Structure and CO Tolerance of a PtMo/C Electrocatalyst

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In this work, the performance of PtMo/C electrocatalysts obtained by the formic acid reduction method was evaluated [1]. Studies were conducted on PtMo/C materials submitted to thermal treatment at different temperatures and environments and tested as anode catalysts for proton exchange membrane fuel cells (PEMFC) supplied with hydrogen/CO. The materials were characterized by X-ray absorption spectroscopy (XAS), and the results correlated to the performance in the PEMFC.

PtMo/C electrocatalysts were synthesized by reduction of H_2PtCl_6 – Aldrich and $(NH_4)_6Mo_7O_{24}.4H_2O$ – Mallinckrodt, in the presence of carbon powder (Vulcan XC-72, Cabot), using formic acid [1]. The Pt:Mo compositions were 80:20 and 60:40 with 20 wt.% metal/carbon ratio. The materials were submitted to heat treatment under oxidizing (air, 200 ^oC, 1h) and reducing (H_2, 500 ^oC, 1h) atmospheres, and combination of both. The PtMo/C materials were used to prepare the catalyst layer of gas diffusion electrodes for PEMFC, as described previously [2]. The metal loading was 0.4 mg cm^{-2} for both, anode (PtMo/C) and cathode (Pt/C – E-tek). Fuel cell polarization measurements were carried out galvanostatically with the single cell (5 cm^2, geometric active area) at 85 ^oC, using oxygen saturated with water at 90 ^oC and 1.7 atm, and either pure hydrogen or mixture of hydrogen with 100 ppm CO (H_2/CO) saturated with water at 100 ^oC and 2.0 atm. X-ray absorption studies were conducted *in situ* and the samples consisted of pellets formed with the heat-treated and the un-treated materials, agglutinated using polytetrafluorethylene and containing 10 mg cm^{-2} of metal. Data were collected in the transmission mode at the platinum L_{III} edge, exploring both, the XANES and EXAFS features.

Figure 1 shows single cell polarization curves for pure H_2 and a mixture of H_2/CO (100ppm) for the as-prepared and the heat-treated PtMo/C (60:40) electrocatalysts. For the as prepared and the material treated at 200 ^oC under air, the electrocatalytic activity for the hydrogen oxidation is high in the presence of CO, with loss of only 100 mV at 1 A cm^{-2}, as compared to the results for pure H_2. This behavior may be related to the formation/stabilization of active oxygenated Mo species for CO oxidation by the formic acid. In contrast, the heat treatment at reductive atmosphere leads to a decrease of the electrocatalytic performance, probably due to the destabilization of the active Mo species.

Figure 2 shows XANES spectra and Fourier transform of the EXAFS signals at the Pt L_3 edge, obtained for Pt foil, Pt/C, and PtMo/C electrocatalysts. In Fig. 2a it is observed an increase of the white line magnitude for PtMo/C 60:40 treated under hydrogen. From Figure 2b it is seen that the Pt/C and PtMo/C treated in H_2 present the *fcc* structure of bulk platinum, as indicated by the similarity of the FT features. These results show evidences of formation of a PtMo real alloy phase, particularly for the material treated at 500 ^oC under hydrogen.

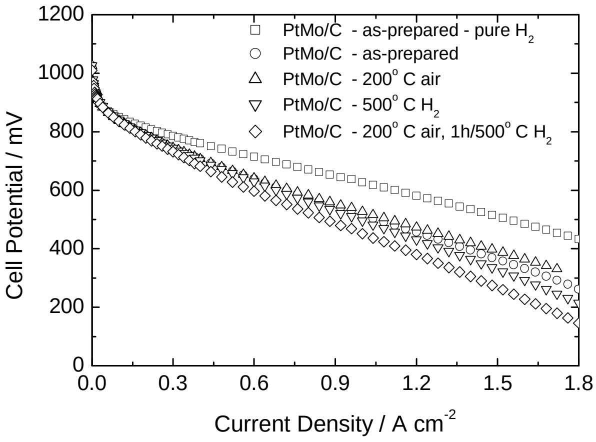

Figure 1 - Polarization curves for PtMo/C (60:40) heat treated at different atmospheres and temperatures.

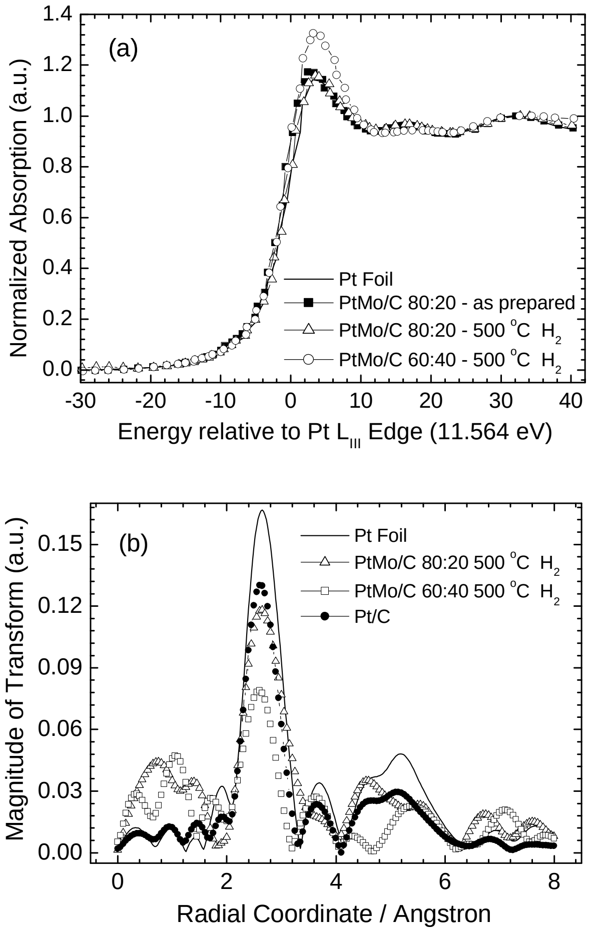

Figure 2 – XANES spectra (a) and Fourier transform of the EXAFS signals (b) at the Pt L_{III} edge of the PtMo/C electrocatalysts at 0.1 V.

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