SURFACE STUDIES OF PALLADIUM AFTER INTERACTION WITH HYDROGEN ISOTOPES

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Abstract: Several pairs of cold rolled palladium cathodes (40 μm thick) were electrolyzed in series for various times up to six minutes. One of each pair was in light water electrolyte and the other in heavy water electrolyte. Atomic force microscopy (AFM) studies performed six months after electrolysis of the heavy water cathodes revealed asperities, craters, and nodules, suggesting that localized melting and recrystallization had occurred, as we reported previously on specimens electrolyzed for longer times. AFM studies 1.5 years later revealed loose, nanometer-sized particles, indicating that the heavy water cathodes continued to change during storage, long after electrolysis was performed, which we also reported previously on other cathodes. The morphology of palladium cathodes electrolyzed in light water electrolyte remained nearly identical to that of the unelectrolyzed control, even two years after electrolysis.

Introduction: Pons and Fleischmann reported that heat not only is generated during the electrolysis of heavy water with a palladium cathode, but also afterward, a phenomenon known as heat after death.[1] In our own research, we have studied the surface topography,[2] thermal output and microchemical composition of palladium[3] and titanium cathodes[4] subjected to electrolysis in heavy water. We have found localized concentrations of unexpected elements,[3-5] and an inversion in isotopic abundance at the surface of a palladium cathode.[5] We have also found that changes in surface topography and microcomposition continue long after electrolysis with a palladium cathode has ended.[4]

Here we will report further results on surface topography obtained after electrolysis with palladium cathodes.

Experimental Methods: The electrolyte for this experiment contained 20 ml D_2O and 3.5 ml H_2SO_4 in one cell and 20 ml of deionized H_2O and 3.5 ml H_2SO_4 in another. The components of each solution were allowed to equilibrate for a minimum of 24 hours. A palladium foil (AESAR lot#D12E06 and stock#11514) was cold-rolled into a strip of thickness 40 μm from its initial thickness of 510 μm. Six pieces of 2 cm by 0.8 cm were cut from this, and one end of each piece was spot welded to a long platinum wire, flattened at one end. The foils were utilized as cathodes, three for the light water cell and the other three for the heavy water cell. An extra piece was cut from the palladium foil to study as a control piece. Platinum foils were used as anodes.

Before electrolyzing, the palladium cathodes were ultrasonically cleaned in methanol for eight minutes, after which they were rinsed in deionized water and blown dry. A portion of each cathode was above the electrolyte solution, and a strip of tape was applied above the solution line to prevent the electrolyte from creeping upward.

Each experiment used two cells linked in series, one containing D_2O electrolyte and the other containing H_2O.[3] These cells were connected to a constant current DC power supply (Harrison 6202B) to produce an ionic current through the solutions. One pair of cathodes underwent electrolysis for six minutes before manual shut down. A second pair of cathodes was afterwards electrólyzed within the same solution for four short periods totaling 1 minute and 45 seconds. A third pair of cathodes was electrolyzed for slightly above three minutes. Upon terminating the experiments, the palladium cathodes were ultrasonically cleaned in methanol, rinsed in deionized water, dried, and stored in petri dishes. AFM studies were performed six months later for all cathodes, which were then returned to their petri dishes, until 1.5 years later, when each was once again studied in the same way on both sides.

Observations were made on a Nanoscope III (Digital Instruments) in air at room temperature, using both height-mode and force-mode methods. The height mode allowed for quantitative measurements for the vertical scale. A resolution of 50 nm was typically achieved to image nodules and other features. A metallurgical microscope (AH-2 Olympus) was used in support of the AFM for low magnifications.

Results and Discussion: All D_2O cathodes bent toward their anodes during electrolysis. The submerged cathode ends were between 45° and 90° to their unsubmerged parts. The H_2O cathodes bent only slightly toward their anodes.

Metallurgical microscope photographs (produced 2 years after electrolysis) illustrate the differences between a sample electrolyzed for six minutes in H_2O electrolyte and a sample electrolyzed for six minutes in D_2O electrolyte (Fig. 1). The parallel lines from cold rolling are readily apparent in the former (similar in appearance to the unelectrolyzed sample) but not in the latter. The pitting observed for the palladium cathode electrolyzed in D_2O electrolyte suggests extensive erosion during electrolysis in the heavy water electrolyte, implying that the metallic bonding of this palladium cathode is lessened by electrolysis in D_2O. There was no chemical dissolution of palladium during immersion in the H_2SO_4-D_2O solution for one hour at 27°C.[2] Therefore, the erosion during electrolysis in heavy water

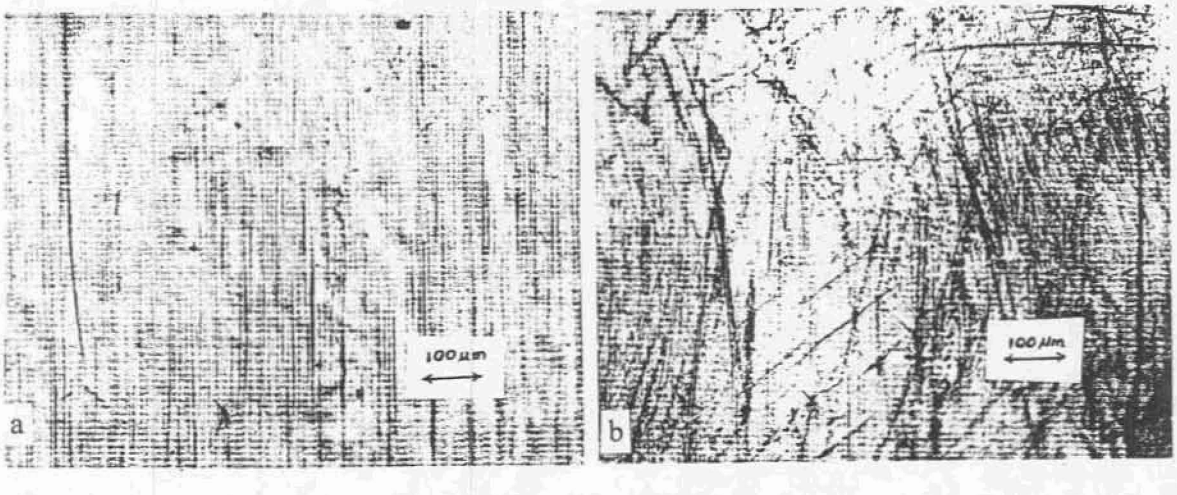

Figure 1. Metallurgical microscope images comparing surfaces electrolyzed for six minutes in a light water solution (a) and a heavy water solution (b).

electrolyte must be caused by the deuterium produced at the cathode and absorbed by the palladium.

An AFM force-mode image and section profile of the palladium cathode electrolyzed for 1 minute and 45 seconds (Fig. 2a) shows an asperity, which appears to be the result of localized surface melting followed by recrystallization. This is similar to features observed on a 12 minute palladium cathode after electrolysis in D_2O electrolyte.[2] The angle, 70.5°, between the two sets of parallel lines suggests that these are traces of {111} planes. An AFM section analysis (Fig. 2b) indicates that this feature rises about 1 μm above the surrounding surface.

Comparing a second set of AFM images taken 1.5 years later than those taken originally from the six minute electrolyzed sample in the D_2O solution, we observed changes of surface characteristics (Fig. 3). In addition to the surface anomalies observed six months after electrolysis, there are now high concentrations of particle debris, an effect likely associated with the 'heat after death' phenomenon.[1] The three minute heavy water electrolyzed sample, which originally showed fewer topographical features than its corresponding six minute heavy water sample, also contained particle debris after two years, but to a lesser extent. The sample electrolyzed repeatedly for 1.75 minutes total in heavy water also acquired granularity after two years. Grains easily detached from the palladium surface were affected by the relative movement of the AFM atomically sharp tip. These grains moved in response to its linear motion. Real time grain motion appears as 'skid marks' viewed on the video screen (Fig. 3b and 4a). High scan frequencies usually resulted in a destroyed tip. Subsequent ultrasonic cleaning removed the observed loose grains from the heavy water samples. None of the palladium samples electrolyzed in H_2O solutions, in contrast, exhibited any granularity during any of our studies (Fig. 4b), even after two years.

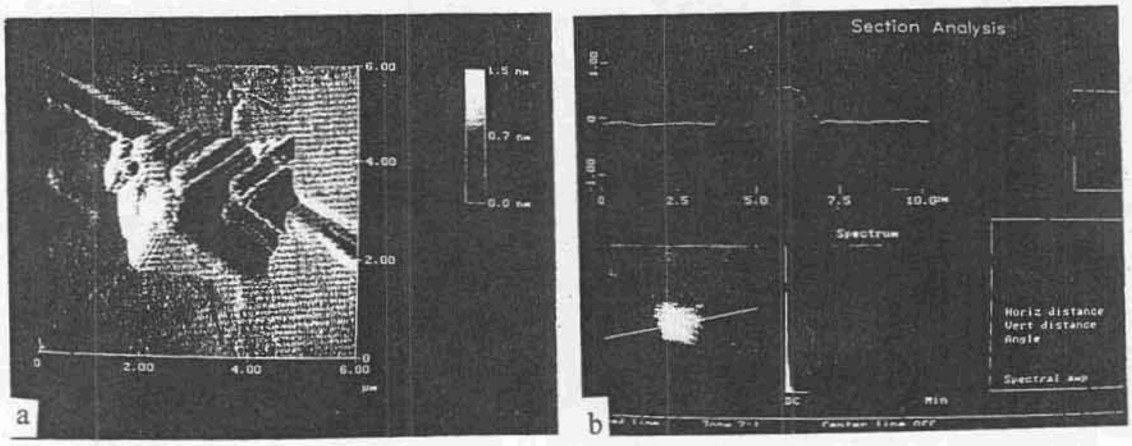

Figure 2. An AFM force-mode image (a) of the palladium cathode side facing away from the anode, electrolyzed for 1 min, 45 sec. Angles of facets suggest the traces of {111} planes. A section (b) analysis indicates the asperity rising about 1 μm above the surrounding surface.

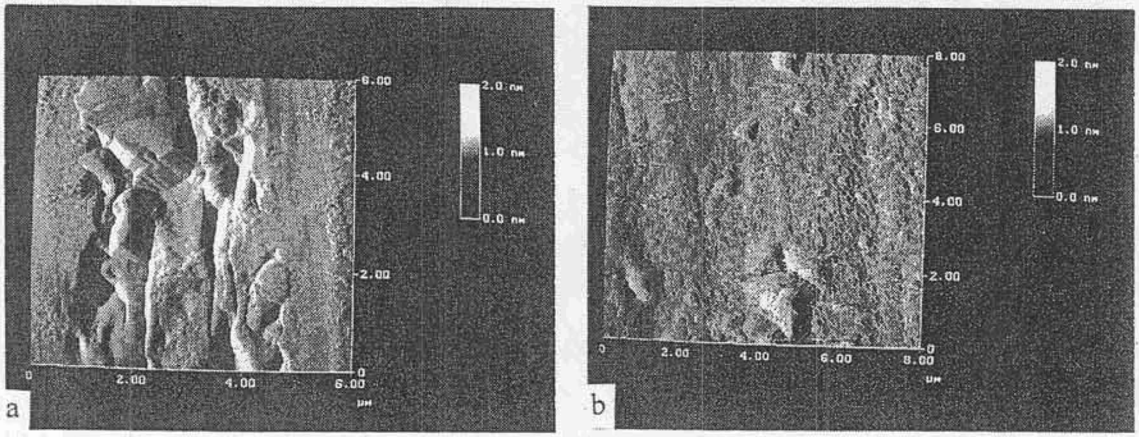

Figure 3. An AFM force-mode image of the D_2O electrolyzed sample (a) 6 µm area, and (b) 8 µm area two years after electrolysis, illustrating an increased granular texture.

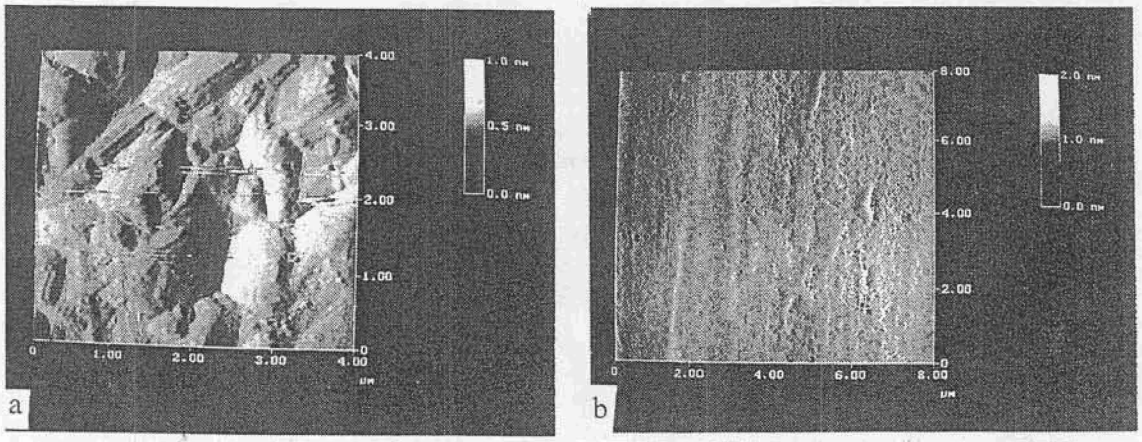

Figure 4. An AFM force-mode image of the six minute sample electrolyzed in (a) D_2O electrolyte shows 'streaks,' unlike that exposed to the (b) H_2O electrolyte.

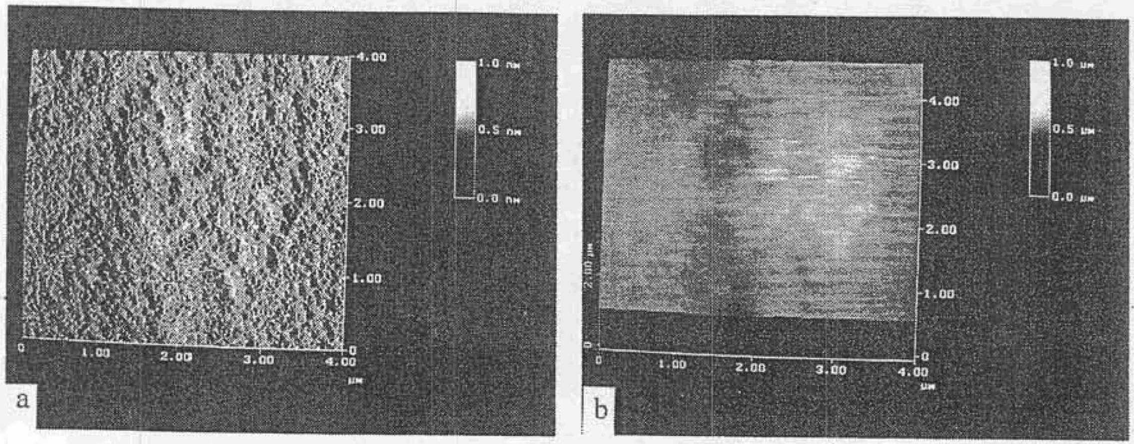

Figure 5. Intensive granularity imaged from both the (a) force-mode and (b) height-mode AFM scans for the six minute D_2O sample two years after electrolysis.

Secondary ion mass spectrometry has also been performed on the H_2O and D_2O samples electrolyzed for six minutes. Inversions of isotopic abundance were observed for the D_2O but not the H_2O sample.[6]

Conclusion: Macroscopic and microscopic deformation of the palladium is produced from the beginning of electrolysis. The prominent microscopic features are: a) micron-sized craters, b) surface asperities, such as nodules, c) crystal planes, indicating melting, evaporation, and recrystallization. Pit formation followed by an increase in asperity and loose particle debris suggest continuous evolutionary changes over the surface.

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REFERENCES

1. S. Pons and M. Fleischmann, *Trans. Fusion Technology*, **26**, 87 (1994).
2. D. S. Silver, J. Dash, and P. S. Keefe, *Fusion Technology*, **24**, 423 (1993).
3. J. Dash, G. Noble, and D. Diman, *Trans. Fusion Technology*, **26**, 299 (1994).
4. J. Dash, R. Kopecek, and S. Miguet, *Proceedings of the 32nd Intersociety Energy Conversion Engineering Conference*, **2**, 1350 (1997).
5. J. Dash, *Proceedings of the 6th International Conference on Cold Fusion*, **2**, 477 Hokkaido, Japan, (1996).
6. D. S. Silver, Ph.D. Dissertation, Portland State University (1998).