Ammonia as a fuel in solid oxide fuel cells

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Abstract

The use of ammonia as a source of hydrogen for fuel cells has received little attention until now. Ammonia offers several advantages over hydrogen as a fuel and is produced commercially in massive quantities and as a biogas. This paper describes the results of a solid oxide fuel cell-based system running on ammonia and compares the performance with respect to hydrogen. A novel catalyst concept has been devised and employed with success. Results indicate that the ammonia performance, using the catalyst is comparable to hydrogen suggesting ammonia can be treated as an attractive alternative fuel.
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1. Introduction

The potential impact of ammonia as a fuel for solid oxide fuel cells has not been fully appreciated by the SOFC community. In the 1980s, Vayanas and co-workers [1–3] investigated the use of ammonia in a solid electrolyte reactor using platinum electrodes, with the aim of producing NO as a useful chemical feedstock in addition to producing electricity. The idea of developing an SOFC system which avoids the formation of NO_x by producing N_2 as the sole nitrogen containing product is both novel and timely. Ammonia presents a cheap and convenient way of storing hydrogen, and is particularly suitable for transportation or for small scale portable systems. Pure ammonia is easily liquefied at room temperature by the application of modest pressures and has a comparatively narrow combustion range. Ammonia has been compared with other liquid fuels such as methanol and gasoline [4,5].

Ammonia is regarded as toxic but its strong odour aids leak identification. It can also be dissolved in water up to very high levels (ca. 30% by volume) offering further advantages for delivery. Ammonia is produced in massive quantities by the chemical industry as a feedstock and for fertiliser production. It also a significant biogas.

Ammonia had been considered as a mixed fuel with alcohol for SOFC systems [6,7], but other than the cited work on platinum, there has not been a definitive study on the use of ammonia as the sole source of hydrogen for the solid oxide fuel cell. The purpose of the present study was to establish the basics for an ammonia system, and to demonstrate that ammonia could be used directly in an SOFC.

Although ammonia is the fuel, its role would be to act as a source of hydrogen as far as a fuel cell is concerned. Ammonia is commercially manufactured by the Haber–Bosch process. The industrial synthesis of ammonia requires the reaction of hydrogen and nitrogen over a catalyst such as alkali doped iron at temperatures around 500 °C and pressures around 250 atm and can simply be represented by the following reaction:

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$
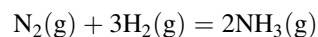
The reverse reaction can be regarded as the ''catalytic cracking'' of ammonia.

$$2NH_3 = N_2 + 3H_2$$
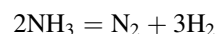
The product gas contains three parts hydrogen to one part nitrogen.

This reaction is carried out on a catalyst, such as iron, Fe_2O_3, or a nickel-based compound. The reaction is carried out typically at 450 °C.

In this work, a novel concept was developed which combines the cracking of ammonia over an iron-based

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catalyst, with electrochemical conversion of the hydrogen so produced. This in situ approach is ideal for tubular SOFC systems as it facilitates incorporation of the catalyst inside the tube, in a similar way to a packed bed reactor. Studies were carried out using both silver and platinum anodes. Silver was selected because it was considered to be relatively inert to oxidising atmospheres and also because its perceived activity toward ammonia could be advantageous. Platinum was chosen because it has already been demonstrated to be a good catalyst for the conversion of ammonia to NO [1]. Several permutations of fuel/electrode/catalyst were investigated in order to fully optimise and characterise the work. In future studies nickel cermet anodes will also be investigated.

2. Theory

SOFCs are attractive fuel cell concepts because of their ability to accept a range of fuels, other than pure hydrogen. SOFC conventionally run at temperatures above 500 °C (typically 800–1000 °C), and one of the advantages of this is that the cracking process, necessary to free the hydrogen from the fuel, and the generation of electricity can be combined. In other words ammonia may be directly input into the SOFC without any pre-treatment.

The overall reaction for complete combustion of ammonia is

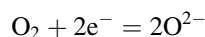$$4NH_3(g) + 3O_2(g) = 2N_2(g) + 6H_2O(g)$$
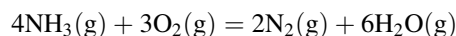
In the solid oxide fuel cell, oxygen is transported through the solid electrolyte (typically yttria stabilised zirconia) from the cathode to the anode.
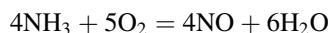
The desired anodic reaction for ammonia is

$$2NH_3 + 3O^{2-} = N_2 + 3H_2O + 6e^-$$
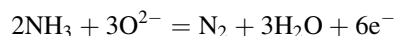
The corresponding cathodic reaction is the reduction of oxygen from air:

$$O_2 + 2e^- = 2O^{2-}$$

This ideal situation is likely to be complicated by the energetically less favourable partial oxidation reaction to form NO

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

This has been shown to be particularly selective with platinum rhodium-based catalysts. The initial electrochemical step is

$$2NH_3 + 5O^{2-} = 2NO + 3H_2O + 10e^-$$

This is then followed by a second step to form nitrogen:

$$4NH_3 + 6NO = 5N_2 + 6H_2O$$
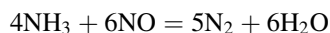
No previous studies have investigated the selectivity of nitric oxide formation on iron or nickel-based catalysts under the conditions experienced in an SOFC system. In the current study an iron-based catalyst was chosen for the SOFC system because of its ability to directly decompose ammonia to its constituent elements:

$$2NH_3 = N_2 + 3H_2$$
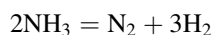
If this reaction is fast relative to the NO formation reaction, then the selectivity for NO may be reduced to zero.

3. Experimental

The SOFC tubes used in this study were supplied pre-sintered, 2.5 mm outside diameter, 200 μm wall thickness and 30 cm in length. The composition was 8 mol% Y_2O_3, balance ZrO_2. The silver electrodes were applied using a suspension of silver powder in an organic vehicle based on terpineol. The anode was applied to the inside of the zirconia tube by sucking the diluted suspension up the inside of the tube using a pipette filler, and then allowing the excess fluid to drain out. The electrode coating was then allowed to dry before applying the electrodes to the outside. The outside electrodes (cathode and reference) were applied using a flexible fibre flail as bands 1 cm in length located close to the centre of the SOFC tube. A 5 mm gap was left between
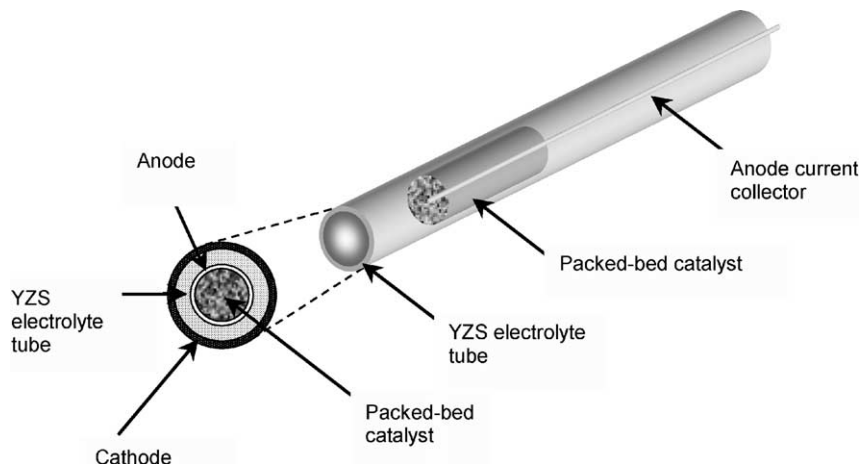

Fig. 1. A schematic drawing of the fuel cell structure employed showing the packed bed catalyst in situ in the electrolyte tube.

the cathode and reference electrode. After drying at room temperature, the coated tubes were heated in a furnace to 800 °C for 1 h to fire on the electrodes. Two such cells were produced. A similar process was used to apply platinum electrodes to a third tube.

The iron catalyst was packed inside one of the silver electrode-based SOFC tubes. The catalyst consisted of a mixture of steel fibre ("steel wool") and finely divided iron powder. The structure of the iron-based silver cell, awaiting assembly can be seen in Fig. 1. To determine the effectiveness of the catalyst in activating the ammonia, a comparison in cell performance was also made using hydrogen as the fuel. All fuels were diluted in pure nitrogen carrier gas. The studies on platinum were made without any in situ packed bed catalyst.

The temperature of a cell under test was determined by attaching a small diameter thermocouple (type-K) to the outside of its zirconia tube. The position of the measuring tip could be moved relative to the tube. The electrical measurements were made using a 2 A potentiostat (Thompson) connected to the cell via digital meters to measure the current and voltage characteristics. The current interruption method was used to determine internal cell resistance and these results will be presented in a future publication.

Ammonia was supplied to the cell from a concentrated aqueous solution (25 vol.%, Fisher Scientific). This was done by diluting the stock solution in de-ionised water up to a volume of 100 ml and then transferring it to a glass storage bottle connected to the flow control system using flexible plastic tubing (4 mm inside diameter). Hydrogen was supplied from a premixed gas cylinder (10% balance nitrogen, "forming gas"). Two ammonia concentrations were used, first the undiluted stock solution, and then a 32% dilution of the stock solution. This latter dilution had previously been observed to provide exactly the same amount of hydrogen atoms in the gas phase as the 10% H_2/N_2 fuel supply. The ammonia was transferred to the gas phase by passing a carrier of pure nitrogen through the storage bottle. Unless otherwise stated, the ammonia concentration referred to in the discussion was that equivalent to the 10% hydrogen supply. The flow control system allowed a rapid changeover between the hydrogen, ammonia and pure nitrogen supplies. Fine adjustment of the gas flow in the cell was achieved with a multi-turn needle valve attached to a rotameter. Flows were calibrated with a bubble flow meter using pure nitrogen at room temperature.

4. Results and discussion

4.1. Silver anode with no catalyst

In the first part of the study, ammonia was supplied directly to the SOFC tube equipped with a silver anode, but no additional catalyst. This was to test for direct electrochemical activity of ammonia on silver. The current voltage (IV) data in Fig. 2 exhibits exponential behaviour
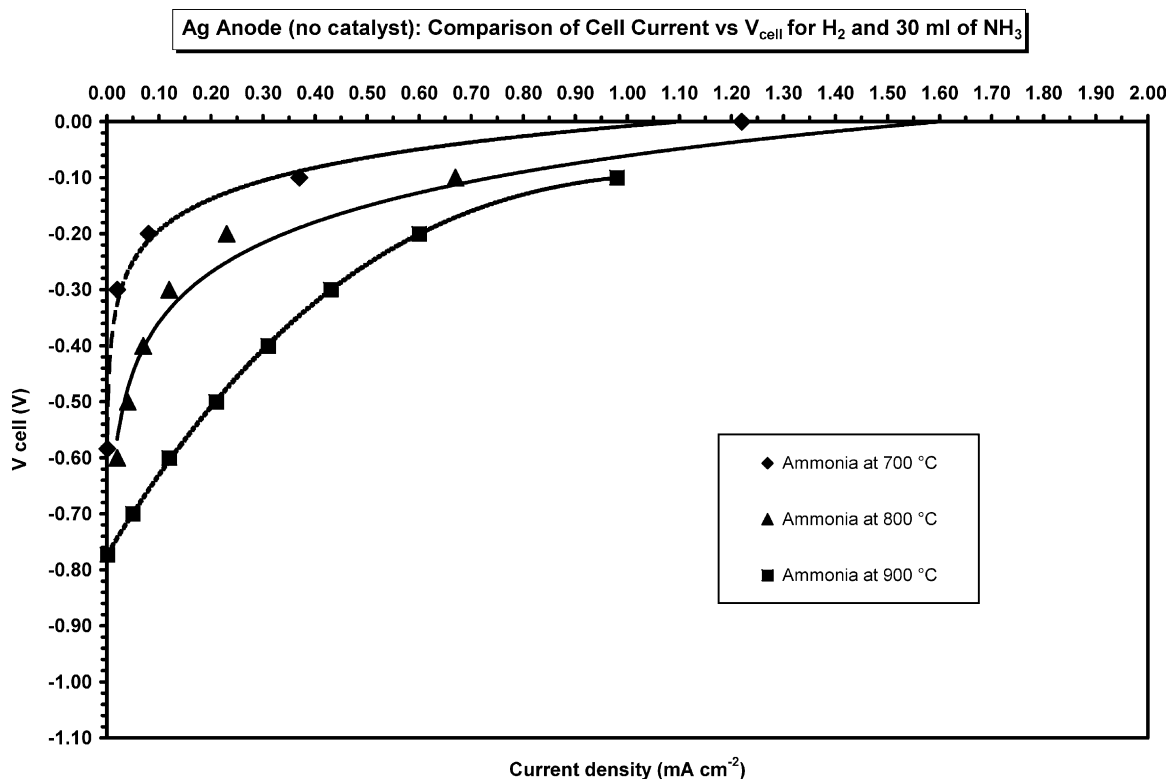

Fig. 2. A graph of activity for ammonia when fed directly to the SOFC tube with no catalyst, the IV plot exhibits exponential behaviour commensurate with electrochemical kinetic limitation.
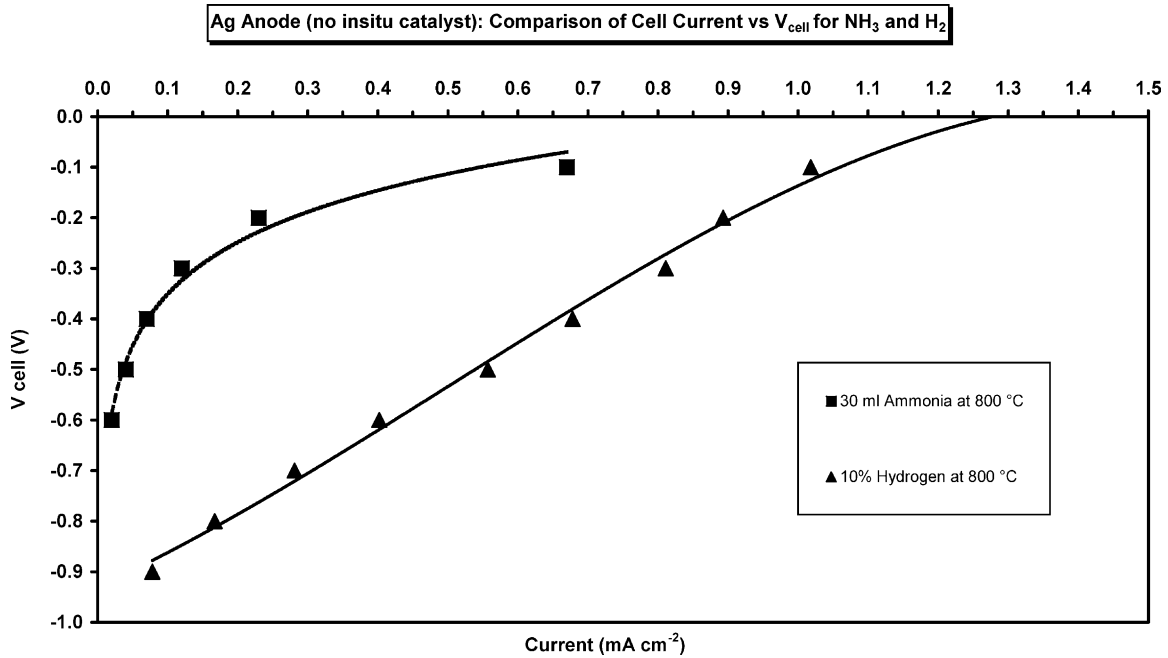
Fig. 3. *IV* plot for an SOFC having an input fuel of ammonia and a further plot showing the activity of the same cell having an input fuel of hydrogen. No catalyst was in use. The results confirm that ammonia is relatively inactive without the catalyst.

commensurate with electrochemical kinetic limitation. This is particularly the case at the lower temperature of 700 °C. Fig. 3 compares the behaviour of ammonia with hydrogen. A significantly higher performance was obtained on hydrogen, indicating that ammonia is relatively inactive on silver without the catalyst.

4.2. Silver anode with iron catalyst

The effect of adding the iron catalyst to the SOFC tube is clearly demonstrated in Fig. 4. The performance with ammonia is increased by a factor of 5 over the no-catalyst runs. Fig. 5 shows a similar comparison with hydrogen.
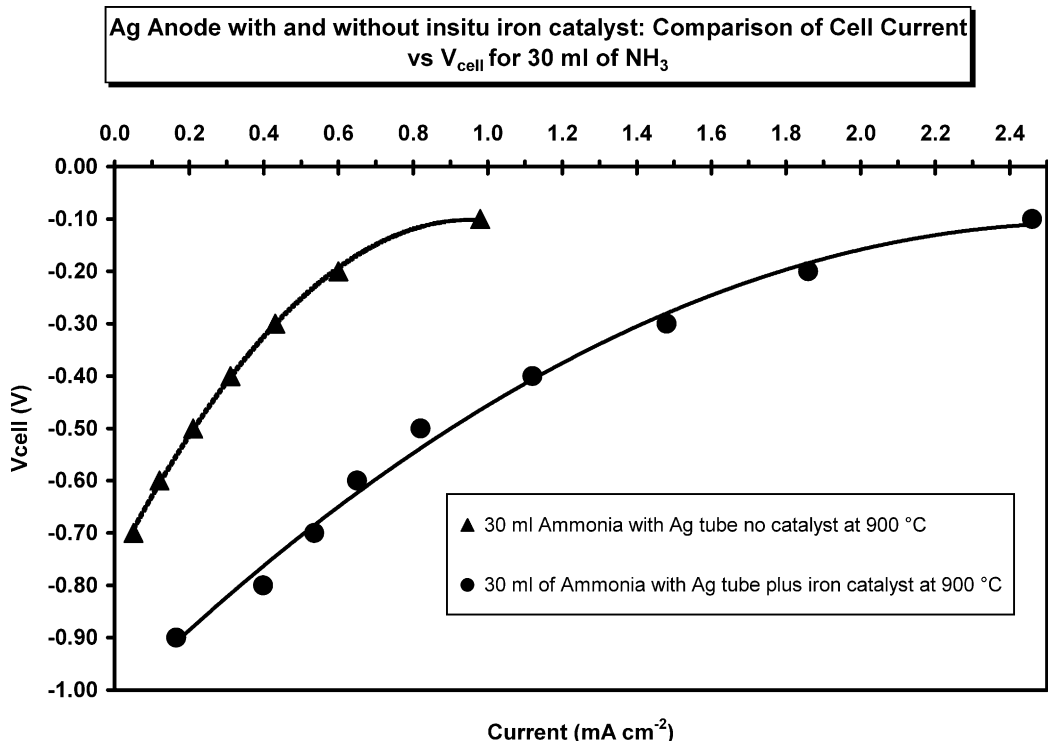

Fig. 4. *IV* plots for an SOFC fuelled by ammonia but with and without in situ iron catalyst clearly showing that the catalyst improves the electrokinetics.
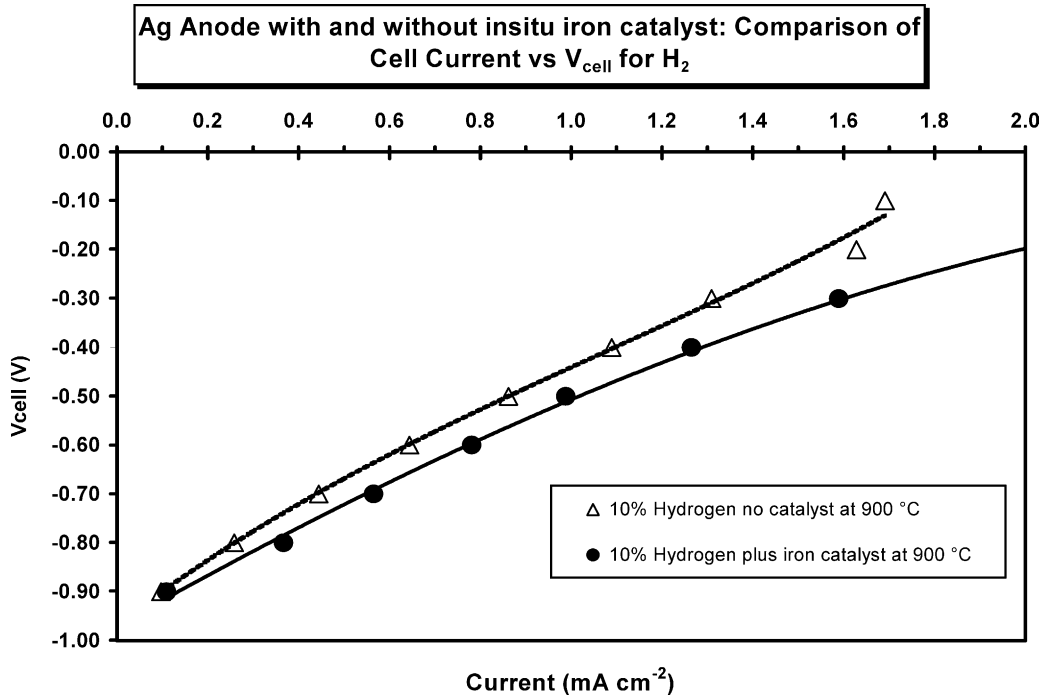
Fig. 5. *IV* plots of an SOFC fuelled by hydrogen with and without in situ iron catalyst. A much smaller increase in activity is observed compared with the increase demonstrated in Fig. 4.

There is much less difference in this case; the catalyst increases the performance only by about 10%. The catalyst was not expected to affect the performance when using hydrogen, and the modest improvement was surprising. It may simply reflect an increase in the residence time of the hydrogen as a consequence of the packed catalyst bed, leading to an improved conversion efficiency, rather than a true catalytic enhancement over silver alone.
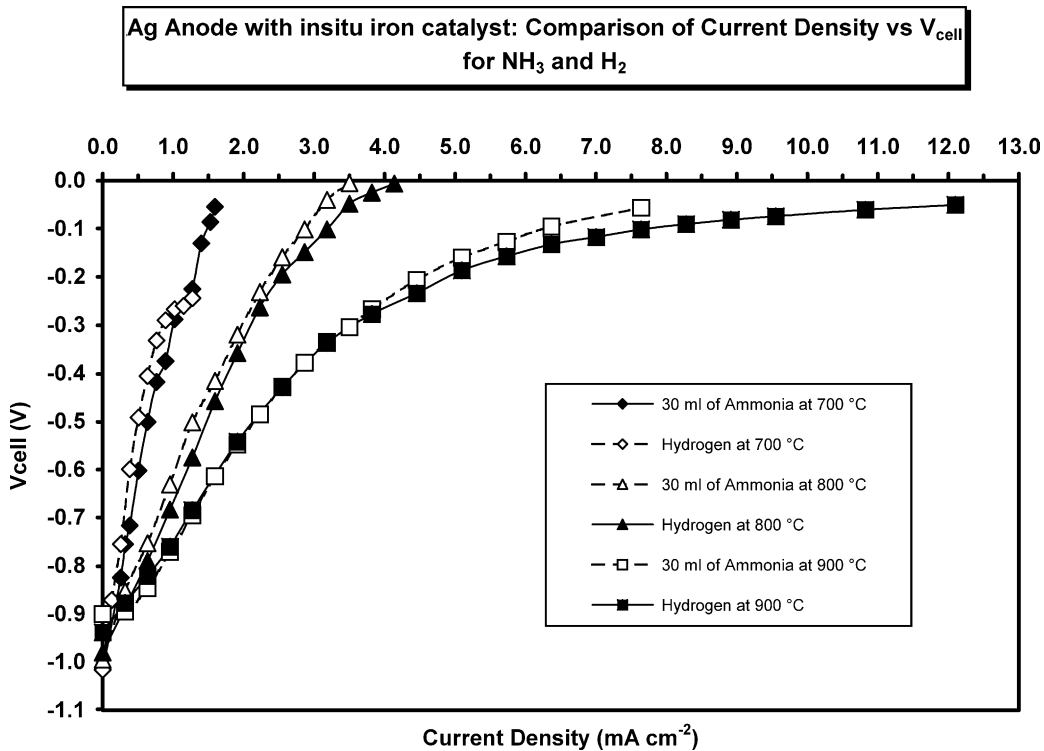

Fig. 6. The activity of test SOFCs fuelled by ammonia and the equivalent amount of hydrogen with in situ iron catalyst and silver anodes. The performance with ammonia and hydrogen fuels is identical.
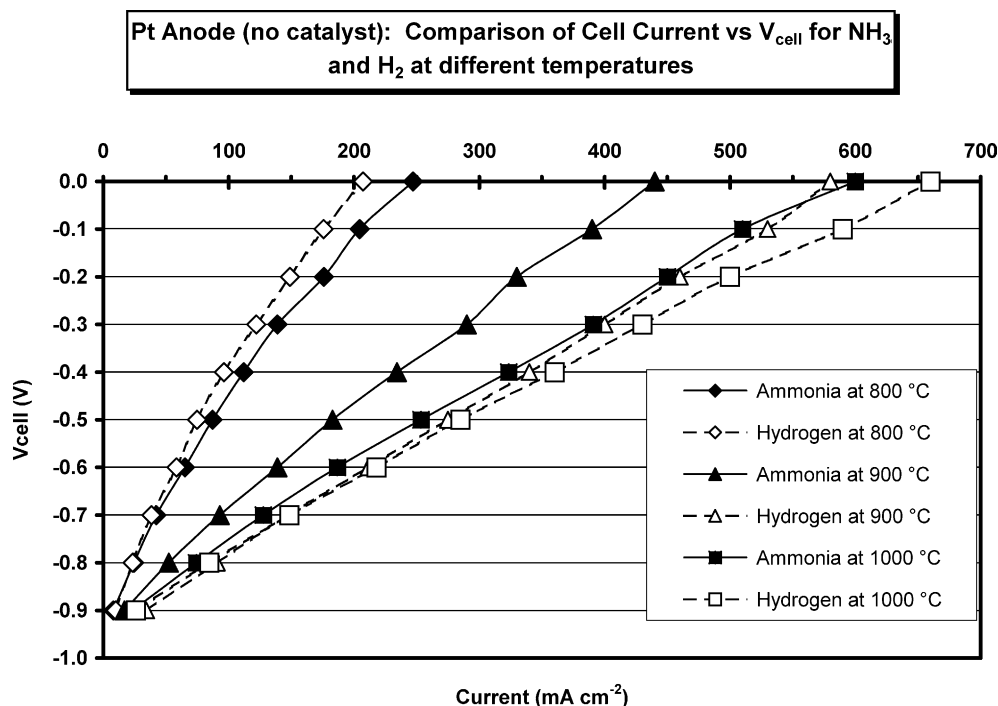
Fig. 7. A graph similar to that in Fig. 6, but for a platinum cell, comparing ammonia and the equivalent hydrogen fuel at different temperatures, without additional catalyst. It should be noted that the current densities are much higher than observed with silver electrodes. The improved performance can be ascribed to morphological and area effects.

Fig. 6 shows a direct comparison between ammonia and hydrogen for three temperatures 700, 800 and 900 °C. The responses are almost identical.

4.3. Platinum anode without iron catalyst

The results obtained on a platinum anode are given in Fig. 7. No added catalyst was used in this part of the study, although this is planned in future work. Fig. 7 compares ammonia with hydrogen for the temperatures 800, 900 and 1000 °C. Ammonia gave quite similar performance to hydrogen in this case, although not identical. The magnitudes of the measured currents were about 200 times greater in the platinum cell experiments than in the corresponding silver cell experiments. This is can be explained by the much higher active surface area of platinum. It is well known that platinum provides many more reaction sites than silver does. The reason is that silver tends to densify during the heat treatment, and so blocks the passage of oxygen from the electrolyte surface. The current densities observed on platinum under these conditions approached those required for a commercial fuel cell.

5. Conclusions

A solid oxide fuel cell running on ammonia as the fuel feed has been demonstrated. The staged experiments prove that ammonia can be used directly as a fuel in an SOFC system. Various electrode/catalyst combinations were tested and with a silver anode coupled to an in situ iron catalyst, ammonia gives a power performance similar to that obtained from an equivalent supply of pure hydrogen. The iron catalyst was based on a novel combination of steel fibres and finely divided iron powder. When a platinum anode was used, the power densities increased enormously up to respectable levels suitable for a commercial system. This increase was largely due to the very high surface area of the platinum paste used, and high porosity within the anode microstructure. By comparison, silver probably formed rather dense, low porosity electrodes. Platinum, however, is not a practical solution for a commercial system, due to the high cost, and also the problem of NO_x formation. Higher surface areas can be achieved by using metal cermet anodes, such as those based on nickel/zirconia. Moreover, nickel is also catalytic for ammonia cracking to form H_2 and N_2. This leads to the conclusion that ammonia could work very well in an SOFC system based on nickel anodes and also incorporating nickel or iron-based catalysts. This is a very encouraging conclusion, since nickel is already the standard choice for the anode in commercial SOFC systems. Another possibility is to mix iron with silver to form a composite catalytic anode. These aspects will be investigated in future studies.

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