

Short communication

## Evaluation of the water-gas shift and CO methanation processes for purification of reformat gases and the coupling to a PEM fuel cell system

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### Abstract

In this work, the water-gas shift (WGS) and the CO methanation reactions on a Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and the coupling of these reactors to a proton exchange membrane fuel cell were investigated. Results of chromatographic analyses showed that when the reactors are fed with a H<sub>2</sub>/CO (1000 ppm) mixture, high conversions of CO into methane (90%) or CO<sub>2</sub> (83%) are observed for the methanation and WGS processes, respectively. These reactions are strongly influenced by the presence of carbon dioxide, particularly in absence of water, for which the methanation of CO<sub>2</sub> is clearly observed. In both cases, some additional production of CO is also apparent. The fuel cell polarization data showed a reduction of the CO poisoning effect for fuel cells with a PtRu/C anode fed with H<sub>2</sub>/CO (1000 ppm) mixture, after the coupling with the methanation or the WGS reactors. In agreement with chromatographic analyses, higher fuel cell efficiency was observed when the coupling was made with the methanation reactor.

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### 1. Introduction

The development of low emission vehicles using fuel cells has been attracting a lot of attention, because of the ever-increasing environmental pollution problems caused by internal combustion engine vehicles. The proton exchange membrane fuel cell (PEMFC) is currently the leading candidate for applications in vehicles because of its higher power density and fast start-up compared to other fuel cell technologies [1].

For most practical applications, the utilization of a hydrogen-rich gas mixture produced by the reforming of primary fuels for feeding the PEMFC is mandatory. The interest

in liquid fuels (smaller volume), free from sulfur and metals and with a low melting point has directed attention to the ethanol steam reforming for hydrogen production [2–4]. The bio-ethanol-to-hydrogen system has the significant advantage of being nearly carbon dioxide neutral, since the produced CO<sub>2</sub> is consumed for the biomass source growth, thus offering a nearly closed carbon loop.

Unfortunately, carbon monoxide (CO) is also produced in high levels (depending on catalyst used, temperature of reaction, metal content, etc) as a by-product of the steam reforming of ethanol. This product strongly adsorbs on Pt, usually employed as the anode catalyst, blocking the adsorption and oxidation of hydrogen and drastically decreasing the PEMFC performance. Recently, the advantages of the hydrogen production by steam reforming of ethanol (400 °C) on Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with high cobalt contents have been discussed [5]. The results showed conversion near to 100% for ethanol and an average gaseous composition of 67% H<sub>2</sub>, 24% CO<sub>2</sub>, 9% CH<sub>4</sub> and 800 ppm (0.08%) of CO. Although

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this amount of CO is considered small for a reforming reactor outlet, it is still too high for the direct use in a PEMFC.

Two or three stages are usually required to reduce the levels of CO produced in the reform: the water-gas shift (WGS) reaction, the preferential oxidation of CO (PROX), or the use of a CO filtering membrane. The water-gas shift reaction,



is an exothermic process ( $\Delta H = -41.1 \text{ kJ mol}^{-1}$ ), implying that the equilibrium conversion of carbon monoxide is favored at lower temperatures [6]. Alternately, a methanation reaction ( $\Delta H = -206.2 \text{ kJ mol}^{-1}$ ) can be also applied to diminish the CO concentration,



This involves the conversion of CO to methane with some consumption of hydrogen. It is also known that above  $530^\circ\text{C}$  the methanation reaction stops because the  $\Delta G$  of reaction (2) becomes positive [7]. Independent of the way used to decrease the CO concentration, WGS, PROX, or methanation, it should lead to acceptable CO levels (of the order of 100 ppm) to be attractive for supplying a PEMFC system, even if working with CO-tolerant electrocatalysts in the anode. These catalysts are usually formed by fine particles of a PtRu composite supported onto a high surface area carbon (PtRu/C), which has emerged as one of the more promising materials for the development of CO-tolerant anodes for the PEMFC system [8,9].

In this work, the performance of a PEM single cell with a PtRu/C anode catalyst fed with CO-contaminated hydrogen was evaluated with and without the coupling with water-gas-shift or methanation reactors containing a Co/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst. The composition of the gases emerging from both reactors was analyzed in independent experiments, using an appropriate gas chromatographic set up. In the case of the methanation reactor no previous study of the practical consequences of the presence of  $\text{CH}_4$  in the hydrogen fuel in the PEMFC performance was found.

## 2. Experimental

The Co/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst used in the WGS and methanation reactors was prepared by the incipient wetness impregnation of the  $\gamma$ - $\text{Al}_2\text{O}_3$  (Degussa) support by using an aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98%, Aldrich). The excess of water was removed in a rotative evaporator and the sample was dried at  $100^\circ\text{C}$ . Then, the catalyst was obtained by the calcination of the sample in air at  $600^\circ\text{C}$  for 6 h. The characterization of this material was presented and discussed in a previous paper [5] and the results indicated formation of  $\text{Co}_3\text{O}_4$  with a proportion of 18 wt.% of Co with respect to the total mass of Co and  $\gamma$ - $\text{Al}_2\text{O}_3$ .

The composition of the gas leaving the WGS and methanation reactors was monitored as a function of time by using an

apparatus consisting of a flow controller system, the reactor unit and the analysis system. The flow system is equipped with a set of mass-flow controllers (Allborg 4 channels), which accurately control the flow of the gases ( $\text{H}_2$ ,  $\text{CO}_2$ , 1%  $\text{CO}/\text{He}$ ) entering the reactor. The catalyst was placed in a fixed-bed system inside a continuous flow micro-reactor (13 mm diameter). Prior to the experiments, the Co/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst (150 mg) was activated by in situ reduction in  $\text{H}_2$  atmosphere ( $40 \text{ cm}^3 \text{ min}^{-1}$ ) at  $650^\circ\text{C}$  ( $10^\circ\text{C min}^{-1}$ ) for 1 h. After this pre-treatment, the sample was kept at  $400^\circ\text{C}$  under a pure  $\text{N}_2$  atmosphere.

Analyses of the gaseous products were carried out on-line by gas chromatography (Varian, model 3800) with two thermal conductivity detectors. The outlet stream was divided into two aliquots inside an automated injection valve, and then analyzed in a different way in order to obtain accurate and complete quantification of the reaction products. One of the aliquots was used to analyze hydrogen and methane, which were separated by using a 13X molecular sieve ( $3 \text{ m} \times 1/8 \text{ in.}$ ) packed column, using nitrogen as carrier gas. The other aliquot was used to analyze  $\text{CO}_2$ ,  $\text{CH}_4$  and CO. Helium was employed as carrier gas and separation was accomplished by a porapak N ( $2 \text{ m} \times 1/8 \text{ in.}$ ) and 13X molecular sieve ( $3 \text{ m} \times 1/8 \text{ in.}$ ) packed columns. The lower limit for carbon monoxide detection is 200 ppm. The product yield, denoted as %  $Y_{\text{product}}$ , was calculated by: %  $Y_{\text{product}} = F_{i(\text{out})}/F_{\text{CO}(\text{in})}$ , where  $F_i$  represents the molar flow rate of the product species measured at the reactor outlet and  $F_{\text{CO}}$  the corresponding flow rate of CO at the inlet.

The PtRu/C (50:50 atomic ratio, 20 wt.% metal/C) catalyst was synthesized by an impregnation method, which consisted of the dissolution of the ruthenium precursor ( $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ , Aldrich) and hydrogen hexachloroplatinate ( $\text{H}_2\text{PtCl}_6$ , Aldrich) in ethanol (99%, Mallinckrodt) and in the presence of carbon Vulcan XC-72 [10]. The impregnation of the metals on the carbon support was concluded after two steps of heat treatment (i)  $100^\circ\text{C}$  for 1 h in inert atmosphere (Ar) and (ii)  $550^\circ\text{C}$  for 3 h in reducing atmosphere ( $\text{H}_2$ ) [10].

Gas diffusion electrodes were prepared with standard gas diffusion and catalyst layers [10–11]. The gas diffusion layer consisted of carbon powder (Vulcan XC-72, Cabot) with 15% (w/w) of polytetrafluoroethylene (PTFE—TE-306A, Du Pont), deposited by filtration onto both faces of a carbon cloth substrate (PWB-3, Stackpole). The catalyst layer was prepared by application of inks composed of 35.5 wt.% of Nafion® (Aldrich, solution with 5 wt.% in alcohol mixture) and 64.5 wt.% of the catalyst in isopropanol, on one of the faces of the diffusion layer. The metal loading was  $0.4 \text{ mg cm}^{-2}$  for both the anode and cathode. In all experiments, Pt/C (20%, E-tek) and 115 Nafion® membranes ( $\text{H}^+$ , Du Pont) were used as the cathodes and electrolyte, respectively. Membrane and electrode assemblies (MEA's) were prepared by hot pressing the anode and the cathode to a membrane at  $125^\circ\text{C}$  and  $1000 \text{ kgf cm}^{-2}$  during 2 min [11].

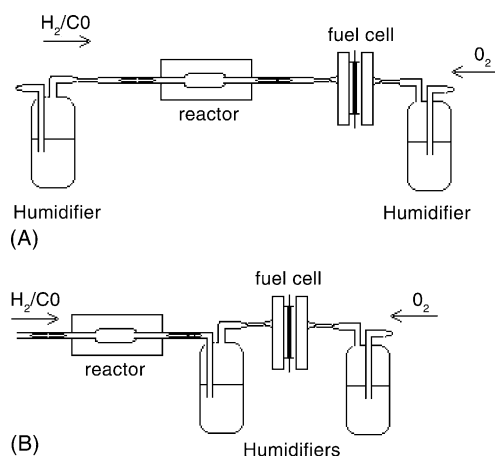


Fig. 1. Scheme of reactor-fuel cell apparatus for (A) WGS and (B) methanation CO removing experiments.

External saturation of the reactant gases with water is required to maintain the Nafion<sup>®</sup> membrane continuously humidified and consequently, to avoid polarization losses due to decrease of the proton conductivity. The single cells were coupled to the WGS or methanation reactors as illustrated in Fig. 1. For this purpose, the Co(18%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst ( $m = 300$  mg) was settled to a fixed-bed quartz tubing reactor in an isolated oven, which was connected to the single cell in two ways: (i) between the fuel humidification bottle and the single cell in the case of WGS reactor (Fig. 1A) and (ii) before the humidification chamber in the case of methanation reactor (Fig. 1B). Prior to the polarization measurements, the reactors were kept at 400 °C in hydrogen atmosphere in order to reduce the cobalt oxides (mainly CO<sub>3</sub>O<sub>4</sub> [5]). During the experiments the reactor was maintained at 400 °C.

Single cell (4.6 cm<sup>2</sup> geometric active area) polarization measurements were made galvanostatically with the cell at 85 °C, using oxygen saturated with highly purified water (>18 M $\Omega$ , Milli-Q) at 90 °C and 1.7 atm. The performance of the anode was evaluated for pure hydrogen and for mixtures of H<sub>2</sub>/CO (100 ppm) and He/CO (1%) diluted in pure hydrogen to form H<sub>2</sub>/CO (1000 ppm), both humidified with purified water at 100 °C at 2.0 atm. The total flow rate of all fuel gases were maintained at 100 cm<sup>3</sup> min<sup>-1</sup>, corresponding to 1.5 times the stoichiometric value at 2 A cm<sup>-2</sup>, while for oxygen the flow rate was 670 cm<sup>3</sup> min<sup>-1</sup> (a large excess). Before the polarization experiments the single cell was conditioned either at 0.7 V for 2 h for pure H<sub>2</sub> or at 0.8 V for 2 h for H<sub>2</sub>/CO, in order to reach the steady-state condition. During the polarization experiments, the cell potential at each current density was recorded only when it reached a constant value in an interval of at least 1 min between two consecutive lectures.

### 3. Results and discussion

Fig. 2 presents the product yields as a function of time measured by 'on line' gas chromatographic analyses at the

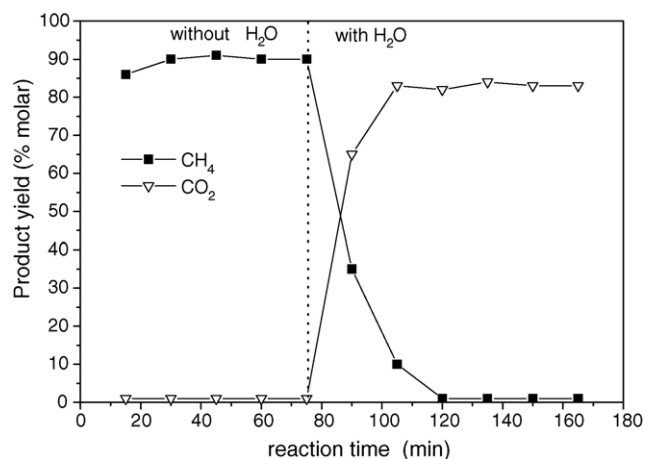


Fig. 2. Formation of methane and CO<sub>2</sub> during the reaction of H<sub>2</sub>/CO (1000 ppm) on the Co (18%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 400 °C in the absence and in presence of water vapor, respectively.

outlet/inlet of a Co(18%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (150 mg) reactor fed with a H<sub>2</sub>/CO (1000 ppm) mixture, with and without water vapor. In the absence of water, large amounts of methane are formed, while the CO<sub>2</sub> production is negligible. As soon as water is supplied to the system, there is an inversion of the CH<sub>4</sub>/CO<sub>2</sub> relative distribution. These results confirm that in the absence of water the methanation reaction (Eq. (2)) is operative, while in the presence of water the CO removal occurs via WGS reaction (Eq. (1)). In both cases, high levels of CO conversion (around 90%) were evident. The absence of methane at the outlet of the WGS reactor is in agreement with a previous report of Haga et al. [12].

A real reformat gas usually contains ca. 20% of CO<sub>2</sub>, besides H<sub>2</sub>, CH<sub>4</sub> and CO [5]. Fig. 3 shows the effects of the presence of carbon dioxide in the methanation and WGS reactions for the Co(18%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reactor operating at 400 °C and supplied with a gas mixture similar to those obtained from the ethanol steam reforming, i.e., H<sub>2</sub>/CO<sub>2</sub> (64:23%, v/v) and

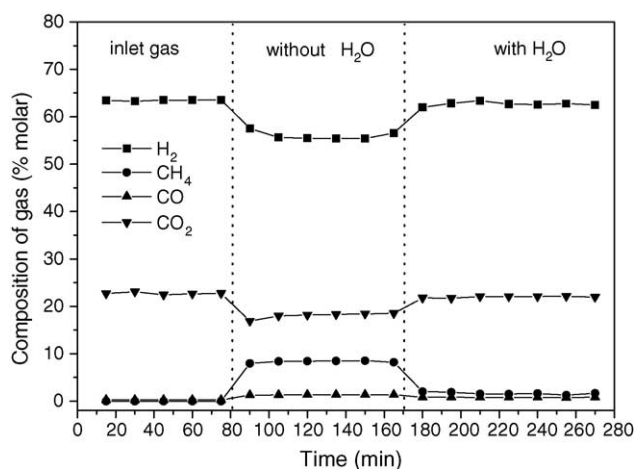


Fig. 3. Product distribution on the Co/ $\gamma$  Al<sub>2</sub>O<sub>3</sub> catalyst (150 mg) fed with 50 cm<sup>3</sup> min<sup>-1</sup> of a gaseous mixture of 65% H<sub>2</sub>, 23% CO<sub>2</sub> and 2300 ppm of CO.

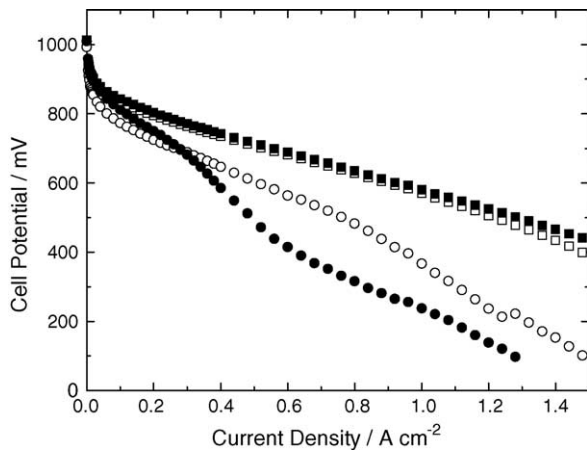
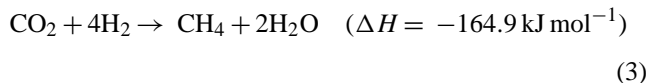


Fig. 4. Polarization curves for PEM single cells with a PtRu/C (50:50 atomic ratio, 20 wt.%) anode. Solid symbols: only the PEM single cell; open symbols: PEM single cells coupled to the WGS reactor. System fed with (□, ■) pure hydrogen and (○, ●) H<sub>2</sub>/CO (1000 ppm). The cathode was fed with pure O<sub>2</sub>.  $T_{\text{cell}} = 85\text{ }^{\circ}\text{C}$ , oxygen humidifier at  $90\text{ }^{\circ}\text{C}$  and hydrogen humidifier at  $100\text{ }^{\circ}\text{C}$ ;  $p_{\text{H}_2} = 2.0\text{ atm}$ ;  $p_{\text{O}_2} = 1.7\text{ atm}$ . Catalyst loading =  $0.4\text{ mg cm}^{-2}$ . Anode flow rate =  $100\text{ cm}^3\text{ min}^{-1}$  and cathode flow rate =  $670\text{ cm}^3\text{ min}^{-1}$ .

traces of CO [5]. In the absence of water, there is consumption of H<sub>2</sub> and CO<sub>2</sub> and production of CH<sub>4</sub> and CO, suggesting that methane is formed by carbon dioxide hydrogenation, which is a thermodynamically favorable process [13]:



On the other hand, the increase of carbon monoxide content can be attributed to the reversing of the WGS reaction (Eq. (1)) [6].

In the presence of water, the composition of the gas in the reactor outlet is similar to that in the inlet, with just a small increase of the CH<sub>4</sub> and CO concentrations. These results show that the CO<sub>2</sub> hydrogenation reaction does not occur appreciably in the presence of water. However, some increase is noted for the CO concentration, implying that the reversing of the WGS reaction takes place, although in a much smaller extent compared to the previous case. These facts contrast to those observed in the absence of CO<sub>2</sub> where a considerable reduction of the CO content was seen (Fig. 2) for both the methanation and WGS reactors. In the presence of CO<sub>2</sub>, the results indicate that the coupling of the reactors to a fuel cell would not be appropriate. Actually, the reactions reported in this paper (WGS, reverse-WGS and methanation of CO or CO<sub>2</sub>) are interplay between CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O [14].

In view of the above facts, the coupling of the WGS and methanation reactors to the PEMFC was considered only for gases without CO<sub>2</sub>. In Fig. 4 the polarization curves for a single fuel cell formed with a PtRu/C anode coupled to the WGS reactor supplied with pure hydrogen or H<sub>2</sub>/CO (1000 ppm) are shown. For comparison, the polarization response for the same single cell supplied with H<sub>2</sub>/CO (1000 ppm) without the

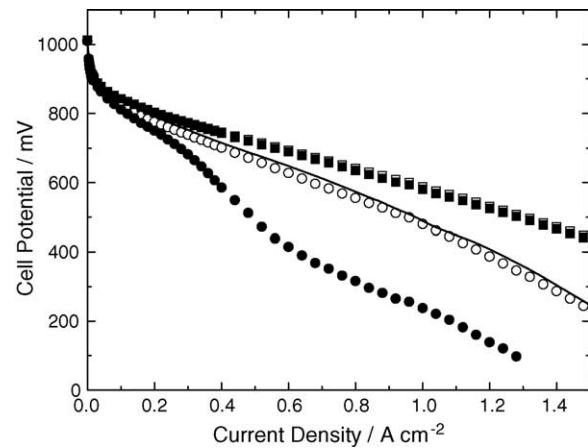


Fig. 5. Polarization curves for PEM single cells with a PtRu/C (50:50 atomic ratio, 20 wt.%) anode. Solid symbols and line: only the PEM single cell; open symbols: PEM single cells coupled to the methanation reactor. System fed with (□, ■) pure hydrogen and (○, ●) H<sub>2</sub>/CO (1000 ppm); (line) H<sub>2</sub>/CO (100 ppm). The cathode was fed with O<sub>2</sub>.  $T_{\text{cell}} = 85\text{ }^{\circ}\text{C}$ , oxygen humidifier at  $90\text{ }^{\circ}\text{C}$  and hydrogen humidifier at  $100\text{ }^{\circ}\text{C}$ ;  $p_{\text{H}_2} = 2.0\text{ atm}$ ;  $p_{\text{O}_2} = 1.7\text{ atm}$ . Catalyst loading =  $0.4\text{ mg cm}^{-2}$ . Anode flow rate =  $100\text{ cm}^3\text{ min}^{-1}$  and cathode flow rate =  $670\text{ cm}^3\text{ min}^{-1}$ .

reactor is also presented. The polarization curves obtained for the single cell supplied with pure hydrogen [15,16] resulted similar to those for the system without the WGS reactor, indicating that no disturbance is caused by the reactor coupling. With H<sub>2</sub>/CO (1000 ppm) in the absence of the reactor, a significant decrease of the cell potential compared to pure hydrogen is evidenced due to a strong catalyst CO poisoning. Despite this, the poisoning effect on this PtRu/C catalyst is much lower than that occurring in the conventional Pt/C material, which presented no activity for the HOR (hydrogen oxidation reaction) under this condition (data not shown). In fact, the PtRu/C catalysts prepared in this work using an impregnation method demonstrated an excellent CO tolerance, in agreement to previous results obtained for H<sub>2</sub>/CO (100 ppm) [10].

The polarization response of the fuel cell coupled to the WGS reactor supplied with the H<sub>2</sub>/CO (1000 ppm) mixture shows a clear decrease of CO poisoning effect compared to the cell without the reactor. This is surely related to the reduction of the CO concentration in gas channels inside the fuel cell, as confirmed by the chromatography analyses (Fig. 2).

The polarization curves for the PEM single cell coupled to the methanation reactor (in the absence of water) supplied with pure hydrogen and with H<sub>2</sub>/CO (1000 ppm) are shown in Fig. 5. For comparison, the polarization curve for the same single cell without the reactor and supplied with H<sub>2</sub>/CO (100 ppm) is also presented. Similarly to the previous case the polarization responses for pure hydrogen were the same for the cell with or without the methanation reactor. The polarization curve indicates a significant improvement in the performance for the cell with the reactor compared to that without the reactor, when the feeding gas was H<sub>2</sub>/CO (1000 ppm). The performance is similar to that ob-

tained with H<sub>2</sub>/CO (100 ppm) without the methanation reactor. This similarity indicates that the methanation reaction is operative with an effective conversion of CO into CH<sub>4</sub> equivalent to 90%, in agreement with the chromatography analyses (Fig. 2). These results also indicate a contamination of the hydrogen entering the cell with ca. 900 ppm of CH<sub>4</sub>, which seems to not substantially affect the fuel cell performance.

#### 4. Conclusions

Results have shown that when H<sub>2</sub>/CO (1000 ppm) is fed to the reactor in absence of water, the methanation reaction is operative, while in the presence of water, CO removal occurs via the WGS reaction. In both cases, high levels of CO conversion (around 90%) were evident. These reactions are strongly influenced by the presence of carbon dioxide, particularly in absence of water, for which the methanation of CO<sub>2</sub> is clearly evident. In both cases, some additional production of CO is noted.

The polarization response of the fuel cell coupled to the WGS reactor supplied with the H<sub>2</sub>/CO (1000 ppm) mixture shows a clear decrease of CO poisoning effect compared to the cell without the reactor. Results also indicate additional improvement in the performance, for the cell with the methanation reactor, which presented a performance similar to that for H<sub>2</sub>/CO (100 ppm) without the reactor. In both cases, results are consistent with an effective conversion of CO of the order of 90%, in agreement with the chromatographic analyses. The results also indicate that the contamination of the hydrogen entering the cell with ca. 900 ppm of CH<sub>4</sub>, does not substantially affect the fuel cell performance.

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