Assembly of a Cost Effective Anode for Alkaline Fuel Cell

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Instructor Guide

Purpose: To select a cost-effective anode material for alkaline fuel cell using cyclic voltammetry technique.

Objectives

- To build a carbon paste electrode (CP) as an economical alternative for a working electrode.
- To modify carbon paste (CP) and glassy carbon (GC) electrodes with palladium nanoparticles (PdNP) as catalyst for fuel cells.
- To understand the difference between geometric area versus surface area.
- To compare how the superficial area affects the catalytic activity of the anode in the electrochemical oxidation of ethanol.

Introduction

Researchers have been working on developing cleaner energy sources that can replace oil and reduce greenhouse gas emissions such as fuel cell.¹ ² Fuel cells are electrochemical devices that transform chemical energy to electricity using a fuel.³ ⁴ These devices consist of two electrodes an anode and a cathode, and a polymer electrolyte membrane that transports positive (e.g. H⁺) or negative ions (e.g. OH⁻). At the anode, an oxidation reaction takes place in which the electrons are removed from the fuel. Then, the electrons move to the cathode through an external circuit where a reduction reaction occurs. Negative ions migrate through the membrane towards the anode to form water, energy and other byproducts depending on the fuel. In the general process a redox reaction takes place to produce electrical energy (see Figure 1). Advances in fuel cells will result in cleaner energy sources and therefore in the design for portable electronics and electric vehicles.

Although fuel cells are a promising technology, there are significant scientific challenges that must be overcome before they become commercially competitive. One of the issues that have to be resolved is the high cost and durability of the materials. Some approaches have been followed to overcome these limitations; such as, (a) to enhance activity of the catalyst using nanoparticles, and (b) to explore a variety of less expensive catalyst such as palladium.⁴
Currently ethanol and oxygen are being used to produce electricity. Ethanol is used as fuel due to its low toxicity and because it can be obtained from fermentation of sugar containing materials.\(^5\)

**Overall reaction:** \[ \text{CH}_3\text{CH}_2\text{OH} + 12 \text{OH}^- \rightarrow 2 \text{CO}_2 + 9 \text{H}_2\text{O} + 12 \text{e}^- \] (1)

![Figure 1. Schematic of an alkaline fuel cell.](image)

**PRE-LABORATORY (HOMEWORK)**

Part A. These questions must be completed before the Experimental Section.

1. Answer:
   a). How does a fuel cell work?
   *The fuel cell converts the chemical energy of fuel to electricity using an anode and a cathode, which produces water and energy.*

   b). What are the parts of a fuel cell?
   *The principal parts of a fuel cell are an anode, a cathode, an electrolyte and an external circuit.*

   c). What reactions occur at the cathode and anode?
   *Ethanol oxidation occurs in the anode and oxygen reduction in the cathode. Oxidation refers to the loss of electrons while reduction refers to the gain of electrons from one species to another.*
d). What is the function of the electrolyte in the cell?  
*The electrolyte’s function is the charge transport.*

e). Where do the electrons come from to reach the external circuit?  
*The electrons come out from the oxidation of the fuel at the anode of the cell.*

f). Identify in the following half reactions what is oxidized and what is reduced:

\[
\begin{align*}
\text{Zn} (s) & \rightarrow \text{Zn}^{2+} (aq) + 2e^- \ (\text{oxidation}) \\
\text{Cu}^{2+} (aq) & + 2e^- \rightarrow \text{Cu} (s) \ (\text{reduction})
\end{align*}
\]

**Write the overall reaction:**

\[
\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}
\]

This reaction is an example of zinc oxidation, which occurs spontaneously in the presence of copper in an aqueous media solution. When this unwanted oxidation occurs in metals it is called **corrosion**.

We can predict the tendency of materials to be oxidized based on their standard reduction potential. For example, Zn\(^{2+}\) needs a potential of -960 mV vs Ag/AgCl to be reduced to Zn. Cu\(^{2+}\) needs 143 mV vs Ag/AgCl to be reduced to Cu. The material that presents the lower standard reduction potential has the lower tendency to be reduced and greater tendency to be oxidized. In the reaction presented above, zinc as a good electron donor has the higher tendency to be oxidized (see **Figure 2**), while copper with a higher standard reduction potential has more resistance to corrosion.

![Figure 2](image.png)  
**Figure 2.** Standard reduction potential for Zn\(^{2+}\) and Cu\(^{2+}\) related to the redox state of the species.

Part B. Select the electrode.
1. Answer:

a). Electrical conduction in metals is due to the movement of electrons. What is the relationship between resistivity and conductivity?

The reciprocal of conductivity is resistivity.

2. Fill in the blanks for Table 1, based on the information provided in the table for each material.

Table 1. Properties of different materials used as electrodes for fuel cells.

| Material         | Catalytic activity for ethanol oxidation | Resistivity (Ωm) | Conductivity (S/m) | Standard Reduction Potential (mV) vs Ag/AgCl | Resistance to corrosion (order from high to low) | Cost ($/g) |
|------------------|------------------------------------------|------------------|--------------------|---------------------------------------------|-----------------------------------------------|------------|
| Platinum (Pt)    | Yes                                      | 1.1 x 10^{-7}    | 1 x 10^{-7}        | 991                                         | 3                                             | 15-20      |
| Zinc (Zn)        | No                                       | 6.0 x 10^{-8}    | 2 x 10^{-7}        | -960                                        | 5                                             | 5          |
| Palladium (Pd)   | Yes                                      | 1.1 x 10^{-7}    | 1 x 10^{-7}        | 718                                         | 4                                             | 11         |
| Glassy Carbon (GC)| No                                       | 3.5 x 10^{-5}    | 3 x 10^{4}         | Inert                                       | 1                                             | 3.5        |
| Graphite         | No                                       | 7.8 x 10^{-6}    | 1 x 10^{5}         | Inert                                       | 2                                             | 0.05       |

*The standard reduction potential (E) is measured with respect to silver/silver chloride (Ag/AgCl as the reference electrode.

3. Based on the properties of conductivity, resistance to corrosion, and cost in Table 1, choose the most appropriate materials (cost effective) to use as electrodes. Arrange them in descending order (best to worst electrode). Explain. 1. Palladium  2. Graphite  3. Glassy Carbon

Students are expected to discard Zn and Pt because of the low resistance to corrosion, and the cost, respectively.
LABORATORY

In this laboratory experience you will select an anode for a commercial alkaline fuel cell. The criteria for your selection should be sustained with the electrochemical studies of the following electrodes: palladium (Pd), carbon paste (CP), and glassy carbon (GC) in the presence of ethanol.

Part I. Preparation of the carbon paste electrode (CP) and determination of the electrode geometric area.

Materials:

- 2 melting point capillary tubes (CAS. No. 34500-99)
- 150 mg graphite powder (CAS. No. 7782-42-5)
- 75 µL mineral oil (CAS. No. 8042-47-5)
- 1 mortar and pestle
- 1 spatula
- 2 pieces of 6 cm copper wire without protective coating (make sure the cooper wire fits inside the capillary tube)
- 5 mL acetone (CAS. No. 8006-64-2)
- 5 mL nanopure water (or distilled)
- 1 test tube (10 cm height x 1 cm diameter)
- Flat filter paper or paper sheet
- Delicate use towels "Kimwipe" and paper towel
- Parafilm
- Balance
- 1 scissors and 1 ruler (cm)
- Micropipette and tips (1-100 µL)

Experimental Procedure:

Use of lab coat, safety glasses and gloves are essential at all times while performing the experiments.

A. Build an electrode with an inexpensive and electrically conductive material.8-9

For each team:

1. Two pieces of copper wire about 6 cm long will be provided to each group (avoid bending the copper wire).
2. Answer:
   a). Why use a copper wire?

   **The copper wire is a good conductor.**

3. Prepare a solution of 5 mL distilled water with 5 mL acetone.

4. Place two pieces of copper wire in a test tube with the acetone:water (1:1) solution and place the test tube in the sonic bath for 3 minutes (see **Figure 3a**).

5. Weigh 150 mg of graphite and transfer it to a mortar.

6. Add 75 µL of mineral oil with a micropipette to the graphite and begin mixing with the pestle until all the powder becomes a paste (see **Figure 3b**).

7. Get a capillary tube and break the closed end of the capillary tube by tilting it in an angle on a hard surface and push until it breaks. **Make use of a paper towel to cover the tube when it breaks to avoid pieces of glass being thrown out** (see **Figure 3c**).

8. Place the capillary tube with the open end that did not break over the paste and start to gently tap into the paste until it enters the tube. Repeat as necessary until 2 cm of the paste is in the tube (see **Figure 3d**).

9. Remove a copper wire from the sonic bath and rinse with distilled water. Then dry the copper wire with a kimwipe.

10. On a filter paper vertically place the capillary tube with the paste already inside. Then carefully insert a clean and dry copper wire in the capillary tube until it touches the graphite paste. (The graphite paste should be compacted within the capillary tube and the copper wire should **NOT** get to the end of the capillary tube).

11. Level the surface of the graphite paste in the tube by gently sliding it on the filter paper.

12. Clean the exterior walls of the capillary tube with a kimwipe.

13. Then seal the top of the capillary tube with parafilm to ensure that the copper wire does not come out (see **Figure 3e**). Repeat steps 7 to 13 to have an extra electrode as a backup. Keep the two carbon paste electrodes drying at room conditions with the graphite side up until the next laboratory section (at least 24 hours).
B. Determine the geometric area of the different electrodes.

1. Measure and record in Table 2 the diameter of the electrodes conductive surface (do NOT include the Teflon insulator material): CP, GC and Pd electrodes (see Figure 4).

![Figure 4. Measuring the diameter of the different working electrodes.](image)

Table 2. Geometric area of the different electrodes

| Electrodes | Electrodes surface diameter (cm) | Radius (cm) | Geometric area of the electrodes (cm²) |
|------------|---------------------------------|-------------|---------------------------------------|
| Pd         | 0.3                             | 0.15        | 0.0706                                |
| CP         | 0.1                             | 0.050       | 0.00780                               |
| GC         | 0.3                             | 0.15        | 0.0706                                |

Formula for geometric area (\(A_g\)): \(A_g = \pi r^2\)  \(\text{(2)}\)

Where \(\pi = 3.14\) and the radius (\(r\)) = diameter / 2
Part II. Electrodes with catalytic activity.

1. Answer:

a). What is a catalyst?

*A catalyst is a material that accelerates a chemical reaction.*

b). How does a catalyst affect the activation energy of a reaction?

*The catalyst decreases the activation energy.*

Nanotechnology gives us the versatility to prepare nanoscale catalysts such as nanoparticles.

c). What is the difference between 1 mL of macroparticles and 1 mL of nanoparticles of the same material?

*The principal difference is that nanoparticles have more superficial area that allow for more sites to react.*

We need a material that will accelerate the oxidation of ethanol to produce energy, since glassy carbon and graphite do not have catalytic activity for ethanol oxidation.

d). Which material would you choose to accelerate the oxidation of ethanol based on Table 1? Why?

*The palladium material because it has a high resistance to corrosion and high catalytic activity toward ethanol. In addition, it is low-cost in comparison with platinum.*

e). How would you use nanotechnology to improve the catalytic activity of the material chosen? Why?

*Nanotechnology provides versatility to design and improves the catalytic activity of a material using nanoparticles by increasing the surface area.*

f). Considering Table 1 and the fact that glassy carbon and graphite do not have catalytic activity in the oxidation of ethanol, how would you impart that property to a glassy carbon or carbon paste electrode?

*Glassy carbon and carbon paste electrodes can have catalytic activity by the modification of the electrode surface with palladium nanoparticles.*
A. Synthesis of unsupported palladium nanoparticles (PdNP) via chemical reduction

For the Instructor:

Materials:
- 1.0 g palladium chloride (PdCl₂) (CAS. No. 7647-10-1)
- 0.88 M sodium borohydride (NaBH₄) (CAS. No. 16940-66-2)
- Stirring plate and magnetic bar
- Filtration system
- 0.1 µm filter (CAS. No. 111105)
- Burette (25 mL)
- Beaker (500 mL)
- Nanopure water

Experimental Procedure:
Use of lab coat, safety glasses and gloves are essential at all times while performing the experiments.

1. The chemical reduction will be done by mixing 1.0 g PdCl₂ with 350 mL of deionized water under constant stirring.
2. Then, an excess of the reducing agent (0.88 M NaBH₄ in 100 mL of water) will be slowly added drop by drop, while continuously stirring.
3. After adding the NaBH₄, the solution will be stirred for an additional 2 hours.
4. Finally, the solution will be filtered and washed copiously with deionized water and dried at room temperature. The reduction reaction is shown below.

\[ \text{PdCl}_2 + 2 \text{NaBH}_4 \rightarrow \text{Pd} + 2 \text{NaCl} + \text{B}_2\text{H}_6 + \text{H}_2 \]

Note: This synthesis by chemical reduction using sodium borohydride is very easy.

B. To prepare palladium nanoparticles (PdNP) ink

Materials:
- Isopropanol, 99.5 % (CAS. No. 67-63-0)
- Nafion perfluorinated resin solution, 5 wt.% (CAS. No. 31175-20-9)
- Palladium nanoparticles (PdNP) powder
- Sonic bath
- 4 mL clear vial, screw top (CAS. No. 27137)
• 1 spatula
• Balance
• Micropipette and tips (1-200 µL)

**Experimental Procedure:**
Use of lab coat, safety glasses, and gloves are essential at all times while performing the experiments.

1. Weigh approximately 0.50 mg of PdNP powder.
2. Calculate the amount of isopropanol and Nafion you need to add to the PdNP to form the ink. Nanoparticles are diluted with isopropanol, and Nafion “polymer” is used to fix nanoparticles on the electrode surface.

Formula for determining the amount of isopropanol needed:

\[
\text{mg isopropanol} = \frac{(\text{experimental weight of PdNP}) \times 250 \mu L \text{ isopropanol}}{0.50 \text{ mg}}
\]  \hspace{1cm} (3)

Formula for determining the amount of Nafion needed:

\[
\text{mg Nafion} = \frac{(\text{experimental weight of PdNP}) \times 8 \mu L \text{ Nafion}}{0.50 \text{ mg}}
\]  \hspace{1cm} (4)

3. Add the amount of isopropanol and Nafion calculated to your weighed PdNP.
4. Then sonicate the mixture for 30 minutes.

*Note: The sonic bath water should not be too hot because it damages the Nafion.*

**C. Cyclic voltammetry**

The cyclic voltammetry technique can be used to find the best catalyst. This technique studies the transfer of electrons at the interface between an electroactive species in solution and the working electrode surface. The current response in function of potential (voltage) is represented as a cyclic voltammogram. The voltammogram shows an oxidation peak going to positive potentials and a reduction peak going to negative potentials (see **Figure 2**). The peaks correspond to the electron transfers that occur at the working electrode surface. Figure 5 shows the components of an electrochemical cell: working electrode (where the oxidation or reduction occurs), reference electrode (used to control and measure the difference in potential between the working electrode and reference electrode) and auxiliary electrode (provides a surface for a redox reaction to balance the one occurring at the working electrode surface and allows the current flow).
Cleaning of palladium (Pd) and glassy carbon (GC) electrodes

Materials:

- Nanopure water
- Electrochemical cell of ~ 5 mL
- Plastic pipettes (*CAS. No. 13-711-7M*)
- 25 mL of 0.10 M sulfuric acid solution (H$_2$SO$_4$) (*CAS. No. 7664-93-9*)
- 1 GC electrode (BASi, MF-2070)
- A reference electrode, silver/ silver chloride (Ag/AgCl) (3 M NaCl) (*BASi, MF-2079*)
- An auxiliary electrode, platinum (Pt)
- 1-20 µL micropipette and tips
- 25 mL beakers
- 1 waste container
- N$_2$ tank
- 1 Pd electrode (*BASi, MF-2018*)
- 1.0, 0.3 and 0.05 µm Alumina (*CAS. No. 40-6305-016*)
- Micro-cloth (*CAS. No. 40-7218*)
- PdNP “ink”
- Potentiostat (SP-50 Bio-Logic Science Instrument)
**Experimental Procedure:**
Use of lab coat, safety glasses and gloves are essential at all times while performing the experiments.

1. Place some alumina in a "micro-cloth." Polish the electrode doing an eight-shaped movement for 2 minutes. Wash the electrode with nanopure water. Then sonicate the electrode for 5 minutes in nanopure water.

2. Add approximately 1 mL of 0.10 M H$_2$SO$_4$ solution with a plastic pipette to the cell. Construct the electrochemical cell with their respective working (GC), reference (Ag/AgCl) and auxiliary (Pt) electrodes (see Figure 5). Immerse the three electrodes in the solution and connect them to the potentiostat.

*Note: Beware of the H$_2$SO$_4$ solution because is dangerous to the skin and eyes.*

**Potentiostat Operating Instructions**

1. Turn on the computer and potentiostat.

2. Open the potentiostat program and select cyclic voltammetry technique.

3. Enter the experimental conditions. The initial potential ($E_0$) is 0.00 V, $E_1 = 1.30$ V (the high potential), the final potential ($E_2$) is 0.00 V using a reference electrode of Ag/AgCl. The scan rate is 100 mV/s and the number of cycles is 3 (6 segments) for GC electrode.

4. Repeat the polishing step and the 3 cycle electrochemical cleaning until you get the typical clean surface voltammogram (see Figure 6a). Then remove the working electrode from H$_2$SO$_4$ solution and rinse it with nanopure water.

5. Carry out the electrochemical cleaning for Pd electrode in 0.10 M H$_2$SO$_4$ solution using 15 cycles (30 segments) at 100 mV/s. Repeat the polishing step and the electrochemical cleaning as necessary (see Figure 6b).

*Note: After three repetitions of the cleaning steps if the voltammogram of GC and Pd electrodes are very different to the examples shown below, change the working electrode or ask for help from the instructor. **For the instructor: The working electrode can be sonicated with ethanol for 10 minutes.***
6. Then dry the surface of both working electrodes with a nitrogen (N₂) flow.

*Note: Do not immerse the carbon paste electrode in H₂SO₄ solution, because it damages the electrode.*

**Modification of glassy carbon (GC) and carbon paste (CP) working electrodes**

**For GC electrode:**

1. Add 10 µL of the solution of palladium nanoparticles (PdNP) using a micropipette on the GC electrode conductive surface and allow to dry for 5 minutes (see Figure 7a).

*Figure 7a. GC electrode modification with PdNP.*
2. Once the working electrode with PdNP is dried, place the electrode in the electrochemical cell with 0.10 M H₂SO₄. Scan from 0.00 to 1.30 V vs Ag/AgCl at 100 mV/s for 1 cycle to obtain a voltammogram that confirms the presence of PdNP on the GC surface (see Figure 7b).

![Cyclic voltammogram of PdNP on GC surface in 0.10 M H₂SO₄ at 100 mV/s.]

**Figure 7b. Cyclic voltammogram of PdNP on GC surface in 0.10 M H₂SO₄ at 100 mV/s.**

Figure 7b shows the cyclic voltammogram for PdNP-modified GC electrode in 0.10 M H₂SO₄ solution. The cyclic voltammograms show features corresponding to the Pd oxide (PdO) formation when scanning towards positive potentials and PdO reduction formed at the electrode surface when scanning towards negative potentials. The cyclic voltammogram shows a single cathodic peak (0.28 V) which is attributed to reduction of the Pd oxide monolayer. The mechanism for PdNP is described in the following equations:\(^{10,11}\)

\[
Pd + H_2O \leftrightarrow PdO + 2H^+ + 2e^- \quad (5)
\]

\[
PdO + 2H^+ \leftrightarrow Pd^{2+} + H_2O \quad (6)
\]

Write the overall reaction: \( Pd \rightarrow Pd^{2+} + 2e^- \)

**For carbon paste electrode:**

1. Add a total of 10 µL (divided in five aliquots; air dry between additions) of PdNP solution with a micropipette onto the surface of the CP electrode and allow to dry for ~ 1 minute.

*Remember: Do not put the CP electrode without the PdNP in 0.10 M H₂SO₄!*
Part III. Ethanol oxidation using the different electrodes

Cyclic voltammetry will be used to measure the amount of current that the ethanol fuel produces. The signal obtained from the electron transfer between the ethanol and the electrode surface is measured as current.

Materials:

- Electrochemical cell of ~5 mL
- Plastic pipettes
- A GC and CP electrodes modified with PdNP ink
- A reference electrode, silver/silver chloride (Ag/AgCl) (3 M NaCl)
- An auxiliary electrode, platinum (Pt)
- 25 mL beakers
- 5 mL solution of 1.0 M KOH
- 5 mL solution of 1.0 M ethanol in 1.0 M KOH, (CAS. No 64-17-5) and (CAS. No. 1310-58-3), respectively
- Balance
- Scissors
- Printer
- Calculator
- White paper

Note: The instructor will provide the 1.0 M KOH solution for the students.

Experimental Procedure:

1. Answer:

a). What characteristic does a voltammogram show when a voltage is applied to the working electrode in a positive direction?

_We can observe anodic peaks corresponding to the oxidation of the electroactive species at the electrode/solution interface._

2. Discard the solution of 0.10 M H$_2$SO$_4$. Carefully rinse the electrochemical cell components with water. Add 1.0 M KOH as blank solution. Change the window potential: $E_0 = -0.90$ V, $E_1 = 0.40$ V, $E_2 = -0.90$ V, and obtain the voltammogram scanning at a rate of 100 mV/s for 1 cycle for each working electrode.

3. Change the solution of step 2 and add 1.0 M ethanol in 1.0 M KOH solution to the electrochemical cell. Keep the window potential of step 2, but run 5 cycles.

4. Run the electrochemical oxidation to detect ethanol using the different working electrodes (a) Pd electrode, (b) GC modified with PdNP and (c) CP modified with PdNP, just change the working electrode.
6. After obtaining the cyclic voltammograms for each electrode in 1.0 M KOH background solution and in 1.0 M ethanol in 1.0 M KOH, it is important to calculate the surface area of these electrodes. Print out the cyclic voltammogram for each working electrode in 1.0 M KOH solution.

8. Answer:
a). Identify the peak corresponding to PdO reduction in the following cyclic voltammograms (see Figure 8):

The PdO reduction peak correspond to -0.35 V vs Ag/AgCl.

![Figure 8](image)

Figure 8. Cyclic voltammogram of Pd electrode in 1.0 M KOH solution.

9. Calculate the surface area of palladium in cm$^2$ using the palladium oxide (PdO) reduction peak for each cyclic voltamograms in 1.0 M KOH (see Figure 8).
a). Cut the PdO reduction peak, measure and record the mass in grams.
b). Cut a rectangular known area using the same paper of the point b (see Figure 9), measure and record the mass in grams.

![Figure 9](image)

Figure 9. Area of a rectangle used to calculate surface area of Pd.
c). Use the units of the cyclic voltammograms in the x-axis and y-axis and calculate the area of PdO reduction peak (see equation 7):

\[ A_{Pd} = \left( I_{\text{rectangle}} (A) \right) \times \left( \frac{E_{\text{rectangle}} (V)}{\text{Peak mass (g)}} \right) \times \left( \frac{\text{Rectangle mass (g)}}{\text{Peak mass (g)}} \right) \]  

(7)

Where, \( A_{Pd} \) = Area of Pd reduction peak, \( I_{\text{rectangle}} \) = rectangle current in Amperes (A) units, consequently, \( A = C/s \), \( C \) = coulombs and \( s = \) seconds, \( E_{\text{rectangle}} \) = rectangle potential in Volts (V) units and the peak and rectangles mass in grams (g) units.

d). Use the result obtained from equation 7 and divide it by the scan rate (V/s) used to carry out the cyclic voltammetry in KOH. What units are used in the final expression?

\[ = A \times V \]
\[ = C/s \times V, \text{ this is divided by the scan rates, V/s} \]

Hence, the end unit = C

e). Use this theoretical\(^{11} \) value 424 \( \mu \)C/cm\(^2\) which is the charge density associated with the reduction of a monolayer of PdO to obtain the square centimeter (cm\(^2\)) of Pd for each working electrode (see equation 8). This final value is the Pd Surface Area. Write the value in Table 3 for each electrode.

\[ \text{cm}^2 \text{ of Pd} = \mu \text{Coloms obtained experimentally} \times \frac{1 \text{ cm}^2 \text{ Pd}}{424 \mu \text{C}} \]  

(8)

Note: The micro (\( \mu \)) unit is a factor of \( 10^{-6} \).

Table 3. Determination of surface area and current density of ethanol oxidation in GC/PdNP, CP/PdNP and Pd electrodes.

| Electrodes | Surface area (cm\(^2\)) of Pd | Anodic Peak Potential, \( (V) \text{ vs. Ag/AgCl} \) | Anodic Peak Current, \( (A) \) | Current density, \( j \) (A/cm\(^2\)) Geometric area | Current density, \( j \) (A/cm\(^2\)) Surface area |
|------------|--------------------------------|-------------------------------------------------|-----------------|-----------------------------------------------|-----------------------------------------------|
| Pd         | 0.2129                         | -1.87 \times 10^{-1}                             | 6.60 \times 10^{-1} | 9.30 \times 10^{-3}                           | 3.1 \times 10^{-3}                           |
| CP/PdNP    | 0.3543                         | -1.07 \times 10^{-1}                             | 1.24 \times 10^{-1} | 1.59 \times 10^{-1}                           | 3.5 \times 10^{-3}                           |
| GC/PdNP    | 1.777                          | -4.90 \times 10^{-2}                             | 9.66 \times 10^{-3} | 1.37 \times 10^{-1}                           | 5.4 \times 10^{-3}                           |
Note: Current values can change depending of the arrangement of PdNP on the electrode surface.

10. Determine the maxima anodic peak current and the potential to ethanol oxidation for each working electrode and write them in Table 3. (see Figure 10).

11. Calculate the current density ($j$) in units of A/cm$^2$ for Pd using the maxima anodic peak current for ethanol oxidation divided by the geometric area obtained in Table 2. Write the values for each electrode in Table 3.

![Cyclic voltammogram of CP/PdNP (solid line), GC/PdNP (dash line) and Pd (circle line) electrodes in 1.0 M ethanol in 1.0 M KOH solution.](image)

Figure 10. Cyclic voltammogram of CP/PdNP (solid line), GC/PdNP (dash line) and Pd (circle line) electrodes in 1.0 M ethanol in 1.0 M KOH solution.

Initially, figure 10 show that both peaks are anodic, these are due to ethanol oxidation. We are not showing reduction peaks. Plots showed typical ethanol oxidation behavior in alkaline conditions.

As you can see in Table 2, there is a difference between the geometric and surface area. Values for both areas are remarkably different. This is because surface area takes into account all the exposed palladium to the surface and the geometrical area takes only the palladium circle of the electrode. This means that those are the currents obtained when 1 cm$^2$ of each catalyst was studied. The final conclusion is that PdNP is the best anode towards ethanol oxidation since equal surface area when compared to (CP, GC and Pd electrodes) showed higher currents.
12. Answer:

a). How many peaks are shown in the positive direction in the cyclic voltammogram of ethanol in 1.0 M KOH?

*One peak is observed in the voltammogram in the positive direction.*

b). In the forward scan applying a positive potential, what happens to the ethanol?

*The ethanol at the electrode interface is oxidized.*

At even more positive potentials palladium oxides are formed. This Pd oxides (PdO) block the catalytic activity of ethanol.

c). How does the PdO contribute to the cyclic voltammogram?

*The anodic peak decreases as PdO amount increases at the electrode surface.*

d). How many peaks are observed in the negative direction?

*One peak is observed in the negative direction.*

Commonly a voltammogram in negative direction shows the reduction of electroactive species with a peak current in the opposite direction to the oxidation peak.

e). What species is responsible for the peak in the negative direction?

*Ethanol oxidation is responsible for the peak in the negative direction too.*

f). Do the peaks in the positive and negative directions show the same peak potential values? Why?

*No, the peak in the negative direction has a more negative potential because PdO blocked the catalytic activity for ethanol, but at more negative potential PdO is reduced to metallic Pd triggering the catalytic oxidation of ethanol.*

The peak in the negative direction appears in the region between -0.30 to -0.60 V vs Ag/AgCl. This peak towards negative potential occurs because palladium oxide is reduced to Pd. The presence of the reduced palladium catalyzes the ethanol oxidation. The mechanism for the ethanol oxidation on palladium is described in the following equations.
\[ \text{Pd} + \text{CH}_3\text{CH}_2\text{OH} \leftrightarrow \text{Pd}-(\text{CH}_3\text{CH}_2\text{OH})_{\text{ads}} \]  

(9)

\[ \text{Pd}-(\text{CH}_3\text{CH}_2\text{OH})_{\text{ads}} + 3\text{OH}^- \rightarrow \text{Pd}-(\text{CH}_3\text{CO})_{\text{ads}} + 3\text{H}_2\text{O} + 3e^- \]  

(10)

\[ \text{Pd}-(\text{CH}_3\text{CO})_{\text{ads}} + \text{Pd}-(\text{OH})_{\text{ads}} \rightarrow \text{Pd}-(\text{CH}_3\text{COOH}) + \text{Pd} \]  

(11)

\[ \text{Pd}-(\text{CH}_3\text{COOH}) + \text{OH}^- \rightarrow \text{Pd} + \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]  

(12)

The increase in the anodic current peak of the ethanol oxidation may vary when changing the KOH and/or ethanol concentrations. For this laboratory experience the concentrations of ethanol and KOH solutions are constant during the whole experiment. Furthermore, the current is only affected by the exposed area of the different working electrodes (CP and GC modified PdNP electrodes).

13. Answer:

a). Observe the last cyclic voltammogram and identify the peaks with the corresponding redox process.

Both peaks correspond to the ethanol oxidation in solution.

Discussion Questions:

1. Why does the GC electrode modified with PdNP present a better catalytic activity in comparison with the CP/PdNP and Pd electrode, based on the current obtained from the ethanol oxidation?

Because the current obtained was compared with equal area surface (1 cm$^2$) for each catalyst. As a result, GC/PdNP showed a better catalytic activity toward ethanol oxidation since equal surface area when compared to CP/PdNP and Pd electrodes, showed higher currents.

2. Is there a difference between the values obtained using the geometric area versus active area? Explain.

Yes, there is a difference between geometric area versus the active area. The geometric area of the electrode is just the area of the one dimension catalyst face exposed. The surface area is the area of all faces including curved faces of the catalyst exposed to the medium (matrix solution). The smaller the catalyst particle size, the bigger will be the surface area and better will be the catalysts effect.
3. If you increase the geometric area of the carbon paste electrode, how will the catalytic activity compare to the carbon paste electrode that you built?

*It will enhance the catalytic activity because the surface area will increase too.*

4. If you were to commercialize the anode for alkaline fuel cells with the materials studied, which one would you choose? Why?

*I would choose the CP modified with palladium nanoparticles because is cheaper. The best catalyst should present the higher value for the ratio of ethanol current obtained/geometric area of the electrode. *This is an open answer because the current values for ethanol oxidation could vary depending of PdNP arrangement at the electrode surface.*

5. What is the function of the electrodes in the electrochemical cell?

*For the electrochemical measurements we use an electrochemical cell with its respective electrodes: working, reference and counter. The working electrode is where the reaction of interest takes place, in the counter electrode an electrical current flows and the reference electrode measures the difference in potential with respect to the working electrode.*

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