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Laboratories and Demonstrations

An Electrochemical Puzzle: The Catalyzed Anodic Dissolution of I-coated Palladium in Halide-Free Acid Solutions

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This laboratory uses a series of electrochemical procedures that are designed to investigate this unique oxidative process.

Iodine adsorbed on a Pd electrode has been shown to catalyze the anodic dissolution of Pd in halide-free acidic solutions. An undergraduate instrumental analysis laboratory experiment has been developed that enables students to use basic electrochemical techniques (cyclic voltammetry and chronocoulometry) to detect and confirm this phenomenon. Cyclic voltammograms of clean Pd and I-coated Pd were done in 0.5 M sulfuric acid solutions containing iodide and iodine as well as halide free 0.5 M sulfuric acid. The large currents noted in the halide-free solution indicate an anodic process that is not related to the oxidation process in solutions containing iodine species. Chronocoulometry was used to determine the total charge that was passed in the 0.5 M sulfuric acid solutions for clean and I-coated Pd electrodes. The results of these experiments point to a unique catalyzed corrosion process for this otherwise inert metal.

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Introduction

Instrumental laboratories that teach multiple electrochemical techniques while investigating very unique and timely chemical phenomena are few. Several years ago, we noted that cyclic voltammograms of Pd electrodes that had been previously dipped in iodide solutions to prevent air oxidation exhibited huge oxidation currents [1]. The procedures in this instrumental analysis laboratory experiment characterize this anomalous oxidation peak and allow students to investigate the oxidative process that is occurring.

This laboratory uses a series of electrochemical procedures that are designed to investigate this unique oxidative process. It also provides the student with a growing body of knowledge, including data from two surface-analysis techniques, thermal desorption mass spectrometry (TDMS) and x-ray photoelectron spectroscopy (XPS). This will aide the student in making valid conclusions. In many laboratory experiments, the student compiles data without understanding. In this experiment the student is made to think about the purpose and significance of the results of each step as they perform the experiment.

The student is exposed to two electrochemical procedures in this laboratory. Cyclic voltammetry (CV) is used as a qualitative tool to identify the anomalous electrochemical behavior and identify its source [2]. Often called *electrochemical spectroscopy*, cyclic voltammetry measures the intensity of electron transfer (current) versus applied energy (potential). The potential at the electrode/solution interface is ramped through a predetermined range of potentials and the current that flows across the interface is recorded. This current is a function of the type and concentration of the species found at the interface. Chronocoulometry (CC) is used quantitatively to understand the magnitude of the dissolution process [2]. The potential is stepped from an inert or quiet potential region to a potential that will drive a redox reaction at the electrode/solution interface. This technique records the total charge that passes as a function of time during the application of a potential step.

The student will use four different procedures in order to investigate the oxidative process which is occurring at the electrode surface. Procedure #1 reproduces the cyclic voltammograms that reveal the large anomalous oxidation currents that occur on the I-coated Pd electrode. Procedure #2 investigates the role of iodine-containing species on the magnitude of the oxidation currents. Procedure #3 uses chronocoulometry to

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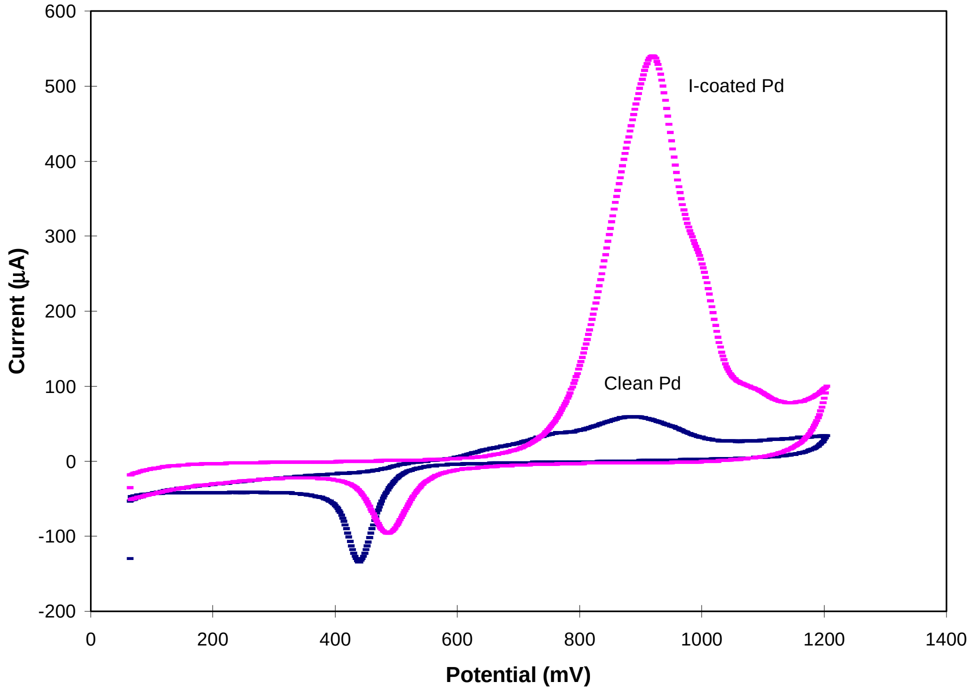

FIGURE 1. CYCLIC VOLTAMMOGRAM OF A CLEAN Pd ELECTRODE IN 0.5 M SULFURIC ACID AT A SCAN RATE OF 20 mV s^{-1}.

quantify the magnitude of the oxidation currents. Finally, procedure #4 probes the stability of the I-adlayer during the oxidative processes.

These experiments should be completed in two laboratory periods. Procedures #1 and #2 should be completed in the first period. Performing the cyclic voltammetry experiments first will allow students to determine the correct potential steps which should be used in the chronocoulometry section of the experiment (procedures #3 and #4).

In order to complete the experiment, the student is provided with background knowledge specific for each procedure being performed. For the cyclic voltammograms in halide free acidic solution (procedure #1), the student is told about the electrochemical reactivity of palladium. Because palladium is known to absorb hydrogen readily into its lattice, all CVs should avoid the potential region below 60 mV as seen in Figure 1. When the Pd electrode is exposed to voltages greater than 550 mV, the surface is oxidized, forming a PdO layer which passivates the surface.

$$\mathrm{Pd} + \mathrm{H_2O} \rightleftharpoons \mathrm{PdO} + 2\mathrm{H}^+ + 2e^-$$

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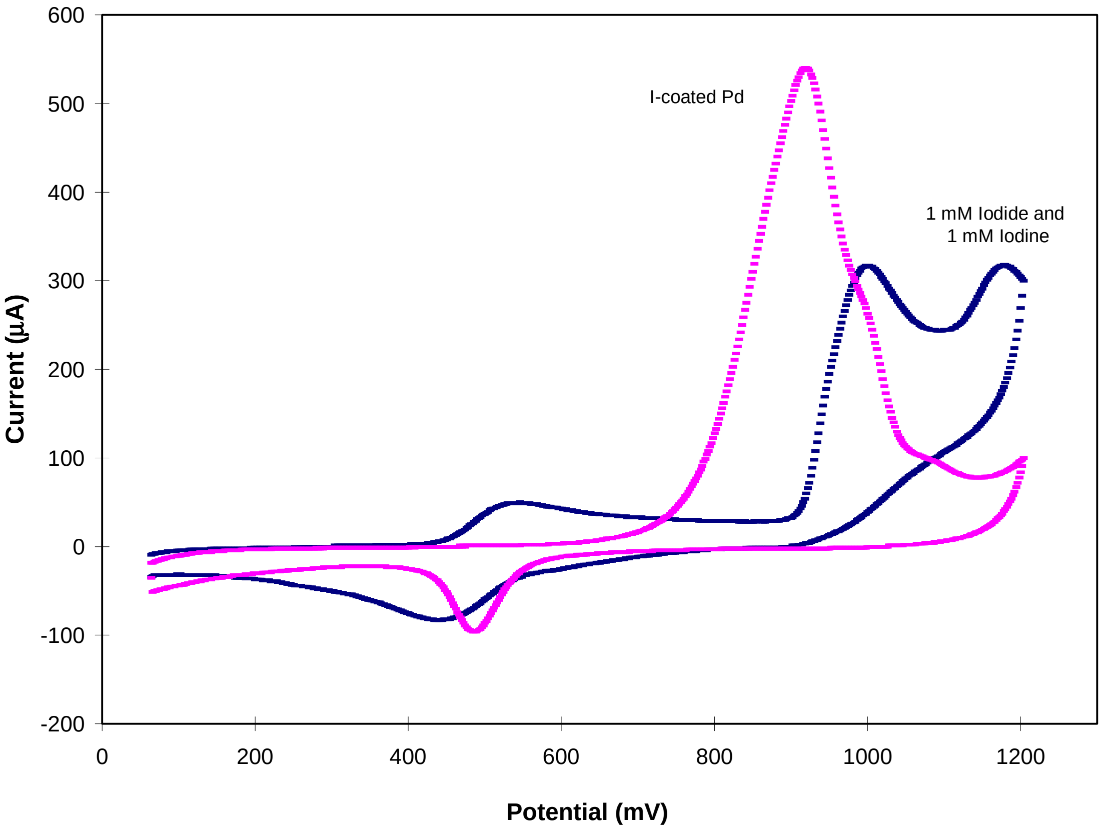

FIGURE 2. CYCLIC VOLTAMMOGRAMS COMPARING AN I-COATED Pd ELECTRODE IN 0.5 M SULFURIC ACID TO AN I-COATED ELECTRODE IN 1 mM IODIDE SOLUTION/0.5 M SULFURIC ACID. ALL SCANS WERE RUN AT 20 mV s^{-1} WITH A Ag/AgCl REFERENCE ELECTRODE.

This passivating oxide layer renders Pd quite resistant to corrosion and subsequent dissolution. When Pd is dipped in an iodide solution, the iodide oxidatively adsorbs to the Pd forming a monolayer of zerovalent iodine on the surface [3, 4]. For over a decade, this I adlayer has been used in research laboratories to protect Pd from air oxidation during experiments requiring clean Pd. Once the I-coated Pd electrode is put into solution, the iodine monolayer is reductively desorbed, leaving behind a clean Pd electrode. A similar technique is also used for other noble metals such as Pt and Rh.

The cyclic voltammograms run in acidic solution containing iodide and iodine involve an examination of the three oxidation states of iodine, namely –1, 0, and +5. Both iodide and iodine are oxidized ultimately to iodate. Figure 2 shows the oxidation of iodide to iodine (around 550 mV, a one electron process) and the further oxidation to iodate (around 1000 mV, a five electron process).

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$$IO_3^- + 6H^+ + 5e^- \rightarrow \tfrac{1}{2} I_2 + 3H_2O \qquad E^0 = 980\text{mV}$$

$$I_2 + 2e^- \rightarrow 2I^- \qquad E^0 = 400\text{mV}$$

$$Pd^{2+} + 2e^- \rightarrow Pd \qquad E^0 = 700\text{mV}$$

The oxidation of Pd to Pd^{+2} begins at approximately 700 mV. When an electrode is set at a potential where two reactions can occur, the process that is energetically favored, that is, having the more cathodic or negative potential, will predominate.

In order to quantify the results found in procedures #1 and #2, the student will perform chronocoulometry (Q versus t), or chronoamperometry (i versus t) experiments in order to measure the amount of charge passed during the oxidative process. These are known as potential-step techniques. Both allow for investigation of the Faradaic processes that are occurring at the electrode as a function of potential. The electrode is polarized to a given potential in a region where no Faradaic processes are occurring. The potential is then stepped to a region of the oxidative process as indicated on the CVs in Figure 3. When the potential is stepped, the current flows until equilibrium is reached, which is indicated by a steady-state current. The steady-state current is usually related to the diffusion current which is limited by the rate of diffusion of the redox species to and from the electrode/solution interface. In this case, however, we are dealing with a surface process which is dependent on the electroactive surface area of the electrode. When Pd is oxidized to PdO, the current will decay and approach zero. It is possible to form several oxide layers on the electrode, but each successive layer is slower in forming and requires more positive potentials.

The current that is expected in a dissolution process would not tend to decay and should be substantially larger than that for the oxidation of the surface. The current will be proportional to the surface area but, because the surface layer being oxidized is a soluble species, the surface is continually renewing itself. In addition, the surface may become rougher during the process and the electroactive surface may increase. This would lead to larger currents as a function of time.

The final procedure is designed to investigate the role of iodine in the dissolution process.

A catalyst is a substance that enhances the kinetics of a process, but remains chemically unchanged by the process. Iodine’s role as a catalyst could be confirmed if

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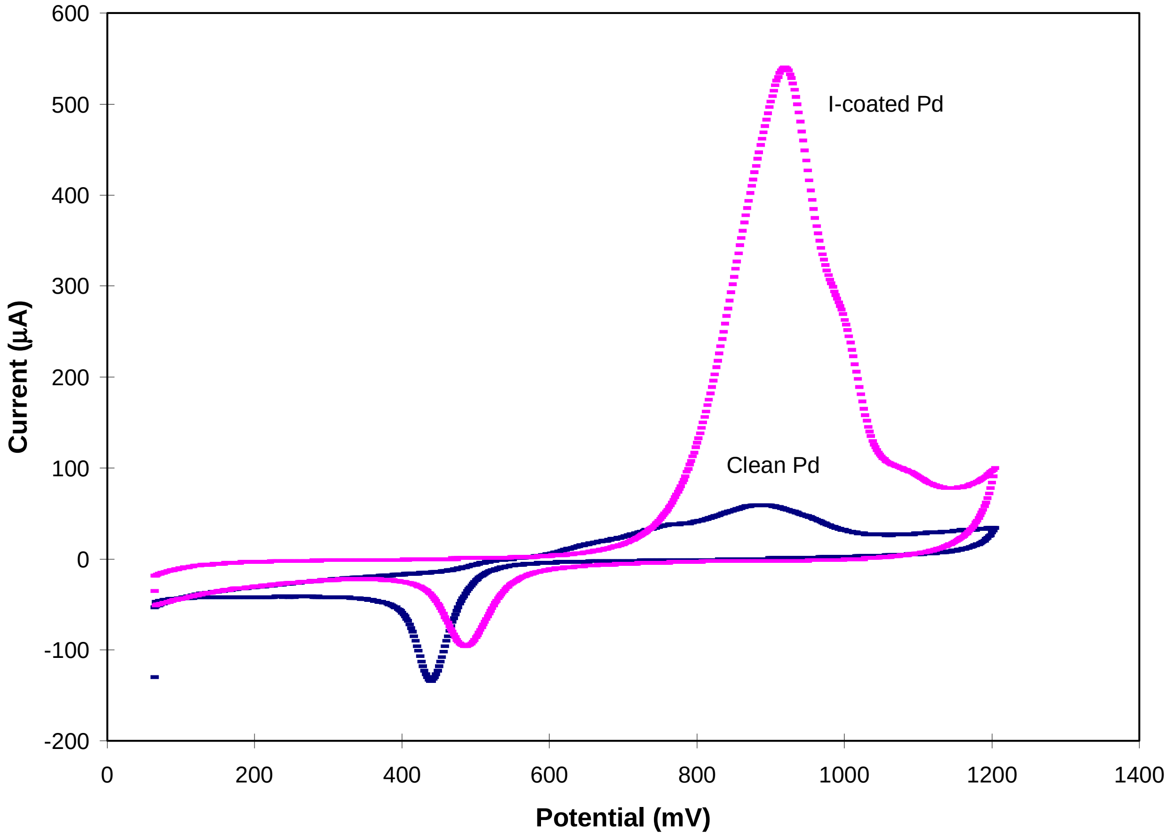

FIGURE 3. CYCLIC VOLTAMMOGRAMS COMPARING CLEAN AND I-COATED Pd ELECTRODES. THE SCANS WERE DONE IN 0.5 M SULFURIC ACID AT A SCAN RATE OF 20 mV s^{-1}.

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it can be demonstrated that the I adlayer remains intact during and after the dissolution process. If the iodine were oxidized during the process and desorbed from the surface, the dissolution process should cease or be inhibited. The question should be asked: At what potential is the surface I adlayer oxidized and rendered ineffective as a catalyst? Figure 4 indicates that the amount of iodine on the surface decreases dramatically between 1000 mV and 1200 mV.

Experimental

Any potentiostat that has the capability to perform cyclic voltammetry and chronocoulometry can be used for this laboratory. This laboratory has been performed using a BAS CV-27 (West Lafayette, IN) connected to a Houston Instruments *XY* recorder (Austin, TX) and an EG&G PAR 273A galvanostat/potentiostat (Princeton, NJ) interfaced to a 286 computer with EG&G electrochemical software.

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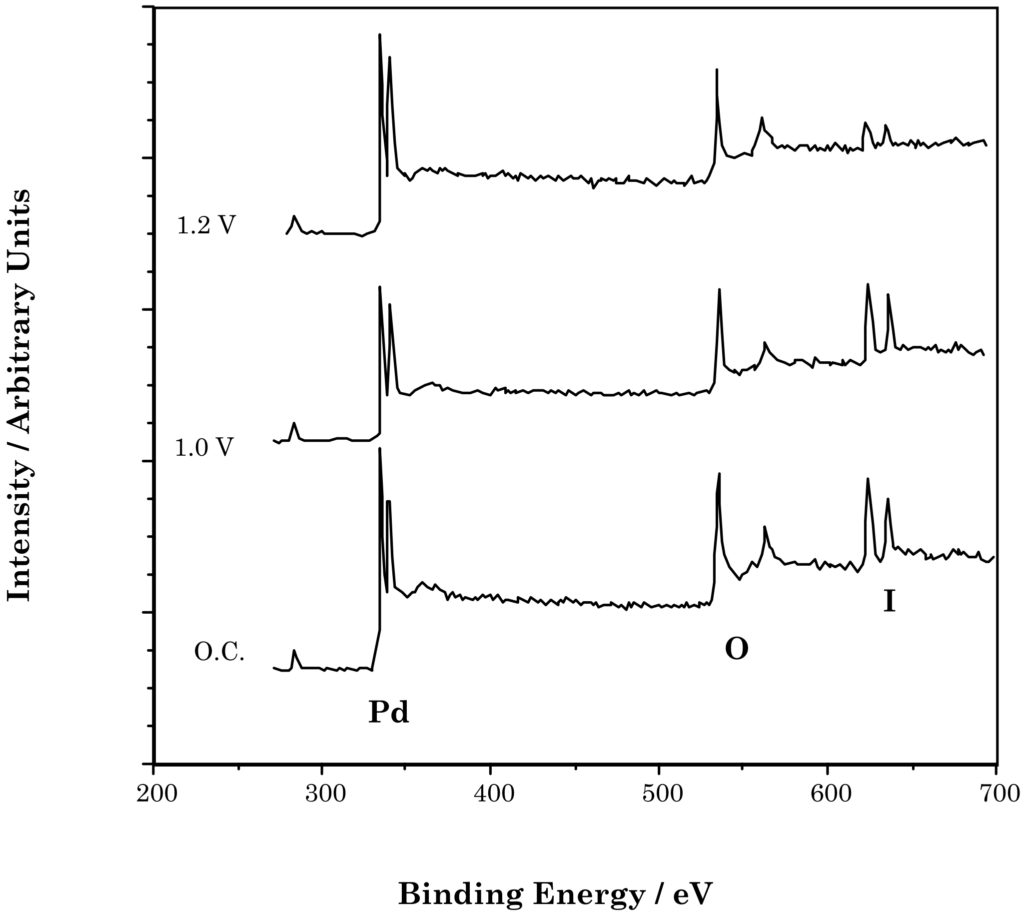

FIGURE 4. X-RAY PHOTELECTRON SPECTROSCOPY OF I-COATED Pd ELECTRODES AS A FUNCTION OF EMERSION POTENTIAL.

A three-electrode electrochemical cell using either Pd wire or Pd foil as a working electrode, a Pt-mesh counter electrode and a Ag/AgCl reference electrode was used along with a BAS 10 mL glass cell with a teflon cap. All voltages are stated versus a saturated Ag/AgCl reference electrode.

Four solutions are required for this experiment: (1) 500 mL of a 0.50 M sulfuric acid solution, (2) 100 mL of 5 mM sodium iodide dipping solution at pH 10 (add 0.1 M NaOH dropwise until pH = 10), (3) 100 mL of 1 mM sodium iodide in 0.50 M sulfuric acid, and (4) 100 mL of 1 mM iodine in 0.50 M sulfuric acid. Use the sulfuric acid solution (1) to make solutions 3 and 4.

Before and after each scan, the Pd electrode is cleaned by heating the electrode to a red hot glow in a gas flame, immediately immersing into Nanopure water, and dipping in

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6 M nitric acid. The electrode is then rinsed with water again and either dipped for 60 seconds in the iodide dipping solution or placed in the electrochemical cell.

New palladium usually comes with impurities that migrate to the surface upon annealing. It is important to pretreat the Pd electrode material to reduce the amount of these impurities in the bulk metal. In order to pretreat the electrode, the electrode is heated in a flame to glowing red, followed by immediately dipping the hot electrode into concentrated nitric acid for 60 s. After rinsing with Nanopure water , the electrode is placed in a 0.5 M sulfuric acid solution. The potential is stepped to 1200 mV for 60 seconds, then to –1000 mV for 60 s. The potential treatment is repeated up to ten times. The voltage is finally set to 700 mV and the current is allowed to decay to zero. Cyclic voltammetric scans are then run in the sulfuric acid solution from 100 mV to 1200 mV to make sure the scans are reproducible. This procedure need only be performed on new Pd material before it is used for the first time. Since the procedure is time-consuming and must be performed properly, it is recommended that the Pd be prepared by the instructor prior to the laboratory.

It is essential that all glassware be extremely clean. For this reason, glassware should be kept in a NoChromix glass-cleaning solution and should be rinsed only with Nanopure water. Gloves should be worn whenever handling the glassware to prevent the transfer of contaminants.

Each time a new solution is used, the electrochemical cell should be rinsed a minimum of five times with Nanopure water and finally rinsed once with the new solution that will be used for the next experiment.

Procedure #1: Comparison of the Cyclic Voltammograms of Clean Pd and I-coated Pd in Sulfuric Acid Solution

This procedure is designed to reproduce the anomalous current found with the I-coated Pd electrode. Two cyclic voltammograms are run in 0.50 M sulfuric acid. One CV should use a clean Pd electrode and the other should use an I-coated Pd electrode. In order to add the I adlayer, the Pd electrode is held in a gas flame until glowing red then dipped into a 1 mM NaI solution, pH 10, for 60 seconds. The CVs are run from 60 mV to 1200 mV and back to 60 mV at a scan rate of 20 mV s^{-1} and are recorded using the same scale so they can readily be overlaid and compared. Figure 3 shows these two CVs done on a 1.0-cm-long piece of 0.5-mm-diameter Pd wire. Pd foil gives more

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dramatic results. Previous experiments using Pd foil have yielded charges that were three orders of magnitude larger on I-coated electrodes versus clean palladium electrodes.

Because this procedure is designed to investigate the possible causes of the large oxidative current found with the I-coated Pd electrode, the student is provided with several possible causes along with explanations that will aid in understanding each process being investigated. The student is presented with the following possibilities:

A. *A solution species is being oxidized*. The only solution species present in both cases are sulfuric acid and water. If this process did involve a solution species, then there would not be a drastic drop in current beyond the oxidation peak. This region is known as the diffusion limited current region and is a function of the rate at which a solution species diffuses to the surface and is typically marginally smaller than the peak current.

B. *The I adlayer is being oxidized*. The I adlayer could be oxidized to iodate and desorb from the surface. Because there is a limited amount of I_{ads} to be oxidized, the current should decay after the I adlayer is oxidized. This can be tested by doing chronocoulometry (see Procedure # 3). Another calculation that can help investigate this possibility entails the integration of the peak of the I-dipped CV scan and comparison to the theoretical amount of charge that would be needed to totally oxidize one monolayer of iodine to iodate (see procedure # 3).

C. *The Pd is being oxidized*. Figure 1 shows that Pd is oxidized but the size of the currents are relatively small. Only the surface layer is oxidized to PdO, forming a passivating layer and limiting the amount of current that will flow. However, there is virtually an unlimited amount of Pd that can be oxidized to Pd^{2+} and dissolved in solution if the surface is not passivated by an oxide layer as shown in Figure 4. If the Pd were being oxidized then the current would not decay at the potentials found in the large oxidation peak noted in Figure 3. If the oxidation currents were due to the oxidation of the I adlayer, the potential at which the oxidation process began would be consistent with the oxidation of iodide or iodine in solution.

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TABLE 1. The Influence of pH on Polycrystalline Pd Corrosion: Results of Chronocoulometry and ICP.

Electrode/Electrolyte	pH 0 mC[b] (ppm)[c]	pH 4 mC[b] (ppm)[c]	pH 7 mC[b] (ppm)[c]	pH 10 mC[b] (ppm)[c]
Clean/Clean[a]	1.53 (0.11)	0.80 (0.00)	0.19 (0.00)	1.36 (0.00)
I-coated/Clean[a]	192.90 (15.32)	0.20 (0.00)	0.26 (0.00)	0.80 (0.00)
I-coated/1mM NaI	45.00 (0.04)	15.30 (0.00)	5.26 (0.00)	0.98 (0.00)
I-coated/1mM I_2	9.15 (0.67)	N/A	N/A	N/A

[a] No I-containing species present in electrolyte.
[b] Total charge was measured after 180 s at 0.9 V versus Ag/AgCl reference.
[c] Concentration in ppm measured using ICP-OES analysis.

Procedure #2: Comparison of the Cyclic Voltammograms of Clean Pd and I-Coated Pd in Sulfuric Acid Solution Containing Iodide and Iodine

Elemental analysis has shown that when either iodide or iodine are present in the solution, there is no significant dissolution of the palladium substrate (see Table 1). Figure 2 shows that, in the presence of the I solution species, there is an oxidative process that occurs that is easier (less positive potential) than the oxidation of Pd to Pd^{2+}; therefore, the oxidation of the I-species is favored. In the absence of aqueous halide species, the oxidation of Pd is possible. This procedure is designed to show that the dissolution of Pd does not occur when halide species are present in solution because it is less energetically favorable than the oxidation of iodide to iodine.

The student will run four CVs in solutions of 1 mM iodide in sulfuric acid and 1mM iodine in sulfuric acid: two on a clean Pd electrode and two on an I-coated Pd electrode. The scans should be run from 60 mV to 1200 mV at 20 mV s^{-1}. The scans

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can then be overlaid in order to compare the processes occurring on the clean Pd and I-dipped Pd electrodes.

The student is asked to identify the potentials and the peaks that coincide to the oxidation of iodide to iodine and iodine to iodate. They are also asked if the I-coated Pd electrode lends itself to large oxidation currents similar to those noted in procedure #1. The students are asked to explain why the Pd dissolution process is inhibited by the presence of iodide and iodine in the solution. Lastly, with the knowledge that the total charge or integrated area under each peak is proportional to the number of electrons passed in the oxidation process, the student is asked to explain the magnitude of the peak currents for the two oxidative processes.

Procedure #3: Quantitative Analysis of the Anodic Dissolution Phenomenon

In order to quantify the results obtained in procedures #1 and #2, the student performs a series of chronocoulometry or chronoamperometry experiments. The student should use the scans obtained from the first two procedures in order to determine the appropriate stepping potentials to be used in these potential-step experiments. Starting potentials should be chosen in a region that displays no Faradaic processes. According to Figure 3, a potential less than 500 mV should be chosen for the starting potential. Then, several potentials should be chosen that can be used to distinguish the two oxidation processes: the formation of a passivating oxide layer and the dissolution of the Pd. From Figure 3, 700 mV, 900 mV, 1100 mV and 1500 mV were chosen as the step potentials, and the charge that is passed at 60 s, 120 s and 180 s was recorded. The final potential chosen was 1500 mV because this step would result in the instantaneous oxidation and desorption of the I adlayer on the electrode, and therefore the dissolution would be minimal. The same four coulograms are run on an I-coated electrode.

If the laboratory has the capability to do trace elemental analysis by AA or ICP, a correlation could be made between the amount of charge that is passed and the concentration of Pd ions versus the maximum potential of each potential-step experiment. Figure 5 and Table 2 examine this data and support the assumption that the anomalous current is a two-electron oxidation of the Pd electrode. Samples can be generated and saved for AA or ICP analysis in a separate laboratory period. If this is attempted, the volume of the solution must be measured carefully, because the

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TABLE 2. Corrosion of I-coated Polycrystalline Pd in 0.5 M H_2SO_4: Results of Chronocoulometry and ICP.

E_f of Potential Step [a]	Q_{tot} [b] mC	[Pd]exp. [c] ppm	[Pd]calc. ppm	ML [d]
0.7 V	3.96	0.37	0.34	4.35
0.8 V	26.8	2.42	2.357	29.5
0.9 V	238	18.1	21.97	261
1.0 V	435	31.4	34.43	478
1.1 V	11.2	0.39	0.969	12.3

[a] Potential steps were done from an E_0 of 0.5V to E_f. E versus Ag/AgCl reference.

[b] Charge passed was measured after 180 seconds at E_f.

[c] Concentration measured by ICP-OES.

[d] Number of monolayers, calculated based on geometric area of 2 cm^2 and $Pd = Pd^{2+} + 2e^-$.

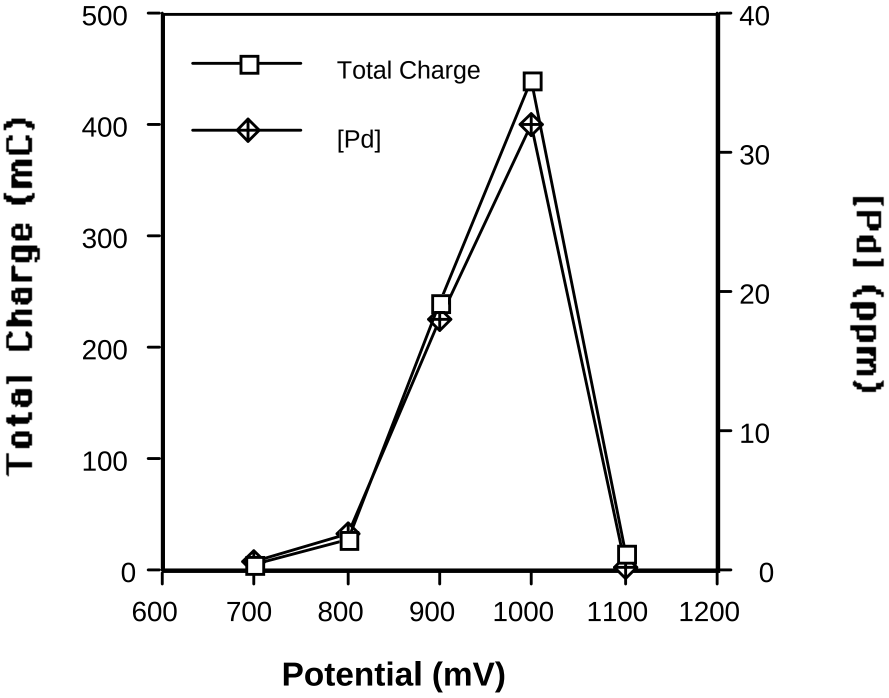

FIGURE 5. THE TOTAL CHARGE MEASURED USING CHRONOCOULOMETRY AND [Pd] ARE PLOTTED VERSUS THE FINAL STEP POTENTIAL FOR AN I-COATED POLYCRYSTALLINE Pd ELECTRODE IMMERSED IN 0.5 M SULFURIC ACID AT 500 mV. SOLUTION SAMPLE SIZES WERE APPROXIMATELY 6.0 mL.

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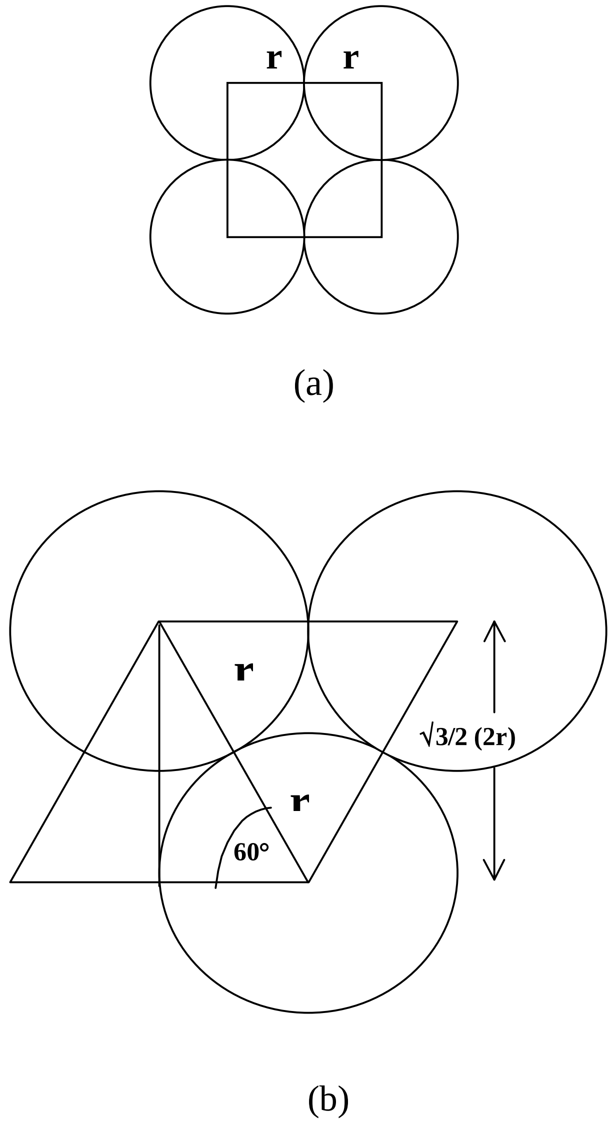

FIGURE 6. SCHEMATICS OF (a) Pd(100) AND (b) Pd (111) USED IN MONOLAYER CALCULATIONS.

concentration of Pd must be converted to the number of moles of Pd dissolved in order to calculate the value of *n* in the equation

$$Q_{passed} = nF\left[Pd^{n+}\right]$$

The student is asked to compare the amount of charge that is passed on the clean Pd and the I-coated Pd electrode. Because it is known that there is a two-electron process occurring for both the oxidation and the dissolution processes, the student is able to calculate the number of monolayers.

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$$Pd \leftrightarrow Pd^{2+} + 2e^-$$

of Pd which are oxidized as a function of potential, surface pretreatment, and time.

Determining The Number of Pd Atoms Per Unit Area of a Polycrystalline Electrode

In order to determine the number of monolayers of Pd which are oxidized, it must be assumed that the surface consists of two single-crystal domains, Pd(111) and Pd(100), at a 1 to 1 ratio. This is a good approximation for a freshly annealed polycrystalline Pd electrode. Pd(100) is a face-centered cubic (fcc) lattice and Pd(111) is a hexagonal close packed (hcp) lattice (Figure 6).

The two-dimensional geometry of the hcp and the fcc unit cells can be used to determine the area occupied by a single atom. The reciprocal will yield the number of Pd atoms per unit area. The weighted average of the two crystal lattices will give the approximate surface coverage of Pd atoms.

The weighted average indicates that 4.55×10^{-4} C will be passed for each cm^2 of Pd atoms that are oxidized. For a 1-cm^2 Pd electrode, this amount of charge is needed for each monolayer of Pd atoms that is oxidized.

There is the possibility that Pd is being dissolved during the oxidation of the clean Pd electrode. As Table 1 shows, dissolution is occurring, but it is very slow. When elemental analysis is done on the solutions, high concentrations of Pd ions are only seen as a result of the oxidation of the I-coated Pd electrode. A dramatic demonstration of this can be seen by dipping the clean and the I-coated electrodes in warm 6 M nitric acid. The dissolution of the I-coated electrode is readily observed, while no significant reaction is noted on the clean electrode.

The data supports the assumption that the large oxidative current is due to Pd dissolution. Based on this data, relevant questions which could be posed to the student include: What is the state of the I adlayer during the dissolution process? How does potential affect the I-adlayer? Will the I-adlayer remain intact indefinitely?

Procedure #4: Verification of Iodine as a Catalyst in the Dissolution Process

This last procedure is designed to determine whether the iodine adlayer functions as a catalyst in the Pd dissolution process or is consumed in the reaction. This is accomplished by determining the potential range in which the I adlayer is stable. In order to determine this potential range, the electrode is coated with an I adlayer and potential-step experiments are run from a region of non-Faradaic potential (between 600 mV and 500 mV, or open circuit) to a potential where oxidation begins, then reversed to the initial potential. A subsequent scan should be run to a point 100 mV more positive than the first scan. This process should be continued until a marked difference is noted in the oxidation scan. It may be convenient to use the same potential limits as those used in procedure #3 of this laboratory.

It should be noted that each subsequent scan retraces the previous scans until a maximum potential is reached that changes the effectiveness of the I adlayer in catalyzing the dissolution process. At that point, any subsequent scans will reveal much smaller currents due to reduced anodic dissolution of the palladium substrate. Because each subsequent scan retraces the previous scan without any sign of the reverse reaction (the reduction of the surface), the I-coated Pd electrode must not be significantly changed by each scan; therefore, the large charges passed can only be explained by the dissolution of Pd. The I adlayer must remain intact because it is the key ingredient to the dissolution of the Pd as seen in Table 1 and Figure 3. When potentials are reached that will oxidize the I adlayer to iodate, the palladium electrode is easily oxidized to PdO and significant dissolution ceases. Because the I is now gone, any subsequent scans will not reproduce the enhanced dissolution.

The results of this procedure will allow the student to determine whether a catalytic process is occurring, that is, the I adlayer is unaffected by the passing of these large oxidative currents. They are asked to explain why the steps to high anodic potentials stop the catalytic process and why this process is called I-catalyzed anodic dissolution of Pd in halide-free acidic solution.

Summary

It has been shown that Pd metal, a noble metal that is resistant to corrosion, can be made to dissolve readily if coated with a monolayer of I atoms and oxidized in acidic solutions. Normally, the Pd would form an oxide layer which would passivate the metal to dissolution, but the I adlayer prevents oxygen from reaching the electrode (see Figure 7). When the Pd is oxidized to a +2 oxidation state, it is ejected through the I adlayer while the I adlayer remains intact. It is possible to anodically desorb the I adlayer at high positive potentials by oxidizing the I to IO_3^-. If one desires, the

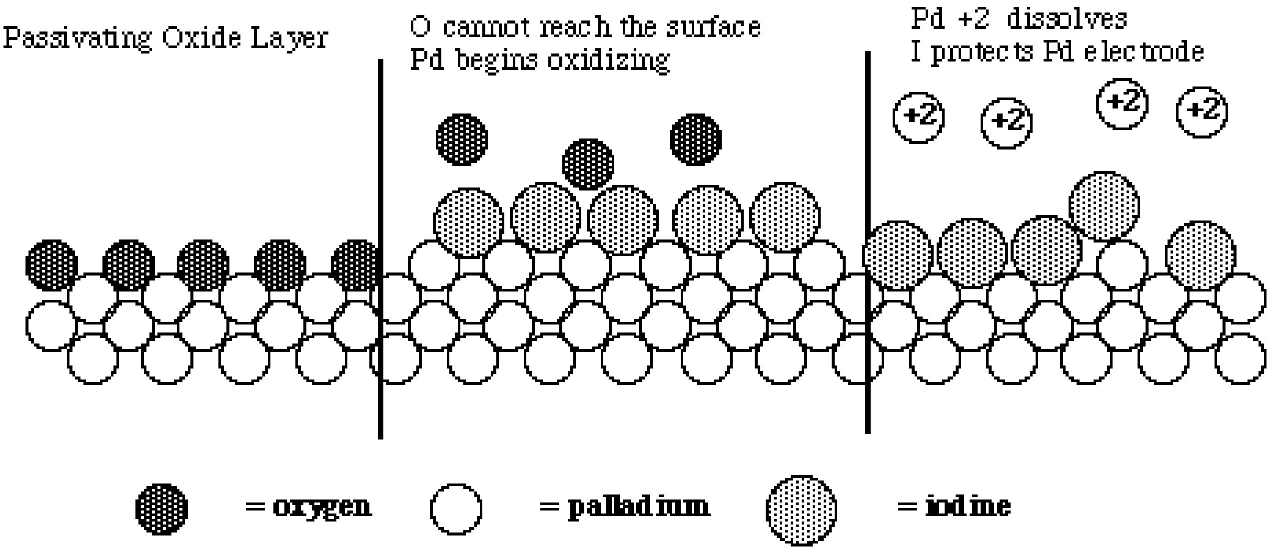

FIGURE 7. ROLE OF I-ad LAYER IN DISSOLUTION OF Pd ELECTRODE.

dissolution process can be the center of further investigations during subsequent laboratory periods. Trace metal analysis can be used to detect and quantitate the amount of dissolved Pd. This phenomenon can also be examined for dependence on the solution pH and the acid anion. Previous studies have demonstrated that the dissolution only occurs at pH <4 and the magnitude of the dissolution is anion dependent ($SO_4^{2-} > ClO_4^{-} > PO_4^{3-}$) [5]. It is also interesting to note that this dissolution does not occur if there is any I^- in the solution. The dissolution is enhanced by having a halide-free environment, which is contrary to most corrosion events.

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