

A hydrogen refill for cellular phone

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Abstract

A device has been designed to generate hydrogen for a fuel cell powered cellular phone. The device is based on the chemical reaction between NaBH_4 and hydrochloric/water solution to satisfy the hydrogen request at room temperature and pressure. The operation mechanism and controlling method is based on the Kipp's gas generating apparatus. A prototype has been built and tested to evaluate the optimum salt/acid and acid/solution ratios and check the hydrogen mass flow rates upon operation and the pressure variation in stand-by condition. The system works delivering hydrogen flows ranging between 0 and 10 ml min^{-1} . In a typical test the hydrogen flow was set to 5 ml min^{-1} to match a 1 W power fuel cell. The working pressure was slightly higher than the atmospheric one. The hydrogen capacity was as high as 2.5% (w/w). By converting this amount of hydrogen in electricity by a fuel cell working at 0.8 V it is possible to achieve a system energy density of about 720 Wh kg^{-1} , four times larger than commercial high energy density lithium-ion batteries.

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1. Introduction

In the general frame of a progressive conversion towards “cleaner way” to produce electrical energy, the use of fuel cells represents a goal to be necessarily attained. A strong limitation to the diffusion of large-scale fuel cell powered devices is the difficulty to store hydrogen. Among the different hydrogen storage techniques the most promising one is the “on site” hydrogen production via hydrolysis of NaBH_4 since it is favorable in terms of energy density, safety, easy handy and cost.

Several approaches have been proposed and tested for hydrogen production from hydride hydrolysis. Kong et al. [1] compared different hydrides while Kojima et al. [2] reported on the LiBH_4 performance. Anywhere, most of the works related about the promising results obtained from NaBH_4 , in particular when in alkaline solution. The hydrolysis is activated by a catalyst, namely Ni_xB [3] or Ru [4,5]. Millennium Cell built a refuel for laptops and cellular phones by using a NaBH_4 -based device [6]. NaBH_4 is dissolved in alkaline water to stabilize the solution.

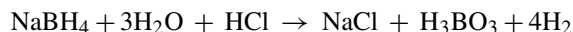
Fast hydrogen production is achieved by flowing the solution over a catalytic bed. Otherwise, in order to avoid the pH increase due to the formation of sodium hydroxide, Aiello et al. [7] proposed to use steam instead of water.

Our approach to speed up the reaction for producing hydrogen for a fuel cell powered cellular phone is to neutralize the sodium hydroxide by using hydrochloric acid.

In this paper a study devoted to define the basic concept and to built a hydrogen generator based on hydrochloric acid assisted NaBH_4 hydrolysis, is presented.

2. Experimental

Hydrogen production resulted from the following reaction:



We used commercial NaBH_4 (VenPure AF granules 98+, Aldrich) and 37% hydrochloric acid (Aldrich). Deionized water (Millipore) was used to prepare the solutions. The reaction was conducted in the homemade apparatus shown in Fig. 1.

It is a modified version of the Kipp's gas generating apparatus and its conceptual scheme is shown in Fig. 2. Two chambers, one filled with solid, granular NaBH_4 (2), the other with a solution of HCl in water (1), are connected by a narrow tube (3). A

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Fig. 1. A picture of the apparatus for reactant ratio optimization.

pressure slightly higher than the atmospheric pressure set by the regulation valve (4) was reached by flowing hydrogen in the system. Opening the outlet valve (6) causes a pressure decrease. When the pressure becomes lower than the set value, it causes the regulation valve (4) to close. Further pressure decrease forces the acid solution to pass into the reaction chamber (2) where it comes in contact with NaBH_4 , producing hydrogen. When the outlet valve is closed, the produced hydrogen over-pressurizes the chamber making the acid solution to go back and stopping the reaction. If the pressure inside the system increases to reach the set pressure for the safety valve (5), the excess of hydrogen produced will be eliminated avoiding dangerous overpressure.

Opening or closing the outlet valve allows therefore the reaction to start or stop; hydrogen is produced only when necessary, as expressed by the “on demand” concept.

The instantaneous mass flow have been determined by a 30 NI h^{-1} Bronkhorst mass flow meter. The total hydrogen produced was evaluated by flow integration. The flow meter has been calibrated by comparing the calculated H_2 volume with water displacement on a graduated container. The mass flow meter signal was acquired and recorded by using a PC.

Two measurement sets have been performed. A “constant flow” set in which the output valve was opened until a constant fixed mass flow was reached. A “variable flow” set in which increasing flows were delivered for various periods of time to

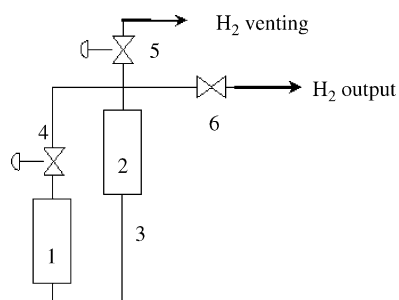


Fig. 2. A scheme of the apparatus showed in Fig. 1: 1, HCl chamber; 2, reaction chamber; 3, connection channel; 4, pressure regulation valve; 5, safety valve; and 6, H_2 outlet valve.

get the same hydrogen mass; the hydrogen flowing periods were interrupted by rest periods in which the outlet valve was closed. A third set of measures was obtained by monitoring the pressure increase during the rest period.

3. Results and discussion

The apparatus showed in Fig. 1 has been used to check the validity of the idea, to optimize the $\text{HCl}/\text{H}_2\text{O}/\text{NaBH}_4$ ratios and to evaluate the system self-discharge.

We found that to have high hydrogen flow rates the acid/hydride ratio must be set equal to 1. This allows to keep the reacted mixture neutral since only neutral species are produced (sodium chloride and boric acid). It is worth to note that the exhausted products are not dangerous, therefore, the used device can be easily wasted.

Looking for the minimum water amount, we tested different acid/solution ratios. We found that the molar amount of water needed to completely convert the NaBH_4 is larger than the theoretical ratio of 3 to 1 described by reaction (1). The excess of water is probably related to the formation of salts in their hydrated form. The best $\text{HCl}/\text{H}_2\text{O}$ ratio was found 1.6 to 1 (ml ml^{-1}). Consequently the best acid solution/ NaBH_4 ratio was found 3.6/1 (ml g^{-1}). These ratios have been used for all the experiments.

The hydrogen flow released from the reaction under constant hydrogen output is reported in Fig. 3. The set mass flow rate (0.31 h^{-1}) corresponds to 1 W power. We were able to obtain a very stable hydrogen mass flow rate during the entire device lifetime as shown in Fig. 3. 1.1 l of hydrogen was obtained by using 0.5 g of NaBH_4 . As the theoretical value is 1.2 l, the reaction yield was 92% indicating that almost all the NaBH_4 reacted with the acid.

The weight of 1.1 l of H_2 is about 0.1 g. Referring to the reactant weight (hydride + acid solution) of 2.5 g, the percentage of hydrogen is as high as 4 wt%. Considering a 0.8 V fuel cell, 1 W power corresponds to an hydrogen mass flow of 10 ml min^{-1} . A 1 W hydrogen mass flow has been released for more than 2.5 h. The energy density when the hydrogen is converted in electricity

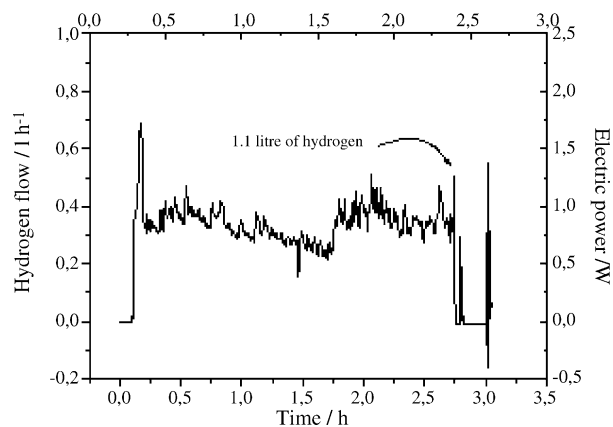


Fig. 3. A “constant output mass flow” measure. The delivered hydrogen flow rate is reported as a function of time. On the right is reported the fuel cell correspondent power.

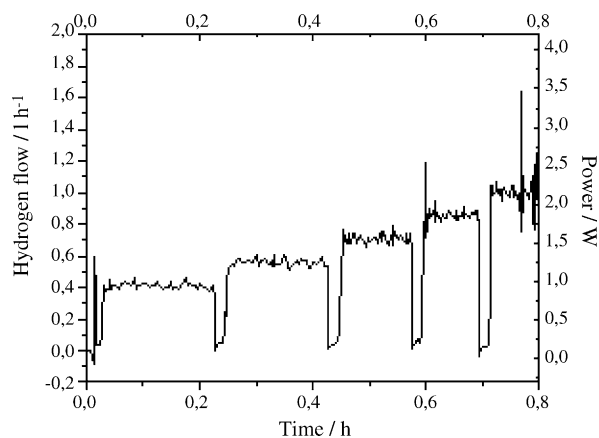


Fig. 4. A “variable output mass flow” measure. The delivered hydrogen flow rate is reported as a function of time. On the right is reported the fuel cell correspondent power.

by a fuel cell, is very impressive when compared to a state of the art lithium battery (720 Wh kg^{-1} versus 170 Wh kg^{-1}).

In Fig. 4 a “variable flow” experiment result is shown: the output was set to various mass flow rates in the 1–2 W power range; among two H_2 production periods, the H_2 flow was stopped by closing the outlet valve. The system auto-regulates the reaction rate to the required output hydrogen mass flow up to 20 ml min^{-1} . Larger output mass flow rates generates instabilities in the system. Foam is produced and the reaction products expelled out from the reactor chamber.

During the rest periods the reaction does not stop immediately. The NaBH_4 wetted by the acid continues to react determining a pressure increase. Fig. 5 show that the pressure increase has a 0.5 power dependence on time; the measured pressure inside our device reached 8 bar after 16 h in stand-by conditions.

The theoretical NaBH_4 hydrogen dissociation capacity is 6.2 wt%. When also considering the water and acid weight the practical capacity drops to 4.0 wt%. To obtain the amount of hydrogen for a 6 Wh device (0.3 g) we need 7.5 g of “chemicals”; if we want to have a total system hydrogen storage capacity not

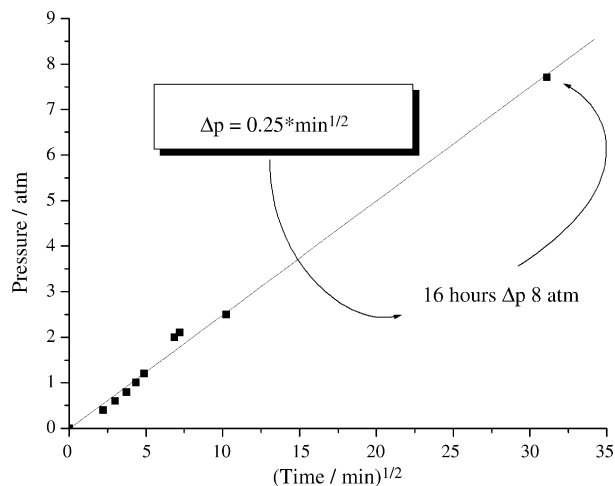


Fig. 5. Pressure increase as a function of time square root during a rest period.

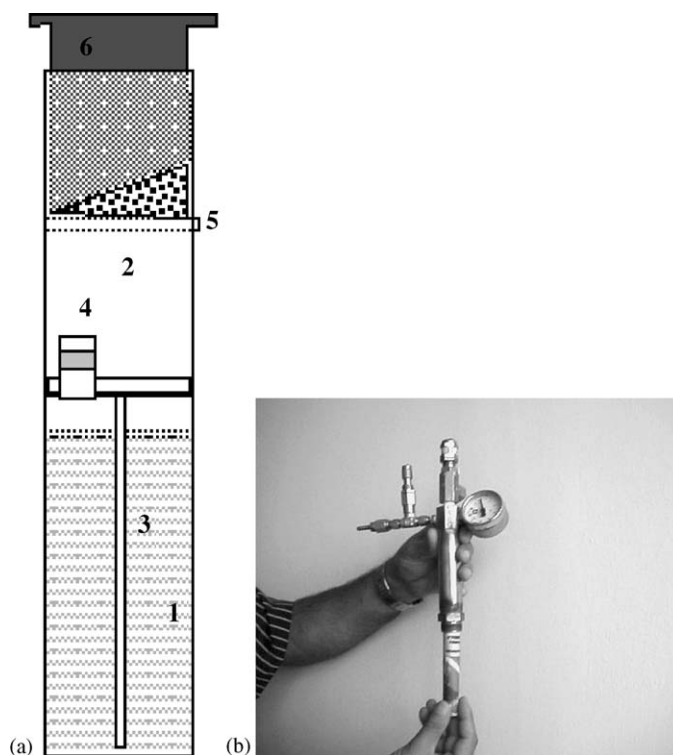


Fig. 6. (a) A schematic of the hydrogen producing device: 1, HCl chamber; 2, reaction chamber; 3, connection channel; 4, pressure regulation valve; 5, diaphragm; 6, activation button; and (b) insertion of the device in the reaction chamber.

lower than 2.5%, the maximum weight allowed for the envelope is 4.5 g.

As the main issue of the research activities resulted to find a suitable technological solution for sufficient light materials and a proper design, a second version of the apparatus was built and it is schematically shown in Fig. 6. It was made by two chambers connected by a central channel. Since the pressurized chamber is built-in on the cellular phone, the refill case has not to sustain any pressure. In such a way, light plastic can be used to build the case. The refill is activated by pressing the button on the top of the device; this allow NaBH_4 entering in the reaction chamber by disrupting a diaphragm. The refill can now be inserted into the pressure chamber inside the cellular phone. Fig. 6a shows the prototype and its insertion in the reaction chamber (6b).

A conservative estimation of the refill cost can be carried out by considering only the more expensive material, NaBH_4 . The cost of a 250 g batch at 98% purity as sold by a chemical distributor is 250 € kg^{-1} . Lower costs are expected for larger amounts. A refill able to work 9–10 day needs of about 1.5 g NaBH_4 . The cost of a 250 g batch is about 40 cents of euro. The total cost for 1 year service is 13.5 €. The refill commercial price is therefore low enough to allow the NaBH_4 based device to became a very large consume object.

4. Conclusions

A device has been designed and built for producing hydrogen for fuel cell feeding. It is based on the “hydrogen on demand”

concept and take advantage of NaBH_4 hydrolysis. The output hydrogen mass flow rate has been dimensioned for mobile applications. The estimated energy density and cost make such a device competitive with state of the art commercial batteries; a cheap and light refill could supply hydrogen for 3 h full power operation. After use, it could be wasted with very low environmental impact.

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