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

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Presentation Summary

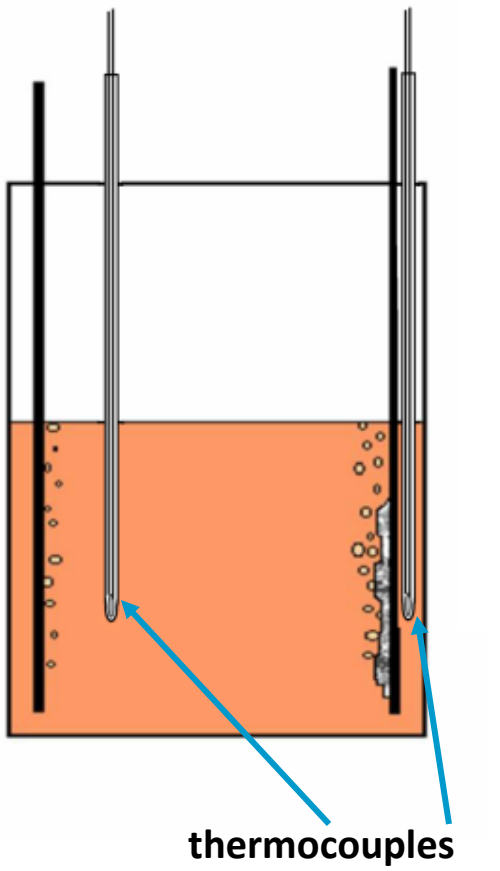
- A wide variety of Co-deposition protocols have been “successfully used
- Co-deposition has always been credited with producing high loading ratios
- Magnetic and/or electric fields may to be important
- Fukai suggests that loading ratios could be even higher with production of SAV’s >1:1
- Implications: 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?

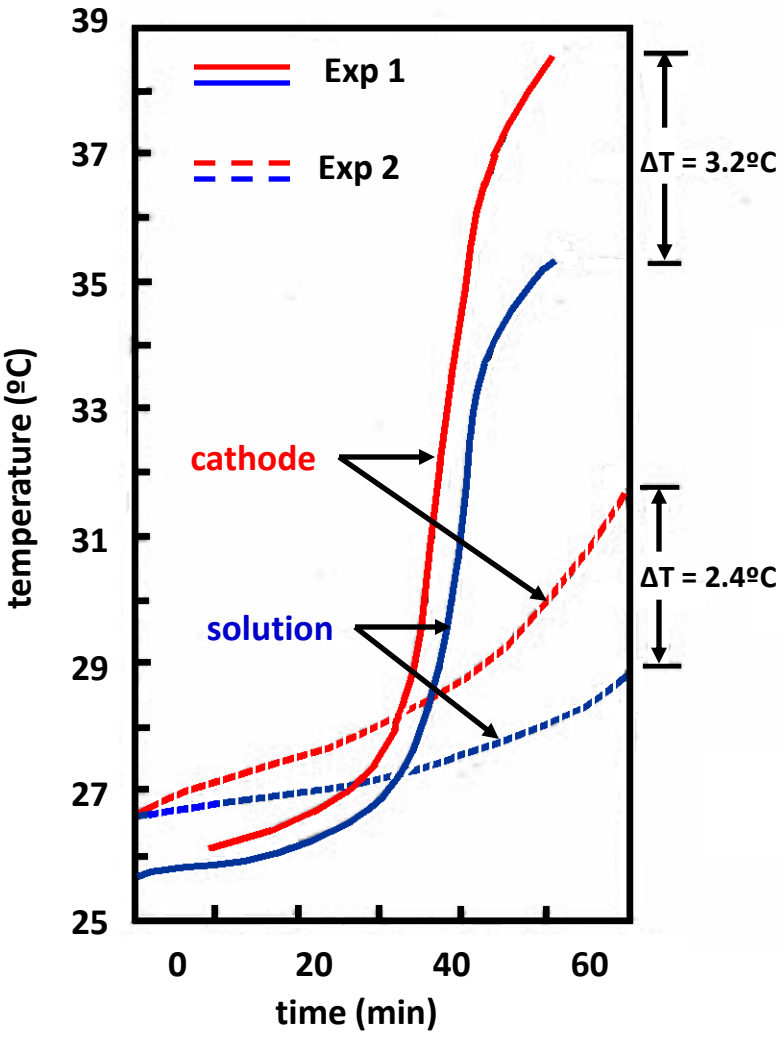
Evolution of Co-Deposition

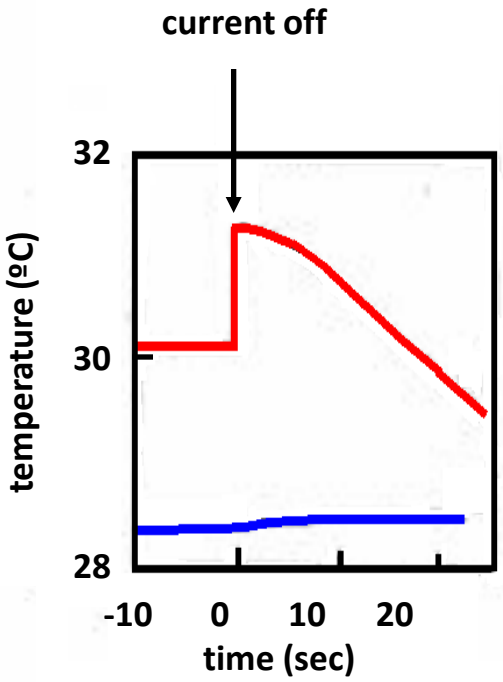
- Fleischmann - Pons effect published [PonFlH89]
  - Cathode: bulk palladium (Pd)
  - Long loading time of 2-4 weeks
  - Excess heat difficult to replicate
- Szpak - Boss co-deposition published [SzpMoS91]
  - Cathode: electrodeposited Pd on Cu and other materials
  - Modest loading time of days
  - 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)



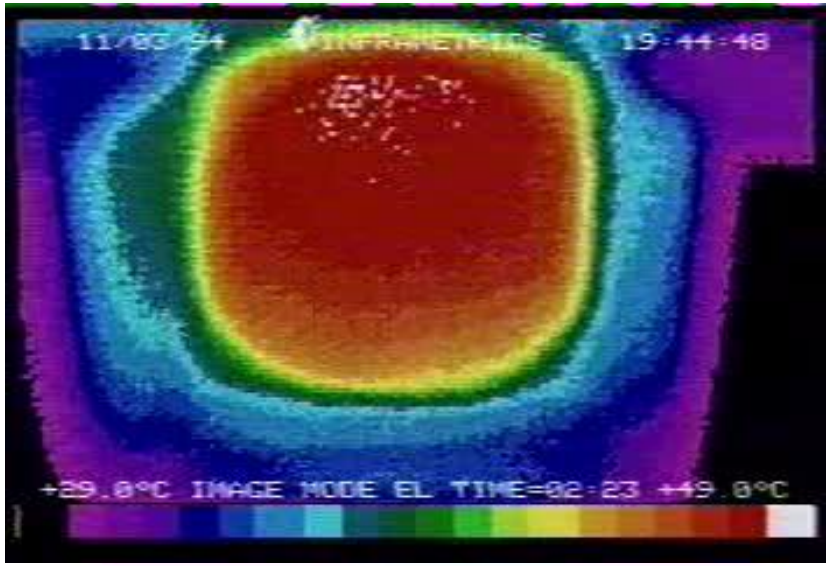




The Electrode is warmer than the Solution!

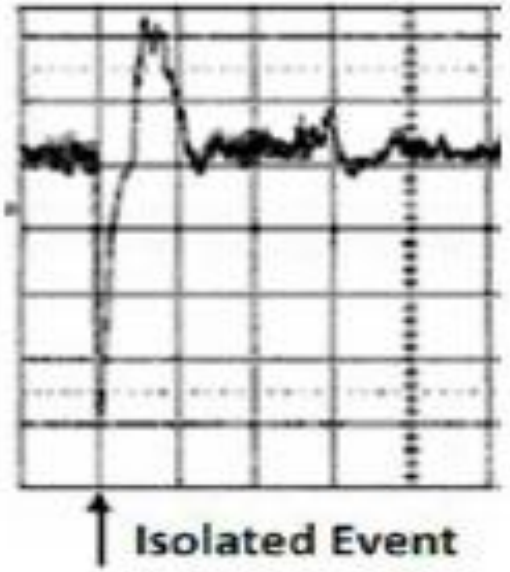
“Hot Spots” and “Mini-Explosions”

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



a

a – hot spots



b

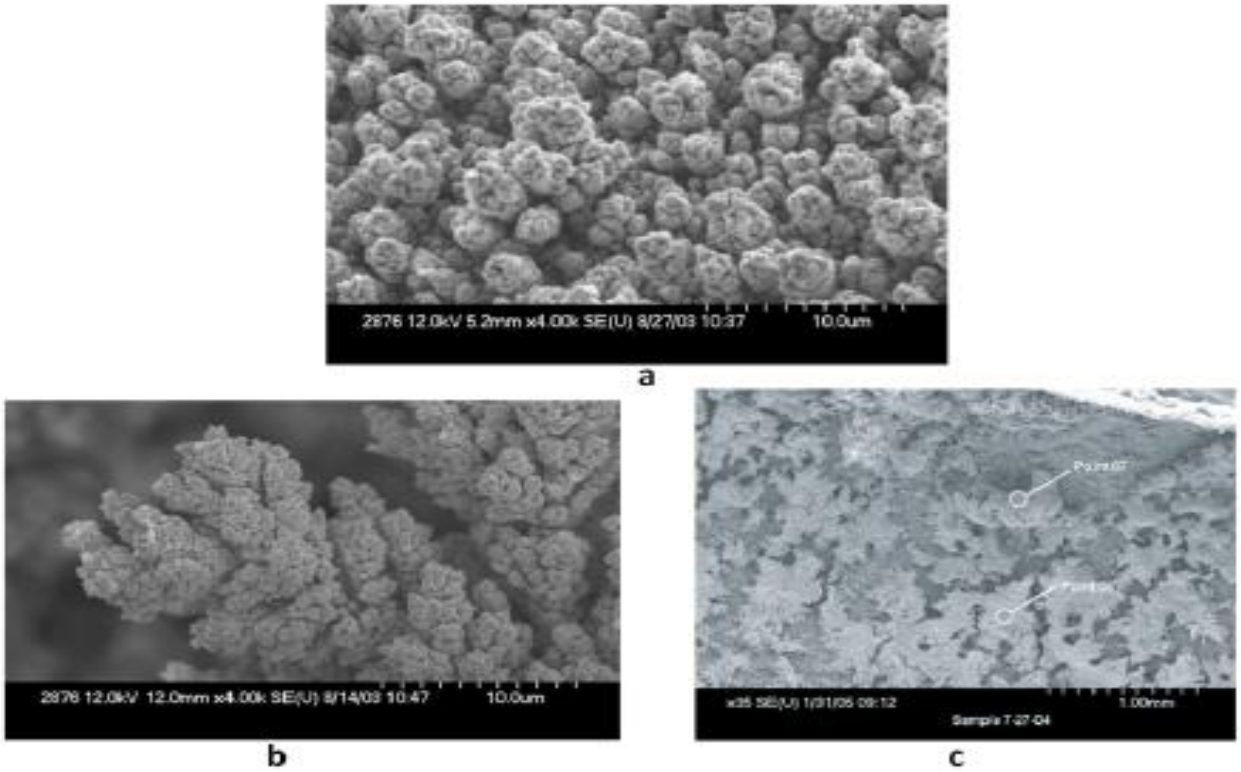
b - piezoelectric

Infrared camera and polarized ferroelectric PZT transducer responses

SEM of Co-Deposited Pd/D Film

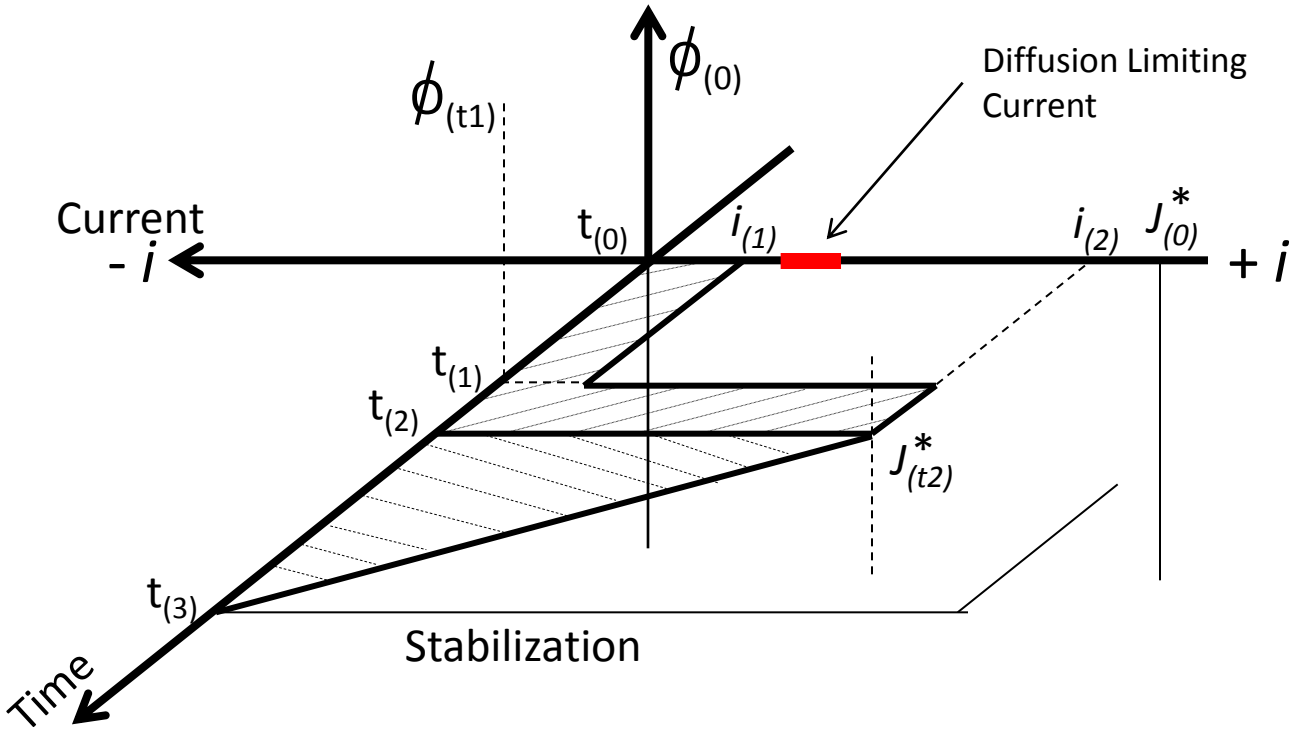
J. Electroanal. Chem. 580 pp284-290 (2005)

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



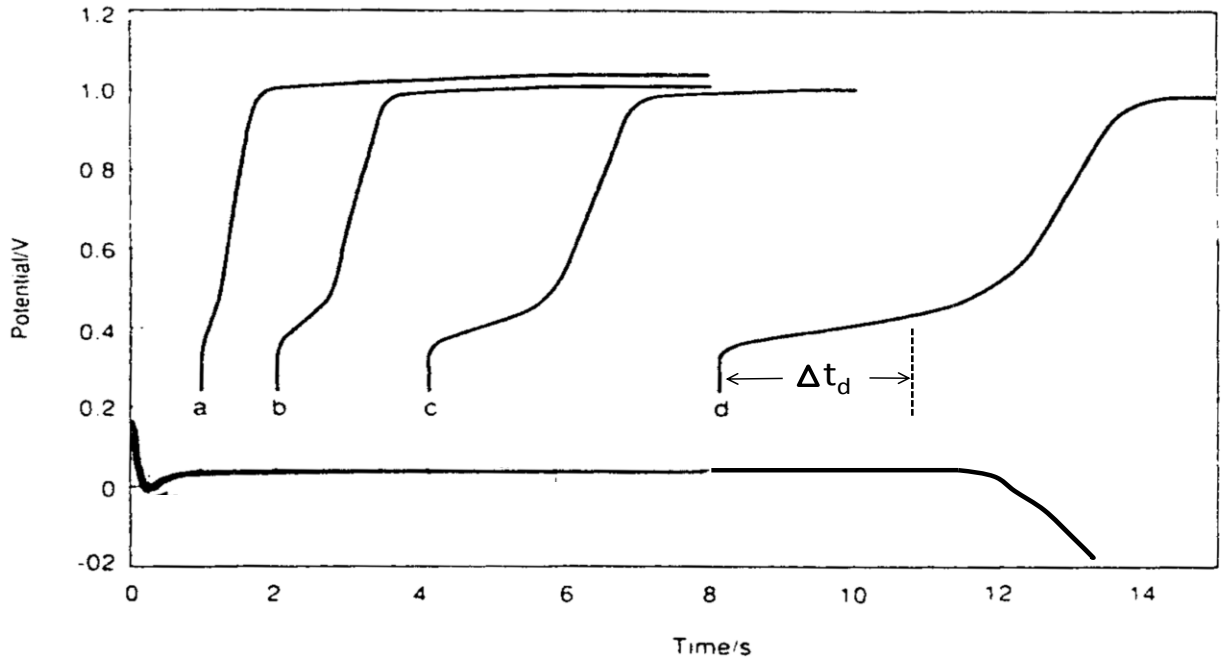
a – after completion of co-deposition,
b – exposed to external electric field, c – exposed to magnetic field

Electrochemical Co-Deposition Processes



Deuterium Up-take

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

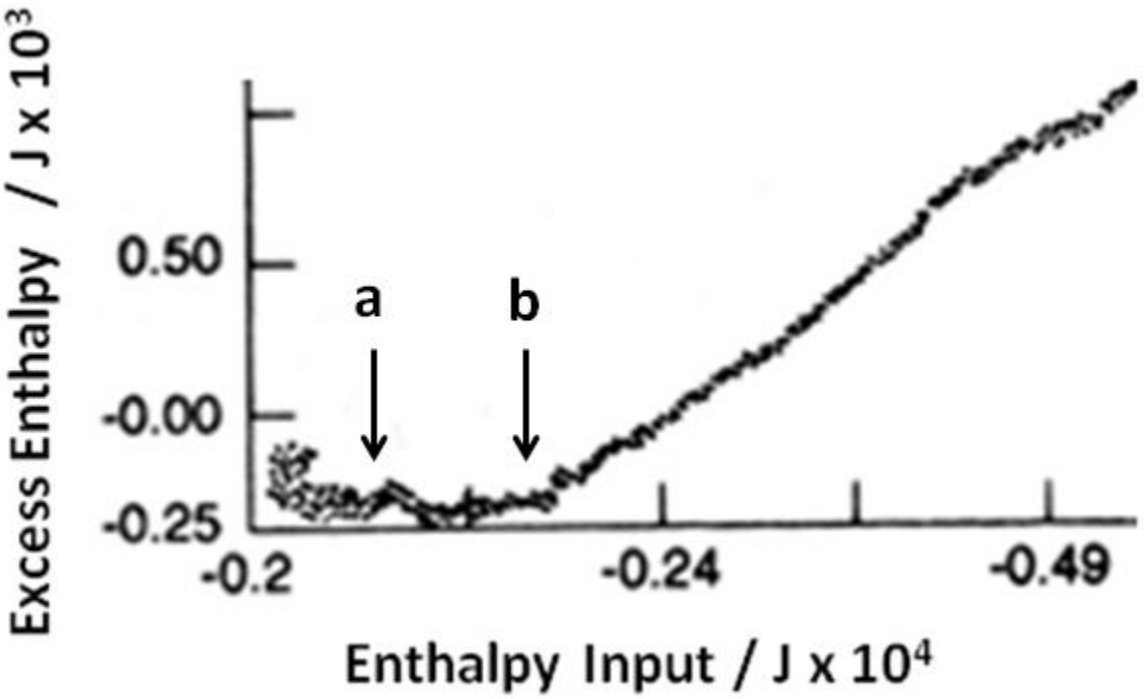


Deuterium up-take during co-deposition. jc = - 5mAcm^{-2} and ja = 5 mAcm^{-2}, with cell current reversal at 1,2,4, and 8 seconds.

High loading ratios are achieved during co-deposition

Initial Co-Deposition Thermal Behavior

Fusion Technology 36 pp234-241 (1999)



endothermic absorption – 0_iQ_iA $[0_iQ_ia]$,
endothermic absorption balanced by exothermic reaction $-a_iQ_ib$ $[aQ_ib]$,
exothermic reaction dominates Q_ia $[bQ_i]$

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)

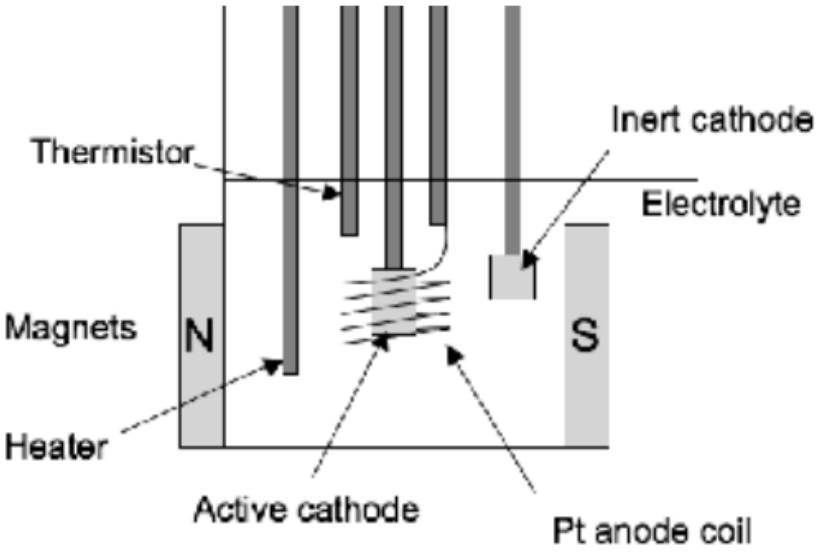
- Successfully demonstrated nuclear particle tracks in CR-39

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 $PdCl_2$
  - 99.9% D_2O
- Current profile
  - 1.3, 2.6, 6.3 mA/cm^2
  - Applied in steps
- Additional conditions
  - Unknown if magnets were used
- Did not produced excess power (heat)

Modified SPAWAR Method in [LetHag12]

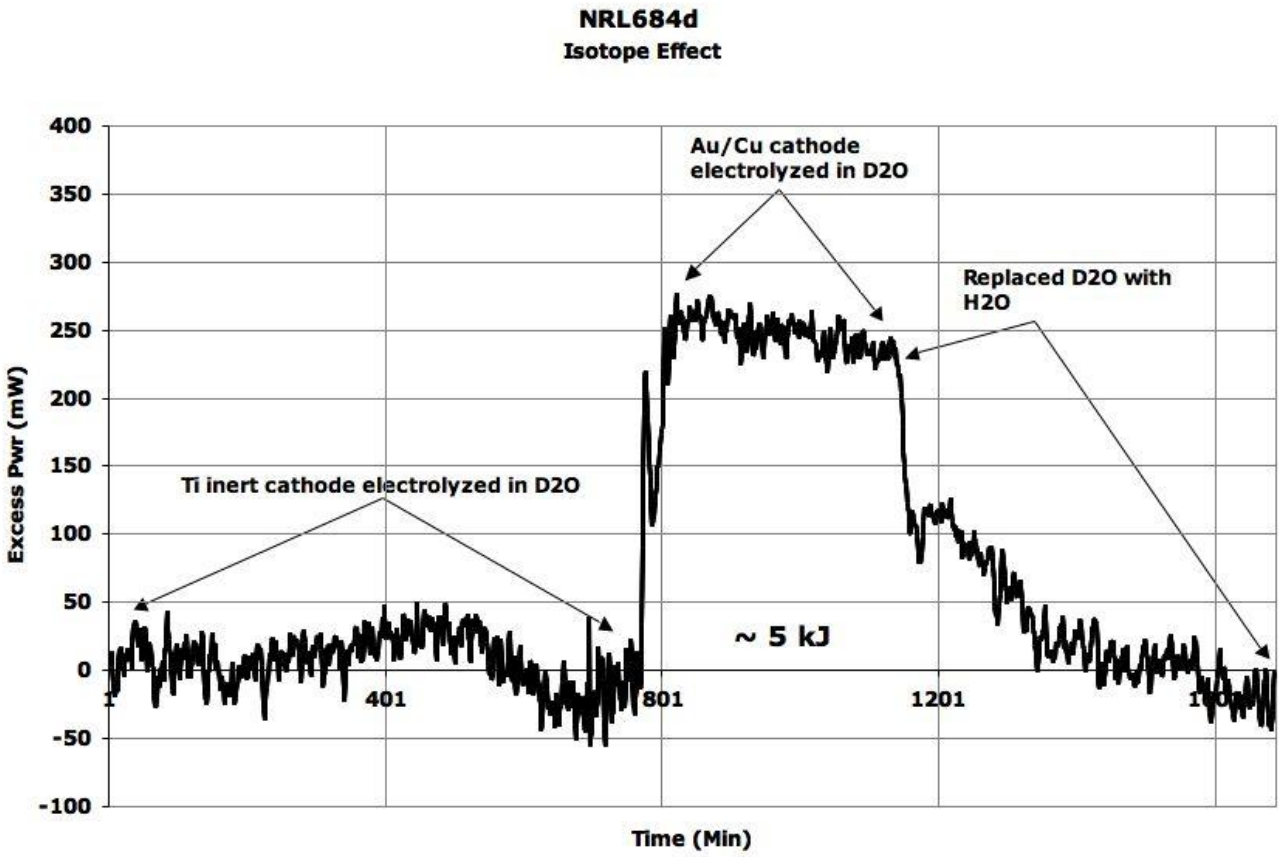
- **Electrodes**
  - Anode: 0.999 Pt wire in the form of multi-turn spiral coil
  - Cathode: Copper substrate gold plated (0.5 cm^2)
- **Electrolyte**
  - 0.15 M LiCl
  - 0.00125 M Pd concentration (0.44 g PdCl2 solution .5 wt % solution in 10 wt % HCl)
  - 99.9% D_2O from Aldrich
- **Current profile**
  - Co-deposition done at ~500 mA/cm^2 (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


Thermistor
Inert cathode
Electrolyte
Magnets
N
S
Heater
Active cathode
Pt anode coil


FEB 16 2010

Letts-Hagelstein Results

JCMNS 6, 2012 pp44-54



0-800 minutes: Calibration with D_2O, LiCl
800 – 1100 minutes: 0.44 ml PdCl II 5%wt, 10%wt HCl
1100-end minutes: D_2O replaced with H_2O
Current at 500 mA/cm^2 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

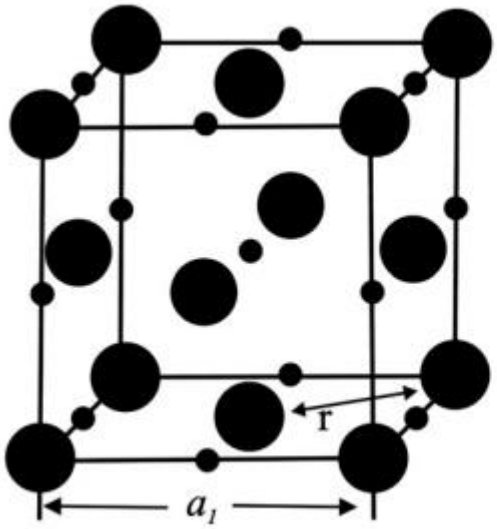
- In an ICCF15 (2009) presentation McKubre and coworkers at SRI showed that some of the conditions that must be meet to replicate the Fleischmann/Pons excess energy from Pd cathodes during heavy water electrolysis were:
  - D/Pd loading > 0.85, perhaps 0.95
  - Long waiting period of 2-4 weeks before 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)?

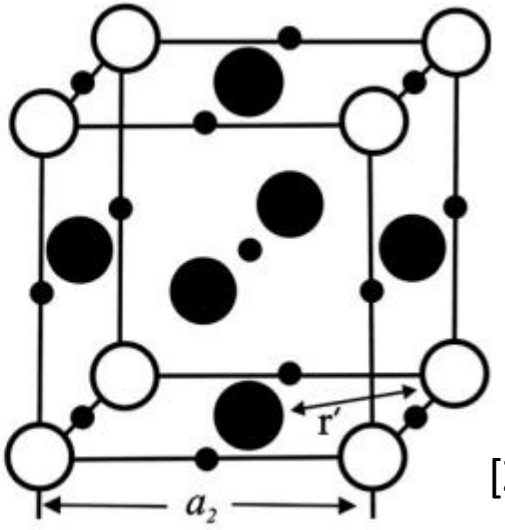
Normal vs. SAV lattice Hydrogen loaded

●: 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

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