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AMMONIA FOR HIGH DENSITY HYDROGEN STORAGE

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One of the main goals of the automotive industry is the development of low-emission engine technology for vehicles to reduce their environmental impact. However, the combustion of hydrocarbons in air generates various pollution gases, including carbon monoxide, carbon dioxide, ozone, nitrogen- and sulphur oxides. Among the various solutions considered hydrogen appears to be a very promising alternative for automotive applications. Use of hydrogen fuels would require only minor modifications to existing engine designs. In alternative propulsion technologies, such as electric vehicles, hydrogen can be used in fuel cells. Electric energy generated by the fuel cell can either be stored in batteries or used directly to feed an electric motor to power the electric vehicle. One problem with hydrogen, however, is the safe handling. The use of hydrogen as a fuel for wide-spread distribution in either gaseous or liquid form poses numerous safety, technical, and economic problems that make its use as a fuel prohibitively difficult. In the absence of a hydrogen pipeline network, small-scale users purchase merchant hydrogen as compressed gas in steel cylinders, or as liquid hydrogen in cryogenic containers. One approach to resolve the drawbacks of hydrogen as a fuel includes considering less expensive, simpler, and cheaper materials that can act as hydrogen carrier. Several on-site methods of producing hydrogen can be considered, for example via steam reforming of natural gas or hydrocarbons, via water electrolysis, by reforming of methanol and by ammonia dissociation.

Ammonia has been identified as a suitable hydrogen carrier. Ammonia is essentially non flammable and is readily obtained and handled in liquid form without need for expensive and complicated refrigeration technology. In addition, ammonia contains 1.7 times as much hydrogen as liquid hydrogen for a given volume. Compared to hydrogen, ammonia therefore offers significant advantages in cost and convenience as a vehicular fuel due to its higher density and its easier storage and distribution. Ammonia is produced and distributed world-wide in million of tons per year. Procedures for safe handling have been developed in every country. Facilities for storage and transport by barges, trucks and pipelines from producer to ultimate consumer are available throughout the world. Therefore liquid anhydrous ammonia is an excellent storage medium for hydrogen even though the endothermic ammonia cracking results in some

efficiency penalty. The fuel capacity per weight of ammonia is higher compared to methanol and the price per kW is lower [1,2] as also seen in Table 1 and 2.

Table 1: Thermodynamic data for some candidate fuel-cell reactions under standard conditions at 25 °C [3]

| Fuel | Reaction | - H° [kJ/mol] | - G° [kJ/mol] |
|-------------|----------------------------------------------------------------------------------------|-------------------------------|--------------------------|
| Hydrogen | $\text{H}_2 + \frac{1}{2} \text{O}_2 \Rightarrow \text{H}_2\text{O}$ | 286 | 237.3 |
| Methane | $\text{CH}_4 + 2 \text{O}_2 \Rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$ | 890.8 | 818.4 |
| Methanol | $\text{CH}_3\text{OH} + 1,5 \text{O}_2 \Rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$ | 726.6 | 702.5 |
| Ammonia | $\text{NH}_3 + 0,75 \text{O}_2 \Rightarrow 0,5\text{N}_2 + 1,5 \text{H}_2\text{O}$ | 382.8 | 338.2 |

The comparison of the power density indicates ammonia as a cheap fuel with high power density. The given table assumes conversion efficiencies of 40-50 % and is based on current retail fuel prices in 1998 [4].

Table 2: Power density and cost of fuels [4]

| Fuel | Kwhr/kg | c /kWh | kWhr / liter |
|--------------------------|----------------|---------------|---------------------|
| H ₂ (156 atm) | 83.4 | 2535 | 0.28 |
| Propane | 1.96 | 34 | 1.15 |
| Methanol | 1.45 | 379 | 1.15 |
| NH ₃ | 1.87 | 117 | 1.45 |

Further advantages of ammonia for fuel cells are given in an easy cracking device.

Ammonia can be cracked into hydrogen and nitrogen in a suitable separation unit according to the reaction: $2 \text{NH}_3 \Rightarrow 3 \text{H}_2 + \text{N}_2$

With ammonia there is no shift converter, selective oxidizer or further co-reactants like water required as in other hydrocarbon or alcohol fuel cell power devices. The generated nitrogen can be released to the atmosphere without significant environmental impact. So, an important reason for using ammonia as fuel is that the dissociation of ammonia offers by far the simplest approach. It allows a single feed stream, simplicity of start-up and low overall equipment weight.

The dissociation rate is depending on temperature, pressure and used catalysts. For low ammonia concentration as necessary for PEMFC's the dissociation should therefore take effect at higher temperatures (up to 900 °C). Otherwise, pointing to the future use of hydrogen from ammonia cracking it should be

mentioned that the alkaline fuel cell is insensitive to small amounts of NH_3 and therefore does allow an efficient cracking process (contrary to the acidic PEM or PAFC systems).

System studies demonstrate that hydrogen derived from anhydrous liquid Ammonia, via a dissociator and following hydrogen purifier, offers an alternative to conventional methods of obtaining pure hydrogen for small-scale use. Hydrogen from ammonia dissociation would be the preferred option for the smallest plant sizes where it is projected to be competitive with hydrogen via natural gas of comparable purity [5].

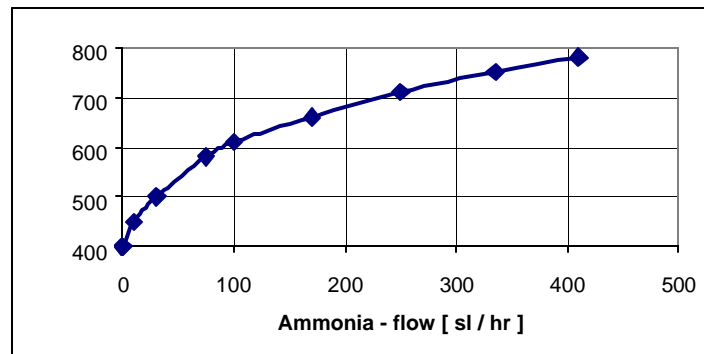
Laboratory studies

Conversion rates of ammonia are dependent on a variety of influence factors. According to literature the chemical reaction kinetic is accelerated by catalysts such as Fe, Co, Cu and Ni. Ammonia cracking devices for small transportable applications were investigated with different system designs [4,6,7,8]. Portable ammonia dissociators with small residual amounts in ppm-range of ammonia for low power applications up to 200 W electrical output at the added fuel cell are described in a volume range less than 6 liters [4,6]. Studies with commercial available simple catalyst materials like nickel oxide or iron oxide on aluminum and the influence of the addition of noble metals were done with lab scale reactors [9]. Decomposition rates of ammonia on noble metal wires were examined and compared at temperatures from 500 to 1900 K [10]. New catalytic investigation obtains better cracking efficiency with new catalyst materials based on Zr, Mn, Fe, Al- Alloy Catalysts [11].

To get easily producible and cheap catalyst materials the research at TU- Graz was done on improvement of commercially available catalyst materials. The catalyst was prepared starting from catalyst pellets (SÜD-Chemie 27-2, nickeloxide on aluminumoxide) by addition of noble metals like platinum, rhodium, palladium, lanthanum oxide and ruthenium including combinations of these additives. Best results were found by simple addition of ruthenium salts to the nickel oxide catalyst. The catalyst pellets were smashed and sieved to obtain an average particle size of 1 to 1,5 mm, followed by the addition of 0,3 g ruthenium /100 g catalyst.

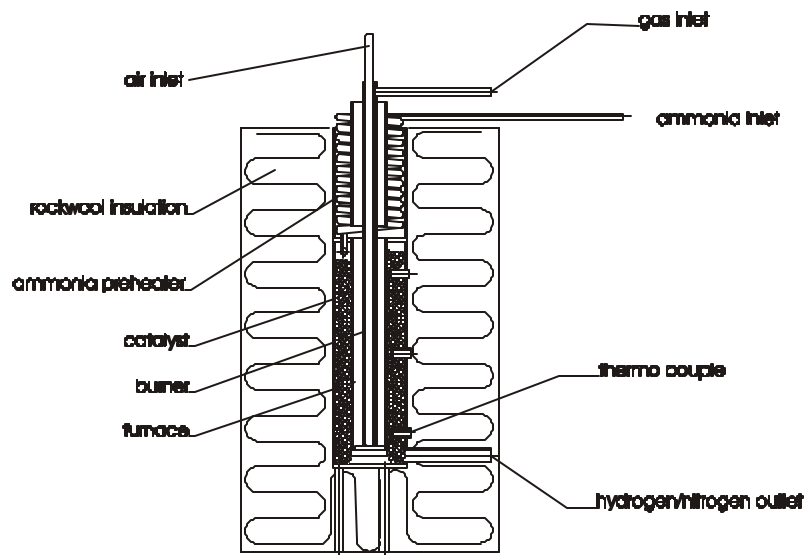
The catalyst test reformer unit was a tube (inner diameter 12 mm, heated length 130 mm) filled with 20 g of the prepared catalyst. The unit was isolated and heated electrically. The performance of this reactor is presented in Figure 1. The temperature was measured inside the catalyst with thermocouples at different positions. Ammonia was preheated to obtain a constant temperature over the full catalyst length. The temperature of the reactor is plotted as a function of ammonia throughput at a conversion rate higher than 99,99 %. The pressure drop in the reactor was depending on the ammonia flow from 0 to 70 hPa.

Figure1. Cracking efficiency (> 99,99 conversion) of 20 grams Ni-Ru - Catalyst (slm - standard liters per minute)



Based on the results of the catalyst research, the design and development of an lab-scale ammonia cracking reactor was done at the institute (Figure2). In laboratory studies the ammonia which is used is preheated to about the same temperature of the catalyst before contacting the ammonia cracking material. Such preheating has been found to improve the efficiency of the cracking reaction and provide higher flow rates. In further applications this preheating will be done by heat exchangers to use the heat released from the cracked hydrogen / nitrogen mixture. Using fuel cells with a mixture of hydrogen and nitrogen as fuel causes a hydrogen containing anode off-gas which can be used for heating this reactor to permit the endothermic cracking process.

Figure 2: Anode off-gas heated cracker prototype



Conclusions

By using materials which are more or less commercially available it is possible to construct a hydrogen generating plant using ammonia as fuel, thus eliminating the problems of hydrogen storage and transport. At the high cracking efficiency of the developed catalyst the ammonia cracker could be constructed at modest mass and volume. The system using ammonia feedstock is technically simple, no recycle loops are required. Especially with alkaline fuel cells high efficiency systems are possible as small amounts of ammonia in the cracked gas are permitted to enter the fuel cell and can be burned in an anode off-gas heated cracker device.

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