Abstract. Hydrogen storage in materials (hydrides) is challenging for vehicular applications, due to the large amounts of heat that must be removed in a short period of time during the filling process. It is proposed that rehydrogenation of the hydride instead is performed outside the vehicle, and linked to hydrogen production by water electrolysis at the filling station. The waste heat removed from the hydride during filling can be used to heat the electrolysis cell, increasing its efficiency. This solution can speed up the filling process, increase the efficiency of the hydrogen production, increase safety during filling, eliminate the need for massive transportation of hydrogen, and open the arena for many new hydrogen storage materials.

Keywords: Hydrogen storage; electrolysis; fuel cells; filling stations

1. Introduction

Hydrogen is commonly believed to become a major energy carrier, replacing fossil fuels in the energy system [1-5]. Hydrogen should then be produced from renewable energy sources, to ensure reduced emission of carbon dioxide [6]. Among the most important obstacles for the introduction of a hydrogen economy is the lack of a proper system for hydrogen storage, particularly for vehicular applications [7-10].

Storage of hydrogen in materials, e.g. in the form of metal hydrides, is often proposed for automotive use of hydrogen – then hydrogen is absorbed at interstitial sites in intermetallic compounds (interstitial hydrides) or is stored in complex metal hydrides via phase transitions [8, 11]. Both these options involve removal of heat when hydrogen is loaded, the amount of heat given by the hydrogenation enthalpy. However, there is still much to desire from this solution, and recharging of the storage tank has been identified as a particularly challenging task. If hydrogenation is to be done at moderate hydrogen pressure and temperature, the hydride formation enthalpy must be around -40 kJ/mol [11], which is heat that must be rejected during the recharging step. A typical target of the filling process is to recharge around 5 kg hydrogen during a few minutes, which implies that heat in the order of MW must be transferred during hydrogenation. To handle such large heat rates with on-board heat exchangers would be both expensive and space demanding [12], if possible at all.

Adding to the complexity, even to obtain a recharging speed in the order of kg H₂/min is a formidable challenge which is far from solved; this is particularly so for the complex hydrides, where complicated phase transitions inhibit rapid (de-)hydrogenation. Thus, the hydrogenation kinetics of most hydrogen storage materials with acceptable hydrogen density are far slower than what is required for rapid filling of a large tank. Distribution of hydrogen is another important technical challenge [13].
Distribution along city gas pipelines has been proposed as an option, but this kind of infrastructure is missing in many places. Also, hydrogen is notoriously difficult to contain, and many existing pipelines may not be adequate for hydrogen distribution. Another fundamental issue concerning metal hydrides is the high net energy consumption associated with their hydrogenation and dehydrogenation [14], which deteriorates the overall energy efficiency.

An alternative is instead to distribute the energy in the form of electricity. Hydrogen should then be produced locally at the filling station, using water electrolysis. One obvious advantage with such a scheme is the already existing infrastructure in the form of electricity grids [15], even if the capacity may have to be increased [16]. This is also versatile with regards to the energy source; the source can easily be changed without the need to replace any hydrogen production or distribution units. This has been used in several demonstration projects worldwide (e.g. Refs. [17, 18]), linked to hydrogen stored as liquid or at high pressure.

The efficiency of water electrolysis depends on the operating temperature, and it is a large advantage to operate at temperatures close to or even above the boiling point of water [19]. Solid oxide steam electrolysis is a particularly interesting option with very high potential [20-23]. There can thus be a need for significant amounts of heat and power at the hydrogen filling station, in order to increase efficiency of ordinary electrolysis or to achieve high temperatures needed for advanced electrolysis.

A previous study compared the efficiency and cost of production of hydrogen from natural gas centrally or distributed, as well as hydrogen stored in various ways [24]; it was found that central production and hydrogen storage in materials was the most energy efficient combination. Another study focused on exergy as the most important parameter to assess the different approaches [25]. Distributed production of hydrogen using small-scale reforming of methane was recently studied to evaluate the optimal investment strategy of hydrogen refuelling stations [26].

This paper suggests a new strategy, in which hydrogen is produced by electrolysis at hydrogen stations, and hydrogen is stored in materials. A detailed description of the concept is given in Sec. 2, along with potential advantages and requirements. A brief case study is then presented, to demonstrate the feasibility of the concept.

### 2. Description of the concept

The crucial point in making solid state storage of hydrogen viable for vehicular applications is to move the recharging step out of the vehicle. This has usually been associated with transportation of the vehicle tanks to a central processing unit where recharging is to be performed, which is inevitable for chemical hydrides and non-reversible metal hydrides like AlH$_3$ [27]. However, such a solution implies large challenges related to transportation and logistics of hydrogen storage tanks, and many of the participants in the field are reluctant to pursue this idea.

The alternative solution which will be advanced in this paper, however, is to recharge the hydrogen tanks locally at the filling station. This will reduce the need of tank transportation to a minimum, since the hydrogen tanks will be stored at the filling station during and after filling. Furthermore, this solution can be coupled with local production of hydrogen at the filling station, eliminating the need to transport hydrogen completely. The best way of producing hydrogen would then be by water electrolysis, using grid electricity (or local electricity sources) as the energy input. Since heat will be produced during hydrogenation of the tanks, high-temperature electrolysis should be used in order for this heat to be exploited; we will come back to the details of this later. An outline of the concept is shown in Fig. 1.
Fig. 1. Outline of an automated filling station for hydrogen fuelled vehicles with solid state hydrogen storage. An empty storage tank is automatically replaced by a filled one. Independently, filling of storage tanks is taking place in a hydrogenation unit. The hydrogenation unit is closely linked with an electrolysis unit, which produces hydrogen from water and electricity. The electrolysis unit makes use of heat from the hydrogenation process, which enhances efficiency. Any additional heat from the hydrogenation process can be used for other purposes.

This concept has many advantages over solutions traditionally proposed for hydrogen fuelled vehicles. One benefit is that recharging of the storage units may be done during night and low-peak periods, which opens for utilization of low-cost electricity from the grid [28]. Using electricity to transport energy is furthermore relatively simple to introduce, and in many cases the existing grid would be suitable at least during initial phases. Electricity also implies flexibility regarding the energy source, and is particularly suitable for renewable energy sources producing electricity. The concept is less suitable for fossil energy sources; production of hydrogen from fossil fuels should most probably be performed centrally in a single process, to avoid loss of efficiency and facilitate carbon sequestration.

A refuelling system involving removal and insertion of metal hydride tanks between vehicles and the filling station obviously imposes special requirements on both the vehicles, the filling station, and their interface. An integrated design with standardized solutions is crucial to achieve global implementation of the solution. A more detailed discussion of the advantages and requirements of the concept is presented in what follows.

Starting with the vehicle, the first and most important benefit is that refuelling may in principle be done during seconds, since only storage units need to be replaced at the filling station. This compares very favourably with other hydrogen storage systems; even refilling a tank with liquid hydrogen, which ideally is as fast as refuelling gasoline, takes longer time – in the order of a minute [29]. Filling a high-pressure hydrogen tank takes many minutes, especially if complete filling is to be achieved.
The filling time will be additionally increased if the pressure range is increased to 700 bars. The most dramatic speedup, however, is when compared to on-board refuelling of solid state hydrogen materials. Due to limitations of hydrogenation kinetics and heat management in material based hydrogen storage tanks, refuelling them can take significantly longer time than filling a high-pressure tank. Complex hydrides, which include the materials with highest gravimetric hydrogen density, exhibit particularly slow kinetics, which has led many to speculate that this problem may be the ultimate show-stopper for vehicular hydrogen storage in materials.

In order to facilitate efficient change of tanks, the tanks should have a universal design. Vehicles of different size could then contain a number of tanks corresponding to their size. This means that a method of switching from one tank to another as the hydrogen source in large vehicles during driving operation will be needed. It also means that all tanks should be easily accessed from the vehicle at the filling station, for efficient replacement of the tanks. A standardized placement of tanks (or rather, of their entrance channel) would further enable adequate design of the vehicle-filling station interface. Closely linked to this is the launching system for replacing the tanks. This should be automated, both since the tanks will be heavy, and to avoid risks associated with manual management. Also, a wireless communication system would most likely be needed for the interface to be efficient. This could assist in the alignment between vehicle and delivery system, and aid during the process of exchanging tanks. Such a communication system could serve additional roles, including automatic payment.

An automated system will also contribute to reducing the overall risk related to hydrogen as a fuel, since no manual handling is required. Adding to this, the concept implies that no highly pressurized hydrogen is needed during the refuelling process. This is particularly beneficial compared to on-board filling of gas tanks or material based tanks, where high-pressure hydrogen must be introduced all the way to the vehicle.

Management of heat in the order of MW involves large, heavy, and relatively expensive equipment. To have on-board rehydrogenation would mean that such heat management units were needed in every vehicle. When the process is moved to a central unit at the filling station, however, this dramatically reduces the need for the size of such an apparatus on-board the vehicle. The remaining requirement of the on-board heat management system is to provide sufficient dehydrogenation rates during driving operation.

Moving to the filling station, this will need to have at least three main parts in addition to the interface with the vehicle: a water electrolysis unit for hydrogen production, a hydrogenation unit filling tanks with hydrogen, and a storage unit for empty and filled tanks. All movement of tanks should be robotized. Furthermore, the electrolysis and hydrogenation units should be closely linked, allowing for precise management of heat and pressure, which can simultaneously optimize the conditions for hydrogen production and hydrogenation of tanks. Thus the overall energy consumption for hydrogen production and filling of tanks can be minimized.

To perform such an optimization, it is necessary to compare the amount of heat released during the hydrogenation step to that needed for high-temperature water electrolysis. We assume that the same amount of hydrogen is produced by electrolysis as is absorbed in the hydrogen storage material. The target of the hydrogenation enthalpy of the storage material (hydride) is often stated to be around -40 kJ/mol H₂ [11] or 20 MJ/kg H₂; this translates to an equilibrium pressure of around 1 bar at room temperature, and would be ideal for a fuel cell operating at or below 100 °C. It is instructive to compare this to the energy required for a high-temperature solid oxide electrolysis cell (SOEC). The enthalpy of heat for hydrogen gas at a typical temperature for a SOEC, 800 °C, is 123.8 MJ/kg H₂. Water electrolysis can at this temperature run with a cell voltage down to 1.1 eV, which corresponds to a theoretical electricity consumption of only 105.3 MJ/kg H₂. The deficiency of energy must be supplied in the form of heat; thus approximately 18.5 MJ/kg H₂ heat is needed to keep the reaction running at this temperature (thermoneutral condition). Taking losses of a few percent into account, this is exactly the amount of heat which is available from the hydrogenation reaction! Such a fortuitous coincidence seems to make the proposed concept particularly suitable also from a thermodynamic
point of view: all the heat energy from the hydrogenation reaction which otherwise would have been lost, could be directly utilized as energy input to the electrolysis process.

However, the temperature of the hydrogenation waste heat is considerably lower than 800 °C; we have required that it be around 300 K at atmospheric pressure. The equilibrium temperature can be increased by increasing the hydrogen pressure. This is governed by the van’t Hoff equation \( \ln(P_1/P_0) = -\Delta H / RT + \Delta S / R \), where \( R \) is the gas constant, \( P \) is the equilibrium pressure at a given temperature \( T \), and \( \Delta H \) and \( \Delta S \) are the enthalpies and entropies of hydrogenation, respectively. From this we see that the equilibrium temperature can fairly easily be increased to 100 °C by using a pressure of approximately 30 bar. However, to reach an equilibrium temperature of 800 °C, a hydrogen pressure of more than 100 kbar is necessary. This is clearly not feasible, and the output temperature of the hydrogenation unit will thus be lower than what would be required for a high-temperature SOEC.

Alternatively, a hydride with larger hydrogenation enthalpy could be used. If increasing (the absolute value of) \( \Delta H \) to -60 kJ/mol \( H_2 \), the equilibrium temperature is 177 °C at atmospheric pressure, which should provide enough heat to move into the regime of steam. It has been shown that operation at 230 °C can significantly increase efficiency \([30]\), a temperature that can be reached with a pressure of only 5 bar if \( \Delta H = -60 \text{ kJ/mol } H_2 \).

It is important that the working temperature and pressure of the hydride are also matched to the fuel cell onboard the vehicle; that is, the onboard fuel cell and the off-board electrolysis cell should operate at comparable temperatures. Even if PEM fuel cells are reckoned as most promising today, it is conceivable that fuel cells with higher temperature can be operable in the near future \([31]\).

It should be emphasized that this concept is also relevant for hydrogen fuelled vehicles running on internal combustion (IC) engines. The amount of waste heat from IC engines is significantly larger than that available from fuel cell vehicles, and the temperature is also higher. Thus, releasing hydrogen from a hydride storage tank by utilizing waste heat should be straightforward also in the case of IC hydrogen vehicles.

A change of the target for hydrogenation enthalpy to -60 kJ/mol \( H_2 \) could mean new possibilities for hydrogen storage in materials. Many of the lightest hydrides are too stable for use together with PEM fuel cells \([8]\), but could be much better suited to this concept. Also, the problem with poor hydrogenation kinetics is not so imperative when moving the hydrogenation out of the vehicle, since the time needed for recharging of a tank can be adapted to the particular hydride being used. In order to achieve the hydrogenation kinetics required for a typical filling station, the number of parallel hydrogenation units can simply be changed – we will come back to this in the case study of the next section. The number of useable hydrides can thus with this scheme be dramatically increased; the most important limitation will most probably be the kinetics of dehydrogenation in driving mode.

Since the waste heat from the hydrogenation reaction has too low temperature to be completely utilized by the electrolysis process, there will probably be a net excess heat from the filling station. This can represent either a problem or an advantage depending on the circumstances. The excess heat can improve the economy and efficiency of the filling station if used for applications in other areas like district heating, cogeneration, etc.

Another opportunity of improving economy lies in the produced oxygen. If this is utilized for e.g. medical use or other industry, the economic feasibility could be further enhanced \([32, 33]\).

Finally, since such filling stations will normally be grid connected, they can contribute with achieving peak power control of the electrical grid \([34]\), by reversing electrolysis to produce electricity when electricity demand and prices are high.

3. Case study

In order to illustrate the viability of the concept, a very simple case study will be presented in this section. It is emphasized that this is by no means meant to be realistic; its main purpose is to demonstrate that the magnitudes of the various system components can be well harmonized to each other.
A small to medium sized filling station is envisioned, with the ability to serve 120 vehicles per day, each vehicle filling 5 kg $\text{H}_2$. With a driving range of around 100 km/kg $\text{H}_2$, this translates to a petrol filling station serving the same number of vehicles with totally approximately 6000 litres of petrol or diesel per day (assuming an average driving range of 10 km/litre petrol or diesel). Averaged over the whole day this means that a continuous hydrogen production of 25 kg/h is required. Note that this is significantly less than the hydrogen flux needed for on-board filling of hydrogen, which must be in the order of kg/min if excessive filling time is to be avoided. This means that, even if only one tank is to be filled at a time, the hydrogenation kinetics can be considerably decreased compared to a system in which rehydrogenation must happen on board the vehicle. To further decrease kinetics requirements, or to scale up production, several tanks can be loaded in parallel.

As mentioned above, high-temperature electrolysis requires a specific power input in the order of 100 MJ/kg $\text{H}_2$. For the case study this means a continuous electricity consumption of slightly less than 1 MW for the production of hydrogen. It is relieving to see that this will be accessible many places using existing grid infrastructure; as an example, 20 kV electricity lines have capacities up to 10 MW. For large filling stations a higher voltage line would be needed, which can have capacities up to hundreds of MW or even the GW range.

When it comes to the hydrogenation unit, the amount and temperature of heat that must be removed depends on the hydride material which is chosen. For a material with $\Delta H = -40 \text{ kJ/mol } \text{H}_2$, the heat removal rate will in average be 140 kW for this test case. If the system is working at around 20 bar, the corresponding temperature will be around 100 °C. This changes to 210 kW at 280 °C if $\Delta H$ is changed to $-60 \text{ kJ/mol } \text{H}_2$, and 245 kW at 310 °C if $\Delta H = -70 \text{ kJ/mol } \text{H}_2$. Even the lowest of these rates is probably too high to be achievable in a single tank, and hydrogenation should most likely take place in several tanks in parallel. The rate of heat is too high to be fully exploited in the electrolysis process, and the excess heat will have to be either discarded or utilized e.g. as district heating.

4. Summary

It has been demonstrated how the challenge of hydrogen storage for transportation can be solved by using material based storage (hydrides) with rehydrogenation taking place off-board, at hydrogen filling stations. This should be combined with local production of hydrogen from water electrolysis, using waste heat from the hydrogenation process to increase the efficiency of electrolysis. In this way, energy is transported to the filling station as electricity, and no transport of hydrogen is necessary.

Challenges remain before this can be implemented in large scale; the most important are how to exchange the hydride tanks with the vehicle, and how to optimize the pressure and temperature needed during electrolysis and rehydrogenation. However, these are technical challenges that most likely can be solved. This is different from some of the problems still facing other proposed solutions to the storage problem, which are physical restrictions that possibly never can be solved: the poor volumetric density of gaseous hydrogen storage, large losses from boil-off associated with liquid hydrogen storage, as well as long filling times combined with excessive heat removal rates required by solid state hydrogen storage with on-board refuelling.

The advantages with the concept are many and profound: In addition to increasing the overall efficiency of hydrogen production and storage, it can significantly speed up the filling process, since only tanks are exchanged at the filling station. This also means that safety during filling is improved, and that transportation of hydrogen is virtually eliminated. Last, but not least, this could open the arena for many new hydrogen storage materials with high hydrogen density, possibly leading to a breakthrough in solid state storage of hydrogen. Implementation of the proposed concept may thus mean a major step towards successful introduction of hydrogen as a fuel for transportation.

References