# Are Oxide Interfaces Necessary for FPE?

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# Theoretical Arguments Against D-D Fusion

1989

- A.B. Hassam and A.N. Dharamsi, “Deuterium Molecule in the Presence of Electronic Charge Concentrations: Implication for Cold Fusion,” *Phys. Rev. A*, **40** (1989) 6689-6691.

- Z. Sun and D. Tomanek, “ Cold Fusion: How Close Can Deuterium Atoms Come Inside Palladium?”, *Phys. Rev. Lett*., **63** (1989) 59-61.

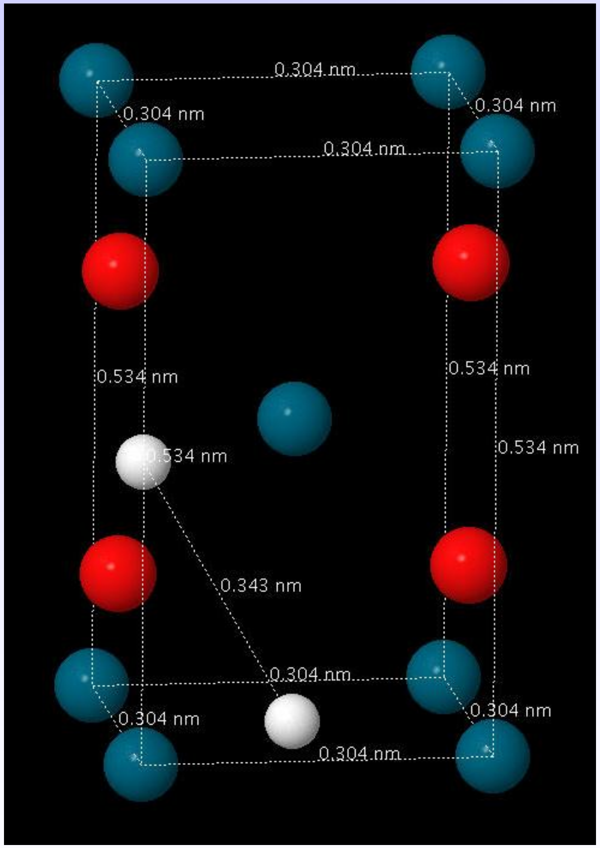
- F. Liu, B.K. Rao, S.N. Khanna and P. Jena, “Nature of Short Range Interaction Between Deuterium Atoms in Pd,” *Solid State Commun*., **72** (1989) 891-894.

- X.W. Wang, S.G. Louie and M.L. Cohen, “ Hydrogen Interactions in $PdH_n$ ($1 \leq n \leq 4$),” *Phys. Rev. B*, **40** (1989) 5822-5825.

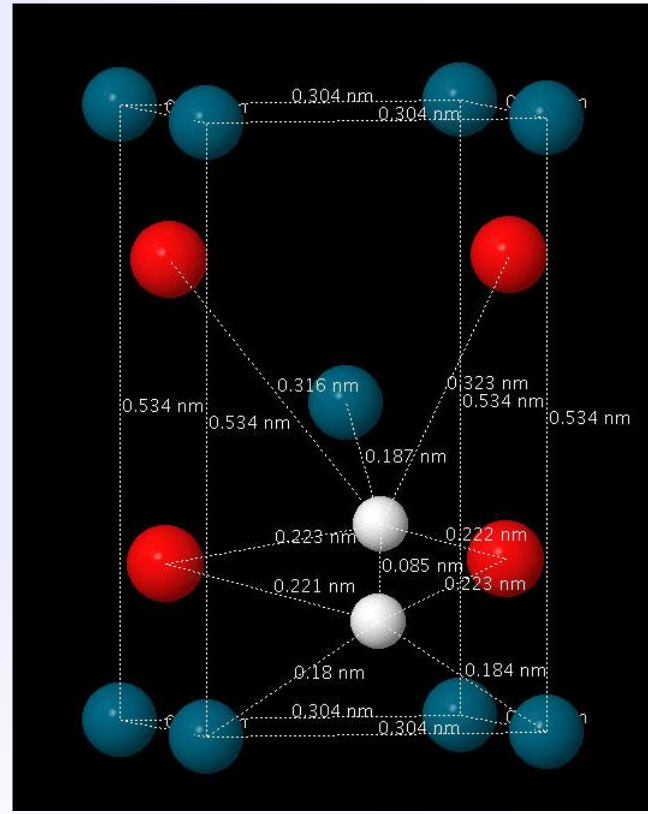
- J.W. Mintmire, B.I. Dunlap, et al., “Chemical Forces Associated with Deuterium Confinement in Palladium,” *Phys. Lett. A*, **138** (1989) 51-54.

# Preliminary Results:

NVT *Born–Oppenheimer* MD Calculation at 100K




Initially add two deuterium atoms in O-sites in the unit cell



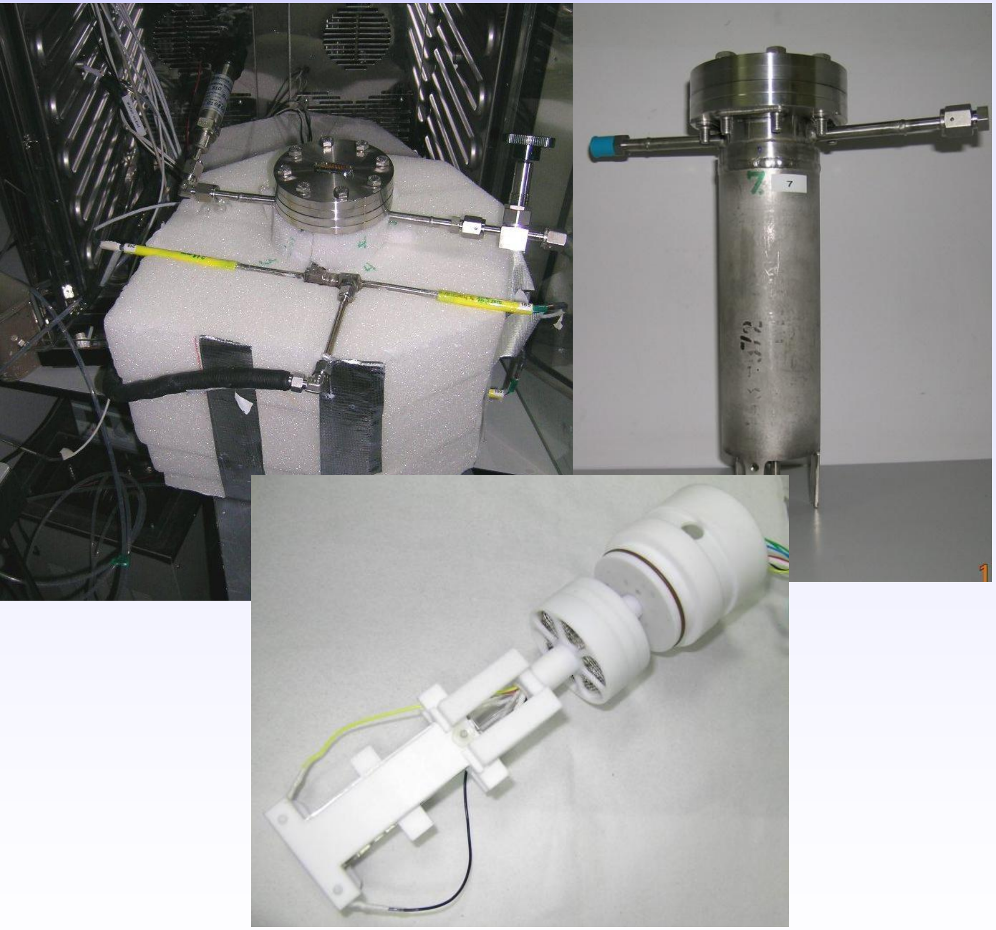

Preliminary Results: $D_2$ molecules forms in PdO with D-D separation around 0.85 Å.

# Outline – Are Oxides Interfaces Necessary for FPE?

- Describe Electrochemical cells/calorimeters
- Materials investigated/morphology
- Results – Oxide interface formation
  - what we see
  - what we don't understand
- Model of Pd oxide interface interacting with $D_2$
- Conclusions

# High Current Density Closed Cells

## Three Energetics Closed Cells



## Three Hart Closed Cells

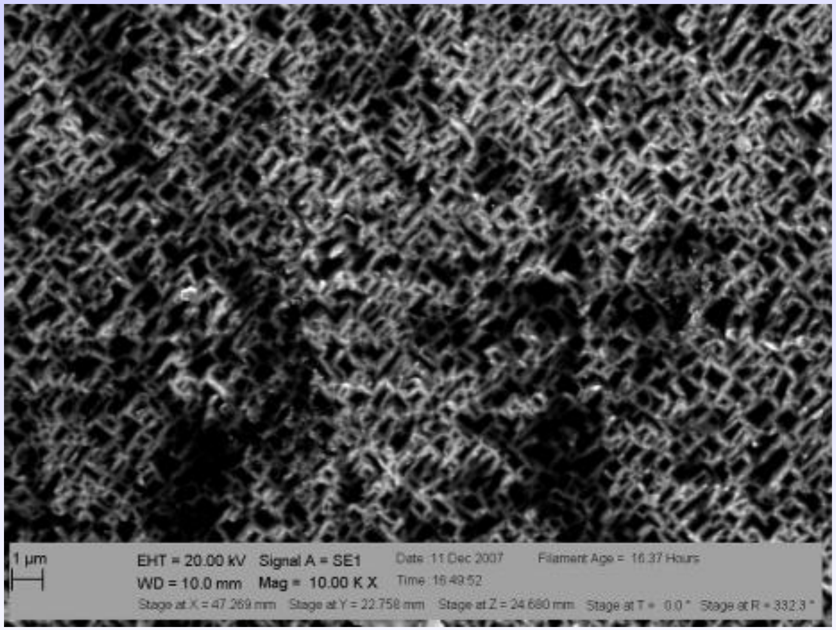
**based on the ENEA / Violante design**

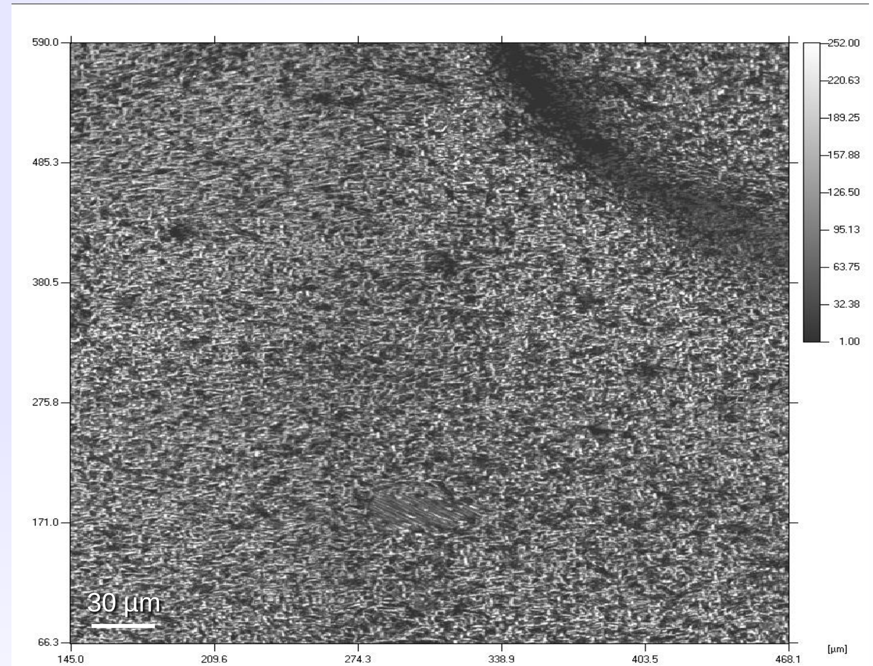
We currently use two different catalysts: 0.5% Pd on alumina and Johnson Matthey Pt electrode on Carbon Fiber Paper

# Material Development for Electrochemical Studies

- Traditional Rolling, Annealing, Etching
- Ultrasound Etching
- Electrochemical/Chemical De-alloying
- Templated Materials
- Oxidation Followed by $D_2$ Reduction
- Ion Implantation (Ar, He)
- Impurity additions – **Raney Ni (50:50 Ni:Al alloy)**, **Al powder**, Fe powder, Ni nanopowder, alumina, silica, cobalt chloride, bismuth citrate, Pd zeolite, Pd ammonium chloride, rhodium sulfate, boric acid, phosphoric acid, sodium tetraborate, NaI, KI, sodium dichromate, lithium carbonate, polyethylenimine, thiourea, uranyl acetate

# Grating/Labyrinth Structure




(NRL Produced)

L64 - Energetic's "Gold Standard"

- Large grains
- < 1 um deep grooves
- Large power gain for many hours

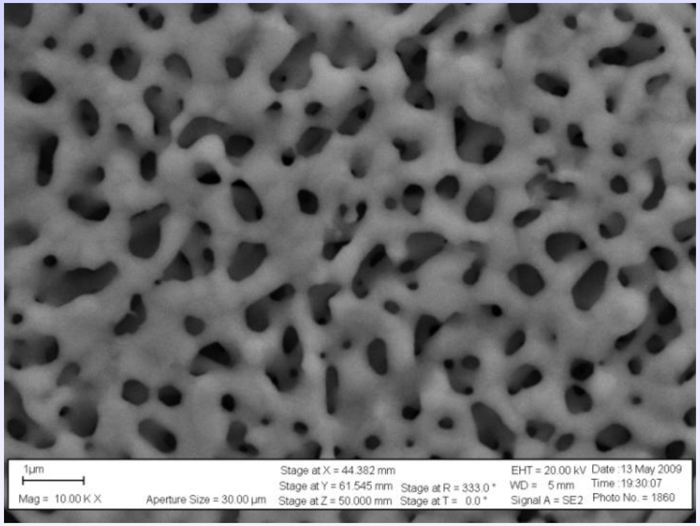
Morphology Important !

Ultra-Sound Etched ESPI Cathode

- No excess heat at <250 mA/cm$^2$ for 3 foils

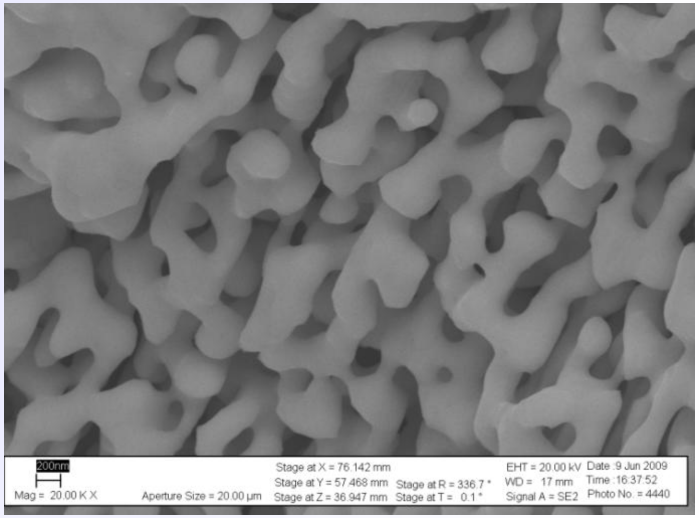
# Nanoporous Materials

## Electrolysis of Nanoporous Pd




- $Pd_{20}Co_{80}/Pd/Pd_{20}Co_{80}$ sandwich bonded by cold rolling and thermal annealing
- Electrochemical dealloying in 0.1M $H_2SO_4$
- Coarsening of porous structures by vacuum annealing at 500ºC for 120 min

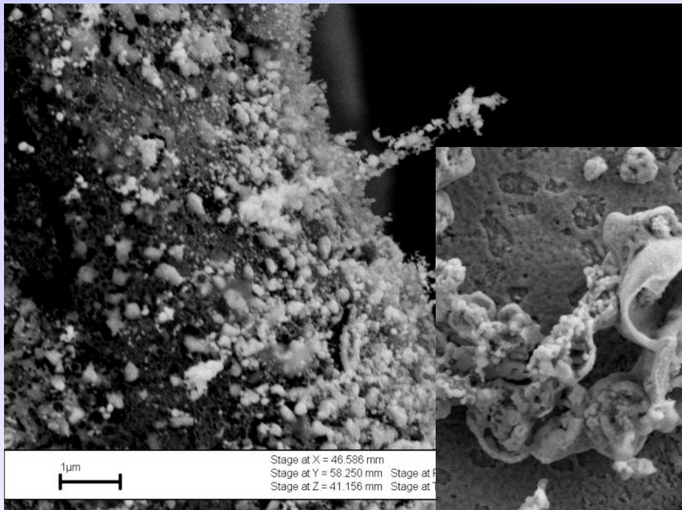
## Pd Nanoparticles in Nanoporous Gold



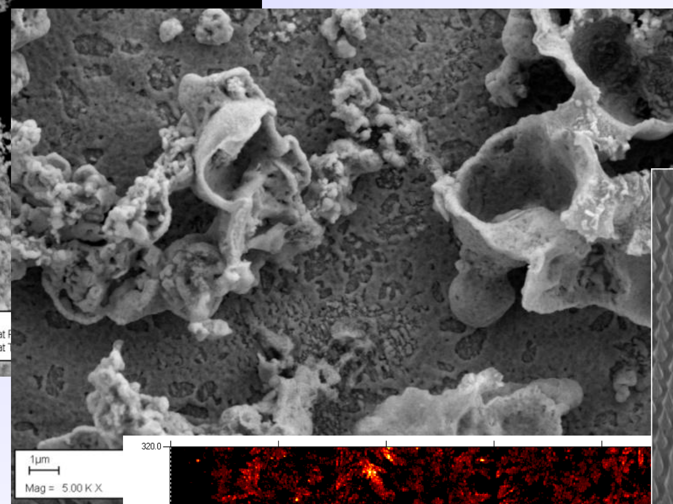

- $Au_{30}Ag_{70}/Au/Au_{30}Ag_{70}$ sandwich bonded by cold rolling and thermal annealing
- Chemical dealloying in conc. $HNO_3$
- Soaked in $PdCl_2$+HCl solution overnight
- Reduction of Pd in 760 Torr $H_2$ at 400ºC for 30 min

No excess heat observed

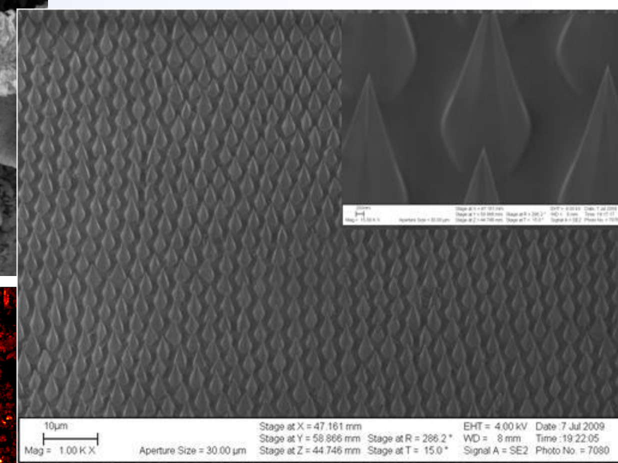
# Other Cathode Materials Under Development




Carbon nanotubes coated with Pd



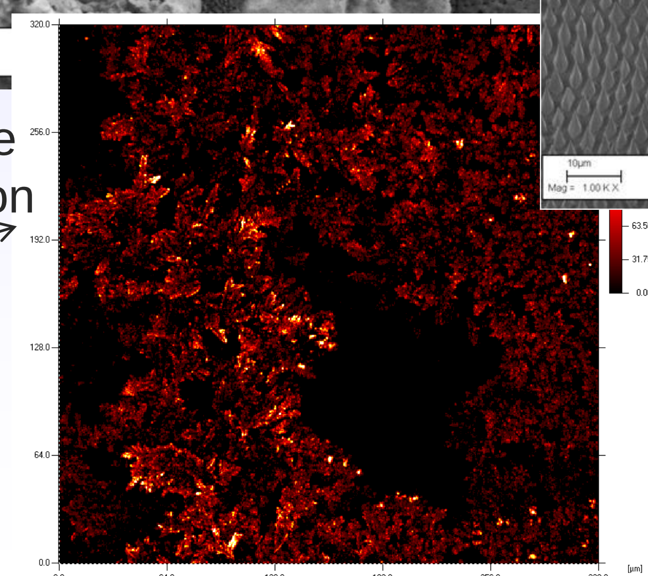

Pd foil after oxidation/reduction procedure




Nanotip Arrays

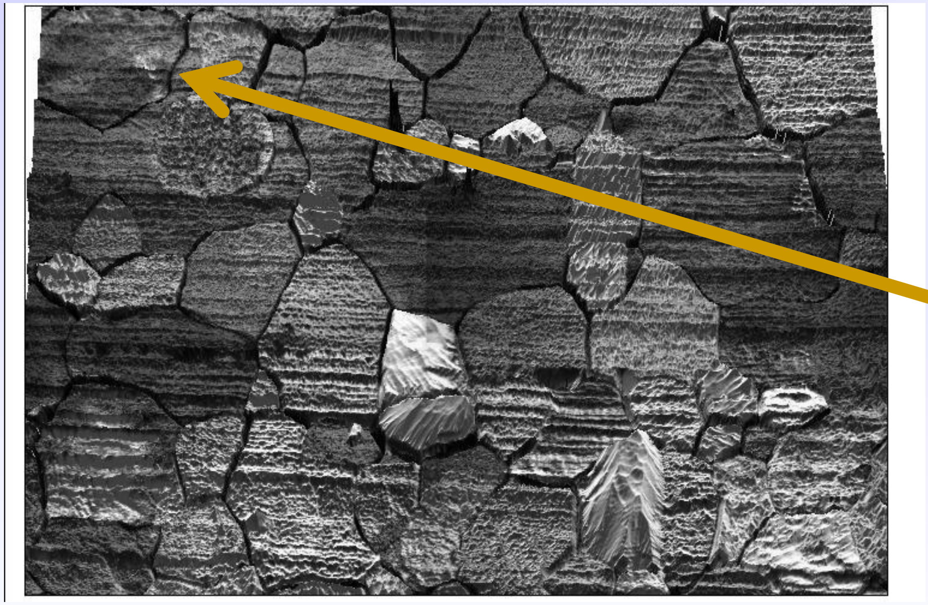
Tip radii of curvature ~ 25nm

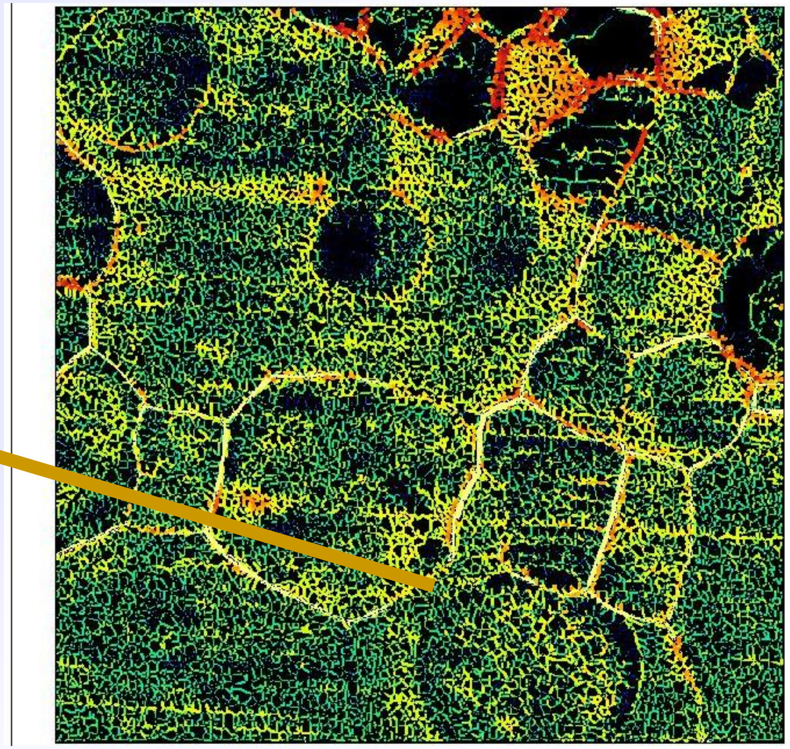
High surface area cathode produced by Co-Deposition



# Pd 98%, Pt 1% and Rh 1%

Recent Success Producing L64-type Morphology





- Well defined grain boundaries
- Partial coverage of labyrinth-like structure

# Cathode Materials Investigated

| | | Energetics | Hart | DTA | Total |
|---|---|---|---|---|---|
| **Pd/LiOD** | | | | | |
| | Platexis | 2 | | | |
| | Holland Moran | 1 | | | |
| | Vittorio | 10 | 15 | 3 | |
| | ESPI | 7 | 6 | | |
| | Alfa Aesar | | 1 | | |
| | Goodfellow | 2 | 18 | | |
| | G&S | | 3 | | |
| | **Total** | **22** | **43** | **3** | **68** |
| | | | | | |
| **Pd/LiOH** | | | | | |
| | Vittorio | 2 | | | |
| | ESPI | 2 | 4 | | |
| | Alfa Aesar | | 2 | | |
| | Goodfellow | | 3 | | |
| | **Total** | **4** | **9** | | **13** |
| | | | | | |
| **misc** | | | | | |
| | Ni/LiOH | | 1 | | |
| | Goodfellow Pd/KOD | | 1 | | |
| | Vittorio Pd/H2SO4 | | 1 | | |
| | **Total** | | **3** | | **3** |

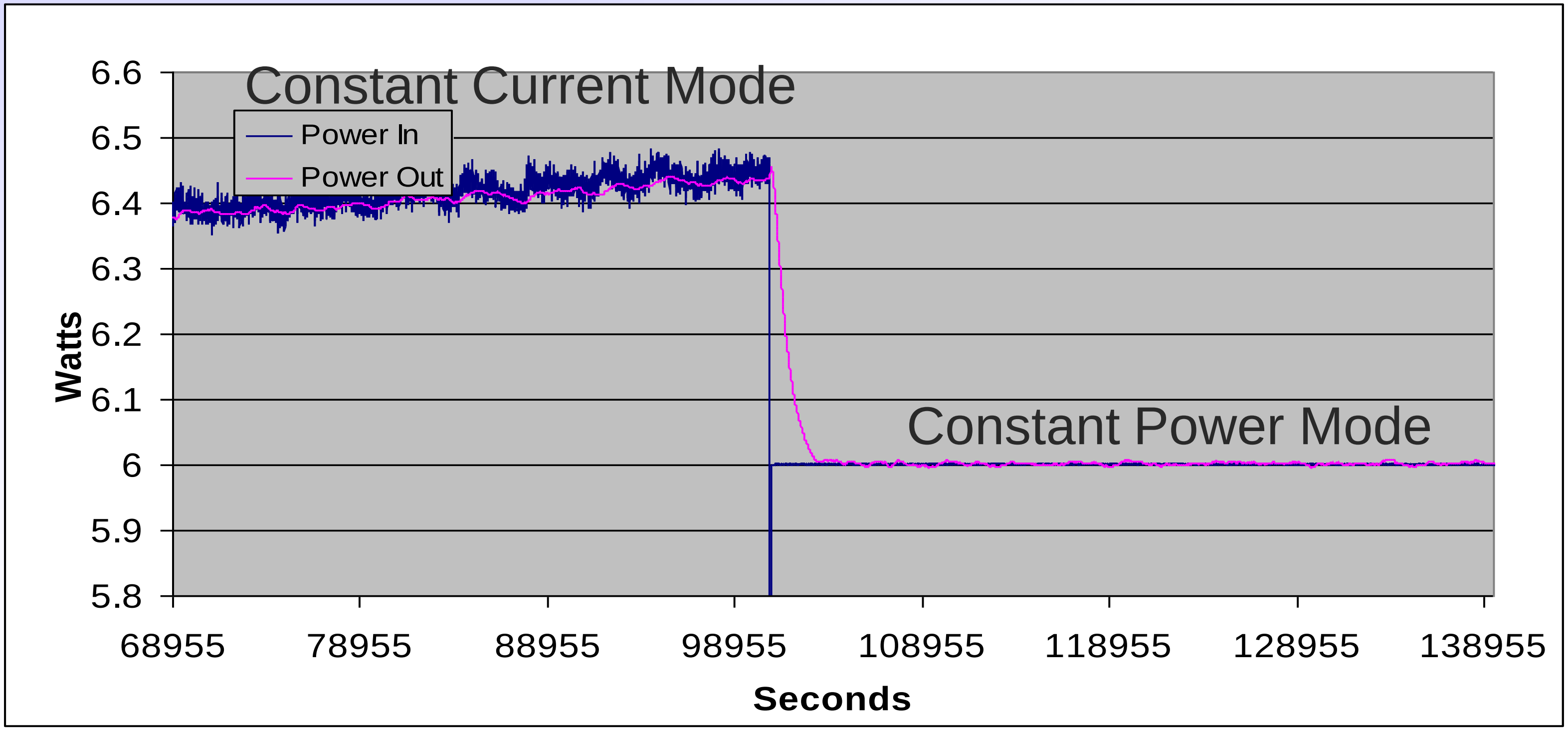
# Cathode Materials Investigated (continued)

| | | Energetics | Hart | DTA | Total |
|---|---|---|---|---|---|
| **x/LiOD** | | | | | |
| | Pd/0.25% B | | 2 | | |
| | Pd/0.75% B | | 2 | | |
| | Pd-C nanofoam | | 1 | | |
| | Pd nanoparticles in nanoporous Au | | 1 | | |
| | Nanoporous Pd | | 1 | | |
| | Ni | | 3 | | |
| | Nb | | 3 | | |
| | Ta | | 2 | | |
| | Pd/5% Ru | | 2 | | |
| | Ni/Pd | | 2 | | |
| | Ni/Pd/Ni | | 1 | | |
| | Pd 98%/Pt 1%/Rh 1% | | 2 | | |
| | Pt | 6 | 5 | | |
| | **Total** | **6** | **27** | | **33** |
| **Grand Total** | | | | | **117** |

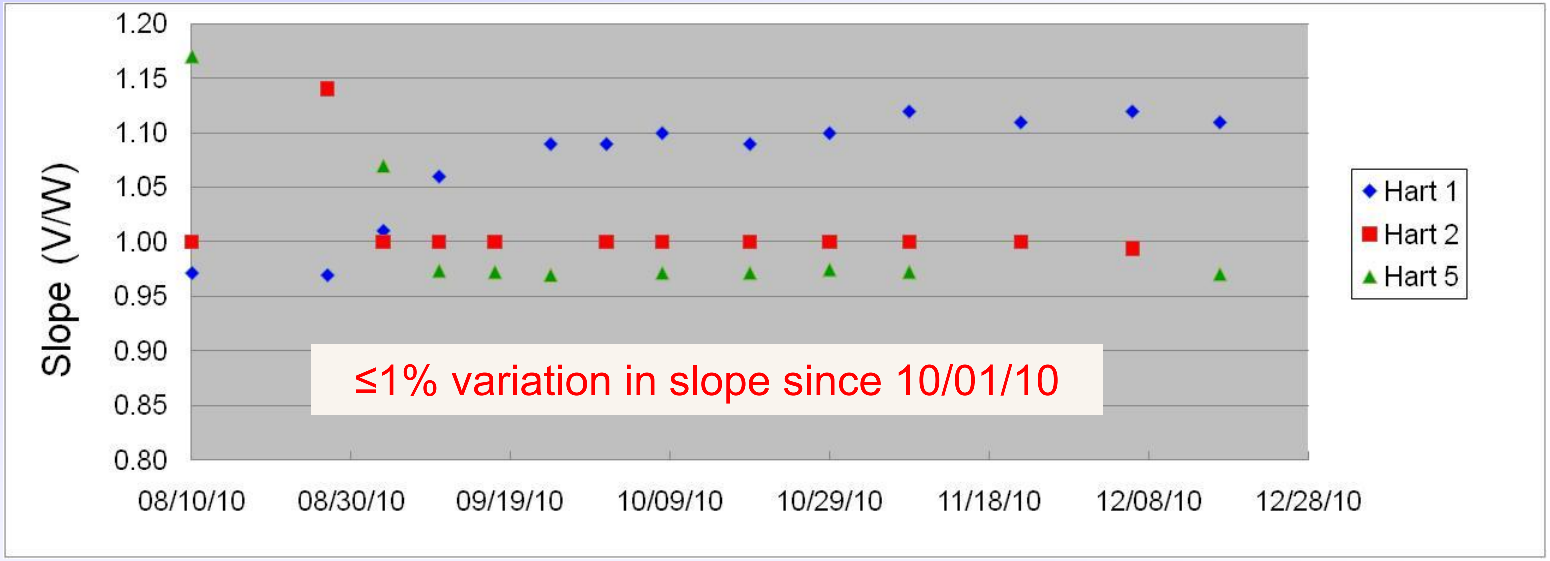
# Electrolytic Loading:

Original Fleishmann and Pons Approach

- Many experiments, over 24 months, with consistent results
  - $Power_{in} = Power_{out}$



# Hart Fitting Coefficients




Calorimeter calibration stable over many months!

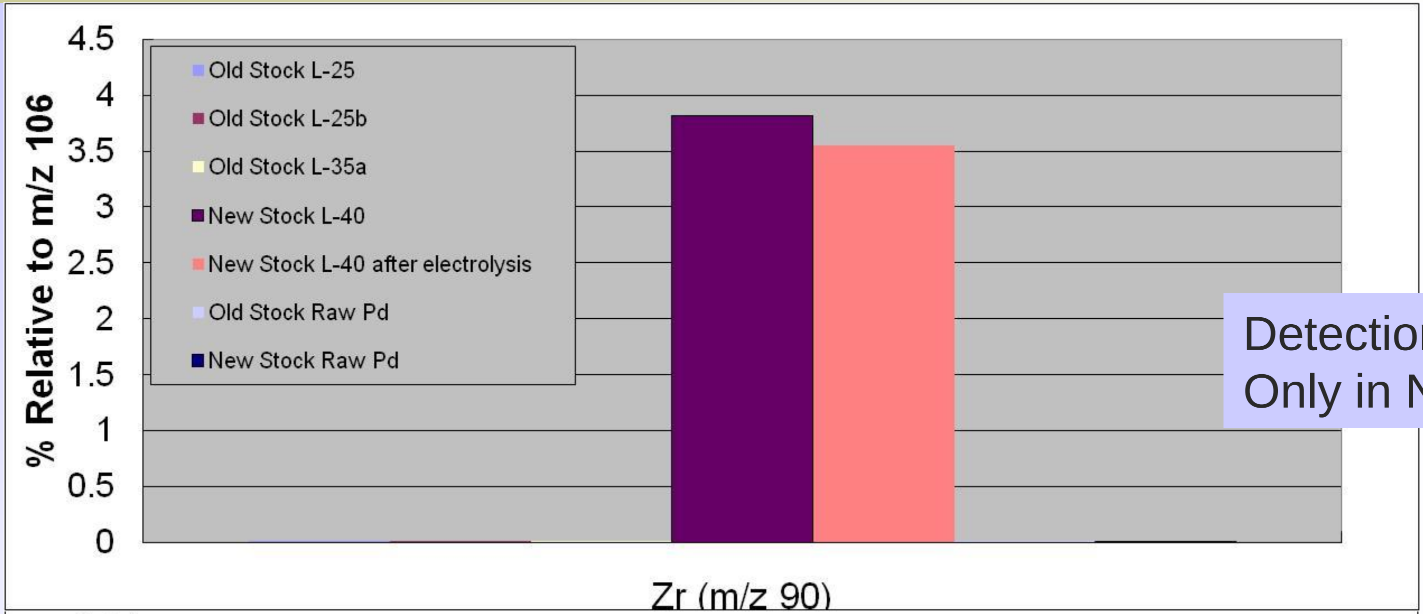
# Analysis of trace impurities

Inductively-Coupled Plasma Mass Spectrometric Analysis

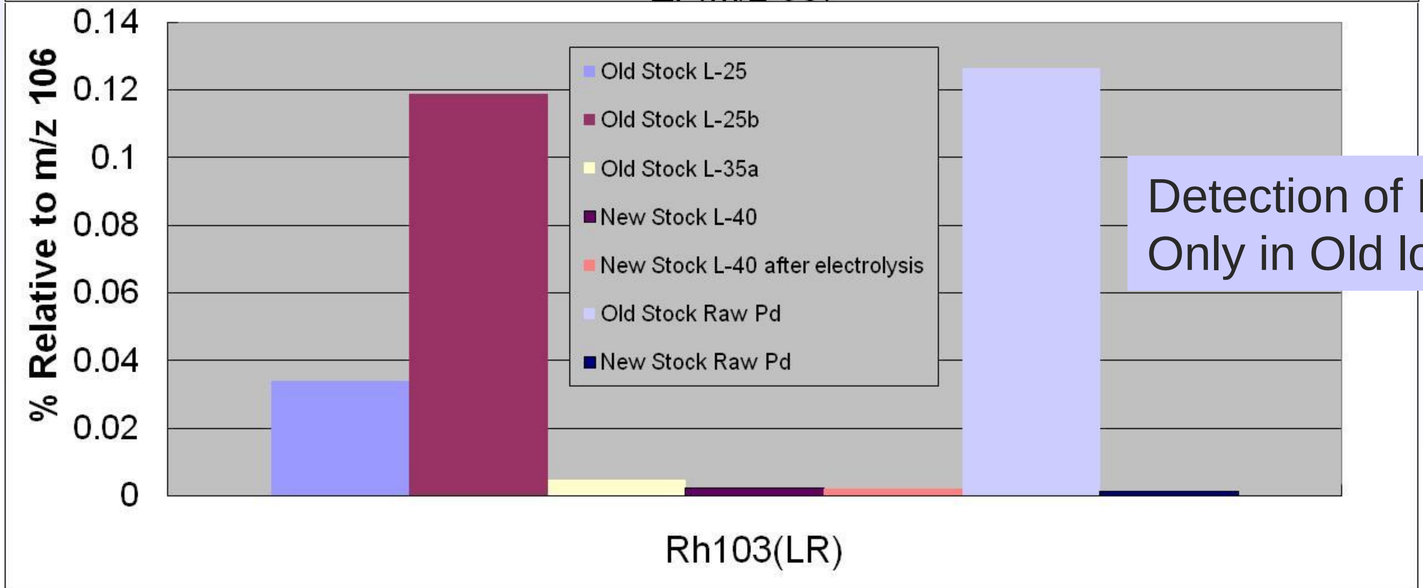
- Older lots of Palladium, that appeared to produce substantial heat, likely had only ONE source – Engelhard
- ICP-MS analysis shows different impurity profiles than current palladium lots
  - Older lots appear to have recycled Pd from catalytic converters as **rhodium** and **platinum** are present
  - Current lots are much purer in these elements but have **zirconium**, **yttrium**, and **hafnium** present
    - Likely change in crucibles for melting to Zirconia
    - Rhodium prices may drive recovery as a separate element
- Are the impurities responsible for FPE??

# Examples of trace impurities

Inductively-Coupled Plasma Mass Spectrometric Analysis



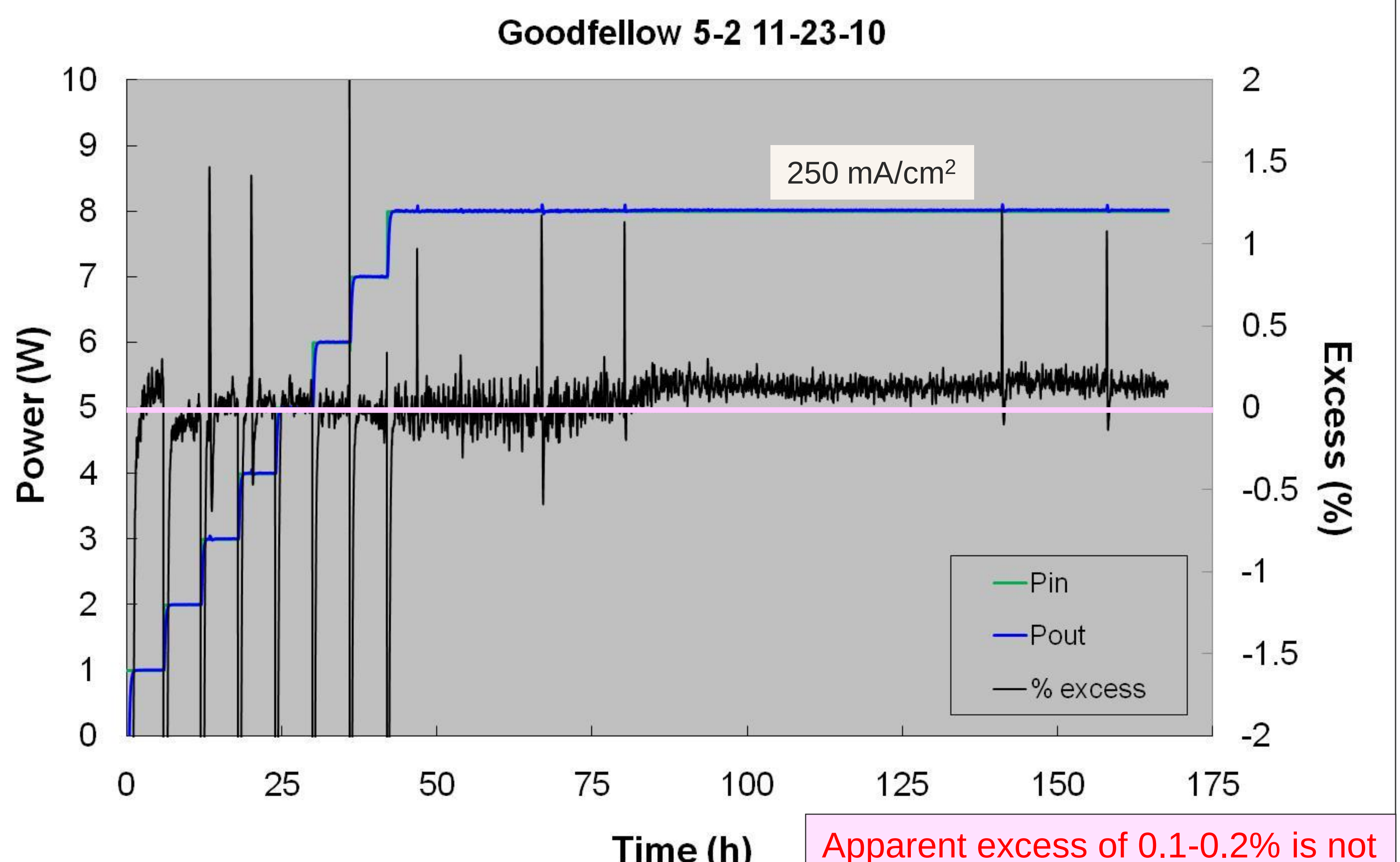

Detection of Zr
Only in New lots




Detection of Rhodium
Only in Old lots

# Goodfellow Pd Cathode

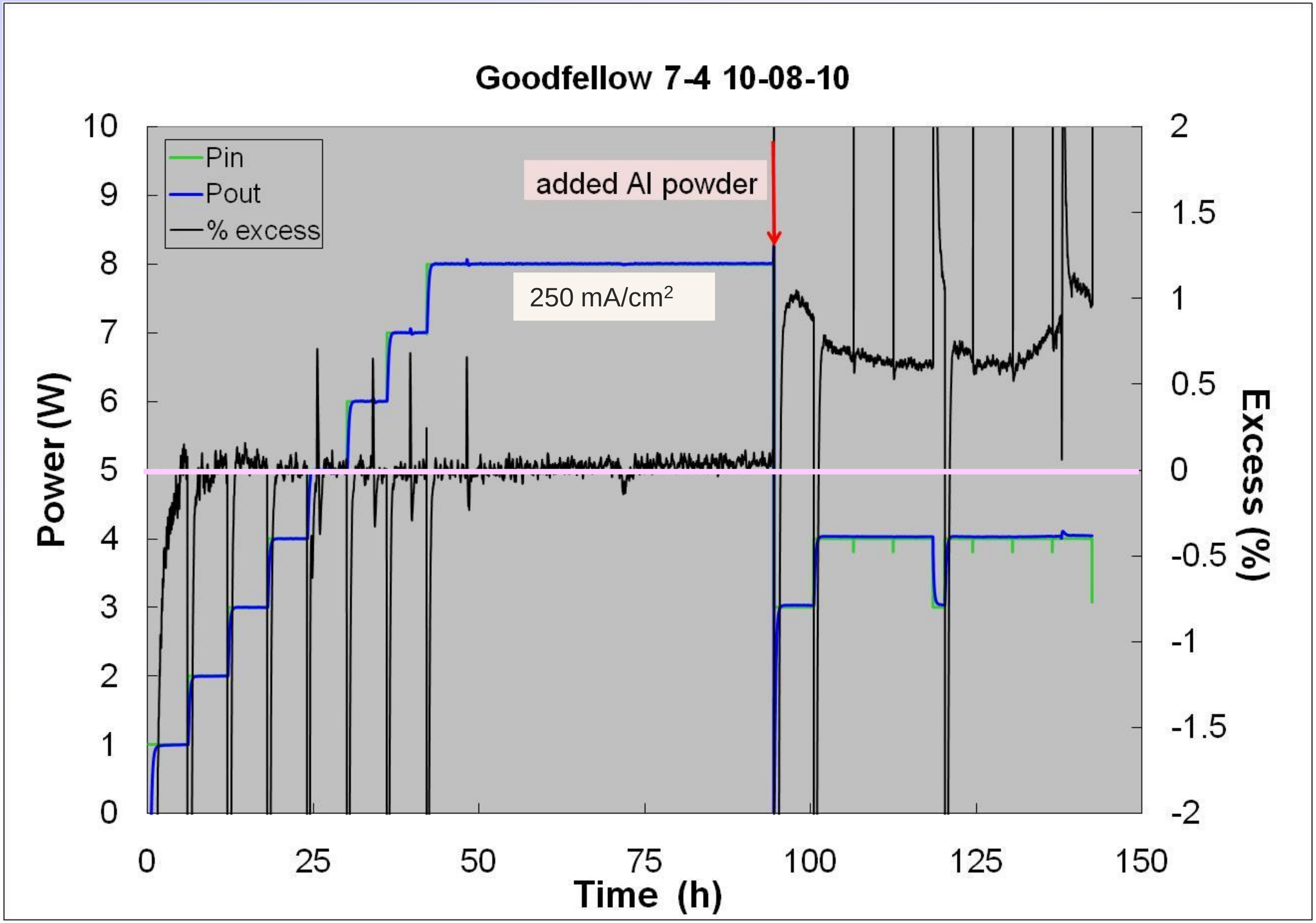
Hart Calorimeter - No Addition




Apparent excess of 0.1-0.2% is not convincing evidence for FPE

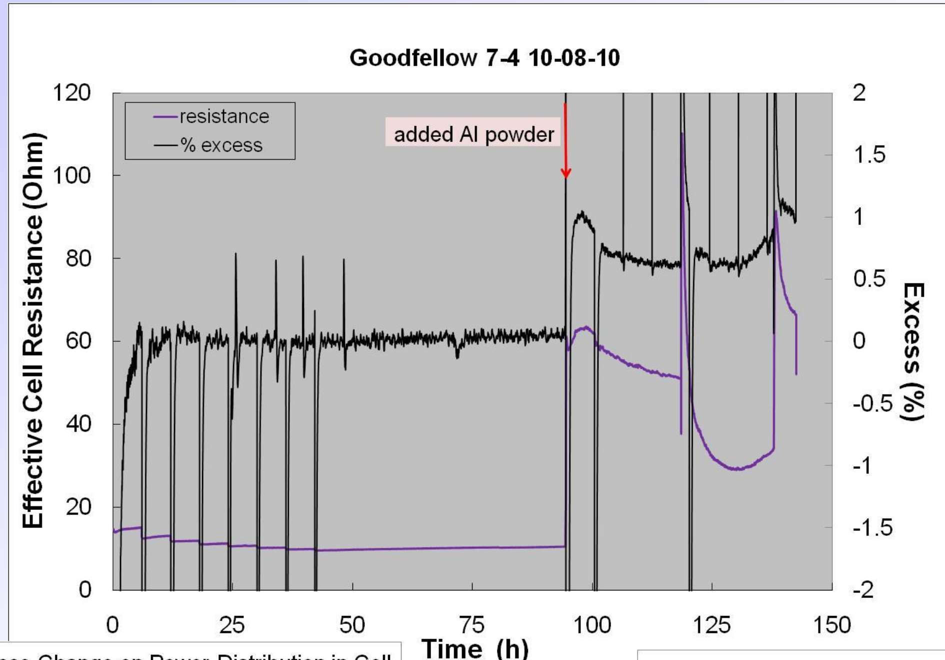
# Do Aluminum Additions Produce Excess Heat?

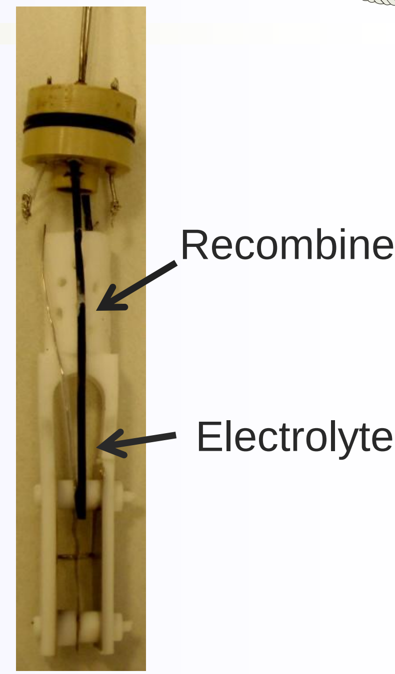
Hart Calorimeter

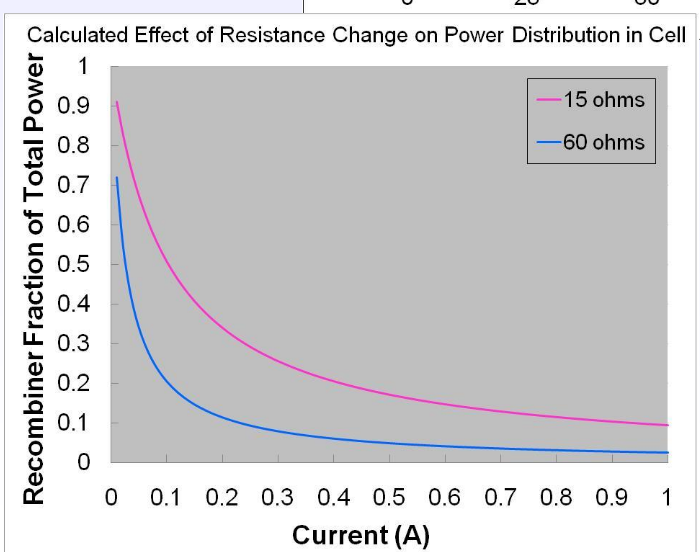


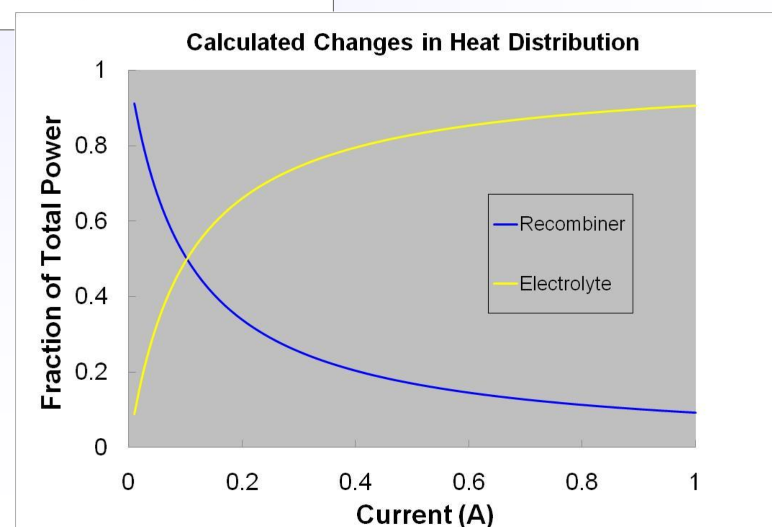
# Is Heat Redistribution Responsible for Excess Heat?

Hart Calorimeter



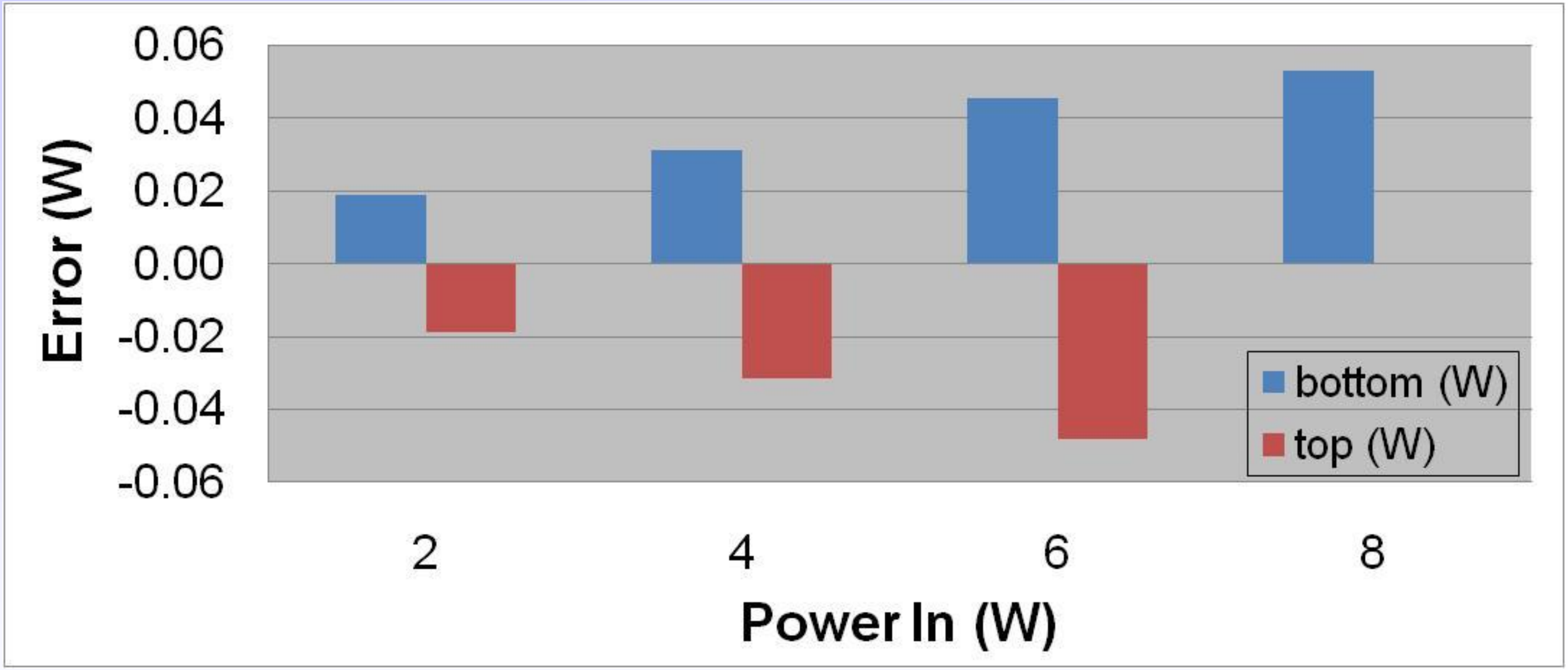



# Two Resistor Calibration of Hart Calorimeter

Worst Case Scenario

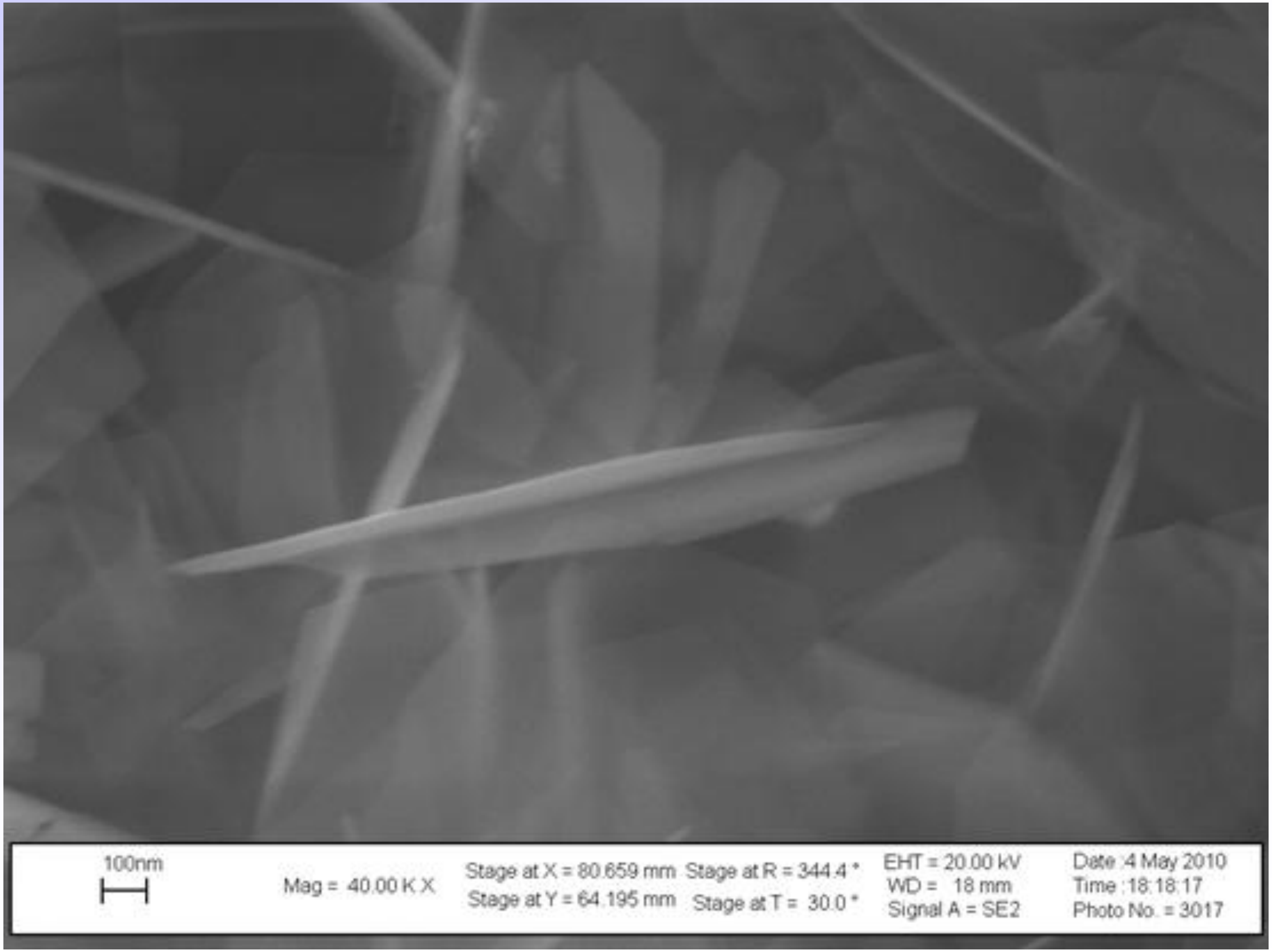



At 8W input power, ±50 mW error is worse case with all heat generated at one end of cell (top or bottom)

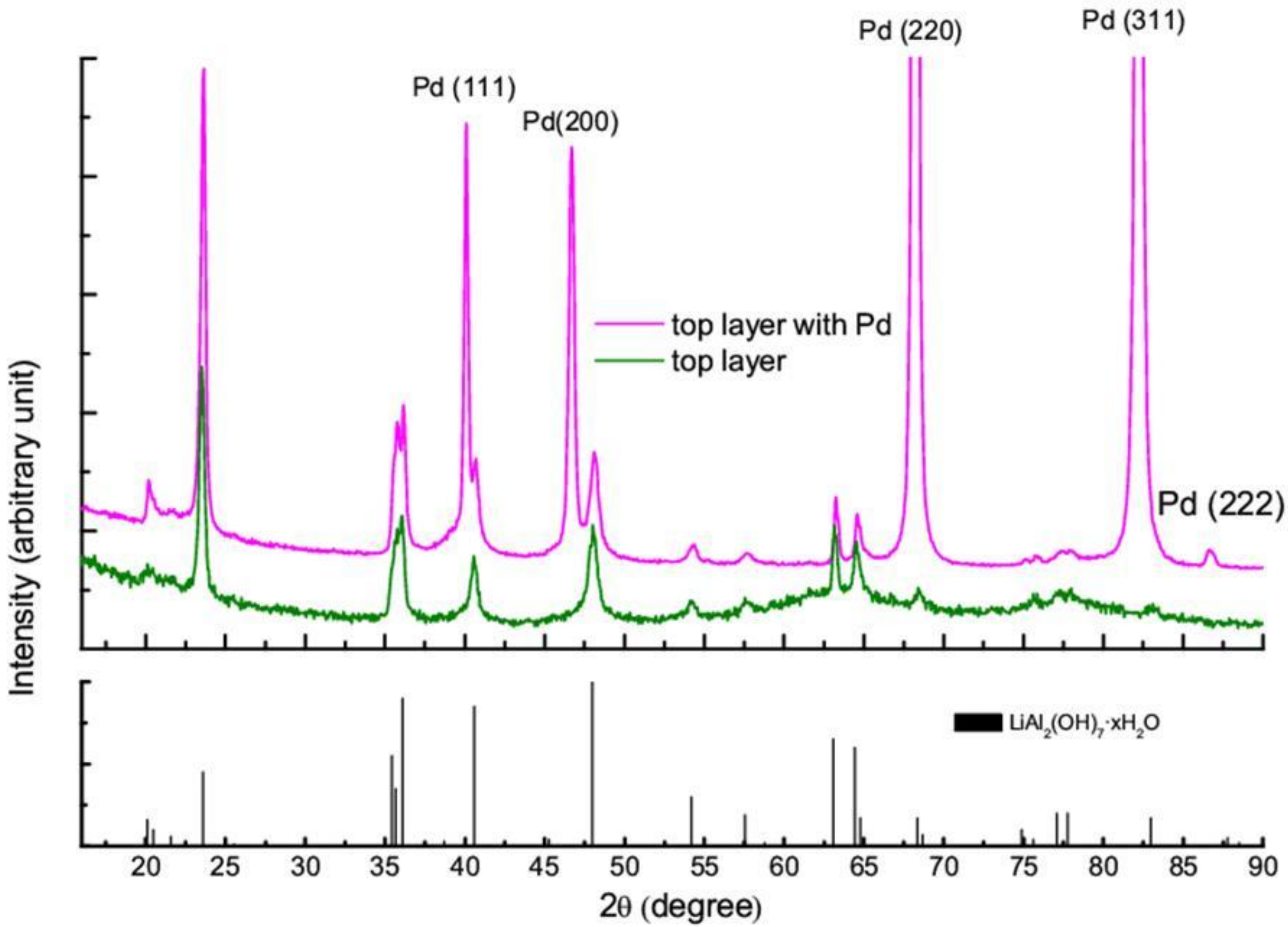
Apparent excess of 0.5-1% for Goodfellow 7-4 Pd cathode might be attributed to heat redistribution in the cell upon the addition of Al powder

# White Material Isolated from Hart Cells:

Lithium Aluminum Hydroxide

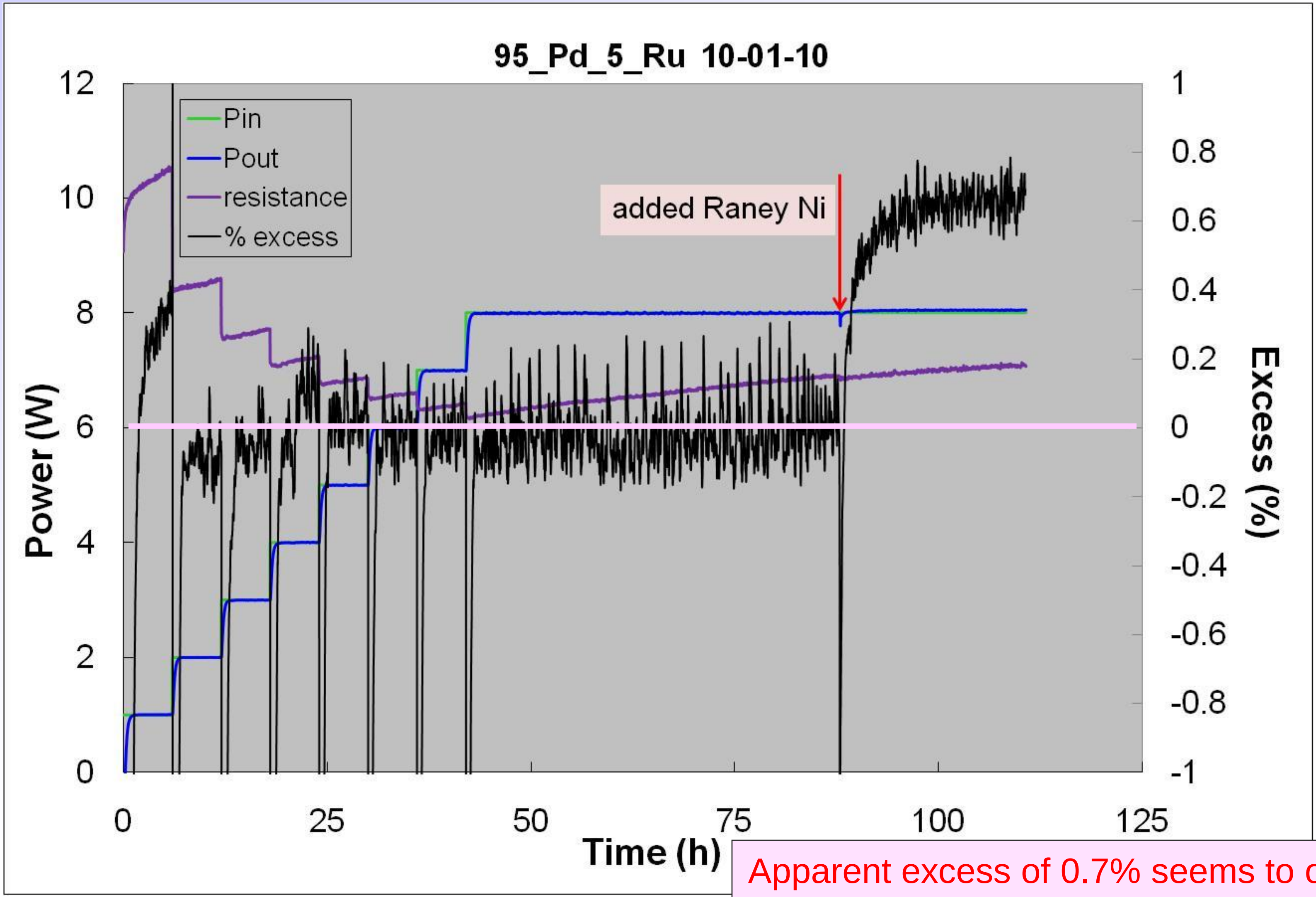


# XRD of Goodfellow Pd with Possible Excess Heat



# Pd 95%, Ru 5%

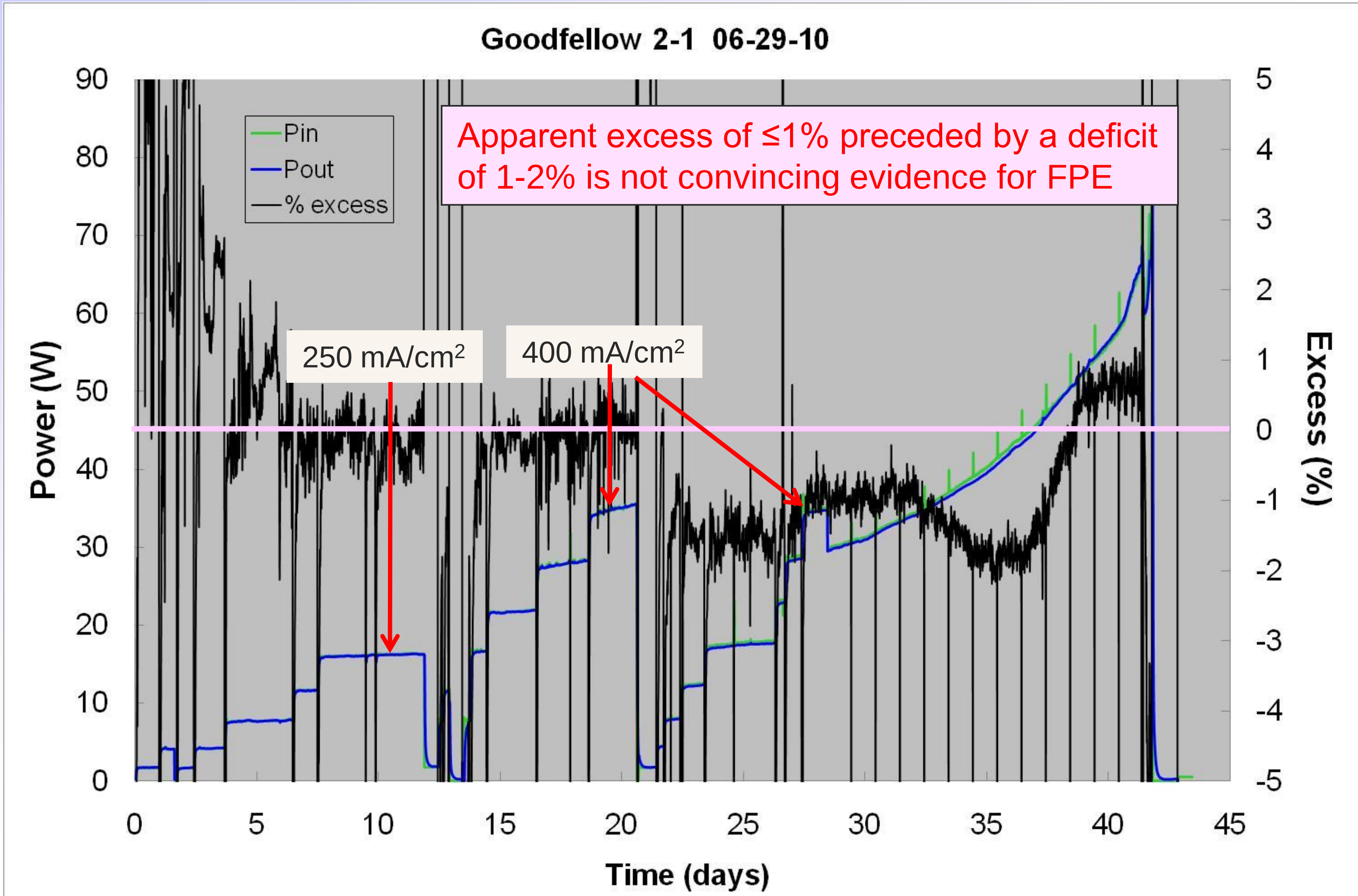
Hart Calorimeter




Apparent excess of 0.7% seems to occur without heat redistribution in the cell

# Goodfellow 2-1

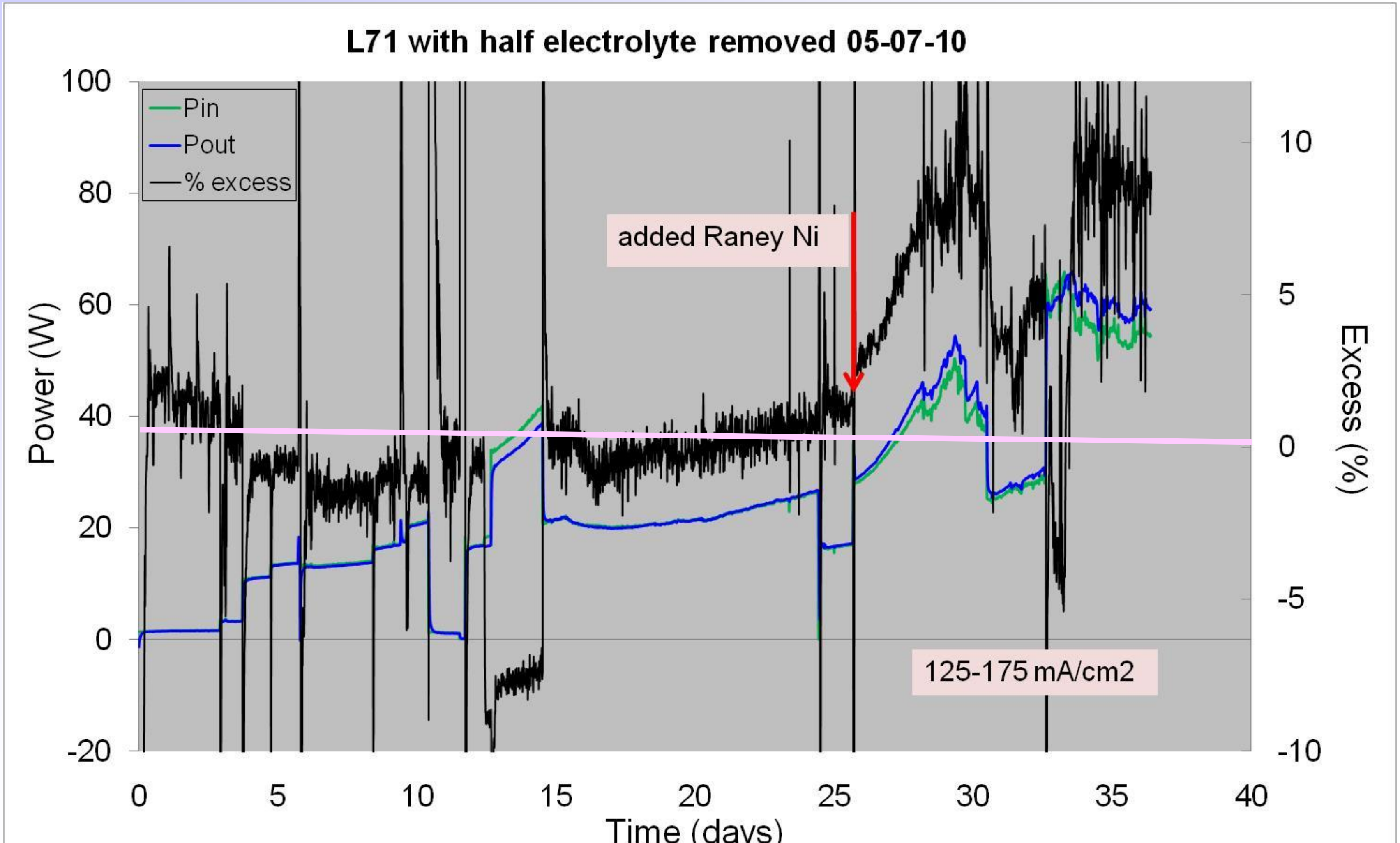
Energetics Calorimeter - No Addition



# L71

## (Half of Electrolyte Removed/Pd Cathode Partially Uncovered)

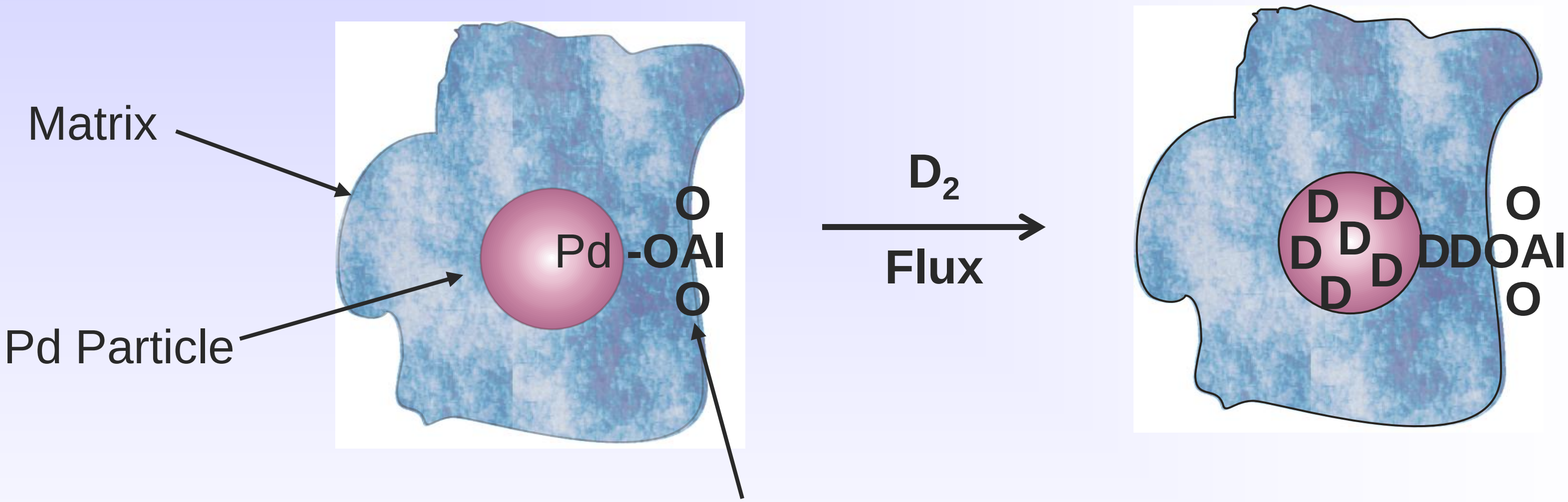
Energetics Calorimeter




An apparent excess of 5-10% is intriguing, BUT heat redistribution in the Energetics cell upon addition of Raney Ni needs to be examined!!!

# Model of Possible Reaction Requirements

Support oxide interacting with palladium nanoparticle




Strong electric fields – up to 95V/nm

C. Otero Areán, *et al*., “Thermodynamics of hydrogen adsorption on the zeolite Li-ZSM-5”, *Chemical Physics Letters* **370** (2003) 631–635.

A strong electric field might be a requirement for FPE

# Other Supporting Evidence for the Role of Oxide Interfaces in FPE

- M. McKubre – 200 ppm addition of aluminum or silicon in metallic or oxide form
- M. Miles – glass tube (silica)
- V. Violante – glass cell (silica)
- F. Celani – Pd wire coated with Pd nanoparticles (nanoporous alumina)
- Cravens & Letts – “pixie dust”
- Arata – Zr, Ni, Pd oxides
- D. Kidwell – Pd zeolites (aluminosilicates)

# Conclusions

- Older, more successful, Pd Materials all had a common production and different impurity profile than current Pd
  - Trace elements may be important for FPE
- Pd morphology may be a necessary but insufficient condition for FPE
- Many different cathode materials investigated in both Hart and Energetics calorimeters
  - No convincing positive results found
  - Some intriguing results keep us motivated to continue
- Oxide interfaces may be necessary for the production of FPE
  - Addition of materials that form oxide interfaces appears helpful
  - The requirements and generation mechanism for FPE are unclear

# Acknowledgements

The views, opinions, and/or findings contained in this presentation are those of the presenter and should not be interpreted as representing the official views or policies, either expressed or implied, of the Naval Research Laboratory or the Department of Defense.

# Questions