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HIGHLY EFFICIENT CONVERSION OF AMMONIA IN ELECTRICITY BY SOLID OXIDE FUEL CELLS

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Highly efficient conversion of ammonia in electricity by Solid Oxide Fuel Cells

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Abstract

Hydrogen is the fuel for fuel cells. A drawback for the use of hydrogen is the low energy density storage capacity, even at high pressures. Liquid fuels such as gasoline and methanol have a high energy density but lead to the emission of the greenhouse gas CO_2. Ammonia could be an alternative fuel, having a high energy density at relative low pressure and no (local) CO_2 emission.

Ammonia as a fuel for the Solid Oxide Fuel Cell appears to be very attractive. Cell tests were performed with Electrolyte Supported Cells (ESC) as well as Anode Supported Cells (ASC) of 100 cm^2. The cell voltage was measured as function of the current, temperature and NH_3 flow. Due to the high temperature and the catalytic active Ni containing anode, NH_3 cracks in the anode compartment into $3H_2$ and N_2. The formed H_2 is converted into electricity. Measurements have shown that electrical cell efficiencies up to 70% (LHV) can be achieved at 0.35 A/cm^2 and 60% (LHV) at 0.6 A/cm^2. The cell degradation was not affected by the presence of NH_3.
At temperatures above 700^{o}C, the conversion of NH_3 is nearly 100% due to the withdrawal of H_2 by the electrochemical cell reaction and is close to the thermodynamic equilibrium. The NO_x outlet concentration of the fuel cell was measured to be below 0.5 ppm at temperatures up to 950^{o}C and around 4 ppm at 1000^{o}C.

SOFC systems fuelled with ammonia are relative simple compared with carbon containing fuelled systems, since no humidification of the fuel is necessary to prevent carbon deposition. Also, the endothermic NH_3 cracking reaction consumes part of the heat produced by the fuel cell, by which less cathode flow is required for cooling of the stack compared with H_2 fuelled systems. Therefore the system for a NH_3 fuelled SOFC will have relatively low parasitic power losses and smaller heat exchangers.

Introduction

Ammonia is produced in high quantities, mostly used as raw material for the production of artificial fertilizer and nitric acid [1]. Ammonia could also be used as a fuel. Since ammonia becomes liquid at a moderate pressure of 8 bar, the volume energy density is much higher compared with compressed H_2. Liquid fuels such as gasoline and methanol have a comparable energy density as ammonia but contribute to the greenhouse effect by the CO_2 emission.

It has been shown that NH_3 as contaminant in biogas is converted in a SOFC into electricity. The most likely mechanism is that NH_3 is first cracked in $3H_2$ and N_2 after which the formed H_2 is electrochemically converted into electricity. Direct electrochemical conversion of NH_3 in electricity is not likely to occur [2]. Recently it was shown that SOFCs can convert pure NH_3 into electricity by using Fe, Ag or Pt anodes [3]. Only with the Pt anode a reasonable current density was measured. Ni/Al_2O_3 is known to be an active catalyst for the cracking of NH_3 [4-6]. Therefore it is very likely that a SOFC with a standard Ni/YSZ anode can convert pure NH_3 into electricity.

In the project "Ammonia Cracking for Clean Electric Power Technology" (ACCEPT), partly funded by the European Commission within the Fifth Framework Programme, ammonia is evaluated as fuel for both Solid Polymer Fuel Cells (SPFC) and Solid Oxide Fuel Cells (SOFC). The study includes a safety study, life-cycle analysis, issues concerning ammonia production and storage, testing of the ammonia sensitivity of a SPFC, development of an ammonia cracker for use with the SPFC, system integration and testing of a 10 kW_{el} SPFC system. Besides, pure ammonia without external cracker was tested as fuel for a SOFC. In this paper the results will be given of the measurements of the ammonia fuelled SOFC.

Experimental

Two type of cells were tested, namely Electrolyte Supported Cells (ESC) and Anode Supported Cells (ASC).

The ESC consists of a TZ3Y electrolyte of 150 μm thickness, as made by tape casting. After sintering, the Ni/8YSZ anode with a thickness of 50 μm and the $La_{0.7}Sr_{0.2}MnO_{3-\delta}$ (LSM) cathode of 50 μm thickness were applied by screen printing. The area of the electrolyte was 100 cm² (10x10 cm²). The active area of the cell is determined by the area of the electrodes, being 81 cm² (9x9 cm²).

The anode of the ASC consists of a Ni/8YSZ layer with a total thickness of about 500 µm, as made by tape casting. On top of the anode, an 8YSZ electrolyte of 5-10 µm and a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode of 15 µm were screen printed. The area of the anode and electrolyte was 100 cm² (10x10 cm²). The active area of the cell is determined by the area of the cathode of 81 cm² (9x9cm²).

The operating temperature of the ESC cell is between 850 and 1000°C. The high operating temperature of the ESC is necessary in order to have a reasonable performance caused by the low ion conductivity of the relative thick supporting electrolyte. Due to the thinner electrolyte and the use of the LSCF cathode, the operating temperature of the ASC cells is in the range of 700 to 800°C. Both type of cells were supplied by Innovative Dutch Electro Ceramics InDEC B.V. (www.InDECpp.com) as part of their standard cell delivery programme.

The cells were tested in a test-rig with a ceramic cell housing, sealed at the fuel side on the electrolyte (ESC) or on the anode (ASC) by a gold seal. The electrical contact was made by a Ni-grid on the anode side and a Pt-grid on the cathode side. The anode and cathode gasses were provided in a co-flow configuration.

The cells were characterized by measuring the cell voltage as function of the current density, anode gas composition, flow and temperature. The standard gas for the measurements in the SOFC was pure NH_3. In order to determine the effect of the internal NH_3 cracking on the cell voltage, various mixtures of $3H_2/N_2$ and NH_3 were applied simulating an equivalent gas with 0, 25, 50, 75 en 100% NH_3. In table 1, an overview of the gas mixtures is given relative to 100 units of NH_3.

	NH3	H2	N2
H2-ref	-	150	-
0% NH3	0	150	50
25% NH3	25	113	38
50% NH3	50	75	25
75% NH3	75	38	13
100% NH3	100	0	0

Table 1. Overview of the anode gas mixtures, equivalent with a gas of 100 units of NH_3.

Two anode flow rates were used, namely a nominal and a high flow rate having 100% fuel utilization at 0.4 and 0.7 A/cm² respectively. On the cathode side, the air flow rate was constant for all experiments. The maximum O_2 utilization was 50% for a current density of 0.7 A/cm².

For a series of measurements under NH_3, the outlet gas was analysed on NO_x and NH_3.

Results and discussion

In Fig. 1 the cell voltage of the ESC is given as function of the current density at 900-1000°C for the gas mixtures as shown in Table 1 with 0-100% NH_3. For all temperatures it is clearly seen that the cell voltage is independent of the gas composition for the high flow rate, as also measured at the nominal fuel flow rate (not shown). Due to the independency of the cell voltage on the NH_3 content, it was shown by calculations that the ammonia must be cracked in $3H_2$ and N_2 directly at the inlet of the anode of the cell.

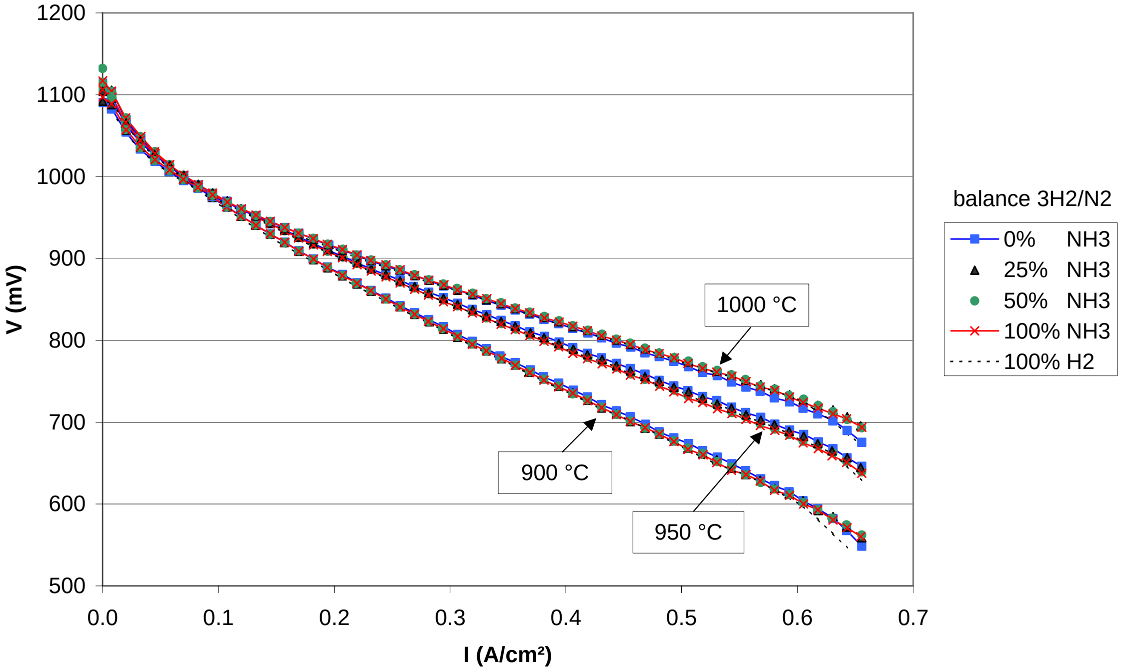


Fig. 1. Cell voltage as function of the current density and fuel composition (ESC with LSM cathode, 900-1000°C, 100% fuel utilization at 0.7 A/cm² (high flow))

In Fig. 2 the cell voltage of the ASC is given as function of the current density at 700-800°C for the same conditions as the ESC of Fig. 1. In this temperature range the cell voltage of the ASC is much higher than for the ESC cell. At 800°C and 750°C, again the cell voltage is nearly independent of the NH_3 content, while at 700°C the cell voltage becomes lower at increasing NH_3 content. This effect was less pronounced for the nominal fuel flow rate. Apparently at 700°C the NH_3 cracking rate is limited by the kinetics of the NH_3 dissociation at the anode, by which less H_2 is available for the electrochemical reaction at the inlet of the fuel cell resulting in a slightly lower performance.
In order to determine the NH_3 conversion, the NH_3 outlet concentration was measured for the ESC and ASC at a fuel utilisation of 75% (nominal flow, Fig. 3).

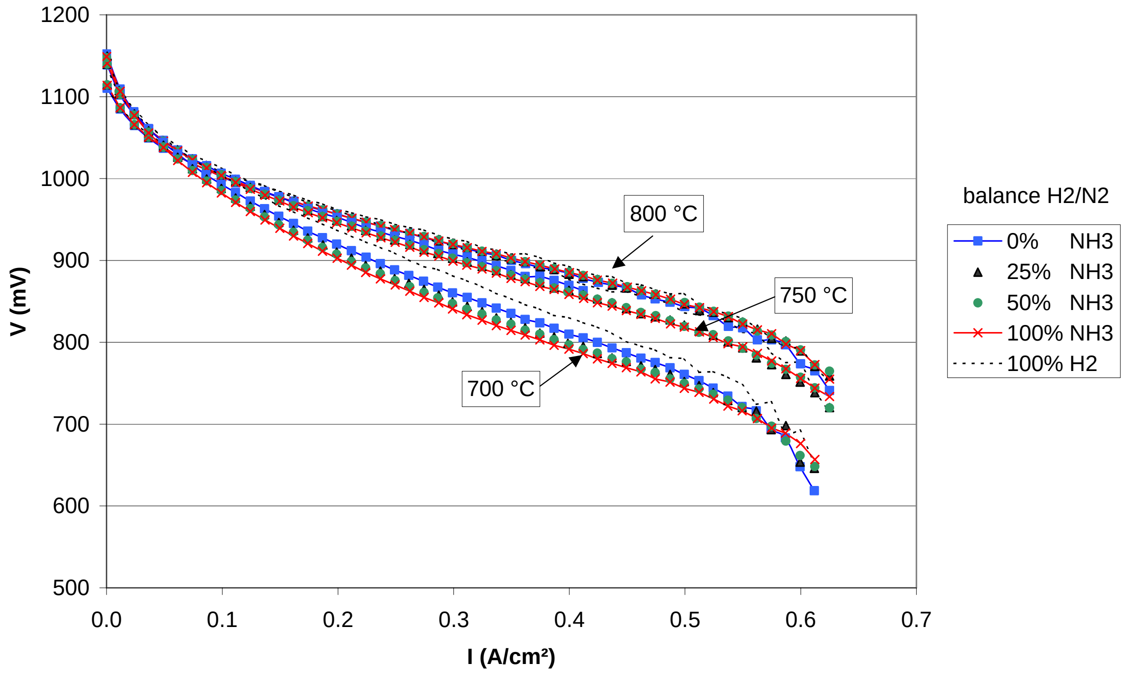


Fig. 2. Cell voltage as function of the current density and fuel composition (ASC with LSCF cathode, 700-800°C, 100% fuel utilization at 0.7 A/cm² (high flow))

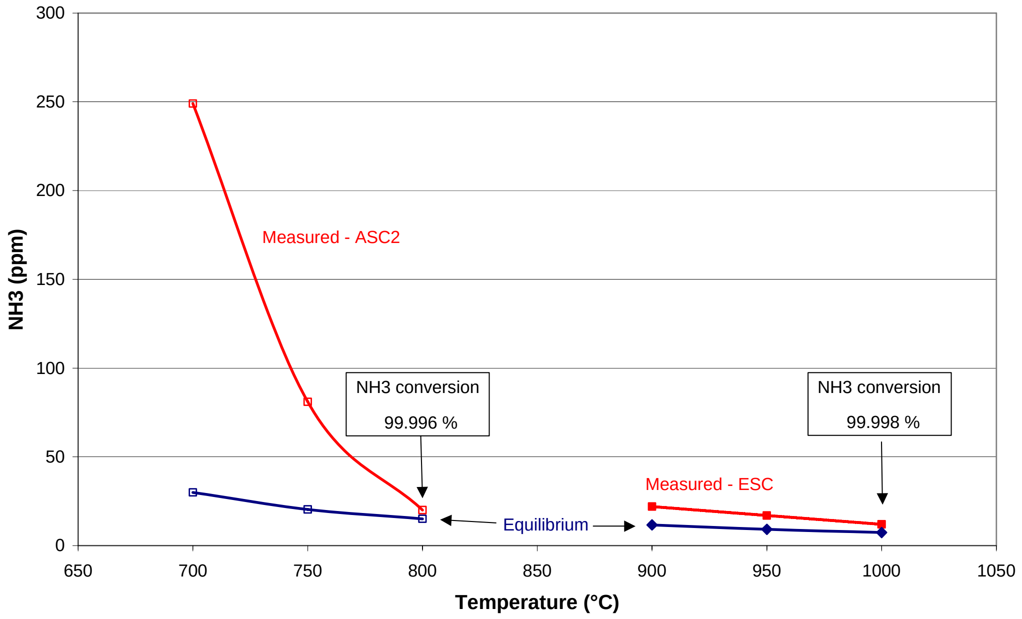


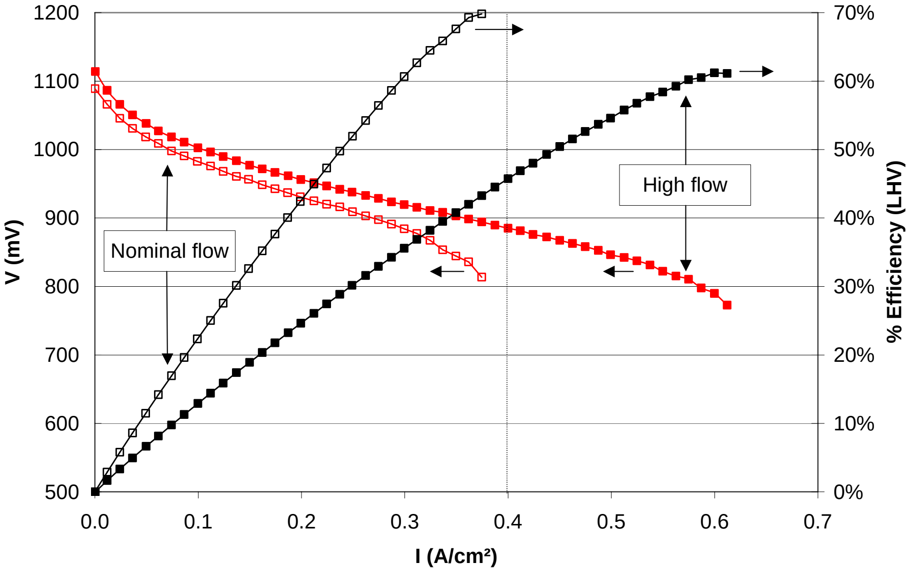
Fig. 3. Measured and equilibrium NH_3 outlet concentration as function of the temperature (ESC and ASC cells, 75% fuel utilization, nominal NH_3 flow)

At 1000°C, the outlet concentration of the ESC cell was nearly equal to the equilibrium composition, as based on the thermodynamics of the reactions. The measured NH_3 conversion is 99.998%. By lowering the temperature to 900°C, the NH_3 concentration is about a factor 2 higher than the equilibrium value.

For the ASC the NH_3 conversion at 800°C is 99.996%, again close to the equilibrium composition. Apparently the NH_3 cracking rate of the ASC at 800°C is higher than the cracking rate of the ESC at 900°C. The higher rate must be ascribed to the 10 times higher Ni content of the anode of the ASC cell compared with the ESC cell, supporting the conclusion that the NH_3 cracking rate is limited by the kinetics of the anode for this reaction. By lowering the temperature to 700°C, the NH_3 cracking rate becomes limited by the finite reaction rate of the anode, resulting in a higher NH_3 concentration at the outlet of the cell.

In a stack with a co-flow configuration and ASC cells, the temperature will be in the range of 700 to 800°C for the inlet and outlet temperature, respectively. The high outlet temperature will assure that most NH_3 is converted in the stack. The remaining NH_3 will be burnt in the afterburner of the system, as needed to convert the remaining H_2 of the anode off-gas. Due to the lower cracking rate at the lower inlet temperature of the cell, the zone with the cracking reaction is spread over the inlet part of the cell, which reduces the thermal stresses as caused by the highly endothermic cracking reaction. Therefore the operating window of 700-800°C of the ASC cells seems to be quite optimal. For the ESC the high cracking rate could result in defects by thermal stresses near the inlet of the cell. This was not the case for the long term test during 3000 hours, as shown later on in this paper.

Fig. 4. Cell voltage and efficiency as function of the current density (NH_3, ASC with LSCF cathode, 800°C, 100% fuel utilization at 0.4 A/cm² (nominal flow) and 0.7 A/cm² (high flow))

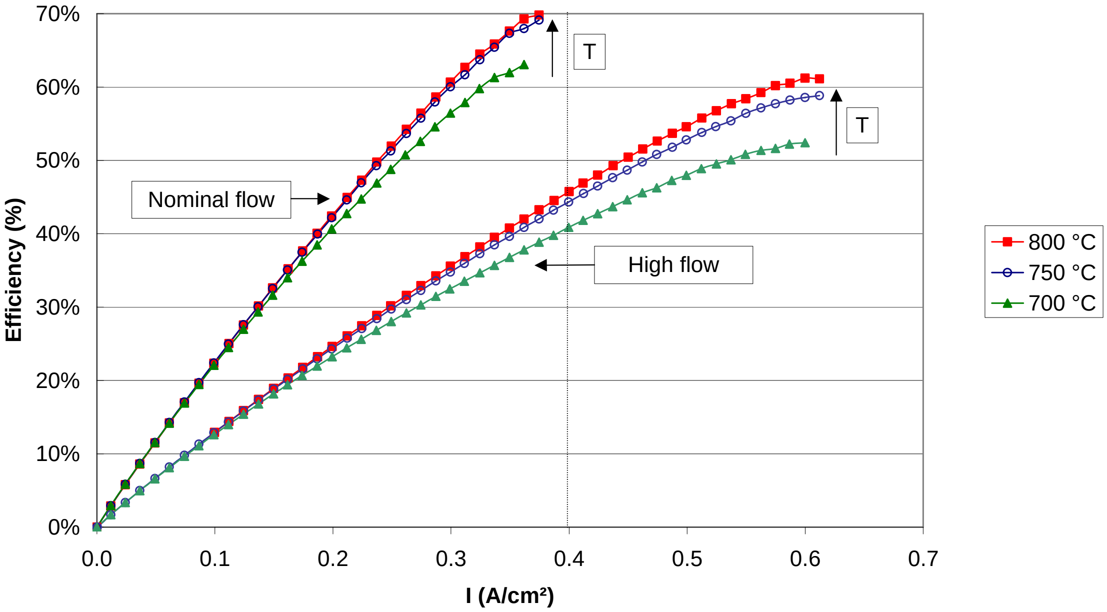


In Fig. 4 the cell voltage and electrical efficiency are given for the ASC cell at 800°C at the nominal and high fuel flow. The electrical efficiency is defined as the electrical power output, divided by the NH_3 fuel input (LHV).

For the nominal flow, the maximum electrical efficiency was about 70% (LHV). The very high fuel efficiency is due to two reasons. Firstly, the cell voltage is high, comparable with dry hydrogen. Secondly, part of the heat of the cell is internally used by the cracking reaction, by which the electrical efficiency is increased by 13% compared with dry hydrogen. The maximum efficiency at the higher flow rate is 60% (LHV), which is lower due to the higher current density.

In Fig. 5 the efficiency of the ASC is given as function of the temperature. For the temperatures between 700 and 800°C, the maximum efficiencies are in the range of 63-70% and 52-60% for the nominal and high flow rate, respectively. The efficiencies of the ESC in the temperature range of 900-1000°C are slightly lower, namely 57-61% and 47-59% under equal conditions (not shown).

Fig. 5. Efficiency as function of the temperature and current density



(NH_3, ASC with LSCF cathode, 800°C, 100% fuel utilization at 0.4 A/cm² (nominal flow) and 0.7 A/cm² (high flow))

The cells were also tested during 3000 hours in order to determine their long term stability under pure NH_3. In Fig. 6, the cell voltage and efficiency is given in time for the ASC at 750°C, fuel utilisation of 75%, high flow rate and a current density of 0.54 A/cm². The average voltage degradation rate was less than 1%/1000 hours. The degradation tends to become lower with time. For the ESC the degradation rate was 0.74%/1000 hours (950°C, U_f = 75%, nominal flow, 0.3 A/cm²), which is comparable with the ASC taking into account the lower current density. For both type of cells, the degradation is comparable with other cells tested under H_2 in a test-rig with a ceramic housing and gold seals. Therefore it must be concluded that the presence of pure NH_3 does not increase the degradation rate of the cells.

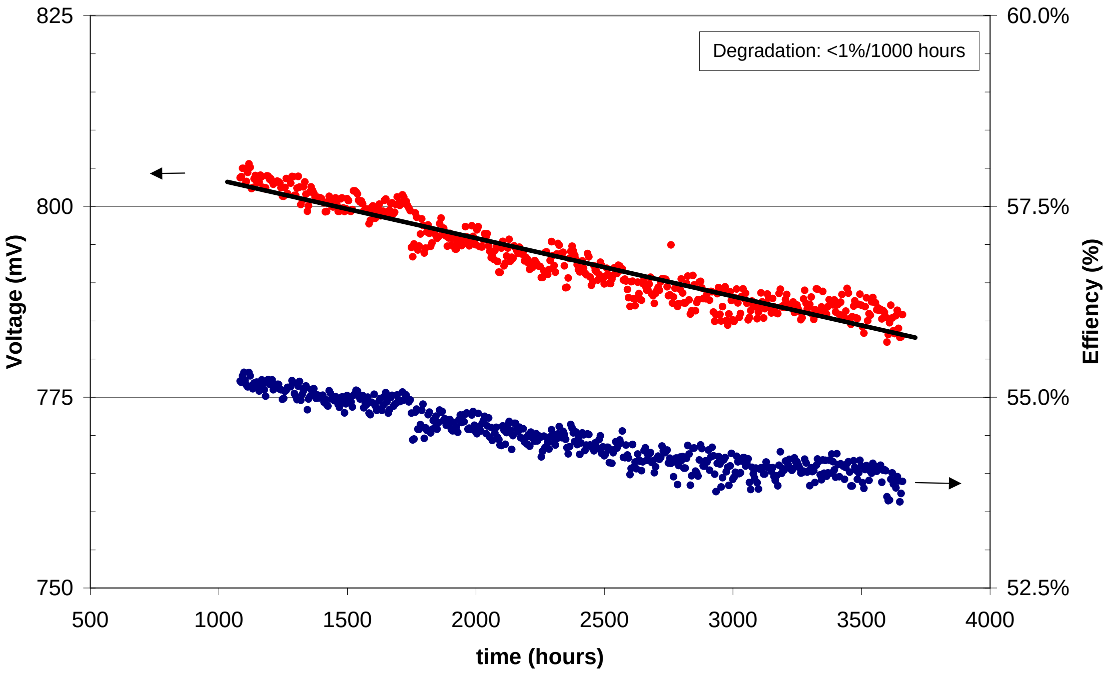


Fig. 6. Cell voltage and efficiency with time (ASC with LSCF cathode, 750°C, high flow, 0.55 A/cm², 75% fuel utilization)

An ammonia fuelled system configuration can be very simple. The anode inlet gas is heated up in a heat exchanger by the anode outlet gas. The anode outlet gas from the fuel heat exchanger is burnt with the cathode outlet gas and some additional air. The outlet gas of the burner is used in an air heat exchanger to heat up the air stream to the required cathode inlet temperature. Due to the high electrical efficiency of the stack, the heat production in the stack is low limiting the required airflow. Still calculations with ASPEN+ showed that the air heat exchanger for heating up the incoming air is a large component. The size of this heat exchanger can be about halved by placing two stacks in the system, in which the cathode outlet flow of the first stack is connected to the cathode inlet flow of the second stack. The temperature of the outlet gas of the first stack is lowered to the inlet temperature of the second stack by adding a limited amount of cold air [7]. From the efficiency point of view the 2 configurations do no differ much, only the size of the air heat exchanger of the second system is smaller.

Compared with a NG fed system, the ammonia fuelled system configuration is very simple since no recycle blower or humidification of the fuel is required in order to prevent carbon deposition. The system efficiency is much higher, since the performance of the stacks is higher and therefore less cooling air is required resulting in lower parasitic losses of the air blower.

Conclusions

It was shown that 100% NH_3 can be applied as a fuel in standard SOFCs with Ni/YSZ anodes. At the anode the NH_3 is internally cracked into $3H_2$ and N_2, after which the H_2 is electrochemically converted into electricity. The efficiency is high due to two factors. Firstly, the voltage is high, comparable with dry H_2. Secondly, the internal endothermic cracking reaction consumes part of the heat of the fuel cell, by which the electrical efficiency becomes 13% higher compared with H_2. The efficiency depends on the current density and the type of cell. The maximum efficiency (LHV) of an Anode Supported Cell (ASC) at 800 °C is 70% at 0.35 A/cm² and 60% at 0.6 A/cm². The efficiency (LHV) of an Electrolyte Supported Cell (ESC) at 950°C is 60% at 0.35 A/cm² and 53% at 0.6A/cm². The degradation of the cells during 3000 hours under NH_3 was lower than 1%/1000 hours, which is comparable with former tests using the same ceramic cell housing with a gold seal and H_2 as fuel.

The NH_3 conversion at 800°C (ASC) and 1000°C (ESC) was >99.996%, close to the thermodynamic equilibrium. In a system the remaining NH_3 will be converted in the afterburner, which is necessary for the burning of the anode-off gas. The NO_x concentration at temperatures up to 950°C was lower than 0.5 ppm, while at 1000°C 4 ppm was measured.

The system configuration can be very simple, since no anode recycling or humidification is required to prevent carbon deposition which is the case using carbon fuels. The required cathode flow for cooling the stack in the system is low due to the high efficiency of the stack, which reduces the size of the air heat exchanger.

Acknowledgement

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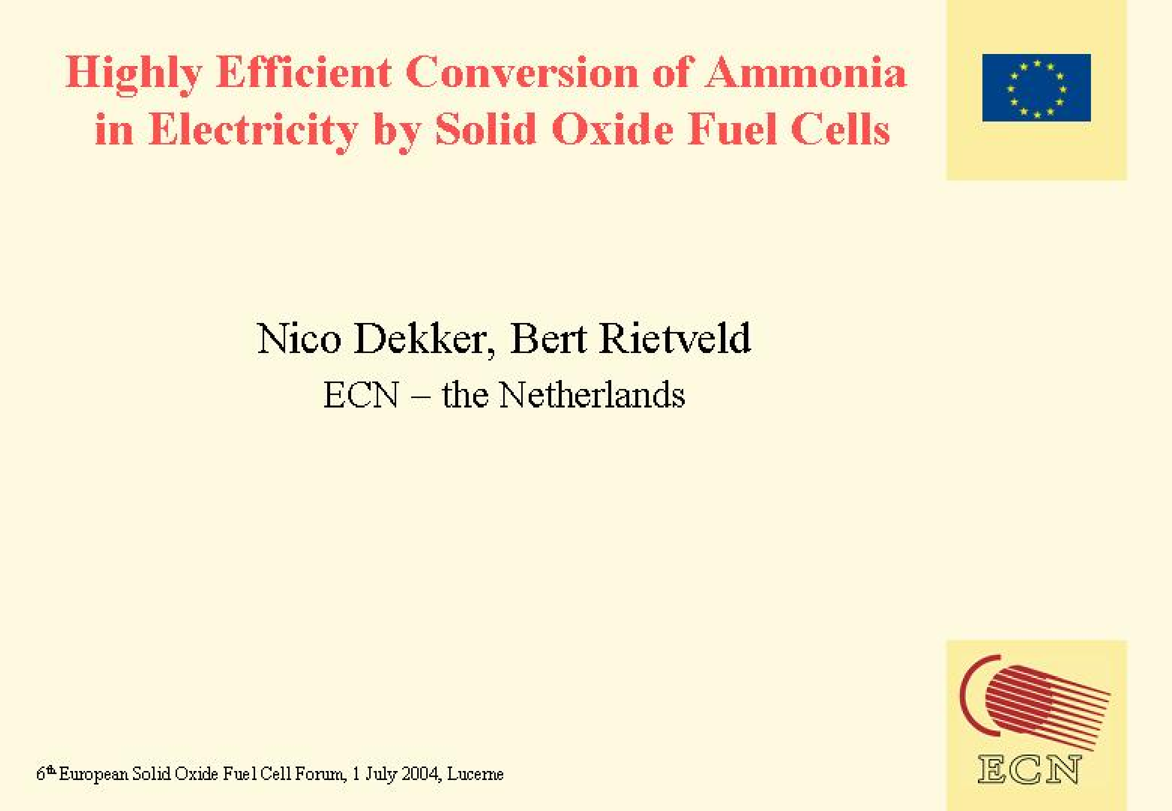

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ECN – the Netherlands

6th European Solid Oxide Fuel Cell Forum, 1 July 2004, Lucerne

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6th European Solid Oxide Fuel Cell Forum, 1 July 2004, Lucerne

EU project "ACCEPT"

ACCEPT: Ammonia Cracking for Clean
Electric Power Technology

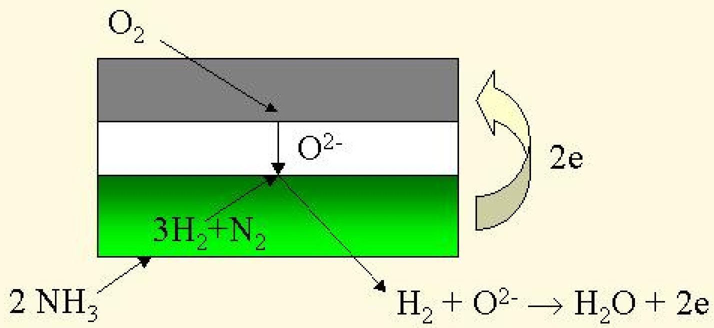
Advantages of ammonia:

- High power density (liquid at 8 bar)
- No (local) CO_2 emissions

Project issues:

- Safety, infrastructure and storage, efficiency and cost
- PEMFC (2 kW_e) with external NH_3 cracker (& absorber)
- **SOFC fuelled with 100% NH_3**

Principle of Ammonia Fuelled SOFC



$H_2 + O^{2-} \rightarrow H_2O + 2e$

Overall: $4\ NH_3 + 3\ O_2 \rightarrow 6\ H_2O + 2\ N_2 + W_{el}$

Cells and Test Conditions

Cells (supplied by InDEC B.V.)

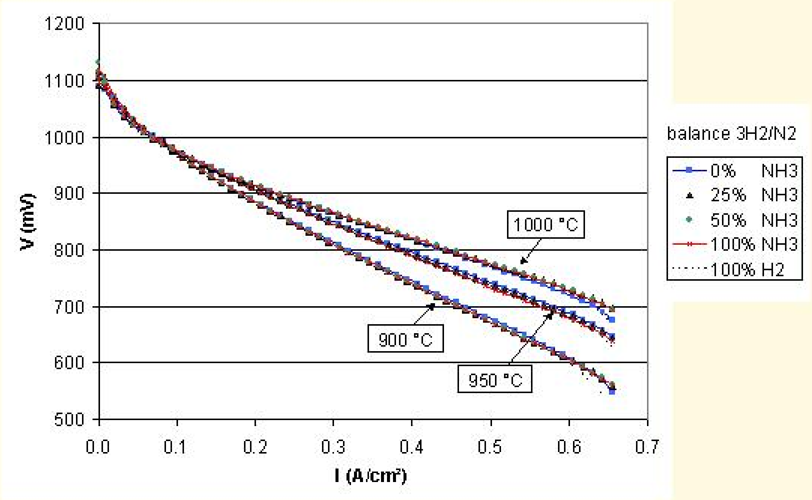
- ESC (Ni-GDC/TZ3Y/LSM-YSZ)
- ASC (Ni-YSZ/YSZ/YDC/LSCF)
- Active area: 81 cm^2

Test conditions

- H_2, 0-25-50-75-100% NH_3 (balance $3H_2/N_2$)
- 700-800°C (ASC), 900-1000°C (ESC)
- Nominal (0-0.4 A/cm^2) and High Flow (0-0.7A/cm^2)

ESC as function of the temperature

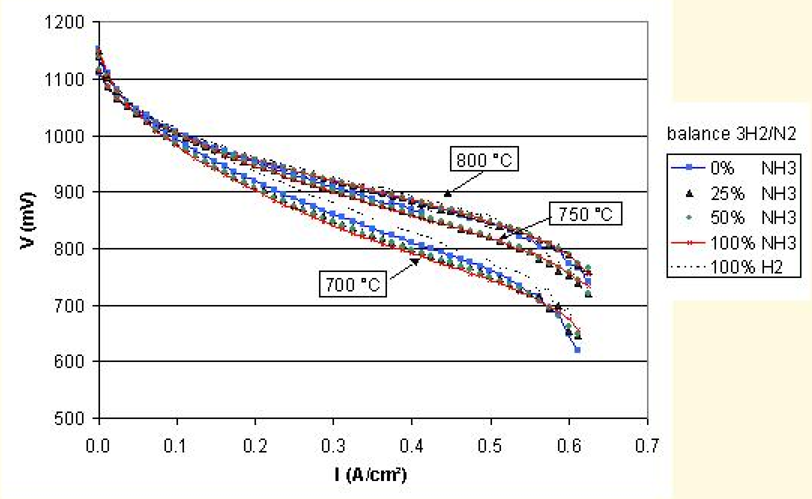
- High flow -



No difference in performance between H_2 and NH_3

ASC as function of the temperature

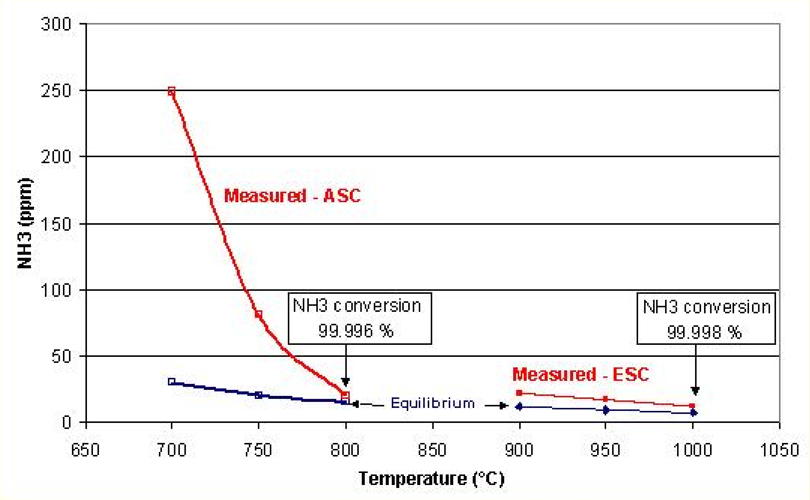
- High flow -



Performance ASC is higher than for the ESC

NH_3 conversion

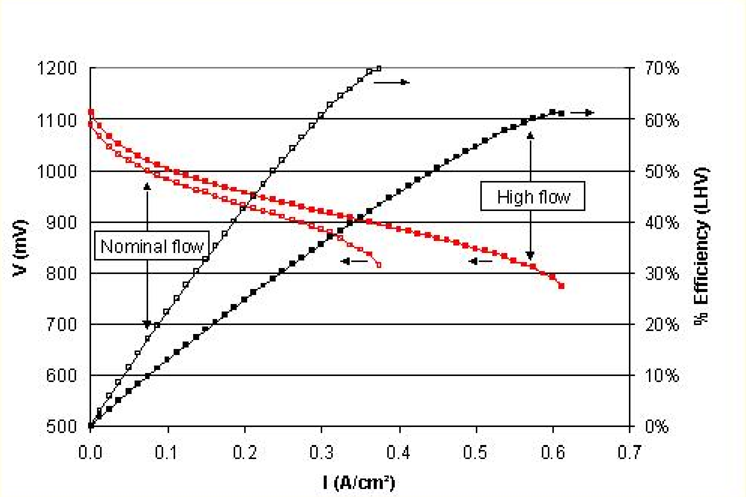
- Nominal flow, U_f = 75% -



Nearly 100% NH_3 conversion at ‘outlet’ temperature

ASC: Cell voltage and Efficiency

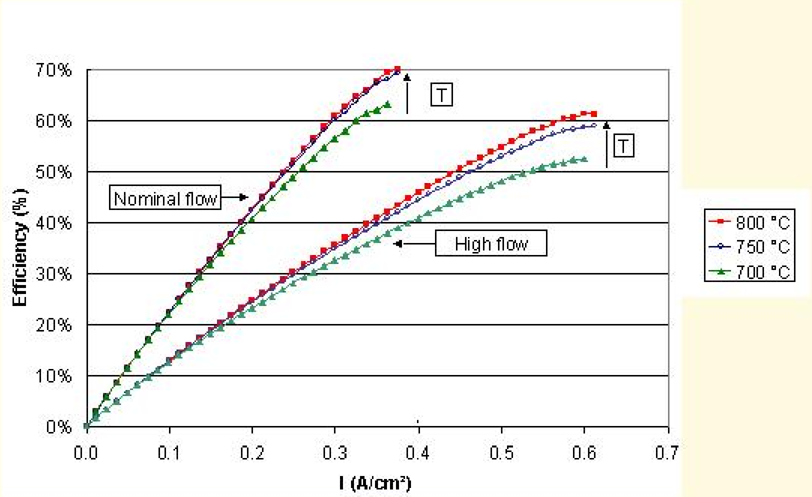
- 800 ^oC -



High efficiency: high voltage & endothermic cracking reaction

ASC: Efficiency

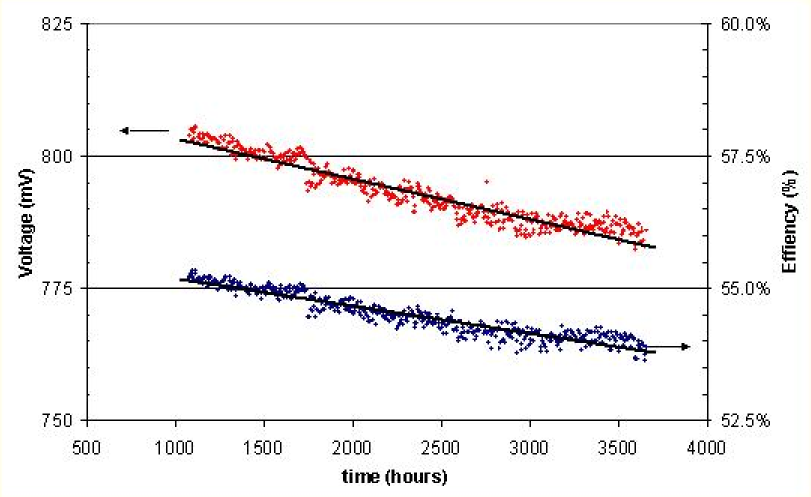
- as function of the temperature -



High efficiency for all temperatures and flows

Performance in time - ASC

- High flow, 750 °C, 0.53 A/cm^2, U_f = 75% -



Degradation < 1% / 1000 hours

Conclusions

Ammonia fuelled SOFC:

- Cell voltage comparable with H_2
- High efficiency
- Low degradation
- High ammonia conversion