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Metal Hydride Hydrogen Storage Units for LT PEMFC Power Systems

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Uninterrupted power systems (UPS) for telecommunication installation (mobile phone transmitting towers, internet backbone computing facilities, etc) has been identified as a niche market for hydrogen based low temperature proton exchange fuel cells (LT PEMFCs). Typical power requirements for telecom backup systems range from 1 - 10 kW for single small-scale installations [1] to 5-100kW for larger multipurpose installations [2]. 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 hours, and that the total annual duration of the operation is typically less than 300 hours per year [1]. Other fuel cell companies (e.g., Ballard) have demonstrated PEMFC stack lifetime up to 11,000 hours [3]. Hence, there seems to be a good business case for hydrogen based LT PEMFCs for UPS telecoms.

A national competence centre on Hydrogen & Fuel Cell Technology Systems (HySA Systems) has newly been established at the South African Institute for Advanced Materials Chemistry (SAIAMC), University of the Western Cape (www.saiamc.org). HySA Systems is part of a large and long-term (15-year) research, development and innovation programme, sponsored by the Department of Science and Technology in South Africa. The main objective with HySA Systems is to perform technology validation and system integration in three key areas relevant to hydrogen and fuel cell technologies: (1) Combined Heat and Power, (2) Portable Power, and (3) Hydrogen-fuelled Vehicles.

The HySA portable power programme includes several R&D projects related to the UPS telecom market, including a project entitled “Metal Hydride H_2-Storage for LT PEMFC Power Systems” (Project KP2-S01). The main objective with the project is to develop and manufacture MH-based hydrogen storage units in South Africa, and supply these units to local and international portable and small-scale stand alone power system markets. The specific goals in the project are to: (1) Develop a series of MH-storage units suitable for 0.5-5 kW portable and stand-alone power H_2-based LT PEMFC and (2) Integrate MH-storage units into power systems based on LT PEMFCs with fast start-up and efficient control at variable loads. Preliminary results from this project, which started up in 2009, are presented in this paper.

Storing hydrogen in the solid-state hydride form holds a volumetric advantage over (compressed) gaseous and liquid hydrogen. Solid hydrogen storage systems also have features of low-pressure operation, compactness, safety, delivery pressure, and scalability (modular design) [4]. Commercial MH companies (e.g. Texaco Ovonic Hydrogen Systems LLC) have successfully manufactured MH hydrogen storage systems for portable power applications [5,6]. These MH-systems, consisting of several MH-units, were capable of storing 320 g (~3.5 Nm^3) of hydrogen in total, which is sufficient to run a 1 kW PEM fuel cell for more than 240 minutes at full power. These pre-commercial MH-units showed no degradation after more than 500 charge/discharge cycles.

The work in this project focuses on the development and system integration of MH hydrogen storage units for PEMFC power systems to be operated below 120°C. Hence, the focus is on “low-temperature” AB_5- (A=rear earth; B=Ni, Co, Mn, Al), AB-alloys (A=Ti; B=Fe, Mn, V), or AB_2- (A=Ti, Zr; B=Mn, Cr, V) type of hydrogen storage materials, which are characterized by fast hydrogen absorption / desorption kinetics at moderate temperatures (10-100°C). In order to achieve fast start-up of the PEMFC and to minimize the power consumption during hydrogen supply (MH hydrogen discharge), the MH-unit must have a hydrogen equilibrium pressure (P_D) higher than the pressure of hydrogen to be supplied to the PEM fuel cell.

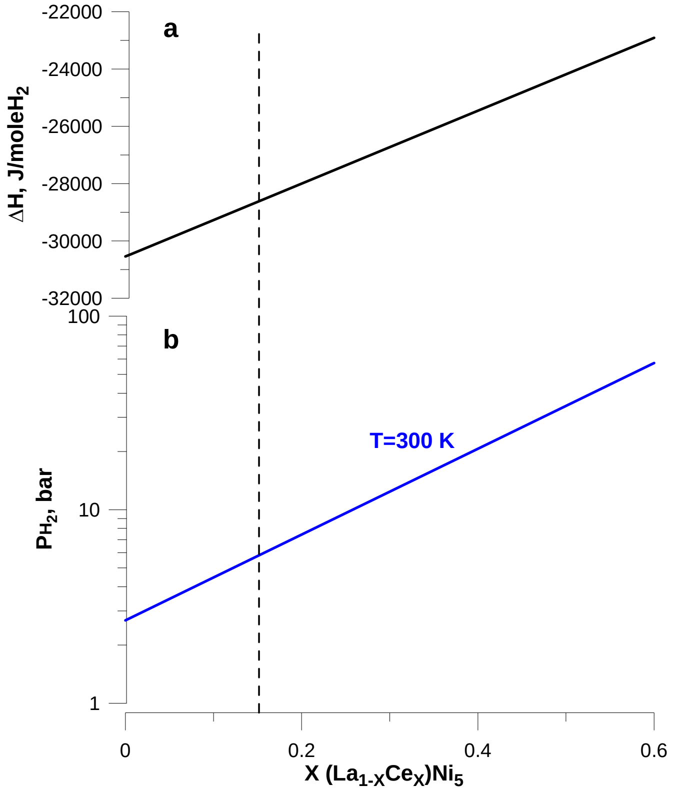

Figure 1: (a) Estimated enthalpies of hydride formation for cerium-substituted intermetallide $LaNi_5$ and (b) corresponding values of equilibrium hydrogen pressure at room temperature calculated assuming the entropy of the hydride formation equal to –110 J/(mole H_2·K).

An AB_5-type of material with a P_D = 5-10 bar (i.e. the required operating pressure for the hydrogen storage system) at room temperature was selected for the first phase of this project (other materials suitable for hydrogen storage pressures will be investigated in the next phase). AB_5-alloys are the most frequently used materials for MH-applications. Their main advantages are: low sensitivity to poisoning by impurities, easy activation, fast hydrogen absorption / desorption kinetics, and wide pressure range at near ambient temperatures [7]. Figure 1a shows our estimated values for formation enthalpies of the intermetallic hydrides $La_{1-x}Ce_xNi_5H_y$ based on available reference data [8], while Figure 1b show the corresponding calculation of hydrogen equilibrium pressures assuming ΔS^0= -110 J/(mole H_2·K). From this it can be deducted that the composition $La_{0.85}Ce_{0.15}Ni_5$ can give an equilibrium pressure at room temperature of about 5 bar, which satisfies the pressure requirements of the given application.

Two batches of 100 kg with a $La_{1-x}Ce_xNi_5$ alloy specified for the project were manufactured by two independently Chinese industrial companies. Results from characterization (XRD, SEM, TEM, H sorption) of the MH-materials showed that both batches had almost identical properties. Hence, the MH-material can be produced on a larger industrially scale, and is suitable for high volume production of MH-units for portable and/or stand-alone power LT PEMFC applications.

Figure 2 shows the XRD-patterns (Cu-K_α) of the delivered alloy and the product of its hydrogenation (Hydrogenation was carried out in a Sieverts setup at a H_2 pressure of 50 bar and room temperature, followed by stabilization of hydride phase by the exposition of the hydrogenated material on air at the liquid nitrogen temperature). The starting alloy contained a single AB_5-phase (space group $P6/mmm$, #191; a = 4.9919 Å, c = 3.9960 Å; V_0 = 86.236 Å^3; ρ_{calc} = 8.327 g/cm^3) (Figure 2a), while the product after hydrogenation was found to be a two-phase containing AB_5H_x hydride (70 vol.%) with increased unit cell volume (a = 5.3877 Å, c = 4.2617 Å; V = 107.133 Å^3; $\Delta V/V_0$=24.2%; ρ_{calc} = 6.703 g/cm^3), and α-solid solution $AB_5H_{\sim 0}$ (30 vol.%) (Figure 2b). The appearance of the α-phase is most probably caused by decomposition of the unstable β-hydride during carrying of the sample to the difractometer and XRD. Volumetric measurements of the pressure, composition, and temperature relationships (PCT) for the $La_{0.85}Ce_{0.15}Ni_5$ - hydrogen system were carried out at T = 0-80°C and P = 0.01-100 bar. Quite small hysteresis was observed (P_{ABS}/P_{DES}<1.2), so both absorption and desorption datasets were processed together. The experimental data was fitted using the model of phase equilibrium in metal – hydrogen systems [9]. Figure 3 and Table 1 summarize the results.

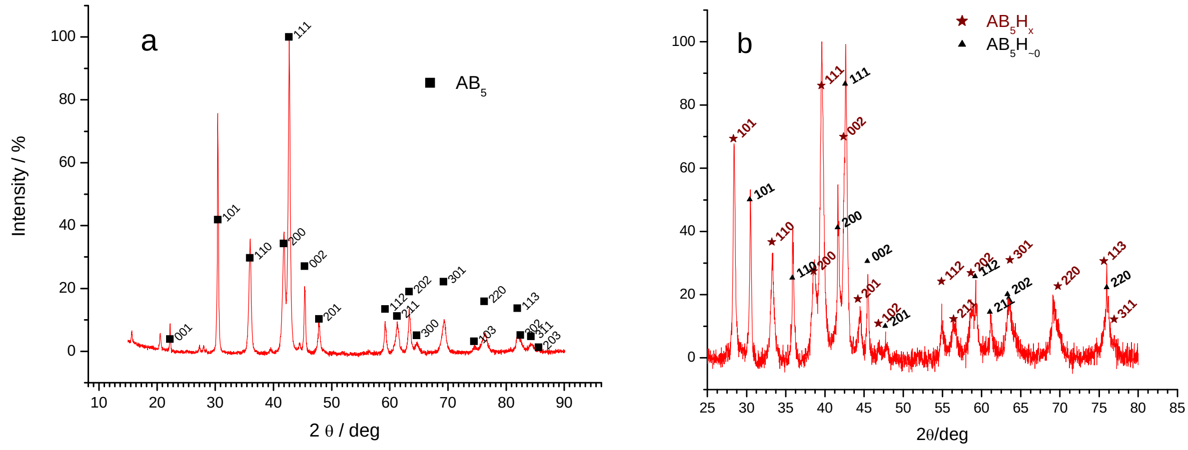

Figure 2: (a) Indexed XRD patterns of the as-delivered and (b) hydrogenated $La_{0.85}Ce_{0.15}Ni_5$ alloy.

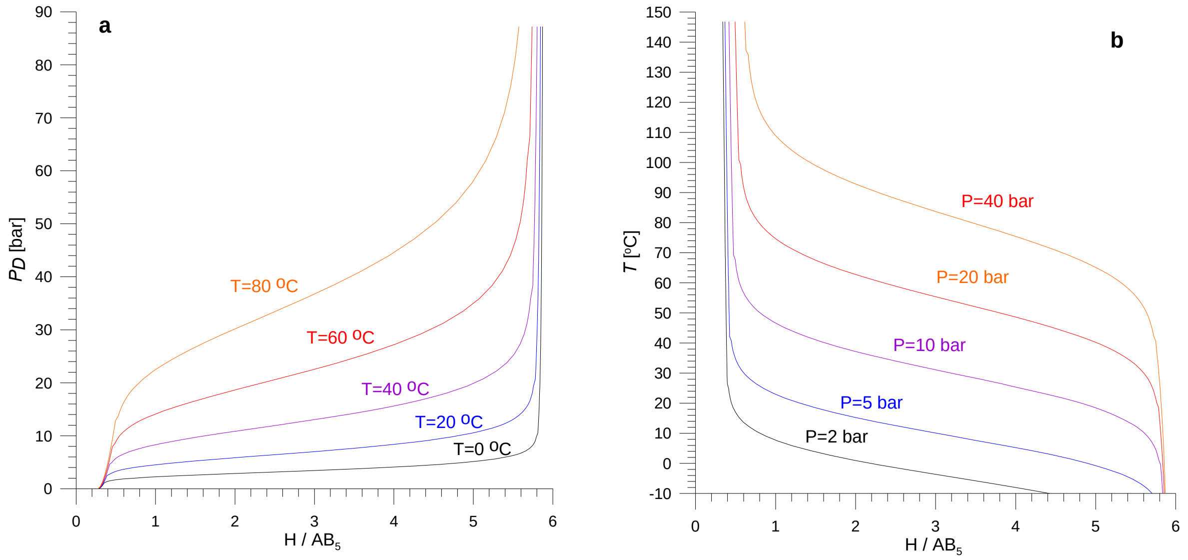

Figure 3: **(a) Calculated isotherms and (b) isobars of hydrogen sorption in $La_{0.85}Ce_{0.15}Ni_5$ alloy.**

Table 1: **Summary of calculated *PCT*-properties for the $La_{0.85}Ce_{0.15}Ni_5$ hydrogen storage alloy.**

Parameter	***T* = 20°C**	***T* = 40°C**	***T* = 60°C**
Plateau midpoint (C_0), H/AB_5	3.060	3.041	3.015
ΔS^0, J/moleH$_2$/K (C=C_0)	-96.61		
ΔH^0, kJ/moleH$_2$ (C=C_0)	-23.548		
d(Ln P)/d(H/ AB_5)	0.171	0.175	0.181
P (C =C_0), bar	7.09	13.14	22.62
C (P =1 bar), H/AB_5	0.34	0.33	0.33
C (P =20 bar), H/AB_5	5.76	5.02	2.35

From the above it can be deducted that the equilibrium hydrogen pressure (P_D) for the selected alloy (Table 1) is greater than 1 bar at temperatures T > 0°C. In practice, this means that the MH-unit will be able to supply sufficiently high hydrogen pressure to the LT PEMFC stack, as long as the MH-unit operates at T > 0°C. In an air cooled/heated MH-unit these operating conditions can be achieved by providing ambient heat or hot exhaust air from the PEMFC-stack. In a water cooled/heat MH-unit more direct heat exchange with the PEMFC-stack can be achieved, but this requires a water cooled PEMFC-stack. The reversible hydrogen capacity of the material at T=30°C and P=1-10 bar is higher than 5 H/AB_5, or 130 L H_2 STP per 1 kg of the alloy.

The dynamic behavior of the hydrogen absorption /desorption in the selected AB_5-material was studied in a 150 cm^3 cylindrical reactor equipped with four thermocouples for the measurement of radial temperature distribution in the middle of MH bed (Figure 4a). The reactor was filled with 600 g of the $La_{0.85}Ce_{0.15}Ni_5$ H storage alloy. The alloy showed reproducible H_2 absorption / desorption dynamics after completion of just one activation cycle: (1) initial evacuation, (2) 24-hours charging with H_2 at P=50 bar, (3) H_2 desorption at P=1 bar, and (4) final evacuation. All the operations were carried out at T=30°C. The evacuation was done using a rotary pump with a residual pressure of $5*10^{-2}$ bar. Both charge and discharge of the MH-reactor were carried out at constant pressures (1.5-5 bar for the desorption and 10-50 bar for the absorption); the unit was immersed in a thermostat (T=20-50°C). During the charge / discharge, hydrogen flow rate was logged, together with the temperatures in the centre of the MH-bed (T1), in between the centre and the wall of the reactor (T2), and on the inner (T3) and outer (T4) surfaces of the reactor wall.

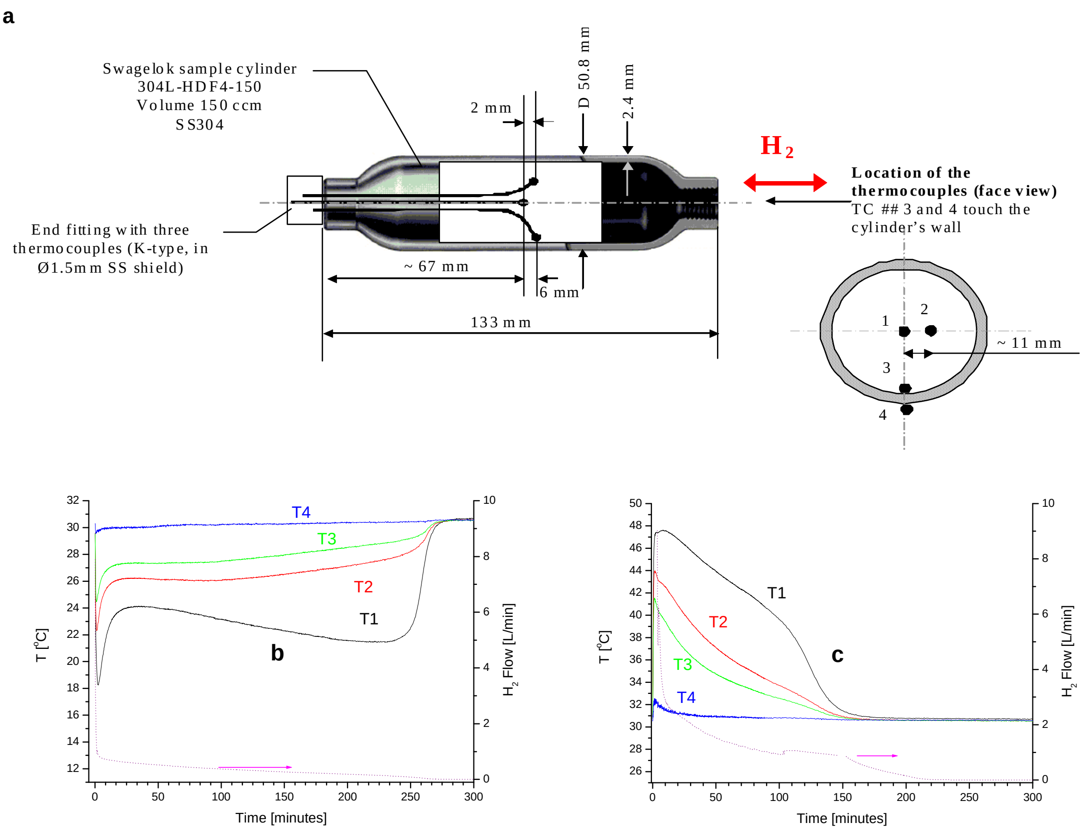

Figure 4: (a) Schematic of placement of thermocouples (1-4) in experimental MH-unit, (b) temperatures during desorption (*P*=2 bar, *T*= 30°C), and (c) temperatures during absorption (*P*=10 bar, *T*= 30°C).

Examples of the dynamic behavior of the MH-reactor are illustrated in Figure 4b (desorption, P=2 bar, T= 30°C) and Figure 4c (absorption, P=10 bar, T= 30°C). The heating/cooling of the MH-reactor during desorption (endothermic) and absorption (exothermic), which is limited by poor thermal conductivity in the MH-powder, significantly affects the hydrogen desorption/absorption flow rates. Initially, (first 2-3 minutes) the flow rates rapidly slow down from ~10 L H_2 (STP)/min to ~1 L/min during desorption, and 2.5 L/min during absorption. Over time the temperature approaches its initial value (thermostat setting), and the hydrogen flow rates slows down. The hydrogen desorption and absorption processes are fairly slow, ca. 5 and 2.5 hours respectively. The desorption is slower than the absorption due to a smaller difference between the operating pressure and the equilibrium pressure (driving force for both absorption and desorption), slower reaction rates, and a more complicated thermal behavior in the MH bed (as observed in the temperature profile in the centre of the MH bed (T1) Figure 4b). This is likely to be caused by exothermic re-absorption of hydrogen in the cold central region, resulting in the temporary temperature increase. Similar effects have been observed in other studies [10], where it was concluded that temperature gradients induce composition gradients within the hydride bed, making the local temperatures, composition or reactions rates very different from the average values.

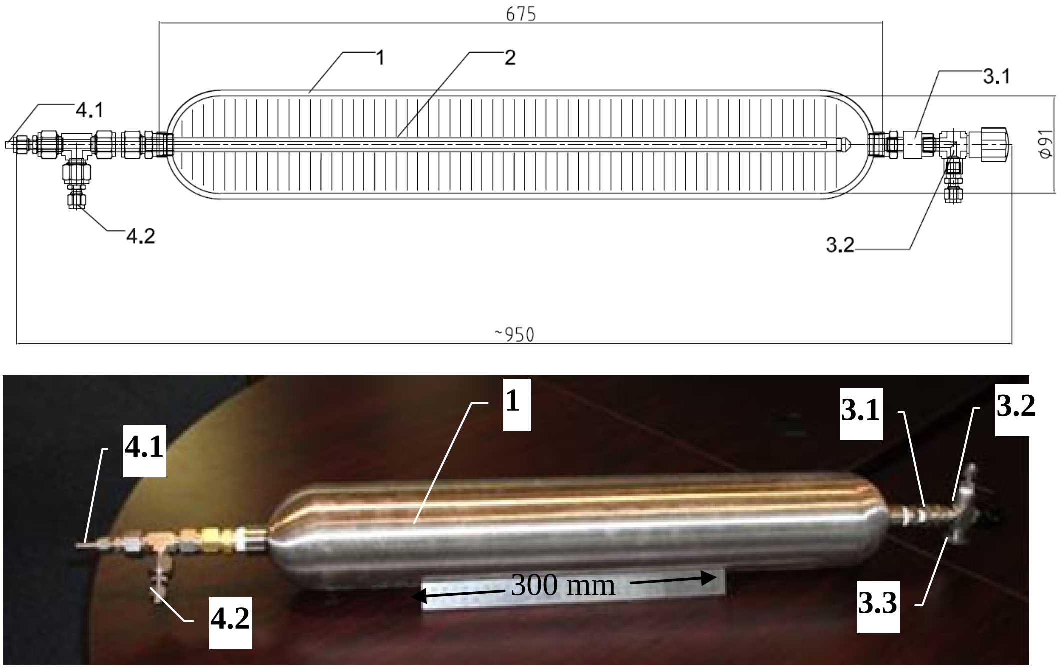

Figure 5: **Schematic drawing (top) and photo (bottom) of the MH hydrogen storage unit, where 1 = stainless steel container; 2 = heat exchanger; 3 = H_2 manifold: 3.1 = filter, 3.2 = valve, 3.3 = overpressure protection (rupture disc); 4 = water manifold: 4.1 = inlet, 4.2 = outlet.**

A prototype water-cooled MH hydrogen storage unit for a LT PEMFC application has been designed and developed (Figure 5) on the basis of the characterizations and heat and mass transfer analyses described above. The MH-unit (Figure 5) was assembled from standard components (Swagelok), except for the self-made heat exchanger (2) consisting of ½-inch OD copper tubing with copper fins (thickness 0.5 mm, pitch 10 mm). The supply of the heating/cooling water is provided via an internal ¼'-inch OD stainless steel tube connected to input pipeline (4.1) of the water manifold (4). Hydrogen charging of the MH-unit and hydrogen supply to the input pressure regulator of PEMFC-stack is provided via a hydrogen manifold (3) consisting of an in-line gas filter (3.1), shut-off valve (3.2), and a rupture disc with a burst pressure of 133 bar (3.3). The main part of the MH-unit is an one gallon (3.7 liter) Swagelok sample cylinder filled with 12 kg of $La_{0.85}Ce_{0.15}Ni_5$ H storage alloy. This gives a bulk density of the material of ca. 3.5 g/cm^3, or ca. 52% density of the material in the hydrogenated state, which is below the upper limit (61%) for safe packing of AB_5-type hydrides in MH containers [11]. The MH-unit, with a total weight of 22 kg, has a hydrogen storage capacity of 1560 liters with H_2 (STP), which can provide more than 2 hours of full-load operation of a 1 kW LT PEMFC-stack. Additional hydrogen storage capacity can simply be achieved by integrating several units in a modular hydrogen storage system. Detailed thermal modeling studies on the MH-unit are currently being performed by a research group at Tswhane University of Technology, a HySA Systems partner. The results from these studies will be used to re-design new and more efficient MH-units.

Acknowledgements

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