Research Article

Anomalous Isotopic Distribution of Silver in a Palladium Cathode

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Abstract

This paper demonstrates that during cold fusion experiments by electrolysis of heavy water with palladium cathodes, there is production of silver. By Secondary Ion Mass Spectroscopy, it is shown that silver detected is not due to contamination, but probably to transmutation of palladium by absorption of a deuterium nucleus, because only the ^{107}Ag-isotope is present, and not ^{109}Ag, as in natural silver. Another important result of this study is the determination of the depth at which the reaction occurs: 1.3 μm below the cathode surface.

Keywords: Electrochemistry, Isotopes, Palladium, Silver, Transmutation

1. Introduction

Since the discovery of Cold Fusion by Fleischmann and Pons [1], an important question remains: what are the reactions responsible for excess heat? Helium-4 has been measured and correlated with excess heat [2], but also silver was detected, which was not present in the original palladium cathode [3]. Therefore, it is very likely that in addition to the fusion reaction of deuterium, there is also transmutation and production of silver by transmutation of palladium. These measurements having been made by EDX in Scanning Electron Microscopes, no isotopic analysis was available [3–5]. This is important because the best proof that silver is due to transmutation, is its possible anomalous isotopic distribution. EDX produces only chemical information. Mass spectroscopy is necessary to measure isotopic distribution.

During their stay in France at IMRA, Pons and Fleischmann did a number of very successful experiments with the ICARUS-9 calorimeter [6]. In 2001, Stanley Pons gave me a palladium cathode which according to him produced a lot of excess heat. I kept it many years. In 2018, I had access to a Secondary Ion Mass Spectroscopy (SIMS) equipment, and an analysis was made. In this paper it is shown that silver detected in this palladium electrode by SIMS has an anomalous isotopic distribution.

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2. Experimental

The palladium cathode came from an experiment performed in an ICARUS-9 type calorimeter [6]. Figure 1 shows a schematic of the calorimeter. It is composed of a Pyrex tube 25 mm diameter, 50 cm long, inserted into a double wall aluminum casing. The two walls are separated by an insulating material. Inside the Pyrex tube the cathode is a palladium rod 10 cm long and 2 mm in diameter, surrounded by a platinum anode wire. The electrolyte is composed of 100 ml D_2O and 0.1 M LiOD. The calorimeter is placed inside a constant temperature water bath. Temperatures are measured by three pairs of thermistors located at different levels along the tube. For each pair one thermistor is located near the Pyrex tube, and the other one near the surface of the aluminum casing. Finally, one is inserted inside the Pyrex tube near the cathode to measure the temperature of the electrolyte. After several weeks of electrolysis at low current (20 mA), the current is raised, and the cell boils. There is a condenser section in the upper parts of the calorimeter, so that the water vapor condensates on the walls of the Pyrex tube and fed back to the electrolyte. The main advantage of this design is that it permits boiling for a long period of time.
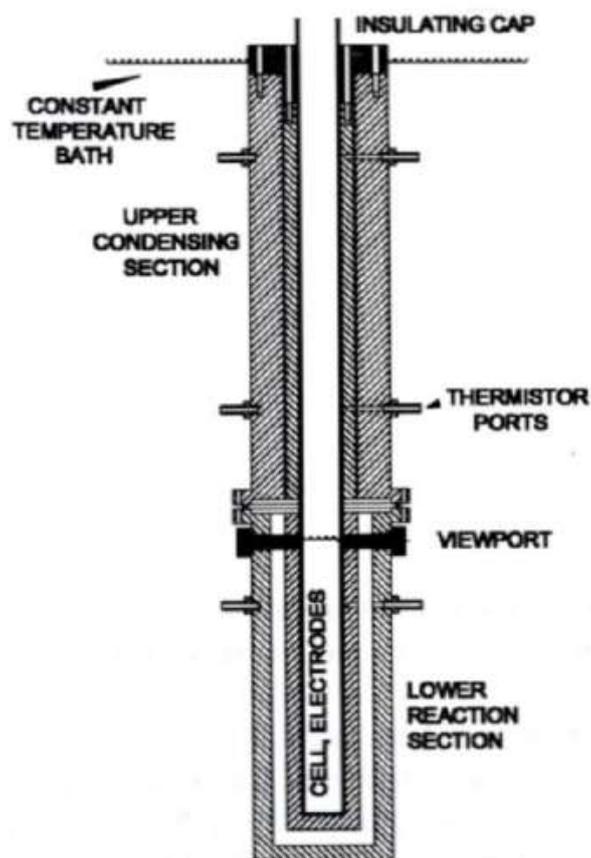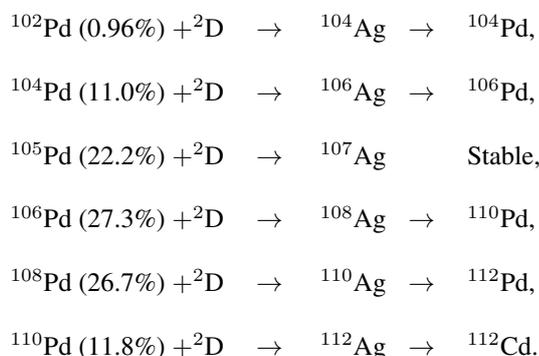

Figure 1.   Schematic of the ICARUS-9 calorimeter.

3. Search for Silver

Palladium and silver are next to each other in the periodic table. The natural isotopes of palladium are: ^{102}Pd, ^{104}Pd, ^{105}Pd, ^{106}Pd, ^{108}Pd and ^{110}Pd. Those of silver are ^{107}Ag and ^{109}Ag. Therefore, there is no mass interference between Pd and Ag. Two types of mechanisms can be imagined explaining the possibility of transmutation of palladium into silver. The first one assumes the fusion of a palladium nucleus with a deuterium nucleus, and the other one, fusion of a palladium nucleus with a di-neutron. This latter mechanism supposes that a deuterium nucleus transforms itself into a di-neutron by an unknown mechanism, which can then easily fuse with a palladium nucleus. The first mechanism is difficult to imagine, due to the strong repulsive Coulomb force, without some unknown catalytic mechanism.

3.1. Assumption 1: Pd and D fuse

If the stable palladium isotopes and deuterium fuse, the following reactions would occur.

$$^{102}\text{Pd} \ (0.96\%) + {}^{2}\text{D} \quad \rightarrow \quad {}^{104}\text{Ag} \quad \rightarrow \quad {}^{104}\text{Pd,}$$

$$^{104}\text{Pd} \ (11.0\%) + {}^{2}\text{D} \quad \rightarrow \quad {}^{106}\text{Ag} \quad \rightarrow \quad {}^{106}\text{Pd,}$$

$$^{105}\text{Pd} \ (22.2\%) + {}^{2}\text{D} \quad \rightarrow \quad {}^{107}\text{Ag} \quad \quad \text{Stable,}$$

$$^{106}\text{Pd} \ (27.3\%) + {}^{2}\text{D} \quad \rightarrow \quad {}^{108}\text{Ag} \quad \rightarrow \quad {}^{110}\text{Pd,}$$

$$^{108}\text{Pd} \ (26.7\%) + {}^{2}\text{D} \quad \rightarrow \quad {}^{110}\text{Ag} \quad \rightarrow \quad {}^{112}\text{Pd,}$$

$$^{110}\text{Pd} \ (11.8\%) + {}^{2}\text{D} \quad \rightarrow \quad {}^{112}\text{Ag} \quad \rightarrow \quad {}^{112}\text{Cd.}$$
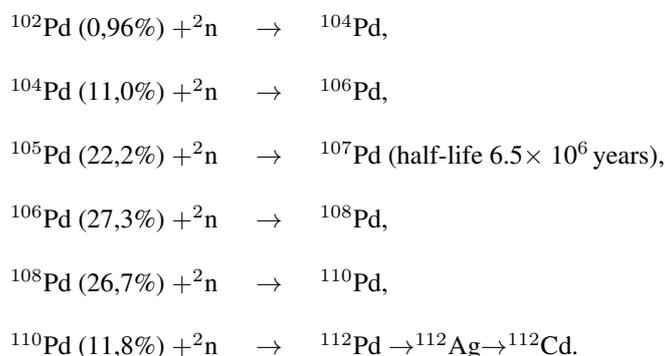
The palladium isotopes would transmute into unstable silver isotopes (except ^{107}Ag). They would quickly transmute into stable palladium isotopes, and stable ^{112}Cd. What is interesting here is the absence of ^{109}Ag, or any other mass 109 element.

3.2. Assumption 2: Pd and ^{2}n fuse

If the stable palladium isotopes and a di-neutron fuse, the following reactions would occur. Palladium isotopes would transmute into stable palladium isotopes except for ^{107}Pd which has a very long half-life, and ^{112}Pd which would quickly transmute into stable ^{112}Cd. What is interesting here also, is the absence of ^{109}Ag.

Because the masses of ^{107}Ag and ^{107}Pd are very close, it would be impossible to distinguish them with the SIMS equipment used in this study. Therefore, if palladium transmutes into silver, we should see only mass 107, which could be either silver or palladium. Therefore, with this type of analysis, it is not possible to distinguish between fusion of palladium with D or ^{2}n. However, in both cases there should be formation of ^{112}Cd. It is important to note that in both mechanisms, there is absence of mass 109.

$$^{102}\text{Pd} \ (0{,}96\%) +\ ^2\text{n} \quad \rightarrow \quad ^{104}\text{Pd},$$

$$^{104}\text{Pd} \ (11{,}0\%) +\ ^2\text{n} \quad \rightarrow \quad ^{106}\text{Pd},$$

$$^{105}\text{Pd} \ (22{,}2\%) +\ ^2\text{n} \quad \rightarrow \quad ^{107}\text{Pd (half-life } 6.5\times 10^6 \text{ years}),$$

$$^{106}\text{Pd} \ (27{,}3\%) +\ ^2\text{n} \quad \rightarrow \quad ^{108}\text{Pd},$$

$$^{108}\text{Pd} \ (26{,}7\%) +\ ^2\text{n} \quad \rightarrow \quad ^{110}\text{Pd},$$

$$^{110}\text{Pd} \ (11{,}8\%) +\ ^2\text{n} \quad \rightarrow \quad ^{112}\text{Pd} \rightarrow ^{112}\text{Ag} \rightarrow ^{112}\text{Cd}.$$

4. SIMS Analysis

The dynamic SIMS equipment used for the analysis was a Cameca 4f. Figure 2 shows a photograph of a piece of the cathode that was analyzed, and Fig. 3 shows SEM images of the surface at various magnifications.

The Cameca 4f instrument is a dynamic SIMS, composed of an oxygen ion beam which etches the surface and a high-resolution mass spectrometer that collects the emitted ions generated by the beam. Therefore, it is possible to have mass analysis as a function of etch time. When etch time is calibrated using a calibration sample of known thickness, then it becomes possible to determine elemental composition versus depth. Masses are either atoms or molecules. It is possible that deuterium remaining in the cathode could give false identification. Indeed, a molecule composed of ^{105}Pd and D would have a mass of 107. in order to eliminate this interference, the cathode was heated at 600°C in air prior to SIMS analysis.

To calculate the depth profile, the etch rate was calibrated using a 100 nm film of palladium deposited on a silicon wafer. Not knowing the actual composition of the cathode, one piece of the cathode was hand filed in order to reach the bulk of the cathode and be analyzed by SIMS. As shown in Fig. 4, there was no silver present, only palladium. Figure 4 shows a depth profile for comparison between ^{106}Pd, ^{107}Ag and ^{109}Ag in the bulk of the cathode. We can see that there is almost no silver present.

Figure 5 shows a depth profile of the palladium cathode. Masses corresponding to ^{106}Pd are shown in black; ^{107}Ag is in red; and ^{109}Ag is in green. Natural silver has the following ratios: ^{107}Ag (51.4%) and ^{109}Ag (48.7%). The masses are almost equal. However, in Fig. 5, it can be seen that at the surface mass 107 is three times larger than mass 109.

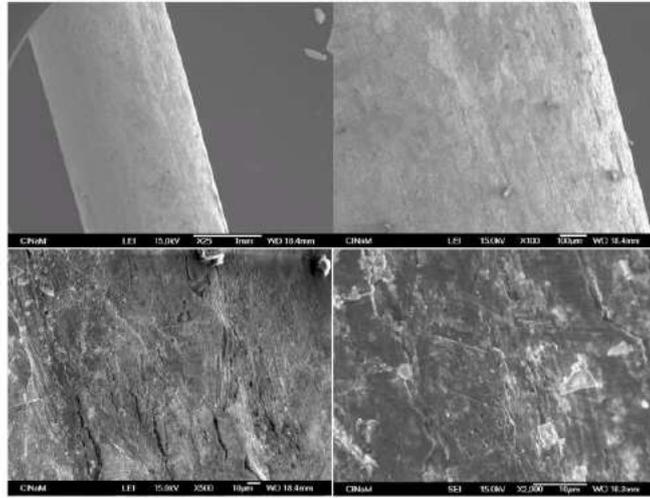**Figure 2.** Photograph of a piece of the palladium cathode.

Figure 3.   SEM images of the surface of the palladium cathode at various magnifications.

After about 400 s of etching, ^{107}Ag and ^{109}Ag peaks are almost equal, as expected with natural silver. This indicates that there is an excess of ^{107}Ag at the surface.

The surface of the palladium cathode is not uniform. We have discovered hot spots. In Fig. 6, the depth profile
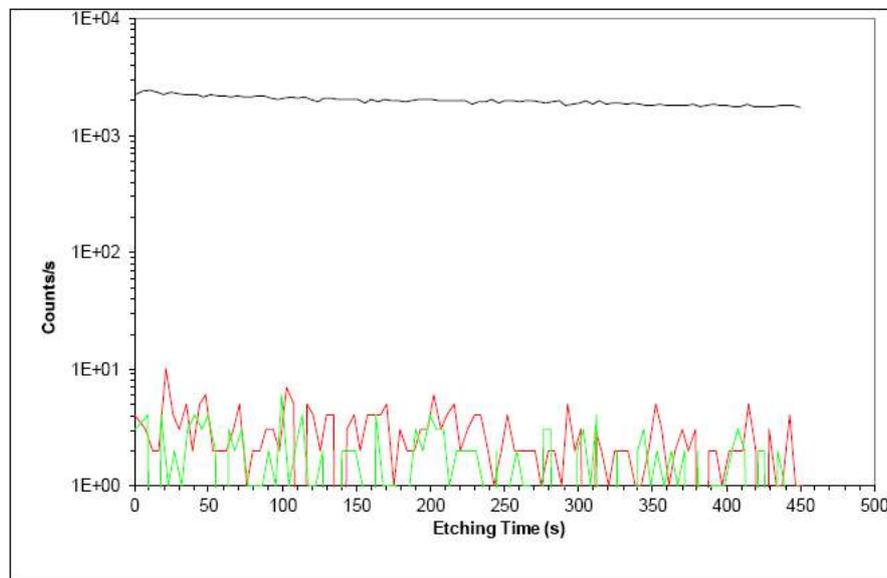

Figure 4.   Depth profile of the bulk of the palladium cathode. ^{106}Pd (*black*), ^{107}Ag (*red*) and ^{109}Ag (*green*).
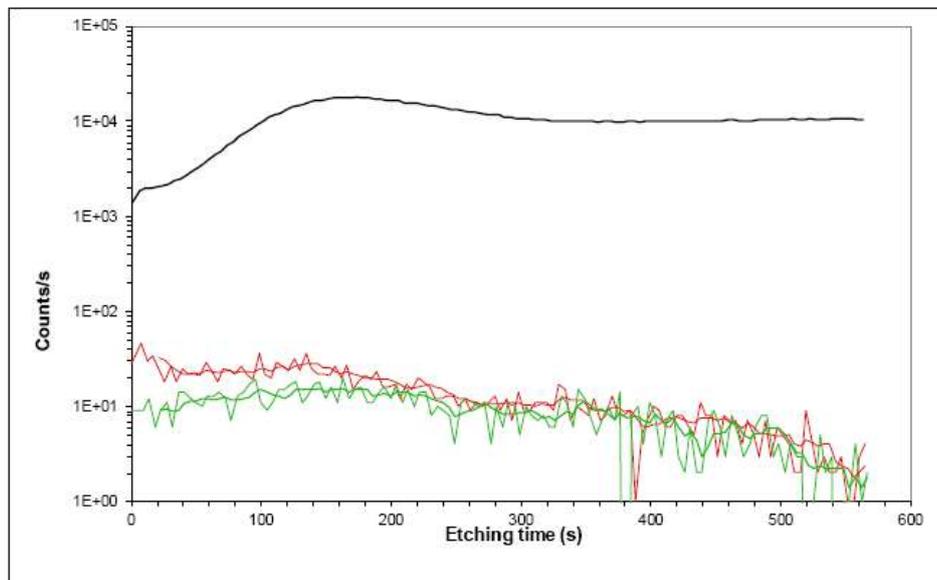
Figure 5. Depth profile of the palladium cathode. ^{106}Pd (*black*), ^{107}Ag (*red*) and ^{109}Ag (*green*).

shows that at the surface, the ratio ^{107}Ag/^{109}Ag is larger than 10. Here too, at 650 s of etching, the ^{107}Ag and ^{109}Ag peaks are equal. As both peaks should be almost equal in natural silver, we have subtracted ^{109}Ag from ^{107}Ag, so that
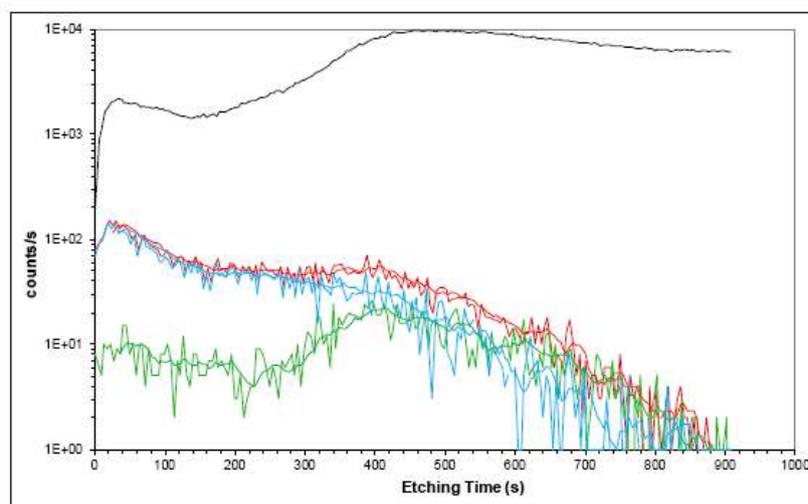

Figure 6. Depth profile of the palladium cathode. Pd-106 (*black*), ^{107}Ag (red), ^{109}Ag (*green*). The blue line shows the ^{107}Ag peak corrected for ^{109}Ag.
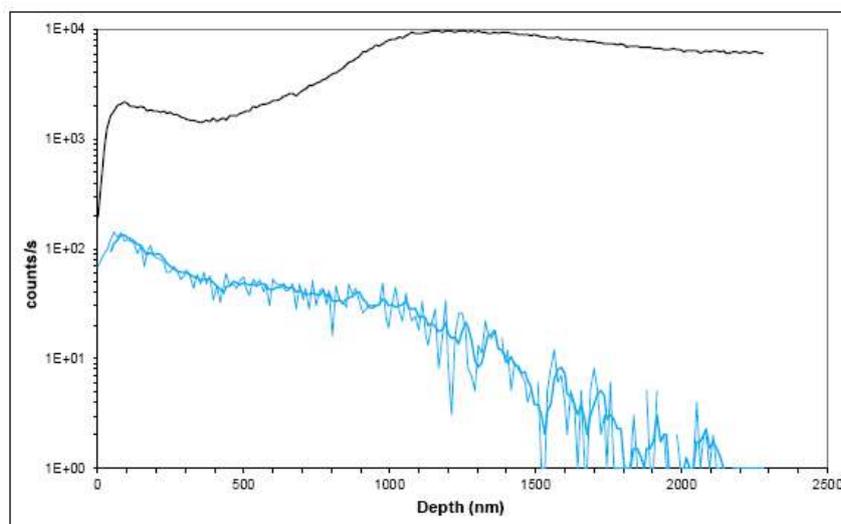
Figure 7. Depth profile of the palladium cathode. ^{106}Pd (*black*), the ^{107}Ag peak corrected for ^{109}Ag (*blue*).

the curve in blue displays only anomalous ^{107}Ag (Fig. 7). Using the etch rate calibration (2.4 nm/s), Fig. 7 shows the ^{106}Pd peak and the ^{107}Ag peak corrected of the ^{109}Ag peak by subtracting the signal of ^{109}Ag from ^{107}Ag.

It is interesting to note that after 1.3 μm, the amount of ^{107}Ag has decreased by a factor of 10. This is an indication of how far the reaction occurs under the surface of the cathode.

5. High Resolution ICP-MS Analysis

In order to check the validity of these observations, the surface of the palladium cathode was etched in aqua regia and sent for analysis to the CNRS (Centre National de la Recherche Scientifique) laboratory in Villeurbanne, France. The Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) analysis shows 3/1000 increase of ^{107}Ag from natural ^{107}Ag. Even though this increase is at the upper limit of the natural variation in ratio of the two isotopes of silver, this result confirms the SIMS analysis. The question of why we did not find the ratio ^{107}Ag/^{109}Ag $= 10$ is certainly due to the fact that it was only measured in hot spots, and not uniformly on the sample. Therefore, the ICP-MS results are compatible with the SIMS data.

6. Discussion

In this study, we have shown the presence of mass 107, but unfortunately, during the first run we did not check for mass 112. In a second run, in spite of all our attempts, we could not find another hot spot, so we could not check for the presence of mass 112.

Another question is the possible interference with ZrO_2 masses. Zirconium and ZrO_2 have the following isotopes shown below:

$$^{90}\text{Zr} \ (51.5\%) \qquad ^{106}\text{ZrO}_2,$$

$$^{91}\text{Zr} \ (11.2\%) \qquad ^{107}\text{ZrO}_2,$$

$$^{92}\text{Zr} \ (17.1\%) \qquad ^{108}\text{ZrO}_2,$$

$$^{94}\text{Zr} \ (17.4\%) \qquad ^{110}\text{ZrO}_2,$$

$$^{96}\text{Zr} \ (2.8\%) \qquad ^{112}\text{ZrO}_2.$$

Therefore, mass 107, could be either ^{107}Ag or $^{107}\text{ZrO}_2$. Even though this is a potential interference, this is very unlikely, as there was no detectable Zr in the cathode.

7. Conclusion

In this paper, it is shown that during electrolysis of a palladium cathode in a heavy water electrolyte, there is production of silver. However, only ^{107}Ag is formed, which corresponds to a possible fusion of palladium atoms with deuterium atoms, with an unknown mechanism. Silver was detected only in hot spots, and not all over the electrode. Also, an important fact regarding this analysis is that silver is detected only down to 1.3 μm under the surface. This shows that in the case of this type of experiments it is a surface effect and not a bulk one that is involved.

Unfortunately, mass 112, corresponding to ^{112}Cd has not been measured in this work. This sheds some uncertainty on the above conclusion. More work should definitely be done to clarify this point.

Acknowledgement

References

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