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Coulometric Assay of Deuterium Loading Levels in Palladium Electrodes

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We report in this paper measurements of hydrogen (H) and deuterium (D) loading stoichiometries in Pd electrodes. We accomplished these analyses using an electrochemical method developed for in situ determination of palladium deuteride stoichiometries. The electrochemical method quantifies the amount of deuterium incorporated into the metal lattice by collecting the charge released during the potential controlled discharge of deuterium loaded Pd electrodes. In addition, ex situ gravimetric analyses were used to confirm electrochemically measured D/Pd atom ratios. Gravimetric analyses were also used in cases where the diameter of the Pd electrode precluded the relatively slow diffusion-limited electrochemical discharge method. A variety of electrolytic factors were studied to determine what conditions, if any, promote the greatest absorption of deuterium into the Pd lattice. We observed loading values of 0.73 ± 0.02 deuterium atoms per Pd lattice atom under all the electrolytic conditions studied in LiOD and D_2SO_4 solutions. As found in previous studies, H/Pd values were approximately 10% higher than D/Pd values. (cont.)

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These measurements of D/Pd stoichiometries indicate that interfacial parameters, i.e. current density, pD, charging time and surface purity have a negligible effect on the maximum deuterium concentration within Pd electrodes.

COULOMETRIC ASSAY OF DEUTERIUM LOADING LEVELS IN PALLADIUM ELECTRODES

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Abstract

We report in this paper measurements of hydrogen (H) and deuterium (D) loading stoichiometries in Pd electrodes. We accomplished these analyses using an electrochemical method developed for in situ determination of palladium deuteride stoichiometries. The electrochemical method quantifies the amount of deuterium incorporated into the metal lattice by collecting the charge released during the potential controlled discharge of deuterium loaded Pd electrodes. In addition, ex situ gravimetric analyses were used to confirm electrochemically measured D/Pd atom ratios. Gravimetric analyses were also used in cases where the diameter of the Pd electrode precluded the relatively slow diffusion-limited electrochemical discharge method. A variety of electrolytic factors were studied to determine what conditions, if any, promote the greatest absorption of deuterium into the Pd lattice. We observed loading values of 0.73 ± 0.02 deuterium atoms per Pd lattice atom under all the electrolytic conditions studied in LiOD and D_2SO_4 solutions. As found in previous studies, H/Pd values were approximately 10% higher than D/Pd values. These measurements of D/Pd stoichiometries indicate that interfacial parameters, i.e. current density, pD, charging time and surface purity have a negligible effect on the maximum deuterium concentration within Pd electrodes.

Keywords: Palladium hydride, palladium deuteride, stripping analysis, coulometry, gravimetry.

Introduction

It has been known for over one hundred years[1,2] that certain metals absorb large quantities of hydrogen and its isotopes. The alleged cold fusion phenomena[3,4] is based on the premise that deuterium atoms confined within a metal lattice undergo an unknown process which leads to nuclear fusion. Intuitively, it is difficult to imagine conditions whereby the energy required to fuse deuterium ($\approx 10^5$ eV) could be furnished within an electrochemical cell (<10 eV). If one assumes for a moment that a nuclear phenomenon is responsible for the anomalous behavior observed in "cold fusion" electrochemical cells, it is clear that the quantity of deuterium loaded into the metal would be a critical component in understanding the mechanism and energetics involved. Unfortunately, deuterium loading values are rarely reported in papers reporting positive results in this field[3-8]. Therefore, we began an extensive investigation of deuterium loading in Pd electrodes with an emphasis on finding conditions which would result in maximum deuterium absorption.

Several methods have been used in the past for monitoring the absorption of hydrogen and deuterium in metals[9-14]. Typically, the uptake of H or D is measured ex situ by weighing the metal before and after loading[7] or by measuring the volume of gas stored inside the metal[12-14]. This paper presents D loading values measured using an *in situ* coulometric method. This method is based on quantifying the charge passed during controlled potential discharge of deuterium loaded Pd cathodes. Gravimetric determinations were used to verify the accuracy of the electrochemical method and in cases where the electrochemical method was not suitable (vide infra).

Experimental

Materials and Reagents. The Pd electrodes used in this study were made from wires and rods. Several different sizes and sources of Pd were used. The Pd electrodes had diameters of 0.127 mm (Aldrich, 99.99%), 0.50 mm (Johnson-Matthey, 99.9975%), 1.0 mm (Johnson-Matthey, 99.9975% or Hoover and Strong, 99.9%) and 4.0 mm (Johnson-Matthey, 99.99%).

The wires were used as received unless otherwise stated. In all but one experiment discussed below, the electrodes were weighed immediately before use. Following weighing, the Pd wires were spot-welded to 0.5 mm-diameter Pt wire leads (Aldrich, 99.9%). The portion of the Pt lead that was submerged in the electrolyte was tightly wrapped in teflon tape to prevent electrolysis at the Pt-solution interface. Ni or Pt wire coils were used as anodes (0.5 mm Ni (Johnson-Matthey, 99.9%) was used in LiOH and LiOD electrolytes; 0.5 mm Pt (Aldrich, 99.9%) was used in D_2SO_4 electrolyte).

LiOH and LiOD solutions (0.10M) were prepared under an argon atmosphere by dissolution of 99.9% Li metal (Alfa) in purified H_2O (Milli-Q, Waters) and D_2O (Isotec, 99.9%). D_2SO_4 solutions (0.12M) were prepared by diluting 99.5 atom% D_2SO_4 (Aldrich) in D_2O (99.9%, Isotec). All other reagents were purchased in purest form and used as-received.

Electrochemical Cells and Equipment. All electrochemical charging and discharging experiments were conducted using an EG&G Princeton Applied Research model 273 potentiostat. Discharge curves (current-time) were collected using an X-Y recorder. The total quantity of charge passed during charging and discharging of the Pd electrodes was measured using the potentiostat's digital coulometer.

The cell schematic is shown in Figure 1. Electrochemical experiments were conducted in acid/base resistant 50 mL polymethylpentene centrifuge tubes (Nalge). The anode and cathode were connected to the potentiostat through rubber septa inserted in the cell cap. A syringe needle was inserted through a third septa (See Figure 1a) allowing the oxygen and hydrogen gases, produced during the loading of the electrode, to escape while minimizing direct exposure of the electrolyte to water and CO_2 in the lab atmosphere. A saturated calomel reference electrode (SCE) was inserted in place of the septa/needle during the discharge portion of the experiments (Figure 1b). All electrode potentials are reported vs. SCE.

Electrochemical Method. We describe below the potential step coulometric method used in this study for the determination of D/Pd atom ratios. To illustrate the method, we first provide background information necessary to understand deuterium loading in Pd electrodes. In addition, we describe an *initial diagnostic experiment which led to the development of the* coulometric method.

The relevant electrode reactions are shown below for heavy water:

$$Pd + D_2O + e^- \leftrightarrow Pd\text{-}D_{surf} + OD^- \text{ (basic or neutral solution)} \qquad (i)$$

$$Pd + D_3O^+ + e^- \leftrightarrow Pd\text{-}D_{surf} + D_2O \text{ (acidic solution)} \qquad (ii)$$

$$Pd\text{-}D_{surf} + Pd\text{-}D_{surf} \leftrightarrow D_2 \qquad (iii)$$

$$Pd\text{-}D_{surf} \leftrightarrow D_{lat} \qquad (iv)$$

$$Pd\text{-}D_{surf} + D_2O + e^- \leftrightarrow D_2 + OD^- \qquad (v)$$

where Pd represents a surface palladium atom, Pd-D_{surf} represents an adsorbed deuterium atom and D_{lat} represents an absorbed deuterium atom. Several studies have characterized the rate of deuterium absorption (reaction iv) into Pd and other metals[15-21]. In general, the rate of absorption of deuterium into the bulk of the metal is diffusion limited at clean surfaces[15]. In the presence of carbon or sulfur species, however, the competing recombination reaction (iii) is favored, slowing the rate of absorption[16,20]. Reaction (v) is the primary electrode reaction after the electrode is fully loaded with deuterium.

Initially, cyclic voltammetric measurements were used to characterize the behavior of Pd electrodes in 0.1M LiOD[22]. Voltammetric waves are shown in Figure 2 for a 3.6 cm length of 0.127 mm-diameter Pd wire in 0.10M LiOD. Curve (a) was obtained during a continuous scan from +0.4V to -1.5V at 50 mV/sec. The cathodic wave at -1.5V is the reduction of water producing adsorbed deuterium (reaction i). During the subsequent positive sweep, an anodic wave was observed at approximately 0.0V. We attribute this peak to the anodic stripping of absorbed deuterium. Curves (b) and (c) were obtained following 10 and 20 second pauses at -1.50V, respectively. We ascribe the increase in the anodic wave to greater concentrations of deuterium incorporated into the Pd electrode during the pauses at -1.5V. This explanation is supported by visual observations of the Pd electrode which were made while holding the electrode at -1.5V. Initially, no gas evolution was observed at the electrode even though cathodic current was flowing. After several minutes, however, gas evolution (reaction v) was evident as bubbles begin to form on the electrode surface, indicating saturation of the electrode with deuterium.

Noting the similarity between this "voltammetric stripping" of deuterium and conventional anodic stripping voltammetry, we attempted quantitative measurements of the amount of deuterium loaded into the Pd wire. The quantity of incorporated deuterium was determined by stepping the potential of the deuterium loaded electrode and counting the charge associated with the oxidative discharge of the absorbed deuterium. A detailed description of the experimental method is provided below.

The electrodes were loaded with deuterium in the galvanostat (controlled current) mode using a two electrode configuration (See Figure 1a). Current densities were calculated based on the surface area of the Pd electrode assuming a surface roughness factor of unity.

The deuterium-loaded electrodes were discharged potentiostatically. Typically, towards the end of the constant current charging portion of the experiment, an SCE reference electrode was added to the cell (Figure 1b). At this point, the SCE was not connected to the potentiostat, but was used to measure the potential difference between the working electrode and the SCE while the charging current was passing. The potential difference was measured using a digital voltmeter. The current was then momentarily interrupted while the SCE reference *was* connected in the standard three electrode mode. The potential measured above between the SCE and working electrode was then applied. Thus, the same approximate current density was applied under potential control as during the preceding constant current portion of the experiment. The cell was at open circuit during the switch from constant current to potentiostatic control for approximately ten to fifteen seconds. The electrode was allowed to charge for several minutes following the insertion of the reference electrode, to overcome any loss of deuterium incurred during the open circuit.

Following the charging portion of the experiment described above, the potential was stepped to a region where deuterium stored within the Pd cathode was discharged. The exact electrode potential used to discharge deuterium-loaded electrodes was determined using cyclic voltammetry. For this determination, a fully deuterium loaded 0.127 mm-diameter Pd electrode was prepared by holding the electrode at a potential of -1.5V for approximately 20 minutes. The electrode potential was then scanned positively and held at a series of potentials in the region of the anodic wave, monitoring the decay of the anodic current attributed to stripping of absorbed deuterium. At 0.0V, the anodic current decayed to zero in a short time. If the scan was then continued positively from 0.0V following this pause, anodic currents were no longer observed indicating that the deuterium had been quantitatively removed from the Pd electrode.

Thus, 0.0V was chosen as the discharge potential in alkaline media because it led to the rapid discharge of absorbed deuterium. Experiments in which the discharge potential was set at successively more positive potentials (+0.1, +0.2 and +0.3V), did not alter the measured D/Pd values. An additional factor in choosing 0.0V as the discharge potential was the separation (by ca. 400 mV) of the discharge potential from the onset of Pd-oxide formation. This separation avoids the possibility of the oxide formation reaction contributing to the anodic charge attributed to the stripping of deuterium. Using the cyclic voltammetric procedure described above, 1.2V was chosen for the discharge potential for Pd electrodes in D_2SO_4. The more positive potential with respect to alkaline solutions is related to the change in half wave potential responsible for the discharge of deuterium in acid.

Immediately following the discharging potential step, absorbed deuterium diffuses to the electrode surface where it is electrochemically oxidized. From the total amount of anodic charge collected following the potential step, the D/Pd atom ratio can be calculated using the following equation:

$$D/Pd = \frac{Q\ (\text{Coulombs})}{F\ (\text{Coulombs/mole } e^-)\bullet(1 \text{ mole } e^-/1 \text{ mole D})\bullet\text{moles Pd}} \qquad (1)$$

where Q is the number of coulombs collected during electrode discharge, F is Faraday's constant and moles Pd is calculated from the initial mass of the electrode. This equation is valid assuming the discharge of absorbed deuterium is the only electrolytic reaction at the working electrode and that deuterium is quantitatively removed from the electrode.

Electrodes were typically charged and discharged several times with little change in the maximum D/Pd atom ratio. After repeated loading and unloading cycles, however, the response becomes sluggish, i.e. longer times were required to quantitatively remove absorbed deuterium. This effect was most evident in larger electrodes (0.5 to 1.0 mm-diameter) which required several hours to discharge and in experiments where poisons were purposefully added to the electrolyte. We attribute this deactivation effect to impurities which built up on the electrode surface with time[23]. These impurities were present in low concentrations in the electrolyte[24], and were also introduced by the SCE reference electrode (chloride ions). The sluggish discharge, however, did not change the final D/Pd values measured. Thus, no special steps were taken to clean the electrolyte or separate the SCE from the electrolysis chamber.

The effect of dissolved D_2 gas, present as a by-product of the electrolysis, was also studied. This study was important because D_2 gas is also oxidized at the discharge potential of 0.0V. Thus, if this reaction occurred at appreciable rates, the assumption that the stripping of deuterium was the only electrolytic reaction occurring at the working electrode would be incorrect. Such an occurrence would provide misleading D/Pd atom ratios. This potential problem was investigated by making a number of D/Pd measurements in cells with and without N_2 saturation. High loading current densities (600 mA/cm^2) were used to produce copious amounts of D_2 gas. No significant difference in the D/Pd values was observed between the N_2 degassed and undegassed solutions. Thus, the effect of dissolved D_2 is negligible and the electrolytes were not degassed in further D/Pd measurements.

Gravimetric Method. In order to test the analytical merit of the electrochemical method, we compared D/Pd atom ratios obtained using the electrochemical method with D/Pd values measured gravimetrically. The details of two sets of gravimetric analyses are provided below.

As in electrochemical measurements, the Pd electrodes were weighed immediately before electrolysis. Larger diameter Pd electrodes (1 mm; 99.9975% Johnson-Matthey) were used in these studies to decrease the analytical uncertainties associated with the relatively small difference in mass of virgin and deuterium loaded electrodes.

A gold-coated alligator clip was used for quick disconnection of the deuterium loaded Pd electrodes. Following two days of electrolysis at 60 mA/cm^2 in 0.10M LiOD, the electrode was disconnected, quickly wiped dry and reweighed. The electrode was then returned to the cell, electrolyzed for several more days and weighed again. The time from disconnection of the electrode to measurement of the mass was less than one minute. The D/Pd ratio was calculated from the following equation:

$$D/Pd = \frac{\Delta W/(2.014 \text{ grams/mole D})}{\text{moles Pd}} \qquad (2)$$

where ΔW is the weight change of the Pd electrode before and after electrolysis.

The effect of extremely long electrolysis times was studied in a second set of gravimetric experiments. Instead of building cells specifically for this study, however, we used a set of existing cells which had been part of an unsuccessful attempt to reproduce reports of tritium production in D_2O electrolysis cells[25]. The cells were connected in several series circuits and electrolyzed at 60 mA/cm^2 using DC power supplies. A detailed description of the experimental procedure and results of our unsuccessful search for tritium can be found elsewhere[25].

We studied nine electrodes that were electrolyzed from a minimum of 99 to a maximum of 145 days in 0.1 to 0.2M LiOD. Eight of these electrodes were made from 1 mm-diameter Pd wire. Of these eight electrodes, 6 were obtained from Hoover and Strong (99.9%), while 2 were made from puratronic Pd distributed by Johnson-Matthey (99.9975%). Three of these 8 electrodes were pretreated by vacuum annealing at approximately 900°C (10^{-6} Torr), three were etched for fifteen minutes in 5M HCl and two were used as-received. The remaining electrode was a 4 mm Pd electrode (99.99% Johnson-Matthey).

In this gravimetric study, measurement of the D/Pd ratio was complicated by the fact that the electrodes had not been weighed before use. Thus, the difference in weight was inferred by the removal of the deuterium after incorporation. The electrodes were removed from their cells immediately after the current was turned off, wiped dry and weighed. The electrodes were heated to 150°C in vacuum (10^{-3} Torr). The electrodes were reweighed every two days after cooling until the weight remained the same on three consecutive weighings. The D/Pd ratio was calculated using equation 2.

Results and Discussion

Figure 3 presents a typical discharge curve for a 0.127 mm-diameter Pd electrode in 0.10M LiOD. The potential step to 0.0V versus SCE is indicated by the near vertical drop in current (from the cathodic D_2O electrolysis current to the anodic stripping current) at the left of Figure 3. An anodic (double layer charging) spike is observed immediately after the potential step. A plateau region follows which is associated with the stripping of D from the bulk of the Pd. When all of the D has been stripped, the current decays to zero. While the area under the curve in Figure 3 gives the stripping charge, for convenience, we obtained stripping charges using a digital coulometer.

Figure 4 presents results of a multiple charge and discharge experiment. The electrode was charged for 1.2 minutes in 0.1M LiOD; the electrode was then discharged and the anodic charge counted. The newly discharged electrode was then charged again, this time for 2.4 min; the D introduced was then stripped again. This process was repeated for charging times of 7.7, 12.5, 18.8 and 28.8 minutes. In all cases, the charge injected was less than that required to saturate the Pd electrode with deuterium.

The data obtained were analyzed via plots of anodic stripping charge (and corresponding D/Pd ratio) versus quantity of cathodic charge passed during the charging period (Figure 4). If all the charge passed during the charging period went to inserting D into the Pd lattice, the slope of the stripping charge versus input charge plot would be unity. In fact, slopes of 0.78 were observed. These data indicate that, during the early part of the charging process, the deuterium absorption reaction is ca. 78% efficient. Experiments in 0.1M LiOH (H absorption) and 0.12M D_2SO_4 produced linear plots with similar charging efficiencies. Other workers have shown that the efficiency of the absorption process is strongly dependent on the degree of purity at the electrode surface[16]. Higher charging efficiencies are obtained using a thoroughly clean system[15].

A plot of D/Pd atom ratio versus input charge is also included in Figures 4. This plot is also linear. Hydrogen and deuterium loading of Pd was found to be linear with respect to charge input in all experiments below the saturation level, i.e. H/Pd or D/Pd atom ratios less than 0.65. At higher loading levels, however, the electrode approaches saturation and the plots level out, as shown in Figure 5. As will be discussed below, electrolyzing for longer times (as long as 145 days) does not appreciably raise the deuterium concentration within the Pd electrode.

Table 1 presents electrochemically determined H and D/Pd atom ratios in fully loaded Pd electrodes electrolyzed in LiOH, LiOD and D_2SO_4 solutions. Note first, that the maximum D/Pd ratio reported here (ca. 0.72) is in quantitative agreement with values obtained in previous investigations [9,11,26]. Furthermore, our observation that the maximal H/Pd value is higher than the maximal D/Pd value is also in agreement with previous measurements[9,11,26-28]. The agreement between D/Pd ratios measured in acidic versus alkaline electrolytes indicate an independence of the D/Pd ratio on solution deuteron activity. In addition, no difference could be found in D/Pd values measured as a function of LiOD concentration (0.1, 0.2 and 0.3M).

Finally, gravimetric determinations of D/Pd ratio produced values which were identical to the electrochemically-determined values, thus validating this electrochemical method.

One of the studies conducted was aimed at determining whether extremely long electrolysis periods might result in higher D/Pd ratios. We have found no evidence for such elevated D/Pd ratios. For example, the D/Pd ratio after 1 week of electrolysis at 60 mA/cm^2 was identical to the ratio obtained after 145 days of electrolysis (0.74 ± 0.02).

We were also interested in determining whether extremely high current densities could force more D into the Pd lattice. Table 2 presents D/Pd measurements obtained in 0.10M LiOD as a function of charging current density. The similarity of the D/Pd ratios at different charging current densities indicates that D/Pd stoichiometry is virtually independent of the magnitude of the charging current density.

In another study, Soriaga and coworkers[29] measured the true electrode potential as a function of current density using a current interrupt electrochemical method[30]. They observed that changes in the true applied potential were very small as the current density was increased. Instead, the higher current and higher voltage result primarily in resistive heating[29]. It is known that palladium deuteride stoichiometry decreases with increasing temperature[9,31]. Thus, one would, in fact, expect the D/Pd ratio to decrease at high current densities if resistive heating has a pronounced effect on the cell temperature. We were unable to observe this high current density phenomenon, as the cells used in the above current density study contained relatively small electrodes (0.127 mm-diameter) and large volumes of electrolyte (approximately 40 mL). Wolf[32], however, has observed this effect using 1 mm-diameter Pd electrodes and smaller electrolyte volumes (approximately 12 mL). Wolf quantified D/Pd stoichiometries using a device which measures the change in length of a Pd electrode associated with the volume increase accompanying deuterium loading[33]. As the current density was increased and the cell temperature increased, the D/Pd ratio calibrated with wire length decreased.

In addition to the measurements discussed above, in relatively clean electrolytes, we were prompted to study the effect of poisons after the alleged success of Storms and Talcott[5] in raising D/Pd levels by poisoning of the electrode surface. In order to study these effects, we carried out several D/Pd measurements in electrolytes poisoned with thiourea and arsenic. In one study, the D/Pd ratio was measured in 0.10M LiOD containing approximately 5 mM thiourea. The D/Pd atom ratio obtained electrochemically in this solution was 0.72.

A second study was carried out using a 10 mM solution of As_2O_3 in 0.10M LiOD. The electrochemical measurements indicated D/Pd ratios of 0.9 and higher. Gravimetric measurements were immediately carried out to confirm this result; the gravimetric determination yielded a D/Pd ratio of 0.77. The disagreement between the two methods was resolved by consulting a table of half-wave potentials[34]; As_2O_3 is easily oxidized at the discharge potential of 0.0 V. Thus, we attribute the anomalously high D/Pd values measured electrochemically to discharge currents that included both absorbed deuterium and solution As_2O_3 oxidation. We see no indication of anomalous concentrations of deuterium, reported to approach D/Pd values of unity, in electrodes electrolyzed in clean[35] or poisoned[5] electrolytes.

The electron micrographs shown in Figure 6 demonstrate the effect of loading and unloading deuterium on the surface of Pd electrodes. Other workers have demonstrated that the volume of the Pd metal expands by approximately 11% when fully loaded with deuterium[36]. This expansion during loading, and contraction after unloading of the electrode, undoubtedly leads to the roughening of the surface observed in these electron micrographs. Micrographs of electrodes charged at higher current densities indicate a higher degree of roughening and cracking.

Conclusions

The electrochemical method of measuring D/Pd stoichiometry proved to be both accurate and precise. One drawback of the method, however, was the requirement that the deuterium be removed from the electrode in order to quantify it. This was impractical in electrodes that were being used in active experiments. In addition, electrode size was an important consideration in measuring D/Pd ratios using this method. Most of the coulometric measurements discussed herein, were made with 0.127 mm and 0.5 mm diameter Pd electrodes. Smaller diameter electrodes were studied due to the considerable length of time required to fully discharge larger electrodes because of slow diffusion of deuterium out of the Pd. Thus, the primary use of this coulometric method would be for diagnostic studies of the effect of solution conditions on the D/Pd stoichiometry. Other methods, such as gravimetric or in situ measurement of changing electrode length would be best suited for measurements of D/Pd values in operating cells.

We have measured D/Pd atom ratios in Pd electrodes under a variety of electrolytic conditions. The average D/Pd atom ratio in fully loaded Pd electrodes was found to be 0.73 ± 0.02. We have seen no indication for anomalously high D/Pd ratios in over two hundred coulometric and thirty gravimetric determinations. Reproducible D/Pd atom ratios above 0.8 have been recorded only at reduced temperature. The highest recorded D/Pd atom ratio was approximately 1.0 at temperatures below 12K[37].

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Table 1. Typical electrochemical and gravimetric determinations of D/Pd (H/Pd) ratio.

	D/Pd or H/Pd Ratio	
Electrolyte	**Electrochemical**	**Gravimetric**
0.10M LiOD	0.72± 0.01	0.74 ± 0.01
0.10M LiOH	0.80 ± 0.01	
0.12M D_2SO_4	0.73 ± 0.01	

Table 2. D/Pd atom ratios as a function of current density determined electrochemically for Pd electrodes loaded in 0.10M LiOD.

Current Density mA/cm^2	D/Pd
20	0.73 ± 0.01
40	0.73 ± 0.01
60	0.73 ± 0.01
120	0.72 ± 0.02
600	0.73 ± 0.02

Figure Captions

Figure 1. Schematic diagrams of electrochemical cell used in the determination of D/Pd atom ratios. (A) is the cell configuration when the Pd cathode was charged in the galvanostatic mode. (B) is the configuration for electrode discharge.

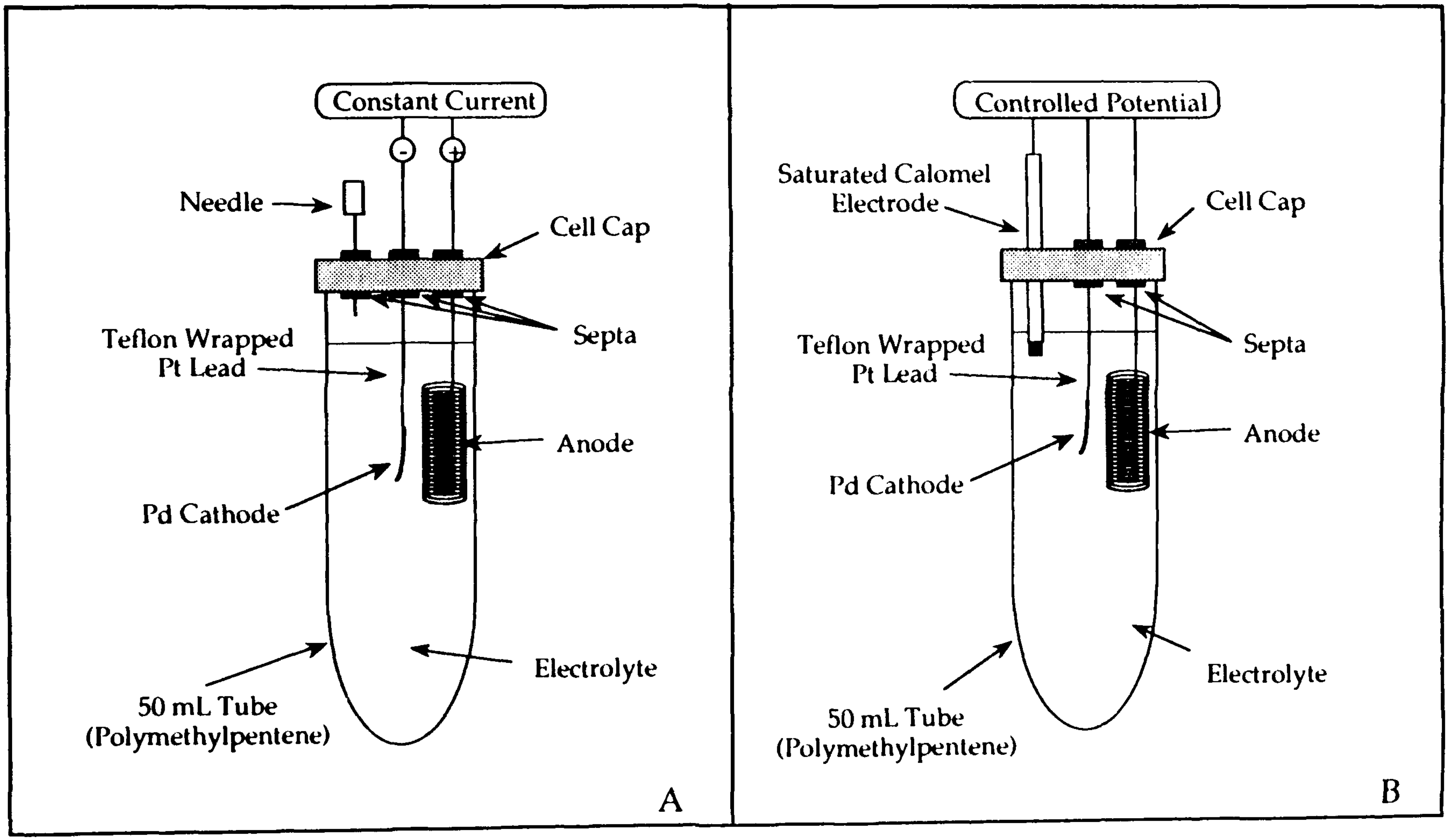
Figure 2. Cyclic voltammogram of a 0.127 mm-diameter Pd cathode in 0.10M LiOD. Curve (a) is the scan from +0.4V to -1.5V. Curve (b) is the sweep after the potential was held at -1.5V for 10 seconds. Curve (c) is the sweep after the potential was held at -1.5V for 20 seconds. The scan rate was 50 mV/sec.

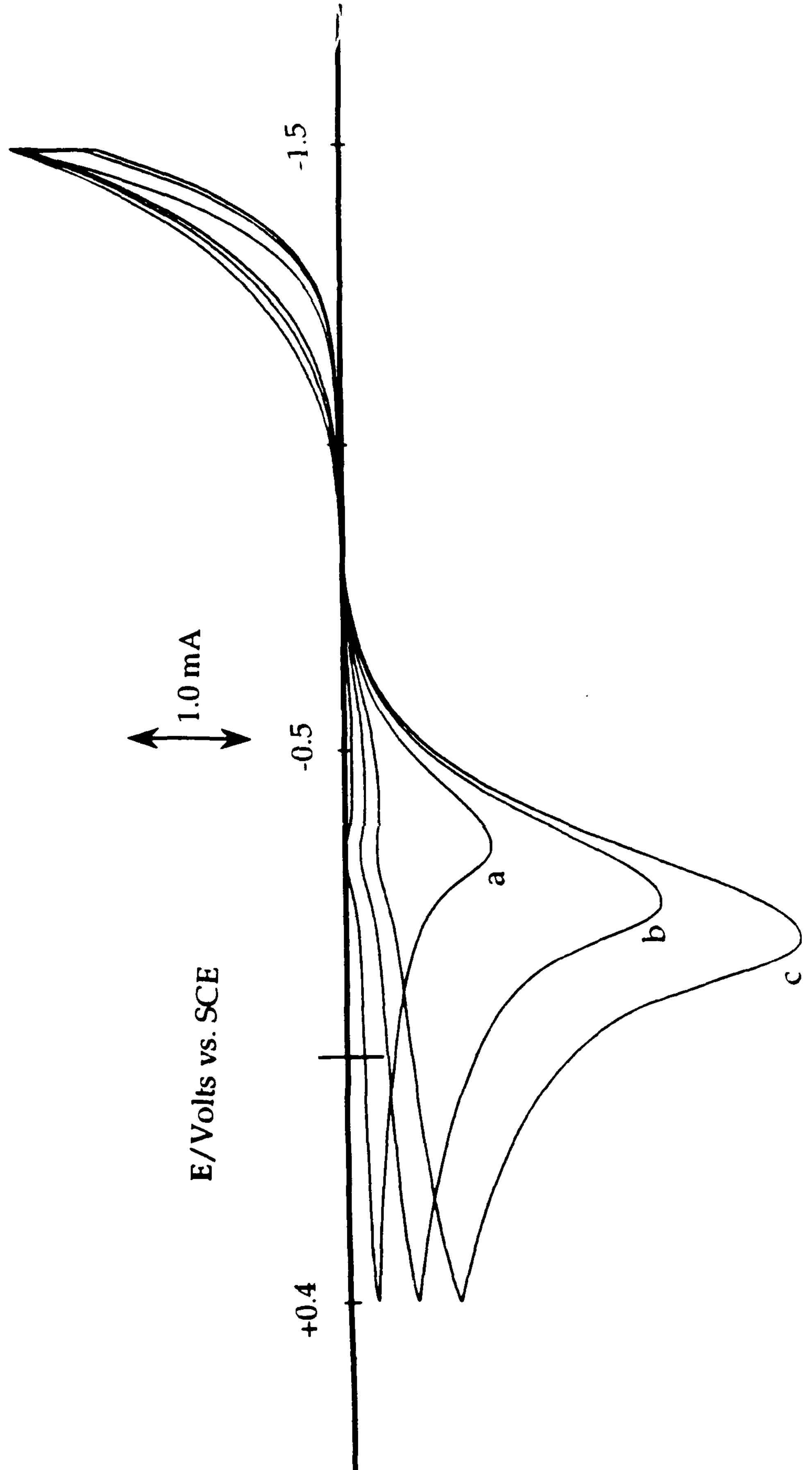
Figure 3. Current-time transient for discharge of a 0.127 mm-diameter Pd electrode in 0.10M LiOD. The potential was stepped from -1.91V to 0.0V versus SCE.

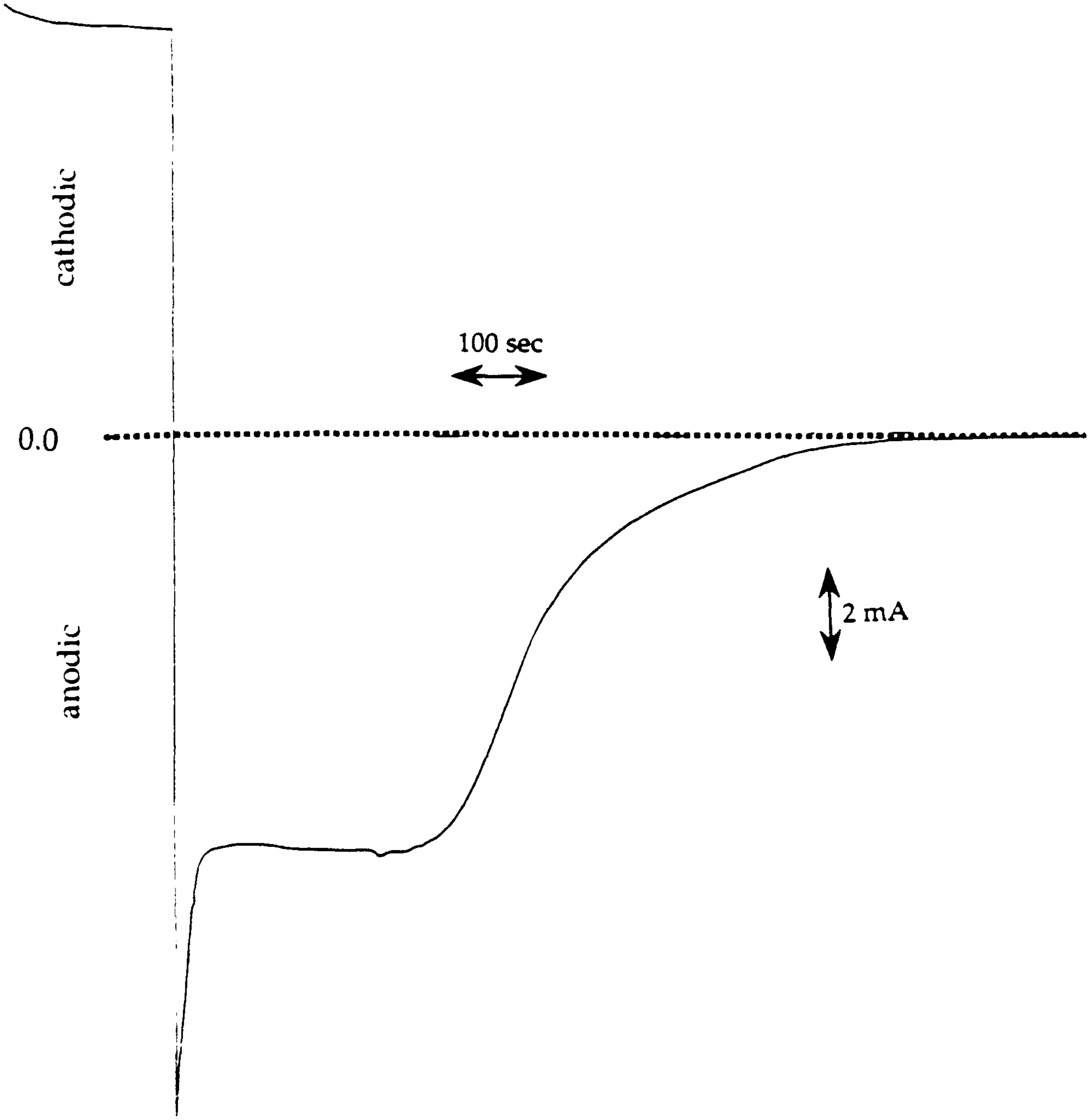
Figure 4. Plot of collected current (--○--) and D/Pd atom ratio (—•—) versus input charge for a 0.5 mm-diameter Pd electrode charged and discharged in 0.10M LiOD. The charging current density was 60 mA/cm^2.

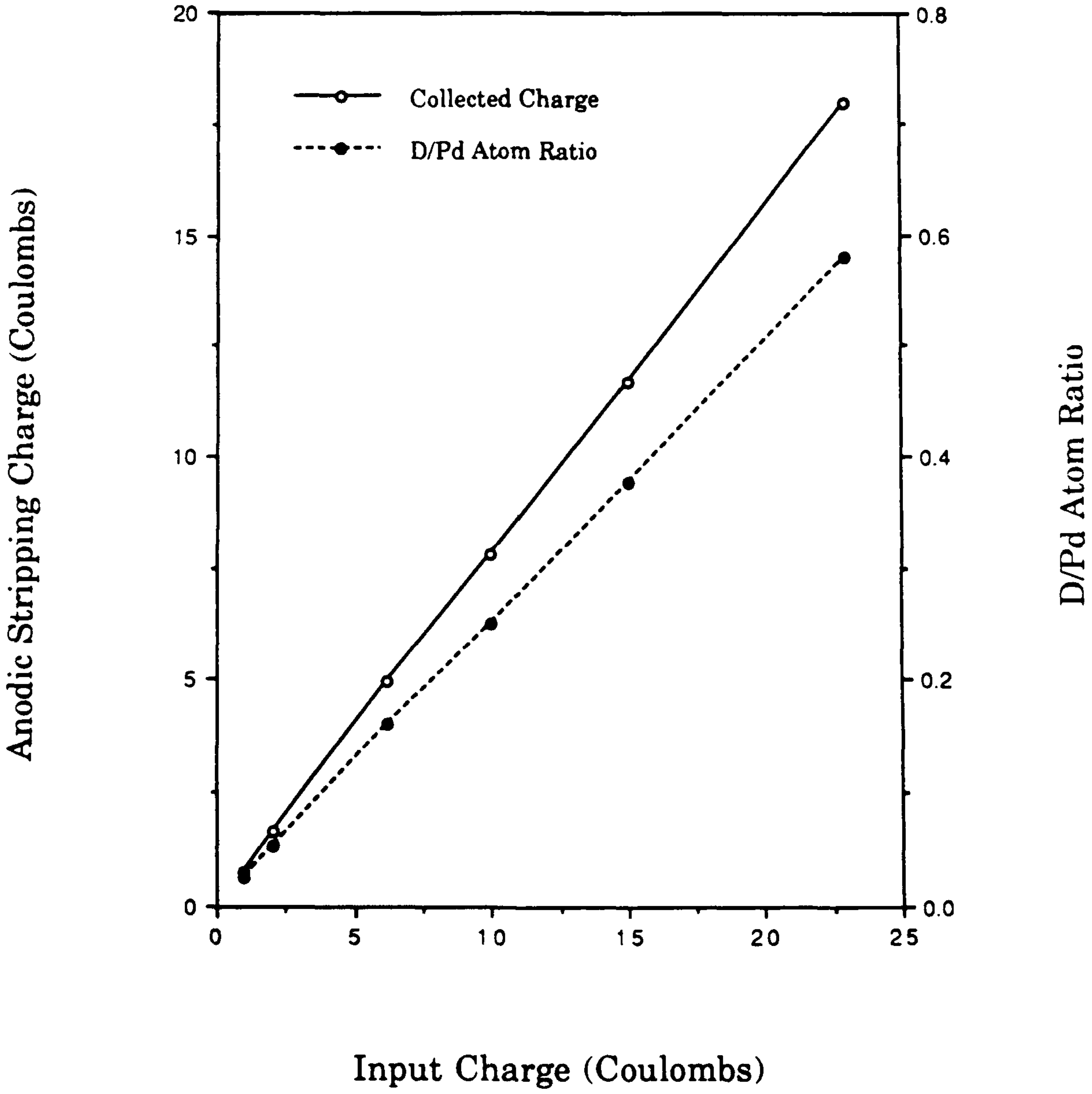
Figure 5. Plot of D/Pd atom ratio versus input charge for a 0.5 mm-diameter Pd electrode showing saturation of the electrode with deuterium in 0.10M LiOD. The charging current density was 60 mA/cm^2.

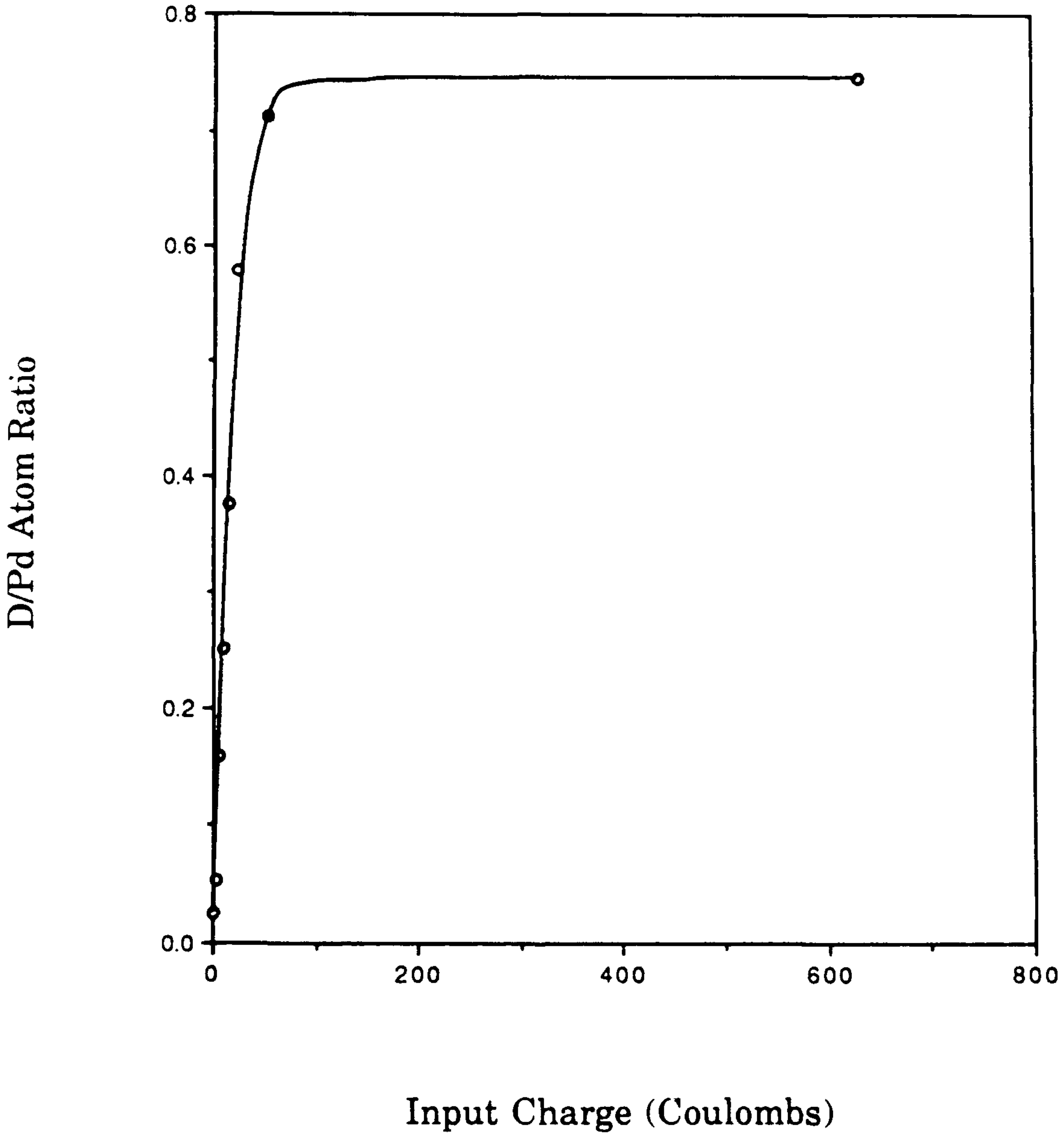
Figure 6. Scanning electron micrographs of (A) virgin 0.5 mm-diameter Pd wire and (B) 0.5 mm-diameter Pd wire after loading and unloading of deuterium.

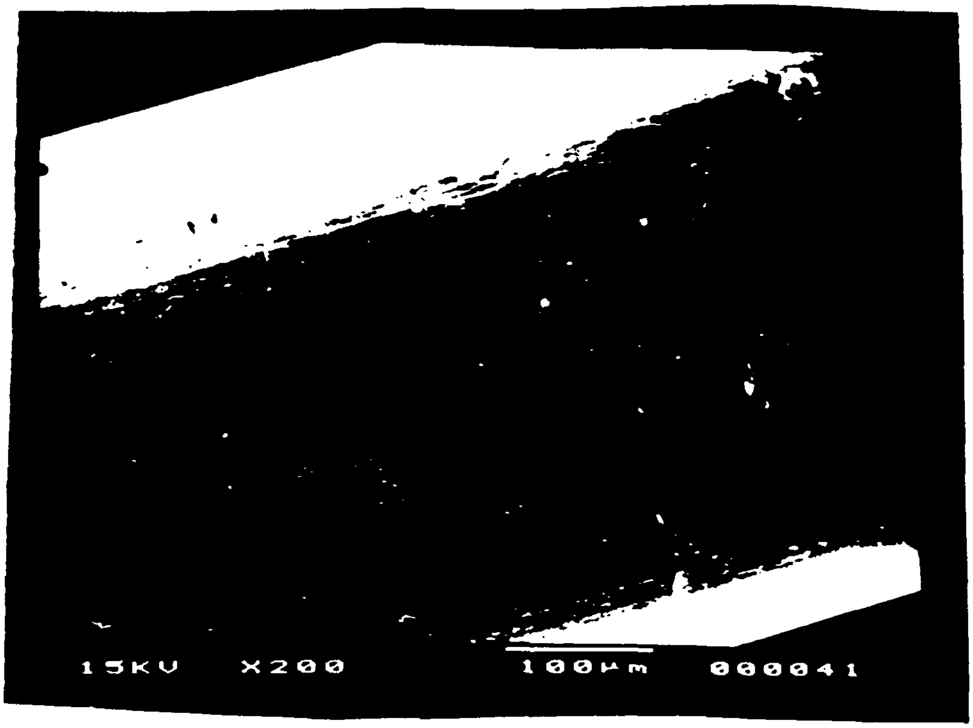

Constant Current
-
+
Needle
Cell Cap
Septa
Teflon Wrapped Pt Lead
Anode
Pd Cathode
Electrolyte
50 mL Tube (Polymethylpentene)
A
Controlled Potential
Saturated Calomel Electrode
Cell Cap
Septa
Teflon Wrapped Pt Lead
Anode
Pd Cathode
Electrolyte
50 mL Tube (Polymethylpentene)
B


-1.5
-0.5
+0.4
1.0 mA
E/Volts vs. SCE
a
b
c

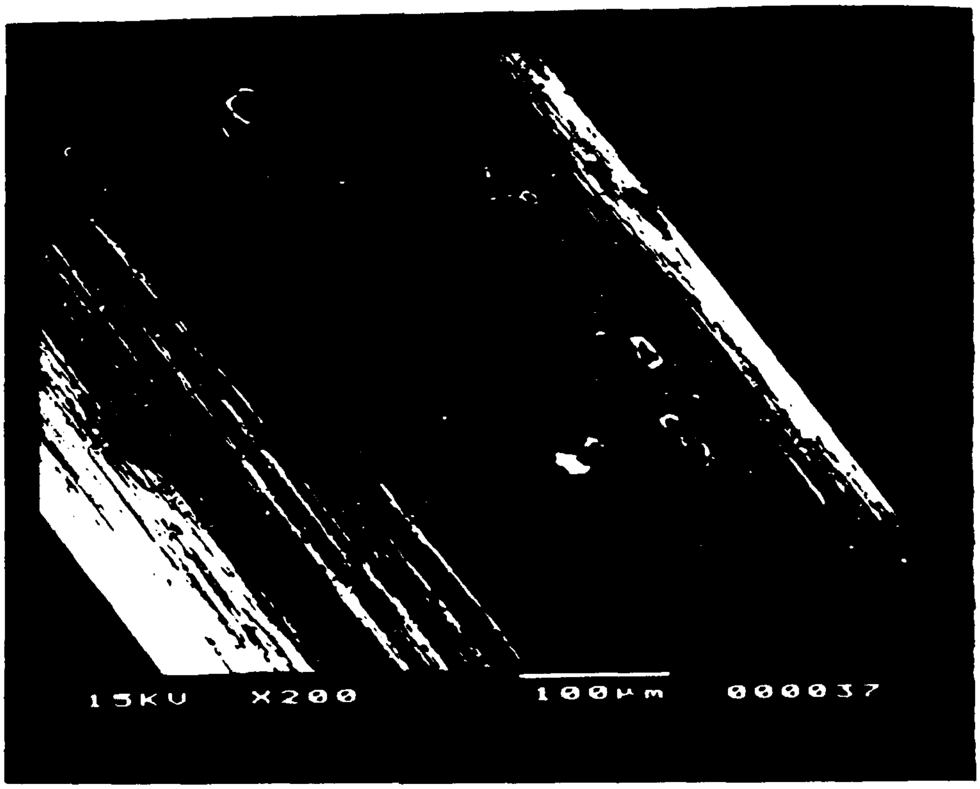

cathodic
100 sec
0.0
anodic
2 mA


Collected Charge
D/Pd Atom Ratio
Anodic Stripping Charge (Coulombs)
D/Pd Atom Ratio
Input Charge (Coulombs)
20
15
10
5
0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25


0.8
0.6
0.4
0.2
0.0
D/Pd Atom Ratio
0
200
400
600
800
Input Charge (Coulombs)



A



B