

**DEVELOPMENT OF NEW SYSTEMS OF NANO-DISPERSE
Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C ELECTROCATALYSTS TOLERANT TO CARBON
MONOXIDE (CO) FOR PEMFC ANODES**

J. Nandenha^a, R. A. Isidoro^a, M. A. Dresch^a, V. C. Fernandes^a,
E. M. Aricó^a, E. I. Santiago^a, G. Rothenberg^b, W. S. Oliveira^c, M. Linardi^a

^a Centro de Células a Combustível, IPEN/CNEN-SP, São Paulo – SP, Brasil

^b Van't Hoff Institut for Molecular Science, University of Amsterdam – Netherlands

^c Engenharia Química, Unicamp, Campinas – SP, Brasil

ABSTRACT

The nanophase material (powder) of Ce_{0.9}W_{0.1}O₂ was synthesized via coprecipitation of oxalates of cerium (IV) and tungsten cations. Pt-Ce_{0.9}W_{0.1}O₂ (2 wt% Pt) was prepared by an alcohol-reduction process using H₂PtCl₆.6H₂O as source of Pt, Ce_{0.9}W_{0.1}O₂ as support and ethylene glycol as solvent and reducing agent. Pt-Ce_{0.9}W_{0.1}O₂ was physically mixed with commercial Pt/C E-TEK (20 w% Pt) to produce the Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C electrocatalyst. The prepared electrocatalysts were characterized by energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and CO stripping. The performances of Pt/C E-TEK and Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C electrocatalysts were tested in single fuel cell fed with a mixture H₂/CO (100 ppm of CO). The results showed that the mixture of 2%Pt-Ce_{0.9}W_{0.1}O₂ and Pt/C E-TEK increases the CO tolerance in a single fuel cell operating at 85 °C compared with Pt/C E-TEK.

Introduction

The pollution generated by burning fossil fuels and the possible shortage of fuel (mainly oil) are reasons to hasten the search for alternative energy sources. In this context, fuel cells have emerged as a promising alternative for portable, mobile and stationary applications due its high efficiency and fuel flexibility. PEMFC (Proton Exchange Membrane Fuel Cell) is the most promising among the various fuel cell types. Platinum is the main metal used in anodes and cathodes of PEMFC increasing the kinetics of electrochemical reactions and enabling the use of fuel cells [1].

Hydrogen gas (H₂) is the fuel that provides the best fuel cell efficiency and can be obtained by water electrolysis or by steam reforming of hydrocarbons. Despite the purity of hydrogen gas obtained by electrolysis, the production cost of this method is very high and therefore most of the H₂ produced in the world comes from the reforming of hydrocarbons, however, in this process carbon monoxide (CO) is produced as by-product. Carbon monoxide adsorbs strongly on the Pt surface and poison the electrocatalyst. In this manner, few ppm of CO in the feed of H₂ leads to a decrease in fuel cell performance in more than 80%. An alternative to circumvent this problem is the addition of

co-catalysts such as Ru and ceria (CeO_2) that provide oxygen species at low potential, facilitating the oxidation of CO to CO_2 [1, 2].

The objective of this work was modify the commercial Pt/C E-TEK electrocatalyst by the addition of 2%Pt- $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$ giving rise to the electrocatalyst called Pt-(2%Pt- $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$)/C. The obtained material was characterized by XRD, EDX and CO stripping and tested as anode in single fuel cell operating with H_2/CO (100 ppm of CO) at 85 °C.

Experimental

The chemicals reagent of P. A. grade and deionized water of specific conductivity less than 0.1 $\mu\text{S}/\text{cm}$ were used in the synthesis of the materials. The nanophase material (powder) of $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$ was synthesized via coprecipitation of cerium (IV) oxalates and tungsten cations [3, 4].

The 2%Pt- $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$ material was prepared by an alcohol-reduction process [2] using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) as source of platinum, ceria doped with tungsten $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$ as support and ethylene glycol as solvent and reducing agent. Briefly, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$ were added in a solution of ethylene glycol/water (75/25, v/v). After this, 2 mL of KOH 1.0 mol. L^{-1} was added [5] and the resulting mixture was treated in a ultrasonic bath for 20 min and submitted to reflux at 140 °C for 3 h. The resultant solid suspension was filtered, washed with water and dried at 70 °C for 3 h. The Pt- $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$ material was prepared with 2 wt% of Pt.

2%Pt- $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$ material was physically mixed with commercial Pt/C E-TEK (20 wt% Pt) to produce the Pt(2%Pt- $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$)/C electrocatalyst with a mass ratio of 70:30 in the following manner: commercial Pt/C E-TEK and 2%Pt- $\text{Ce}_{0.9}\text{W}_{0.1}\text{O}_2$ were dispersed in a mixture of water/2-propanol and treated in a ultrasonic bath for 15 min. Subsequently, the suspension was submitted to mechanical stirring for 2 h and finally was dried at room temperature and open atmosphere.

EDX analysis were performed using a scanning electron microscope, Philips XL30 model with an electron beam of 20 kV and equipped with microanalyser EDAX DX-4 model.

X-ray diffraction was performed in a Rigaku diffractometer (MuniFlex II model) using a radiation source of $\text{CuK}\alpha$ ($\lambda = 1.54056 \text{ \AA}$). The experiments were performed in the creaks of $2\theta = 20^\circ - 90^\circ$ with the scan speed of $2^\circ(2\theta)/\text{min}$.

The CO stripping experiments were performed in fuel cells, using the potentiostat-galvanostat (Autolab) and connected to active booster (BSTR10A-Autolab) and coupled to computer. In the CO stripping, the anode was used as work electrode and the cathode as reference electrode and counter electrode. The CO stripping experiments were performed using the injection of the mixture of H_2/CO (1000 ppm of CO) at the scan rate equal to 20 mV. s^{-1} in the range 0.1 to 0.9 V at room temperature.

The polarization measurements were performed in a single cell of 5 cm^2 of active geometrical area, with the anode and cathode humidified externally at 100 °C and 90 °C, respectively. For the experiments was maintained a pressure of 2 bar in the anode and cathode. The cell temperature was 85 °C with the flow of H_2/CO (100 ppm of CO) equal to 300 $\text{mL} \cdot \text{min}^{-1}$ and 516 $\text{mL} \cdot \text{min}^{-1}$ of O_2 .

Results and discussion

In Table 1 is shown the comparison of the nominal mass ratio and the mass ratio obtained by EDX of the components of 2%Pt-(Ce_{0.9}W_{0.1}O₂)/C electrocatalyst prepared by the physical mixing process.

Table 1: Nominal mass ratio and mass ratio obtained by EDX of the Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C electrocatalyst

Mass proportion of Pt-(2%Pt-Ce _{0.9} W _{0.1} O ₂)/C		Nominal mass ratio	Mass ratio (EDX)
Pt	Ce _{0.9} W _{0.1} O ₂	Pt:Ce:W	Pt:Ce:W
70	30	72:25:03	66:30:04

The results shows that the obtained Pt:Ce:W mass ratio by EDX is similar to the nominal mass ratio.

In Figure 1 are shown the X-ray diffractograms of Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C 70:30 and commercial Pt/C E-TEK electrocatalysts. Pt/C E-TEK presents four peaks at about $2\theta = 40^\circ$, 47° , 68° and 82° that are associated to the (111), (200), (220) and (311) planes, respectively, which are characteristic of the face-centered cubic (fcc) structure of Pt [2]. For Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C besides the peaks of Pt(fcc) structure it is also observed the peaks at about $2\theta = 29^\circ$, 33° , 47° , 56° , 59° , 69° , 77° , 79° and 88° attributed to (111), (200), (220), (311), (222), (400), (331), (420) and (422) planes, respectively, CeO₂ phase [2]. The crystallite sizes of Pt(fcc) and CeO₂ phases of the Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C electrocatalyst were calculated using Scherrer equation and the obtained values are 2 and 16 nm, respectively.

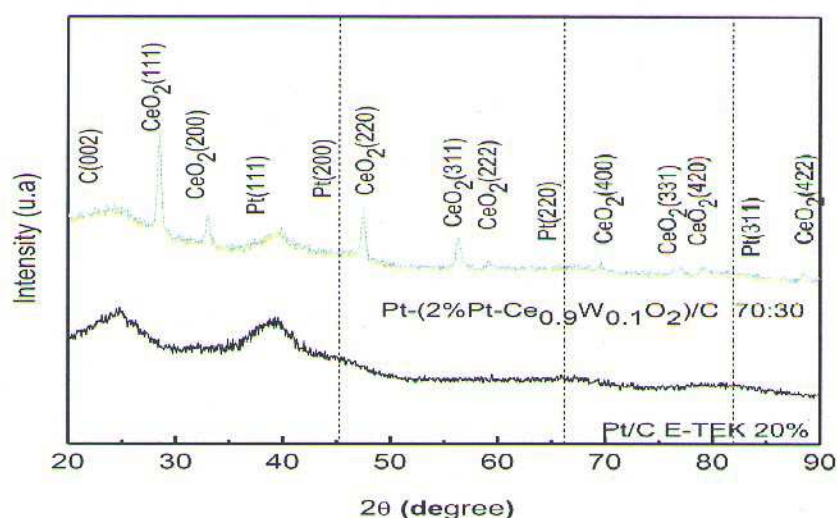
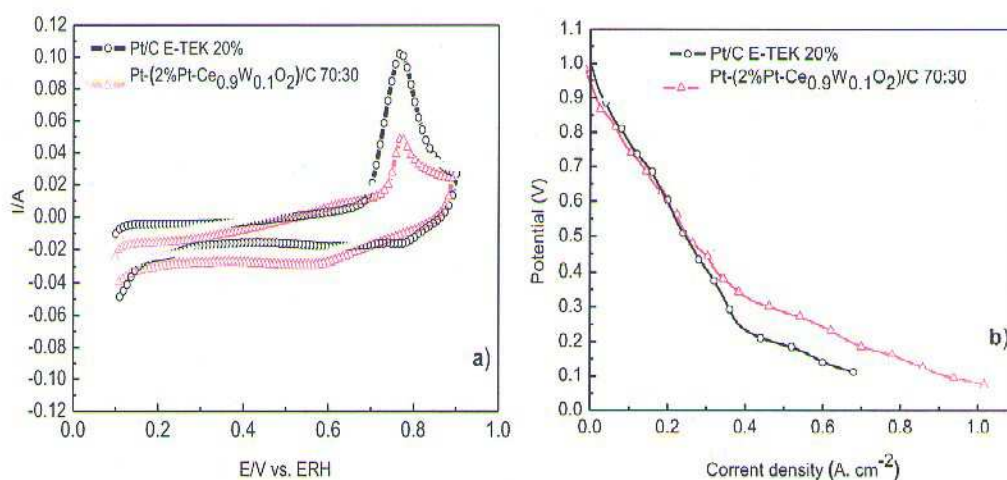


Figure 1: X-rays diffractograms of the Pt/C E-TEK 20 % and Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C 70:30 prepared by the physical mixing process.

In Figure 2a are shown the CO stripping voltammograms of the Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C and commercial Pt/C E-TEK. It is observed that the CO oxidation starts in less positive potentials (0.3 V) for Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C electrocatalyst when compared to Pt/C E-TEK (0.68 V). This can be justified by the formation of oxygen species (CeO₂-OH_{ads}) at low potential that help to oxidize CO molecules adsorbed on the surface of Pt by the bifunctional mechanism [6, 7].

In Figure 2b are shown the polarization curves of single cells operating with a mixture of H₂/CO (100 ppm of CO) and Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C and commercial Pt/C E-TEK as anode electrocatalysts. It is observed that the commercial Pt/C E-TEK shows a more pronounced fall of potential compared to the Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C electrocatalyst, which is in concordance with CO stripping measurements.



Figures 2a and 2b: 2a) CO Stripping of the Pt/C E-TEK (○) and Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C 70:30 (Δ) electrocatalysts, $v = 20 \text{ mV} \cdot \text{s}^{-1}$, $T = 25^\circ\text{C}$ and 2b) Comparison of the polarization curves of the single cells using Pt/C E-TEK (○) and Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C (Δ) as anodes electrocatalysts fed with H₂/CO (100 ppm of CO) in the anode and O₂ in the cathode. Absolute pressure of 2 bar at 85°C .

Conclusions

Pt-(2%Pt-Ce_{0.9}W_{0.1}O₂)/C electrocatalyst prepared by physical mixture of commercial Pt/C E-TEK and 2%Pt-Ce_{0.9}W_{0.1}O₂ obtained by an alcohol-reduction process showed a superior performance for oxidation of H₂/CO mixture in a single cell at 85°C compared to commercial Pt/C E-TEK. These preliminary results showed that the obtained system is very promising for PEMFC operating with H₂ produced by steam reforming.

Acknowledgements

IPEN-CNEN/SP, Pro-H₂ MCT, CAPES, FINEP

References

1. F. Du Melle, "The global and urban environment: the need for clean power systems". *Journal of Power Sources*, 71 (1-2): 7-11 (1998).
2. A. Oliveira Neto, A. L. Farias, R. R. DIAS, M. Brandalise, M. Linardi, E. V. Spinacé. "Enhanced electro-oxidation of ethanol using PtSn/CeO₂-C electrocatalyst prepared by an alcohol-reduction process". *Electrochemistry Communications*, 10 (9): 1315-1317 (2008).
3. A. E. C. Pamqvist, M. Wirde, U. Gelius, M. Muhammed. Surfaces of Doped Nanophase Cerium Oxide Catalysts. *NanoStructured Materials*, 11 (8): 995-1007 (1999).
4. G. Rothenberg, E. A. (Bart) de Graaf, A. Blik. Solvent-Free Synthesis of Rechargeable Solid Oxygen Reservoirs for Clean Hydrogen Oxidation. *Angew. Chem. Int. Ed.* (42) 3366 – 3368 (2003).
5. D. M. Gu, Y. Y Chu, Z. B. Wang, Z. Z. Jiang, G. P Yin, LIU, Y. "Methanol oxidation on Pt/CeO₂-C electrocatalyst prepared by microwave-assisted ethylene glycol process". *Applied Catalysis B: Environmental*, 102 (1-2): 9-18 (2010).
6. Z. Hou, B. Yi, Z. Lin, H. Zhang. "CO tolerance of PtRu-HxMeO₃/C (Me = W, Mo) made by composite support method". *Journal of Power Sources*, 123 (2): 116 – 125 (2003).
7. E. I. Santiago, M. S. Batista, M. E. Assaf, E. A. Ticianelli. "Mechanism of CO tolerance on Molybdenum-Based Electrocatalysts for PEMFC". *Journal of the Electrochemical Society*, 151 (7): A944 – A949 (2004).