Room temperature micro-hydrogen-generator[☆]

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Abstract

A new compact and cost-effective hydrogen-gas generator has been made that is well suited for supplying hydrogen to a fuel-cell for providing base electrical power to hand-carried appliances. This hydrogen-generator operates at room temperature, ambient pressure and is orientation-independent. The hydrogen-gas is generated by the heterogeneous catalytic hydrolysis of aqueous alkaline borohydride solution as it flows into a micro-reactor. This reactor has a membrane as one wall. Using the membrane keeps the liquid in the reactor, but allows the hydrogen-gas to pass out of the reactor to a fuel-cell anode. Aqueous alkaline 30 wt% borohydride solution is safe and promotes long application life, because this solution is non-toxic, non-flammable, and is a high energy-density ($\geq$2200 W-h per liter or per kilogram) hydrogen-storage solution. The hydrogen is released from this storage-solution only when it passes over the solid catalyst surface in the reactor, so controlling the flow of the solution over the catalyst controls the rate of hydrogen-gas generation. This allows hydrogen generation to be matched to hydrogen consumption in the fuel-cell, so there is virtually no free hydrogen-gas during power generation. A hydrogen-generator scaled for a system to provide about 10 W electrical power is described here. However, the technology is expected to be scalable for systems providing power spanning from 1 W to kW levels.
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1. Introduction

Fuel-cell power-sources have three major components: (A) the fuel supply; (B) the fuel-cell; (C) control and power-conditioning electronics. Practical fuel-cells and control electronics have been available, but a compatible practical fuel has remained elusive. Hydrogen is a highly desired fuel, because there are polymer electrolyte membrane (PEM) fuel-cells available that will steadily and stably make electrical power for many thousands of hours, as long as the PEM fuel-cell is supplied hydrogen and air [1]. Unfortunately hydrogen storage is typically bulky and hazardous, which has been one of the main obstacles preventing commercialization of the hydrogen-air fuel-cell as a hand-carried power-source. A new hydrogen supply system reported here can surmount the hydrogen-supply problems and lead to a feasible fuel-cell system as a practical portable power-source.

A power-source system with high energy-density has been increasingly desired for powering hand-carried electronics applications (such as, cell phones, laptop computers, radios, palm pilots, etc.) as more features, complexity and subsequently increased power demands are introduced to these electronic appliances. Our first system goal is to develop an integrated power-source system that provides tens of Watts of power and has an energy-density greater than 300 W-hour per liter (or kilogram) of the power-source system.

Fig. 1 shows a block diagram of such a power-source system and its key components.

2. Experimental

All gases used were high purity grade or better (Air Products) and all other reagents were reagent grade or better. The hydrogen storage solution was made by preparing a 30 wt%
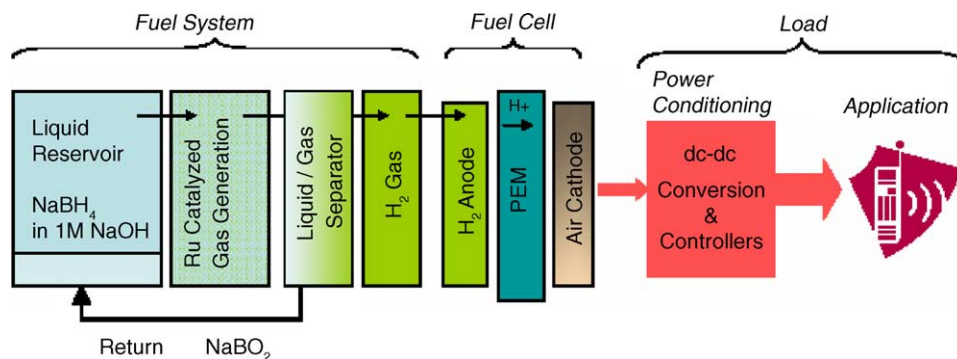
Fig. 1. The block diagram of the fuel-cell system showing the key components: (a) hydrogen-generator; (b) fuel-cell; (c) power conditioning and controllers.

solution of sodium borohydride (Aldrich reagent grade) in 1 molar (4 wt%) sodium hydroxide (Aldrich) water (Millipore 18 MΩ) solution. This alkaline aqueous borohydride solution was filtered through a 0.2 micron polycarbonate filter (Nucleopore) to give a clear colorless solution. Ruthenium on alumina catalyst was made by soaking high surface area gamma alumina pellets in a 2 or 5 wt% $RuCl_3$ solution in DI water for 12 h. The solution was decanted off and the $RuCl_3$-coated alumina pellets were dried at room temperature before drying in a tube furnace at 100 °C under helium. Samples were then heated under 5% hydrogen, balance helium. The temperature was ramped at 100 °C h^{-1} to at least 150 °C, and as high as 700 °C with a 6 h dwells for comparison. The result was a mainly Ru metal on alumina support as determined by energy dispersive absorption X-ray (EDAX) spectroscopy. Gas flow was measured using an Agilent ADM 2000 flow meter. Gas and liquid separation was achieved by using a Celgard 4560 Gas Permeable membrane. All seals were made using Viton gasket filled with non-conducting carbon only (Eagle Elastomer, Westlake, OH). Fuel-cells were made with Nafion 117 membrane purified by soaking in: 1 M sulfuric acid, then 30 wt% peroxide, then three times in DI water at 70 °C. The purified membrane was sandwiched by two E-TEK (Summit NJ) V3 ELAT electrodes (0.5 mg Pt per centimeter squared). First the electrodes had been treated with 1 wt% alcoholic Nafion solution to give 1 mg of Nafion per centimeter squared of electrode (mass electrode ≅ 50 mg).

After the electrodes were air dried at 70 °C for 1 h, they were hot pressed onto the Nafion membrane at 120 °C and 800 N cm^{-2} for 2 min. Fuel-cell polarization curves were obtained with hydrogen as the fuel and either air or oxygen as the oxidant. Polarization measurements were made galvanostati-

cally using a Keithley 2420 Source meter controlled by a custom Labview program. Cell resistance was determined from the high frequency intercept of a electrochemical impedance scan done with a Solartron 1286 potentiostat coupled to a Solartron 1250 Frequency Response Analyzer controlled by Z-Plot software (Scribner Associates). Polarization data were recorded when the voltage change at constant load was less than 1 mV per minute, which insured the fuel-cell was at steady state. The humidity of flowing gases was measured with an Omega CT 485B meter. This was done with a humidity sensor sealed in a chamber (100 ml) with two holes. Gas was admitted into the chamber through one hole and allowed to escape through the other. The exit was protected from back diffusion of air. After a time (depending on the flow rate) the chamber volume was exchanged with test gas, and the relative humidity of test gas was measured repeatedly over many hours to insure accuracy.

3. Discussion and results

3.1. Fuel Supply

This paper mainly concerns the first block of the fuel-cell system, shown in Fig. 1, the fuel system. The fuel system consists of: (i) compact and safe hydrogen storage solution; (ii) low power pumps to move the liquid fuel; (iii) a catalytic reactor to release hydrogen from the hydrogen storage solution; (iv) an orientation-independent gas–liquid separator.

(i) The specific hydrogen storage solution used as the fuel is an aqueous alkaline (1 M sodium hydroxide,

Table 1
Borohydride solution and H_2 gas flows to sustain electrical power

Current (A)	Liquid fuel flow (microliter min^{-1} NaBH4-30)	Molar flow (mole min^{-1})	H_2 gas flow (sccm)	P at 0.7 V (W)
0.1	1	3.1E−05	0.7	0.07
1	10	3.1E−04	7.0	0.7
2	20	6.2E−04	14	1.4
10	100	3.1E−03	70	7

1 l of NaBH4-30 solution stores 66 g of H_2 equivalent to 789 l of H_2 gas. The freezing point of NaBH$_4$-30 is −13 to −36 °F. The boiling point is ∼120 °C.
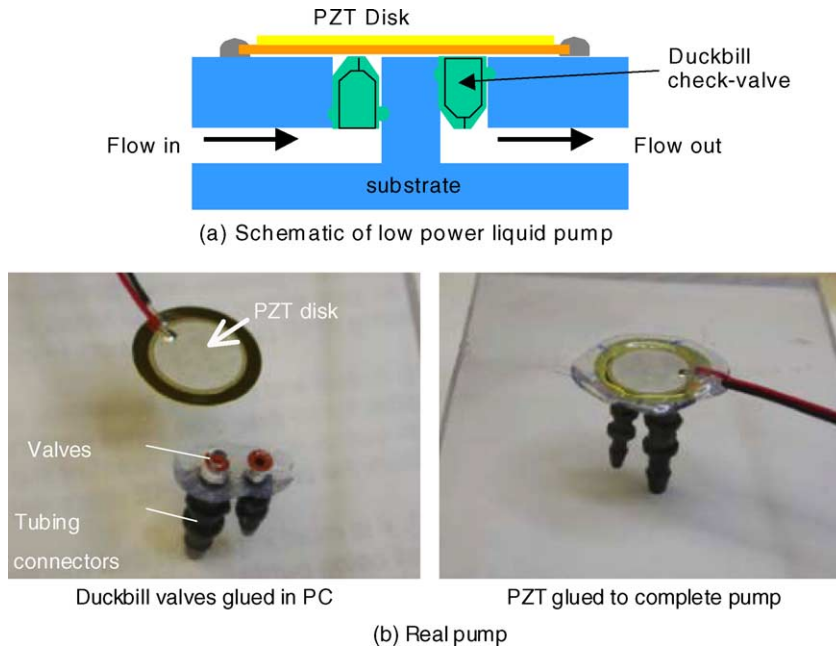
Fig. 2. (a) Schematic diagram of piezo-pump with bubble tolerant duckbill valves; (b) actual pump components; valves and tube glued in a plastic housing (left) and then with the wired piezo-element glued to the housing to make a completely assembled pump.

pH = 14) solution containing 30 wt% sodium borohydride (energy-density = 2200 W-hour per liter, 450 day shelf half-life, [2]). When this borohydride solution is flowed into micro channels coated with supported heterogeneous catalyst, like ruthenium [3–5] metal on alumina, hydrogen is catalytically generated by the hydrolysis of the sodium borohydride [3–5]. Table 1 gives the ideal liquid and gas flows for generating hydrogen and electricity. The hydrogen storage solution is very safe. It does not burn (even when in contact with a spark or flame) and does not release hydrogen until it passes over the catalyst.

(ii) Piezo pumps have been developed that can provide a wide range of liquid flow (microliter to milliliter per minute) by controlling the piezo excitation voltage and frequency. The pumps develop a 5 psi pressure head, are self-priming, gas-bubble tolerant, low in cost (<\$1) and are efficient, that is, the pumps draw very little power from a battery or fuel-cell. Fig. 2a is a schematic diagram of the pump design showing the essential features: the piezo element (PZT disk), the check valves and the housing, which is typically plastic laminate. Fig. 2b shows actual pump components and an assembled pump.

At a given voltage, flow rate varies with frequency (maximum frequency used is 100 Hz), and at a given frequency, flow rate varies with voltage (maximum voltage used is 100 V). Fig. 3 shows the liquid flows obtained using these piezo-pumps under a variety of conditions. The piezo pump with a 35 mm PZT disk and duck bill check valves outputs a maximum one-way liquid flow of 1.7 ml min^{-1} of 30% alkaline borohydride solution. This flow would generate 1700 sccm H_2, or enough hy-
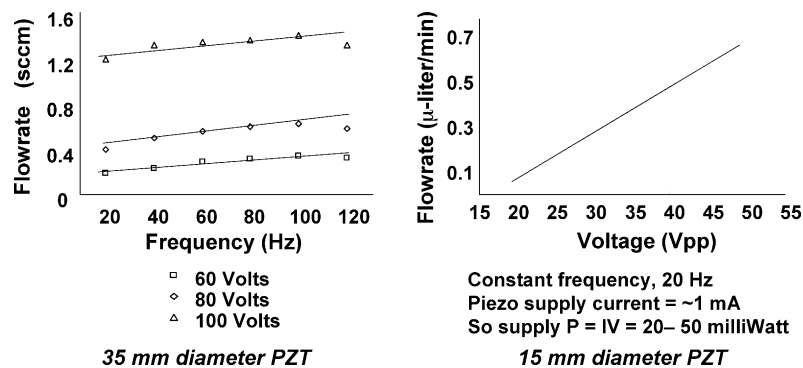

Fig. 3. Results when pumping liquids with piezo pumps: (left) the flow generated with a 35 mm piezo element when supplied 60, 80 and 100 ac volts at frequencies between 20 and 120 Hz; (right) flow generated with a 15 mm piezo element at a constant 20 Hz excitation frequency for ac volts between 15 and 55 V.
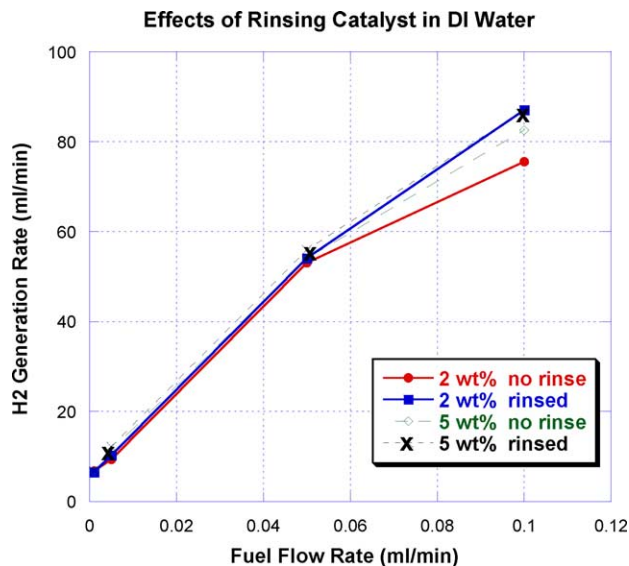
Fig. 4. Gas-generation vs. liquid flow into the reactor, as shown in Fig. 5 below. The actual weight% of ruthenium in ruthenium on alumina pellet for both the 2 and 5 wt% solutions is 4.6 wt% as determined by EDAX and visual observations of volume of colored cross-section. No H_2 flow was observed when Ru on alumina was replaced by equivalent weight of alumina only.

drogen to generate over 120 W of electrical power. This pump is self-priming and bubble-tolerant. Typically, a piezo-pump costs ∼$0.2; can provide a controllable flow (micro liter to milliliter per minute depending on pump drive voltage and frequency) and is readily integrated with electronic controllers used in the fuel-cell system. These pumps draw low parasitic power (10 mW for a pump to supply the borohydride solution to a 1 W fuel-cell, and 0.5 W for pump to supply a 100 W fuel-cell).

These low-power piezo-pumps are the preferred means for pumping the liquid feed into the micro reactor. They allow for a controlled, self-generated hydrogen flow from the reactor, through the gas liquid separating membrane to the fuel anode, while the liquid
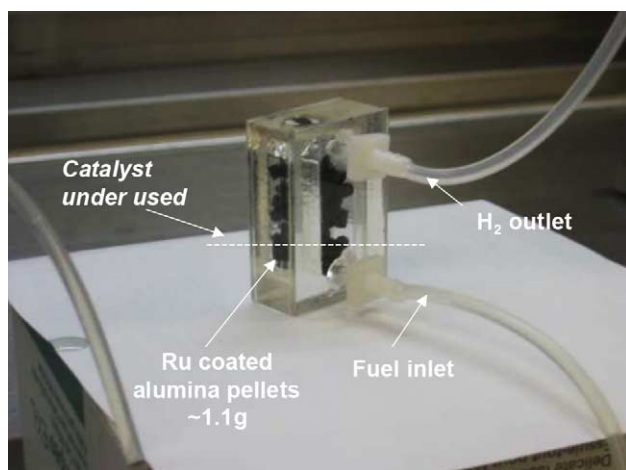

Fig. 5. Hydrogen-generating reactor used for experiment to get results in Fig. 2 above.
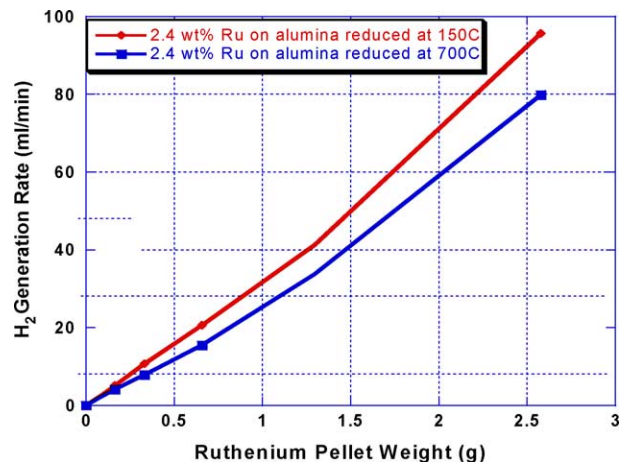

Fig. 6. Rate of hydrogen-gas generation in the presence of excess borohydride as a function of catalyst weight.

by product is pumped back to a bladder in a the space in the fuel cartridge that was originally occupied by the hydrogen storage solution. This controlled flow is desired because it insures no excess hydrogen builds up in the system during power generation.

(iii) Having a steady generation of hydrogen from the alkaline borohydride hydrogen storage solution is the key feature that enables a new low temperature fuel-cell system. The hydrogen-generating micro-reactor is designed to operate under mass transfer control. That is, as soon as the hydrogen storage solution flows over the catalyst surface in the micro-reactor, the reaction between the water and alkaline borohydride occurs and proceeds to completion. To have a steady generation of hydrogen requires an active catalyst for the room temperature hydrolysis of alkaline borohydride solution, and the hydrolysis catalyst should have no appreciable deactivation as it is used over practical periods of time. In our hands, we have found that ruthenium metal support on gamma alumina is such a suitable hydrolysis catalyst. It is an active, stable and cost effective catalyst. The
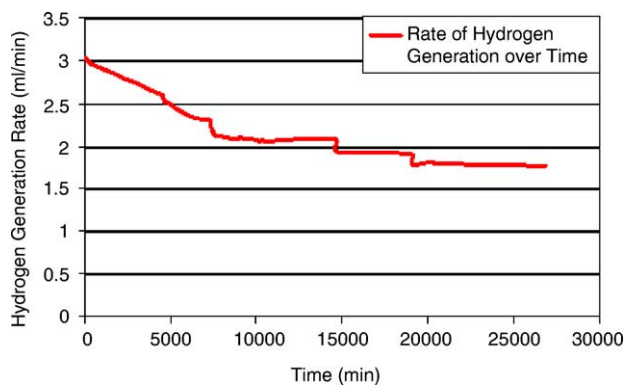

Fig. 7. Hydrogen-gas generation over time with 90 mg of 2.4 wt% Ru on alumina catalyst in excess sodium borohydride ($NaBH_4$) solution.
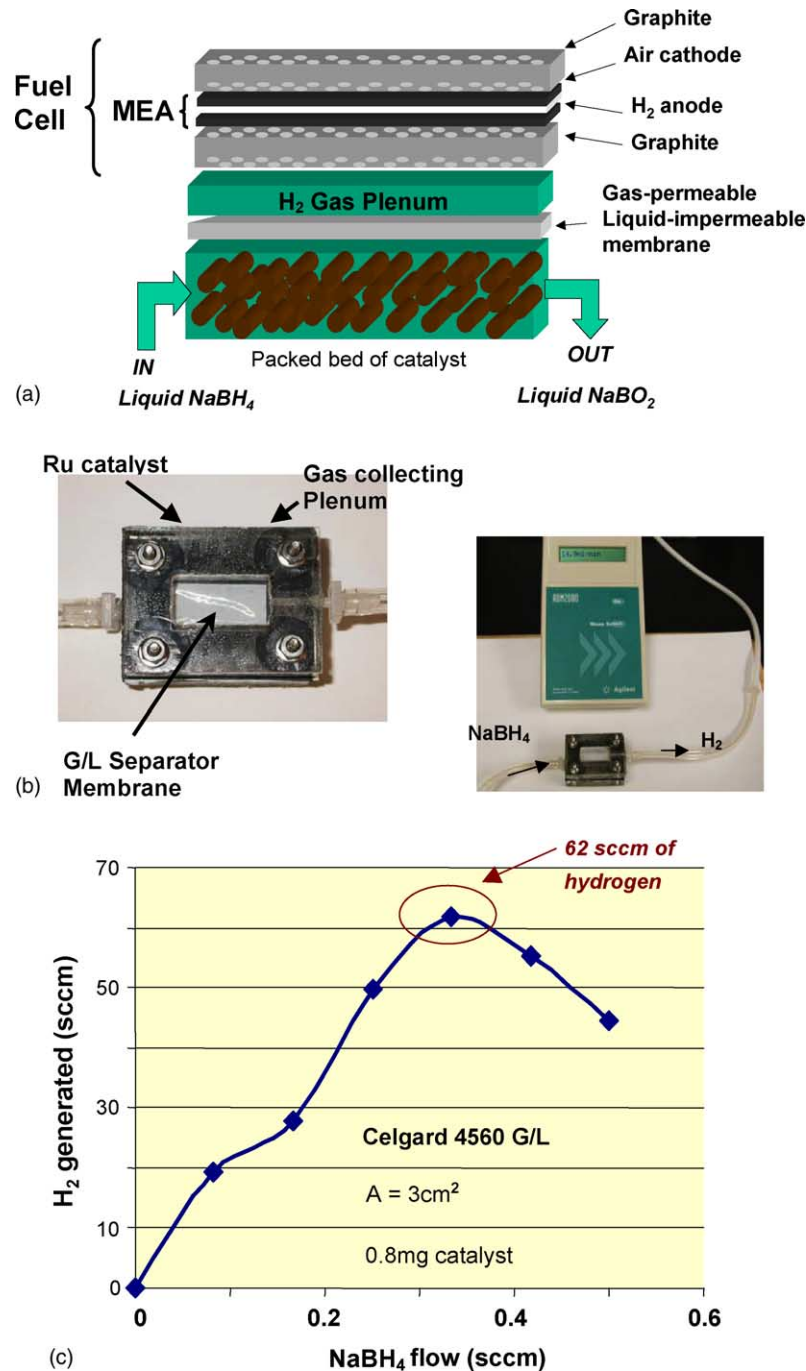
Fig. 8. (a) Schematic diagram of an orientation-independent hydrogen-generator that employs a gas/liquid separating membrane (bottom) integrated to a fuel-cell (top). The gas exit of the reactor goes to a plenum that supplies hydrogen to the fuel-cell anode. (b) Actual laboratory prototype of an orientation-independent hydrogen (H_2) generator with gas liquid separating membrane [6]. The weight of the Ru on alumina in the reactor was 0.895 g in which the 2.4 wt% of this is Ru. (c) Hydrogen generation through gas-liquid separating membrane in orientation-independent hydrogen-generator. Membrane area = 3 cm^2.

following discussion and results explain our approach to developing this catalyst and a catalytic reactor.

Fig. 4 shows results for a hydrogen-generator (shown in Fig. 5) in which the hydrogen generation rate was linearly dependent on the rate of mass transport of liquid alkaline borohydride hydrogen-storage solution into the catalytic reactor. The reactor (shown in Fig. 5)

was 'overbuilt' in that it contained an excessive amount of Ru on alumina catalyst.

The reactor (shown in Fig. 5) was not optimized for catalyst amount or size. It used excessive amounts of Ru (52 mg). To optimize Ru utilization, one needs to know the activity of Ru on alumina for catalyzing the hydrolysis of aqueous borohydride solution (as it is

used to generate hydrogen-gas). One useful metric of catalyst activity is the mass of the catalyst needed to promote a specific rate of reaction. Fig. 6 shows the rate of hydrogen-gas generation as a function of catalyst weight in the presence of excess alkaline borohydride solution. As can be seen in Fig. 6, it was found that the H_2 gas flow is approximately linearly proportional to the catalyst weight. Considering that Ru costs approximately $30 per gram, and that approximately 10 sccm of hydrogen is needed to produce a Watt of electrical power, then the weight of the Ru metal need per Watt of electricity corresponds to less than 25 cents of Ru.

Fig. 7 addresses the issue of the stability of the catalyst activity. It shows the hydrogen-gas flow generated by a fixed amount (90 mg) of Ru on alumina catalyst in excess sodium borohydride solution. From Fig. 7 and similar longer-term data, we conclude that Ru is an active catalyst for the hydrolysis of borohydride solution, and that its activity did not change for thousands of hours. The decline in the hydrogen-gas generation (hydrogen-gas flow shown in Fig. 7) is not due to loss of catalyst activity, but is due to the decline in the concentration of the excess sodium borohydride solution. The observed decrease in hydrogen-gas generation is as predicted by the rate equation, in which the rate of H_2 generation is equal to the product of the rate constant (k) times the catalyst area (A) times concentration of sodium borohydride [$NaBH_4$], or rate $= k\,A\,[NaBH_4]$. Therefore, it is clear that the Ru lost no activity for catalyzing the hydrolysis (hydrogen generation) reaction over the entire time of the measurement. This stability of the catalyst activity is important when designing a practical hydrogen-generating device.

(iv) Orientation-independent gas-liquid separation is needed for a practical power-source system. Recently, a refined embodiment of the hydrogen-generator has been developed that is orientation and gravity independent. This orientation-independent hydrogen-generating reactor is described in Fig. 8a–c. The orientation independence is derived from the use of a gas and liquid separating membrane (Celgard 4560). Fig. 8a is a block diagram that shows the design for an orientation-independent hydrogen-generator (bottom) mated with a fuel-cell (top).

Fig. 8b shows an actual orientation-independent hydrogen-generator. The hydrogen-generating reactor of Fig. 8b is essentially the bottom three layers shown in Fig. 8a.

Fig. 8c shows the actual performance of the reactor shown in Fig. 8b.

Hydrogen, but no alkaline solution, passes through the Celgard membrane, even if the generator is 'upside down' and completely covered with the liquid alkaline borohydride solution. No change was observed for a pH paper on the fuel-cell side of the membrane during hydrogen generation. With a 3 cm^2 membrane forming one wall of the reactor, the

hydrogen generation linearly increased with increasing flow of borohydride solution into the reactor. When the liquid feed flow passed 0.4 ml per minute, a maximum hydrogen flow of 60 sccm was attained. Apparently this is the limit. An outward bulge was seen in the membrane when the hydrogen flow approached 60 sccm. So, for every centimeter squared of the membrane, at least 20 sccm of hydrogen freely passes, which enough hydrogen to sustain making three Watts of electrical power. The cause of the decline in hydrogen generation with increasing liquid feed (see liquid flows past 0.4 ml per minute in Fig. 8c) is not certain. Regardless, the trace shown in Fig. 8c does not change, even when the reactor is fed many times at liquid supply rates between 0 and 0.5 ml per minute.

3.2. Fuel-cell

A fuel-cell that can utilize the hydrogen made by the hydrogen-generator is discussed net. The fuel-cell is to be fed hydrogen stream generated the hydrolysis of sodium borohydride solution as is flowed over a catalyst in an orientation-independent hydrogen-generating reactor being developed for making a 10 W power-source.
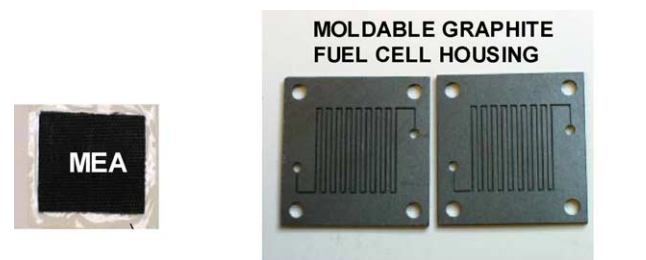
(a) Membrane electrode assembly (MEA, on the left) and moldable graphite current collecting flow field with serpentine flow field (on the right); overall dimensions: 38 x 38 x 2mm.
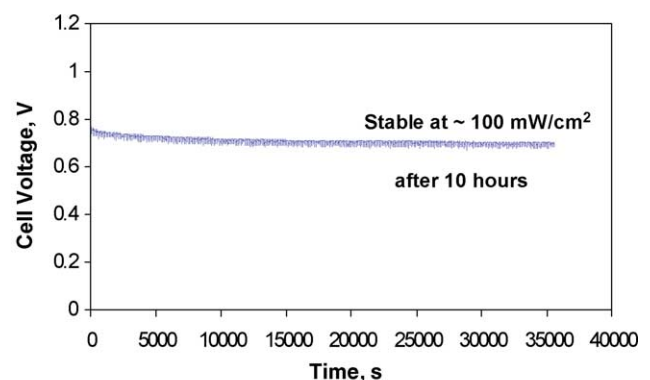
(b) Cell voltage at constant load (130 mA/cm²) in time for MEA with 4.5 mg Nafion in 50 mg E-TEK electrode

Fig. 9. Fuel-cell hardware and fuel-cell performance: (a) on top show fuel-cell hardware and (b) bottom is performance at constant load (130 mA cm^{-2}) for the MEA in a conventional (Fuel-cell Technologies) fuel-cell test housing. Anode feed: pure humidified (100% RH) hydrogen. Cathode feed: pure dry oxygen. Each electrode is a Pt catalyzed gas-fed porous electrode (E-TEK, 0.5 mg Pt per cm^2 of electrode).

Fig. 9a shows actual hardware for making a portable fuel-cell and a representative fuel-cell performance. Fig. 9a shows MEA (left) and the current-collecting moldable graphite plates (right) that are used to house the MEA. The plates have serpentine gas channels. One of the plates supplies hydrogen-gas to the anode and the other plate supplies oxygen to the cathode. Fig. 9b shows fuel-cell performance for a home-made membrane electrode assembly (MEA) tested in a standard test fixture. The goal is to reproduce MEA performance (shown in Fig. 9b) that was gotten in standard test fixture in the new test fixture hardware (Fig. 9a) using the hydrogen generated from the reactor (shown in Fig. 8, above). Alternatively, there are many commercial MEAs that have been similarly made using Nafion membrane and porous gas-fed Pt-catalyzed electrodes. Commercial MEAs could be used in conjunction with our hydrogen-generator instead of our homemade MEA, since the hydrogen-generator makes pure wet (100% RH) hydrogen, which is ideal for feeding these commercial MEAs.

3.3. Control and power-conditioning electronics

The fuel-cell power-source system is expected to be a hybrid of a fuel-cell, a battery, maybe a capacitor and will require dc–dc converter, control electronics, temperature sensing, battery charge/discharge control etc. to make a complete 'battery substitute' power-source. In, addition the fuel-cell must maintain operation in a specific voltage/current region to avoid damage to the cell or membrane and to maintain maximum efficiency. This is a formidable project in engineering and beyond the scope of this paper.

4. Conclusions

Described here are all of the necessary elements needed to make an orientation-independent hydrogen-generator that operates at room temperature, ambient pressure and uses a high energy-density liquid fuel, alkaline borohydride solution. Using alkaline borohydride hydrogen-storage with a high efficiency mini $H_2–O_2$ PEM fuel-cell offers a means for obtaining clean portable reliable power for longer appliance life than with a battery of same size and weight. The proposed fuel-cell system offers applications longevity owing to its more concentrated (up to 10 wt% H_2) hydrogen storage than found with H_2 stored under common tank pressures or in typical metal hydrides. This fuel-cell system is ideal for hand-carried appliances because it operates at room temperature and the alkaline borohydride solution is non-toxic and non-flammable. Liquid would leak slowly and safely from a punctured liquid alkaline borohydride storage-solution tank, whereas a ruptured pressurized tank of H_2 is hazardous and H_2 would be lost nearly instantaneously. Using proven H_2-O_2 PEM fuel-cell together with innovative borohydride fuel

technology assures meeting system power and energy goals and system reliability. To enable the borohydride hydrogen storage and generation in a practical fuel-cell system still requires further work on optimizing a micro-channel hydrogen-generator interfaced to the gas-liquid separator membrane and fuel-cell in a moldable graphite housing, as well as integration to a number of ancillaries, such as, a piezo liquid pump, fan for air supply, a system controller and power conditioning electronics.

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