

## MICROANALYSIS OF PALLADIUM AFTER ELECTROLYSIS IN HEAVY WATER

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### ABSTRACT

The morphology and microcomposition of palladium after electrolysis in heavy water were studied. Fibers which appeared on the surface were observed to change with time. Evidence which supports the possibility of transmutation is presented.

### INTRODUCTION

Previously we reported finding concentrations of unexpected elements on palladium cathodes after electrolysis in an electrolyte containing  $\text{H}_2\text{SO}_4$  and  $\text{D}_2\text{O}$  (1,2). We report here the results of analysis of palladium 0.315 mm thick used as a cathode for 25 hours and then inadvertently as an anode for 170 minutes.

### EXPERIMENTAL METHODS AND RESULTS

The electrolysis experiments have been carried out, first, for about 5 hours during summer 1993, and then for about 23 hours during summer 1994.

For the first 5 hours of operation, the experimental setup consisted of two cells in series, one (light water control cell) containing 0.06 mol fraction  $\text{H}_2\text{SO}_4$  (analytical reagent) in deionized  $\text{H}_2\text{O}$ , the other (heavy water cell) contained 0.06 mol fraction  $\text{H}_2\text{SO}_4$  in  $\text{D}_2\text{O}$  (99%  $\text{D}_2$ ) and both containing a cold-rolled Pd cathode and a Pt anode. The anodes were made from 99.9% platinum and the cathodes were made from 99.9% palladium. Chemical analyses of the palladium and platinum were provided by the supplier. The palladium foils were produced by cold rolling from the initial 0.5 mm thickness to 0.315 mm.

For the next 20 hours of operation, a new setup was used. Two cells were connected in series but, this time, the control cell contained two Pt electrodes, and the experimental cell contained the previous Pd cathode and Pt anode of the heavy water cell. Both contained acidified heavy water (0.06 mol fraction  $\text{H}_2\text{SO}_4$  ).

In the last experiment, the palladium was used inadvertently as an anode. After electrolysis for 170 minutes, the cell current rapidly dropped to zero. When the cell was opened, we found that the lower part of the palladium had dissolved. The electrolyte, originally a clear liquid, was now a black powdery solid. Some of this black solid was attached to the platinum anode but the platinum was not damaged.

In this series of experiments, a recombination catalyst consisting of a substrate coated with platinum black (Los Alamos type electrode, 20% Pt on carbon) was utilized to recombine the off-gases in a closed system. Electrolysis was performed at current densities ranging from 0.75 to 1.5 A per  $\text{cm}^2$ .

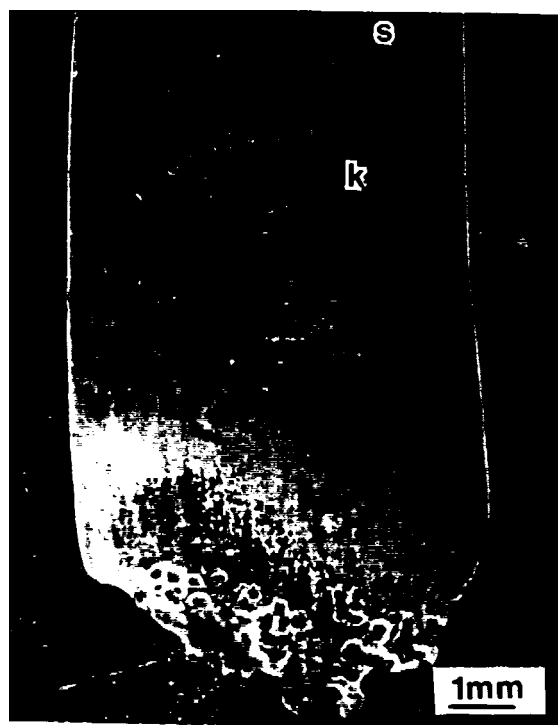
Excess heat compared with the control was observed during both the 1993 and the 1994 experiments.

Surface chemical analyses of the palladium cathode were performed with a LINK AN10,000 Energy Dispersive Spectrometer (EDS) attached to an ISI-SS40 Scanning Electron Microscope (SEM). The thin window of the EDS detector was in place, thus allowing detection of atomic number six and above. The cathode was tilted 45 degrees along the longitudinal axis for efficient X-ray detection and enhancement of the surface relief.

We report here the results of analyses of the concave side and the edges of the palladium cathode.

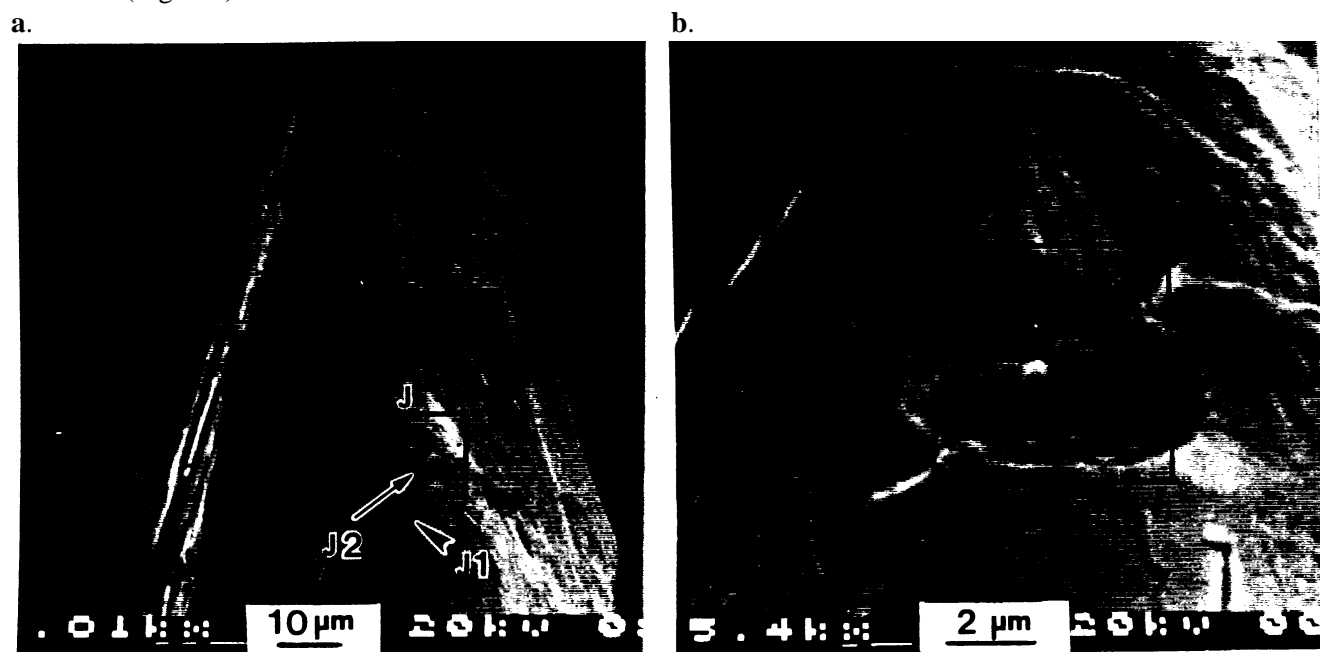
Fig. 1 shows the lower part of the concave side of the palladium cathode after the last electrolysis experiment during which anodic dissolution occurred. The smooth, rounded features near the bottom are believed to be the result of electropolishing; although localized melting might also produce similar features. Comparison of the crystal size in the upper and lower parts of this electrode may be helpful in deciding this question. This has not yet been done.

Microchemical analyses were obtained from the bottom of the electrode and from the areas indicated by the letters **k** and **s** in Fig. 1. Unexpected elements observed on the bottom edge include aluminum and titanium.

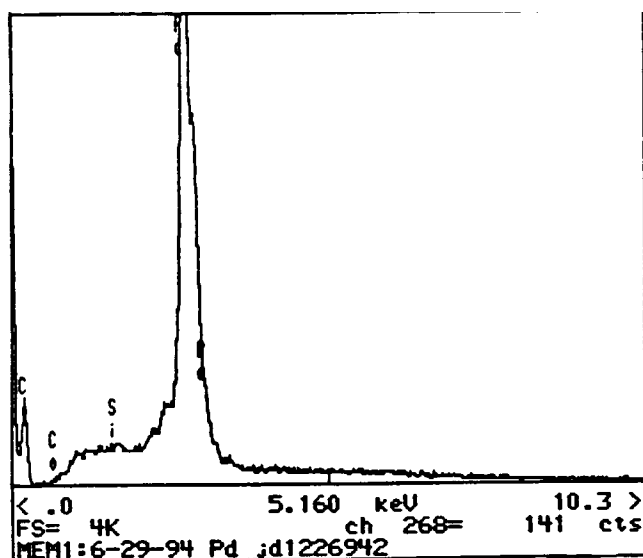


**Fig. 1** Lower part of the concave side of the palladium cathode. This side faced the counter electrode during all of the electrolysis experiments. The region indicated by the letter **k** is approximately at the electrolyte level.

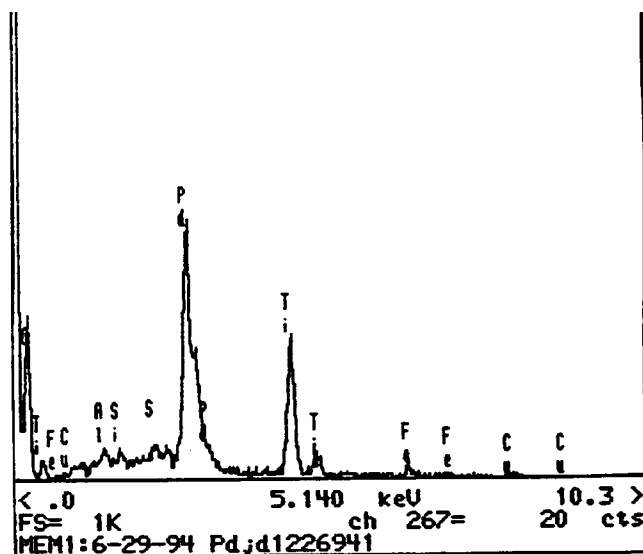
An example of the location of titanium is shown by the region labeled j in Fig. 2a, which is enlarged in Fig. 2b. The spot labeled **J1** has no titanium (Fig. 3a), whereas the spot labeled **J2** contains about 25% titanium (Fig. 3b).



**Fig. 2(a)** Portion of the lower edge of the palladium electrode. **(b)** Enlargement of the region **J** in Fig. 2a.



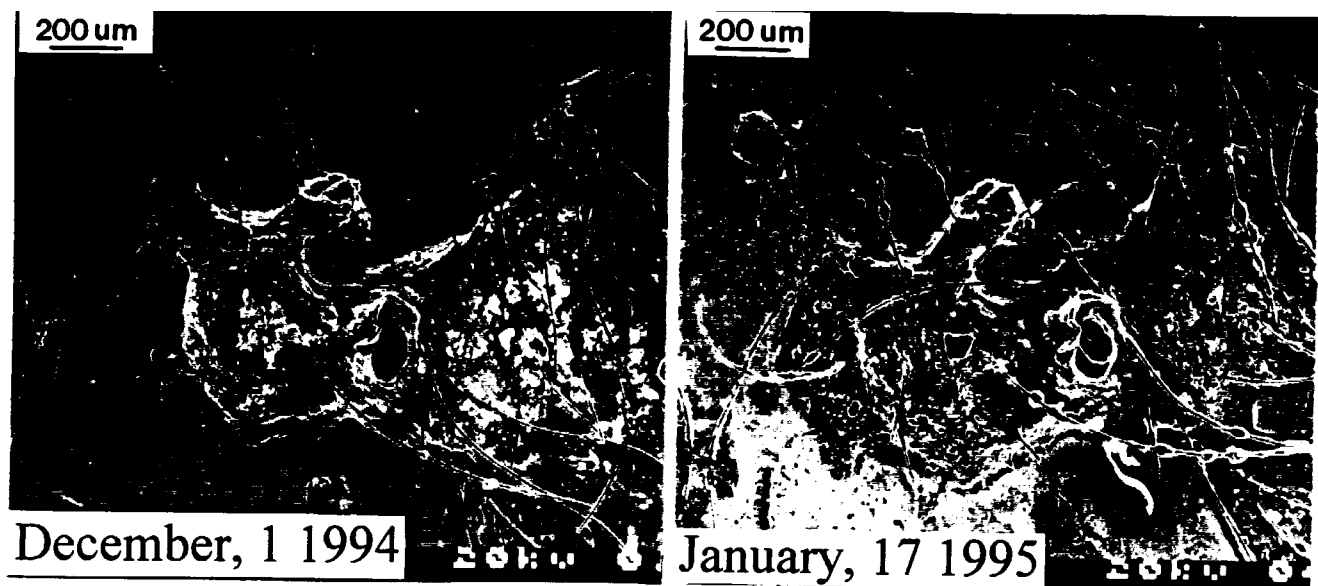
**Fig. 3a** EDS spectrum of spot **J1** in Fig. 2a



**Fig. 3b** EDS spectrum of spot **J2** in Fig. 2a

A black blob appeared on the palladium electrode, near the electrolyte level, after 10 hours of electrolysis, in June 1994. This persisted for 15 more hours of electrolysis and through numerous washings with deionized water. The portion of the blob in region **k** of Fig.1 is shown in Fig. 4a as it appeared on Dec.

1, 1994. Here it is obvious that fibers protrude from the blob. Apparently, changes occurred in both the blob and the fibers, either while the lower part of the electrode was being examined in the SEM or during storage between successive SEM examinations. For example, Fig. 4b shows that bulges occurred along the fibers.



**Fig. 4** Enlarged view of region **k** in Fig. 1 (a) 12-1-94. (b)1-17-95

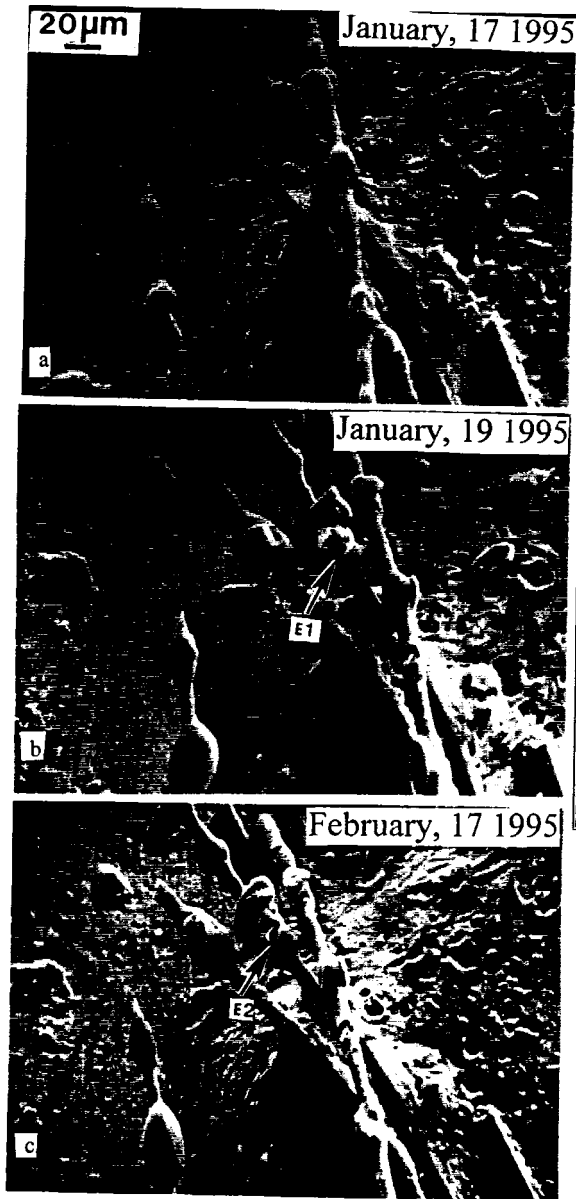
The fibers are composed mainly of palladium, sulfur, carbon, and oxygen, but the proportions of these elements are quite variable. The bulges also have variable composition, which appears to change with time. This can be seen in Fig. 5. The bulge labeled **E1** in Fig. 5b gave the spectrum shown in Fig. 5d, in which peaks for silver  $L\alpha$  and silver  $L\beta$  are labeled. The ratio of the intensities of these two peaks is 0.57. About one month later, the bulge changed in appearance (point **E<sub>2</sub>** in Fig. 5c), and the ratio of the two silver peaks increased to 0.82 (Fig. 5e). Because the silver  $L\beta$  peak coincides with the cadmium  $L\alpha$  peak, a possible explanation for the change in peak ratio is that silver has been slowly changing to cadmium. This is consistent with our observation on another palladium cathode which had been electrolyzed in heavy water. Silver was observed in high, localized concentrations shortly after electrolysis. Examination 15 months later showed the presence of cadmium in addition to silver.

## DISCUSSION OF RESULTS

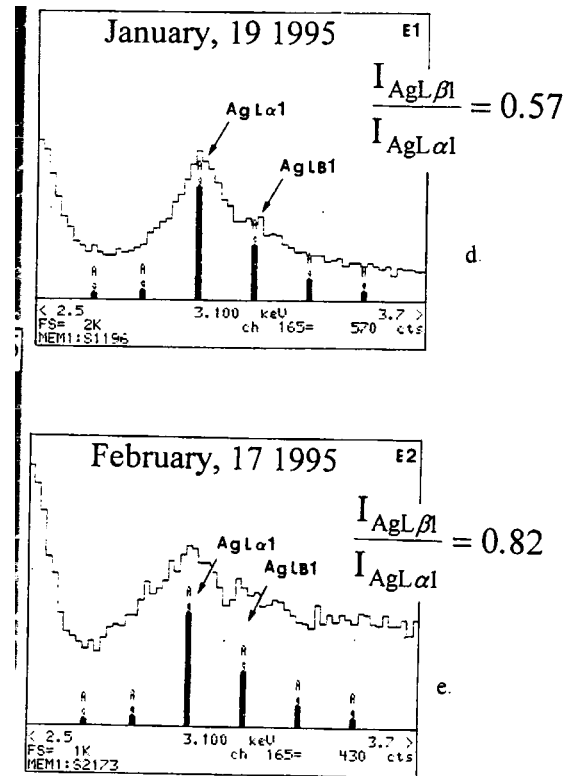
The results presented here for a palladium cathode after electrolysis in heavy water are consistent with those presented previously in that localized concentrations of elements not expected from impurities in the system have been observed. Whereas we previously found gold and silver on the surface, we here report aluminum and titanium concentrated inside the palladium, in addition to silver on the surface. A new finding is the appearance of fibers on the surface, whose composition appears to change with time. Similar fibers have been observed by others after electrolysis of palladium in heavy water (3).

## ACKNOWLEDGEMENT

The electrolysis experiments were performed by Daniel Fredrickson, Grant Noble, Maureen Breiling, and Elizabeth McNasser.



**Fig. 5** Changes in morphology and EDS spectra of the features in the square shown in Fig. 4a. These changes occurred during storage at room temperature with no further electrolysis.



## REFERENCES

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