



Short communication

Ammonia as efficient fuel for SOFC

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ABSTRACT

Ammonia is a possible candidate as the fuel for SOFCs. In this work, the influence on the performance of a tubular SOFC running on ammonia is studied. Analysis of open circuit voltages (OCVs) on the cell indicated the oxidation of ammonia within a SOFC is a two-stage process: decomposition of the inlet ammonia into nitrogen and hydrogen, followed by oxidation of hydrogen to water. For comparison, cell was also tested with hydrogen as the fuel and air as oxidant at different temperatures showing a similar behaviour. The performance of the cell tested under various conditions shows the high potential of ammonia as fuel for SOFCs.

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1. Introduction

Current SOFC technology based on oxide ion conductors, such as yttria stabilised zirconia (YSZ) and doped ceria is well established. There are, however, still problems hindering their practical development, such as store and hydrogen distribution, material incompatibilities and coking within the anode compartment when using hydrocarbon fuels [1].

Recently, some investigations have been focused on the development of new anode materials, in which nickel is replaced by other metal, in order to avoid coke formation [2,3]. A little progress has been made in this sense. Other interesting option to accelerate the commercialisation of SOFCs may be the exploration of possible alternative fuels, being ammonia a suitable choice [4].

Ammonia is a good hydrogen carrier and is carbon free. It might be a fine substitute for hydrogen and hydrocarbons for the following reasons. The price of ammonia is as competitive as hydrocarbons. It can be easily liquefied, the volumetric energy density of liquefied ammonia is higher than that of liquid hydrogen, which is useful in transport and storage. Furthermore, ammonia is less flammable compared with other fuels and the by-products of its cell reaction are merely nitrogen and water, so no greenhouse gases are emitted as with hydrocarbons and there are no concerns about anode coking. On the other hand, although ammonia is toxic, the leakage

can be easily detected by human nose under 1 ppm, so there are no severe safety concerns.

As an indirect fuel for fuel cells operated at low temperatures, ammonia has been extensively researched [5–7], but there are significant barriers to be overcome for successful commercial implementation. Direct utilisation of ammonia in SOFCs should be more seriously considered, but there are only a few reports in this area. Wojcik et al. [8] first tried to directly fuel yttrium-stabilised zirconia (YSZ) based SOFCs with ammonia and using Pt as electrodes, a maximum power density of 50 mW cm^{-2} was obtained at 800°C . Staniforth and Ormerod [9] indicated that ammonia completely decomposed at Ni-YSZ anode and no nitrogen oxide was produced at the anode when oxygen-ions transferred from cathode to anode. Some protons-conducting SOFCs also have been investigated [10,11], but as a more mature commercialised system, YSZ based SOFCs still deserve further investigations. Recent studies have been focused on evaluating the benefits of using ammonia as a sustainable fuel for mobile and remote applications based on fuel cell technology [12].

The main purpose of this work was to evaluate if ammonia might be used as direct fuel for SOFC without reducing its performance, in comparison with hydrogen. For that, a wide range of compositions for anodic feeding, combining hydrogen and ammonia, has been studied until total ammonia replacement of hydrogen in the stream.

The feasibility of operating a SOFC with hydrogen streams containing low ammonia concentrations (up to 1000 ppm), similar to a hydrogen stream obtained by a catalytic reforming process, have been demonstrated in our previous researches [13].

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2. Experimental

Experiments were carried out using a commercial microtubular SOFC (Adelan) consists of a Ni/YSZ anode, LSM cathode and YSZ electrolyte [14] in a home-developed cell-testing system. A silver wire was used as current collector at cathode and a nickel mesh was inserted down the tube and connected to a platinum wire which goes through the exhaust end to collect the anode current. The test cell inlet was linked to a set of mass flow controllers (MFC) and micrometric valves to feed the reactant gases in anodic side, enabling evaluation over a full range of operation conditions and fuel composition. Cathode was exposed to air atmosphere. A constant flow of 40 ml min^{-1} of gas mixture, hydrogen and ammonia in different ratio, was fed in the anodic side. Anode was previously reduced *in situ* in the test system at 850°C for 24 h under a stream of humidified hydrogen. The inlet gases passed through the humidifiers at room temperature to get a humidity of 3% approximately.

The operating temperature of the cell varied between 700°C and 900°C . The cell was characterized by measuring the cell voltage as function of the current density, anode gas composition, flow and temperature. A constant current demand of 0.05 A was applied, using a DC electronic load (DC Hewlett Packard 6060B), in order to achieve a cell potential of 0.8 V approximately. Frequent polarization scans shortened the required time to reach stable performance. The control and data acquisition system, based on LabView software, was developed in our lab. The test system allows that the performance and durability of the fuel cell can be simultaneously evaluated during the study of the effect of ammonia in the fuel feeding to the anodic side of SOFC.

Firstly, SOFC performance was evaluated for 120 h at 700°C under humidified hydrogen. After that, hydrogen was gradually replaced with increasing amounts of ammonia. Long periods of time were used for ammonia cell exposures (5 hours) and at least 1 hour for recovering in order to reach a steady power output. Polarisation curves were measured before and after each ammonia exposure and recovery cycle.

When hydrogen was totally substituted by ammonia exposition time was increased in order to obtain responses at long time (18 h). Finally, SOFC performance was evaluated in function of the fuel, hydrogen or ammonia, and the operation temperature.

A scanning electron microscope (SEM, Hitachi S-2500) was employed to observe the microstructure of the cell after testing.

3. Results and discussion

The microtubular SOFC under study was operating on ammonia and hydrogen at $700\text{--}900^\circ\text{C}$ and a cell potential of 0.78 V during 400 h and total ammonia exposure time was 51 h. The global cell performance, cell voltage, current and temperature are shown in Fig. 1. Ammonia exposure sequences in the anodic feeding, mixtures H_2/NH_3 or exclusively NH_3 , are shown as grey solid bars in this figure.

In the first part of the study the effect of the hydrogen replacement with ammonia (10–100%) on the cell voltage was evaluated in the same SOFC, at 700°C under current demands and open circuit. Previous to the NH_3 exposure experiments, the cell performance was stable during 120 h at 700°C . The open circuit voltage was 1.09 V, operating with humidified hydrogen stream, whereas it decrease to 0.82 V under a current demand of 0.05 A.

After stabilisation, the cell underwent 6 sequences of NH_3 exposure, varying from 10% to 100% of ammonia in the fuel fed to the anodic side (run time between 120 h and 350 h). Fig. 2 shows the cell voltage as a function of the ammonia concentration and current demand for the gas mixtures. Notice that cell voltage gradually decreases with the increment of ammonia concentration in the hydrogen stream. For different hydrogen–ammonia mixtures volt-

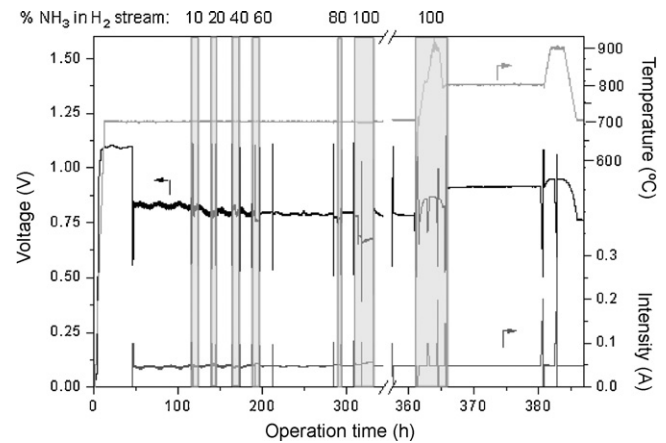


Fig. 1. Global cell performance under different operating conditions.

age remains nearly constant, at a current demand of 0.1 A the cell voltage was 0.6 V and no significant degradation was detected. I – V curves were obtained before and after each ammonia exposure and recovery cycle and they are shown in Fig. 3a and b together with the cell power density.

For compositions between 10% and 80% NH_3/H_2 I – V curves are nearly similar (Fig. 3a and b). However, when hydrogen was totally replaced with ammonia, after a stabilisation period, the cell voltage slightly decreased, 0.68 V and 0.41 V under 0.05 A and 0.1 A current demand, respectively, in comparison with voltage of the cell fuelled with humidified hydrogen, 0.79 V (0.05 A) and 0.52 V (0.1 A). The reason for this phenomenon can be attributed to a lower partial pressure of hydrogen due to the co-production of nitrogen when ammonia is used as fuel. Cell recovered its initial performance when feeding was changed to humidified hydrogen (Fig. 2).

After checking the feasibility of using ammonia as fuel in SOFC the effect of increasing temperature on the open circuit voltage operating on ammonia or hydrogen was evaluated. Fig. 4 presents open circuit values (OCVs) of the cell at different temperatures and fuels. It can be observed that in both cases, operating on humidified hydrogen or ammonia, the OCVs essentially decrease with increasing temperature. OCVs values obtained for SOFC operating on ammonia (1.03, 1.02 and 0.99 V for 700, 800 and 900°C , respectively) are lower than on humidified hydrogen (1.09, 1.08 and 1.06 V) due to the lower partial pressure of hydrogen, as it has been explained before. This cell behaviour allows to elucidate the mechanism for ammonia conversion. Table 1 compares ΔG° and E° for the oxidation of ammonia (reaction (1)) with the oxidation of hydrogen (reaction (2)).

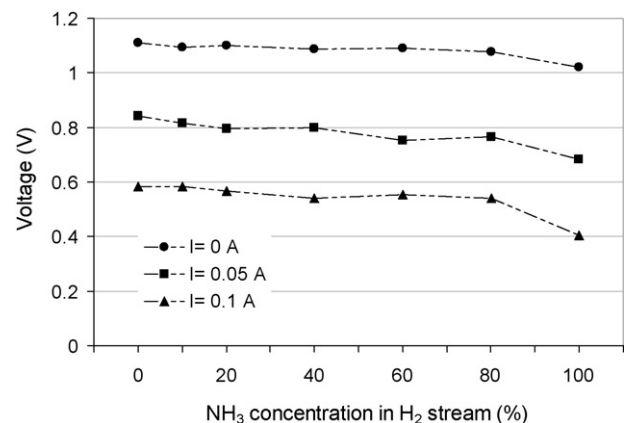


Fig. 2. Cell voltage as a function of the fuel composition and current demand.

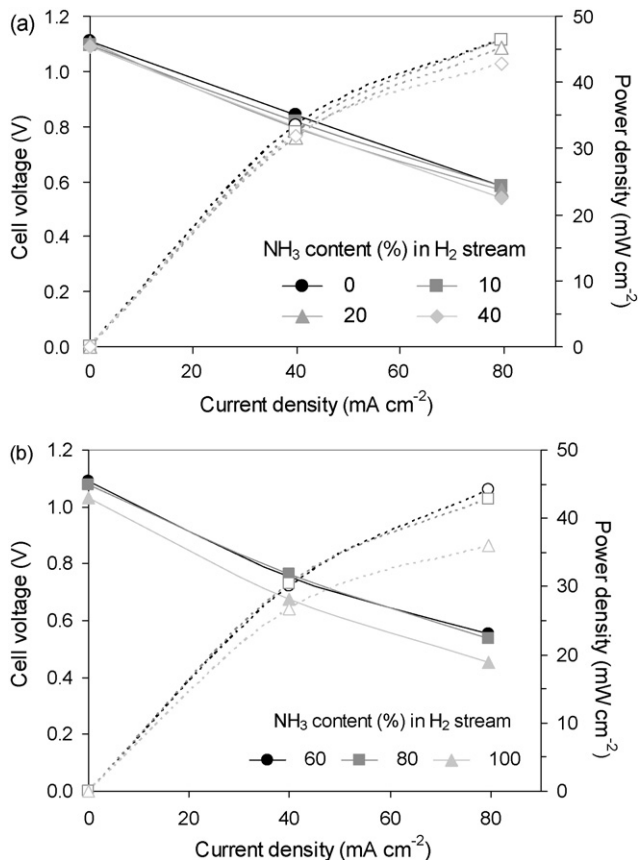


Fig. 3. I - V (solid) and I - P (hollow) curves of the fuel cell fueled by mixtures of ammonia and hydrogen at 700 °C. (a) 0–40% and (b) 60–100% ammonia in H_2 stream.

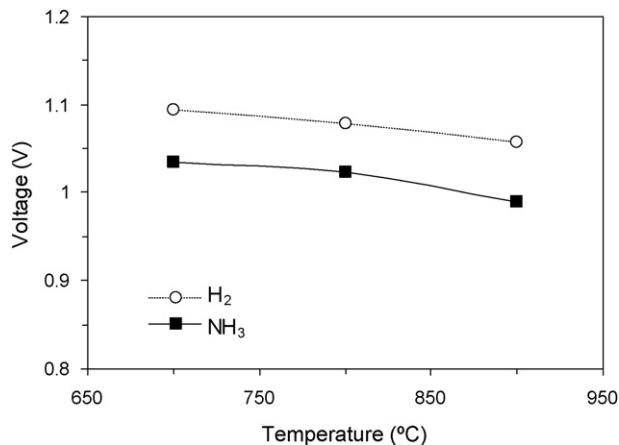


Fig. 4. OCVs of the cell with ammonia or hydrogen as fuel at different temperatures.

It can be seen from data in Table 1 that the amount of energy potentially available from electrochemically oxidising ammonia in a SOFC is effectively twice that from oxidising hydrogen. The thermodynamic data for ammonia oxidation (reaction (1)) suggest that the open circuit voltage of the SOFC should increase with operating

Table 1

Comparison of thermodynamic data for the oxidation of ammonia and the oxidation of hydrogen.

Reaction	ΔG_{298K}° (kJ mol ⁻¹)	ΔG_{1123K}° (kJ mol ⁻¹)	E_{298K}° (V)	E_{1123K}° (V)
$2NH_3 + \frac{3}{2}O_2 \rightarrow N_2 + 3H_2O$ (1)	-652.8	-772	1.13	1.33
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (2)	-228.6	-179	1.19	0.93

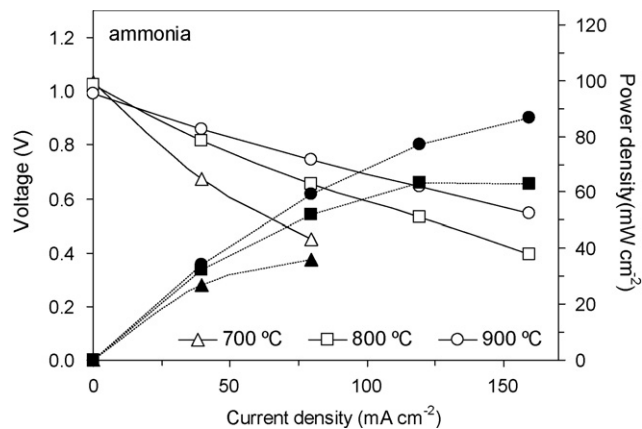


Fig. 5. Cell voltage (solid) and power density (hollow) as a function of current density of the cell operating with ammonia at different temperatures.

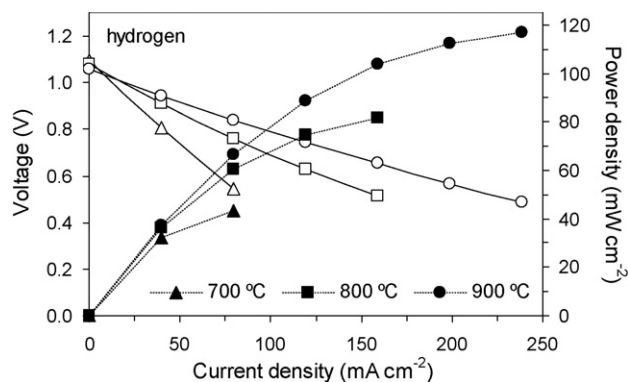


Fig. 6. Cell voltage (solid) and power density (hollow) as a function of current density of the cell operating with hydrogen at different temperatures.

temperature when ammonia is used as fuel. However, Fig. 3 shows clearly an essentially linear decrease in the open circuit voltage. This is not consistent with the thermodynamics of ammonia oxidation but it is the behaviour expected from the thermodynamics of hydrogen oxidation (reaction (2)). This phenomenon suggests that oxidation of ammonia in a SOFC is a two-stage process, decomposition of ammonia to nitrogen and hydrogen occurs initially (reaction (3)), followed by hydrogen oxidation to water (reaction (4)).



It could be concluded that previously reduced Ni cermet is active for ammonia decomposition at common operating temperature of SOFCs. Generated hydrogen is subsequently oxidised at the cell to produce electricity and hot water. Only reaction (4) is effective for the fuel cell performance.

Fig. 4 shows I - V curves together with the power density of the fuel operating with ammonia at different temperatures. For their comparison, I - V curves and power density for the same cell operating with hydrogen are shown in Fig. 5.

It must be noted that the cell performances in function of the current density is similar operating with both fuels, ammonia or hydrogen, although power densities are slightly lower in the case of ammonia fueled cell. At 900 °C, and a current density of 159 mA cm⁻², the power densities were 88 and 104 mW cm⁻² for ammonia and hydrogen respectively, it means a 15% lower in the case of ammonia fueled cell. The decreasing power output when cell is operated using ammonia compared to hydrogen could be attributed to the lower partial pressure of hydrogen. For both, ammonia and hydrogen, the power density decreases as temperature decreases because the cell resistance increases.

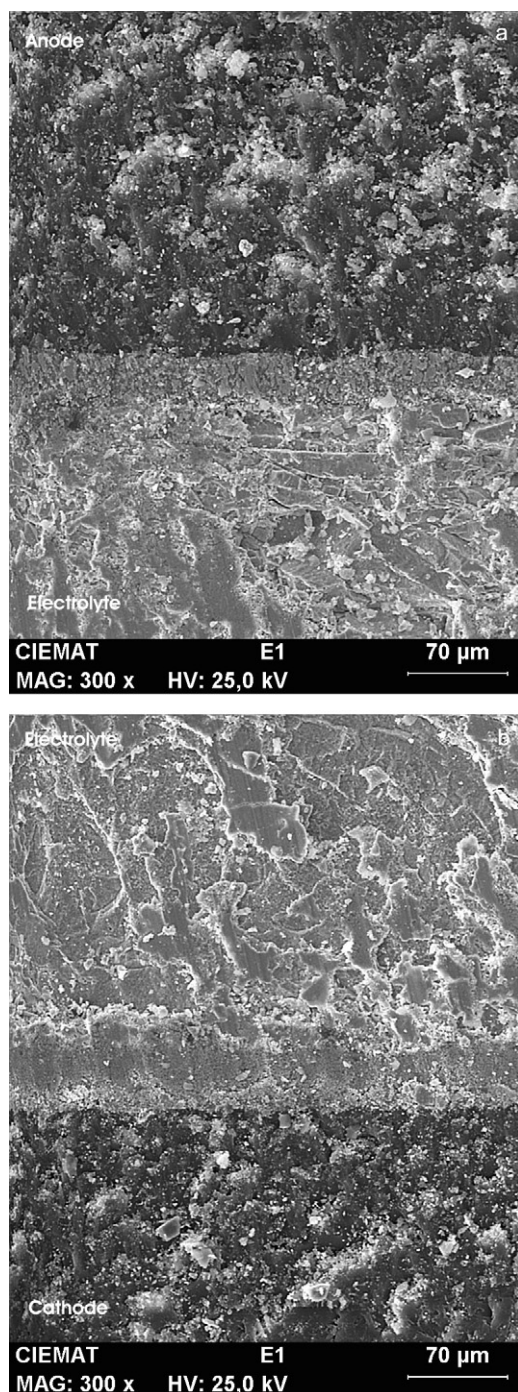


Fig. 7. SEM micrographs of a cross-section of the tested cell. (a) Anode/electrolyte and (b) electrolyte/cathode.

Relationship between the cell voltage and the current density is practically linear at 800–900 °C for ammonia or hydrogen fueled cell (Figs. 5 and 6) which implies a constant internal resistance within the range of 0–250 mA cm⁻² as well as a complete decomposition of the ammonia into H₂ and N₂. However, it should be noted that in the case of ammonia fueled cell when operating temperature was decreased to 700 °C, a nonlinear relationship was observed between voltage and current densities, specially at low current density. This fact could be explained on the basis on a more slowly ammonia decomposition into H₂ and N₂ at this relative low operating temperature (700 °C). For that, hydrogen formation slows down and activation polarization resistance increases. At this operating temperature the ammonia decomposition is a rate-determining step for the whole cell reaction.

From the slopes of the *I*-*V* curves (Figs. 5 and 6), the total resistance were calculated by linear fitting to be 2.77 Ω cm⁻² and 2.37 Ω cm⁻² in ammonia and humidified hydrogen at 900 °C, respectively. Values are nearly close independently of the used fuel which indicates a similar internal resistance for cells fueled with ammonia and hydrogen, under cited operating conditions. However, some differences in the polarization resistance exist depending on the used fuel, more significantly at low temperatures and current demands.

SEM micrographs of a cross-sectional view of the post-test cell Ni-YSZ/YSZ/LSM are shown in Fig. 7. It can be seen that YSZ film is free from pores and cracks within the scale of SEM observation. Both, Ni-YSZ and LSM films, appear as porous uniform layers and well-bonded to the YSZ substrate, no fault or irregularities of the microstructure are observed. These results indicate that no significant degradation of the cell microstructure occurs after ammonia exposition and total operation time.

The efficiency of a SOFC operated with ammonia is highly based on economical and environmental benefits. Similar performance, in comparison with hydrogen fueled cells, is achieved operating with ammonia. Humidified gases are not necessary because no carbon deposits can be formed. The ammonia decomposition is an endothermic reaction and therefore part of heat from the cell can be consumed in this process increasing the electrical efficiency of the system.

4. Conclusions

Having previously shown that solid oxide fuel cells can be run directly on hydrogen containing ppm of ammonia, without affect to its performance, the influence of ammonia exposures, at higher concentration (10–100%) and time periods, in the decay or recovery rates and their effect in the fuel cell performance, was tackled in this work to better explore the feasibility of ammonia as a substitute fuel for SOFC.

The fuel cell performance was evaluated constantly for 400 h, within the range of 700–900 °C, under different anodic feeding. After evaluated the influence on the cell performance of increasing amount of ammonia in the hydrogen anodic feeding, at 700 °C, cell was also tested using ammonia as unique fuel at different temperatures. Similar tests were carried out under humidified hydrogen for their comparison.

Results have demonstrated that SOFC can actually utilise the ammonia as fuel to produce electrical power. Direct electrochemical oxidation of the ammonia does not occur; ammonia is first catalytic decomposed into H₂ and N₂ over the nickel cermet and generated hydrogen is then electrochemically converted to water and electrical power. The decomposition of ammonia was both sufficient and fast in the anode chamber, in the range of operating temperatures under study, and cell voltage and power densities were similar to those obtained under hydrogen feeding, taking into account the

lower partial pressure of hydrogen when cell was operated with ammonia.

The cell internal resistance seems to be independently on the used fuel and only slight differences exist on the polarization resistance at 700 °C and low current density, probably due to a more slowly ammonia decomposition at this temperature.

No severe changes or deterioration were undergone on cell performance after long operation period. The close performance of cell fueled by ammonia and hydrogen suggest that ammonia has a potential as a substitute fuel for H₂ and it can be viewed as an attractive fuel for SOFCs.

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References

- [1] P. Ranran, Y. Wu, L. Yang, M. Zongqiang, *Solid State Ionics* 177 (2006) 389–393.
- [2] A. Atkinson, S. Barnett, R.J. Gorte, J.T.S. Irvine, A.J. McEvoy, M. Mogenssen, S.C. Singhal, J. Vohs, *Nature* 3 (2004) 17–27.
- [3] A. Fuerte, R.X. Valenzuela, L. Daza, *J. Power Sources* 169 (2007) 47–52.
- [4] N.J.J. Dekker, G. Rietveld, *J. Fuel Cell Sci. Technol.* 3 (2006) 499–502.
- [5] S.F. Yin, B.Q. Xu, X.P. Zhou, C.T. Au, *Appl. Catal. A* 227 (2004) 1–9.
- [6] N. Sifer, K. Gardner, *J. Power Sources* 132 (2004) 135–138.
- [7] T.V. Choudhary, C. Sivadinarayana, D.W. Goodman, *Chem. Eng. J* 93 (2003) 69–80.
- [8] A. Wojcik, H. Middleton, I. Damopoulos, J. Van Herle, *J. Power Sources* 118 (2003) 342–348.
- [9] J. Staniforth, R.M. Ormerod, *Green Chem.* 5 (2003) 606–609.
- [10] K. Xie, Q. Ma, B. Lin, Y. Jiang, J. Gao, X. Liu, G. Meng, *J. Power Sources* 170 (2007) 38–41.
- [11] L. Zhang, W. Yang, *J. Power Sources* 179 (2008) 92–95.
- [12] C. Zamfirescu, I. Dincer, *J. Power Sources* 185 (2008) 459–465.
- [13] A. Fuerte, R.X. Valenzuela, T. González, L. Daza, Effects of trace NH₃ from biogas on solid oxide fuel cell performance, in: *Proceedings of the 2006 Fuel Cell Seminar*, Honolulu, Hawaii, USA, 2006.
- [14] K. Kendall, C.M. Finnerty, G. Saunders, J.T. Chung, *J. Power Sources* 106 (2002) 323–327.