

Advances, aging mechanism and lifetime in AFCs with circulating electrolytes

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Abstract

Alkaline fuel cells (AFCs), although known to have a high efficiency, were considered to be only useful for space applications due to their high price, their low lifetime and their high carbon dioxide sensitivity. In fact, AFCs can be built low-cost and CO₂ reconcilable with sufficient lifetimes for vehicles and backup systems. The key is a liquid circulating electrolyte which avoids many problems membrane systems have, like the water and the heat management. The drawbacks of AFCs diminishing the lifetime were also discussed, whereby solutions to overcome these problems were given.

Finally, ammonia (NH₃) as alternate fuel for an 300 W alkaline fuel cell system was introduced.

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1. Introduction

Interests in the alkaline fuel cell, which has been a stepchild for many years, rose again recently, as the development of low cost PEMFCs took much more efforts than expected. Especially for medium-size systems (0.5–50 kW), the simplicity of AFCs with liquid electrolytes (like heat and water management) and their capability of being started up fast and being shut down for long periods of time, caused some companies and institutions to concentrate on this system. The main task was to increase the long-time stability of the AFC electrodes, which usually showed lifetimes up to a few thousands of hours.

The decrease of performance during operation is mainly caused by a wetting of the electrodes. The electrolyte slowly fills up the pores and this increases the diffusion path for the reaction gases to the reaction sites; a drop in cell voltage occurs. By improving the electrode structure, especially the hydrophobic agents in the diffusion layers, this effect can be diminished.

Another research topic in the AFC field is the use of non-noble metal catalysts, especially silver for oxygen reduction. This possibility of significant cathode cost reduction is also of major interest for zinc/air cells.

A well-known drawback of AFCs is the carbon dioxide sensitivity, as carbonate crystals are well known to destroy

the carbon pores. Fortunately, the situation is much better than widely believed; the CO₂ can be absorbed easily using soda lime or using an integrated cleaning system (with electrolyte). Again, the use of liquid circulating electrolyte is a major advantage, as a certain amount of CO₂ in the feed gas can be accepted (approximately 100 ppm). An AFC can afford any fuel as long as the feed gas is low on CO₂. Especially ammonia as a hydrogen-rich fuel, which can be reformed at low temperatures (AFC accept small amounts of ammonia), has been a center part of recent research.

2. State of development

Already in the late 1930s, Bacon [1] started his important work on alkaline fuel cells, which lead to a number of larger demonstration units, like his 5 kW unit [2] and the 15 kW tractor of Allis Chalmers Manufacturing [3]. Finally, Pratt & Whitney Aircraft licensed the Bacon patents and built the power units for NASA's Apollo capsules. Although interests in fuel cells decreased strongly after the Apollo Program was abandoned, NASA continued to improve their alkaline system for their space shuttle (Orbiter). Today, their system is considered fully developed, which can be seen by the fact that there is no back-up electric power installed on the space craft. The cost is still quite high, but this is compensated by a high lifetime of 5000 h and more. This might not look much, but it equals more than 20 space flights. For more detailed data on the Orbiter technology see [4].

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These systems, however, cannot be used for terrestrial stationary and mobile applications but some niche markets (e.g. submarines). All systems mentioned above work with an immobilized caustic electrolyte which is highly sensitive to carbon dioxide (CO_2). Any carbonate crystals formed inside the pores of the electrodes cannot be removed and do not only block the diffusion paths, but can also destroy the electrode mechanically. Hence, either air and also fuel gas, if it is coming from a hydrocarbon reformer, have to be cleaned very carefully, or pure gases must be used.

Already in the 1950s, Union Carbide Corp. (UCC) started their research and development on alkaline fuel cells with circulating electrolyte. Using that approach, UCC took advantage of several features of having a fluid media in each of the cells.

2.1. Simple thermal management

Having a circulating liquid inside each cell not only allows removing the reaction heat from the system, but also speeds up the start-up procedure by simply heating the electrolyte in the tank using a hybrid rechargeable battery.

2.2. Simple water management

A common problem of membrane systems is their sensitivity to incorrect water balance; flooding or drying out is observed regularly. A circulating electrolyte can guarantee a certain water concentration all over the stack, which of course changes a little bit along the electrode surface, but never reaches a critical concentration (high or low), even if the power density is changed rapidly.

2.3. Bubble buildup not critical

Any gas bubbles penetrating the gas diffusion electrodes are washed away keeping the total electrode surface wetted.

2.4. Reduction of concentration gradient

The current-carrying ions (OH^-) are produced on the cathode side and used up on the anode side. As the electrolyte flow is rather turbulent (due to a plastic mesh placed between the electrodes), it diminishes the concentration gradient and therefore slightly increases the cell performance.

2.5. Monopolar cell design possible

While membrane systems are always bipolar, a system with circulating electrolyte can also be constructed a monopolar way, which again brings several advantages. First, it is low cost, because no bipolar plates are needed; just cheap plastic screens are used to avoid an internal short circuit. Second, stack thickness decreases as there is only one gas chamber between two electrodes (see Fig. 1). Third, no mechanical pressure is needed to build the stack (like for MEAs); gluing or welding techniques are used. Finally, monopolar designs allow configuring the finished stack to several different voltage/current ratios to customers needs. For example, a 2 kW stack (32 cells, 0.8 V at 200 mA/cm², 400 cm² active area, 25 V, 80 A) can support 25 V/80 A, 12.5 V/160 A, 8.3 V/320 A, etc. by just changing the external current connectors.

Accumulated impurities removable: During operation of an alkaline fuel cell, impurities like carbonates, carbon particles, corrosion products and alike, accumulate slowly. These impurities can not only be filtered out of the liquid electrolyte, but the whole electrolyte can easily be exchanged like the oil in the car every few hundred operating hours.

UCC first developed thick pitch-bonded carbon plate electrodes (6.4 mm thick), but soon changed to plastic-bonded (mainly PTFE) thin carbon electrodes with metallic current collectors. Up to the 1970s, a number of systems had been built for US Army and US Navy, for General Motors (“Electrovan”) and others. One famous milestone of terrestrial fuel cell development was Kordesch’s Austin A-40. All

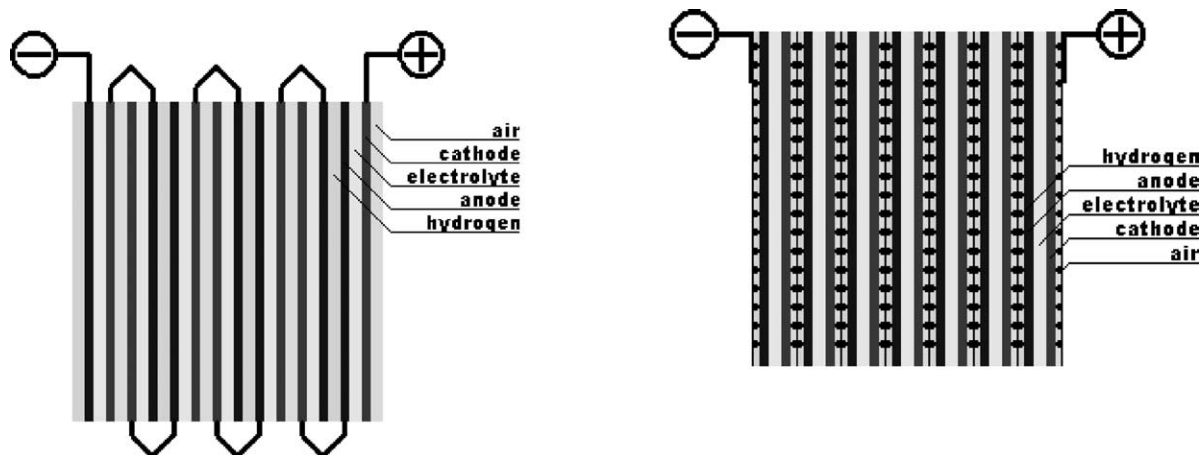


Fig. 1. The two ways of stack construction.

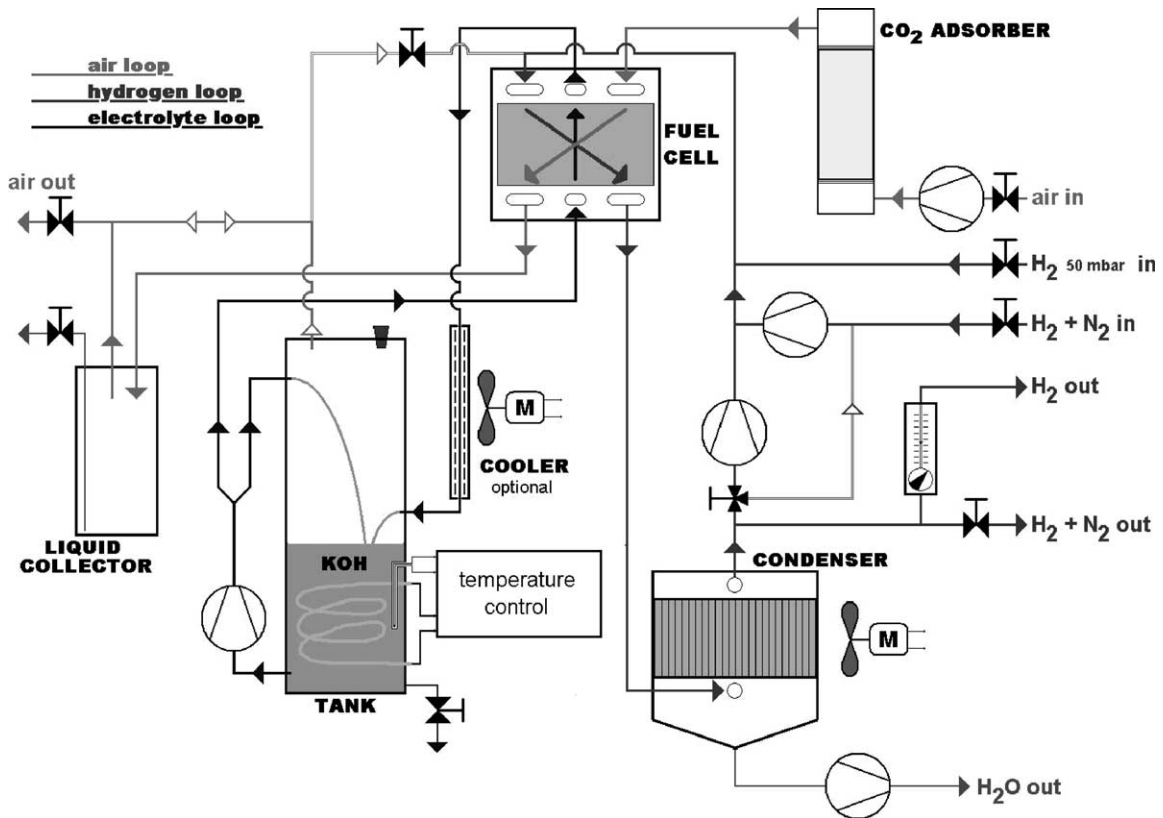


Fig. 2. Schematic view of the accessories of an alkaline fuel cell.

these systems were well described in [5]. Unfortunately, the fuel cell program was one of the projects UCC abandoned after their accident in India.

Today, worldwide only about four companies concentrate on alkaline fuel cells for terrestrial applications, and most of them base their technology on that UCC project. Zetek Power, for example, based their knowledge from the fuel cell research of Elenco for the Hermes Power Plant (the projected manned space craft of the European Space Agency, ESA), consisting of a circulating caustic electrolyte and thin carbon gas diffusion electrodes.

An H_2 /air system with circulating caustic electrolyte commonly consists of the parts shown in Fig. 2; it shows the AFC system of Fig. 6. The hydrogen loop looks complicated, but it allowed the use of pure H_2 as well as N_2 -containing fuel gas coming from a NH_3 cracker (see Section 4).

Usually, the electrode is mounted vertically, electrolyte is on the active layer side. The numbers of active and/or diffusion layers may differ (1–3 diffusion layers, 1 and 2 active layers).

Today, a standard alkaline fuel cell electrode for liquid electrolyte consists of several PTFE-bonded carbon black layers (Figs. 3 and 4), sometimes also containing other hydrophobic materials like paraffin, wax or other plastics like polyethylene (PE) or polysulfone (PSU). Other additives are graphite (for increasing the electric conductivity) and pore-formers (like sugar). Sometimes, porous PTFE foils are pressed onto the gas side.

In monopolar cell assemblies, the use of a metallic current collector is necessary. Commonly, nickel, nickel-plated steel or gold-plated materials are used. Porous metal plates were used at UCC, however they were very expensive.

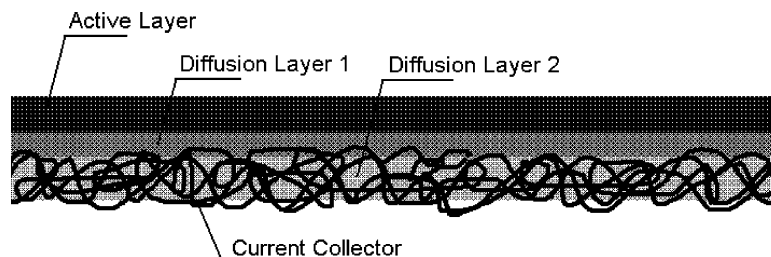


Fig. 3. Schematic cut through an AFC electrode.

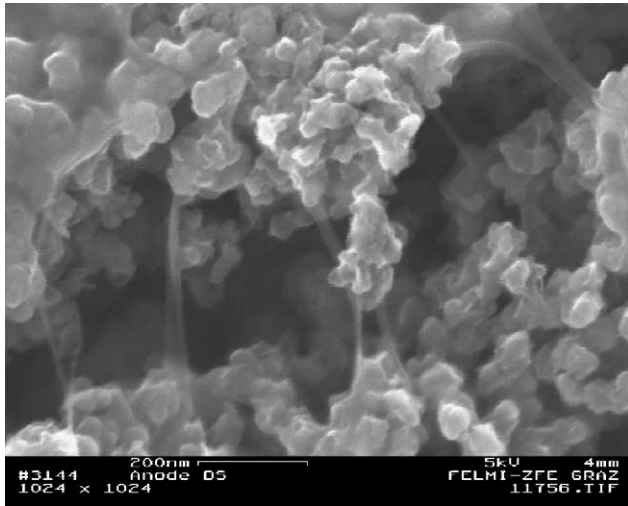


Fig. 4. SEM picture of a PTFE-bonded carbon layer; the hydrophobic PTFE “glue” is visible.

Therefore, meshes, screens and expanded metals are used. Carbon fleeces were considered also, but performing a good external electric connection is difficult.

The electrodes are produced by rolling, pressing and sintering procedures and finally framed for stack construction (Fig. 5). The frames are either glued (like the one in the picture) or welded; no screws are necessary.

One often mentioned advantage of alkaline fuel cells is the possibility to use low-cost non-noble metal catalysts. For cathodes this could be silver, some perovskites and spinels, silica and also carbon itself. A catalyst for anodes is

Raney-nickel. However, the use of noble metals for cathodes (Pt) and anodes (Pd, Pt, Ru, Rh) is still common because the number of AFC systems produced is low. AFCs always have a higher open circuit voltage than acid systems [6], and a smaller catalyst loading leads to the same power output compared to acid systems. Recent performance curves of alkaline systems were reported in [7,8].

3. Life limiting effects

Besides the large number of advantages, alkaline fuel cells fight one big drawback: The poor lifetime. In practical applications, not more than 5000 operating hours could be obtained. It is obvious that most efforts of any research group dealing with AFCs is not to decrease the cost as this is low compared to other fuel cell systems anyway, but to increase the lifetime.

There are several effects that shorten the lifetime and not all of them will be discussed here. The most common effects are corrosion, electrode weeping, mechanic electrode destruction by carbonate crystals and catalyst decomposition. Then, in a stack or during galvanostatic experiments, the death of a cell finally occurs because of a cell reversion; gas bubbles destroy the carbon layers mechanically.

3.1. Corrosion

Hot caustic electrolyte is highly corrosive, so only a few materials can be used for electrode, stack and system construction.

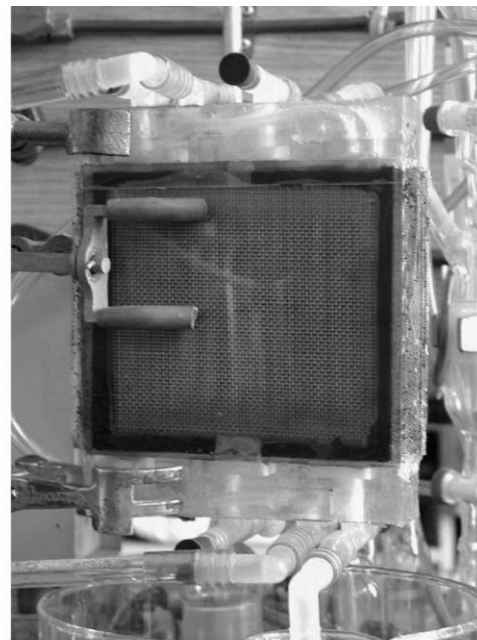
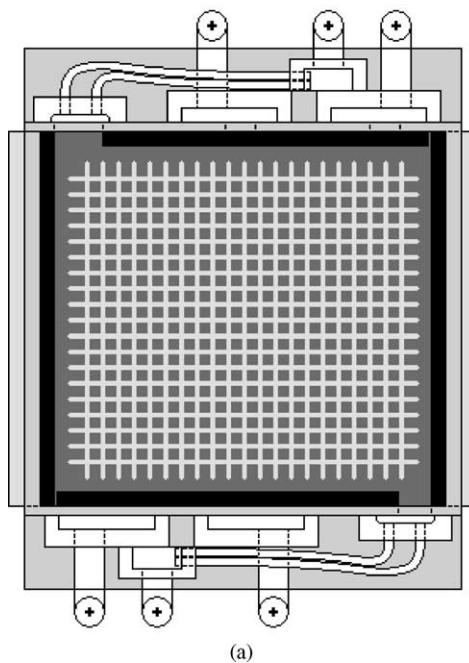


Fig. 5. (a) Schematic view (left) of an 100 W AFC stack produced at University of Technology, Graz. Top left and bottom right tubes: H₂; top right and bottom left tube: scrubbed air; center tubes: electrolyte. (b) Right picture: seven-cell stack under test.

Carbon is not corroded by KOH, but oxidized by O₂ and air at higher temperatures. The situation is much less serious at 75 °C, which is the normal operation temperature of AFCs with liquid electrolytes, than at >200 °C, which is the operation temperature of phosphoric acid fuel cells (PAFCs) and some AFC types used in space (NASA's Apollo Project). Anyway, as mentioned in the section above, carbon alone also catalyses oxygen reduction; a feature which is of interest for zinc/air batteries which work at ambient temperature. However, the most active sites "burn" first; the higher the temperature the faster is the loss of activity. Regarding oxygen reduction, this burning is not critical for electrodes catalyzed otherwise.

Plastic binders, even PTFE, is attacked by the hot caustic electrolyte. The electrolyte always contains peroxides, which were produced during incomplete oxygen reduction. These peroxides can induce radical chain destruction. Along with the destruction of the polymers the electrode loses mechanical stability (crack formation) and hydrophobicity (weeping, see below). This problem can be diminished by introducing radical collectors into the chains (e.g. styrenes) or using improved catalysts with lower peroxide formation.

The current collectors commonly consist of nickel. Nickel passivates in caustic environments, however, it forms an oxidic layer on the surface which increases the internal resistance of the electrode. If nickel-plated steel is used, special care has to be taken that the steel is completely covered. In cathodes, the danger of nickel dissolution is much higher than in the reducing environment and potentials at the anode side. A complete protection of the steel and the nickel can only be obtained by layers of gold and other resistant but expensive materials. Another approach is to graphite-coat or embed the current collector into the diffusion layer (Fig. 3), so nearly no metal gets into direct contact with the electrolyte.

It is obvious that all accessories like tubes, pumps, the tank and alike must consist of pure nickel, nickel alloys or special plastic materials (PTFE, PSU, . . .). In the latter case, it is most important to consider that these plastic materials do not contain flexibilizers, because these surface-active substances, once dissolved, neutralize the electrode's hydrophobicity.

3.2. Electrode weeping

In contrast to electrode "wetting", which is the situation during normal operation (electrolyte filled pores and gas filled pores inside the active layer side by side; no electrolyte inside the diffusion layer), "weeping" describes electrolyte penetrating through the electrode. This can happen because the electrode contains cracks (so called "mud cracks"), the hydrophobicity was destroyed for any reason (see above) or a cold hydrogen feed gas (on anodes). Mud cracks appear during drying steps during electrode preparation; only an optimized electrode production can inhibit that effect (dry preparation techniques).

Anodes suffer from cold hydrogen. The chemical reaction at the anodes produces water which dilutes the electrolyte inside the pores of the anodes, where it finally evaporates. Also, the reaction heat is produced at that site, hence the vapor pressure is very high at that point, compared to the rest of the fuel cell. If cold fuel gas enters the cell, it cools the anodes from the gas side, the vapor pressure drops until the water condenses inside the pores of the diffusion layer, no matter if there is a hydrophobic surface or not. This not only blocks the diffusion paths of the fuel gas but also causes the buildup of paths of liquid through the whole electrode. Hence, the fuel gas has to be heated first, simplest by using the electrolyte.

3.3. Carbon dioxide

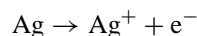
The biggest danger coming from that acidic gas is the formation of large crystals of carbonate inside the electrolyte-filled pores. These crystals not only block the diffusion paths but also destroy the layers mechanically. The solubility of these carbonates depends on the electrolyte concentration, the temperature, the amount of liquid electrolyte and the type of electrolyte. The type of electrolyte also affects the shape of the crystals formed. NaOH, for example, has a lower solubility of CO₃²⁻ than KOH, but the crystals are very much smaller and can easily be washed away. In case of K₂CO₃, the crystals remain inside the pores. It is obvious that AFCs with immobilized electrolytes suffer much more from carbonate formation and cannot support even trace amounts of CO₂.

Strongly bonded electrodes can support unscrubbed air for a longer period of time (several thousands of hours [9]), but there is always a buildup of carbonates in the electrolyte, causing negative effects like a slower kinetic due to a lower OH⁻ concentration, a reduced electrolyte conductivity, a reduced O₂ solubility and an increased electrolyte viscosity.

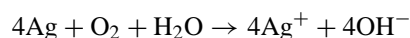
Kordesch showed during daily operation of his car [5] that partly scrubbing of the air using soda lime and removing about half of the CO₂, together with replacing the liquid electrolyte every few hundred operation hours, lowers the carbonate content to a tolerable level.

3.4. Catalyst decomposition

Noble metals appear to be very stable in caustic electrolytes, and the decrease of activity is commonly covered by the wetting and weeping effects described above. Silver and its alloys, however, show a strong dissolution at open circuit voltages:



Total reaction at cathode:



The silver ions (Ag^+) get reduced at the anode again, as soon as power is drained from the cell again, harming the catalysts of the anode. To prevent silver from being dissolved, the fuel cell has always to be “on power”. When no power is needed, a high ohmic resistance, a rechargeable battery or alike should be connected to the fuel cell.

Also, a small “electrolytic” cell which consists of two nickel plates can also be added to the electrolyte stream to remove any silver from the electrolyte. Such a cleaning cell would also remove carbon particles and other impurities inside the electrolyte.

3.5. Cell reversal

As soon as one cell cannot support the current drained from the stack, the cell will be reversed. The other cells, still in normal operation, force a current through the damaged cell, but the normal reactions (O_2 reduction and H_2 oxidation) do not proceed, but H_2 and/or O_2 evolution starts. The fuel cell becomes an electrolysis cell. The carbon-based electrodes cannot support gas evolution very long, a mechanical damage occurs. To prevent cell reversal, a careful control of all cells during production and also during operation is necessary.

4. Ammonia as hydrogen source

As described above, CO_2 containing gases could cause trouble and decrease the lifetime of the electrodes. Hence, a CO_2 -free fuel is preferred for fueling AFCs. The use of pure compressed or liquefied hydrogen, although widely considered for future terrestrial applications, could be a very simple

Table 1
Advantages of ammonia as fuel

High H_2 density	50% more H_2 than liquid H_2 at same volume
Very low-cost today	Third largest chemical produced (worldwide) NH_3 : US\$ 1.17 $(\text{kWh})^{-1}$; methanol: US\$ 3.79 $(\text{kWh})^{-1}$; H_2 : US\$ 25 $(\text{kWh})^{-1}$ [10]
Liquid at low pressure	8–9 bar at ambient temperature
Strong smell	Leakages easy detectable
Environmentally friendly	Fertilizer, neutralizes acid rain
Technology available	For production, distribution and storage for daily use
Simple reforming	In small units at low temperatures if used with AFCs [11] No cleaning of the reformed gas necessary (H_2 , N_2 , NH_3)

solution, however its use certainly brings along a number of safety risks, which cannot be ignored. All alternative hydrogen sources, which are in discussion today, contain carbon: methanol, methane, propane, liquid gas, etc.

The third largest chemical produced today worldwide in millions of tons per year has been forgotten somehow. This material contains 50% more hydrogen per liter than pure liquid hydrogen, and it is carbon-free: it is ammonia, NH_3 .

This gas can be liquefied easily at ambient temperatures using pressures of 8–9 bar, which is quite the same as butane in lighteners. Hence, no high-pressure vessels are needed. In fact, the technology of producing, shipping (transportation), storage and supplying is very old and well developed. Ammonia was used in every refrigerator, before it was replaced by the environmentally critical chlorofluorocarbons, CFCs. For larger areas to be cooled, like on every big ship,



Fig. 6. AFC system running on cracked ammonia and air.

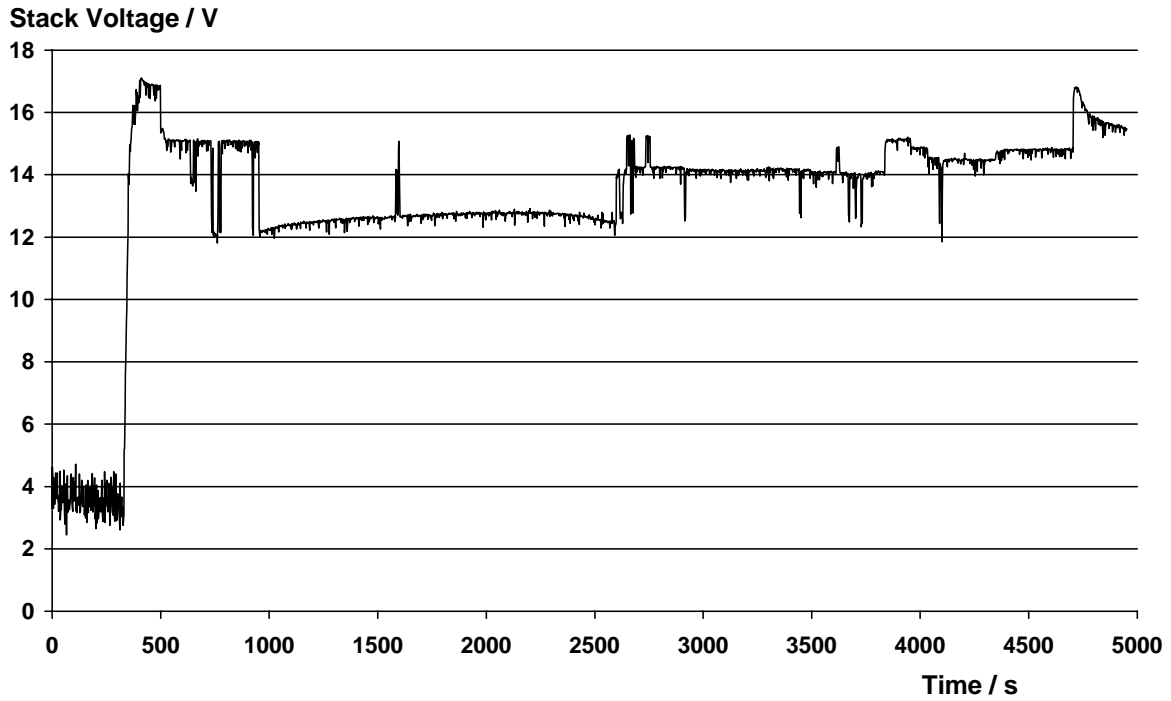


Fig. 7. AFC System of Fig. 6 under test $H_2(N_2)$ from ammonia/air: 40 °C, 9 M KOH; left side: startup.

for cooling skating rinks and bobsleigh lanes, ammonia is still used. Most of the ammonia produced today is used up for the production of fertilizers (like phosphates) and many other products (urea, nitric acid, ...). Some of the pure

liquid ammonia is used for fertilizing directly. In this case, ammonia is sprayed into the ground directly, and many farmers, especially in China and Africa, but also in some parts of the USA and other countries, own a tank of ammonia.

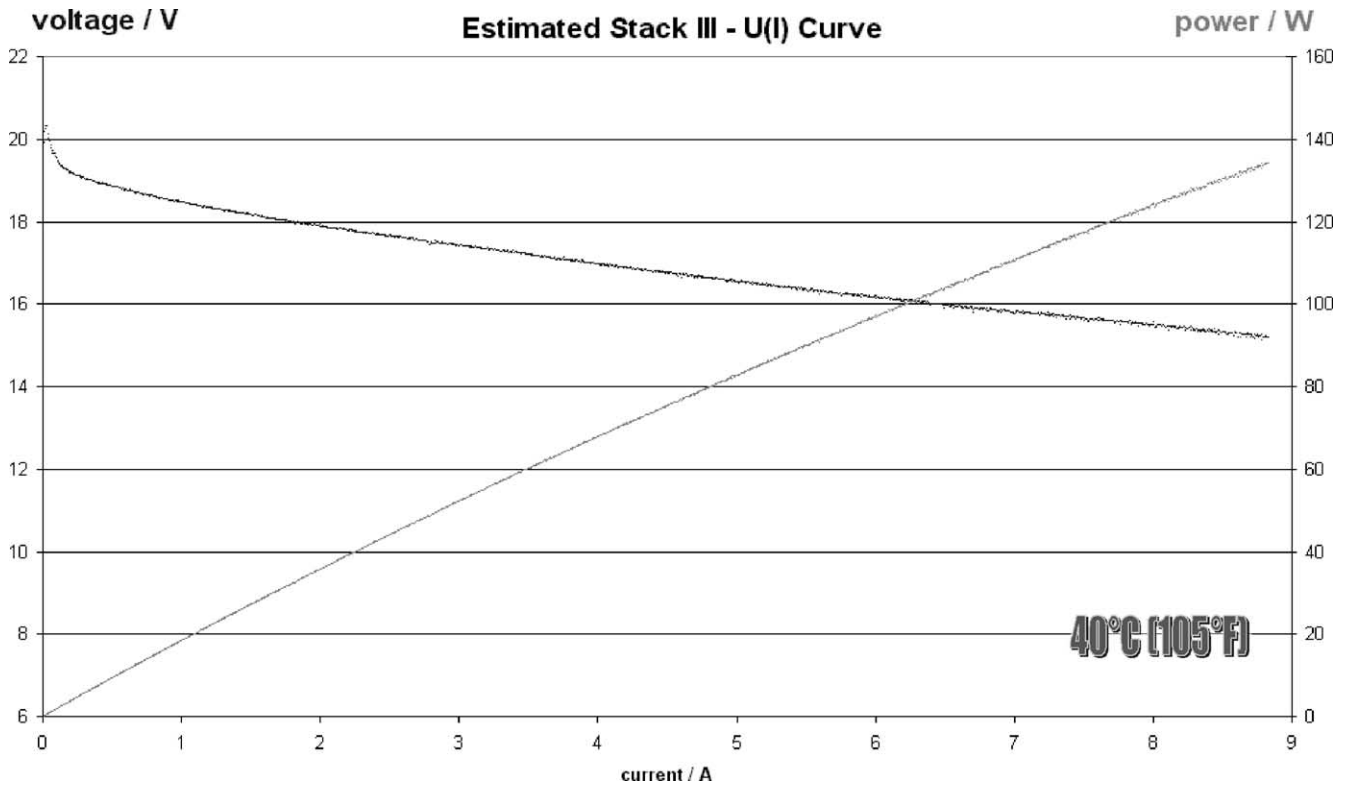


Fig. 8. Performance of the AFC Stack of Fig. 6, 7 m KOH.

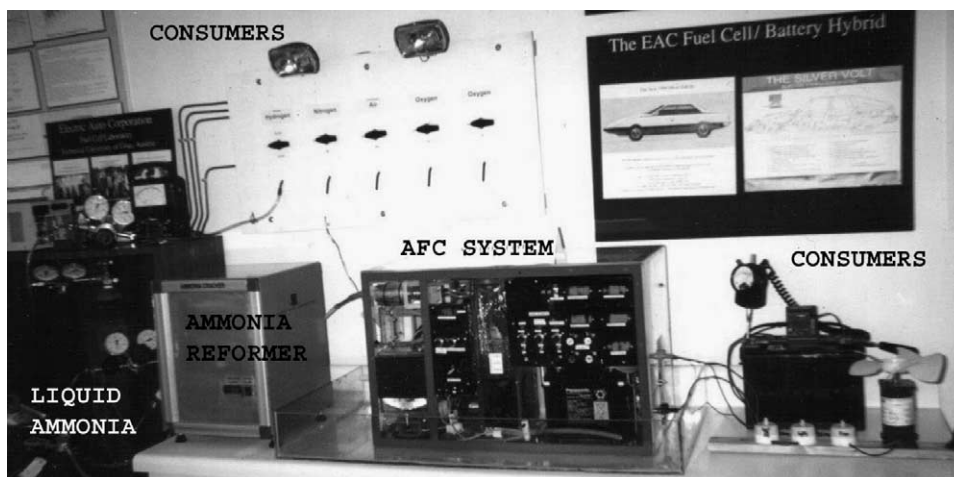
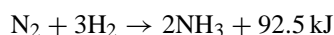


Fig. 9. AFC System demonstration operated with ammonia as fuel.

Ammonia is produced out of hydrogen and nitrogen using the well-known Haber-Bosch process. The basic raw material today is natural gas (methane).



Ammonia is transported the same way as liquid gas: compressed in bottles, via trucks and ships and also in pipelines.

One argument against ammonia is its toxicity. In fact, the danger is not as large as commonly expected. First, it has an extremely strong smell, which is an alarming signal. Therefore, NH_3 poisoning was (and still is) very rare, the lethal dose is $1.5\text{--}2.5 \text{ gm}^{-3}$ ($\approx 2\text{--}31$ pure NH_3 per m^3) for 1 h! Smaller amounts of gaseous ammonia lead to irritations of eyes and skin, higher amounts cause etching. However, in contrast to poisoning by methanol, which is mainly irreversible, poisoning by ammonia is nearly fully reversible.

Second, ammonia is environmentally friendly (fertilizer!), hence any leakages do not cause sustainable problems. Everybody knows the efforts needed if gasoline and alike get into the ground. Methanol is even worse. It is water soluble and gets into the groundwater easily, poisoning it for a long time.

Third, the explosion range of ammonia in air is very narrow (15–28 vol.%), outside that range it does not support burning.

Table 1 below summarizes the advantages of ammonia as fuel. Of course, some of the arguments can be seen as disadvantages also, but when looking at the facts objectively and comparing it with the risks of existing fuels (gasoline, diesel, liquid gas), a decrease of danger is obvious.

To prove the capability of an alkaline fuel cell to run on cracked hydrogen, two ammonia reformers were built and connected to a laboratory AFC system with circulating electrolyte (Fig. 6). These two reformers were of different type: one was heated by burning hydrogen which left the fuel cell as bleed gas, the second one was heated electrically (for details see [11]).

The first test was made using the chemically heated cracker. Different loads were drained from the AFC system (lights, motors, resistors, internal heater, battery recharging, ...) while the data was obtained by a data acquisition system continuously (curves like Fig. 7). All cells (19) showed good properties, 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 (Fig. 8). The hydrogen was circulated inside the AFC system via a fan-cooled water condenser; however, as there was a nitrogen buildup in the hydrogen loop, the hydrogen-rich bleed gas was used for heating the cracker (internal burner) and carry on the endothermic cracking reaction. Although there was a direct burning of hydrogen and oxygen (from air) in presence of nitrogen, no NO_x could be detected. This was expected, as NH_3 , which was also present, is known to prevent the buildup of NO_x .

Numerous presentations were given in Fort Lauderdale, USA, where visitors could see the AFC system in operation together with the electrically heated cracker (Fig. 9).

It could be proven that ammonia could be a powerful way to store hydrogen while keeping the risks low. However, as very common acidic fuel cell types like the PEMFC cannot support the caustic gas NH_3 , and a reduction of NH_3 in the reformer off-gas can only be accomplished by increasing the reformer temperature up to 900°C or more, which then increases the problems with startup and materials, the use of pure ammonia as fuel will stay just one of the big advantages of alkaline fuel cells.

Acknowledgements

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