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Towards an ammonia-mediated hydrogen economy?

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Abstract

Materialization of a hydrogen economy could provide a solution to significant global challenges. In particular, the possibility of improving the efficiency and simultaneously minimizing the environmental impact of energy conversion processes, together with the opportunity to reduce the dependency of fossil fuels, are main drivers for the currently increasing research and development efforts. However, significant technological breakthroughs are necessary for making a hydrogen economy feasible. In particular, it is necessary to develop appropriate hydrogen storage and transportation technologies. Recently, metal ammine salts were proposed as safe, reversible, high-density and low-cost hydrogen carriers. Here, we discuss how this development could provide a platform for using ammonia as a fuel for the hydrogen economy. We do that by comparing various possible hydrogen carriers with respect to energy and cost efficiency, infrastructure requirements, safety concerns and also environmental impact. Based on this, it appears that in several scenarios, the use of metal ammines offers significant new opportunities.

Keywords: Hydrogen; Ammonia; Desorption

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1. Introduction

The scientific and technological challenges associated with the development of a hydrogen economy continue to attract significant attention. Additionally, the commitment of governments and major industries to support and engage in these efforts also appears to increase. This resolve can be attributed mainly to increasing concerns about the future availability of fossil fuels and also to concerns about possible climate changes. The most significant virtues of a hydrogen economy are an improved energy efficiency due to the possibility of achieving a higher efficiency of fuel cell systems than of combustion engines, reduced environmental impact as the only by-product of fuel cell systems is clean water, and the possibility of finding a long-term energy solution since hydrogen can be produced both from fossil fuels, renewable resources and atomic energy. However, despite these considerable advantages of a hydrogen economy compared to the current fossil fuel economy, there are still significant challenges that must be overcome before this shift in energy paradigm can occur [1]. Fuel cell technology must be further improved to make cost competitive energy systems widely available and simultaneously an infrastructure for transporting and distributing hydrogen must be developed. In particular, for mobile systems, such as cars, the need for efficient hydrogen storage strategies is evident [2]. Even for stationary units it might prove advantageous to use a suitable hydrogen carrier rather than relying on distribution of hydrogen gas in pipes, since this will avoid massive infrastructure investments and eliminate the risk associated with distribution of hydrogen gas.

There are many requirements for the perfect hydrogen carrier. The optimal candidate should not be more expensive than hydrogen (for the same volumetric or gravimetric energy content), it should be safe, and also fully recyclable or otherwise available in inexhaustible amounts. Currently, most attention is focused on the use of metal hydrides, complex hydrides, methanol and ethanol as possible hydrogen storage media. However, none of these alternatives meet all requirements for the optimal hydrogen storage material. Thus, it appears that the preferred hydrogen storage solution will in the

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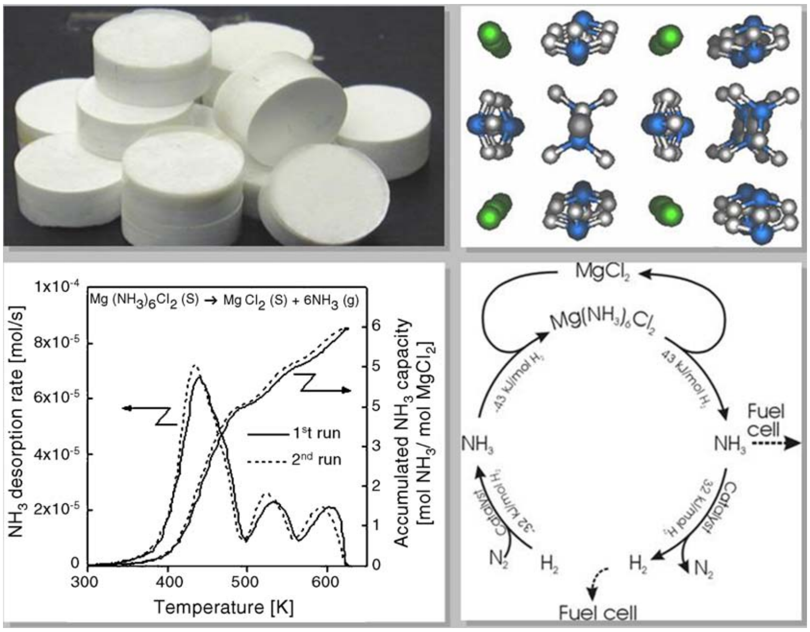

Fig. 1. Upper left panel: compact tablets of $Mg(NH_3)_6Cl_2$. Upper right panel: structure of $Mg(NH_3)_6Cl_2$ as deduced from DFT. Ammonia is coordinated to magnesium in an octahedral arrangement. Lower left panel: reversible absorption and desorption of ammonia. Lower right panel: integrated cycles for ammonia/hydrogen production and storage.

end present an acceptable compromise between the different desires. Recently, the use of metal ammines as possible hydrogen storage materials was proposed [3]. Fig. 1 briefly summarizes key aspects of this new concept for hydrogen storage. Rather than storing hydrogen, it was suggested to store ammonia in the form of metal ammine complexes such as $Mg(NH_3)_6Cl_2$. Hexaamminemagnesium chloride is formed simply by passing ammonia over anhydrous magnesium chloride at room temperature and the absorption and desorption of ammonia is completely reversible. Once ammonia is released from the salt it can easily be converted into hydrogen and nitrogen by an ammonia decomposition catalyst, which can be integrated within the ammine salt container.

Importantly, $Mg(NH_3)_6Cl_2$ can be shaped into completely compact bodies essentially without any void space. Thus, the integrated solid metal ammine salt/ammonia decomposition reactor provides a compact, high-density hydrogen storage solution since the ammine salt itself has a gravimetric hydrogen content above 9 wt.% and a volumetric hydrogen content of approximately 105–110 kg H_2/m^3.

In this paper, we compare this new concept for hydrogen storage with some of the currently most promising alternatives. We briefly consider the energy and cost efficiencies, infrastructure requirements, safety concerns and also the environmental impact.

2. Ammonia as a hydrogen source

There are two main reasons for trying to find useful hydrogen carriers instead of simply fuelling the hydrogen society via an infrastructure based on pressurized hydrogen distributed in pipes. These two reasons are safety concerns and energy density considerations. Additionally, the investments required to build the necessary hydrogen infrastructure for such a scenario also seems prohibitive. The fact that hydrogen is very volatile and difficult to contain combined with its very low flash point, its tendency to explode in air, and the fact that hydrogen fires are invisible present severe difficulties for storing and transporting energy in the form of hydrogen. Furthermore, the volumetric energy content of pressurized hydrogen is too low to make it useful in mobile units, such as cars [2]. Even liquefied hydrogen only has a volumetric energy content which is about 1/3 of that of gasoline, and this is not actually an option due to the high-energy consumption required for hydrogen liquefaction [2]. In addition, even a well-insulated liquid hydrogen container (−253 °C) has a continuous boil-off, which makes medium to long-term storage difficult. Thus, it is clear that a hydrogen carrier is needed and also that there are many considerations involved in selecting the appropriate hydrogen carrier(s).

In many respects, ammonia could be considered the perfect hydrogen carrier, since it is already:

- produced at essentially the same cost as hydrogen;
- available in larger quantities than any other pure chemical;
- distributed through an existing, world-wide infrastructure.

These properties are of course, a result of the extended global use of ammonia as fertilizer [4]. An additional key property of ammonia is that it can be easily decomposed into hydrogen and nitrogen. This fact has led to several proposals for using ammonia as a fuel for the hydrogen economy [5,6]. As a hydrogen carrier, ammonia could even be CO_2-neutral if appropriate sequestration strategies were implemented at the central production facilities. Interestingly, similar considerations have already formed basis for a proposal for an ammonia economy [7] in which fossil fuels are replaced directly by ammonia in combustion engines.

Ammonia has one important drawback as a preferred energy carrier, namely the fact that it is toxic. So far, this toxicity has prohibited most serious considerations of its extended use as a fuel both in combustion engines and for fuel cells. It is this difficulty that is addressed through the use of metal ammines for hydrogen storage.

3. Direct and indirect hydrogen storage solutions

Hydrogen storage technologies can be categorized as being either direct hydrogen storage or indirect hydrogen storage solutions. In this categorization, the direct hydrogen storage technologies involve compounds that liberate hydrogen directly when they are heated and/or the pressure is lowered. Metal hydrides and particularly complex hydrides appear to be the currently most promising candidates [2]. The indirect hydrogen storage solutions involve compounds that require one or more separate chemical transformations to produce pure hydrogen from the storage compound. The most studied indirect hydrogen storage solutions include steam reforming of hydrocarbons or methanol, hydrolysis of (complex) hydrides, and decomposition of ammonia.

At first sight, the direct hydrogen storage solutions appear to be particularly attractive since only absorption/adsorption and desorption processes are involved. Particularly, for low-temperature fuel cells, the use of a direct hydrogen storage solution is advantageous. However, all currently known direct hydrogen storage materials fall short of the US Department of Energy targets for gravimetric hydrogen density [1,2]. Actually, it is not at all clear that it will prove possible to find a widely available and inexpensive material that features completely reversible storage of hydrogen with the required density and which, at the same time, allows hydrogen desorption at a sufficiently low temperature without also causing an unacceptably high hydrogen pressure at ambient conditions. Additionally, the hydrogen storage material must have sufficiently fast desorption kinetics at the relevant temperatures. Typically, for currently known materials, the solid-state diffusion of atomic hydrogen in the storage material and desorption of molecular hydrogen from the surface of the storage materials is too slow to reach acceptable hydrogen production rates. To circumvent this difficulty, a catalyst is occasionally added to the storage material and the storage material is transformed into nanosized particles, e.g. by high-energy ball-milling [2]. However, with the latter solution it should be noted that this will introduce significant void space and consequently an even further lowering of the volumetric hydrogen storage density in real systems. Furthermore, nanoparticles tend to sinter towards more compact structures after many cycles. As a final complication, it should be noted that many direct hydrogen storage materials spontaneously ignite when exposed to the ambient air or explode when brought into contact with water.

For the indirect hydrogen storage solutions, it is an obvious drawback that they all inherently require at least one further chemical transformation to produce the hydrogen fuel. On the other hand, these solutions often provide significantly higher energy storage densities than those currently possible with the direct hydrogen storage materials. Examples of possible indirect hydrogen carriers are hydrocarbons, methanol, ethanol and ammonia. For fuel cell systems that do not require essentially pure hydrogen, the indirect hydrogen storage solutions actually appear to be preferable in many cases. Specifically, the solid oxide fuel cell is able to operate directly, e.g. on a methanol, methane or ammonia feed, and this has distinct advantages. First of all, the heat required for the endothermic reforming or decomposition reactions to produce hydrogen is supplied directly from the waste heat of the fuel cell and, at the same time, this helps cooling the cell and thus extends its life-time. However, for low temperature fuel cells, such as the proton exchange membrane fuel cell, the requirement for almost completely CO-free hydrogen necessitates the introduction of a CO clean-up system if the hydrogen is produced by steam reforming of carbon-containing feeds [8]. Thus, among the possible indirect hydrogen storage solutions, all seem to have their advantages and disadvantages, particularly with respect to their applicability with low temperature fuel cells. In Table 1, it is attempted to rank the most promising alternatives according to a few selected key parameters.

In connection with a low temperature fuel cell system, it is highly undesirable to conduct reforming of the fuel at an excessively high temperature and consequently hydrocarbons are not attractive hydrogen carriers for this purpose. Ethanol, which has many appealing features as a hydrogen carrier especially with respect to toxicity and renewability, is available only by expensive fermentation of carbohydrates and therefore this does also not appear to be a viable solution at the moment. However, both methanol and ammonia could be useful hydrogen carriers and it has been shown that they offer very comparable overall efficiencies [9]. The main objection to the widespread use of these is related to the toxicity of the two compounds. So far, mostly methanol has attracted attention to the point that a methanol economy has been proposed [10]. However, ammonia could also be an attractive source of hydrogen since the purification, which amounts to adsorption of unconverted ammonia, is quite simple compared to that required for methanol. Furthermore, use of ammonia as a hydrogen carrier could, as mentioned, lead to a CO_2-neutral energy supply. On the other hand, it is also clear that handling of liquid ammonia involves significantly higher hazards than the handling of methanol.

Table 1
Applicability of various indirect hydrogen storage solutions for use with low temperature fuel cells

Compound	Cost	Reforming temperature	Purification needed
Hydrocarbons	Low	High	Moderate
Methanol	Moderate	Low	Moderate
Ethanol	High	Moderate	Moderate
Ammonia	Moderate	Low	Low

Fig. 2. Tablets of hexaamminemagnesium chloride (featuring the logo of the Technical University of Denmark) can be handled conveniently in the palm of a hand. Each pellet is approximately 1 cm^3 in size, contains ~0.62 g NH_3 and correspondingly 0.11 g of pure hydrogen. The hydrogen content is roughly 1.3 l gaseous H_2 (STP). This corresponds to a virtual hydrogen pressure of about 1300 bar in the tablets.

Fig. 3. Upper left: original tablet of $Mg(NH_3)_6Cl_2$ prior to ammonia desorption. Lower left: tablet broken into half before ammonia desorption. Upper right: original tablet of $Mg(NH_3)_6Cl_2$ after to ammonia desorption. Lower left: tablet broken into half after ammonia desorption. The slight coloring of the tablet after desorption is due to impurities introduced from the sample holder.

4. Metal ammines versus methanol for hydrogen storage

Metal ammines are solid salts, in which ammonia is coordinated to a metal ion. Numerous metal ammines are known. So far, only hexaamminemagnesium chloride has been considered in some detail as an indirect hydrogen carrier [3,11] since it has both high gravimetric and volumetric hydrogen content. Furthermore, it is prepared from magnesium chloride, which is abundant, inexpensive, binds ammonia reversibly, and can be considered complete safe. Additionally, hexaamminemagnesium chloride can be compacted into a dense material, which holds approximately 615 kg NH_3/m^3, or 110 kg H_2/m^3, almost the same volumetric ammonia content as that of liquid ammonia. Due to a much lower ammonia pressure (~2 mbar) and release rate at room temperature, it is actually possible to handle this material safely at ambient conditions in the palm of a hand as shown in Fig. 2.

Since metal ammine salts are solids, it could be expected that the compacted tablets would suffer from some of the same drawbacks as the direct hydrogen storage materials, specifically the slow desorption kinetics. In other words, is it possible to desorb ammonia through distances of several centimeter solid storage material? It turns out that upon desorption of ammonia from the shaped, dense hexaamminemagnesium chloride materials, a nanoporous structure is created while the material maintains its original shape [11] as shown in Fig. 3.

During desorption, the material gradually becomes more porous, which could be pictured as a shrinking-core of saturated material that gradually is reduced as the desorption front progresses. However, the process is slightly more complicated since diammines, monoammines, and pure $MgCl_2$ form. Furthermore, it is noteworthy that by physically separating the hydrogen storage material from the hydrogen generation, it is simpler to efficiently catalyze the hydrogen formation. This difference between direct and indirect hydrogen storage solutions is illustrated in Fig. 4.

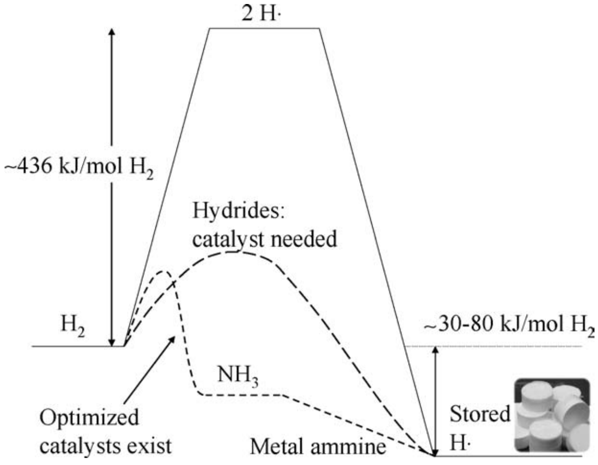

Fig. 4. A schematic energy diagram for direct and indirect hydrogen storage. Storage in hydrides or complex hydrides requires dissociation of the stable H–H bond, i.e. for all practical purposes a catalyst is needed. Using metal ammine complexes for indirect storage, the dissociation or formation of hydrogen does not take place in the storage container/material, but on a highly optimized catalyst: the ammonia synthesis or decomposition catalyst.

Table 2
Comparison of the safety of storing hydrogen as methanol, liquid ammonia and ammonia as metal ammine

	Vapor pressure, $p_{i,293\ K}$ (bar)	IDLH (NIOSH)[a] (ppm)	Relative volatility $p_{i,293\ K}$/IDLH
Methanol	0.13	6000	21.6
Liquid ammonia	~8	300	$\sim 2.7 \times 10^4$
Ammonia $[Mg(NH_3)_6Cl_2]$	1.4×10^{-3}		4.65
Ammonia $[Ni(NH_3)_6Cl_2]$	2.0×10^{-4}		0.68

The volatility is compared with concentration levels, which are dangerous to life or health.

[a] NIOSH immediately dangerous to life or health concentration.

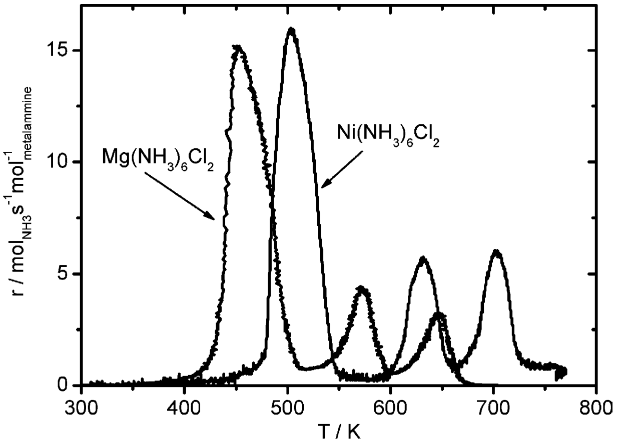

Fig. 5. Temperature programmed desorption of ammonia from $Mg(NH_3)_6Cl_2$ and $Ni(NH_3)_6Cl_2$. Both ammine salts reversibly binds six ammonia molecules. Ni binds ammonia stronger than magnesium. This lowers the vapor pressure of ammonia but also necessitates higher desorption temperature.

Activation of the stable hydrogen bond for the formation of atomic hydrogen—as is needed for direct storage in hydrides—requires a catalyst at the metal hydride surface in order to achieve reasonable kinetics [2]. By using the ammine-approach, storage of hydrogen is, as already mentioned, done in two steps: first by ‘‘activating’’ hydrogen over an ammonia synthesis catalyst and subsequently by storing ammonia safely in a metal ammine. The generation of hydrogen is achieved by desorbing ammonia and leading it through a small catalytic cracker, which should be placed close to or even inside the storage container. Both the hydrogen activation (ammonia synthesis) and hydrogen generation (ammonia decomposition) are well-known catalytic systems. In fact, it has been shown that the same catalyst is not optimal for both ammonia synthesis and decomposition [12].

It was argued above that methanol and ammonia are almost equally useful indirect hydrogen storage materials based on cost and efficiency. In terms of the needs for hydrogen purification for use with low temperature fuel cells, ammonia seemed to offer some advantages, which, however, are more than counterbalanced by the hazards associated with its handling. In the metal ammines, ammonia is coordinated to the metal ion and consequently the vapor pressure of ammonia is significantly lowered. Thus, it is highly interesting to make a simple comparison of the safety of metal ammines and methanol. Table 2 shows the vapor pressure of methanol and ammonia over liquid ammonia and two different hexaammines at room temperature and relates this to the concentration, which is considered to be immediately dangerous to life or health.

From the table, it is clear that binding ammonia in metal ammines dramatically lowers the risks associated with handling liquid ammonia—especially considering that the compacted metal ammines tablets contain essentially the same amount of ammonia per unit volume. Particularly, for hexaamminemagnesium chloride it is striking that the safety risk is comparable to that of methanol. Additionally, it is clear from Table 2 that it is possible to further lower the ammonia vapor pressure over the hexaammine salt simply by choosing a different metal ion that binds ammonia more strongly—here shown by substituting magnesium by nickel. As illustrated in Fig. 5, such a salt will obviously require a higher desorption temperature. With $Ni(NH_3)_6Cl_2$ it is clear that a somewhat lower gravimetric hydrogen content results (7.7 wt.%) but the volumetric hydrogen content is almost unchanged. Thus, selection of the appropriate metal ammine salt could easily represent a compromise between efficiency and safety.

5. Conclusion

Recently, metal ammine salts were proposed as safe, reversible, high-density and low-cost hydrogen carriers [3]. Here, we have argued that this concept could build on all the well-known benefits of using ammonia as the hydrogen carrier, i.e. low cost, wide availability, existing infrastructure, limited need for hydrogen purification, and the possibility of producing CO_2-neutral energy. Most importantly, the use of metal ammines simultaneously minimizes the hazards associated with ammonia. It is clear that implementation of a hydrogen economy will require numerous special safety precautions no matter which hydrogen carrier is used. Obviously, safe storage containers will also be required in any application. We have indicated that by use of metal ammines, the safety of an ammonia economy relying on a fuel cell for procuring electricity could be comparable or even better than what is possible for methanol with regard to toxicity. Accordingly, the new concept for hydrogen storage based on metal ammines appears to hold significant promise and warrants further investigations. It would be particularly useful if improved ammonia decomposition catalysts, designed for the relevant reaction conditions [13], were developed.

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