

Performance Assessment of an Integrated PEFC and an Hydrogen Storage Device Based on Innovative Material

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ABSTRACT

Storage of hydrogen in solid materials has the potential to become a safe and efficient way to store energy, both for stationary and mobile applications. An integrated small scale system, integrating a small hydrogen tank and a 25 cm² PEFC single cell, has been tested to assess the performance of an innovative hydrogen storage material based on manganese oxide anchored to a polymeric matrix. A prototype small hydrogen tank, with a capacity of 18 cm³ made of a stainless steel tube, has been filled with the hydrogen storage material, previously characterized and reaching an hydrogen storage capacity of about 1 wt%. The system included a temperature and pressure sensors and a mass flow to control the desorption rate. A Labview software application has been developed for data logging and control of the test set-up. Sorption process has been achieved by fixing the charging time and recording pressure vs time. The electrochemical tests were performed at 80°C (PEFC cell temperature) and several discharge-charge cycles have been performed at different pressure and two discharge rates (i.e. 100 and 200 ml/min). The nominal power produced by the PEFC cell has been between 6-10 W, with an average discharge time of 400-500 s, depending on charging time and pressure. This material, which adsorbs H₂ in no drastic condition and safe as inert when in contact with ambient air, has demonstrated both a good cycle reversibility in terms of H₂ charge and discharge and, moreover, not affected by the packing in the tank

Keywords: Hydrogen storage material; H₂ tank and Fuel Cell integration; electrochemical tests



1. Introduction

The excessive use of energy that exploits fossil fuels has led to an increased environmental pollution and energy crisis. Recently, a deep research has been done on renewable resources in order to eliminate the dependence on fossil fuels. For the characteristics of unlimited supply, zero emissions of greenhouse gas and high energy efficiency, hydrogen has been identified as the principal candidate for the energy industry of the future [1-2]. However, hydrogen has a low density, only 0.0899 g/L at standard temperature and pressure and its storage is one of the predominant barriers to be overcome for its use as an energy carrier. In fact, the main problem is related to the development of safe, compact and high capacity storage systems for molecular hydrogen [3]. In addition, to permit a wide application on board it is necessary to comply the technical and cost requirements of the automotive industry [4-6]. However the possibility to store this gas in a tank depends on its physic form. Actually, three different methodologies to store such a gas are available and consist in: storing as a pressurized gas in steel or metallic alloy tank at high pressure (800bar) [7-8]; storing as a liquid form in tanks able to maintain a cryogenic temperature (77K) [9]; storing onto solid matrices able to adsorb/desorb hydrogen through chemical or physical sorption at given temperature and pressure conditions [10-11]. The last one is the most investigated method due to both the simplicity of the energetic system and the economic advantages. Sever classes of materials are investigated that could be split up in metallic hydrides and their alloys [12-15], metallorganic framework (MOF) [16] and carbonaceous materials [17-20]. Among these materials, the metallic hydride are in a commercial stage and the most used is LaNi_5 , which storage capacity corresponds to about 1.6wt% in no drastic conditions of temperature and pressure. On the contrary, the limiting steps for its diffusion on a large scale are the high production costs, the difficulty to handle due to its instability in air environment, the need of activation cycles and the high weight. The other classes of materials possess the advantages of light weight, low sensitivity to air and hydrogen storage comparable to metal hydrides but, on the contrary, the storage capacity is activated in drastic conditions of temperature and pressure. Recently, a new class of materials widely investigated is based on transition metal oxides supported on polymeric matrices [21-22]. From previous studies, it was demonstrated that the manganese oxide anchored on a polymeric matrix (functionalized Polyetheretherketone) showed interesting hydrogen storage properties, reaching about 1wt% at 110°C and 60bar. The encouraging results obtained on this material seems to be promising for the development of a prototype, in fact its good hydrogen storage and the light weight render this material promising for real application. In this work, a prototype consisting of a tank with a capacity of 5-8Nl of hydrogen, useful for feeding a fuel cell, was designed, realized and characterized. The electrochemical characterizations were carried out by coupling the prototype to a 25cm² single cell, in order to feed the anode with the hydrogen stored in the tank.

2. Experimental

2.1. Synthesis of the material

A highly chlorosulphonated PEEK, obtained through an electrophilic aromatic substitution reaction [21], was used as polymeric matrix. The precursor PEEK (450PF Victrex) was treated with chlorosulphonic acid at 30°C under stirring for 24 hrs and the resulting polymer had a sulphonation degree around 100%. This polymeric material was successively treated with a KMnO_4 solution to obtain a composite material with different MnO_2 in weight percentage. The amount of the oxide was calculated weighting the residual mass at 1000°C, above the decomposition temperature of the polymer. A more detailed procedure for the chlorosulphonation and manganese oxide reaction is reported elsewhere [21]. Following this procedure, a scale-up of the composite material synthesis (from 2 to 20 g) was carried out and a good reproducibility was confirmed by XRD analysis (fig. 1).



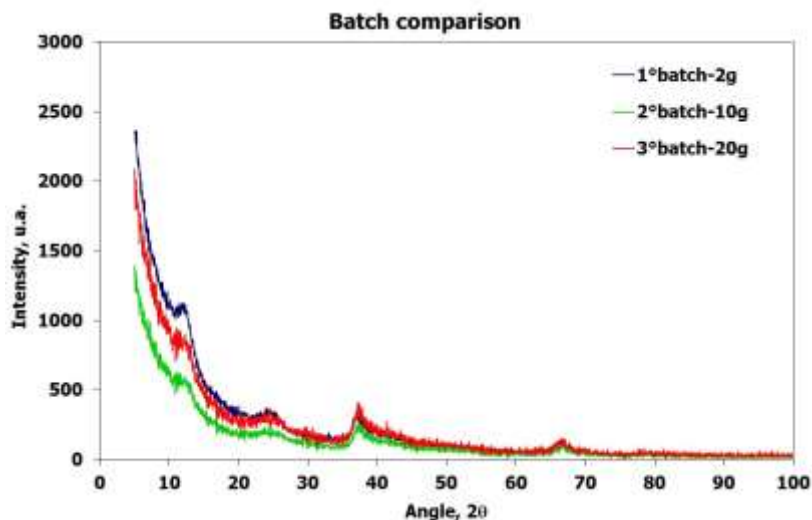


Fig. 1 – XRD batch profiles

2.2 Design of the tank

The synthesized material was already characterised in terms of H_2 storage [21-22] showing a H_2 sorption of 1.1%wt at $T = 110^\circ\text{C}$ and $P=60$ bar. Starting from these features, to feed a 25cm^2 single cell with about 20g of material, the following parameters (Table 1) were considered to size the tank:

Table 1. Theoretical electrochemical parameters with 20 g of sample

Parameter	Amount	Unit
H_2 Stoichiometry	1	-
Composite material amount	20	g
Absorption ratio	1	% mass
Absorbed H_2	0.20	g
PM H_2	2	g/mol
Absorbed H_2 moles	0.10	mol
Constant molar volume	22.41	Nl/mol
Absorbed H_2 volume	2.24	Nl
H_2 volume at 50 bar	0.04	l
Single cell active area	25	cm^2
Specific Power	400	mW/cm^2
Single cell Power	10	W
Cell Potential	0.60	V
Cell Current	16.67	A
H_2 consumed	$8.636\text{E-}05$	mol/s
Lifetime	1158	s
Lifetime	19.30	Min.



The lifetime of the test was calculated from the molar consumption of reagents (Faraday's law) of the cell at the fixed current, while the potential was chosen to compare the data with other tests performed in a fuel test station. From this data sheet, the cylinder has a H_2 molar volume of 2,24 Nl, able to feed a 25 cm^2 single cell with a 400 mW/cm^2 power density at 0.6 V, corresponding a total power of 10 W. Such system should have a lifetime of about 20 min. The tank was designed considering three basic experimental parameters: the initial mass of the material (20 g), its apparent density (1.8 g/ml) and the internal tank diameter of the cylinder (1.65 cm). The design was performed using the Solid Edge program (fig. 2).

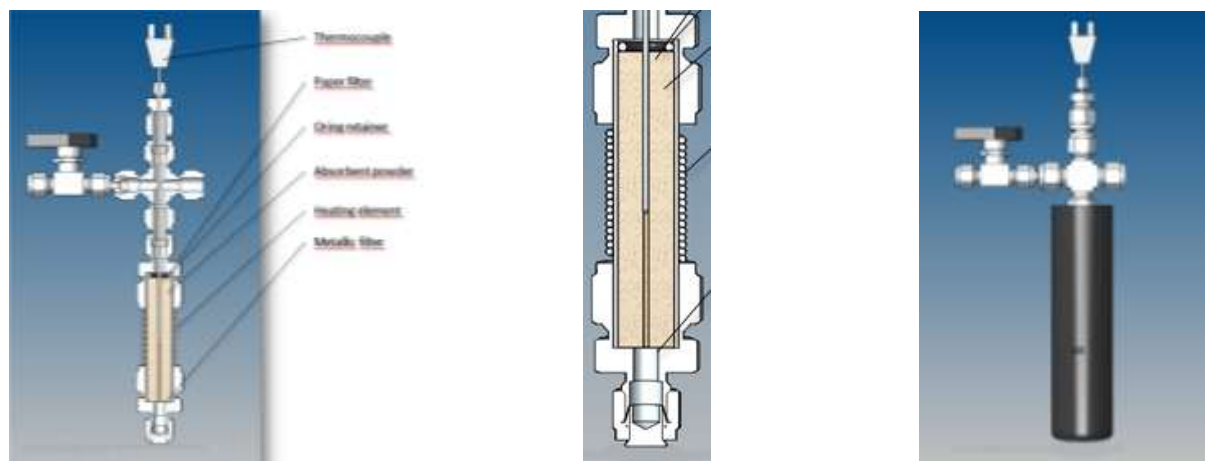


Fig. 2 – Prototype tank design

The prototype tank before and after the loading of the material is shown in fig. 3. The thermal insulation of the cylinder was made using a polymeric material having high temperature resistance.



Fig. 3 – Prototype tank

Having to operate at different temperatures, a thermo resistance was been winded on the cylinder. The assembly cylinder- thermo resistance was thermally insulated to the outside through two layers of insulator, the inner in ceramic sheath (for high T) while the outer one in polymeric material (for T less than 100°C).

2.3 Design and control of the measurement system

The measurement system was realized by interfacing a fuel cell test station and a NI Compact RIO controller connected it to a PC. The monitored signals were:

- the output gas pressure of the tank by means of a pressure transducer;
- the output gas flow rate of the tank and the input gas into the cell, controlled by the fuel cell test station.

3. Results and discussion

Two types of test were performed to measure the performance of the small tank. The first test includes the measurement of the quantity of gas released by the tank filled with the synthesized material. This parameter was recorded through a mass flow controller. The monitored (and recorded) quantities are tank pressure and gas mass flow versus time. The measurements were performed at two constant flow rates, respectively 100 ml/min and 200 ml/min. After each test, the hydrogen tank is recharged at 60 bar(g) and 110°C and different recharge time. The recharge time is recorded to understand the most convenient value relative to desorption performance. The experimental setup for the first test is configured as follows: the hydrogen tank outlet has a shutoff valve and it is connected to a first pressure regulator, which reduces the pressure from the storage value (i.e. 60 bar) down to 10 bar(g); then a second pressure regulator further decreases the pressure to a value compliant to mass flow specification. This latter pressure does not influence the desorption process flow rate because the flow is already limited by the mass-flow controller at the set point. It is necessary to insert a small dead volume between the second pressure regulator and the mass-flow to dump pressure fluctuations generated by the pressure controller and the mass-flow controller regulations, resulting in a fluctuating pressure and unstable flow rate. This added volume, plus piping, connections and controllers volume, false the measurement by giving an additional capacity for hydrogen storage which is not related to the actual storage capacity of the adsorption material. Hence it is needed to estimate this “blank” volume and reduce the measured capacity resulting from the test. This test, made following the same procedure of the complete system test, was performed at 60 bar(g) and ambient temperature (25°C), excluding the hydrogen tank. The result is in an autonomy of approx. 2 minutes (110s), from 60 bar(g) down to 0 bar(g), ambient temperature and at a constant flow of 100 ml/min.

After blank volume estimation, the system was tested as previously described. A total of 6 tests have been performed and their results summarized in table 2.

Table 2. experimental data for charge/discharge of prototype tank

Test	Charge (min)	Discharge (min)	Flow (ml/min)	Net discharge time (min)
1	30	13	100	11
2	120	23	100	21
3	420	25	100	23
4	60	11	200	9
5	120	15	200	13
6	220	12	200	10

Test results show a pretty constant performance in terms of gas output, while the staircase aspect for the pressure plot is caused by the upstream pressure regulator action. The average duration of the gas flow is approx. 15 minutes at a



flow rate of 200ml/min (tests n. 4-6) and 23 min at 100ml/min (tests n. 1-3). Plots of test n.6, performed at 200ml/min, and test n. 2, performed at 100ml/min, are shown respectively in figg. 4a-b.

The non-proportional result of the discharge time at 100ml/min and 200ml/min is related to a leakage, which is obviously more evident at higher pressure and lower flow, while it reduces its influence at lower pressure and higher flow. Despite this issue, the net measured flow is still comparable to the theoretical value as calculated in tab. 1.

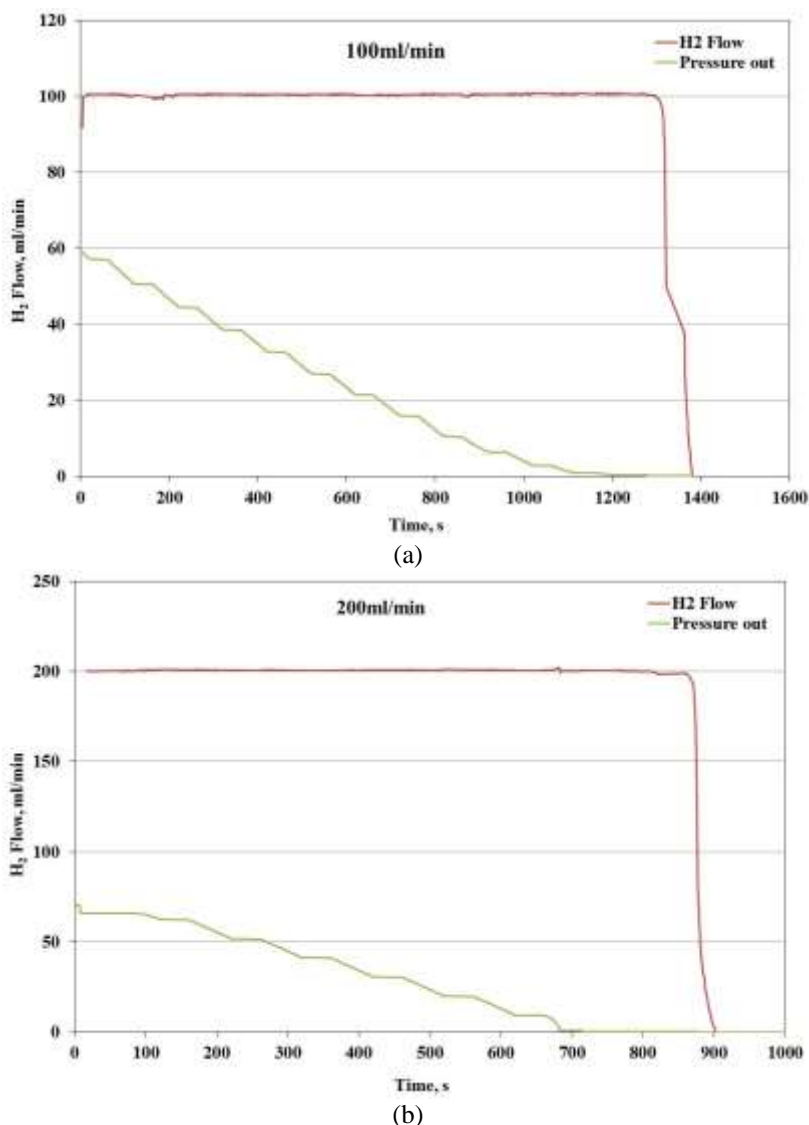


Fig. 4 – Discharge profile at 100ml/min (a) and 200ml/min (b)

Discharge time versus charge time are then plotted to highlight their correlation (i.e. the tendency to a plateau which shows the end of the absorption process) and any possible anomaly (i.e. significant gas leakage) (fig. 5). As shown in fig. 5, an increase of charge time did neither lead to a proportional increase nor a constant value of discharge time,



confirming that, while the blank volume is promptly filled, the adsorption process requires a longer time while adding a little, but still measurable, more autonomy to the system.

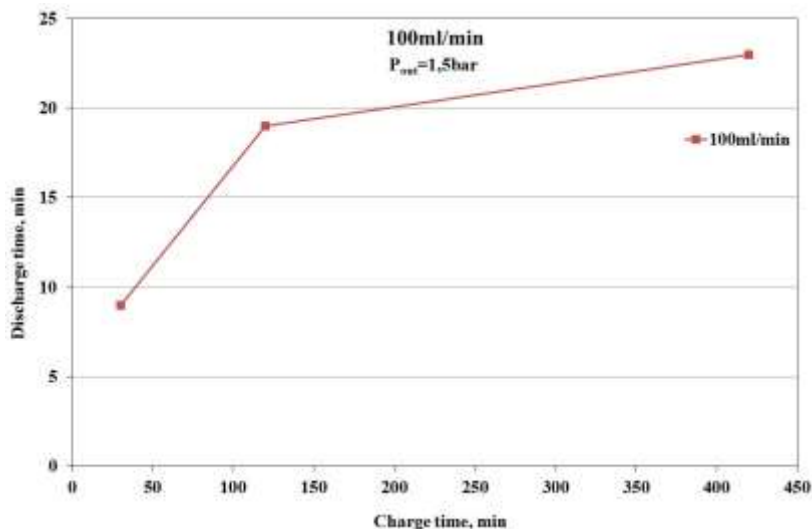


Fig. 5 – Discharge vs charge time at 100ml/min.

A second test was performed by connecting the tank to a Polymer Electrolyte Fuel Cell. This is a 25 cm^2 (active area) single cell operating in dead-end mode, so that the hydrogen desorption and the consumption rate can be measured theoretically by using the Faraday Law and measuring the current of the fuel cell. Previously the cell was tested at 80°C -100%RH by feeding with air and H_2 from the lab pipeline. This is needed to create a performance baseline to be compared with the data obtained from the complete system test. Afterward, the anode was fed with the hydrogen supplied by the prototype tank. In figure 6, an image of the test set up is shown.



Fig. 6 - 25 cm^2 single cell and experimental set up.

In figure 7a) a comparison between the electrochemical test at 80°C 1.5 bar at 0.6V is reported. The blue line represents the performance of PEFC under standard testing conditions while the green line represents the

performance of the actual system. In the latter case, the potentiostatic test shows an unstable behavior while galvanostatic test show a more stable behavior, as reported in figure 7b). This is explained by Faraday's Law, because under galvanostatic condition the gas consumption rate is constant, while under potentiostatic condition any current change leads to a flow instability.

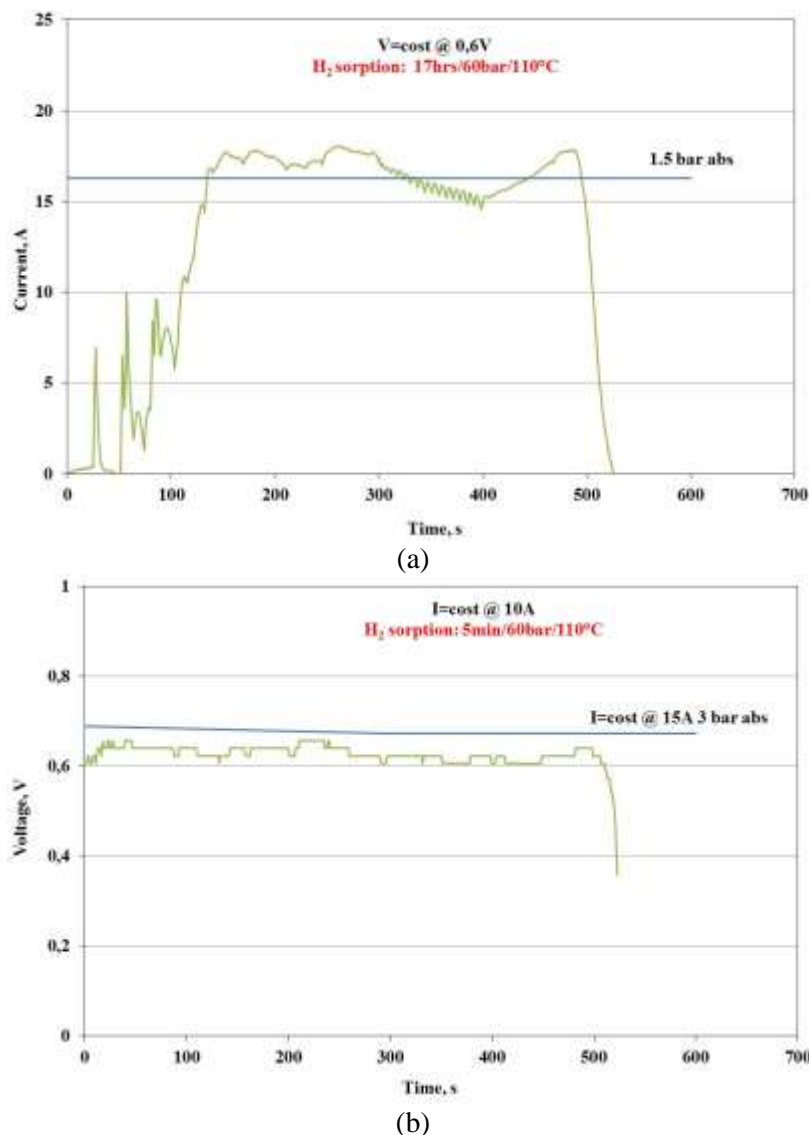


Fig. 7 - Comparison of fuel cell performance at fixed potential (a) and current (b) by using standard and prototype H₂ feeding

The different performance of the PEFC single cell (blu line vs. green line) is related to the different operative conditions when the cell is fed with the hydrogen from the pipeline (3 bar, 80°C, fully humidified hydrogen, 2.5 stoich at the actual current) or from the tank (80°C, 1.5 bar, dry hydrogen, stoich. value at the actual current). Again,



hydrogen leakage reduced the tank autonomy, this time reducing the duration to 10min instead of the actual discharge time of 20min measured in the first test.

4. Summary and perspectives

This paper shows that, despite its intrinsic simplicity, such a prototype can still be used to demonstrate the feasibility of a simple solid storage system able to operate in a real environment also when connected to a simple load such as a small fuel cell. Leakage problem at higher pressure affects the precision of results, currently losing almost 50% of the storage capacity. This prototype also gives some hints for the next development of such system, for example to avoid to keep two regulation valves (the pressure reducer and the mass flow controller) too close, otherwise resulting in an unstable flow and hence the need to put an additional dead volume to dump pressure variations. The fuel cell performance were comparable to that of a standard testing, showing that the innovative material used for hydrogen storage can be used for practical applications, although still many aspects need to be enhanced such as material storage capacity and system design.

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