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Effect of carbon dioxide on the contamination of low temperature and high temperature PEM (polymer electrolyte membrane) fuel cells. Influence of temperature, relative humidity and analysis of regeneration processes

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ABSTRACT

An experimental investigation of the performance and contamination of low and high temperature PEMFCs (polymer electrolyte membrane fuel cells) operating with different concentrations of CO_2 at the anode inlet is presented. 50 cm^2 MEAs are used in the investigation: Nafion membranes with catalyst Pt loading 0.5 mg cm^{-2} for both anode and cathode for the low temperature cell, and Celtec P1000 PBI MEAs with catalyst loading 0.75 mg cm^{-2} in anode and 1 mg cm^{-2} in cathode for the high temperature cell. An analysis of the relative humidity influence in the contamination process for low temperature polymer electrolyte membrane fuel cells and the temperature effect for both low and high temperature operation range are also investigated in this work. The results show that the performance loss is larger than expected if only a dilution effect were considered, so that a real contamination process occurs in the cell when CO_2 is fed to the anode, due to the RWGS (reverse water gas shift) reaction. This contamination effect is analysed and quantified by comparing the polarization curves of the contaminated cell with the ones corresponding to the cell operating with pure hydrogen, following the method described in section 2. The overpotentials for different current densities, CO_2 concentrations, relative humidity, and cell temperatures are presented and discussed for both types of fuel cells. Two different regeneration processes (anode feeding with pure H_2 and with air) are also presented and discussed. The analysis of the effectiveness of each regeneration strategy also supports that CO produced via the RWGS reaction is adsorbed onto the catalyst.

1. Introduction

PEMFCs (polymer electrolyte membrane fuel cells) are considered as a promising alternative to the current internal combustion engines [1–4]. This type of system generates electrical energy directly and with a high efficiency from the chemical energy stored in reactants, producing water and heat. The main characteristic of this kind of fuel cells is that it uses a solid polymer electrolyte with a high ionic conductivity instead of a liquid electrolyte. The PEMFCs fueled by hydrogen show some advantages compared to other fuel cells: low temperature operation (20–90 °C) with the consequent quicker start-up, easier anode kinetics for the HOR (hydrogen oxidation reaction) and high power density [3,5–15].

Currently, approximately 95% of hydrogen (H_2) is produced by the steam reforming of natural gas or methane [8,16]. In the feed obtained using this process, besides H_2, there are different impurities like CO (carbon monoxide), CO_2 (carbon dioxide), CH_4 (methane) and others such as N_2 (nitrogen), H_2S (hydrogen sulfide) or NH_3 (ammonia). Hence it is important to determine how they can affect the fuel cell performance. The presence of these impurities can have a highly negative effect on the fuel cell performance even at low concentration levels, decreasing the overall system

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efficiency and, depending of the type of impurity, the degradation of the different components which comprise a fuel cell can be highly irreversible [17,18]. For this reason, the presence of impurities in the reacting flows will influence the durability and the efficiency of a fuel cell.

In literature, the most extensively investigated contaminant is CO. The presence of CO in the fuel has been deeply studied due to the high performance losses obtained when this impurity is present in the feed supplied to the anode [18–29]. Even the presence of small concentrations of CO causes a high decrease in performance. CO can block the active Pt surfaces and also displace the H_2 adsorbed from Pt because the bond between CO and Pt in Reaction 1 is much stronger than that between H_2 and Pt in Reaction 2 [19].

$$CO + Pt \rightarrow Pt - CO \tag{1}$$

$$2CO + 2(Pt - H) \rightarrow 2Pt - CO + H_2 \tag{2}$$

Thus, the presence of CO adsorbed onto the catalyst surface limits the electro-oxidation reaction of H_2 (Reactions 3 and 4), decreasing the overall performance.

$$H_2 + 2\ Pt \rightarrow 2H - Pt\ \text{Tafel reaction} \tag{3}$$

$$Pt - H \rightarrow H^+ + e^- + Pt\ \text{Volmer reaction} \tag{4}$$

However, there are other impurities which can be present in the fuel. The stream obtained from a reformation process is typically formed by a mixture of H_2 (40–70%), CO_2 (15–25%), CO (1–2%) and small quantities of N_2, water vapour and sulphur impurities [17].

Among all the impurities, the study of the influence of CO_2 on the performance of a PEMFC is of considerable interest due to the high concentration of this contaminant in a typical reformate mix. The presence of CO_2 in the fuel can produce performance losses that cannot be underestimated [17,18,27,30–37].

CO_2 is commonly considered as an inert gas. That means that the losses are typically only attributed to the H_2 dilution. However, a CO_2/H_2 mixture produces larger polarization losses than a N_2/H_2 mixture [32,33,38]. This can be explained if it is considered the production of CO through the RWGS (reverse water gas shift reaction) as stated by Gu et al. [38] who presented experimental results consistent with the RWGS reaction. The reactions occurring are:

$$2\ Pt + H_2 \rightarrow 2\ Pt - H \tag{5}$$

$$CO_2 + 2\ Pt - H \rightarrow Pt - CO + H_2O + Pt \tag{6}$$

The RWGS can produce CO concentrations of about 10–100 ppm approximately [18,30]. This reaction can take place under normal operating conditions of a PEMFC and with the presence of a catalyst. It means that even a non-containing CO fuel can produce a drastic degradation on the performance if enough concentration of CO_2 is present.

Due to the endothermic nature of the RWGS reaction, temperature is one of the main parameters when the production of CO is studied. De Bruijn et al. [30], from thermodynamic calculations, showed in their study the influence of the temperature over the production of CO. The authors concluded that for each specific relative humidity there is a range of temperature where the CO production decreases. However, it exists a temperature range where the higher the temperature the greater the CO production. This means that temperature highly influences the CO production process. Nevertheless Gu et al. [33] claimed that temperature does not have a strong influence on the CO coverage.

The CO electro-oxidation depends also on the humidity degree [39]. On account of the fact that degradation in PEM fuel cells operating with H_2/CO_2 mixtures is directly related to the CO production, it is of high interest to study the influence of the relative humidity in the contamination process regarding the presence of CO_2.

The CO_2 effect on high temperature PEMFCs has been investigated and reported in the literature to a much minor extent. Andreasen et al. [27] operated a BASF Celtec P2100 high temperature PEM MEA with CO/CO_2 mixtures, using Electrochemical impedance spectroscopy (EIS) to characterize the performance decrease. However there is a general lack of concluding results regarding the effect of CO_2 on high temperature fuel cells.

The aim of the present work is therefore to evaluate both low and high temperature fuel cells performance, operating with hydrogen feeds containing different concentrations of CO_2. The effect of the operation temperature for both types of cells and the relative humidity influence are also addressed. The performance results are presented and discussed, obtained for pure H_2, H_2/CO_2 (90/10%), H_2/CO_2 (75/25%) and H_2/CO_2 (50/50%). Finally, the efficiency of two methods of regeneration for anode contamination is analysed: feeding pure H_2 and feeding air into the contaminated anode.

2. Materials, operating conditions and experimental description

The experimental work was conducted with a CT-1000 test station from FuelCon located at the Fuel Cell laboratory at the National Institute for Aerospace Technology (INTA). The test station is able to operate cells up to 600 W and a maximum intensity of 100 A. It is possible to work with both galvanostatic and potentiostatic modes, and with a dead end or flow-through operation (all tests were carried out with flow-through). The operating parameters that can be controlled are: flow of fuel and oxidant (0.2–10 Nl min^{-1} in the anode and 0.4–20 Nl min^{-1} in the cathode), temperature and relative humidity of the reactants, pressure of both anode and cathode, cell temperature, and pressure in anode and cathode. All the bench piping and cell can be purged by N_2.

2.1. Low temperature PEMFC experiments

For the low temperature experiments, seven layer commercial MEAs produced by Paxitech with active surface area of 7 × 7 cm^2 have been used. These MEAs consisted in a 50 μm polymer electrolyte membrane (perfluorinated cation exchange membrane) coated on both sides with a catalyst ink, and combined with a GDL (gas diffusion layer), 15 μm sub-gasket material and silicon gaskets around the active layers from GDL edge to outer edge of the polymer electrolyte. GDLs are pressed onto the catalyst active area and are made of a carbonised non-woven material with a Polytetrafluoroethylene (Teflon) (PTFE) surface treatment. The sub-gasket material protects the active layer/GDL contact area and the polymer electrolyte membrane border. The catalyst Pt loading is 0.5 mg cm^{-2} both in the anode and in the cathode.

The cell used consisted of graphite bipolar plates from Electrochem Inc. with a five-channel serpentine flow field design and with an area of 50 cm^2. Serpentine bipolar plates have five parallel channels and nine rows. Channel and land width is 0.71 mm and 0.86 respectively. Total plate thickness is 9.5 mm. An external heater controlled by a Proportional-integral-derivative controller (PID) is used to maintain the operating temperature chosen for the test. This external heater consists on a flexible resistance surrounding the cell. Due to the exothermic nature of the reaction, once 400 mA cm^{-2} is reached, a fan is necessary in order to avoid an