The enthalpy of formation of PdH as a function of H/Pd atom ratio and treatment

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Production of the LENR effect involves achieving a large concentration of D in the PdD lattice structure. A great deal of effort has been applied to understanding how this can be accomplished and the nature of the resulting structure. The bulk properties play a role in this process but are sensitive to the impurity content and treatment. The influence of the bulk properties on this process has not been fully explored.

This paper describes a new method to directly measure the bond energy between the PdH structure and the contained H atoms in real time as a function of H/Pd ratio from zero to the maximum H content using the electrolytic method and $H_2SO_4+H_2O$ to react Pd with H. A unique and very accurate calorimeter (±5 mW) is used to measure power during the loading reaction. This method is applied to several types of Pd including commercial Pd sheet, extra pure Pd, and a zone refine single-crystal of Pd after each is subjected to several treatments. These treatments include repeated loading-deloading cycles, annealing at 900°C, and reduction in thickness. The bond energy is found to be sensitive to purity, treatment, and H/Pd ratio, with good agreement with published measurements being achieved after certain treatments. In addition, three methods to measure the average H/Pd ratio are described and compared. These methods use weight gain, orphaned oxygen, and recombiner temperature. A great deal of information about the reaction process can be obtained by combining these three methods because they are sensitive to different possible errors and behaviours.

Figure 1 compares the initial loading process and Fig. 2 compares the enthalpy of formation for the three different samples before the effect of treatment is explored. The bond between H and the lattice becomes repulsive (endothermic) as the upper H/Pd limit is approached.

The study has revealed unexpected behaviour and a new method to explore the environment in which LENR occurs.

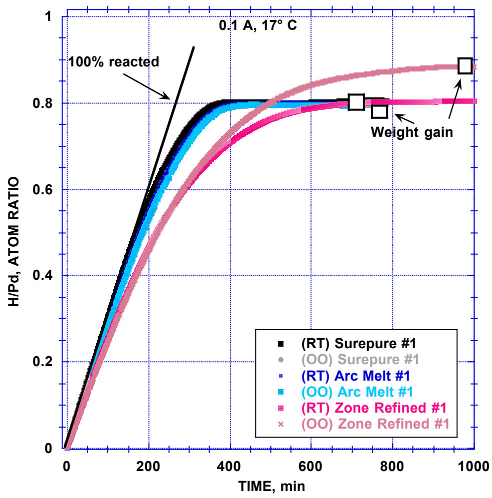

Fig. 1. Examples of loading behaviour by comparing the three different measurements of H/Pd ratio, where RT is recombiner temperature and OO is orphaned oxygen.

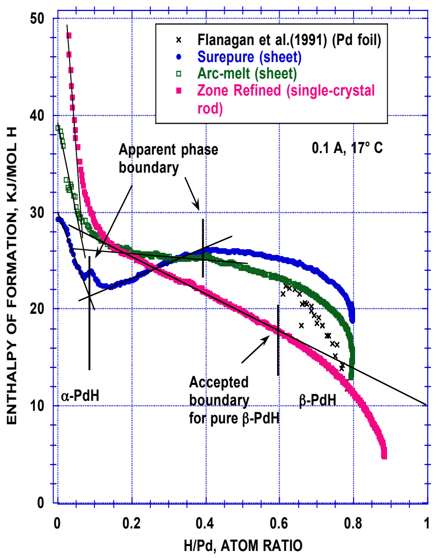

Fig. 2. Enthalpy of formation of the three types of Pd before treatment. Values are measured every minute.

The enthalpy of formation of PdH as a function of H/Pd atom ratio and treatment with other useful information

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A new method using the recombiner temperature reveals:

1. The D/Pd ratio of the Pd cathode.
2. The enthalpy of formation of PdD.
3. The errors caused by periodic recombiner failure.

Measurements Used:

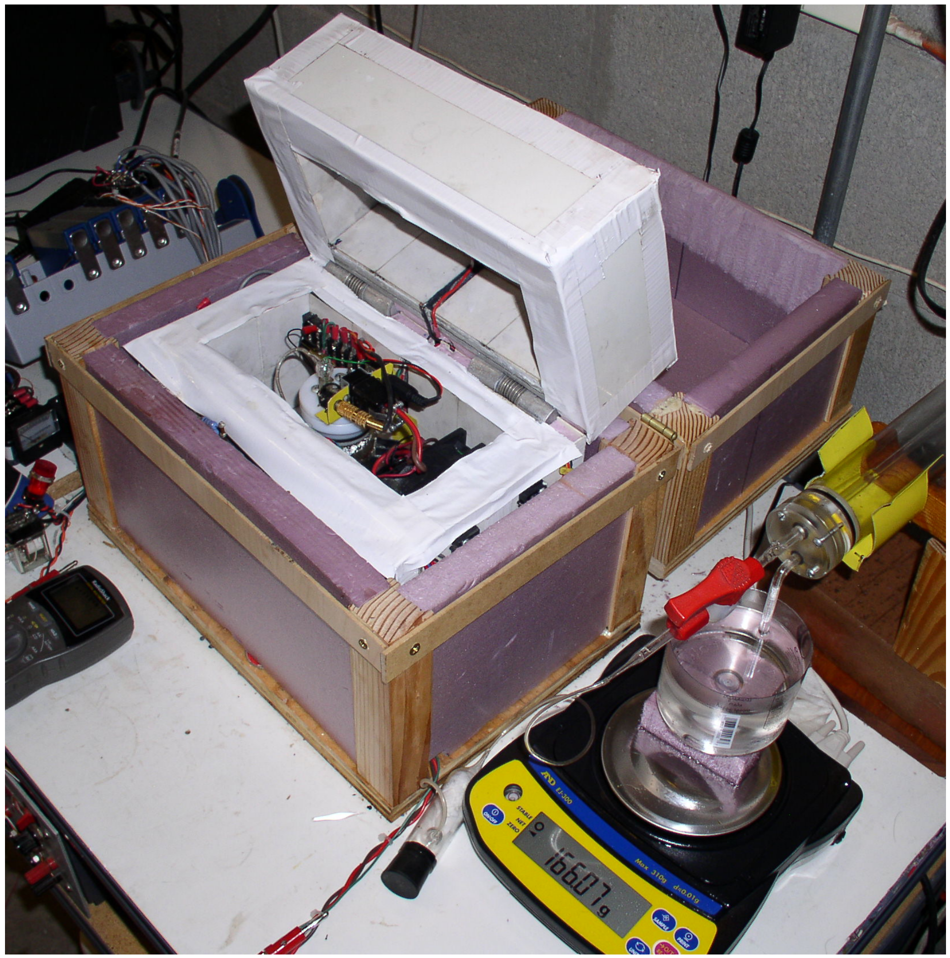
A. Electrolyte of 0.5 ml H_2SO_4+30 ml H_2O

B. Seebeck type calorimeter

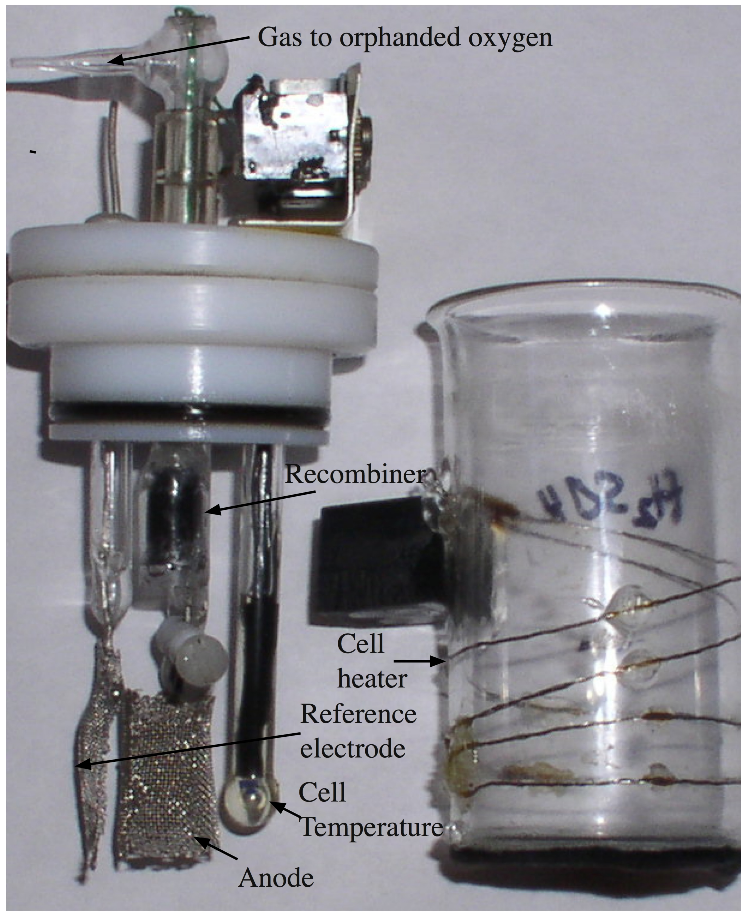
C. Three different sources of Pd

1. Commercial sheet, 99.5 %
2. Arc-melted pure Pd, 99.95 %
3. Zone-refined single-crystal rod

OPEN CALORIMETER

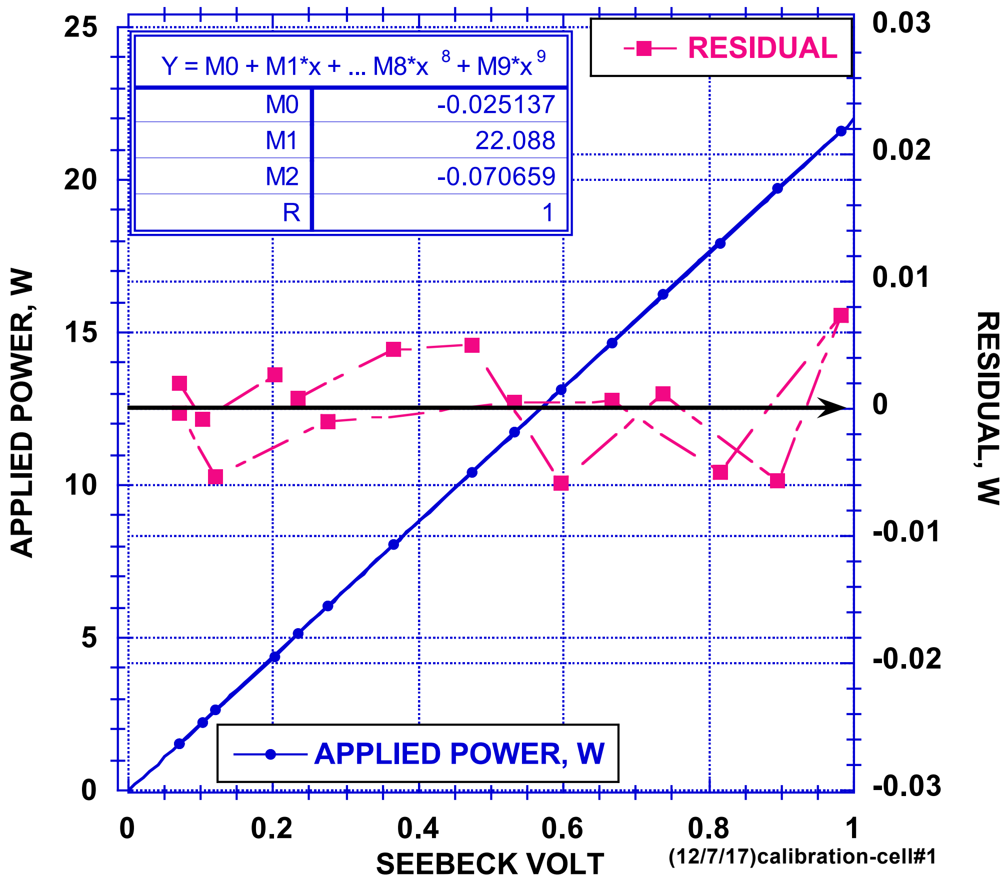


REACTION CELL

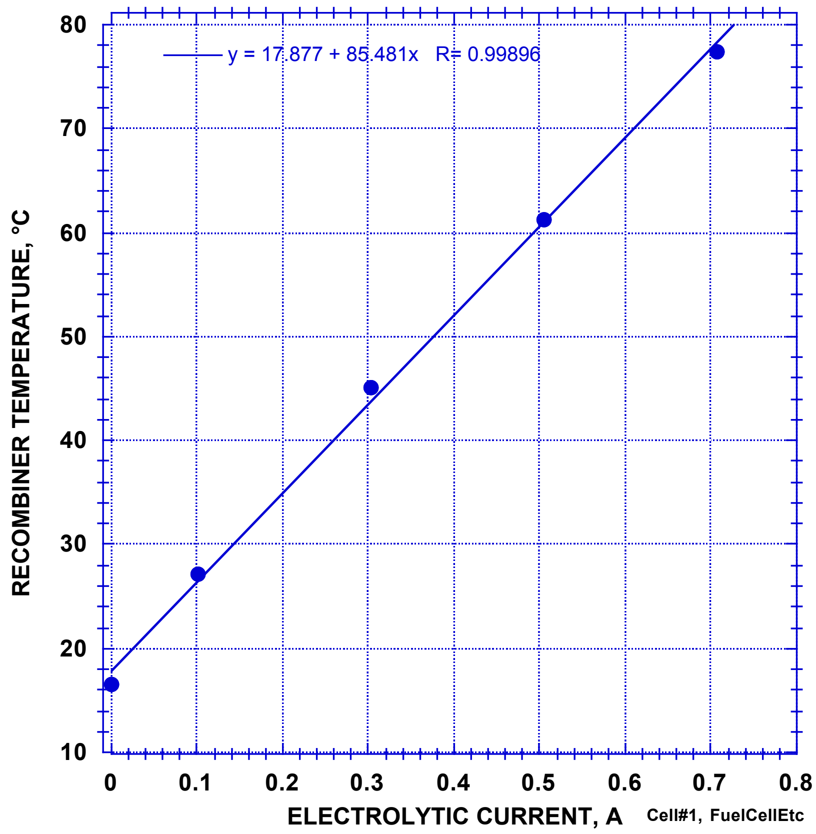


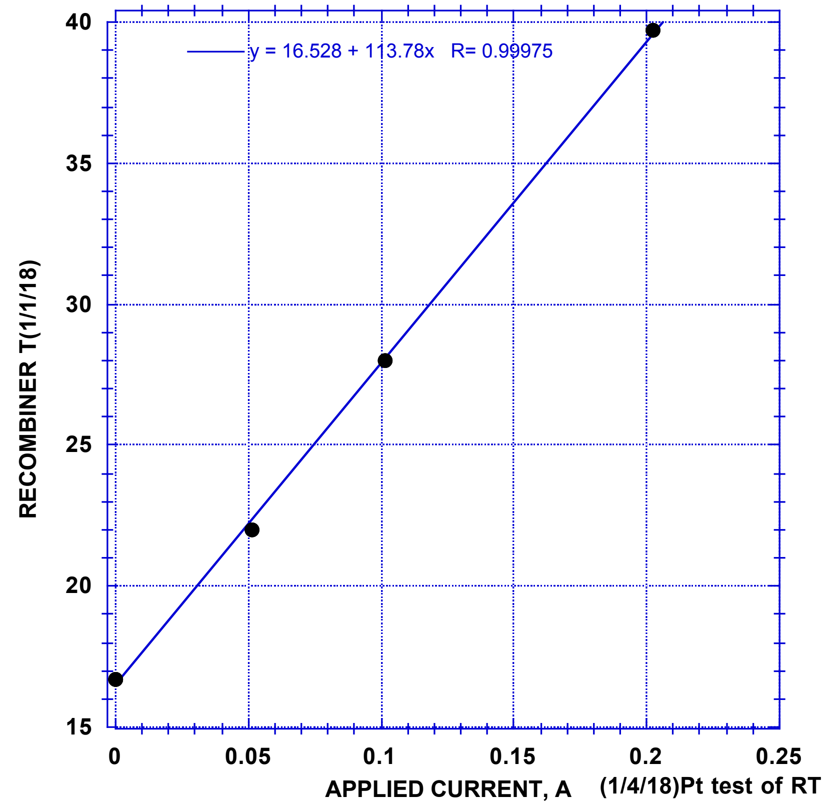
CALIBRATION OF CALORIMETER

Three methods can be used with all giving the same result.

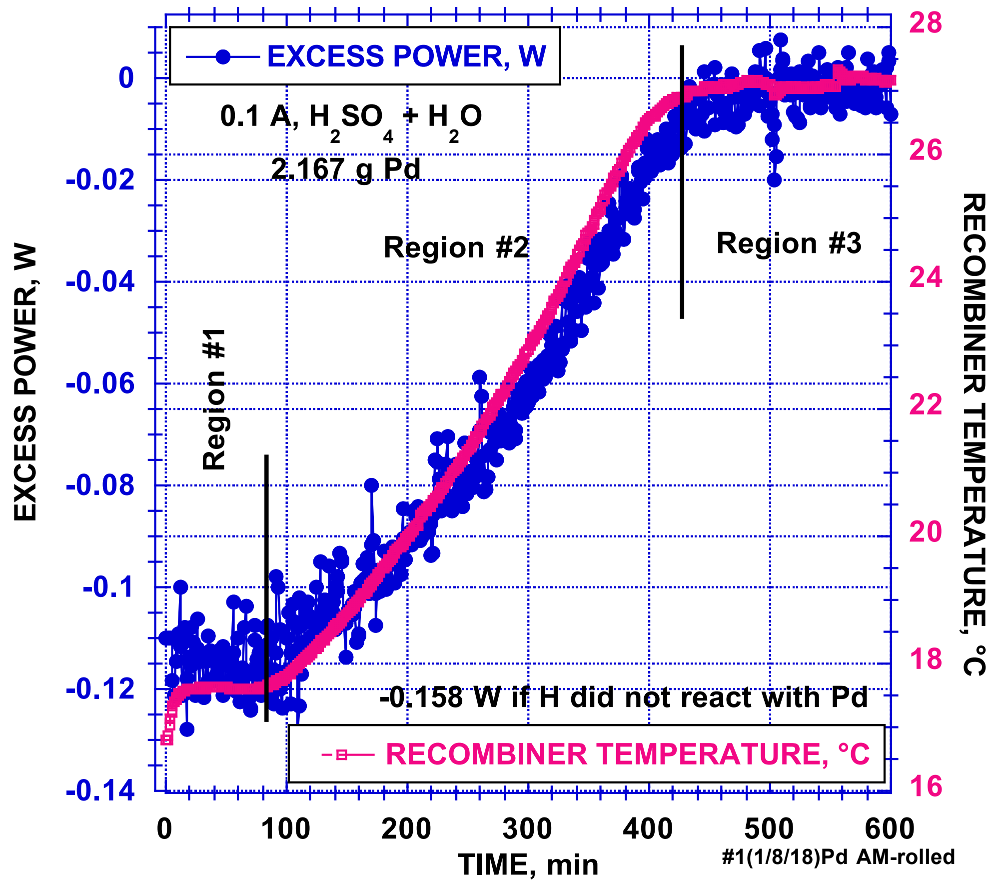


CALIBRATION OF RECOMBINER





EXAMPLE OF MEASUREMENTS



DATA TREATMENT

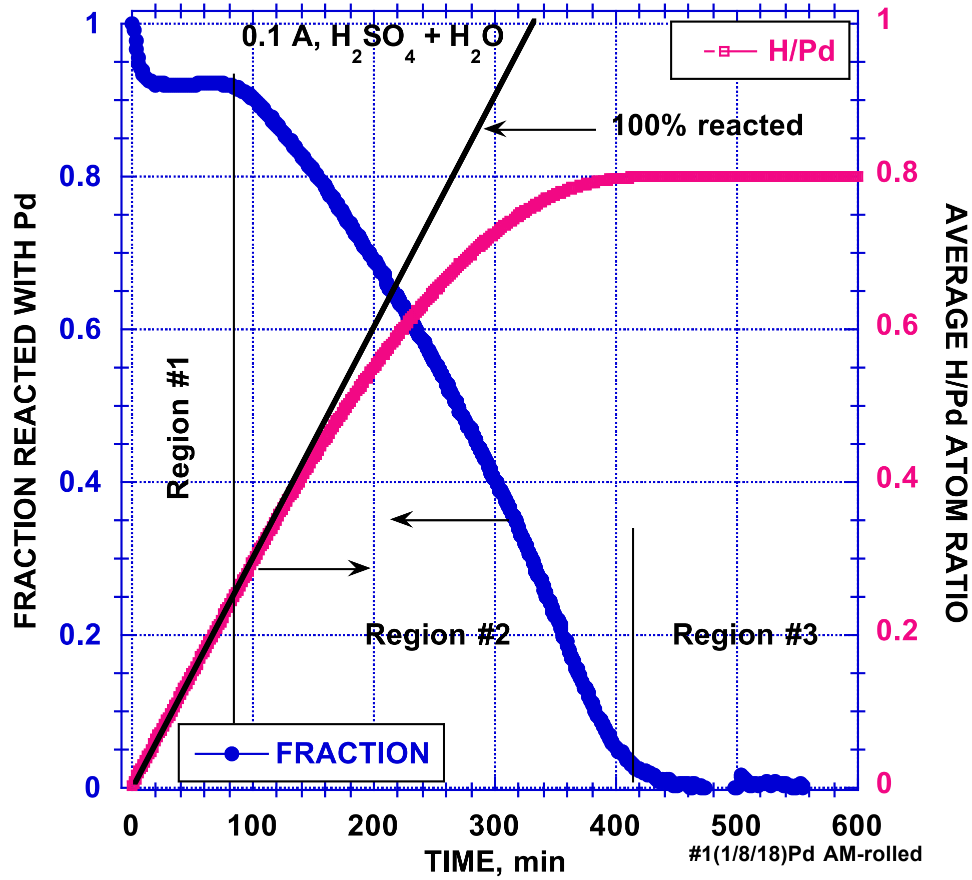
CALCULATION OF FRACTION OF HYDROGEN REACTED

- Fraction reacting with metal = F = 1 - $(T_m - T_i)/(T_f - T_i)$
- Where: T_m is the recombiner temperature at the measured time
- T_i is the initial recombiner temperature when all H reacts with the metal.
- T_f is the final recombiner temperature when no net H reacts with the metal.

CALCULATION OF H/Pd ATOM RATIO

- The number of moles of hydrogen being supplied by electrolysis can be determined using the equation:
- Moles H or D = M = seconds * current/98485.
- Because the time interval is 60 seconds and the current is 0.101 A for this study, the number of atomic moles of hydrogen generated in the cell during the measurement interval is:
- M_D = 60*0.101/98485 = 6.15×10^{-5} moles/min
- Total H reacted = $\sum$ [fraction *6.15×10^{-5}]

EXAMPLE OF RELATIONSHIP BETWEEN FRACTION REACTED AND H/Pd RATIO

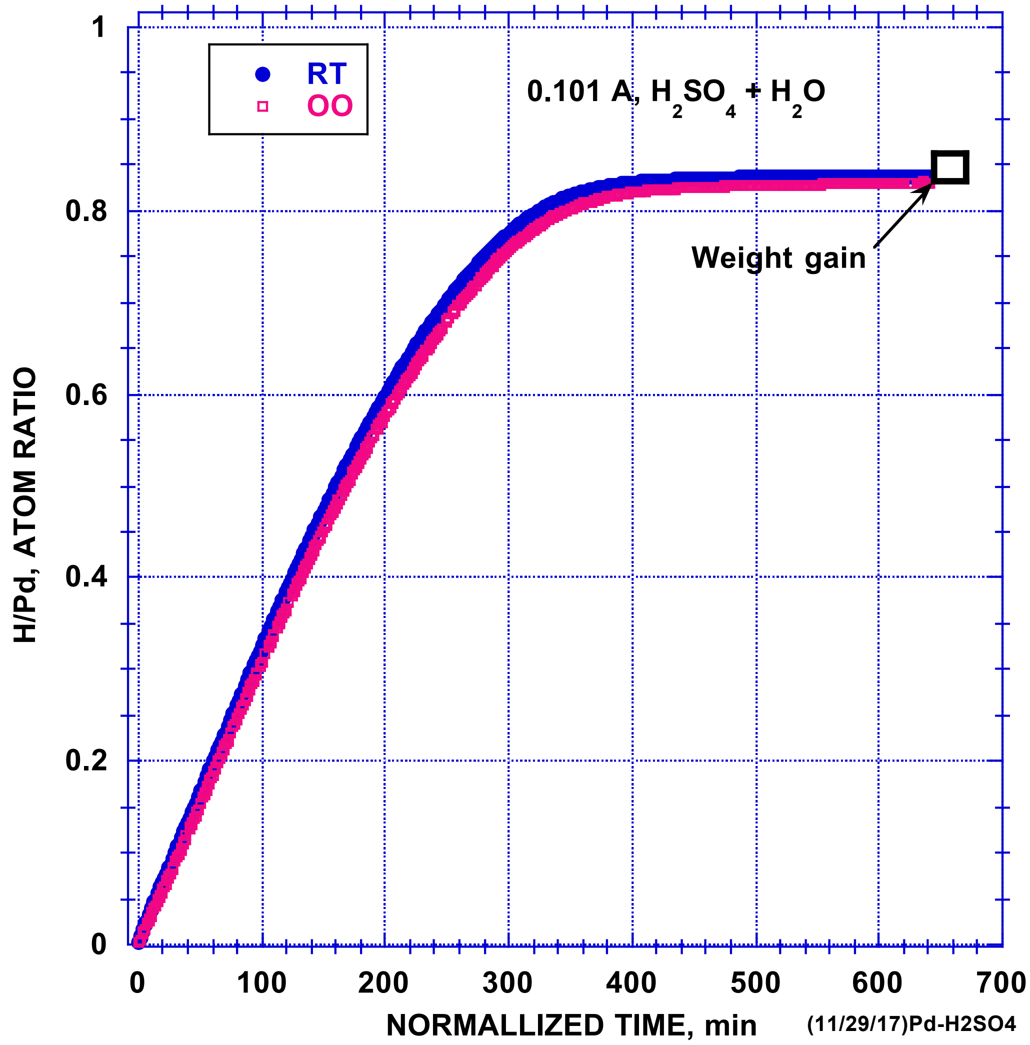


COMPARISON BETWEEN OTHER MEASUREMENTS OF AVERAGE H/Pd RATIO

Recombiner Temperature (RT)

Orphaned oxygen (OO)

Weight gain (WG)



MEASUREMENT OF ENTHALPY OF FORMATION

Equations used to obtain values:

- Power (W) to form PdD = P = (excess power) + 1.482 * (applied current) * (fraction hydrogen reacted)

- Energy released during each measurement interval = E(J) = 60 * P

- Total Energy = sum of each measurement interval

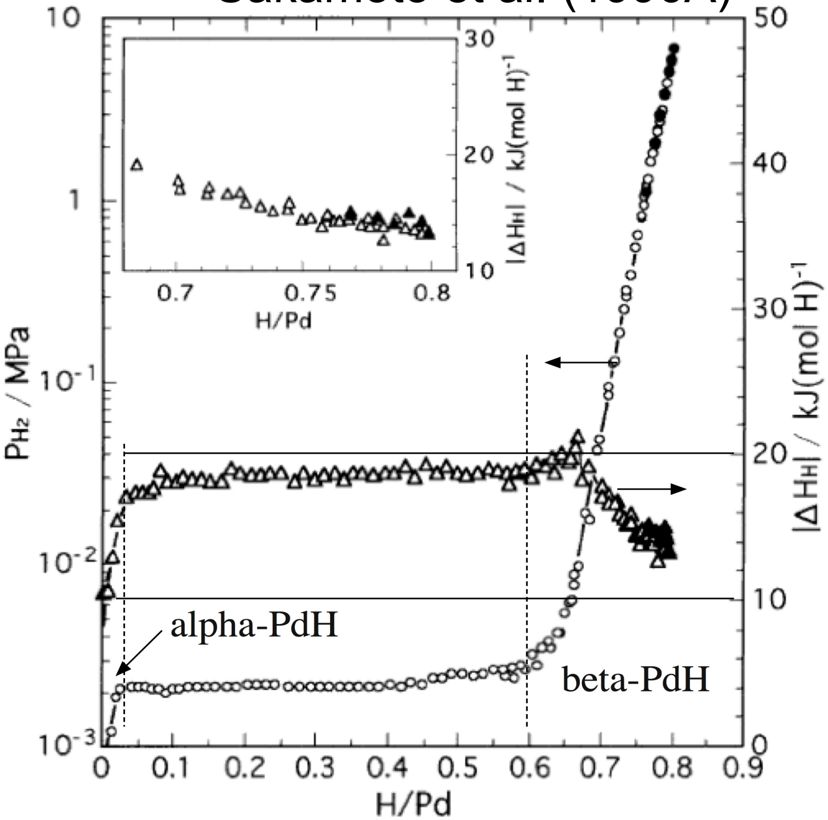
- M_D = 60*0.101/98485 = 6.15×10^{-5} moles/min
- Total H reacted =∑ [fraction *6.15x10^{-5}]

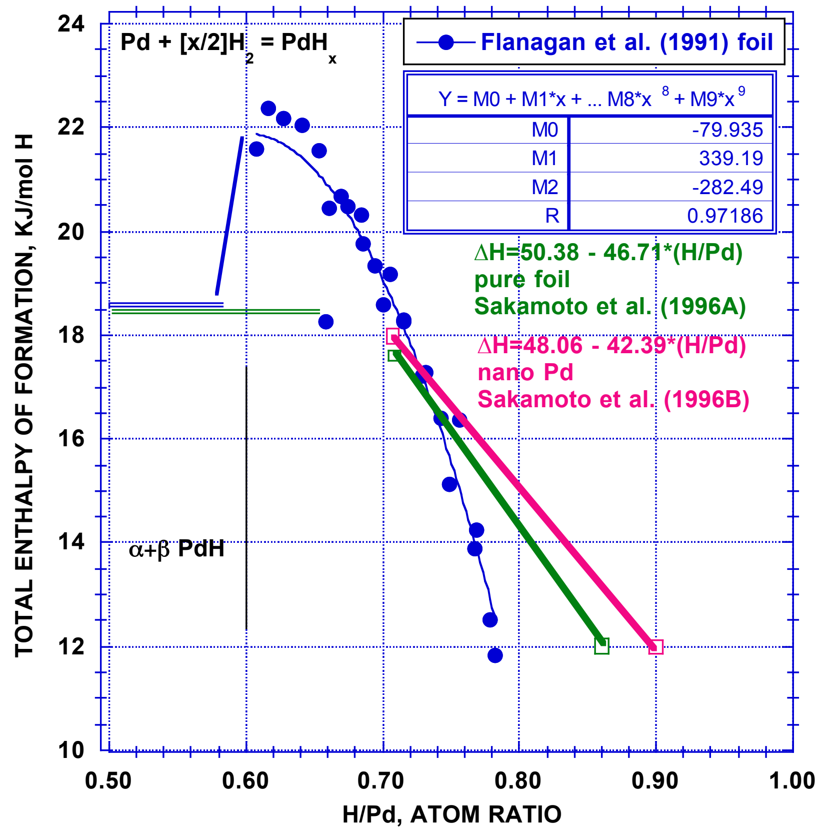
- Composition gradients are present that can compromise the values.

ENTHALPY OF FORMATION

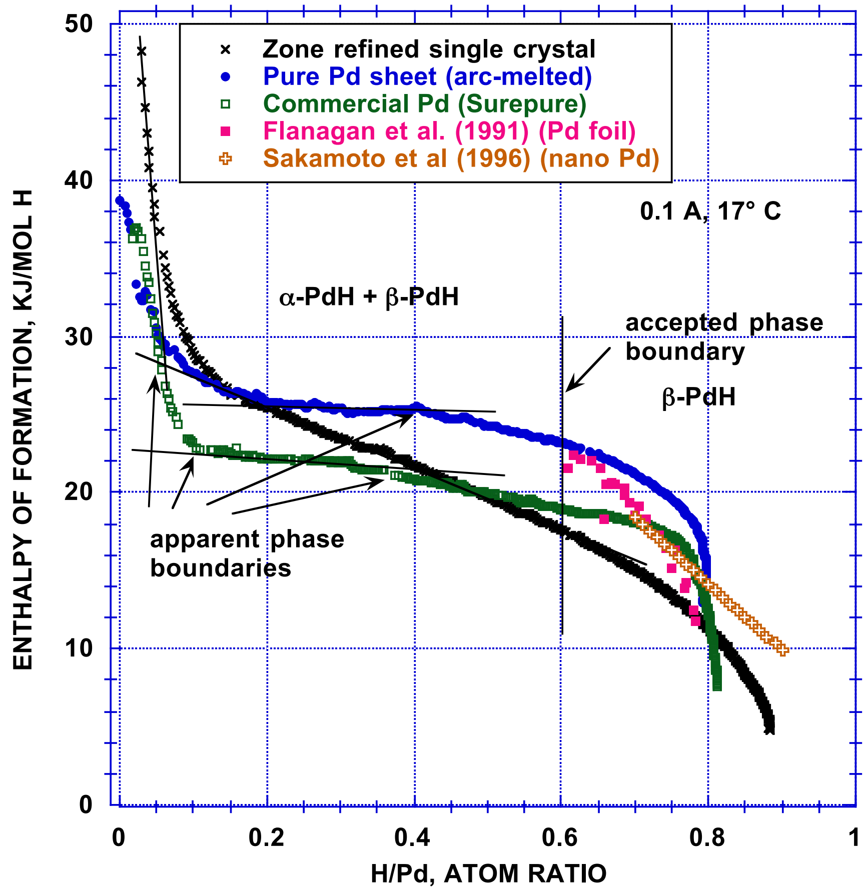
$Pd+[x/2]H_2=PdH_x$ (gas reaction after 10 loading-deloading cycles)

Sakamoto et al. (1996A)

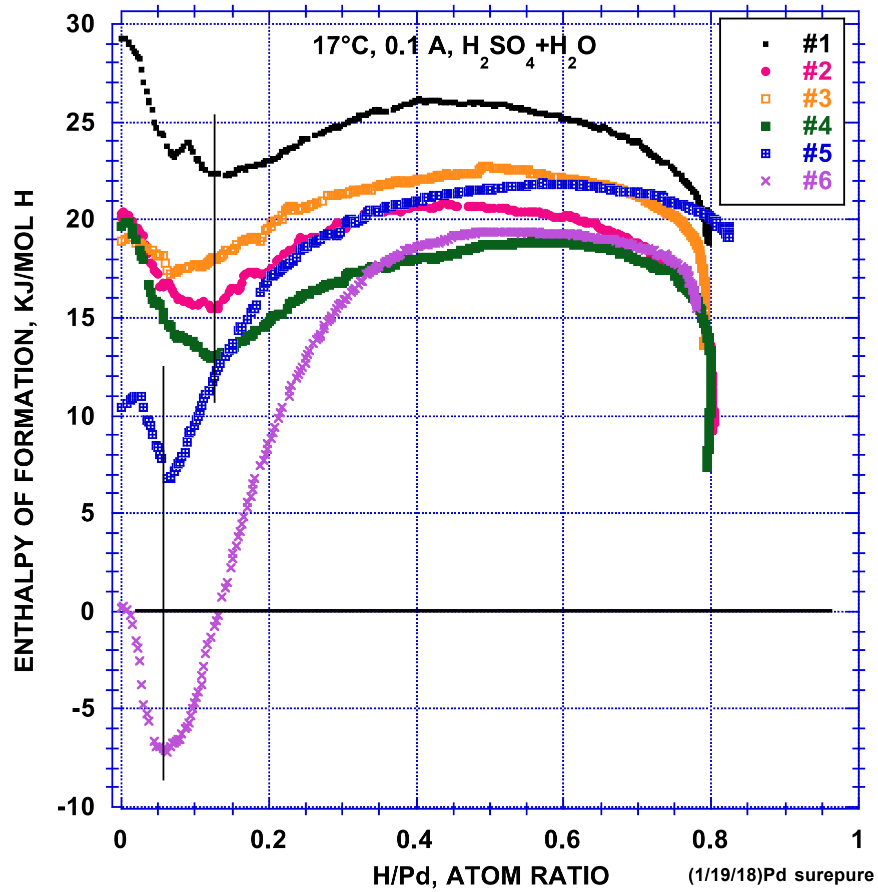




COMPARISON BETWEEN DATA SETS AND PUBLISHED VALUES

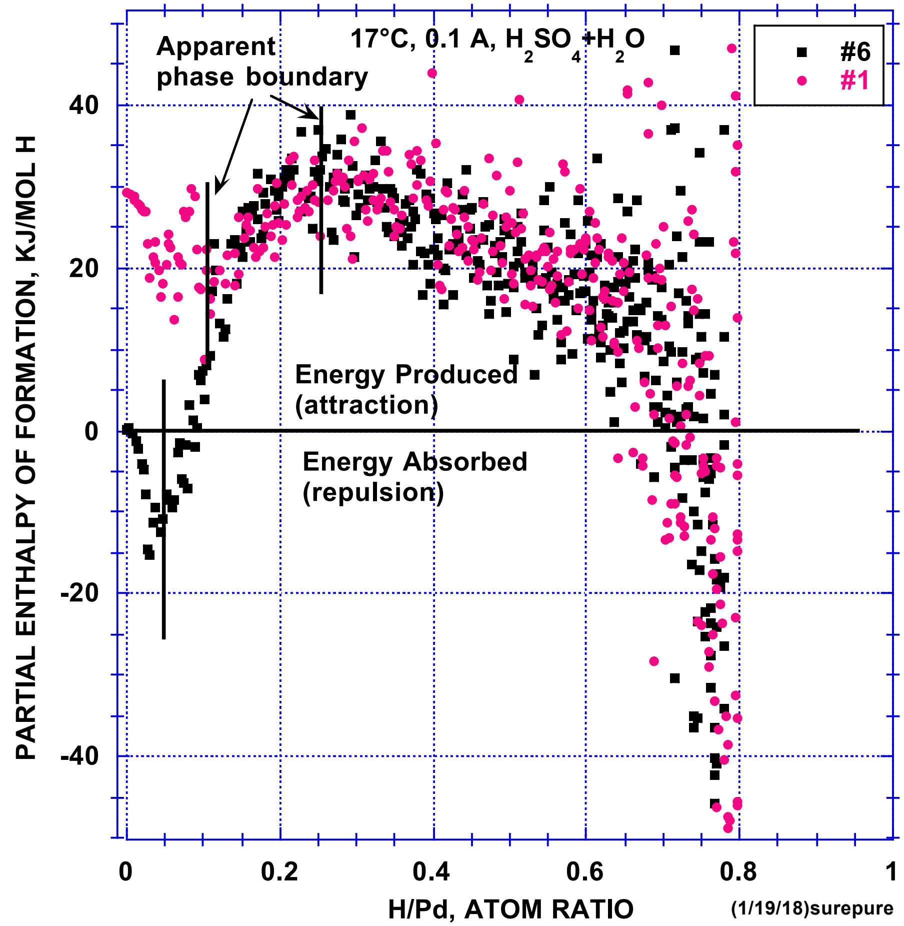


Effect of repeated loading and deloading using 99.9 % Pd

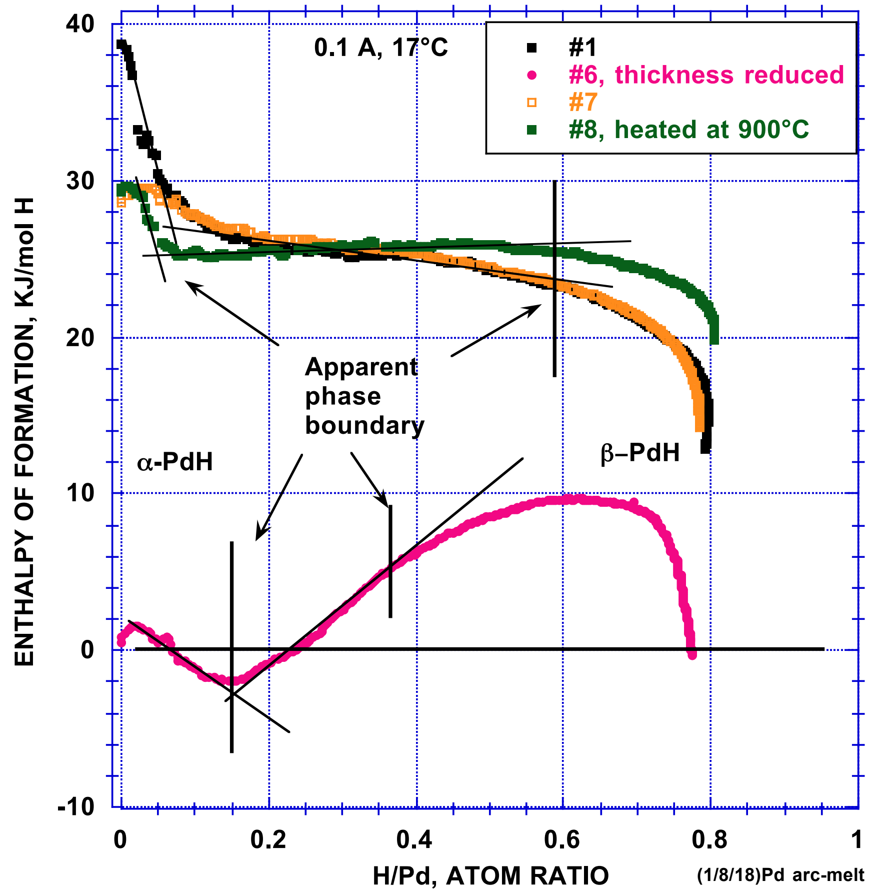


Effect of treatment on bond energy

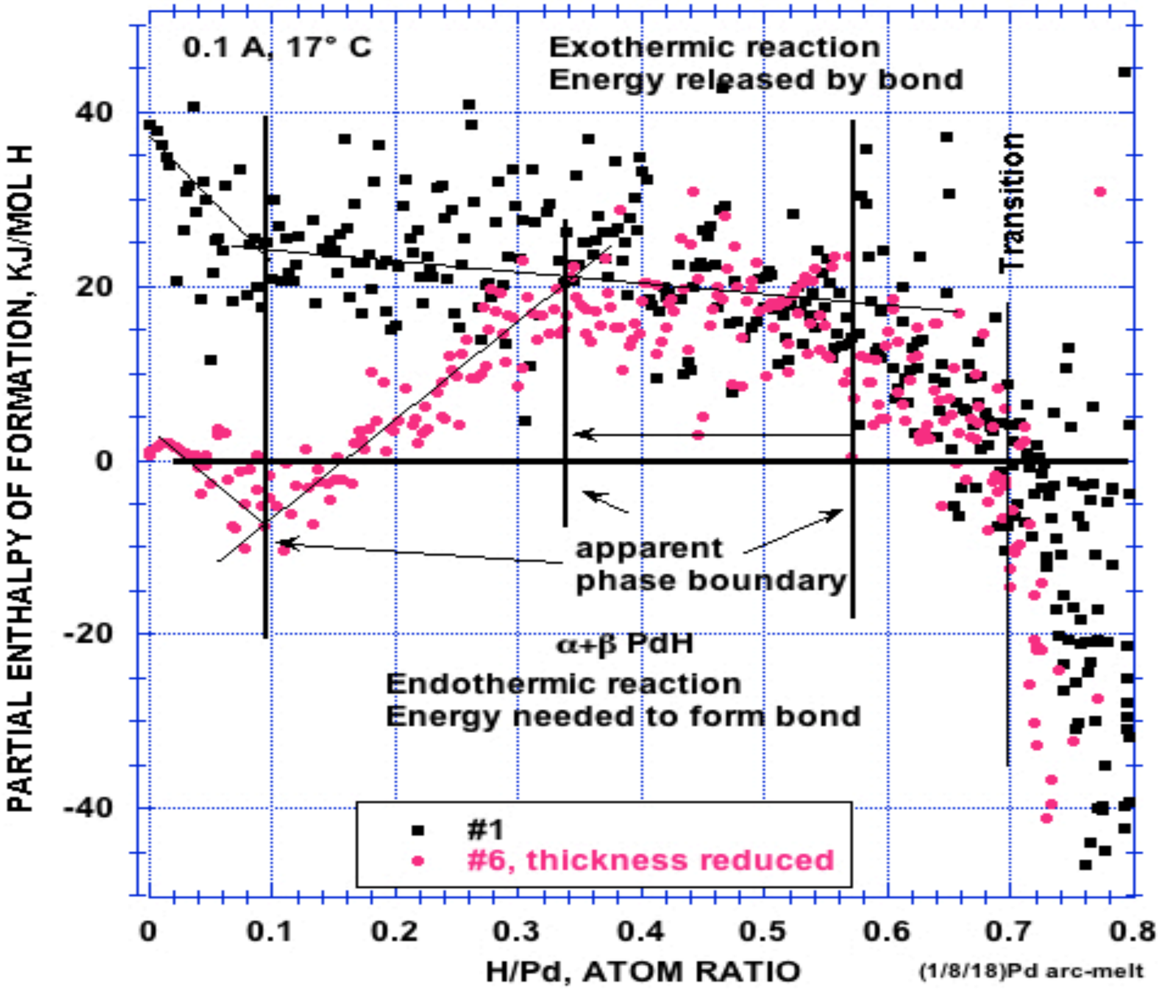
(measured every minute)



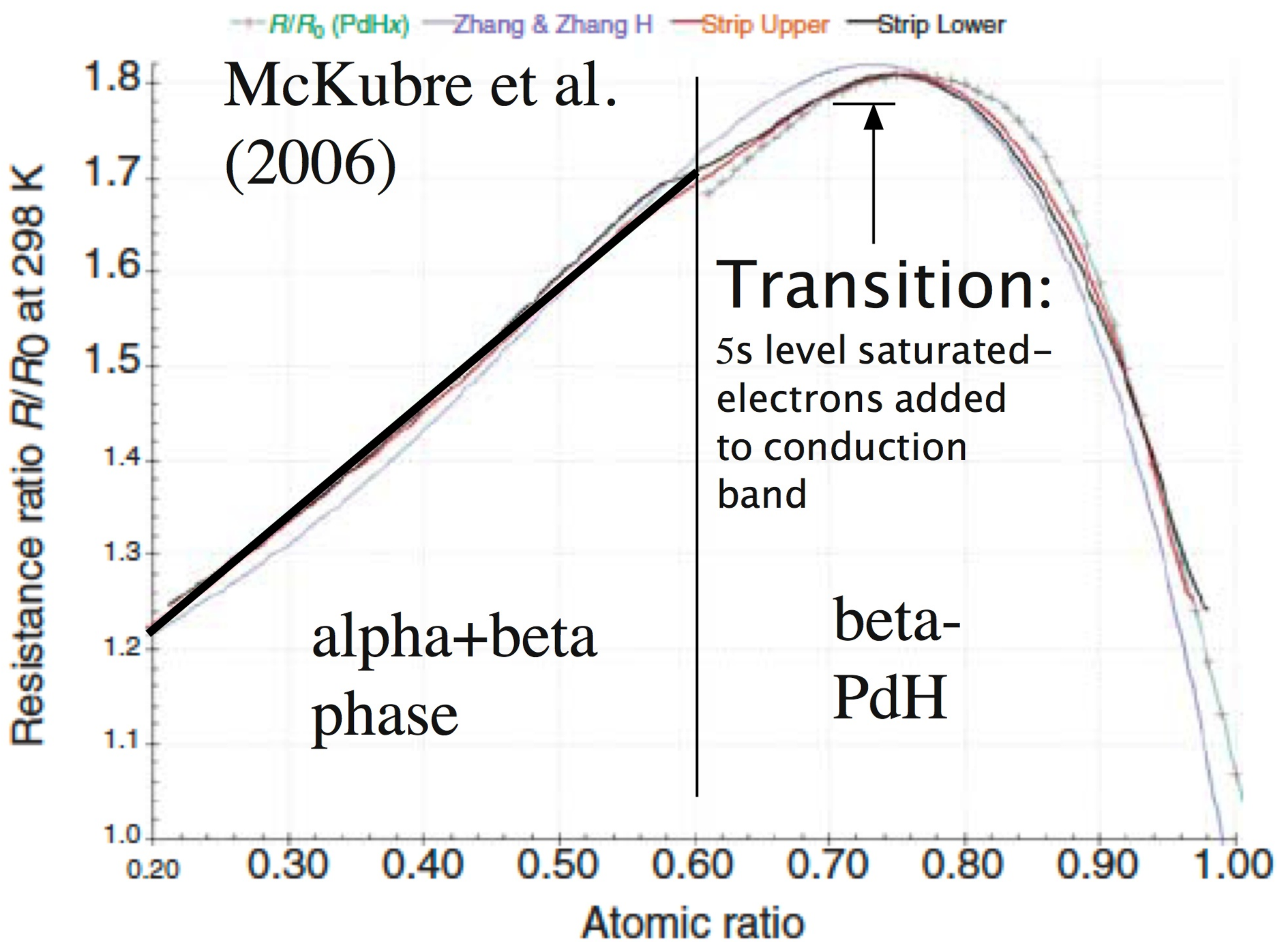
EXAMPLE OF THE EFFECT OF TREATMENT



BOND ENERGY vs AVERAGE H/Pd RATIO



RESISTANCE RATIO FOR PdH_x



Addition of hydrogen to β-PdH above about $PdH_{0.75}$ produces increased nonbonding between Pd and H as the added electrons enter the conduction band rather than bonding orbits.

SUMMARY

- Measurement of recombiner temperature allows H/Pd ratio and bond energy to be determined.
- Behavior of H/Pd vs time provides important information about the loading mechanisms.
- Behavior of bond energy gives information about how the LENR mechanism might function.

CONCLUSIONS

- The stability of alpha-PdH is very sensitive to purity and treatment.
- The stability of beta-PdH becomes increasingly negative at H/Pd ratios above about 0.75.
- The composition of the alpha and beta phases at their phase boundaries is sensitive to purity and treatment.