Short communication

Current status of combined systems using alkaline fuel cells and ammonia as a hydrogen carrier

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Abstract

In order to solve the hydrogen storage problem ammonia is considered as a storage compound. Hydrogen is supplied by a cracking process. According to equilibrium conditions traces of ammonia are expected, which are known to negatively affect PEM-based fuel cells. Experiments with alkaline fuel cells were carried out. No negative effects on the cell performance were found, when the feed gas contained low concentrations of ammonia.
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Keywords: Ammonia; Fuel cell; AFC; Hydrogen supply

The issue of the fuel storage is a major challenge for portable applications of fuel cells. Although there had been attempts to use methanol as a fuel in combination with direct methanol fuel cells (DMFC) [1], it seems that only hydrogen-based fuel cells provide an efficiency of energy conversion that justifies the change of technology in the field of vehicle propulsion. Considering the fundamental differences of properties between hydrogen and conventional fuels for internal combustion engines (ICE) the design of vehicles driven by fuel cells powered engines includes the development of a new fuel storage technology. The following concepts have been investigated so far

(1) Direct storage of hydrogen:
   - pressurized in high pressure tanks;
   - as a liquid in cryogenic tanks;
   - in form of reversible storage alloys, e.g. LaNi$_6$.
(2) The use of hydrogen containing storage compounds which are converted into hydrogen and by-products by a more or less irreversible chemical reaction in a separate process:
   - carbon containing liquid compounds, e.g. methane, LNG, methanol;
   - carbon-free liquid compounds: ammonia;
   - (solid) metal hydrides, e.g. NaBH$_4$ and stoichiometric hydrides of elements of the first and second group of the periodic table of the elements.

Each of these solutions has advantages and disadvantages. Technologies applying the direct storage of hydrogen are dependent on the existence of a hydrogen distribution infrastructure which – although proposed under the slogan "hydrogen economy" – did not exist 15 years ago and is currently established by ambitious projects with large amounts of public funds in the United States [2] and the European Union [3]. Technologies which provide hydrogen by conversion of storage compounds can rely on existing fuel distribution infrastructure, in the case of ammonia at least in the United States and China [4,5,8]. On the other hand the introduction of reforming components increase the complexity of the system and the feed gas to be introduced into the anodic compartment of the fuel cells contains unwanted by-products as carbon monoxide, carbon dioxide and methane in the case of hydrocarbons and nitrogen in the case of ammonia.

Using ammonia it is possible to avoid catalyst poisoning by carbon monoxide and the conversion reaction is simplified compared to the reforming of hydrocarbons.

1. Thermodynamics and stoichometry

The thermodynamic fundamentals of the reaction

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \leftrightarrow NH_3$$
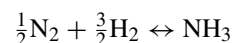
are well established since the beginning of the 20th century, when the formation of ammonia became one of the most important industrial processes. The corresponding thermodynamical

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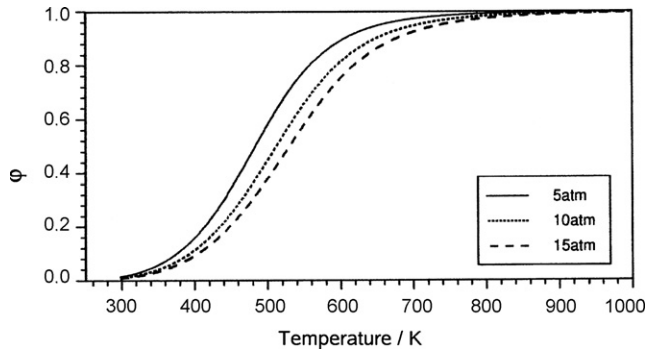 *E-mail address:* kmno2@aol.com (K. Kordesch).

Fig. 1. Numerical calculated values for φ based on a interpolation algorithm on data points from Ref. [7] and Eqs. (1)–(3).

data are accessible via standard information sources [7,8]. From these data the conversion factor φ for the decomposition reaction can be calculated according to

$$\varphi = \sqrt{\frac{K_x}{K_x + \sqrt{27}/4}} \tag{1}$$

φ assumes values between 0 and 1 with the meaning of no ammonia decomposition taking place at a hypothetical value of 0 and complete decomposition for a hypothetical value of 1.

Fig. 1 shows φ calculated according to Eq. (1) for a temperature range from 300 K to 1000 K. K_x was calculated using Van't Hoff's equation

$$\ln K_p(T) = \int_{298\,K}^{T} \frac{\Delta H_R(T)}{RT^2} dT + \ln K_p(298\,K) \tag{2}$$

with

$$K_x = K_p \frac{1}{P} \tag{3}$$

because the number of molecules increases by 1 in the reaction regarded. The software LabPlot [6] was used to approximate $\Delta H_R(T)$ on the basis of data points from Ref. [7] formulated as a fourth order polynomial

$$\Delta H_R(T) = 36.405 + 0.042686T - 3.9322 \times 10^{-5}T^2$$
$$+ 2.2384 \times 10^{-8}T^3 - 6.4 \times 10^{-12}T^4 \tag{4}$$

The accuracy of the approximation can be described by

$$\overline{\Delta(\Delta H_R(T))} = \frac{1}{n}\sum_{i=1}^{n} \Delta(\Delta H_R(T))_i = 1.49 \times 10^{-3}\,kJ\,mol^{-1} \tag{5}$$

and

$$S^2 = \frac{1}{n-1}\sum_{i=1}^{n}(\Delta(\Delta H_R(T)) - \overline{\Delta(\Delta H_R(T))})^2$$
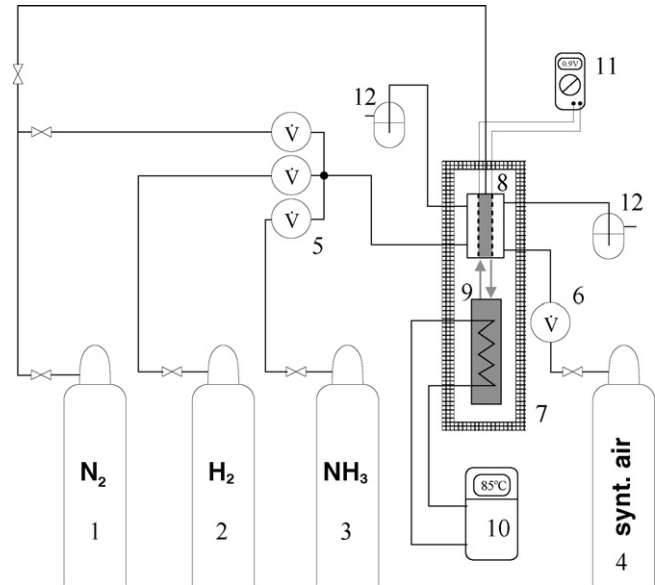$$= 1.14 \times 10^{-3}\,kJ\,mol^{-1} \tag{6}$$

with $n = 11$.

Fig. 2. Experimental setup: gas sources (1–4), gas flow control (5,6), thermal insulation (7) and temperature control (10), fuel cell (8), electrolyte storage tank (9), electric data acquisition (11), and exhaust gas outlet (12).

Assuming that ammonia which is not split into hydrogen and nitrogen can be burned after passing the anode compartment of the fuel cell and contributes to the heat supply for the endothermal decomposition reaction it is possible to shift the operating temperature of the cracker to comparably low values, i.e. below 400 °C. Under these circumstances the feed gas contains several percent of ammonia, so the question arises if this affects the fuel cell performance.

From PEM-based fuel cells it is known that they are highly sensitive to even traces of ammonia [9,10], so either high cracker temperatures [11] or a gas cleaning system is required. Here we report our experiences with alkaline fuel cells.

2. Experimental

The experimental setup is displayed in Fig. 2: The fuel cell – in single cell design – was fed by a mixture of hydrogen, nitrogen and ammonia on the anode side, as well as synthetic air on the cathode side. The electrolyte was forced to circulate between the fuel cell and the storage tank by a small stream of nitrogen and a sophisticated cell design described in detail elsewhere [12]. The electrodes were prepared using established technology [13,14]. Platinum catalysts was used as a catalyst both on the anode and the cathode, the geometrical area of the electrodes was 12.5 cm^2. Voltages were recorded with IR-correction using a Kordesch-Marko-bridge [15–17] in the case of current voltage characteristics.

3. Results and discussion

In Fig. 3 current–voltage characteristics with hydrogen (1 ml s^{-1}), a hydrogen/nitrogen mixture (0.8 ml s^{-1}/0.3 ml s^{-1}) and a hydrogen/nitrogen/ammonia
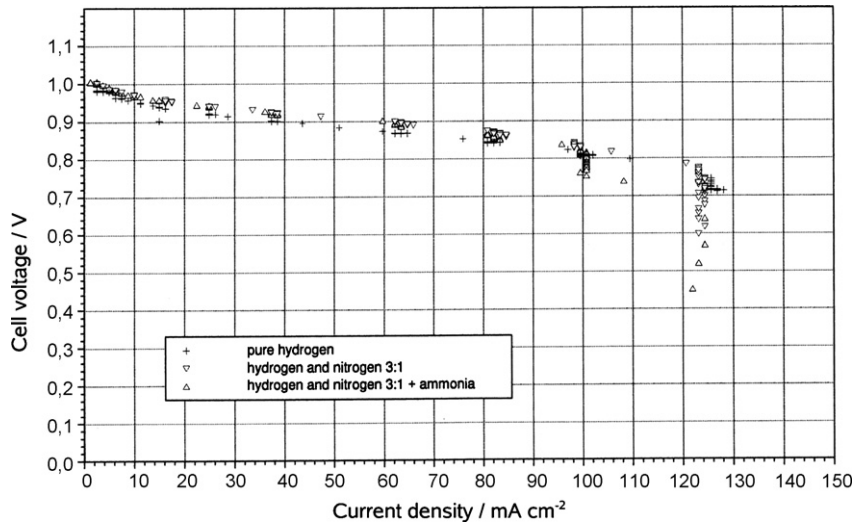
Fig. 3. Single cell performance of an alkaline test cell with pure hydrogen and mixtures of hydrogen and nitrogen, respectively hydrogen, nitrogen and ammonia.

mixture $(0.71\,\mathrm{ml\,s^{-1}}/0.23\,\mathrm{ml\,s^{-1}}/0.09\,\mathrm{ml\,s^{-1}})$ are compared (the air flow in these experiments was set to $1.5\,\mathrm{ml\,s^{-1}}$). It can be seen that the gas mixtures with and without ammonia show similar performance for current densities up to $100\,\mathrm{mA\,cm^{-2}}$. The flowfield of the test cell was not optimized, the performance decay at $120\,\mathrm{mA\,cm^{-2}}$ may be attributed to diffusion effects in the pores of the diffusion zone of the anode.

Experiments with an ohmic load of $10\,\Omega$ were performed to study the response of the cell to a potential breakdown of the ammonia cracker with the focus on the recovery behaviour. An example of this type of experiment is shown in Fig. 4. Initially the cell was fed with an hydrogen/nitrogen/ammonia mixture $(0.8\,\mathrm{ml\,s^{-1}}/0.24\,\mathrm{ml\,s^{-1}}/0.09\,\mathrm{ml\,s^{-1}})$. At $t = 0\,\mathrm{s}$ the cell was exposed to a stream of ammonia, until a significant response of the cell voltage was recorded. Then the initial gas flow was restored. The cell voltage was recorded with an accuracy of $\pm 1\,\mathrm{mV}$ at a sampling rate of $3\,\mathrm{min^{-1}}$.

The cell showed an initial voltage of $0.85\,\mathrm{V}$ (no IR-correction) and a sharp decay, obviously when the backside of the anode was flooded with ammonia. The cell voltage recov-

ered, when the initial gas flow was restored, to the initial value of $0.85\,\mathrm{V}$.

These results indicate that ammonia does not irreversibly affect the performance of alkaline fuel cells. Due to the high pH only small amounts of ammonia dissolve in the electrolyte. No attempts were made to measure these small concentrations, they are supposed on the basis of equilibrium considerations. Because the duration of the corresponding experiments was limited to $100\,\mathrm{h}$ catalyst poisoning cannot be completely ruled out, although it is very unlikely on the basis of existing data.

4. Conclusion

Experimental data showed that alkaline fuel cells are – in contrast to acid PEM fuel cells – tolerant to ammonia. Because of the simplicity of the conversion reaction and the absence of carbon monoxide and carbon dioxide, hydrogen produced by the cracking of ammonia is the ideal fuel supply for alkaline fuel cells [18].

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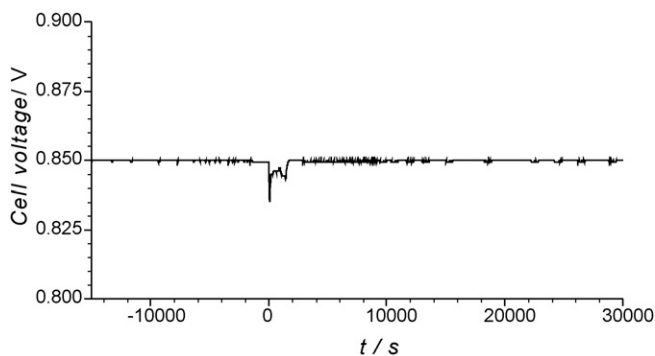[10] K. Heikrodt, Felderprobung Fa. Viessmann, WBZU workshop, Ulm, March 3, 2005.

Fig. 4. Voltage response of the cell in experiments carried out to study the recovery from a simulated cracker breakdown.

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