

LANR Cathode Preparation for Electrolysis Experiments: A Comparison of Protocols and Implications

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Presentation Summary

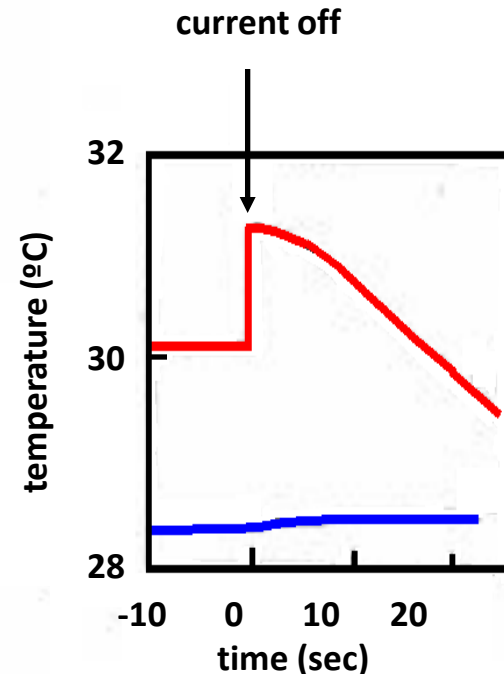
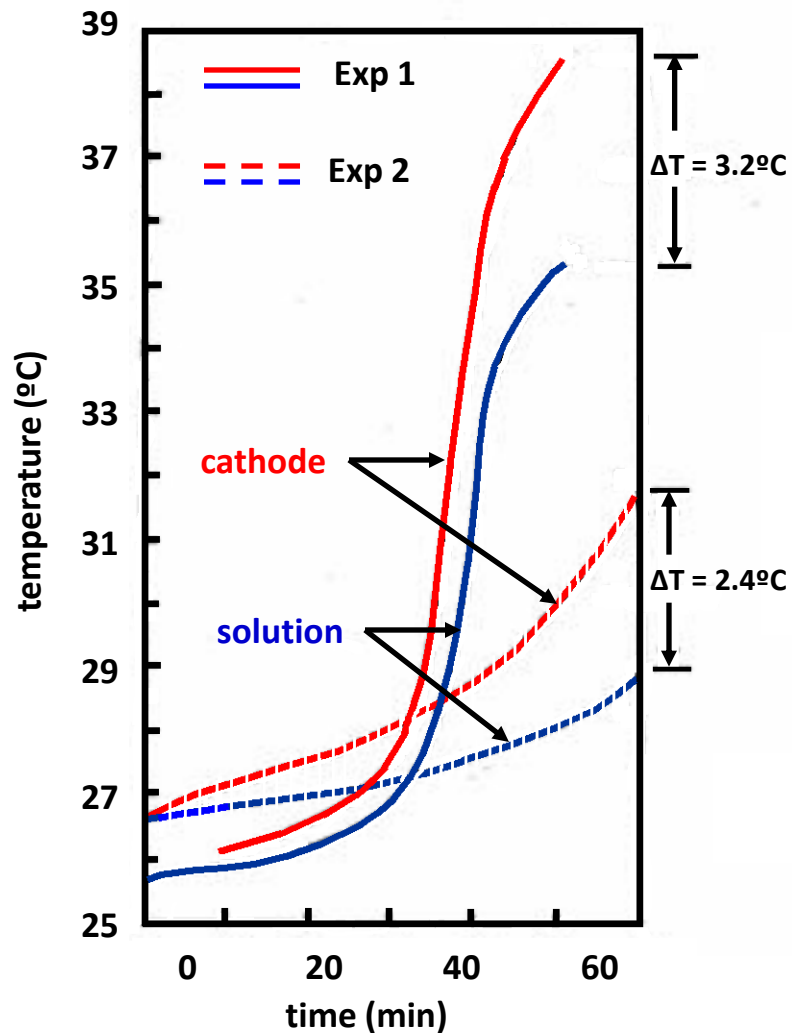
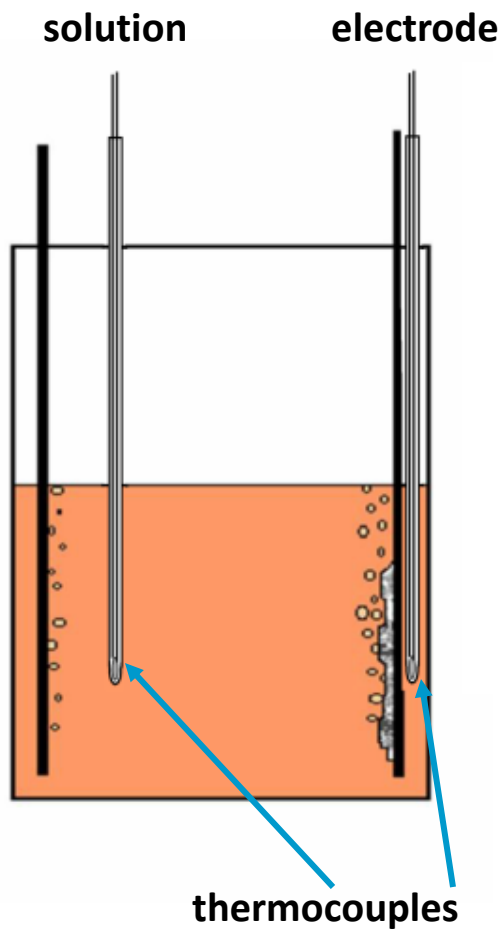
- A wide variety of Co-deposition protocols have been “successfully used
- Co-deposition has always been credited with producing high loading ratios
- Magnetic and/or electric fields may to be important
- Fukai suggests that loading ratios could be even higher with production of SAV's >1:1
- Implications: Suggests a lot more experimentation with co-deposition
 - Chemistry vs current density and profile vs magnetic field vs ???
 - Are products (heat, radiation) different for different conditions?
 - At what lattice concentration does hydrogen become a poison?

Evolution of Co-Deposition

- Fleischmann - Pons effect published [PonFlH89]
 - Cathode: bulk palladium (Pd)
 - Long loading time of 2-4 weeks
 - Excess heat difficult to replicate
- Szpak - Boss co-deposition published [SzpMoS91]
 - Cathode: electrodeposited Pd on Cu and other materials
 - Modest loading time of days
 - Excess heat replicable
- Many others have used/are using co-deposition
- Letts – Hagelstein protocol published [LetHag12]
 - Cathode: electrodeposited Pd on Au coated Cu
 - Different concentrations of Pd
 - Higher current density resulting in short co-deposition time
 - Excess heat reported

Temperature vs Time Profile

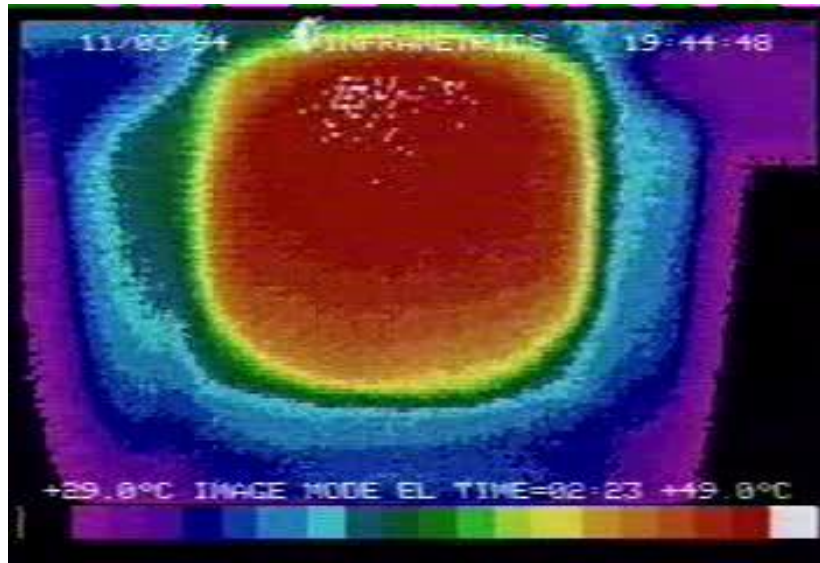
J. Electroanal. Chem., Vol.302, pp. 255-260 (1991)



The Electrode is warmer than the Solution!

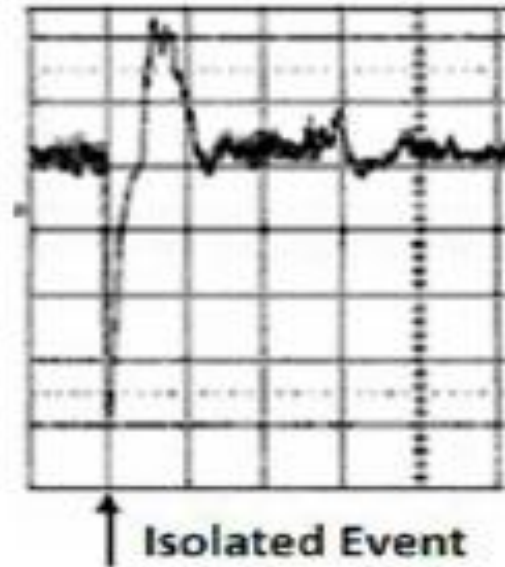
“Hot Spots” and “Mini-Explosions”

Il Nuovo Cimento, Vol 112A, pp. 577-585 (1999)



a

a – hot spots



b

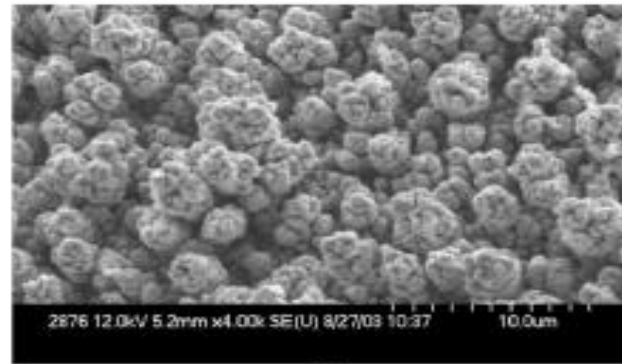
b - piezoelectric

Infrared camera and polarized ferroelectric PZT transducer responses

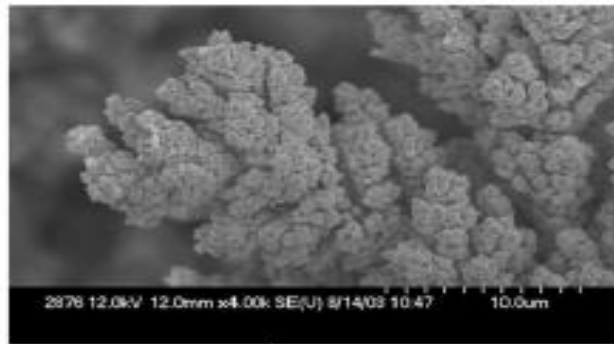
SEM of Co-Deposited Pd/D Film

J. Electroanal. Chem. 580 pp284-290 (2005)

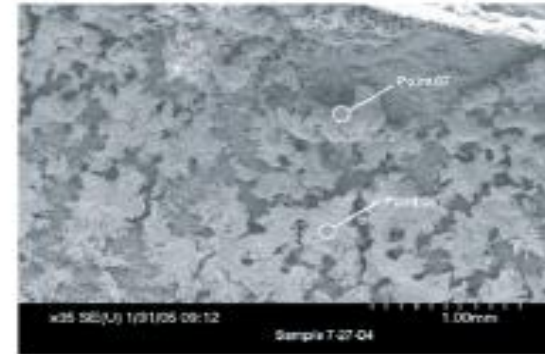
Eur Phy J Appl Phys 40 pp293-303 (2007)



a



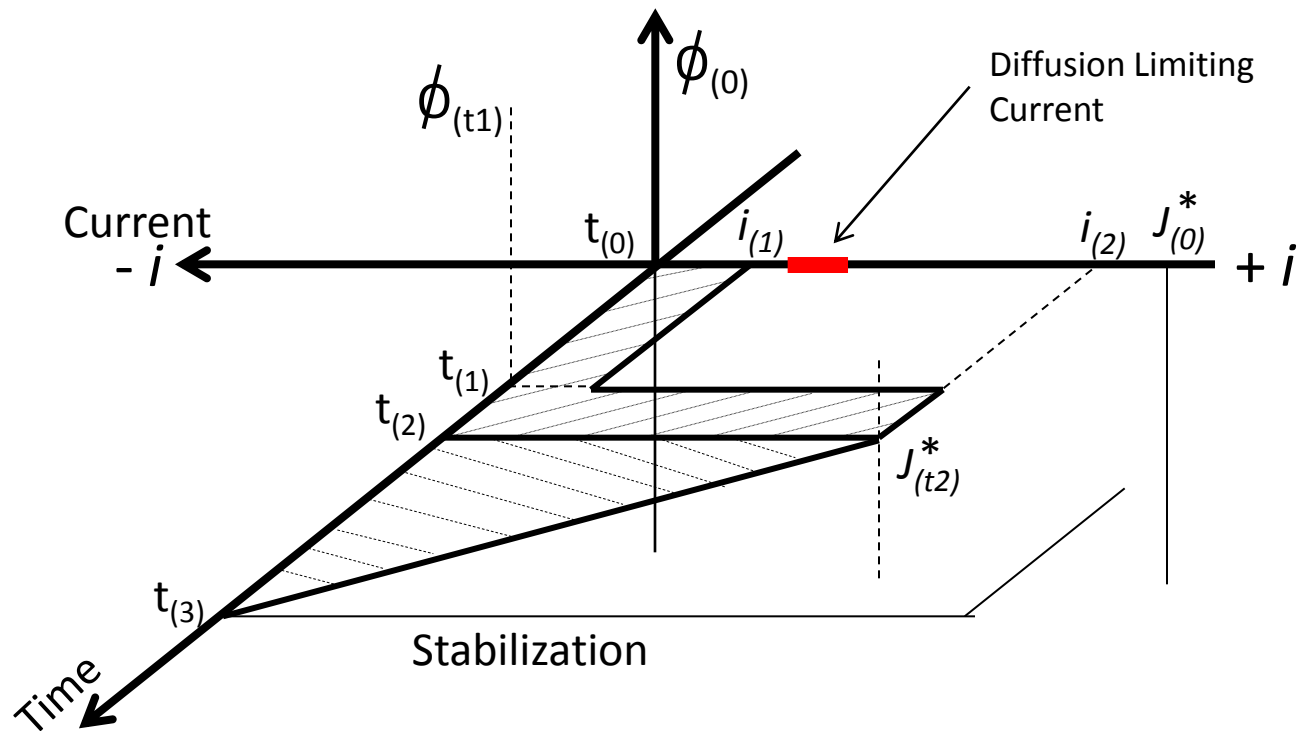
b



c

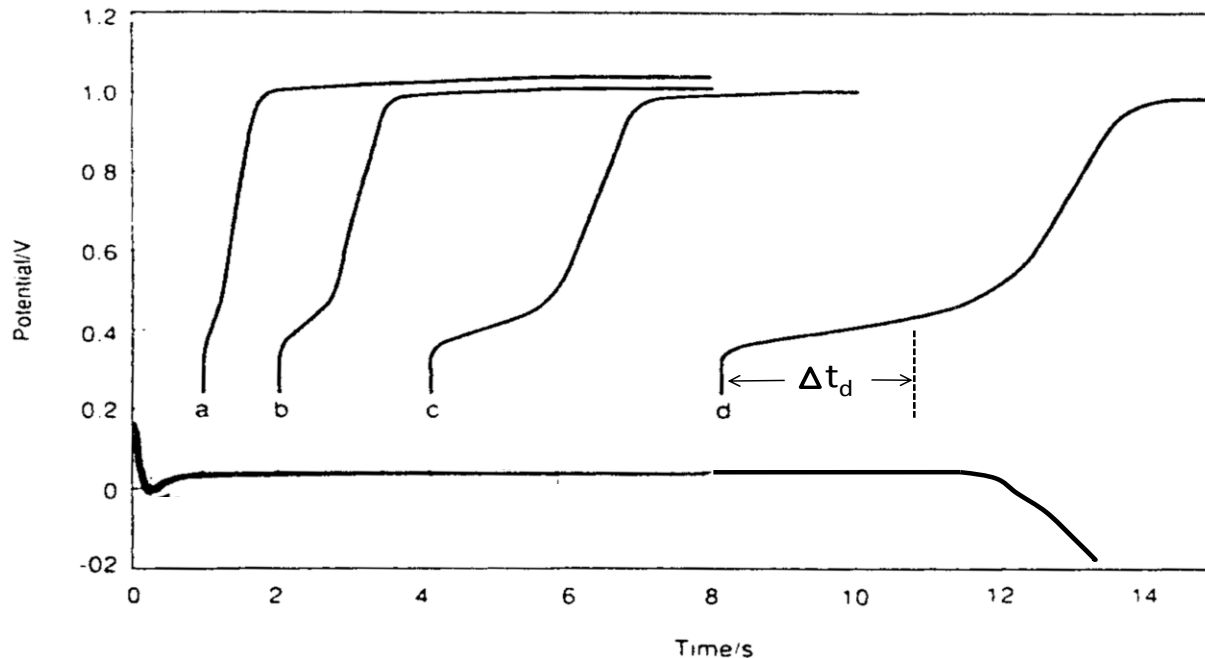
a – after completion of co-deposition,
b – exposed to external electric field, c – exposed to magnetic field

Electrochemical Co-Deposition Processes



Deuterium Up-take

J. Electroanal. Chem. 379 pp 121-127 (1994)

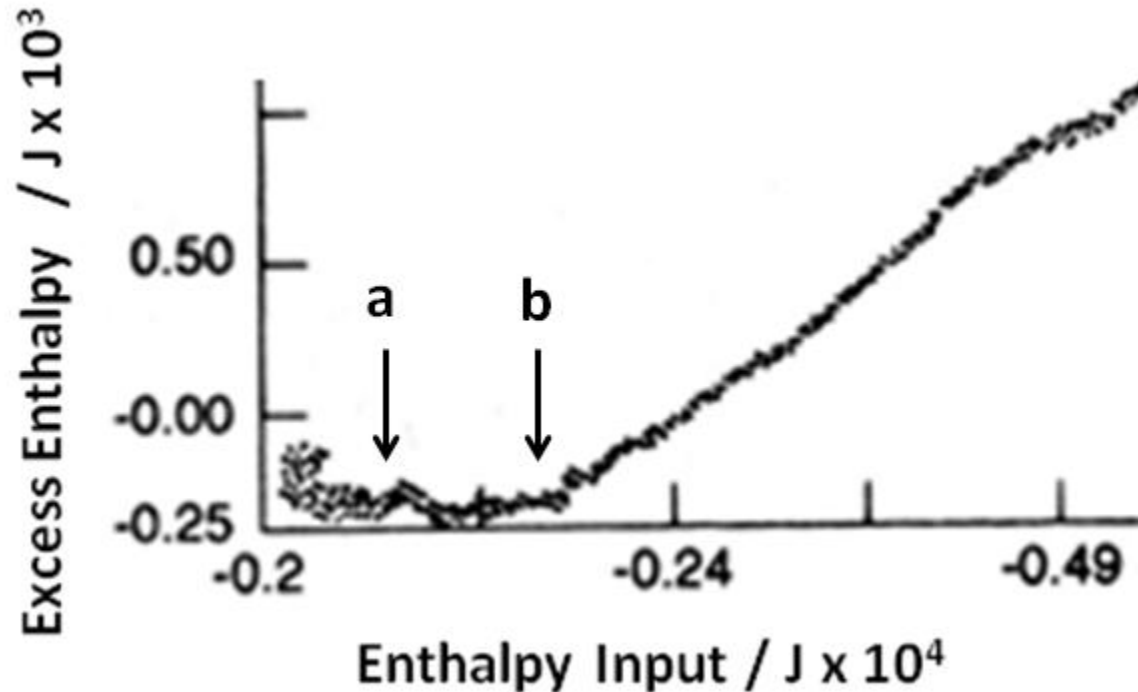


Deuterium up-take during co-deposition. $j_c = -5 \text{ mAcm}^{-2}$ and $j_a = 5 \text{ mAcm}^{-2}$, with cell current reversal at 1, 2, 4, and 8 seconds.

High loading ratios are achieved during co-deposition

Initial Co-Deposition Thermal Behavior

Fusion Technology 36 pp234-241 (1999)



endothermic absorption – $0_i Q_i A$ [$0_i Q_i a$],

endothermic absorption balanced by exothermic reaction – $a_i Q_i b$ [$a Q_i b$],

exothermic reaction dominates $Q_i a$ [$b Q_i$]

Galileo “Protocol”

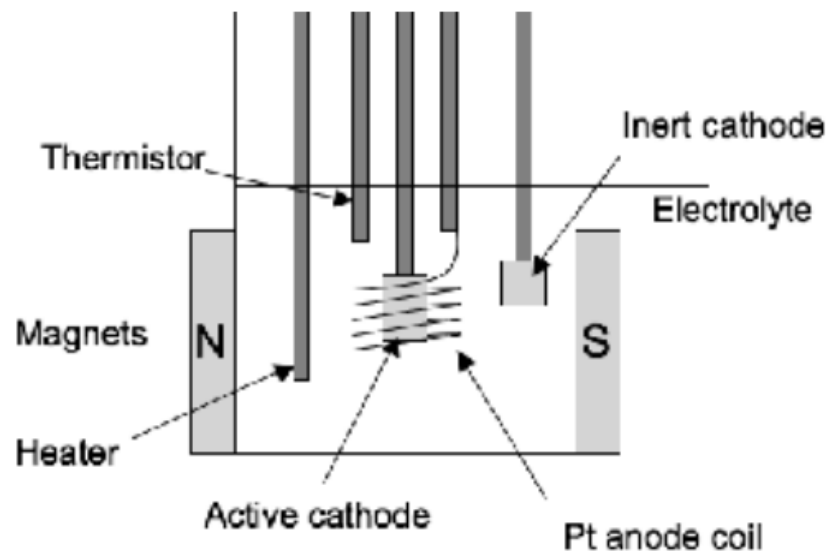
- The co-deposition protocol developed at SPAWAR by Szpak and Mosier-Boss as part of the Galileo Project to confirm nuclear particle generation using CR-39 as an archival particle detector
- Protocol and projects results reported in:
<http://newenergytimes.com/v2/projects/tgp/2007TGP/2007GalileoProjectReport.pdf>
- Protocol summary:
 - A plating phase (approximately 2 weeks)
 - A loading phase (approximately 1 week)
- Successfully demonstrated nuclear particle tracks in CR-39

Szpak Mosier-Boss (SPAWAR) Protocol as Used in [LetHag12]

- Substrate – Prepared copper
- Electrolyte (subsequently diluted 50% to reduce Pd build-up)
 - 0.30 M LiCl
 - 0.05 M PdCl₂
 - 99.9% D₂O
- Current profile
 - 1.3, 2.6, 6.3 mA/cm²
 - Applied in steps
- Additional conditions
 - Unknown if magnets were used
- Did not produced excess power (heat)

Modified SPAWAR Method in [LetHag12]

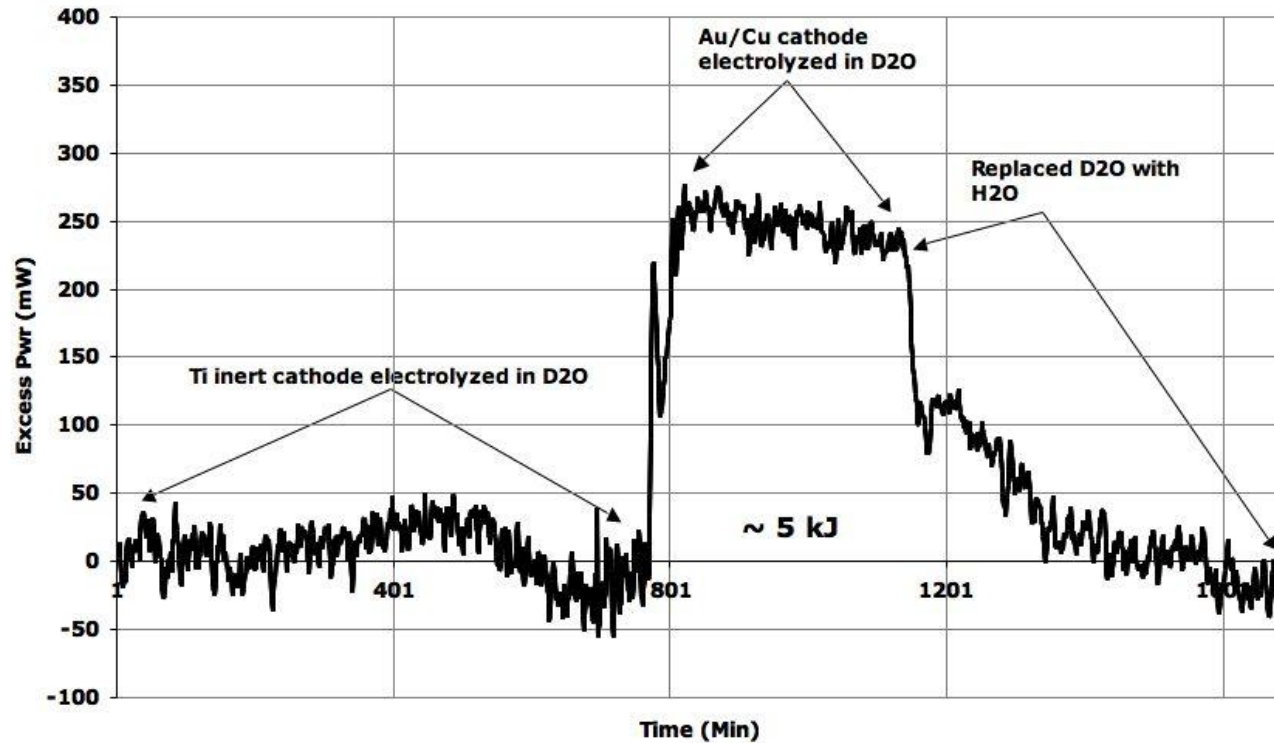
- **Electrodes**
 - Anode: 0.999 Pt wire in the form of multi-turn spiral coil
 - Cathode: Copper substrate gold plated (0.5 cm²)
- **Electrolyte**
 - 0.15 M LiCl
 - 0.00125 M Pd concentration (0.44 g PdCl₂ solution .5 wt % solution in 10 wt % HCl)
 - 99.9% D₂O from Aldrich
- **Current profile**
 - Co-deposition done at ~500 mA/cm² (Solution clears in a couple of hours)
 - Applied immediately
- **Additional conditions**
 - Cell were closed
 - Gasses recombined with 1/8 in. alumina pellets coated with 0.5% platinum reduced
- **Experimental results:**
 - excess energy produced



Letts-Hagelstein Results

JCMNS 6, 2012 pp44-54

NRL684d
Isotope Effect



0-800 minutes: Calibration with D₂O, LiCl

800 – 1100 minutes: 0.44 ml PdCl II 5%wt, 10%wt HCl

1100-end minutes: D₂O replaced with H₂O

Current at 500 mA/cm² throughout

Important Events in the Search for Excess Heat in Pd-D

- Szpak and coworkers [SzpMoS91] showed that electrolytic codeposition of Pd and D from a solution containing LiCl
- In an ICCF15 (2009) presentation McKubre and coworkers at SRI showed that some of the conditions that must be met to replicate the Fleischmann/Pons excess energy from Pd cathodes during heavy water electrolysis were:
 - D/Pd loading > 0.85, perhaps 0.95
 - Long waiting period of 2-4 weeks before excess heat observed
- At ICCF-17 Letts and Hagelstein speculate “... about the importance of vacancies in producing the excess power effect in deuterated palladium cathodes.”

[LetHag13]

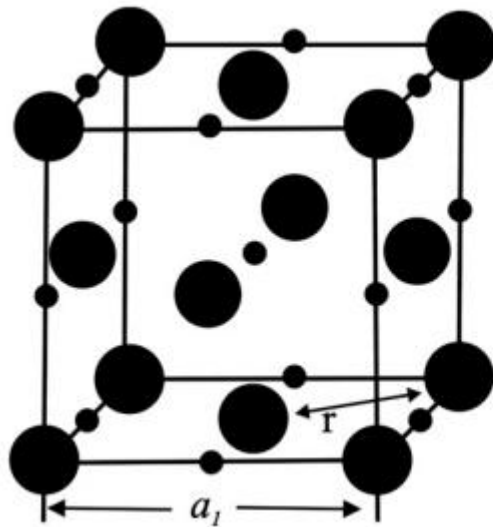
 - “... [We] found only one parameter that increased by 340% with a 13 degree increase in cell temperature – the number of vacancies in the palladium cathode, ...”

What are “Superabundant Vacancies” (SAV)?

Normal vs. SAV lattice

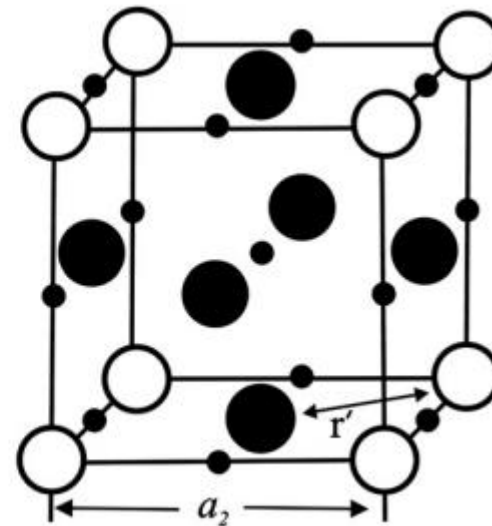
Hydrogen loaded

●: M, ○: Vacancy



f.c.c

Max loading 1:1



[Zag&al10]

Vacancy-ordered $L1_2$ structure,
 Pd_3VacH_n maximum $n = 4$

Max loading 4:3

[Fukai95]

Superabundant Vacancies (SAV) [Fukai 93 - 07]

- One of the important recognitions gained from the SAV formation is that the most stable structure of M-H alloys is in fact a defect structure containing a large number of vacancies
- “... in all metals investigated by ion implantation experiments, H atoms are trapped by vacancies, up to six atoms per vacancy, with rather large binding energies”
- In metal-hydrogen (M-H) alloys at high temperature and high hydrogen pressure “the lattice parameter of Ni and Pd decreased over several hours until it reached a limiting value ~1.5% smaller”
- There is “the possibility of creating SAVs without any extreme conditions, namely by electrolytic deposition “
- In electrodeposition “the stable structure should be reached directly as H and M atoms are deposited simultaneously incorporating vacancies in appropriate proportions”

Observations and Questions

- Co-deposition has been successfully used in a wide variety of experimental protocols
 - What is the roll of a magnetic and/or electric field?
 - Can different protocols lead to different reaction paths?
- Was the F-P experiment really a co-deposition experiment?
 - Did co-deposition occur during the 2-4 week “loading” period?
 - Were SAV’s created in the bulk during that time?
- What is the roll of SAV’s?
 - Were Pons and Fleischmann lucky with their protocol?
- Co-deposition produces both high surface area and SAV’s.
 - Are SAV’s involved in gas loading of nano-particles?

So far, the main thing that I’m learning is how much I don’t know!

Acknowledgments

- Mitchell Swartz et al. for organizing the meeting
- Stan Szpak, Pam Mosier-Boss and the SPAWAR team
- Dennis Letts and Peter Hagelstein
- To everyone working in the field and contributing to the advancement of LANR