SURFACE MORPHOLOGY AND MICROCOSPOSITION OF PALLADIUM CATHODES AFTER ELECTROLYSIS IN ACIDIFIED LIGHT AND HEAVY WATER: CORRELATION WITH EXCESS HEAT

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Abstract

Experiments were performed using Pt anodes and Pd cathodes. The electrolyte contained H\textsubscript{2}O and H\textsubscript{2}SO\textsubscript{4} in one cell and D\textsubscript{2}O and H\textsubscript{2}SO\textsubscript{4} in a similar cell connected in series. Excess heat, localized melting, and localized concentrations of Au or Ag were observed. It is concluded that nuclear fusion is the most probable explanation for the excess heat, localized melting, and localized concentrations of unexpected elements.

Experimental Methods and Results

We recently reported on the electrolysis of D\textsubscript{2}O acidified with H\textsubscript{2}SO\textsubscript{4}, using a Pd cathode made from a single crystal cold rolled into a foil\textsuperscript{1}. Rimmed craters occurred on the surface of this cathode after electrolysis for 12 minutes, suggesting that localized melting had occurred. We also recently reported on comparative heat measurements during electrolysis from two cells in series, one containing H\textsubscript{2}O and H\textsubscript{2}SO\textsubscript{4}, the other containing D\textsubscript{2}O and H\textsubscript{2}SO\textsubscript{4}, and both containing cold-rolled, 0.35 mm thick polycrystalline Pd cathodes\textsuperscript{2}. The anodes were Pt foil 0.03 mm thick. A recombination catalyst was used in both. Excess heat was observed from the D\textsubscript{2}O cell for the first 300 hours of operation, after which excess heat was observed from the light water cell for the final 100 hours of operation. Subsequent to our published report\textsuperscript{2}, we have begun to study the surface topography and composition of the Pd cathodes from both cells. The electrodes were cleaned ultrasonically in deionized water before this study.
A low magnification scanning electron microscope (SEM) photograph of these electrodes is shown in Fig. 1. The appearance of both electrodes is similar. After about 400 hours of electrolysis, the original rectangular cross sections have become oval, and the original rectangular longitudinal shapes have become tapered and bent concave toward the anodes. The concave side of each electrode is depicted in Fig. 1. The original smooth, shiny surfaces changed to dull, corrugated topography. Dark spots are present on the lower ends of both cathodes, where the shape changes were greatest. These dark spots most probably were caused by localized differences in topography, but localized differences in chemical composition also were observed by using an energy dispersive spectrometer (EDS) attached to the SEM. EDS gives surface analysis to a depth of about one μm.

![Fig. 1. Heavy water (left) and light water (right) Pd cathodes, concave side, after electrolysis for about 400 hours.](image)

For example, Fig. 2 is a higher magnification photograph of a small portion of the bottom of the light water Pd cathode on the concave side. The composition of a smooth area such as A is given by the spectrum in Fig. 3. This relatively smooth, flat area with little contrast appears to have no heavy elements other than Pd. On the other hand, region B, which appears darker and rougher with more contrast, gave the spectrum in Fig. 4. This spectrum shows an appreciable amount of Pt and Au in addition to Pd. Similar spectra were obtained from regions C and D. It is likely that Pt is plated from
the electrolyte where it occurs due to slow dissolution of the Pt anode. Au, however, is not expected to arise from a pure Pt anode. Nor is it expected to occur inhomogeneously as an impurity in Pd because Au and Pd are completely miscible in the solid state\textsuperscript{3}.

Fig. 3. EDS spectrum from region A of the H\textsubscript{2}O cathode shown in Fig. 2.

Fig. 4. EDS spectrum from region B of the H\textsubscript{2}O cathode shown in Fig. 2.
Similar analysis of the bottom of the heavy water Pd cathode on the concave side also revealed Au in localized regions. The concentration of Au on the heavy water cathode appears to be greater than on the light water cathode. For example, analysis of an active area of $10^{-3}$ mm$^2$ on the heavy water cathode gave 6% Au compared with 3% Au for an active area of the same size on the light water cathode.

Both cells used the same materials, except that the heavy water cell contained D$_2$O (Baker Analyzed G210-05) and the light water cell used deionized H$_2$O. Both cells were electrolyzed for exactly the same time with exactly the same current. Therefore, it is difficult to explain how a greater concentration of Au could be deposited on the D$_2$O cathode either by plating from the electrolyte or by diffusion from within the cathode.

A possible mechanism for the occurrence of Au on these Pd cathodes is transmutation caused by neutrons. The heavy water cell produced more excess heat than the light water cell, and the concentration of Au on the heavy water Pd is greater than that on the light water Pd. If the excess heat was caused by nuclear fusion, then neutrons may have been released. In the presence of hydrogen, transmutation may be greatly enhanced. If a neutron is captured by Pt$^{196}$, an abundant isotope, it becomes Pt$^{197}$, which quickly decays to Au$^{191}$, a stable isotope.

Assume that region B in Fig. 2 has a concentration of 20% Au atoms in a surface area 4 $\mu$m$^2$ and 1 $\mu$m deep. The number of Au atoms in this volume is about $6.4 \times 10^{10}$. If 2.5 MeV is released along with each neutron from the assumed fusion reaction, then the energy produced by $6.4 \times 10^{10}$ events is $2.6 \times 10^{-2}$ J. This means that about 0.6% of the cathode volume would produce about $6.4 \times 10^{-5}$ J excess heat. Transmutation by-products would be concentrated in minute areas, requiring microscopic analytical techniques such as we have used.

In an additional experiment, the same cells were used in series with the same electrolytes (0.06 mol fraction H$_2$SO$_4$) but without the recombination catalyst. A cell diagram is shown in Fig. 5.

The two identical open electrolytic cells were run in series, using 0.03 mm Pt foil anodes and 0.055 mm Pd foil cathodes. The electrodes were made from the same lots used for the electrodes in the experiment described above. The water jacket of the heavy water cell contained 8 g more water than that of the light water cell. Thus, the mass of the D$_2$O cell exceeded the mass of the H$_2$O cell by about 8 g. The current density was about 0.7 A/cm$^2$, and the voltages of the cells were controlled by adjusting the proximity of the electrodes and the immersed surface area of the anode. A PC-based data acquisition system manufactured by Kiethly-Metrabyte recorded thermocouple voltages at four positions in the water jackets around the circumference of each cell. The thermocouples (copper-constantan with electronic icepoints) were accurate to $\pm$ 0.5°C.

Electrolysis was performed for five hours, and then the power was turned off. The palladium cathodes were washed with deionized water, and then cleaned ultrasonically in
acetone prior to being examined and photographed with a light microscope, and with a scanning electron microscope.

A program was written which averaged the four water jacket temperatures in each cell. The average in the H cell was then subtracted from the average in the D cell for every data point. Then, the average, maximum, and minimum of this difference was recorded for every ten minutes of data. The power value for each cell was also averaged and the minimum and maximum recorded over the ten minute periods.

The power input to the heavy water (D) cell was maintained at least 0.1 watt less than to the light water (H) cell. Although the mass of the D cell exceeded that of the H cell, the temperature of the D cell was the same or higher than that of the H cell throughout the experiment, as shown by the graphs in Fig. 6. The graphs show the difference in power input and the difference in temperature between the H and D cells during an experiment. One can clearly see a positive value for the average D-H temperature, and a negative value for the difference (D-H) in power input. This indicates that the D cell was producing more heat per unit power in, than the H cell.

![Diagram of open cells and circuit](image)

Fig. 5. Schematic diagram showing components of open cells and circuit used for electrolysis of light and heavy water cells in series.

An obvious change in surface morphology occurred during electrolysis, as shown in Fig. 7. The edges of the foil became rounded and spherical globules formed on the surface on the concave side, suggesting that localized melting and chemical reaction with sulfate in the electrolyte occurred during electrolysis. Using an energy dispersive spectrometer attached to a scanning electron microscope, chemical composition was determined in regions which had topography suggestive of localized melting. A spectrum (Fig. 9A) of the entire region in Fig. 8 has a strong peak at 2.84 KeV, indicating that its composition...
Fig. 6.A. Difference in power input to the heavy water (D) cell and light water (H) cell during electrolysis for five hours. The negative values indicate that more power was input to the H cell throughout the experiment.

Fig. 6.B. Difference in water jacket temperature of the D cell and H cell. The positive values indicate that the D cell power output exceeded the H cell power output throughout the experiment.
is overwhelmingly Pd, but a peak for Pt is also present. The intensities of the Pt and Pd peaks suggest that the average surface composition of the entire area of Fig. 7 is about 85% Pd and 15% Pt. As mentioned above; Pt from the anode codeposits with H and D at the Pd cathode in this system.

Spectra from the four numbered asperities in Fig. 8 are shown in Fig. 9B, 9C, 9D, and 9E for spots 1, 2, 3, and 4, respectively. In all of these the predominant peak is at 2.98 KeV, which corresponds to Ag. The inflections at about 2.84 KeV indicate that Pd is still present, especially in spectrum D from spot 3. Pt peaks also occur in all of these spectra, and peaks for S occur in spectra B and C from spots 1 and 2, respectively. The occurrence of S at spots 1 and 2 but not at spots 3 and 4 or in the overall area of Fig. 8 may be due to inhomogeneous interaction with sulfate from the electrolyte. Localized heating may have been more intense at points 1 and 2, causing inhomogeneous chemical interaction.

Fig. 7.A. Pd cathode before electrolysis. The lines on the surface and the edge cracks were caused by cold rolling.

Fig. 7.B. Pd cathode after electrolysis. Changes were probably caused by localized melting and reaction with sulfate in the electrolyte.

The possibility of electroplating silver from this cell is minimal. The anode was high purity Pt, and electrolyte was made from analytical reagents, and the container was glass. The possibility of Ag occurring as an inhomogeneous impurity in the Pd cathode also is minimal because the Ag-Pd system exhibits complete miscibility in all phases.

A possible mechanism for the occurrence of Ag in such areas is transmutation caused by neutrons. For example, if the excess heat observed for the heavy water cell was caused by nuclear fusion, then neutrons may have been released. If a neutron is captured by Pd$^{108}$, it becomes Pd$^{109}$, which rapidly decays to Ag$^{109}$, a stable isotope.
Assuming excess heat production at the rate of 0.1 watt, the total excess heat produced by the heavy water cell was 1800 J. The particle indicated by point 4 on Fig. 8 contains about 50% Ag. Assuming that this concentration occurs in a volume $25 \times 10^{-9}$ mm$^3$, this particle contains about $2.14 \times 10^{12}$ atoms, half of which are Ag. Assuming that 2.5 MeV is released along with each neutron from a fusion reaction, then about 0.4 J would have been produced along with the Ag in the particle at point 4. Assuming average specific heat of 0.26 J/g°C and a mass of $3 \times 10^{-10}$ g for the particle, the temperature of the particle would have increased to the melting point by absorption of about $10^{-6}$ J. The observed 1800 J of excess heat could have been produced by about 0.4% of the volume of the electrode.

![Fig. 8. Portion of the concave surface of the Pd cathode near the edge where localized melting was observed. EDS spectra indicate that Ag is present at points 1, 2, 3, and 4, but the spectrum from the whole area did not indicate the presence of Ag.](image)

**Discussion of Results**

In the experiments described above, unexpected elements were found in amounts roughly commensurate with measured excess heat. These elements were found only in high current density areas where the surface either had erupted or had been drastically altered.
Fig. 9.A. EDS spectrum from entire area of Fig. 8. The spectra in B, C, D, and E were obtained from spots 1, 2, 3, and 4, respectively, on Fig. 8.
from the original cold-rolled condition. Gold was found on palladium cathodes from both light water and heavy water cells which had been electrolyzed in series for about 400 hours. More gold was found on the heavy water cathode than on the light water cathode. This seems to correlate roughly with the excess heat measurements; i.e., more excess heat was observed for the heavy water cell than for the light water cell. Gold was observed only on the highest current density portions of each cathode, and on a highly convoluted surface. The initial thickness of the palladium electrodes on which gold was observed after electrolysis was 0.35 mm.

In the second experiment, the same cells were used with platinum anodes from the same lot used for the first experiment. The palladium cathodes also were made from the same lot of palladium used in the first experiment, but the thickness was 0.055 mm. Excess heat was observed over the span of the five-hour experiment; i.e., the output of heat from the heavy water cell exceeded that produced by the light water cell. Evidence of surface melting and chemical reaction of sulfate from the electrolyte with the palladium cathode was observed on the concave side of the heavy water cathode near the edges but not on the convex side of the cathode, which faced away from the anode. Silver was detected at surface eruptions near the edges where melting occurred, but not elsewhere. Gold was not observed on this electrode. The evidence for surface melting which was found on the thin palladium cathode was not apparent on the thicker palladium cathode which had gold deposits but not silver. It seems likely that the thinner palladium cathode reached a higher temperature during electrolysis, so that kinetics may have been more rapid on the thinner palladium.

The occurrence of gold and silver in these experiments seems unlikely to have been caused by impurities being deposited in the localized, high concentrations which were observed. On the other hand, these elements could have been produced by transmutation if slow neutrons were present. It is estimated that the average energy of a neutron is reduced by 50% in each collision with a proton. Consider a group of 1 MeV electrons. After about 14 collisions with protons, half of these will have energies less than 1 eV. Neutrons to be used for transmutation are commonly slowed down in paraffin. In our system, protons are present in the electrolyte and in the palladium.

In summary, we have observed excess heat from electrolysis of palladium in both light and heavy water, both of which contained H₂SO₄. Unexpected elements were detected. These may have been produced by transmutation caused by neutrons from fusion reactions which occurred in only a small fraction of the palladium cathodes.

It is essential that these experiments are repeated, using the highest purity materials available, in order to determine if the results reported here are reproducible.
References


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