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# The influence of impurities in high temperature polymer electrolyte membrane fuel cells performance

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## ABSTRACT

This work investigates the influence of carbon dioxide and non-reacted methanol, present in the reformat stream obtained via methanol steam reforming, in the performance of high temperature polymer electrolyte membrane fuel cells (HT-PEMFC), operating between 160 °C and 180 °C.

The HT-PEMFC anode was fed with pure hydrogen, hydrogen balanced with carbon dioxide (75%/25% vol.) and synthetic reformat mixture, considering also vaporized methanol solution in the reformat content (up to 10% vol.). The synthetic reformat was feed during cycles of 420 min. The fuel cell was characterized based on the polarization curve and electrochemical impedance spectroscopy (EIS) analysis. Additionally, acid–base titrations were performed to access the phosphoric acid content in different sections of the MEAs as well as scanning electron microscopy (SEM).

A low impact in the fuel cell performance was observed when three cycles of synthetic reformat containing methanol solution were performed. When the number of cycles was increased, the performance of HT-PEMFC decreases and irreversible degradation of performance was observed. The cycles with synthetic reformat increased the ohmic resistance and high frequency resistance associated with anodic processes, but decreased the intermediate frequency resistance associated with cathodic processes. Additionally, by increasing the number of cycles, the phosphoric acid content of Celtec<sup>®</sup> MEAs and the thickness of the membrane decreased.

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## Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are electrochemical devices that have been considered for stationary applications and as an alternative to internal combustion engines. PEMFC are limited to a maximum operating

temperature of 90 °C due to use of perfluorinated membranes as electrolyte, which presents very high conductivity under humidified conditions. The increase of operation temperature of PEMFC is desirable due to electrochemical kinetics improvements, simplified water management, heat recovery and increased CO tolerance [1]. High temperature polymer electrolyte membrane fuel cells (HT-PEMFC) operate between

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160 °C and 180 °C and are based on phosphoric acid doped polybenzimidazole (PBI) membranes.

PEMFC devices can achieve high power densities, without any emissions besides water vapor, when pure hydrogen is fed to the anode. Hydrogen storage systems do not present yet the required capacity, cost and operating simplicity. Hydrogen can be produced by the reforming of fuels such as methane, methanol or ethanol and then feed to the fuel cell. Due to its high hydrogen/carbon ratio and absence of carbon to carbon bonds, methanol is a more attractive fuel for *in-situ* hydrogen production. Additionally, methanol can be used directly in direct methanol fuel cells (DMFC), but they present considerably lower performance [2] due to poor oxidation kinetics and methanol crossover from the anode to the cathode.

A high temperature DMFC was first studied in the 1990's using phosphoric acid doped PBI as electrolytes [3–5]. The assembled DMFC reached a maximum of 0.1 W cm<sup>-2</sup>, at 200 °C [4]. More recently, a PBI-based HT-DMFC was used by Lobato et al. to study the effect of temperature, methanol/water ratio, and oxygen partial pressure [6]; a power peak close to 0.14 W cm<sup>-2</sup> was obtained at 200 °C.

Methanol steam reforming (MSR) reaction is an endothermic reaction, producing hydrogen and carbon dioxide; the presence of carbon monoxide in the reaction products can be attributed to side reactions, namely methanol decomposition and reverse water gas shift. The effect of CO<sub>2</sub> and especially CO on the performance of HT-PEMFCs was reported by several authors [7–11]. CO adsorbs strongly on platinum surface, used as electrocatalyst, reducing its activity. A good tolerance (voltage loss within 30–50 mV) of a Pt/C catalyst was observed with 3% and 5% of CO at 180 °C, at moderate values of cell voltage [10]. The presence of CO<sub>2</sub> in the reformat dilutes the fuel and limits the maximum current density of the fuel cell and can have a negative effect due to formation of CO via the reverse water–gas shift reaction on platinum surface [12].

Pan et al. integrated a HT-PEMFC stack, based on acid-doped PBI membranes, with a MSR [13]. The reformat was directly fed into the stack and a voltage decrease was seen in all current density range when compared with pure hydrogen; one of the factors may be the effect of residual methanol from the reformer. Su et al. [14] integrated a methanol fuel reformer positioned upstream of a HT-PEMFC and observed a decrease in the fuel cell power peak from 0.22 W cm<sup>-2</sup> to 0.12 W cm<sup>-2</sup>, when pure hydrogen was replaced by methanol reformat obtained at 240 °C, due to the presence of CO and CO<sub>2</sub>. Avgouropoulos et al. [15–17] proposed the internal methanol reforming by incorporating the reforming catalyst in the HT-PEMFC anodic compartment. In the latest communication [17], the MSR catalyst was deposited on a gas diffusion layer and was separated from the MEA by a plate, being in indirect contact. The authors reported a cell voltage of 642 mV at 0.2 A cm<sup>-2</sup>, at 210 °C, when the anode was supplied with a mixture of methanol, water and helium.

Up to now, very few studies were performed concerning the effect of methanol slip from the MSR on the performance of HT-PEMFC. Methanol oxidation presents a complex reaction mechanism, being several orders of magnitude slower than H<sub>2</sub> oxidation [18]. Furthermore, the possible permeation of methanol via diffusion from the anode to the cathode (e.g. during a transient) depolarizes the cathode and reduces O<sub>2</sub>

availability [5]. Araya et al. [19] performed a HT-PEMFC durability test, at 0.2 A cm<sup>-2</sup> and 160 °C; the degradation rate increased when pure hydrogen was replaced with hydrogen/methanol-water vapor mixture (5% or 8% vol.). The same research group analyzed the effects of methanol and water vapor on the performance of HT-PEMFC, between 140 °C and 180 °C [20]. The authors observed a negligible effect when simulated stream considering methanol reforming conversion of 90% (3% vol. methanol vapor) was used in the anode gas feed. Both studies did not consider the influence of CO<sub>2</sub> and CO but in another study the authors performed a multi-level factorial design of experiments to evaluate the interdependence among the concentrations of unconverted methanol-water vapor mixture, CO and CO<sub>2</sub> in gas feed [21]. The poisoning effect on the fuel cell by the methanol showed to be more pronounced when other impurities were also present in the feed gas, especially at higher methanol concentrations.

Understanding the influence of contaminants present in the reformat stream on the HT-PEMFC performance is vital for power supplies with reformat fuel feed development. This work aims to study the influence of methanol-water vapor mixture slip (up to 10% vol.) and CO<sub>2</sub> (up to 25% vol.) on the performance of HT-PEMFC, working at moderate current density. The supply of reformat containing methanol solution was performed in cycles of 420 min at 0.6 A cm<sup>-2</sup>. These conditions are more extreme than the ones already reported, in an attempt to understand clearly the effect of methanol slip.

## Experimental

The MEAs used in this study were Celtec<sup>®</sup> – P2100 MEA from BASF Fuel Cell, with an active area of 45 cm<sup>2</sup>. The MEAs were activated accordingly to supplier's specifications, at constant load of 0.20 A cm<sup>-2</sup> and at 160 °C for at least 50 h, with stoichiometry of 2 for air and 1.2 for hydrogen. After activation and during experiments the MEAs are operated with stoichiometry of 1.5 for hydrogen.

The tested were carried out in an in-house made fuel cell test bench, described elsewhere [22], using a *Pragma* single cell assembled with a torque of 5.5 N m. The experimental conditions were controlled using an application developed in *LabView* (National Instruments) and the electrochemical tests were performed using a *Zahner* IM6e electrochemical workstation coupled with a potentiostat PP-241.

In the experiments, besides pure hydrogen, gas mixtures were used to evaluate the effect of impurities: hydrogen balanced with carbon dioxide (75%/25% vol., hereafter referred as carbon dioxide mixture) and hydrogen balanced with carbon dioxide and methanol solution, hereafter referred as synthetic reformat. The experiments with synthetic reformat were performed in cycles of 420 min, at constant 0.6 A cm<sup>-2</sup>, starting with two cycles with 7% vol. methanol solution (and therefore 18% of carbon dioxide) followed with cycles with 10% vol. methanol solution (and therefore 15% of carbon dioxide). The synthetic reformat stream was produced using a methanol evaporating system comprising a methanol solution (steam to carbon ratio of 1.5) reservoir, a

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