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## **SURFACE STUDIES AFTER LOADING METALS WITH HYDROGEN AND/OR DEUTERIUM**

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### **Abstract**

Surface studies of 40  $\mu\text{m}$  thick Pd foils after electrolysis in  $\text{D}_2\text{O} / \text{H}_2\text{SO}_4$  electrolyte for six minutes found inversions in isotopic ratios. Anomalous isotopic ratios were also found on the surface of a 350  $\mu\text{m}$  thick Pd foil after electrolysis in the same electrolyte for 74 hours.

### **Introduction**

Our 1994 publication [1] presented evidence of localized, microscopic surface concentrations of gold and silver on palladium cathodes which had been electrolyzed in an electrolyte containing either  $\text{H}_2\text{SO}_4$  and  $\text{D}_2\text{O}$  or  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ . The unique capabilities of a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) made it possible to locate concentrations of these elements on a microscopic scale. Our experiments included the detection of excess heat. We suggested that the excess heat and unexpected elements could be explained by the energy released during transmutation of platinum to gold and palladium to silver in the presence of thermal neutrons.

A previous study by another group also reported elemental anomalies on the surface of palladium after electrochemical loading of deuterium [2]. A near surface enrichment of rhenium and silver was detected by x-ray photoelectron microscopy (XPS). These elements are present as impurities in the starting palladium at levels (50 ppm Rh and 100 ppm Ag), well below the XPS detection limit. It is not clear why nickel, which is present before electrolysis as an impurity at the 200-300 ppm level, was not similarly enriched to a concentration which could be detected by XPS. This report does not include a bulk analysis of a Pd cathode after electrolysis. The authors concluded that surface segregation of Rh and Ag impurities is most likely due to the forcing current and time during long-term electrolysis.

In another study by the same group [3], time-of-flight-secondary ion mass spectroscopy (TOF-SIMS) measurements of the Pd blank (no electrolysis) and Pd electrolyzed in  $\text{H}_2\text{O}$  gave the natural abundances of the stable Pd isotopes. However, two samples electrolyzed in  $\text{D}_2\text{O}$  had more than 20% increases in Pd 106 intensities and decreases in Pd 105 intensities. These researchers suggested the possibility that Pd 105 obtained a neutron and became Pd 106. Although this SIMS research seemed promising, it was not

mentioned in a later publication from this group [2]. Apparently, this research was terminated.

In 1994 we also published a report on the changes in surface topography and microcomposition of a palladium cathode caused by electrolysis in acidified light water [4]. A thin palladium cathode became bent and torn during electrolysis in acidified light water. Localized changes in composition, including the possibility of the formation of silver by neutron absorption, were reported.

Results of our SIMS study of Pd foils before and after electrolysis were presented in 1996 [5]. We found that there was an isotopic inversion on the surface of a Pd foil cathode which had been electrolyzed in acidified heavy water. In the spectrum from the control (unelectrolyzed Pd foil), the signal from Pd 106 (natural abundance 27.33 at.%) was slightly greater than the signal from Pd 108 (natural abundance 26.46 at.%). However, a SIMS spectrum from an electrolyzed Pd foil had a more intense signal from Pd 108 than from Pd 106. The difference between these two abundances decreases with increasing sputtering time. After sputtering for 50 minutes to a depth of about 0.3  $\mu\text{m}$ , these two isotopes have the same abundance.

The same report included data on excess thermal power (0.3 W maximum) which was observed from electrolysis of acidified heavy water with a Pd foil cathode, compared with an identical cell containing a Pt cathode. After about 70 hours of electrolysis and a dormant period of 75 days, the cells were again electrolyzed. In 5 consecutive experiments totaling 20 hours over a period of 2 weeks the cell with the Pt cathode produced as much as 0.3 W excess thermal power compared with the cell containing a Pd cathode.

In 1997 we published the results of electrolysis experiments with titanium cathodes [6]. One experiment produced about 1 W excess thermal power compared with a control. Geiger-Mueller counters used to monitor radiation emitted by the cells showed no significant difference compared to background. LiF chips sealed in plastic and placed inside the cells before electrolysis also showed no significant difference compared to background. The Ti cathodes were examined before and after electrolysis, using SEM and EDS. A new microscopic feature on a cathode after electrolysis contained appreciable vanadium, one atomic number higher than titanium, just as silver is one atomic number higher than palladium and gold is one atomic number higher than platinum.

In the same publication [6], we presented evidence of microscopic, time-dependent changes in fibers on the surface of a Pd cathode which had been electrolyzed about 6 months earlier. Distinct changes in the morphology of one of the fibers occurred in two days during storage at room temperature and atmospheric pressure. An EDS spectrum of a new, oval-shaped feature showed that it contained an appreciable amount of silver. A spectrum from the same spot one month later suggested that silver was changing to cadmium, which is one atomic number greater than silver. This is further evidence which supports the possibility of transmutation.

## **Experimental methods**

Palladium (AESAR stock # 11514) was cold rolled from 500 to 40  $\mu\text{m}$  thickness. Each cathode was prepared from a piece of this foil 2 cm long and 0.8 cm wide which was spot

welded to a Pt lead wire. The anodes were prepared in the same way, using Pt foil spot welded to a Pt lead wire.

The electrolyte contained 20 ml D<sub>2</sub>O and 3.5 ml H<sub>2</sub>SO<sub>4</sub> in one cell. A second cell contained 20 ml deionized H<sub>2</sub>O and 3.5 ml H<sub>2</sub>SO<sub>4</sub>. The heavy water and light water cells were connected in series (Fig. 1).

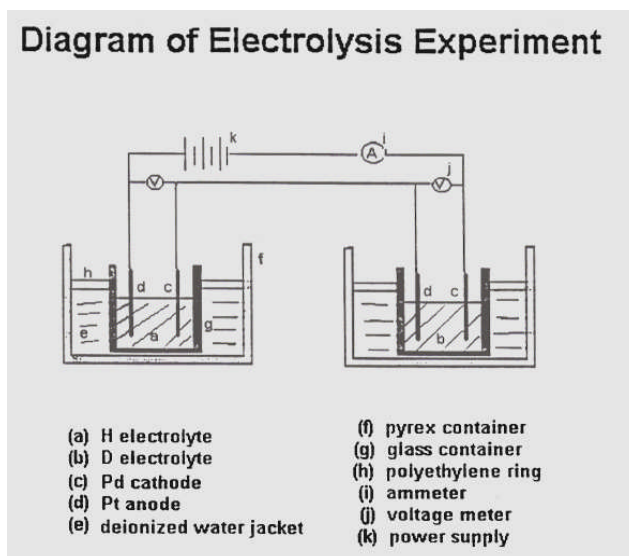


Fig.. 1. The heavy water and light water cells are connected in series. Each cell has a Pd cathode and a Pt anode. All heavy water cathodes bent toward their anode 45 to 90 degrees, but the light water cathodes bent toward their anode only slightly.

In one experiment the time of electrolysis was 6 minutes at a current density of about 0.25 A per cm<sup>2</sup>. After microscopy of the electrodes was completed, SIMS analysis was performed on a control (no electrolysis) Pd foil from the same cold rolled strip, and on the Pd cathodes from the light water and heavy water cells.

The instrument used for these analyses was a PHI II SIMS, Model 3500, linked to a General Balzer 16 mm rod quadrupole mass spectrometer. Each sample was bombarded with a 3 KV Cs ion beam which scanned an area of about 1.4 mm x 1mm. Pd was sputtered from the cathode at the rate of about 0.1 nm per second. By sputtering for long times, it was possible to obtain the relative abundances of the isotopes versus depth.

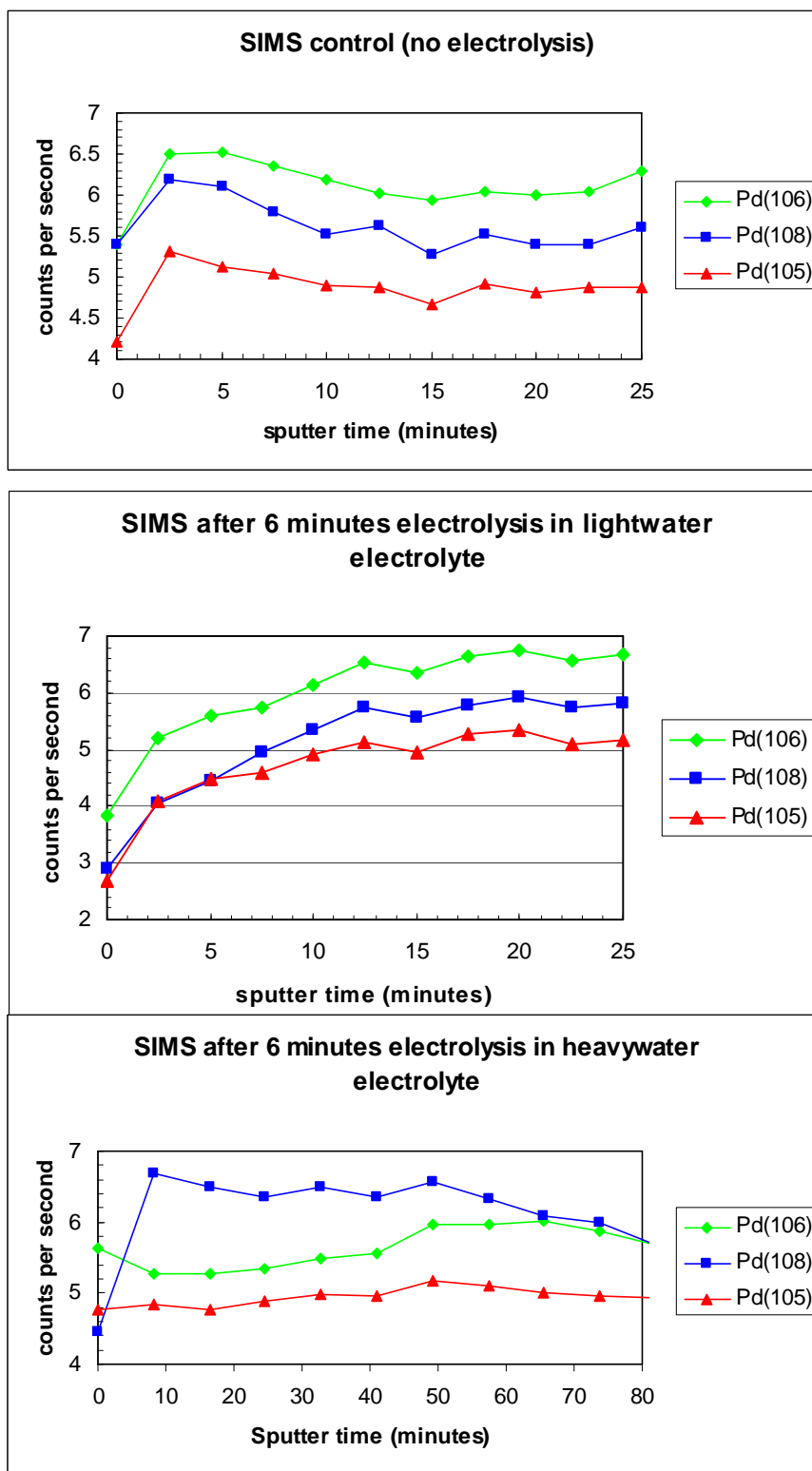


Fig. 2. Depth profiles for the most abundant Pd isotopes : top – control (no electrolysis) ; center – after H<sub>2</sub>O electrolysis; bottom – after D<sub>2</sub>O electrolysis.

## Results and discussion

The uppermost graph in Fig. 2 gives the signal intensities for the three most abundant Pd isotopes as a function of sputtering time for the control (no electrolysis) foil. As expected, Pd 106 gives the highest signal intensity (counts per second CPS), Pd 108 is next, and Pd 105 gives the lowest signal intensity. There is no significant change in signal intensity with increasing sputter time, i.e. with increasing depth into the sample. This is similar to the three other depth profiles taken from other locations on the unelectrolyzed control foil.

The SIMS results for the Pd foil which was electrolyzed for 6 minutes in H<sub>2</sub>O electrolyte are given in the center graph, Fig. 2. After sputtering for 5 minutes, the relative intensities are in proportion to their natural isotopic abundances, i.e., 27.3% for Pd 106, 26.5% for Pd 108, and 22.3% for Pd 105. After 12 minutes of sputtering, the signal intensities are almost constant for all three isotopes until sputtering was stopped after 25 minutes. Four other regions on the same sample gave very similar depth profiles.

SIMS profiles were taken from nine different regions of the Pd foil which was electrolyzed in D<sub>2</sub>O electrolyte. The bottom graph, Fig 2, shows a typical profile. After sputtering for about 10 minutes, there is clearly an inversion in signal intensity : Pd 108 now has greater signal intensity than Pd 106, whereas the opposite is expected, based on natural abundances. All nine of the depth profiles from this foil show this inversion. This suggests the possibility that Pd 106 absorbs a neutron, and becomes Pd 107 which beta decays to produce Ag 107, a stable isotope. Another possibility is that 106 PdD forms during electrolysis. This would appear in the SIMS spectrum as mass 108, thus increasing the Pd 108 signal and diminishing the Pd 106 signal.

The bottom graph in Fig. 2 shows that the difference in signal intensities of Pd 106 and Pd 108 diminishes with increasing sputtering time. After 65 minutes, corresponding to a depth of about 0.4  $\mu\text{m}$ , the signals from these two isotopes are identical. It appears that the process which caused the changes in signal intensities is confined to the outermost layers of the cathode surface. This is not surprising because the time of electrolysis was

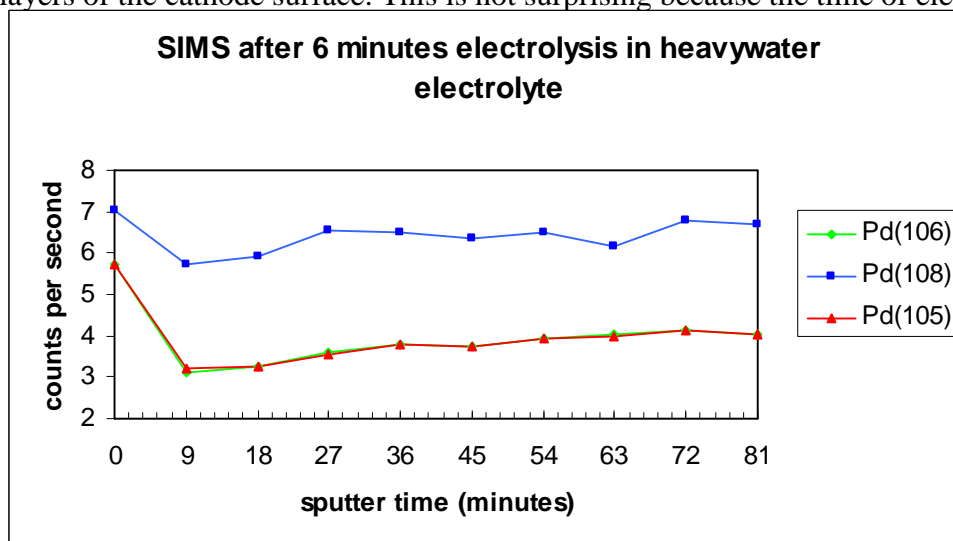


Fig. 3. SIMS depth profile from a different area of the same Pd cathode.

only 6 minutes, which would be insufficient for uniform hydride or deuteride formation.

Fig. 3 shows a SIMS depth profile from a different area of the same Pd cathode after electrolysis for 6 minutes in D<sub>2</sub>O electrolyte. The signal from Pd 106 is far less than expected. It coincides with the signal from Pd 105 which has a natural abundance 5 at.% less than Pd 106. The signal from Pd 108 is consistently greater than that from Pd 105 and Pd 106 throughout the 81 minute sputtering time. There is no tendency for merger of the Pd 106 and Pd 108 signals, such as that shown in the bottom graph, Fig. 2.

SIMS profiles for 8 of the 9 analyzed areas of the heavy water electrolyzed Pd cathode show that there is also an inversion in the abundance of Pd 104 (11.14 at.% natural abundance) and Pd 110 (11.72 at.% natural abundance). Data for the control and for the light water and heavy water electrolyzed Pd cathodes are given in Fig. 4. The signal from Pd 110 is greater than the signal from Pd 104 throughout 25 minutes of sputtering, both for the control (upper graph) and for the 6 minute H<sub>2</sub>O electrolyzed Pd cathode (center graph). The lower graph gives data for the Pd cathode after electrolysis for 6 minutes in D<sub>2</sub>O electrolyte. It shows that the signal from Pd 110 is only about half the intensity of the signal for this isotope in the upper 2 graphs, whereas the signal from Pd 104 for this cathode is only slightly less than that in the upper 2 graphs. The inversion is almost constant throughout the 81 minute sputtering time. Its cause may have a similar explanation to those suggested above for the 106/108 inversion.

In another experiment, Pd from the same stock was cold rolled from 0.5 to 0.35 mm thickness. A cathode 25 x 23 x 0.35 mm<sup>3</sup> was prepared from this. Electrolyte was prepared containing 6.7 g D<sub>2</sub>O : 1 g H<sub>2</sub>SO<sub>4</sub> and about 0.02 g Ti per ml of solution. Electrolysis was performed for about 6 hours per day for 8 days. Excess power compared to a control cell was observed for every run. It ranged from 0.5 to 2.6 W. The average was 1.8 W.

During electrolysis the Pd cathode bent toward the Pt anode to form a concave surface facing the anode. After electrolysis both the concave and convex surfaces were analyzed blind by National Renewable Energy Laboratory (NREL) scientists. The analyses included SIMS, SEM, and Auger Electron Spectroscopy (AES). SEM and AES data are given in Figs. 5 and 6 and Tables 1 and 2.

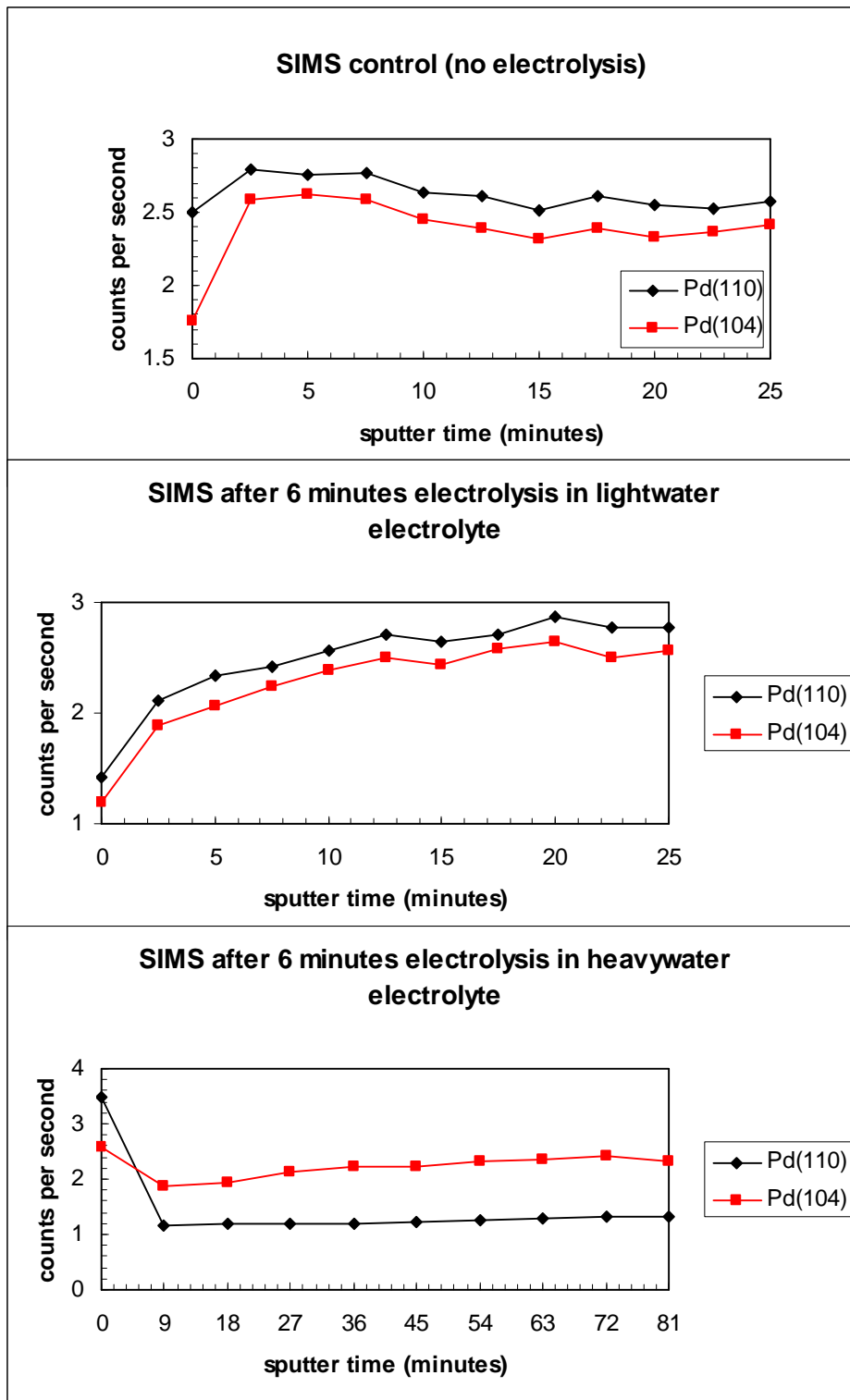


Fig. 4. SIMS depth profiles for Pd 104 and Pd 110.

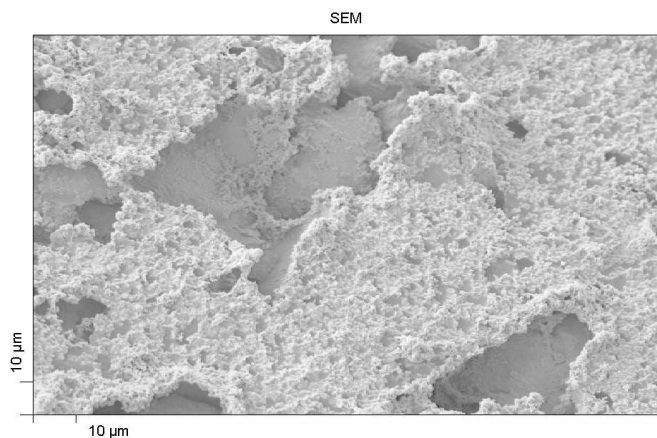


Fig. 5. SEM photo of the concave side of the Pd cathode. AES analyses were taken from the two large dark gray areas and from the light gray area.

Dark gray	C	O	S	N	Pd	Pt
As-received	48.5	21.6	2.3	12.4	12.0	3.1
20 sec sputter	45.9	14.6	3.3	13.1	21.2	1.9

Light gray	C	O	S	N	Pd	Pt
As-received	54.2	17.4	1.9	10.3	6.4	9.9
20 sec sputter			2.6		79.0	18.4

Dark gray	C	O	S	N	Pd	Pt
As-received	54.3	16.9	2.9	12.6	10.3	3.0
20 sec sputter	45.5	14.8	4.0	13.9	15.5	6.3

Table 1. AES analyses (at.%) of dark gray and light gray areas in Fig. 5. The dark gray areas have large concentrations of C, O, and N before and after sputtering. These elements were also found on the light gray area as received, but not after sputtering.

Data for the convex side of the Pd cathode after electrolysis are given in Fig. 6 and Table 2.



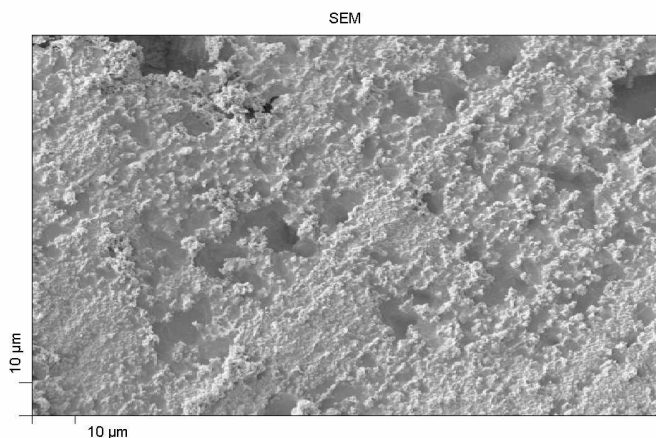


Fig. 6. SEM photo of the convex side of the Pd cathode after electrolysis.

Dark gray	Cl	O	S	N	Pd	Pt
As-received	2.4	13.9	2.2	11.3	68.0	2.1
20 sec sputter	1.1	9.8	3.3	9.8	73.5	2.6

Light gray	Cl	O	S	N	Pd	Pt
As-received	3.0	9.8	1.1	8.3	75.0	2.8
20 sec sputter	0.7		0.6		94.5	4.2

Table 2. AES analyses (at.%) of the convex side of the Pd cathode after electrolysis. Carbon was not detected on this side of the cathode. After sputtering, oxygen and nitrogen were not detected. Chlorine was detected on both light and dark gray areas.

Figs. 5 and 6 show that both sides of the Pd cathode contain a mixture of smooth, dark gray areas in a matrix of mottled, light gray areas. As received, the outermost layers of the concave side of the Pd cathode contain about 50 at.% C, but C was not detected on the convex side. It is difficult to accept that this difference could be caused by contamination. The main difference between the two sides is that the concave side had higher current density during electrolysis. If C was deposited on the concave side, it should have also been deposited on the convex side, but to a lesser extent.

The origin of the Cl on the convex side only is also puzzling. Again, contamination or deposition during electrolysis is expected to affect both sides.

The SIMS data on the same Pd cathode after electrolysis does not contain any inversions of isotopic abundance such as those in Figs. 2 – 4, but there are significant differences compared with the control, a pure (99.999 %) Pd foil which had not been electrolyzed. For example, there are no changes in isotopic abundance in the depth profiles for the control. Fig. 8 shows the count rate for masses 107 and 109 for the convex side of the

electrolyzed Pd foil. The average count rate is about 50% greater for mass 107 than for mass 109,

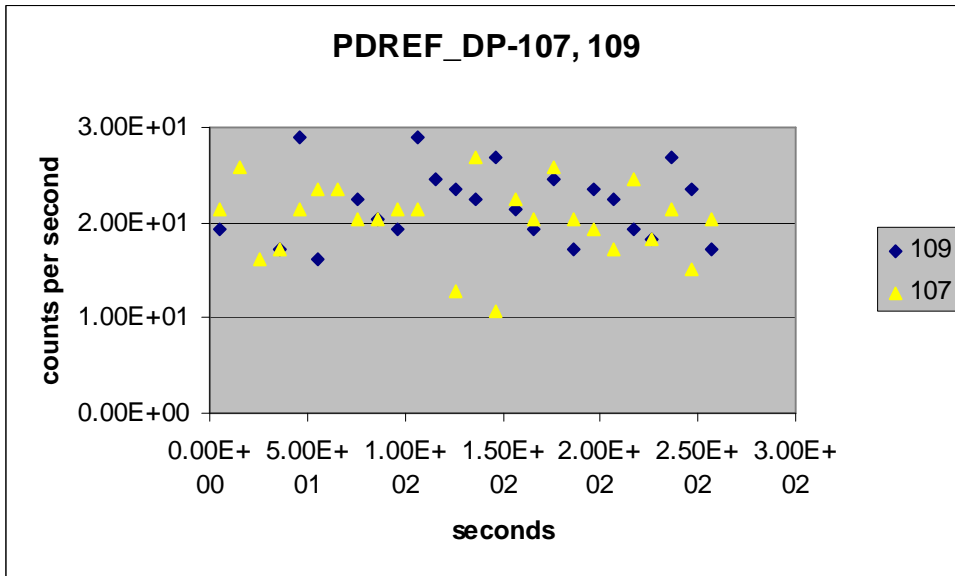


Fig. 7. Counts per second for the control Pd foil from masses 107 and 109. The count rate does not change with increasing depth into the foil. The average counts per second is about 22 for both masses.

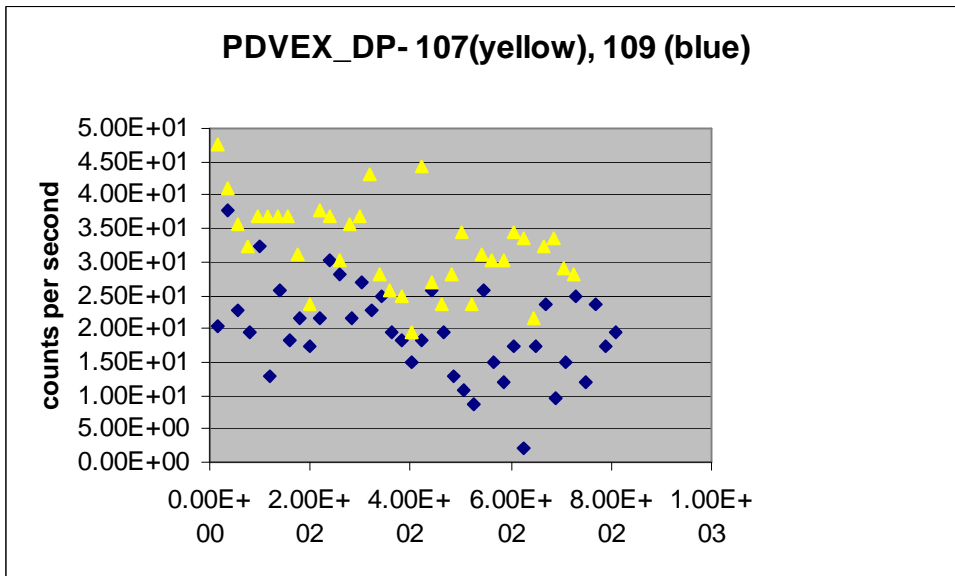


Fig. 8. Counts per second versus sputtering time (seconds) for the convex side of the electrolyzed Pd foil, which faced away from the anode during electrolysis. Compared with the control, there is less overlap of the data for mass 107 (yellow) with the data for mass 109 (blue). The average counts per second is about 30 for mass 107 and 20 for mass 109.

The SIMS depth profiles for masses 107 and 109 from the concave side of the electrolyzed Pd cathode are shown in Fig. 9. Here, it is apparent that the count rates for both 107 and 109 decrease with increasing sputtering time, and the count rate for 107 is

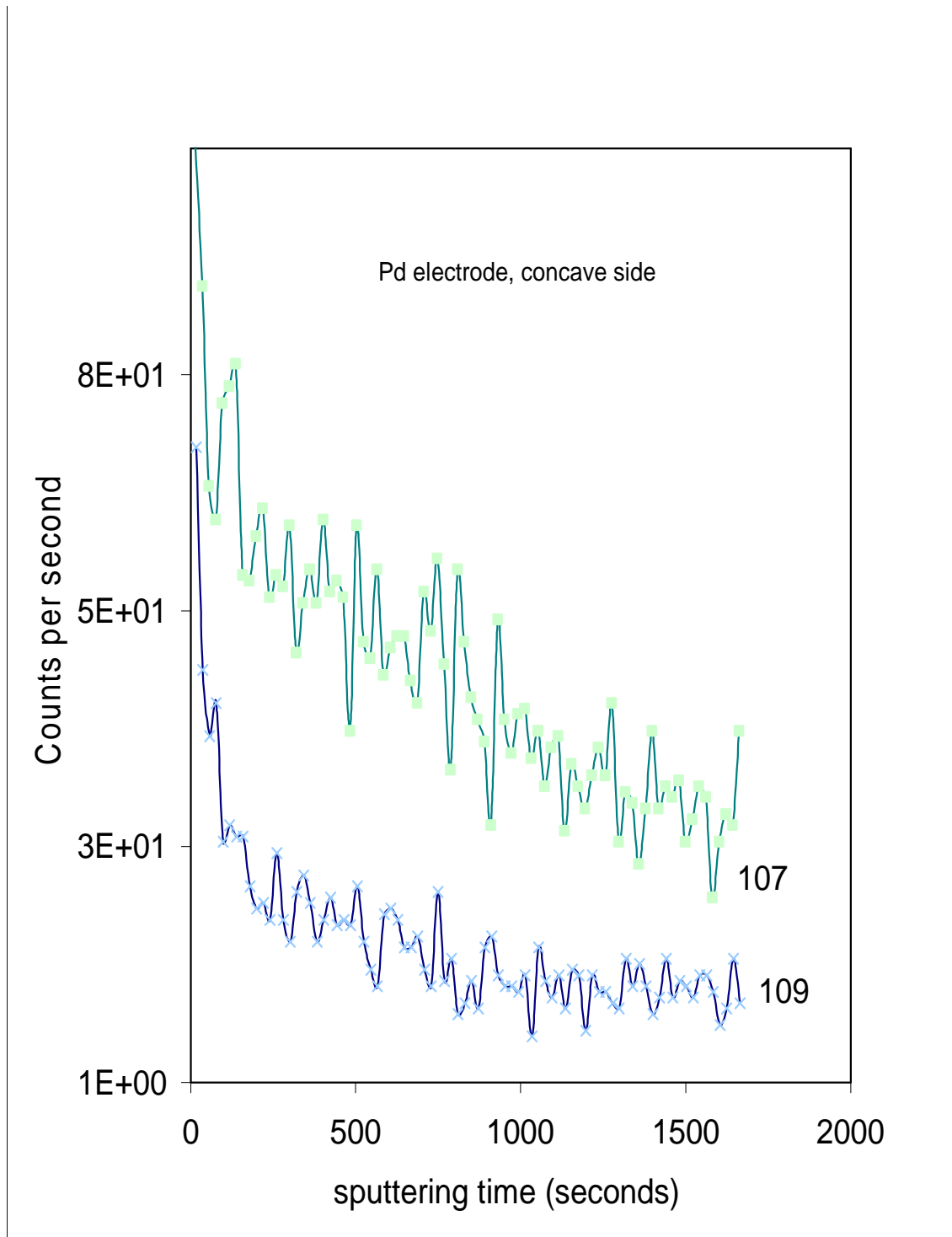


Fig. 9. Depth profile of the signals from masses 107 and 109 for the Pd cathode after electrolysis (concave side).

about double that of 109 throughout 1700 seconds of sputtering. There is no overlap of the count rates from these two masses. At the start of sputtering the signal from mass 107 is about 90 cps, and this falls to about 35 cps at the end of sputtering. The signal from mass 109 falls from about 75 cps to about 15 cps during the same time period.

Masses 107 and 109 are stable isotopes of Ag, so transmutation by absorption of thermal neutrons is one possible explanation for the presence of these isotopes. Another possibility is that PdH and PdD are formed. Then,  $^{105}\text{PdD}$  would appear at 107. This could be an explanation for the ratio  $107/109 \sim 2$  in Fig. 8, whereas the expected ratio is  $\sim 1.1$  for Ag. However, if  $^{105}\text{PdD}$  is present, then  $^{108}\text{PdH}$  should also be present. This would appear at mass 109 in the SIMS spectrum, and the 109 signal would be enhanced. Fig. 8 shows that there is enhancement of the 109 signal for several hundred seconds sputtering time compared with the 109 signal from the control in Fig. 7. Because there is no change in abundance with depth into the control Pd foil and because the  $107/109$  ratio is as expected, it seems likely that the signals from these two isotopes are due to Ag impurity which is uniformly distributed throughout the control Pd foil.

Fig. 10 gives another example of changes in isotopic abundance on the concave surface of the 0.35 mm thick Pd cathode with increase in sputtering time. At the surface, the ratio of the isotopic abundance of  $^{105}\text{Pd}$  to that of  $^{104}\text{Pd}$  is about six, whereas the natural abundance ratio for these two isotopes is about two. After rising initially, the abundances of these two isotopes fall and converge, so that the abundance ratio is about 2.5

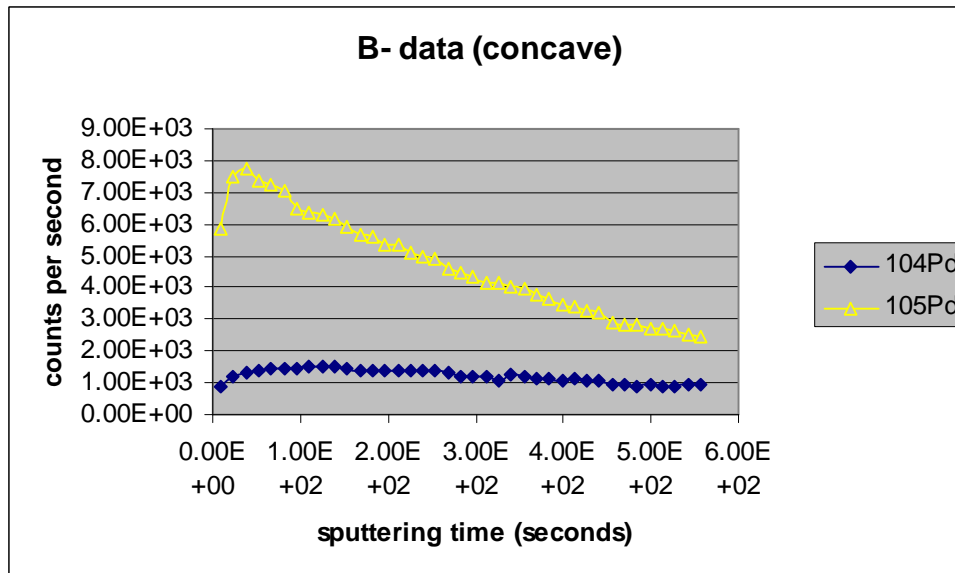


Fig. 10. Variation of isotopic abundance on the concave side of a 0.35 mm thick Pd cathode with increase in sputtering time. The rate of sputtering is about 0.8 nm per second, so the data in this figure represents isotopic abundance to a depth of about  $0.4\mu\text{m}$ .

after sputtering for about 550 seconds. On the convex side, the isotopic abundance of 104 and 105 Pd changes with increasing sputtering time, but the ratio 105 Pd / 104 Pd is close to the natural abundance.

## Summary and Conclusions

SIMS spectra from 40  $\mu\text{m}$  thick Pd foil cathodes after electrolysis in  $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$  electrolyte for 6 minutes show no significant changes in isotopic abundance compared with the control which was not electrolyzed. However, Pd foil cathodes electrolyzed in  $\text{D}_2\text{O}/\text{H}_2\text{SO}_4$  electrolyte had inversions in which the Pd 108 signal exceeded the Pd 106 signal and the Pd 104 signal exceeded the Pd 110 signal. These inversions may have been caused by the formation of PdD and PdH. For example, 106 PdD would appear at 108, thus increasing the abundance of Pd 108. Also, 102 PdD would appear at 104, thus increasing the abundance of Pd 104. Another possibility is that transmutation to Ag occurred. This would require the presence of thermal neutrons [7].

A much thicker Pd foil (350  $\mu\text{m}$  thick) electrolyzed for 74 hours in  $\text{D}_2\text{O}/\text{H}_2\text{SO}_4$  electrolyte did not show inversions of isotopic abundance, but it did show significant differences in the SIMS spectra compared with the control. The occurrence of weak signals of almost the same intensity from the control at masses 107 and 109 suggests that Ag is present as an impurity in the control. The SIMS spectrum from the concave side of the electrolyzed Pd foil has about twice the intensity of the signal at mass 107 compared with mass 109. Based on natural abundance, the ratio of the signals should be 107/109  $\sim$  1.1, instead of the observed 2. Any attempt to explain these results should include the effects of PdH and PdD which are formed during electrolysis. PdH would appear in the SIMS spectrum at 107 and 109, but their ratio should be  $\sim$  1, not the observed 2. Another possibility is that transmutation to Ag occurred. Ag was detected by EDS in localized concentrations on both sides of this Pd cathode after electrolysis. Large concentrations of C on the concave side were detected by EDS studies, in agreement with the AES results. EDS also detected C on the convex side of the Pd cathode, but at much lower concentrations. This suggests that the C content is related to the current density during electrolysis. The high C content is on the concave surface which faced the Pt foil anode and therefore had much higher current density than the convex surface, which faced away from the anode. The changes in the SIMS spectra are also much greater on the concave side. Fig. 9 shows one example. There are others, too numerous to present in this report.

Since 1989, there have been many other reports of anomalous elements resulting from the interaction of metals with hydrogen isotopes [ 8-14]. The results reported here add to that growing body of evidence.

## Acknowledgement

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