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Morphological differences between hydrogen-loaded and deuterium-loaded palladium as observed by scanning electron microscopy

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INTRODUCTION

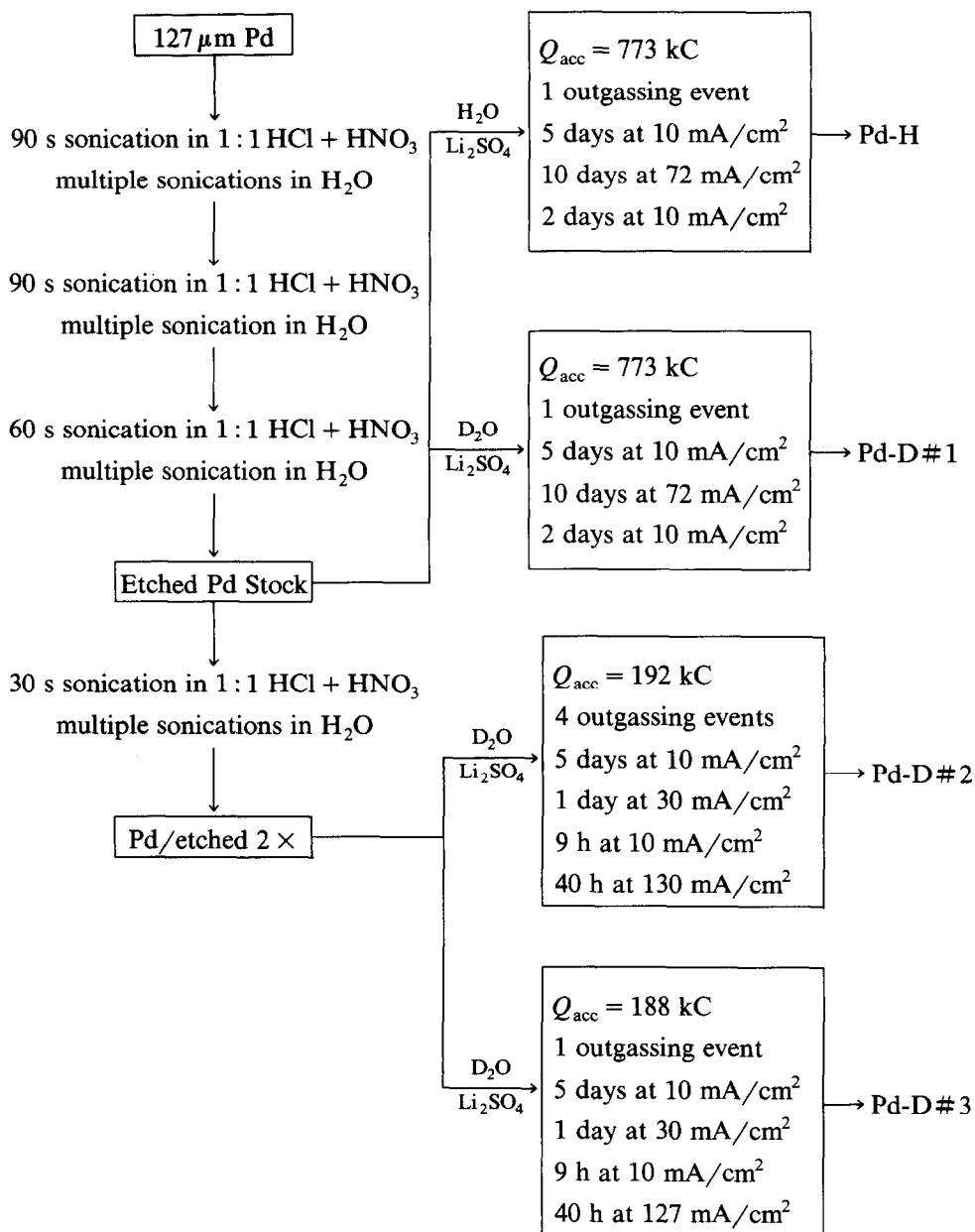
Among researchers achieving success in the replication of the Fleischmann–Pons effect [1], the necessity to determine the physical, chemical, and metallurgical nature of the palladium surface before and after long-term electrolysis of D₂O solutions has been emphasized [2,3]. Our efforts to characterize the Pd–D₂O system have focused on the surface analysis of Pd foils before and after electrochemically loading the Pd with hydrogen or deuterium and a number of anomalous results have been obtained by mass spectrometry and X-ray photoelectron spectroscopy [4–6].

Scanning electron micrographic (SEM) surveys of the surface morphology of Pd foils after electrolysis of H₂O and D₂O also indicated that some differences result, but it became clear that the starting morphology of the etched Pd foil affected the development of the characteristic morphological features and structures observed for the Pd after electrolysis. With this as a concern, two series of experiments were run where the starting morphology of the etched Pd foil was known. This paper describes briefly the structural and intragranular differences that result when, as electrochemically prepared, deuterium-loaded and hydrogen-loaded Pd are compared.

EXPERIMENTAL

A large piece of 0.127 mm Pd foil (99.9% pure, as determined by spectrographic analysis [5], and oriented, primarily in the $\langle 200 \rangle$ direction [4]) was etched in 1:1 HCl + HNO₃ as described in Scheme 1. Ultrasonication of the viscous etchant was

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Scheme 1. Etch procedure used to prepare two sets of Pd with known initial etch morphology and the electrochemical conditions and charging history of the resulting samples.

used to minimize the adherence of the acid to the surface of the foil and to maximize the effectiveness of the rinsing steps. This piece of Pd is referred to as the etched Pd stock; a portion was reserved for SEM analysis. All electrode samples are derived from this piece of etched Pd.

The electrochemical cell, described previously [4], conformed to the Fleischmann and Pons design [1], so that the Pt-wire anode (99.999%, Alfa), wound around a glass-rod cylindrical cage, surrounded the Pd foil cathode concentrically. A spot-welded contact was made between the Pd foil and Pd wire (0.5 mm diameter, 99.9%, Aldrich). The Pd was electrochemically loaded with H or D (as appropriate) by charging at a constant current of 10 mA/cm² using the galvanostatic mode of a EG&G PAR Model 173 potentiostat/galvanostat. Cell voltage was monitored by connecting the reference and auxiliary electrode leads to the electrometer (EG&G PAR Model 178). Solutions were 0.1 M Li₂SO₄ (anhydrous, Alfa) in H₂O, triply distilled from quartz, or D₂O (Cambridge Isotope Laboratories). The Pd electrodes were ultrasonicated in the appropriate solvent before immersion in electrolyte.

Two 1.5 × 4.2 cm strips were cut from the etched Pd stock and identically charged (see Scheme 1) to a total accumulated charge of 773 kC, one in H₂O (designated as Pd-H) and the other in D₂O (designated as Pd-D #1). The remaining portion of the etched Pd stock was re-etched in 1:1 HCl + HNO₃, see Scheme 1; this piece is designated as Pd/Etched 2 ×; a portion was reserved for SEM analysis. Two strips (~ 0.95 × 3.8 cm), cut from Pd/etched 2 ×, were charged to ~ 190 kC of total accumulated charge in D₂O. This set of samples differs in the number of outgassing events imposed during the charging history, as summarized in Scheme 1. An outgassing event is defined as the vigorous outpouring of gas bubbles observed at the surface of a Pd cathode when the charging current (or the electrochemical cell) is shut off. Pd-D #2, charged to 192 kC, had four outgassing events, while Pd-D #3, similarly charged to 188 kC, had only one outgassing event.

Scanning electron microscopy was performed with a Hitachi Model S-800 Field Emission electron microscope. Photomicrographs, derived from the secondary electron signal from the samples, were made in the normal mode and, to emphasize surface topography, in the differential mode.

RESULTS AND DISCUSSION

The etched pieces of Pd have clearly defined grain boundaries visible by eye and at 40 ×. The general level of contrast at this low magnification reveals greater brightness for some crystal grains, indicative of greater intragranular roughness; this is confirmed by study at higher magnification. The relative brightness of the roughened grains, as observed at 40 ×, increases after electrolysis of D₂O. Characteristic of both the etched Pd stock and Pd/etched 2 × is the presence of some (~ 20–30% of the surface) dark crystal grains, which are smooth and essentially featureless at high magnification.

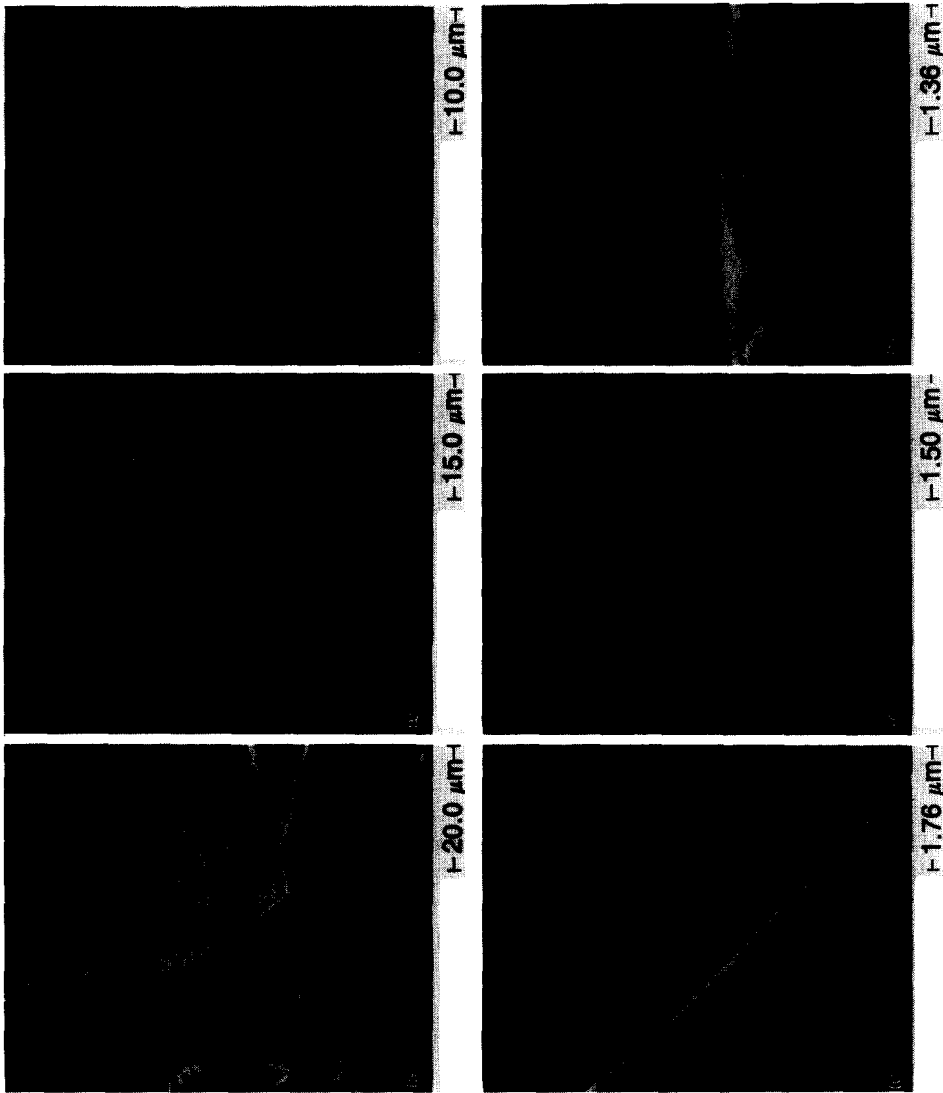


Fig. 1. Photomicrographs (normal mode) comparing the etched Pd stock before electrolysis (a, d) and after electrolysis of 0.1 M $\text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ (Pd-H, b, e) and electrolysis of 0.1 M $\text{Li}_2\text{SO}_4 + \text{D}_2\text{O}$ [Pd-D#1, (c) and (f)]: (a) tilt = 30°; (b) tilt = 22°; (c) tilt = 30°; (d) tilt = 30°; (e) tilt = 30°; (f) tilt = 30°.

H-loaded Pd vs. D-loaded Pd

We observed Pd surfaces with minimal electrodeposited contaminants [4] due to the lesser etchant nature of Li_2SO_4 solutions relative to LiOD or LiOH solutions. Figure 1 documents the characteristic way in which these two types of grains – dark, smooth, and unstructured vs. bright and structured – alter from the initial etch morphology (Fig. 1, a and d), through electrolysis of H_2O (Fig. 1, b and e), and electrolysis of D_2O (Fig. 1, c and f).

The grains representative of the roughened grains for the etched Pd stock are shown in Fig. 1a, upper right; on the micrometer scale, this roughened structure can be seen to be sponge-like and relatively superficial (Fig. 1d, upper right). The dark, smoother grains for the etched Pd stock are seen in the lower left of Fig. 1, a and d.

After electrolysis of $\text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$, the structured grains characteristic of Pd-H are those seen in Fig. 1b, lower right. Compared on a scale of tens of micrometers, the Pd-H features are more homogeneous across the grain and the surface appears more polished relative to the surface structure of the roughened grains of the etched Pd stock. On the micrometer scale, the structure is that of regularly spaced and shaped mounds (Fig. 1e, upper right). Dark, smooth grains persist after H_2O electrolysis and are seen in Fig. 1b, upper left and Fig. 1e, lower left.

After electrolysis of $\text{Li}_2\text{SO}_4 + \text{D}_2\text{O}$, the bright, structured grains characteristic of Pd-D#1 are those seen in Fig. 1c, lower half, where the features are both more intragranularly homogeneous than the etched Pd stock and individually more rugged than Pd-H. On the micrometer scale (Fig. 1f, upper half), the peaked, “alpine” appearance of this structure is apparent. Again, dark, smooth grains persist after D_2O electrolysis, as seen in Fig. 1c, upper half and Fig. 1f, lower half.

What is not apparent across the grain surfaces of Pd-D#1 and Pd-H, even at high magnification, are cracks and fissures indicative of catastrophic release of D_2 or H_2 upon breaking the electrochemical circuit. Because the degree of etching is sufficient to remove the cold-worked layer and reveal well-defined grain boundaries, the outgassing event is probably less mechanically disruptive in these samples than when the grain boundaries are buried.

What is apparent is that the etched grains restructure with electrolysis to form a uniformly featured, high surface area morphology. Surprisingly, the nature of the surface morphology upon electrochemical restructuring differs for H-loaded Pd vs. D-loaded Pd, even when the initial etch morphology is the same.

D-loading of Pd / etched 2×

Further etching of the etched Pd stock leaves a starting morphology of greater uniformity across those crystal grains which do roughen; the patchy nature of the etch as seen for the etched Pd stock (Fig. 1a, upper right) is gone. Dark, smooth crystal grains persist, however, as seen in Fig. 2a. The nature of the structured grains after electrolysis of D_2O is related to that seen for Pd-D#1, but the features are deeper and more developed and dramatic in appearance. Three characteristic morphologies are observed for Pd-D#2 and Pd-D#3; the number of outgassing events did not affect the types of characteristic surface structures observed.

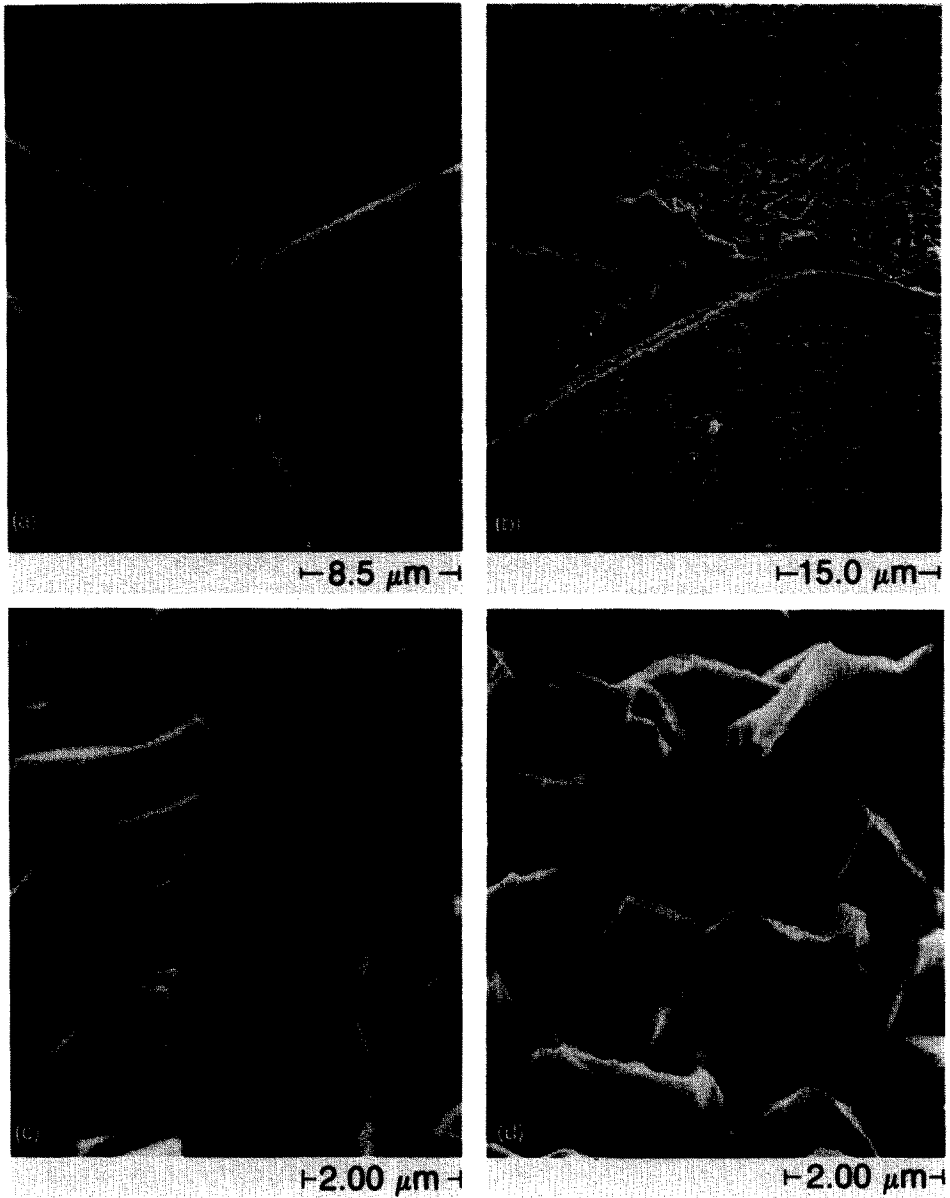


Fig. 2. Photomicrographs (normal mode) comparing Pd/etched 2× before (a) and after electrolysis of 0.1 M $\text{Li}_2\text{SO}_4 + \text{D}_2\text{O}$: (a) tilt = 30°; (b) Pd-D#3, tilt = 30°, (c) Pd-D#2, magnification of the characteristic "alpine" structure seen in (b), lower half; tilt = 22°; (d) Pd-D#3 magnification of the intertwined structures seen in (b), upper right; tilt = 22°.

Figure 2b captures the intersection of these three characteristic intragranular structures: dark, smooth, featureless grains persist (upper left); the fine, rugged morphology seen for Pd-D#1 is again observed (lower half); and an intertwined morphology is observed (upper right). On the micrometer scale, the “alpine” morphology is that of parallel, thin-edged ridges, see Fig. 2c, whereas the intertwined structures are revealed as perhaps the beginnings of crystal faceting, see Fig. 2d.

Intergranular topographical variance of Pd-D

As the starting Pd foil is primarily oriented in the $\langle 200 \rangle$ direction, it is tempting to assign the structured grains to an $\langle n00 \rangle$ orientation, which is more open in the fcc structure, and presumably more susceptible to etching and reaction. Likewise, the persistence of some essentially unstructured, featureless intragranular surfaces after strong etch conditions and long-term electrochemically reactive conditions (to form the hydride or deuteride forms of Pd) strongly suggests a crystal orientation that is resistant to reactive attack. Obviously, the etch (which removes on the order of tens of micrometers of material from the surface) does remove Pd from these grains or topological relief would be evident upon etching and is not. Lewis shows micrographs of the $\langle 100 \rangle$ and $\langle 111 \rangle$ faces of single-crystal Pd after electrolytic loading with hydrogen; however, the initial morphologies, conditions of loading, and even the scale of the micrograph are not given (ref. 7, p. 48).

Photomicrographs taken in the differential mode for the Pd-D samples did unveil elevational differences between the structured grains and the smooth, unfeatured grains. Stereopairs were made in 2–3 locations for the etched Pd stock, Pd/etched



Fig. 3. Stereopair of Pd-D#3 showing the elevational uplift of the structured crystal grains relative to the dark, smooth crystal grains, (a) tilt = 22° ; (b) tilt = 30° .

$2\times$, Pd-H, and all Pd-D samples. The field and magnification were chosen to include an entire dark, smooth grain surrounded by structured grains, as shown by the stereopair of Fig. 3. Elevational differences were only apparent for the Pd-D samples. Study of the stereopairs through a stereoviewer revealed that the structured grains were uplifted relative to the dark, smooth grains for Pd-D#1, Pd-D#2, and Pd-D#3.

The force uplifting the structured grains above the smooth, featureless grains is unlikely to be due to mechanical expansion of the crystal lattice caused by formation of the palladium deuteride phase since the palladium lattice must expand even more to form palladium hydride [7], and no uplift was found for Pd-H. The quantification of the height of the uplift is under way, but qualitatively, there appears to be no dramatic difference between Pd-D#2 and Pd-D#3, indicating that multiple outgassing events do not increase the magnitude of uplifting. There also appears to be an equivalent degree of uplift when comparing Pd-D#1, with four-fold greater accumulated charge, to Pd-D#3.

When the electrochemical circuit is broken and a vigorous burst of gas rushes out of the Pd cathode, the outgassing is visibly more explosive and copious for the Pd-D₂O system than for the Pd-H₂O system. This observation accords with the fact that D is held less strongly by the Pd lattice and is faster diffusing in Pd than is H [7,8]. During a non-equilibrium process, such as deuterium or hydrogen unloading due to loss of potential or current control, the initial explosion of gas from the near-surface region of the Pd would be expected to be greater for D than for H.

These experimental and observational facts, i.e., (i) the persistence of smooth, featureless, crystal grains, apparently unaffected by deuterium or hydrogen loading, which are sunken relative to the crystal grains which actively restructure with electrolysis, but only for deuterium loading, (ii) a visibly more explosive discharge of D₂ than of H₂ when the electrochemical circuit is broken, and (iii) no obvious increase in the magnitude of the intergranular uplift/depression with multiple loading/unloading events, lead us to assign the uplifting of the electrochemically restructured crystal grains to the premier episode of outgassing when the rapid and mechanically stressful outrush of D₂ from these highly loaded grains (probably along the well-defined grain boundaries) leaves the less D-loaded, possibly unloaded, featureless crystal grains behind.

CONCLUSION

Our SEM results show that the degree of the initial etch regulates the development of the surface structures that form with electrolysis of D₂O and H₂O, doing so probably through the number of reaction sites, as the more highly etched surfaces provide greater initial reactive surface area. Electrolysis of either light or heavy water at Pd restructures these roughened grains and produces greater intragranular homogeneity and features of higher surface area; in addition, a different structure results for PdD_x than for PdH_x. An additional series for PdH_x and PdD_x with a

starting morphology akin to Pd/etched $2 \times$ is being prepared to confirm this latter observation.

The "alpine" features observed for PdD_x, with parallel rows of sharply edged ridges, may offer some of the asperity characteristic of dendrites. One of the crystal orientations remains featureless and unstructured with electrolysis in either D₂O or H₂O. These unstructured grains are depressed in elevation relative to the structured grains, but only for PdD_x. Our results are in accord with the idea that the reactivity of cathodic surfaces depends on at least three microscopic factors: grain orientation, surface preparation and the nature of the species being reduced.

On a speculative note, our SEM results imply that studies of the Fleischmann-Pons effect with Pd single-crystals of an orientation characteristic of the smooth, featureless crystal grains would be spectacularly unproductive. Attempts to determine microscopically the crystal orientation of the structured and smooth grains are under way.

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REFERENCES

- 1 M. Fleischmann, S. Pons, and M. Hawkins, *J. Electroanal. Chem.*, 261 (1989) 301; err. 263 (1989) 187.
- 2 Panel Discussions, 1st Annu. Conf. on Cold Fusion, Salt Lake City, UT, 28-31 March 1990.
- 3 L.E. Murr, *Scripta Metallurg. Mater.*, 24 (1990) 783.
- 4 D.R. Rolison and W.E. O'Grady, Proc. NSF-EPRI Workshop on Anomalous Effects in Deuterated Metals, Washington, DC, 16-18 October 1989.
- 5 D.R. Rolison and W.E. O'Grady, in preparation.
- 6 D.R. Rolison, W.E. O'Grady, R.J. Doyle, Jr., and P.P. Trzaskoma, Proc. 1st Annu. Conf. on Cold Fusion, Salt Lake City, UT, 28-31 March 1990.
- 7 F.A. Lewis, *The Palladium Hydrogen System*, Academic Press, London, 1967.
- 8 G.T. Cheek and W.E. O'Grady, *J. Electroanal. Chem.*, 277 (1990) 341.