

Hydrogen and Fuel Cell Technologies at the Hydrogen South Africa (HySA) Systems Competence Centre

Technological achievements and breakthroughs with emphasis on platinum group metals beneficiation work to date under the HySA Systems Initiative

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The Hydrogen South Africa (HySA) programme is based upon the beneficiation of South Africa's large platinum group metal (pgm) resources. The present article summarises some of the progress by HySA Systems, one of the three Competence Centres under the HySA Programme, since 2008. Work has been carried out on membrane electrode assembly and stack development for high-temperature proton exchange membrane fuel cells (HTPEMFCs) for use in combined heat and power (CHP) supplied by natural gas and hydrogen fuelled vehicle (HFV) applications. The emphasis is on improved carbon monoxide tolerance and simplified heat and humidity management, allowing simpler fuel cell systems to be designed. Metal hydrides modified with palladium are being explored as poisoning-tolerant hydrogen storage materials for stationary and special mobile applications, and metal organic frameworks (MOFs) modified with platinum as light-weight hydrogen storage with a high hydrogen storage capacity. Lastly research into hydrogen purification using Pd membrane reactors is focused on membrane support synthesis, hollow fibre seeding and development of the plating procedure.

1. Introduction

HySA Systems is one of three National Competence Centres which makes up HySA. Initiated by the Department of Science and Technology (DST) and approved by the Cabinet in May 2007, HySA is a long-term (15-year) programme within their Research, Development and Innovation (RDI) strategy, officially launched in September 2008 (1). This National Flagship Programme is aimed at developing South African intellectual property, innovation, 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. HySA also focuses 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 turn resulting in commercialisation ventures and a viable industry around mineral beneficiation.

The principal strategy of HySA is to execute research and development (R&D) work, with the main aim of achieving an ambitious 25% share of the global hydrogen and fuel cell market using novel 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, and exporting added value pgm materials, components and complete products. The first five years of funding focused on developing infrastructures at each centre with a major emphasis upon human capacity development. Relevant international expertise was recruited by each centre to access technical support and well-established implementation networks and to ensure the programme and its deliverables remain market related and world-class. Collaborations with institutions and partners from R&D, academia and industry are underway (1,2).

There are a number of Key Programmes (five in total) including CHP and HFVs, among others. This article focuses on a selection of projects involving pgms, including MEA development, stack design, and the storage and purification of hydrogen.

2. Combined Heat and Power

Fuel cell based CHP systems have entered early commercialisation recently and are being deployed in thousands in Japan (Ene-Farm) and Europe (Ene.Field, Callux). In Japan, 34,000 units were installed at the end of 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).

HySA Systems, however, is focusing on HT-PEMFC based CHP systems in the range 1–2 kW_{el}, fuelled by natural gas. Although the electrical efficiency of HT-PEMFC is lower than that of LT-PEMFC, the overall efficiency (electricity + heat) is higher for HT-PEMFC based CHP systems. Moreover, HT-PEMFC can tolerate carbon monoxide poisoning better than LT-PEMFC and does not require a complex water management system, making HT-PEMFC ideal for CHP applications. 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 **Figure 1**.

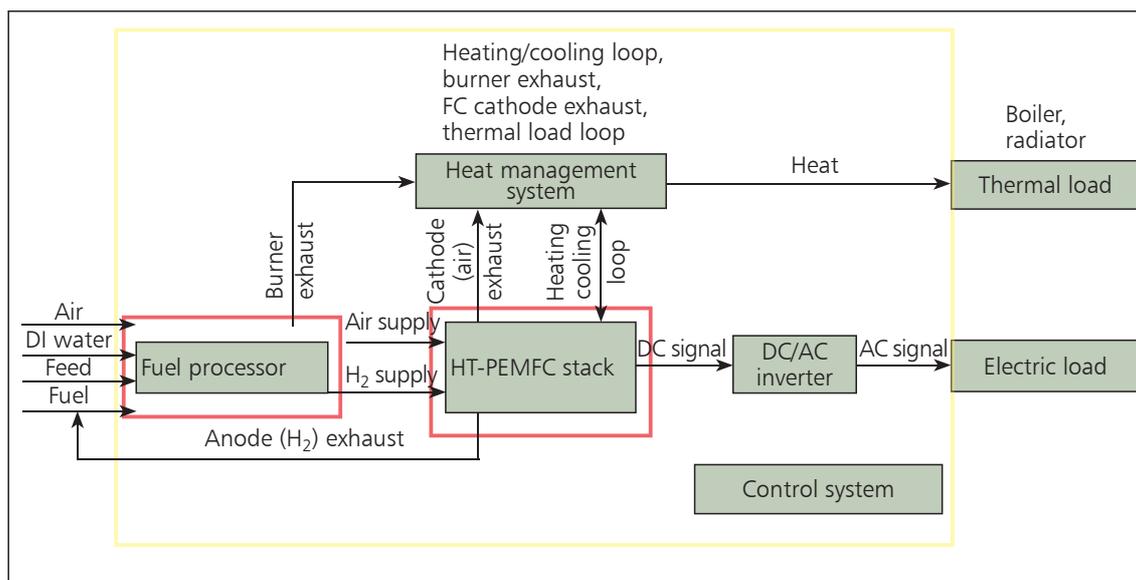


Fig. 1. Block diagram of the HT-PEMFC based CHP system

The red blocks show 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 test bench in collaboration with Zentrum für Sonnenenergie-und Wasserstoff-Forschung (ZSW, the German Centre for Solar Energy and Hydrogen Research), 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. Hydrogen Fuelled Vehicle

The scope of this HySA Key Programme is to develop and integrate systems and modules that can be used in niche fuel cell vehicles, based on HySA technologies. This includes on-board hydrogen storage (including metal hydrides), the fuel cell system (the fuel cell stack and its controller), power electronics and the 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.

4. Research and Development and Key Technologies

4.1 High Temperature Membrane Electrode Assembly

MEAs are the core of fuel cells and detailed understanding of the phenomena within the MEA is necessary to improve the durability and reduce the overall cost of the fuel cell. Although extensive research and development has already been carried out in LT-PEMFC MEAs, HT-MEA is relatively new. HT-PEMFCs are gaining momentum with the number of 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 PEM, 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 catalyst coated membrane (CCM) MEA preparation methods. This includes air assisted spraying, ultrasonic spraying and electrophoretic deposition (EPD).

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 (Figure 2).

The main reason for the performance was found to be the preparation conditions 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, Figure 3. 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 operation 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.

Focused efforts are also targeted at improving and optimising the GDEs. Various binders, proton conductors and acid controlling layers are currently being studied and the effect of the various binders on the performance of the MEA was investigated (4). Five different binders: Nafion[®], polybenzimidazole (PBI), polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF) and a PBI-PVDF blend, were studied

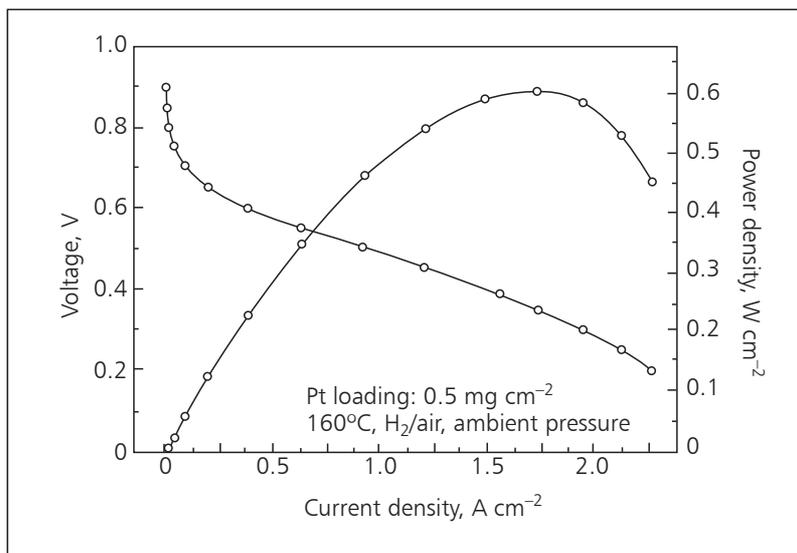


Fig. 2. Polarisation and power density curves of PA-doped AB-PBI fuel cell using GDEs prepared by the catalyst spraying under irradiation

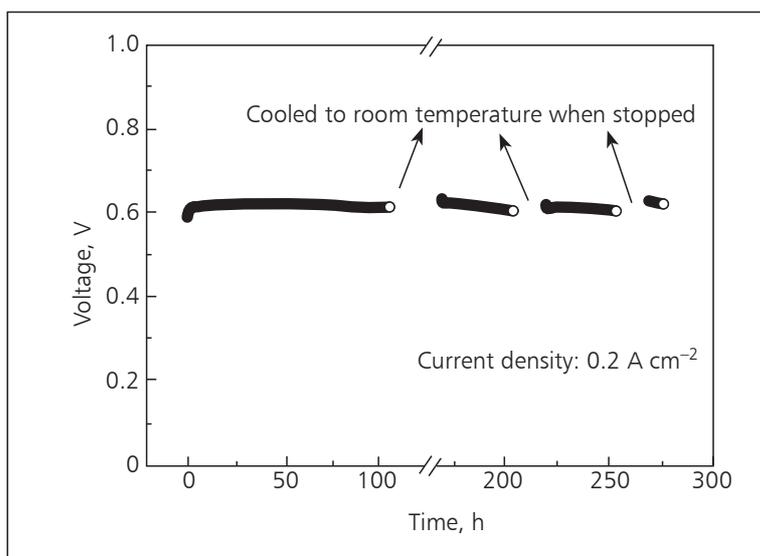


Fig. 3. Stability of the MEA at 160°C and 0.2 A cm⁻², H₂/air, ambient pressure

(Figure 4). As expected, Nafion[®] was found to be unsuitable for HT-MEAs, obviously due to its proton conductivity limitations at the operation 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 have also set up a pilot-scale MEA manufacturing line and the components and operation are currently being optimised.

4.2 High Temperature Proton Exchange Membrane 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 perfluorosulfonic acid (PFSA)-membrane based LTP-PEMFC technology. The developed materials and components exhibit performances that would allow commercialisation (6). The high operation temperature of HT-PEMFC at 150°C–180°C leads to some of the key advantages of the technology over LTP-PEMFC. The main advantage is tolerance to CO in the anode gas supply which enables supply with reformat gas without the need for a complex

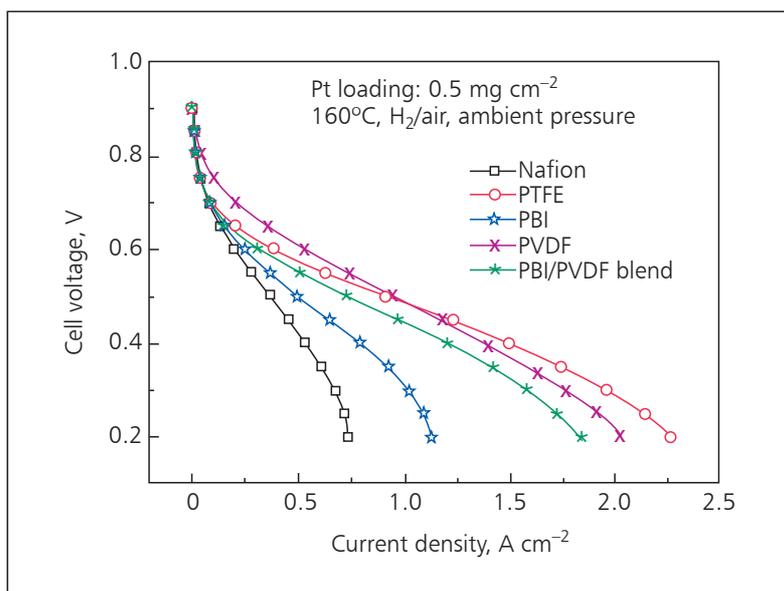


Fig. 4. Polarisation curves of the MEAs based on PB-doped AB-PBI with GDEs prepared with different binders

purification process. Tolerance of up to 5% CO in the anode supply gas was reported for a single HT-PEM cell (7). Secondly, the 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 on phosphoric 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 reformat fuel.

In the field of HT-PEM fuel cell technology HySA Systems focuses on R&D, technology development and applications. 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 Stack Development

Proper thermal management of the HT-PEMFC stack is a crucial issue. A 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 thermally conductive fluids have to be used. Externally oil-cooled stack design is one of the possible options for HT-PEMFC stack cooling that ensures a 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 the micrometre range. To meet all the requirements of stack component production, a high precision micro milling computer numerical control (CNC) machine, KERN Evo-765, is available at the HySA Systems laboratory together with a three-dimensional (3D) laser scanner, GOM ATOS II Triple Scan System. Together these are used for the manufacturing and quality validation of the stack components.

In 2012, a 96-cell 2 kW_{el} HT-PEMFC stack was manufactured in South Africa in HySA Systems labs (Figures 5(a) and 5(b)). The South African HT-PEMFC stack has been integrated within a CHP prototype breadboard system (Figure 5(c)) and tested. The test was performed at 160°C, atmospheric pressure, pure hydrogen and air conditions; the polarisation curve of the stack measured during the test is shown in Figure 5(d). A peak power of 2.2 kW_{el} was measured at 0.4 A cm⁻². Further testing includes operation on reformat and long term steady-state will be performed to validate the quality of the product. HySA

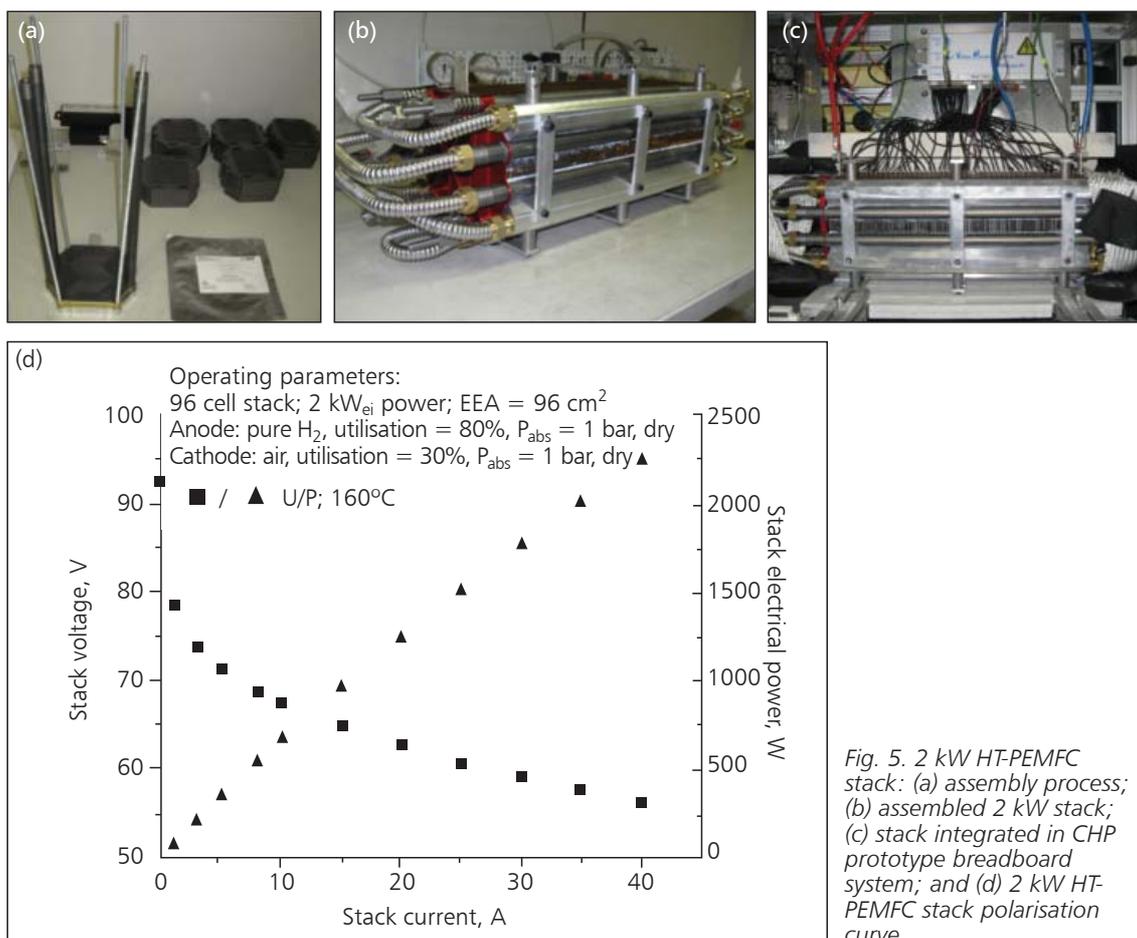


Fig. 5. 2 kW HT-PEMFC stack: (a) assembly process; (b) assembled 2 kW stack; (c) stack integrated in CHP prototype breadboard system; and (d) 2 kW HT-PEMFC stack polarisation curve

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 Stack Validation and Characterisation

The fuel cell stack is the key component of every fuel cell system, its performance, efficiency and lifetime depends strongly on operating conditions. At HySA Systems commercial and in-house built stacks are being tested and their performances are measured at a wide range of operating conditions. Testing and validation of HT-PEMFC stacks is performed with the aid of commercially available testing stations. The 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 in-house testing setups. The electrochemical impedance spectroscopy (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 a 150 W_{el} unit are very promising; for example, a current density of 0.78 A cm⁻² and almost 0.35 W cm⁻² were measured. A 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 vs. CO concentration. The highest stack performance was obtained at a power density of 225 mW cm⁻², at 160°C and at 0.4 A cm⁻² measured using pure hydrogen. The stack showed a reasonable CO tolerance of up to 0.5% CO at 160°C. A more detailed description of the 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 Stack Applications

The advantages of HT-PEMFC make the technology attractive for stationary applications. A very promising

area is natural gas supplied CHP systems in which the reformer is integrated as a fuel processor. To investigate the possibilities of HT-PEMFC applications in a CHP system, a 2 kW_{el} CHP prototype breadboard system designed in cooperation with ZSW has been installed and tested at HySA Systems (Figure 6).

The system has been validated at various operating conditions. Figure 7 shows an example of results obtained at different operating temperatures. The highest power density of 0.22 W cm⁻² was measured at 160°C, +0.5 V mean cell voltage and 0.45 A cm⁻². As can be observed, the operating temperature has a significant influence on the stack performance and the increase in temperature from 120°C to 160°C results in a power gain of almost 10%.



Fig. 6. 2 kW CHP system installed at HySA Systems laboratories

at high current densities at low temperature is not possible because the cell voltage drops below the safe operation level. The stack was also tested at different carbon dioxide concentrations and no significant decrease in performance was observed at CO₂ concentrations up to 20%. A thorough characterisation of the 2 kW CHP test-rig with CO and simulated reformat gas will be performed and a FLOX[®] reformer will be integrated.

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 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 MOFs. Note that all MOFs activities have recently been transferred to HySA Infrastructure since the financial year of 2013/2014.

4.3.1 Metal Hydrides

Hydrogen storage materials based on reversible metallic hydrides have found a number of promising applications in processes of considerable economic potential, such as hydrogen storage, separation and recovery, thermally-driven compressors, heat

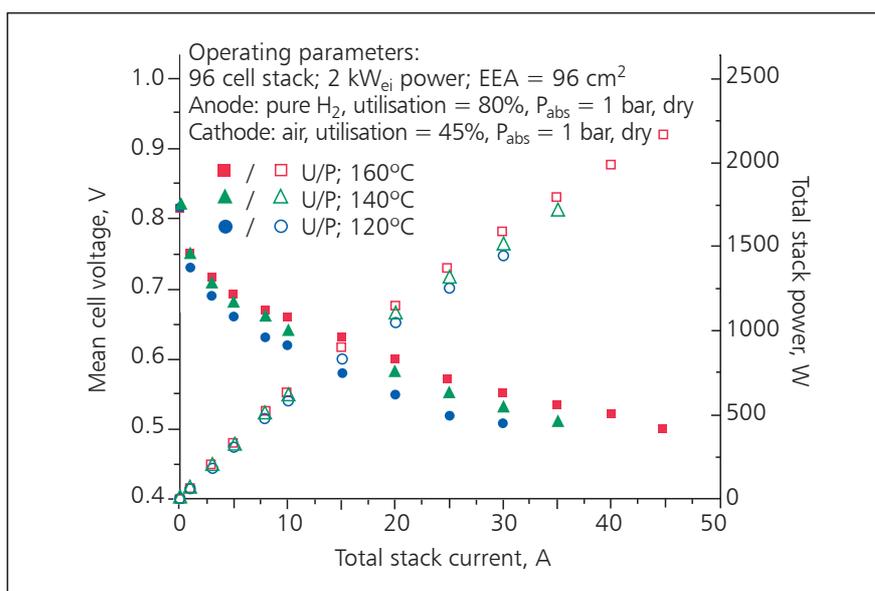


Fig. 7. Polarisation curves and power characteristics of the 2 kW HT-PEM stack installed in CHP test-rig system, recorded at temperature range 120°C–160°C

pumps and NiMH batteries (12, 13). Much of this work is on non-pgm systems utilising South Africa's rich mineral reserves and established mining infrastructure. However, the focus of the present article is on those applications involving the use of pgms. These include poisoning-tolerant surface modified metal hydride materials.

The selectivity of reversible hydrogen interaction with hydride-forming materials allows for the development of simple and efficient pressure or 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, $H_2 > 50\%$) which contain relatively innocuous admixtures, mainly nitrogen and argon (14). At the same time, the gases associated with processing coal, petrol, natural gas and other carbonaceous fossil fuel feedstock, in addition to hydrogen, may contain significant amounts of other components, mainly CO_2 and CO, which in most cases cause the deterioration of hydrogen sorption performances of metal hydrides (15). The poisoning tolerance of hydride-forming materials can be improved by modifying their surface. The existing surface modification methods use two approaches, the first of which is aimed at the improvement of surface catalytic activity while 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 (16).

Surface modification with a pgm such as Pd has been shown to significantly improve hydrogen sorption kinetics and poisoning tolerance. Pre-functionalisation of the metal hydride substrate with water-soluble aminosilanes facilitates the electroless deposition of pgm resulting in denser and more uniform coatings than conventional deposition techniques. 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 (16, 17).

AB_5 -type material surface modified by fluorination and Pd electroless deposition (18, 19) were found to have good poisoning tolerances (Figure 8), even for large (~1.5 kg) batches. The feasibility of their application for H_2 separation from gas mixtures (up to 30% CO_2 and 100 ppm CO) was demonstrated by testing a prototype H_2 separation system. The H_2 separation was characterised by stable performances during hundreds of absorption/desorption cycles (20, 21).

4.3.2 Metal Organic Frameworks

MOFs are crystalline coordination materials attractive for their microporous channels (<2 nm) and high specific surface areas (for example, $3500 \text{ m}^2 \text{ g}^{-1}$ for MOF-5), which can be significantly greater than that

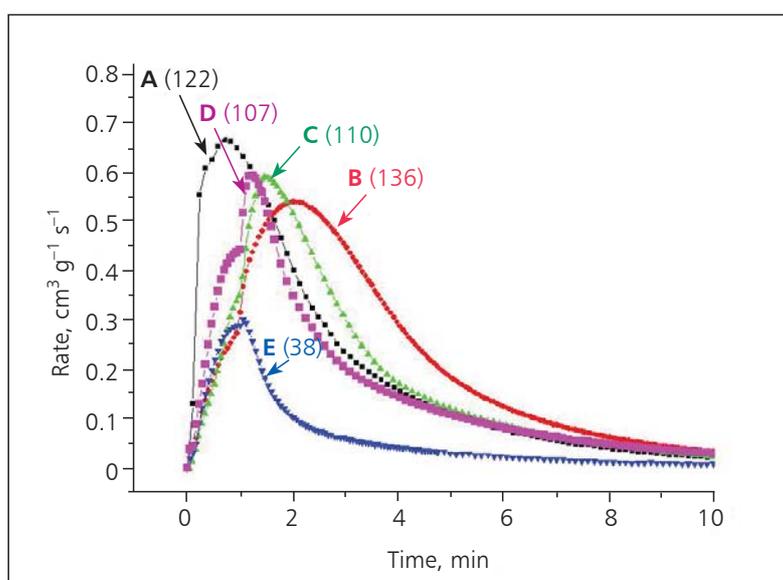


Fig. 8. Dynamics of hydrogen absorption by the surface-modified with palladium $La(Ni,Co,Al,Mn)_5$ alloy in running-flow mode at $T=20^\circ\text{C}$. The partial H_2 pressure and flow rate are 2 bar and 0.25 L min^{-1} , respectively. The values in brackets correspond to maximum hydrogen absorption capacity ($\text{cm}^3 \text{ g}^{-1} \text{ STP}$): **A** Pure H_2 ; **B** 25% H_2 + 10% CO_2 + N_2 (balance); **C** 25% H_2 + 10% CO_2 + 100 ppm CO + N_2 (balance) Cycle 1; **D** 25% H_2 + 10% CO_2 + 100 ppm CO + N_2 (balance) Cycle 16; **E** 25% H_2 + 28% CO_2 + 0.33% CO + N_2 (balance)

exhibited by zeolitic materials, and their subsequent high hydrogen storage capacities (22). They are constituted of divalent or trivalent metal ion centres connected by large organic linkers. A multitude of MOF structures exist, and 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 (23). The materials typically contain microporous networks, with microcavity diameters known to range from 10 Å–13 Å. The materials are typically prepared through a solvothermal route, in which the metal ion precursor and molecular ligand are incubated under mild thermal conditions. 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 (24). 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 (25). 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 consideration of the 'hydrogen spillover' phenomenon, which has the potential to increase room temperature hydrogen adsorption properties of adsorptive materials. Pt 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 (26). During the hydrogen spillover phenomenon, Pt catalytic particles cleave the bond in the dihydrogen (H₂) molecule leading to dissociation and generation of hydrogen 'atoms' (Figure 9). The H atoms then migrate to a substrate material where they can be used for various surface processes or spillover again to a secondary receptor (27). In these types of composite hydrogen storage materials, AC could be

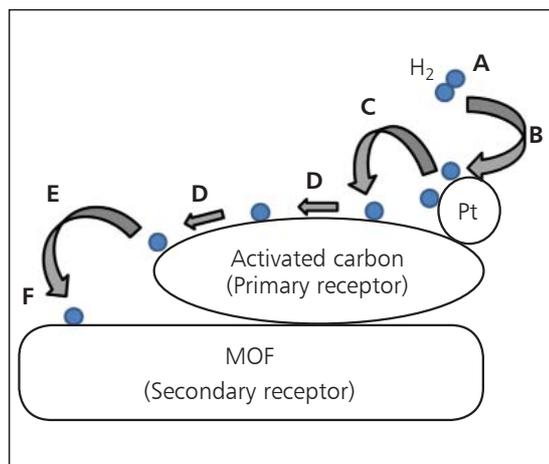


Fig. 9. Graphical representation of the hydrogen spillover process: **A** migration to the Pt catalyst; **B** dissociative chemisorption; **C** primary H spillover to the primary receptor; **D** surface diffusion; **E** secondary spillover to the secondary receptor; **F** surface adsorption and storage

considered a primary hydrogen atom receptor, after the dissociation of H₂ by the Pt nanoparticles, with the MOF as a secondary receptor eventually storing the H atoms in its microstructure (28).

The Pt-AC material can be prepared *via* a chemical reduction method or can 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 (for example, sucrose, fructose, glucose) and this has been demonstrated to significantly enhance hydrogen storage capacities (29). 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.

The catalytic particles can be deposited onto high-surface-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 introducing 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 (30). 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 non-uniform Pt/AC particle interconnectivities and inconsistent mixing of Pt/AC, sucrose and MOF particles. MOF activities are no longer within HySA Systems' Projects Portfolio since 2013.

4.4 Palladium-based Membrane for Hydrogen Purification

Roughly 96% of the global annual demand for H₂ is currently derived from fossil based fuels using reforming processes. The reformation reaction product stream is typically a mixture of H₂, CO, CO₂ and methane 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 of CO with steam (H₂O) into 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 of the LTWGS a pressure swing adsorption (PSA) system is needed to separate the H₂ from the CO₂ and traces of other gases. Needless to say, the CO conversion and gas purification cost greatly impact the cost of fuel cell grade H₂.

Continuous films of Pd material are known for their exceptionally high selectivity towards H₂. So called 'Pd membrane reactors' have these films applied in close proximity to 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 H₂ production yield. With the use of Pd-based 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 must 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.

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

- Membrane support synthesis. The support material forms the foundation for the membrane and needs to form a smooth surface that is 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 zirconium dioxide hollow fibre supports. The production system and SEM images of hollow fibres with the desired 'sponge like structure' are depicted in **Figure 10**.
- Investigation of the most effective seeding procedure of hollow fibres. Commonly applied seeding procedures are typically repeated ten times to form a sufficient number of seeds well distributed over the surface of

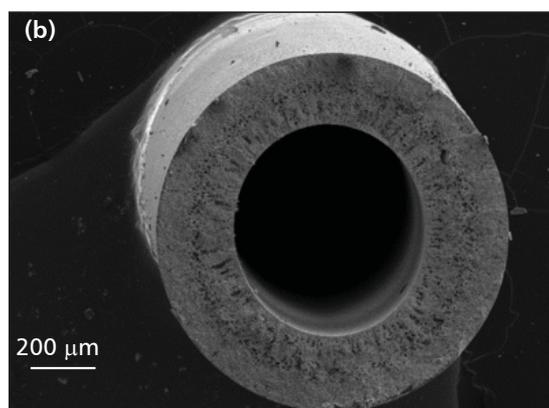


Fig. 10. (a) Photograph of the phase inversion setup developed to produce the hollow fibre support; (b) SEM image of a fibre showing the desired sponge like structure of the fibre outer area

the support. **Figure 11** shows that the seed formation has a great impact on the formation of the film.

- 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 ZrO_2 in a well dispersed manner, a coalescence film can be produced.

Results related to the membrane selectivity and permeance are currently being collected.

5. Publications and Patents

HySA Systems has been active in disseminating their work in high impact journals (**Figure 12**) and innovating. For example, since 2008 two major patents have been generated by the Centre (32, 33).

6. Conclusions

This limited review has only been able to cover the major steps in pgm beneficiation work – there is much other work that is outside the scope of the present Journal. Nevertheless it can be stated that HySA Systems is delivering successfully in all of its remitted areas. 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. In areas from CHP to HFV, developments in the HT-MEA technology and stack design are making progress towards allowing a simplified design of fuel cell systems especially suitable for small scale applications. Improved hydrogen storage and purification, based on pgm technologies, will also enable the cost of H_2 fuel to be reduced. Work is ongoing in all these areas.

Acknowledgements

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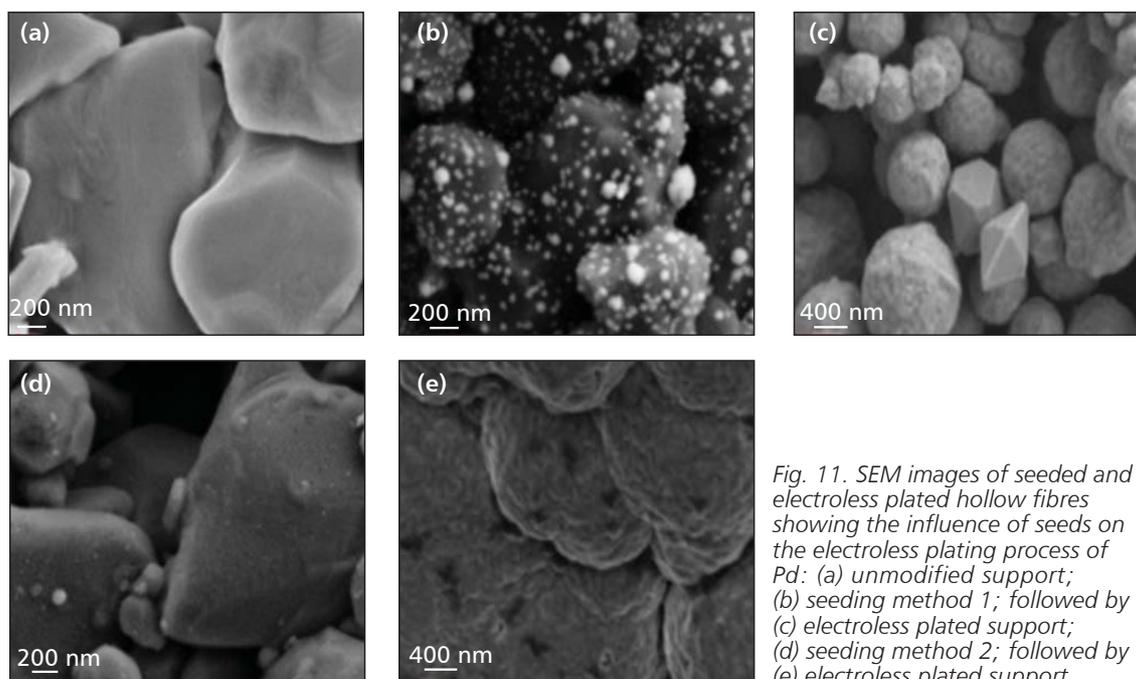


Fig. 11. SEM images of seeded and electroless plated hollow fibres showing the influence of seeds on the electroless plating process of Pd: (a) unmodified support; (b) seeding method 1; followed by (c) electroless plated support; (d) seeding method 2; followed by (e) electroless plated support

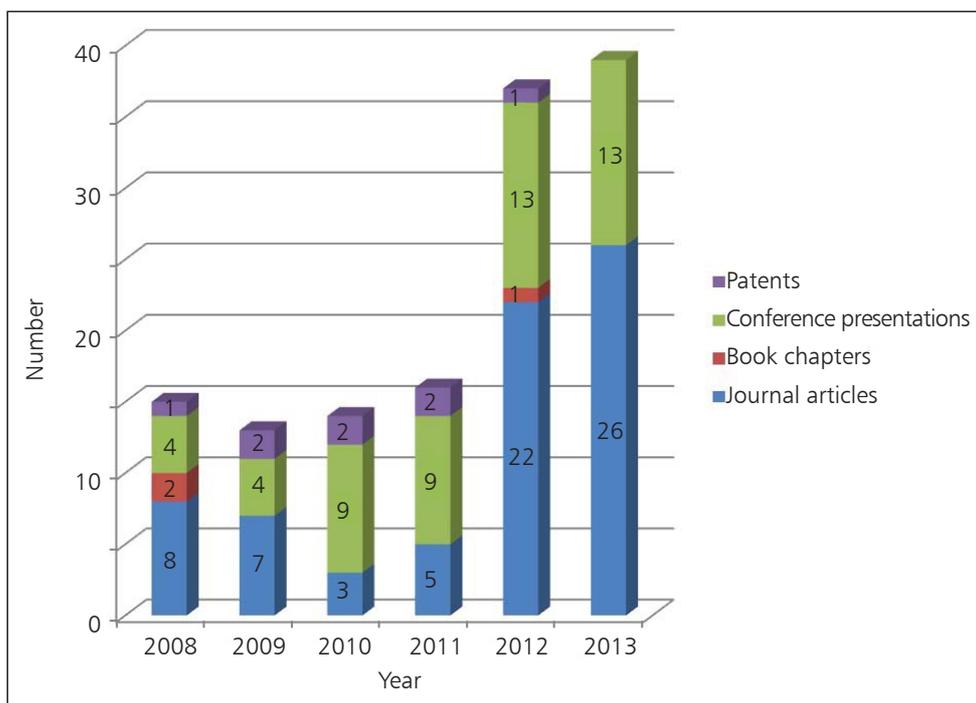


Fig. 12. Chart showing the number of publications per annum since the creation of HySA Systems in 2008

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References

- 1 The HySA Systems Integration & Technology Validation Competence Centre: <http://www.hysasystems.org/> (Accessed on 11th February 2014)
- 2 S. Barrett, 'HySA Infrastructure: Producing and Using Hydrogen for Energy in South Africa – Part 1', October 2013: <http://www.renewableenergyfocus.com/view/34110/hysa-infrastructure-producing-and-using-hydrogen-for-energy-in-south-africa-part-1/> (Accessed on 17th February 2014)
- 3 H. Su, S. Pasupathi, B. J. Bladergroen, V. Linkov and B. G. Pollet, *J. Power Sources*, 2013, **242**, 510
- 4 H. Su, S. Pasupathi, B. Bladergroen, V. Linkov and B. G. Pollet, *Int. J. Hydrogen Energy*, 2013, **38**, (26), 11370
- 5 C. Felix, T.-C. Jao, S. Pasupathi and B. G. Pollet, *J. Power Sources*, 2013, **243**, 40
- 6 T. J. Schmidt and J. Baurmeister, *J. Power Sources*, 2008, **176**, (2), 428
- 7 Q. Li, R. He, J.-A. Gao, J. O. Jensen and N. J. Bjerrum, *J. Electrochem. Soc.*, 2003, **150**, (12), A1599
- 8 C.-Y. Chen and W.-H. Lai, *J. Power Sources*, 2010, **195**, (21), 7152
- 9 J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Song, T. Navessin, Z. Shi, D. Song, H. Wang, D. P. Wilkinson, Z.-S. Liu and S. Holdcroft, *J. Power Sources*, 2006, **160**, (2), 872
- 10 J. Scholta, W. Zhang, L. Jörissen and W. Lehnert, *ECS Trans.*, 2008, **12**, 113
- 11 P. Bujlo, S. Pasupathi, Ø. Ulleberg, J. Scholta, M. V. Nomnqa, A. Rabiou and B. G. Pollet, *Int. J. Hydrogen Energy*, 2013, **38**, (23), 9847
- 12 G. Sandrock, 'Applications of Hydrides', in "Hydrogen Energy system: Production and Utilization of Hydrogen and Future Aspects", ed. Y. Yürüm, Kluwer, NATO Advanced Science Institutes Series, Springer Science+Business Media, Dordrecht, The Netherlands, 1995, pp. 253–280

- 13 P. Dantzer, *Mater. Sci. Eng.: A*, 2002, **329–331**, 313
- 14 M. Au, C. Chen, Z. Ye, T. Fang, J. Wu and O. Wang, *Int. J. Hydrogen Energy*, 1996, **21**, (1), 33
- 15 G. D. Sandrock and P. D. Goodell, *J. Less-Common Met.*, 1984, **104**, (1), 159
- 16 M. V. Lototsky, M. Williams, V. A. Yartys, Y. V. Klochko and V. M. Linkov, *J. Alloys Compd.*, 2011, **509**, (2), S555
- 17 M. Williams, M. V. Lototsky, A. N. Nechaev and V. M. Linkov, Eskom Holdings Ltd, 'Method of Surface Modification of Metallic Hydride Forming Materials', *US Patent* 8,354,552; 2013
- 18 M. Williams, M. V. Lototsky, A. N. Nechaev, V. M. Linkov, Eskom Holdings Ltd, 'Hydride-Forming Material', *South Africa Appl.* 2008/09123
- 19 M. Williams, M. V. Lototsky, V. M. Linkov, A. N. Nechaev, J. K. Solberg and V. A. Yartys, *Int. J. Energy Res.*, 2009, **33**, (13), 1171
- 20 M. Lototsky, K. D. Modibane, M. Williams, Y. Klochko, V. Linkov and B. G. Pollet, *J. Alloys Compd.*, 2013, **580**, (1), S382
- 21 K. D. Modibane, M. Williams, M. Lototsky, M. W. Davids, Y. Klochko and B. G. Pollet, *Int. J. Hydrogen Energy*, 2013, **38**, (23), 9800
- 22 F. Afsahi, H. Vinh-Thang, S. Mikhailenko and S. Kaliaguine, *J. Power Sources*, 2013, **239**, 415
- 23 J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 2005, **44**, (30), 4670
- 24 D. Saha and S. Deng, *Sci. Technol.*, 2010, **15**, (4), 363
- 25 R. M. Kumar, J. V. Sundar and V. Subramanian, *Int. J. Hydrogen Energy*, 2012, **37**, (21), 16070
- 26 Y. Li and R. T. Yang, *J. Am. Chem. Soc.*, 2006, **128**, (3), 726
- 27 A. D. Lueking and R. T. Yang, *Appl. Catal. A: Gen.*, 2004, **265**, (2), 259
- 28 Y. Li and R. T. Yang, *J. Am. Chem. Soc.*, 2006, **128**, (25), 8136
- 29 Y. Li, R. T. Yang, C.-j. Liu and Z. Wang, *Ind. Eng. Chem. Res.*, 2007, **46**, (24), 8277
- 30 N. R. Stuckert, L. Wang and R. T. Yang, *Langmuir*, 2010, **26**, (14), 11963
- 31 M. W. J. Luiten-Olieman, L. Winnubst, A. Nijmeijer, M. Wessling, N. E. Benes, *J. Membrane Sci.*, 2011, **370**, (1–2), 124
- 32 M. Lototsky and M. W. Davids, University of the Western Cape, 'Method for Preparing Hydride-Forming Alloys', *South Africa Appl.* 2011/03817
- 33 M. W. Davids, M. Lototsky, M. Williams, J. M. Sibanyoni, B. G. Pollet and V. M. Linkov, University of the Western Cape, 'Method for Preparation of Hydride Forming Material on the Basis of Nanostructured Magnesium Hydride', *South Africa Appl.* 2012/08851

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