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Effects of carbon monoxide, carbon dioxide, and methane on nickel/yttria-stabilized zirconia-based solid oxide fuel cells performance for direct coupling with a gasifier

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ABSTRACT

This work focuses on the role of CO and CO_2 usually present in syngas generated by biomass gasification when they are flowed in a Ni-YSZ-based SOFC. Polarization, power versus intensity and electrochemical impedance spectroscopy measurements are performed and the theoretical aspect is enhanced with comparison with values of the Nernst potentials of the two H_2O/H_2 and CO_2/CO couples. The CO as electrochemical reactant is clearly highlighted, and also compared to H_2. Indeed, power density values of 460 mW cm^{-2} and 540 mW cm^{-2} are obtained at 750 °C when the cell is fueled with a 50% CO–50% N_2 mixture and a 50% H_2–50% N_2 mixture respectively, and the use of CO leads to higher power density values when the percentage of the fuel in the Fuel/N_2 mixture is lower than 27%, the use of higher amounts of CO inducing a large increase of the total resistance of the cell. The impact on the efficiency of the cell of the presence of CH_4 is also examined using electrochemical measurements. Finally, power density values of 502 mW cm^{-2} is obtained at 750 °C when the cell is fueled with a 50% N_2-20% CO-17% H_2-10% CO_2-3% CH_4 mixture which appears to a be a realistic composition corresponding to the exhaust of the gasifier.

Introduction

Energy transition involves using a mix of renewable energy including biomass. Reusable gases can be extracted from that biomass [1–4]. Currently, more heat power than electrical power is produced from that source. Moreover the global electric yield is between 20 and 30% when conversion devices are motors, which are the common way to get electrical power

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from biomass gasification. Also those kinds of motors emit harmful gases, especially mono-nitrogen oxides, during combustion.

In order to improve the electric yield and to avoid noxious gases, the gas conversion into electricity can be operated by solid oxide fuel cell (SOFC) [3–11]. These kinds of fuel cell can double the electric yield and cogeneration is possible thanks to high operating temperatures (700°C–900 °C), which increases the global yield.

This paper is a preliminary study that takes part of the VALORPAC project, which consists in integrating a SOFC in a gasification process. In this project, the power source is produced by a fixed bed downdraft wood gasifier. Indeed, this type of gasifier is known to produce cleaner syngas with low tars rate compared to updraft or fluidized bed reactors [12,13], and S3D has patented recently (n° PCT/FR2011/052318) a gasifier reactor specially designed to produce high quality syngas which could be used nearly directly to fuel a SOFC. Indeed experimental tests were done with wood pellets and wood chips, and preliminary measurements of the composition of the corresponding gasifier exhaust are given in Table 1 [4,14]. The aim of the present work is to study the electrochemical response of the cells used in the project when they are fueled by the gas issued from the wood gasifier patented by S3D, i.e. a mixture of H_2, CO and CO_2, in presence of small amounts of CH_4. The originality of the work is to establish the cells limitations associated to each component of the fuel, to specify gasification parameters acceptable for a direct use of the cells, and finally to validate the feasibility of the VALORPAC project.

Usually SOFC are fueled with hydrogen and their operation is known to be dependent on any pollutant [4,11,15]. Even if it has been established in literature that CO can be used as a fuel for SOFC [15–19], the real potential of CO is not clearly evaluated, because it is not estimated for its own electrochemical significance, but only for its capacity of reforming by the thermodynamic reaction of water gas shift:

$$CO + H_2O \rightleftarrows H_2 + CO_2 \quad (1)$$

Nevertheless, CO can react directly with O^{2-} according to:

$$CO + O^{2-} \rightarrow CO_2 + 2e^- , \quad (2)$$

in a reaction which is similar to the reaction involving H_2:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- . \quad (3)$$

Table 1 – Average amounts of the main components measured in the gas issued from the gasifier [14].

Component	Amount
N_2	45–55% vol.
H_2	15–20% vol.
CO	15–25% vol.
CO_2	10–15% vol.
CH_4	<3% vol.
H_2O	5–15% vol.
Tars and particles	<1g/Nm^3

The fact that CO is both a fuel and a reactant involved in numerous equilibria [20] leads to a rather complicated situation, which requires a comparison to thermodynamic data. In the present study the effect of carbon dioxide on SOFC, which is often unknown or disregarded, is also highlighted. Indeed, in mixtures issued from gasifier, CO_2 is also present, and it has been reported that this gas may have a negative influence on the SOFC performance [15,21]. This gas is also in equilibrium with CO, through Boudouard equilibrium (4):

$$2CO \rightleftarrows C + CO_2 \quad (4)$$

or water gas shift reaction [20]. For these two reasons, the influence of this gas onto the performance of the SOFC has been also carefully studied.

In the present paper, voltage and power versus current density curves were obtained at temperatures comprised in the 750–850 °C range with cells fed by variety of fuel mixtures, i.e. firstly mixtures of H_2–N_2, and then CO–N_2, H_2–CO–N_2 and H_2–CO_2–N_2 mixtures. The influence of the presence of small amounts of CH_4 in the fueling mixture was also studied. In order to indentify the origin of the cell resistances, impedance diagrams have also been recorded. The tests are repeated several times, in order to eliminate possible cell-to-cell variations, and results are correlated to thermodynamic data.

Experimental

Cell

The SOFC is a Fiaxell circular shaped planar anode-supported 2R-Cell™ [22], schematized in Fig. 1, and composed of commonly used materials, i.e. a Ni/Yttria-stabilized zirconia (YSZ) anode, prepared in situ by reduction of a YSZ/NiO cermet [23,24], an YSZ electrolyte covered by a gadolinium-doped ceria layer GDC [15,21,25] containing cobalt oxide, and a $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ cathode [21]. Four cells are employed, called 107.2, 107.3, 107.9 and 166.31. They are similar, 10 cm^2 cathode area.

Apparatus and temperature program

The experimental setup [22,26] contains an oven where two stage of temperature (intermediate and final temperature duration) and two ramps are programmable. Inside the kiln, the cell is placed in an inconel support elaborated to avoid gas leak isolated by ceramic insulation plates (p). Two aluminum

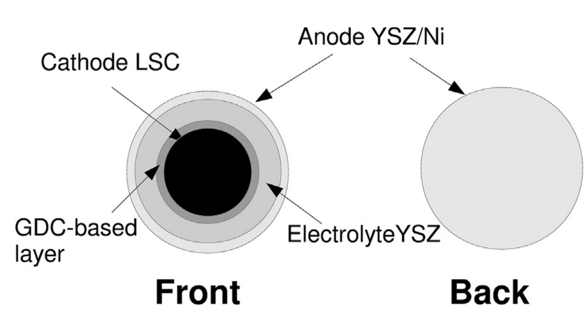

Fig. 1 – Schematic representation of the cell.