

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he





Hydrogen South Africa (HySA) Systems Competence Centre: Mission, objectives, technological achievements and breakthroughs



Bruno G. Pollet^{*}, Sivakumar Pasupathi, Gerhard Swart, Kobus Mouton, Mykhaylo Lototskyy, Mario Williams, Piotr Bujlo, Shan Ji, Bernard J. Bladergroen, Vladimir Linkov

HySA Systems Competence Centre, South African Institute for Advanced Materials Chemistry, Faculty of Natural Science, University of the Western Cape, Robert Sobukwe Road, Private Bag X17, Bellville 7535, South Africa

ARTICLE INFO

Article history: Received 30 September 2013 Received in revised form 27 November 2013 Accepted 28 November 2013 Available online 31 January 2014

Keywords: Hydrogen South Africa MEA PEMFC Stacks Metal hydride Li-ion Power module

ABSTRACT

A long-term (15-year) Hydrogen and Fuel Cell Technologies (HFCT) Research, Development, and Innovation (RDI) strategy was officially launched in September 2008 by the Department of Science and Technology (DST) in South Africa. The Hydrogen South Africa (HySA) programme is based upon the beneficiation of the country's large Platinum Group Metal (PGM) resources. HySA comprises of three Centres of Competence: HySA Catalysis, HySA Infrastructure and HySA Systems. HySA Systems, a Systems Integration and Technology Validation Competence Centre on HFCT was established in 2007 at the South African Institute for Advanced Materials Chemistry (SAIAMC) at the University of the Western Cape (UWC). The main objective with HySA Systems is to (i) develop Hydrogen and Fuel Cell systems, demonstrators, prototypes and products, (ii) perform technology validation and system integration and (iii) focus on system oriented material R&D in two key HySA-programmes: (1) Combined Heat and Power (CHP) and (2) Hydrogen Fuelled Vehicles (HFV). HySA Systems is also responsible for the development, prototyping, testing and commissioning of the following key technologies: High Temperature (HT) Membrane Electrode Assemblies (MEAs), HT-Proton Exchange Membrane (PEM) fuel cells, metal hydrides for hydrogen storage and compression systems, hydrogen fuel cell/battery power modules, palladium membranes, and lithium-ion batteries. HySA Systems has successfully: a) implemented some pilot plant manufacturing facilities/capabilities for HFC components and systems in South Africa, b) been partnering with key international HFC and local industries, c) established a local Supply Chain of SMMEs, d) set up industrial/commercial agreements with national/international HFC players, e) been disseminating their findings/work in High Impact Factor

* Corresponding author. Tel.: +27 (0) 714840323.

E-mail addresses: bgpollet@hysasystems.org, bgpollet@uwc.ac.za (B.G. Pollet). URL: http://www.uwc.ac.za, http://www.hysasystems.org

⁰³⁶⁰⁻³¹⁹⁹ Copyright © 2013, The Authors. Published by Elsevier Ltd on behalf of Hydrogen Energy Publications, LLC. Open access under CC BY license. http://dx.doi.org/10.1016/j.ijhydene.2013.11.116

Journals and National/International Conferences, and f) innovated and thus generated Intellectual Property in key HFC technologies.

Copyright © 2013, The Authors. Published by Elsevier Ltd on behalf of Hydrogen Energy Publications, LLC. Open access under CC BY license.

1. Introduction

HySA Systems is one of three National Competence Centres which makes up HySA (Hydrogen South Africa). Initiated by the Department of Science and Technology (DST) and approved by the Cabinet in May 2007, HySA is a long-term (15year) programme within their Research, Development, and Innovation (RDI) strategy, officially launched in September 2008. This National Flagship Programme is aimed at developing South African intellectual property, knowledge, human resources, products, components and processes to support the South African participation in the nascent, but rapidly developing international platforms in Hydrogen and Fuel Cell Technologies. The programme strives towards a knowledgedriven economy meaning that innovation will form the basis of South Africa's economy; this includes an aggressive capacitydevelopment programme's approach. HySA also focusses on (i) the "Use and Displacement of Strategic Minerals", (ii) ways of harnessing South Africa's mineral endowments to promote both the hydrogen economy and renewable energy use, and (iii) seeking the most cost-effective and sustainable ways of incorporating PGM-based components in hydrogen fuel cell and other technologies, in turns resulting in commercialisation ventures and a viable industry around mineral beneficiation (see speech from Derek Andre Hanekom - the South African Minister of Science and Technology http://www.info. gov.za/speech/DynamicAction?

pageid=461&sid=39338&tid=119629).

Indeed, HySA has been implemented in the context of the DST's various innovation strategies, the Department of Mineral Resources' (DMR) minerals beneficiation strategy, the Department of Energy's (DoE) Integrated Resource Plan and the Department of Trade and Industry's (DTI) industrial development strategies. The principal strategy of HySA is to execute research and development work, with the main aim of achieving an ambitious 25% share of the global Hydrogen

and Fuel Cell market using novel Platinum Group Metal (PGM) catalysts, components and systems since South Africa has more than 75% of the world's known PGM reserves. In order to achieve this, the structure is aimed at the parallel development of knowledge and technology across all areas of the Hydrogen and Fuel Cell value chain, allowing for the establishment of a strong R&D Hydrogen and Fuel Cell Technology exporting added value PGM materials, components and complete products. Each Centre has a unique responsibility, but all three are complementary within the common vision of fostering proactive innovation and developing the human resources required to undertake competitive R&D activities in the field of Hydrogen and Fuel Cell Technologies. The first five years of funding focused on developing infrastructures at each Centre with a major emphasis upon Human Capacity Development (HCD). Relevant international expertise was recruited by each Centre to access technical support and wellestablished implementation networks, and to ensure the programme and its deliverables remain market related and world-class. Furthermore, to achieve the HySA strategy objectives, the three HySA Centres of Competence Fig. 1 form a national network of research 'Hubs' and 'Spokes' through collaboration with institutions and partners from the R&D sector, higher education, as well as industry.

The HySA programme consists of five Key Programmes – see Table 1.

HySA Systems focuses on two Key Programmes and Key Technologies as shown in Fig. 2 and detailed below:

2. Key Programme 1 – combined heat & power

Fuel cell based Combined Heat and Power (CHP) systems have entered early commercialisation recently and are being deployed in 1000's in Japan (Ene.Farm) and Europe (Ene.Field,



Fig. 1 – HySA structure and stakeholders.

Table 1 $-$ HySA's five main Key Programmes.		
KP	HySA Key Programmes	Competence Centres
KP1	Combined Heat and Power	HySA Systems
KP2	Portable Power Systems	HySA Catalysis
KP3	Hydrogen Fuelled Vehicles	HySA Systems
KP4	Hydrogen Filling Stations	HySA Infrastructure
KP5	Renewable Hydrogen Production	HySA Infrastructure

Callux). In Japan, 34,000 units were installed at the end 2012 and the objective is to have over 5 million units installed by 2030. Most of the CHP systems deployed so far are based on Low Temperature PEMFC (LT-PEMFC). Although the electrical efficiency of LT-PEMFC is higher as compared to High Temperature PEMFC (HT-PEMFC), the overall efficiency (electricity + heat) is higher for HT-PEMFC based CHP systems, moreover, it can tolerate CO poisoning better than LT-PEMFC and does not require a complex water management system, making HT-PEMFC ideal for CHP applications.

HySA Systems is focussing on HT-PEMFC based CHP systems in the range $1-2 \text{ kW}_{el}$, fuelled by natural gas. The main scope is to develop internationally competitive components, specifically MEAs and stacks for the CHP market, however, there is also a concerted effort to develop systems in the above specified range. The block diagram of the CHP system being developed is provided in Fig. 3.

The red blocks shows the core R&D areas carried out by HySA and the yellow block shows the level of system integration that is currently being carried out at the centre. HySA Systems has successfully completed a breadboard CHP testbench in collaboration with ZSW, the German Center for Solar Energy and Hydrogen Research in Germany, and is validating various HT-PEMFC stacks in this configuration. Currently the efforts are targeted at the integration of a natural gas reformer with the breadboard system, to study and analyse the operation of the system at various operating strategies and conditions. The plan is to integrate a 1 kW_{el} CHP system by 2014 and then to introduce locally produced components including the reformer and fuel cell catalysts from HySA Catalysis. HySA Systems is collaborating and also extending collaboration with various other institutions and companies, locally and overseas, to realise the objective of this programme.

3. Key Programme 3 – hydrogen fuelled vehicle

When the European Commission (EU) launched their Clean Fuel Strategy in January 2013, high-level plans to reduce EU oil-dependence in the transport industry were provided. The document indicates that member states are planning to have over 9 million Electric Vehicles (EVs) deployed by 2020 [1]. This includes Fuel Cell Vehicles (FCVs), and though their initial share may be modest, the International Energy Agency (IEA) estimates that by 2050 more than 10 million FCVs will be sold globally each year [2].

The largest demand for FCVs is expected to be in passenger vehicles, with several models already being displayed by automakers across the world. Encouraged by the significant government investments and progressively harsher emission legislations, all of large automotive companies have performed significant R&D in this field. It seems however, that infrastructure, overall cost and fuel cell durability remain significant challenges that are still holding back the market uptake of FCVs. Rather than trying to compete directly with these large companies and national programmes, HySA's strategy is to pursue opportunities in niche vehicles with the expectation that if successful, its technologies will spillover into the mainstream automotive field. There are many potential niche FCVs to consider, including material handling vehicles (e.g. forklifts), light passenger vehicles (e.g. threewheelers, golf carts and micro-cars) and special-purpose vehicles (e.g. mining locomotives). An added advantage of this segment of vehicles is that they are mostly operated in fleets, where customer infrastructure can more easily be established and where the technology benefits are more easily realised.

The scope of HySA Key Programme 3 is to develop and integrate systems and modules that can be used in these niche vehicles, based on HySA technologies. This includes the on-board Hydrogen storage (including Metal-Hydrides), the Fuel-Cell System (the FC-stack and its controller), power



Fig. 2 – HySA's main Key Technologies.



electronics and Li-ion Battery System. Through a modular design and standardised interfaces the 'HySA Power Module' will be designed so that it can be retro-fitted into existing small battery-powered vehicles with minimal changes to the vehicle itself.

The figure below shows the key technologies and how they are integrated into various vehicular platforms (Fig. 4).

4. R&D and key technologies

4.1. High temperature Membrane Electrode Assembly

Membrane Electrode Assemblies (MEAs) are the core of fuel cells, and detailed understanding of the phenomenon within the MEA is necessary to improve the durability and reduce the overall cost of the fuel cell. Although extensive research and development is being already carried out in LT-PEMFC MEAs, High Temperature MEA (HT-MEA) is relatively new. HT-PEMFCs are gaining momentum with the publications nearly doubled in 2012 (~1100) as compared to five years ago (~650). Most of the R&D is dedicated to the development of the Polymer Electrolyte Membrane, although efforts are also made to develop suitable catalysts and gas diffusion electrodes. Some of the R&D areas focus on:

- Novel membranes that can operate between 40 °C and 200 °C without humidification requirements.
- Development of suitable PGM-based catalysts, that are active and durable.
- Suitable support materials for the catalysts, to overcome carbon support corrosion/dissolution.
- Suitable MEA architecture to reduce catalyst loading, minimise acid leaching and improve durability.

At HySA Systems, the focus is on the MEA architecture aiming at reducing the catalyst loading and improving the durability, with the membranes sourced from commercial suppliers. Various coating techniques are being developed and used for both Catalyst Coated Substrate (CCS) and



Fig. 4 - Integration of HySA technologies into niche FCVs.



Fig. 5 – (a) – Polarisation and power density curves of PA-doped AB-PBI fuel cell using GDEs prepared by the catalyst spraying under irradiation. (b) – Stability of the MEA at 160 °C and 0.2 A cm⁻², H₂/Air, ambient pressure.

Catalyst Coated Membrane (CCM) MEA preparation methods. This includes air assisted spraying, ultrasonic spraying and electrophoretic deposition (EPD) to name but a few.

MEA performances comparable to the best results reported so far have been achieved under similar conditions [3]. The GDEs in this case were prepared by a novel automatic catalyst spraying under irradiation technique, at usual operating conditions (160 °C, H₂/Air, ambient pressure), the peak power density of the single cell reached 0.61 W cm⁻², and the current density at +0.6 V was up to 0.38 A cm⁻² (Fig. 5(a)).

The main reason for the performance was found to be the preparation condition of the MEA and is reported elsewhere [3]. Another crucial factor for the MEA, apart from the performance, is its durability under standard operating conditions. A short term durability test was performed on the MEA at 160 °C with H₂/Air, and a constant load of 0.2 A cm⁻², Fig. 5(b). The cell voltage reached a steady state within 4 h of operation and was found to be stable for a period of about 100 h. Following this, intermittent operations of the fuel cell, was carried out to mimic 'real' operating conditions, with cooling to room temperature while shutting down. During this study for about 275 h operation, no appreciable degradation was noticed.

Focussed efforts are also targeted at improving and optimising the GDEs, where various binders, proton conductors and acid controlling layers are currently being studied. For example the effect of the various binders on the performance of the MEA was investigated [4]. Five different binders; Nafion[®], PBI, PTFE, PVDF and PBI–PVDF blend, were studied (Fig. 6(a)). As expected, Nafion[®] was found to be unsuitable for HT-MEAs, obviously due to its proton conductivity limitations at the operations conditions of 160 °C. PVDF was found to be a better binder at low current densities, whereas PTFE was found to be suitable for high current densities.

Other MEA fabrication methods are also being studied including the CCM and EPD methods, recently some promising results have been obtained with the EPD method [5] and further studies are currently being carried out in this area. HySA Systems also have set up a pilot-scale MEA manufacturing line, and the components and operation are currently being optimised. Fig. 6(b) shows a series of polarisation curves for commercial HT-MEAs compared to HySA Systems HT-MEAs.

4.2. High temperature PEM fuel cell

HT-PEMFC technology has been under fast and intensive development for the past two decades and is currently becoming an attractive alternative to conventional PFSA-membrane based LT-PEMFC technology [6]. The developed materials and components exhibit the performances that allow commercialisation. The state of development and possible applications allow benefiting from the properties that HT-PEMFC possess. High operation temperature of HT-PEMFC 150–180 °C reflects in some



Fig. 6 – (a) – Polarisation curves of the MEAs based on PB-doped AB-PBI with GDEs prepared with different binders. (b) – Polarisation curves comparing the performance of HySA Systems HT-MEAs vs. various commercial HT-MEAs.

of key advantages of the technology over LT-PEMFC. The main advantage is tolerance to CO in anode gas supply what enables supply with reformate gas which does not require complex purification process. The tolerance of up to 5% CO concentration in anode supply gas was reported for single HT-PEM cell [7]. High operating temperature and temperature difference simplifies the heat management system thus the electrically generated waste heat can be efficiently removed and captured. Finally, the membrane conduction mechanism which is not dependent on humidity or water content but sulphuric acid doping level simplifies the water management system and eliminates the need for the supplied reactants to be humidified [8]. These properties enable the design of simple fuel cell systems, especially for small-scale power generation supplied with reformate fuel.

In the field of HT-PEM fuel cell technology, HySA Systems focuses on the R&D, technology development and application. The main objective is to integrate and validate complete CHP systems. To achieve this goal the conducted work is divided into three main streams (i) HT-PEMFC stack development, (ii) HT-PEMFC stack validation and characterisation and (iii) HT-PEMFC stack applications, focused mainly but not only, on stationary applications.

4.2.1. HT-PEMFC stack development

Proper thermal management of HT-PEMFC stack is a crucial issue as the stack steady temperature has to be maintained because degradation processes are strongly temperature dependent [9]. Water cannot be used as a cooling medium due to the high operating temperature. For this reason, alternative stack cooling strategies have to be developed and suitable thermo conductive fluids have to be used. Externally oilcooled stack design is one of the possible options for HT- PEMFC stack cooling that ensures its long lifetime [10]. The design has been developed by ZSW and HySA Systems produces the stacks for laboratory testing and validation. The production of graphite bipolar plates requires high precision tooling as the tolerances of machining are in micrometres range. To meet all the requirements of the stack components production, a suitable high precision micro milling CNC machine KERN Evo-765 is available at HySA Systems, a 3-D laser scanner GOM ATOS II Triple Scan System is used for qualification of the stack components.

In 2012, a 96-cell 2 kW_{el} HT-PEMFC stack was manufactured in South Africa in HySA Systems labs (Fig. 7(a) and (b)). The South African HT-PEMFC stack has been integrated within a CHP prototype breadboard system (Fig. 7(c)) and tested. The test was performed at 160 °C, atmospheric pressure, pure hydrogen and air conditions; the polycurve of the stack measured during the test is shown in Fig. 7(d). A peak power of 2.2 kW_{el} was measured at 0.4 A cm⁻². Further testing that includes operation on reformate and long-term steady-state will be performed to validate the quality of the product. HySA Systems R&D work in the field of HT-PEMFC stack will also focus on the development of stack design up to 1 kW_{el} power.

4.2.2. HT-PEMFC stack validation and characterisation

The fuel cell stack is the key component of every FC system, its performance, efficiency and lifetime depends strongly on operating conditions. At HySA Systems commercial and inhouse built stacks are being tested and theirs performances are measured at wide range of operating conditions. Testing and validation of HT-PEMFC stacks is performed with the aid of available commercial state-of-the-art testing stations. The





Fig. 7 – 2 kW HT-PEMFC stack (a) assembly process, (b) assembled 2 kW stack, (c) stack integrated in CHP prototype breadboard system and (d) 2 kW HT-PEMFC stack polarisation curve.



Fig. 8 – (a) 2 kW CHP System installed at HySA Systems labs; (b) Polycurves and power characteristics of the 2 kW HT-PEM stack installed in CHP test-rig system, recorded at temperature range 120–160 °C.

characterisation of stack units up to 5 kW_{el} can be performed. Short stacks up to 200 W_{el} are being tested with the use of inhouse built testing setups. The EIS method is employed to investigate electrochemical processes that take place during the stack operation. Short 5-cell stacks have been assembled and validated. Preliminary results of conditioning and performance testing of 150 Wel unit are very promising, for example, current density of 0.78 A cm⁻² and almost 0.35 W cm⁻² was measured. 1 kW_{el} externally oil-cooled stack has been also thoroughly characterised. The tests focused on thermal and electrical output at various operating conditions as well as stack resistance to operation at CO concentration. The highest stack performance was obtained at a power density of 0.23 W cm⁻² at 160 °C and at 0.4 A cm⁻² that was measured using pure hydrogen. The stack showed a reasonable CO tolerance of up to 0.5% CO at 160 °C. More detailed description of results of stack testing has been reported and is available elsewhere [11]. The stack will be further characterised and long-term stability operation and voltage degradation rate will be studied.

4.2.3. HT-PEMFC stack applications

HT-PEMFC advantages make the technology attractive for stationary applications. Very promising area is in the natural gas supplied CHP systems in which reformer is integrated as a fuel processor. To investigate possibilities of HT-PEMFC applications in CHP system, a 2 kW_{el} CHP prototype breadboard system designed in cooperation with ZSW has been installed and tested at HySA Systems.

The system has been validated at various operating conditions. Fig. 8 shows an example of results obtained at various operating temperatures. The highest power density of 0.22 W cm^{-2} was measured at $160 \degree \text{C}$, +0.5 V mean cell voltage and 0.45 A cm^{-2} . As it can be observed, the operating temperature has significant influence on the stack performance and the increase of the temperature from 120 to $160 \degree \text{C}$ results in power gain of almost 10%. The operation at high current densities at low temperature is not possible because of the cell voltage drop below safe operation level. The stack was also tested at different CO_2 concentrations and no significant decrease in performance was observed up to 20% of CO_2 concentration. A thorough characterisation of the 2 kW CHP test-rig with CO and simulated reformate gas will be performed followed then by the integration of a commercial reformer (FLOX (R)).

4.3. Solid-state hydrogen storage and related applications

HySA Systems' activities within this key technology are aimed at the development, testing and validation of safe and efficient technologies for hydrogen storage, compression and separation/purification utilising solid-state hydrogen storage materials. Mainly, these activities are focused on materials and systems development for stationary and special mobile applications on the basis of "low-temperature" metal hydrides. In addition, HySA Systems carries out exploratory R&D in light-weight hydrogen storage materials based on nanostructured magnesium hydride and Metal Organic Frameworks (MOFs).¹

4.3.1. Metal hydrides

Hydrogen storage materials on the basis of reversible metallic hydrides (Metal Hydrides, MH) have found a number of promising applications in processes of considerable economic potential, such as hydrogen storage, separation and recovery, thermally-driven compressors and heat pumps, NiMH batteries, etc. [12,13]. These materials exhibit a favourable combination of their properties, including reversibility and selectivity of hydrogenation/dehydrogenation at mild conditions, high volumetric density of

¹ From Fiscal Year 2013/14, all MOF activities undertaken at HySA Systems have been transferred to HySA Infrastructure.

hydrogen in the solid, significant heat effects of hydrogenation/dehydrogenation. Thus, they are very flexible in various applications and offer to an end-user safe, efficient and cost-saving solutions.

In addition to well-developed PGM industry, South Africa has a well-established mining infrastructure, and can produce a number of metals which are important components to various metal hydride-forming alloys, including titanium, vanadium, nickel, manganese, rare-earth metals, etc. (Fig. 9). This feature may become a key driver for the development of new high tech industries for the manufacturing of MH materials, and systems realising MH technologies.

Metal hydride related activities at the South African Institute for Advanced Materials Chemistry have started since 2004. The works included the preparation and analysis of the properties of hydrogen storage composites composed of metal hydrides with silica [14], metal hydrides with nanoscale carbon [15,16], development of poisoning-tolerant surface modified MH materials [17–20]. After the establishment of HySA Systems in 2008, R&D activities focussing on "lowtemperature" MH materials and technologies have continued within the HySA Systems' projects. At present, the SAIAMC and HySA Systems MH-related activities include:

- (i) Poisoning-tolerant surface modified MH materials and MH systems for H_2 separation and purification.
- (ii) AB- and AB₂-type materials on the basis of Ti: preparation routes and characterisation.
- (iii) MH hydrogen storage systems for stationary LT-PEMFC applications.
- (iv) Thermally-driven MH H₂ compressors.
- (v) MH hydrogen storage and refuelling systems for utility vehicles.

4.3.1.1. Poisoning-tolerant surface modified MH materials. Selectivity of reversible hydrogen interaction with hydride-



Fig. 9 – Availability of mineral deposits for the manufacturing MH alloys in South Africa.

forming materials allows for the development of simple and efficient pressure/temperature swing absorption-desorption systems for hydrogen separation from complex gas mixtures and its fine purification [12,13]. However, so far, this approach has been successfully implemented only for hydrogen-rich feed gases (vent streams in the ammonia synthesis loop, H₂ >50%) which contain relatively innocuous admixtures, mainly nitrogen and argon [21]. At the same time, the gases associated with processing of coal, petrol, natural gas and other carbonaceous/fossil fuels feedstock, in addition to hydrogen, may contain significant amounts of other components, mainly carbon dioxide and monoxide, which in most cases cause the deterioration of hydrogen sorption performances of MHs [22]. Improvement of poisoning tolerance of hydrideforming materials can be achieved by modification of their surface. The existent surface modification methods use two approaches, first of which is aimed at the improvement of surface catalytic activity, and the second protects the surface from an impurity attack, by the creation of protective coatings permeable for hydrogen but not permeable for the impurity species [23].

Our developments use both approaches for the improvement of activation performances and poisoning tolerance of hydride-forming materials. The surface modification by the deposition of metals (including PGM), possessing high catalytic activity towards the dissociative H₂ chemisorption, has been applied using electroless deposition [17,19,20,23-26] or CVD [27] techniques, for the substrates on the basis of AB₅ [17,19,20,23-25] or TiFe [26,27] hydride-forming intermetallides. Surface modification with PGM (e.g. Pd) has been shown to significantly improve hydrogen sorption kinetics and poisoning tolerance. Pre-functionalisation of the MH substrate with water-soluble aminosilanes facilitates improved electroless deposition of PGM resulting in more dense and uniform coatings, as distinct to conventional deposition technique. The improvements have been found to be due to chemical bonding between the PGM nuclei and surface oxygen, via functional groups formed from aminosilane molecules.

The AB₅-type materials surface modified by the fluorination and Pd electroless deposition [18,20] were found to have good poisoning tolerances (Fig. 10(a)), even for the large (~1.5 kg) batches. Feasibility of their application for H₂ separation from gas mixtures (up to 30% CO₂ and 100 ppm CO) was demonstrated by testing of a prototype H₂ separation system. The H₂ separation was characterised by stable performances in the duration of hundreds absorption/desorption cycles [28,29].

4.3.1.2. AB- and AB₂-type materials on the basis of Ti. Ti-based AB and AB₂-type hydride-forming materials have shown to be very promising hydrogen storage alloys due to their reasonable reversible hydrogen storage capacity at near ambient conditions, abundance and low cost [12,13]. Ti-based hydride-forming alloys are less expensive when compared to AB₅ alloys. However, due to huge price increases for titanium metal during the last decade [30], the cost for these materials prepared by conventional method of melting the metallic components has become unacceptably high. At the same time, the available titanium-containing raw materials are



Fig. 10 – (a). Dynamics of hydrogen absorption by the surface-modified La(Ni,Co,Al,Mn)₅ alloy in running-flow mode at T = 20 °C. The partial H₂ pressure and flow rate are 2 bar and 0.25 L/min, respectively. The values in brackets correspond to maximum hydrogen absorption capacity [cm³ g⁻¹ STP]: 1 – Pure H₂; 2 – 25% H₂ + 10% CO₂ + N₂ (balance); 3 – 25% H₂ + 10% CO₂ + 100 ppm CO + N₂ (balance); a – cycle # 1, b – cycle #16; 4 – 25% H₂ + 28% CO₂ + 0.33% CO + N₂ (balance). (b) – Hydrogenation performances of the AB₂-type hydride-forming alloy prepared from ilmenite (P = 40 bar, T = 20 °C): A – first hydrogenation without vacuum heating, B – second and consequent hydrogenations of the material dehydrogenated by heating to 300 °C in vacuum during 1 h, C – hydrogenation of the de-hydrogenated material after 10 min-long exposure to air.

much more cost-effective. According to the data reported by Van Vuuren [31], the corresponding average prices sharply increased from USD 0.09 kg⁻¹ for ilmenite and USD $0.4-2.1 \text{ kg}^{-1}$ for titanium dioxide of different grades to 10, 20 and USD\$ 40 kg⁻¹ for titanium sponge, ingot and mill products, respectively. Such large differences are mainly caused by the complexity and high costs of production of metallic titanium, whereby a significant part of the process is related to the separation and refining of the pure metal. Of the number of titanium-containing raw materials, ilmenite (FeTiO₃) is characterised by the lowest cost and widest availability. Thus, it is a very attractive feedstock for the manufacturing of titanium-containing metal hydrides. In the preparation of TiFe-based hydride-forming alloys from the ilmenite, the separation of iron and titanium is not necessary, yielding a strong motivation for the development of the corresponding methods related to direct reduction of FeTiO₃ to TiFe.

HySA Systems has developed a novel process for the preparation of Ti-based hydride-forming alloys via the reduction of ilmenite [32–34], allowing achieving a maximum yield of the target product of a reasonable quality. Synthesis of TiFe-based metal hydride-forming alloy from mixed titanium-iron oxide (ilmenite, FeTiO₃) was carried out by a twostage reduction of the latter using H₂ and CaH₂ as reducing agents. The reversible hydrogen absorption capacity of the TiFe-based material was about 0.5 wt.% H, that is significantly lower than the corresponding values (~1.8 wt.% H) reported in the literature. The main reason was due to the high amount of oxygen present in the as-prepared TiFe alloy. Thus in order to improve the hydrogen absorption of the raw TiFe, the material was further alloyed together with Zr, Cr, Mn, Ni and Cu to yield an AB₂ alloy. For the as-prepared AB₂ alloy, the reversible hydrogen sorption capacity was about 1.3 wt.% H at P = 40 bar and >1.8 wt.% at P = 150 bar, which is acceptable for stationary applications. Finally, the material was found to be superior

when compared to known AB₂-type alloys, with regard to their activation and poisoning tolerance (Fig. 10(b)).

4.3.1.3. MH H storage systems for stationary LT-PEMFC applications. Uninterrupted Power Systems (UPS) for telecommunications have been identified as a niche market for hydrogen based LT-PEMFCs. Typical power required for telecom backup ranges from 1 to 10 kW for single, small-scale installations [35] to 5–100 kW for larger multipurpose installations [36]. Field experience made by fuel cell companies in this market (e.g. Hydrogenics) show that the required time of continuous operation of such facilities typically varies from 1 to 24 h and that the total annual duration of the operation is typically less than 300 h per year [35]. Other fuel cell companies (e.g. Ballard Fuel Cells) have demonstrated PEMFC stack lifetime up to 11,000 h [37]. Hence, there seems to be a 'good business case' for hydrogen based LT-PEMFCs for UPS telecoms.

HySA Systems developed a prototype water-heated-cooled MH hydrogen storage system for LT-PEMFC applications [38]. The system uses "low-temperature" hydrogen storage materials on the basis of commercially available AB₅- or AB₂-type alloys characterised by fast hydrogen absorption/desorption kinetics at moderate temperatures (10-100 °C). To provide fast start-up of the PEMFC and to minimise power consumption in the course of hydrogen supply, the MH materials are characterised by H₂ equilibrium pressure higher than the pressure of hydrogen to be supplied to the FC (~1 bar). The MH unit (Fig. 11) comprises cylindrical external shell (1) equipped with two hemispherical end caps. One of the end caps carries gas supply and removal fittings (3), while the opposite end cap is fitted with a "tube in tube" internal heat exchanger comprising a finned core tube (2), and a manifold (4) for input and output of a heating/cooling fluid. The prototype MH unit became a basis for further development of liquid heated-cooled MH containers for hydrogen storage and compression having similar layout. 10-15 kg of the MH material



Fig. 11 – Schematic drawing (top) and photo (bottom) of the MH hydrogen storage unit, where 1 = stainless steel container; 2 = heat exchanger; $3 = H_2$ manifold: 3.1 = filter, 3.2 = valve, 3.3 = overpressure protection (rupture disc); 4 = water manifold: 4.1 = inlet, 4.2 = outlet.

loaded in the container provided hydrogen storage capacity of $1.6-2 \text{ m}^3 \text{ H}_2$ (STP) and stable hydrogen discharge flow rate about 20 L H₂ min⁻¹ that is equivalent to the operation together with 1.2 kW fuel cell stack.

4.3.1.4. Thermally-driven MH H₂ compressors. A promising method for hydrogen compression driven by low-grade heat and not requiring the usage of moving parts, is the application of MHs. However, being up-scaled to higher productivities necessary for industrial processes (i.e., ≥ 1 m³ H₂/h STP), the method will inevitably meet a number of problems related to complications of the system layout, high costs and significant labour resources for the manufacturing, and low thermal efficiency.

Since 2008, SAIAMC and HySA Systems have been developing advanced engineering solutions for MH hydrogen compression from 5–10 to \sim 200 bar [39–42]. The developed MH compressors are thermally-driven and only require water cooling at T = 15-25 °C and heating by low-grade steam or superheated water at T = 120–140 °C. Fig. 12 shows one of the developed MH compressors with average output productivity up to 1 m³ h⁻¹ STP [42]. The compressor has a two-stage layout whereby the first stage uses AB5- and the second AB2-type hydride-forming intermetallic alloys. A special engineering solution [41] allows for the use of large MH containers (~2 m³ STP H₂ capacity), so that the required productivity is provided by just four containers assembled in two compression elements each of which comprises one first- and one secondstage MH containers. The compressor layout also provides heat regeneration, thus reducing the consumption of hot and cold heat transfer fluids and increasing the overall efficiency.

4.3.1.5. MH Hydrogen storage and refuelling systems for utility vehicles. The focus in this activity is to develop and integrate a metal hydride hydrogen storage system for a fuel cell powered forklift, with a capacity of 3 tonnes and 10 kW nominal fuel cell output. Based on a fuel cell efficiency of 50%, the required consumption of H_2 fuel is estimated to be 6.7 N m³ h⁻¹. Hence,

a permanent operation of the forklift for 8 h will require about 54 Nm³ H₂. This amount of hydrogen can be stored in a ca. 300 kg of MH material with a storage capacity of 180 L of H₂ per kg (estimated volume of the MH powder about 100 L). To store the same amount of hydrogen in high-pressure (350 bar) composite cylinders available on the market, it is necessary to use 28 cylinders with the capacity 6.8 L, or 21 cylinders with the capacity of 9 L; the total volume of the gas-cylinder storage system is about 2 times higher than that of metal hydride. In addition, a compressed gas cylinder solution would require a high pressure hydrogen compressor, which typically has challenges with service costs, safety and reliability.

A novel system concept for fuel cell powered utility vehicles with on-board MH hydrogen storage units has been proposed by HySA Systems. The system (Fig. 13) includes the following sub-systems:

- a) Utility vehicle with on-board fuel cell and metal hydride hydrogen storage system on the basis of "low-temperature" MH (equilibrium pressure at T~0 °C above 1 bar);
- b) Stationary hydrogen refuelling system consisting of a lowpressure hydrogen supply and a metal hydride hydrogen compressor.

4.3.2. Light-weight hydrogen storage materials

The exploratory activities of HySA Systems in the area of lightweight hydrogen storage materials for mobile applications focus on R&D of nanostructured magnesium hydride and Metal Organic Frameworks (MOFs).¹

4.3.2.1. Nanostructured magnesium hydride. Magnesium dihydride MgH₂ is an attractive hydrogen storage material. It has a high reversible hydrogen storage capacity (7.6 wt.% H/ 110 kg H m⁻³); magnesium metal is inexpensive and abundant. At the same time, slow hydrogenation/dehydrogenation kinetics at temperatures below 350 °C and high stability (that corresponds to an equilibrium hydrogen pressure of 1.0 bar at



Fig. 12 – MH hydrogen compressor (200 bar H_2 , up to 1 m³ h⁻¹ STP) developed by SAIAMC/HySA Systems.

T ~300 °C) are the major obstacles for hydrogen storage applications on the basis of MgH₂.

During the last 15 years, intensive studies by many research groups worldwide resulted in the development of hydrogen storage composites on the basis of catalysed nanostructured MgH₂ which are characterised by the greatly improved hydrogenation/dehydrogenation performances. This research has been implemented in highly-efficient hydrogen storage materials and large-scale hydrogen storage systems on the basis of nanostructured MgH₂ [43]. A significant contribution to the R&D field has been achieved as a result of recent activities of HySA Systems with Norwegian, Chinese, Russian and Ukrainian collaborators [44–49]. This yielded valuable results important for the development of highly-efficient hydrogen storage nanocomposites on the basis of Mg H₂.

4.3.2.2. Metal Organic Frameworks¹. MOFs are crystalline coordination materials attractive for their microporous channels (<2 nm) and high specific surface areas (e.g. 3500 m² g^{-1} for MOF-5), which can be significantly greater than that exhibited by zeolitic materials and their subsequent high hydrogen storage capacities [50]. They are constituted of divalent or trivalent metal ion centres connected by large organic linkers. A multitude of MOF structures do exist, where their framework topology, pore size, and surface area can be tailored simply by the exchange of linker groups or molecular bridges in the synthesis stage [51]. The materials typically contain microporous networks, with microcavity diameters known to range from 10 to 13 Å. The materials are typically prepared through a solvothermal route, in which the metal ion precursor, and molecular ligand are incubated under mild thermic condition. However, attractive storage capacities are only achieved under energy-intensive cryogenic conditions. Applications of these materials for ambient temperature absorption of hydrogen proved ineffective, with IRMOF-8 exhibiting <2.0 wt.% at 298 K and 10 bar H₂, thus failing to meet US DOE targets [52]. This drastic decrease in the hydrogen storage capacities of MOFs is a direct result of the

decrease in the binding energy between hydrogen molecules and the MOF surface.

HySA Systems R&D has been focused on both the synthesis of MOF materials exhibiting high specific surface area, and the post-synthetic PGM treatment of these materials in order to facilitate high hydrogen storage capacities under ambient conditions of temperature and pressure [53]. Syntheses of materials have been centred on the preparation of MOF-5, MOF-177, and IRMOF-8. Our post-synthetic treatment of the MOF materials has been dedicated towards catalytic additions to the MOF materials to make them suitable for room temperature adsorption of hydrogen for on-board storage systems of Fuel Cell Electric Vehicles (FCEVs). This is achieved through considerations towards the "hydrogen spillover" phenomenon, which has the potential to increase room temperature hydrogen adsorption properties of adsorptive materials. Platinum catalysts are known to promote the hydrogen spillover effect, and when supported onto high surface area materials, such as Activated Carbon (AC), has the potential to enhance the hydrogen storage capacity of the MOF materials [54]. During the hydrogen spillover phenomenon, Pt catalytic particles cleave the bond in the dihydrogen (H_2) molecule leading to dissociation and generation of hydrogen "atoms" (Fig. 14). The H atoms then migrate to a substrate material where it can be used for various surface processes, or spillover again to a secondary receptor [55]. In these types of composite hydrogen storage materials, AC could be considered a primary hydrogen atom receptor, after the dissociation of dihydrogen by the Pt nanoparticles, with the MOF as a secondary receptor eventually storing the hydrogen atoms in its microstructure [56].

The Pt-AC material can be prepared *via* a chemical reduction method, or could be purchased as a fuel cell catalytic material with various metal loadings available. Further bridging of MOF with the Pt/AC materials can be enhanced by the carbonisation of simple sugars (e.g. sucrose, fructose, glucose), and has been demonstrated to significantly enhance hydrogen storage capacities [57]. The enhancement is a direct result of an increase in the binding energy from 9.65 kJ mol⁻¹ for unmodified IRMOF-8 to 21.7 kJ mol⁻¹ for H on the "bridge" site of IRMOF modified with Pt/AC and sucrose.

¹ From Fiscal Year 2013/14, all MOF activities undertaken at HySA Systems have been transferred to HySA Infrastructure.



Fig. 13 – General layout of the main and auxiliary systems for H₂-fuelled forklifts with MH hydrogen storage and refuelling.

The catalytic particles can be deposited onto the highsurface-area MOF receptors, for hydrogen storage by spillover, either by physically mixing the MOF material with a supported metal catalyst (such as Pt/AC), or by introduction of the metal onto the receptor through chemical doping. In both cases, additional bridging between catalytic particles is needed for further enhancement of hydrogen spillover processes for room temperature hydrogen adsorption [58]. However, it was observed that reproducibility of H₂ spill-over storage on the bridged MOF samples is very difficult to bring into fruition, based on the nature of bridge building and nonuniform Pt/AC particle interconnectivities and inconsistent mixing of Pt/AC, sucrose and MOF particles.



Fig. 14 — Graphical representation of the hydrogen spillover process: (1) migration to the Pt catalyst; (2) dissociative chemisorption; (3) primary H spillover to the primary receptor; (4) surface diffusion; (5) secondary spillover to the secondary receptor; (6) surface adsorption and storage.

4.4. Pd-based membrane for hydrogen purification

Roughly 96% of the global annual demand for H₂ is derived from fossil based fuels using reforming processes. The reformation reaction product stream typically is a mixture of H₂, CO, CO₂ and CH₄ of which the composition is controlled by reaction equilibria. Major capital investment is required to increase the H₂ yield and to separate the H₂ from the reaction mixture to produce fuel cell grade H₂. The commonly applied process to convert high concentrations on carbon monoxide (CO) with steam (H₂O) into carbon dioxide (CO₂) and H₂ is known as the High Temperature Water Gas Shift (HTWGS) process which is typically followed by a Low Temperature Water Gas Shift (LTWGS) to reduce the CO levels in the product gas stream below 1000 ppm. Downstream the LTWGS a Pressure Swing Adsorption (PSA) system is needed to separate the H_2 from the CO_2 and traces of other gasses. Needless to say, the CO conversion and gas purification cost greatly impact the cost of fuel cell grade H₂.

Continuous films of Palladium (Pd) material are known for their exceptionally high permeability towards H₂. So called 'Pd membrane reactors' have these films applied in close proximity of the reforming catalyst enabling H₂ to be removed from the reaction zone, allowing a continuous shift of the reforming and WGS reaction equilibrium resulting in significantly higher hydrogen production yield. With the use of Pdbased membranes, fuel cell grade H₂ can be produced without the need for HTWGS, LTWGS or PSA technology, offering a great cost reduction potential. The production of Pd films is rather challenging as a successful membrane may not exhibit any defects (to ensure high H₂ selectivity), must preferably be less than 5 µm in thickness (to show sufficient permeance) and finally should exhibit both the mechanical and thermal stability needed to survive the harsh gas reforming environment during its operational lifetime.



Fig. 15 — (a) Photograph of the phase inversion set up developed to produce hollow fibre support; (b) SEM image of a fibre showing the desired sponge like structure of the fibre outer area.

HySA Systems R&D has been focused on the following:

- (i) Membrane support synthesis. The support material forms the foundation for the membrane and need to form a smooth surface of material mechanically and chemically stable in a reducing environment up to 600 °C. In order to achieve a highly permeable support structure with high packing density, phase inversion technology is used to produce thin asymmetric ZrO_2 hollow fibre supports. The production system and SEM images of hollow fibres with the desired "sponge like structure" are depicted in Fig. 15(a) and (b) respectively.
- (ii) Investigation of the most effective seeding procedure of hollow fibres. Commonly applied seeding procedures are typically repeated 10 times to form a sufficient number of seeds well distributed over the surface of the support. Fig. 16 shows that the seed formation has a great impact on the formation of the film.
- (iii) Development of the plating procedure. After a large number of nanoseeds not contaminated with highly mobile metals such as tin, are deposited on a smooth

surface of ZrO₂ in a well dispersed manner, a coalescence film can be produced.

The selectivity and permeance results of the Pd membranes will be published shortly.

4.5. CombiLit batteries

The term "CombiLit" describes a hybrid energy storage device that combines a high power density supercapacitor electrode with a high energy density Li-ion battery electrode in one cell. This unique technology can be tailored to provide varying levels of high power discharge and charge with increased energy storage, long cycle life and low cost.

4.5.1. Carbon coating of $LiMn_2O_4$ (cc $LiMn_2O_4$) cathodes and ccPbSO₄ anodes for aqueous cells

Alkali Metal-Ion Intercalation Compounds (AMICs), e.g. $LiMn_2O_4$, and $NaMn_2O_4$, show stable cyclability, good rate capability, and high capacity in aqueous electrolytes. Practical usage of AIMCs as cathodes in aqueous energy storage cells



Fig. 16 – SEM images of seeded and electroless plated hollow fibres showing the influence of seeds on the electroless plating process of Pd.

has proven viable in "hybrid" cells containing Activated Carbon (AC) anodes, with commercial development of AC/ NaMn₂O₄ cells for energy storage applications currently underway. However, in order to achieve practical levels of energy and power density in 'real' cells at battery scale, high mass loadings of electrode material are required on current collectors. This is accompanied by increased electrode resistance and thus less power can be obtained. Therefore, to improve energy and power retention at high mass loading we have carbon-coated LiMn_2O_4 to facilitate better electronic transport. Fig. 16 shows the higher energy retention of carboncoated ccLiMn₂O₄ vs. uncoated LiMn_2O_4 .

Secondly to obtain higher energy density from the aqueous cells we investigated a novel, alternative anode material, carbon-coated PbSO₄ (ccPbSO₄) against LiMn₂O₄. Fig. 17(b) shows the cell's discharge voltage of +1.4 V, which gives a practical energy density of ~50 Wh kg⁻¹ matching that of lead acid cells, and Fig. 17(c) and (d) the stable cycling and Coulombic efficiency of the cell. Since LiMn₂O₄ offers a lower cathode voltage than the PbO₂ lead acid cathode (+1.2 V and +1.69 V *vs.* SHE respectively), the cell does not require highly acidic electrolyte and thus uses light stainless steel current collectors in pH 5 electrolyte in place of the heavier, acid-resistant, Pb grid current collectors. Consequently, the ccPbSO₄/LiMn₂O₄ cell matches lead acid cells in energy density, but uses less hazardous ~ pH7 electrolyte, ~60% less Pb,

and thus provides a promising cheaper candidate for grid storage of renewable energy sources.

4.5.2. ccPbSO₄-LMO cells

Cycling of the ccPbSO₄ against LMO in 1 M Li₂SO₄ produced a marked improvement in capacity over the previously studied Pb granules, with ccPbSO₄ matching the capacity of LMO at 80 mAh g⁻¹, two times that of AC (Fig. 17(d)). The C/5 rate is also used by Aquion Energy[®] for their AC/NMO cells resulting in similar predicted up-scaled cells at ~50 Wh kg⁻¹, which suit energy capture from renewable power sources.

4.5.3. Prototypes

High powered hybrid Li-ion battery cells were also developed. These cells are made of two long electrodes, one made from AC/graphite coated on Cu current collectors, and the other from commercial NMC materials coated on Al current collectors. The electrodes were wound together with Celgate separator and then placed into cylindrical cell cases and filled with electrolyte, LiFP₆, in a dry room. Cells charged at 1 C with 5 C discharge showed excellent cycle life performance. Only after 1000 cycles, the capacity of this cell drops by 15%, which is much better than conventional Li-ion cells. Fig. 18 shows produced pouch cells (15–20 Ah; (a)) and cylindrical cells (2 Ah; (b)) at pilot scale.



Fig. 17 – (a) Ragone plot showing improved energy retention of carbon-coated $LiMn_2O_4$ (red plot) compared to uncoated $LiMn_2O_4$ (black plot) in an AC/LiMn_2O_4 cell; (b) Cycling of the ccPb/LiMn_2O_4 cell at 1 C, (c) Cycling of ccPbSO₄/LMO, voltage/ time plot; (d) Coulombic efficiency/capacity plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 18 – Produced pouch cells (15–20 Ah) and cylindrical cells (2 Ah) at pilot scale at the University of the Western Cape.

4.6. Energy system engineering

Optimising of energy utilisation has to be approached from a total system perspective. Optimisation can only be performed once a cost function is defined, i.e., the value system has to be established. It is difficult to compare the environmental impact of generating energy with the environmental impact of consuming energy. Renewable energy sources are only environmentally neutral during energy generation, but what about the impact during manufacturing? What is the cost of convenience, 5 min refuel vs. 8 h recharge, personal transport vs. public transport, etc?

Well-to-wheel analyses do provide comparative information regarding fuel types and energy sources [59,60] but do not address availability and convenience factors associated with the various energy sources and methods of use. The latter are strongly influenced by location and the socio-economic status of the region. HySA Systems focus on tank-to-wheel optimisation using various prototypes as development and demonstration platforms.

4.6.1. Vehicle prototypes

4.6.1.1. Golf cart. An existing battery electric road-legal urban vehicle, ideally suited as shuttle vehicle, is fitted with a H₂ LT-PEMFC as a range extender. Both High Pressure (HP) and Metal Hydride (MH) H₂ storage methods are being evaluated. Although the vehicle is fitted with a 5 kW electric drive system, a 1.2 kW FC is sufficient to maintain the charge of the 12 kWh Pb-A traction battery pack for extended usage, resulting in a more than 60% additional range. This is achieved by consuming 155 g of H₂ stored in 2×6.8 L HP cylinders at 160 bar. The weight penalty of this range extender is approximately 15% of the total weight of the Pb-A traction battery pack. Fig. 19 shows a comparison of logs of vehicle battery voltage, in the battery - (a) and hybrid (Pb-A traction battery + FC)-powered (b) modes shows that in the latter mode the battery discharge takes place much slower, and the significant voltage drop is observed only after shutting the PEMFC stack down when hydrogen fuel is no longer available (c).

A theoretical range increase of up to 110% can be achieved should the H_2 filling pressure be increased to the maximum HP cylinder capacity of 300 bar. This prototype vehicle (Fig. 20(a)) is a plug-in hybrid; the recharging of the traction battery pack is primarily done using the off-board battery charger. The drive cycle has an average energy consumption of 2.5 kW, which suggests a requirement for a 2.5 kW FC (ignoring efficiencies) if H_2 is the only energy source.

4.6.1.2. E-Scooter. The range of a high-way capable battery electric scooter is extended by adding a H_2 LT-PEMFC in a typical storage box, as well as 2 MH storage cylinders (easily mistaken as exhaust pipes, see Fig. 20(b)) without compromising the ride quality significantly (effect is less than a passenger).

4.6.1.3. Forklift. Material handling vehicles are often required to have "environmentally friendly" emissions. The only byproducts of H_2 FCs are water, heat, and electricity. Such a power pack is ideally suited for refrigerated warehouses with perishable goods; conditions where the traditional Pb-A battery packs are compromised, resulting in poor energy capacity performance. HySA Systems are initiating the development by generating representative duty cycles for a 3tonne capacity battery electric forklift (Fig. 20(c)). This will form the basis for the future conversion to a H_2 FC material handling vehicle.

4.6.1.4. Three wheeler. A recent addition to the prototype fleet of HySA Systems is a three wheeler electric vehicle manufactured by Microcab Industries UK Ltd (Fig. 20(d)). This rear wheel drive configuration has a 5 kW direct current (DC) motor with motorbike-like throttle and brakes on the steering. The $2 \times$ Pb-Acid batteries have a combined useable energy capacity of 1.2 kWh resulting in an expected operating range of less than 20 km. This vehicle is a useful platform for the development of an energy system concept for a community transport vehicle.

4.6.2. System engineering process

4.6.2.1. Requirement management. The first steps in the prototype development process are to establish the user requirement and derive the system specification. This is often the first practical application of the technology (outside the ideal conditions of a laboratory) and therefore not advisable to have strict pass/fail criteria. HySA Systems, adapt the approach targets or goals, typically in the form of specifications rather than 'let's see what we get'.



Fig. 19 – Logs of vehicle battery voltage taken during driving of the vehicle: (a) – battery powered, (b) – hybrid (FC + battery)powered, (c) – comparison of the trend lines. The horizontal dashed lines in (a) and (b) correspond to the states of battery discharge indicator (BDI), and the vertical dashed line in (c) – to the moment of shut-down of the FC stack (out of H_2) [61].

Concept designs are evaluated against these agreed specifications, compromises clearly noted and accepted. Safety, however, cannot be compromised, and a HySA Systems documented Safety Process is followed which includes a full risk analysis and hazard operability (HAZOP) study. HySA Systems also make use of an independent safety certification authority to ensure safe operation, where appropriate.

4.6.2.2. Integration. Integration of the various sub-systems, which the system comprises of, is already initiated during the concept design phase. Interfaces are defined and controlled, resulting in typically a smooth assembly process.

4.6.2.3. Configuration management. Formal configuration control utilising strict change control via Engineering Change Proposals (ECPs), Product Configuration Management Board meetings (PCMBs) etc., can easily stifle the experimental and research nature of the prototypes. It is however essential to keep track of changes, especially from a safety perspective. Uncontrolled changes can easily nullify previous test data, not only costly but also time consuming. HySA Systems makes use of a configuration status spreadsheet to capture changes and record current configuration.

4.6.3. Validation

4.6.3.1. FCV Emulator. HySA Systems recently procured a 20 kW FCV Emulator for acceptance testing of sub-systems prior to integration and evaluation in road vehicles Fig. 21. This provides an essential platform for repetitive testing according to a pre-programmed duty cycle with excellent repeatability. It also enables extensive instrumentation and data recording, if required, which is not always possible on the road. Road hazards are also eliminated and driver fatigue is not an issue during endurance testing.

4.6.3.2. Field testing. "The proof of the pudding lies in the eating" and practical 'real-life' testing is required for maturing the technologies. Maturing the technologies imply not only optimising performance, but also manufacturing costs, robustness to manufacturing tolerances and processes, as well as comprehending maintenance requirements.

4.7. Manufacturing of energy components

SAIAMC and HySA Systems Competence Centre have, for the first time in South Africa, set up fully functional Pilot Plant Component Manufacturing for: a) MEA and b) Li-ion battery. A



Fig. 20 — Fuel cell powered vehicles at HySA Systems: (a) golf cart (Melex), (b) e-scooter (Melex), (c) forklift (STILL International), (d) three-wheeler (Microcab).

metal hydride pilot plant, supported by the DST, is currently being constructed. On the basis of completed materials studies, the details of influence of preparation routes on the properties of MH materials have been clarified, and target compositions of the MH alloys for various applications,



Fig. 21 – View of the FCV Emulator.

including hydrogen storage, compression and separation/purification, have been identified. The primary objective of the pilot plant is to build-up knowledge base and infrastructure for the manufacturing of MH materials for various applications in South Africa using local natural and labour resources. Facilities for the manufacturing (induction melting and annealing) of the AB₅- and AB₂-type MH alloys with capacity of 25 kg/day are being developed together with a South African company; the commissioning is scheduled in Q1 of 2014.



Fig. 22 – Number of academic outputs since HySA Systems creation in 2008.

5. Publications and patents

In response to the need for the generation and application of PGM-related knowledge and innovation in South Africa, HySA Systems has been active in innovating and disseminating its work (Fig. 22), with a major focus on its 'research impact', e.g. job creation. For example, since 2008 the Centre has generated >70 academic R&D publications in peer-reviewed journals, >70 publications in national and international conferences and books (including presentations, posters, abstracts, book chapters, conference proceedings papers etc.), and >5 patents. For example, since 2008 two major patents have been generated by the Centre:

M. Lototskyy, M.W. Davids. Method for preparing hydrideforming alloys. Patent ZA2012/03824

The invention relates to a method for preparing of hydrideforming alloys on the basis of titanium and iron using ilmenite as a main primary feedstock. The patented process includes:

- (i) gas-phase reduction treatment of raw ilmenite, by its heating in the flow of a reducing gas to convert the ilmenite into a mixture of metallic iron and titanium oxides;
- (ii) metal-thermic reduction treatment of the mixture of metallic iron and titanium oxides, by its mixing with a powdered reducing agent followed by thermal treatment in inert atmosphere whereby the formation of a primary hydride-forming alloy on the basis of TiFe occurs;
- (iii) alloying the primary hydride-forming alloy on the basis of TiFe with additional metallic components, to yield either AB- or AB₂-type hydride-forming alloy; and
- (iv) separation of by-products formed on the step of the alloying and/or the metal-thermic reduction.

The two-step reduction of ilmenite including gas-phase and metal-thermic processes, allows one to prepare hydrogen storage alloys for various applications, starting from cheap and widely available raw material. As distinct from conventional direct metal-thermic reduction, the approach used within the scope of invention allows to minimise the contribution of side reactions resulting in the formation of mixed oxides and oxygen capturing by the final product that worsen its hydrogen sorption performances. In addition, it reduces the consumption of reducing agent taken for the metal-thermic reduction.

M.W. Davids, M. Lototskyy, M. Williams, J.M. Sibanyoni, B.G. Pollet, V.M. Linkov. Method for preparation of hydride-forming material on the basis of nanostructured magnesium hydride. Patent Application ZA2012/08851

The invention relates to a method of preparation of hydride-forming materials on the basis of nanostructured magnesium hydride. The patented process includes:

- (i) loading magnesium and at least one additive to be a mixed titanium – iron oxide (TiFeO₃) into a grinding container;
- (ii) sealing the grinding container;
- (iii) filling the container with hydrogen; and

(iv) mixing and grinding the magnesium with the additives (including sp^2 hybridised carbon) in the container under hydrogen pressure.

The method for preparation of hydride-forming material on the basis of nanostructured magnesium hydride by reactive mechanical grinding (including high energy reactive ball milling) of magnesium metal in hydrogen atmosphere with an additive of a mixed iron—titanium oxide (including natural ilmenite) allows one to prepare lightweight materials for hydrogen storage and heat management applications, starting from cheap and widely available raw materials. As distinct from similar preparation methods within the prior art, the approach used within the scope of the invention allows to shorten the preparation time and to produce materials with improved dehydrogenation and re-hydrogenation performances.

6. Conclusions

HySA Systems has delivered successfully and has advanced extremely well against their Business Plans since 2008. The Centre:

- (i) has established some manufacturing facilities/capabilities for HFC components and systems in South Africa;
- (ii) has been partnering with key international HFC and local industries to 'leap-frog' the technologies for both domestic and automotive applications;
- (iii) has been disseminating their findings/work in High Impact Factor Journals & National/International Conferences;
- (iv) has generated Intellectual Property in key HFC technologies; and
- (v) is working very closely with the HFCT markets and has a competitive edge in some technologies.

In other words, HySA Systems is on track for the implementation of a Fuel Cell Industry in South Africa involving: a) international commercial partners, b) South African supply chain and c) South African manufacturers and (d) South African innovation. From 2013 onwards, a large emphasis has been on implementing and advancing R&D vehicular system integration, and broadening systems engineering activities to improve HySA technology maturity and commercialisation.

Acknowledgements

First and foremost, the authors would like to thank the Department of Science and Technology (DST) for their financial support under the Hydrogen and Fuel Cell Technologies RDI Programme (HySA) as well as Dr Cordelia Sita, Chief Director of Hydrogen and Energy; Ms Mandy Nompumelelo Mtyelwa, Deputy Director of Hydrogen and Energy and Dr Cosmas Chiteme, Director of Alternative Energy at the DST for their guidance, encouragement and kind support.

Some application-related studies, including surfacemodified MH, hollow fibre synthesis and their application for hydrogen separation and purification, as well as the development of MH compressors, were supported by Eskom Holdings Ltd (South Africa). The activities on MH hydrogen storage and refuelling systems for utility vehicles were also supported by Impala Platinum Ltd (South Africa). Investments from these industrial funders have been leveraged through the Technology and Human Resources for Industry Programme, which is jointly managed by the South African National Research Foundation and the Department of Trade and Industry (NRF; THRIP projects TP2010071200039, TP2011070800020, and TP1207254249). The authors are grateful to: (a) Melex Electrovehicles, (b) Microcab Industries UK Ltd, (c) the Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (Centre for Solar Energy and Hydrogen Research Baden-Württemberg, ZSW) in Germany, (d) the Institute for Energy Technology IFE in Norway, and (e) other national and international industrial and commercial partners for their kind and continuous support. The authors would also like to thank: (a) HySA Catalysis (University of Cape Town and Mintek), (b) HySA Infrastructure (North West University and the Council for Scientific and Industrial Research), (c) HySA Systems' Spoke partners, and (d) the University of the Western Cape for their support. Last but not least, the authors are grateful to the HySA Systems' Technical Steering Committee for their technical and commercial advices and recommendations.

REFERENCES

- [1] EU launches clean fuel strategy. European Commission; 24/ 01/2013. Press release IP/13/40, http://europa.eu/rapid/pressrelease_IP-13-40_en.htm.
- [2] Technology roadmaps electric and plug-in hybrid electric vehicles (EV/PHEV). Paris: International Energy Agency; 2011.http://www.iea.org/publications/freepublications/ publication/EV_PHEV_Roadmap.pdf.
- [3] Su H, Pasupathi S, Bladergroen BJ, Linkov V, Pollet BG. Enhanced performance of polybenzimidazole-based high temperature proton exchange membrane fuel cell with gas diffusion electrodes prepared by automatic catalyst spraying under irradiation technique. J Power Sources 2013;242:510–9.
- [4] Su H, Pasupathi S, Bladergroen BJ, Linkov V, Pollet BG. Optimization of gas diffusion electrode for polybenzimidazole-based high temperature proton exchange membrane fuel cell: evaluation of polymer binders in catalyst layer. Int J Hydrogen Energy 2013;38:11370–8.
- [5] Felix C, Jao TC, Pasupathi S, Pollet BG. Optimisation of electrophoretic deposition parameters for gas diffusion electrodes in high temperature polymer electrolyte membrane fuel cells. J Power Sources 2013;243:40–7.
- [6] Schmidt TJ, Baurmeister J. Properties of high-temperature PEFC Celtec[®]-P 1000 MEAs in start/stop operation mode. J Power Sources 2008;176:428–34.
- [7] Li Q, He R, Gao JA, Jensen JO, Bjerrum NJ. The CO poisoning effect in PEMFCs operational at temperatures up to 200°C. J Electrochem Soc 2003;150:A1599–605.
- [8] Chen CY, Lai WH. Effects of temperature and humidity on the cell performance and resistance of a phosphoric acid doped polybenzimidazole fuel cell. Int J Hydrogen Energy 2010;195:7152–9.

- [9] Zhang J, Xie Z, Zhang J, Tang Y, Song C, Navessin T, et al. Self-assembly of nanostructured proton exchange membranes for fuel cells. J Power Sources 2006;160:872–91.
- [10] Scholta J, Zhang W, Jörissen L, Lehnert W. Conceptual design for an externally cooled HT-PEMFC stack. ECS Trans 2008;12:113–8.
- [11] Bujlo P, Pasupathi S, Ulleberg Ø, Scholta J, Nomnqa MV, Rabiu A, et al. Validation of an externally oil-cooled 1 kWel HT-PEMFC stack operating at various experimental conditions. Int J Hydrogen Energy 2013;38:9847–55.
- [12] Sandrock G. Applications of hydrides. In: Yurum Y, editor. Hydrogen energy system. Production and utilization of hydrogen and future aspects. Dordrecht/Boston/London: Kluwer Acad Publ.; 1995. pp. 253–80.
- [13] Dantzer P. Properties of intermetallic compounds suitable for hydrogen storage applications. Mater Sci Eng A 2002;329–331:313–20.
- [14] Grinberga L, Kleperis J, Bajars G, Vaivars G, Lusis A. Estimation of hydrogen transfer mechanisms in composite materials. Solid State Ionics 2008;179:42–5.
- [15] Ndungu P, Nechaev A, Khotseng L, Onyegebule N, Davids W, Mohammed R, et al. Carbon nanomaterials synthesized using liquid petroleum gas: analysis toward applications in hydrogen storage and production. Int J Hydrogen Energy 2008;33:3102–6.
- [16] Suttisawat Y, Rangsunvigit P, Kitiyanan B, Williams M, Ndungu P, Lototskyy MV, et al. Investigation of hydrogen storage capacity of multi-walled carbon nanotubes deposited with Pd or V. Int J Hydrogen Energy 2009;34:6669–75.
- [17] Williams M, Lototsky MV, Nechaev A, Linkov V. Method of surface modification of metallic hydride forming materials. Patent US 8354552 B2 (ZA 2007/09455, W02009/066263).
- [18] Williams M, Lototsky MV, Nechaev A, Linkov V. Hydrideforming material. Patent ZA 2008/09123.
- [19] Williams M, Nechaev A, Lototsky MV, Yartys VA, Solberg JK, Denys RV, et al. Influence of aminosilane surface functionalization of rare earth hydride-forming alloys on palladium treatment by electroless deposition and hydrogen sorption kinetics of composite materials. Mater Chem Phys 2009;115:136–41.
- [20] Williams M, Lototsky MV, Linkov V, Nechaev A, Solberg JK, Yartys VA. Nanostructured surface coatings for the improvement of AB_5 -type hydrogen storage intermetallics. Int J Energy Res 2009;33:1171–9.
- [21] Au M, Chen C, Ye Z, Fang T, Wu J, Wang O. The recovery, purification, storage and transport of hydrogen separated from industrial purge gas by means of mobile hydride containers. Int J Hydrogen Energy 1996;21:33–7.
- [22] Sandrock GD, Goodell PD. Cyclic life of metal hydrides with impure hydrogen: overview and engineering considerations. J Less-Common Met 1984;104:159–73.
- [23] Lototsky MV, Williams M, Yartys VA, Klochko YV, Linkov V. Surface-modified advanced hydrogen storage alloys for hydrogen separation and purification. J Alloy Compd 2011;509:S555–61.
- [24] Ren J, Williams M, Lototskyy MV, Davids W, Ulleberg Ø. Improved tolerance of Pd/Cu-treated metal hydride alloys towards air impurities. Int J Hydrogen Energy 2010;35:8626–30.
- [25] Williams M, Lototsky M, Nechaev A, Yartys V, Solberg JK, Denys RV, et al. Palladium mixed-metal surface-modified AB₅-type intermetallides enhance hydrogen sorption kinetics. S Afr J Sci 2010;106(9/10) [Article #310].
- [26] Williams M, Lototsky MV, Davids MW, Linkov V, Yartys VA, Solberg JK. Chemical surface modification for the improvement of the hydrogenation kinetics and poisoning resistance of TiFe. J Alloy Compd 2011;509:S770–4.

- [27] Davids MW, Lototskyy M, Nechaev A, Naidoo Q, Williams M, Klochko Y. Surface modification of TiFe hydrogen storage alloy by metal-organic chemical vapour deposition of palladium. Int J Hydrogen Energy 2011;36:9743–50.
- [28] Lototskyy M, Modibane KD, Williams M, Klochko Y, Linkov V, Pollet BG. Application of surface-modified metal hydrides for hydrogen separation from gas mixtures containing carbon dioxide and monoxide. J Alloy Compd 2013 December 15;580(1):S382–5.
- [29] Modibane KD, Williams M, Lototskyy M, Davids MW, Klochko Y, Pollet BG. Poisoning-tolerant metal hydride materials and their application for hydrogen separation from CO₂/CO containing gas mixtures. Int J Hydrogen Energy 2013;38:9800–10.
- [30] U.S. Geological Survey. Titanium statistics. In: Kelly TD, Matos GR, editors. Historical statistics for mineral and material commodities in the United States: U.S. Geological Survey data series 140. http://pubs.usgs.gov/ds/2005/140/; 2008.
- [31] Van Vuuren DS. Keynote address: titanium an opportunity and challenge for South Africa. In: The 7th international heavy minerals conference, the Southern African Institute of Mining and Metallurgy 2009. pp. 1–7.
- [32] Lototskyy MV, Davids MW. Method for preparing hydrideforming alloys. Patent ZA 2012/03824.
- [33] Davids MW, Lototskyy MV. Influence of oxygen introduced in TiFe-based hydride forming alloy on its morphology, structural and hydrogen sorption properties. Int J Hydrogen Energy 2012;37:18155–62.
- [34] Davids MW, Lototskyy MV, Pollet BG. Manufacturing of hydride-forming alloys from mixed titanium – iron oxide. Adv Mater Res 2013;746:14–22.
- [35] Dogterom J. Hydrogen and fuel cell business development in Canada. Case study: fuel cell telecom installations. In: HySA systems business seminar 2 November 2009. Cape Town.
- [36] DOE/GO/10217-T1 Teledyne Brown Engineering report: fuel cell power systems for remote application; 1998.
- [37] Büchi FN, Inaba M, Schmidt TJ, editors. Polymer electrolyte fuel cell durability. Springer; 2009.
- [38] Ulleberg Ø, Lototskyy M, Ntsendwana B, Klochko Y, Ren J. Metal hydride hydrogen storage units for LT-PEMFC power systems. In: 18th world hydrogen energy conference (WHEC 2010); Essen/Germany May 16–21, 2010. pp. 101–8. Book 4.
- [39] Lototsky M, Halldors H, Klochko Y, Ren J, Linkov V. 7–200 bar/60 L/h continuously operated metal hydride hydrogen compressor. In: Schur DV, Zaginaichenko SY, Veziroglu TN, Skorokhod VV, editors. Hydrogen materials science and chemistry of carbon nanomaterials/ICHMS'2009, XI international conference Yalta – Crimea – Ukraine, August 25–31, 2009. Kiev: AHEU; 2009. pp. 298–9.
- [40] Lototsky M, Linkov V. Hydride container. Patent ZA2009/ 02427.
- [41] Lototskyy MV, Klochko Y, Linkov V. Metal hydride hydrogen compressor. Patent ZA2011/01351 (WO 2012/114229 A1).
- [42] Lototskyy M, Klochko Y, Linkov V, Lawrie P, Pollet BG. Thermally driven metal hydride hydrogen compressor for medium-scale applications. Energy Procedia 2012;29:347–56.
- [43] Delhomme B, de Rango P, Marty P, Bacia M, Zawilski B, Raufast C, et al. Large scale magnesium hydride tank coupled with an external heat source. Int J Hydrogen Energy 2012;37:9103–11.

- [44] Løken S, Solberg JK, Maehlen JP, Denys RV, Lototsky MV, Tarasov BP, et al. Nanostructured Mg–Mm–Ni hydrogen storage alloy: structure–properties relationship. J Alloy Compd 2007;446–447:114–20.
- [45] Wu Y, Lototsky MV, Solberg JK, Yartys VA, Han W, Zhou SX. Microstructure and novel hydrogen storage properties of melt-spun Mg–Ni–Mm alloy. J Alloy Compd 2009;477:262–6.
- [46] Lototsky MV, Denys RV, Yartys VA. Combustion-type hydrogenation of nanostructured Mg-based composites for hydrogen storage. Int J Energy Res 2009;33:1114–25.
- [47] Denys RV, Riabov AB, Maehlen JP, Lototsky MV, Solberg JK, Yartys VA. In situ synchrotron X-ray diffraction studies of hydrogen desorption and absorption properties of Mg and Mg–Mm–Ni after reactive ball milling in hydrogen. Acta Mater 2009;57:3989–4000.
- [48] Lototskyy M, Sibanyoni JM, Denys RV, Williams M, Pollet BG, Yartys VA. Magnesium-carbon hydrogen storage hybrid materials produced by reactive ball milling in hydrogen. Carbon 2013;57:146–60.
- [49] Williams M, Sibanyoni JM, Lototskyy M, Pollet BG. Hydrogen absorption study of high-energy reactive ball milled mg composites with palladium additives. J Alloy Compd 2013 December 15;580(1):S144–8.
- [50] Afsahi A, Vinh-Thang H, Mikhailenko S, Kaliaguine S. Electrocatalyst synthesized from metal organic frameworks. J Power Sources 2013;239:415–23.
- [51] Rowsell JLC, Yaghi OM. Strategies for hydrogen storage in metal-organic frameworks. Angew Chem Int Ed Engl 2005;44:4670–9.
- [52] Saha D, Deng S. Hydrogen adsorption on metal-organic framework MOF-177. Tsinghua Sci Technol 2010;15:363–76.
- [53] Kumar RM, Sundar JV, Subramanian V. Improving the hydrogen storage capacity of metal organic framework by chemical functionalization. Int J Hydrogen Energy 2012;37:16070–7.
- [54] Li Y, Yang RT. Significantly enhanced hydrogen storage in metal-organic frameworks via spillover. J Am Chem Soc 2006;128:726–7.
- [55] Lueking AD, Yang RT. Hydrogen spillover to enhance hydrogen storage – study of the effect of carbon physicochemical properties. Appl Catal A Gen 2004;265:259–68.
- [56] Li Y, Yang RT. Hydrogen storage in metal-organic frameworks by bridged hydrogen spillover. J Am Chem Soc 2006;128:8136–7.
- [57] Li Y, Yang RT, Liu CJ, Wang Z. Hydrogen storage on carbon doped with platinum nanoparticles using plasma reduction. Ind Eng Chem Res 2007;46:8277–81.
- [58] Stuckert NR, Wang L, Yang RT. Characteristics of hydrogen storage by spillover on Pt-doped carbon and catalyst-bridged metal organic framework. Langmuir 2010;26:11963–71.
- [59] Brinkman N, Wang M, Weber T, Darlington T. Well-to-wheel analysis of advanced fuel/vehicle systems – a North American study of energy use, greenhouse gas emissions, and criteria pollutant emissions http://www1.eere.energy. gov/bioenergy/pdfs/well_to_wheels_analysis.pdf; May 2005.
- [60] Pollet BG, Staffell I, Shang JL. Current status of hybrid, battery and fuel cell electric vehicles: from electrochemistry to market prospects. Electrochim Acta 2012;84:235–49.
- [61] Tolj I, Lototskyy MV, Davids MW, Pasupathi S, Swart GP, Pollet BG. Fuel cell-battery hybrid powered light electric vehicle (golf cart): influence of fuel cell on the driving performance. Int J Hydrogen Energy 2013;38:10630–9.