



# Performance evaluation of a solid oxide fuel cell coupled to an external biogas tri-reforming process



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## ABSTRACT

This study deals with an investigation of the performance of a biogas-fed solid oxide fuel cell (SOFC) operating in combination with an external tri-reforming system. The tri-reforming process is carried out using a ceria supported Ni catalyst (1.75-wt.% Ni/CeO<sub>2</sub>), prepared by combustion synthesis. The catalytic tests are carried out at 800 °C with fixed CH<sub>4</sub>/CO<sub>2</sub> molar ratio. Different O<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>O/CH<sub>4</sub> molar ratios are investigated to evaluate the influence of different feed compositions on the performance of the integrated SOFC and tri-reforming system. The SOFC can tolerate different percentages of CO, CH<sub>4</sub> and CO<sub>2</sub> in the reformat stream without the need of steam addition. However, the SOFC performance varies consistently with the different reformat compositions; this effect is strongly related to the tri-reforming catalyst performance. The results indicate that the process using biogas tri-reforming and SOFC is promising for application in small and medium sized stationary power systems.

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## 1. Introduction

The increasing use of fossil fuel results in environmental issues involving polluting emissions (e.g., SO<sub>x</sub>, NO<sub>x</sub>, particulate) and causing the greenhouse effect due to CO<sub>2</sub> and unburned CH<sub>4</sub>. The scientific community is now addressing such issues and the global warming by focusing research efforts on technological solutions which allow a reduction of pollutants and greenhouse gas emissions. Many studies have evaluated the use of biomasses, from refuse and in particular from biogas, in energy applications according to the recent regulations of the European Union [1–3]. The biogas is one of the most known and widespread renewable fuels, obtained from a variety of biomasses and processes such as degradation of urban and industrial waste, landfills, co-digestion of zootechnical effluents, agricultural wastes and energy crops. There is an urgent need in Europe to increase the use of renewable fuels to comply with the EU 20–20–20 objectives. As an example, in Italy, where the “Green Certificates” have been adopted from several years, there is a new interest for biogas plants; from a recent census of CRPA (Research Center for Animal Production), compared to 2010, biogas plants in agricultural and zootechnical sectors have increased from 273 to 521 [4]. The biogas composition is related to the starting substrate, basically it consists of 50–75% CH<sub>4</sub>, 25–45% CO<sub>2</sub>, 2–7% H<sub>2</sub>O (at 20–40 °C), 2% N<sub>2</sub>, <1% H<sub>2</sub> with traces of H<sub>2</sub>S, O<sub>2</sub>, NH<sub>3</sub>, halides and siloxanes [5,6]. At present, biogas is mainly used to produce electricity and heat by cogeneration systems; internal combustion engines (ICE) and gas turbines represent the most used technology. However, especially in small biomass

gathering terminals, the biogas production and the related production of electricity by conventional engines would lead to low electrical conversion (18–25%) and high levels of noise, maintenance, and pollutant emissions [7–9]. Recently, the use of biomass-derived fuels in combination with fuel cells (FCs) coupled with reforming processes has been proposed [10–13]. Fuel cells (FCs) appear to be very promising because of their high efficiency, low emissions and negligible noise [7,14]. The choice of solid oxide fuel cells (SOFCs), and in particular the intermediate temperature-SOFCs (IT-SOFCs), compared to other fuel cell technologies, is not only related to the above mentioned advantages, but also to their operating temperature (500–800 °C) allowing the use of biogas with fuel processing. A purification step, to remove poisoning agents such as sulphur species is always necessary to avoid material degradation problems. Purification of gas stream from sulphur species is carried out by using a high surface area active carbon such as Norit (BET 1300 m<sup>2</sup> g<sup>-1</sup>). The SOFC technology allows a good thermal integration between fuel cell stack, fuel processor, purification section (abatement of H<sub>2</sub>S, NH<sub>3</sub>, halides and siloxanes) [5]. Moreover, the fuel cell can provide both the facility's electricity and the heat required for the digester, resulting in a combined heat and power (CHP) efficiency between 80% and 90%. The utilization of a biogas processing step, instead of its direct use in SOFC after desulphurization, is principally due to the necessity to prevent the risk of carbon deposition at the Ni-based SOFC anode [15]. Fuel cells coupled with a pre-reforming process may reduce the risk of carbon deposition at the anode increasing cell stability. This is a pre-requisite to enter the market of the medium scale electricity generators (5–100 kW<sub>e</sub>). Biogas processing can be carried out by using dry reforming (DR), steam reforming (SR) and partial oxidation (POX). Each of these processes presents several problems principally related

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to the severe operating conditions resulting in catalyst deactivation by coke deposition and/or sintering of the metallic phase and support [16–19]. Recently, a new catalytic process called Tri-Reforming (TRM), allowing the achievement of a desirable  $H_2/CO$  ratio using  $CO_2$  in the flue gas has been proposed for fossil fuel-based electric power plants [20,21]. The process involves a combination of dry reforming, steam reforming and partial oxidation of methane in a single step. The presence of steam can promote steam reforming and water gas shift reactions, reducing the problem of carbon deposition occurring in the dry reforming reaction, while the addition of  $O_2$  compensates for the endothermic reforming reactions. However, appropriate catalysts are necessary to achieve suitable conversion rates in the tri-reforming process [22]. Moreover, the active phase must be finely dispersed on the support to avoid the occurrence of sintering and agglomeration during operation. Despite the relevant interest of a combined process including tri-reforming and SOFC, limited efforts have been addressed to this regard. In this work, we have focused our efforts to the investigation of the combined process on a micro-scale to individuate the most proper operating conditions and any relevant drawback. Moreover, a Nickel–Ceria catalyst, prepared by combustion synthesis, was used for the tri-reforming process. There are earlier reports on Ni/ $CeO_2$  catalyst for different kinds of reforming reactions regarding methane (dry, steam and autothermal reforming) [23,24]. This type of catalyst has already shown a promising catalytic activity and stability in a propane oxy-steam-reforming process. In such process, the relationship between the composition and the catalytic activity was affected by dispersion of the active nickel phase [25]. However, this type of catalyst has neither been investigated in the presence of biogas nor for  $CO_2$  conversion. Thus, it is relevant to test such type of catalyst in a biogas tri-reforming process. Moreover, this process was combined with a state-of-the-art anode supported SOFC in order to investigate the flexibility of such approach.

## 2. Experimental

### 2.1. Ni/ $CeO_2$ catalyst preparation and SOFC fabrication

The ceria supported Ni catalyst (1.75-wt.% Ni/ $CeO_2$ ) was prepared by a self-combustion synthesis [25]. Stoichiometric amounts of  $(NH_4)_2Ce(NO_3)_6$ ,  $Ni(NO_3)_2 \cdot 6H_2O$  and  $C_2H_6N_4O_2$  (oxalyldihydrazide, as fuel) in aqueous solution were mixed in a borosilicate dish and heated at 350 °C, after water evaporation, and the mixture was ignited with a cold flame leaving a sponge-like solid. After preparation, the catalyst powder was pelletized, crushed, sieved to 200–600  $\mu m$ .

A conventional SOFC design was used in this study. The button cell (2  $cm^2$  active area) consisted of several layers [26]. The planar cell included anode support: composite of Ni/YSZ ( $Zr_{0.92}Y_{0.08}O_2$ ) catalyst; electrolyte membrane: YSZ ( $Zr_{0.92}Y_{0.08}O_2$ ) (thickness: 10  $\mu m$ ); CGO ( $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ ) buffer layer (8  $\mu m$ ) and LSCFO ( $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ ) cathode.

Inert gold grids were used as current collectors on both sides. Previous studies have shown that these current collectors do not affect significantly the power density [27,28].

### 2.2. Material chemical–physical characterizations

Powder XRD patterns were collected with a Philips X-Pert 3710 diffractometer, using a  $Cu K\alpha$  radiation at 40 kV and 30 mA. The  $2\theta$  angle was scanned at a rate of 1.5°/min within the range of  $25^\circ < 2\theta < 75^\circ$ . Peak position and broadening as well as lattice parameter were determined by a fitting procedure using the Marquardt–Levenberg algorithm. The crystallographic phases of fresh and spent catalyst were identified by using the JCPDS (Joint Committee of Powder Diffraction Standards) database. The mean crystallite size ( $d$ ) was determined from the X-ray broadening ( $\beta$ ) by the Scherrer equation ( $d = \lambda\alpha / \beta \cos \theta$ ); the half maximum line width of  $CeO_2$  (111) reflecting planes was used.

Temperature programmed reduction (TPR) measurements were carried out by using 5% hydrogen in an argon mixture (30  $cm^3 \text{ min}^{-1}$ , STP), as reducing gas, in a dedicated reactor. The investigated temperature range was 0–1100 °C, with a heating rate of 20 °C  $\text{min}^{-1}$ . Hydrogen consumption was monitored by a thermoconductivity detector (TCD). The TCD response was quantitatively calibrated by monitoring the reduction of a  $CuO$  standard [29]. Transmission electron microscopy (TEM) analysis was carried out by FEI CM12-EDX instrument operating at 120 kV and equipped with  $LaB_6$  filament. The sample was dispersed in ethanol in an ultrasonic bath; a few drops of this solution were deposited on a copper grid. Elemental analysis of the light elements (CHNS-O) for the catalyst after operation was carried out with a Carlo Erba Instrumentation (Mod. EA 1108). The surface area of the catalyst powder was determined by the Brunauer–Emmet–Teller (BET) method using a Thermoquest 1990 Series Sorptomatic. The sample was first degassed at 200 °C for 3 h. The nitrogen adsorption and desorption were conducted in the relative pressure (partial pressure) range between 0 and 1.

Post-operation cell analysis was made by Scanning Electron Microscopy (SEM XL30FEI instrument) to investigate the morphological modifications.

### 2.3. Microscale equipment and experimental set up

A flowchart of the experimental equipment is shown in Fig. 1. It consists of the following main sections: reforming feed section (for tri-reforming process and catalyst reduction), SOFC feed section (for SOFC conditioning), tri-reforming reaction section, tri-reforming analysis section (gas-chromatographic measurements) and electrochemical analysis section (electrochemical polarization and ac-impedance measurements).

An amount of 0.5 g of Ni/ $CeO_2$  catalyst was placed between two quartz wool plugs in the centre of a quartz tube (6 mm internal diameter), inserted into a furnace, heated to the reaction temperature and controlled through a temperature controller. A thermocouple close to the catalytic bed was allowed to precisely control the operating temperature. This catalyst was reduced at 450 °C in a flow of 5%  $H_2/N_2$  mixture before the experiments. The tri-reforming reaction of simulated biogas was carried out at 800 °C under atmospheric pressure; the gaseous feed ( $CH_4$ ,  $CO_2$ ,  $O_2$ , and small amount of  $N_2$  as internal standard) was regulated by mass flow controllers. Steam was added to the feed by an isocratic pump and a specially designed vaporizer. The feed and reaction products were analysed using an Agilent 6890 Plus gas chromatograph equipped with thermal conductivity (TCD) and flame ionization detectors (FID). The catalytic tests were initiated by heating the reactor, from ambient temperature to 800 °C, under  $N_2$  flow. Subsequently,  $N_2$  flow was stopped and the reaction mixture was allowed to flow through the reactor; on-line chromatographic analysis of the reaction products was carried out every 20 min during each test. The experiments were carried out for different  $O_2/CH_4$  and  $H_2O/CH_4$  molar ratios in the feed, while the gas hourly space velocity (GHSV) was fixed at 15,000  $h^{-1}$ , and the total reagent flow was 100  $cm^3/\text{min}$ .

Conversion of reactants was calculated according to:

$$X_{\text{reactant}}(\%) = \frac{F_{\text{reactant in}} - F_{\text{reactant out}}}{F_{\text{reactant in}}} \times 100$$

where  $F_{\text{in}}$  and  $F_{\text{out}}$  were the molar flow rates of the specie X measured at inlet or outlet of the reactor, respectively.

The outlet reformate gas was passed through a drexel at room temperature to remove water from the stream by using a  $MgClO_4$  bed before feeding the gas to the SOFC anode.

The SOFC button cell was mounted on an alumina tube and sealed with quartz adhesive (AREMCO). It was initially heated with a stream of He at the anode before conditioning in  $H_2$ , whereas, the cathode

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