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Molybdenum carbide-based electrocatalysts for CO tolerance in proton exchange membrane fuel cell anodes

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ABSTRACT

The activity, stability and CO tolerance of molybdenum carbide-based electrocatalyts were studied in anodes of proton exchange membrane fuel cells (PEMFCs). To this purpose, carbon-supported molybdenum carbide (Mo_2C/C) was prepared by an ultrasonic method, and was used as catalyst support in the anode of a PEMFC. Pt and PtMo nanoparticles were deposited on this Mo_2C/C by the formic acid reduction method. The physical properties of the resulting electrocatalysts were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray absorption near edge structure (XANES), scanning electron microscopy (SEM) and wavelength dispersive spectroscopy (WDS). Electrochemical characterizations were carried out by single cell polarization measurements, CO stripping, cyclic voltammetry (CV) and online mass spectrometry (OLMS). CV and OLMS experiments were performed to evaluate the stability and CO tolerance of the electrocatalysts. The results obtained for the carbide-based electrocatalysts were compared with those obtained for carbon-supported PtMo and Pt electrocatalysts. It was observed that Pt and PtMo supported on Mo_2C/C present a better stability than PtMo supported on carbon. CV and WDS results evidenced a partial dissolution of Mo from the anode and its migration toward cathode during the cell operation. On the basis of polarization measurements and cyclic voltammograms, it was concluded that the stability of anode electrocatalysts can be improved by the use of molybdenum carbide as catalyst support.

1. Introduction

Fuel cells are considered as alternative electrical power sources for the near future. Among the various types of fuel cells used today, the most promising is the proton exchange membrane fuel cell (PEMFC), which is particularly useful for portable applications, because of its relatively high power density despite the low temperature of operation [1]. The electrocatalysts most commonly used for hydrogen oxidation in the PEMFC anode mainly contain Pt, which ensures a good electrocatalytic activity. However, the hydrogen obtained from reformate fuel stream contains carbon monoxide (CO) impurities that are easily adsorbed on the Pt surface, thus reducing the Pt surface available for hydrogen adsorption and eventually reducing the cell performance [2]. Therefore, a transition metal such as Ru or Mo is typically added to the Pt in order to increase the CO tolerance of the anode electrocatalysts by desorbing CO molecules from Pt surface [3,4]. Unfortunately, the high price of these metals, particularly Pt and Ru, and wear of the catalysts, still prevent the large-scale commercialization of PEMFCs. Transition metal carbides have been studied because of their catalytic activities for many chemical reactions including hydrodenitrogenation, hydrodesulfurization, methanol steam reforming and water-gas shift (WGS) reactions [5,6]. These carbides can be produced having large surface area and catalytic properties resembling those of the Pt-group metals (PGMs) [7,8].

In particular, molybdenum carbide (Mo_2C) has been investigated as anode electrocatalyst for PEMFCs [9,10], although its catalytic activity for H_2 electro-oxidation is not high enough to meet the requirements for fuel cell applications [11]. However, the catalytic activity of this carbide can be noticeably improved by the addition of Pt. In a recent study conducted to evaluate the use of molybdenum carbide as electrocatalyst in fuel cell anodes, it has been reported that Pt-Mo_{carb} supported on carbon black has shown a superior activity for methanol electro-oxidation in comparison with Pt supported on carbon [12]. In another study it was observed that molybdenum carbide has a high activity for the

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dissociation of methanol and water, as well as a relatively low CO desorption temperature of around 330 K [13]. Moreover, Weigert et al. [9] observed that Pt-modified Mo-C has enhanced activity and stability compared to Pt supported on carbon.

Summarizing, some research data can be found in literature regarding the activity of Mo_2C/C either for methanol oxidation or oxygen reduction, however, the CO tolerance and stability of this material has not been studied in detail. Thus, in this work, molybdenum carbide was prepared and used as support of Pt and PtMo electrocatalysts for hydrogen electro-oxidation in the presence of 100 ppm CO in PEMFC anodes. In addition to physical and electrochemical properties, the stability of these electrocatalysts was studied, in comparison with carbon-supported PtMo and Pt electrocatalysts.

2. Experimental

2.1. Preparation of electrocatalysts

The molybdenum carbide support (30 wt%, Mo_2C/C) was prepared by sonicating a slurry of molybdenum hexacarbonyl (Mo $(CO)_6$, Aldrich) and carbon powder (Vulcan XC-72R) in hexadecane, with a high intensity ultrasonic horn at 90 °C for 3 h. The resulting mixture was filtered, washed several times with purified pentane and heated at 90 °C until a black powder was obtained. This powder was transferred to a tubular quartz reactor and placed in a furnace. It was then exposed to an argon flow at 100 °C during 1 h. The argon was then replaced by a 1:1 CH_4/H_2 mixture and the temperature was increased at a rate of 5 °C min^{-1}, firstly until 300 °C for 1 h, secondly until 400 °C also for 1 h and finally until 500 °C for 12 h, in order to carburize the black powder and obtain the molybdenum carbide [14,15]. Pt (20 wt%) was deposited on this carbide support by the formic acid reduction method [16–18], which consisted of the reduction of dihydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6.6H_2O$, Aldrich), in the presence of the molybdenum carbide, using formic acid as reducing agent. In addition, PtMo (20 wt%) was deposited on Mo_2C/C and Vulcan XC-72R, also by the formic acid method. Pt supported on Vulcan XC-72 carbon also with 20 wt% metal/C was supplied by E-TEK. The Pt and PtMo loading in all the electrocatalysts was maintained at 20 wt%.

2.2. Physical characterizations

The metal content of the Mo_2C/C support as well as the metal loadings (Pt and Mo) of the catalysts were determined by energy dispersive x-ray spectroscopy (EDS) in a scanning electron microscope LEO, 440 SEM-EDX system (Leica-Zeiss, DSM-960) with a microanalyzer (Link analytical QX 2000) and a Si (Li) detector, using a 20 keV incident electron beam. The BET surface areas of the catalyst samples were determined by using a Micromeritics AutoChem II Chemisorption Analyzer. X-ray diffraction (XRD) patterns were recorded in a RIGAKU XRD RU200B diffractometer using CuKα radiation, in the 2θ range from 10 to 90°. Particle size distributions were determined by transmission electron microscopy (TEM, Tecnai G2F20 transmission electron microscope). The average crystallite sizes of the catalysts were determined by the Scherrer equation [19], using the Pt (220) diffraction peak and were compared with the results from TEM. The electronic properties of Pt in the electrocatalysts were investigated by x-ray absorption spectroscopy (XAS) (beamline D041 XAFS1 at the Brazilian Synchrotron Light Laboratory, LNLS) focused on the x-ray absorption near edge structure (XANES) region of the Pt L_3 absorption spectrum, that provides information about the electronic structure of the Pt 5d band and thus on the reactivity of the catalysts. These experiments were conducted by using a homemade spectro-electrochemical cell which

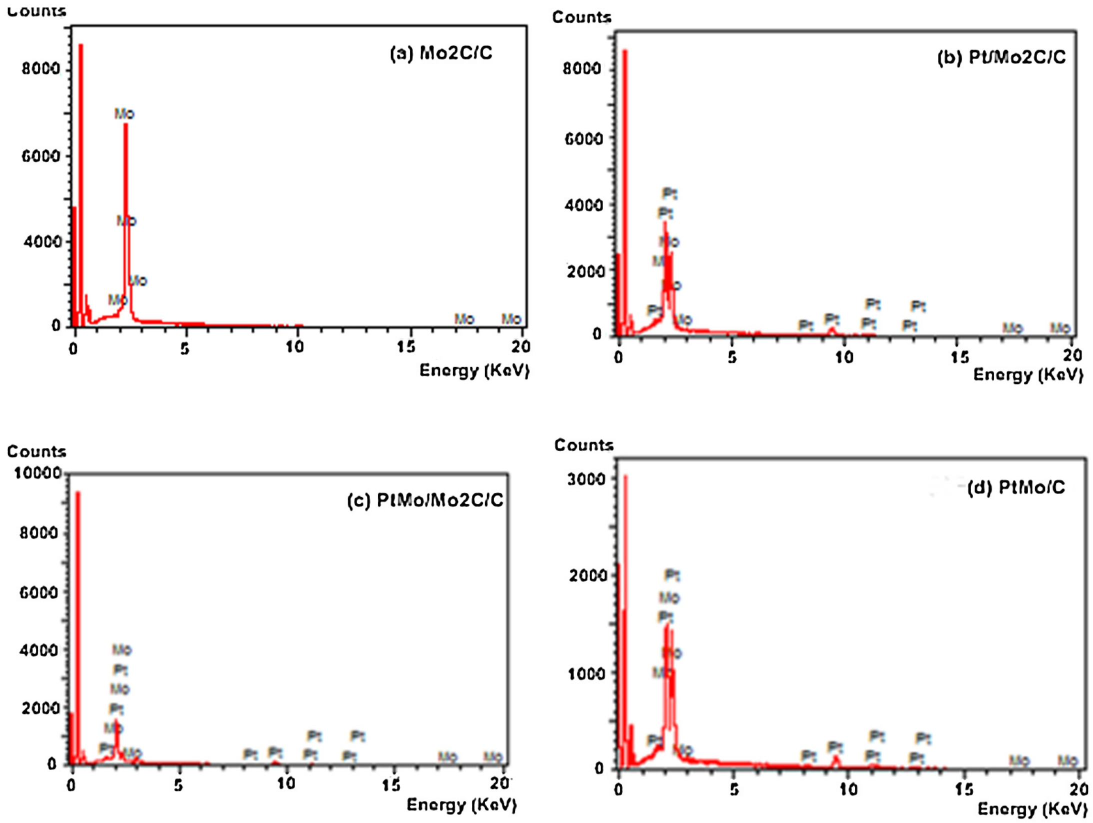

Fig. 1. EDS spectra of Mo_2C/C support and the $Pt/Mo_2C/C$, $PtMo/Mo_2C/C$ and PtMo/C electrocatalysts.