

# Ammonia as Hydrogen Source for an Alkaline Fuel Cell–Battery Hybrid System

by

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## Introduction

The biggest obstacle to commercialize Fuel Cells is the supply with proper fuels. Whilst high temperature fuel cells such as SOFCs and MCFCs allow the direct use of hydrocarbons (methane, natural gas and alike), low temperature fuel cells like PEMFCs, AFCs and PAFCs are restricted to a very small number of direct fuels. Besides hydrogen ( $H_2$ ) just methanol is being considered today. The use of hydrazine ( $N_2H_4$ ) is only of historical interest due to its toxicity. Adding a fuel reformer to the fuel cell system increases the variety of fuels, which all have in common that they are rich of hydrogen. Although the reforming of the fuel is quite simple, the following cleaning of the reformer off gas is complicated ( $CO$ ,  $CO_2$ ,  $NH_3$ , hydrocarbons ...). Hence, it is obvious that a proper combination of fuel, reformer and also fuel cell type is necessary for making the whole system as simple (and therefore low-cost) as possible.

Such a combination is ammonia ( $NH_3$ ), ammonia cracker and an alkaline fuel cell (AFC). Ammonia is globally available at low cost together with a good infrastructure. Cracking ammonia into hydrogen ( $H_2$ ) and nitrogen ( $N_2$ ) is also relatively easy, and the reformed gas can be used without a cleaning step directly as fuel gas for the AFC, which alkaline electrolyte rejects the caustic  $NH_3$ . Adding a rechargeable battery to the system for startup and peak power completes a simple system for mid power (1 to 20 kW) applications.

## Facts on Ammonia

Almost all of the ammonia produced today comes from Haber-Bosch synthesis out of its constituent elements, whereby the total production quantity grows continuously (e.g. 1980: 70 million tons per year; 2000: 105 million tons per year). Although the main raw material for ammonia production today is natural gas (especially methane,  $CH_4$ ) via a steam cracking process and hydrogen as intermittent product, ammonia can also be produced from any other source of hydrogen. Especially regarding hydrogen economy, renewable sources like water, wind or solar energy via electrolysis could be considered (minimizing the  $CO_2$  problem). Being produced in very high quantities, ammonia is of very low total cost (\$ 1,20 per kWh; for comparison: methanol: \$ 3,80; hydrogen: \$ 25,40) [1].

Pure ammonia is used today as fertilizer, most commonly it is applied directly to the soil from anhydrous ammonia tanks. Also, ammonia is widely used in various branches of chemical industry as catalyst, neutralizing agent or reactant in rubber, plastic and textile industry, ammonia-soda (Solvay) process, fertilizer industry (nitrate, phosphate ...), metallurgy... One gram of ammonia absorbs approx. 1,4 kJ of heat when vaporizing, therefore it is also frequently used as cooling agent in air-conditioning systems, ice skating rinks and refrigeration (especially in bigger ships, therefore many harbors are equipped with ammonia fueling stations).

Due to that wide use, the infrastructure as well as standards for the use of ammonia is well established. It is either transported in cylinders at -33 deg.C (~ -27 deg.F) at ambient pressure or at approx. 8 bar (120 psi) at ambient temperature. In addition, pipelines for ammonia exist all around

the world. Ammonia has a very specific and strong odor. Very often considered to be a disadvantage, leaks in the system can easily be detected by the strong smell before dangerous situations arise (compare with the not smellable and highly explosive hydrogen). Ammonia is flammable within a small range when mixed with air (15 to 34 vol.%). In contrast to methanol, ammonia is not an environmental poison, because it serves as nutrient source for plants and bacteria. It is lighter than air and evaporates fast. As being part of the natural nitrogen cycle, it is recycled naturally in the environment and therefore does not last long there. Once released to air, it is rapidly removed by rain or snow, or by reaction with other chemicals in the air, especially acids.

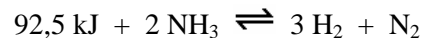
To a certain extent ammonia is toxic. However, the lethal amount is more than one thousand times higher than the limit of perception (see table 1).

**Table 1:** Toxicity limits of ammonia [2]

	ppm	mg / m <sup>3</sup>
Limit of perception	5	3,5
MAC	50	35
Disturbance	250	175
Symptoms of poisoning	2500	1750
Lethal dose	> 5000	> 3500

### Ammonia as Hydrogen Source

Liquid ammonia (pressurized or cooled, see above) contains 1,7 times more hydrogen than liquid hydrogen for a given volume. Therefore, ammonia offers a significant advantage in cost and convenience over pure hydrogen. Hydrogen can be released from the ammonia molecule by shifting the formation reaction back to the elements:



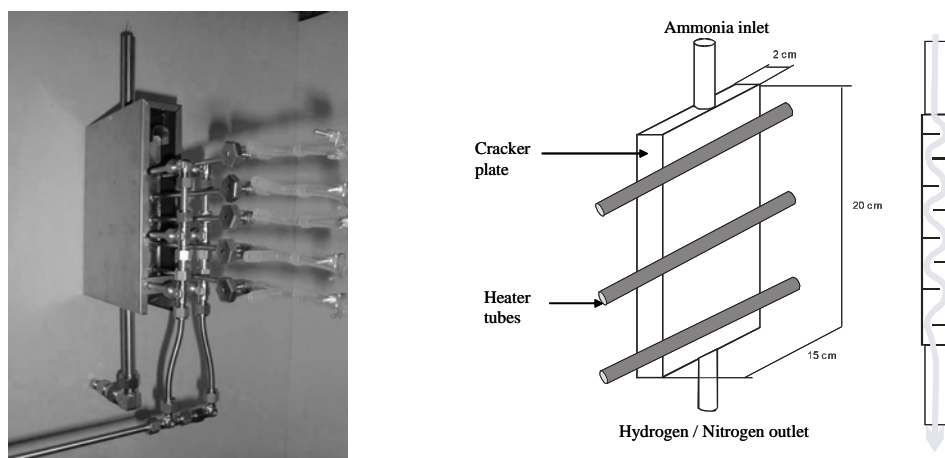
The formation reaction of ammonia is exothermic. As ammonia is of industrial importance, its equilibrium data has been available since the beginning of the century for a wide range of temperature and pressure [3, 4]. According to this data, the equilibrium of the equation on the right side at temperatures exceeding 500 K (low pressure provided). However this equilibrium is not achieved due to bad kinetic properties and high activation energies. So, an excellent catalyst is necessary, and extensive studies all around the world have already been done based on several different approaches [e.g. 5 to 11].

After extensive studies at University of Technology, Graz, a commercial nickel oxide catalyst (on aluminum oxide), treated with ruthenium salts, was chosen [12]. First tests were made with an electrically heated tube cracker (Prototype II). It was easier to handle than the foregoing model (Prototype I), which was heated by an internal burner, especially for testing different types of catalysts. From a practical point of view, considering an operation with a fuel cell, the cracker was not satisfying, because it needed power from the grid. However, the rate of ammonia conversion was high. At approx. 500 deg.C, the amount of NH<sub>3</sub> in the reformer off gas was below 10 ppm.

The higher the temperature the more ammonia is converted; however, the more problems arise. At high temperatures (1000 deg.C), hydrogen strongly attacks the common stainless steel and makes it brittle. Hence, very special and therefore expensive qualities of steel must be used. Those high

temperatures are necessary if one considers to use an ammonia reformer together with an PEMFC, as this acid-type fuel cell is strongly harmed by traces of ammonia (salt formation). In case of an AFC, ammonia is not critical. Therefore, the reformer temperature can be much lower. Best results have been obtained around 550 deg.C. At that temperature, common stainless steel is not reasonably affected by H<sub>2</sub>.

After tests using another tubular cracker with burner inside (Prototype III), reformer development shifted to a plate design (Prototype IV, figure 1). It was heated by burning a hydrogen-rich off gas coming from an alkaline fuel cell and was fitted with ten temperature sensors. One plate like the one shown in the figure could produce enough hydrogen for continuous operation of a 2 kW fuel cell.

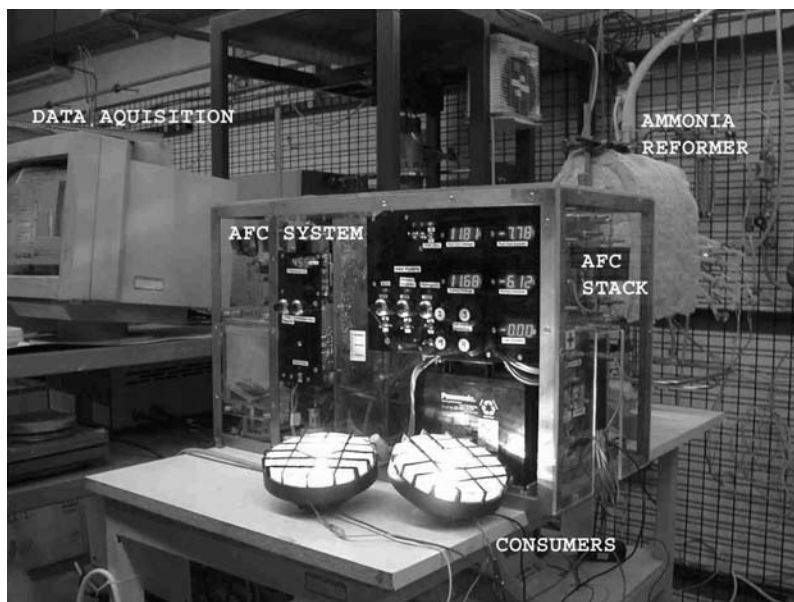


**Figure 1:** Ammonia Reformer Prototype IV. This plate-type reformer is heated by hydrogen and supplies hydrogen for a 2 kW fuel cell system.

### Alkaline Fuel Cell Running on Ammonia

Due to the fact that the reformed hydrogen gas contains 25% nitrogen, the purge rate on the anode side of the fuel cell has to be rather high to prevent the buildup of an inert atmosphere inside the fuel cell stack. The hydrogen content of the anode off gas depends on the current drawn from the fuel cell, but it is high enough to feed the burner of the reformer. Hence, no hydrogen is lost. The waste heat of the fuel cell (air at 70 deg.C; liquid alkaline electrolyte at 70 deg.) is used to preheat the ammonia as well as the ammonia tank, because, as mentioned in the beginning, evaporating ammonia strongly cools down the tank.

Figure 2 shows an AFC under test, fueled with hydrogen from the NH<sub>3</sub> reformer described above (Prototype IV). Different loads were drained from the AFC system (using lights, motors, resistors, internal heater, battery recharging ...) while the data was obtained by a data acquisition system continuously. The system showed good properties throughout the tests, although the cracker was operated at only 500°C, which left a smellable amount of ammonia in the hydrogen stream. The voltages were comparable with those obtained with pure hydrogen from a compressed source. Although there was a direct burning of hydrogen and oxygen (from air) in presence of nitrogen, no NO<sub>x</sub> could be detected. This was expected, as NH<sub>3</sub>, which was also present, is known to prevent the buildup of NO<sub>x</sub>.



**Figure 2:** AFC under test when fueled with hydrogen coming from an ammonia reformer

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