Characterization of Proton Exchange Membrane Fuel Cell Catalysts
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Abstract: the structures of the Proton Exchange Membrane Fuel Cells Catalysts were investigated by transmission electron microscopy (TEM), energy dispersive analyses (EDS), X-ray Diffraction (XRD) were used to evaluated the semi-quantitative composition of the catalysts. The electrochemical behavior was analyzed by cyclic voltammetry (CV) and polarization curves (Uxi).

Introduction
The demand for green energy in this century will increase and in this context fuel cell technology seems to be an important way to generate distributed green energy[1].

One important issue to be addressed is the choice of the fuel, hydrogen is the best choice however it logistic remains costly. In order to overcome this problem liquid fuels such as methanol and ethanol can be used for fuel cell applications. In this work we synthesized some ternary catalysts that were tested with transmission electron microscopy (TEM), energy dispersive analyses (EDS), X-ray Diffraction (XRD) used to evaluated the semi-quantitative composition of the catalysts. The electrochemical behavior was analyzed by cyclic voltammetry (CV) and polarization curves (Uxi). These catalysts systems were tested in real fuel cells systems with hydrogen/oxygen (H₂/O₂) hydrogen contaminated with carbon monoxide simulating reforming gas, methanol and ethanol. One important field in fuel cell research consists on the development of new catalysts aiming to increase electrochemical activity for H₂/CO, methanol and ethanol oxidation. Aiming to minimize the contamination caused by the CO adsorption on Pt sites, different synthesis of catalysts has been reported in the literature[2-8]. In this work different catalysts has been synthesized by the colloid method also known as the Bönneman method[9] which gives a crystallite with an average size between 1.5 to 3.0 nm well dispersed in the carbon matrix[10].

Experimental
Bönnemann’s method: this method consists on a formation of a stable colloid prepared in an inert and dried atmosphere. The proper amount of the chloride salts of the metals involved were dissolved in anhydrous tetrahydrofuran (THF) with tetracrilamoniouym bromide [N(oct)₄Br], while the reducing agent was prepared by the dissolution of tetracrilamoniouym bromide [N(oct)₄Br] in THF, adding potassium triethylhydroborate [KHB(ET)₃]. After stirring a strong reduce agent is formed (trietilhydroborate of tetaoctalamoniyoum [N(oct)₄HBr(ET)₃]) according to equation 1:

\[
N(oct)_4Br + KHB(ET)_3 \rightarrow N(oct)_4HBr(ET)_3 + KBr \quad \text{Eq.(1)}
\]
In order to perform the reduction of metallic ions 1.5 times of the stoichiometric amount of the reducing agent [N(oct)4HBr(Et)3] was employed, added to the solution of metals salts and heated under stirring. The reduction is followed by the darkening of the solution and hydrogen evolution, as shown in the equation 2. After that an stable colloid with the average size between 1.5 and 3.0 is formed. The stable colloid formed was dropwised in a Vulcan carbon black suspension filtered and washed several times with THF and ethanol.

\[
\text{MeX}_n + \text{N(oct)}_4\text{HB(et)}_3 \rightarrow \text{Me}^* [\text{N(oct)}_4]^+ + n\text{B(et)}_3 + \frac{n}{2} \text{H}_2 \uparrow + n\text{X}^- \quad \text{Eq.(2)}
\]

THF colloid

After the preparation of the catalysts a thermal treatment described elsewhere[11] was employed to eliminate the impurities on the surface of the catalyst. The ternary systems developed in this work were PtRuMo, PtRuNi and PtRuDy in order to evaluate their electrochemical behavior while operating with reformed gas, methanol and ethanol. The PtRu system was adopted as a reference catalyst, since is well established.

**Structural Characterization:** the electrocatalysts powder were investigated by EDX in a Philips XL 30 scanning electron microscopy with EDX performing semi-quantitative analysis of the composition of the systems. X-rays powder diffraction was carried out on a STOE STADI-P powder diffractometer, with germanium monochromatized CuKα radiation and a position-sensitive detector with 40° aperture in transmission mode, with 20 scanned from 10 to 90° and scan rate of 0.03° s-1 and a Philips CM 20 with an acceleration voltage of 200 kV and tungsten cathode was applied for high resolution images of the supported catalysts. Additionally the microscope was equipped with a nano-EDX device to check the catalysts composition in nm-sized regions. Samples were prepared by suspending the catalyst powder in methanol and depositing a drop of the suspension on a standard copper grid covered with carbon. These analysis (XRD and HRTEM) were performed in the Materials Science Institute of the Technical University of Darmstadt in collaboration with Materials Science group of professor Hartmut Fuess. Electrochemical characterization: the catalyst systems developed were investigated by cyclic voltammetry (CV) in an EGG Princeton Applied Research Model 273 in a 0.5 mol L⁻¹ H₂SO₄ saturated with N₂. Thin porous layer of the catalyst was done and act as working electrode, while the reference electrode a RHE and the counter electrode was Pt platinized plate. The polarization curves were performed in a 25 cm² fuel cell from Electrochem, while The operation of the unit cell was performed with variable fluxes (by volume) of H₂ and O₂ corresponding to 1.5 times the stoichiometric figures. The conditions of the operation utilizing H₂/O₂ were: unit cell operation temperature 65°C, moisten temperature 85 ºC, anode and cathode operation pressure 1 atm. Variable fluxes of reactants calculated for 50% excess over stoichiometric figures. The operational conditions for direct oxidation of ethanol were: unit cell operation temperature 85°C, ethanol temperature 125°C, anode and cathode operation pressure 1 atm[12-16].

The MEAs were tested in commercial unit cells Electrochem® (USA), the gases were supplied by White Martins, ethanol and methanol were supplied by Casa Americana.

**Results**

The composition of the ternary catalysts systems developed in this work are summarized in Table 1 below and their compositions were checked by carbon analysis and the other elements were quantified by EDS.
Table 1: Catalyst composition (wt%)

<table>
<thead>
<tr>
<th>Sistema</th>
<th>C %</th>
<th>Pt %</th>
<th>Ruthenium %</th>
<th>3º element %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRu</td>
<td>80,0</td>
<td>14,1 ± 0,1</td>
<td>4,0 ± 0,1</td>
<td></td>
</tr>
<tr>
<td>PtRuMo</td>
<td>87,9</td>
<td>4,4 ± 0,1</td>
<td>1,8 ± 0,1</td>
<td>1,3 ± 0,1</td>
</tr>
<tr>
<td>PtRuNi</td>
<td>82,1</td>
<td>7,7 ± 0,1</td>
<td>1,2 ± 0,1</td>
<td>4,6 ± 0,1</td>
</tr>
<tr>
<td>PtRuDy</td>
<td>84,7</td>
<td>10,4 ± 0,1</td>
<td>2,1 ± 0,1</td>
<td>2,8 ± 0,1</td>
</tr>
</tbody>
</table>

In order to verify the structure of the catalyst X-ray diffraction was performed and
de the diffractogram of these catalysts are presented on Figures 1-4.

![Figure 1: diffractogram of platinum and ruthenium catalyst supported on carbon black](image1)
![Figure 2: diffractogram of platinum, ruthenium and nickel catalyst supported on carbon black](image2)
![Figure 3: diffractogram of platinum, ruthenium and molybdenum catalyst supported on carbon black](image3)
![Figure 4: diffractogram of platinum, ruthenium and dysprosium catalyst supported on carbon black](image4)

The ternary catalyst systems developed in this work presented only platinum fcc
structure identified by x-ray diffractogram. The average crystallite size of the catalysts
was calculated according to Scherer equation.

Table 2: Average crystallite size of the ternary catalysts systems[17].

<table>
<thead>
<tr>
<th>Radiação Cukα</th>
<th>Scherer equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sistema</td>
<td>d (nm)</td>
</tr>
<tr>
<td>PtRu</td>
<td>5,5</td>
</tr>
<tr>
<td>PtRuNi</td>
<td>2,2</td>
</tr>
<tr>
<td>PtRuMo</td>
<td>2,2</td>
</tr>
<tr>
<td>PtRuDy</td>
<td>3,1</td>
</tr>
</tbody>
</table>
Except for the PtRu/C system the other catalysts presented 2 to 3.1 nm. The PtRu/C system developed presents 5.5 nm.

Transmission electron microscopy analyses of the catalysts systems synthesized confirm that colloid method produces catalysts in the range of 2.2 to 5.5 nm for this work. The catalysts are widespread and homogeneous on the support in accordance to literature the catalysts structure can be observed in Figures 5 and 6. The electrochemical behavior is discussed bellow.

![Figure 5: Transmission electron micrograph for PtRuNi catalyst.](image1)
![Figure 6: Transmission electron micrograph for PtRuMo catalyst (The bar corresponds to 4 nm).](image2)

In order to identify the surface structure of the catalysts XPS measurements were performed and the results are presented in Table 3.

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding energy (eV)</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>72.1</td>
<td>Pt</td>
</tr>
<tr>
<td>Pt 4f</td>
<td>74.2</td>
<td>PtO₂</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>463.1</td>
<td>RuO₂</td>
</tr>
<tr>
<td>Ru 3p</td>
<td>465.6</td>
<td>RuO₂·xH₂O</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>232.1</td>
<td>(NH₄)₂MoO₄</td>
</tr>
<tr>
<td>Mo 3d5/2</td>
<td>232.8</td>
<td>MoO₃</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>168</td>
<td>Dy₂O₃</td>
</tr>
</tbody>
</table>

According to the results of XPS measurements except for platinum the other components were identified as oxides that may improve the catalysts performances when the bi-functional mechanism is present.

The electrochemical behaviors of the catalysts were analyzed with cyclic voltammetry and polarization curves (I x U). The voltammetry technique was used to identify the best catalyst system and after that the polarization curves were performed. The results of the electrochemical investigations are presented on Figures 7, 8, 9 and 10.

In Figure 7 one can see the current-potential anodic scans for H₂/CO 100 ppm oxidation and PtRuMo ternary catalysts presented the higher electrochemical activity among others catalysts for H₂/CO oxidation. This result allows us to investigate the catalysts performance in a real fuel cell environment.
In the Figures 8, 9 and 10 the polarization curves for H₂/CO, methanol and ethanol oxidation are presented. The data presented in Figure 8 confirms the voltammetry results and the PtRuMo is a better catalyst than the other ternary systems for H₂/CO and in Figure 9 the PtRuMo presents the best result for methanol oxidation.

For direct ethanol oxidation the best catalyst was PtRuDy system and it electroactivity is comparable to the PtSn₃ catalyst developed by other groups.

**Conclusions**

The colloid method was suitable to synthesize the catalysts systems with structural and electrochemical activity for fuel cell applications.

The catalysts systems present a Pt fcc structure with oxides that are necessary to a good electrochemical behavior.

For reformate gas (H₂/CO) and methanol oxidation the PtRuMo system presents the best results among others systems.

For ethanol oxidation the PtRuDy system presents the best electrochemical activity among all systems.

Further investigations on PtRuDy system are necessary to identify the best composition of the catalyst.
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Bibliography