CO tolerance of proton exchange membrane fuel cells with Pt/C and PtMo/C anodes operating at high temperatures: A mass spectrometry investigation

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ABSTRACT

The performance of proton exchange membrane fuel cells (PEMFC) with Pt/C and PtMo/C anodes has been investigated using single cell polarization and on line mass spectrometry (OLMS) measurements in a wide range of temperature (70–105 °C) for the system supplied with hydrogen containing different amounts of CO. As expected a higher CO tolerance is observed at higher temperatures for both catalysts. The anode exit gas analysis revealed that CO_2 is produced already at the cell open circuit potential, and it increases with the increase of the anode overpotential. The CO tolerance phenomena are assigned to different processes depending on the catalyst nature. For the Pt/C containing anodes, at temperatures above 80 °C, thermal desorption, reduced CO oxidation potential and CO oxidation by O_2 crossover are responsible for enhanced tolerance, whilst PtMo/C shows greater tolerance due the occurrence of a MoO_x-mediated water gas shift reaction (WGS), which is activated at high temperatures. Although the occurrence of WGS leads to the anode poisoning in the presence of CO_2, the polarization results show that only small additive contamination effect occurs by the combined presence of $CO + CO_2$ in the hydrogen stream.

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1. Introduction

Proton exchange membrane fuel cells (PEMFC) have been gaining large attention as an alternative electric power source, since they are very efficient for the conversion of chemical energy into electrical energy [1]. However, before the effective use of this technology, the problem of large power losses caused by low levels of carbon monoxide have to be solved, particularly when reformate hydrogen is used as anode reactant. In such a case, a strong CO adsorption [2–4] occurs on the Pt anode catalyst, which severely hinders the adsorption and oxidation of hydrogen [5]. Additionally, the operating environment/conditions are known to have an impact on the fuel cell's durability, and this includes exposure to impurities (on both, the anode and cathode), start-up from subfreezing conditions, and high operation temperatures [6].

In the CO tolerance context, the operating temperature [7] and the oxygen crossover [8] are shown to be important factors for improving the PEMFC performance, but some other approaches have been attempted to reduce the poisoning problem [9–11]. So, several Pt-based catalysts have been investigated to improve the CO tolerance, such as Pt–Fe [12], Pt–Ru [13–15], Pt–Mo [7,14,15], Pt–W [16] and Pd–Pt [17]. The higher CO tolerance of these materials, as compared to Pt alone, is usually assigned to two distinct mechanisms: the so-called bifunctional and electronic mechanisms. In the first, the presence of a second metal promotes the electro-oxidation of CO to CO_2 after a spillover process of Pt–CO to OH-species formed on the oxophilic sites on the second metal [18]. As for the electronic effect [19,20], the presence of the second metal modifies the Pt electronic properties and thus changes the CO chemisorption properties, ultimately reducing the CO coverage and leaving freer Pt sites available for the H_2 oxidation. Also, other known ways to reduce the CO poisoning is the promotion of CO oxidation by oxygen either deliberated introduced in the fuel stream or coming from the cathode after crossing the membrane [8], and the occurrence of the water gas shift process (WGS) which corresponds to the reaction of CO with water catalyzed by specific catalysts, particularly on PtMo/C [14]. This catalyst had been also tested for the performance on hydrogen reformate (40 ppm CO, 25% CO_2) [15], where the occurrence of the reverse WGS process is proposed for explaining the poisoning effect observed for CO_2.

This work presents results showing how the increase of temperature (up to 105 °C), and the CO and CO_2 concentrations (ranging from 0.01 to 2% CO and 25% CO_2) affect the CO tolerance of PEMFC anodes formed by Pt/C and PtMo/C. By using on line mass spectrometry (OLMS) it was possible to elucidate the reactions and processes involving CO, occurring in parallel with the hydrogen oxidation reaction. The results provide new insights to the CO tolerance mechanism for PEM single cells as well on the extension of O_2 crossover from the cathode to the anode, and its role on the CO oxidation.

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2. Experimental

The PEMFC single cell studies were performed with membrane and electrode assemblies (MEA) prepared with standard gas diffusion electrodes containing Pt/C or PtMo/C catalysts for the anodes and only Pt/C for the cathode. Both anode and cathode electrodes (4.62 cm^2, each) contained 0.4 mg cm^{-2} of metal loading. The materials and preparation methods employed are described elsewhere [2–4,14,16,17,21]. For preparation of PtMo/C eletrocatalysts the formic acid reduction method [2–4,14,16,17,21] was used, which consisted in the simultaneous reduction of dihydrogen hexachloroplatinated (H$_2$PtCl$_6$, Aldrich) and tetrahydrated ammonium molybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O) with formic acid solution, in the presence of high-surface area carbon powder (Vulcan XC-72, Cabot), at 80 °C. Briefly, the catalysts were prepared by adding the desired amount of Pt and Mo precursors in a solution containing formic acid and the high-surface area carbon at 80 °C. After completion of the adding step the mixture was filtered and washed thoroughly to remove impurities, and at last dried at 80 °C for 2 h before usage for the electrode preparation. The Pt/C catalyst was purchased from E-Tek.

The catalysts were characterized by X-ray diffraction (XRD, RIGAKU Ultima IV, KαCu radiation 1.5416 Å) and transmission electron microscopy (TEM, Philips CM 120, LaB$_6$ filament) to obtain structural information as well as the mean crystallite/particle size distribution. Energy dispersive spectroscopy (EDS, Leica-zeiss LEO 440 SEM-EDX e-beam at 20 kV with microanalyzer Link Analytical QX 2000 with SiLi detector) and X-ray photoelectron spectroscopy (XPS, SPECS Phoibos HSA3500 150 MCD9 with KαAl 1487 eV X-ray source and pass energy of 20 eV) measurements were also conducted to assess the average and local chemical compositions, specifically for PtMo/C. Finally, the electronic properties of Pt in the PtMo/C catalyst were investigated by X-ray absorption Spectroscopy (beam line D04B XAFS1 at the Brazilian Synchrotron Light Source, LNLS), focused in the X-ray absorption near edge structure (XANES) portion of the absorption spectra, which can provide evidence of electronic structural changes on the Pt 5d band and thus on the atom reactivity. These experiments were conducted at a specially designed spectro-electrochemical cell which enables virtually the same humidification, temperature and gas flux as in a real fuel cell.

Fuel cell polarization measurements were carried out galvanostatically (Electronic Load HP 6050A) with the cell at several temperatures using the gases saturated with water at temperatures above that of the cell, by 15 °C for hydrogen and 5 °C for oxygen. Details on the humidification system, temperature and pressure control can be found elsewhere [22]. For all temperatures, the system was initially maintained at a cell potential of 0.7 V with pure H$_2$ and at 0.8 V with H$_2$/0.01–2% CO, for 2 h each, prior to the data acquisition. To achieve the desired composition in the anode fuel streams a mixture of hydrogen (99.99%), primary mixtures of 100, 1000 or 20,000 ppm carbon monoxide in hydrogen balance, nitrogen (99.996%), carbon monoxide (99.5%) and carbon dioxide (99.997%) were employed. At all times both anode and cathode reactant streams were kept at 1 bar partial pressure. This means that the total pressure in the chambers was 1 bar above the vapor pressure of water at the considered humidification temperature. The gas-mixing system was formed by a set of four mass flow controllers (MKS 1179A MFC and MKS 247D Four-Channel Readout unit), keeping the total flow rate at 250 mL min^{-1} for the cathode gas and 300 mL min^{-1} for the anode side. Pure oxygen (99.5%) was used as the cathode feed. All gases were purchased from White Martins.

Cyclic voltammetry and CO stripping experiments were conducted at several temperatures for helping to understand the reasons of the CO tolerance, for both Pt/C and PtMo/C anodes.

Table 1
Composition and structural parameters of the Pt/C and PtMo/C electrocatalysts.

Material	Pt:Mo/at.%	Lattice constant/nm	Crystallite size/nm	Particle size/nm
Pt/C	–	0.393	2.2	2.2
PtMo/C	66–55:34–45	0.393	2.0–2.4	2.3–2.4

The experiments were performed using a potentiostat–galvanostat (Solartron 1285) in the standard fuel cell hardware, with the anode fed with argon or CO mixture (for CO adsorption) as the working electrode while the cathode was constantly fed with hydrogen and used as both counter electrode and the reversible hydrogen electrode (RHE). As the current level during these experiments was below 2 A, usage of the RHE also as the counter electrode does not incur in potential drift as hydrogen was constant fed into this electrode. Prior to potential scanning at 2 mV s^{-1}, CO was admitted to the anode side for 20 min under potentiostatic control (c.a. 50 mV vs. RHE), and then flushed with argon for 40 min.

The anodic exit gas composition was measured with on-line mass spectrometry (OLMS) to understand the CO oxidation processes occurring in the fuel cell anodes [13,14,17,23,24]. A mass spectrometer (Pfeiffer Vaccum GSD 301 Omnistar, quadrupole QMS 200 Prisma, W filament 70 eV electron energy with SEM 1000 V common voltage) was connected to the single cell anode outlet by a capillary heated at 170 °C for on line measurements of the O$_2$ crossover, detection of changes in the inlet CO concentration, and the quantification of the CO$_2$ amount formed at distinct experimental conditions. Data corresponding to the CO$_2$ ionization currents were converted into CO$_2$ contents using an analytical calibration curve obtained with five different concentrations of CO$_2$ in H$_2$, at the same experimental conditions (temperature, pressure) of the experiments. The calibration procedure was performed for both catalysts, not showing any change in the slope of the analytical curve, and indicating that the nature of the catalyst was irrelevant for the system calibration. The curve (not shown) shows a linear coefficient correlation factor of 99.9%, ensuring the good quality of the calibration procedure.

To assess the specific effect of the CO contamination on the fuel cell, the overpotential of the hydrogen electrode in the presence of CO (η_{CO}) was obtained as a function of current density. The overpotential was obtained at each current density from the values of cell potential in the presence ($E_{H_2/CO}$) and absence of CO (E_{H_2}), by using the expression,

$$\eta_{CO} = E_{H_2} - E_{H_2/CO_2} + \eta_{H_2} \cong E_{H_2} - E_{H_2/CO} \qquad (1)$$

where, η_{H_2} is the overpotential of the anode electrode due the hydrogen oxidation reaction. Taking into account that this reaction has a fast kinetics in acidic media, its overpotential can be neglected without introducing any appreciable errors in our analysis even at high current densities [25].

3. Results and discussion

3.1. Chemical and morphological structure of the PtMo/C catalyst

X-ray diffraction patterns obtained for the Pt/C and PtMo/C catalysts are quite similar to the data available in the literature [14,26,27], and so will not be presented here. The TEM images obtained for the PtMo/C material are shown in Fig. 1. A collection of the catalyst chemical and morphological properties obtained from these data are summarized in Table 1. Results show that the overall atomic ratio of Pt:Mo, as measured by EDS, are in the range of 55–66:45–34 in the PtMo/C material, while the metal/C ratios are very close of 20 wt.%. The average particle and crystallite size is around 2.2–2.4 nm, and so very much similar for both catalysts,