Development of a Compact Hydrogen Generator from Sodium Borohydride

S. Galli[1], M. De Francesco[1], G. Monteleone[1], R. Oronzio[2] and A. Pozio[1]

[1]ENEA - Energy Technologies Dept., 301 via Anguillarese, Rome, Italy
email: galli_s@casaccia.enea.it - www.enea.it
[2] University of Rome "La Sapienza", Chemical Engineering Dept., Roma, Italy
email: rosanna.oronzio@enea.it

Abstract

Chemical hydrides can be a simple and safe hydrogen vector for polymer fuel cells. In particular the catalytic hydrolysis of sodium borohydride ($NaBH_4$) is here envisaged to produce on-demand hydrogen to be supplied to a small solid polymer fuel cell in a portable energy generator.
A compact hydrogen generator is designed around a tubular catalytic reactor, whose catalytic powder is hold in place by magnetic field. The gas is generated by the exothermic hydrolysis reaction of an aqueous sodium borohydride solution in contact with no-noble catalyst particles inside the reactor. The reaction produces wet hydrogen and borate, which is soluble in water and not harmful to the environment. When hydrogen demand stops, the reactor is emptied and the hydrolysis reaction ceases.
A generator was then tested showing a smooth operation and a reasonably good performance. Correct choice of operating conditions and start-up procedures are requested to have a hydrogen production adequate to the fuel cell needs.

Keywords: *hydrogen production, sodium borohydride, portable fuel cell, reaction engineering,*

1 Introduction

The actual capabilities of consumer electronic devices, e.g. in telecommunication and laptop computer technologies, are mainly limited by the capacity and size of battery. Far to solve any energy issues related to power generation and transport, fuel cell technologies could represent an effective energy-source alternative for battery in small and portable power supplies. Considerable R&D on micro fuel cell has been under way in the industries and research institutes, in part funded by the military to power future-day soldiers. Some prototypes of micro (power range: 0.1÷30 W) and mini (30÷150 W) fuel cells are just proposed on the market, claiming a net improvement of continuous non-stop runtimes before recharging.

If the technological challenges in mini-fuel cell systems are more difficult to solve due to extreme miniaturization of components, those in non-consumer application power range (e.g. auxiliary power, back-up power and remote power) look more affordable and less-demanding in term of energy density and size. For on-field soldiers or others needing unconnected and easily portable power, the technical solution could be a small energy fuel cell system designed to be recharged by spare fuel cartridges.

The choice of the fuelling system remains strictly linked to the fuel cell technologies. For portable applications fuels presently proposed include methanol, formic acid, borohydride, butane, and hydrogen. Every fuel choice has pros and cons aspects, regarding to energy density, safety, ease handling and, of course, cost.
When pure hydrogen is requested, the chemical hydrides ($NaBH_4$, KBH_4, LiH, NaH) look as an effective alternative for their rather good energy density and safe handling. Among all, sodium borohydrides ($NaBH_4$) show a rapid hydrolysis reaction rate only in presence of a catalyst, allowing an easily controlled hydrogen production.
During $NaBH_4$ hydrolysis, every mole of sodium borohydride, as solid or in alkaline solution, reacts with water to produce 4 moles of hydrogen according to the exothermic ($\Delta H = -300$ KJ/mol) catalytic reaction:

$$NaBH_4 + 2H_2O \overset{\text{catalyst.}}{\Rightarrow} NaBO_2 \cdot x\ H_2O + 4\ H_2 \qquad (1)$$

where x can be 4 or 8, depending on the sodium metaborate ($NaBO_2$) concentration and solution temperature.

The alkaline-stabilized $NaBH_4$ aqueous solution can be stored on shelf or loaded into the energy generator, and hydrolyzed to produce hydrogen and borate only when in contact with specific catalysts, even a room temperature. With no catalyst the reaction proceeds very slowly and stops with the addition of a few percent of a NaOH/water solution.

Our previous studies and testing were focused on the kinetics studies of the catalytic $NaBH_4$ hydrolysis [1]. A no-noble catalyst was then developed [2], showing on one side a good chemical stability in that alkaline environment but on the other a not so high catalytic activity, in part offset by adopting solution recycling for higher $NaBH_4$ conversion. Later our activities were focused on the design and testing of a reactor able to keep catalyst powder magnetically during hydrolysis reaction, avoiding entrainment and losses of catalyst in the two-phase stream during hydrogen production [3].

In the present paper the tubular reactor is integrated into a hydrogen generator able to supply hydrogen fuel continuously or on-demand to the anodic compartment of a solid polymer fuel cell.

2 Hydrogen generator – fuel cell concept

The energy system here proposed consists of a generator, charged with a $NaBH_4$ solution, capable to produce hydrogen for a solid polymer fuel cell (fig. 1).

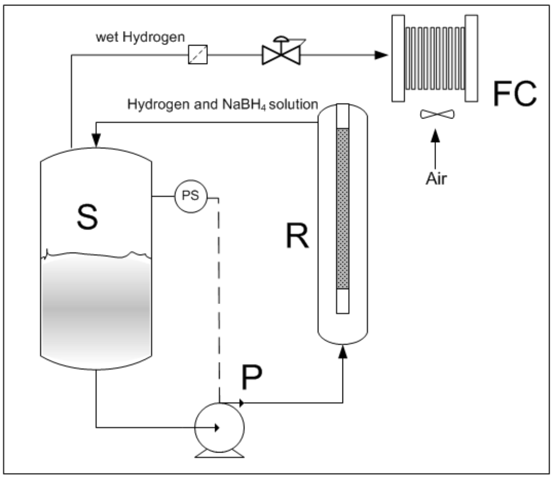

Fig. 1. Schematic of the hydrogen generator and the polymer fuel cell and energy system

When energy is requested, the $NaBH_4$-rich solution in the reservoir S is pumped by a pump P into the catalytic reactor R. The reactor consists of a double tube: inner tube has the catalyst powder on the external surface, kept there magnetically by magnetic elements put inside the tube. The solution, flowing in the annulus and in contact with catalyst, produces hydrogen gas.

The two-phase stream flows upwards and gets out from the reactor to return into the solution reservoir. The wet hydrogen separates from solution and, after filtering, enters the anodic compartment of the fuel cell. Due to the hydrogen purity, the fuel cell can run in the dead-end mode.

The returning solution mixes with the rest of the solution inside the reservoir, whose temperature and borate concentration increase continuously. The solution is again pumped into the reactor to produce further hydrogen.

Generally the production rate of hydrogen doesn't match its consumption in the fuel cell. In order to balance the supply with the hydrogen demand, a pressure regulator is installed between generator and fuel cell: the surplus of the produced hydrogen is accumulated inside the empty room above solution in the reservoir and supplied to the anodic side of the fuel cell, according to the need, by the pressure regulator.

When the pressure inside the generator reaches a set maximum value, a pressure switch (PS) inverts the rotating direction of pump, emptying the reactor and stopping the hydrogen production.

During emptying some small amounts of solution adhere on the catalytic surface, producing more hydrogen and increasing further the pressure inside generator.

Generator operation starts again when hydrogen consumption in the fuel cell reduces pressure inside the generator vessel, and pressure switch allows the straight pump operation.

This design of the generator requires that the unit has to be stay vertically, to avoid any undue mixing of reactants and an uncontrolled hydrogen production.

Pressure regulator could be substituted with a calibrated check valve: if this simplifies the system, at the same time the gas supply to fuel cell could have an irregular behavior.

In this scheme a source is requested to supply energy for pumping, even if the energy consumption is low for the small flow rate and the limited hydraulic resistance in the circuit.

In theory a simpler scheme of the generator could be envisaged with no moving part equipment and no external power supply: in fact the solution flow could be achieved exploiting the different densities in the reactor and in the reservoir, caused by the higher temperature and gas bubbles in the reactor. A valve should be installed at the reactor outlet to start and stop the hydrogen production.

By the way in the present application a peristaltic pump was installed to study the operation of reactor at different and controlled solution flow rates.

The hydrogen generator was sized for a portable power generator service, able to supply a solid polymer fuel cell of 50 W peak power for maximum 24 hours of continuous operation, generating a total energy amount of about 1.2 kWh.

When a 15% wt of $NaBH_4$ solution is loaded into the system, the system needs about 2.5 liters of fresh aqueous solution of sodium borohydride at start up to operate fuel cell according to this specifications.

As the borate dissolves in the solution, its increase of concentration in the solution limits the mass transfer inside the reactor. A decrease of the hydrogen production rate should be observed, with a higher risk to reach the solubility limits of borate, and its precipitation on catalyst and tubing, with reduced efficiency and eventual clogging of the circuit.

In the present case, at ambient temperature and with all the sodium borohydride reacted, the eventual average borate concentration is enough far from solubility limit.

The overall system operates in a batch mode: when the hydrogen production gets too slow, due to the reduced reacting hydride concentration and the higher mass transfer resistance in the reactor, the system is stopped and the storage is emptied (borate solution is not harmful to the environment). After charging fresh sodium hydride aqueous solution (or directly mixing fresh water with some $NaBH_4$ tablets inside reservoir) the generator can run again.

3 Hydrogen generator design

The main equipment in the hydrogen generator are the reactor, the reservoir of the solution, and a pump to flow the solution from the reservoir to the reactor and to empty it during shut-down.

Various designs of generator were envisaged in order to have a compact design and to reduce volume and weight. Eventual version has the reactor installed inside the reservoir, with pump placed just under the assembly (fig. 2).

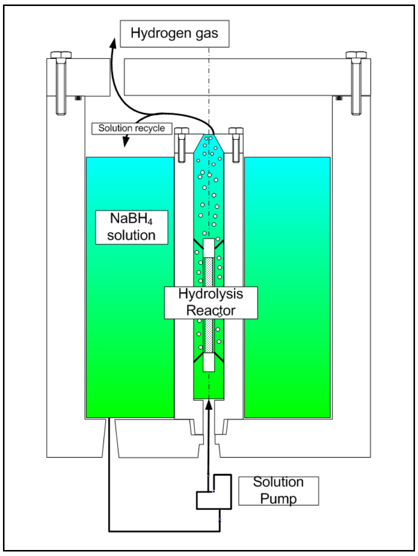

Fig. 2. The H_2 generator design

Such a scheme has some advantages as the capability not to dissipate the reaction heat during start-up, using it to warm the bulk of solution in the storage, and favouring a smooth increase of reaction temperature.

In such a scheme the fresh $NaBH_4$ solution is charged into the reservoir, leaving some room above the liquid level to hold some pressurized hydrogen. When the system is on, pressure inside reservoir controls the pump. The solution is pumped into the reactor and flows upwards in the annulus contacting the catalyzed surface. A two-phase stream, consisting of wet hydrogen gas, un-reacted solution and dissolved borate, exits from the upper end of the reactor. The hydrogen flows outside to supply the fuel cell, while solution returns to the solution tank.

The core of the generator system consists of a tubular reactor where a catalyst is kept in place on the external surface of the inner tube, as shown in figure 3.

Fig. 3. Catalytic reactor for $NaBH_4$ hydrolysis

The ferromagnetic Co-powder catalyst is magnetically attracted on the surface by small cylinder elements (d_o=4 mm) (Supermagnete), whose radial magnetic field was demonstrated to be more effective than the axial one in order to expose the catalysts grains to the contact with flowing solution. The reactor was assembled placing the inner tube with the catalytic powder (50 mm high) into a Plexiglas tube (d_i=16 mm). Overall height of the assembly was 150 mm. The catalyst amount (1 gr) was evaluated to have a continuous hydrogen production slightly greater than the nominal amount requested by fuel cell (0.5 L/min).

Particular care was taken in the design of annular section inside reactor: even if the magnetic field strength of cylinder elements was over the calculated value, the high local turbulence inside reactor, due to high production rate at the start up with fresh catalyst, could cause the entrainment of some of the most external grains of catalyst. On the other side if the annulus area is too large system response could be slower and the empting time too long, with a large hydrogen production during shut down phase.

The reservoir consists of a Plexiglas cylinder able to accept the starting solution (2500 cc). For this testing a transparent material was chosen for reservoir and reactor to allow experimenters to observe phenomena in the reactor and the generator, very useful when two-phase flow happens. Reservoir was completed with two flanges in Lexan, where all fittings for connections and measurements are installed.

The pump is a small peristaltic (Wartson–Marlow 400 F/A) one, capable to deliver up to 20 ml/min of solution and to reverse rotation to empty reactor during shut down phase. Estimated power requested is less than 1 W. During testing a bench peristaltic dosing pump was run as well to check accurately the solution flow inside reactor.

The complete set-up of testing of the hydrogen generator is shown in figure 4. The pump is on the left, on its control unit, while in the background is the gas flow-meter.

Fig. 4. The experimemtal set-up

4 Testing and results

The objective of testing the generator was to determine the hydrogen production rate at different solution flow rates, and the overall efficiency of the system. The system efficiency is defined as the ratio of hydrogen produced to the hydrogen available in the starting solution plus hydrogen provided by water according to the reaction (1).

Due to the exothermic behaviour of reaction, the temperature of solution will increase during testing, improving the kinetics inside the reactor.

A test rig was then realized to collect the hydrogen flow rates and temperature measurements. Three T-type thermocouples were installed to measure the temperatures of the solution entering the reactor, of hydrogen exiting the generator and one in contact with the upper magnetic element inside reactor. Hydrogen production measurement was performed by periodic observations of hydrogen flown through a rotary piston flow-meter (S.I.M. Brunt). The test pressure of the system was atmospheric.

In every test 200 cc of an aqueous solution with 8% (w/V) of sodium borohydride and 10 % (W/V) sodium hydroxide (as stabilizer) was charged into the reservoir. Maximum hydrogen production was about 38 L. The tests here presented were performed with solution flow rates of 5 and 10 cc/min, with an estimated hydrogen flow rate, at 10 cc/min, of 25 NmL/min of hydrogen.
The small amount of solution and the lower initial $NaBH_4$ concentration were chosen to have moderate reaction conditions inside reactor and limited test time (every test lasted about 90 min).

In figure 5 the hydrogen production is shown for the two flow rates (5 and 10 cc/min).

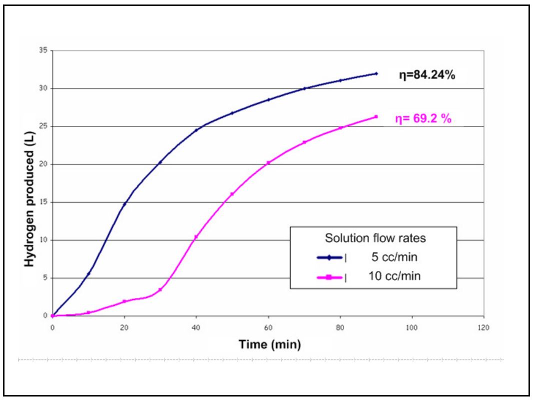

Fig. 5. Generator test: hydrogen production trends

The production rate at the lower solution flow rate is higher for the slower filling of the reactor volume at the start-up, the increase of temperature inside the reactor and the enhanced kinetics of the $NaBH_4$ hydrolysis reaction.

In fig. 6 the trends of the temperature of the solution entering the reactor show a quicker heating at 5 cc/min flow rate, but a late peak of temperature at higher flow rate, when the larger amount of reaction heat produced warms the solution incoming the reactor.

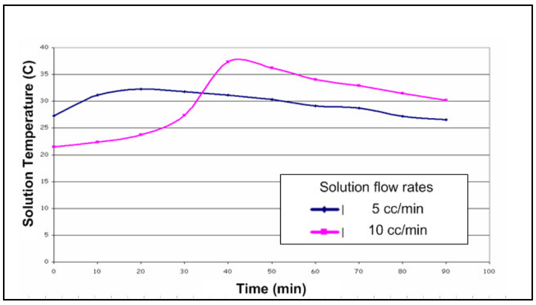

Fig. 6. Generator test : incoming solution temperature trends

The faster warm-up at lower flow rates, when the reaction heat is provided only to the catalyst surface and the still solution inside reactor, with an increase of their temperature and the hydrolysis reaction rate, could be exploited at every start up of the generator or to match the fuel cell demand.
After those peaks the heat losses from the reservoir balance the reaction heat and the eventual generator temperature gets stable.

The increase of temperature inside reactor is more evident when the temperature inside the reactor, in contact with magnetic element, is observed: here an early peak shows the warm-up always present during the filling phase of reactor, and the next higher peak for the overall heating of the system and the following balance with the heat losses.

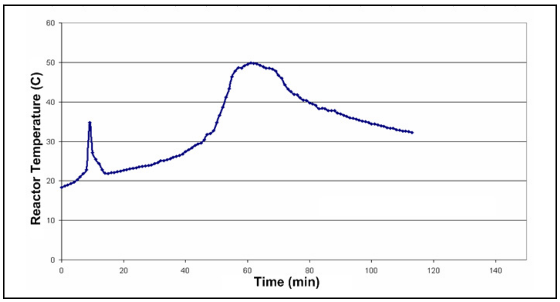

Fig. 6. Generator test: inner reactor temperature trends

The system efficiency is strictly linked with the thermal behaviour of the systems and its operating conditions. In fact performance of generator at lower flow rate and higher initial temperature is higher then at higher flow rates (84.2% vs. 69.2%), of course considering the test limited in the time. Extending the testing time, the conversions between the two flow-rate conditions converge.

Conclusions

A hydrogen generation system for portable energy applications (about 50W and 1 kWh), based on the $NaBH_4$ solution hydrolysis, has been developed and tested.

The generator consists of a minimum of components and is designed for a future integration with a fuel cell into a portable power generator.
Hydrogen generator works properly and its dynamic response and performance look adequate to be coupled with a solid polymer fuel cell. Measured conversions are promising (more than 80%), and proprietary catalyst shows a good chemical stability.
Further work will be focused on defining optimal operating conditions and start-up procedure.

References

[1] R. Oronzio, M. De Francesco, P. Di Lemma, S. Galli, G. Monteleone, and A. Pozio, Catalyst preparation and testing for sodium borohydride hydrolysis, *EMCC5*, Cetraro (CS), Italy, 24-29 May 2008

[2] M. De Francesco, A. Pozio, Magnetic containment device for Hydrogen generation from alkaline borohydrides, *EP1496014A1,* **2005**

[3] A. Pozio, M. De Francesco, G. Monteleone, R. Oronzio, S. Galli, C. D'Angelo, M. Marrucai, Apparatus for the production of hydrogen from sodium borohydride in alkaline solution, *Int. J. Hydrogen Energy ,* Vol 33 (2008) 51-56