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Laboratory Experiment

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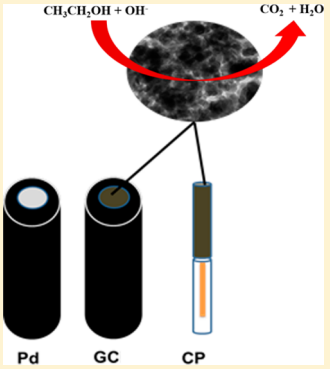
Assembly of a Cost-Effective Anode Using Palladium Nanoparticles for Alkaline Fuel Cell Applications

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Supporting Information

ABSTRACT: Nanotechnology allows the synthesis of nanoscale catalysts, which offer an efficient alternative for fuel cell applications. In this laboratory experiment, the student selects a cost-effective anode for fuel cells by comparing three different working electrodes. These are commercially available palladium (Pd) and glassy carbon (GC) electrodes, and a carbon paste (CP) electrode that is prepared by the students in the laboratory. The GC and CP were modified with palladium nanoparticles (PdNP) suspensions. The electrodes efficiencies were studied for ethanol oxidation in alkaline solution using cyclic voltammetry techniques. The ethanol oxidation currents obtained were used to determine the current density using the geometric and surface area of each electrode. Finally, students were able to choose the best electrode and relate catalytic activity to surface area for ethanol oxidation in alkaline solution by completing a critical analysis of the cyclic voltammetry results. With this activity, fundamental electrochemical concepts were reinforced.



KEYWORDS: *Upper-Division Undergraduate, Nanotechnology, Laboratory Instruction, Analytical Chemistry, Electrochemistry, Problem Solving/Decision Making*

Researchers have been working on developing cleaner energy sources that can replace oil and reduce greenhouse gas emissions such as fuel cells.[1,2] These electrochemical devices transform chemical energy to electricity using a fuel and oxygen.[3,4] These devices consist of two electrodes, an anode and a cathode, and a polymer electrolyte membrane. 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. In alkaline fuel cells, negative ions migrate through the membrane toward 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).

$$\text{Overall reaction: } CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

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]

This experience reinforces fundamental electrochemical concepts, such as electron transfer and redox reactions. In addition, the experience exposes students to factors that prevent fuel cells from becoming commercially available, such as high initial cost of the manufacturing process

Here we present a laboratory experience in which students study a cost-effective anode for fuel cells and understand electrochemical concepts[5] using cyclic voltammetry (CV) technique.

EXPERIMENTAL OVERVIEW

CV is a technique that measures current as a function of applied potential.[6] This technique uses an electrochemical cell with three electrodes: working, reference, and counter. Different working electrodes (e.g., Pd, GC, or CP) are studied as the anode. Platinum and Ag/AgCl electrodes were used as counter and reference. This laboratory involves students in the use and interpretation of cyclic voltammograms and determination of electro-active surface area for different electrodes to evaluate the anode performance of the cell.

This experience was divided into a prelaboratory and three experimental parts that gradually increase the level of reasoning. It has been implemented four times in the undergraduate instrumental analysis laboratory course. A total of 180 undergraduate students have been impacted so far. In each laboratory section, the students were divided in groups of 2 members for a total of 12 groups. The activity was done in two laboratory periods of 3 h each. In the first period, the following parts were carried out: discussion of the prelaboratory,

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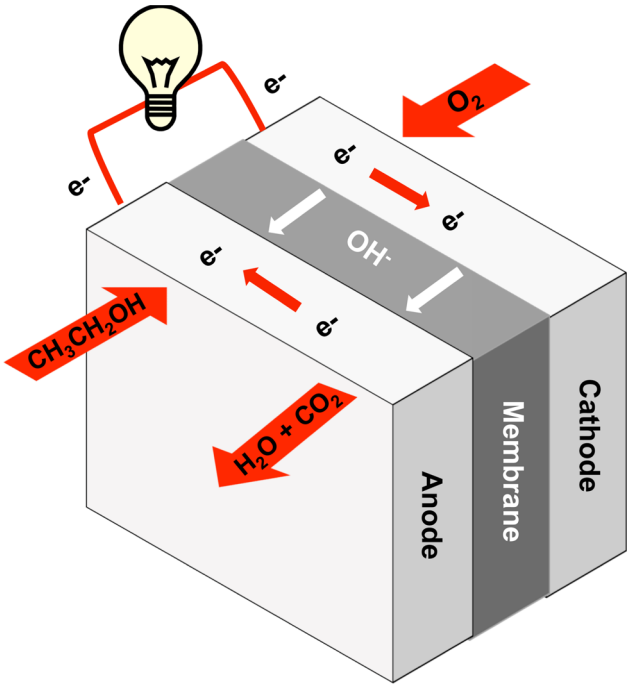


Figure 1. Schematic of an alkaline fuel cell.

preparation of the aqueous solutions and construction of the home-built CP electrode, including the measurement and calculation of the geometric area of the three different electrodes. In the second period, they worked on the PdNP ink preparation, modification and electrochemical testing of the electrodes, and data analysis for ethanol oxidation. The experience served to provide connections between the different components of fuel cells, nanotechnology, fundamental electrochemical concepts, surface area, and the use of the CV technique.

Prelaboratory

As a prelaboratory activity, students performed a literature search to predict and select the best materials to construct a fuel cell anode. Students calculated conductivity for the different electrodes materials. In addition, they determined the resistance to corrosion and chose the most appropriate electrode based on conductivity, resistance to corrosion, and cost. Table 1 summarizes some of the properties that students considered to select the best material for the construction of the fuel cell anode. This activity was done by the students as homework and discussed in the classroom.

EXPERIMENTS

Part I: Carbon Paste Electrode Preparation

The undergraduate students constructed a home-built CP electrode in the laboratory[9,10] using mineral oil, graphite, and a copper wire (see Supporting Information). Once the electrode was constructed, the students measured the diameter of the CP surface using a ruler and calculated the geometric area. They then repeated the same procedure for the different commercial electrodes: Pd and GC.

Part II: Electrodes with Catalytic Activity

In this session, students were exposed to the concepts of nanotechnology and surface area. The PdNP were synthesized via a simple chemical reduction using sodium borohydride (see Supporting Information). The students prepared a PdNP ink paste by mixing 0.50 mg of PdNP with 2-propanol and Nafion solution in a vial and placing it in an ultrasonic bath for 30 min. Then, 10 μL of the PdNP ink paste was placed on the GC and CP surface and allowed to air-dry at room temperature. Once dried, the working electrodes (GC and CP) with PdNP were placed in the electrochemical cell with 0.10 M H_2SO_4 solution. Students were required to generate their own cyclic voltammograms using an applied potential from 0.00 to 1.30 V vs Ag/AgCl at a scan rate of 100 mV/s with the PdNP modified electrodes. Then, they interpreted the generated cyclic voltamograms for each electrode and compared their results with the literature.

Part III: Ethanol Oxidation Using the Different Electrodes

In this part, the surface areas of different electrodes were calculated using data obtained from voltammograms in 1.0 M KOH solution. The catalytic activity for ethanol oxidation in 1.0 M KOH solution was tested using the CP and GC electrodes modified with PdNP. The working electrode was placed in the electrochemical cell, and the applied potential was cycled between −0.90 and 0.40 V vs Ag/AgCl at a scan rate of 100 mV/s. This step was repeated for the commercial Pd electrode. Once the cyclic voltammograms were obtained, the students determined the peak current density for ethanol oxidation using the electrode geometric and surface area and compared the results for each working electrode tested.

HAZARDS

Students must wear a lab coat, goggles and gloves at all times during the lab. Concentrated sulfuric acid is dangerous to the skin and eyes; they must be used in a fume hood. Potassium hydroxide causes severe skin burns and eye damage. Sodium borohydride is irritant and corrosive.

Table 1. Properties of Different Materials Used as Electrodes for Fuel Cells[a]

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)[7,8]
Platinum (Pt)	Yes	1.1×10^{-7}	1×10^{7}	991	3	15
Zinc (Zn)	No	6.0×10^{-8}	2×10^{7}	−960	5	5
Palladium (Pd)	Yes	1.1×10^{-7}	1×10^{7}	718	4	11
Glassy Carbon (GC)	No	3.5×10^{-5}	3×10^{4}	Inert	1	3.5
Graphite	No	7.8×10^{-6}	1×10^{5}	Inert	2	0.05

[a]The values in Table 1 were obtained from references7 and 8. Standard reduction potentials are referred to aqueous solutions at 25 °C, 1 atm. versus Ag/AgCl (3 M NaCl).

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RESULTS AND DISCUSSION

In the prelaboratory activity, students analyzed the requirements for an effective anode using the information in Table 1 and their own literature search. Then, they selected the materials to be tested as an anode. In part I, they measured each working electrode surface diameter and calculated the geometric area. With this data collection, students were able to see a difference in the diameters for the different electrodes.

In Part II, an introduction to CV technique was given to students. Then, the presence of PdNP on the GC and CP electrodes was confirmed using the CV technique in 0.10 M H_2SO_4 solution and a potentiostat. Figure 2 shows the cyclic voltammograms for bare GC and GC modified with PdNP in 0.10 M H_2SO_4 solution. The bare GC electrode did not show oxidation and reduction peaks. However, GC modified with PdNP showed current peaks corresponding to the palladium oxide (PdO) formation at positive potential and PdO reduction at negative potential.[11,12] The students were guided to make a detailed interpretation of each cyclic voltammogram, explaining the characteristic peaks and its corresponding redox reaction.

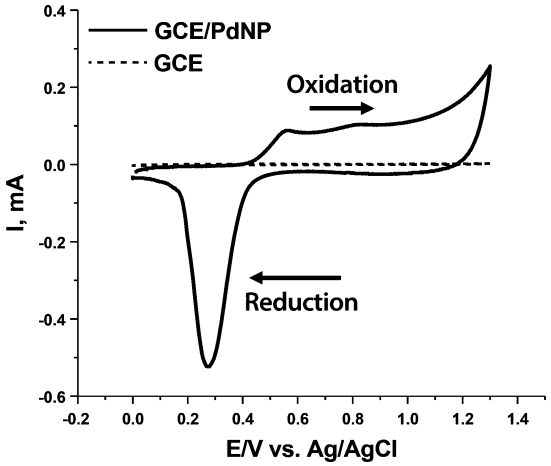


Figure 2. Cyclic voltammogram of GC electrode modified with PdNP (solid line) and bare GC electrode (dash line) in 0.10 M H_2SO_4 solution.

In Part III, the student calculated the active surface area of Pd using the voltammograms obtained from in 1.0 M KOH for each electrode (see Supporting Information). The results obtained were collected in Table 2. In addition, the students tested the catalytic activity for ethanol oxidation using the different electrodes modified with the PdNP. The obtained results were compared with the voltammogram of the commercial Pd electrode. The current density was calculated using the ethanol oxidation peak current divided by both the electrode geometric and surface areas for each electrode, and the results were compared. The potential, current, and current density values were written in Table 2.

Figure 3 shows cyclic voltammograms of the ethanol oxidation using an alkaline medium, i.e., 1.0 M ethanol and 1.0 M KOH. Students observed two peaks: the first peak appears in the potential region from −0.50 to 0.00 V vs Ag/AgCl during the forward scan (positive direction). At positive potentials, the formation of PdO blocks the catalytic activity for ethanol oxidation.[12−14] In the reverse scan (negative direction), PdO is reduced to metallic palladium starting at −0.30 V, returning the ethanol oxidation catalysis, and showing an anodic peak again. Students observed this second peak in the region between −0.30 and −0.60 V vs Ag/AgCl in 1.0 M ethanol and 1.0 M KOH solution. This voltammetry experiment showed that both peaks are anodic, a typical ethanol oxidation behavior in alkaline conditions. We are not showing reduction peaks.

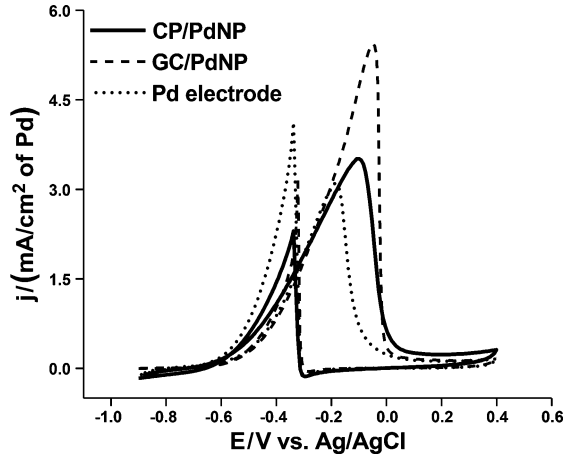


Figure 3. Cyclic voltammogram of CP/PdNP (solid line), GC/PdNP (dashed line), and Pd (dotted line) electrodes in 1.0 M ethanol and 1.0 M KOH solution.

Finally, the students choose the best cost-effective anode electrode for an alkaline fuel cell through the literature search, experimental method, and analysis of data summarized in Table 1 and the results are presented in Table 2.

Results shown in Table 2 will allow students to learn about the effect of the electrode active surface area on the performance of the electrode. It is expected that they understand that electrodes with equal area surface (1 cm^2) for each catalyst will have high catalytic surface area and will produce a higher peak current density.

CONCLUSION

A new laboratory experience that introduces students to applications of nanotechnology and fuel cells was successfully implemented in the Instrumental Analysis Laboratory course. During this experience, students developed skills related to literature search, and interpretation and analysis of electro-

Table 2. Determination of Surface Area and Peak Current Density of Ethanol Oxidation for the Different Electrodes in 1.0 M KOH and 1.0 M of Ethanol in 1.0 M KOH

Electrodes	Geometric area (cm^2)	Surface area (cm^2) of Pd	Anodic Peak Potential, (V) vs Ag/AgCl	Anodic Peak Current, (A)	Current density, j (A/cm^2) Geometric area	Current density, j (A/cm^2) Surface area
Pd	7.06×10^{-2}	0.2129	-1.87×10^{-1}	6.60×10^{-4}	9.30×10^{-3}	3.1×10^{-3}
CP/PdNP	7.80×10^{-3}	0.3543	-1.07×10^{-1}	1.24×10^{-3}	1.59×10^{-1}	3.5×10^{-3}
GC/PdNP	7.06×10^{-2}	1.777	-4.90×10^{-2}	9.66×10^{-3}	1.37×10^{-1}	5.4×10^{-3}

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chemistry data related to fuel cell. In the prelaboratory, they were encouraged to convert resistivity values to conductivity, resistance to corrosion, and to consider the economical aspect in the selection of materials for anode electrodes. In the experimental process, they were exposed to fundamental electrochemical concepts, and tested and analyzed how different parameters such as material and surface area affect the catalytic activity for ethanol oxidation in alkaline media.

The principal limitations confronted in the experience were related to students' previous knowledge of fuel cells components and the use of the CV technique. In spite of the wide use of CV in academic and research, this technique was not well understood by the students in comparison to other instrumental techniques such as chromatography and spectroscopy. At the beginning of the experience, the students demonstrated poor understanding of the concepts involving the CV technique such as the peculiar shape of the voltammograms. Therefore, a brief description of the CV technique and operation of fuel cells components presented in most textbooks is insufficient to attain a comprehensive understanding. It was necessary to explain the technique in detail to the students with an emphasis on the analysis of the voltammograms to characterize the function of the fuel cell components.

The most challenging part for the students was the interpretation of the cyclic voltammograms obtained for ethanol oxidation. Since in most textbooks CV is explained using voltammograms where oxidation and reduction peaks are observed, the ethanol oxidation voltammogram was confusing for the students, because the reduction peak was absent. This is a typical behavior for ethanol oxidation in alkaline conditions. This behavior was explained in detail to the students with the use of the literature.

■ ASSOCIATED CONTENT

Supporting Information

Student and instructor manuals. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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