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PLACEMENT REPORT – DUT 2 CHIMIE

Synthesis and characterization of catalytic nanoparticles on carbon support for oxidation of formaldehyde in fuel cell

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This work was carried out in Chemistry Department at the Electrocatalysis Laboratory in Faculdade de Filosofia Ciências e Letras de Ribeirão Preto at the University of São Paulo.

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My warmest thanks go to Dra. Fabiana Lopes da Silva Purgato for being by my side and always being available and Rodrigo Garcia da Silva and Thiago Cavassani for their availability and the many tips they gave to me.

Thank you to all the staff of the laboratory for their warm hospitality and availability. The joy that you release will remind me just good memories of you!

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General introduction

Since these last years, major climate changes and the increase of greenhouse gases emissions are two major problems in industrialized countries. Moreover, the sharp decline of oil and gas reserves show it is now essential to develop new sources of energy. The fuel cell appears as an interesting alternative. In fact, the fuel cell has to principle the direct conversion of chemical energy into electrical energy. Due to their very low CO_2 emissions, high efficiency and silent operation, they are considered like a promising technology.

Today, these cells mainly use hydrogen as fuel. However this gas, which is however the most abundant element on earth, does not exist in the natural state (only water). The problem of production, storage and transport, compromises the development of this type of battery.

Formaldehyde is an interesting molecule with simple structure that can be used as a model molecule in investigations of the behavior of larger organic species. Formaldehyde is present in quantity in the waste of hospitals. The use as fuel can be interesting in the place of hydrogen in oxidation side of fuel cell. During this work, cathode side will not be study.

In addition, the most common material for electrocatalysts is platinum. It is added on cathode and anode to allow the oxidation and the reduction. The fact is that platinum is a precious metal with a high cost (about 40euros/gram).

To overcome these barriers, in this laboratory many researches are implemented to develop catalysts combining several metals to use for the oxidation of organic fuel.

The preparation of new catalysts using “Water in oil” method was made combining different metals using their catalytic properties at the macro scale. The objective is the oxidation of formaldehyde at low potential and pass by the oxidation of formic acid without creating CO intermediate species (poison for catalyst).

À refaire entièrement

CHAPTER I

Presentation of the University of São Paulo

1.1/University of São Paulo

The University of São Paulo (USP) was created in 1934 and it has now become the most important institution of high school and research in Brazil. It offers a great opening to the international enabling it to form a large part of the Brazilian masters and doctors of higher education and research institutes.

The University of São Paulo is a free and public university. It is also one of three public universities in the state of São Paulo. The others are University of Campinas (UNICAMP) and University of the State of São Paulo (UNESP).

Admission is authorized to USP students selected by the vestibular (equivalent to French Bachelor). It has nearly 88.000 students to about 5.000 teachers.

The University of São Paulo is made up of 11 campuses. Four of them are located in São Paulo itself, others are located in the cities of Bauru, Lorena, Piracicaba, Pirassununga, Ribeirão Preto and São Carlos (both campuses). It has many infrastructures: 40 units of formation and research, five hospitals, five museums, five specialized agencies etc.

Actually it is the most prestigious university in Brazil and South America. Requests for admissions are very important, about 180 000 applications for just 13.000 places each year. In 2010, the USP was between the 101st and 150th ranking of institutions of high school in the world. Moreover it is corresponding more than 50% of the scientific production of the state of São Paulo, and 25% of Brazil, which is considerable. [1]

1.2/ Ribeirão Preto campus

Every year on the campus of Ribeirão Preto, 1300 seats are available for new students. 24 different courses are offered to them such as philosophy, law, music, mathematics, medicine etc.

The chemistry department belongs to the Faculty of Philosophy, Sciences and Letters of Ribeirão Preto but teachers want to make this department, an institute. This would allow them to be independent, to have more resources and therefore improve their hardware. This department has many research laboratories in organic, inorganic, analytical, physics or biology.

This internship is realize in the laboratory LEEARP (Laboratório Eletrocátalise e Eletroquímica Ambiental of Ribeirão Preto). This laboratory is supervised by two professors: Professor Dr. Paulo Olivi which focuses its research on new catalysts for fuel cells and Professora Dra, Adalgisa Rodrigues de Andrade, which focuses mainly on biofuel cells with the use enzyme.

In this lab, students conduct their researcher on the development of fuel cells using simple fuels such as methanol, ethanol, and formaldehyde. Further researches are conducted to develop multi-metallic catalysts to reduce the amount of platinum and thus reduce the cost of batteries. [2]

CHAPTER II

Generality

2.1/ Generality on the Fuel cell

A fuel cell is an autonomous electric generator which allows processing of chemical energy directly into electrical energy. It has for principle to make the reverse reaction of electrolysis.

A unit cell is composed of two electrodes, the anode and the cathode, separated by an electrolyte. It can be solid or liquid. The two compartments of the cell are fed continuously: the anode with a fuel or a reducing (hydrogen, methanol ...) and the cathode with an oxidizer or oxidant (typically air or oxygen). Unlike the conventional batteries, the reagents are renewed and products are continuously evacuated thereby obtain a continuous current.

The most widely used is the Hydrogen-Oxygen cell:

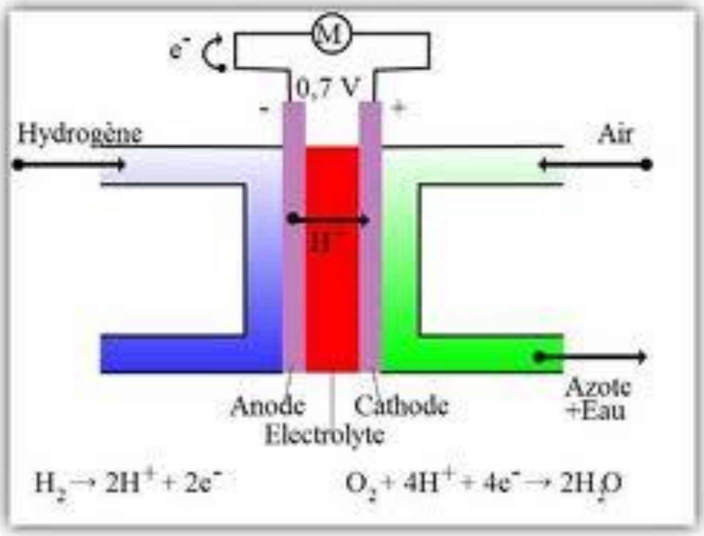

Figure 1: scheme of fuel cell

In view of this scheme, we obtain the net equation: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

Pure hydrogen is now regarded as the best fuel for cells. However, many problems arise when the use of this fuel. It can be obtained by electrolysis of water, which is a specific process, but the performance is still too low. It can also be produced by reforming hydrocarbons, but this process releases large amounts of CO_2. In addition, others problems arise at the safety, handling, storage and distribution of this gas. This is why many searches are conducted to find alternative fuels such as methanol, ethanol and formaldehyde. [3] During this work, formaldehyde is used in place of dihydrogen.

2.2/ Generality on the experiment

2.2.1/ water in oil method

The method of synthesis known as microemulsion "water in oil" is a colloidal[1] method, allowing various roads of synthesis, based on the use of two immiscible solvents. An aqueous phase is introduced into a phase alkane (or organic solvent). In the presence of a surfactant, various microscopic structures stable can be obtained depending on the volume ratio between the two phases: micelles, reverse micelles, etc. When the volume of organic phase is much higher than that of the aqueous phase, a system of reversed micelles is formed. From a macroscopic point of view, the solution seems to be homogeneous, but the nanometer scale, the solution is heterogeneous, composed of nanogoutelettes aqueous dispersed in a continuous organic phase. [4]

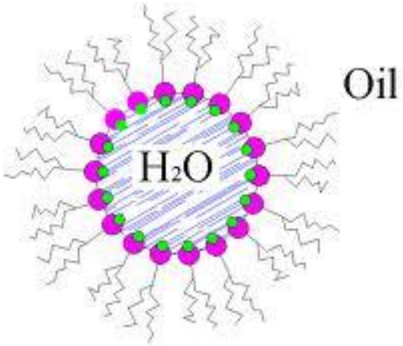

Figure 2: scheme of reverse micelle water in oil

Hydrophilic portion of the surfactant molecules surround water droplets while the hydrophobic portion is directed to the organic phase (n-Heptane Lab Synth) to stabilize the system. In addition, the volume of surfactant plays an important role in the size of the micelles thus formed for a constant volume of water. Their size is inversely proportional to the volume of surfactant present in the microemulsion.

The surfactant Brij® 30 (5 wt. % by aliphatic alcohol, Sigma Aldrich) was chosen. It is a nonionic surfactant in order to avoid interactions between the surfactant and the metal ions. It has a flexible structure enough to be permeable to a reducing agent or allow interaction and exchange between micelles when collisions occur within the microemulsion.

For the manipulation, a total metal concentration of 0.2 $Mol.L^{-1}$ in 1 ml of water must be obtained. So it is important to use metal salts soluble in water.

An optimal ratio between the concentration of surfactant and water, called the report ω was determined with $\omega = n[water] / n\ [surfactant]$. this parameter was set to $\omega = 3.8$ which means that 5.6 ml of Brij® 30 were added to 1 ml of aqueous solution containing metal salts present in the reactor. All parameters will allow obtaining particles of a size of 3 nm.

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[1] Colloidal: A system in which finely divided particles, which are approximately 10 to 10,000 angstroms in size, are dispersed within a continuous medium in a manner that prevents them from being filtered easily.

A molar ratio between reducing agent and metal salts is from 15 to provide an excess of reducing agent.

The amount of carbon Vulcan XC 72 added is 60% of the total catalyst mass. So the total mass of metal salts will be 40%. [5]

2.2.2/X-rays diffraction

X-rays diffraction (XRD) is non-destructive analytical techniques which reveal information about the crystal structure, chemical composition, and physical properties of materials. The general method consists in bombarding the sample with X-rays, and look at the X-ray intensity which is distributed according to the space orientation. The scattered X-rays interfere with each other, therefore intensity present maxima in certain directions: this phenomenon is called "diffraction". The intensity detected is recorded as a function of the deflection angle 2θ ("two theta") of the beam and the curve obtained is called "diffraction. [6]

Here, use of x rays will permit to have an approximation of the size of the particles to know if the water in oil method is valid.

2.2.3/Cyclic voltammetry

Cyclic voltammetry consists in applied to the working electrode a potential which varies linearly with time between two extreme values : E_{sup} and E_{inf}. The unity of the potential is the volt (V).

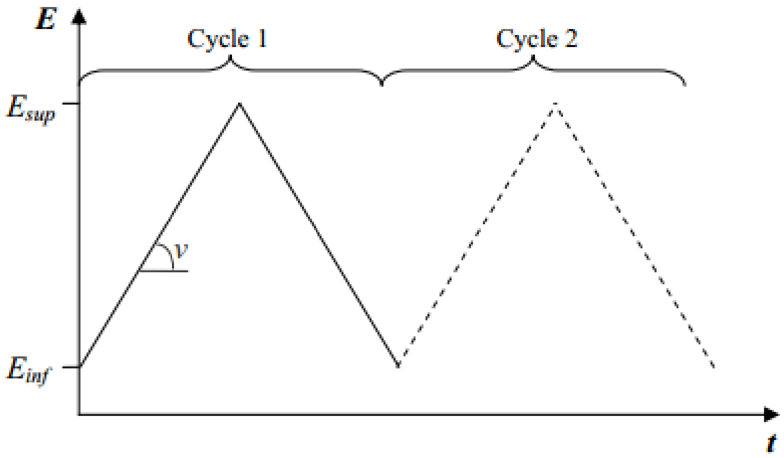


Figure 3: Evolution of the potential with time

The current response is then recorded as a function of potential. The potential is measured between the reference electrode and the working electrode, and the current between the working electrode and the counter electrode. This technique allows studying the electrochemical phenomena occurring at the surface electrode / electrolyte.

The electrochemical cell used for the experiments consists of three electrodes: the working electrode, the reference electrode and the counter electrode. They are all three placed in an electrolyte solution of sulphuric acid (H_2SO_4 0.5 mol.L^{-1}). [7]

2.2.4/ chronoamperometry

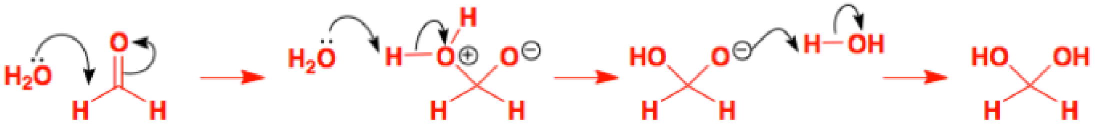
This electrochemical technique allows studying the reactions that occur on the working electrode by imposing a constant potential (the set potential being slightly higher than the start of oxidation of the fuel) and recording the current response over time.

This technique is mainly used to determine the catalytic activity of a catalyst. When the chronoamperometry is performed several times for the same catalyst, it is possible to verify the stability of the curves overlap or not. [8]

2.3/Fuel

2.3.1/Formaldehyde

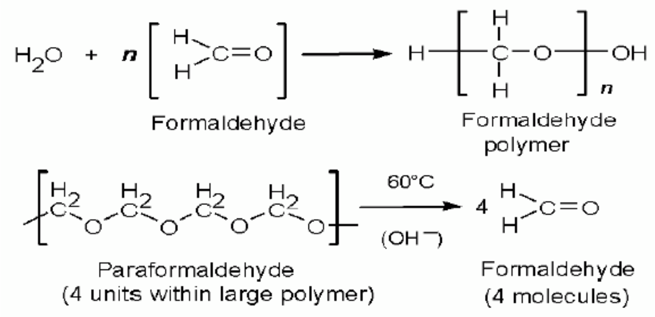
The simple structure of formaldehyde makes him an interesting organic molecule to be studied in the fuel cell. Although the experimental data make that analyzes are complicated due to the existence of chemical equilibrium involving formaldehyde and methylene glycol, which is the principal species in the aqueous solution [9].



Equation 1: Hydratation of formaldehyde in aqueous solution

This reaction is realized at 99% in aqueous solution. [10]

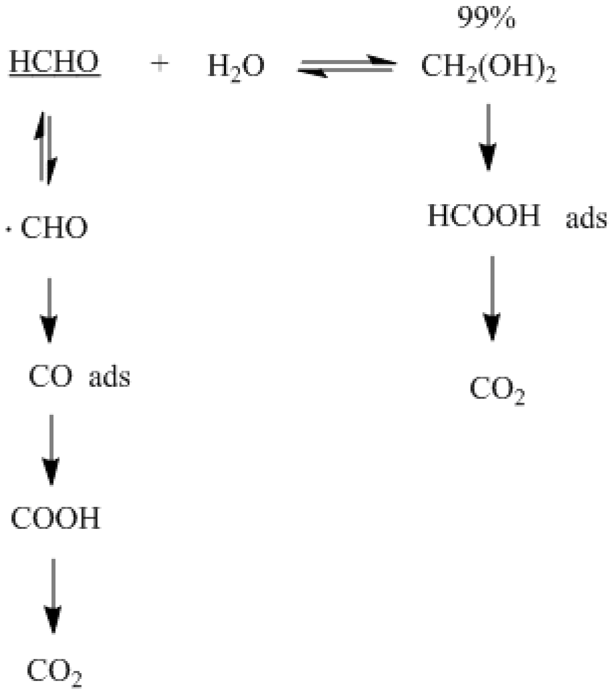
The hydrated methylene ($CH_2(OH)_2$) contains two hydrogen attached to a carbon atom and there are no C-C connections that need to be broken. The methylene hydrated molecule reacts with one another, combining to form polymer (as shown below). The liquid known as formalin containing 37-40% formaldehyde and 60-63% water (by weight), with most existing low-formaldehyde polymer (n = 2-8 in the formula given in figure below).



Equation 2: Formation of formaldehyde polymer and depolymerization of paraformaldehyde

The commercial formaldehyde solution contains approximately 10% methanol as a stabilizer. The methanol is absorbed in the noble metal electrode [11], leading to the adsorption of CO and other intermediates in which affect the results obtained when commercial formaldehyde solution are used [12]. Formaldehyde commercial solution contain 10% methanol, added by the manufacturer because it decreases leading to their eventual precipitation polymerization in paraformaldehyde. A 4% formaldehyde solution made from commercial solution therefore contains 1% methanol. It also contains a small amount of formic acid. These ions are derived from Canizzaro reaction in which two molecules of formaldehyde react with each other, one being reduced in methanol and the other is oxidized in formic acid. Because of its slow reaction rate, the concentration of ions format and methanol slowly increases with prolonged storage of the solution. [13, 14-15].

The oxidation of formaldehyde can be achieved in different ways as shown in the diagram below:



Equation 3: Different ways of oxidation of formaldehyde

The objective is to replace hydrogen by formaldehyde in oxidation side of the fuel cell and oxide formaldehyde in formic acid. The other pathway involves CO abs by the catalyst and that CO is oxide as high potential and therefore causes a blockage of catalyst sites.

Chapter III
Experiments

3.1/ Preparation of Catalyst

3.1.1/ choice of the carbon support

The most common material used as a support for catalyst in fuel cell is carbon black especially Vulcan XC-72 carbons due to its good report cost / performance. However, this support has disadvantages when used in real application in fuel cells, especially at the level of its durability / stability due to corrosion phenomena and the management of water in the middle of the pile because of its hydrophobicity. The objective is to study anodic oxidation reaction and this support is very available and study so the choice of materials was made on the Vulcan XC-72 carbons.

In order to remove any contaminants that may be absorbed on Vulcan XC-72 carbon commercial, in particular traces of sulfur, heat treatment is performed prior to use in the synthesis of the catalysts

This treatment is commonly used in the laboratory and consists in treating the carbon (from Cabot) powder for 4 h at 400 ° C under a stream of N_2. [16]

So the following program is being chosen:

Table 1: physical properties of the carbon used as a support for catalysts

Temperature (°C)	Time (min)	Rate of increase of temperature (°C/min)
250	30	30
350	30	30
400	240 (4 hours)	30

3.1.3/ Micro emulsions method

Metal salts used for the synthesis are as follows:

Or - $HAuCl_4.3H_2O$, Alfa Aesar, 99.99%
Platine - $H_2PtCl_6.6H_2O$, sigma aldrich, 99.9 %.
Ruthenium - $RuCl_3.H_2O$, Acros organics, 99.9%
Palladium - $PdCl_2$, Acros organics, 99.999%

Summary of operatory condition:

- Molar ratio ω= n[water]/n[surfactant] equal at 3.8.
- Organic solvent with a volume by synthesis of 27.35 ml.
- Metallic salt concentration in the aqueous solution of 0.2 $mol.L^{-1}$.
- Volume fraction of brij® 30 in the microemulsion is 16.5%.
- Molar ratio between the reducing agent and the metal salt of 15.
- Ambient temperature.

Starting from this, the manipulation will occur like this: [17]

- Dissolve in 1 ml of ultra pure water metal salts to obtain a concentration of 0.2 $Mol.L^{-1}$.
- Take 27.35 ml of n-heptane (merk) and put it in the aqueous solution. After this, stir.
- Add 5.6 ml of brij® 30) in the solution
- Mix slowly until obtaining a homogeneous solution and translucent.
- Add the reducing agent $NaBH_4$ (sigma Aldrich)
- Once the gassing of H_2 finished, add the Carbon Vulcan XC-72.
- Stirring with ultrason bath for 2 hours.
- Wash and filter the solution with 20 ml of acetone, 20 ml of ethanol and a mix of 50% of water and acetone.
- Repeat the washing step
- Dry the filter containing the catalyst in an oven for at least 12 hours at 75 ° C.

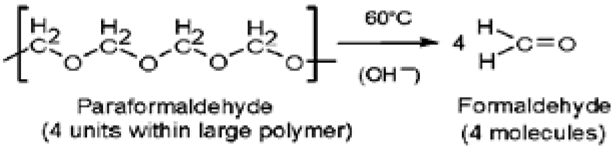
3.2/ Preparation of solution

3.2.1/ Distillation of n-heptane

N-heptane date of 2009 without has been opened. However, HPLC quality is requested, so the n-heptane is distilled according to the procedure.

Solid sodium is added to a balloon filled with n-heptane (HPLC quality from Lab Synth made in 2009). Sodium removes traces of water and will react with impurities. Distillation is then carried at 98.42 °C. For 1L of heptane to be distillate, the first and the last 100 ml of the distillate are not used. [18]

3.2.2/ Synthesis of formaldehyde



Equation 4: synthesis of formaldehyde starting from paraformaldehyde

A reflux at 60°C is performed. Concentration of paraformaldehyde in the flask is 0.2 $mol.L^{-1}$ and 10^{-3} $mol.L^{-1}$ for the sulfuric acid. [19]

So for 100 ml:

- 6.006g of paraformaldehyde is adding.
- 0.00533 ml of sulfuric acid
- Make up to 100 ml with water.

- 3 ml are pipetting and add in the electrochemistry cell.

3.2/ Characterization of catalyst

3.2.1/ X-rays diffraction

Diffraction patterns of the catalysts were obtained with an X-ray diffractometer (Siemens D5005) with Cu-K radiation (λ = 1.5406 Å) produced at 40 kV and 40 mA. The following parameters were kept constant during the analysis: the scale 2θ = 20°-90°, step = 0.03 °, time step: s = 3, and the total analysis time = 1.97 h. [20]
To obtain the size of particles, the software Profile Plus Executable, is use.

3.2.2/ Cyclic voltammetry

Preparation of working electrode:
First, an ink is prepared.

- 2 mg of solid catalyst
- 120 µL eau
- 30µL of isopropanol
- 67 µL nafion

- Take 3 µL of this solution (ink) and place on vitreous carbon electrode and allowed to harden.

After, all the cyclic voltammetry analyzes occurs like this:

- Add 50 ml of Electrolyte solution in the electrochemistry cell.
- Pass for 5 to 10 minutes, a stream of dinitrogen through the electrolyte solution to remove all traces of oxygen.
- Hydrogen generation at the reference electrode: Connect the hydrogen reference (HRE) electrode as working electrode and usually the cons electrode. Impose: i=10mA for t =35s.
- This step consists to clean and active the surface of the catalyst. For this it is necessary to apply a potential variation in the working electrode for 100 cycles at a rate of 100 mV.s^{-1}. Connect the ERH like reference electrode.
- The same operation is performed but this time only for 2 cycles at a speed of 50, 20 and then of 10 mV.s^{-1}. These slower speeds allow better visualization of the behaviour of the catalyst. Three speeds allow seeing whether differences in the behaviour of oxidation are present.
- Add formaldehyde or formic acid to obtain a concentration of 0.1 mol.L^{-1}.
- Make the analysis of this solution with 2 cycles at a speed of 50, 20 and then of 10 mV.s^{-1}

- For make others analysis, the solution and the catalyst must be replace.

3.2.3/ Chronoamperometry

The chronoamperometry is realized after cyclic voltammetry. It must be choose a potential at the top of the oxidation peak selected and the time of analysis is 1800 seconds. The software for the treatment is Autolab. [21]

3.2.4/ Fuel cell

If the electrochemical characterization is successful, that is if the catalytic activity is quite high and the initial oxidation potential low, an application to the fuel cell is then possible.

Here, $Pt_{50}Ru_{50}/C$ is used to oxide formaldehyde in fuel cell because it's the best catalyst for oxidation of formaldehyde.

First, the solution containing the catalyst is prepared. In a pill, are placed 52.9 mg of catalyst, 475 µL of ethanol and 24 µL of Nafion. The solution is then placed about 10 minutes in the ultrason bath. It must then file the solution on the anode. Indeed on the cathode is a commercial solution of platinum and carbon is deposited.

The cathode, ion exchange membrane and anode are then adjoins. For that these three elements are placed in a press preheated to 130 ° C. A pressure of 35 $kg.cm^{-3}$ must be applied for 2 minutes and 30 seconds. The complex, cathode, anode and Nafion, can be placed in a montage which allows to the fuel and the oxidant to pass. The fuel cell is then performed.

The parameters to be taken into consideration when applying in battery are:

The area of tissue of the anode and the cathode is 5.29 cm^2 for a square of 2.3 cm side.

- The oxygen pressure should be close to 2 bar.
- The fuel concentration is 2 $mol.L^{-1}$.
- The set temperature of the oxygen is still larger than that of the fuel 5 °C.
- The experiment was conducted five times, each time at a different temperature: 50 °C, 60 °C, 70 °C and 80 °C.

This manipulation provides a graph of the power vs. current density. Compared to a $Pt_{50}Ru_{50}/C$ E-TEK, it is possible to see the effectiveness of the method of synthesis.

Chapter IV
Results and discussion

4.1/ Results

4.1.1/ Validation of water in oil method

The water in oil method is realized for gold nanoparticles.

To see if the water in oil method is valid and allows obtaining particles of 3 nm, X-ray diffraction verification is necessary.

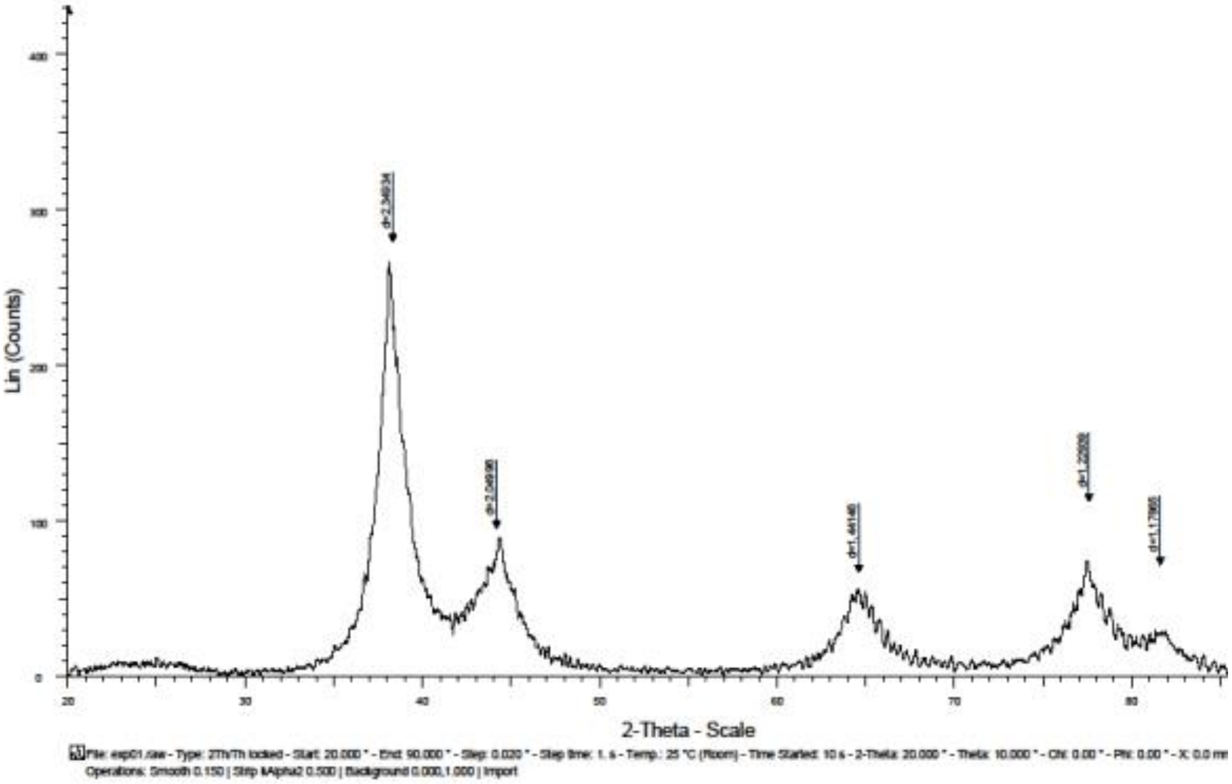


Figure 4: Graphic analysis by X-ray diffraction of the gold catalyst by oil in water method

After treatment on the software "profile plus", you can get the following data:

Table 2: X-Rays diffraction results for water in oil method for gold nanoparticles

2θ	D-space	Peak intensity	Peak area	Full width at half maximum			Breadth	Crystal size
				left	Right	Both		
64.6	1.44030	42.01	117.1	2.6182	2.6182	2.6182	2.787	3.75 nm

Only the peak at 2θ = 64.6631° is used because it is away from the zone of influence of carbon located 20 to 50° (2θ) and this peak is isolated unlike the other two peaks at 80°.

The result given by “profile plus” is an approximation that allows us to observe if the synthesis gives correct results. It was expected particles of 3 nm. For gold nanoparticles the water in oil method looks available. Other catalytic tests and size measurement are made:

Table 3: X-Rays diffraction results for water in oil method for $Pd_{90}Au_{10}/C$ nanoparticles

2θ	D-space	Peak intensity	Peak area	Full width at half maximum			Breadth	Crystal size
				left	Right	Both		
67.5	1.38547	24.39	80.3	3.0945	3.0945	3.0945	3.2940	3.22 nm

It can therefore be considered that the synthesis worked because profile plus gives a result of 3.75 nm for gold catalyst, and 3.22 nm for $Pd_{90}Au_{10}/C$ catalyst.

The method being validated, it produced a series of catalysts which are then analyzed. Catalytic properties oxidation of formaldehyde and formic acid are thus determined.

4.1.2/ Analysis of catalyst

A first series of catalysts are analyzed: $Pd_{80}Au_{20}/C$; $Pd_{90}Au_{10}/C$; Pd/C and Au/C.

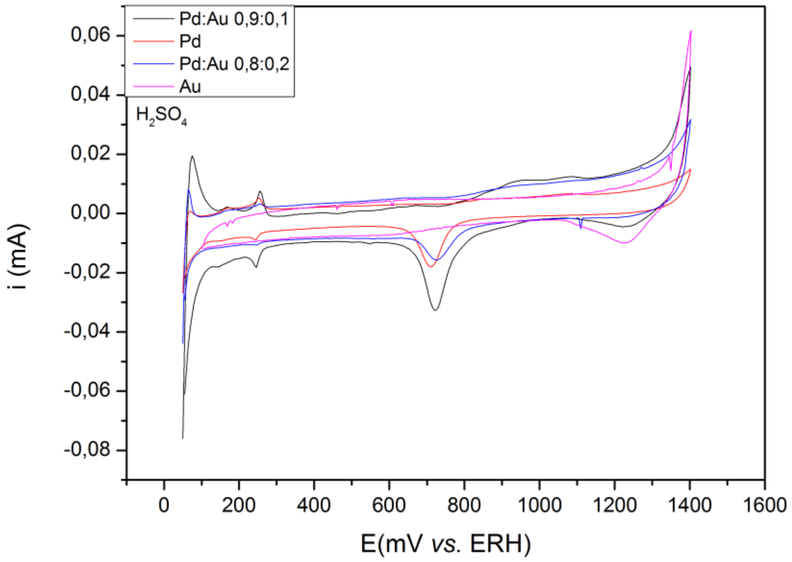


Figure 5: Cyclic voltammetry of Au/C, Pd/C and PdAu/C catalyst in H_2SO_4 0.5 mol L^{-1} medium V=10mV s^{-1}

At 200 mV there is hydrogen absorption at side of positive intensity, and desorption of the hydrogen at side of negative intensity. At 700 mV, the conventional peak of the reduction of Pd-O is observed, as well as from oxidation is at 800 mV. This corresponds to a classic voltammogram palladium catalyst in acid medium. The same sort of voltammogram is visible for platinum and for mixture of Pd/X or Pt/X in their experiments in acid medium (X: any element).

For the formic acid:

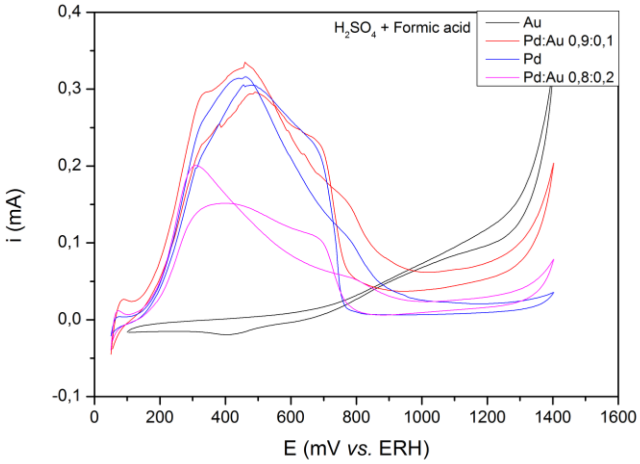


Figure 6: Cyclic voltammogram of Au/C, Pd/C and PdAu/C catalyst in H_2SO_4 0.5 mol $L^{-1}$and formic acid 0.1mol L^{-1} medium

The beginning of formic acid oxidation is approximately the same for all the catalyst. For $Pd_{90}Au_{10}$/C the intensity is a little higher than the others. And gold catalyst doesn’t oxide formic acid.

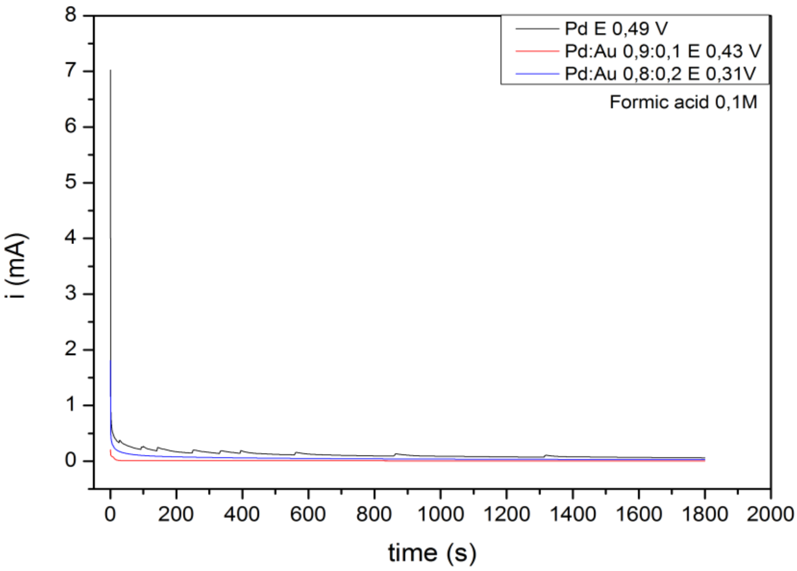


Figure 7: Chronoamperometry of Pd and Pd/Au in H_2SO_4 0.5 mol L^{-1} and formic acid 0.1 mol L^{-1} medium

This chronoamperometry shows that $Pd_{90}Au_{10}$/C not gives remarkable intensity. In addition, knowing that Pd/C is performed has a higher potential than $Pd_{80}Au_{20}$/C, we cannot conclude on that gives better results because the potential is not the same. With the cyclic voltammogram, $Pd_{90}Au_{10}$/C gives the best results because of the highest peak of oxidation. In spite of this, results for $Pd_{90}Au_{10}$/C are not so good to be use in fuel cell.

For the formaldehyde:

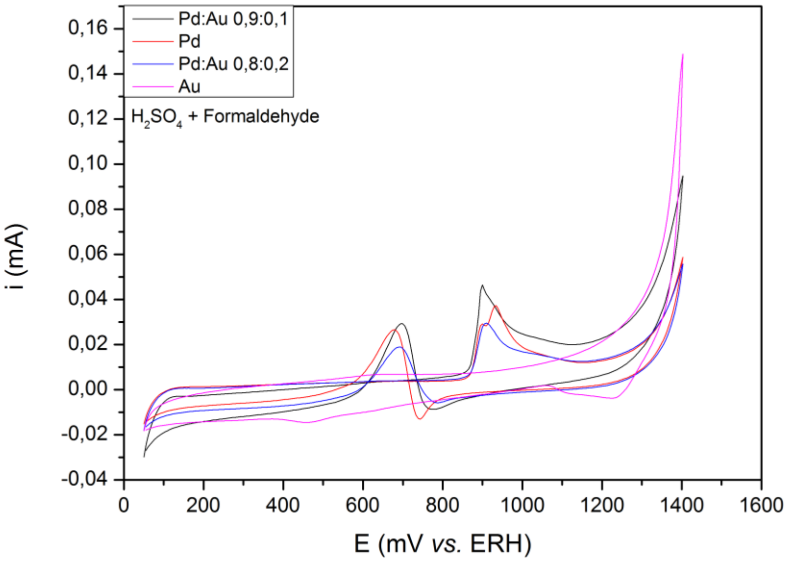


Figure 8: Cyclic voltammogram of Pd, Au and Pd/Au catalyst in H_2SO_4 0.5 mol L^{-1} and Formaldehyde 0.1 mol L^{-1} medium V=10 mV s^{-1}

For all catalysts, the oxidation of formaldehyde occurs at high potential (0.9 V vs. HRE). Moreover, the intensity of oxidation is very low (Just a little more high for $Pd_{90}Au_{10}/C$ catalyst). Two peaks can be shown for Pd catalyst. But the first peak is not visible for higher rate of analysis.[2]

The Chronoamperometry confirm this because intensity becomes 0 A after a few seconds.[3] Results are not enough good and show that the oxidation don't occurs very good. We can suppose that the oxidation of formaldehyde gives CO who is a poison for catalyst.

- **The mixture $Pd_{90}Au_{10}/C$ seems more appropriate for formaldehyde.**
- **The mixture $Pd_{80}Au_{20}/C$ seems more suitable for formic acid.**
- **The gold alone does not oxidize formaldehyde and formic acid.**

But finally, results do not allow the use in a fuel cell. A second series of catalyst is Synthesized and analyzed. These catalysts are: Pt/C, $Pt_{50}Pd_{50}/C$ and $Pt_{50}Ru_{50}/C$.

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[2] Annexes : figure I.

[3] Annexes : figure II.

For the formic acid:

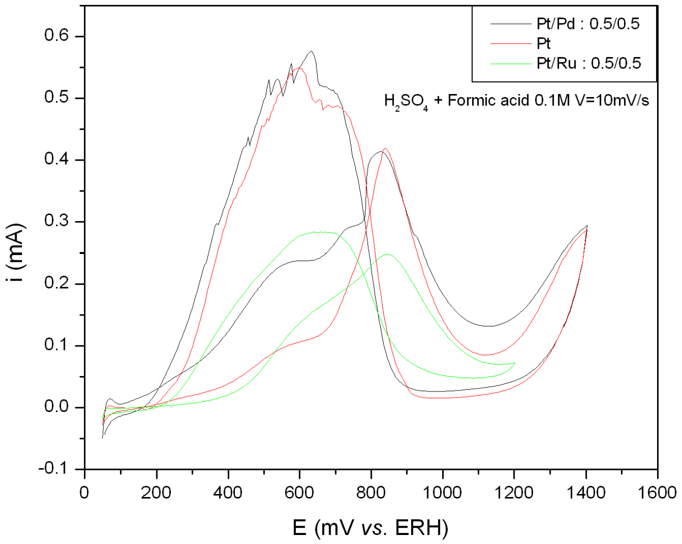

Figure 9: Cyclic voltammetry of Pt/C, $Pt_{50}Pd_{50}$/C and $Pt_{50}Ru_{50}$/C catalyst in H_2SO_4 0.5 mol L^{-1} and formic acid 0.1 mol L^{-1} medium v=10 mV s^{-1}

In formic acid medium, $Pt_{50}Pd_{50}$/C catalyst has the lower oxidation energy (0.1 V vs HRE). It looks more appropriate for the oxidation of formaldehyde than others. Moreover, three types of oxidation can be seeing (three peaks) for $Pt_{50}Pd_{50}$/C catalyst. Just two peaks can be seeing for Pt/C and $Pt_{50}Ru_{50}$/C catalyst. Changing the scanning speed, some peaks are visible more preferably.[4]

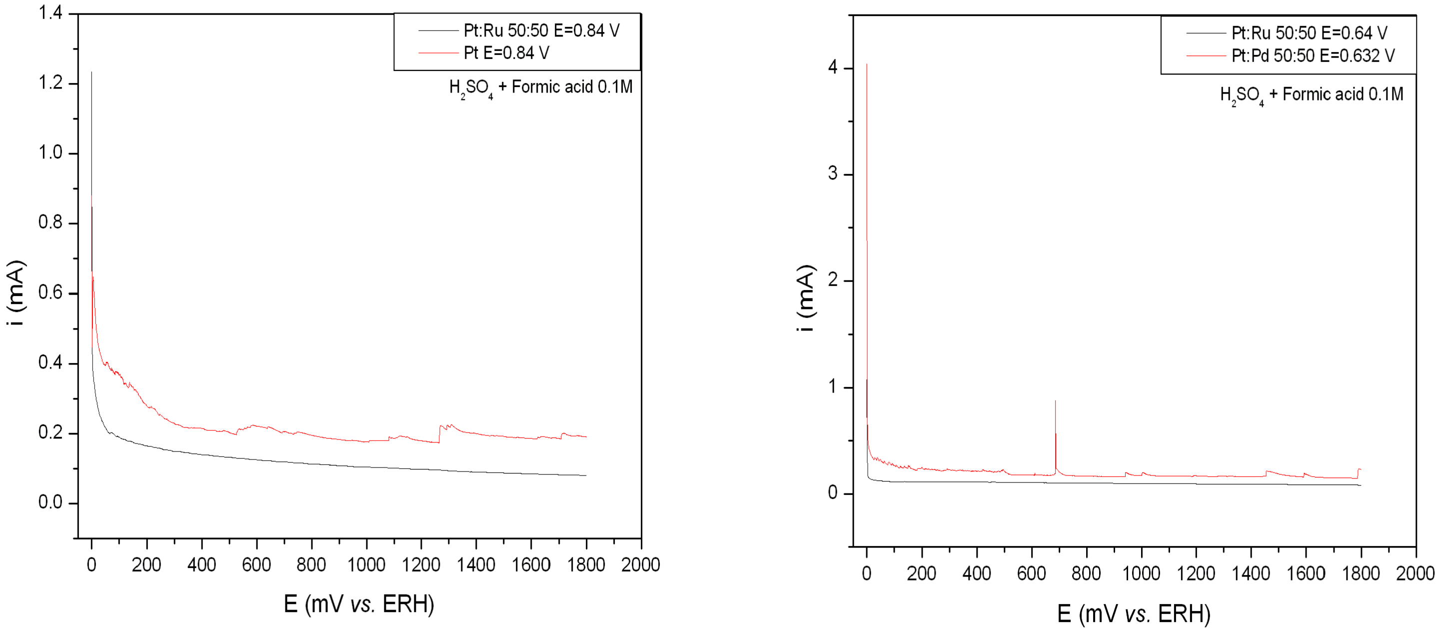

Figure 10: Chronoamperometry of catalyst in H_2SO_4 0.5 mol L^{-1} and formic acid 0.1 mol L^{-1} medium

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[4] Annexes: figure III, IV, V.

The left chronoamperogram shows a slightly higher intensity for the Pt catalyst at the same potential. It is therefore more suitable that $Pt_{50}Ru_{50}/C$ for the oxidation of formic acid.

The right chronoamperogram shows a higher intensity for the $Pt_{50}Pd_{50}/C$ at the same potential. It is therefore more suitable that $Pt_{50}Ru_{50}/C$ for the oxidation of formic acid.

With chronoamperogram and cyclic voltammogram, we can say that $Pt_{50}Pd_{50}/C$ catalyst is better for the oxidation of formic acid than Pt/C and $Pt_{50}Ru_{50}/C$.

*** $Pt_{50}Pd_{50}/C > Pt/C > Pt_{50}Ru_{50}/C$**

For the formaldehyde:

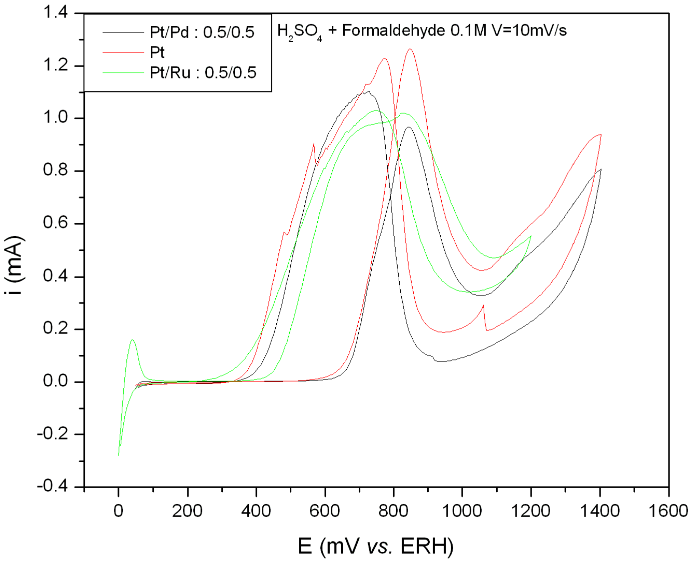

Figure 11: Cyclic voltammetry of catalyst in H_2SO_4 0.5 mol L^{-1} and formaldehyde 0.1 mol L^{-1} medium V=10mV s^{-1}

In formaldehyde medium, $Pt_{50}Ru_{50}/C$ has the lowest energy of beginning of oxidation (0.45 V vs. HRE). Pt/C and PtPd/C have approximately the same (0.65V vs. HRE). Just one peak of oxidation can be seeing for PtPd/C and Pt catalyst. For a rate of 10 to 50 mV/s. $Pt_{50}Ru_{50}/C$ have two peaks of oxidation of formaldehyde and for a rate of 50 mV.s^{-1}, the peak two become more important than the first.[5]

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[5] Annexes : figure V

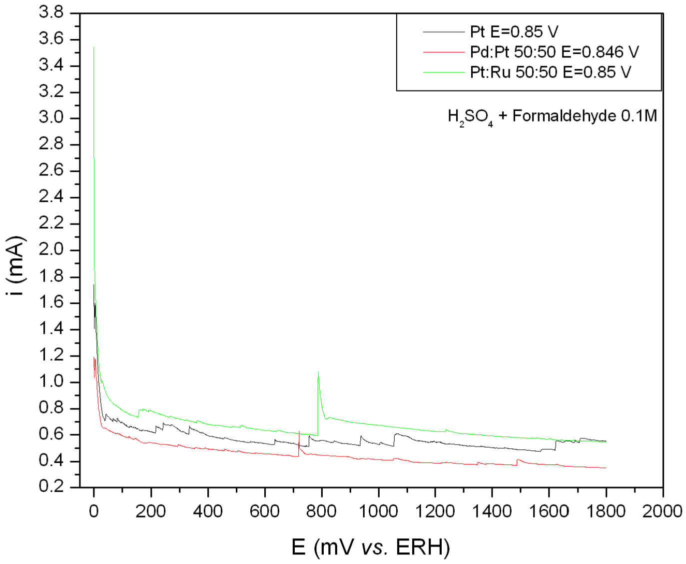

Figure 12: Chronoamperometry of Pt/C, $Pt_{50}Ru_{50}$/C and PtPd/C catalyst in H_2SO_4 0.5 mol L^{-1} and formaldehyde 0.1 mol L^{-1} medium

Here, all the potentials are the same, so it's easy to make a good comparison. So $Pt_{50}Ru_{50}$/C gives the higher intensity then Pt/C and PtPd/C.

With results of chronoamperometry and cyclic voltammetry, it can say that $Pt_{50}Ru_{50}$/C is the more suitable for the oxidation of formaldehyde, then Pt/C and $Pt_{50}Ru_{50}$/C.

- **The mixture** $Pt_{50}Ru_{50}$/C **is more appropriate for formaldehyde.**
- **The mixture** $Pt_{50}Pd_{50}$/C **seems more appropriate for formic acid.**

4.1.3/ Application to the fuel cell

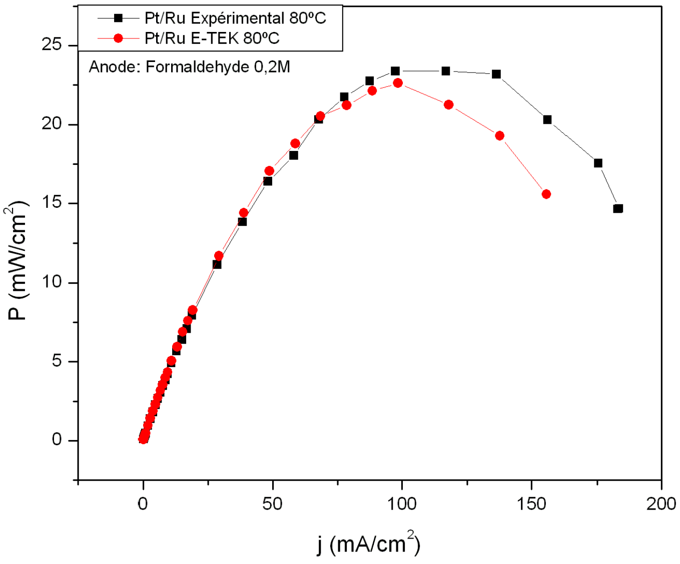

Figure 13: P = F (j) for a fuel cell with a PtPd/C at the anode side and formaldehyde as fuel

For analysis at 80 º C, the $Pt_{50}Ru_{50}/C$ synthesized by oil in water method is more active than $Pt_{50}Ru_{50}/C$ E-TEK. It means that $Pt_{50}Ru_{50}/C$ synthesized oxide better formaldehyde.

4.2/ Discussion

It is widely known that Pt/C is a very good catalyst for the electrooxidation of small organic molecules. However, this metal is easily poisoned by strong adsorbed species that block the electrode surface. . In this work it was demonstrated that $Pt_{50}Pd_{50}/C$ and $Pt_{50}Ru_{50}/C$ are better catalysts than Pt/C for the electrooxidation of formic acid and formaldehyde, respectively. The main objective was to find a good catalyst for the oxidation of formaldehyde and form formic acid without the formation of CO that is a poison for Pt catalysts.

Cyclic voltammograms showed that for a lot of catalyst, they have two or three peaks of oxidation of formic acid. It means that the catalyst surface present regions with different adsorption energies and therefore do not interact in the same way the species and that formic acid is oxidizing with different mechanisms. [22]

One of the most accepted mechanisms for formic acid oxidation is described below. The first mechanism, called “direct pathway” involves direct oxidation of the acid to carbon dioxide.

$$\mathrm{HCOOH} + \mathrm{Me} \longrightarrow \mathrm{CO_2} + 2\mathrm{H^+} + \mathrm{Me} + 2e^-$$

Me: catalyst

Equation 5: direct oxidation of formic acid

A second mechanism occurs when carbon monoxide adsorbs onto a “Me” surface, and two electrochemical steps follow:

$$\mathrm{HCOOH + Me \rightarrow Me\text{-}CO + H_2O}$$
$$\mathrm{Me + H_2O \rightarrow Me\text{-}OH + H^+ + e^-}$$
$$\mathrm{Me\text{-}CO + Me\text{-}OH \rightarrow 2Me + CO_2 + H^+ + e^-}$$

Equation 6: indirect oxidation of formic acid

The direct oxidation of formic acid occurs at the lowest potential because the increase of the scan rate during the cyclic voltammetry experiments influences preferably the first peak.[6] Direct oxidation is kinetically faster so a scanning speed high permits to show preferably the direct oxidation. Moreover, the direct oxidation appears simpler to realize than the indirect oxidation because indirect oxidation need to remove the CO of the metal which requires more energy. This argument also leads to the conclusion that the direct oxidation takes place at lower potentials than indirect oxidation. For catalysts that have three peaks of oxidation, like $Pt_{50}Pd_{50}/C$, it’s possible to suppose that another oxidation mechanism occurs or that the difference of energy leads to a catalyst with a heterogeneous surface able to present this additional peak.

In the case of formaldehyde oxidation, just Pd/C and $Pt_{50}Ru_{50}/C$ catalyst showed two

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[6] Annexes: figure III, IV, V

peaks of oxidation in cyclic voltammogram. This additional peak, in the case of $Pt_{50}Ru_{50}/C$, was observed at potential values lower than any others.

We can say that one of the peaks is the oxidation of formaldehyde in CO_2 but the reaction pass by CO. The other peak is the reaction of oxidation of the hydrate form of formaldehyde to acid formic and this is the desired reaction. This reaction occurs at more low potential than the first reaction. So we can suppose that just $Pt_{50}Ru_{50}/C$ and Pd/C can give formic acid. But $Pt_{50}Ru_{50}/C$ does the oxidation at more low potential and with good intensity than Pd/C.

The chronoamperometry gives bad results for the first series of catalyst: Pd/C, PdAu/C and Au/C. However for Pd/C and PdAu/C, the cyclic voltammetry shows that the oxidation occurs. These bad results can be explained by the fact that the oxidation gives CO and it is not oxidized by the catalysts in the applied potential. So, the carbon monoxide species block the surface of the catalysts very fast and the oxidation is inhibited.

The results of analyses of $Pt_{50}Ru_{50}/C$ in fuel cell fed with formaldehyde show that the prepared $Pt_{50}Ru_{50}/C$ catalyst is more active than the commercial $Pt_{50}Ru_{50}/C$ from E-TEK. Since the commercial catalyst presents particle sizes in the same range of the prepared one, about 2-3nm [23], it is supposed that the observed difference can be attributed to the catalyst structure.

Conclusion

The objective of this work was the synthesis of catalysts with controlled size by the oil in water method to achieve the oxidation of formaldehyde to formic acid and then form CO_2. At the end of this work, some conclusions may be derived and prospects of continuation of this work considered.

The experimental study conducted on the catalysts provides the following observation:

- The oil in water method allows obtaining nanoparticles of controlled size.
- All catalysts prepared oxide formic acid directly and indirectly.
- The modification of speeds analyzes can change the oxidation preferably carried.
- Only the $Pt_{50}Ru_{50}/C$ catalyst allows oxidation of formaldehyde to formic acid.
- Pd/C and PdAu/C can't oxide CO at low potential in the condition of experiments.
- Pt_{50} Pd_{50}/C catalyst is the best to achieve the oxidation of formic acid.
- $Pt_{50}Ru_{50}/C$ catalyst is the best to achieve the oxidation of formaldehyde.
- $Pt_{50}Ru_{50}/C$ E-TEK is worse in fuel cell application than the experimental $Pt_{50}Ru_{50}/C$.

With the aim to continue this work, it would be well to consider some points as:

- Perform the experiments in basic environments to see the impact on the oxidation of formaldehyde
- Do a tri-metallic catalyst Pd, Pt and Ru to try using of goods properties of $Pt_{50}Ru_{50}/C$ on the oxidation of formaldehyde and the goods properties of PtPd/C on oxidation of formic acid. It can afford to spend of the oxidation of formaldehyde to formic acid and formic acid to CO_2 more easily.

More personally, this work placement has allowed me to build a scientific capital in the field of metal catalysis while creating my own thinking on the subject. Moreover, in a work placement abroad in particular, information is mostly in English and thus helps us to improve our English. In addition, listen more other languages permits after three months to have very goods basis for national language, here the Portuguese.

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Illustration tab

Figures

Equation:

Table:

Annexes

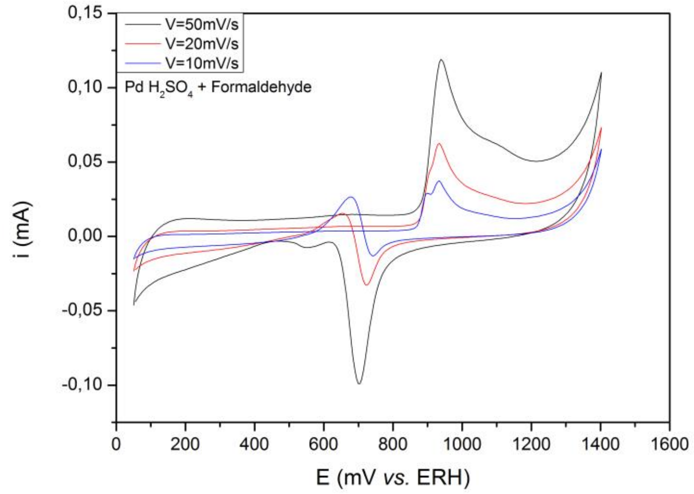

Figure I: Cyclic voltammogram Results for Pd/C catalyst.

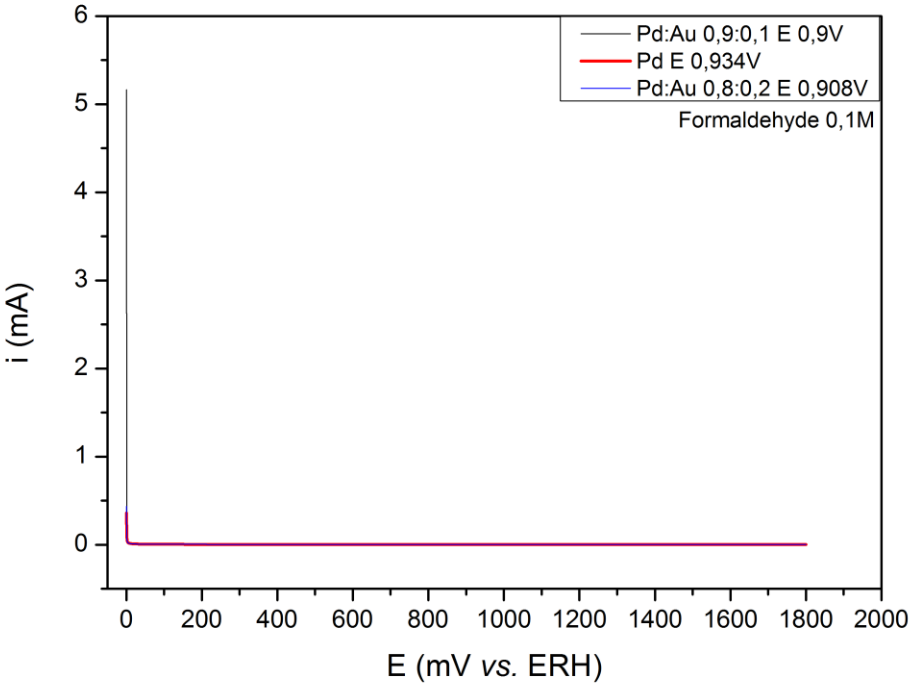

Figure II: Chronoamperometry Results for $Pd_{90}Au_{10}$/C, $Pd_{80}Au_{20}$/C and Pd/C catalyst in formaldehyde oxidation.

Pt/C :

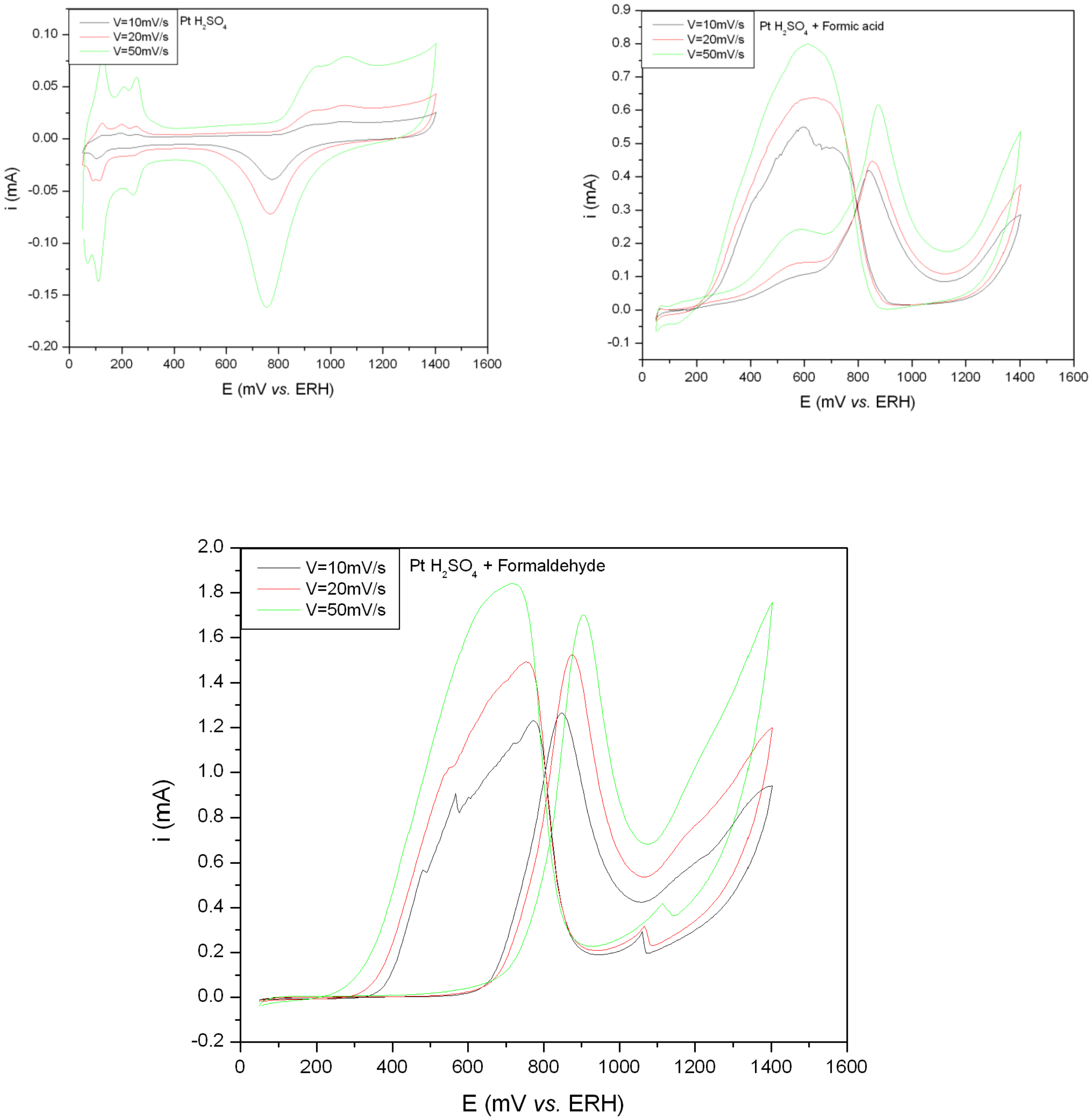

Figure III: Cyclic voltammogram Results for Pt/C catalyst.

$Pt_{50}Pd_{50}/C$:

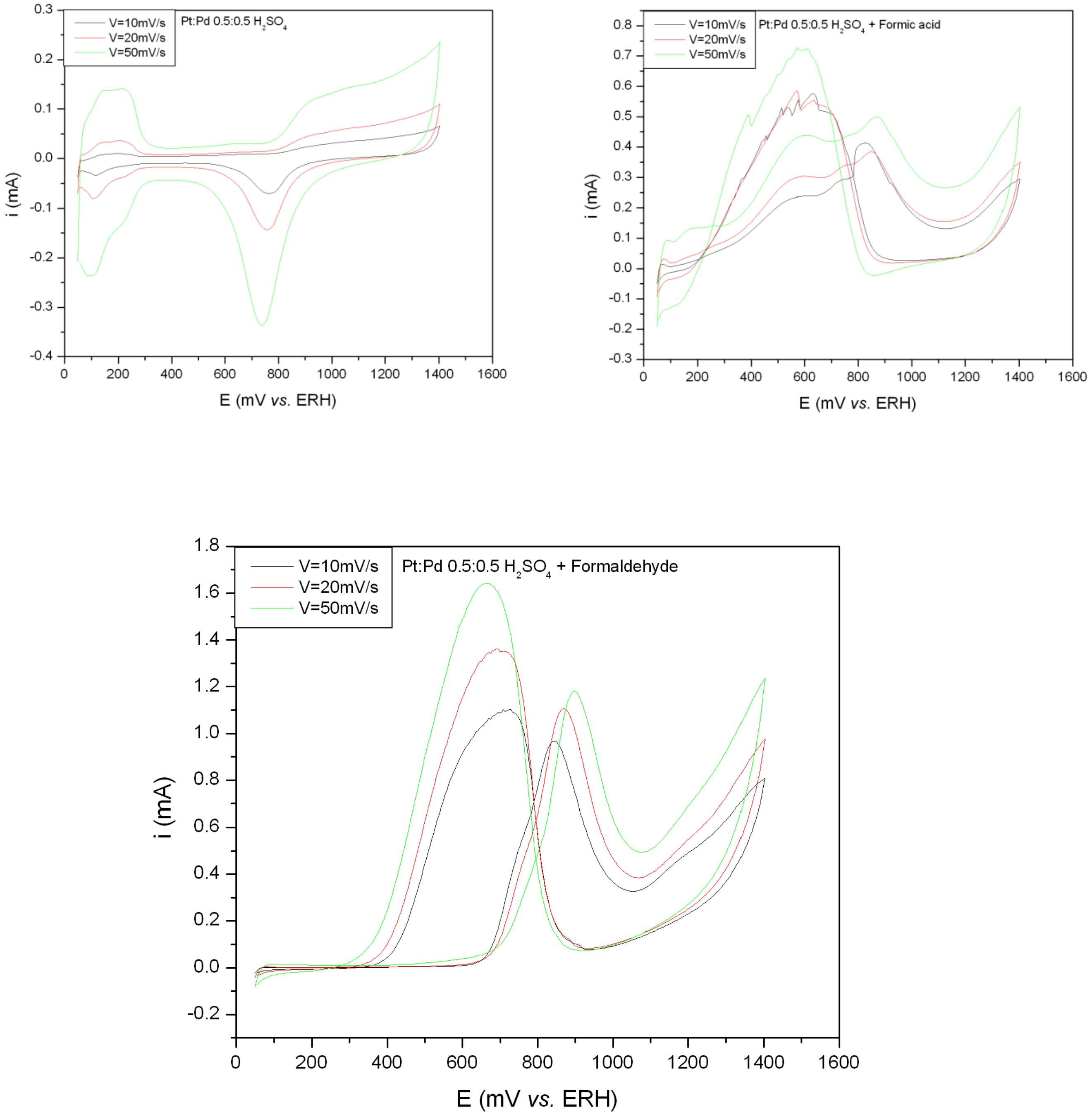

Figure IV: Cyclic voltammogram Results for $Pt_{50}Pd_{50}/C$ catalyst.

$Pt_{50}Ru_{50}/C$:

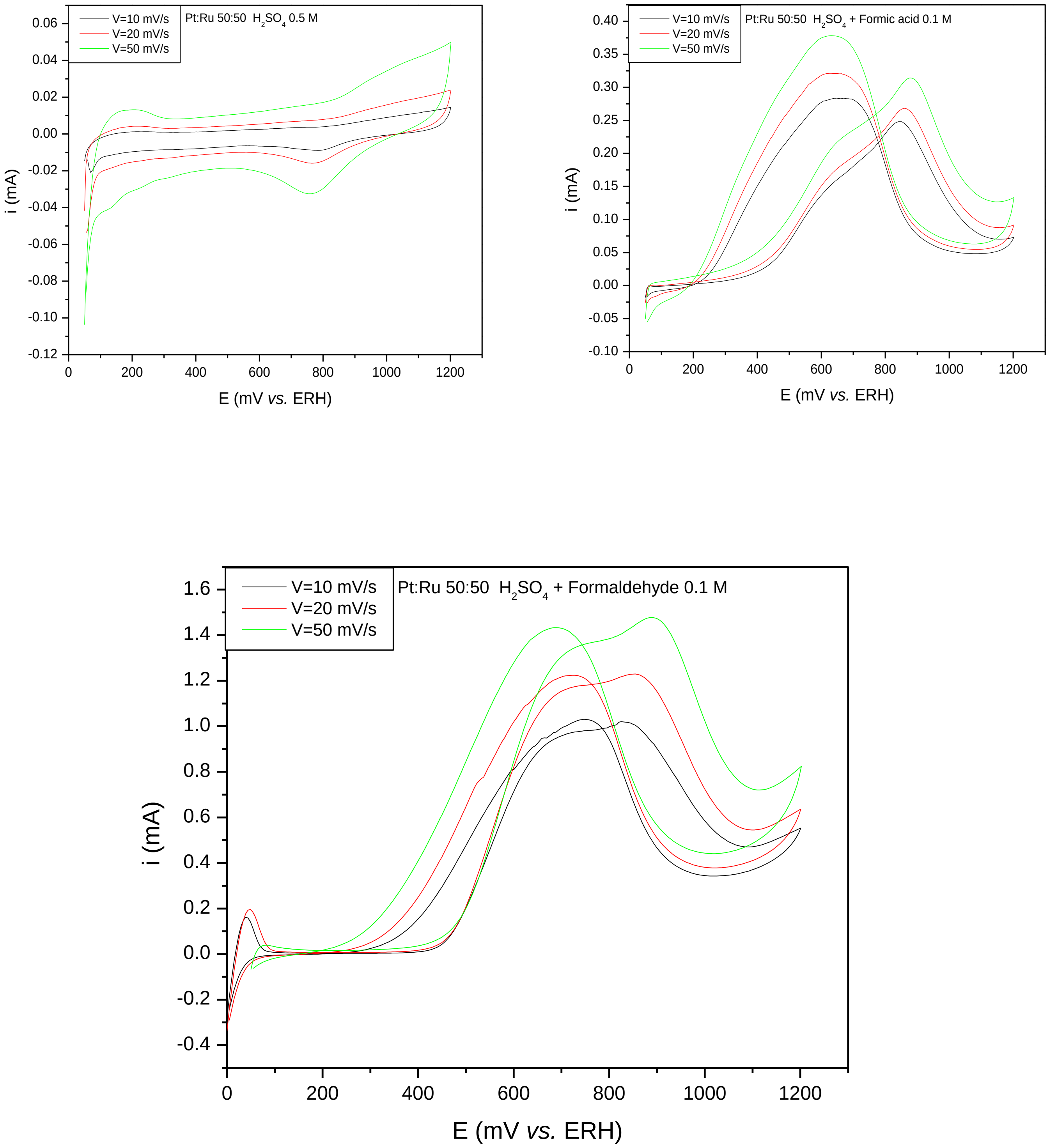

Figure V: Cyclic voltammogram Results for $Pt_{50}Ru_{50}/C$ catalyst.

Abstract

The work presented in this report talks about the synthesis by the “oil in water” method and the characterization of catalysts for the oxidation of formaldehyde in a fuel cell. The principle of the oil in water method consists in introducing an aqueous phase in an alkane phase in the presence of a surfactant. Different stable microscopic structures can be obtained depending on the volume ratio between the two phases.

The characterization of the catalysts was carried out by cyclic voltammetry and chronoamperometry. These methods will permit to determine potential and intensity of all catalysts. The study of the oxidation of formaldehyde and formic acid will tell if the synthesized catalysts can oxidize formaldehyde to formic acid and formic acid to CO_2.

The results showed that the oil in water method permit to obtain nanoparticles of the desired size. In addition, analyzes have shown that the catalysts $Pt_{50}Ru_{50}/C$ is the most suitable for the oxidation of formaldehyde and the $Pt_{50}Pd_{50}/C$ is the most suitable for the oxidation of formic acid.

Keywords: catalysts, oil in water, electrochemistry, cyclic voltammetry, chronoamperométry, analysis, formaldehyde, formic acid, oxidation, nanoparticles, X-rays diffraction.

Résumé:

Le travail présenté dans ce rapport traite de la synthèse par la méthode « oil in water » et la caractérisation de catalyseurs pour l’oxydation du formaldéhyde dans une pile à combustible. Le principe de la méthode oil in water consiste à introduire une phase aqueuse dans une phase alcane en présence d’un tensioactif. Différentes structures microscopiques stables peuvent ainsi être obtenues en fonction du rapport volumique entre les deux phases.

La caractérisation des catalyseurs est réalisée par voltammétrie cyclique et par chronoampérométrie. Ces méthodes permettront de déterminer le potentiel et l’intensité d’oxydation propre à chaque catalyseur. L’étude de l’oxydation du formaldéhyde et de l’acide formique permettra de dire si les catalyseurs synthétisés permettent d’oxyder le formaldéhyde en acide formique et l’acide formique en CO_2.

Les résultats ont montrés que la méthode oil in water a bien permit d’obtenir des nanoparticules de la taille voulu. De plus, les analyses ont montrées que le catalyseur $Pt_{50}Ru_{50}/C$ est le plus adapté à l’oxydation du formaldéhyde et que le catalyseur $Pt_{50}Pd_{50}/C$ est le plus adapté à l’oxydation de l’acide formique.

Mot clés: catalyseurs, oil in water, électrochimie, voltammetry cyclique, chrono amperométrie, analyse, formaldéhyde, acide formique, oxydation, nanoparticules, diffraction de rayon X.