

**Evaluation and Comparative Analysis of Pt-Mo/C Catalysts Synthesized by Different Methods for
Application as Anodes in Direct Methanol Fuel Cells**

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ABSTRACT

It has been found that Pt-Mo catalysts can play an important role in direct methanol fuel cell systems. This activity is explained by some authors in terms of different mechanisms such as the bifunctional mechanism, the ligand effect, the hydrogen spillover effect and it has also been proposed a physical blocking effect of some Pt sites by Mo species. In this work, constant composition materials (Pt_{0.8}Mo_{0.2})_{0.25}/C_{0.75} were synthesized in two different ways, in order to have different surface structures and to compare their activities towards methanol oxidation. The first catalyst consists of two active phases (Pt and Mo) simultaneously deposited on the carbon support. The second catalyst is obtained by the synthesis of monometallic materials (Pt/C and Mo/C) that are mixed and vigorously stirred in suspension, in diethyl ether.

Monometallic and bimetallic materials were synthesized by a carbonyl thermolysis method using, as precursors, molybdenum hexacarbonyl (Mo(CO)₆) and hexachloroplatinic acid (H₂PtCl₆) and using Vulcan XC-72 carbon as support. The synthesized materials were studied by cyclic voltammetry and current-sampled voltammetry tests to evaluate their activities. X-ray diffraction and transmission electron microscopy were carried out in order to determine the relationships between the active phases.

1. Introduction .

Platinum is recognized as the most active catalyst for the oxidation reaction of methanol and, so far, it has been indispensable in the formulation of such materials. However, the formation of different organic intermediates during the methanol oxidation reaction, which are adsorbed on the surface of Pt, cause metal poisoning, reducing its efficiency as a catalyst. Previous studies indicate that the modification of the Pt catalyst with other transition metal lead to interesting results in the methanol oxidation at low potential (lower than in pure Pt) [1]. Some studies suggest that the presence of metal oxides at the catalyst surface can supply oxygen-containing species, promoting the removal of CO (which is the major contaminant) and other organic species adsorbed at Pt sites [2,3].

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It is well known that bimetallic materials showed increased activity in the electro-oxidation reaction of CO, yielding CO₂. This activity is explained by some authors in terms of the so-called bifunctional mechanism whereby the formation of reactive species containing oxygen takes place at lower potential than in pure Pt, promoting the complete oxidation of CO [2,3]. However, other researchers propose that it is an electronic effect (or binder) [4], responsible for the increased activity. In this case, the presence of a second metal modifies and weakens the bond Pt-organic species so that the adsorption energy of CO on these materials is different [4]. Other theories suggest the existence of a hydrogen spillover effect. In this phenomenon, a proton (H⁺) migrates from a Pt site to form metallic bronzes in the promoting phase and leaving Pt active sites available for adsorption of a methanol molecule [5]. Moreover, it has been suggested that, by modifying the surface of a Pt catalyst with metallic molybdenum and MoO₃ species the chemisorption of CO on the surface of Pt (110) can be suppressed due to a physical partial blocking effect of Pt sites by molybdenum, allowing the presence of free active sites for the oxidation reaction and preventing the adsorption of CO at the crystalline platinum plane in which it most strongly adsorbs [6].

Currently the most widely used catalysts to direct methanol fuel cells (DMFC) are formulated with Pt and Ru. Recent works have demonstrated the influence of the structure of particles formed by different oxidation states of Ruthenium in this kind of catalysts to improve the performance of devices using these materials [7, 8]. It is commonly accepted that the Pt-Ru electrocatalyst provides superior activity for the electro-oxidation of methanol in DMFC's. However it has been reported that Ruthenium from several commercial catalysts dissolves into and migrates through the proton exchange membrane (PEM). This process results in loss of activity from oxidation of fuel in the anode and the Pt catalyst activity for oxygen reduction at the cathode decreases [9].

Some research groups and industry laboratories are working on proton exchange membrane fuel cell (PEMFC) with the objective of achieving power densities useful in technological applications and reduce costs to facilitate market entry. Different synthesis methods and characterization techniques for these catalysts and devices have been proposed [10]. Among the commonly used methods to synthesize these materials are: the thermolysis of metal carbonyls [11]; the chemical reduction to obtain small particles at low temperatures (below 100 ° C), and the support treatment to achieve optimal performance [12-18].

Studies on the catalytic effects that take place on bimetallic surfaces, product of pure metals and modified by the deposition of a second metal, are related to the technological development of low temperature fuel cells. One of the main objectives in this research field is the understanding of the CO oxidation. Some researchers have emphasized the use of CO as a test molecule to show the electronic effect associated with this reaction. The CO desorption energy is apparently related to strong intermetallic bonds and mixed orbitals of the active phases. Methanol is probably the most studied one-carbon atom molecule, because it is a fuel with high energy density, that can power fuel cells at low temperature. Hence, a catalyst with high activity for the oxidation reaction of methanol must also have high activity for CO oxidation [19]. In this work, we prepared and studied catalysts

formulated with constant Pt and Mo loadings. One series of these materials was prepared with both active phases simultaneously supported on carbon. The second series consisted of monometallic, carbon-supported Pt and Mo solids, that were mixed in suspension. From the comparison of results from the characterization tests carried out for both series, it is expected to establish if long distance effects between active phases can take place in the methanol electrochemical oxidation.

2. Experimental

2.1 Catalysts synthesis.

As a first step, Pt hexacarbonyl complex was synthesized by bubbling CO, at $25 \text{ cm}^3 \text{ min}^{-1}$, during 24 h, through an aqueous H_2PtCl_6 dissolution. This complex is used as the precursor for the Pt phase in the catalysts and this synthesis procedure allows to have control on the Pt particle size [12,20,21]. The Pt-Mo/C catalyst preparation was carried out by the thermolysis of Pt and Mo carbonyl complexes. Commercial Mo hexacarbonyl (Aldrich) was employed. The adequate amounts of the metallic carbonyl species to obtain solids with a formulation $(\text{Pt}_{0.8}\text{-Mo}_{0.2})_{0.25}/\text{C}_{0.75}$ in weight percent, are dissolved in 1,2-dichlorobenzene and Vulcan XC-72R is added as a suspended phase simultaneously. The temperature of the system is increased up to 110°C and maintained during 4 h, with vigorous stirring. After this stage, the solvent is distilled. The solid is washed twice with diethyl ether and placed in N_2 atmosphere, at 400°C during 2 h. The bimetallic material designed (**Pt-Mo/C**) is thus obtained.

In a second step, starting with the Pt hexacarbonyl and Mo carbonyl complexes, monometallic materials were separately synthesized. Afterwards, the Pt/C and Mo/C solids, were mixed by mechanical stirring in diethyl ether suspension during 5 hr at room temperature, to yield the same overall composition as the bimetallic catalyst. The solid is placed in N_2 atmosphere, at 400°C during 2 h. The obtained product from this suspension mixture shall be designated (**Pt+Mo/C**).

2.2 Electrode preparation and electrochemical measurements.

An ink containing 1 mg of each catalyst dispersed in a $10 \mu\text{L}$ 2-propanol, $10 \mu\text{L}$ NafionTM resin liquid mixture, was prepared. The dispersion was placed in an ultrasound bath during 15 min and $5 \mu\text{L}$ of the ink were placed on the tip of a commercial vitreous carbon disk electrode with the aid of a micropipette. The solvent is evaporated at ambient temperature and a catalytic solid layer is obtained. The catalyst content in this electrode is 2.54 mg cm^{-2} , referred to the geometrical surface area of the disk. (0.5 cm diameter). Cyclic voltammetry experiments were carried out in a three electrode cell at 25°C .

The catalyst layer was used as working electrode, a saturated calomel electrode (SCE) was used as reference and a graphite rod as counter electrode. An aqueous $0.5 \text{ M H}_2\text{SO}_4$ solution was employed as supporting electrolyte in all experiments. The working solution is a 1.0 M methanol, $0.5 \text{ M H}_2\text{SO}_4$ electrolyte. Working media were degassed by bubbling nitrogen during 15 min previous to each experiment. Voltammetry results presented here were obtained at a potential scan rate of 30 mV s^{-1} , with a Voltalab 50 potentiostat. Potentials are referred to the

Normal Hydrogen Electrode (NHE). Before each experiment, electrodes were activated by applying 50 potential cycles, between 300 and 1000 mV vs. NHE in a sulfuric acid solution.

2.3 Characterization by physical techniques

The materials were analyzed by means of High Resolution Transmission Electron Microscopy in a JEOL 2010 microscope working at 200 kV and by Scanning Electron Microscopy. The catalysts were dispersed in isopropanol, in an ultrasound bath for 1 h and the microscope copper grids were impregnated with the liquid.

3. Results and discussion.

(Pt-Mo) catalysts displayed better performances than the (Pt+Mo) material. This performance is observed as a decrease in the oxidation potential of organic species. In figure 1, the voltammetry results of the last potential cycle from the Pt+Mo/C and Pt-Mo are presented. A higher current is observed with (Pt-Mo), suggesting that this material provides an increase in the oxidation catalytic activity. The methanol adsorption – oxidation peak appears at a lower potential than with (Pt+Mo). The same behavior is observed in the reverse sweep, where the organic intermediates oxidation – desorption peak is observed. Furthermore, an analysis of the cyclic voltammetry curves showed that the active phases simultaneously deposited display methanol oxidation current peaks higher than the material obtained from suspension mixing. Much higher electrical charges transferred per VC cycle are obtained in the bimetallic catalyst.

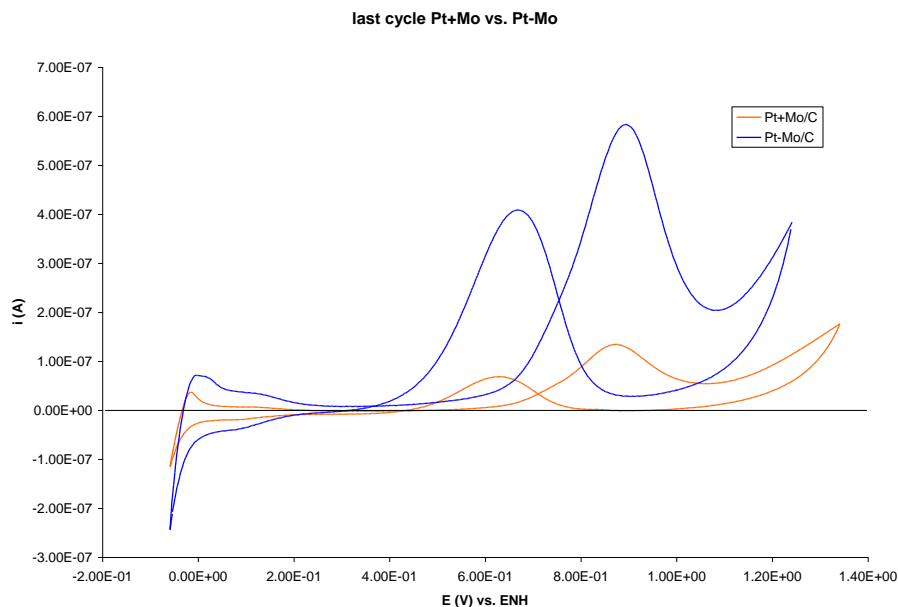


Figure 1. Cyclic voltammetry results from the Pt-Mo/C and Pt+Mo/C materials, in 1.0 M methanol, 0.5 M H_2O_4 , at 30 $mV s^{-1}$.

SEM and TEM images of the (Pt-Mo/C) material, presented in figure 2, reveal that particle sizes of all active phases are not homogeneous, as there are particle sizes from 5 nm to clusters between 50 and 100 nm. In the case

of this materials, a uniform dispersion of the metals on the carbon support is observed although the metallic phases reveal agglomeration in some regions. This can be related to the high activity obtained with this material: if water dissociation is expected to occur on Mo surfaces, and organics adsorption – oxidation takes place on Pt, then the fact of having molybdenum adjacent to platinum can play a role in the catalytic performance improvement.

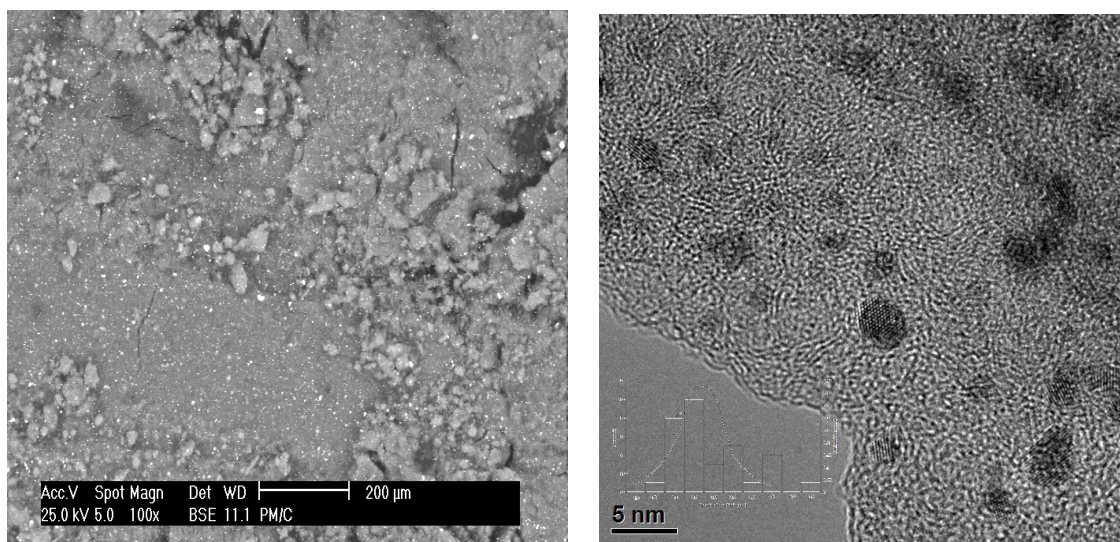


Figure 2. SEM and TEM Micrographs of the Pt-Mo/C material.

In figure 3 is shown an analysis of the charge transferred per cycle in the VC, the difference is large because the transferred charge into the (Pt-Mo) material is higher than the material that was mechanically mixed. This could support theories on the different proposed mechanisms, such as the bifunctional mechanism, the ligand effect, and even the physical blocking effect of Pt sites by Mo species.

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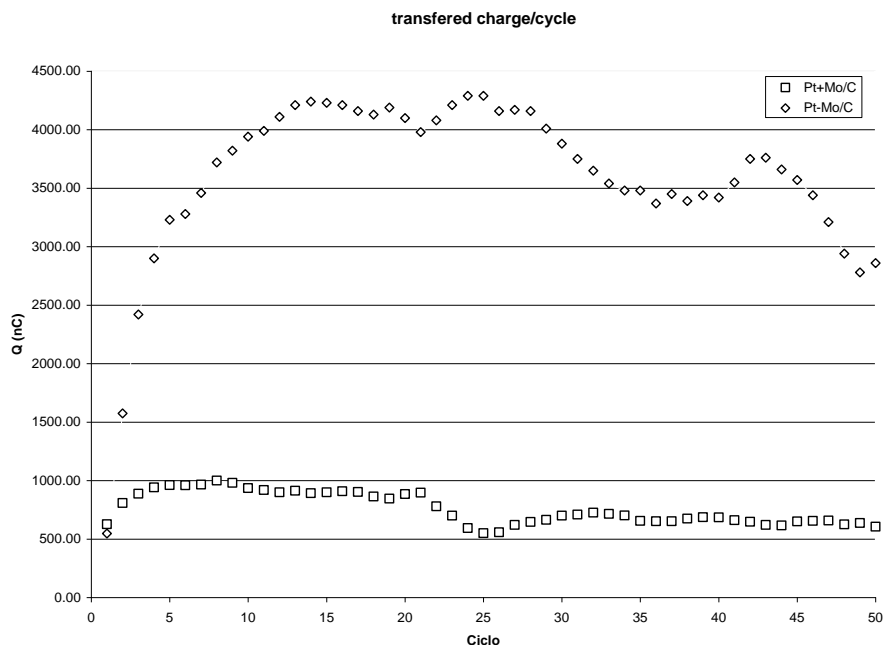


Figure 3. Transferred charge vs. cycle of materials Pt+Mo and Pt-Mo.

4. Conclusions.

The synthesis method allowed to retain the original proportions, although the particle size is not homogeneous, with particles sizes ranging from 5 nm to 100 nm.

The presence of molybdenum allowed the decrease of reaction potentials, which results in a higher catalytic activity. The transferred charge is greater in the material obtained by simultaneous synthesis. This suggests that the promoting role of Mo is due to a short distance effect.

As in previous studies, in this work we demonstrate that Pt – Mo materials can be employed in this kind of device with similar performances and lower production costs than Pt-Ru. The obtained results show that the catalysts synthesized by this method present all the requirements to be efficiently used in direct methanol fuel cells or can be employed in this kind of device with similar performance and lower production costs.

5. Acknowledgements

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6. References.

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Appendix.

Figure 1. Cyclic voltammetry results from the Pt-Mo/C and Pt+Mo/C material, in 1.0 M methanol, 0.5 M H₂ O₄, at 30 mV s⁻¹.

Figure 2. SEM and TEM Micrographs of the Pt-Mo/C material.

Figure 3. Transferred charge vs. VC cycle of Pt+Mo and Pt-Mo materials.