

Ammonia as a feedstock for a hydrogen fuel cell; reformer and fuel cell behaviour

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Abstract

In this paper, an indirect ammonia fuel cell system is proposed which circumvents the problem of hydrogen storage. System analysis shows that the specific energy density (kWh/kg or kWh/m³) of such a system is very attractive compared with that of a direct hydrogen fuel cell system. The fuel cell stocks have an important impact on these figures. However, both the indirect ammonia and the direct hydrogen systems use the same type of fuel cells, and improvement in fuel cell characteristics will improve the specific power and energy densities of both systems. Earlier work also showed that ammonia is a more attractive fuel than methanol for an indirect fuel cell. Ammonia therefore merits more attention as a fuel cell feedstock.

Introduction

In an earlier paper [1] it was shown that ammonia is an attractive fuel for fuel cells on a specific energy basis, compared with hydrogen or methanol.

Hydrogen can be used directly in a fuel cell, whereas ammonia or methanol must be transformed to hydrogen and nitrogen or carbon dioxide, respectively. When fuel cell efficiency, fuel processor temperature, fuel processor efficiency, and mass and volumes of tanks are taken into account, the specific energy of ammonia cracked at 650 °C at an efficiency of 70%, then used in an alkaline fuel cell at an efficiency of 60% is 1.03 kWh_e/kg or 0.91 kWh_e/l.

For methanol steam-reformed at 450 °C at a reformer efficiency of 70% using the reformate in an acid fuel cell at an efficiency of 40%, the corresponding figures are 0.68 kWh_e/kg and 0.96 kWh_e/l.

Apart from these advantageous figures, ammonia has a further advantage with respect to methanol in that during cracking no poisons are generated. During steam-reforming of methanol carbon monoxide is generated. This is a severe poison for most low-temperature electrocatalysts.

In this paper we describe an ammonia cracker designed to operate in a once-through mode to produce hydrogen for a standard hydrogen fuel cells. The behaviour of such fuel cell using hydrogen/nitrogen feedstock is presented.

Using these results, specific energy figures for a real ammonia system will be estimated.

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System envisaged

Ammonia, a compressed liquid fuel (pressure 8 atm at 20 °C), which is stored in a pressure vessel, is evaporated and passed through a cracking reactor to produce a hydrogen/nitrogen mixture. This mixture is passed directly into the fuel cell, where the majority of the hydrogen is consumed to produce electricity. The anode off-gases are burned to supply the heat of the reforming reaction.

The anodic portion of the system is shown in Fig. 1. It is described by the following equations:

$$X_u1 + X_u2 + X_u3 + X_u4 = 1 \quad (1)$$

$$X_{ri1} + X_{ri2} + X_{ri3} + X_{ri4} = 1 \quad (2)$$

$$X_{ru1} + X_{ru2} + X_{ru3} + X_{ru4} = 1 \quad (3)$$

$$X_{f3} + X_{f4} = 1 \quad (4)$$

$$F_0 \times 1.5\varphi + (F_u - F_s) \times X_u1 = F_{ri} \times X_{ri1} \quad (5)$$

$$F_0 \times 0.5\varphi + (F_u - F_s) \times X_u2 = F_{ri} \times X_{ri2} \quad (6)$$

$$F_0 \times (1 - \varphi) + (F_u - F_s) \times X_u3 = F_{ri} \times X_{ri3} \quad (7)$$

$$(F_u - F_s) \times X_u4 = F_{ri} \times X_{ri4} \quad (8)$$

$$F_{ri} \times X_{ri1} = F_{ru} \times X_{ru1} + qI/(nF) \quad (9)$$

$$F_{ri} \times X_{ri2} = F_{ru} \times X_{ru2} \quad (10)$$

$$F_{ri} \times X_{ri3} = F_{ru} \times X_{ru3} \quad (11)$$

$$F_{ri} \times X_{ri4} = F_{ru} \times X_{ru4} - \alpha qI/(nF) \quad (12)$$

$$F_{ru} \times X_{ru1} = F_u \times X_u1 \quad (13)$$

$$F_{ru} \times X_{ru2} = F_u \times X_u2 \quad (14)$$

$$F_{ru} \times X_{ru3} = F_u \times X_u3 + F_f(1 - X_{f4}) \quad (15)$$

$$F_{ru} \times X_{ru4} = F_u \times X_u4 + F_f \times X_{f4} \quad (16)$$

$$F_0(1 - \varphi) = F_f \times X_{f3} \quad (17)$$

$$F_{ri} \times X_{ri1} = RqI/(nF) \quad (18)$$

$$F_s(X_u1 \times \Delta H1)\eta_2 = c1 + (c2 + c3\varphi)F_0 \quad (19)$$

$$F_f \times X_{f4} = \beta F_{ru} \times X_{ru4} \quad (20)$$

The equations represent molar balances and have been solved by means of a computer program (MAPLE V). The solution allows us to obtain all the parameters as a function of current. Equations (17), (18) and (19) need some explanation. Equation (17) indicates that all the traces of ammonia entering the system are taken out by the water leaving the condenser, since ammonia is very soluble in water. However, the highest possible ammonia conversion will be attempted, so that the amount of ammonia entering the system will be very small compared with the water produced. Equation (18) is determined by the fuel cell characteristics, since it must be fed by an amount of hydrogen that is R times the stoichiometric amount. Equation (19) represents the amount of hydrogen leaving the system, which must be sufficient to

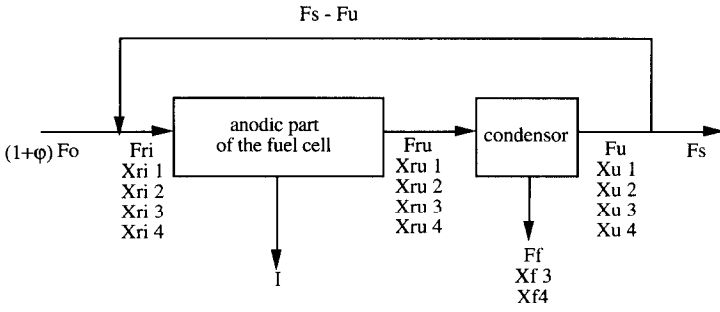


Fig. 1. Schematic representation of the anodic part of the fuel cell.

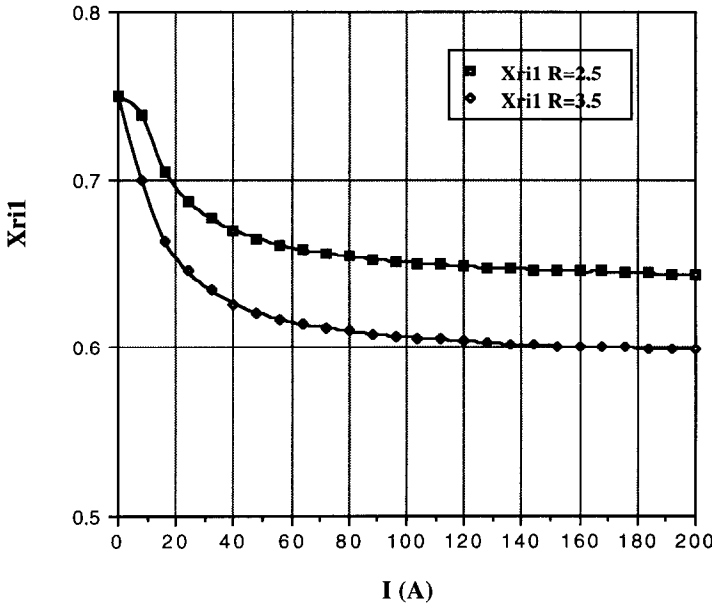


Fig. 2. Hydrogen fraction at the inlet of the fuel cell ($\alpha=0.5$; $\beta=0.95$; $\eta_2=0.5$, and $\varphi=0.99$).

supply the heat for the crackup reaction. The right-hand side of eqn. (19) represents the energy requirement for the fuel processor as a function of ammonia throughput and conversion.

The set of equations has been solved for the cracking reactor and the fuel cell described below. The solution has allowed us to test a fuel cell on a synthetic hydrogen/nitrogen mixture under realistic conditions. In Fig. 2 the fraction of hydrogen at the inlet of the fuel cell is plotted as a function of total current. The fraction at the inlet is less than 75% corresponding to the composition of the hydrogen/nitrogen mixture leaving the reformer. This results from the presence of the recycle loop in the anodic gas stream. Figure 3 shows the total molar gas flow at the inlet of the fuel cell as a function of total current. The results in Figs. 2 and 3 have allowed a test of the performance of a fuel cell with a realistic fuel flow.

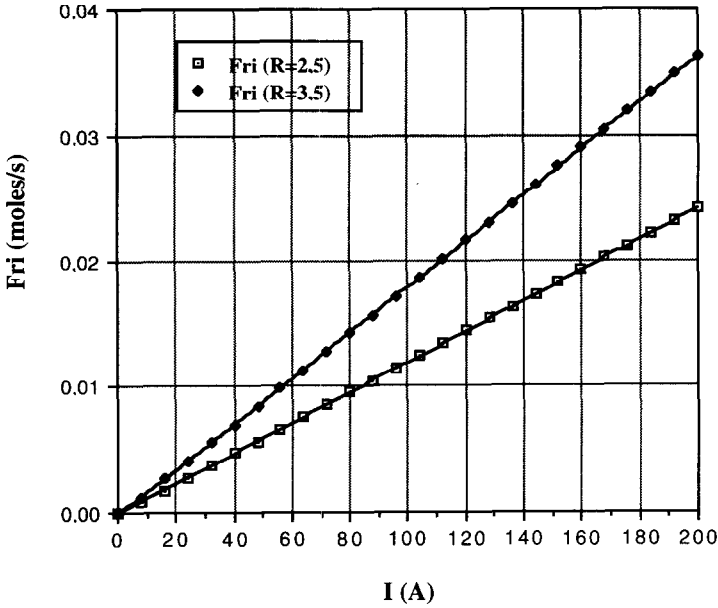


Fig. 3. Total molar flow at the inlet of the fuel cell ($\alpha=0.5$; $\beta=0.95$; $\eta_2=0.5$, and $\varphi=0.99$).

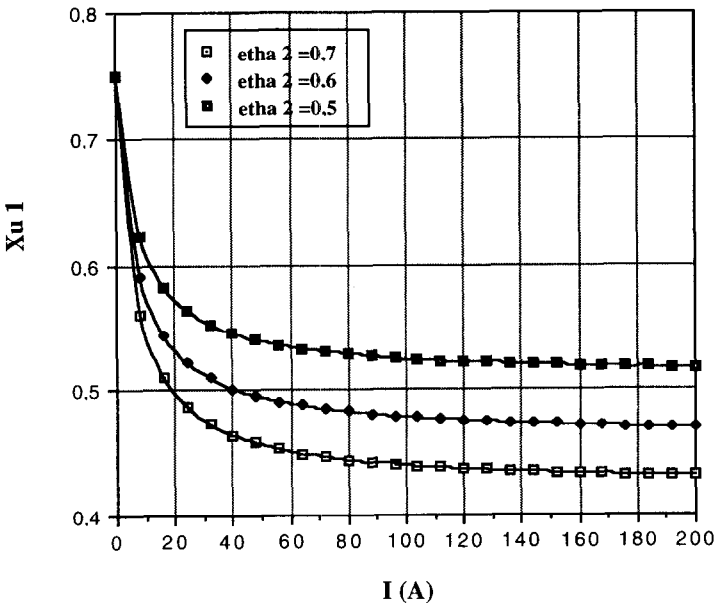


Fig. 4. Hydrogen fraction at the outlet of the system ($R=2.5$; $\alpha=0.5$; $\beta=0.95$, and $\varphi=0.99$).

In Fig. 4 the fraction of hydrogen in the gas leaving the system is plotted as function of the total current. This fraction is unexpectedly high (about 50%), and depends on the efficiency at which the off-gases are burned. Figure 5 shows the total

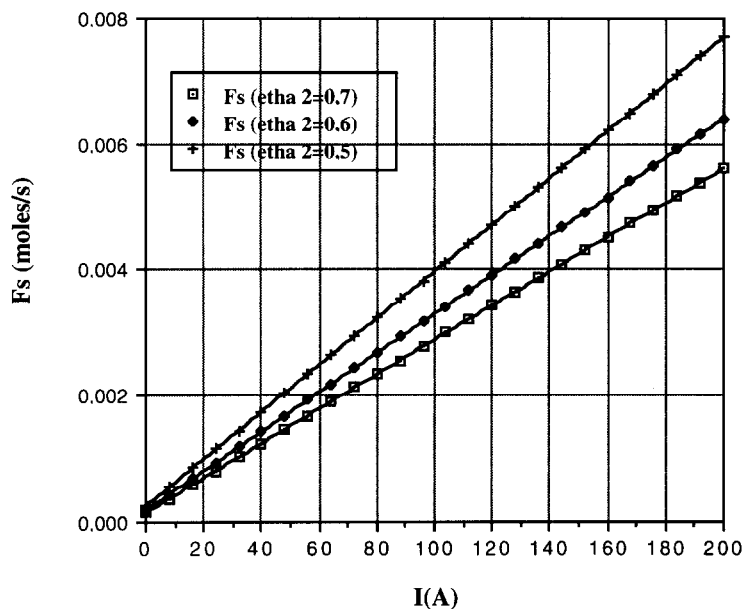


Fig. 5. Total molar gasflow leaving the system containing one fuel cell ($R=2.5$; $\varphi=0.99$; $\alpha=0.5$, and $\beta=0.95$).

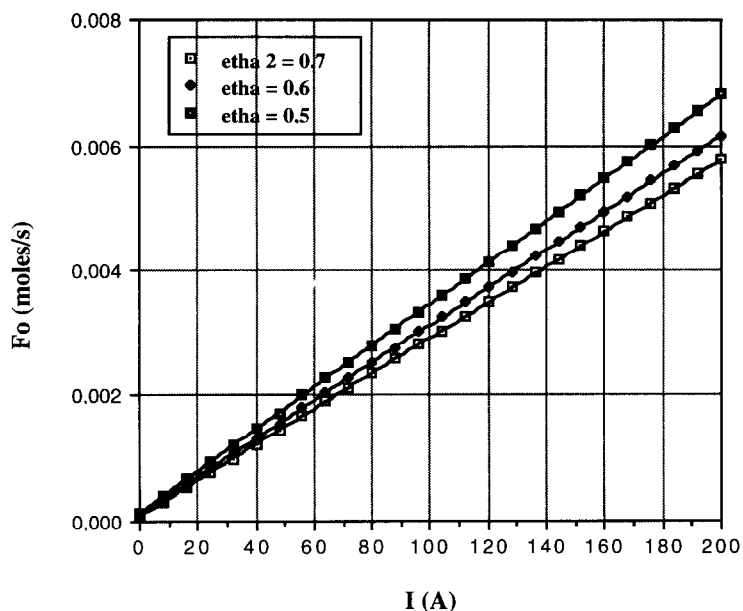


Fig. 6. Molar ammonia consumption of the system containing one fuel cell ($R=2.5$; $\varphi=0.99$; $\alpha=0.5$, and $\beta=0.95$).

molar gas flow leaving the system, and in Fig. 6 the ammonia consumption as function of total current is plotted as a function of the efficiency of burning fuel cell anode off-gas.

Reforming unit

The reformer unit was a simple tube (diameter: 40 mm, length: 750 mm) filled with a commercially available ammonia synthesis catalyst (Atochem magnetite, Fe_3O_4). The average particle size was 0.6 mm. The mass and volume of the reactor were 15 kg and 80 l. The reactor was covered with a 200 mm thick fibrothal insulation ($U=0.0572$ W/k). It was heated electrically.

The performance of this reactor is presented in Figs. 7 and 8.

In Fig. 7, the temperature of the reactor is plotted as a function of ammonia throughput at various conversions. The reactor temperature was limited to 600 °C, allowing crackup of 3 Nm³/h of ammonia at a conversion of 99%. The pressure drop in the reactor was 0.3 bar.

A heat-exchange efficiency (η_1) of 50% between the hot gases leaving the reaction (hydrogen/nitrogen) and the cold ammonia feedstock was assumed. Using this value, the net powder needs of the reactor may be calculated. The result is plotted in Fig. 8 as a function of conversion. This energy would be furnished by burning the fuel cell anode off-gas with an efficiency of η_2 , the efficiency appearing in eqn. (19).

Fuel cell and its behaviour

The fuel cell tested was an alkaline system with a nominal power of 432 W. It contained 24 cells operating at 0.7 V and 100 mA/cm² at 70 °C (6 groups in series,

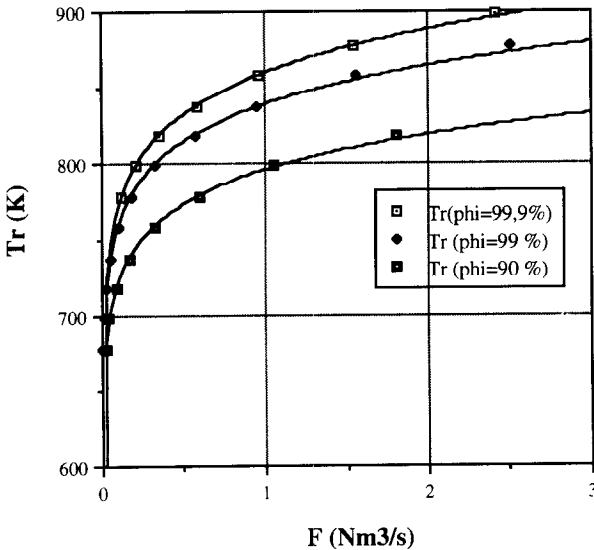


Fig. 7. Reformer temperature as function of ammonia throughput and conversion (catalyst: Atochem; $\eta_1=0.5$; $U=0.0572$ W/K and $P=1$ bar).

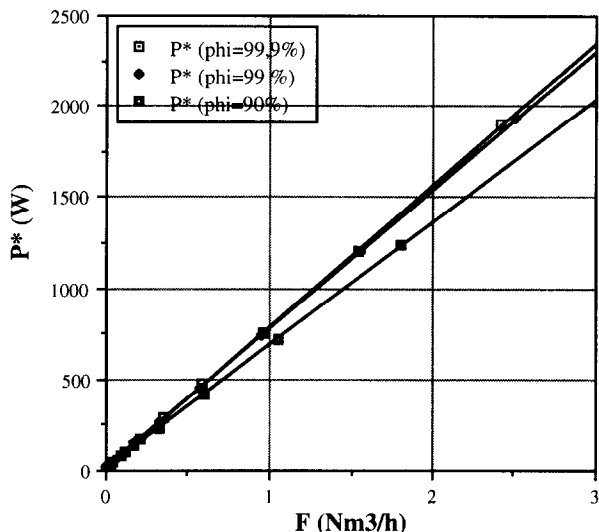


Fig. 8. Net powder needs of the reformer as function of ammonia throughput and conversion (catalyst: Atochem; $\eta_1 = 0.5$; $U = 0.0573$ W/K and $P = 1$ bar).

each group containing 4 fuel cells in parallel). The platinum catalyst loading was 0.4 mg/cm² at both anode and cathode. The mass and volume of the fuel cell were 15 kg and 15 l. Both air and fuel were supplied at close ambient pressure.

Air was passed through a soda-lime filter, and was used in 2.5 times the stoichiometric requirement.

The fuel cell was fed with a hydrogen/nitrogen flow following the mathematical model given earlier. The results are given in Fig. 9. This figure shows that the loss in fuel cell power on a mixture containing only 40% of hydrogen is only 3% compared with operation on pure hydrogen for an output in the current region where mass-transport limitations are unimportant. Figure 10 shows the *IR*-free voltages of the fuel cell as a function of total current after determination of ohmic resistance via the interruptor technique.

It can be seen that the fuel cell starts to suffer from mass-transport problems starting at a total current from about 20 A. With a lean hydrogen mixture, mass-transfer problems at the anode play an important role. Improvement of anodic mass-transfer resistance is therefore necessary to improve fuel cell power density.

During fuel cell operation it appeared that for low-current loads (<40 A), the ratio *R* should be 2.5, whereas in the higher current regions *R* could be lowered to 1.5. This is of great importance since with *R*=1.5, the excess hydrogen leaving the fuel cell anode corresponds reasonably well to the amount needed to supply heat for the crackup reaction. The fuel cell can then be operated in a once-through mode, so that the recycle loop may be eliminated. With a once-through mode ammonia cracker, the system as a whole is then extremely simple.

During fuel cell operation it was noted that electrolyte breakthrough occurred at the hydrophobic electrodes. This is normal for alkaline fuel cells, and is in fact an advantage since it permits CO₂ scrubbing form air with the electrolyte itself. In this way the soda-lime filter may not be necessary in a real system, at the expense of consuming potassium hydroxide. However, using this 'spent' electrolyte as a CO₂ scrubbing medium also offers a solution for humidifying process air.

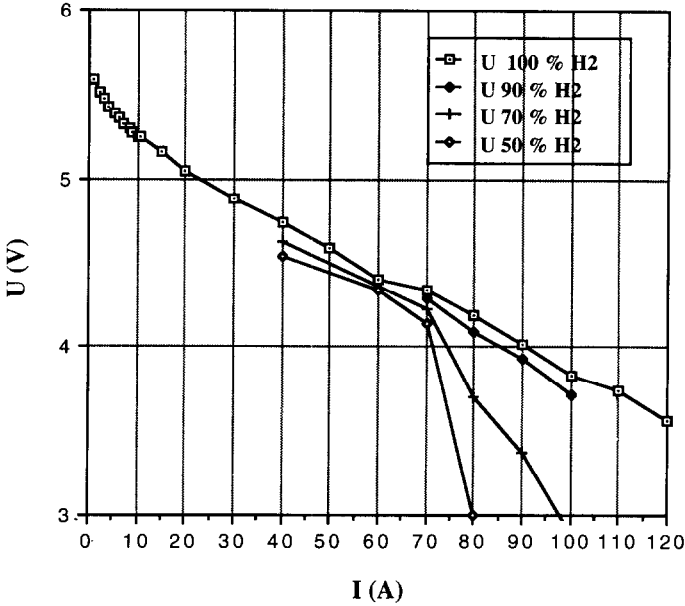


Fig. 9. Fuel cell performance under various hydrogen fractions. ($T_{\text{fuel cell}} = 70\text{ }^\circ\text{C}$; $R_{\text{air}} = 2.5$; $R_{\text{fuel}} = 1.5$; both fuel and air supplied at near ambient pressures, all polarization losses included.)

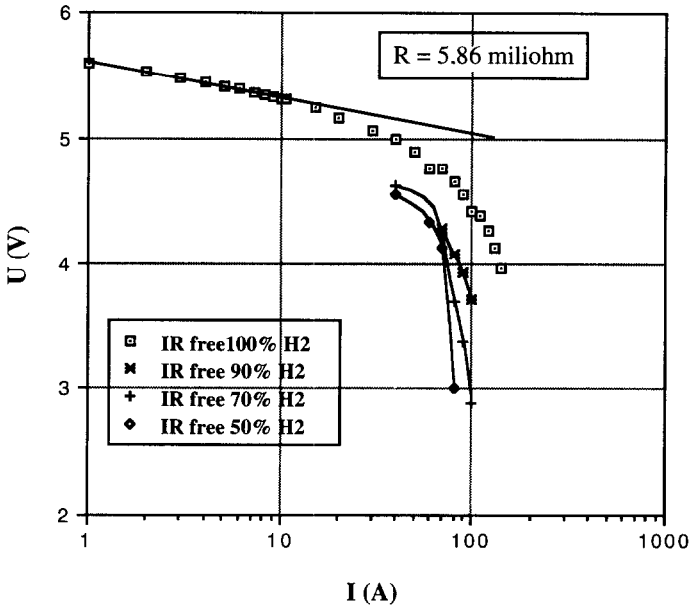


Fig. 10. IR-free polarizations curves of the fuel cell fed with various hydrogen fractions. ($R_{\text{air}} = 2.5$; $R_{\text{fuel}} = 1.5$; $T_{\text{fuel cell}} = 70\text{ }^\circ\text{C}$; both air and fuel supplied at near ambient pressure.)

Discussion

It is not within the scope of this paper to present all the possible theoretical relationships which may be obtained using the mathematical model given here. Complete results are reported elsewhere [2]. However, both mathematical modelling and practical observations point to the desirability of a fuel cell system using ammonia as a feedstock. The system proposed here would consist of 14 standard hydrogen fuel cells and one ammonia cracker, as described above.

The system has been analysed for a fuel supply to give a range comparable to that of 50 l of gasoline. The storage system requirements of various fuels are presented in Table 1 [3]. Using these data, we can compare the specific energy and the specific power of both indirect ammonia and direct hydrogen systems.

Figure 7 shows that at 99% ammonia conversion and a reactor temperature of 877 K (600 °C) 3 Nm³/h (33.3 mmol/s) of ammonia may be cracked. If the fuel cell operates at 54% efficiency (corresponding to 4 V in our fuel cell unit) then from Fig. 9, the fuel cell unit will furnish 80 A on a 60:40 hydrogen/nitrogen mixture, or 90 A on pure hydrogen.

From Fig. 6, a system containing one fuel cell unit consumes 0.0024 mol/s of ammonia to produce 80 A. Thus, with the above assumptions (see Table 2), the reformer described, with a mass and volume of 15 kg and 80 l, can supply about 14 fuel cell units. These will produce 4.48 kW (56 V, 80 A), and have a mass and volume of 210 kg and 210 l, respectively. With the ammonia consumption given in Fig. 6, a system containing 14 fuel cell units with a tank containing 87 kg of ammonia will have an endurance of 42.3 h, producing 189.5 kWh_e.

If the 14 fuel cell units were supplied with 100% hydrogen, the system would produce 5.04 kW_e (at 54% efficiency) and consume 39.2 mmol/s of hydrogen, not taking into account any requirements. This system would have an endurance of 47.9 h, producing 241.2 kWh_e.

The real specific power (kW/kg and kW/l) and energy (kWh_e/kg and kWh_e/l) densities of the two systems are given in Table 2. For comparison, figures for a standard lead/acid battery are also presented [4]. In this comparison, the electrolyte pump and air compressor have not been taken into account. The mass and volume of the electrolyte pump are negligible compared with the mass and volume of the complete system. However, the air compressor has a non-negligible mass and volume, and consumes a considerable amount of electrical energy. No reliable data were available to estimate its parameter, which will influence design features of both direct hydrogen and indirect ammonia systems. The soda-lime filter has not been taken into account, since a portion

TABLE 1

Storage system requirements for carrying the energy equivalent to 50 l of gasoline

Compound	Volume fuel (l)	Mass fuel (kg)	Lower heating value (LHV) (kWh/kg)	Mass tank (kg)	Volume tank (l)
Gasoline	50	36.8	455	41.3	54.2
H ₂ (g, 200 bar)	794	13.5	455	410	1720
H ₂ (l, 252 °C)	190	13.5	455	121	757
NH ₃ (l, 20 °C, 8 bar)	137	87	455	140.5	258

TABLE 2

Specific energy and power densities for an indirect ammonia fuel cell system, a direct hydrogen fuel cell system and a lead/acid battery system^a

System	System weight (kg)	System volume (l)	Nominal power (KW _e)	Energy produced (kWh _e)	Specific power density		Specific energy density	
					(W/kg)	(W/l)	(Wh/kg)	(Wh/l)
NH ₃ indirect	452	547	4.48	189.5	9.9	8.2	419	346
H ₂ (g, 200 bar)	633	1930	5.04	241.2	8.0	2.6	381	125
H ₂ (l, 252 °C)	344	967	5.04	241.2	14.7	5.2	700	249
Lead/acid (C5)					7.0	14	35	70

^aR_{hydrogen} = 1.5; R_{air} = 2.5; φ = 0.99; η₁ = 50%; η₂ = 50%; α = 0.5, and β = 0.95.

Energy stored: 455 kWh based on LHV of the fuels.

of the electrolyte breakthrough at the alkaline fuel cell electrodes may be used to scrub CO_2 from the air supply.

Table 2 shows that the indirect ammonia system has attractive volumetric power and energy densities compared with the direct hydrogen system using either liquid or gaseous hydrogen storage. On a mass basis, the liquid hydrogen system is more attractive. Both hydrogen and ammonia system have favourable specific energy densities compared with those of a classical lead/acid battery.

Conclusions

Analysis of an indirect ammonia fuel cell system shows that its specific power and energy densities are attractive compared with those of a fuel cell system using hydrogen directly.

Using materials which are more or less commercially available it would be possible to construct a generating plant using ammonia as the fuel, thus eliminating the problems of hydrogen storage and transport. While hydrogen is produced in very large amounts throughout the world, it is nearly completely consumed on-site for the production of refined oil products, methanol, ammonia and chemical products. Ammonia and methanol are the two major products of the chemical industry, and are both easy to handle and transport.

Although an absolute comparison between methanol and ammonia systems was not the subject of this paper, we consider that the indirect use of methanol as a fuel is less interesting than that of ammonia for the following reasons [1, 2]:

(i) Using hydrogen as a starting material, it is easier to produce ammonia from ambient air than it is to produce methanol from carbon dioxide from ambient air. No production plants exist for the production of methanol from this source, although the product cement plants could perhaps be used.

(ii) Ammonia for use in fuel cells has a higher specific energy than methanol for the same application.

(iii) Ammonia can be used in an alkaline fuel cell, whereas methanol must be used in an acid system. Unlike acid fuel cells, alkaline systems can in principle operate without noble metal catalysts.

(iv) Based on the lower heating value of methane (the raw material for both methanol and ammonia production, used as feedstock for the overall system efficiency) is higher for ammonia than for methanol (33 versus 23%).

(v) The system using ammonia feedstock is technically simple. No recycle loops are required, which facilitates system operation.

(vi) An ammonia cracker has a modest mass and volume compared with that of the overall system. Improvement system of specific power and energy mainly depends on improvement in the fuel cell characteristics. That ammonia is a more attractive fuel than hydrogen will not be influenced by fuel cell improvements.

List of symbols

q	number of unit fuel cells in series, –
n	number of electrons transferred, –
F	Faraday constant, C/eq
I	current, A

F_0	molar ammonia flow, mol/s
F_{ri}	molar gas flow at the inlet of the fuel cell, mol/s
F_{ru}	molar gas flow at the outlet of the fuel cell, mol/s
F_u	molar gas flow out of the condenser, mol/s
F_f	molar liquid flow out of the condenser, mol/s
F_s	molar gas flow at the outlet of the system to be burned to supply the heat of the reforming reaction, mol/s
R	ratio of carburant or comburant to stoichiometric amount, –
X_i	molar fraction of the i th species, –
	index 1 = hydrogen
	index 2 = nitrogen
	index 3 = ammonia
	index 4 = water
ΔH_1	lower heating value of hydrogen, J/mol
U	overall heat-transfer coefficient of the insulation layer of the reformer, W/K

Greek symbols

α	ratio of water in the fuel cell anode exit gas stream to the stoichiometric amount of water produced, –
β	efficiency of water removal in the condenser, –
φ	ammonia conversion, –
η_1	heat-exchange efficiency between hot gases exiting reformer reactor and gas entering the reformer, –
η_2	thermal efficiency for burning anode exit gas stream, –

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