

# Ammonia for Renewable Energy Systems

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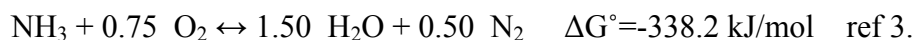
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## 1) Introduction

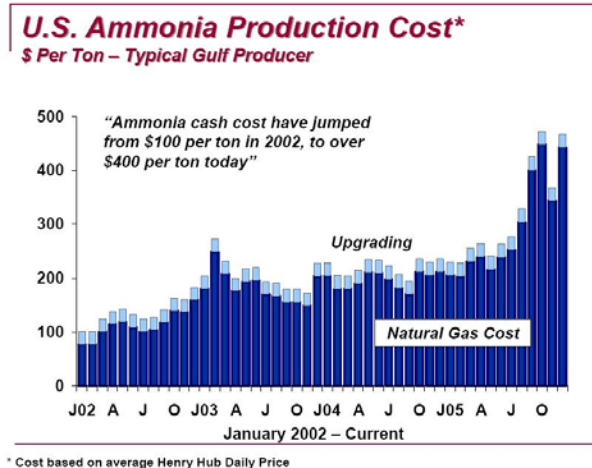
Renewable energy sources such as solar and wind operate intermittently, and therefore require an energy storage system to supply continuous electricity. In addition, the economy needs a fuel carrier that can be distributed cheaply and safely. Substantial attention has been given to hydrogen gas as a clean energy currency, but methods of storing hydrogen are wrought with low system energy density and risk of explosion.<sup>1</sup> Using ammonia (NH<sub>3</sub>) as an energy carrier is an idea that has appeared feasible for the last 40 years, but has yet to gain popular acceptance. Ammonia has several distinct advantages over hydrogen gas. It can be stored at much lower pressures, is not explosive, is already distributed in millions of tonnes per year, and has a greater hydrogen concentration by volume than liquid hydrogen.<sup>2</sup>

The elemental components of ammonia are plentiful and readily accessible - the atmosphere consists of 78% nitrogen and the earth's surface is covered 71% by water. By converting the abundant nitrogen and water to oxygen and ammonia, one can imagine a fully nitrogen-based energy economy in the place of the current carbon-based one. The following reaction cycles between reduced nitrogen (NH<sub>3</sub>) and reduced oxygen (H<sub>2</sub>O), releasing energy as the ammonia oxidizes to nitrogen.



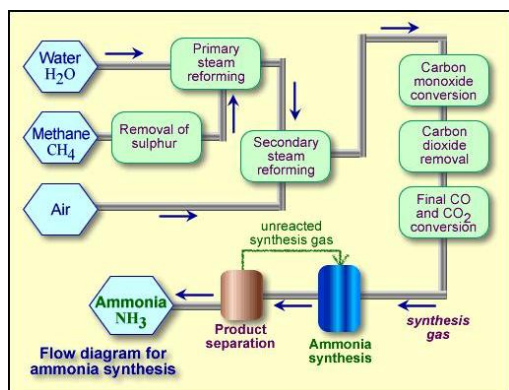
With current technology ammonia could be used to significantly displace foreign oil. Both internal combustion engines and solid oxide fuel cells can use ammonia as a fuel. The current US ammonia consumption is already of tremendous scale - equal to 6.8% of US petroleum imports by volume.<sup>4,5</sup> Ammonia costs \$1.09/gallon in 2005,<sup>2</sup> corresponding to a cost of \$2.59 per energy equivalent of a gallon of gasoline.<sup>6</sup> The limit on expanding the ammonia production is dominated by the cost of the natural gas feedstock as in Fig. 1.<sup>7</sup> As renewable hydrogen production sources mature, ammonia has promise to rise as a carbon-free energy currency.

Fig. 1.



## 2) Generation of Ammonia

Current worldwide ammonia production is 130 million tonnes per year, using about 1% of the world's total energy.<sup>4,5</sup> Nearly all ammonia is produced using the Haber-Bosch process (Fig. 2), a reaction developed in 1909 by Fritz Bosch and Carl Haber to reduce nitrogen. The steam reforming of natural gas produces a hydrogen-rich synthesis gas that is combined with nitrogen at high temperature and pressure to yield ammonia. Modern ammonia plants operate at around 350-550 °C and 100-250 atmospheres while consuming about 30-38 MJ per kg of ammonia



produced.<sup>4</sup> Substantial research is ongoing to replace the Haber-Bosch process with lower temperature and pressure reactions for the production of ammonia.

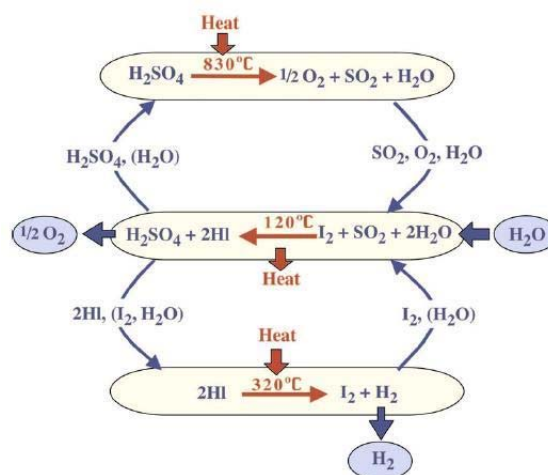
The Haber-Bosch process is a good initial market for hydrogen produced by solar and wind power. Whether the hydrogen is generated by electrolytic, thermochemical, or photoelectrochemical means it can be stored as ammonia

through this well-known process. Using natural gas as a feedstock, ammonia production releases 246 million tonnes of CO<sub>2</sub> each year that could be circumvented by a carbon-free source of hydrogen.

### a) Renewable Sources of Hydrogen

Significant progress has been made in hydrogen production from water electrolysis powered by renewable energy. According to NREL technical reports,<sup>8</sup> modern electrolyzers require 55-70 kWh of electricity per kilogram of hydrogen produced, corresponding to efficiencies of 56-73%. In 2005, industrial electrolyzers produced hydrogen at \$4.09/kg, paying \$1.63/kg in fixed costs and \$2.41/kg of electricity (at \$0.05/kWh). The Department of Energy goal of \$2-3/kg clean hydrogen would be possible with either \$0.03-0.04/kWh electricity or much lower fixed costs.

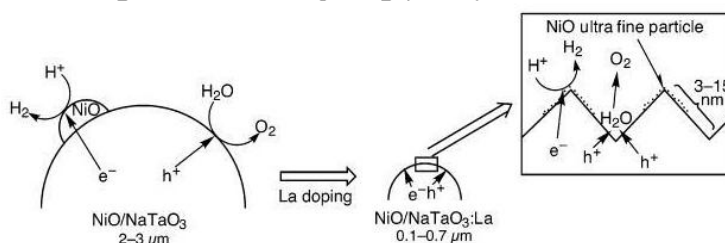
Fig. 3. Iodine-Sulfur Cycle (ref 10)



Thermochemical methods have also been considered to use heat energy for water splitting reactions. A system based on iodine and sulfur (Fig. 3) has received the most attention from the nuclear energy community<sup>9</sup> but other sources of heat, namely solar thermal, are also well suited. The cycle consists of three reaction zones, one releasing oxygen and sulfur dioxide from sulfuric acid, the second releasing hydrogen and iodine from hydroiodic acid, and the third using water to reform sulfur dioxide and iodine back into the starting materials.<sup>10</sup> The Japan Atomic Energy Authority has constructed small scale IS cycles capable of producing 2 kg/hr of hydrogen. Large reactors planned by General Atomic are anticipated to operate at 50-60% energy efficiency and to provide hydrogen at \$1.50-2.00/kg.<sup>9</sup>

Photoelectrochemical water splitting is another research topic that could provide very low cost hydrogen production from water and light. One of the most active materials for the reaction is NaTaO<sub>3</sub>:La loaded with NiO catalyst particles (Fig. 4), as developed by Kato et al.<sup>11</sup> Using ultraviolet irradiation at 270 nm for water splitting, they attained a quantum efficiency of 56% and an energy efficiency of 15.2%.

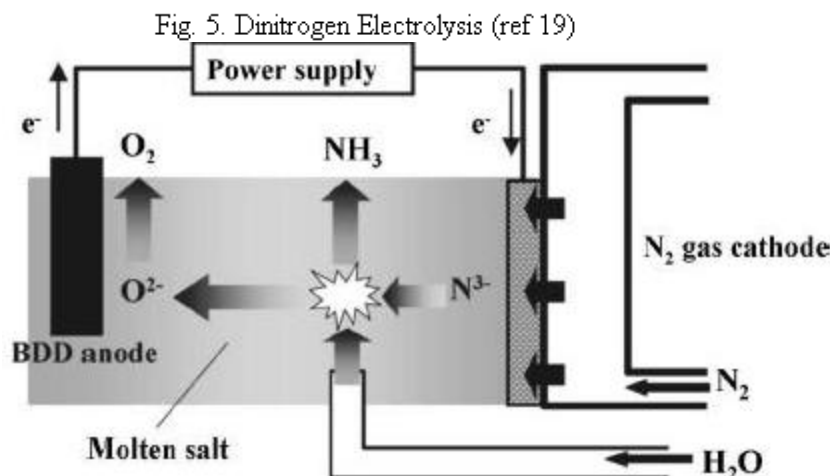
Fig. 4. UV Water-Splitting (ref 11)



Work is underway in band gap engineering and catalytic Z-schemes to design new systems that accomplish water splitting with visible light.<sup>12</sup>

### b) New Reactions for Dinitrogen Reduction

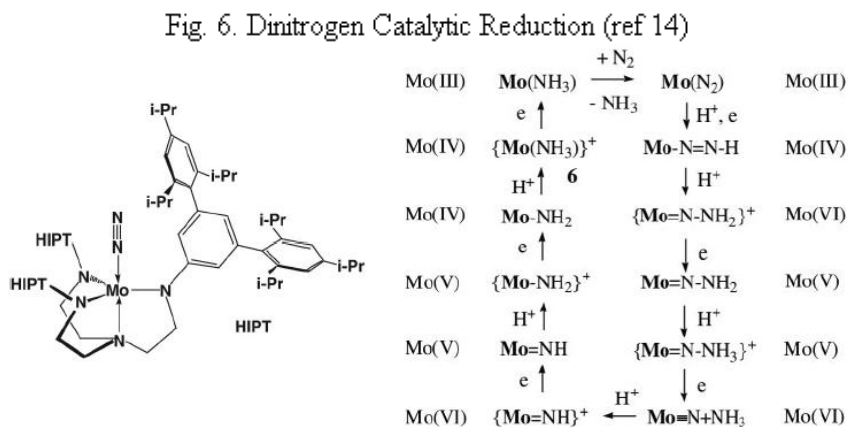
The scale of ammonia production has prompted much work in making new catalysts to allow the Haber-Bosch process to operate more mild conditions. The high temperatures of the current ammonia production are necessary to improve the rate of the reaction. Ternary nitrides such as  $X_3Mo_3N$  where X is Fe, Co, or Ni have shown activities 2-3 times greater than traditional iron catalysts.<sup>4</sup> In another study, coupling a solid oxide proton conductor such as  $CaIn_{0.1}Zr_{0.9}O_3$  to the traditional iron catalysts increases the activity by 13 times.<sup>15</sup> In principle a 1300% rate increase could allow for lower operating pressures, reducing the typical 100-250 atm to 70-190 atm.



melt to convert dinitrogen and water directly to ammonia and oxygen (Fig. 5). A porous Ni electrode reduces dinitrogen to  $N^{3-}$  ions that react with water vapor to form ammonia and  $O^{2-}$  ions. A boron-doped diamond anode oxidizes the  $O^{2-}$  ions to molecular oxygen. The cell operates at 3.1 V with a molten electrolyte of LiCl, KCl, CsCl at 300 °C. The initial activity of the cell reaches 37% energy efficiency, demonstrating the potential of this method. However, parasitic reactions of the  $O^{2-}$  ions degrade energy efficiency to 4% within 30 minutes, as hydroxide generated from a side reaction evolves hydrogen at the cathode.

A branch of inorganic chemistry is devoted to mimicking the nitrogenase enzyme for dinitrogen reduction to ammonia. The reduction of dinitrogen happens biologically on the order of 3.5 billion tonnes per year at ambient conditions.<sup>4</sup> Schrock et al designed the first

working catalytic system operating at room temperature and pressure (Fig. 6).<sup>14</sup> Inspired by the  $MoFe_7S_9$  cluster in the enzyme active site,<sup>13</sup> Schrock used a sterically protected Mo catalyst. With dinitrogen bound to the Mo complex, protons were added with an organic acid and electrons were added



with a chromocene reductant. The two nitrogen atoms in dinitrogen are converted to ammonia sequentially, resulting in a catalytic selectivity of 68%. Modifying the system to use other sources of protons and electrons (such as hydrogen gas) would enable the elusive ‘ambient’ Haber process.

### 3) Utilization of Ammonia

Today 85% of worldwide ammonia production is used as fertilizer with the remaining amount divided between textiles, explosive, and other industries.<sup>4</sup> As a fertilizer, agricultural equipment sprays liquid ammonia directly on the soil. There is an ammonia pipeline extending through much of the Midwest US and constant transport via ships, trains, and trucks.<sup>2</sup> Safety procedures are well developed and the distribution of ammonia is established. Ammonia can be stored as a liquid at 25 °C under 25 atm, or as a compressed gas at 5-10 atm. By contrast hydrogen is usually compressed around 400-500 atm to increase its energy density by volume.<sup>16</sup>

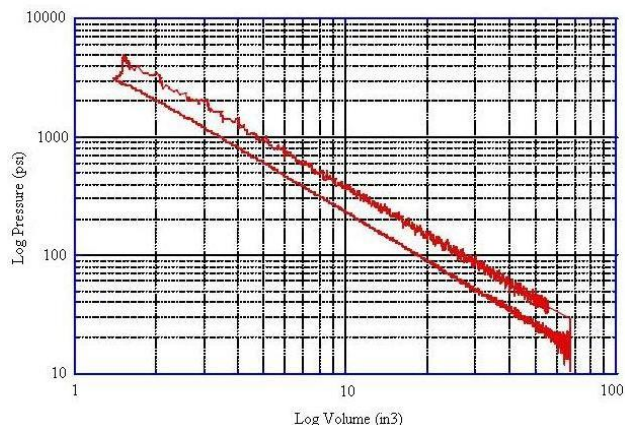
Fig. 7. US Ammonia Pipeline (ref 2)



#### a) Internal Combustion and Fuel Cells

For utility-scale energy storage, the energy stored in ammonia may be accessed in a number of ways. By itself or in a mixture with hydrocarbons, ammonia is compatible with internal combustion engines, allowing the fuel to have an immediate place in the current energy infrastructure.<sup>17</sup> Sandia National Laboratory tested ammonia in advanced internal combustion engines with a compression ratio of 48:1 and obtained high efficiencies of 50%.<sup>18</sup> Traditional gasoline engines run at a compression ratio closer to 12:1, and are compatible with mixtures of ammonia, alcohols, and hydrocarbons. Ammonia added to traditional gasoline engines actually decreases NO<sub>x</sub> production as residual NH<sub>3</sub> combines with NO<sub>x</sub> to form dinitrogen and water.<sup>17</sup>

Fig. 8. PV Curve of Combustion of Ammonia (ref 18)



Ammonia can also be used in fuel cells with a cracking system to decompose it into its elemental components and use the hydrogen as fuel. Ammonia crackers usually operate at temperatures reaching 500-800 °C with metal catalysts such as ruthenium or nickel. At these temperatures the equilibrium conversion of NH<sub>3</sub> to its constituent elements is greater than 99% complete, but catalysts are necessary to obtain at a significant rate.<sup>20</sup>

The two fuel cells designs most compatible with residual ammonia are solid oxide and alkaline fuel cells.<sup>3</sup> Solid oxide cells in particular operate at temperatures near 1000 °C, hot enough to crack the ammonia directly.<sup>21</sup> These also happen to be the two cheapest cells due to their ability to draw high current without precious metal electrodes.<sup>22</sup> Once hydrogen is generated it can be combusted directly or utilized in many types of fuel cells.

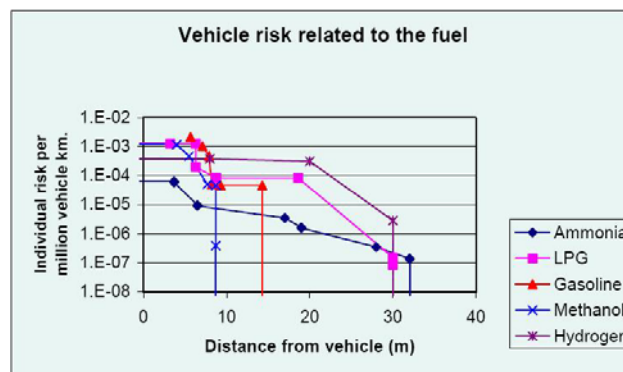
## b) Consumer Transportation Fuel

Although ammonia is a good candidate for utility-scale energy storage, it may also find applications as a consumer transportation fuel. Two main arguments against adoption of ammonia as a fuel are the toxicity and the strong odor (Table 1).<sup>2,16</sup> Ubiquitous ammonia use could accumulate to detectable odor in heavily trafficked areas. Before ammonia can be accepted as a consumer energy carrier, the emissions of vehicles should be as low as hundreds of ppb. Still, in many studies the low limit of perception of ammonia is interpreted as an advantage for leak detection and accident prevention. Hydrogen is odorless and likely to cause explosions from undetected leaks. In fact, most accidents in modern ammonia plants are fires caused by hydrogen leaks rather than ammonia exposure.<sup>23</sup>

Table 1. Ammonia Perception and Toxicity

Effect	NH <sub>3</sub> concentration in air (by volume)
Least perceptible odor	5 ppm
Readily detectable odor	20-50 ppm
No discomfort or impairment of health for prolonged exposure	50-100 ppm
General discomfort and eye tearing; no lasting effect on short exposure	150-200 ppm
Severe irritation of eyes, ears, nose and throat, no lasting effect on short exposure	400-700 ppm
Coughing, bronchial spasms	1,700 ppm
Dangerous, less than ½ hour exposure may be fatal	2,000-3,000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5,000-10,000 ppm
Immediately Fatal	10,000 ppm (1%)

Fig. 9. Collateral Damage of Vehicle Failure (ref 16)



To ascertain the risk associated with the toxicity of ammonia, in February 2005 Risø National Laboratory in Denmark performed a full risk assessment of pressurized ammonia as a transportation fuel.<sup>16</sup> The study conducted a thorough comparison of the hazards associated with gasoline, hydrogen, liquid petroleum gas (LPG: butane and propane), and ammonia. For individual vehicles, the risks of ammonia-powered cars are similar to those of LPG (Fig. 9) except that the collision ratings of the pressurized fuel tanks must be higher for ammonia storage. In terms of ammonia transport to fueling stations, they determined that refrigerating the ammonia for distribution at ambient pressure reduces the risk below that of LPG. Finally, the study considered leaks and accidents at fueling stations, calculating risk of 'serious dangers' up to 150 m from the facility compared to the 40 m hazard radius from hydrocarbon fueling. To minimize this risk ammonia fueling stations would have to be located at least 70 m from residential areas. With these safety factors in place ammonia fuel would be no more dangerous than current use of LPG.

## 4) Conclusions

Ammonia is a viable answer to the problem of storing the energy produced from renewables. Methods of generating hydrogen from electricity, thermal, and light energy are constantly improving and the Haber-Bosch process already converts some 23 million tonnes of hydrogen to ammonia every year. Compressed ammonia requires only 2% of the pressure to store compressed hydrogen, and as a liquid fuel ammonia has 45% more hydrogen by volume than liquid hydrogen itself. The energy stored in ammonia can be accessed with the current technology of internal combustion engines. Moving into the future, researcher will continue to develop improved processes for the production of ammonia as well as more efficient fuel cell designs and crackers for its use.



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