



OXYGEN REDUCTION STUDIES ON CARBON – SUPPORTED Pt-M CATALYSTS (M: Ru, W, Mo)

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ABSTRACT

The activities of a series of carbon-supported bimetallic catalysts, with different active phases loadings, were tested towards the oxygen reduction reaction. Pt was used in all materials and its proportion was kept constant. Mo, W and Ru were used as promoting phases. Rotating Disk electrode experiments revealed that Pt-Ru displayed the best performance in oxygen reduction among the studied materials. The materials with the highest loadings of the second metal revealed the highest activities.

Keywords: Oxygen reduction reaction, fuel cell catalyst.



1. INTRODUCTION

The oxygen reduction reaction is a limiting factor in the development of low-temperature fuel cells, mainly because of the complex reaction mechanisms and the involved slow kinetics [1,2]. Catalysts formulated with platinum supported on carbon have been used in a large number of works, as cathode electrodes because they have proven to be efficient for the four-electron reduction reaction of O_2 to yield water [3,4]. Combination of Pt with other transition elements such as W, Mo, Ru, Sn, [5,6] has revealed better performances of the cathodic catalyst layers. It has been proposed that tungsten promotes hydrogen peroxide reduction [7,8], an intermediate in the complete Oxygen Reduction Reaction (ORR). It has also been reported that Ru-based catalysts exhibit good activity towards the ORR [9].

The aim of this work is to evaluate the performance of Ru, W and Mo as promoting phases, in combination with Pt, in cathode catalysts, and to evaluate the effects related to the proportions of each component.

2. EXPERIMENTAL PROCEDURE

2.1 Catalysts synthesis and electrodes preparation

The synthesis of Pt-Mo/C catalysts was carried out in a reflux system where Pt carbonyl complex, the second metal (M) carbonyl complex, and vulcan XC72R carbon were dissolved or suspended in o-xylene [10]. The temperature was kept at 140 °C and reflux was maintained for 24 h. Once the reaction time was elapsed, the xylene was distilled, the catalysts were washed with diethyl ether three times and heated at 400 °C in N_2 atmosphere for 1 hour. The nominal composition of each material is presented in table 1. As it can be seen, the platinum loading was constant in all cases, and the proportions of M and vulcan carbon changed.

A catalytic ink was prepared with 1 mg of the electrocatalyst and 16 ml of a Nafion solution (3% isopropanol). Electrodes were prepared by the deposition of 5 μ L of the ink onto the surface of a glassy carbon rotating disk electrode, with a 0.5 cm diameter. This corresponds to a 2.5 μ g catalyst loading in these electrodes. The film was left to dry at room temperature during



12 h before the tests. In a previous work, the morphology of these layers was investigated by means of Scanning Electron Microscopy, and revealed no important differences in porosity or electrode surface area as a function of the catalyst composition [11].

Table 1. Prepared catalysts, where M designates Ru, W or Mo.

Catalyst	Weight percent		
	Pt	M	Carbon
Pt/C	20	0	80
Pt50-M50	20	20	60
Pt67-M33	20	10	70
Pt80-M20	20	5	75
M/C	0	20	80

2.2 Electrochemical experiments

The electrolyte employed in all cases was 0.5 M H₂SO₄ in bidistilled, deionized water. The electrolytes were first degassed by bubbling N₂ for 15 minutes. The open circuit potential was then measured and cyclic potential sweeps, between -300 mV and 1400 mV vs. Standard Calomel Electrode (SCE) were applied in order to activate the working electrode. Afterwards, a potential step was applied at -300 mV vs. SCE to clean the surface. The electrolyte is then oxygenated by bubbling O₂ (99.99 %) during 15 minutes.

ORR studies are then carried out in a conventional three-electrode cell, with SCE as reference, a graphite rod as counter electrode and the catalyst on the RDE as working electrode. The experiments consisted of a potential scan from 670 to -200 mV vs. SCE with varying rotation speeds, from 0 rpm to 2000 rpm. Scan rate was kept at 10 mV/s for all experiments.

3. RESULTS AND DISCUSSION

As an example of the obtained results, in figure 1 is presented the series of polarization curves obtained with Pt67-Ru33, at the studied rotation speeds. Similar curves were obtained with all Pt-containing materials. Here, a diffusion peak can be observed at 0.5 V vs. SCE in the curve without agitation (0 rpm) and in those with low rotating speeds (100 and 250 rpm). This is due to the ORR entering the mass transfer control regime. A diffusion control plateau is then



observed in all curves between 0.3 and -0.05 V vs. SCE. In this domain the reaction is under steady state conditions and the limiting current can be recorded. At potentials below -0.1 V vs. SCE the cathodic current increases again due to the H₂ discharge.

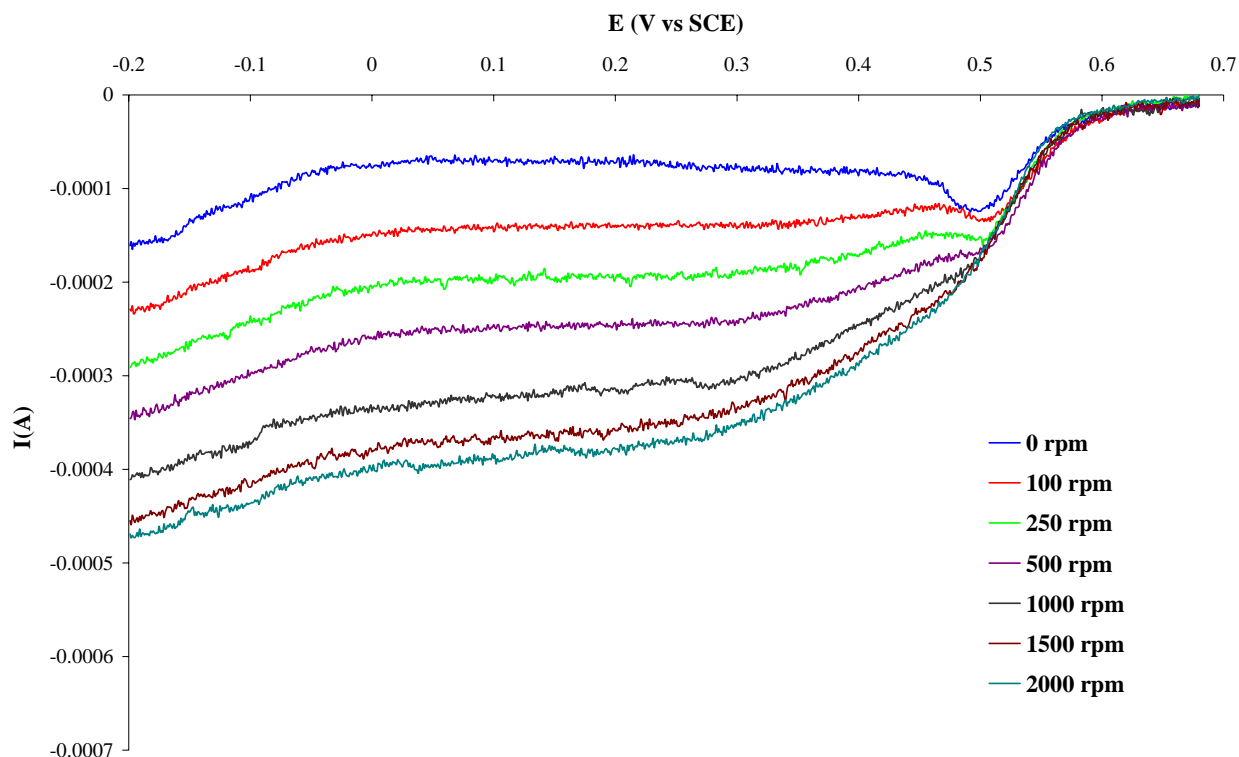


Figure 1. Typical polarization curves obtained from Pt67-Ru33 at varying rotation speed

In figure 2, the limiting current is recorded for each set of curves at 0 V vs. SCE and plotted against the square root of the rotation speed ($\omega^{1/2}$). A linear dependence of I_L with ω is observed at low rotation speeds. At high ω values, a deviation from this behavior occurs. It can be seen that Pt50-M50 is, in all cases, the proportion that provides the highest current. Among the three studied promoting phases, ruthenium is the metal that offers the best performances with electrical currents about 2 mA higher than Pt/C.

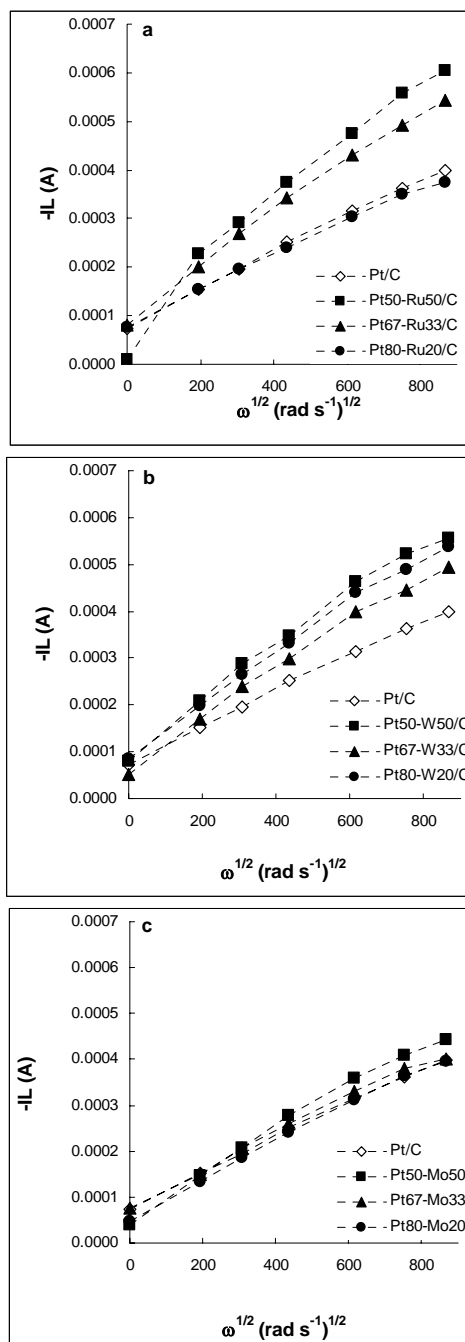


Figure 2. Dependence of the limiting current, recorded at 0 V vs. SCE, on the rotation speed ($\omega^{1/2}$) for each catalyst.
a) Pt-Ru; b) Pt-W; c) Pt-Mo



4. CONCLUSION

Catalysts with constant Pt loadings and different proportional quantities of a second metal (Ru, W or Mo) and vulcan carbon were synthesized. Ru proved to be the best material to activate, in combination with Pt, the Oxygen Reduction Reaction. Mo yielded poor results when compared with Pt-Ru materials, but still, the electrical currents obtained with Pt50-Mo50 were higher than those observed on Pt alone. High loadings of the second metal improved the catalysts performances, since for all the studied materials Pt50-M50 is the composition that offers the best results. The use of Pt cannot be avoided because none of the M/C materials revealed any oxygen reduction activity.

5. REFERENCES

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