# The Effect of Microstructure on Deuterium Loading in Palladium Cathodes

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## Abstract

The effect of micro structure on deuterium loading in palladium cathodes was investigated. Cathode micro structure is determined by thermomechanical processing that includes electrode deformation (swaging) and the annealing conditions (time and temperature). Results will be presented on the extent of deuterium loading in rod-shaped (0.4 cm in diameter and 3.5 cm long) cathodes with controlled microstructure produced at The Naval Research Laboratory (NRL). Loading on NRL cathodes will be compared with that attained on commercially available electrodes routinely used at other laboratories.

Deuterium loading of the electrodes was accomplished electrochemically in 2.5 cm diameter by 15 cm length borosilicate-glass cells containing 0.1M LiOD in $D_2O$ as the electrolyte and a cylindrical Pt anode. Loading was monitored in-situ by measuring the change in the axial resistance of the cathode and comparing the measured values with the known relationship between resistance and the D/Pd atomic ratio. Comparison of deuterium loading in well-controlled electrochemical experiments on Pd cathodes with different microstructure indicate that loading is facilitated in cathodes with large grains. In addition, it was found that commercially processed, high purity Pd (99.99% or better) produced limited grain growth compared to lower purity material under the typical annealing conditions (1100°C for 20 hours in vacuum) because of small residual stress.

## Introduction

Anomalous effects, which include the production of excess power, helium-4, tritium and other forms of low energy radiation, have been reported in deuterated Pd systems. The experimental observations of anomalous effects are not generally reproducible, however. Many reasons for the lack of reproducibility have been postulated. These include variations in the composition and microstructure of the electrode materials, differences in the electrode geometry, and levels of deuterium loading attained. Results are presented in which the electrode material was thermomechanically processed to control the microstructure, characterized both chemically and metallurgically, and loaded electrochemically with either deuterium or hydrogen. The extent of loading is correlated with Pd microstructure. Loading on NRL Pd cathodes is compared to that attained on commercially available material used at other laboratories.

**Experimental**

**Palladium Electrode Material Processing and Characterization.** Thermomechanical processing was done to produce an electrode material with a homogeneous composition, controlled microstructure, and minimal defects. A single batch of high purity (nominally 99.999%) Pd sponge from Johnson Matthey was used as the starting material for cathode preparation. Both rod and plate cathode geometries were prepared. Processing for rod-shaped electrodes (0.4 cm diameter × 3.5 cm length; surface area = 4.5 cm$^2$) consisted of arc-melting, casting, swaging, machining, and annealing. For plate electrodes (0.07 cm × 0.7 cm × 3.5 cm; surface area = 4.9 cm$^2$), processing involved arc-melting, rolling, annealing, rolling again, machining, and re-annealing. For both rod and plate cathodes, arc melting was carried out in a water-cooled copper hearth, dry machining was used to avoid contaminating the cathode material with oil or water, and annealing was done in a vacuum of 10$^{-5}$ torr or better. Annealed samples were cooled slowly in the furnace under an argon atmosphere to room temperature.

Cathode microstructure was determined by controlling the deformation and the annealing conditions. A separate metallurgical study was undertaken to examine grain growth behavior in Pd rod-shaped cathodes. The results of this study are shown in Figure 1 for Pd at a deformation level of 80% cold-rolled at 650°C and 950°C. In Figure 2 the grain size variation in a Pd rod annealed at 650 °C for 1 hour is shown in an optical micrograph. The grain size variation was related to the deformation.
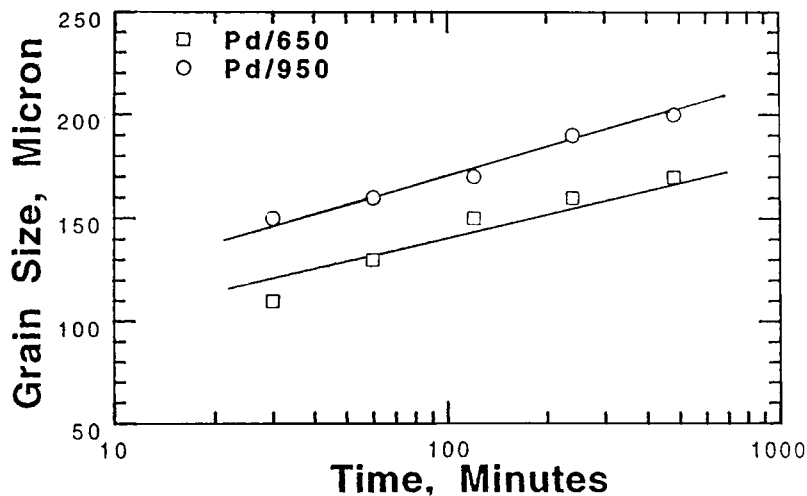


Figure 1. Grain growth vs. time plots for palladium cathodes (rods) processed at NRL. The starting materials were deformed to 80% by cold rolling and annealed at 650°C and at 950°C.

400 μm

Figure 2. Optical micrograph of NRL palladium rod after annealing in vacuum ($<10^{-5}$ torr) at 650°C for 1 hour. The micrographs show large grains close to the center and finer grains near the surface because of the gradient of residual stress before annealing.

Plate electrodes were examined because the microstructure of plates is easier to control than that of rods since plates undergo less deformation in processing. As such, plate electrodes were expected to have a more uniform cross-section. Cross-section uniformity was expected to (1) remove diffusion barriers due to stresses present in the rods, (2) lead to more uniform loading and (3) lead to faster loading.

Grain size variations in rod and plate electrodes were obtained by varying the annealing conditions (time and temperature). Samples of rod and plate electrodes were given simultaneous annealing treatments for comparison. One pair of rod and plate electrodes was not annealed, a second pair of each was annealed at 650°C for 1 hour, and a third pair of each was annealed at 1100°C for 20 hours. The processing resulted in electrodes with elongated grains from cold working the material and those with equiaxed grains. A comparison of optical micrographs for the corresponding rod and plate cathodes showed little or no difference in microstructure. Electrodes annealed at 650°C and 1100°C had average grain sizes of 44 and 600 μm, respectively. Since the unannealed electrodes likely had more defects and strain than the annealed electrode, the effects of these on loading were also investigated.

Glow-Discharge Mass Spectroscopic (GDMS) Analysis (Shiva Technologies, Inc.) was used to determine the chemical composition of the Pd electrode materials. GDMS is a direct elemental analysis method for solids. The method analyzes for 76 elements in one cycle and has detection limits in the ppb concentration range. GDMS is considered to be a pseudo-"bulk" analysis

technique since samples are analyzed end-on and several mm of sample are consumed in the analysis. The precision of GDMS analysis is generally ±10-15%, although light elements and halogens may have larger errors.

Two separate GDMS analyses were made on the as-received Pd sponge starting material. Selected elements from the analytical reports of these samples are shown in Table 1. As seen from the Table, the sponge had several metallic impurities present at the ppm concentration level: Na,, Ti, Cr, Fe, Ni, Rh, Ag, Ta, W, Pt, and Au. Differences noted in the analyses are attributed to inhomogeneities in the different samples of starting material. The purity of the starting material was found to be 99.99%, not 99.999% as specified.

GDMS analyses of NRL-processed Pd rod and plate cathodes (Table 1) showed an increased concentration of Cu, W and Pt over the starting material. Although care was taken to avoid contamination, these impurities were likely introduced into the samples during processing from the arc melter and the tools used to handle the material. In spite of the higher concentrations of these few impurities, the analyses showed that the purity of the processed materials remained essentially 99.99%.

Table 1 - Selected Elements from Glow-Discharge Mass Spectroscopic Analyses of NRL Palladium Cathodes (concentration in ppm by weight)

| Element | Pd sponge 9/16/92 | Pd sponge 3/31/94 | Pd rod 3/31/94 | Pd rod 11/28/94 | Pd plate 3/31/94 |
|---------|-------------------|-------------------|----------------|-----------------|------------------|
| B | 0.1 | 0.007 | <0.005 | <0.001 | <0.005 |
| C | 5 | <10 | <1 | 0.01 | <0.1 |
| N | 1 | <0.1 | <0.1 | 0.03 | <0.1 |
| 0 | 10 | <20 | <0.5 | 0.36 | <1 |
| Mg | 0.1 | <0.01 | 1.2 | — | 1.7 |
| Al | 0.5 | 0.06 | 0.3 | 0.52 | 0.3 |
| Si | 0.6 | 0.15 | 1 | 0.32 | 9.6 |
| Ca | 0.5 | <0.05 | 0.8 | 0.67 | 1.1 |
| | | | | | |
| Cr | 2.5 | 2.8 | 1.1 | 1.2 | 1.8 |
| Mn | 0.9 | 1.3 | 0.75 | — | 1.1 |
| Fe | 45 | 31 | 30 | 33 | 50 |
| Ni | 1.3 | 1.1 | 0.84 | 0.96 | 1.3 |
| Cu | 0.8 | 0.44 | 31 | 24 | 12 |
| Zn | 0.9 | 0.3 | 1 | 1.1 | 2 |
| Rh | 8 | 6.3 | 9.3 | 10.5 | 11 |
| Ag | 1.5 | 1.6 | 1.1 | 1.1 | 1.7 |
| W | 1 | 0.01 | 0.5 | 3.4 | 3 |
| Pt | 12 | 6.3 | 31 | 29 | 26 |
| | | | | | |
| Total | 92 | 82 | 111 | 106 | 124 |

**Electrode Pretreatment and Cell Assembly.** After machining the electrodes with four grooves for the Pt resistance wires, cathodes were either annealed or left as processed. Regardless of the treatment, Teflon-coated Pt lead wires were attached to the cathodes by spot welding. A 30 second etch in either "heavy" or "light" aqua regia followed the spot-welding to remove contaminates from the cathode surface. Other NRL work [1] showed that the etch also increases the initial reactive surface area of the Pd and aids in the development of surface structures that form with $D_2O$ or $H_2O$ electrolysis. The isotopically appropriate water was used to rinse the cathodes after an etch. Either Pt-clad Nb mesh, Pt mesh, or Pt helical anodes were used in the electrochemical loading experiments. Anodes were cleaned by immersion in a 50-50 mixture of concentrated nitric and sulfuric acids, rinsed with triply distilled water and oven dried in air.

Borosilicate-glass test tubes (2.5 cm O.D. × 15 cm length) were used as electrolysis cells in our experiments. The cells were fitted with Teflon stoppers and sealed with Viton o-rings. Cell tops held small diameter Teflon tubing for exit gases and electrolyte additions. Cathodes were centered within the circumference of the cell and cylindrical anodes were place symmetrically around the cathode. Cell assembly was done on the benchtop using clean, latex gloves to avoid excessive handling of the cell components. Serious attempts were made to avoid introducing impurities into the electrolytic cells in order to obtain reproducible electrochemical experiments. As such, only high purity reagents were used and precautions were taken to minimize the exposure of all reagents to the ambient atmosphere to avoid contamination with light water. Unopened bottles of deuterium oxide (Cambridge Isotope Laboratories, 99.9% or Ontario Hydro, 99.93%), cans of lithium foil (Johnson Matthey, 99.9%), aluminum shot (Johnson Matthey, 99.999%) and deuterated hydrochloric, nitric, and sulfuric acids were taken into a glove box with a boil-off nitrogen atmosphere for storage on receipt of the materials. Freshly prepared, 0.1 M LiOD electrolyte was made in the glove-box by dissolving Li metal in heavy water before each new electrochemical experiment. Reagents for light water experiments were stored outside the glovebox on the benchtop.

## Results and Discussion
**Electrochemical Loading Experiments on NRL Cathodes.** Two nearly identical electrolytic cells were connected electrically in series in each electrochemical loading experiment. Usually, one cell contained heavy water while the second cell contained light water. Cells were run under galvanostatic control. Electrode loading was started as soon as possible after electrolyte addition (electrolyte volume was 30 mL). Initial charging was usually done with current densities of 20-25 mA cm$^{-2}$ on the cathodes. For 0.4 cm diameter rod electrodes, initial charging took 2-3 days. Deuterium or hydrogen loading reached a D(H)/Pd atomic ratio of 0.70-0.75 during this time. The current density was then increased in 20-25 mA cm$^{-2}$ steps every day or two to continue the loading.

Electrolyte was replenished with $D_2O$ or $H_2O$ before the total volume in the cell was 5 mL below the starting level. This procedure kept the cathode and anode completely submerged. The frequency of additions varied depending on the current density applied. For 0.4 cm diameter Pd cathodes at low current densities (25-50 mA cm$^{-2}$), additions were made every two or three days. At higher current densities (100-200 mA cm$^{-2}$), additions were made daily. Some electrolyte additions contained small amounts (typically 120-275 ppm) of dissolved aluminum metal.

Aluminum was added to facilitate the I attainment and maintenance of high D(H)/Pd loadings as described by McKubre et al. [2].

During all experiments cathode loading was monitored *in situ* by measuring the change in the axial resistance of the Pd with deuterium or hydrogen content as described by McKubre [14]. The resistance measurements were made with a standard 4-point probe technique. D/Pd and H/Pd loading atomic ratios were estimated from the resistance measurements and plots of the resistance ratio-loading variations in the H/Pd and D/Pd systems at room temperature as shown in papers by McKubre et al. [3]. Loading atomic ratios, H/Pd and D/Pd, are often inferred from these plots, but care is taken in assuming a precise level of loading based on resistance measurements alone since other factors (temperature, electrode cracking, loading inhomogeneities, electrode impurities) can affect the Pd resistance [4].

Electrochemical loading experiments were carried out on six pairs of NRL Pd electrodes with different microstructures. Several observations regarding cathode loading were noted from these experiments. First, deuterium loading in both rod and plate cathodes did not exceed a D/Pd atomic ratio of 0.7-0.75, despite the extent of electrode processing. This level of loading corresponds to the α, β mixed-phase region; loading beyond this level would occur in the β-phase. Second, hydrogen loading into the pure β-phase, where the H/Pd atomic ratio was 0.8-0.85, occurred in the Pd rod with large grain morphology. Hydrogen loading did not exceed a H/Pd atomic ratio of 0.7-0.75 in rod cathodes with less processing. Third, hydrogen loading in Pd plates increased with electrode processing although all the plate cathodes loaded into the β-phase. Hydrogen loading reached a level where the H/Pd atomic ratio was 0.8-0.85 in an electrode with no processing, but it increased to where the H/Pd atomic ratio was approximately 0.95 with electrode processing. The comparison of hydrogen loading in rod and plate electrodes provided evidence that reducing the strain in the Pd led to higher loading.

Our experiments on Pd rod and plate electrodes with different microstructures showed that deuterium loaded more slowly in cathodes with a large grain morphology. Slower loading appeared to be advantageous for attaining higher levels of loading. In addition, thin plate electrodes were found to load more rapidly to D(H)/Pd~0.7 than 0.4 cm diameter rod electrodes with comparable grain sizes. Faster loading in plate electrodes can likely be attributed to the more uniform cross-section of the plates and to their higher surface area to volume (A/V) ratio. The influence of the A/V ratio on loading Pd with hydrogen to the β-phase had been observed by Hoare [5] who compared loading ratios in foils, wires and beads in acid solution.

Eventually, deuterium loading into the β-phase was routinely achieved in NRL rod and plate cathodes with large grain morphology. This was accomplished by improving the cathode surface preparation and better controlling the electrolyte purity. The changes decreased the thickness of surface films that deposited on the Pd and prevented high cathode loading. Resistance ratio-time variations for two pairs of these cathodes are shown in Figure 3 as a function of the applied current. Note that the resistance of the Pd shows a dynamic response to current.

**Comparison With Commercial Cathodes.** GDMS analyses of as-received, commercially available Pd rod and wire were done to confirm the purities of the materials acquired and to identify the impurities present. Selected elements from the analyses are shown in Table 2. As seen from the table, all the materials examined had essentially the purities specified. The Johnson Matthey 99.997% Pd wires (stock#10960) had the highest purity. Both lots (W12954 and W7403) had exceptionally low Fe and Pt concentrations. Lot W7403 had an elevated Si content, however. Pt, Rh, Fe and Si were the major impurities found in the majority of materials at the ppm concentration level. In addition, some 99.9% materials had relatively high concentrations of B, O, Al, Cu and Ag. Other impurities present at the ppm level included C, N, Ca, Cr, Mn, Ni, Zn and W.
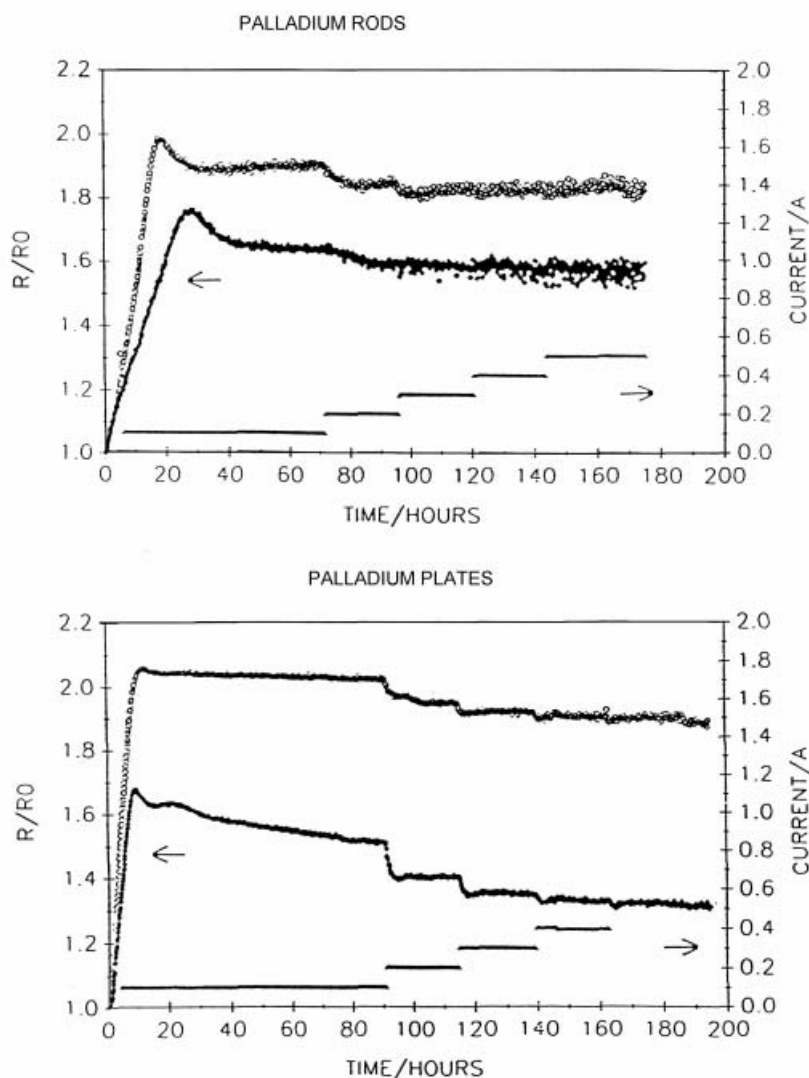


Figure 3. Resistance ratio ($R/R_0$) vs. time variations for two pairs of NRL palladium cathodes as a function of applied current. Open symbols - deuterium, closed symbols - hydrogen.

The commercial Pd rods and wires were annealed at 1100°C for 20 hours to examine the grain morphology produced. The morphology of the grain depends not only on the annealing conditions, but also on how much residual stress was in the sample before annealing. Optical micrographs of the annealed materials showed that samples responded differently to the annealing conditions based on their processing history. For example, the annealing conditions we used produced a large grain morphology in all of the 99.9% materials and the 99.99% Johnson Matthey rod. However, the Johnson Matthey 99.997% wires (stock #10960) and a Goodfellow 99.99+% wire (stock #005155/11 - not analyzed by GDMS) had either fine, equiaxed grains or elongated grains after the anneal. In other words, the commercially processed, high purity (99.99% or better) wires produced limited grain growth compare to the lower purity (99.9%) materials under the annealing conditions because of residual stress in the materials. The grain morphologies observed reflected different thermomechanical treatments of the samples.

Table 2 - Selected Elements from Glow-Discharge Mass Spectroscopic Analyses of Commercial Palladium Cathodes (concentration in ppm by weight)

| Element | J. Matthey 99.9% Wire K11C06 | J. Matthey 99.997% Wire | J. Matthey 99.997% Wire W12954 | Goodfellow 99.95% Wire 005150/11 | Engelhard #3 99.9% Rod | J. Matthey 99.99% Rod | J. Matthey 99.9% Rod F13E05 |
|---|---|---|---|---|---|---|---|
| B | 17 | 0.01 | 0.007 | 2.5 | 140 | 23 | 4.1 |
| C | <5 | <1 | <1 | <1 | <1.8 | <1 | <0.1 |
| N | <0.1 | <5 | <3 | <0.1 | <0.23 | <0.1 | <0.05 |
| 0 | <10 | <20 | <10 | <10 | <290 | <20 | <6 |
| Mg | 0.29 | 0.008 | 0.009 | 0.04 | 0.59 | 0.09 | 0.09 |
| Al | 59 | 0.34 | 0.63 | 2.3 | 12 | 1.1 | 7.6 |
| Si | 67 | 43 | 3.5 | 6.6 | 280 | 1.8 | 16 |
| Ca | 7.3 | 0.11 | 0.29 | <0.05 | 66 | 7.5 | 5.1 |
| Cr | 5.3 | 0.25 | 0.21 | 0.68 | 15 | 1.3 | 1.6 |
| Mn | 1.6 | 0.01 | 0.004 | 0.17 | 0.51 | 0.22 | 0.84 |
| Fe | 95 | 1.1 | 2.9 | 30 | 69 | 14 | 37 |
| Ni | 54 | 0.05 | 0.03 | 1.4 | 1.7 | 0.58 | 1.4 |
| Cu | 24 | 0.11 | 0.76 | 22 | 13 | 2.6 | 6.5 |
| Zn | 5.2 | 0.1 | 0.02 | 2.5 | <0.021 | 0.55 | 3.6 |
| Rh | 110 | 0.56 | 4.2 | 6 | <9.3 | 24 | 71 |
| Ag | 29 | <0.1 | 0.45 | 13 | <76 | 1.6 | 0.7 |
| W | 1.4 | 0.15 | 0.1 | 0.2 | 1.1 | 0.06 | 0.91 |
| Pt | 1100 | 1.9 | 2.2 | 80 | 22 | 28 | 960 |
| | | | | | | | |
| Total | 1591 | 74 | 29 | 179 | 930 | 128 | 1123 |

Based on this limited sample set, a possible correlation was found between sample purity and grain morphology. For example, in the high purity (99.99% or better) wires, hardly any grain growth occurred on annealing whereas all of the lower purity (99.9%) materials readily grew large grains. Very pure samples are generally expected to have very rapid rates of grain growth. Other factors such as the amount of deformation encountered during cold working and the grain size before cold working can have an adverse effect on grain growth.

**Loading Experiments on Commercial Cathodes.** Almost all of the commercial Pd cathode materials (except the Goodfellow 99.99+% wire #005155/11) were used in deuterium loading experiments. The materials were either annealed before being used in the experiments or left as processed. Metallurgical analysis of the annealed materials showed that the grains enlarged in these samples as result of the annealing treatment. Unannealed samples likely had elongated or small, equiaxed grain morphology although a metallurgical analysis was not done on all of these samples.

Electrochemical deuterium loading experiments on the commercial cathode materials were carried out as described in the section on NRL cathodes. In deuterium loading experiments on annealed cathodes with large grain morphology five out of six cathodes were loaded into the β-phase: 1 Johnson Matthey 99.99% rod, 1 Johnson Matthey 99.9% wire (#K11C06), 1 Goodfellow 99.9% wire (#005150/11), and 2 Engelhard #3 99.9% rods supplied by SRI. The annealed cathode that failed to load into the β-phase was a Johnson Matthey 99.99% rod.

Five deuterium loading experiments with unannealed, commercial cathodes were carried out. Only two of these loaded into the β-phase: a Johnson Matthey 99.9% wire (#K11C06) and a Johnson Matthey 99.9% rod (#F13E05). The three unannealed materials that did not load into the β-phase were 2 Johnson Matthey 99.997% wires (#W12954 and W7403) and 1 Goodfellow 99.9% Pd rod (#007940/5).

Based the these results, a possible correlation was found between sample morphology and deuterium loading. Specifically, most samples with a large grain morphology loaded into the β-phase of Pd while those with elongated or small grains were not as readily loaded.

**Conclusions**
1. Electrochemically loading Pd cathodes into the β-phase with deuterium or hydrogen is facilitated in a material with a large grain morphology.
2. Hardly any grain growth occurred on annealing high purity (99.997%) Pd wires at 1100°C for 20 hours whereas high purity rods fend lower purity (99.9%) materials readily grew large grains.
3. Pd cathodes with elongated or small grains did not load into the β-phase while large grain materials loaded readily.

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