



Methane-free biogas for direct feeding of solid oxide fuel cells

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ABSTRACT

This paper deals with the experimental analysis of the performance and degradation issues of a Ni-based anode-supported solid oxide fuel cell fed by a methane-free biogas from dark-anaerobic digestion of wastes by pastry and fruit shops. The biogas is produced by means of an innovative process where the biomass is fermented with a pre-treated bacteria inoculum (*Clostridia*) able to completely inhibit the methanization step during the fermentation process and to produce a H₂/CO₂ mixture instead of conventional CH₄/CO₂ anaerobic digested gas (bio-methane). The proposed biogas production route leads to a biogas composition which avoids the need of introducing a reformer agent into or before the SOFC anode in order to reformat it.

In order to analyse the complete behaviour of a SOFC with the bio-hydrogen fuel, an experimental session with several H₂/CO₂ synthetic mixtures was performed on an anode-supported solid oxide fuel cell with a Ni-based anode. It was found that side reactions occur with such mixtures in the typical thermodynamic conditions of SOFCs (650–800 °C), which have an effect especially at high currents, due to the shift to a mixture consisting of hydrogen, carbon monoxide, carbon dioxide and water. However, cells operated with acceptable performance and carbon deposits (typical of a traditional hydrocarbon-containing biogas) were avoided after 50 h of cell operation even at 650 °C. Experiments were also performed with traditional bio-methane from anaerobic digestion with 60/40 vol% of composition. It was found that the cell performance dropped after few hours of operation due to the formation of carbon deposits.

A short-term test with the real as-produced biogas was also successfully performed. The cell showed an acceptable power output (at 800 °C, 0.35 W cm⁻² with biogas, versus 0.55 W cm⁻² with H₂) although a huge quantity of sulphur was present in the feeding fuel (hydrogen sulphide at 103 ppm and mercaptans up to 10 ppm). Therefore, it was demonstrated the interest relying on a sustainable biomass processing which produces a biogas which can be directly fed to SOFC using traditional anode materials and avoiding the reformer component since the methane-free mixture is already safe for carbon deposition.

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1. Introduction

The high flexibility of solid oxide fuel cells on fuel typology allows foreseeing their future use with a large spam of fuels. Among these, a sustainable route is considering fuels produced by biomass.

Biomass is generally processed following two main paths, gasification and anaerobic digestion. The first one consists in the thermal breakdown of the starting biomass into a combustible gas, volatiles, char, and ash in an enclosed reactor or gasifier. Gasification is a two-step, endothermic process. First, the pyrolysis takes place; the volatile components of the fuel are vaporized at temperatures below 600 °C by a set of complex reactions. Included in the volatile vapours are hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tars, and water vapour. In the sec-

ond step, the char is gasified through reactions with oxygen, steam, carbon monoxide and hydrogen. The heat needed for the endothermic gasification reactions is generated by combustion of part of the fuel, char, or gases, depending on the reactor technology.

A second path for biomass processing is linked to biological transformation. Among the biological processes, dark anaerobic fermentation represents an efficient procedure to obtain biogas in a sustainable way, especially if organic wastes are used. Biomass undergoes through a fermentative process with the result of formation of gaseous compounds whose composition depends on the biomass typology and on the employed bacteria microflora and its treatment. A conventional biogas from anaerobic digestion is essentially a mixture of CH₄/CO₂, with CH₄ in a richer molar fraction (typically 60/40 vol%), plus various gaseous species depending on the biomass selected for the process.

Solid oxide fuel cells have been demonstrated to work in combined operation with biomass gasifiers as shown in the work

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by Aravind [1], Baron et al. [2], Hofmann et al. [3] and Frank et al. [4].

Integration of gasifiers and solid oxide fuel cell systems have been recognized as a very attractive energy solution for distributed generation in particular when thinking about indirect gasification with heat provided by the thermal integration with the SOFC system. Particular interest relies on the TopCycle-Concept proposed by Technical University of Munich where the waste heat of a high temperature fuel cell is recovered to supply the required heat for the endothermic gasification reactions to an allothermal gasifier. In that solution high temperature (800 °C) heat is provided by a sodium heat pipes-cooled SOFC stack [5].

Despite such important achievements, it has been shown how the integration of gasifiers and SOFC systems is quite a complex task, essentially because the cell degradation with pollutants and the tars' effect, which is a topic not still, cleared. Further, the system integration and the medium or high temperature gas cleaning is still a technological challenge.

The utilization of a biogas from anaerobic digestion with SOFCs could then represent a more immediate and effective opportunity (provided the risks of cell degradation are reduced) to couple SOFCs and biomass; in fact, the system integration is much easier and cheap and further, low temperature gas cleaning is much more reliable and technically available. It is necessary to specify, however, that gasification and anaerobic digestion are not necessarily two competing technology since they often exploit different kinds of biomass (e.g. wood is generally used for gasification, but not for anaerobic digestion—even if nowadays special pre-treatment processes are under investigation and could be used to make lingo-cellulosic biomass suitable for fermentation).

About conventional biogas from anaerobic digestion, it has been proven to be potentially dangerous for SOFCs' anodes if directly fed to them [6]. Such a mixture is likely to undergo the dry reforming to produce H₂ and CO to electrochemically react on the TPB of the anode electrode, but reactions as methane cracking (disaggregation) or Boudouard reaction are likely to occur as well, thus generating the carbon formation onto the anode surface, which eventually lead to a fast degradation and in some cases to the mechanical failure of the anode. To overcome these problems, a possible way is the modification of the classical materials used in the anode layer. More encouraging results have been found by employing carbon tolerant anode compositions [7,8]: in Ref. [7] the direct feeding of a Scandia-based anode-supported SOFC with CH₄/CO₂ mixtures is demonstrated up to 50 h without any voltage drop and carbonaceous deposits. In Ref. [8] solid oxide fuel cells (SOFCs) with NiO–ScSZ and Ni_{0.9}Mg_{0.1}O–ScSZ-based anodes were operated by directly feeding a fuel mixture of CH₄, CO₂ and N₂ (CH₄ to CO₂ ratio of 3:2): stable operation under constant current load (200 mA cm⁻²) was achieved with a NiO–ScSZ type anode during 200 h operating hours at 900 °C. Less stable operation occurred with a Ni_{0.9}Mg_{0.1}O–ScSZ-based anode.

A complementary and new approach, discussed in this paper, is the modification of the biogas composition before its utilization with the SOFC cell; the approach based on the modification of the conventional biological path of the biogas production, in order to obtain a methane-free biogas from anaerobic digestion which could directly be used in solid oxide fuel cells.

The methane-free biogas is produced by a Clostridia bacteria microflora in a wastewater sewage sludge which is previously treated with HCl to inhibit the production of methane; the pre-treated sludge is then used as inoculum in a carbohydrate-rich medium as carbon source (vegetables and fruit wastes, previously finely crumbled). The produced biogas is an high quality fuel in terms of permanent gas compounds and impurities, consisting mainly of CO₂ (ranging from 70 to 50%), hydrogen (ranging from 30 to 50%), and traces of CO and H₂S. This paper shows the feasi-

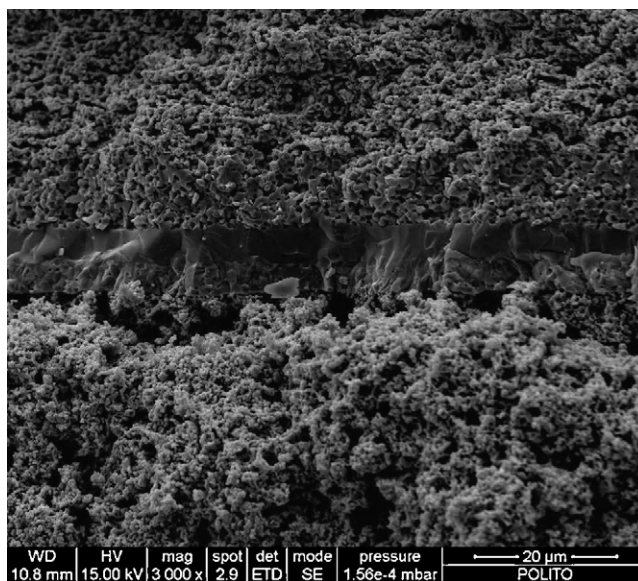


Fig. 1. Cross-section of an anode-supported SOFC fed by biogas (from top to bottom: Ni/8YSZ anode-support, Ni/8YSZ anode active layer, 8YSZ dense electrolyte, YDC barrier interlayer, LSCF cathode).

bility of direct utilization of biogas from that innovative anaerobic digestion route with Ni-based SOFC anodes.

2. Experimental assessments and experiment purposes

The experiments were done at the LAQ IN.TE.S.E. of Politecnico di Torino. A test stand for testing planar SOFCs is installed, equipped with several devices for the characterization of fuel cells including an electronic load by Kikusui and an impedance spectrometer by Gamry. The rig is also equipped for testing SOFCs with a variety of fuels including synthetic mixtures consisting of hydrogen, carbon monoxide, carbon dioxide, nitrogen and methane. Further details about the test-rig can be found in Ref. [9].

The employed cells were circular planar cells with 80 mm of diameter consisting of a (1) three layers anode (2 μm NiO current collector layer, 500 μm NiO/YSZ diffusion layer and 5 μm NiO/YSZ functional layer); (2) a 5 μm 8YSZ electrolyte with a 3 μm YDC barrier layer; (3) a 40 μm LSCF cathode. In Fig. 1 it is shown a SEM analysis of an investigated cell after operation with an outline of the different layers. A deep analysis of the cell geometry and microstructure can be found in Ref. [10].

In a first experimental session, simulated H₂/CO₂ mixtures, representative of the considered bio-hydrogen, were used to evaluate the performances and degradation issues of a conventional Ni/8YSZ anode-supported cell at different fuel composition and temperatures. For comparison, also H₂/N₂ mixtures were tested. This first experimental session had the aim to:

- experimentally assess the feasibility of feeding SOFCs with a syn-gas consisting of H₂/CO₂ mixtures (before the tests with the real biogas from anaerobic digestion);
- detail the effect of different fuel diluents (N₂, CO₂) with reference to the typical thermodynamic operating conditions of the fuel cell;
- relate the SOFCs behaviour with the thermodynamic properties of feeding mixtures, taking into account the effect of side reactions which can finally modify the transport properties of reactive species, the chemical activity and the energy balance on a volume close to the cell surface.

Afterwards, medium-term endurance experiments (50 h) were performed considering simulated bio-hydrogen and bio-methane fuel mixtures. The experiments were performed keeping constant all the operational cell parameters including temperature and fuel utilization. The main aim of this experiment was the demonstration of the capability of a direct feeding of an SOFC with bio-hydrogen whereas the direct utilization of bio-methane was no longer feasible due to the formation of carbon deposits and performance drop.

Finally, an experimental session was performed with the aim to evaluate the use of the real biogas produced by a fermentative process of organic wastes. The biogas consisted of H₂/CO₂ mixtures and it was generated in a reactor located in the BioEnergy Lab in the Environment Park of Torino. Tedlar® sample bags were used to store the gas and bring it to the SOFC test-station. A peristaltic pump was then used to pump the biogas from the bags to the cell furnace. The flow rate was measured by using air rotameters with a correction factor in order to take into account the physical properties of the biogas.

The effective demonstration of the operation of the fuel cell with such biogas is essential to assess practical integration of the two technologies by designing a continuous biogas fuel supply and a proper gas cleaning systems.

3. Biogas production

Hydrogen represents a promising alternative to fossil fuels that can be produced in several ways: electrolysis of water, steam reforming of hydrocarbons, gasification and biological production. Among the biological processes, dark anaerobic fermentation represents an efficient process to obtain hydrogen in a sustainable way, especially if organic wastes are used. Bacteria involved in hydrogen production belong to the Clostridial species, as reported by Kim et al. [11]. *Clostridium* spp. are anaerobic, Gram positive and spore-forming bacteria, able to resist to shocks like heat treatment or acid–basic treatment. Moreover, *Clostridium* spp. can achieve the highest H₂ yield per mole of glucose in dark anaerobic fermentation (1.61/2.36 mol H₂/mol glucose), as reported by Taguchi et al. [12]. Mixed microflora should be preferred to pure culture in order to make bio-hydrogen production more cost-effective. In this sense, a good solution is represented by the use of digested sludge, rich in Clostridiaceae, at mesophilic temperatures (Fang et al. [13], Lin and Lay [14] and Zhang and Shen [15]). The inoculum used in the pilot plant for bio-H₂ production, located in the BioEnergy Lab in the Environment Park of Turin, was obtained from an anaerobic digested sludge, derived from the municipal wastewater treatment plant of the city of Turin (SMAT S.p.A.). The main results on physical–chemical properties of the sludge are reported in Table 1.

During the fermentative process, after the acidogenic step, during which hydrogen is produced, methanogenic or sulphate-reducing bacteria consume hydrogen to form methane. Many pre-treatments were proposed to inhibit the methanogenic bioactivity in a batch process: for example acidification, basification, freezing and thawing or thermal shock (Mu et al., [16]; Mohan et al., [17]; Ting and Lee [18]), being *Clostridium* spp. spore formers and consequently resistant to these treatments. In this work, the sludge was pre-treated with HCl 1N for 24 h till pH 3/4 in order to inhibit methanogenesis as reported by Mu et al., [16]. Concentration of *Clostridium* spp., in terms of CFU/ml (Clostridial plate count after 48 h at 30 °C), in the inoculums before and after the acid pre-treatment, do not change appreciably, as shown in Table 2.

Fang et al. [13], found that predominant bacteria present in a mixed culture enriched by acid pre-treatment belong to species in the genera *Clostridium*, *Enterobacter* and *Citrobacter*. Some species, i.e. *Clostridium butyricum* and *Clostridium tyrobutyricum*, produce butyrate and acetate as their main fermentation by-products,

Table 1
Sludge properties.

Property	Units of measurement	Measured value
pH	pH	7.3
Dissolved oxygen	mg l ⁻¹	2.3
Density	g ml ⁻¹	1.03
Suspended solids	mg l ⁻¹	26,184.0
Total solids	%	3.09 ± 0.88
COD	mg l ⁻¹	15,981.5
BOD ₅	mg l ⁻¹	3,775
Ammonium nitrogen	mg l ⁻¹	670.3
Nitrite	mg l ⁻¹	7.3
Nitrate	mg l ⁻¹	47.5
Total organic carbon	mg kg ⁻¹	4,490
Organic nitrogen	mg kg ⁻¹	220
C/N ratio	mg kg ⁻¹	16.2
Total phosphorus	mg kg ⁻¹	1,358.0
Fats and vegetal and animal oils	mg l ⁻¹	19.0
Bacterial charge at 37 °C	CFU/100 ml	89,000

according to the following reactions which take into account sucrose as main source of carbon:



As a source of carbon organic wastes (pastry and fruit unsold stock) was dissolved in a medium of salts and micronutrients consisting of (all in mg g⁻¹ of total sugar): NaHCO₃ 26.8, NH₄Cl 53.58, KH₂PO₄ 53.6, K₂HPO₄ 53.6, CaCl₂ 10.72, NiSO₄·6H₂O 1.16, MgSO₄·7H₂O 6.86, FeCl₃ 0.43, Na₂B₂O₇·10H₂O 0.15, Na₂MoO₄·2H₂O 0.30, ZnCl₂ 0.49, CoCl₂·6H₂O 0.45, CuCl₂·H₂O 0.21, MnCl₂·4H₂O 0.64, yeast extract 1.07 (Fang et al. [13]), in order to guarantee a good nutritional supply (COD/N ≥ 50; the acronym signifying the ratio between the chemical oxidation demand, COD, and the total nitrogen concentration, N).

Dark anaerobic fermentation was carried out in batch conditions in a reactor of 250 l, fed with acidly pre-treated inoculums (10%, v/v) and medium (salts, micronutrient and crumbled wastes) in order to obtain a total reactant volume of 200 l. The reactor is mixed thanks to the action of a recirculation system activated by a centrifugal pump, in order to avoid stratification inside the reactor and to provide a better distribution of nutrients among the bacteria involved in the fermentative process. Anaerobic conditions were created by insufflating nitrogen at the bottom of reactor, till no oxygen could be detected. During fermentation temperature was maintained at room conditions (20–25 °C) without being regulated in order to improve the global energetic balance.

The pressure inside the reactor was set at values of 20–30 mbar by regulating a relief valve; as soon as the pressure inside exceeds the backpressure, gas passes through the valve and is collected in another vessel of 2.5 l connected to a compressor which pressurizes the gas, then ready to be stored in gas sampling bags SKC, 232 series. The gas produced was constantly measured with a volumetric gascounter (Sacofgas S1ATG4), as well as pH, ORP (Oxidation Reduction Potential) and temperature which was logged through a data acquisition system.

After a lag phase of about 48 h, necessary for the bacteria sporulation, fermentation began, reached its exponential phase and stopped after approximately 5 days, leading to a gas mainly consisting of hydrogen (35%), carbon dioxide (56%) with traces of methane

Table 2
Concentration of *Clostridium* spp. before and after acid pre-treatment.

	Sludge before pre-treatment	Sludge after pre-treatment
<i>Clostridium</i> spp. (CFU ml ⁻¹)	6.66 × 10 ⁴	5.93 × 10 ⁴

(0.0052%) and hydrogen sulphide (110 ppm). The maximum value of specific hydrogen production rate was about 0.05 l of hydrogen produced per hour per litres of reactant volume.

Along fermentation pH decreased constantly from 7.0 to 4.0, due to the formation of volatile fatty acids (VFAs), while ORP reached its minimum in correspondence of maximum hydrogen production rate, indicating that a reducing atmosphere was established along fermentation. Experimental results show that hydrogen production was limited by pH decrease rather than carbon source consumption; production stopped when pH reached values lower than 4.0 and the substrate was not completely consumed.

The schematic diagram for the biogas production is shown in Fig. 2.

4. Thermodynamic findings

When dealing with multi-species fuels and SOFCs it is required to take into account eventual side reactions which can proceed to a certain extent according to several factors, including fuel composition, thermodynamic state (temperature and pressure), nature of the employed catalysts in the cell anode. The most important of these side reactions are the water gas shift reaction, methane steam reforming and dry reforming:



The possibility of achievement of equilibrium in SOFC conditions has been widely discussed and, sometimes, results have been contradictory. Some experimental and theoretical investigations have confirmed that chemical equilibrium is achieved in many SOFC operating conditions [19,20].

Before starting with experiments, a thermodynamic simulation was performed concerning H_2/CO_2 and CH_4/CO_2 equilibrium mixtures on the SOFC anode in operation. The equilibrium calculations were based on the minimization of the Gibbs free energy, which is an appropriate and simple method to calculate the equilibrium compositions of any reacting system. For a reacting system with N species, the total Gibbs free energy is given by

$$G^t = \sum_i^N n_i \cdot \bar{g}_i = \sum_i^N n_i \cdot \mu_i = \sum_i^N n_i \cdot \bar{g}_i^0 + RT \cdot \sum_i^N n_i \cdot \ln \frac{\hat{f}_i}{f_i^0} \quad (6)$$

where G^t is the total Gibbs free energy, \bar{g}_i the partial molar Gibbs free energy of species i , \bar{g}_i^0 the standard Gibbs free energy, μ_i the chemical potential, R the molar gas constant, T the temperature of the system, P the pressure of the system, \hat{f}_i the fugacity in the system, f_i^0 the standard-state fugacity, and n_i the mole of species i . For reaction equilibrium in gas phase $\hat{f}_i = y_i \cdot \hat{\phi}_i \cdot P$, $f_i^0 = P^0$, $\bar{g}_i^0 = \Delta \bar{g}_{f_i}^0$ are assumed, where y_i the gas phase mole fraction, $\hat{\phi}_i$ the fugacity coefficient of species i , $\Delta \bar{g}_{f_i}^0$ is the standard Gibbs energy of formation of species i , P^0 the standard-state pressure of 101.3 kPa.

Six species were considered to exist at the equilibrium: hydrogen, methane, carbon monoxide, carbon dioxide, water steam and nitrogen. It was found a variation of equilibrium compositions depending on the temperature and CO_2/H_2 and CO_2/CH_4 ratios. In particular, in the case of bio-hydrogen, the equilibrium mixtures mainly consisted of hydrogen, carbon dioxide, carbon monoxide, water steam and some methane (especially at 650 °C). In fact, Reverse Water Gas Shift reaction is promoted in this domain of thermodynamic conditions of the fuel cell; further, at the lower temperature, results also suggest that the Reverse Steam Reforming Reaction proceeds to a certain extent.

As different species are present in the product gas as a result of chemical equilibrium, the calculation of the Nernst voltage was made with the oxygen partial pressure on the anode side (oxygen partial pressure assumed on the cathode side: 0.21 atm). This corresponds to evaluate the following formula:

$$\text{OCV} = \frac{RT}{4F} \ln \left(\frac{P_{\text{O}_2, \text{cath}}}{P_{\text{O}_2, \text{an}}} \right) \quad (7)$$

The simulation of open circuit voltages was made considering the equilibrium composition of the fuel gas as previously discussed. The calculated Nernst voltage corresponds to the one established at the entrance of the fuel cell or to the one when the cell is operating at open circuit.

The anode partial pressure can be calculated either by the H_2 - H_2O equilibrium or the CO - CO_2 equilibrium, since the Nernst voltage has to be the same in equilibrium conditions. The partial pressure at the anode, considering the hydrogen oxidation reaction at equilibrium, can be then evaluated as:

$$\ln P_{\text{O}_2, \text{an}} = \frac{2\Delta G_{0, \text{H}_2\text{O}}}{RT} + 2 \ln \left(\frac{P_{\text{H}_2\text{O}, \text{an}}}{P_{\text{H}_2, \text{an}}} \right) \quad (8)$$

where $P_{\text{H}_2\text{O}, \text{an}}$ and $P_{\text{H}_2, \text{an}}$ are respectively the molar fraction of H_2 and H_2O present in inlet anode gas at the equilibrium.

In the same way, considering the carbon monoxide oxidation reaction at equilibrium, we can write:

$$\ln P_{\text{O}_2, \text{an}} = \frac{2\Delta G_{0, \text{CO}_2}}{RT} + 2 \ln \left(\frac{P_{\text{CO}_2, \text{an}}}{P_{\text{CO}, \text{an}}} \right) \quad (9)$$

where $P_{\text{CO}_2, \text{an}}$ and $P_{\text{CO}, \text{an}}$ are respectively the molar fraction of CO_2 and CO present in inlet anode gas at the equilibrium.

For gas mixtures containing methane as well, an analogous equation should be written for this compound as long we consider its direct oxidation likely to happen. This means that the CH_4 reacts electrochemically before reforming or undertaking other chemical transformation. Anyway, this not the case for the experiments reported here.

Thermodynamic calculations also showed that no carbon deposition was expected using bio-hydrogen in typical operation of SOFCs, which is over 650 °C. In the case of the bio-methane feeding, carbon formation was expected from thermodynamics also at the nominal operating temperature of 800 °C.

5. Assessment of SOFCs behaviour with simulated biogas mixtures

In a first experimental session, bottle gases were used to simulate the bio-hydrogen utilization with a planar anode-supported SOFC with traditional NiO/YSZ cermet. Mixtures of H_2/CO_2 with different concentrations were fed to an anode-supported SOFC at different temperatures. The concentration of CO_2 varied from 20 vol% up to 45 vol%, in particular the following molar fraction ratios of CO_2/H_2 were analysed: 0 (pure hydrogen), 0.25 (20 $\text{CO}_2/80\text{H}_2$), 0.43 (30 $\text{CO}_2/70\text{H}_2$), 0.82 (45 $\text{CO}_2/55\text{H}_2$). A constant flow of 0.6 Nl min^{-1} of hydrogen humidified at 30 °C was fed to the fuel cell, and mixed with the CO_2 dry gas in the desired concentration ratio. The hydrogen flow was kept constant in order to evaluate the CO_2 dilution effect keeping constant the value of fuel utilization (at least the theoretical one). Experiments were done changing the cell temperature between 650 °C and 800 °C with 50 °C steps. Also H_2/N_2 mixtures were tested for comparison (pure dilution of H_2). The effect of such mixtures was measured on cell voltage behaviour.

In order to achieve such result, a detailed experimental session was designed and then performed. During each experiment, once the set-point temperature was reached and stabilized, the cell was put in OCV condition with 0.6 Nl min^{-1} of humidified hydrogen at

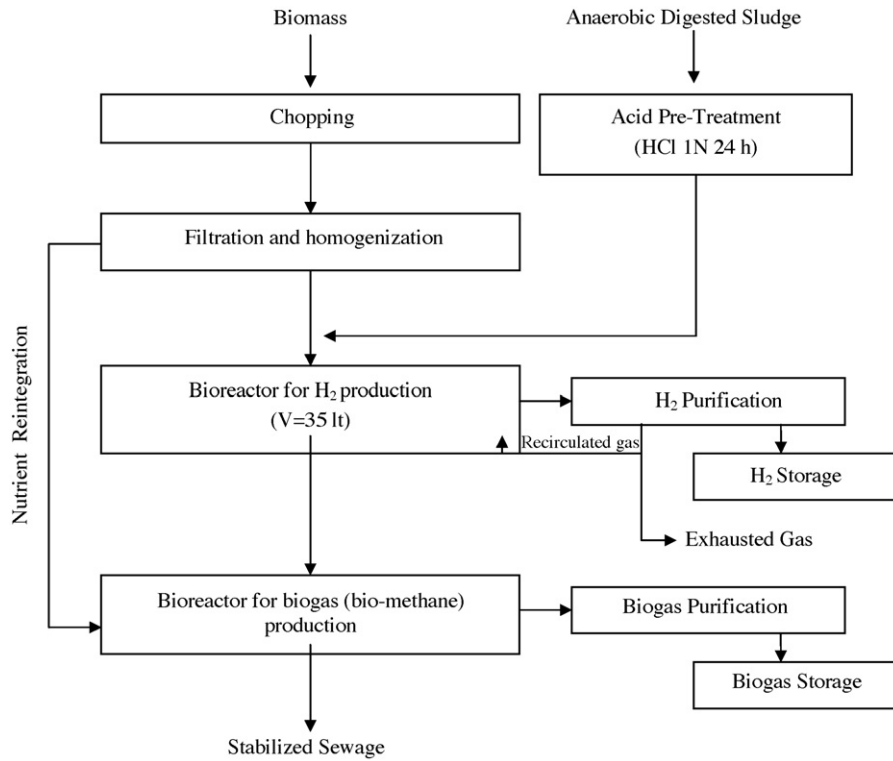


Fig. 2. Schematic diagram for the methane-free biogas production.

30 °C (reference condition of the experiment) and data acquired for 30 min. Afterwards, the hydrogen fuel was diluted according to the scheduled experiment. Data were then acquired for 30 min with the new fuel mixture at OCV condition. The polarization experiment started from the OCV condition until the lowest voltage of 500 mV. The current step was of 1 A and the dwelling time was set at 60 s.

In Fig. 3 the OCVs with CO₂/H₂ mixtures, both measured and simulated, are plotted.

It is possible to see that for H₂/CO₂ mixtures, the simulated OCVs well represent the experimental data. However, for pure hydrogen feeding the open circuit voltage was lower than the theoretical

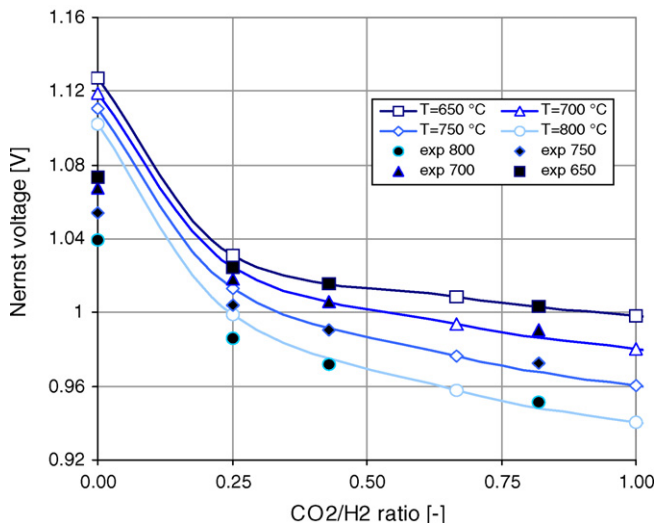


Fig. 3. Theoretical and experimental Nernst voltage with H₂/CO₂ mixtures.

one. This unexpected behaviour has to be probably addressed to the experimental set-up, with unsealed anode and cathode compartments. In fact, the condition with pure hydrogen feeding is characterized by quite low anodic flow (0.6 Nl min⁻¹) and the difference of pressure between anode and cathode side can enhance backflow phenomena of air to the anode side, thus reducing the hydrogen concentration. When mixed with CO₂, the anode flow is increased and this effect is able to recover fuel losses linked to the air backflow. The theoretical values are well reproduced from the experimental results: this is a first confirmation that chemical reactions occur in the thermodynamic operation conditions of SOFCs and, further, they seem to reach the equilibrium.

The full polarization behaviour was investigated in a wide range of temperature, from 650 °C up to 800 °C. This experimental domain was chosen also to evaluate the coupled effect of cell thermodynamic state and fuel property on the cell electrochemistry. In Fig. 4, it is possible to see the measured current–voltage and current–power curves with pure hydrogen, H₂/N₂ and H₂/CO₂ mixtures (55/45 vol%) at 700 °C. The mixtures are obtained respectively with 0.6 Nl min⁻¹ of H₂ humidified at 30 °C; 0.6 Nl min⁻¹ of H₂ and 0.5 Nl min⁻¹ of N₂ both humidified at 30 °C; and 0.6 Nl min⁻¹ of H₂ humidified at 30 °C and 0.5 Nl min⁻¹ of dry CO₂.

First, it is possible to see that the reversible voltages obtained with N₂ and CO₂ dilution are quite different. The worst performance obtained with CO₂ is due to the change on the chemical activity of the fuel mixture because of the chemical side reactions and consequent switching to the equilibrium composition. In fact, in the case of H₂/CO₂ mixtures, the proceeding of side reactions is responsible for the decrease of hydrogen concentration and the increase of carbon monoxide, with the final result to have a lower reversible voltage as shown from theoretical calculations. Moreover, there is a significant difference of behaviour also in terms of polarization. In particular, the difference appears to be more pronounced at high current density where mass transport limitation clearly differentiates the behaviour of these fuels.

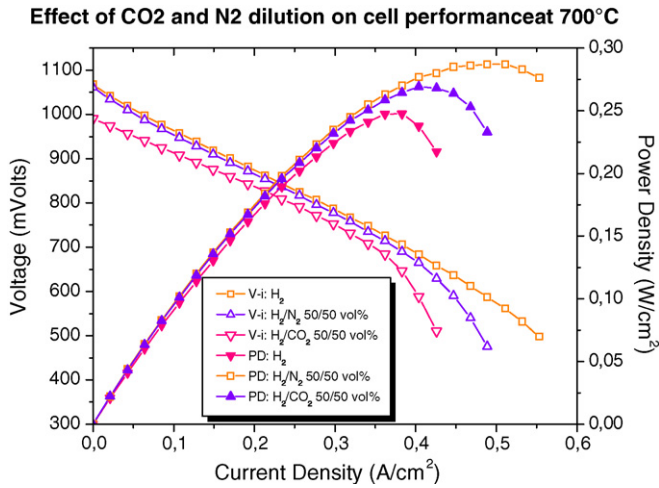


Fig. 4. Effect of N₂ and CO₂ diluents on voltage and power characteristic curves of SOFCs.

The electrochemical behaviour was analysed by using a polarization model for the cells, the following model was employed:

$$V = OCV - R_{lin} \cdot i + \frac{RT}{2F} \ln \left(1 - \frac{i}{i_{al}} \right) + \frac{RT}{4F} \ln \left(1 - \frac{i}{i_{cl}} \right) \quad (10)$$

The model takes into account the reversible potential of the cell as calculated with Eq. (7), a linear contribution which is essentially ohmic but also include a contribution due to the activation of fuel oxidation and oxygen reduction reactions, and finally two terms which refer to the mass transport phenomena in terms of limiting current densities. The linear contribution R_{lin} and the anodic limiting current densities were estimated for all the experimental current–voltage curves.

The limiting current density at the anode side is given by

$$i_{as} = \frac{2Fp_{H_2}^b D_{a(eff)}}{RTt_a} \quad (11)$$

where F is the Faraday constant, p is the pressure in the cell (1 bar), $p_{H_2}^b$ is the partial pressure of hydrogen at the bulk, R is the universal gas constant, T is the cell temperature and t_a is the anode thickness and $D_{a(eff)}$ is the effective diffusion coefficient.

The limiting current density at the cathode side has been fixed because its small contribution on the cell performance (due to very high values of air utilization during the tests) and because of the operating conditions at the cathode side are kept constants during all the experiments. Its value has been evaluated by considering the microstructure at the cathode side in terms of porosity and tortuosity and also the partial pressure of oxygen at the bulk according to the equation:

$$i_{cs} = \frac{4Fp_{O_2}^b D_{c(eff)}}{\left(\frac{p-p_{O_2}^b}{p} \right) RTt_c} \quad (12)$$

where $p_{O_2}^b$ is the partial pressure of oxygen at the bulk and t_c is the cathode thickness. The term $D_{c(eff)}$, is the effective binary diffusion oxygen given by

$$D_{c(eff)} = \frac{\varepsilon}{\tau} \cdot D_{O_2-N_2}(T_{ref}) \cdot \frac{T}{T_{ref}} \quad (13)$$

where $D_{O_2-N_2}$ is the binary diffusion coefficient of O₂ and N₂, ε and τ the average porosity and tortuosity respectively of the cathode layer. The bulk oxygen partial pressure has been set at 0.21 since the air flow is provided with high excess at the cathode side whereas the porosity has been kept at $\varepsilon = 0.3$ and tortuosity at $\tau = 5$. Considering

Table 3

Parameters of the polarization model in case of CO₂ dilution.

	650 °C	Δ	700 °C	Δ
CO ₂ /H ₂ : 0.25				
R_{lin} (Ω cm ²)	1.57	± 0.031	0.663	± 0.0138
I_{al} (A cm ⁻²)	0.35	± 0.023	0.557	± 0.0021
CO ₂ /H ₂ : 0.43				
R_{lin} (Ω cm ²)	1.5352	± 0.0232	0.6453	± 0.0129
I_{al} (A cm ⁻²)	0.3083	± 0.0099	0.5344	± 0.0012
CO ₂ /H ₂ : 0.82				
R_{lin} (Ω cm ²)	1.5937	± 0.0208	0.6462	± 0.0126
I_{al} (A cm ⁻²)	0.2775	± 0.0059	0.4292	± 0.0011
	750 °C		800 °C	
		Δ		Δ
CO ₂ /H ₂ : 0.25				
R_{lin} (Ω cm ²)	0.38371	± 0.0046	0.2443	± 0.0030
I_{al} (A cm ⁻²)	0.95509	± 0.0062	1.2189	± 0.0106
CO ₂ /H ₂ : 0.43				
R_{lin} (Ω cm ²)	0.3779	± 0.0067	0.2402	± 0.0026
I_{al} (A cm ⁻²)	0.9057	± 0.0056	1.1556	± 0.0018
CO ₂ /H ₂ : 0.82				
R_{lin} (Ω cm ²)	0.3724	± 0.0061	0.2478	± 0.0030
I_{al} (A cm ⁻²)	0.7970	± 0.0037	1.0070	± 0.0020

a cathode thickness of 30 μ m, the limiting current density at the cathode has been found to be around 7.5 A cm⁻².

In Table 3 an example of the estimation of some parameters of the model is reported in the case of CO₂ dilution at different temperatures.

First, it is interesting to notice how the linear part of the curve (which is mainly dependent on the thermally activated processes such as activation of electrochemical reaction and charge transport) seems not so much affected by the chemical activity of the mixtures. In fact, at fixed temperature the variation of R_{lin} with the CO₂ dilution was very limited.

The effect of dilution was particularly effective in the mass transport limitation. This is clear looking at Fig. 4 where the mass transfer limitation in case of CO₂ dilution is higher than in case of nitrogen dilution and in case of pure hydrogen. Also, this effect is shown looking at the values of limiting current densities obtained by the experimental data fitting and summarized in Table 3: in fact, with the increase of CO₂ concentration the limiting current densities decrease. Also the effect of temperature in the variation of limiting current densities is significant. This is due to the fact that, in case of CO₂ dilution, the reactive molecules have to diffuse in a mixture which has a higher molecular mass than the H₂/N₂ mixtures even when side reactions are taken into account, and this reduces the mass transport rates and the reactant concentration in the active sites.

The medium-term stability of the Ni-based anode with a direct feeding of H₂/CO₂ mixtures was also analysed and compared with the cell behaviour in the case of direct utilization of CH₄/CO₂. In order to obtain such information, a galvanostatic experiment of 150 h was performed with 0.5 A cm⁻² of current density and 800 °C of temperature and around 30% of fuel utilization. Both simulated bio-methane, obtained from traditional method, and bio-hydrogen, obtained from the innovative processing path, was directly utilized with a planar SOFC with Ni/YSZ cermet anode.

Cells were tested at 800 °C with hydrogen, bio-hydrogen and bio-methane from bottles. Each experiment lasted 50 h and the stability of the cell to operate with a direct feeding of each fuel was investigated. Also the performance of the cells was evaluated keeping constant the operating conditions of fuel utilization and temperature for the different investigated fuels.

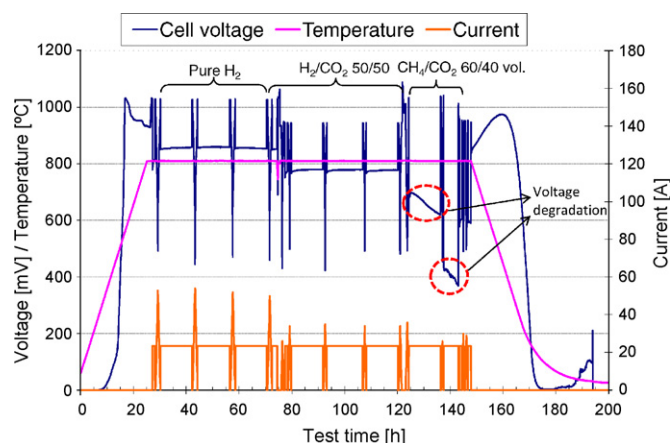


Fig. 5. Medium-term behaviour of an anode-supported SOFC with H_2/CO_2 mixtures.

The flows were set at 0.5 Nl min^{-1} for H_2 (hydrogen fuel), 0.5 Nl min^{-1} for H_2 and 0.5 Nl min^{-1} for CO_2 (bio-hydrogen fuel), 0.19 Nl min^{-1} for CH_4 and 0.13 Nl min^{-1} for CO_2 . With these gas flows, it was expected to operate the cell with the same theoretical fuel utilization: in the case of bio-methane feeding the calculation was done by considering the moles of the reactive species (H_2 and CO) at the equilibrium condition from dry methane reforming reaction.

A current–voltage curve was measured every 12 h. In Fig. 5, the results obtained during this experiment are reported.

In the first experiment with humidified hydrogen (30°C bubbler temperature), the cell voltage arises in the first 12 h of operation due to the electrodes' activation. The cell then operates with a stable voltage of around 860 mV at 0.5 A cm^{-2} with a power density of 0.43 W cm^{-2} . After 50 h of operation the fuel composition was changed, the cell operated with simulated bio-hydrogen (H_2/CO_2 50/50 vol%) for further 50 h with a stable voltage of around 780 mV at 0.5 A cm^{-2} and a power density of 0.39 W cm^{-2} . Finally, the fuel composition was varied in order to simulate direct utilization of bio-methane in the SOFC anode. A fuel mixture of CH_4/CO_2 with 60/40 vol% of composition was fed to the cell; thermodynamic calculations revealed that carbon formation was likely to occur in the considered thermodynamic operating state of the fuel cell.

From Fig. 5 it is shown that during the first hours of operation the cell voltage had a small gain in performance; afterwards, the voltage quickly decayed until the cell was operated at higher polarization conditions and a dramatic loss of performance was measured. The first phenomenon has been already reported [6] and it concerns with the related enhancement of anode electronic conductivity due

to the deposits of solid carbon. When the amount of carbon deposits increase, other phenomena are likely to occur like the reduction of triple phase boundary and pore filling: the constant decay of voltage of Fig. 5 is believed to be related to these two mechanisms. Despite the cell showed a strong decay of voltage (80 mV in 12 h of operation from initial 700 mV with CH_4/CO_2), we continued the experiment in order to further analyse the continuous degradation effect of carbon deposits. A polarization experiment was performed after 12 h of operation with bio-methane, the cell voltage had a strong decay and it was 400 mV at the end of the test, this experiment also ended with the cell break as revealed by the reduced open circuit potential (around 950 mV on H_2) and post-operation inspection.

The stability of the anode structure was also investigated by post-operation analysis using SEM and microanalysis techniques. Both surface and cross-section analysis on the anode substrates were performed indicating that solid carbon did not deposit neither in the anode current collector layer (forming a blocking layer) nor in the Ni particles of the electrochemical active zone in the case of bio-hydrogen feeding. In Fig. 6, a microanalysis performed on the anode current collector layer showed the main elements of the structure being essentially Ni with some Zirconia. The analysis shows the important result that carbon deposition did not occurred in normal operating conditions of SOFC when bio-hydrogen was considered as fuel. In the case of bio-methane feeding, carbon was detected by means of microanalysis and EDAX analysis; however the cell was found broken after such experiment and the anode partially oxidized. In Fig. 7 the results obtained by SEM and EDS on an anode operated with CH_4/CO_2 are shown.

6. Experiments with the produced biogas

Approximately 80 l of biogas have been produced and stored in two sample bags and then fed to the fuel cell through the experimental test-rig described before. The analysis of the gas was performed by E-on Ruhrgas and the results are summarized in Tables 4 and 5.

The gas mainly consists of carbon dioxide (56 mol%) and hydrogen (35 mol%) with very small traces of methane, carbon monoxide and higher hydrocarbons. The results suggest the successful application of the biogas production process in terms of inhibition of the methanization step. However, the hydrogen content was a bit lower than the expected one: this is due to the fact that the production has been done in batch process, and therefore the concentration of hydrogen represents the average value during the whole process; actually, the hydrogen content has an increase during the process, reaching the value of 46% in the final biogas (which would represent the concentration in a continuous process). The presence of nitro-

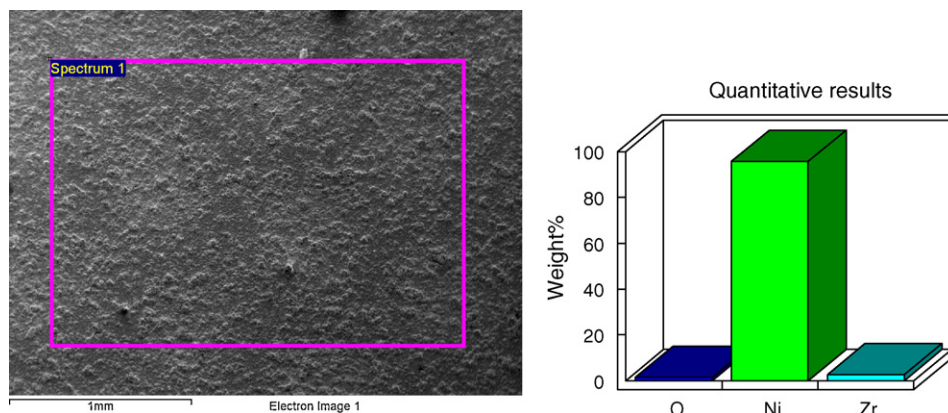


Fig. 6. Microanalysis on the anode current collecting layer fed with H_2/CO_2 mixture.

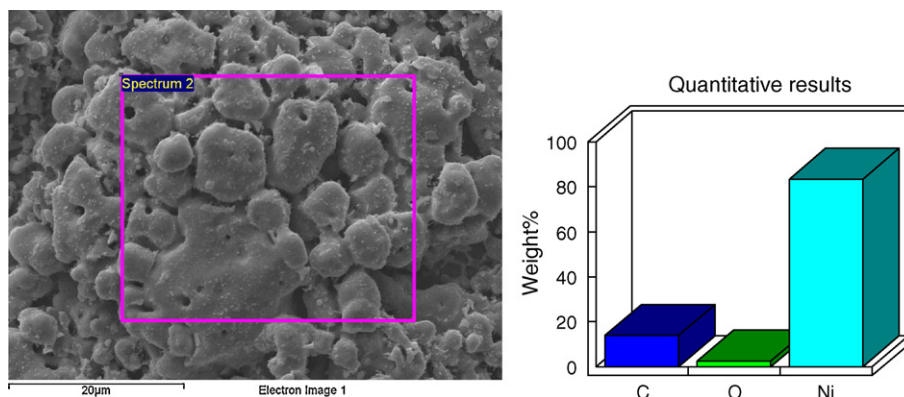


Fig. 7. Microanalysis on the anode current collecting layer fed with CH_4/CO_2 mixture.

Table 4
Biogas permanent species as measured by gas chromatography.

Biogas species as measured from gas analysis (mol%)		
Helium	He	0.2
Carbon dioxide	CO_2	56.4
Nitrogen	N_2	5.4
Oxygen + argon	$\text{O}_2 + \text{Ar}$	2.1
Hydrogen	H_2	34.5
Carbon monoxide	CO	<0.001
Methane	CH_4	0.0052
Ethane	C_2H_6	0.0001
Propane	C_3H_8	<0.0001
Propene	C_3H_6	<0.0001
n-Butane	n- C_4H_{10}	<0.0001
i-Butane	i- C_4H_{10}	<0.0001
Butene + butadiene	$\text{C}_4\text{H}_8 + \text{C}_4\text{H}_6$	<0.0001
n-Pentane	n- C_5H_{12}	<0.0001
i-Pentane	i- C_5H_{12}	<0.0001
neo-Pentane	neo- C_5H_{12}	<0.0001
HC in the range of hexane	C6-HC	0.0050
HC in the range of heptane	C7-HC	0.0019
HC in the range of octane	C8-HC	<0.0001
HC in the range of nonane	C9-HC	<0.0001
HC in the range of C10	C10 + -HC	0.0006
Benzol	C_6H_6	<0.0001
Toluol	C_7H_8	<0.0001
Xylole	C_8H_{10}	<0.0001
Unknowns	$\text{H}_2\text{O}/\text{unknowns}$	1.35

gen and oxygen may suggest a small change in the gas composition by air diffusion inside the Tedlar bags.

According to gas analysis also some physical properties of the mixture were evaluated: at the temperature of 25°C and 1.01325 bar of pressure, the density was 1.2507 kg m^{-3} , the high and low heating values were respectively 4.45 and 3.74 MJ m^{-3} , while the Wobbe index was respectively 4.53 and 3.74 MJ m^{-3} .

The analysis was also focused on the measurement of sulphur compounds present in the biogas. The results are summarized in Table 5 and they take into account the results obtained by gas chromatography analysis. The presence of sulphur compounds was

Table 5
Sulphur compounds as measured by gas chromatography.

		GC (mg m^{-3})
Hydrogen sulphide	H_2S	153
Carbonyl sulphide	COS	<0.4
Methyl mercaptan	$\text{CH}_3\text{-SH}$	9.9
Ethyl mercaptan	$\text{C}_2\text{H}_5\text{-SH}$	0.6
Methylthiomethane	$\text{CH}_3\text{-S-CH}_3$	1.9
Carbon disulphide	CS_2	10
Tetrahydrothiophene	THT	<0.6

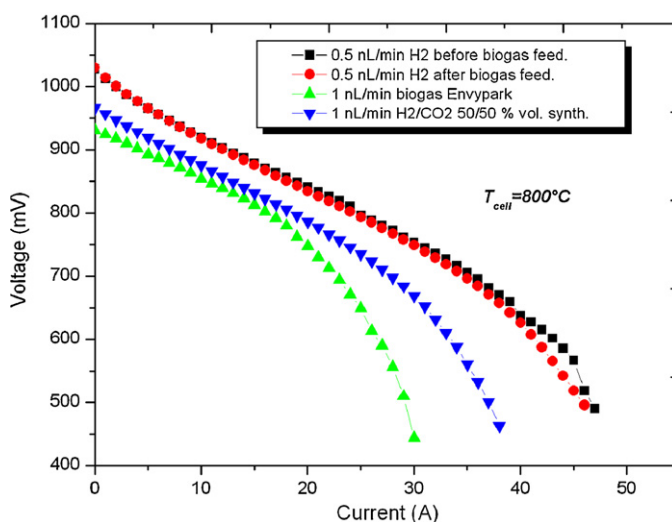


Fig. 8. Polarization curves of an anode-supported cell with biogas as fuel compared to pure hydrogen and CO_2/H_2 simulated mixture.

significant: around 103 ppm of H_2S ; further, different mercaptans were found in the mixture: their concentration was up to 10 ppm with a big contribution of methyl mercaptan and carbon disulphide.

This biogas was then fed to the SOFC without any cleaning. The operating temperature was fixed at 800°C and the biogas flow was set at 1 N l min^{-1} . The procedure for the testing of the biogas fuel has been the following:

- feeding with 0.5 N l min^{-1} of 4% humidified pure hydrogen and polarization measurement;
- feeding with 1 N l min^{-1} of syngas (simulated biogas) mixture H_2/CO_2 with a composition of 50/50 vol%;
- feeding with 1 N l min^{-1} of biogas for 2 h: 1 h in OCV for thermochemical stabilization and then current–voltage measurements;
- feeding with 0.5 N l min^{-1} of 4% humidified pure hydrogen with polarization measurement to verify eventual degradation of the cell.

All the measured polarization curves are reported in Fig. 8.

The biogas fuel gave acceptable polarization performance if compared with both the pure hydrogen fuel and the synthetic H_2/CO_2 mixtures; the calculated Nernst voltage from the molar compositions at equilibrium was approximately 0.92 V, and this value is very close the experimental one which is 0.93 V.

The lower performance achieved by the real biogas polarization curve in respect to the pure hydrogen feeding is essentially due to the lower hydrogen content present in it; and the effect is particularly evident from the OCV gap between the two curves. Moreover at high current densities the polarization curve is bending off due to a typical low fuel availability condition; this could be also an effect of the high presence of sulphur in the real biogas.

The eventual effect of sulphur seems to be however reversible as shown by the polarization curve measured with humidified hydrogen after the biogas experiment. From our short test-lab test with a high sulphur-poisoned biogas, we did not encounter significant degradation effects: when fed with hydrogen, the performance of the cell in terms of polarization curve has been similar before and after biogas feeding.

This obviously does not mean that sulphur was not poisoning the anode, but just that the test was probably too short in time to observe any deleterious effects. In fact, even a low amount of sulphur in the fuel entering the anode side is known to severely affect the Ni catalytic properties, as well as blocking electrochemical active sites as reported by Lohsoontorn et al. [21], Nabelek and Smith [22], Sasaki et al. [23] and Matsuzaki and Yasuda [24].

7. Discussion

We succeeded in producing a bio-hydrogen gas from a novel anaerobic digestion technique which deploys a specific treatment to the initial bacteria culture in order to inhibit the methane formation, responsible in many SOFC operating conditions of carbon deposition onto the anode, which eventually can cause catastrophic failure of the whole cell. The as-produced biogas potentially eliminate the need of adding further steam, carbon dioxide or air into the inlet fuel stream in order to promote dry reforming, steam reforming, partial oxidation or a combination of those.

Simulated biogas mixtures in different molar fractions ratio of H_2/CO_2 have been reproduced to assess biogas basic thermodynamic considerations. The results we found out fit quite well thermo-chemical equilibrium calculations. The aim of this part of the experimental session was to verify the equilibrium condition of H_2/CO_2 mixtures in SOFC operating condition and provide a reference for the real biogas operation.

Medium-term experiments were also performed in order to demonstrate the capability of direct utilization of bio-hydrogen with Ni-based anodes whereas the direct utilization of bio-methane was demonstrated to be destructive for the cell's anode after few hours of operation.

It has to be said that diluting CH_4/CO_2 with a proper amount of a reformer agent could easily inhibit carbon formation. In particular, from thermodynamic equilibrium calculations, a steam to carbon ratio around 0.5 at $800^\circ C$ would avoid carbon cracking (steam to carbon ratio defined as the moles of steam over the moles of methane present inside the biogas). Further, steam could be easily introduced in the fuel stream by an external steamer with a waste of thermal energy or by providing a smart solution based on an ejector-driven recirculation system of the anodic depleted stream [29,30]. Moreover, the fuel stream could be diluted by adding air and then encouraging simultaneous partial oxidation and dry reforming reactions.

The use of an ejector system could provide both steam and CO_2 from the depleted anodic flow to promote steam and dry reforming and easily avoid carbon cracking.

At this point of the discussion a system engineer should probably choose between external reforming or (more likely) internal direct or indirect reforming paths (using the waste heat from fuel cell reaction and the anode catalyst to promote the fuel processing or just recovering heat and provide catalytic conditions in integrated

reformer boards). The internal direct is appealing in the sense that a reformer is no longer considered in the system BoP; this solution needs anyway a deep investigation of proper anode materials to allow a direct conversion of methane in the region close to the anode electrodes while avoiding carbon-deposition phenomena (Ni-based, Ceria-based, etc.). Another possible drawback is additional thermal stresses to the cells due to the temperature drop arising from the endothermicity of the reforming reactions.

Further consideration can be done about SOFC systems behaviour with H_2/CO_2 mixtures in terms of global energy balance and efficiencies. H_2/CO_2 mixtures, in the thermodynamic operating state of SOFCs, lead to Reverse Water Gas Shift which is known to be endothermic. This would provide self-stack cooling and allow reducing air flow for cooling purposes (with a reduction of blower consumption and better system efficiencies). However by comparing with the cooling effect of steam and dry reforming, H_2/CO_2 mixtures surely provide a lower self-cooling of the stack thus requiring a higher air flow or even an external cooling fluid.

On the other hand, many available small scale SOFC systems equipped with POX have a comparable and even a worst behaviour in terms of stack cooling.

Based on these considerations, the solution proposed in the work has a technical significance and relevance, provided a more deep investigation on the thermal management of the stack. In Ref. [25] the authors provided a SOFC system complete model considering different biogas fuel mixtures as input. For an air-cooled stack, the bio-hydrogen route requires almost a double air feed into the stack compared to a conventional methane biogas steam/dry-reformed or fully dry-reformed. This is essentially due to a less endothermic behaviour of the RWGS, with respect to a methane reforming conversion. This aspect is partially mitigated by a more performing cell polarization in the case of bio-hydrogen, which means less internally stack generated heat per electric kW of output (whatever is the fuel producing it). At the end, the bio-hydrogen route performs slightly worse than a biogas steam or dry-reformed as overall electric efficiency, but definitely better than the POX/dry-reformed biogas, which requires even more air than the bio-hydrogen case, being the POX reaction exothermic. In addition to this, the bio-hydrogen feeding actually allows a direct feeding without a proper reforming zone, being a mixture by itself less likely to cause carbon deposition. Moreover, it could open further discussion on the fuel cell side (fuelling a PEM with bio-hydrogen?) and even on the biomass fermentation side (probably a double-stadium production of bio-hydrogen and bio-methane would be the best energetic solution and best fuel for high temperature fuel cells).

Another advantage of having a methane-free biogas is the expected reduced effect of H_2S poisoning; in fact, with a conventional CH_4/CO_2 biogas, even a small amount of H_2S could strongly limit the CH_4 dry reforming and the fuel availability for the electrochemical reaction [23]; with a bio-hydrogen fuel there will be no longer such a reforming deactivation issue. Nevertheless, long term tests have to be performed in order to analyse the degradation effect due to the high amount of H_2S which has been found in the biogas discussed here. In particular, it will be interesting to provide a recommendation on the maximum H_2S ppm tolerance threshold for a conventional Ni/8YSZ anode with a H_2/CO_2 mixture as the anode gas.

In general, it must be said that desulphuring a biogas has certainly some difficulties since the sulphur content in the gas finally reaching the SOFC has to be really low in order to avoid a voltage decrease due to a deactivation phenomena of the electrochemical reactions; in Ref. [26], a maximum total sulphur level of 100 ppb is recommended for operating SOFC systems under NG (natural gas) feeding. Selecting the proper system is also a trade-off between having an economic and durable cleaning system (low maintenance

costs), and having an effective H₂S removal in order to increase the durability of the cells. Many room-temperature systems are easily available if the physisorption is chosen. In Ref. [26] the author, on the basis on a field-experience on Siemens SOFC systems, identifies a double stage desulphurization process as the most successful, durable, and economically feasible way to desulphurize the natural gas from the municipality grid. In this configuration, the cleaning is performed first in a zeolites fixed bed reactor and then in an activated carbons reactor. The choice of order for the physical adsorbent is related to the fact that in NG are present different sulphur compounds (COS, C₂S, mercaptans, H₂S, THT), coming both from the natural gas itself and from purpose of gas smell (e.g. THT and some mercaptans are specifically added in the ppm range as odorants), and each considered adsorbent is not able alone to efficiently remove all the sulphur species [27,28]. Actually the cleaning system for a biogas feeding could not be much dissimilar to the one used for a natural gas fuel flow. Anyway the analogy with the NG desulphurization has still to be carefully analysed for practical applications; the main differences between NG and the biogas here considered are that the latter has no COS and THT compounds, which is clearly a benefit since in particular the COS are reported as the most difficult to remove [26]; on the other hand, the level of H₂S and mercaptans in the biogas are at least an order of magnitude higher than those in the NG. For the sake of completeness, other possibilities instead of the physisorption cleaning route are chemisorption or biological processes, but they generally involve more complex and expensive cleaning systems.

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