Ammonia for hydrogen storage: challenges and opportunities†

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Received 2nd January 2008, Accepted 13th March 2008
First published as an Advance Article on the web 3rd April 2008
DOI: 10.1039/b720020j

The possibility of using ammonia as a hydrogen carrier is discussed. Compared to other hydrogen storage materials, ammonia has the advantages of a high hydrogen density, a well-developed technology for synthesis and distribution, and easy catalytic decomposition. Compared to hydrocarbons and alcohols, it has the advantage that there is no CO₂ emission at the end user. The drawbacks are mainly the toxicity of liquid ammonia and the problems related to trace amounts of ammonia in the hydrogen after decomposition. Storage of ammonia in metal ammine salts is discussed, and it is shown that this maintains the high volumetric hydrogen density while alleviating the problems of handling the ammonia. Some of the remaining challenges for research in ammonia as a hydrogen carrier are outlined.

Introduction

There are significant challenges related to the production, distribution and storage of hydrogen as a significant energy carrier of the future.¹ The requirements of the transportation sector have received particular attention, as outlined in the FreedomCAR 2015 system targets:² high reversible storage capacity (3 kWh kg⁻¹ or 9 wt.% hydrogen and 2.7 kWh L⁻¹ or 0.081 (kg H₂) L⁻¹ system), fast kinetics (0.02 (g H₂) s⁻¹ kW⁻¹), good reversibility (1500 cycles), ambient operating temperature (−40 to 60 °C), low cost ($2 kWh⁻¹ or $67 (kg H₂)⁻¹), high hydrogen purity (<1 ppm CO) and safety (applicable standards).

Among these required properties, research efforts have primarily been focused on finding materials that feature the highest potential hydrogen storage capacity. Meeting this target alone is a significant challenge, which is accentuated by the fact that up to half the storage capacity by weight is often lost in the system integration.³ The search for ultra-high capacity materials has led to the synthesis and characterization of more and more exotic and reactive compounds: complex metal hydrides like NaAlH₄,⁴ LiAlH₄,⁵ and AlH₃,⁶ metal organic frameworks (MOFs),⁷ borohydrides like LiBH₄,⁸,⁹ and Mg(BH₄)₂,¹⁰ destabilized borohydrides,¹¹ ammonia borane¹² and amide/imide systems.¹³ All display high potential storage capacities, but fall short on a number of the other targets. Currently, complex metal hydrides do not reach the target for reversible hydrogen storage capacity, MOFs require operational temperatures around liquid nitrogen (−196 °C), systems based on borohydrides are practically irreversible and suffer from relatively slow kinetics,¹⁴ production and regeneration of ammonia borane is very costly,¹⁵ and the amide/imide systems have low reversible capacity.

Among hydrogen’s main competitors as an energy carrier, methane/natural gas and methanol offer clear advantages in terms of energy capacity and distribution infrastructure, but suffer from their intrinsic carbon content causing end-user CO₂ emissions, since onboard capture is not feasible. Furthermore, the IEA (International Energy Agency) recently projected that a gap between production and demand of natural gas may occur.

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† This paper is part of a Journal of Materials Chemistry theme issue on hydrogen storage and generation. Guest editor: John Irvine.
As soon as 2010–2012, effectively rendering this solution short term and environmentally non-sustainable.

Aside from hydrogen, ammonia provides the only carbon-free chemical energy carrier solution for the transportation sector. Ammonia is not a greenhouse gas (GHG), and in light of the enormous global climate challenges with respect to GHG outlined, e.g., in the Kyoto protocol, combined with a high hydrogen density, NH₃ could be an interesting alternative to hydrogen.

Ammonia is primarily produced from natural gas, but a large number of coal-based ammonia plants are currently being put into production, an aspect which is particularly important for countries like China, with a rapidly expanding need for transportation, limited oil and gas resources, but enormous coal reserves. A highly developed ammonia infrastructure is already in existence, and with a centralized, coal-based production of ammonia with simultaneous sequestration of the produced CO₂, ammonia could offer not only a short term solution to needs of the transportation sector, but a long-term, zero-carbon-emission solution with a projected lifespan of 200 years. Still, ammonia is often disregarded as a potential fuel in the transportation sector, primarily because of its too high toxicity, but recent research on reversible NH₃ storage in metal amines (see Fig. 1), e.g., Mg(NH₃)₆Cl₂ and Ca(NH₃)₈Cl₂, illustrates how a toxicity lower than that of gasoline can be obtained, while maintaining a practical, reversible storage capacity of up to 10 wt.% hydrogen.

For use in polymer electrolyte membrane fuel cells (PEMFC), ammonia must first be decomposed into nitrogen and hydrogen, but NH₃ can be decomposed catalytically at temperatures above 300 °C (Fig. 1) with present-day catalysts. This is, however, an area of active research and the development of superior decomposition catalysts remains a worthwhile challenge for an ammonia-powered transportation sector.

In the following, we review the status, challenges, and perspectives of ammonia stored in metal amines as a carrier material in the transportation sector, and place the results in the context of state-of-the-art in hydrogen storage materials and existing transport fuels.

**Ammonia synthesis**

The use of ammonia as an energy carrier has several advantages. One of these is that most of the technologies for production and transportation are well developed and already in widespread use on an industrial scale. The synthesis of ammonia in the Haber–Bosch process is among the largest and best studied chemical processes in the world. The annual production of ammonia (mainly for agricultural use) exceeds 120 million tons. The synthesis reaction is performed under 200–350 bar pressure over a multi-promoted iron catalyst operated at temperatures from 300 to 550 °C in a reactor with two to four catalyst beds giving around 15% conversion to ammonia. The unconverted synthesis gas is recycled. The hydrogen for the synthesis process is primarily produced from methane by steam reforming and water gas shift reactions. Although ammonia synthesis is an exothermic reaction (Fig. 1), the practical production of ammonia from hydrogen and nitrogen incurs a small energy loss of $1.5 \text{ GJ t}^{-1}$ compared to the $28.4 \text{ GJ t}^{-1}$ energy stored in the ammonia. In comparison, the production of hydrogen has an energy cost of $8.0 \text{ GJ t}^{-1}$. Hydrogen production is necessary for all proposed hydrogen-based energy carriers, but in the case of ammonia, this can also come from other sources than methane. The current price of ammonia is in the range of $225–300 \text{ t}^{-1}$, the equivalent of $1.4–1.7 (\text{kg H}_2)^{-1}$. This price is mainly governed by the price of methane that constitutes above 75% of the running cost of ammonia production.

Ammonia production is a prime candidate for CO₂ sequestration, because CO₂ is being removed from the synthesis gas by scrubbing to avoid deactivation of the ammonia synthesis catalyst. Furthermore, ammonia plants are typically located close to natural gas reservoirs, where the captured CO₂ might be pumped back.

The hydrogen for ammonia synthesis can also be produced from coal by gasification. Coal is interesting for hydrogen production for several reasons; first of all, coal is cheap compared to other hydrocarbon energy sources, secondly, the coal reserves are large enough to last for at least 200 years, and finally, coal can be efficiently converted into hydrogen by gasification with a high efficiency. Thus, even though an intense search for alternatives to coal is continuously on-going, the end result could be that we will need to exhaust all the available coal reserves.

**Ammonia safety**

The risk of explosion is an essential safety concern in the transportation sector, which can block the potential use of any energy carrier. High capacity carriers are generally very reactive, but significant differences can be observed in the flammability and explosion limits (see Table 1).

From Table 1, it is clear that hydrogen is very flammable, as are natural gas/methane, methanol, and gasoline vapors, whereas ammonia is not flammable in air. With respect to explosion limits, both hydrogen and ammonia require significantly higher concentrations than gasoline vapor and natural gas.

The toxicity of ammonia is clearly also an important safety aspect. Comparing the toxicity of liquid ammonia to that of gasoline and methanol, liquid ammonia is approximately three orders of magnitude higher in “apparent toxicity”, i.e. the vapor pressure relative to the toxicity, at room temperature. The apparent toxicities takes both the IDLH (Immediately Dangerous to Life or Health) concentration and the vapor

![Fig. 1](The life-cycle of hydrogen stored as ammonia in metal amines, M(NH₃)ₓX₂.)
pressure into account, since substances with a low vapor pressure can have a low IDLH concentration and still rate safer than a substance with higher IDLH concentration but higher vapor pressure.

For ammonia stored in metal ammines, e.g. Mg(NH3)6Cl2, the apparent toxicity falls below those of both gasoline and methanol; in comparison, the promising and intensely studied borohydrides22 are known to display partial release of highly flammable and toxic diborane during hydrogen desorption.38,39 Safety issues remain a main challenge for using ammonia in the transportation sector, but the considerations outlined above are in line with a recent EU-funded report, which concluded that “the use of ammonia as a transport fuel wouldn’t cause more risks than currently used fuels”.40

### Storage and transportation of ammonia

The infrastructure for handling and transporting bulk ammonia is already well established. Liquid ammonia is being transported around the world in ships, pipelines, trains and trucks.25,41,42 The transportation of liquid ammonia in closed systems to decentralized sites for production and regeneration of metal ammine salts can minimize the overall cost and be scaled up while maintaining safety, but some additional steps need to be taken to minimize the risks involved.40 For automotive applications, the end user should therefore not come in contact with liquid ammonia, only the metal ammines produced and regenerated at a nearby location.

As outlined above, the toxicity and vapor pressure of liquid ammonia make it undesirable for direct use in mobile applications, mainly because of the potential risk of accidents where ammonia is released and because of the technical challenges of securing the end user against contact with liquid ammonia during refilling and while performing periodic maintenance.25,42

The storage of ammonia is currently done in two different ways: for large quantities up to 50 000 t, ammonia is stored at 1 bar and −33 °C in insulated tanks. The temperature is kept down by slow vaporization, and the ammonia vapor is continually compressed back to a liquid. For small tanks, below 1500 t, ammonia is stored under pressure in stainless steel spheres.29

### Ammonia and fuel cells

The direct use of ammonia in high temperature solid oxide fuel cells (SOFC) has been shown to work with a performance similar to pure hydrogen43,44—in fact, even surpassing it at temperatures above 200 °C.45 The SOFC can also run on other fuels like methanol or methane, but these fuels need to be reformed and this gives a possibility of carbon poisoning of the anode.46,47 The carbon oxide-free ammonia can be fed directly into a high temperature SOFC and the endothermic ammonia decomposition reaction will help cool the SOFC, which combined with an entropy gain means that ammonia as a direct fuel increases the fuel cell performance at high temperatures.45

In low temperature fuel cell systems, such as polymer electrolyte membrane (PEMFC) and alkaline fuel cells (AFC), ammonia needs to be decomposed to hydrogen and nitrogen before it is fed to the fuel cell. In some applications, it might be desirable to remove the inert nitrogen to supply a concentrated hydrogen stream. This can be done, e.g., by use of a hydrogen-selective membrane system.48,49 The ammonia decomposition is done catalytically over a suitable catalyst at temperatures from ca. 300 to 520 °C (see below). The ammonia decomposition reaction is equilibrium-limited, so unconverted ammonia must be taken properly into account when the fuel cell system is designed. If the system operates with an AFC, ammonia is tolerated and can be recycled to the decomposition unit.50 For proton-conducting fuel cells such as PEMFC and PAFC (phosphoric acid fuel cell), ammonia is problematic since the acidic electrolyte reacts with ammonia and thereby deactivates. This means that for continuous operation, the ammonia concentration must be below 1 ppm.51

### Ammonia decomposition

The ammonia decomposition reaction has traditionally been studied to gain more information about the ammonia synthesis catalyst.52 This is slowly changing as ammonia is gradually becoming more widely accepted as one of the more promising hydrogen carriers.53 At present, the commercially used catalyst for ammonia decomposition is nickel on alumina,54 which is mechanically strong and heat resistant, but further development and optimization are needed.

During the last ten years, different research groups have developed and optimized catalysts specifically for use in ammonia decomposition for production of CO2-free hydrogen.55–57 There now exists a general consensus that cesium-promoted ruthenium supported on graphite is the best known catalyst.58,59 Several studies have shown that barium is also a useful promoter for ammonia decomposition on ruthenium surfaces.60

The currently best promoted ruthenium catalysts are sufficiently active at temperatures from about 300 °C. In Fig. 2, two different studies of the decomposition rate of ammonia are shown. The first is a study by Rároˇg-Pilecka et al.,58 which shows...
the decomposition rate in a conventional reactor at various ammonia concentrations and at a fixed temperature of 400 °C. The second study shows the rate of ammonia decomposition as a function of temperature, at a constant inlet gas concentration of 20% ammonia in argon and for a constant flow rate. These experiments were performed in micro-fabricated reactors, which feature excellent heat transport to the endothermic reaction.

The challenge with low temperature ammonia decomposition is that the equilibrium conversion is dependent on the temperature and the reaction is endothermic, i.e. the concentration of ammonia at equilibrium increases with decreasing temperature. At 425 °C and 1 bar pressure, the equilibrium conversion of ammonia is 98–99%, which makes unconverted ammonia a significant challenge for the overall system efficiency if the temperature is lowered with a conventional reactor design. Furthermore, the decomposition rate decreases significantly when equilibrium is approached according to the general formula

\[ r = r^0(1 - \beta) \]

where \( \beta \) describes the approach to equilibrium as a factor between 0 and 1. To avoid the equilibrium limitation, removal of the hydrogen through a membrane is an option, which would provide a pure hydrogen feed, free of ammonia and nitrogen, and it will help to increase the conversion by shifting the equilibrium further towards complete conversion.

### Solid storage of ammonia

The idea of using ammonia as a hydrogen carrier has been promoted by the further development of safe storage of ammonia in solid form by binding it in metal ammine complexes. A large number of metal salts are known to form stable metal ammines, and these are generally well described in the classical chemistry literature.

The solid storage of ammonia solves the safety issues of driving with ammonia in liquid form under pressure. At the same time, the volumetric hydrogen density is high for the metal ammines compared to that of liquid ammonia and metal hydrides as shown in Fig. 3. Fig. 3 also compares the mass of the different hydrogen storage materials, and among the solid materials, the metal ammines stand out by being lighter than the metal hydrides, but heavier than the liquids and gases, when the weight of the storage tank is not taken into consideration. The current developments in high pressure hydrogen storage move towards lighter cylinders of composite materials but still with a high weight compared to the stored amount of gas, and the safety issues of driving and refueling to pressures between 35–70 MPa need to be carefully considered. Liquid hydrogen is difficult to handle on a small scale, mainly because of the very low temperature of −252 °C and the evaporation loss of 2–3% per day. The amount of insulation also adds to the mass and volume of the overall storage system. Liquid ammonia needs to be transported in pressurized tanks, and for the safety issues mentioned above, it appears unlikely to obtain the required public acceptance. This leaves the solid storage of hydrogen and ammonia as the best alternatives for mobile use.

From the literature values, suitable metal ammine salts can be selected for a given application. So far, the best studied material is Mg(NH₃)₆Cl₂, which was selected due to the low vapor pressure of 2 mbar at room temperature (see Table 1) and the

![Fig. 2](image1.png)  
Dependence of the ammonia decomposition rate on \( x_{\text{NH}_3} \) over the Ru/C catalyst at 400 °C (left). The temperature dependence of the ammonia decomposition rate for Ru/HSAG in micro-fabricated reactors (right).

![Fig. 3](image2.png)  
Mass and volume of 10 kg hydrogen stored reversibly by 8 different methods, based on the best obtained reversible densities reported in the literature without considering the space or weight of the container.
high gravimetric (9.19 wt.% and volumetric (109 (g H₂ L⁻¹)) hydrogen density available from a compacted tablet. Recently, research on Ca(NH₃)₈Cl₂ has also shown promise for mobile applications, since the hydrogen density is as high as 9.78 wt.% and the release of ammonia is achieved at lower temperatures than that of Mg(NH₃)₆Cl₂, thereby reducing the energy needed to desorb the ammonia, but also the stability at 60 °C.²

The lower desorption temperature of Ca(NH₃)₈Cl₂ results in a higher ammonia vapor pressure at room temperature (0.7 bar), but this is still an order of magnitude lower than that of liquid ammonia.²⁴ The number of metal ammines investigated for use as hydrogen storage materials is still quite small, but due to their similar chemical nature, the general findings can be used as a guideline for the behavior of other metal ammines. This has been tested by detailed modeling using density functional theory (DFT) calculations, which showed good agreement between theoretical calculations and experimental data.²⁴ DFT calculations are able to reproduce the experimentally observed trend in desorption enthalpies for various ammines at all decomposition steps,²⁴ making such calculations a valuable tool in the design and prediction of novel metal ammine compounds with specific stabilities, e.g. by varying the metal or halide components in the ammine salt.

Release of ammonia from metal ammines has been investigated in several papers in the efforts to map out their chemical and physical properties. Generally, metal ammines reversibly absorb and desorb ammonia as shown in Fig. 1, where the desired absorption and desorption enthalpies are also indicated. When the enthalpy of desorption of the first ammonia is below 40 kJ mol⁻¹, the vapor pressure at room temperature is close to 1 bar, making absorption of ammonia in the salt difficult. If the desorption enthalpy of the last ammonia is above 70 kJ mol⁻¹, the temperature needed for desorption is too high for practical applications—with the possible exception of the SOFC, where sufficient heat will typically be easily available.

The desorption kinetics of metal ammines has mainly been studied by temperature programmed desorption (see Fig. 4). These experiments show that generally, the metal ammines have very similar properties and can be formed into compact tablets essentially without any voids that would lead to a loss of volumetric storage capacity. Even in this compact form (>95% of bulk density), they maintain their excellent properties with respect to fast ammonia desorption kinetics.²⁴ Generally, the desorption characteristics can be estimated directly from the desorption enthalpies and the fact that the metal ammines have very similar entropies.²⁷ A main limitation of ammonia desorption is heat transfer, since the activation energy for ammonia desorption is relatively low and because the metal ammines are poor heat conductors; hence the required heat is mainly transported by the ammonia gas.²⁸ Another reason for the fast desorption is the intrinsic formation of a nanoporous, sponge-like skeletal structure from the compact metal ammines during ammonia desorption, which has recently been documented in a detailed in situ small-angle X-ray scattering (SAXS) study.²⁹ This is an important aspect, since compact tablets of metal ammines maintain their physical shape even after desorption of all the ammonia, corresponding to a loss of approximately half the mass and three quarters of the occupied volume. The formation of nanopores has also been investigated by DFT calculations, which show that metal ammine crystals can release ammonia by a change of the lattice constant and a slight internal rearrangement; this can be interpreted as the individual crystallites gradually shrinking to form pores.²⁵

Solid state storage of ammonia has the additional advantage that the storage density can be considered constant at temperatures around 0 °C. This is not the case for liquid ammonia as shown in Fig. 5, where the vapor pressure and volumetric hydrogen density is plotted as function of the temperature in a normal operating interval.

**System integration**

For practical use of ammonia and metal ammines as hydrogen carriers on a larger scale, efficient system integration must be achieved to minimize the energy loss. This means that the waste heat from the fuel cell and the catalyzed ammonia decomposition process must be used efficiently to release ammonia from the metal ammine and to heat the ammonia feed gas.²⁹ The safety
issues concerning liquid ammonia also make it important to design a system where the end user does not come into contact with liquid ammonia during refueling. This can be done by handling the regeneration of the metal ammine salts at decentralized locations, where the heat of formation can also be reused.

If the metal ammine system is integrated with a high temperature SOFC, the waste heat from the fuel cell is more than sufficient to supply the heat required for ammonia release and ammonia decomposition at the anode. As previously mentioned, ammonia has the advantage over reformed methane or methanol in a SOFC that it is carbon-free and that no reformer is needed.\(^8\) The residual ammonia and unused hydrogen can be sent directly to a (catalytic) burner as is common practice with most operating SOFCs, and the ammonia will contribute to lowering NO\(_x\) emissions.\(^8\)

Systems using ammonia together with low temperature fuel cells using proton conducting membranes are more complicated for various reasons. The heat from the fuel cell is available at low to intermediate temperatures, which is sufficient for complete desorption of ammonia from Ca(NH\(_3\))\(_8\)Cl\(_2\), but not for e.g. Mg(NH\(_3\))\(_6\)Cl\(_2\). However, any required additional heat can come from the ammonia decomposition reactor that will operate at temperatures from 300 °C, which is the minimum temperature if the ammonia residue should be below 2%. The challenge is that the decomposition is an endothermic process requiring 46 kJ (mol NH\(_3\))\(^{-1}\). The heat for ammonia decomposition needs to be supplied by electrical heating or by burning hydrogen or ammonia. The remaining ammonia from the decomposition needs to be removed to keep the ammonia concentrations <1 ppm to avoid poisoning of the fuel cell. This can be done efficiently by leading the gas through an acid media which can reduce the ammonia concentration down to ppb levels. More elegantly, the unconverted ammonia could also be removed by absorption into MgCl\(_2\) or CaCl\(_2\) or other even more reactive metal salts, to (re)form the metal ammine.

The possibilities are plentiful and very little research effort has so far gone into this technology compared to other related subjects, such as CO poisoning in PEMFC or DMFC.

**Outlook and perspective**

The utilization of ammonia as a potential hydrogen carrier is still receiving limited attention compared to e.g. the complex metal hydrides and other direct hydrogen storage methods, even though the ammonia technology seems to be significantly closer to market. The research devoted to the use of carbon-based hydrogen carriers as light hydrocarbons and methanol has also been substantial, although the challenges regarding CO\(_2\) for the end user remaining unsolved. In this perspective, ammonia stored in metal ammines appears as an attractive alternative which can solve many of the main targets setup for a hydrogen storage material, i.e. fast kinetics, high hydrogen storage capability, high availability and low cost. The less attractive sides to ammonia as a hydrogen carrier include the current methane-based production of ammonia without carbon sequestration, and the toxicity of the liquid.

Recent research into solid state storage of ammonia in metal ammines has solved many of the problems regarding end user safety, since the main risk of exposure to liquid ammonia has been avoided. The metal ammines also have higher volumetric hydrogen densities than liquid ammonia and other proposed hydrogen storage materials. Desorption of ammonia from metal ammines can easily be controlled and the desorption temperature can be selected to fit a given application. The use of metal ammines is currently being commercialized for automotive applications in connection with SCR catalysts to reduce the amount of NO\(_x\) produced by diesel cars or trucks.\(^2\)

There are several remaining challenges involved with an ammonia mediated hydrogen economy. A technology must be developed to remove CO\(_2\) from the production system, but this is a general challenge for the idea of a carbon-free energy system. Alternatively, it would be very interesting if one could produce ammonia electrochemically in a process analogous to the one certain enzymes, the nitrogenases, use in nature.\(^8\) This would allow decentralized, sustainable ammonia production on the basis of photo-voltaic cells or wind power. Optimization of the use of the energy stored in ammonia is also needed. This is possible, either from better ammonia decomposition catalysts or from better direct ammonia fuel cells. Other alternatives could be electrolysis of ammonia to hydrogen in an alkaline solution.\(^4\) The benefit of electrolysis is clean hydrogen production at low temperature. Current fuel cell research is focusing on bridging the temperature gap between SOFCs and PEMFCs. That could give very efficient direct ammonia fuel cells with running temperatures from 400–600 °C.\(^8\) In terms of storing ammonia in metal ammines, there appear to be many unexplored opportunities for designing suitable salts that feature a desired desorption temperature, as well as in mixtures with other hydrogen storage materials.\(^6\) Finally, the establishment of fully integrated systems is required to achieve the necessary operating experience with all aspects of these systems.

**Acknowledgements**

The Center for Sustainable and Green Chemistry is sponsored by the Danish National Research Foundation and the Center for Atomic-scale Materials Design is supported by the Lundbeck Foundation. The authors acknowledge the European Commission DG Research (contracts SES6-2006-51827/NESSHy and MRTN-CT-2006-032474/HYDROGEN) and the Danish Council for Strategic Research (# 2104-05-0016).

**References**
