

Electrocatalytic Oxidation of Methanol: Study with Pt:Mo Dispersed Catalysts

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A oxidação eletroquímica do metanol foi estudada sobre ligas de Pt:Mo dispersa em carbono, preparadas utilizando um método recentemente desenvolvido neste laboratório. Análises de EDX confirmaram que a redução simultânea dos sais precursores de Pt e Mo conduzem a presença destes metais nas composições nominais inicialmente calculadas. A adição de Mo sobre Pt causa um aumento da corrente de oxidação, mas não produz um efeito catalítico para oxidação do metanol. A partir dos dados de polarização em várias concentrações de metanol foram obtidos diagramas de Tafel que apresentaram duas inclinações. A técnica de espectroscopia de massa diferencial aplicada "on line" a um experimento voltamétrico foi utilizada para investigar a distribuição de produtos e intermediários formados na oxidação de metanol.

The electrocatalytic oxidation of methanol on Pt:Mo dispersed on carbon prepared using an alternative method recently developed in this laboratory was investigated. The EDX analysis confirmed that the simultaneous reduction of the precursor salts of Pt and Mo leads to the presence of these materials at the nominal composition initially calculated. The addition of Mo to Pt causes an increase of the oxidation currents, but does not improve the catalytic effect for methanol oxidation. Tafel plots for various methanol concentrations showed the presence of two slopes. On line differential electrochemical mass spectrometry (DEMS) was used to investigate the distribution of products and intermediates in methanol oxidation.

Keywords: methanol electrooxidation, Pt:Mo dispersed catalysts

Introduction

The direct methanol fuel cell is an attractive alternative solution for electrochemical energy conversion applied to transportation. Liquid and gas feed systems have been proposed for this fuel cell operating with a solid polymer electrolyte membrane¹. Most of the investigations made during the last years in this fuel cell are directed to the elucidation of the mechanism of the methanol oxidation, in order to find the best catalysts (low cost, good activity) for this reaction².

Kinetic studies on Pt indicate the formation of poisoning intermediates, which can be only oxidized at high potentials. Many binary Pt based electrocatalysts have been proposed for this reaction: Pt:Ru³⁻¹¹, Pt:W¹², Pt:Sn¹², Pt:Mo¹²⁻¹⁴ and ternary systems^{12,15-16}, and seem to give better results than Pt alone.

The present work presents a study the electroactivity of Pt:Mo dispersed catalysts towards the oxidation of methanol in acid medium. Various catalyst compositions were

elaborated and the activities investigated in the presence of different methanol concentrations. For the first time, dispersed catalysts on carbon have been investigated by means of differential electrochemical mass spectrometry (DEMS), with the aim to characterize the possible products and intermediates of the methanol oxidation reaction.

Experimental

The catalysts of Pt:Mo dispersed on carbon were obtained by simultaneous reduction of Pt and Mo compounds (H₂PtCl₆ and (NH)₄Mo₇O₂₄·4H₂O) by a method elaborated in this laboratory¹⁷. The atomic composition of the samples was confirmed by EDX. All the samples contained 20% in weight of catalyst dispersed on carbon and the nominal compositions were: 60:40, 70:30, 80:20, 90:10 and 100:0 of Pt:Mo.

The electrochemical characterization of the catalysts was performed using cyclic voltammetry and polarization techniques at room temperature. Thin porous coating electrodes (TPC)^{18,19} employed in these studies were prepared by mixing the catalyst powders with a dilute suspension (2% w/w) of PTFE emulsion (DuPont TM30) and applied into the recess of a conventional rotating electrode. A conventional one compartment electro-

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chemical glass cell was used in the electrochemical experiments. A platinum foil served as the counter electrode and a reversible hydrogen as the reference electrode (RHE). All the experiments were carried out in 0.5 mol L⁻¹ H₂SO₄ solution (Merck). Methanol was Merck p.a. grade and water distilled and purified in a Milli-Q (Millipore) system. The electrolytes were saturated with purified N₂ gas. All the experiments were conducted at room temperature (25±1°C).

X-ray diffraction (XRD) analyses were carried out with a X-URD, Carl Zeiss X-ray system.

For the DEMS measurements a computer controlled quadrupole mass spectrometer, MKS Instruments, was used. Details on this technique are given elsewhere²⁰⁻²². The method allows the on-line detection of volatile and gaseous products of electrochemical reactions during the application of a potential scan. The electrochemical cell was constructed according to the principles described in Ref. 23. A reversible hydrogen and a platinum foil were used as reference and counter electrodes, respectively. The working electrode for the DEMS experiments was prepared by mixing the catalyst powders with a dilute suspension (1% w/w) of PTFE. This mixture was filtered and applied on a gold layer (1.13 cm² area, 50 nm thickness) prepared by sputtering gold onto a SCIMAT® membrane (thickness 60µm, mean pore size 0.17µm, 50% porosity).

Results and Discussion

After preparation, the dispersed Pt:Mo materials with various Pt:Mo ratios were characterised by EDX. These results are presented in Table 1. As seen in this Table, EDX analyses confirm the nominal composition of the samples. Figure 1 presents a comparison of the behaviour of the X-ray diffraction patterns of all catalysts prepared in this work with commercial E-Tek 75:25 Pt:Mo samples. The results confirm that the samples prepared here present the same structure than the E-Tek material. The differences in the peak intensities are due to differences on the alloy concentrations (the E-Tek powder contains 30 % Pt:Mo/C and the samples prepared in this work 20 % Pt:Mo/C).

Table 1. Composition analysis by EDX of the TPC Pt:Mo lectrodes.

Nominal composition of the TPC Pt:Mo catalysts	EDX	EDX
	Pt content Atom %	Mo content Atom %
90 : 10	86	14
80 : 20	77	23
70 : 30	67	33
60 : 40	63	37

Figure 2 shows cyclic voltammograms in absence of methanol, recorded at 10 mV s⁻¹ in 0.5 mol L⁻¹ H₂SO₄, for different thin porous coating Pt:Mo electrodes. The results

show evidences of both Pt and Mo features, although the Pt-H_{upd} region is not as well defined as on Pt/C or Pt:Ru/C electrodes^{19,24}. Also, no evidences of the Pt-hydro-oxides features are seen. When the Mo contents increases from 10 to 40 atom percent, there is a progressive increase in the currents at potentials corresponding to the Pt-H_{upd} and double layer regions of platinum. A redox process is also apparent at around 0.5 V, with a current intensity that increases with the Mo content.

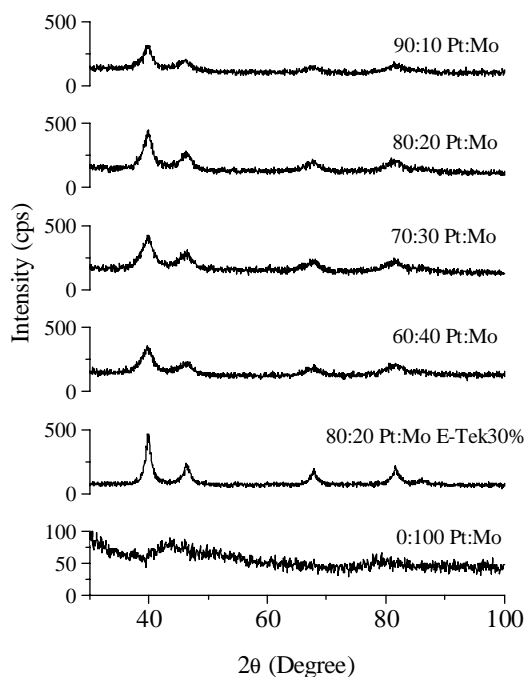


Figure 1. X-ray diffraction results for Pt:Mo catalysts. The compositions are indicated in the Figure.

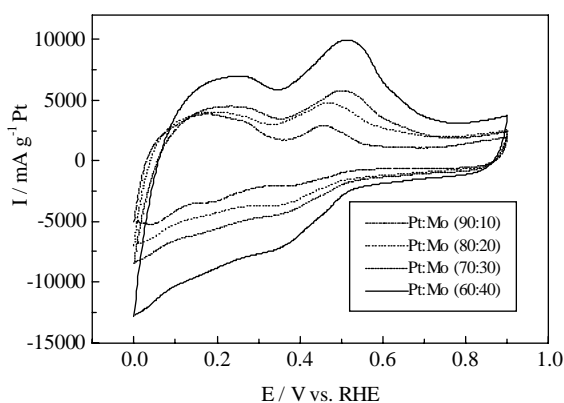


Figure 2. Cyclic voltammograms for the different Pt:Mo electrodes recorded in 0.5 mol L⁻¹ H₂SO₄ at 10 mV s⁻¹. Currents were normalized with respect to the Pt loading.

The increase of current in the double layer region was observed previously with Pt:Ru catalysts²⁴ and various investigations have shown that it is due to the formation of

adsorbed oxygenated species. This may also be the case for the Pt:Mo catalysts, for which X-ray absorption spectroscopy have indicated the presence of oxide layers for potentials as low as 0.1 V²⁵. The presence of the redox process at about 0.5 V has been reported previously for other Pt:Mo catalysts²⁵ and it is most likely due to a $\text{Mo}^{4+} \leftrightarrow \text{Mo}^{6+}$ oxidation state change of Mo.

Figure 3 presents cyclic voltammograms for methanol oxidation on the carbon supported Pt:Mo (70:30) catalyst. Comparing the curves for the different methanol concentrations, only small differences are observed in the potentials corresponding to the onset of the methanol oxidation reaction. Figure 4 illustrates the corresponding $\log(j)$ vs. E curves (Tafel diagrams) obtained from the cathodic scans of the cyclic voltammograms with the currents normalised with respect to the Pt loading. In this case, the results show a potential shift of ca. 25 mV to more positive potentials for the methanol concentration of 1 mol L⁻¹ in comparison with the concentration of 0.1 mol L⁻¹, indicating a smaller catalytic effect at the higher concentration. In all cases the Tafel diagrams present two slopes: $\sim 35 \text{ mV dec}^{-1}$ in the low current region and $\sim 240 \text{ mV dec}^{-1}$ in the high current region.

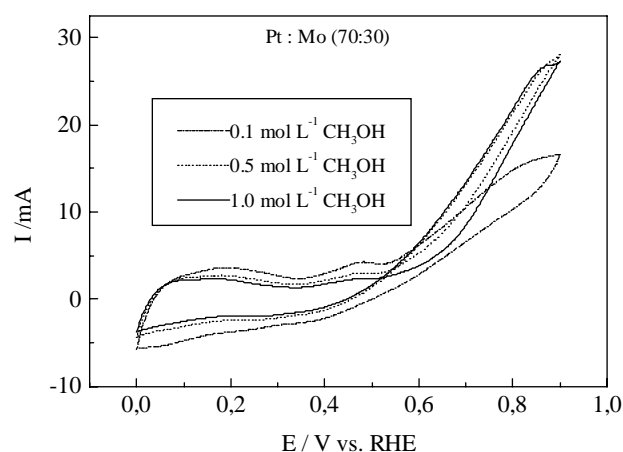


Figure 3. Cyclic voltammograms for Pt:Mo (70:30) recorded in 0.5 mol L⁻¹ H₂SO₄ at 10 mV s⁻¹ in the presence of various methanol concentrations.

Cyclic voltammograms in the presence of 0.1 mol L⁻¹ and 1.0 mol L⁻¹ CH₃OH in 0.5 mol L⁻¹ H₂SO₄ for different Pt:Mo electrodes at 10 mV s⁻¹ are presented in Figure 5. In both cases the currents were normalised with respect to the Pt loading in the electrode. In Figure 6, the results corresponding to the anodic scan for 0.1 mol L⁻¹ methanol were re-plotted after subtraction of the background responses due to the Pt:Mo features in the supporting electrolyte (Figure 2).

In Figure 5, it is seen that the carbon supported 60:40 Pt:Mo catalyst gives the higher current density for the oxidation processes in both methanol concentrations.

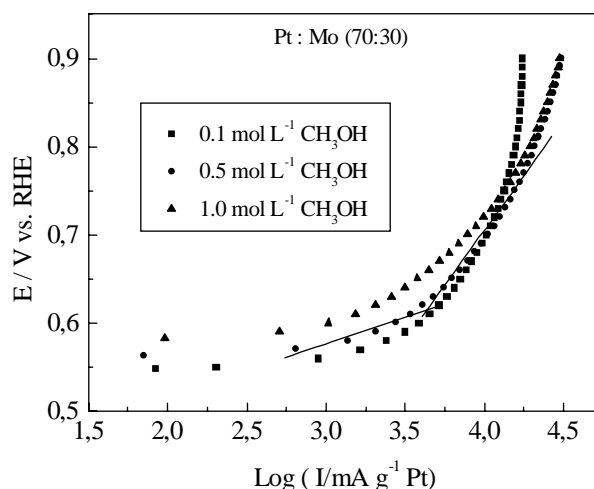


Figure 4. $\log(j)$ vs. E curves for the oxidation of methanol on Pt:Mo (70:30) catalysts in 0.5 mol L⁻¹ H₂SO₄. Currents were normalized with respect to the Pt loading.

However, after correction of background currents (Figure 6), it is observed that the onset of methanol oxidation starts at lower potentials for the catalyst with 90:10 Pt:Mo atomic ratio, demonstrating the higher catalytic activity of this material compared with the other compositions. Figure 6 also shows a comparison of the behaviour of the catalysts used in this work with that of a commercial E-Tek 75:25 Pt:Mo sample. These results clearly show that the commercial sample presents a lower catalytic effect than the catalysts prepared here with alternative method.

Figure 7 presents Tafel diagrams comparing the performance of the several Pt:Mo catalysts with that of pure Pt for methanol oxidation. For all Pt:Mo catalysts, much smaller currents were observed below 0.55/0.6 V, when compared with the response of pure Pt. However, for more positive potentials, the activity of the Pt:Mo catalysts increases with the amount of Mo and the electrodes with 70:30 and 60:40 Pt:Mo present higher oxidation currents than those of the catalyst containing Pt alone. This behaviour indicates that the Pt:Mo catalysts are not much effective for the initiation of the methanol oxidation reaction. However, the increase of the oxidation currents at high potentials denotes a better tolerance to the poisoning species (mainly CO) formed as intermediates in the oxidation of methanol. This observation is in agreement with the improvements in CO tolerance observed with Pt:Mo/C for the hydrogen oxidation reaction at 85°C with 100 ppm CO in the H₂ gas, which show a two to three fold enhancement in performance compared to the current state of the art Pt:Ru/C anodes²⁶.

As in the case of Figure 4, the results in Figure 7 show that for the Pt:Mo catalysts the Tafel plots present two slopes, that is, 30-35 mV dec⁻¹ at low current densities and 230-250 mV dec⁻¹ at high current densities. It is interesting to com-

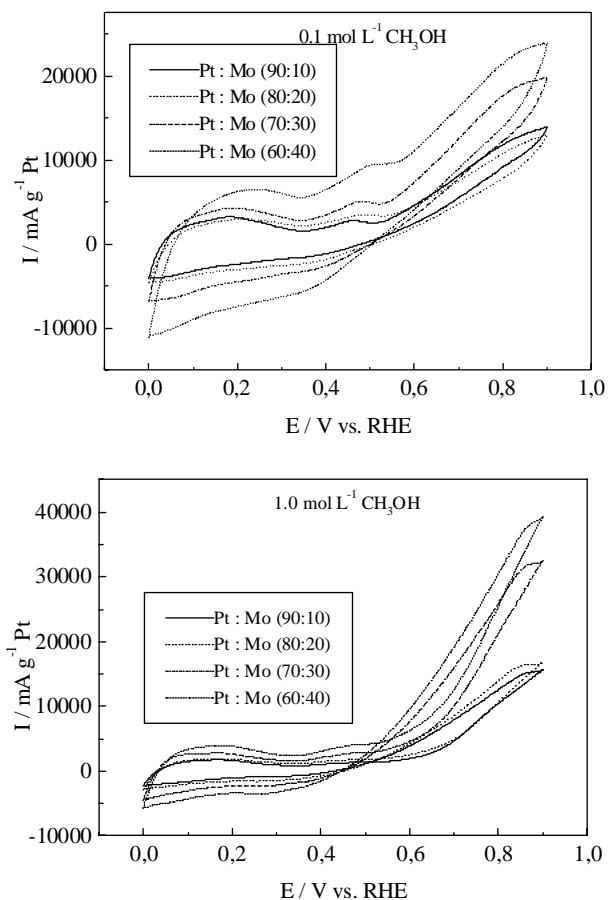


Figure 5. Cyclic voltammograms for the different Pt:Mo electrodes recorded in 0.5 mol L⁻¹ H₂SO₄ at 10 mV s⁻¹ in the presence of 0.1 mol L⁻¹ CH₃OH and 1.0 mol L⁻¹ CH₃OH. Currents were normalized with respect to the Pt loading.

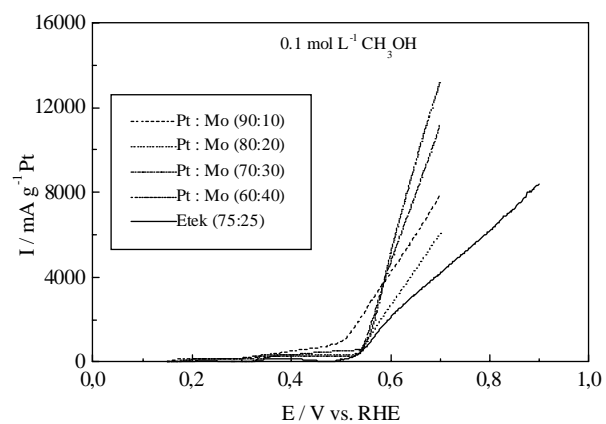


Figure 6. Comparison of current density vs. potential curves of the different TPC Pt:Mo electrodes and for a commercial E-Tek sample in 0.5 mol L⁻¹ H₂SO₄ in the presence of 0.1 mol L⁻¹ CH₃OH. Currents were corrected for the background response and normalized with respect to the Pt loading.

pare these data with those in pure Pt for which the slopes are 100 and 270 mV dec⁻¹. The first value for this catalyst is the same as that reported in the literature²⁶. The different values

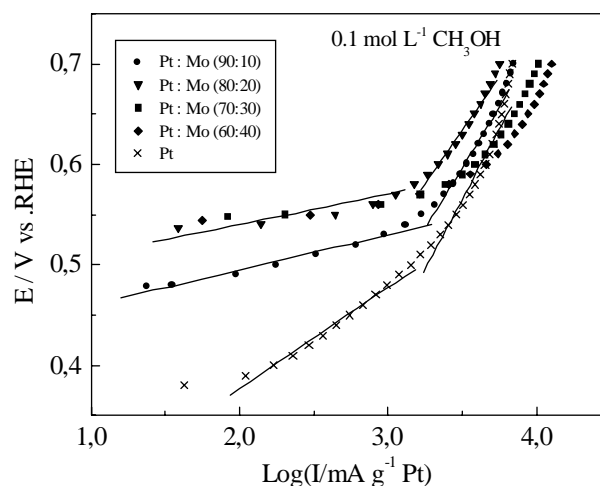


Figure 7. Comparison of Tafel plots for the different TPC electrodes: Pt:Mo and Pt, in 0.5 mol L⁻¹ H₂SO₄ in the presence of 0.1 M CH₃OH.

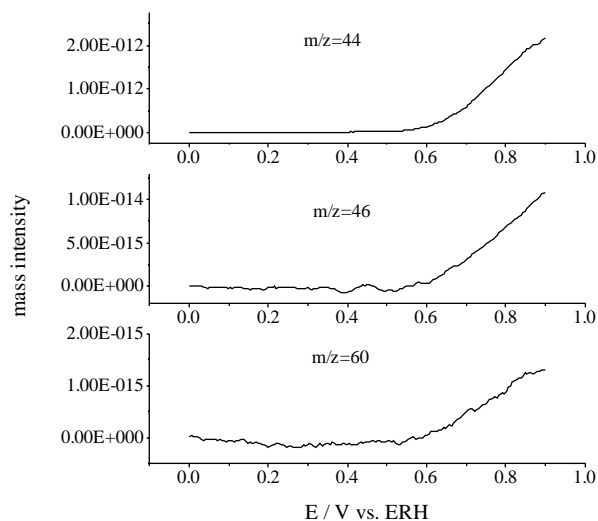


Figure 8. On-line mass signals vs. potential for the DEMS technique for the oxidation of methanol on Pt:Mo (60:40) catalysts in 0.5 mol L⁻¹ H₂SO₄ in the presence of 0.1 mol L⁻¹ CH₃OH at 10 mV s⁻¹: (a) m/z = 44; (b) m/z = 46; (c) m/z = 60.

of the first Tafel slope for the Pt and Pt:Mo catalysts can be related to effects of the particle size and distribution, because these have been shown to play important roles in the mechanism of oxidation of small organic molecules such as methanol, formic acid and carbon monoxide²⁷. However, in the present case, it is more probable that the differences are related to the formation of oxygenated species at low potentials. The presence of these species is evident for Pt:Mo but they are completely absent for pure Pt.

Figure 8 presents the results of DEMS analysis for the oxidation of methanol in the 60:40 Pt:Mo catalyst. The mass signals (m/z) analysed were: 44 (CO₂), 46 (HCOOH) and 60 (HCOOCH₃). It is seen that all mass signals start to increase at about 0.55 V, corresponding to the same potential

where the methanol oxidation starts to take place (Figs. 3 and 5). It is observed that the $m/z = 44$ signal is considerable larger than the others, indicating that the most important product in the oxidation of methanol is CO_2 . This behaviour is consistent with the DEMS analysis of other non-dispersed catalysts^{11,22}. Further studies of the oxidation of methanol are under way to compare the product distributions for Pt:Mo/C with those of other dispersed catalysts.

Conclusion

The experiments described in this work show that the alternative preparation method of the Pt:Mo catalysts leads to active materials. The addition of Mo to Pt causes a significant increase of the oxidation currents, but does not show a catalytic effect for the initiation of methanol oxidation.

The DEMS experiments, performed for the first time in this type of catalyst, show the formation of CO_2 , formic acid and methyl formate at potentials that coincide with the increase of the electrochemical oxidation currents.

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