

Preparation of M-M_xS_y (M = Pt, Rh) Supported Nanoparticles and its Application as Methanol-Tolerant Oxygen Reduction Electrocatalysts

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Introduction

The growing interest in low temperature fuel cells has been a great motivation for the development and study of supported catalysts. In Direct Methanol Fuel Cells (DMFC), one of the main problems which decrease the efficiency of the cell, is the methanol crossover [1]. To overwhelm this problem more selective electrode materials for oxygen reduction reaction (ORR) in the presence of alcohols are necessary. Among these materials, transition metal chalcogenides have shown greater selectivity [2]. The most easily prepared chalcogenides have M_xX_y structure, where M = transition metal and X = S, Se or Te [3]. Despite the variety of methods studied during the past years [2], it is still necessary to develop simpler methods of lower costs. In the present research, the formic acid method [4] was modified for the preparation of M-M_xS_y/C using thiourea (TU) as sulfur source. M-M_xS_y (M = Pt,Rh) supported nanoparticles were prepared using different amounts of thiourea (TU), changing the M: M_xS_y ratio. All materials were well characterized. The electrocatalytic activity towards the ORR in the presence and absence of Methanol was studied. Also, the effect of an electrochemical or thermal treatment was evaluated.

Experimental

For the catalysts preparation the formic acid method [4] was used, with adequate quantities of H₂PtCl₆ and RhCl₃ solutions (to obtain a Pt:Rh 50:50 ratio). The final solution was made to contain different concentrations of thiourea (TU) in the range 1–5 mmol L⁻¹. A material using only H₂PtCl₆ and TU 5 mmol L⁻¹ was prepared for comparison.

Electrochemical experiments were carried out at 25 °C, in H₂SO₄ 0.5 mol L⁻¹. Potentials were measured using a reversible hydrogen electrode (RHE). The working electrode was prepared by applying a thin layer of the supported catalyst on a glassy carbon disk according to a method already described [5]. The ORR experiments were carried out with O₂-saturated solution without and with methanol 0.1 and 0.5 mol L⁻¹, using a rotating disc electrode (RDE).

Part of the materials was thermally treated (TT) at 300 °C for 2 hours in a 20%-H₂/Ar atmosphere. Also, part of them were electrochemically treated by performing 100 cycles between 0.05-1.2 V.

Results and Discussion

Transmission Electron Microscopy (TEM) showed that all prepared materials were well dispersed in the carbon support (not shown). Using X-Ray Diffraction (XRD) (not shown) and X-Ray Photoelectron Spectroscopy (XPS) it was determined that both crystalline metallic and non-crystalline metal sulfide phases were formed. The M:Mt_xS_y ratio increases as the TU concentration increases (Figure 1a). XPS and Extended X-ray Absorption Fine Structure (EXAFS) results showed that the platinum containing chalcogenide phase is mainly PtS and that a Rh_xS_y phase is formed. The materials prepared with TU 5 mmol L⁻¹ can be described as being PtS/C and Rh-Rh_xS_y-PtS/C. All

materials were more tolerant to methanol than the commercial Pt/C (E-TEK). Thermal treatment under H₂ atmosphere reduces almost completely the PtS and less effectively the Rh_xS_y, as can be seen by XPS (Figure 1b and 1c). The electrocatalytic activity towards the ORR increases after these treatment, probably due to the partial reduction of the chalcogenide phases. However, this takes place without a major loss of selectivity (Figure 2), possibly as a result of the remaining PtS and Rh_xS_y after treatment.

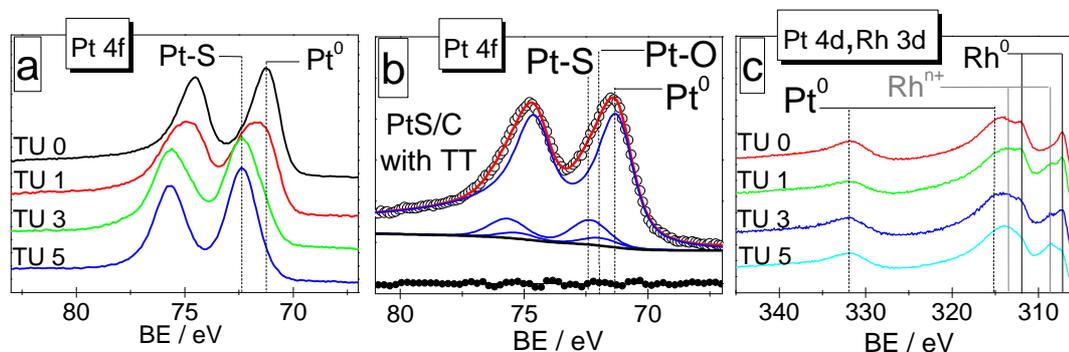


Figure 1. X-ray photoelectron spectra collected at the D04A-SXS beam line of the National Laboratory of Synchrotron light, $h\nu = 1840$ eV, $E_{\text{pass}} = 20$ eV. (a and c) platinum and rhodium containing catalysts. (b and c) Thermally treated catalysts. TU concentration and BE of each core line are indicated in the figure.

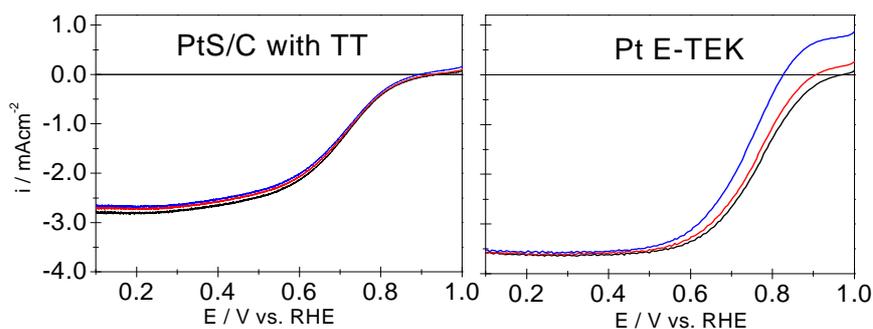


Figure 2. RDE polarization curves. 25 °C, O₂-saturated, H₂SO₄ 0.5 mol L⁻¹, 900 rpm. Without CH₃OH (black), CH₃OH 0.1 mol L⁻¹ (red) and CH₃OH 0.1 mol L⁻¹ (blue).

The electrochemical treatment also improved the catalytic activity of the catalysts (not shown). The activity loss in the presence of methanol was higher than for the thermally treated materials. Nevertheless, the activity loss was lower than for the commercial Pt/C catalyst.

A straightforward methodology for the preparation of supported catalysts based on noble metal sulfides was developed. Improvement in the electrocatalytic activity towards the ORR is easily achieved by thermal treatment in H₂/Ar or electrochemically, although other treatments or combination of them could be used.

Acknowledgements

The authors want to acknowledge CNPq and FAPESP for fellowships and financial support. Also, acknowledges to the National Laboratory of Synchrotron light (LNLS).

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