ANOMALIES IN THE SURFACE ANALYSIS OF DEUTERATED PALLADIUM

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ABSTRACT

The surface and near-surface analytical characterization of thin palladium foils after the electrolysis of H_2O or D_2O was performed with X-ray photoelectron spectroscopy (XPS), high resolution mass spectrometry, time-of-flight secondary ion mass spectrometry (TOF-SIMS), and scanning electron microscopy (SEM). These surface characterizations revealed a number of anomalous results, as summarized below.

INTRODUCTION

Our studies of the Pd-D_2O system, precipitated by the announcement of the Fleischmann-Pons effect [1], have centered on the exploration of the surface character of thin palladium foils before and after electrolysis of pH-neutral solutions of D_2O and H_2O [2-4]. The importance of understanding and controlling the nature of the electrode surface, so as to understand and control electron-transfer reactions occurring at the electrode surface, underlies the field of electrochemistry and has previously been emphasized as critical for the successful hydrogen loading of Pd [5]. In light of the variability of observations made by the myriad researchers exploring the Pd-D_2O system, the imperative need to determine the physical, chemical, and metallurgical nature of the palladium surface has recently been stressed [6,7].

EXPERIMENTAL

Electrochemistry and Chemicals

All electrolyses were performed, with one exception, in 0.1F Li_2SO_4/D_2O or H_2O, as appropriate. The one exception was a solution of 0.1F LiOD in D_2O prepared by dissolving lithium metal in D_2O. H_2O was triply distilled from quartz, 99.9% D_2O [MSD Isotopes for the preliminary experiments, Cambridge Isotope Laboratories for the majority of the experiments] was used as received. Li ribbon [Alfa] and Li_2SO_4 [Alfa, anhydrous] were used as received.

All electrolyses were performed with 99.9% Pd foil, 0.127-mm thick [historical supply of precious metals, Naval Research Laboratory]. X-ray diffraction analysis of this foil showed that it was preferentially oriented, primarily in the <200> direction [2]. The foils were acid etched in 1:1 HC/:HNO_3 to remove surface oxide, rinsed well, and then sonicated in the appropriate solvent prior to use. The anode, with one exception described below, was 99.999% Pt wire [Alfa], wound around a glass-rod cage so as to concentrically surround the Pd cathode.

The Pd foils were cathodically charged at 10 mA/cm^2 using the galvanostatic mode of a EG&G PAR Model 173 potentiostat/galvanostat; higher current densities were then usually applied. The cells and experimental procedure have been described in greater detail elsewhere [2-4].

Mass Spectrometric Measurements

The mass/charge profile encompassing the Pd isotope range (m/z range 100-115) was measured using the static SIMS mode of a TOF-SIMS built in-house at the Naval Research Laboratory [8,9]. Positive-ion spectra were obtained by using primary ions of 14.0-keV cesium ions from a pulsed alkali-ion gun containing a thermionic emitter. Each reported spectrum is the average of two-to-three million spectra. Samples were argon-plasma cleaned, *in situ,* prior to analysis.

High resolution (m/Δm > 50,000) analysis of m/z 3, 4, 5, and 6 of the gases emitted by electrochemically loaded PdD$_x$ was made using a ZAB-2F double-focusing mass spectrometer. Slivers were cut from the Pd foil immediately after electrolysis and placed in glass capillaries; the capillaries were introduced into an electron ionization source via a standard solids probe. This experiment was performed for one sample only. Background pressure was 10^{-8} torr.

The mass/charge region encompassing the Pd isotope window (m/z 102-110) was obtained by wrapping the foils (before and after electrolysis) around a solids probe and fast-atom bombarding with 8 keV Xe; resolution was m/Δm = 3300. 6-10 spectra were signal averaged to produce the obtained spectrum. To gauge the presence of interfering polyatomic species at m/z 106, the ions comprising m/z 106 were mass selected and collided with helium neutrals to induce dissociation of polyatomics.

To obtain the ratio of m/z 7 to m/z 6, lithium salts were dissolved to ≈0.1F with H$_2$O and aliquots of the solution were evaporated on the solids probe.

Bulk and Surface Elemental Analysis

Atomic emission spectrographic analysis of the stock Pd foil showed significant concentrations of the following metals [3]:

Element	Concentration/ppm
Ni	200-300
Pt	200
Ag	100
Rh	50
Cu	50
Si	20-40

Elemental analysis of the Pd surface before and after electrolysis was performed with a Surface Sciences Instruments Model SSX-100-03 X-ray photoelectron spectrometer with a small-spot capability and equipped with an Al anode. Foils analyzed immediately after electrolysis outgassed so severely (> 10^{-7} torr background pressure) that ≈12 h were required to reduce the pressure to the typical analysis pressure of < 5 x 10^{-9} torr [3]. Binding energies are referenced to the adventitious C1s line at 284.6 eV. Overlapping lines were deconvoluted with a graphics package using a χ^2-minimization calculation.

Scanning electron microscopy was performed with a Hitachi Model S-800 Field Emission Microscope. Photomicrographs were taken in the normal mode (using the secondary electrons emitted from the sample) and, to accentuate surface topography, in the differential mode.

RESULTS and DISCUSSION

X-ray Photoelectron Spectroscopic Analyses

Survey scans of the etched Pd, an example of which is shown in Figure 1*a*, consist of the characteristic Pd lines with a trace amount of spectrometer-derived carbon. The small peak at ≈50 eV is due to Pd5p$_{3/2}$; the other platinum-group metals also have weak, higher valence lines in this area making any post-electrolysis assignment of Li1s, by XPS, ambiguous.

After electrolysis of D$_2$O for an accumulation of 1.9 x 10^5 Coulombs of charge, other elemental lines are now evident in the survey scan (Figure 1*b*), *e.g.,* O1s (the small contribution seen for Pd3p$_{1/2}$ at 560 eV shows that the line at 530 eV is predominantly O1s and not Pd3p$_{3/2}$), Na1s (and a Na Auger line), Pt4f, a Mg Auger line, Zn2p, Si2p, S2p, and Cu2p. While elemental components derived from the glass cell (Si, Mg, Na) are present, as is Pt (electrodeposited at the surface as Pt metal from Pt ions generated by the oxidative dissolution of the anode), the surface retains a Pd signature.

Although Rh and Ag are present in our Pd stock at a concentration below the limit of detection by XPS, after electrolysis of either D$_2$O or H$_2$O, Rh and Ag can be detected at the surface of the Pd by signal averaging tens of high resolution scans. The concentrations of Rh and Ag maximize at 3 and 1 atom%, respectively, relative to the Pd signal [3].

Rh and Ag do not electrodeposit, but rather they concentrate towards the interface as a function of the long duration and high accumulated charge of the electrolysis. This was determined in two ways: *(i)* by the absence of Ag signals for the one sample electrolyzed in LiOD – this sample had no Pd signal and strong Pt signals due to electrodeposited Pt; and *(ii)* by using the small-spot capability of the spectrometer, the analysis was centered on a slight scratch made in the surface before placing the sample in the spectrometer – this procedure emphasizes bulk material brought to the surface; the Pt4d$_{5/2}$ line was found to strongly decrease while the area due to the Rh3d$_{3/2}$ line remained unchanged. Both of these results are consistent with a Pt signal dominated by Pt derived from electrodeposition and Ag and Rh signals derived from surface enrichment of Rh and Ag residing in the bulk Pd.

The concentration of the Rh increased as a function of total accumulated charge, but plateaued at ≈3 atom% [3]. The magnitude of the surface enrichment can be gauged by estimating the depth of the enriched layer assuming a uniform 3 atom% concentration. This layer would be ≈0.1-μm thick – which is a serious degree of migration / segregation in a foil on the order of 10^2-μm thick. As both Ag and Rh appear at the surface of Pd charged in either D$_2$O or H$_2$O, a mechanism based on surface segregation and forced diffusion as the Pd lattice is filled with H$^.$ or D$^.$ atoms seems more probable than one relying on known neutron activation reactions of Pd isotopes, some of which yield stable Ag and Rh isotopes [10]. Intriguing though this latter prospect may be, experiments with 99.999% Pd would be required before a physical transport mechanism could start to be discounted.
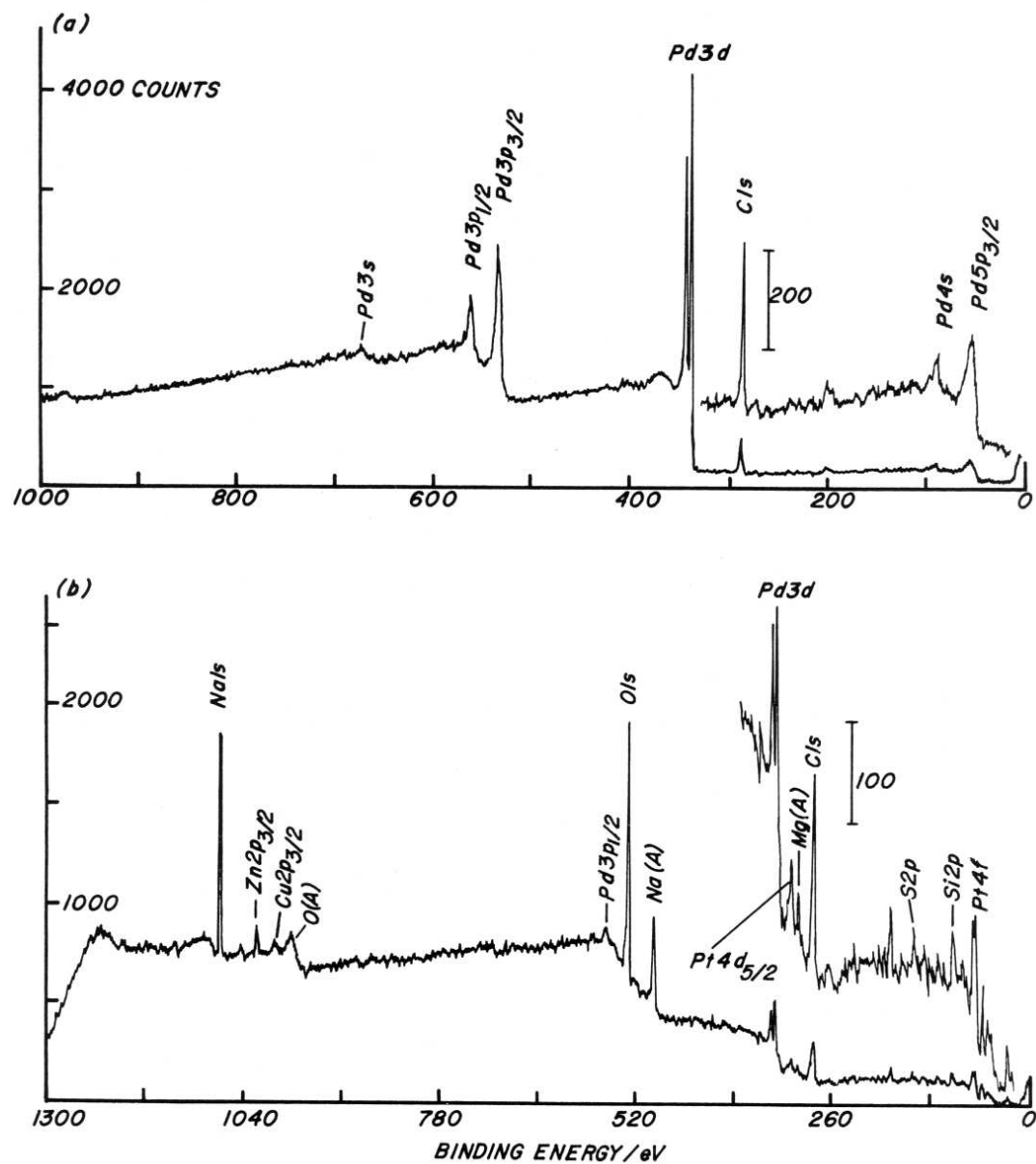
Figure 1. X-ray photoelectron survey scans of Pd foil: *(a)* **after etching in 1:1 HC*l*:HN0$_3$; and** *(b)* **after electrolysis in 0.1*F* Li$_2$S0$_4$/D$_2$O for a total accumulated cathodic charge of 1.9 x 10^5 C.**

Mass Spectrometric Analyses
Pd

TOF-SIMS measurements of the Pd blank (the Pd starting material prior to electrolysis) and Pd electrolyzed in H_2O yielded mass-to-charge vs. amu intensities which mirrored the expected sequence for the stable Pd isotopes (neglecting the 1.02% abundant [102]Pd). The ideal abundances are [11]:

Isotope	Natural Abundance/%
[104]Pd	11.14
[105]Pd	22.33
[106]Pd	27.33
[108]Pd	26.46
[110]Pd	11.72

Two samples electrolyzed in D_2O exhibited greater than 20% enrichments in m/z 106 intensity and diminutions in m/z 105 intensity [2]. This result is provocative because of the implication that [105]Pd obtained a neutron to generate [106]Pd. The more startling [106]Pd enrichment (≈100% over ideal) was observed for the only sample electrolyzed in LiOD; an enrichment of ≈45% was observed for one of the samples electrolyzed in Li_2S0_4. It was shown using the Pd blanks and the sample used to electrolyze H_2O that the conditions of the TOF-SIMS measurements, including *in-situ* plasma cleaning of the samples, were not responsible for the enrichment/ diminution phenomena [2].

Subsequent fast-atom bombardment, high-resolution mass spectrometric measurements on the LiOD sample replicated the TOF-SIMS results, however, mass selecting the ions at m/z 106 and using collisional-induced dissociation showed a loss of oxygen atoms indicating that the intensity at m/z 106 was compromised by the presence of polyatomic ions. It was shown that the species was [90]Zr[16]O, a species with a nearly coincident mass to [106]Pd, 105.8992 and 105.9032, respectively. The zirconium isotopic distribution allows ZrO species to unfortunately overlap most of the Pd isotopic distribution (see Figure *2b),* making high resolution measurements of this region (or the Pd dimer mass/charge region) necessary [12]. After 30 min of bombardment, the isotopic distribution reflected the expected abundances for Pd. The zirconium was present at the surface as $Zr0_2$ (confirmed by XPS), at trace levels, and it derived from the electrochemical (or post-electrolytic) conditions and not from a plasma-generated contaminant.

The Li_2S0_4-derived, [106]Pd-enriched sample was Zr-free according to TOF-SIMS data, see Figure *2a;* unfortunately, it no longer existed in a form compatible with surface-sensitive high resolution mass spectrometry (having earlier been dissolved in 1:1 HC/:$HN0_3$ to pursue other analytical chimera). Other Pd foils used to electrolyze D_2O have shown, by high resolution mass spectrometry, a mass/charge distribution in this region which matches the expected Pd isotopic distribution, including a sample only mildly etched, so that the cold-worked overlayer remained.

The source of the anomaly in the Pd isotopic distribution for the one Li_2S0_4-derived sample remains unexplained. We have recently recognized that this sample was coincidentally contaminated with Cd due to an impurity in the Pt-gauze used as an anode while awaiting receipt of the 99.999% Pt wire. ([106]Cd is a stable isotope but has an abundance of 1.25% [11]; signals for

the significantly more abundant ^{112}Cd (24.13%) and ^{114}Cd (28.72%) are absent in the TOF-SIMS spectrum.) Cd has a high overvoltage for the evolution of hydrogen [13], *i.e.,* the back reaction of D atoms recombining to form D_2 gas is inhibited. Cd may have provided a serendipitous, low-level surface poison and it is conceivable that higher D:Pd levels were achieved in this one experiment than in subsequent experiments. Experiments to test this possibility are in progress.
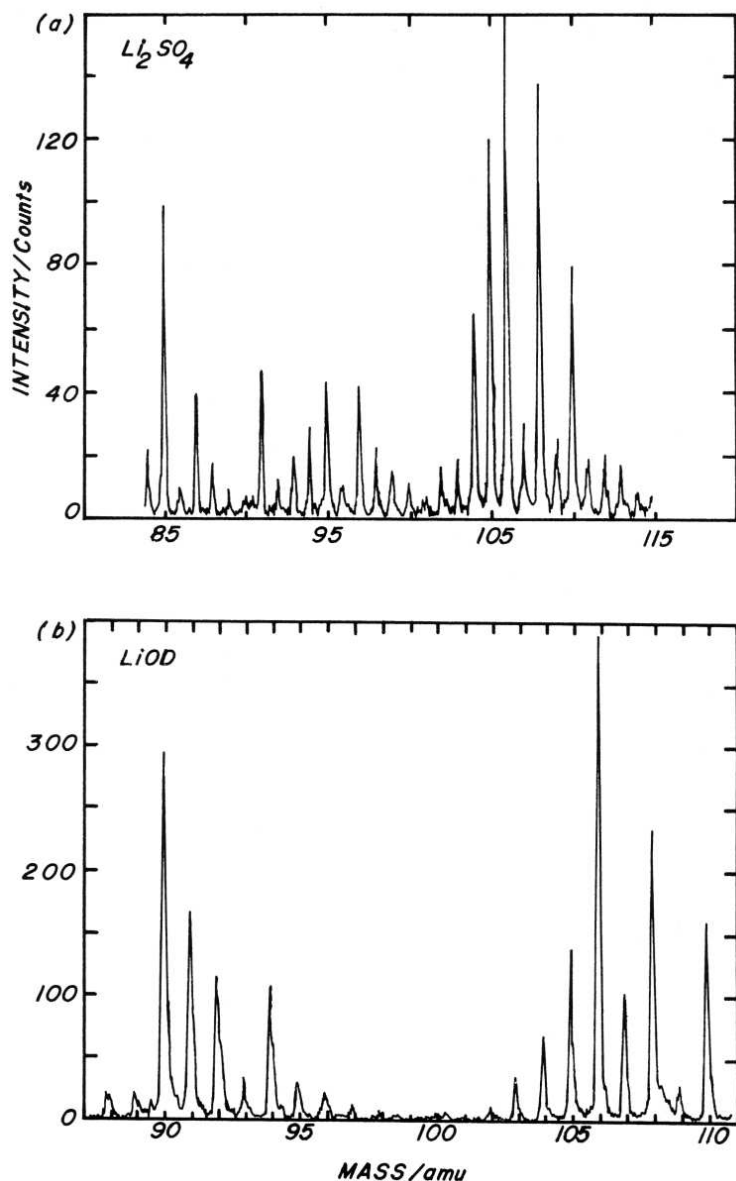

Figure 2. TOF-SIMS spectra obtained for Pd foil after electrolysis in *(a)* **0.1***F* **Li$_2$SO$_4$/D$_2$O for a total accumulated cathodic charge of > 8 x 10^3 C; and** *(b)* **0.1***F* **LiOD/D$_2$O for a total accumulated cathodic charge of 1.4 x 10^6 C. The m/z range is chosen to encompass the Zr and Pd isotopic distributions.**

Li

As has been pointed out by others, the natural abundance of Li isotopes (^{7}Li, 92.5% abundant and ^{6}Li, 7.5% abundant) is not necessarily found in commercial lithium salts due to the extraction of the neutron-scavenging ^{6}Li isotope. Consequently, any determination of the ^{7}Li-to-

^{6}Li ratio for Pd after electrolysis of Li^+/D_2O electrolytes needs to be balanced against the ratio of the starting lithium electrolyte salt. Sampling, via fast-atom bombardment mass spectrometric analysis, of some lithium salts stocked at our laboratory shows how variable the ^{7}Li-to-^{6}Li ratio can be, as summarized below:

Li salt	^{7}Li-to-^{6}Li ratio	Source
Natural Abundance	12.3	Big Bang
LiOD	31 ± 1	Li metal, Alfa
LiB_4O_7	18.2	Johnson Matthey
LiI	11.6	Alfa
LiI	19.4	Aldrich
$LiBO_2$	16.1	Johnson Matthey

H/D/T

The copious explosion of gas that bursts from the surface of the Pd cathode when the electrochemical circuit is broken is followed by long-term outgassing, as can be observed by the gas bubbles that form when the Pd cathode is stored under water after electrolysis. Likewise, even slivers of material cut from the Pd after electrolysis provide ample gas to analyze by mass spectrometry. High resolution analysis of the gases emitted from one Pd foil after charging in Li_2SO_4/D_2O showed that the m/z 3, 4, 5, and 6 peaks were composed of the dimers and readily formed trimers of hydrogen and deuterium with no detectable quantities of tritium-based species.

Scanning Electron Microscopic Analyses

SEM has been used to explore Pd foil before and after use as cathodes to electrolyze H_2O and D_2O [4]. After sufficient etching to leave visible crystal grains, the majority of the grains are roughened, but ≈20-30% of the grains remain smooth and unfeatured even at high magnification (> 15,000 x). The surface morphology changes after electrolysis, with the roughened grains restructuring to yield greater intragranular homogeneity and features of higher surface area, however, smooth and unfeatured grains persist after electrolysis of both D_2O and H_2O electrolytes.

Three characteristic grains have been observed for PdD_x from highly etched stock, the smooth, unstructured grains, and two structured morphologies. On the micrometer scale, as seen in Figure 3, one structure consists of rugged, parallel, thin-edged ridges (Figure 3a), and the other is an intertwined structure (Figure 3b, lower half), which at higher magnification, might be the beginning of crystal faceting [4].

The degree of the initial etch governs the development of the surface structures that form with electrolysis. SEM survey scans of Pd cathodes after electrolysis must be placed in the context of the initial microscopic morphology of a portion of the *same* piece of Pd. We attempted to control this by etching a large piece of Pd foil and then using portions of it for electrolytic preparation of PdH_x and PdD_x using comparable electrolytic histories.

Three PdD_x samples have been prepared, yielding comparable characteristic morphologies, and one PdH_x sample has been prepared, electrolytically analogous to one of the three PdD_x samples. The PdH_x sample also produced restructured grains with greater intragranular homogeneity and higher surface area than the initial etch morphology, however the resulting restructured morphologies differed between H- and D-exposed Pd. The surface of the structured

grains for PdH$_x$ appeared more polished and had features that were less deep and developed than those on the comparably treated PdD$_x$. An additional series will be run to confirm this difference in morphology between electrolytically prepared PdH$_x$ and PdD$_x$.

Cracks and fissures do not appear to be part of the morphology after electrolysis for either system; this may be due to the well-defined grain boundaries, resulting from the etch, which provide non-catastrophic paths for gas release when the electrical circuit is broken.

Photomicrographs taken in the differential mode indicated that intergranular elevational differences resulted between the smooth, unstructured grains and the roughened and structured grains, as seen in Figure 4a. Stereopairs made in 2-3 locations for PdH$_x$, all three PdD$_x$ samples, and reserved samples of the initially etched Pd confirmed the intergranular elevational differences and showed that the structured grains are uplifted relative to the smooth, unstructured grains, but only for the PdDx samples. This topography is somewhat restricted to the nearsurface region in that all intergranular differences in elevation disappeared after a piece of the sample shown in Figure 3 was subjected to ~10 min of fast -atom bombardment, as seen in Figure 4b. In addition, the high surface area features are now absent. Quantifying the depth of the profile is not routinely done in this experiment, so the restructured layer can only be estimated as greater than nanometer, but less than micrometer in depth. We assign the process for uplifting to the premier, rapid episode of outgassing because (i) deformation, due solely to lattice expansion upon formation of the hydride or deuteride would have produced greater deformation for the PdHx sample since palladium hydride expands more than does palladium deuteride [5]; (ii) one of the three PdDx samples was subjected to multiple charge/outgassing cycles and showed a qualitatively similar degree of uplifting as singly outgassed samples; (iii) the smooth grains appear structurally indifferent to hydrogen or deuterium loading; and (iv) the outrush of gas is visibly more explosive for the PdDx system than it is for the PdHx system.
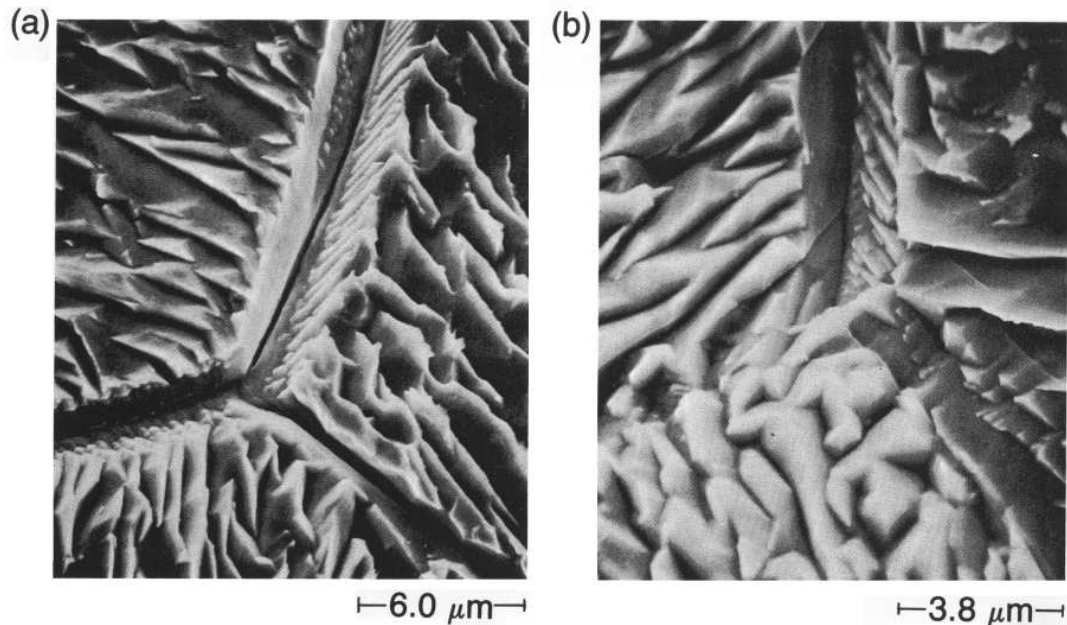

⊢6.0 μm⊣   ⊢3.8 μm⊣

Figure 3. Photomicrographs (normal mode) of the two characteristic restructured grains observed on highly etched Pd foil after electrolysis of 0.1F Li$_2$SO$_4$/D$_2$O (total accumulated cathodic charge = 1.9 x 10^5 C): *(a)* morphology described as rugged, parallel thin-edged ridges (tilt = 30°, 5000x); and *(b)* morphology described as an intertwined structure, lower half (tilt = 22°, 8000x).
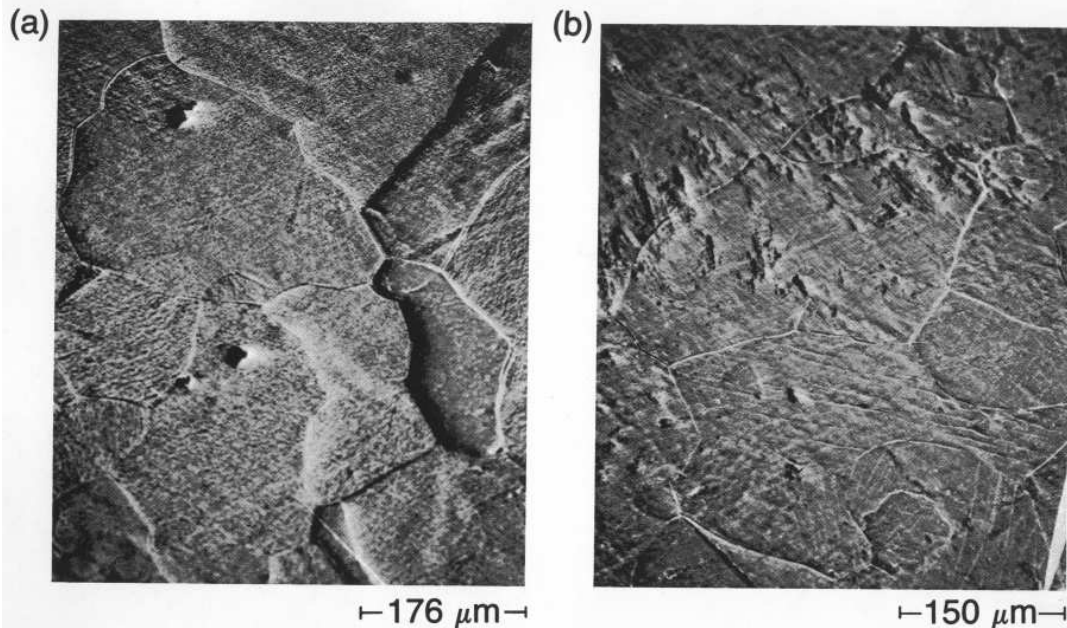
Figure 4. Photomicrographs (differential mode) showing *(a)* **the presence of intergranular elevational differences for the sample of Figure 3 (tilt = 30°, 170x); and** *(b)* **the absence of intergranular elevational differences after fast-atom bombardment of the surface (tilt = 30°, 200 x).**

CONCLUSIONS

Our surface analytical characterizations of Pd-H_2O and Pd-D_2O systems have produced a number of unusual results involving: (i) a relative enrichment at m/z 106 that cannot be attributed to heretofore-identified plausible chemical interferents:

(ii) segregation of metallic impurities (present in the bulk Pd at 10^2-ppm levels) to the surface of the more resistive, but still conductive PdDx or PdHx at atom-% levels; (iii) differently structured morphologies for PdDx and PdHx;

(iv) grains which remain smooth and unstructured even after electrolysis of D_2O or H_2O solutions to 10° C of accumulated charge; and (v) intergranular uplift for the structured grains relative to the unstructured grains, but only for PdDx samples.
Obviously the surface and near-surface characterization of electrolytically prepared PdDx systems requires great care and attention, but with the reward of unusual results.

ACKNOWLEDGMENTS

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[12] We would like to emphasize, yet again, that we have always referred to this observation as a mass/charge anomaly and not as an isotopic anomaly. The result, while valid for this one sample, and certainly intriguing, can only legitimately be described as a mass/charge anomaly when using this experimental approach and the resolution of this experiment.

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