# Thermal Treatment Effects over Carbon Support Properties used in PEMFC Fuel Cells

## 7º Workshop Internacional sobre Hidrogênio e Células a Combustível
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## Campinas, Brazil


Linardi, M.; Poço, J.G.R.; Carmo, M. do; Verjulio-Silva, R.W.

**www.marcelocarmo.tripod.com**
**marcelocarmo1@gmail.com**

# Introduction

**Energy's Sources**

**Petroleum** | **"Clean and Renewable"**

**Vehicles, Machines, Thermoelectrical, etc.**

**Low efficiency, $CO_2$, CO, $NO_x$, $SO_x$ emission and another poluent materials.**

**Fuel Cell !!**

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# Polymer Electrolyte Membrane Fuel Cells:

- Chemical Energy → Electrical Energy + heat
- An efficient system
- „Clean“
  - ✓ $2H_2 + O_2 \rightarrow 2H_2O$ , electricity and heat
  - ✓ $2CH_3OH + 3O_2 \rightarrow 4H_2O + 2CO_2$ , electricity and heat

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# PEM Fuel Cell Applications



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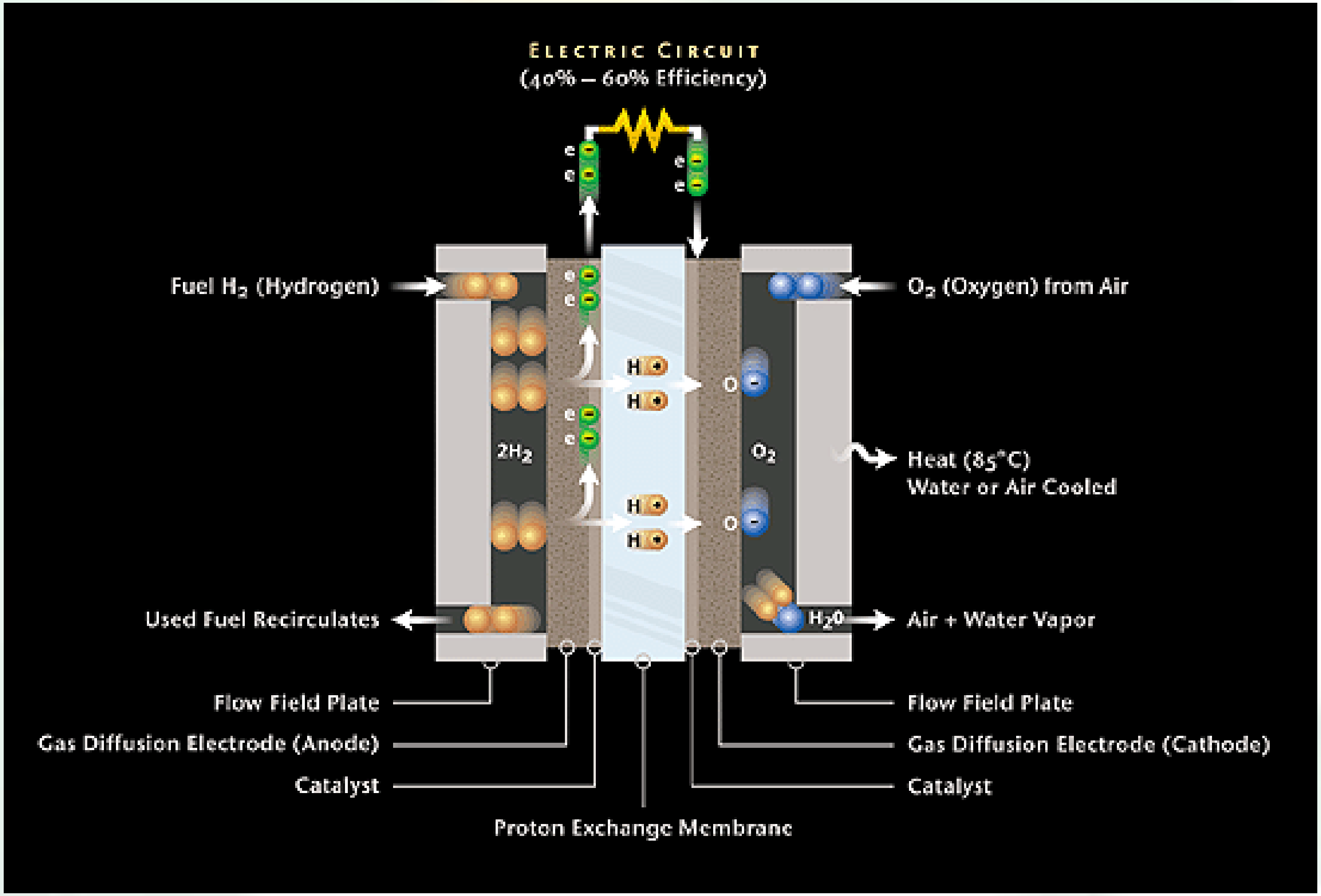
# Polymer Electrolyte Membrane Fuel Cell – PEMFC





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# Direct Methanol  Fuel Cell – DMFC)

**Advantages**:

- - the using of a liquid fuel: methanol aqueous solution
- - low temperatures (<100ºC)
- - methanol production is efficient and known
- - the same storage and similar distribution as gasoline

**Disadvantages**:

- - slow eletrooxidation reaction of methanol
- - Reaction happens with the transfer of 6 electrons
- - sub-products like CO
- - CO poisons Pt impeding that the reaction continues
- - Methanol is toxic
- - Membrane Methanol crossover



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# PEM Stations – IPEN - Brazil



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# Why funcionalization of Carbon Black?

To develop new catalysts with a better performance !!!

↓

Which are the best physical and chemical conditions of those carbon suports??

↓

Apply the best conditions!!!!.

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# 1. Modification of the carbon surface

- In this case the modifications in the level micro/nanoscopic could be:

- Connection of simple organic compositions.
- Connection or macromolecules growth.
- Adsorption
- Chemical reactions

Seeking:

- To encapsulate, to protect
- Change of the hydrofobic/hydrofilic character.
- To alter reactivity
- To develop catalytic properties
- To create composites.
- To alter polarity (zeta potential).

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# Objective

Funcionalization of carbon black surface by the reaction with hydrogen peroxide, aiming meanly:

- Remove carbon black impurities
- Avoid nanoparticle sintherization
- Produce a more homogeneous catalyst

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# Experimental

- Carbon Funcionalization

1.Step – $H_2O_2$ treatment

$$C + H_2O_2 \longrightarrow C\text{-}OH$$

Conditions: $H_2O_2$ 30V – 60°C – 24h

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# Electrocatalysts preparation

$H_2PtCl_6$ in Ethylene Glycol and $RuCl_3$ in 2-Ethoxy-Ethanol

↓

C-OH

↓

Hydrazin

150 $^{o}$C – 15 min

↓

PtRu/C-OH (metal loading 20%)

# MEA Preparation

- Sieve Printing Technique


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# Results

Activated material: Vulcan XC72-OH

- LS Particle Size Analysis - XRD – Zeta potential – Cyclic Voltammetry - BET

Catalysts: PtRu/C-OH 20% metal

- EDX – XRD – TEM – CV – FC: $H_2$/air - Methanol/air

Standart materials: PtRu/C ETEK and HISPEC
Pt/C ETEK and HISPEC

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# C-OH - $H_2O_2$ treatment
# LS Particle Size Analysis

| | Average particle size (µm) |
|---|---|
| **Vulcan XC72** | 14.9 |
| **Vulcan XC 72 $H_2O_2$ Treated** | 11.9 |

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# C-OH - $H_2O_2$ treatment
# BET Results

| | Surface Area ($m^2g^{-1}$) |
|---|---|
| **Vulcan XC72** | 232 |
| **Vulcan XC 72 $H_2O_2$ Treated** | 166 |

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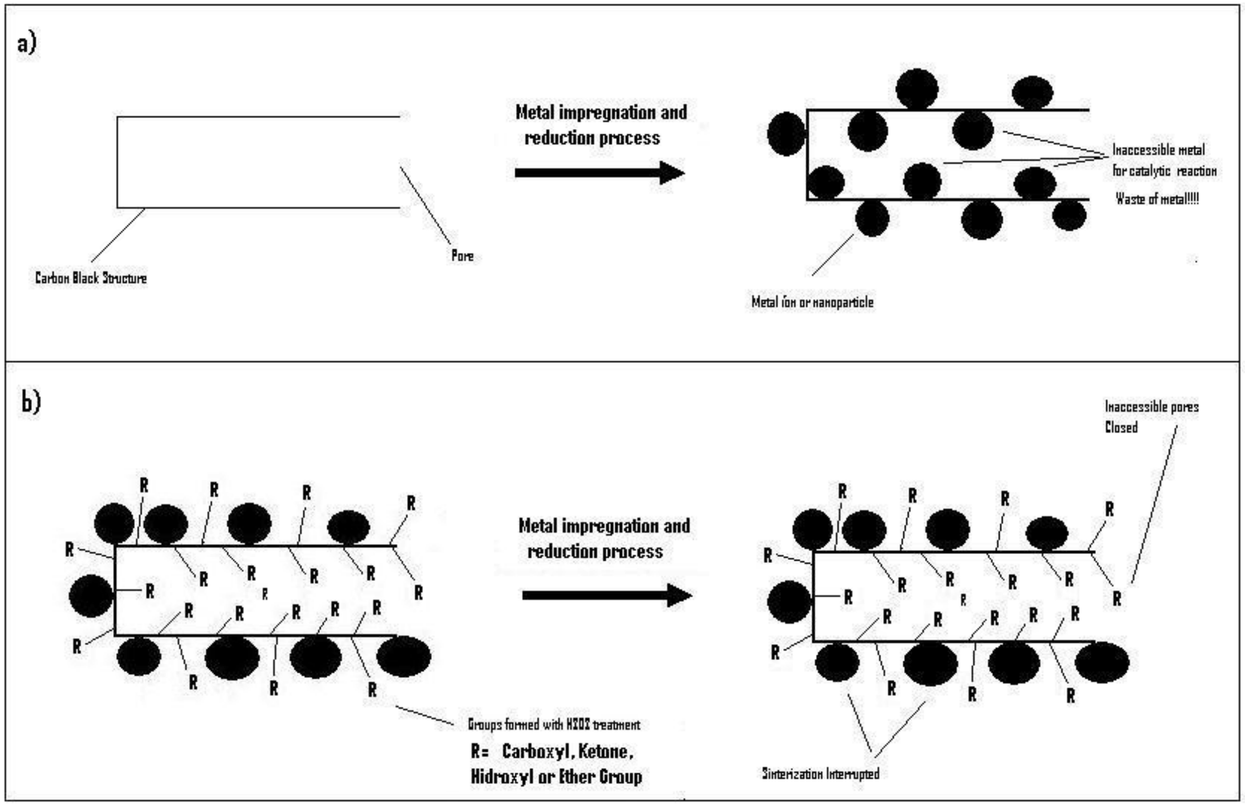
# PtRu/C-OH – $H_2O_2$

## Pore Structure Model – before and after $H_2O_2$ activation

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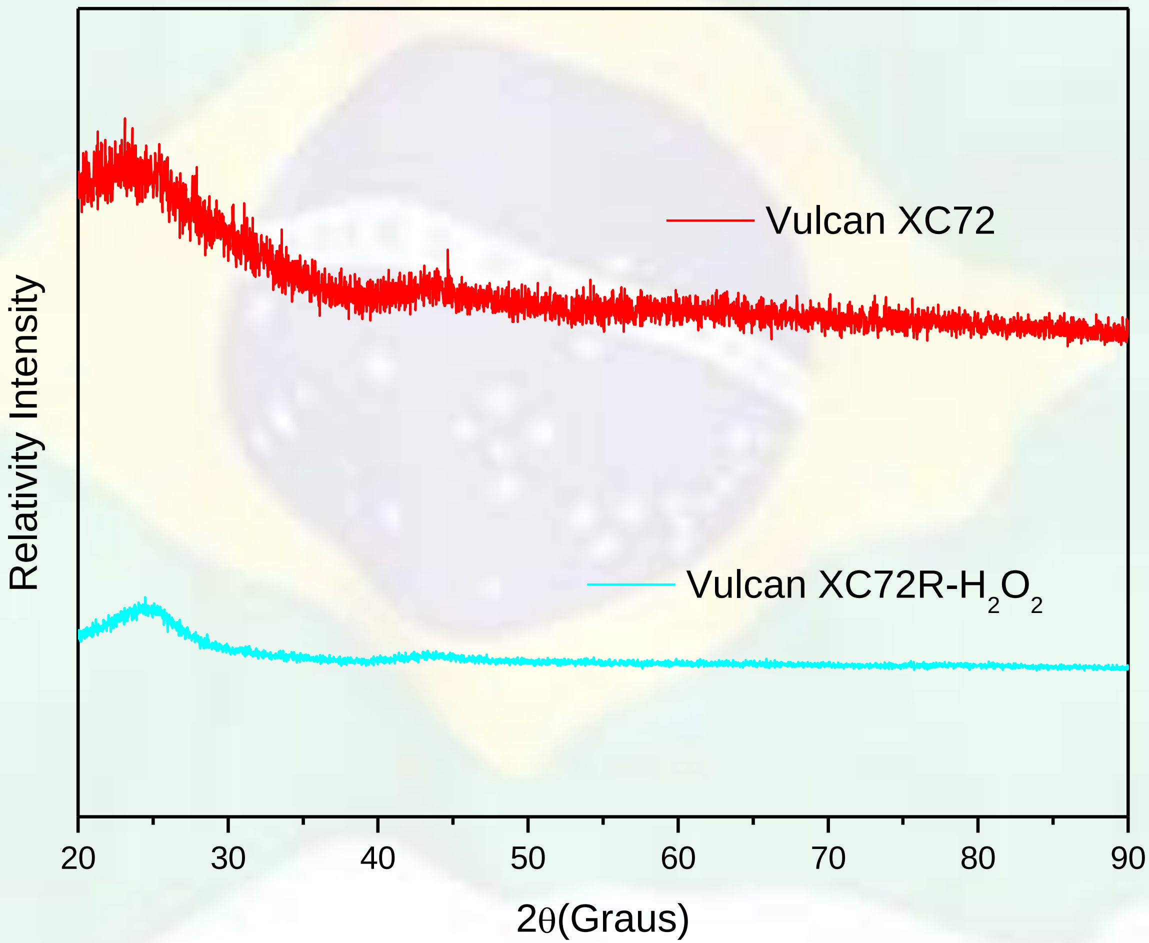
# C-OH - $H_2O_2$ treatment
# XRD

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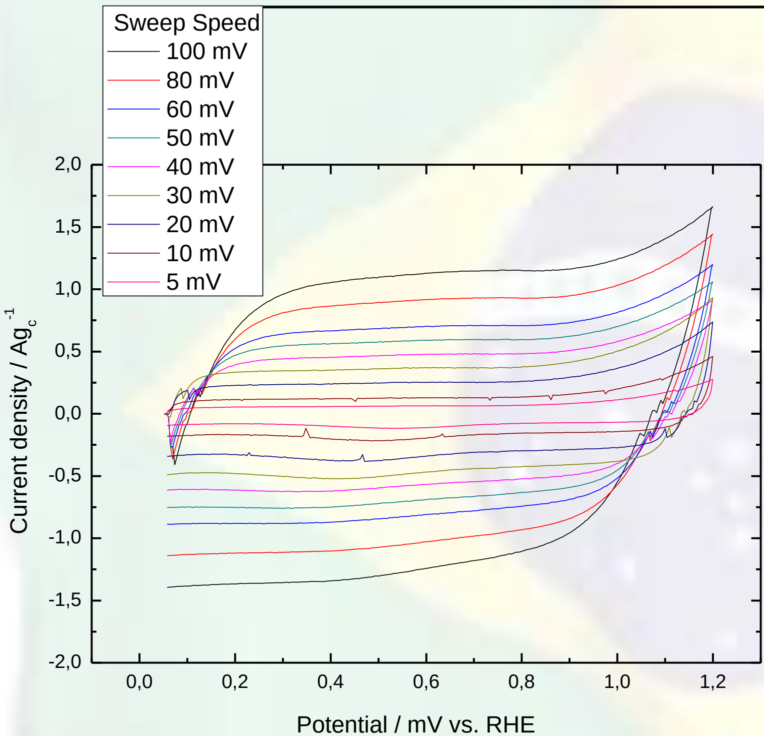
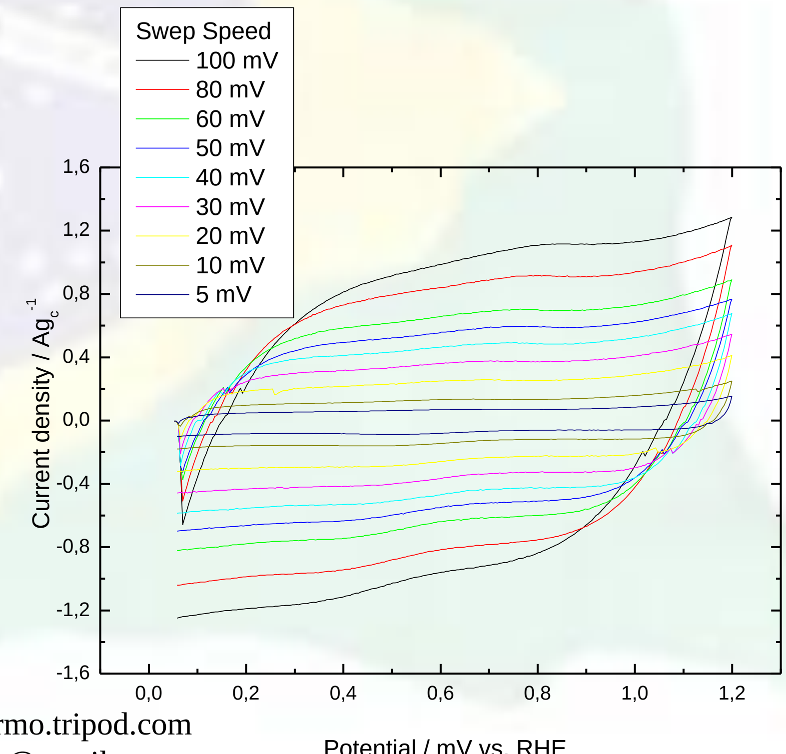
# C-OH - $H_2O_2$ treatment
# Cyclic Voltammetry in $H_2SO_4$ 0.5 $molL^{-1}$




Vulcan XC72

Vulcan XC72 – $H_2O_2$

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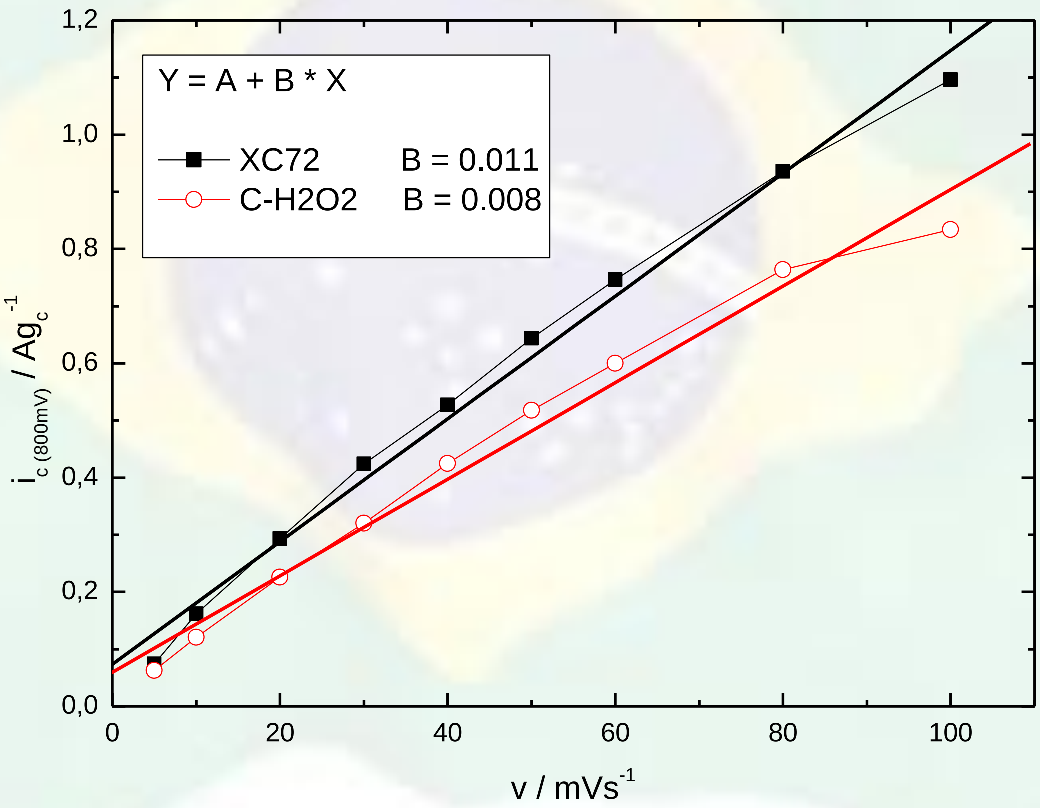
# C-OH - $H_2O_2$ treatment
# Carbon Capacitance evaluation by the CVs

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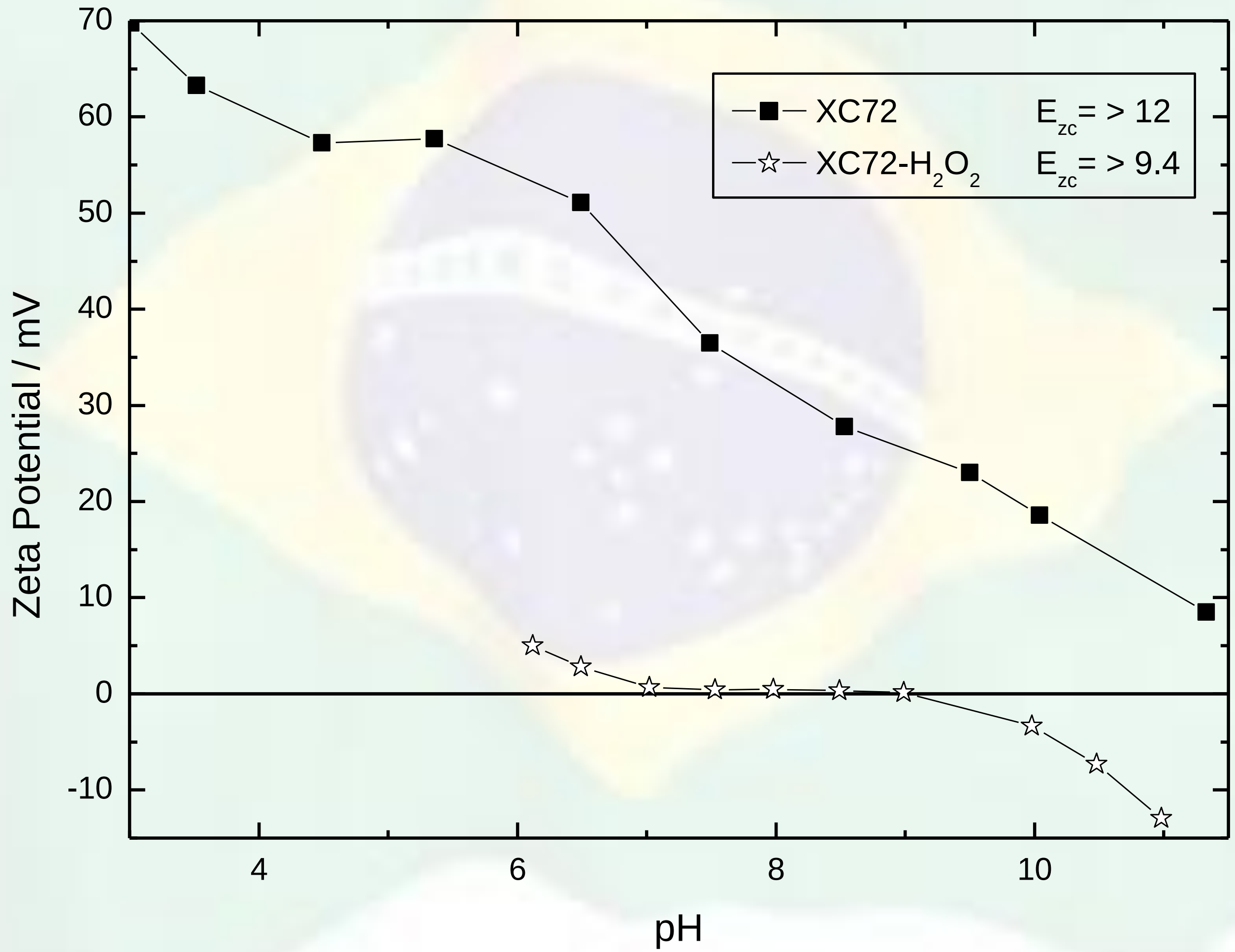
# C-OH - $H_2O_2$ treatment
# Potential Zeta





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# Electrocatalysts physical characterization

**PtRu/C-OH – $H_2O_2$ Activation**

- EDX
- XRD
- TEM

**Standart Materials**

- PtRu/C Hispec and PtRu/C ETEK

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# PtRu/C-OH – $H_2O_2$ Activation EDX

| | Pt nominal composition (atomic %) | Ru nominal composition (atomic %) | Pt (atomic %) | Ru (atomic %) |
|---|---|---|---|---|
| **PtRu/C-$H_2O_2$** | 50 | 50 | 48 | 51 |
| **PtRu/C** | 50 | 50 | 59 | 41 |
| **PtRu/C ETEK** | -- | -- | 51.5 | 48.5 |
| **PtRu/C Hispec** | -- | -- | 50 | 50 |

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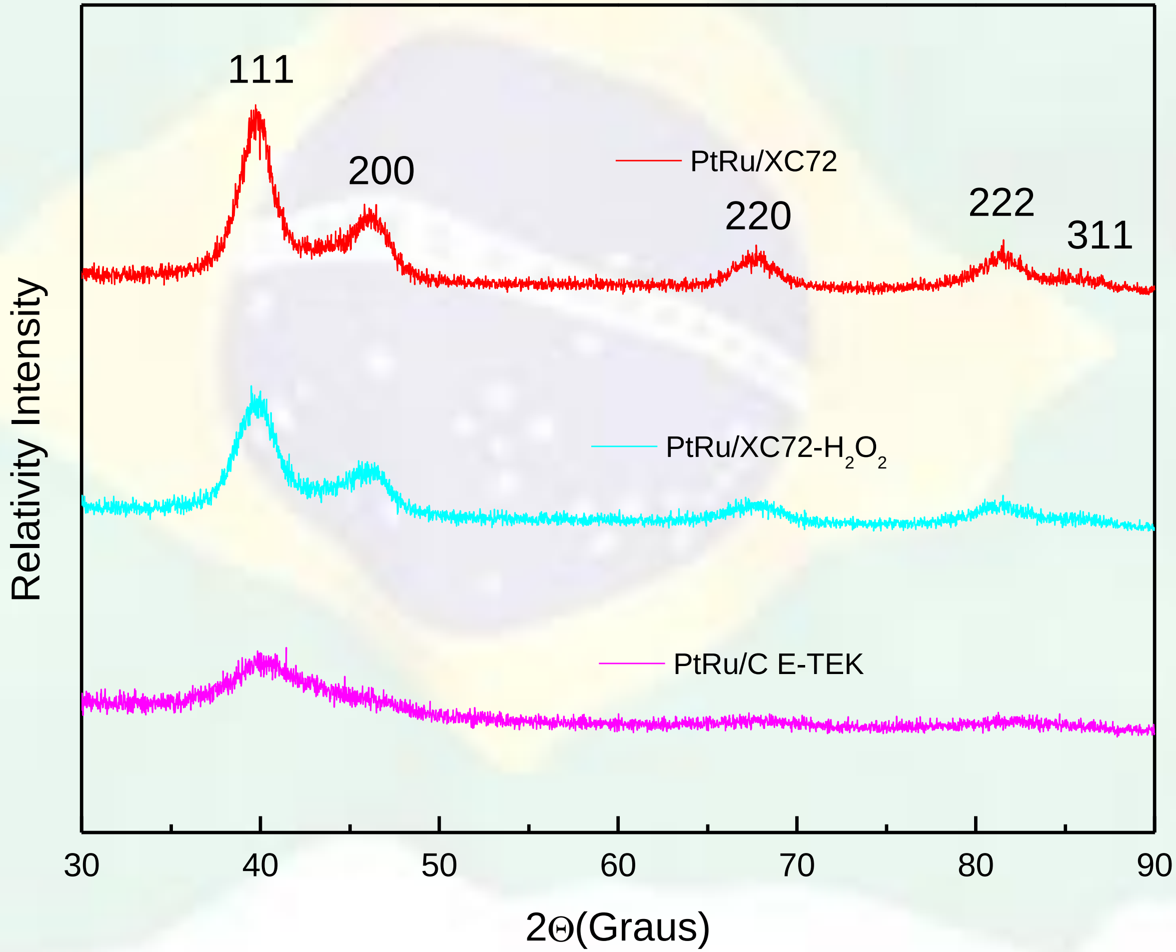
# PtRu/C-OH – $H_2O_2$ Activation XRD

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# PtRu/C-OH – $H_2O_2$ Activation
# Particle size Results – XRD and TEM

| | Size (nm) from XRD | Size TEM (nm) |
|---|---|---|
| **PtRu/C-$H_2O_2$** | 3.4 | 3.7 |
| **PtRu/C** | 4.3 | 4.7 |
| **PtRu/C ETEK** | 1.5 | 2.8 |
| **PtRu/C Hispec** | -- | 3.9 |

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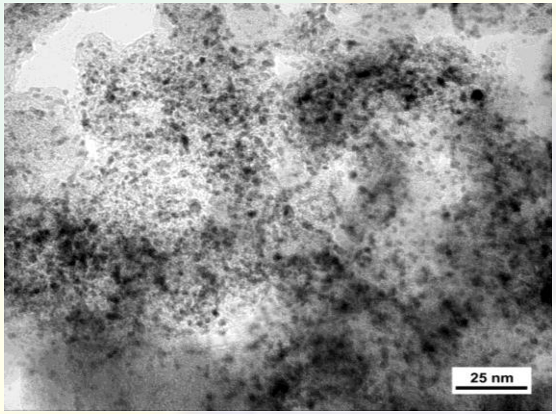
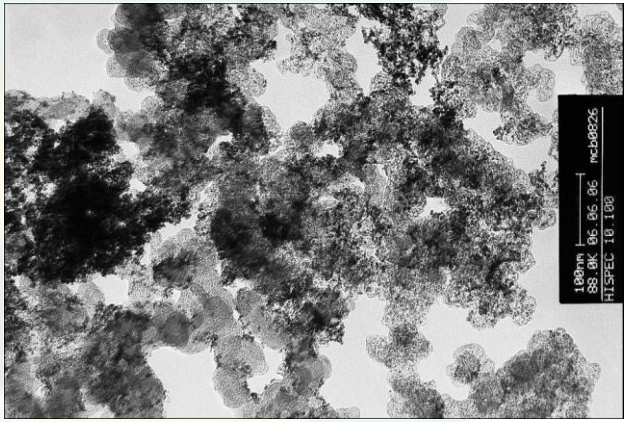
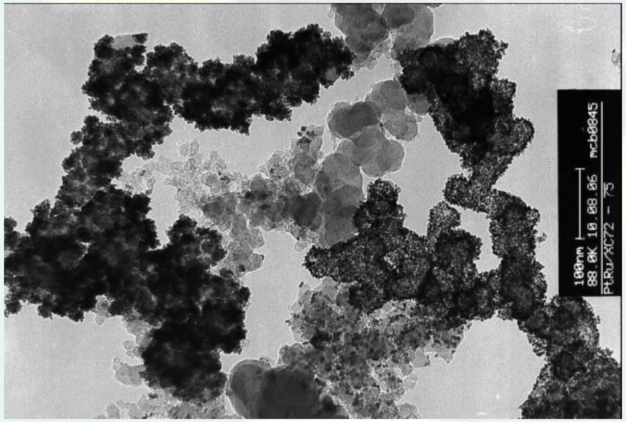
# PtRu/C-OH – $H_2O_2$ Activation TEM



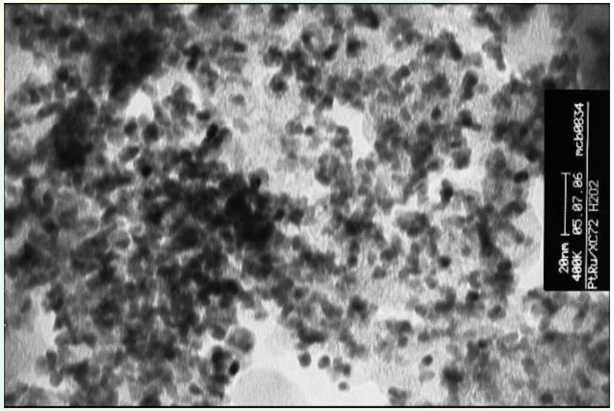

PtRu/C ETEK



PtRu/C HISPEC



PtRu/C



PtRu/C-$H_2O_2$

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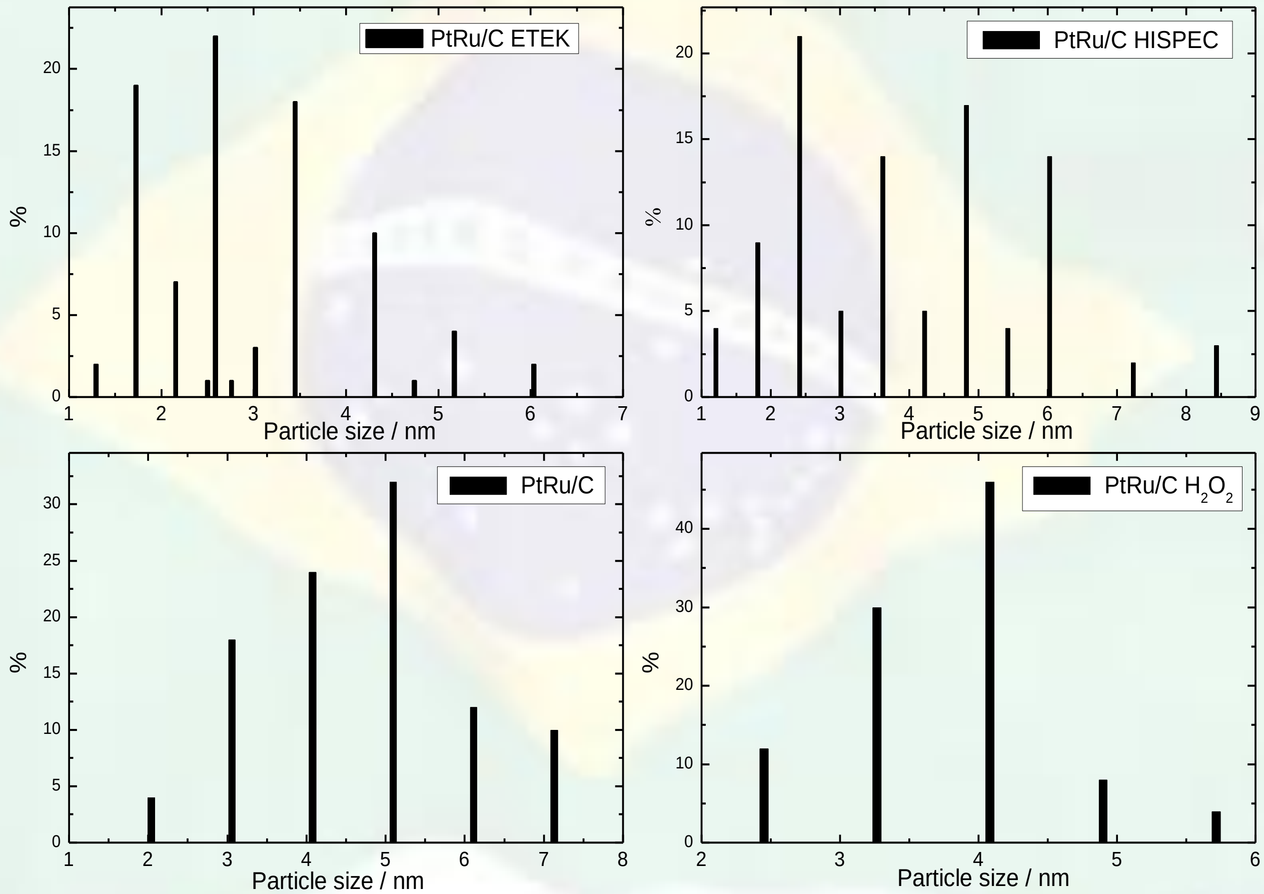
# PtRu/C-OH – $H_2O_2$ Activation TEM Histograms

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# Electrochemical Results

**PtRu/C-OH – $H_2O_2$**

RDE

- Cyclic Voltammetry in $H_2SO_4$ 0.5 $molL^{-1}$ - RDE
- Cyclic Voltammetry for Methanol oxidation in $H_2SO_4$ 0.5 $molL^{-1}$

FUEL CELL

- $H_2$/air PEMFC results
- Methanol/air DMFC Results

**Standart Materials**

Anode: PtRu/C Hispec and PtRu/C ETEK

Cathode: Pt/C Hispec and Pt/C ETEK

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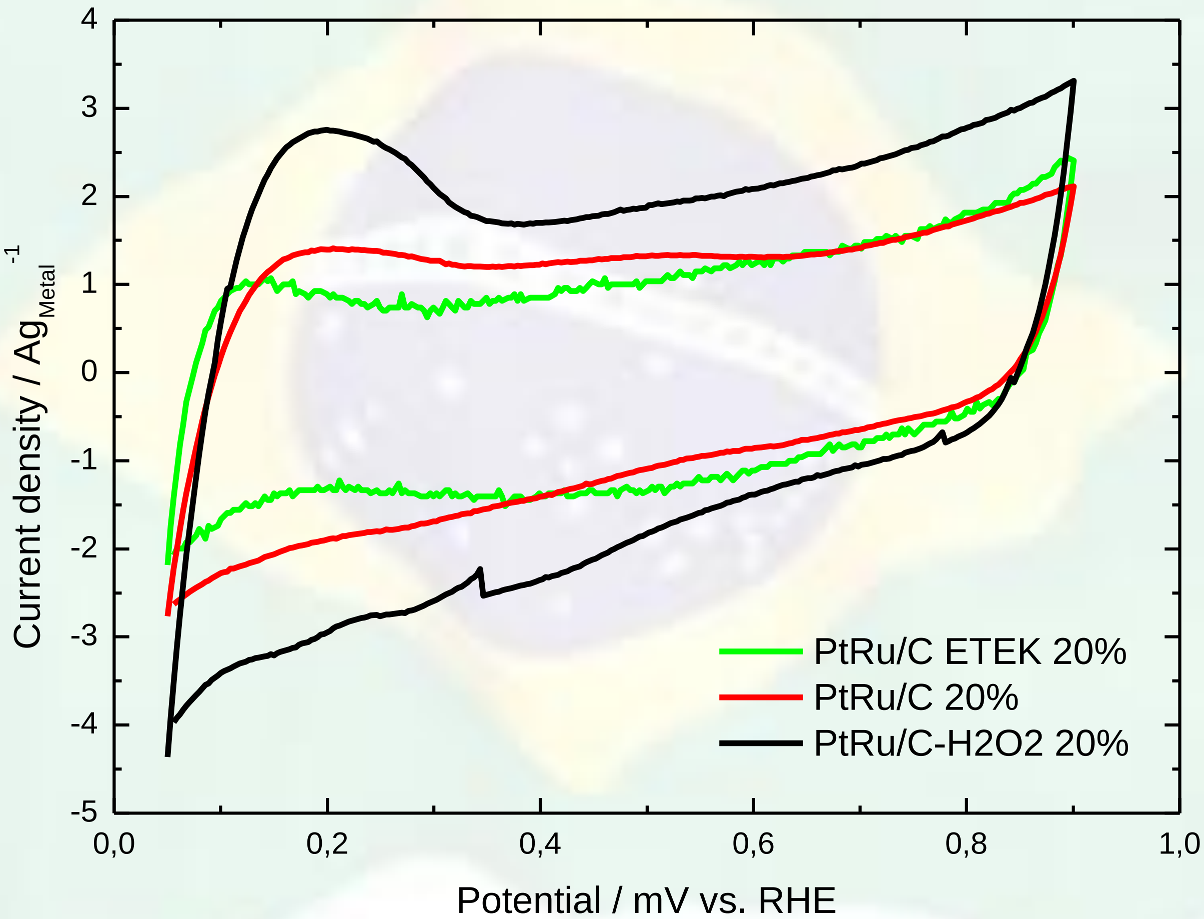
# PtRu/C-OH – $H_2O_2$ Activation
# Cyclic Voltammetry in $H_2SO_4$ 0.5 molL$^{-1}$





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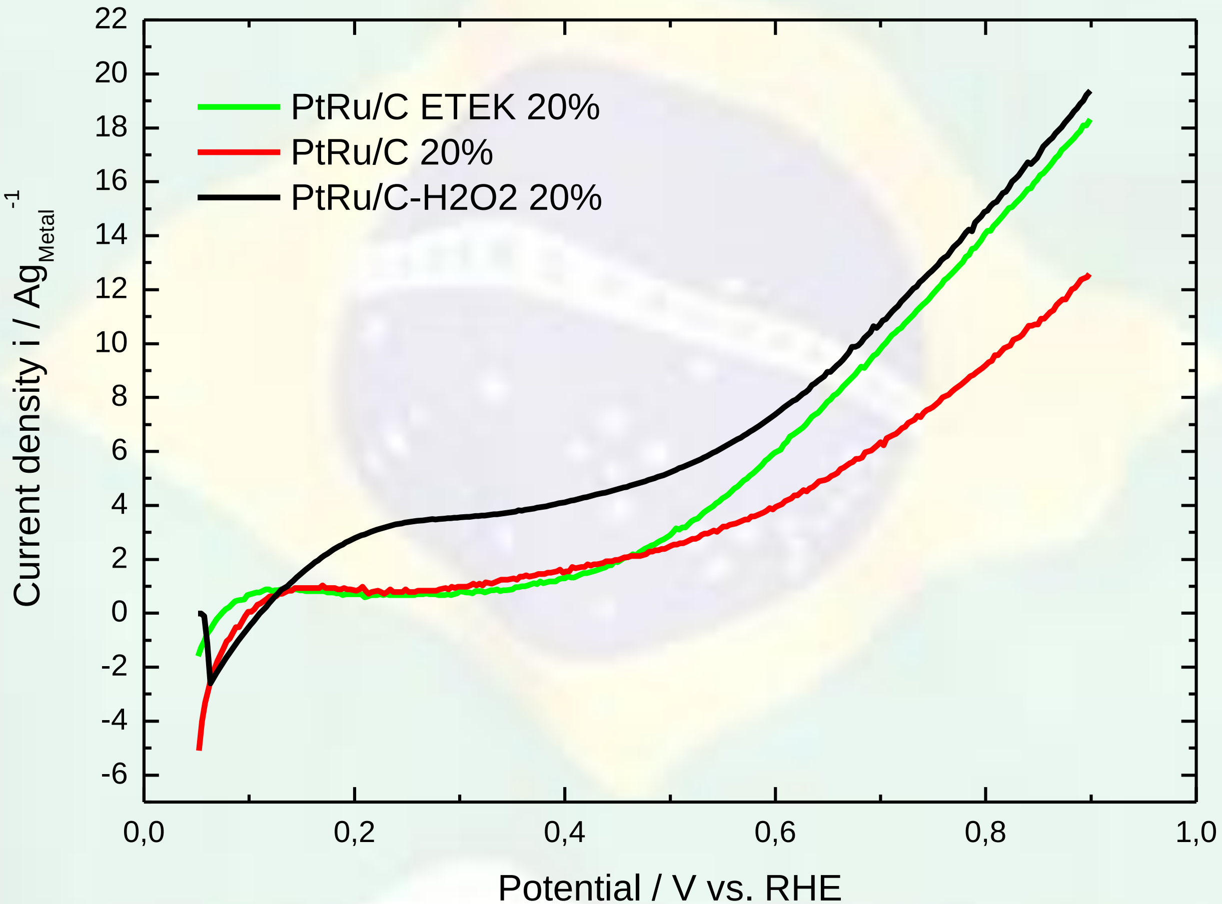
# PtRu/C-OH – $H_2O_2$ Activation

## Ciclic Voltammetry for Methanol 0.5 $molL^{-1}$ Oxidation





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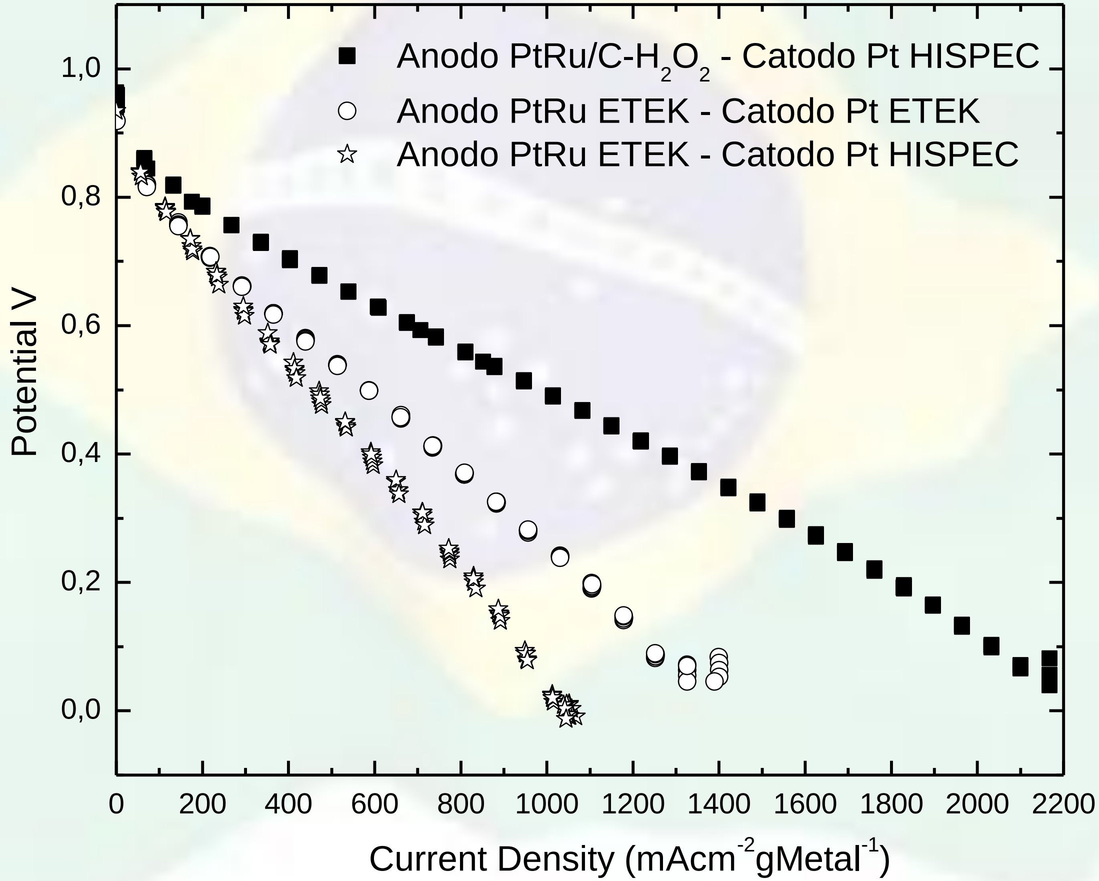
# PtRu/C-OH – $H_2O_2$ Activation $H_2$/air PEMFC results

Testcell: HIAT FC25/125, Cell Torq: 1N/mm2 air: 2.5 NL/min (100% Humidity), $H_2$: 0.8 NL/min (85% Humidity), Temp. 70°C GDLs: Anode Toray, Cathode SGL 10 CC

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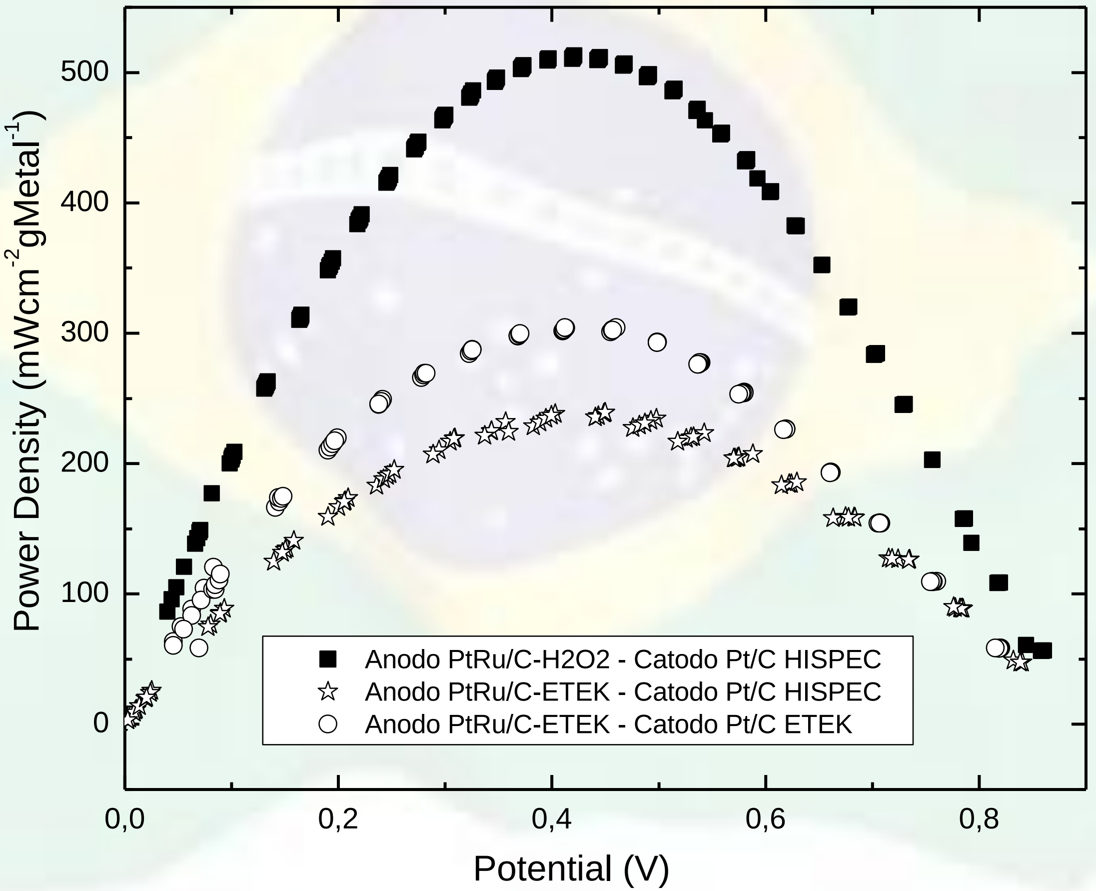



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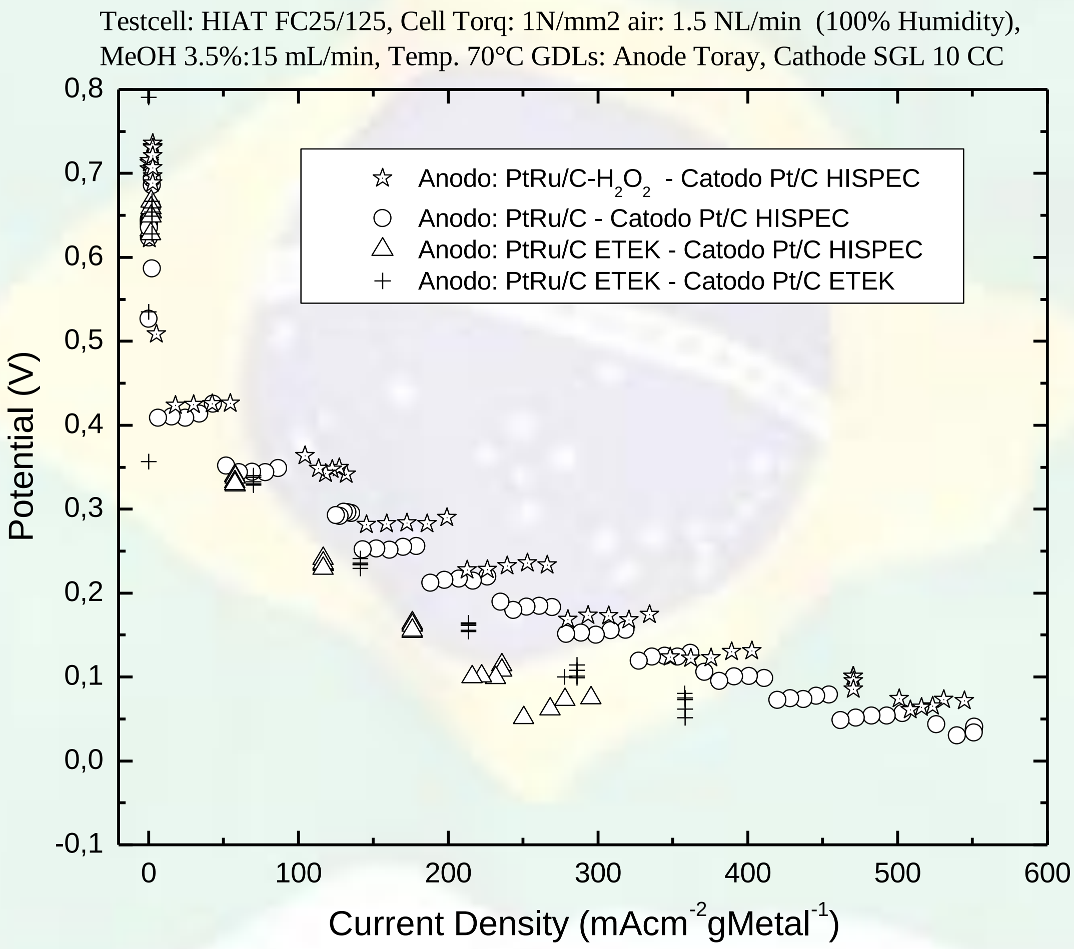
# PtRu/C-OH – $H_2O_2$ Activation
# Methanol/air DMFC results





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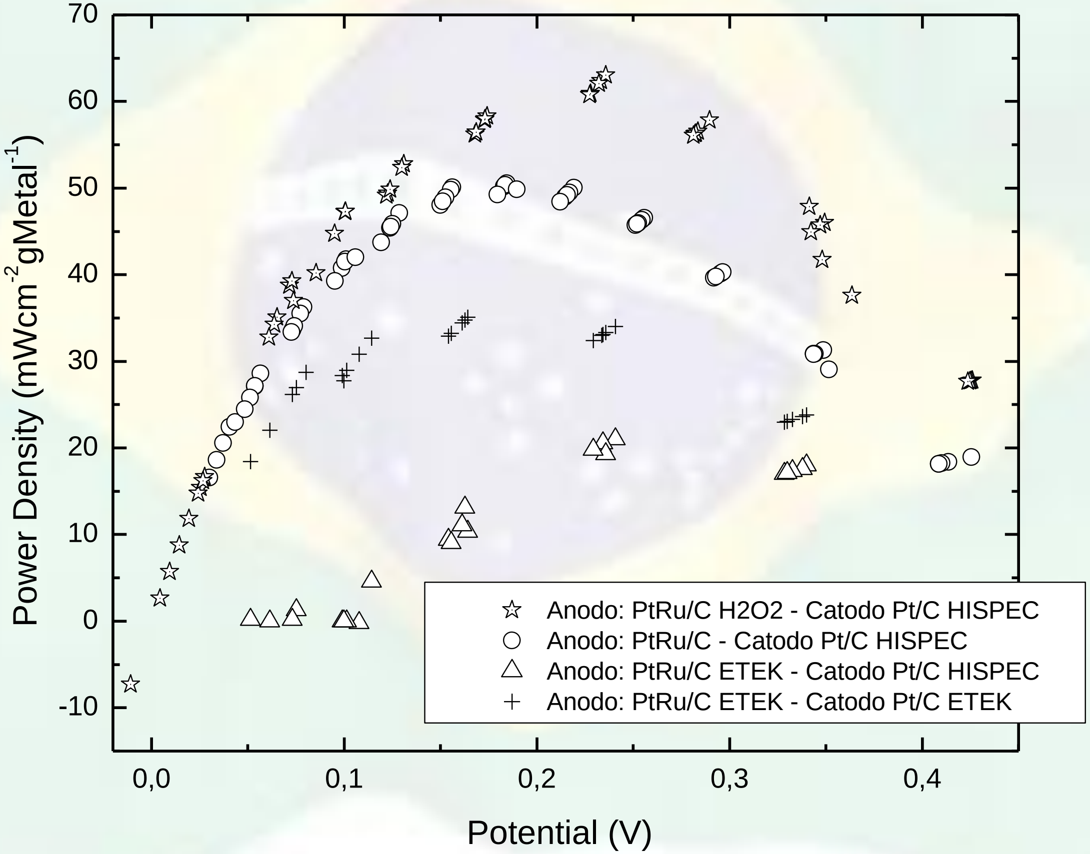
# PtRu/C-OH – $H_2O_2$ Activation
# Methanol/air DMFC results

Testcell: HIAT FC25/125, Cell Torq: 1N/mm2 air: 1.5 NL/min (100% Humidity),
MeOH 3.5%:15 mL/min, Temp. 70°C GDLs: Anode Toray, Cathode SGL 10 CC





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# Conclusions

- Elimination of the impurities and/or volatile materials resulting in a much more pure carbon material and meanly the destruction and/or blocking of the carbon pore structure

- A more amorphous structure for the material chemically treated.

- A decrease in the particle average size compared with the material without treatment, and with a very good homogeneous particles distribution.

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# Conclusions

- CV´s for methanol oxidation showed greater current density for methanol oxidation – start: 200mV, consequently better performance.
- For PEMFC:

PtRu/C-$H_2O_2$ - 519 $mWcm^{-2}g_{metal}^{-1}$,

PtRu/C ETEK 305 $mWcm^{-2}g_{metal}^{-1}$,

- the performance was at least 48% better.

- For DMFC:

PtRu/C-$H_2O_2$ - 65 $mWcm^{-2}g_{metal}^{-1}$,

PtRu/C ETEK 36 $mWcm^{-2}g_{metal}^{-1}$,

- the performance was at least 55% better.

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marcelocarmo1@gmail.com

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marcelocarmo1@gmail.com