temperature measurements were made using Omega Type K thermocouples. Operation of the manifold and collection of temperature and pressure data were done manually. A calibrated volume and equilibrium gas calculations were used to determine hydrogen gas absorption or desorption by the palladium hydride bed. A high temperature hot plate was used as a heat source for the palladium hydride bed, while passive cooling could be

enhanced through the use of a chilling block made of mass of aluminum initially at room temperature. Prior to use, the nafion membrane was isolated from the manifold, and heat tape was used to bake out the manifold and test vessels prior to experimentation.

Initially, both sorption and desorption pressure-composition-temperature (P-C-T) results for dry hydrogen were generated for the palladium hydride system at several temperatures up to 250 C. Selected measurements were repeated in a second run to verify consistency and reproducibility. Subsequently, the system isolation valving was reconfigured to require the hydrogen overpressure gas to contact the water-containing Nafion membrane, so as to enable both absorption and desorption pressure-composition-temperature (P-C-T) measurements with the hydrogen overpressure in contact with the Nafion membrane. Because the vessel containing the Nafion membrane could not be evacuated without also vacuum drying the membrane, the vessel initially contained some room air which was trapped when the Nafion membrane was sealed within the vessel. Upon first opening this vessel to the dry palladium hydride system, a noticeable prompt rise in hydride bed temperature showed that oxygen in the trapped air was promptly reacted with hydrogen at the palladium surface to form water. The cycle of Nafion membrane isolation, palladium hydride system evacuation, and hydride refilling was performed several times to insure that all oxygen in the system had been reacted, and most of the nitrogen from the trapped air in the system had been removed through evacuation, although some residual nitrogen always remained in the system as an inert diluent.

Once the system had been conditioned as described above, both absorption and desorption P-C-T results were obtained for the palladium hydride system at several temperatures up to 250 C while in communication with the Nafion membrane. Again, selected measurements were repeated in a second run to verify consistency and reproducibility.

In both the dry hydrogen PCT measurements, and the membrane-contact PCT measurements, hydrogen pressures and quantities were carefully adjusted to insure that the resultant hydrogen overpressure always corresponded to a palladium hydride composition in the 2-phase region, typically targeted within the range of stoichiometries from 0.2 – 0.4 moles of hydrogen per mole of palladium metal. In this 2-phase region, absorption and desorption pressures versus stoichiometry do not change much with composition, but are primarily a function of temperature. When results are plotted versus composition, the hydrogen equilibrium pressures in the 2-phase region are seen to plateau (i.e. remain relative unchanging with composition). A single measurement value can be taken to describe this plateau pressure. In figure 3, plateau pressures versus temperature for the both the dry hydrogen case, and the membrane-in-contact case, are plotted along with calculated plateau pressures using the derived equations. The measured results appear, within the variance of the experimental data, to be consistent with calculated results for both the dry hydrogen and membrane contact cases. These results would seem to indicate that the contact with the Nafion membrane, and the presence of residual nitrogen diluent did not affect the equilibrium P-C-T performance of the palladium hydride system in any appreciably observable way. This would be consistent with expectation. It should be noted that no specifically kinetic measurements were undertaken to determine whether the kinetics of the P-C-T performance might have been affected, although none seemed apparent. Based on these equilibrium results, it may be concluded that contact between the hydrogen overpressure and the water-containing Nafion membrane had no apparent affect on the equilibrium P-C-T performance of the palladium hydride.

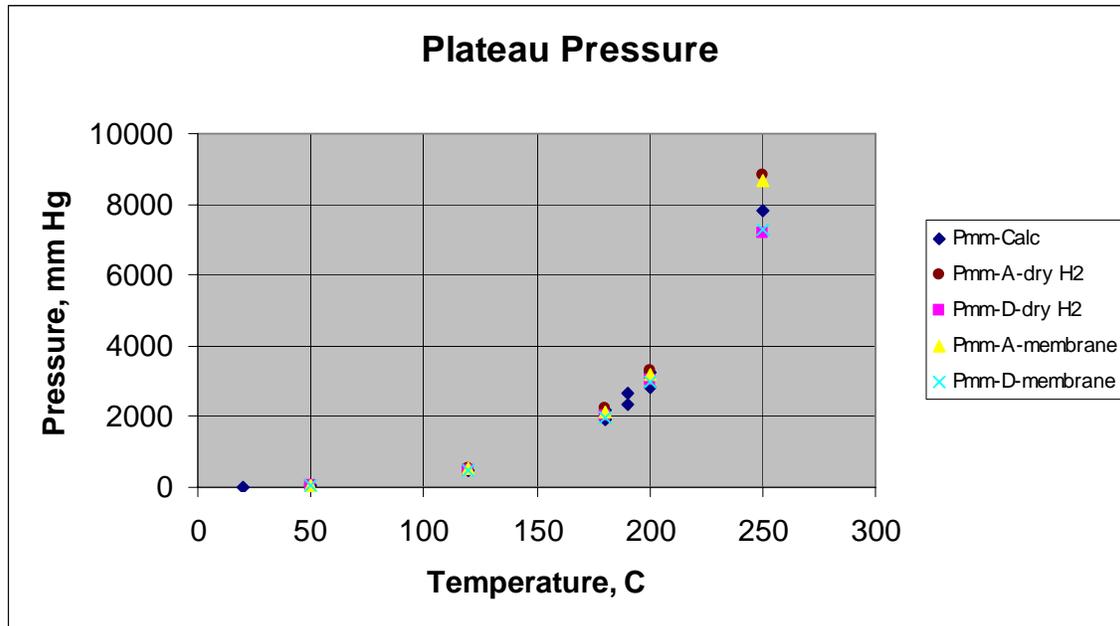


Figure 3. Palladium Hydride Plateau Pressures (2-Phase Region).

Hydrogen Concentration Cell Performance

Electrochemical hydrogen concentration cell performance was investigated primarily using a small single-cell hydrogen fuel cell demonstration cell originally obtained commercially several years ago for an unrelated hydrogen fuel cell project. Supplemental results investigating bipolar contact resistance were obtained using an experimental hydrogen fuel cell stack developed by the principal investigator several years ago for an unrelated hydrogen fuel cell project. The commercial single-cell hydrogen fuel cell consists of a single membrane electrode assembly comprised of a Nafion electrolyte membrane separating two hydrogen gas diffusion electrodes of the Elat type from E-TEK. The Elat electrodes employ platinum-catalyzed carbon powder on the surface of a gas-diffusion sponge-like electrode substrate comprised of a matrix of Nafion powder, Teflon powder, and carbon powder, all together heat-and-pressure sinter-bonded into a sponge-like layer onto an underlying woven carbon fiber cloth ply. These Elat electrodes are then heat-and-pressure bonded to the Nafion electrolyte membrane to form a membrane electrode assembly. This construction constitutes a typical state-of-the-art hydrogen fuel cell membrane electrode assembly. Stainless steel woven wire mesh current collectors sandwiching the membrane electrode assembly within an acrylic flange housing with gas ports complete the electrochemical cell. The single cell is symmetrical, and either electrode may be chosen as the anode or fuel electrode. In the case of a concentration cell, the only distinction between electrodes is their hydrogen operating pressure.

This single electrochemical cell was assembled into a hydrogen manifold as shown schematically in the figure 4. As configured, the manifold allows each electrode to be connected to a separately fillable hydrogen reservoir. The hydrogen pressure in these reservoirs can be separately adjusted so that one can select the hydrogen pressure applied to each electrode. The acrylic flange and wire-mesh current collector provide sufficient support to the membrane electrode assembly to sustain the differential pressure applied across the cell ($\Delta P \sim 3000$ mm Hg, where 760mm of Hg is approximately one atmosphere or 14.7 psia).

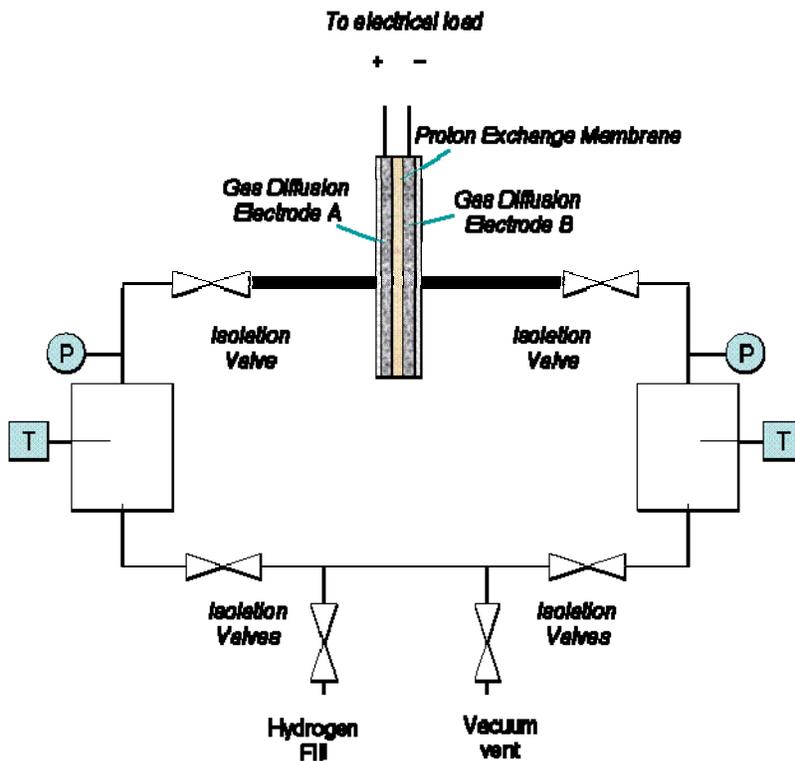


Figure 4. Experimental Arrangement for Electrochemical Concentration Cell

Prior to beginning concentration cell experiments, the electrochemical cell was conditioned by operation for a time, in both the forward and reverse direction, as a hydrogen fuel cell. This was accomplished by disconnecting the selected cathode from the hydrogen manifold, and operating the cathode open to room air. A load resistor was connected across the hydrogen fuel cell to limit operating current to approximately 100 mA/cm², and the cell was operated in this mode steadily for several hours. Subsequently, the configuration was reversed, so that former anode became cathode and vice versa, and operated in that mode steadily for several hours. This conditioning insures that the electrolyte membrane and the gas diffusion electrodes are properly hydrated to support proton transfer associated with electrochemical performance. Once the electrochemical cell and the test manifold had been converted out of fuel cell operation mode, back to hydrogen concentration cell operation mode, the gas diffusion electrodes were flushed with hydrogen gas to sweep any residual air or water vapor out of the electrodes. The hydrogen concentration cell was then ready for test.

With the cathode electrode held at nominal hydrogen gas pressure of 45 mm Hg, the anode electrode hydrogen gas pressure was stepwise increased from 45 mm of Hg while the open cell voltage produced across the hydrogen concentration cell was measured. The result is plotted in Figure 5.

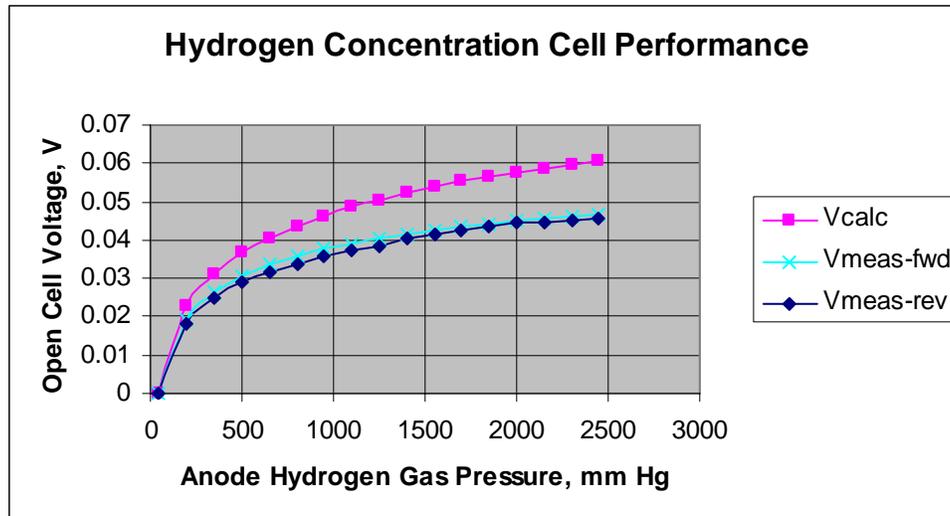


Figure 5. Hydrogen Concentration Cell Performance – Open Cell Voltage

These results confirm the expectation of only tens of millivolts of cell output, but also highlight losses that can be expected in real apparatus. As expected, the actual measured open cell voltage increases with anode hydrogen gas pressure, tending toward an asymptotic approach to a limit of performance some 10 millivolts less than the calculated theoretical voltage, or approximately 85% of the theoretical voltage. Similar results are obtained for cell operation in both the forward and reverse directions, that is, with the electrodes alternating as the higher pressure anode. This is unsurprising since the design of the cell is symmetrically identical in both forward and reverse operation. The open cell voltage available in an actual cell operating at practical pressures and temperature would appear to somewhat less than 50 mV. This suggests some loss due to polarization phenomena or contact resistance between the distributed locations at which the electrochemical voltage is generated on the surface of the electrocatalyst within the electrodes and the terminals at which the voltage can be measured. This loss highlights an unfavorable comparison between the hydrogen concentration cell and the hydrogen fuel cell. Whereas a loss of 10 mV represents only a minor loss for a hydrogen/oxygen fuel cell (theoretical open cell voltage $E = 1.23$ V), this 10 mV loss represents a significant percentage voltage loss relative to the very modest voltages produced by the hydrogen concentration cell. In practice, this means that more cells will be required to be connected in series to produce a given practical output voltage.

An additional series of measurements were conducted to further characterize the hydrogen concentration cell performance. Selected electrical resistance loads were connected across the terminals of the concentration cell to determine the performance under load. Separate measurements were conducted with the concentration cell operating in both the forward and reverse direction - that is, with the electrodes alternating as the higher pressure anode. The results are presented in figure 6.

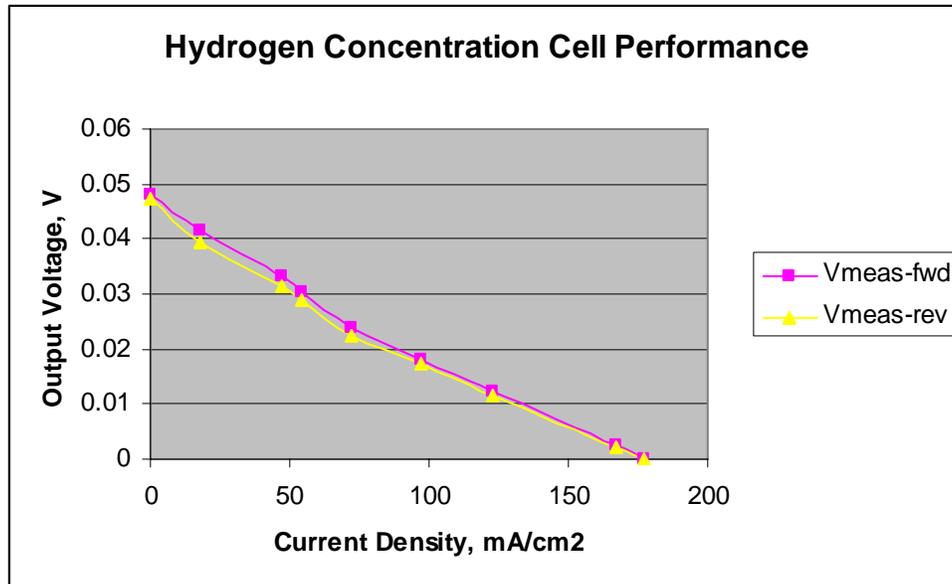


Figure 6. Hydrogen Concentration Cell Performance – Voltage vs. Output Current

These polarization curves represent a typical performance for electrochemical cells based on Nafion solid polymer electrolyte membranes and Elat type gas diffusion electrodes. The drop in output voltage with increasing current density is primarily the result of irreducible internal and contact resistances. More recently, Nafion has become available in increasingly thinner membranes, thus reducing internal resistance of more modern cells approximately proportionately to the thickness of the Nafion membrane employed. The commercially bought electrochemical cell used in these tests uses a DuPont Nafion 117 membrane of thickness 183 microns. The power outputs corresponding to the polarization curves of Figure 6 are presented in Figure 7. As is typical of such cells, power output increases with initial current draw, maximizes over a range of current densities corresponding to best output for the particular cell, and then rolls off with increased current loading. For the electrochemical cell used in this study, power density peaked at slightly less than 1.8 mW/cm².

These polarization and power density curves highlight a second characteristic of hydrogen concentration cells – because they operate at such a modest voltage, internal and contact resistances act to limit the current density, and therefore, power density achievable by the cell to values significantly lower than the actual limit capabilities of the materials of construction. In hydrogen fuel cell operation, similar membrane electrode assemblies are capable of current densities of Amperes/cm², and corresponding power densities on the order of Watts/cm².

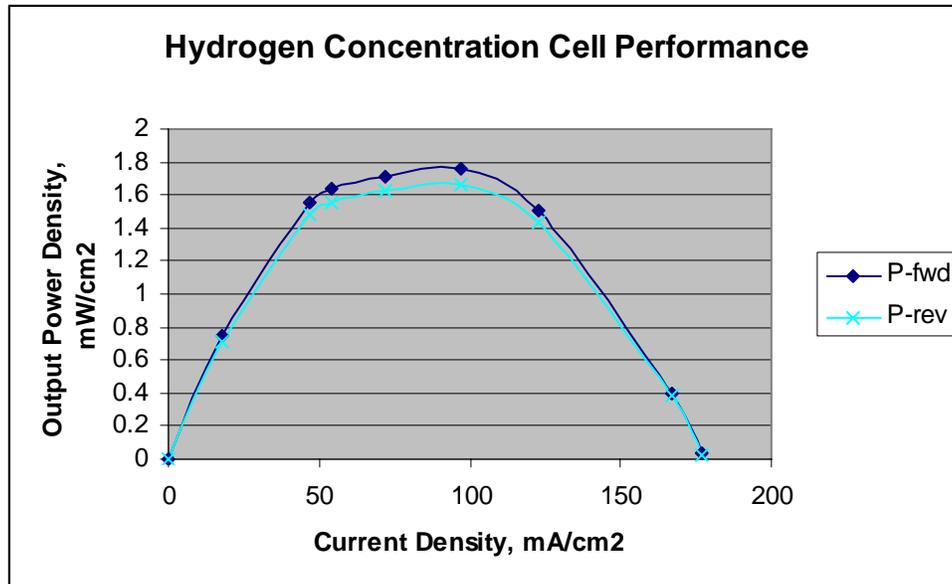


Figure 7. Hydrogen Concentration Cell Performance – Output Power Density

To be sure, these performance comparisons between the hydrogen concentration cell and hydrogen fuel cell relate only to cost-effective utilization of expensive materials of construction; they should not be used to impute any inferiority to the hydrogen concentration cell. Though perhaps underutilized in the hydrogen concentration cell, the Nafion-based membrane electrode assembly has the merit that, in this application, the output current and power densities are well removed from actual materials limits of performance with respect to internal water transport limitations and corresponding catastrophic membrane resistivity buildup. This headroom regarding materials limits of performance can be counted as a distinct advantage for micropower sources employing the hydrogen concentration cell. Of course, as one moves to larger power sources, this advantage becomes offset by cost and modest performance, so that one would not consider hydrogen concentration cells of this design for large power sources. Nevertheless, for micropower sources, the potential has been clearly demonstrated.

Integrated Hydride Bed / Concentration Cell Demonstration

While it had been our intent to conduct an integrated demonstration combining palladium hydride bed source and sink reservoirs coupled to a hydrogen concentration cell converter, in the event, it was not possible to carry through with this activity within the scope of the resources available to the project. Nevertheless, it is encouraging to note that all the needed antecedent results had proved positive, and that there could be every expectation that the integrated demonstration should also be successful. Further, encouraging independent results had demonstrated that microfluidic quantities of energetic liquid fuels could be reacted at catalyst-coated reaction sites, having been delivered to the reaction zone through electrokinetic flow. Consequently, all the elements called for in the conceptual design of the “regenerative flip” concentration cell have now been demonstrated, so that we should have every expectation of success should an integrated demonstration be completed.

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Conclusions and Recommendations for Future Work

Conclusions

The results of this investigation have demonstrated the feasibility of micropower generation from hydrogen concentration cells based on solid polymer electrolyte membranes. Micropower densities of 1.8 mW/cm² were demonstrated using hydrogen operating parameters compatible with palladium hydride gas reservoirs, and hydrogen electrochemical converters adapted from commercial hydrogen fuel cell apparatus. By employing truly state-of-the-art thin Nafion membranes (50 micron thick, and even 25 micron thick membranes have now been demonstrated in the literature), power density improvements of 3X to 5X should be feasible, so that single cell power outputs should approach 5 to 10 mw/cm².

The feasibility of using palladium hydride as source and sink reservoirs for regeneratively cycled hydrogen gas has been reinforced by demonstration that the water-containing Nafion membranes, despite being in continuous contact with the hydrogen “working fluid”, do not appreciably affect the pressure-composition-temperature performance of the hydrogen - palladium hydride interaction. Consequently, it should definitely be feasible to use palladium hydride as the source and sink reservoirs in a “regenerative flip” hydrogen concentration cell power source as proposed for this study.

Finally, though not a part of the reduced scope of work of this study, a separate Sandia LDRD project has successfully demonstrated the microfluidic electrokinetic-pumping of energetic liquid fuels, and the catalytic decomposition of such energetic liquid fuel upon delivery to the catalyst-coated reaction surface.

Therefore all the elements needed to proceed with an integrated demonstration of a “regenerative flip” hydrogen concentration cell micropower source as proposed in this study have been individually demonstrated.

Recommendations for Future Work

Should future funding permit it, the above results would argue that continued development of this technology for small power direct generation applications would appear warranted. Topics for future work include:

1. Higher performance hydrogen concentration cells using state-of-the-art thin Nafion membranes, and improved thick-film gas diffusion electrodes.
2. Development of bipolar hydrogen concentration cell stacks of 10 to 20 cells to achieve stack voltages in the 0.2 – 1.3 V, suitable for further voltage step-up using commercially available power conditioning chips.
3. Demonstration of the “regenerative flip” operation of a hydrogen concentration cell coupled to heated source and passively-cooled sink palladium hydride beds.
4. Demonstration of palladium hydride bed heating by microfluidic electrokinetic pumping of energetic liquid fuel catalytically reacted upon the catalyst-coated surface of the palladium hydride bed containment vessel.

5. Integrated demonstration of the “regenerative flip” hydrogen concentration cell micropower source incorporating all of these elements, as in the original concept proposal.
6. Extended operation of an Integrated “regenerative flip” hydrogen concentration cell micropower source.

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