

Methanol Electro-Oxidation on Bimetallic PtMo/C Catalysts and Pt/C - Mo/C Mechanical Mixtures

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The role of molybdenum in carbon-supported Pt-Mo electrocatalysts was studied with the aim of obtaining active materials to be used as anodes in the methanol electro-oxidation reaction. The catalysts were synthesized by the thermolysis of Mo and Pt carbonyls. Two series were obtained: bimetallic PtMo/C, and Pt/C plus Mo/C mechanical mixtures. The Mo content was changed, with the atomic ratio ranging from 0.0 to 1.0. XRD and XPS analyses of the fresh materials indicated the presence of Pt⁰ and molybdenum oxides (MoO_x). XRD of Mo/C treated electrochemically at constant potential in H₂SO₄ confirmed the formation of molybdenum bronzes with different protonation degrees (H_xMoO₃ 0.3 < x < 2). Cyclic voltammetry indicated that Mo/C does not present the capacity to oxidize methanol nor the intermediate species, but it did show promoter behavior. In the PtMo/C series, low molybdenum contents present the maximum promoting effect on methanol electro-oxidation, as evidenced by lower onset potentials for the methanol oxidation reaction with respect to the Pt/C catalyst. Similar results were registered by the mechanical mixtures, where the Pt sites are separated from the molybdenum bronzes, suggesting that Pt poisoned sites, caused by methanol electro-adsorption, are cleaned by the interaction with molybdenum bronzes (H_xMoO₃) through a process of surface diffusion of oxygen-containing species.

Keywords: PtMo/C, mechanical mixtures, Pt/C, Mo/C, DMFC, methanol electro-oxidation, electrocatalyst.

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