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Effect of fuel utilization on the carbon monoxide poisoning dynamics of Polymer Electrolyte Membrane Fuel Cells

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HIGHLIGHTS

- CO is fed to a single cell in concentrations between 0.18 and 1 ppm.
- Three fuel utilizations are used namely 70%, 40% and 25%.
- The single cell incorporates and anode catalyst loading of 0.05 mg Pt cm^{-2}.
- The drop in performance of the cell is correlated with the exhaust gas composition.

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ABSTRACT

The effect of fuel utilization on the poisoning dynamics by carbon monoxide (CO) is studied for future automotive conditions of Polymer Electrolyte Membrane Fuel Cells (PEMFC). Three fuel utilizations are used, 70%, 40% and 25%. CO is fed in a constant concentration mode of 1 ppm and in a constant molar flow rate mode (CO concentrations between 0.18 and 0.57 ppm). The concentrations are estimated on a dry gas basis. The CO concentration of the anode exhaust gas is analyzed using gas chromatography. CO is detected in the anode exhaust gas almost immediately after it is added to the inlet gas. Moreover, the CO concentration of the anode exhaust gas increases with the fuel utilization for both CO feed modes. It is demonstrated that the lower the fuel utilization, the higher the molar flow rate of CO at the anode outlet at early stages of the CO poisoning. These results suggest that the effect of CO in PEMFC systems with anode gas recirculation is determined by the dynamics of its accumulation in the recirculation loop. Consequently, accurate quantification of impurities limits in current fuel specification (ISO 14687-2:2012) should be determined using anode gas recirculation.

1. Introduction

Prevailing heavy reliance on fossil fuels and increasing environmental concerns have raised interest in Polymer Electrolyte Membrane Fuel Cells (PEMFCs) for automotive applications [1]. The main technical problems of PEMFCs have been solved [2]; however, there is room to reduce costs and improve their durability [3,4]. One of the remaining issues is related to the presence of impurities in the fuel and/or the oxidant since they affect the performance and accelerate the degradation of PEMFCs [5].

PEMFC use hydrogen and oxygen in order to generate electricity and water, releasing heat [6]. While the oxidant composition is not currently regulated, the fuel composition is regulated according to standard ISO 14687-2:2012, which outlines the H_2 fuel specification for road vehicles. This standard limits the amount of impurities such as carbon dioxide (CO_2) to 2 ppm, carbon monoxide (CO) to 0.2 ppm, ammonia (NH_3) to 0.1 ppm and sulfur species (e.g. H_2S and SO_2) to 4 ppb.

Complying with the H_2 fuel specification hinders the market growth of PEMFC vehicles due to the increased fuel costs. This is

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Abbreviations: PEMFC, polymer electrolyte membrane fuel cell; CO, carbon monoxide; ppm, parts per million; H_2S, hydrogen sulfide; SO_2, sulfur dioxide; ppb, parts per billion; MSR, methane steam reforming; PSA, pressure swing adsorption; HOR, hydrogen oxidation reaction; MEA, membrane electrode assembly; Pt, platinum; GC, gas chromatography.

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true especially for H_2 that is produced via methane steam reforming (MSR) [7] and purified using pressure swing adsorption (PSA) [8] as it contains trace amounts of CO. This latter H_2 production process is considered to be the least expensive if methane is available at reasonable price. The increase in cost due to the use of PSA comes from the fact that the lower the level of impurities required, the lower the H_2 yield of the PSA system. This is well illustrated in a paper by Besancon et al. [9].

CO is considered one of the most challenging impurities for two reasons. First, it is difficult to separate and to measure in a cost effective way at a concentration of 0.2 ppm. Second, CO decreases the performance of PEMFCs as it preferentially adsorbs onto the anode catalyst, usually platinum (Pt), hindering the hydrogen oxidation reaction (HOR). The last phenomenon is referred as “CO poisoning”, and its short term effects are well documented [5]. However, there is a noticeable lack of information regarding the impact of CO in the durability of PEMFCs. Franco [10] has recently summarized the efforts made so far to predict the durability of PEMFCs. That author observed a decrease in the corrosion of cathode catalyst support in a long-term test (>600 h) when hydrogen with 5 ppm CO was fed to a PEMFC with an anode catalyst loading $\approx$ 0.2 mg Pt cm^{-2} under load cycling conditions. Those results highlight the importance of studying the synergies between impurities and materials degradation in PEMFCs.

Despite great advances related to understanding CO poisoning, there are at least two issues that need to be studied with greater detail. The first issue is the CO poisoning dynamics, which is still poorly understood for low anode catalyst loadings, i.e. <0.1 mg Pt cm^{-2}. According to Gasteiger et al. [11], only 0.05 mg Pt cm^{-2} would be needed in the absence of impurities. Despite that, current membrane electrode assemblies (MEAs) for automotive PEMFC systems incorporate higher anode Pt loadings [12]. Hashimasa et al. [13] contributed to understanding the effect of catalyst loading on CO poisoning by testing anode Pt loadings between 0.05 and 0.4 mg Pt cm^{-2}. Those authors observed a slower decrease in performance at higher catalyst loadings for a constant CO concentration of 1 ppm. Furthermore, Angelo et al. used an anode Pt loading of 0.1 mg Pt cm^{-2} and CO concentrations of 0.2 ppm [14] and 1 ppm [15] to study the steady state CO poisoning. Those authors observed a decrease in electrochemically active area of the anode after their tests. Despite the importance of catalyst loading on the CO poisoning of PEMFC, it is noted that the most relevant studies in the literature [16–19] have been performed using anode Pt loadings that are not relevant i.e. $>$ 0.3 mg Pt cm^{-2}.

The second issue that must to be studied in greater detail is the effect of the H_2 stoichiometric rate (λ_{H_2}) or fuel utilization rate (μ_f) on the CO poisoning. The H_2 stoichiometric rate and the fuel utilization rate are related according to [6]:

$$\lambda_{H_2} = \frac{1}{\mu_f} \tag{1}$$

It is observed that in most of the studies only one fuel utilization was used, i.e. 17% [17], 50% [14,15,18–20] or 70% [13,21], not corresponding to actual PEMFC systems that may operate on a wide range of fuel utilizations [4,22]. The effect of fuel utilization on CO poisoning has been studied numerically for CO concentrations $\geq$10 ppm [16,23] and CO concentrations in the range 1–5 ppm [24]. The modeling results of Bonnet et al. [24] suggest that the current density, CO coverage and anode overpotential along the flow field is more homogeneous at lower fuel utilizations.

The most representative studies on CO poisoning have been performed using single cells for which the excess exhaust gas is vented to atmosphere [13–21]. Nevertheless, the CO poisoning dynamics is expected to be different in actual automotive PEMFC systems where the fuel is delivered in dead end mode with recirculation [25–29] (Fig. 1). Regarding the effect of impurities, the fuel delivery configuration depicted in Fig. 1 makes it necessary to study the buildup or enrichment of impurities in the recirculation loop [30–32]. The term enrichment of impurities is applied to reactive and/or non-reactive species other than H_2 that may accumulate in the recirculation loop until they are vented to atmosphere. To the best knowledge of the authors, only Matsuda et al. [33] have experimentally studied the enrichment of impurities. However, in their work the anode catalyst loading was 0.4 mg Pt cm^{-2} and the concentration of CO 4.8 ppm. Ahluwalia and Wang [30] have modeled the enrichment of CO and CO_2. Those authors observed that the enrichment depends on the original CO concentration which can reach 175% and 600% of its original value at the stack inlet and outlet respectively.

Regarding the effect of fuel utilization, the fuel delivery configuration of Fig. 1 makes necessary to use high gas recirculation rates since recirculated gas is used to humidify the H_2 at the anode inlet [29]. In this respect, there is a lack of literature documenting the effect of fuel utilization on the CO poisoning dynamics of PEMFC systems with anode gas recirculation.

It is of the utmost importance to analyze the composition of the anode recirculation gas in order to evaluate the enrichment of impurities in PEMFC systems. One approach to gain insight on the enrichment of impurities is to analyze the anode exhaust gas composition in single cells (fuel is fed and exhaust gas is vented). The latter has been applied in a few studies for CO [13–15,18,19,34–36], but again, the CO concentration, and/or the anode catalyst loading and/or the fuel utilization were too high in these studies. In a study by Pérez et al. [35] it was demonstrated that the fuel utilization influences the CO poisoning dynamics for CO concentrations between 15 and 19 ppm, fuel utilizations in the range 55–83% and an anode catalyst loading of 0.4 mg Pt cm^{-2}. In that study, due to the high Pt loading and fuel utilizations used, no significant amount of CO was detected in the anode exhaust gas before a significant drop in the current was observed. In contrast, in the studies by Hashimasa et al. [13] (1 ppm of CO, 0.05–0.4 mg Pt cm^{-2} and 70% fuel utilization) and by Santis [34] (50 ppm of CO, 0.6 mg Pt cm^{-2} and 50% fuel utilization), CO was detected for a marginal drop in performance during galvanostatic [13] and potentiostatic [34] operation.

Obtaining information about the anode exhaust gas composition and CO enrichment in the recirculation loop using low anode

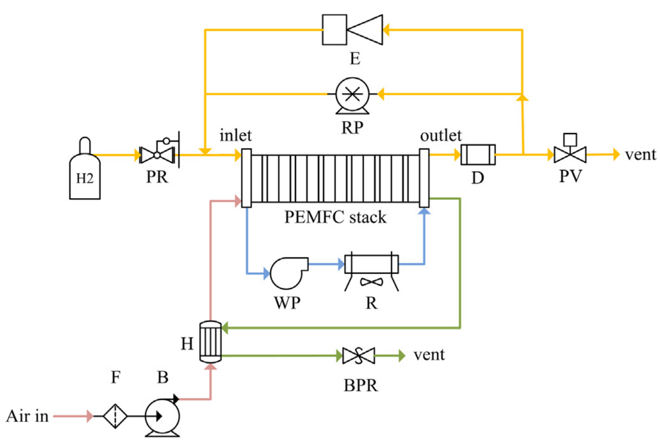

Fig. 1. Simplified diagram of an automotive PEMFC system. PR, pressure regulator; D, demister; PV, purge valve; RP, recirculation pump; E, ejector; F, filter; B, blower; H, humidifier; WP, water pump; R, radiator; BPR, back pressure regulator. Adapted from [22–25].