

# CHANGES IN SURFACE TOPOGRAPHY AND MICROCOMPOSITION OF A PALLADIUM CATHODE CAUSED BY ELECTROLYSIS IN ACIDIFIED LIGHT WATER

J. Dash and G. Noble  
Department of Physics  
Portland State University  
P.O. Box 751  
Portland, Oregon 97207-0751

and

D. Diman  
Carleton College  
Northfield, Minnesota 55077

## ABSTRACT

A thin palladium cathode became bent and torn during electrolysis in acidified light water. Localized changes in composition were observed, including the occurrence of chlorine and possibly silver. Transmutation by neutron absorption may have caused the formation of silver.

## Introduction

It has been shown that electrolysis with a palladium cathode in an electrolyte containing a mixture of sulfuric acid and either light water or heavy water results in greatly altered surface topography [1,2,3], excess heat [2,3] and unexpected elements which could have been produced by absorption of neutrons [3]. For example, silver was observed in high concentrations at microscopic surface aspirates on the 0.060 mm thick palladium cathode after electrolysis in the heavy water electrolyte [3]. But silver was not detected when larger areas which included the surface aspirates were analyzed. Thus, the internal processes which result in surface aspirates and high concentrations of unexpected elements are highly localized.

We report here the results of analysis of a 0.060 mm thick palladium cathode after electrolysis in a light water electrolyte.

## Experimental Methods and Results

Platinum foil (99.9% Pt) was used for the anodes and palladium foil (99.9% Pd) was used for the cathodes. The palladium foil was produced by cold rolling from the initial 0.5 mm thickness to 0.06 mm. The electrolyte consisted of 0.06 mol fraction  $\text{H}_2\text{SO}_4$  (analytical reagent) in deionized  $\text{H}_2\text{O}$  for the light water cell and 0.06 mol fraction  $\text{H}_2\text{SO}_4$  in  $\text{D}_2\text{O}$  (99.9%  $\text{D}_2$ ) for the heavy water cell. The cells were connected in series, and electrolysis was performed for five hours at a current density of about 0.67  $\text{A}/\text{cm}^2$ . Excess gases from electrolysis escaped through the tops of the cells. Excess heat production of about 0.1 watt was observed for the heavy water cell, compared with the light water cell [3].

After electrolysis, the palladium cathode from the light water cell was cleaned ultrasonically in deionized water. It was then examined with a scanning electron microscope (SEM) and analyzed

chemically with an attached energy dispersive spectrometer (EDS).

Fig. 1a shows the upper portion of the palladium cathode which was not immersed in the electrolyte during electrolysis. This is almost as smooth and flat as the original cold rolled palladium before electrolysis. In contrast to this, Fig. 1b shows the distorted and torn lower portion of the palladium cathode which was immersed in the electrolyte during electrolysis.

Using the EDS, spectra were taken from the square areas indicated on Fig. 1a and 1b, using identical experimental conditions. These are shown in Fig. 2. Superimposed on these spectra are vertical bars which indicate the positions and expected relative intensities of six palladium L peaks. The two most intense L peaks are  $L\alpha_1$  at 2.84 KeV with relative intensity 100% and  $L\beta_1$  at 2.99 KeV with relative intensity 42%. Actual relative intensity of  $L\beta_1$  to  $L\alpha_1$  in Fig. 2a is 50% and in Fig. 2b it is 54%. Similar results were obtained by analysis of the remainder of the electrode areas shown in Fig. 1a and 1b. Thus, the ratio of the Pd  $L\beta_1$  intensity to the Pd  $L\alpha_1$  intensity is slightly greater in the electrolyzed portion of the palladium cathode (Fig. 1b) than in the unelectrolyzed portion (Fig. 1a). Changes in this ratio can be caused by factors such as differences in absorption [4]. Overlap with emission lines from another element could also produce changes in this ratio. For example, silver  $L\alpha_1$ , the strongest silver L line [4], occurs at 2.98 KeV. If silver were present in the palladium, it would increase the intensity of Pd  $L\beta_1$  without appreciably changing the intensity of Pd  $L\alpha_1$ . Thus, the presence of silver would increase the ratio of Pd  $L\beta_1$  to Pd  $L\alpha_1$ .

The spectrum in Fig. 2b, which came from the electrolyzed portion of the palladium cathode, has a strong platinum peak. This results from slow dissolution of the platinum anode and subsequent electroplating of Pt on the palladium cathode. The platinum peak is not present in the Fig. 2a spectrum from unelectrolyzed palladium.

The arrow at the bottom left of Fig. 1b indicates an area which is enlarged in Fig. 3a, and enlarged further in Fig. 3b. An EDS spectrum from the feature which protrudes from the surface in Fig. 3b is shown in Fig. 3c. An EDS spectrum from the square area indicated in the lower right-hand corner of Fig. 3b is shown in Fig. 3d.

The protruding feature shown in Fig. 3a and in more detail in Fig. 3b appears to have erupted out of the surface of the palladium cathode. The surroundings are smooth and flat. The protrusion also differs in composition from the surroundings, as indicated by the intense chlorine peak between the platinum and palladium peaks in Fig. 3c and the absence of this peak in Fig. 3d. There is also a weak potassium peak to the right of the palladium peak in the spectrum of the protrusion, but there is no potassium peak in the spectrum from the right of the protrusion (Fig. 3d).

Three more spectra were taken from other positions on the protrusion in addition to that shown in Fig. 3b. Although the relative intensities differed from one position to another, the same elements (Pt, Cl, Pd, and K) were detected in all four spectra.

At about 50 $\mu$ m from the lower edge of the palladium cathode shown in Fig. 3a, the surface topography changes from uniform gray to a dark, mottled appearance, as shown in Fig. 4a. A spectrum from the spot indicated on Fig. 4a is shown in Fig. 4b. This shows the presence of palladium, but there is no peak for platinum such as that in Fig. 3d which was obtained from the uniform gray area on the lower right of Fig. 3b. In the spectrum of Fig. 4b the ratio of Pd  $L\beta_1$  to Pd  $L\alpha_1$  is 0.61, or about 0.1 greater than this ratio in all of the spectra shown above, from either the unelectrolyzed or the electrolyzed portions of the palladium cathode.

The upper portion of Fig. 4a has a fairly uniform, light gray appearance, similar to the region on the lower right of Fig. 3b which contains a large amount of platinum (Fig. 3d). It may be that the platinum peeled off of the lower edge during ultrasonic cleaning of the electrode. The current density was highest at the lower edge, and the electroplated platinum may have been dendritic and loosely adherent.

The mottled structure near the lower edge of the electrode in Fig. 4a is shown at higher magnification in Fig. 5a. The contrast in this photograph is most likely due to topographic differences. Light gray areas are probably higher in elevation than the interspersed dark, sub-micron diameter areas.

The composition of the area within the square indicated above the center in Fig. 5a is given by the spectrum in Fig. 5b. This is similar to the spectrum in Fig. 4b in that platinum is not present. The ratio of the palladium  $L\beta_1$  peak height to the  $L\alpha_1$  peak height is 0.75, which is 0.15 greater than the same ratio in Fig. 4b and about 0.25 greater than this ratio in all the spectra taken at distances more than  $50\mu\text{m}$  above the lower edge of the cathode.

## Discussion of Results

The above results illustrate the drastic changes in surface morphology of a palladium cathode which occur during electrolysis with an electrolyte containing  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  and a platinum anode. The violent interaction of hydrogen with palladium caused inhomogeneous distortion and tearing. Analysis of a surface protrusion revealed the presence of chlorine (probably as a compound) on the protrusion but not on the adjacent area of the palladium cathode. The source of chlorine is not known.

The morphology of the lower edge of the cathode, where current density most likely was highest during electrolysis, shows a large number of sub-micron sized surface pits. Analysis shows a large change in ratio of x-ray fluorescence peaks of palladium. The ratio of Pd  $L\beta_1$  at 2.99 KeV to Pd  $L\alpha_1$  at 2.84 KeV changed from about 0.50 for the upper part of the palladium cathode to 0.75 for the lower edge. It is known that changes in this ratio can be caused by changes in absorption by the sample [4]. But it is not clear why the absorption from a region near the edge should change in such a way as to cause the observed change in intensity ratio. It seems more likely that the change in intensity ratio was caused by the presence of silver which produces an  $L\alpha_1$  peak at 2.98 KeV. If this is the correct explanation, then the region in Fig. 5a from which the spectrum in Fig. 5b was obtained contains about 20% Ag. This is much less than was found in localized areas of a similar palladium cathode electrolyzed in heavy water [3].

If silver is present, then it either diffused from within the palladium, was electroplated, or was produced by transmutation caused by neutrons produced during nuclear fusion of hydrogen or deuterium. The results show that platinum electroplates onto the palladium, but that the platinum probably peeled off of the lower edge during ultrasonic cleaning after electrolysis due to poor adherence of the electroplated layer. Therefore, if silver had been electroplated, it probably would have peeled off with the platinum. The likelihood that silver would diffuse from the interior and concentrate at selected sites on the surface seems extremely remote because silver and palladium are miscible in all phases [5].

We previously concluded that a nuclear fusion reaction may have resulted in silver deposits on a palladium cathode electrolyzed in an electrolyte containing  $\text{D}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  [3]. It seems most probable that the enhanced x-ray intensity at 3 KeV in Figs. 4b and 5b may also be due to transmutation caused by neutrons from a fusion reaction. If a neutron is captured by  $\text{Pd}^{108}$ , an abundant isotope, it becomes  $\text{Pd}^{109}$ , which rapidly decays to  $\text{Ag}^{109}$ , a stable isotope [6].

## References

1. D.S. Silver, J. Dash, and P.S. Keefe. "Surface Topography of a Palladium Cathode After Electrolysis in Heavy Water, *Fusion Technology*, vol 24, p 423 (1993).
2. J. Dash, P.S. Keefe, E. Nicholas, and D.S. Silver, "Comparison of Light and Heavy Water Electrolysis with Palladium Cathodes," Proceedings AESF 80th Annual Conference, Orlando, Florida (June 1993), p 755.
3. J. Dash, G. Noble, and D. Diman, "Surface Morphology and Microcomposition of Palladium Cathodes After Electrolysis in Acidified Light and Heavy Water: Correlation with Excess Heat," Proceedings of 4th International Conference on Cold Fusion, Lahaina, Hawaii (December 1993).
4. G.G. Johnson, Jr., and E.W. White, "X-ray Emission Wavelengths and KeV Tables for Nondifferential Analysis," ASTM Data Series DS 46 (ASTM, Philadelphia, 1970).
5. I. Karakaya and W.T. Thompson, Binary Alloy Phase Diagrams, vol 1 (T. B. Massalski, ed.-in-chief.) Metals Park, Ohio: ASM, 1986, pp 55-56.
6. Handbook of Chemistry and Physics, 41st ed., Cleveland: Chemical Rubber Publishing Co., 1959/60, pp 470-471.

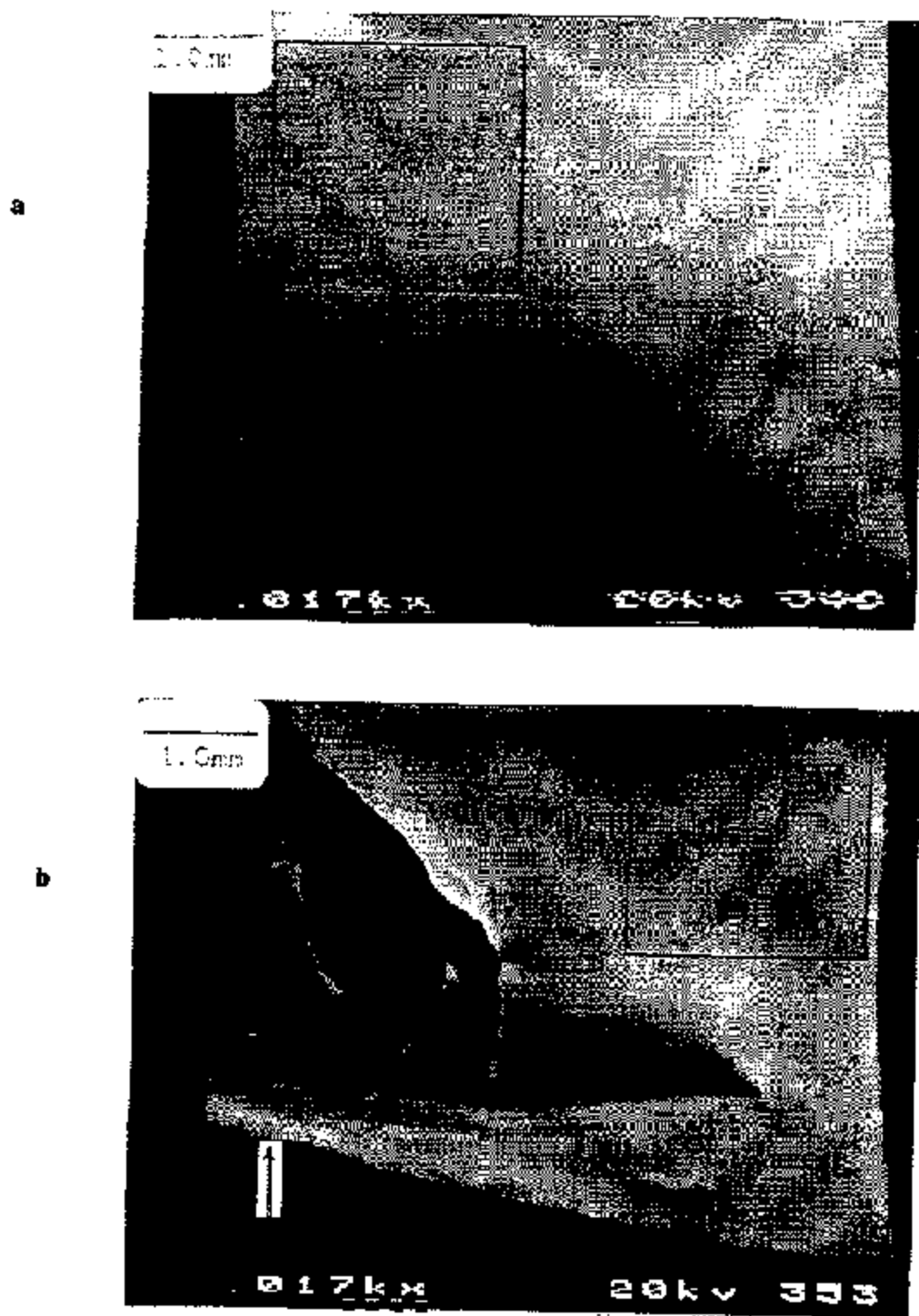
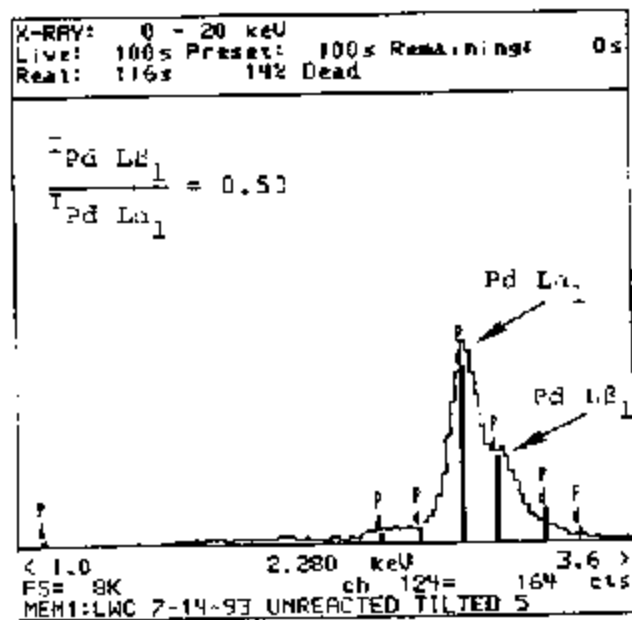


Fig. 1. Palladium cathode after electrolysis in acidified light water. (a) Portion of the cathode above the electrolyte. (b) Portion of the cathode immersed in the electrolyte, concave side (facing anode).

a



b

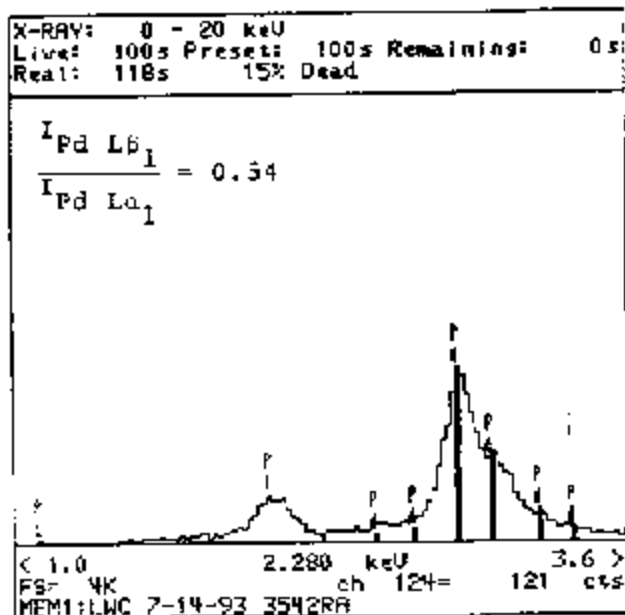


Fig. 2. EDS spectra from a palladium cathode after electrolysis in acidified light water. (a) Spectrum from the square area in Fig. 1a. The positions of Pd  $L\alpha_1$  and Pd  $L\beta_1$  are indicated. (b) Spectrum from the square area indicated in Fig. 1b. The ratio  $I_{Pd L\beta_1} / I_{Pd L\alpha_1}$  is indicated for each.

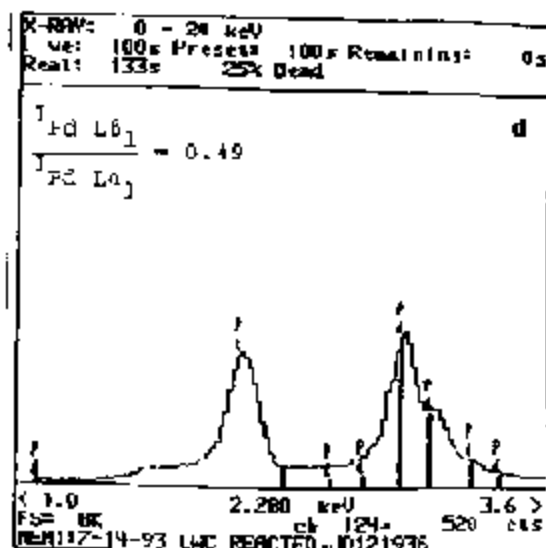
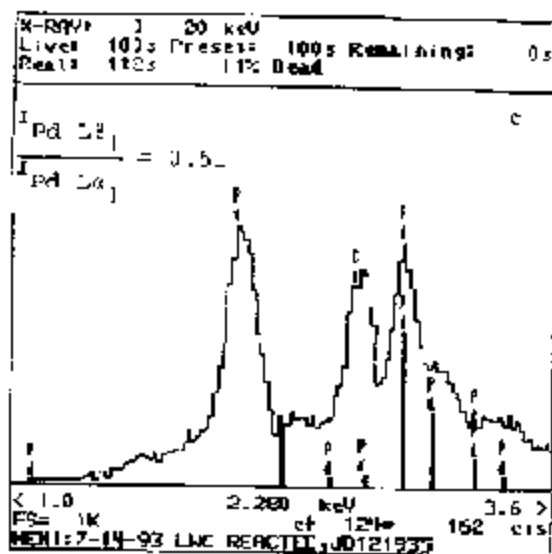


Fig. 3. (a) Enlargement of area near arrow in Fig. 1b. (b) Enlargement to show details of the protrusion near the center of Fig. 3a. (c) EDS spectrum from position 1 on the protrusion in Fig. 3b. (d) EDS spectrum from the square area shown on the lower right of Fig. 3d.

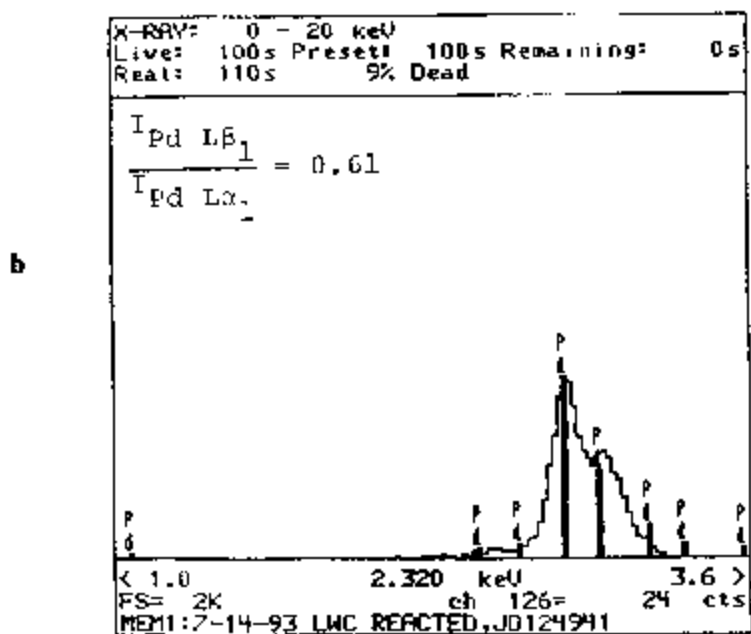
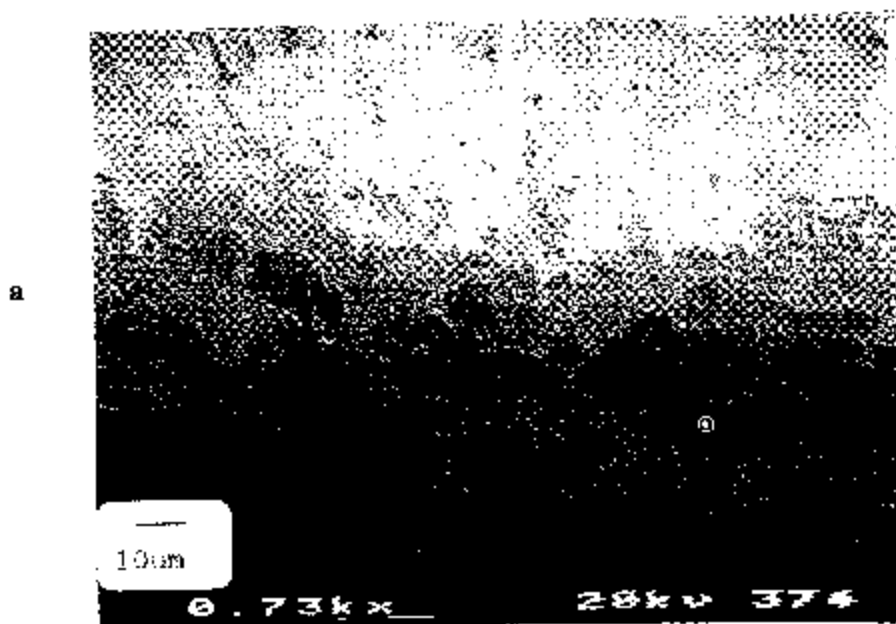


Fig. 4. (a) Enlargement of lower edge of palladium cathode to show changes in surface topography. (b) EDS spectrum from spot shown in Fig. 4a. Note that there is no platinum peak in this spectrum.





b

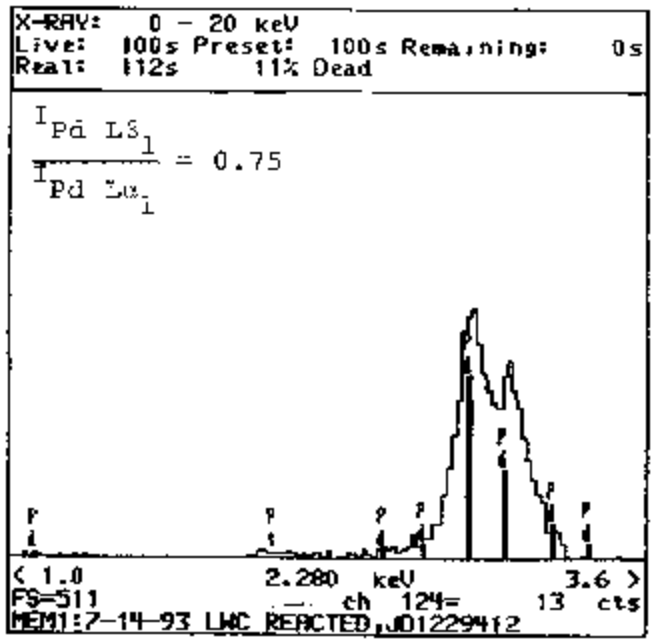


Fig. 5. (a) Enlargement of area a few microns from the lower edge of the Pd cathode. (b) EDS spectrum from square area indicated on Fig. 5a. Note that there is no platinum peak.