An X-Ray Diffraction Study of Lattice Expansion and Phase Transformation in Electrochemically Loaded Palladium Hydrides

D.L. Knies, V. Violante, K.S. Grabowski, J. Hu, D.D. Dominguez, J. He, S.B. Qadri and G.K. Hubler

Time resolved, in-situ, high-energy x-ray diffraction was performed on modified Fleishman-Pons electrolytic cells during electrochemical loading of palladium foil cathodes with hydrogen and deuterium. Concentrations of H and D up to 1:1 in 0.1 M LiOH/LiOD in H$_2$O/D$_2$O electrolytes were obtained with lattice constant data monitored throughout the range of concentrations. In addition to data on lattice constant versus H or D concentration and palladium hydride resistivity, some indication of the rapidity of loading and deloading of hydrogen from the Pd surface was obtained. The alpha-beta phase transformations were clearly delineated but no new phases at high concentration were definitively determined.

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In Situ Energy-Dispersive X-ray Diffraction Study of Thin Pd Foil at D/Pd and H/Pd ~1

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15\textsuperscript{th} International Conference on Cold Fusion, Oct. 4-9, 2009, Rome, Italy
Motivation

- In situ XRD not performed for H/Pd > 0.76 in Fleischmann-Pons electrolytic cells

Possibility of learning

- Does a new γ phase was suggested by Tripodi et. al. for the electrochemically loaded palladium when the composition H/Pd approaching 1 exist?
- Does temperature coefficient of resistivity of PdH versus the concentration of H anomaly show up in Pd crystalline structure (Tripodi et. al.)?
- In the Pd-D system, new phases were found through deuterium thermal desorption spectra. Does anything show up on FPE system (Rybalko et. al.)?
- Report showing oscillating resistivity for palladium hydrides at some concentration range of H/Pd>0.9 (Miley et. al.).

- These proposed phase transitions are only based on indirect experimental data and have not been structurally determined.
Temperature Coefficient of Resistance

Figure 3: Temperature coefficient of resistivity $\lambda$ for all phases. The dashed is the plateau value for $\lambda$. 
Pd Foil Cathodes

- Pd 0.9995 purity fabricated at ENEA by V. Violante

- Rolled from 1 mm thick bar to 50 μm thickness, annealed 850 C for 8 hours, etched in aqua regia for 2 minutes, cleaned in water and alcohol

- 20 mm x 40 mm dimension

- ~100 μm grain size
Electrochemical Cell

- Designed and built by ENEA
- Dual Pt anodes
Electrochemical Cell

Electrochemical Cell [electrolyte: 0.1M LiOD in D₂O]

Catalyst in CLOSED CELL

Pt Anodes

Pd Cathode

Thermocouple

4-Point Probe

D₂, O₂ gas

D⁺
## Experimental Measurements

<table>
<thead>
<tr>
<th>Cell Measurements</th>
<th>X-Ray Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>• <strong>Temperature</strong></td>
<td>• 14 µm tall, 23-µm wide x-ray beam</td>
</tr>
<tr>
<td>- 1 thermocouple in electrolyte</td>
<td>• Diffraction spectra collection</td>
</tr>
<tr>
<td>- 5 RTD's external to cell</td>
<td>time ~5 minutes</td>
</tr>
<tr>
<td>• <strong>Electrolysis</strong></td>
<td>• Ge high resolution detector</td>
</tr>
<tr>
<td>- Current</td>
<td></td>
</tr>
<tr>
<td>- Voltage</td>
<td></td>
</tr>
<tr>
<td>• <strong>Cell Pressure</strong></td>
<td></td>
</tr>
<tr>
<td>- Baratron</td>
<td></td>
</tr>
<tr>
<td>- Safety valve</td>
<td></td>
</tr>
<tr>
<td>• R/R₀</td>
<td></td>
</tr>
<tr>
<td>- 4-point probe @ 1 kHz</td>
<td></td>
</tr>
<tr>
<td>• <strong>Time</strong></td>
<td></td>
</tr>
<tr>
<td>• <strong>Data rate</strong></td>
<td></td>
</tr>
<tr>
<td>- 1/4 Hz</td>
<td></td>
</tr>
</tbody>
</table>

No Calorimetry!
Brightness of NSLS Beam Lines

![Graph showing the brightness of NSLS Beam Lines](image)
X-Ray Transmission through Electrochemical Cell

Absorption thru the Cell with 2.7 cms of H₂O and 0.3 cms of Glass with a density of 2.7 g/cm³.

Energy (keV) vs \( I/I_0 \)
Bragg Condition

\[ 2d \sin \theta = n \lambda \]

\[ E = h \nu, \quad \lambda \nu = c \]

\[ 2d \sin \theta = n ch/E \]

or

\[ Ed \sin \theta = 6.1992n \]

Continuous energy picks out d for properly oriented planes
Detection Volume - $1.6 \times 10^{-12} \text{ m}^3$

collimated X-ray beam is 23 µm wide x 14 µm tall

collimated diffracted beam is 50 µm wide x 500 µm tall

$\theta = 13$ degrees

view from top

Not to Scale
Near surface sampling (Pd x-ray fluorescence observed)
Detection Volume

Bulk sampling (No Pd x-ray fluorescence observed)
Unexpected Challenges & Observations

• Control of geometry difficult due to movement of foil from stresses caused by 13% volume change as cathode was loaded with hydrogen.

• Since beam covered only a few grains, diffraction condition often had to be found by x-y-z position scanning.

• When cell abruptly turned off at high loading fraction, electrolyte turned black and then clarified in ~ 60 seconds. Presumably this was caused by rapid removal of impurities plated on the cathode surface that then dissolved into the electrolyte.

• Observation of spontaneous deloading under current control.

• Observation of highest loading fractions early in loading cycle.
### Cathode Loading Descriptions

**Tentative observations:**
- R/R0 four point probe underestimates loading ratio
- R/R0 is a good in situ qualitative guide for loading ratio
- Thinner foils loaded to higher ratio

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>0.1M LiOD in</th>
<th>R0 mOhm</th>
<th>Total Time</th>
<th>Total Charge (C)</th>
<th>Total Energy (kJ)</th>
<th>Maximum H/Pd Ratio fr resistivity</th>
<th>Maximum (H,D)/Pd Ratio fr lattice const.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRL#2</td>
<td>D$_2$O</td>
<td>3.69</td>
<td>46:15</td>
<td>6337</td>
<td>22.14</td>
<td>0.85</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>L23</td>
<td>D$_2$O</td>
<td>3.82</td>
<td>30:15</td>
<td>5974</td>
<td>18.32</td>
<td>0.87</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>D$_2$O</td>
<td>10.08</td>
<td>48:22</td>
<td>110947</td>
<td>783.24</td>
<td>0.95</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>L5</td>
<td>H$_2$O</td>
<td>5.24</td>
<td>09:56</td>
<td>4354</td>
<td>18.19</td>
<td>0.97</td>
<td>1.01</td>
<td></td>
</tr>
</tbody>
</table>
Observation of Spontaneous Deloading

<table>
<thead>
<tr>
<th>Run Time (s)</th>
<th>Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 $10^4$</td>
<td>0.4</td>
</tr>
<tr>
<td>4 $10^4$</td>
<td>0.3</td>
</tr>
<tr>
<td>6 $10^4$</td>
<td>0.2</td>
</tr>
<tr>
<td>8 $10^4$</td>
<td>0.1</td>
</tr>
<tr>
<td>1 $10^5$</td>
<td>0</td>
</tr>
</tbody>
</table>

D/Pd = 0.89

NRL2 Data

R/R0

Current (A)

Run Time (s)

Deuterium

Hydrogen
Electrochemical History

![Graph showing electrochemical history with data points and labels R/R0, Cell Voltage (V), and D/Pd = 0.93.]
Electrochemical History

\[
\frac{R}{R_0} = 1.02
\]

\[\text{D/Pd} = 1.02\]
Systemmatics of Loading

![Graph showing the relationship between $\chi_0$ and $x$. The graph compares Deuterium and Hydrogen. The $y$-axis represents $\chi_0$, ranging from 0.0 to 2.0, and the $x$-axis represents $x$, ranging from 0.0 to 1.0.](Image)

![Graph showing the relationship between R/R_0 and Lattice Constant a. The x-axis represents Lattice Constant a, ranging from 3.85 to 4.1, and the y-axis represents R/R_0, ranging from 0.8 to 2.0. The graph includes data points represented by crosses.](Image)
Systemmatics of Loading
High Loading Fractions at Early Time
Typical X-Ray Spectrum

Semi-Log Plot

- Intensity falls off at low E due to absorption in electrolyte
- Pd K-edge absorption below 23 keV
- Intensity falls off at high E due to x-ray beam intensity fall-off
- In this spectrum, 10 x-ray diffraction peaks fit well

- Fluorescence peaks for Pb and Sn appear during all cell runs
- Pd fluorescence used to monitor surface

- Only a few instances where Alpha and Beta diffraction seen simultaneously. Therefore, within ~ 3-5 min intervals, the phase change is complete
- Only several grains interrogated
Cathode Loaded with Hydrogen

H/Pd = 1.01

Reached peak in 20 minutes
Summary - Electrolysis of 4 Cathodes

Observations consistent with literature

More difficult to load D than H
Spontaneous deloading under current control
Evidence of large amount of deposited impurities on surface
R/R0 in situ resistivity measurement is a good *qualitative* guide to loading ratio
Once a cathode has been loaded to high a ratio, it can not be loaded a second time

Tentative new observations

Higher starting resistivity foils (thinner foils) loaded to higher D/Pd ratio
Highest loading ratios occur at early time in loading cycle
All four ENEA-prepared cathodes loaded to high D/Pd ratios
Observations consistent with literature

alpha-beta phase change

Tentative new observations

Rapid surface deloading and reloading

Very few x-ray spectra with both Alpha and Beta phases present suggests that within multiple grains, the transformation from Alpha to Beta is very rapid (within the 3-5 minute time resolution of the data)

Highest D/Pd ratio early in loading cycle

New observations

High D content by x-ray diffraction (D/Pd = 1.02)

R/R0 measurement consistently underestimates the loading ratio

No obvious new phase at high loading fractions (for Pd sublattice only)

First time x-ray diffraction performed in FPE cell at concentrations greater than D/Pd > 0.76
Conclusions

• Time resolved, in-situ, high-energy x-ray diffraction was performed on modified Fleishman-Pons electrolytic cells during electrochemical loading of palladium foil cathodes with hydrogen and deuterium.

• Concentrations of H and D up to 1:1 in 0.1 M LiOH/LiOD in H₂O/D₂O electrolytes were obtained.

• While very interesting data in its own right, no new anomalous behavior was observed that identifies a mechanism of FPE.
Table I: Maximum Electrolytic Loading Ratios Achieved in the Pd-H and Pd-D systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Loading Ratios</th>
<th>Loading Conditions and/or Sample Preparation</th>
<th>In Situ X-Ray or Neutron Diffraction</th>
<th>Year</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-D</td>
<td>0.72</td>
<td>0.1 M LiOD</td>
<td>x-ray diffraction</td>
<td>1998</td>
<td>27</td>
</tr>
<tr>
<td>Pd-D</td>
<td>0.92-0.96</td>
<td>1 M LiOD, stepwise changed current density; 0.96 if etched with aqua regia, 0.92 if polished with diamond grit</td>
<td>none</td>
<td>1997</td>
<td>12</td>
</tr>
<tr>
<td>Pd-H; Pd-D</td>
<td>0.78-0.82</td>
<td>0.1 M/1 M LiOH or LiOD, 50 mA/cm²</td>
<td>none</td>
<td>1996</td>
<td>13</td>
</tr>
<tr>
<td>Pd-H; Pd-D</td>
<td><strong>0.76</strong></td>
<td>0.1 M LiOD</td>
<td>x-ray diffraction</td>
<td>1995</td>
<td>14</td>
</tr>
<tr>
<td>Pd-H; Pd-D</td>
<td>0.85-0.90</td>
<td>1 M LiOH and LiOD</td>
<td>none</td>
<td>1995</td>
<td>15</td>
</tr>
<tr>
<td>Pd-D</td>
<td>0.91-0.93</td>
<td>Pd was vacuum annealed and acid etched.</td>
<td>none</td>
<td>1994</td>
<td>16</td>
</tr>
<tr>
<td>Pd-D</td>
<td>0.55</td>
<td>0.1 M Li₂O in D₂O</td>
<td>neutron diffraction</td>
<td>1990</td>
<td>66</td>
</tr>
</tbody>
</table>
Pd-H Phase Diagram

Figure 1: The phase diagram of Pd-H system.

Figure 2: The phase diagram of Pd-D system (Here, $\alpha'$ phase means $\beta$) at low temperatures.
Shifts in XRD peaks with time

Figure 5: Temporal dependence of the intensity of (422) diffraction peaks of $\alpha$ and $\beta$ phases.
D/Pd > 1

1 alpha-beta phase change
2 rapid surface deloading
3 high D content
4 suggestion of phase change

In-situ measurement of D/Pd

Lattice Parameter

Cell Voltage (Volts)

R/Ro Corrected

Time (sec)