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CO-DEPOSITION OF PALLADIUM WITH HYDROGEN ISOTOPES

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ABSTRACT. Palladium was co-deposited with hydrogen isotopes on a Pd cathode. This resulted in enhanced production of excess thermal power. After electrolysis the Pd Lβ / Lα ratio was found to be increased in characteristic x-ray spectra from localized, microscopic areas on the surface of the Pd cathode. This suggests the possibility that appreciable amounts of silver are present in these areas.

INTRODUCTION. In an experiment using a cell with one Pd and one Pt electrode in H_2SO_4-D_2O electrolyte, the polarity was switched by mistake, so that the Pd became the anode and the Pt became the cathode [1]. During the next four hours and many subsequent experiments, this cell produced excess thermal power compared with a control cell. Pd dissolves from the Pd anode and co-deposits with hydrogen isotopes on the Pt cathode. Co-deposition of Pd with hydrogen isotopes has been studied extensively by Szpak and Mosier-Boss [2].

In this report we describe the results of co-deposition of Pd with hydrogen isotopes on a Pd cathode.

EXPERIMENTAL METHODS AND RESULTS. Closed cells were constructed using 200 ml Berzelius beakers (Pyrex, without pouring spouts), Teflon lids fitted to each beaker, perforated Teflon baskets filled with recombination catalyst and suspended above the electrolyte, and thin foil electrodes connected to platinum wires which were threaded through the Teflon tops, Fig. 1.

A control cell and an experimental cell were identical except that the control cell contained two Pt foil electrodes and H_2O-H_2SO_4 electrolyte, whereas the experimental cell contained a Pt anode and a Pd cathode, and D_2O-H_2SO_4 electrolyte. The recombination catalyst was 0.5% Pd on coconut charcoal. The experimental cell electrolyte consisted of H_2SO_4 and D_2O in the ratio 1:6.7. The average temperature of each cell was determined with the aid of a data acquisition system which monitored three thin foil, type K thermocouples attached to the **outside** of each cell. One thermocouple was attached to the bottom of each cell, and one was attached opposite each electrode. The output of the thermocouples was monitored with an automated data acquisition system. The power supply was operated in the constant current mode, and the cells were connected in series. The cells were held in recesses cut into a Styrofoam base. Cell voltages were monitored with a strip chart recorder. The ambient temperature was monitored with a thermocouple in the space between the cells. Each cell was weighed before and after each experiment to determine the extent of energy losses due to incomplete recombination.

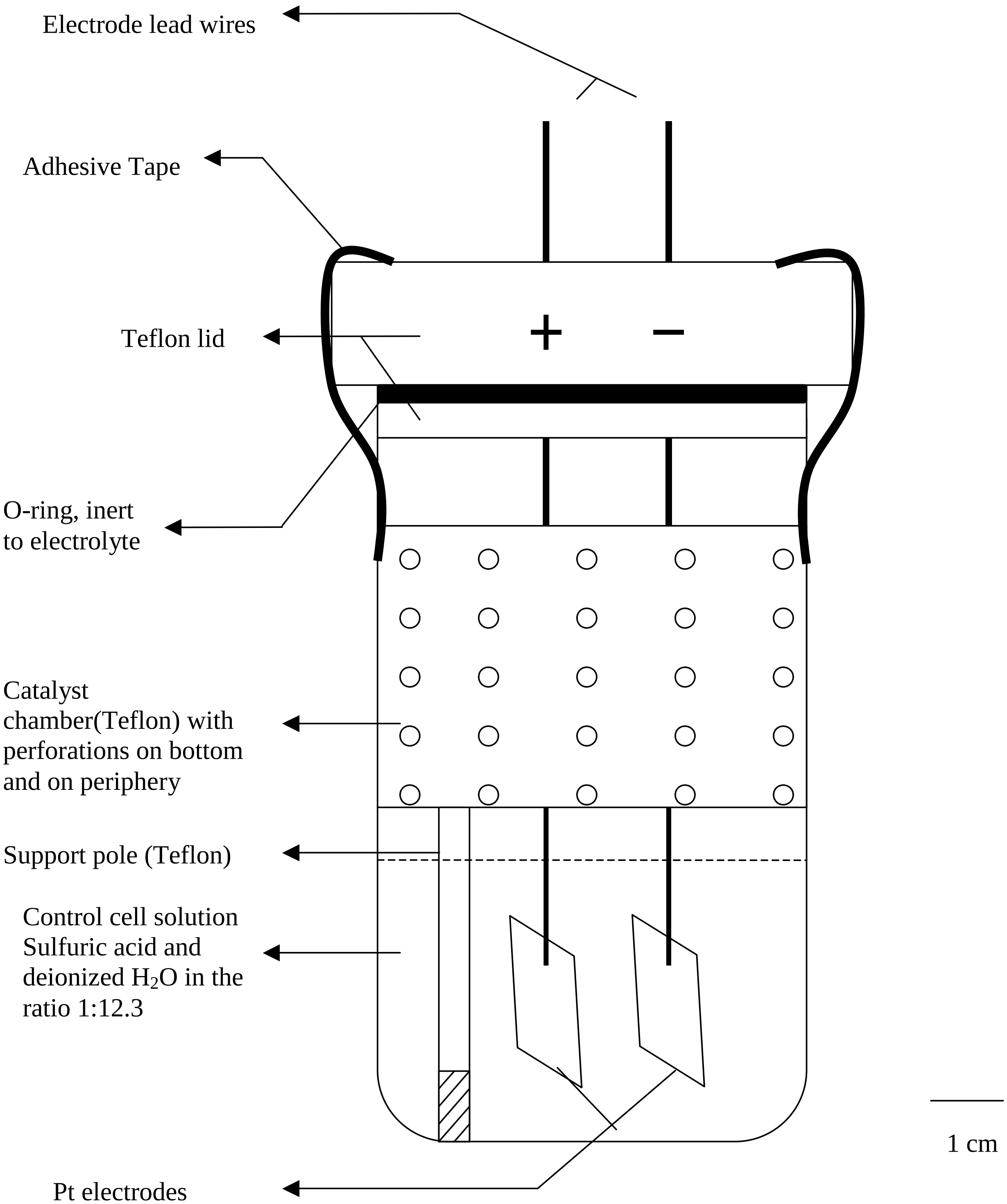


Fig.1. Control cell used for electrolysis in series with an experimental cell.

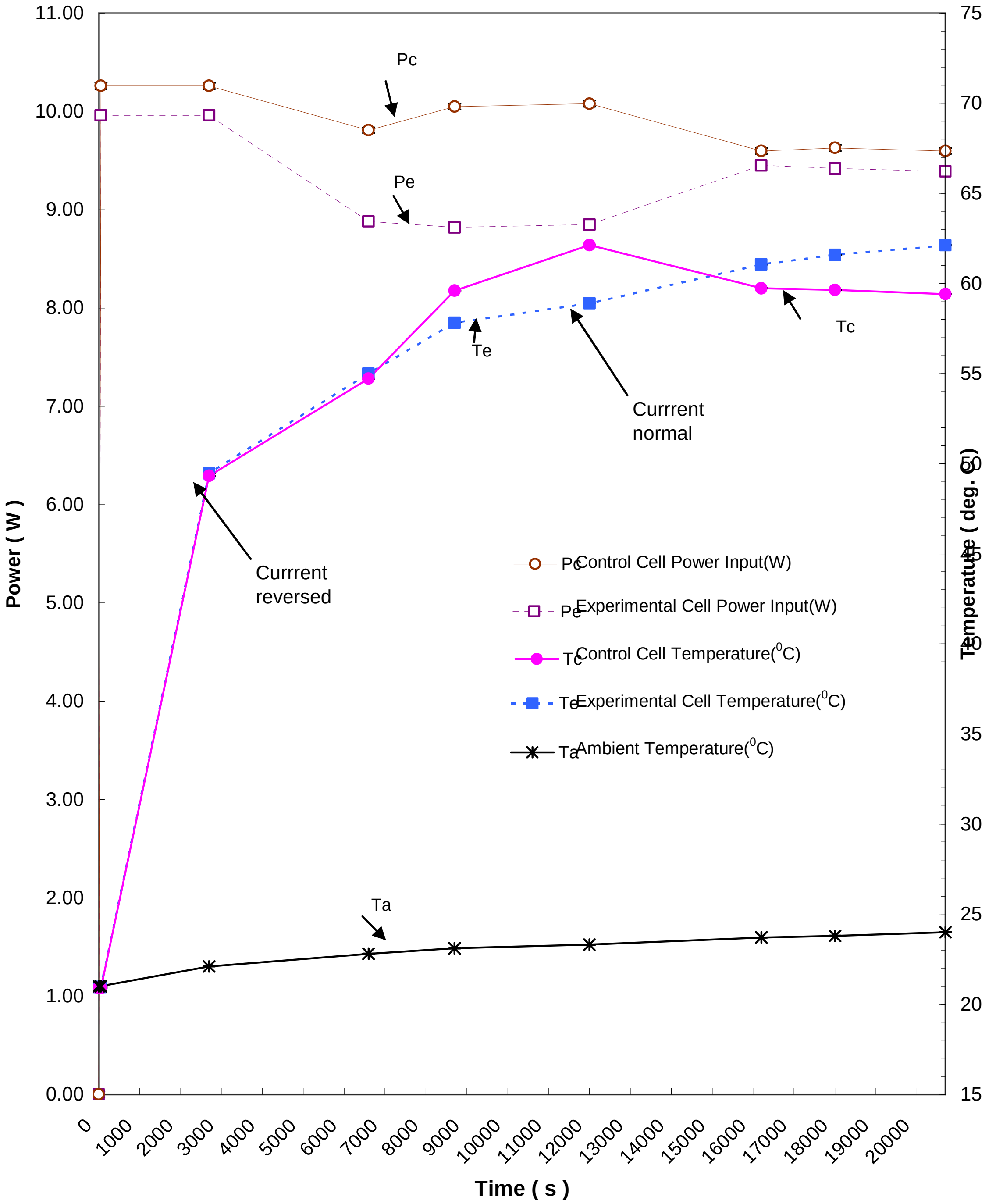
Fig. 2 shows the results of an experiment in which the control cell had greater power input throughout the 5.5 hour experiment, but the experimental cell temperature was about 3ºC higher at the end of the experiment.

During the first 2700 seconds of the experiment, both cells had the same temperature, starting at 21ºC and rising to 50 C. During this period the input power to the control cell was about 0.3 W greater than the input power to the experimental cell. Then the current to both cells was reversed, so that the anode of the experimental cell was now Pd and the cathode was Pt. Both electrodes of the control cell were Pt, but the cathode with a dark surface layer formed during prolonged electrolysis was now the anode.

After the current was reversed, the power input to both cells dropped due to enhanced conductivity. The drop was much greater for the experimental cell than for the control cell, probably because Pd was dissolving from the anode and depositing on the cathode, thus increasing the surface area, which lowered the cell voltage. The control cell received 0.9 W more power than the experimental cell after electrolysis for 6500 seconds, but both cells had the same temperature (55ºC).

After electrolysis for 8700 seconds, the control cell was receiving 1.2 W more power than the experimental cell. Now the control cell temperature was almost 2ºC higher than the experimental cell. After 12000 seconds, there was no change in power input to the two cells, but the control cell temperature was about 3ºC higher. Now the current was again reversed, so that the Pd electrode in the experimental cell was again the cathode. The control cell voltage and temperature began to decrease and the experimental cell voltage and temperature began to increase. After a total of 16200 seconds of electrolysis, the control cell was receiving 0.15 W more power, but its temperature was now about 1ºC **lower** than the experimental cell. Now the cell voltages remained constant for the remainder of the experiment, but the temperatures continued to diverge. After 20700 seconds, the control cell was receiving about 0.2 W more power, but its temperature was now almost 3ºC **lower** than that of the experimental cell.

Fig. 2. Temperature and power results for electrolysis of heavy water with a Pd cathode compared with a control. Pd dimensions: 2.5 cm x 1.25 cm x 0.035 cm. Constant current was 3 A and current density was ~ 0.5 A / sq cm. Error bars are embedded in the data points. Error for power values was +/- 0.03 W and +/- 0.1 C for temperature.



The power output of the experimental cells compared with the control cell was determined at steady state temperature, where the power input was equal to the power output. For the control cell at steady state,

(1) Power in, $V_c I = k(T_c - T_a) + \frac{dH_c}{dt}$, where,

V_c is the cell voltage, I is the constant current, k is the heat transfer coefficient, T_c is the cell temperature, T_a is the ambient temperature, and dH_c / dt is the rate of enthalpy loss due to incomplete recombination. The latter term is determined from the change in weight of the cell and the duration of the experiment. This equation is solved for k, which is then used in a similar equation for the experimental cell.

In the equation for the experimental cell, a term for excess thermal power output is added on the left side to give,

(2) $V_e I + \frac{dH_{xs}}{dt} = k(T_e - T_a) + \frac{dH_e}{dt}$, where

dH_{xs} / dt is excess thermal power, and the subscript e refers to the experimental cell. If the right side of equation (2) exceeds V_eI, the input power to the experimental cell, then excess heat is being produced by the experimental cell..

The temperature and voltage for the control cell data at 27000 seconds, the constant current (3 A), ambient temperature (24°C), and the rate of enthalpy loss caused by incomplete recombination are substituted into equation (1), and the heat transfer coefficient k is calculated. This k is substituted into equation (2), along with the temperature, voltage, and enthalpy loss data for the experimental cell. The excess thermal power is found to be 0.93 W. To estimate the accuracy of this result, the errors involved in power input and power output measurements must be estimated.

The power input is the product of the constant, 3A cell current and the voltage. Because the cells are connected in series, the measurement error for the current has no significant net effect on the power input. The measurement error for cell voltage was +/- 0.01 V. Therefore, the error in input power measurements was +/- 0.03 W, which means that the error bars for input power are embedded within the data points for input power in Fig. 2.

The power output is calculated from temperature and mass measurements. At the beginning of the experiment the control cell temperature was 20.9ºC +/- 0.02, the experimental cell average temperature was 21.0ºC +/- 0.1, and ambient temperature was 21.0ºC. The balance used for measurement of mass has a precision of +/- 0.1 g. Using this data, the uncertainty in the power output is estimated to be about +/- 0.1 W, and the calculated 0.93 W excess thermal power output is statistically significant. Subsequent runs gave similar results.

After a total of 229 hours of electrolysis, the Pd cathode from the experimental cell was examined with a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) in order to characterize surface topography and microchemical composition. Fig. 3 is a low magnification photograph of a portion of the Pd cathode. The topography is varied. The relatively smooth area enclosed in the white rectangle was examined at higher magnification, Fig. 4.

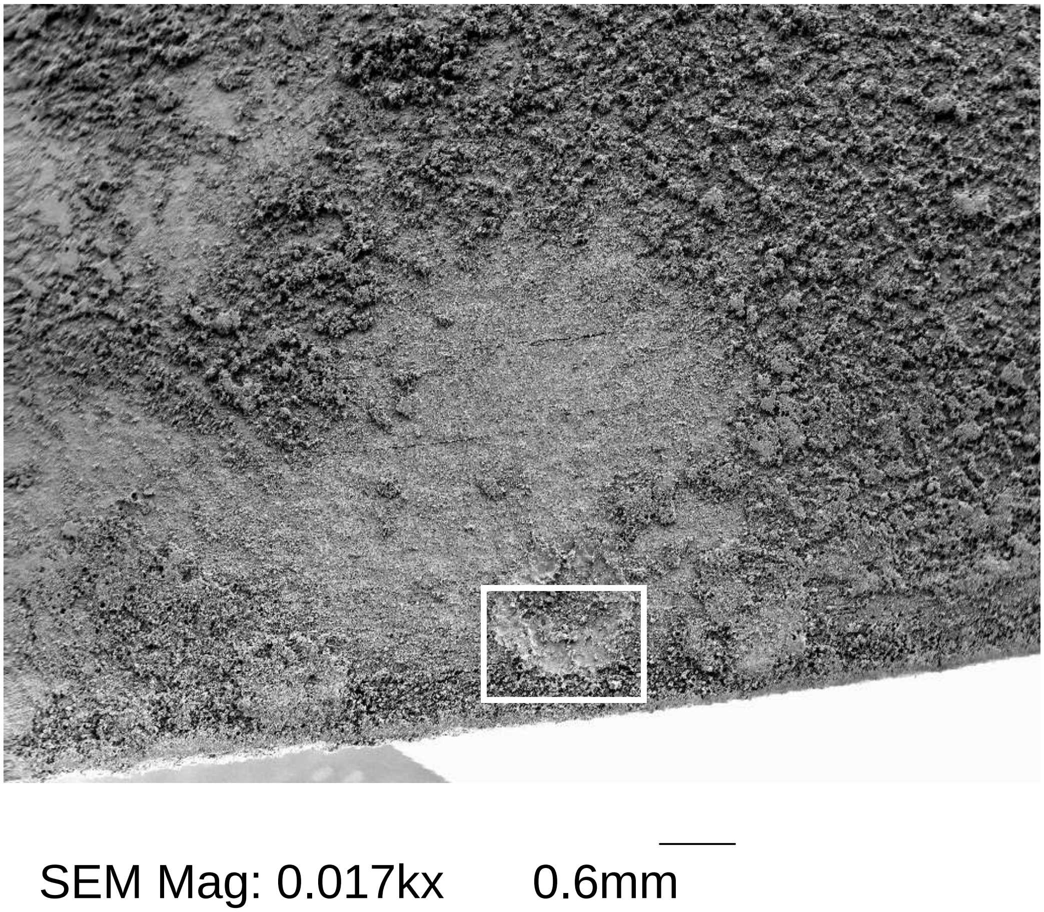


Fig. 3. SEM photograph of a portion of the Pd cathode from the experimental cell. The area within the rectangle was enlarged (Fig. 4).

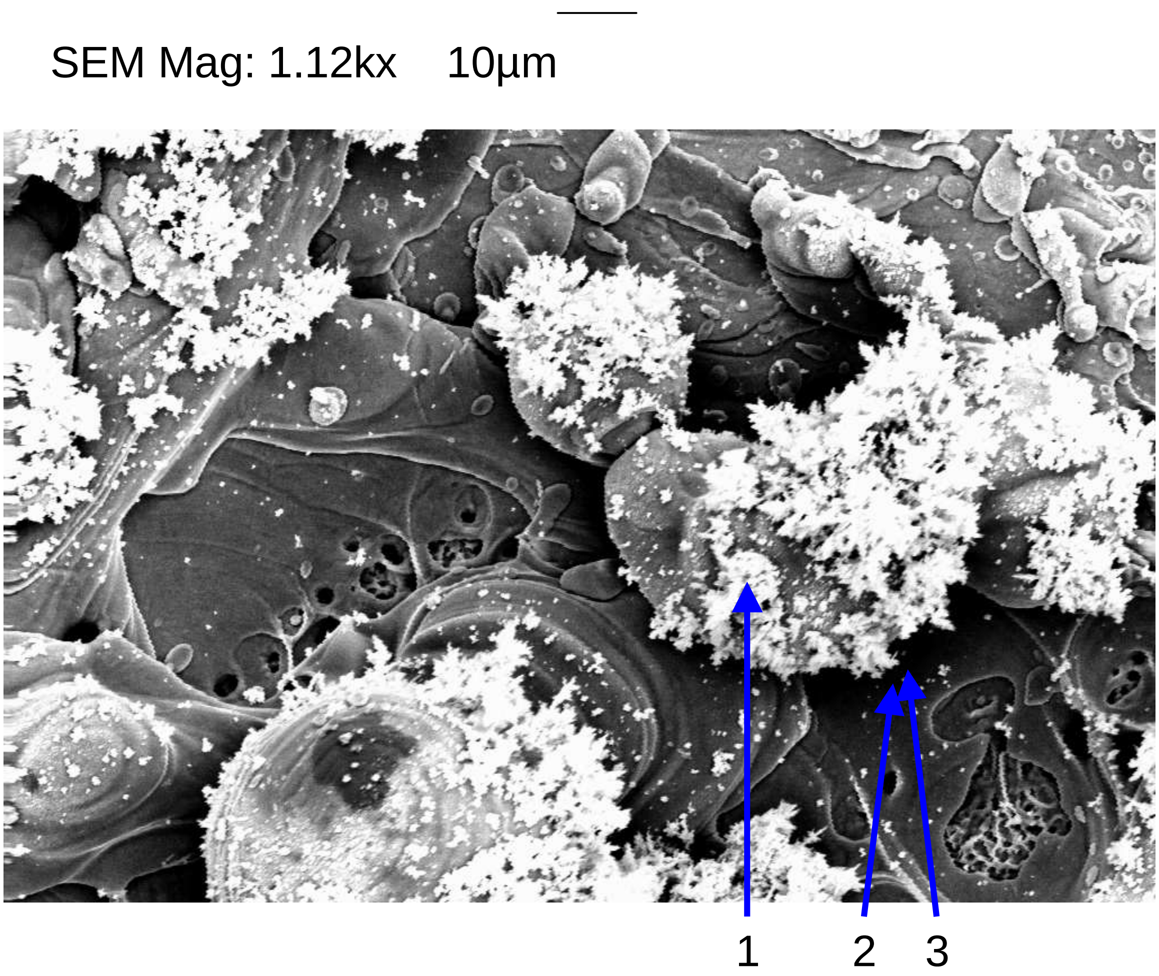


Fig. 4. Enlargement of area within the white rectangle in Fig. 3. The arrows 1, 2, and 3 point to spots from which characteristic x-ray spectra were obtained.

The topography in Fig. 4 is quite varied. The bright, dendritic particles may have resulted from electrodeposition of Pd and Pt after the current reversal, as indicated in Fig. 2. The EDS characteristic x-ray spectrum shown in Fig. 5 was obtained from the bright particle indicated by arrow 1. By fixing the electron beam in the SEM on a spot, it is possible to obtain chemical analyses from about 1 cubic micron on the surface of a specimen. The spectrum in Fig. 5 indicates that the chosen spot contains about 63 weight percent (wt.%) Pd, 24 wt.% Pt, and 13 wt.% C.

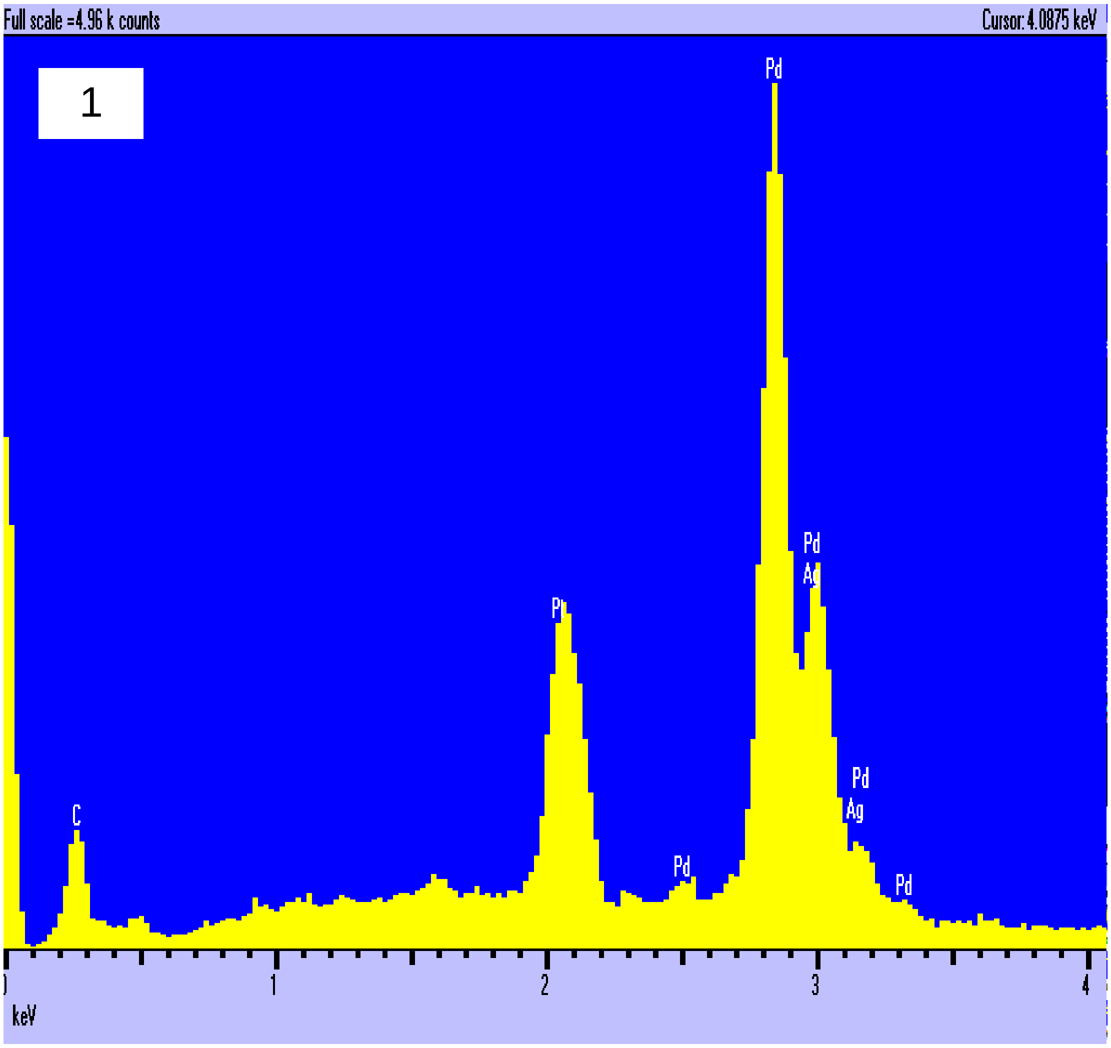


Fig. 5. Characteristic x-ray spectrum from a point on a white particle on the surface of the Pd cathode from the experimental cell. Arrow 1 indicates the location of this point. The most prominent peaks in the spectrum are from Pd, Pt, and C. Pt slowly dissolves from the anode and deposits on the cathode, and C most likely comes from the charcoal catalyst. The Pd Lα peak occurs at 2.84 keV, and the Pd Lβ peak occurs at 2.99 keV. The intensity ratio, Pd Lβ / Lα , is expected to be 0.42 [3]. In this spectrum this ratio is 0.45.

Arrows 2 and 3 indicate two spots on the smooth, dark area shown in Fig. 4. The spectrum in Fig. 6 was obtained from the spot indicated by arrow 2.

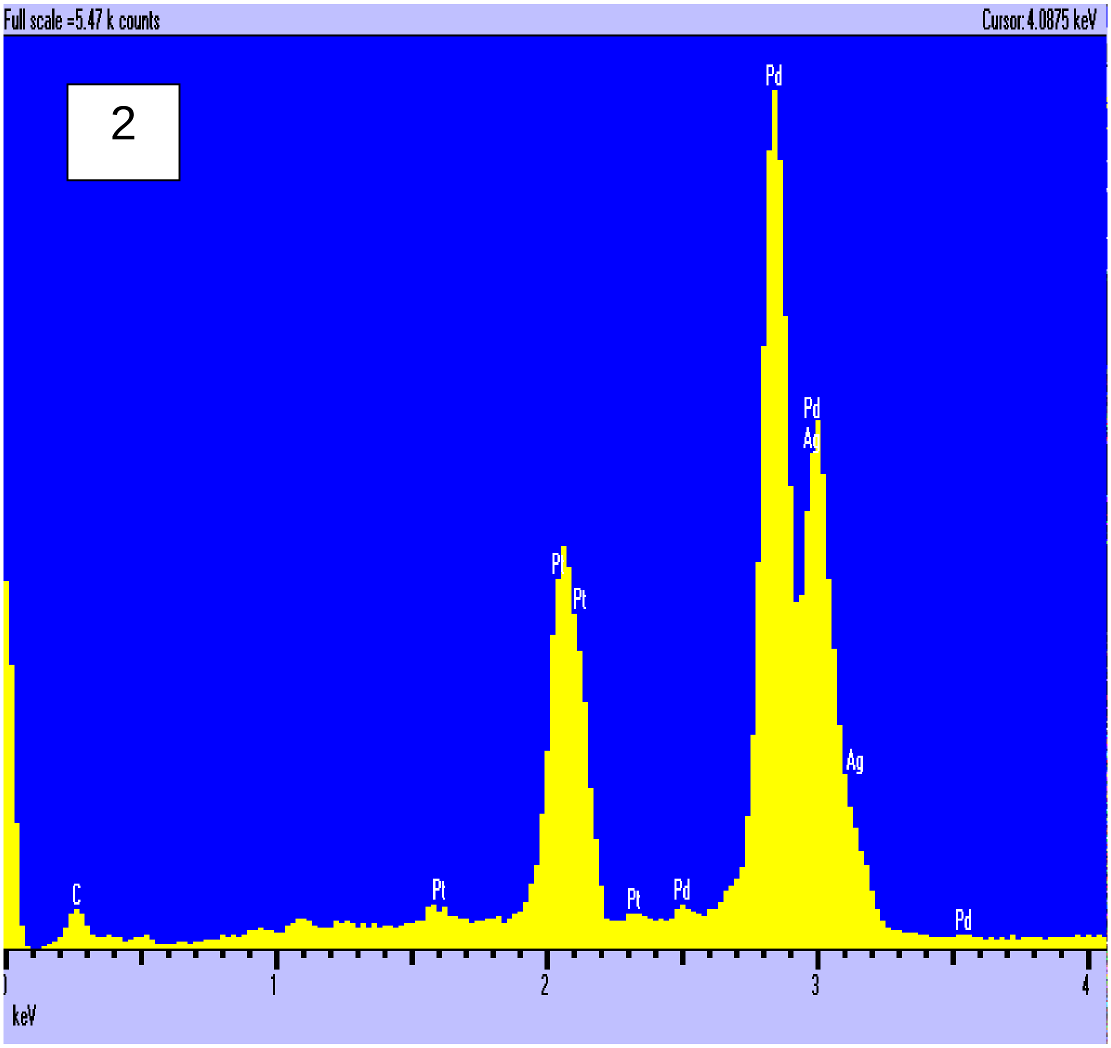


Fig. 6. Characteristic x-ray spectrum from the dark spot indicated by arrow 2 in Fig. 4. The ratio Pd Lβ / Pd Lα is 0.61. This is an increase of 36 % compared with the spectrum in Fig. 5. This increase may be due to overlap with Ag Lα , which occurs at 2.98 keV. If so, then quantitative analysis indicates that this spot contains about 7 wt.% % Ag.

Quantitative analysis of the spectrum in Fig. 6 gave 4 wt.% C, compared with 13 wt.% C from a bright spot (Fig. 5). The other elements in the spectrum, Pd and Pt, are in approximately the same ratio as in Fig. 5. Another difference in Fig. 6 compared with Fig. 5 is that the Pd Lβ / Pd Lα ratio is 0.45 in the latter compared with 0.61 in the former. This difference is possibly due to the presence of Ag , for which the Lα peak occurs at 2.98 keV compared with 2.99 keV for Pd Lβ. If this interpretation is correct, then spot 2 in Fig. 4 contains about 7% Ag.

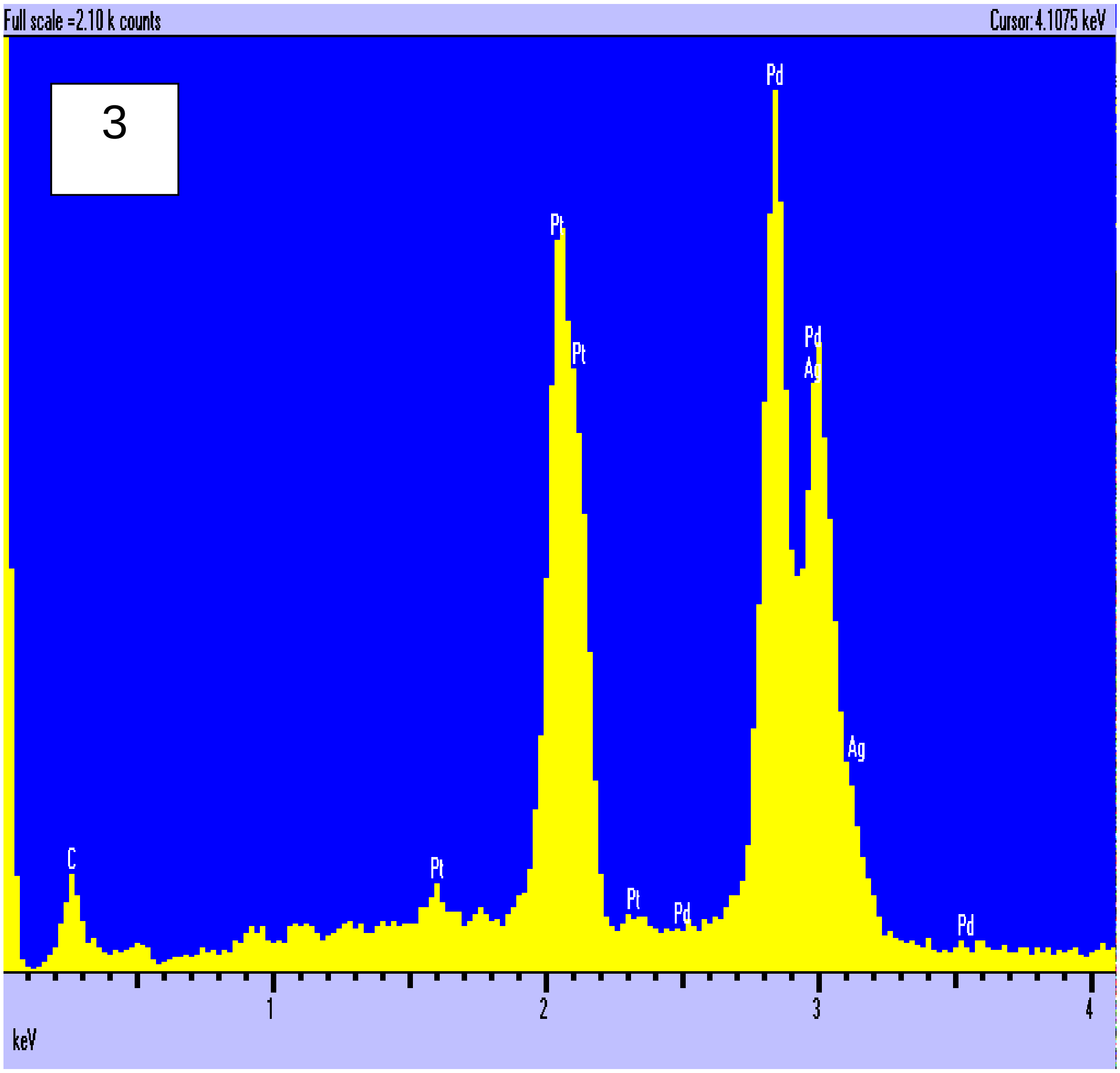


Fig. 7. Characteristic x-ray spectrum from black spot indicated by arrow 3 in Fig. 4. Here the Pd Lβ / Pd Lα ratio is 0.71. This is a 58 % increase compared with this ratio in Fig. 5. If this increase is caused by overlap of Ag Lα with Pd Lβ , then quantitative analysis indicates that this spot contains about 10 % Ag.

The spectrum in Fig. 7, obtained from the black spot indicated by arrow 3 in Fig. 4, is similar to the Fig. 6 spectrum. In Fig. 7 the Pd Lβ / Pd Lα ratio is 0.71, compared with the expected 0.42 for pure Pd [3]. If this increase is caused by the presence of Ag, then the amount of Ag is about 10 wt.%.

DISCUSSION OF RESULTS. The experiment described here shows that co-deposition of Pd with hydrogen isotopes enhances the production of excess enthalpy. Szpak and Mosier-Boss also reported excess enthalpy from their co-deposition experiments [2]. In addition, localized changes in the ratio of Pd characteristic x-ray peak intensities suggests the presence of Ag in these microscopic areas. Confirmation of the presence of silver by some other method such as mass spectroscopy is necessary.

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