Section 10

MASS/CHARGE ANOMALIES IN Pd AFTER ELECTROCHEMICAL LOADING WITH DEUTERIUM

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Introduction

Among the multitude of efforts [1] to reproduce the provocative experiment of Fleischmann, Pons, and Hawkins [2], the focus has been on the production of heat, and/or the generation of neutrons, high energy gamma rays, or the expected chemical byproducts of the fusion of deuterium with deuterium, such as tritium and ^{3}He. Our approach has been to explore the surface character of Pd foils after extensive electrolysis of H_2O or D_2O solutions.

Our experiments with the electrolysis of Pd foil in D_2O did not produce large neutron fluxes, and due to the small volume of the foil, calorimetric measurements were precluded. However, surface analyses by time-of-flight secondary mass spectrometry (TOF-SIMS) of the electrolyzed Pd revealed anomalies with electrolysis. TOF-SIMS was used to survey the effect on the Pd isotopic distribution with electrolysis in D_2O and H_2O. We report here an enrichment of m/z 106 and a diminution of m/z 105 in the surface/near-surface layers of Pd electrolyzed in D_2O. No enrichment of m/z 106 was observed for the starting Pd material or for Pd electrolyzed in H_2O.

Experimental

Materials and Electrolytic Conditions

All experiments were run with samples cut from a piece of Pd foil (0.127-mm thick) obtained from the historical supply of precious metals in the electrochemistry group at the Naval Research Laboratory. X-ray diffraction [Philips/Norelco Model XRG 6000 X-ray Diffractometer] of this foil showed that it was oriented, primarily in the <200> direction.

The Pd foil cathode was cut in the shape of a flag or a rectangular strip. A spot-welded contact was made to 0.5-mm diameter Pd wire [Aldrich, 99.99% pure] for the strip electrode or to Ta ribbon for the flag electrode. The Pd-Ta join was placed well above the solution level during electrolysis. Prior to electrolysis, the Pd foil (which was dull gray) was cleaned in freshly prepared 1:1 HCl:HNO_3 either superficially to remove surface oxide or as follows: the Pd strip was gently moved through the acid for 90 s and then sonicated three times in fresh H_2O; this step was repeated twice; finally the foil (now shiny and showing visible facets) was sonicated in the solvent of electrolysis.

The reaction was run in two different cells. The first cell was a variation on the toroidal dispersion electrolysis cell, previously described [3,4], with an anode of Pt gauze cylindrically surrounding the Pd flag cathode (with a total surface area of 2 cm^2). Solution volume was 30 ml. The second cell was a tall-form beaker where the anode was Pt wire (Alfa, 5N pure) wrapped around the outside of a glass-rod cage, as in the Fleischmann and Pons design [2], to surround a long Pd strip (of varying area, > 1 cm^2), so that the Pd cathode is again concentrically surrounded. Solution volume of this cell was 100 ml. Unless the anode symmetrically surrounds the Pd cathode, electrolysis merely achieves the diffusion of deuterium through (and out of) Pd.

The electrolyte solution for the D_2O experiments was 0.1F Li_2SO_4 [anhydrous, Alfa] in one of two sources of 99.9% pure D_2O [MSD Isotopes or Cambridge Isotope Laboratories]. Reasoning that the pertinent half-cell electrochemical reaction, i.e., the reduction of D_2O at the cathode,

$$D_2O + e^- = D^\cdot + OD^- \qquad (1)$$

occurs in both neutral and basic solutions, we opted for the less resistive and lower etchant electrolyte. One

experiment was prepared under environmentally controlled conditions, i.e., previously unopened D_2O [Cambridge Isotope Laboratories] was placed in a dry box [Vacuum Atmospheres: He atmosphere at < 1 ppm H_2O] and used to prepare 0.1F LiOD from Li metal ribbon [Alfa]. The electrochemical cell was assembled in the dry box, sealed, and removed for electrolysis. Electrolyses in light water were performed with triply-distilled (from quartz) H_2O with 0.1F Li_2SO_4.

The electrochemical loading of D or H in Pd was achieved by applying a constant current of 10 mA/cm^2 for at least one day using the galvanostatic mode of a EG&G PAR Model 173 potentiostat/galvanostat. Cell voltage was measured by connecting the reference and auxiliary electrode leads to the electrometer. After initial charging at 10 mA/cm^2, some cathodes were charged at 50 mA/cm^2 or 140 mA/cm^2, but most were maintained at 10 mA/cm^2. Some experiments were run with a neutron counter [Radiac Probe Model DT-371/PDR-70 and Radiac Model 2 Counter-Timer] placed outside of the cell.

The isotopic profile for Pd (m/z range 102-110) was performed using the static SIMS mode of a TOF-SIMS. The instrument used in these studies was built at the Naval Research Laboratory [5,6] and utilizes a pulsed alkali-ion gun, containing a thermionic emitter which produces 2-5 ns pulses of 14.0-keV cesium ions. Positive secondary ions were detected. Each intensity-amu spectrum is the averaged accumulation of two or three million spectra. Samples (sized approximately 0.5 cm x 1 cm) were argon-plasma cleaned in the analysis chamber prior to analysis.

Elemental analysis of the Li_2SO_4/D_2O solution was performed with inductively coupled plasma emission spectrometry and indicated no trace metallic impurities at sub-ppm levels.

Results and Discussion

During the initial electrochemical experiments with Pd in Li_2SO_4/D_2O, rudimentary neutron counting was performed, and although the results were statistically ambiguous, it seemed that further investigation was warranted. X-ray diffraction of the electrolyzed Pd foil showed that lines for Pd were gone and lines for a Pd deuteride phase were present.

Isotopic Distribution from TOF-SIMS

In TOF-SIMS the velocity of the secondary ions produced from the sample surface is inversely proportional to the square root of the mass/charge ratio. This allows the mass of each ion to be determined by measuring its flight time, and, thus, it is possible to reliably observe isotopic ratios in a sample.

The first TOF-SIMS experiment on a Pd foil electrolyzed in D_2O was focused on the low m/z region to gauge the presence of any Li and H/D/T isotopes. The high m/z range was coincidentally obtained, yielding the startling result that the expected natural isotopic distribution of Pd was altered in the electrolyzed Pd, with m/z 106 significantly enhanced. This is clearly seen in Figure 1, where the Pd isotope range (m/z 102-110) is contrasted for Pd blank (i.e., never-electrolyzed Pd foil) and two deuterated Pd foils: PdD#4 - Pd foil electrolyzed for an accumulated charge of $\approx 8 \times 10^3$ Coulombs with freshly opened D_2O and 0.1F Li_2SO_4; and PdD#10 - Pd foil electrolyzed for 1.4×10^6 Coulombs of accumulated charge with freshly opened D_2O and freshly prepared LiOD.

Figure 1 also includes the TOF-SIMS spectrum obtained for Pd foil electrolyzed in H_2O for an accumulated charge of 40.2×10^3 C (PdH#14). These spectra for the electrolyzed foils show peaks at the Pd isotopic values; they do not show a shifted isotopic distribution at $(m+2)/z$ as expected for PdD or $(m+1)/z$ as expected for PdH. This means that molecular PdD or PdH species do not predominate the ions displaced from the surface. The bond strength of PdH has been theoretically determined to be < 0.1 Hartree [7,8], thus few molecular PdD(H) ions would be expected to survive the secondary ion process.

Assigning the enhanced m/z intensity at 106 amu as due to preferential reaction of a deuteron with ^{104}Pd to generate ^{104}PdD at m/z 106 would require rewriting our chemical understanding of reactions. Isotopic effects are observed in the rate of a reaction, not in the identity of the reaction. Furthermore. $(106/104)^{1/2} = 1.010$ - which is not a large isotopic driving force.

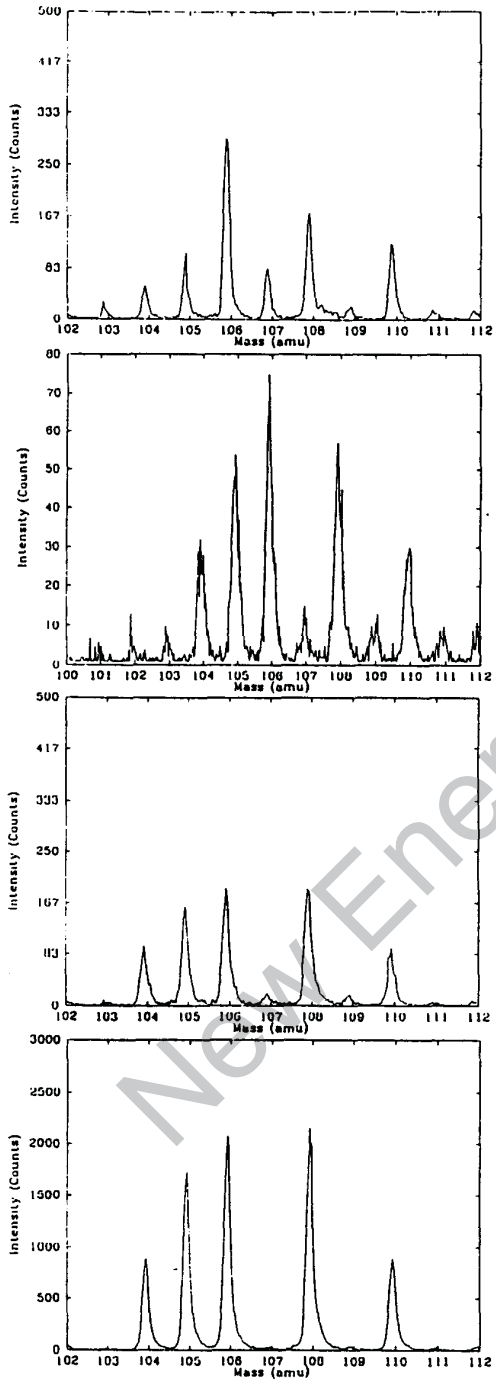

Figure 1: TOF-SIMS spectra obtained for Pd foils before and after electrolysis in D_2O and H_2O.

PdD#10 (0.1F $LiOD/D_2O$)

PdD#4 (0.1F Li_2SO_4/D_2O)

PdH#14 (0.1F Li_2SO_4/H_2O)

Pd foil

Because the samples are cleaned by generating an inert gas plasma inside the TOF-SIMS analyzer chamber, the possibility exists for contamination by constituents of the steel chamber walls; in this m/z range, chromium dimers are an especial worry. Table I lists the naturally occurring isotopes for Pd, Cr, Rh, and Ag. The greatest concern arises with respect to m/z 104, since a dimer of ^{52}Cr (83.8% abundant) would contribute to the signal for ^{104}Pd. Slighter influences from Cr dimers could also affect ^{105}Pd, ^{106}Pd, and ^{108}Pd. As the samples are placed in the chamber and analyzed separately, each experiences slightly different plasma conditions.

TOF-SIMS Analysis of Non-Electrolyzed Pd

To assess the effect, if any, of plasma-generated m/z contamination, three non-electrolyzed Pd foil samples were plasma cleaned in-situ and analyzed. Because m/z 110 cannot be affected by a chromium dimer, it was used as an internal standard: the intensities for m/z 104, 105, 106, and 108 were ratioed to that at m/z 110 for each sample. The results are listed in Table I. Also included in Table I is the percent difference between this ratio and the ratio predicted from the known isotopic abundances of Pd (also listed in Table I); this gives an estimate of the deviation from ideality.

It can be seen that for two of the blanks (Pd#1 and Pd#3) there is no obvious problem from chromium dimers for m/z 105, 106, and 108, as they vary, at most, 15% from ideality, and even m/z 104, the most susceptible m/z, is not severely affected. Pd#2, however, has an enormous excess at m/z 104 (338.7% over ideality); most encouraging, however, is the fact that m/z 105, 106, and 108 are essentially unaffected. This study with non-electrolyzed Pd shows that the use of m/z 110 as an internal standard readily highlights significant contamination ascribable to chromium dimers, and that any peculiarity at m/z 106, as seen in Figure 1, cannot be ascribed to isotopic or molecular contaminants arising from the in-situ plasma cleaning.

As a second check, the intensities were also analyzed as adjusted abundances. This was done by rejecting any information at m/z 104 and summing the areas associated with m/z 105, 106, 108, and 110 (ideally summing to 88.08% of the total), ignoring any minor contribution from m/z 102, and renormalizing to 100% (the factor is 100/88.08 = 1.135). As seen in Table I, this approach also shows that within 15-20%, the expected isotopic distribution for Pd (excluding m/z 104) is obtained, regardless of significant plasma-generated contamination as seen for Pd#2.

TOF-SIMS Analysis of Electrolyzed Pd

With this analytical footing, a number of Pd samples electrolyzed in D_2O and H_2O were analyzed by TOF-SIMS. The normalized intensities, and their percent deviation from the natural abundance, are listed in Table II. Graphically, the normalized results are depicted in Figures 2 and 3 by histograms for each electrolyzed sample and for an averaged value obtained for the three Pd blanks from Table I. Their magnitudes are contrasted with a level drawn for the ideal value.

It is immediately obvious, whether normalizing with m/z 110 (as an internal standard) or adjusting the percent abundance, that two samples, PdD#4 and PdD#10, have been significantly altered at m/z 106, by approximately 45 and 85% respectively, over what was observed for the starting Pd material which mirrors the expected values for normalized ^{106}Pd.

The isotopic distribution for two samples - PdD#4(a) (analyzed by TOF-SIMS four months after termination of electrolysis) and PdD#9 (analyzed two months after termination of electrolysis, and run with air-exposed Li_2SO_4 and D_2O) - are less clearly scrambled. If the internal standard normalization is used, there appears to be a relative enrichment in m/z 106, but not at the levels seen for PdD#4 and PdD#10. If the adjusted abundance normalization is used, these samples closely resemble the ideal ratio at m/z 106 within experimental limits.

Study of the histograms prepared for m/z 105 and 108, as in Figure 3, yields similar conclusions, i.e., clear departure from natural abundances for PdD#4 and PdD#10. In this instance the isotopic abundances of m/z 105 and 108 are clearly diminished for PdD#4 and PdD#10, by either normalization analysis, while PdD#4(a) and PdD#9 are enhanced relative to m/z 110, but appear to be normal using the adjusted abundances.

TABLE I: Isotopic Ratios from TOF-SIMS Intensities - Pd blank

Naturally Occurring Isotope, m/z	% Abundance [a]	Normalized to ^{110}Pd	Pd#1 I_i/I_{110}	Pd#1 % Dev.	Pd#1 Adj. % Abundance	Pd#1 % Dev.	Pd#2 I_i/I_{110}	Pd#2 % Dev.	Pd#2 Adj. % Abundance	Pd#2 % Dev.	Pd#3 I_i/I_{110}	Pd#3 % Dev.	Pd#3 Adj. % Abundance	Pd#3 % Dev.
^{102}Pd	0.96	0.08												
^{104}Pd	10.97	0.93	1.26	+35.5			4.08	+338.7			0.84	-9.7		
^{105}Pd	22.23	1.88	1.72	-8.5	20.1	-9.5	1.79	-4.8	22.6	+1.8	2.03	+8.0	21.9	-1.4
^{106}Pd	27.33	2.31	2.43	+5.2	28.5	+4.4	2.49	+7.8	31.4	+15.0	2.65	+14.7	28.5	+4.4
^{108}Pd	26.71	2.26	2.26	0	27.6	+3.4	1.70	-24.8	21.5	-19.5	2.50	+10.6	26.9	+0.7
^{110}Pd	11.81	1.00			11.7	-0.8			12.6	+6.8			10.8	-8.5
^{50}Cr	4.31													
^{52}Cr	83.76													
^{53}Cr	9.55													
^{54}Cr	2.38													
^{103}Rh	100.00													
^{107}Ag	51.82													
^{109}Ag	48.18													

[a]: From Reference 11.

%Deviation = [(obtained value - ideal)/ideal] x 100.
Adjusted % Abundance = $(m/z)_i/([\text{sum of } m/z(105+106+108+110)] \times 1.135) \times 100$.

TABLE II: Isotopic Ratios from TOF-SIMS Intensities - Electrolyzed Pd

Sample	Accumulated Charge/10^3 C	(m/z)/amu	I_i/I_{110}	% Dev.	Adj. % Abundance	% Dev.
PdD#4	> 8	104	0.49	-47.3		
Pd/0.1F Li_2SO_4		105	1.36	-27.7	15.8	-28.8
D_2O		106	3.35	+45.0	38.9	+42.5
		108	1.88	-16.8	21.8	-18.4
		110			11.6	-1.7
PdD#4(a)	> 8	104	1.38	+48.4		
Pd/0.1F Li_2SO_4		105	2.65	+41.0	24.8	+11.7
D_2O		106	3.03	+31.2	28.3	+3.8
[a]		108	2.74	+21.2	25.7	-3.7
		110			9.4	-20.3
PdD#9	254.5	104	1.14	+31.2		
Pd/0.1F Li_2SO_4		105	2.40	+27.7	23.0	+3.6
D_2O		106	3.05	+32.0	29.2	+7.0
		108	2.76	+22.1	26.4	-1.1
		110			9.6	-18.6
PdD#10	1402	104	0.54	-41.9		
Pd/0.1F LiOD		105	0.95	-49.5	10.4	-53.2
D_2O		106	4.43	+91.8	48.8	+78.8
		108	1.63	-27.9	17.9	-33.0
		110			11.0	-6.8
PdD#11	1402	104	0.91	-2.2		
Pd/0.1F LiOD		105	2.11	+12.2	22.9	+3.2
D_2O		106	2.18	-5.6	23.6	-13.5
		108	2.84	+25.7	30.8	+15.2
		110			10.8	-8.1
PdH#14	40.2	104	0.89	-4.3		
Pd/0.1F Li_2SO_4		105	1.84	-2.1	22.2	0
H_2O		106	1.99	-13.9	24.0	-12.1
		108	2.47	+9.3	29.9	+12.0
		110			12.1	+2.5
Pd	0	104				
Blank (not		105	1.85±0.16	-1.6	21.5±1.3	-3.2
electrolyzed)		106	2.52±0.11	+9.1	29.5±1.7	+9.9
[Average of 3		108	2.15±0.41	-4.9	25.3±3.3	-5.2
samples]		110			11.7±0.9	-0.8

[a]: Sample was a portion of Pd foil ribbon used to contact the flag portion of PdD#4, but analyzed 4 months later.

%Deviation = [(obtained value - ideal)/ideal] x 100.
Adjusted % Abundance = $(m/z)_i/([\text{sum of } m/z(105+106+108+110)] \times 1.135) \times 100$.

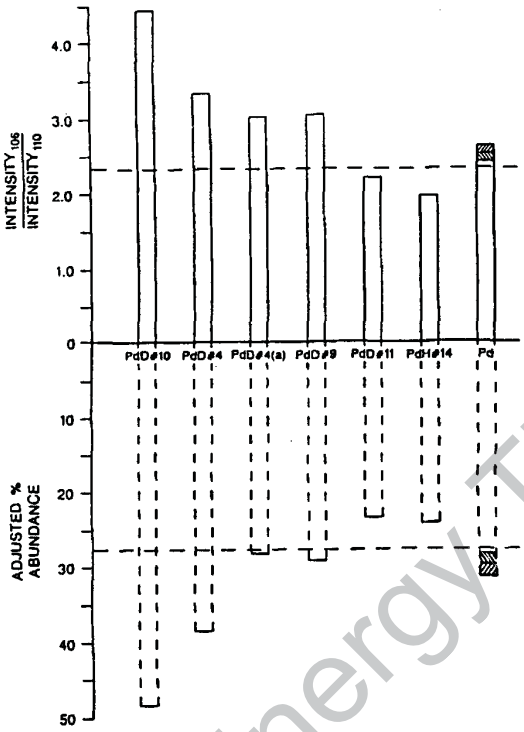

Figure 2: Histograms of the m/z 106 intensity normalized to the m/z 110 intensity (above the x-axis) and normalized as an adjusted % abundance (below the x-axis) for Pd foils before and after electrolysis in D_2O and H_2O. The horizontal dashed line represents the ideal value for m/z 106 by either normalization method.

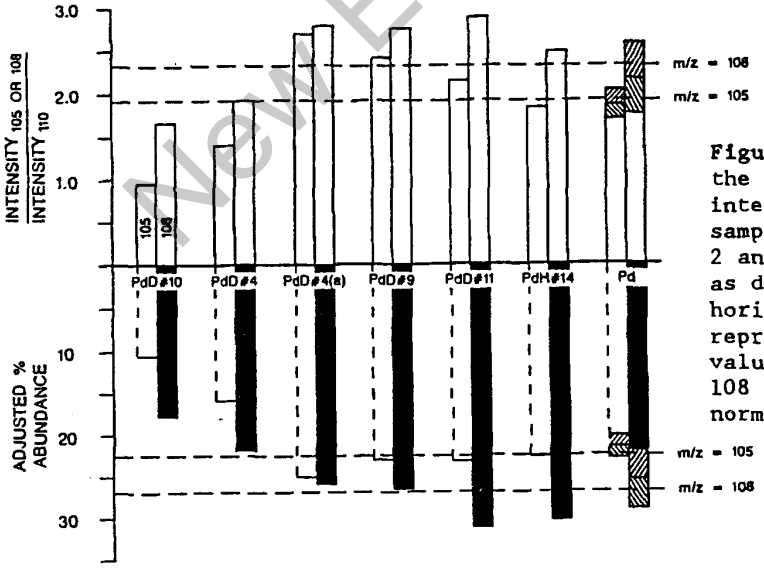

Figure 3: Histograms of the m/z 105 and 108 intensities for the samples shown in Figure 2 and normalized as described above. The horizontal dashed lines represent the ideal values for m/z 105 and 108 by either normalization method.

The isotopic distribution for Pd electrolyzed in H_2O (PdH#14, analyzed by TOF-SIMS two months after termination of electrolysis) has an essentially normal isotopic picture, by either normalization analysis, and resembles the averaged non-electrolyzed Pd values: see Table II and Figures 2 and 3. Only the Pd samples electrolyzed in D_2O exhibit an abnormal isotopic distribution.

Curious as to the depth of this m/z anomaly, we acid etched a piece from PdD#10 - the sample with the most pronounced enhancement at m/z 106 (and diminution of the remaining naturally occurring isotopes) - with 1:1 $HCl:HNO_3$. The etching removes on the order of micrometers of material from the surface. After the acid etch the foil was once again shiny and crystal facets were again visible, i.e., it looked just like acid-cleaned, non-electrolyzed Pd foil. The TOF-SIMS results (Table II and Figures 2 and 3) show that this treated sample (PdD#11) is indistinguishable from the Pd blank. While the depth of the acid etch is on the order of 10 μm, the mass/charge anomaly is clearly not a bulk phenomenon.

Conclusions and Concluding Speculations

During prolonged electrolysis of D_2O at Pd, in addition to stuffing the Pd lattice with deuterons, other processes are occurring, including enrichment of Pd bulk impurities such as Rh and Ag at the surface [9]. The apparent scrambling of the normal isotopic distribution for Pd, which occurs only after electrolysis in D_2O, is another. The possibility of stable, non-Pd isotopes contributing to the m/z 106 signal can be ruled out as follows: (1) the only other stable 106 isotope is ^{106}Cd (1.22% naturally abundant) [10,11]; at the magnitude of the change in m/z 106, the more abundant Cd isotopes (^{112}Cd, 24.07% and ^{114}Cd, 28.86% abundant) would also be present in the TOF-SIMS spectrum; the intensities at m/z 112 and 114 are at background; and (2) a doubly charged 212 amu isotope is even less plausible, as all 212 amu isotopes are radioactive [10].

The fact that the interior of the Pd remains isotopically normal implies two things: (1) that any isotopic scrambling is near surface; and (2) that the enhancement of m/z 106 does not derive from a long range isotopic separation - an isotopic redistribution which leaves the middleweight isotope enriched relative to the light- and heavyweight isotopes is puzzling, especially when the separation factors (calculated as the square root of the ratio of the masses) differ only by parts-per-thousand.

A surface-sensitive, high-resolution mass spectrometric analysis is required to determine if the intensity at m/z 106 is due to only ^{106}Pd or to a mix of ^{106}Pd and another m/z 106 species. Contributions to the m/z 106 intensity by the most plausible plasma-generated polyatomic candidates have been ruled out, as summarized in Table III.

Subsequent to the NSF-EPRI meeting of 16-18 October 1989, high-resolution surface-sensitive mass spectrometric measurements have shown that PdD#10 was contaminated during the electrochemistry with a trace of ZrO_2 [12] (also confirmed by X-ray photoelectron spectroscopy). Zirconium has an isotopic range of:

90 (51.45% natural abundance)
91 (11.32%)
92 (17.19%)
94 (17.28%)
96 (2.76%)

This makes for a coincidental, and unfortunate, overlap of ZrO ions with the Pd isotopic region. $^{90}Zr^{16}O$ has a mass of 105.8992; ^{106}Pd has a mass of 105.9032 making the high-resolution aspect of the mass spectrometric analysis even more critical.

PdD#4, the sample with a nearly 50% enrichment at m/z 106, shows no m/z intensities consistent with zirconium isotopes in its TOF-SIMS spectrum, so the enrichment observed for this sample is not due to this happenstance interference. This sample was dissolved shortly after termination of charging for bulk analysis, so, unfortunately, it does not exist in a form permitting high-resolution, surface-sensitive mass spectrometric analysis. The origin of the m/z 106 enrichment and m/z 105 diminution for PdD#4 is still unknown, but it is not due to either plasma contamination from the conditions of the TOF-SIMS experiment or the zirconium contamination seen for PdD#10.

Table III: Possible Contributing Species to m/z 106

Possible Species	Contributor to m/z 106?	Experimental Evidence
$(^{104}PdD)^+$	no	1. Do not see peaks at (m+2)/z; for the enhancement seen at m/z 106, a peak at m/z 112 (for ^{110}PdD) would be apparent and is not.
$(^{105}PdH)^+$	no	1. No reflection of the Pd isotopic distribution at (m+1)/z for Pd electrolyzed in H_2O or D_2O, in particular, no signal above background at m/z 111 (for ^{110}PdH) is observed. 2. No $(PdH)^+$ species seen for Pd from trace H and H_2O species in the spectrometer.
$^{53}Cr_2^+$, $(^{52}Cr^{54}Cr)^+$	no	1. Control experiments with non-electrolyzed Pd show that plasma-imposed Cr contamination, even when overwhelmingly present, does not contribute to m/z 106 intensity. 2. Electrolyzed Pd shows no dominating increase in m/z 104 intensity.
$(^{52}Cr_2D)^+$	no	1. For this species to cause a 50% increase in m/z 106, m/z 104 should be enormously enhanced (as Cr_2^+ would be more probable than $(Cr_2D)^+$), but is not.
$(^{52}Cr^{54}Fe)^+$; $(^{50}Cr^{56}Fe)^+$	no	If plasma conditions generate Fe ions as well as Cr ions from the walls of the analyzer chamber, the level of m/z 106 enhancement seen would require: a. A large enhancement at m/z 104 for $^{52}Cr_2^+$ (^{52}Cr is 83.8% abundant, while ^{54}Fe is only 5.8% abundant), which is not seen. b. A large enhancement at m/z 104 for $^{52}Cr_2^+$ (^{50}Cr is only 4.3% abundant) with a large signal at m/z 112 (for dimers of 91.7% abundant ^{56}Fe) - also not observed. c. Control experiments with non-electrolyzed Pd show that plasma-imposed Cr contamination, even when overwhelmingly present, does not contribute to m/z 106 intensity and no increase in m/z 112 intensity above background is observed.
$^{106}Cd^+$	no	1. ^{106}Cd is 1.2% abundant; at 50% enrichment, significant intensity at m/z 112 (24.1% abundant ^{112}Cd) and m/z 114 (28.9% abundant ^{114}Cd) should be observed and are not.
Silicate molecular ions	no	1. Such a species would have to be observed for Pd electrolyzed in light water, if not at m/z 106 (for a $(Si\text{-}O)_n$ species charge balanced by alkali) then at m/z <106 for OH forms. PdH #14 has background intensities from m/z 73 to m/z 104.
$(^{53}?)_2^+$	no	1. ^{53}Cr (9.6% abundant) is the only stable 53 amu isotope.
$(^{106}?)^+$	no	1. ^{106}Pd and ^{106}Cd are the only stable 106 amu isotopes.
$(^{212}?)^{2+}$	no	1. All 212 amu isotopes are radioactive.

It is possible that the additional intensity is due to a radioisotope and not ^{106}Pd. The 106 amu radioisotopes, their half-lives, and their decay products are listed in Table IV. The most promising candidate in terms of half-life is ^{106}Ru. Ru is unfortunately difficult to surface analyze by XPS or Auger in this particular chemical system due to interferences from characteristic lines for other elements also present in high concentrations at the surface.

TABLE IV: Possible Radioactive Isotopes at 106 amu [10]

Radioisotope	Half-life	Decay Product
Ru	1.0 y	^{106}Rh
Rh	30 s	^{106}Pd
Ag	8.3 d/24 m	^{106}Pd
In	5.3 m	^{106}Cd

The diminution of m/z 105 in PdD#4 reacted in D_2O implies a reactive or diffusional loss that cannot be explained away by non-Pd species at this m/z value. We are at a loss to explain this near-surface isotopic redistribution (enrichment of m/z 106 and diminution of m/z 105) - admittedly only for a single sample - by polyatomic interferents, leading us to the speculation that the redistribution may be nuclearly induced. **(d,p)** reactions with ^{104}Pd and ^{105}Pd, while also thought to be as improbable as deuterium-deuterium fusion in the Pd lattice, have been recently proposed for this system [13,14]. Isotopic analyses from 100-112 amu of known heat-producing Pd cathodes will be needed to extend (or discount) our provocative experimental observation.

Acknowledgments

We would like to express our gratitude for the timely and expert assistance of Dr. Steven M. Hues (NRL) for the TOF-SIMS measurements, Mr. Robert J. Doyle, Jr. (Code 6110, NRL) for the high-resolution mass spectrometric measurements, Dr. Robert L. Jones (NRL) for the X-ray diffraction measurements, and Dr. Ramanathan Panayappan (NRL) for inductively coupled plasma analysis of electrolyte solutions, and for, in general, the generous aid, comfort, supplies, and equipment of our colleagues in the Chemistry Division at NRL. We thank Drs. Steven King, Gary Phillips, Robert August, and Joseph Cutchin (Code 4616, NRL) for providing their expertise in neutron counting, and Dr. Galen Hansen (NRL) for his assistance, during the early experiments with Pd foil. Provocative discussions with Dr. Jerry J. Smith (DOE) and Dr. Carter White (Code 6110, NRL) are acknowledged with pleasure.

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DISCUSSION (ROLISON)

Rafelski: What atomic numbers are the peaks at mass number 107 and 109?
Rolison: They are silver impurities in the palladium, and they are in the expected ratio of 49:51. The secondary-ion mass spectrometry (SIMS) technique does not have the resolution to determine the masses to a high enough degree of accuracy to identify each isotopic species.
Teller: Does the technique only sample the palladium surface?
Rolison: SIMS is surface sensitive, because the secondary bombarding ions are of low energy and only ionize the surface.
Teller: What is the depth of penetration?
Rolison: Essentially only one or two atomic layers.
Appleby: If you take the Pd-105 peak and add it to the Pd-106 after testing, do you see the same total amount of Pd isotopes as those in the starting sample?
Rolison: Because of the possibility of iron and chromium contamination, we use Pd-110 as an internal reference standard which cannot be compromised by such contamination. On palladium blanks we have seen compromisation at mass number 104, indicating the presence of chromium, i.e., $^{52}Cr_2$. However, if one sums the areas of the peaks, it corresponds rather well to the initial natural abundances of the two isotopes.
Hoffman: Did you try progressive evaporation of surface layers?
Yeager: Using that technique, you would be able to obtain a concentration-depth profile.
Rolison: Such an experiment would have been very useful, but unfortunately our spectrometer does not have that capability.
Bockris: How long was your palladium sample exposed to electrolysis?
Rolison: The lithium sulfate solution in D_2O was electrolyzed for only four days. The thin foils charge with deuterium within a short time, about 1-2 hours. We have typically charged at 10 mA/cm^2 or less. The platinum anode was of 99.999 percent purity. Electrolysis in the LiOD solution corresponded to 1.4 million Coulombs over 26 days.
Yeager: Your palladium surface would certainly not be clean after electrolysis.
Bockris: How did you clean it before obtaining the SIMS results?
Rolison: We cleaned our surfaces using a modified aqua regia etch before electrolysis. After electrolysis, the surface is dull gray; it becomes bright

after etching, and it is quite clean. After exposure to lithium sulfate solution, little silicon contamination from glass was seen by XPS.

Appleby: Do you see platinum on the surface?

Rolison: Yes, the result is shown on one of my figures.

Werth: Were the cell potentials the same in the H_2O and the D_2O solutions?

Rolison: They are a little lower in the H_2O solutions, as one might expect.

Lewis: Even so, the H_2O and D_2O solutions might contain different contaminants which would affect both overpotential and surface composition.

Rolison: They were both analyzed by ICP (inductively coupled plasma atomic spectrometry) to look for problems of metal contamination, and they were both shown to be very clean.

Werth: I asked my question about the cell voltage or overpotential, because if some impurity were coming from the platinum anode, different amounts might be seen at the surface at different overpotentials.

Rolison: One surface analysis which we have carried out in detail is XPS. Results of this kind would certainly stand out if they were important.

Teller: A neutron removed from an atomic species like palladium requires about 7 MeV. If a proton is simultaneously removed, 11 MeV would be required to go from Pd-108 to Pd-106. Instead of an energy input, an excess energy seems to be observed.

O'Grady: The mass number 106 species may not be palladium. What we see is only a mass analysis, not an elemental analysis.

Chubb: We must also account for the apparently missing proton that should be formed with the tritium. Loss of a proton from Pd-106 could conceivably yield a mass number 105 species, going down the periodic table. A silver isotope is also a possible product. When I heard of this result, my immediate reaction was a conclusion that perhaps nuclear physics is indeed happening at the palladium surface.

Rolison: I would like to make a first point. The two electrolyte samples in which palladium electrodes appeared to give a strong enrichment were kept relatively dry, following some of Dr. Huggins' comments about making sure that the D_2O does not absorb water. The lithium sulfate used was sealed and was freshly opened before use, using as much care as possible. With the LiOD solution, all possible precautions were taken, which included loading the cell with electrolyte in a glovebox, followed by sealing.

A further point is that there is only one other stable 106 isotope, namely Cd-106. It has a natural abundance of only 1.2 percent. If it were present, one would expect to see very large peaks for two more abundant Cd isotopes, which are not observed. Other species may still be responsible for this peak. For example,

deposition of silicates on the surface is in principle possible. However, I believe that our light water controls rule out that possibility. One is then left with the possibility of dimers of atomic mass unit (AMU)-52 and -53 species, particularly Cr-53. A doubly-charged AMU-212 is in principle possible, but that would be a radioactive species, since there are no stable 212 isotopes. Other species may still, of course, be possible: for example, ^{90}ZrO, which would add up to 106.

Finally, taking a thickness of 1000 angstroms as that of the reaction zone at the palladium surface, and knowing the enrichment of the AMU-106 species, one can calculate how many new atoms of 106 palladium have been generated in that layer during the time of electrolysis. The results showed apparently about 10^{11} events per second.

Appleby: How large was the surface area of your electrodes in this work?

Rolison: They varied, though they were always more than 1-cm^2 facial surface area, including the front and back sides.

Appleby: The order of magnitude of excess heat that we observed, for electrodes of this size, would certainly correspond to about 10^{11} event/s.

Rolison: That was certainly our impression, although we did not carry out heat or tritium measurements.

Hoffman: Is there a possibility that the Naval Research Laboratory could provide a service for researchers to have their cathodes examined after electrolysis?

Rolison: It would appear that the next generation of experiments will require the use of surface-sensitive equipment, particularly high-resolution surface-sensitive mass spectrometry. We may have that capability at NRL.

Lewis: Could you show us the entire SIMS data over all the AMU range?

Rolison: Unfortunately, I do not have all the data, but our emphasis was on the lower AMU range.

Lewis: Did you also obtain data for the higher AMU range? For example, have you detected any $^{102}RuD_2$ or some other compound whose AMUs might add up to 106?

Rolison: That's what we tried to consider. We can see the cations for chromium and iron, for instance.

Lewis: What other elements did you find in the SIMS?

Rolison: Chromium and the iron were always present, even in the light water blanks. In the higher AMU region, any species seen would have to be molecular. We did not observe anything of this sort. The blank data in light water show that traces may be there, but they do not show any signals in the higher AMU range. One can argue that the 106 species must be ^{104}PdD. Of course, that is ludicrous, since it is impossible to conceive of a preferential isotopic chemical reaction of D with ^{104}Pd.

Kim: It may, of course, be $^{52}Cr_2$.

Rolison: We have ruled that out. If Cr_2 were a problem, it would be seen at AMU 104 in the absence of Pd. We do not see it.

Teller: I continue to be concerned about the ^{108}Pd peak. If you cannot account for this via molecular impurities, its presence is very difficult to explain. To produce it would require energy input, so the laws of physics would be violated.

Kim: There is one possible chain process which could do it: neutron capture by ^{108}Pd producing gamma rays. And gamma rays are about 6 MeV, which could disintegrate deuterons and produce more neutrons.

Rolison: As I have emphasized, our SIMS results lack high resolution for the AMU values detected. Our XPS results show atom percent concentrations of various elements present at the surface relative to palladium. Platinum is an important impurity, and the total amount of it is a function of cumulative charge, so the longer electrolysis is carried out, the more platinum is present on the surface. This is easy to explain, since some platinum goes into the solution at the anode and plates out at the cathode. As one would expect, platinum results are similar in heavy water and light water.

The XPS results, which are highly surface sensitive, show significant amounts of silver and rhodium at the palladium surface, but they are not present in the electrolyte or in the anode. However, they are initially present in our palladium cathode. Analysis of the 99.9 percent pure palladium which we used showed that it contained 100 ppm of silver and 50 ppm rhodium. Both metals form continuous solid solutions with palladium. It has been considered surprising that they segregate at the surface. However, migration is not impossible, since their solubility characteristics may be different in Pd deuteride.

The palladium surface is cleaned using a plasma etch before the SIMS results are obtained. The sample which showed a large surface enrichment of AMU 106 using SIMS showed only the bulk level of rhodium at the surface using XPS, after an acid etch. Before etching, XPS showed 3 atom percent of rhodium at the surface. Reaching this rhodium level in a 0.1-micron surface layer from a bulk value of 50 ppm in a 127-micron foil implies a great deal of segregation. In fact, it indicates that all of the rhodium is in the 0.1 micron surface layer sampled by XPS. Because our palladium was not 99.999 percent pure, and we did have a bulk presence of these elements, we either must say that they are completely segregated near the surface, making the metallurgists unhappy, or that they were produced there by nuclear transformations. Rhodium and silver are near neighbors to palladium in the periodic table, and there are certainly a number of neutron processes that can generate their nuclei.

Bard: What were the results of a similar analysis in the light water samples?

Rolison: At present, we do not have the data.

Lewis: Do you have results on a platinum, not palladium, cathode as a control in the same D_2O electrolytes?

Rolison: We did try that experiment, but the platinum cathode was not ultrapure either.

Voice: Would you review the relative change in AMU 105 and AMU 106 compared with that for AMU 108?

Rolison: The results are shown in detail in our paper.

Bockris: Do you have plans to successively evaporate the surface layers to determine the progressive change in composition?

Rolison: I have already pointed out that we cannot do that in our instrument, and I am not sure if we can do it elsewhere. Such experiments will in any case be criticized, since the surface can be rearranged during the higher energy ion bombardment required for evaporation.

Hoffman: You are using AMU 110 as the internal standard to determine your ratios.

Rolison: Correct.

Hoffman: Have you tried making AMU 108 the internal standard instead, to see the results obtained under those conditions?

Rolison: We have not attempted that. However, we did examine two methods of evaluating the ratios. One was with AMU 110 as an internal standard, and the other used an adjusted percent abundance for the isotopes. Since AMU 104 may possibly be due to chromium dimer contamination, we ignored that peak. In consequence, we added the total of the natural abundances of ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{110}Pd, giving 88 percent. We matched the expected abundances for the light water blank. For heavy water specimens, the results using this alternative method showed an enrichment in ^{106}Pd, with a diminution in the ^{105}Pd and ^{108}Pd.

Voice: If you use ^{108}Pd as a standard, all of the other isotopes appear to be increasing in mass. For example, ^{104}Pd and ^{105}Pd go to ^{106}Pd, and ^{108}Pd goes to ^{110}Pd.

Rolison: Maybe, but we do not obtain a relative increase in AMU 112.

Voice: Relative to ^{110}Pd, does ^{108}Pd become reduced in abundance?

Rolison: Yes.

Voice: Relative to ^{108}Pd as a standard, both ^{110}Pd and ^{112}Pd increase. Using this standard, all of the other isotopes increase in mass.

Rolison: Different methods of analysis will give different results. The important point is that a redistribution of isotope abundances occurs in the case of the D_2O specimens.

Hoffman: If some people are concerned that the surface concentration of ^{108}Pd is reduced, the analysis can be adjusted so that it is no longer a problem.

Voice: But then one has the difficulty that ^{110}Pd is increasing.

Schneider: Alternatively, some other method of treating the raw data should be used which would allow one to extract additional information that one cannot obtain from calculations based on these different hypotheses.

Jordan: Some assumptions can be made based on the various possible nuclear reactions that have been hypothesized.

Rolison: An initial examination of our data might make many groups rush to find a surface-sensitive mass spectrometer.

Rafelski: Could you tell us again how the surface of the specimen was treated after electrolysis for a few hours and before surface analysis?

Rolison: The cathode was charged at the low current density of 10 mA/cm^2 for a time that is probably an order magnitude longer for charging than would be estimated based on diffusion into the palladium volume. The cathode was then either left at this same current density or exposed to a higher current density equal to about 100 mA/cm^2. Before electroylsis, the palladium was cleaned with a 50/50 nitric and hydrochloric acid mixture, which polishes its surface.

Storms: Have you measured the tritium level which you may have developed in your cell?

Rolison: No. In my opinion, the next hurdle in this work will involve heavy isotope analysis, particularly SIMS peak resolution measurements along the AMU axis. These will allow us to follow the Pd isotope enrichment processes, if this process is really applicable. For example, it will allow us to determine if the AMU 107 peak is ^{107}Pd, which has a 6.5 million year half-life. As an alternative, it may be ^{107}Ag occurring without ^{109}Ag.