

3.- Development of the Project

The estimated duration of the Project is three years. It is sub-divided into the following tasks:

Task 1: Data acquisition and analysis of the exhaust gases

A thorough analysis of the plant's exhaust gases will be carried out under this task, to complement those that have been made to-date.

Task 2: The fuel cell

The characteristics of the fuel cell to be employed will be defined under this task. The input hydrogen purity characteristics must be specified so that the design of the purification systems may be efficiently undertaken; it will finally be installed in the plant.

Task 3: Hydrogen purification, adequation and treatment systems

After a state-of-the-art study, the stages of system dimensioning, design and, finally, installation of the infrastructure required for the hydrogen, from when it leaves the plant up to when it is put into the fuel cell, will follow.

Task 4: Output adequation system

The output adequation system shall be designed to covert the continuous outlet voltage from the fuel cell to alternating current susceptible to being employed to supply the plant itself or sold to the local network company.

Task 5: Start-up and assessment

The final tests will be carried out during this stage, the Project reports will be drawn up, and the tasks related to the dissemination of the results will be carried out.

4.- Conclusions

This Project contains a high number of aspects that make it a key demonstrator for fuel cell technology.

- On the one hand, a waste is valorised (the plant outlet gas), producing electric energy in an absolutely clean manner and obtaining only steam in this energy generation process.
- On the other hand, the idea is to demonstrate the feasibility of electric energy generating plants based on fuel cells, for outputs of hundreds of kilowatts; we must take into account the fact that plants with outputs equal to, or greater, exist worldwide, but they are generally projects that produce the hydrogen by means of natural gas reforming, which produces carbon dioxide as a waste.
- Finally, with a project of this nature we are tending towards the distributed generation of electric energy, using clean energy sources, such as those that have begun to appear in the recommendations made lately by international bodies.

ELECTROXIDATION OF ETHANOL USING PtRu/C ELECTROCATALYST PREPARED FROM A SINGLE SOURCE MOLECULAR PRECURSOR

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INTRODUCTION

PtRu/C electrocatalysts have superior activity as anode in direct methanol fuel cell (DMFC) and CO-tolerant proton-exchange membrane fuel cell (PEMFC) [1,2]. Lukehart *et al.* [3-5] prepared a PtRu/C electrocatalyst using the complex $(\eta\text{-C}_2\text{H}_4)(\text{Cl})\text{Pt}(\mu\text{-Cl})_2\text{Ru}(\text{Cl})(\eta^3\text{-}\eta^1\text{-C}_{10}\text{H}_{16})$ as a 1:1 Pt:Ru bimetallic molecular precursor and Vulcan Carbon XC72R as the traditional carbon powder support. The measurements of the catalytic activity as anode catalyst in DMFC revealed that the 50wt% PtRu catalyst showed a superior performance to that of a 60wt% PtRu commercial catalyst (E-TEK[®]). Ethanol is a renewable and attractive fuel for Direct Alcohol Fuel Cell (DAFC) as it is much less toxic than methanol and can be produced in great quantities from biomass resource. In Brazil ethanol is produced, distributed and used as a fuel for internal combustion engine cars for more than twenty years. In this work the PtRu/C electrocatalysts, prepared using the complex $(\eta\text{-C}_2\text{H}_4)(\text{Cl})\text{Pt}(\mu\text{-Cl})_2\text{Ru}(\text{Cl})(\eta^3\text{-}\eta^1\text{-C}_{10}\text{H}_{16})$ as a single-source molecular precursor, were submitted to different thermal treatments and tested for the ethanol oxidation using the thin porous coating electrode technique.

EXPERIMENTAL

The complex $(\eta\text{-C}_2\text{H}_4)(\text{Cl})\text{Pt}(\mu\text{-Cl})_2\text{Ru}(\text{Cl})(\eta^3\text{-}\eta^1\text{-C}_{10}\text{H}_{16})$ was synthesized and characterized as described by Lukehart *et al.* [3-5]. The PtRu/C electrocatalysts (20 wt%, Pt:Ru atomic ratio of 1:1) were prepared in the following manner: The required quantity of complex was dissolved in a small quantity of dichloromethane and to this solution was added the appropriate mass of carbon support (Vulcan XC72R). The resulting slurry was stirred for 30 min under argon and after this the solvent was removed at reduced pressure. The black solid obtained was submitted to different thermal treatments in a tube furnace with controlled atmosphere. The sample treated under hydrogen atmosphere was heated from room temperature to 400°C at 1°C min⁻¹ under argon flow. When the activation temperature was reached, hydrogen gas was introduced and the catalyst was held at that temperature for 2 h. Finally the sample was cooled to ambient temperature under argon flow. The sample treated under argon was submitted to the same conditions under argon flow during all time. The sample treated under hydrogen at 400°C was also submitted to a further treatment: the sample was heated from room temperature to 300°C at 5°C min⁻¹ under air atmosphere for 30 min. Transmission electron microscopy (TEM) was carried out using a Carl Zeiss CEM 902 apparatus with a Proscan high-speed slow-scan CCD camera and digitalized (1024x1024 pixels, 8 bits) using the AnalySis software. The particle sizes distributions were determined by measuring the nanoparticles from micrographs using Image Tool Software. The Pt/Ru atomic ratios were obtained by EDAX analysis using a scanning electron microscope Philips XL30 with a 20 keV electron beam and provided with EDAX DX-4 microanaliser. Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique. The working electrode was constructed using PTFE cylinder with a cavity 0.15 mm deep and 0.36 cm² area. A known amount of the electrocatalysts were treated with a 2% PTFE suspension and transferred quantitatively to the cavity. The reference electrode was a RHE and the counter electrode was a platinumized Pt plate. Electrochemical measurements (Cyclic Voltammetry) were

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made using a Microquímica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquímica software. Cyclic Voltammetry was performed in a 0.5 mol L⁻¹ H₂SO₄ solution saturated with N₂. The evaluation of ethanol oxidation was performed at 25°C in three different concentrations of ethanol: 0.1, 0.5 and 1.0 mol L⁻¹. For comparative purposes a commercial carbon supported PtRu catalyst from E-TEK[®] (20 wt%, Pt:Ru molar ratio 1:1, Lot # 3028401) was used.

RESULTS AND DISCUSSION

The electrocatalysts were prepared by the impregnation of the PtRu complex on the carbon support and the resulting solids were submitted to different thermal treatments. The TEM micrographs of the electrocatalysts are shown in Fig. 1. The electrocatalysts have the metal particles dispersed on the carbon support with an average particle size of 2.5 ± 1.0 nm. The broad area EDAX analysis of the electrocatalysts, on the micron scale, showed the emission lines from Pt and Ru with relative intensities corresponding to Pt/Ru atomic ratios between 1.0 and 1.3. Similar results were described by Lukchart *et al.* [3-5].



Figure 1: TEM micrographs a) electrocatalyst treated at 400°C under hydrogen flow and b) treated at 400°C under hydrogen flow and submitted to the oxidative thermal treatment.

The results of cyclic voltammetry experiments, in the absence of ethanol, are shown in Fig. 2. The electrocatalysts do not have a very defined hydrogen oxidation region, as observed for pure platinum, and the currents in the double layer are larger. These results are characteristic of electrocatalysts PtRu with atomic ratio of 1:1 [6,7]. However, some differences are apparent among the electrocatalysts. The electrocatalysts treated under hydrogen flow and E-TEK[®] have a more characteristic hydrogen region (0.05 - 0.40V) while the electrocatalysts treated under argon flow show a less defined peak in the hydrogen region. The electrocatalyst submitted to the oxidative thermal treatment has the larger currents in the double layer region. Thus, the electrocatalyst treated at 400°C under hydrogen flow and submitted to the oxidative thermal treatment has a more defined hydrogen region and the larger currents in the double layer region.

The electro-oxidation of ethanol was studied varying the concentration from 0.1 to 1.0 mol L⁻¹. In the hydrogen region (0 - 0.4 V) the current values decrease with the increase of ethanol concentration probably due to the increase of ethanol adsorption on the surface [7]. For potentials more positive than 0.5V the current values increase with ethanol concentration, even for 1 mol L⁻¹.

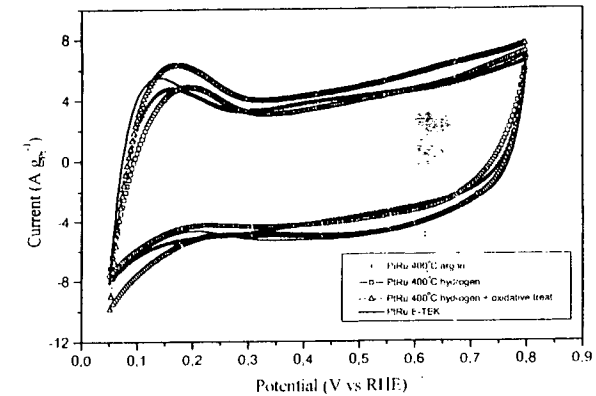


Figure 2: Cyclic voltammetry of the electrocatalysts in 0.5 mol L⁻¹ H₂SO₄ with a sweep rate of 10 mV s⁻¹

The electrocatalysts performance in ethanol oxidation is strongly dependent of the thermal treatment as shown in Fig. 3. In the region of interest for fuel cell applications (0.5 - 0.7 V) the electrocatalyst treated at 400°C under argon flow has the poor performance and this is probably due to the presence of residual chlorine coming from the decomposition of the PtRu complex under these conditions [5]. It is known that even small residual levels of chlorine in DMFC anode catalysts degrade fuel cell performance [3-5,8,9]. When the electrocatalyst is treated at 400°C under

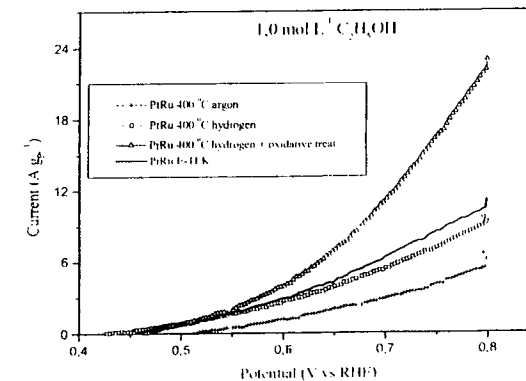


Figure 3: Cyclic voltammetry of the electrocatalysts in 0.5 mol L⁻¹ H₂SO₄ and 1.0 mol L⁻¹ of ethanol with a sweep rate of 10 mV s⁻¹, considering only the anodic sweep.

hydrogen flow the chlorine is eliminated to the gas phase as hydrogen chloride [5,9] and an increase in the current values is observed. The best performance was obtained using the electrocatalyst treated at 400°C under hydrogen flow and submitted to the oxidative thermal treatment. The current values are approximately two times greater than the commercial E-TEK electrocatalyst. The treatment under hydrogen flow leads to enrichment of platinum on the nanoparticles surface and the major part of the ruthenium exists as metallic ruthenium. When submitted to the oxidative thermal treatment the ruthenium segregates to the surface and oxidize ruthenium species are formed while platinum is maintaining preferentially in the metallic form [8,10]. Thus, this electrocatalyst probably have the optimal composition of metallic platinum and oxidize ruthenium species on the PtRu nanoparticles surface, which could be the active species that promote the ethanol oxidation by the bi-functional mechanism proposed for methanol oxidation [10-13].

CONCLUSIONS

The PtRu molecular precursor method showed to be suitable and very promising to produce active PtRu/C electrocatalysts for ethanol electro-oxidation. However, the thermal treatment affects strongly the performance of the catalysts. The electrocatalyst treated under hydrogen flow and submitted to an oxidative thermal treatment has a significant superior performance. This could be attributed to the better control of the metallic platinum and oxidize ruthenium species present on the PtRu nanoparticles surface developed by this treatment.

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EVALUATION OF HYDROGEN TECHNOLOGIES ON THE BASIS OF THE FOUR-SECTOR BENEFIT DIAGRAM

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Abstract. The evaluation of Hydrogen Technologies is generally carried out on the basis of Indices and Indicators designed to support both interested companies and decision-makers in their own strategic choices. The latter, however, are very often not convergent towards an agreed scenario of investments and expected results. In addition, the evaluation parameters used are often heterogeneous, because they derive from different theoretical approaches and disciplines, individually and specifically adequate to different time-space fields of analysis. On the other side, the goal of making the evaluation parameters sufficiently consistent is often achieved by restricting them to a somehow reduced field of analysis. Finally, the evaluations are very often performed more in terms of possible *damages* to be *internalized* than in terms of *external benefits* to be *remunerated*.

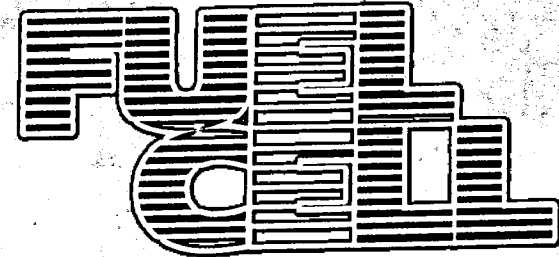
The methodology here presented, on the contrary, is mainly based on the evaluation of the *Benefits* pertaining to the four distinct "Subjects" (and related Sectors) which are usually involved in the global productive process: Benefits to the *Firm* (deriving from the Production process), Benefits to the *Society* (deriving from the commercialization of the new Product), Benefits to the *Environment as a Source* (due to the optimized consumption of natural resources), Benefits to the *Environment as a Sink* (due to the decreased amount of wastes, both in terms of quality and quantity).

The paper thus presents a very general procedure able to handle a huge number of different indicators within an aggregated synthetic picture, obtained as the generalization of well known decision making techniques (e.g., Boston Chart, General Electric Method, etc).

The method proposed starts from the characterization (in terms of selected Indicators) of the four *basic* reference Sectors previously mentioned, which cover the most important aspects that a Policy Maker has to take into account in the complexity of the contemporary society. Such Sectors are symmetrically set with respect to the center of the mentioned diagram because the Decision Maker represents a sort of "referee" in equilibrating different needs and interests, often in contrast with each other, such as the Benefits to the Firm and those to the Society, as well as the Benefits for the Environment as a "donor" and those as a "sink" respectively.

Such a graphic choice would also indicate that the four Sectors cannot be considered as being independent from each other. In fact each Sector is seen as a sub-system of a Whole characterized by a dynamic "circulation of Benefits". To this purpose each Sector is identified by two axes, which point out the fundamental features of its input/output properties respectively. These, in turn, also characterize the main interface relationships between adjacent Sectors.

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ABSTRACTS

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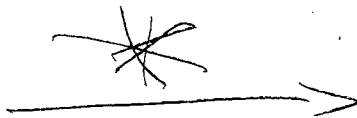
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