Metal hydride systems for hydrogen storage and supply for stationary and automotive low temperature PEM fuel cell power modules

Mykhaylo V. Lototskyy a,*, Moegamat Wafeeq Davids a, Ivan Tolj a, Yevgeniy V. Klochko a, Bhogilla Satya Sekhar a, Stanford Chidziva a, Fahmida Smith b, Dana Swanepoel c, Bruno G. Pollet a

a HySA Systems Competence Centre, South African Institute for Advanced Materials Chemistry (SAIAMC), University of the Western Cape, South Africa
b Impala Platinum Ltd, Springs, South Africa
c TF DESIGN (Pty) Ltd., Stellenbosch, South Africa

Article Info
Article history:
Received 10 December 2014
Accepted 20 January 2015
Available online 7 February 2015

Keywords:
Metal hydrides
Low temperature PEM fuel cells
Hydrogen storage and supply

Abstract
Metal Hydrides (MH) provide efficient hydrogen storage for various applications, including Low Temperature PEM Fuel Cells (LT PEMFCs), when system weight is not a major and critical issue. Endothermic dehydrogenation of MH leading to decreased rates of H2 evolution eliminates the risk of accidents even in the case of rupture of the hydrogen storage containment. At the same time, it poses a number of challenges related to the constant, stable and sufficient H2 supply for stable FC operation.

This paper reviews recent efforts in MH hydrogen storage and supply systems for LT PEMFC applications, including the ones developed at HySA Systems/SAIAMC/University of the Western Cape. The systems are characterised by a series of hydrogen storage capacities ranging from 10 NL to ~10 Nm3 H2 in turns providing stable operation for stationary and mobile FC power modules (from a few W to several kW). The MH systems use unstable hydride materials (equilibrium H2 pressure at ambient temperature around 10 bar) that, in combination with special engineering solutions of MH containers (both liquid- and air-heated-cooled), and optimised system layout, facilitates H2 supply to LT PEMFC stacks.

Introduction
The use of LT PEMFC for stationary and mobile applications is of great interest worldwide as it is a clean and very efficient technology. LT PEMFCs offer a number of attractive advantages, including positive environment impact (the only by-products are pure water and heat), high efficiency, low operating temperature, high power density, fast start-up time and response to fluctuating load changes, simplicity, long-life etc. Because of this, LT PEMFCs are ideal choices for automobiles, scooters and bicycles, golf carts, utility vehicles,
distributed power generation, backup power, portable power, airplanes, boats and underwater vehicles [1].

Main challenge for wide implementation of LT PEMFCs, especially in the mobile applications, is in the development of efficient hydrogen storage and supply systems which have to meet a number of contradictory requirements, including high volume and weight hydrogen storage capacities, short refuelling time, high hydrogen supply flow rates sufficient for the normal operation of LT PEMFC, safety and reliability, low costs, including the ones for the refuelling infrastructure, etc.

Mostly, LT PEMFC power systems use storage of hydrogen as high pressure compressed gas (CGH2) in light-weight composite cylinders at pressures ranging from 350 to 700 bar. This commonly used solution has advantages of quite high weight hydrogen storage capacity, short refuelling time (3–5 min), and virtually unlimited flow rate of hydrogen supply to the fuel cell stack. At the same time, the volume hydrogen storage capacity of the CGH2 systems is still too low. These systems also suffer from two main issues – low safety and extremely expensive refuelling infrastructure – both are associated with high pressure of the stored hydrogen.

The use of metal hydride (MH) technologies characterised by compactness, safety, simplicity and flexibility is a promising option to solving the hydrogen storage problems. Application of MH can provide very high hydrogen storage capacity per unit volume (sometimes higher than the one for liquid hydrogen), safety and reliability, high purity of the supplied H2. It also significantly reduces heat emissions due to endothermic nature of the hydrogen release from MH materials; and improves operational safety (compared to CGH2) due to the lower pressure of stored hydrogen and limited rate of hydrogen release in the case of accidental leaks or even rupture of the hydrogen storage containment. In addition, it simplifies the refuelling infrastructure which otherwise requires expensive and potentially unsafe high pressure hydrogen compressors.

Conventionally the use of “low-temperature” metallic hydrides is characterised by low storage capacity per unit weight (<3 wt.%), but this disadvantage is not critical in stationary and special mobile applications. However, slow charge/discharge of MH hydrogen storage units limited by heat transfer is a serious drawback of the MH systems requiring special engineering solutions to overcome.

The integration of metal hydride hydrogen storage used as H2 supply system for LT PEMFC has been studied and data have been disseminated in several publications and patents [2–14]. Generally, the waste heat generated by the fuel cell stack is transferred to the metal hydride storage bed to supply the required heat for desorption of hydrogen from the MH; the intensification of the heat exchange between the MH and the heat transfer fluid is provided by a heat-conductive matrix formed by fins, metallic foam and/or binder disposed in the containment.

The necessity of speeding up the charge of the MH with hydrogen in the refuelling mode initiated numerous modifications of this approach which have been disclosed, chiefly in patents [5,7]. Generally, these solutions envisage alternative supply of a coolant from refuelling station in the charge mode and the heating fluid from the cooling system of the fuel cell in the discharge one, to heat exchangers built in the MH storage containers. As a rule, the mentioned solutions have complicated layout and require a sophisticated control system.

LT PEMFCs are characterised by a fairly low exhaust heat temperature (≤60 °C) which may not be high enough to provide the driving force for the heating of the MH material sufficiently for the H2 supply for conventional solutions. The most efficient way to address this problem is in the use of hybrid hydrogen storage when the MH material possesses low hydride thermal stability in high pressure composite cylinder thus combining CGH2 and MH hydrogen storage advantages. It allows to significantly increase the volumetric hydrogen storage capacity and decrease storage pressure (as compared to CGH2), as well as to increase flow rate of H2 delivered to fuel cell, and shorten refuelling time (as compared to MH). The features and performances of hybrid hydrogen storage tanks have been presented in Refs. [15–22]. The advantages of hybrid hydrogen storage appear at fairly low fraction of hydrogen stored in MH, above 3–5% of the total amount of stored hydrogen. Their main drawback is in very high costs mainly associated with the expensive high-pressure (up to 350 bar) composite cylinders which, in addition, need to have leak-proof and pressure-rated fittings for the input/output of the heat transfer fluid to/from the high pressure containment. Still high charge pressures, up to 350 bar, are the main cause of the high indirect costs associated with the use of expensive refuelling infrastructure similar to one for CGH2 systems.

This paper presents features and performances of a series of MH hydrogen storage and supply systems for LT PEMFC systems developed at HySA Systems, SAIAMC at the University of the Western Cape.

**Experimental**

**Metal hydride material**

A noticeable contribution in the high cost of MH hydrogen storage systems originates from the expensive MH materials. The way to reduce their costs, is by the use of ‘cheap’ mixed titanium–iron oxide (TiFeO3) as a primary feedstock for the preparation of Ti-based AB- and AB2-type MH alloys as earlier suggested by the authors [23,24]. Importantly, it was shown that the potentially inexpensive alloys have titanium/iron atomic ratio of about 1:1, and tuning of their hydrogen storage performances to application requirements has to be performed by the introduction of other metallic elements. Following the correlation between composition and hydrogenation thermodynamics for the multi-component AB2-type hydrogen storage alloys [24], the target AB2 composition (Al = Ti + Zr; B = Fe + Mn + Cr + Ni; Ti:Fe = 1:1; Ti:Zr = 0.55:0.45) has been identified, and the alloys of the specified compositions were manufactured in 10–100’s of kgs.

The XRD analysis (see Supplementary Information, Section S1.1) showed that the starting alloy contains a single AB2 (C14/ MgZn2-type) intermetallic phase, space group P63/mmc (# 194). The hydrogenation results in a lattice expansion without change of the crystal structure; the XRD pattern of the hydrogenated sample shows the presence of two phases, α-solid
solution of hydrogen in the metallic matrix (AB$_2$H$_x$), and β-hydride (AB$_2$H$_2$) characterised by ~16% volume increase as compared to the parent alloy. The data on real densities of the MH material were further used for the determination of safe filling density of MH material being loaded in MH containers.

Measurements of hydrogen absorption–desorption performances (see Supplementary Information, Section S1.2) showed that during the charge with hydrogen at pressures above 50 bar and temperatures below 60 °C, the material absorbs more than 1.4 wt.% H (up to 1.8 wt.% H at P = 100 bar and room temperature). The residual hydrogen concentration (P = 1 bar, T = 0 °C) was lower than 0.2 wt.% H, so the reversible hydrogen capacity of the material (P = 1–100 bar, T = 0–60 °C) was determined as 1.2 to 1.6 wt.% H.

The material described above was used for the filling of MH containers in the developed hydrogen storage and supply systems. The formation of the MH bed in the containers was carried out in accordance with the advanced engineering solution recently developed at HySA Systems [25]. For the improvement of activation performances, the material powder was mixed with ~10 wt.% of the powder of easily-activated AB$_2$-type hydride-forming alloy. In all cases the MH filling density was below 61% of the material real density in the hydrogenated state (the maximum value providing the safe operation of the MH container [26]). In addition, for the compensation of stresses originated from the swelling of the material during hydrogenation (when the material was loaded in the container in powdered form), ~1 wt.% of thermally-expanded graphite (TEG) powder was added to the mixture.

**System layouts**

Fig. 1 shows typical layouts of MH containers developed at HySA Systems for hydrogen storage and its supply to LT PEMFCs.

In the simplest layout (Fig. 1A) MH powder (2) was loaded in the containment (1) one of end caps of which was equipped with a gas connector (4) with built-in in-line gas filter (3; porous stainless steel, pore size 0.5 μ). Further improvement of the H$_2$ charge/discharge dynamics, by the intensification of heat transfer in the MH bed, was achieved by the introduction of transversal aluminium or copper fins (5); the container of bigger diameter additionally comprised longitudinal fins (Fig. 1C; 6). In the containers of type B, a longitudinal tubular gas filter (3, same material and pore size as for layout A) was assembled with the gas connector (4). The alternative solution (layouts C, E) used the in-line gas filter similar to layout A, and auxiliary longitudinal tubular filter plugged from both ends, for a uniform gas distribution along the MH [27]. The characteristic heat transfer distances in the MH bed (MH powder + fins) for the containers of types B, C and E were about 2.5, 5 and 5 mm, respectively.

Further improvement of the heat transfer in the MH bed was achieved by its making in the form of MH + TEG compacts in combination with aluminium fins ([25]; Fig. 1D, fin pitch 15 mm); a uniform gas distribution along the MH container was provided by an axial hole in the MH bed assembly.

Heat supply and removal in the containers of types A–D was provided from the outside using gaseous (ambient air; T = 15–25 °C) or liquid (circulating water; T = 20–40 °C)

Fig. 1 – Typical layouts of MH containers for hydrogen storage and its supply to LT-PEMFC: 1 – containment; 2 – MH powder, 2a – MH/TEG compacts; 3 – gas filter; 4 – gas connector; 5 – transversal fins; 6 – longitudinal fins; 7 – core of inner heat exchanger; H$_2$ – hydrogen flow; Q – heat supply/removal; H$_2$O – flow of heating/cooling water.
heating-cooling fluid. The liquid heated-cooled container of type E comprised internal heat exchanger, similarly to the layout of MH containers for hydrogen compressors [27,28].

For the integration of liquid heated/cooled MH container with LT PEMFC power system, an original solution combining MH and CGH2 hydrogen storage options was used ([12,29]; see Supplementary Information, Section S1.3, for more details). The solution allowed (i) to increase H storage capacity of the whole system and to reduce H2 charge pressure, as compared to CGH2 cylinders alone; (ii) to shorten charge time in the refuelling mode and to smooth peaks of H2 consumption during its supply to the FC stack; and (iii) to use standard parts with simple layout and low cost, and to add flexibility in the layout and placement of the components of the hydrogen storage system.

Testing procedure

The tests of MH systems were carried out using a specially designed test rig which allowed to monitor flow rates of H2 charge at P = 20–80 bar and discharge at P = 1–15 bar (set by a reducer and a back-pressure regulator, respectively) using a mass flow controller; the latter allowed to limit the H2 charge or discharge flow rates by setting their maximum values. Some of the systems were tested together with LT PEMFC power modules, in the latter cases the H2 consumption was determined indirectly, starting from the measured power of the FC stack; the dependence of the H2 consumption on the FC power was determined in the course of preliminary calibration [30].

Heating and cooling of the MH containers (types 1–6, see Table 1) were provided by ambient air, either in the course of natural convection, or at the air velocity of 2 m/s. For the comparison, the containers of types 1–3 (Table 1) were also heated/cooled by water at T = 25–30 °C in a thermostated bath; the same heating/cooling mode was applied for the container of type 8. The wall temperatures of the containers were measured in 2–3 points by thermocouples; in addition, the temperatures in different points of the MH bed of type 6 and 7 containers were measured as well.

For the liquid heated/cooled container of the type 7 (Table 1) integrated with LT PEMFC power module, the flow of the circulating water was 0.3–0.5 kg/min. In doing so, the temperatures were measured at the water inlet and outlet, as well as in the different points of MH bed of type 6 and 7 containers were measured as well.

It was found that in the discharge mode the temperature differences in various points of container wall, or the MH bed, as a rule, did not exceed 5 K, so the average values will be presented below.

Results and discussion

On the basis of MH materials and layouts described above, HySA Systems has developed a series of metal hydride hydrogen storage and supply systems for small- and medium-size LT PEMFC stacks. The main system elements are MH containers which allow for compact and safe hydrogen storage and its further supply to a consumer using flow of ambient

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<table>
<thead>
<tr>
<th>Type</th>
<th>Layout</th>
<th>H Storage capacity [NL]</th>
<th>FR [L/min STP]</th>
<th>Weight [kg]</th>
<th>Internal fins/pitch [mm]</th>
<th>Gas connection</th>
<th>Other features</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>10.5</td>
<td>0.3</td>
<td>0.07/0.16</td>
<td>Air</td>
<td>Schrader valve, or quick coupling with compression fitting</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>90</td>
<td>1.5</td>
<td>0.52/0.94</td>
<td>Cu/Al</td>
<td>Shut-off valve with compression fitting</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>30</td>
<td>1.0</td>
<td>0.60/0.61</td>
<td>Cu/Al</td>
<td>Shut-off valve with compression fitting</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>30</td>
<td>1.0</td>
<td>0.60/0.61</td>
<td>Cu/Al</td>
<td>Shut-off valve with compression fitting</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>D</td>
<td>90</td>
<td>2.5</td>
<td>0.56/0.82</td>
<td>Cu/Al</td>
<td>Shut-off valve with compression fitting</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>700</td>
<td>10</td>
<td>3.0/0.52</td>
<td>Cu/Al</td>
<td>Shut-off valve with compression fitting</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>E</td>
<td>1900</td>
<td>20</td>
<td>12.2/5.20</td>
<td>Cu/Al</td>
<td>Shut-off valve with compression fitting</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>B</td>
<td>500</td>
<td>7.5</td>
<td>3.5/0.40</td>
<td>Cu/Al</td>
<td>Shut-off valve with compression fitting</td>
<td></td>
</tr>
</tbody>
</table>
The tests of discharge performances of the developed MH containers (see examples in Supplementary Information, section S3) showed that the endothermic desorption of H$_2$ from MH results in a significant cooling of the container that, in turn, slows the H$_2$ supply flow rate down, even at low H$_2$ pressures (~1 bar). First of all, the H$_2$ discharge dynamics depends on the intensity of the heat exchange between the heating-cooling fluid and the wall of the externally heated MH container; the dynamics is significantly improved in the series of MH containers with typical efficiency of 50% (H$_2$ consumption depends upon the heat transfer in the powdered MH). The effect of slowing H$_2$ discharge dynamics down due to the cooling of the MH material results in incomplete consumption of hydrogen supplied from the MH to the FC stack to provide its stable operation. Since the H$_2$ consumption by the stack is approximately proportional to its power, the share of the consumed hydrogen (as to the total H storage capacity of the MH system) will decrease when the stack power increases.

Fig. 3 summarises test results of the developed MH containers (Table 1) as dependencies of fractions of the utilised hydrogen (as respect to the maximum H storage capacity) on the specific (per 1 kg of the MH material) power of LT PEMFC stack with typical efficiency of 50% (H$_2$ consumption 11.1 NL min$^{-1}$ per 1 kW).

It can be observed from Fig. 3 that the container of the smallest size (type 1, 70 g of MH) can provide fairly high utilisation of the stored H$_2$ (>70% at 250 W/kg) that corresponds to the stack power about 17 W) even without intensification of the heat transfer in the powdered MH.

The increase of container size results in a significant reduction of the percentage of utilised hydrogen which can provide stable operation of the FC stack. The scale effect is especially pronounced for the air-heated units (2–4, 6) even equipped with the internal fins. At the same time, the combination of fins and compacting the MH materials with TEG (5; layout D) results in more stable discharge performances in the studied range: more than 75% of the stored hydrogen can provide stable operation at a specific power up to 250 W/kg, or 140 W for the unit of type 5. Further improvement of the dynamic performances was achieved by the utilisation of the heat generated by the air-cooled PEMFC. Despite of quite imperfect realisation of this approach, by just placing the MH container at the exhaust of the stack cooling system (see Fig. 4 in the Supplementary Information), it allowed for >40 min-long stable operation at the stack power of 130 W (225 W/kg(MH)) with the utilisation of >90% of the stored H$_2$.

Fig. 3 also shows that for the bigger size liquid-heated MH container of type 7, a significant decrease of the percentage of the utilised hydrogen takes place when the stack power and, in turn, H$_2$ consumption increase. The drop of H$_2$ utilisation is from 97% at 50 W/kg (610 W in the stack power) to 35.5% at 250 W/kg (3.05 kW). At the same time, the integration of this container with LT PEMFC according to our solution [12,29] resulted in a significant improvement of performances of the hydrogen storage and supply system. After 10–15 min long charge with H$_2$ (P < 100 bar) the MH system operating alone provided ~100 min driving when the FC power module consumed 962 NL H$_2$, or 50.6% of the total hydrogen capacity of the MH tank. When the system additionally comprised CGH2 tanks...
(two 6.8 L gas cylinders) at the same H₂ charge conditions, the FC stack operated for 5 h, i.e. 3 times longer; the total amount of the consumed hydrogen was of 2224.5 NL, of which 1245 NL were delivered from the MH tank that corresponds to 65.5% of its total hydrogen capacity \([29]\); see also Supplementary Information, Fig. 8).

Presently HySA Systems is building-up a MH system for onboard hydrogen storage and its supply to 10 kW LT PEMFC power module for forklift application. The system will be based on 20 × MH containers of type 8 (Table 1) connected in parallel and placed in a common water-heated-cooled jacket. The system integration with FC power module will be done using the “distributed hybrid” MH + CGH₂ hydrogen storage solution \([12,29]\). The expected hydrogen storage capacity will be about 10 Nm³ H₂ and H₂ supply flow rate up to 150 NL min⁻¹.

**Conclusions**

A series of MH hydrogen storage and supply systems for stationary and mobile LT PEMFC applications has been developed. The systems use unstable MH on the basis of AB₂-type intermetallic and range in hydrogen storage capacity from 10 NL to 10 Nm³ H₂. It was shown that slowing down the dynamics of hydrogen supply originated from endothermic H₂ desorption from MH is mostly dependent upon (i) the size of the MH container, (ii) heat supply/removal conditions, (iii) layout features of the MH container related to the intensification of heat transfer in the MH bed. The inhibition of the H₂ supply results in an incomplete hydrogen consumption from MH by the fuel cell stack at H₂ supply flow rate which provides stable operation of the latter at the rated power. This undesired effect can be most efficiently mitigated by the use of MH containers where MH bed is made as MH powder compacted with thermally expanded graphite additionally comprising fins made of high thermal conductivity metal (copper or aluminium). Additional improvement of the H₂ charge – discharge dynamic performances can be achieved by system optimisation where liquid heated-cooled MH containers and compressed gas cylinders are integrated with LT PEMFC power modules.

**Acknowledgements**

This work is supported by the Department of Science and Technology (DST) within the HySA Programme (project KP3-S02), and Impala Platinum Limited; South Africa. Investment from the industrial funder has been leveraged through the Technology and Human Resources for Industry Programme, jointly managed by the South African National Research Foundation and the Department of Trade and Industry (NRF/DTI; THRIP project TP1207254249).

**Appendix A. Supplementary data**

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2015.01.095.

**References**


