PROGRESS ON DUAL LASER EXPERIMENTS

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We have continued our experiments using duel laser stimulation of electrochemically loaded PdD_x. In earlier work, we used two properly oriented and polarized tunable diode lasers which provided stimulation at optical frequencies; interestingly, we found that the excess heat is sensitive to the beat difference frequency. Low-level thermal signals are observed to be triggered at apparent resonances when the difference frequency is 8.3, 15.3 and 20.4 THz.

There seems to be a reasonable connection between beat frequencies of 8.3 and 15.3 THz and characteristic frequencies of the optical phonon spectrum in PdD, but the optical phonon spectrum in PdD does not go up to 20.4 THz. However, 20.4 THz is close to a characteristic frequency of PdH, and we believe that our experiments so far have had significant proton contamination. Exploring the role of H contamination in this experiment is a goal of ongoing experiments.

In previous work, we have been limited in the frequency range over which difference frequencies can be generated. In ongoing experiments we have extended the upper limit, and are using the new set-up to see whether resonances occur at higher difference frequencies.

We are also interested in questions concerning the size of the region responsible for the excess heat, as well as the dependence on laser intensity. There is some evidence to support the hypothesis that the excess heat arises from a region larger than the laser spot in our previous single laser experiments. There is also evidence that the excess heat is initiated once the laser reaches a (low) threshold intensity, but that the excess power is relatively insensitive to the laser intensity above threshold.

Progress on two-laser experiments

Peter Hagelstein, Dennis Letts, and Dennis Cravens

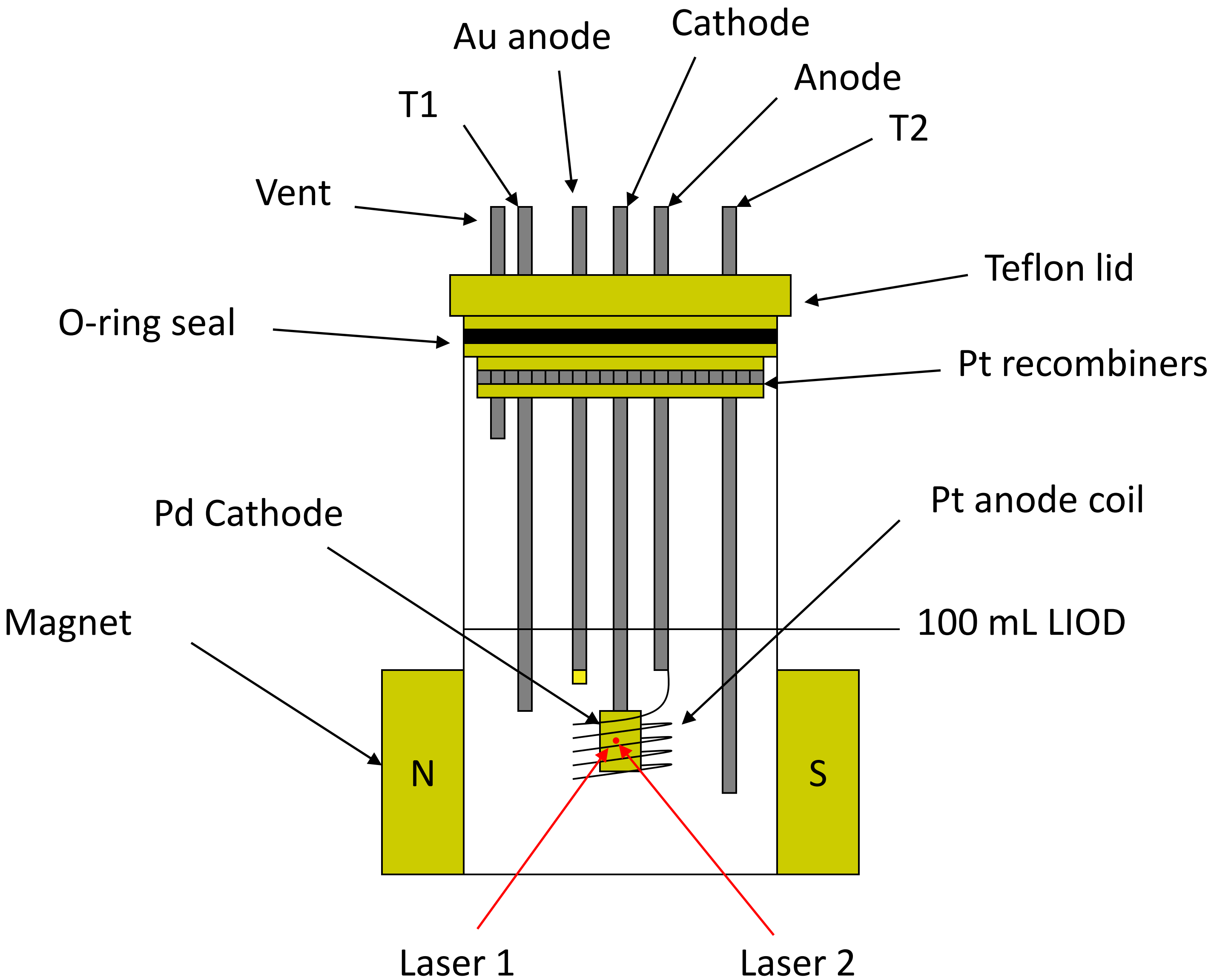
Goal: to see if P_{xs} responds to the beat frequency

- In previous years Letts and Cravens showed that a laser could trigger excess heat

- Hope was that two lasers might trigger excess heat

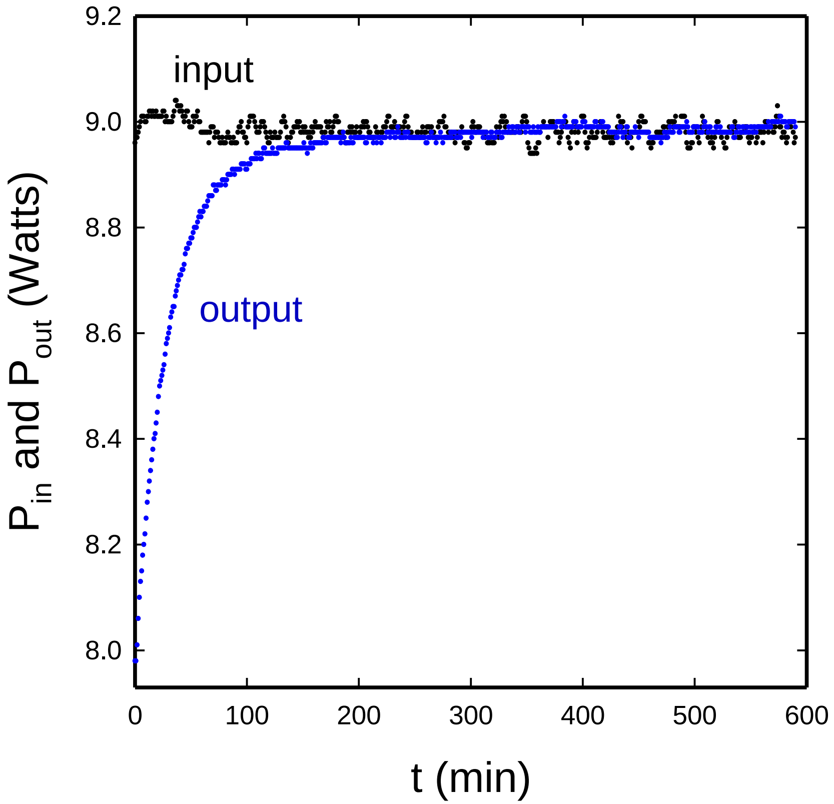
- If so, then could study the dependence of excess heat on the difference frequency

- Possible method to see whether optical phonons involved

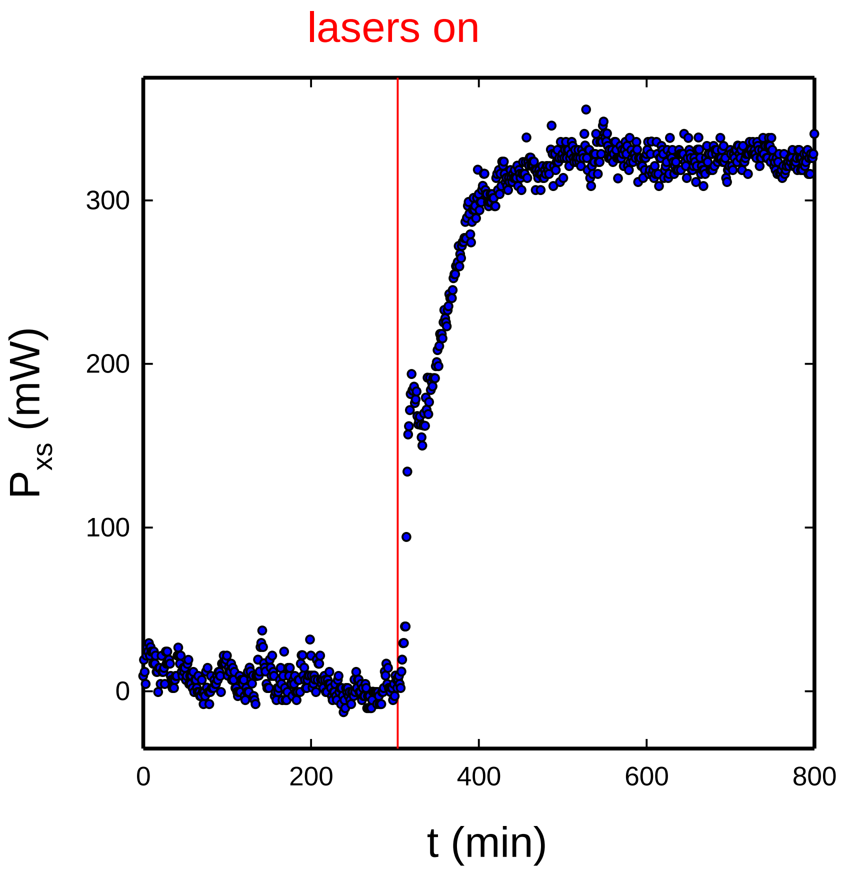


Schematic of experimental set-up

Power balance assuming $P_{th} = K\,\Delta T$, and $P_{in} = I(V - V_0)$



Lasers stimulate excess heat

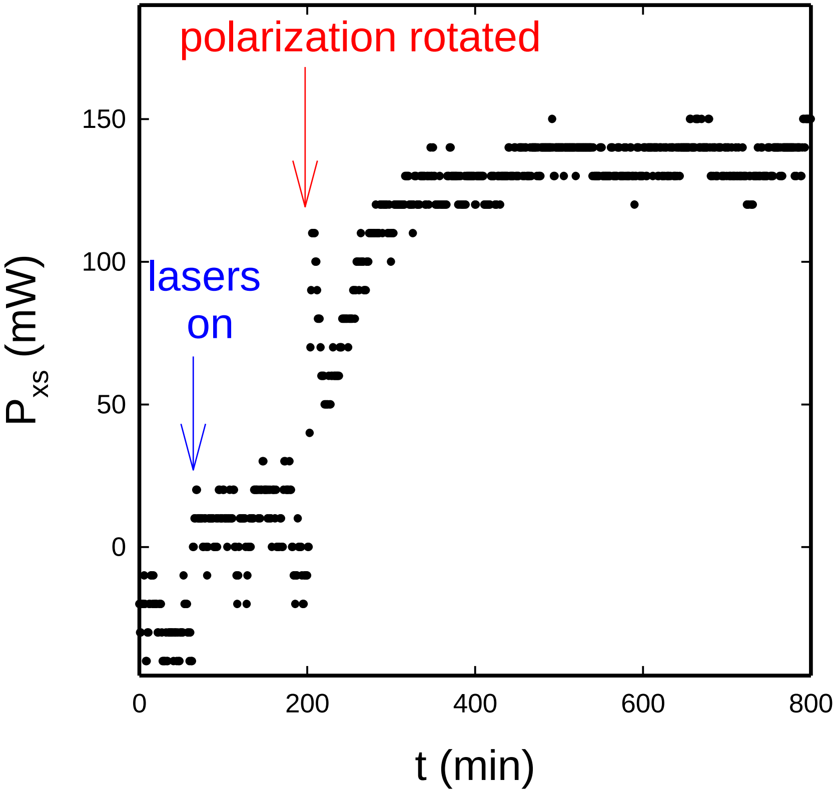


Big response seen at “sweet spots”, little response at other difference frequencies

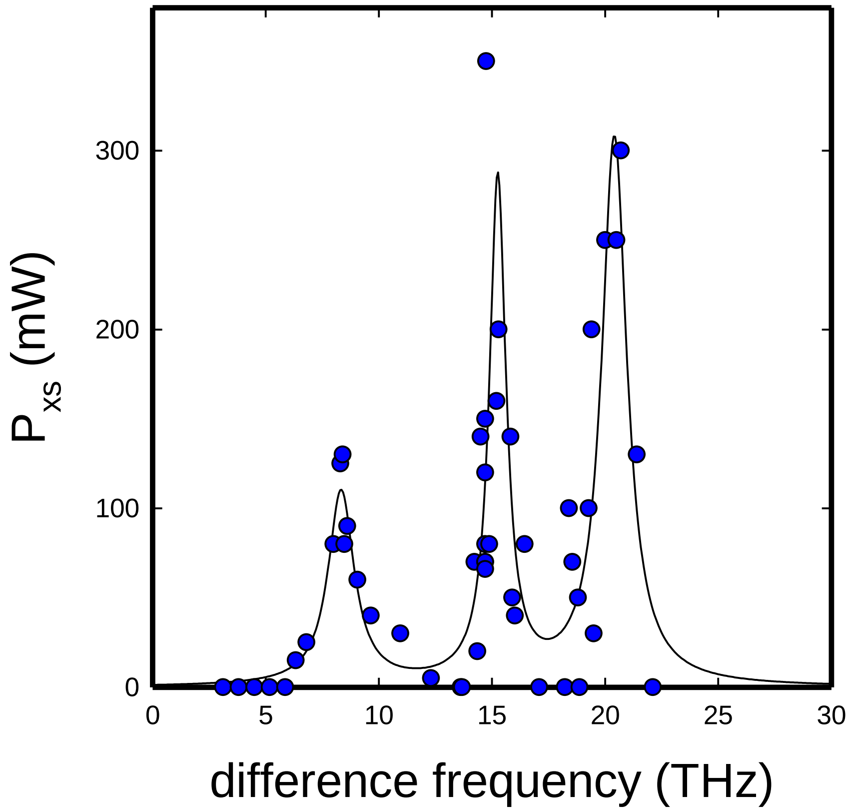
Excess power responds to two laser stimulation:

- p polarization required for both lasers
- Overlap of beams required
- Lasers at different frequencies
- Response only at specific difference frequencies

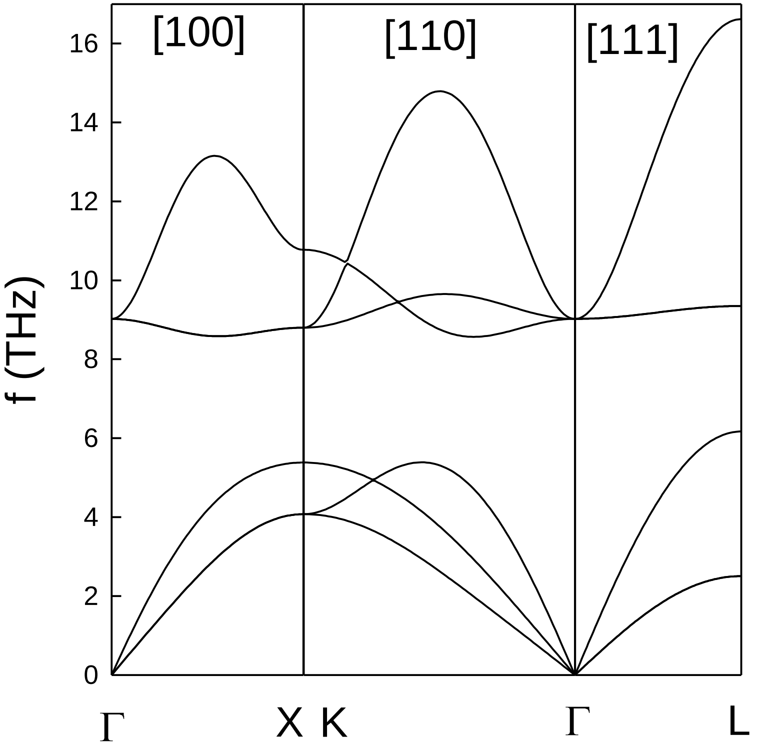
Aligning the polarization leads to excess power



Summary of about 50 measurements over 2 years



Comparison with Pd phonon mode spectrum



Conclusions

- Excess power triggered using two lasers
- Response depends on difference frequency
- Sweet spots (resonances) at 8.3, 15.3 and 20.4 THz
- 15.3 THz is close to L-point compressional optical phonon mode
- 8.3 THz is near Γ-point compressional and transverse modes
- 20.4 THz is close to PdH L-point mode
- Computations with $PdD_{0.75}H_{0.25}$ give L-point mode at 19.7 THz
- Results implicate optical phonons in these experiments

Modeling the SRI loading experiments

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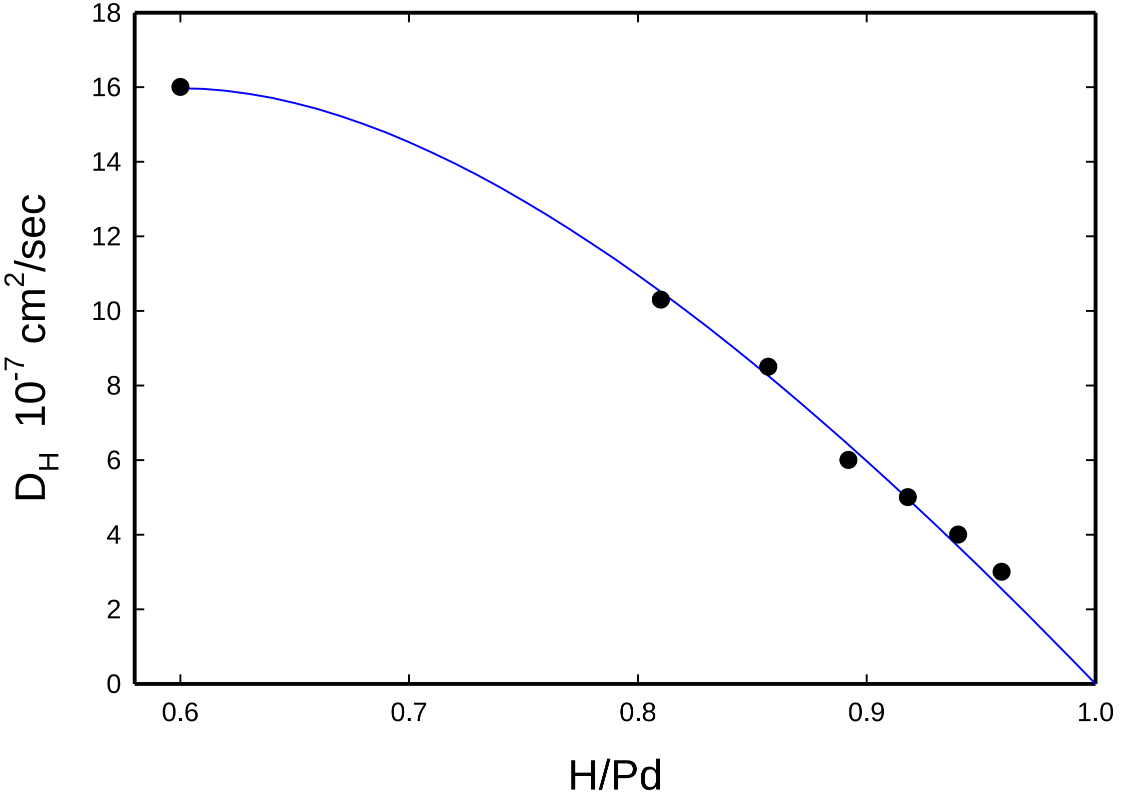
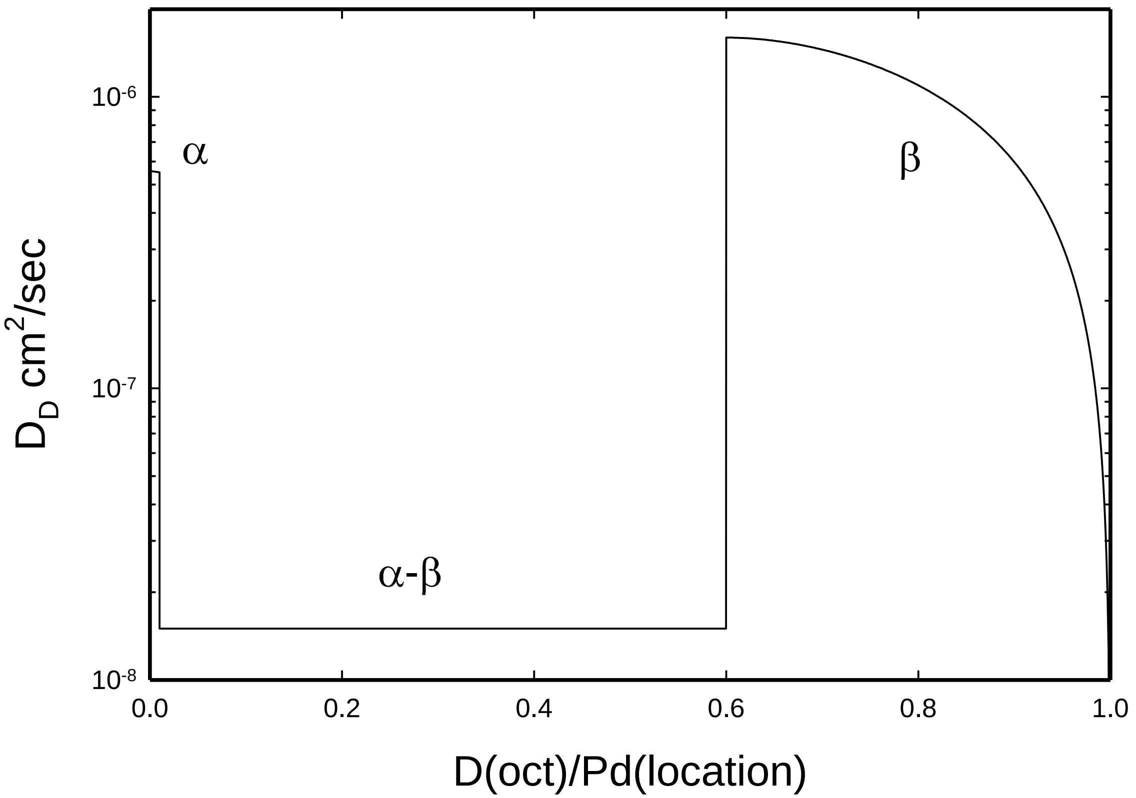
Diffusion coefficient at high loading

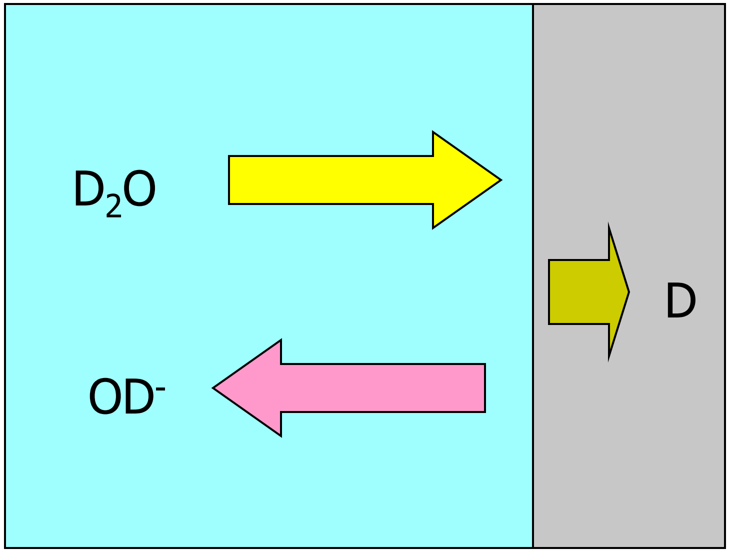


Fit to Baranowski data, and also other experimental data at beta phase boundary

Our diffusion model



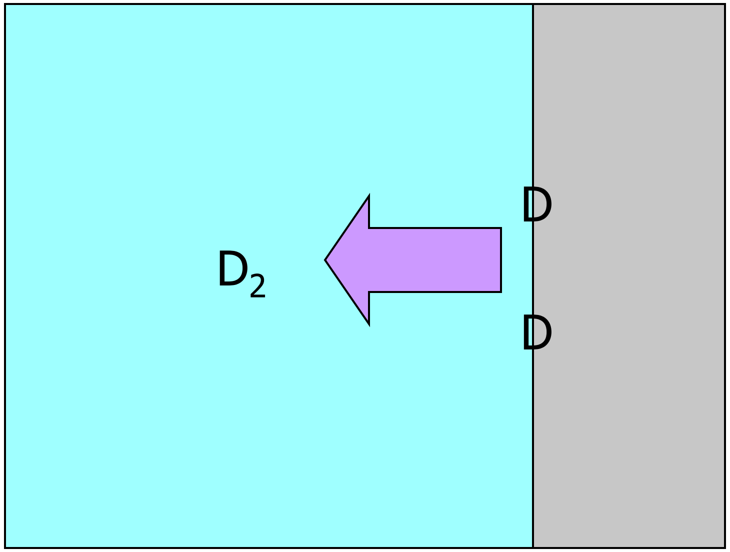
Loading deuterium into Pd



M. Volmer

Electrochemical current density J loads 1 D per charge.

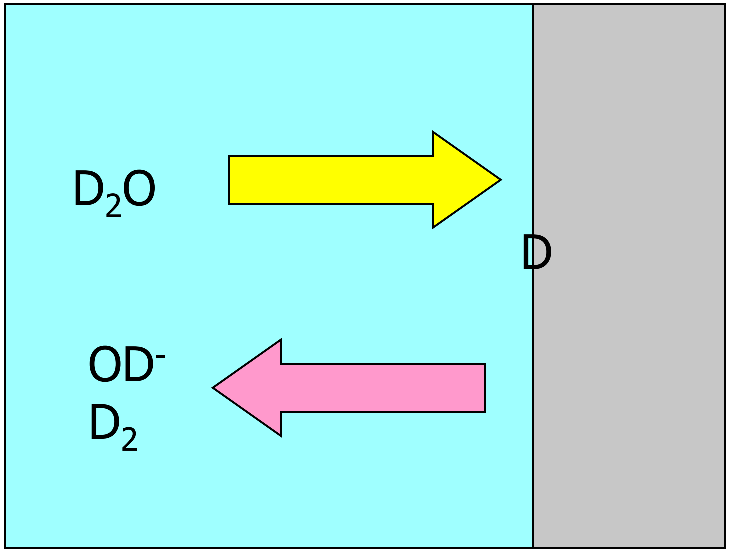
Deuterium loss from PdD



J Tafel

Deuterium on the surface combines to make D_2 gas. Rate depends on deuterium potential and the surface blocking.

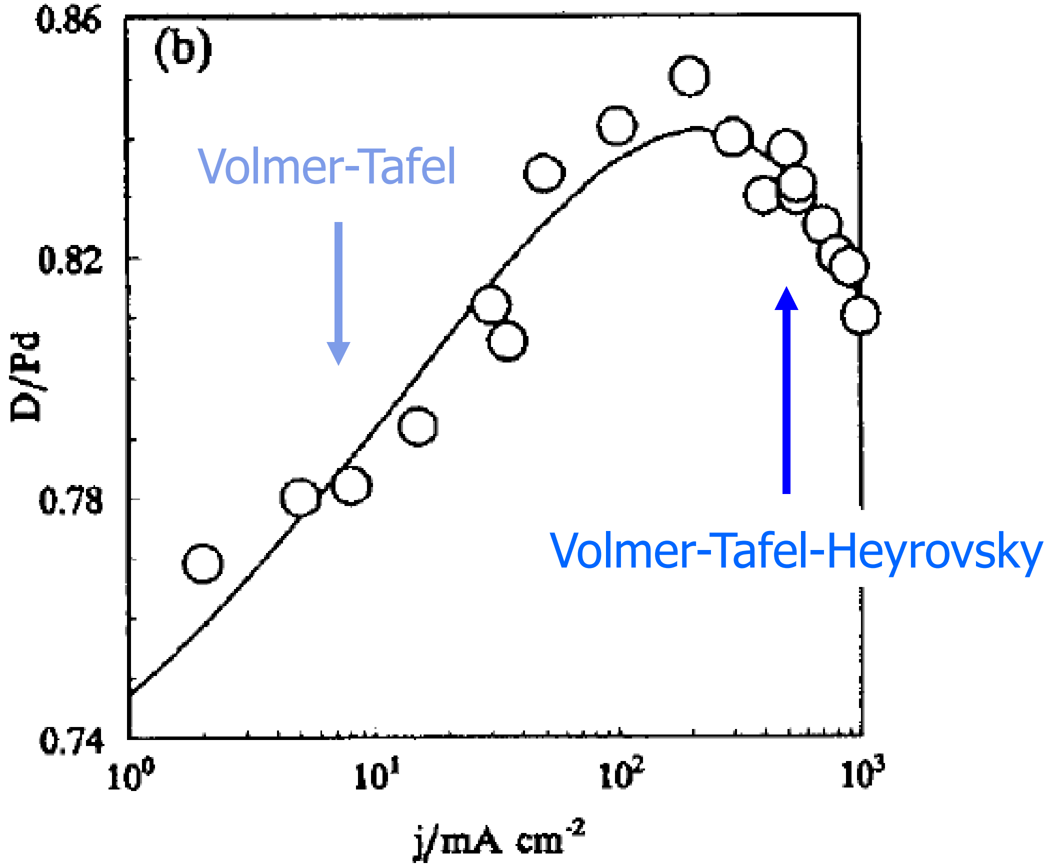
An additional pathway?



J Heyrovsky

If the chemical potential of deuterium is high, then the electrochemical current density J contains a part that deloads deuterium

Explanation for loss of loading



Data of Akita et al, ICCF4 (1994)

Model of Zhang et al, J Electronal. Chem. (1997).

Why are the models broken?

Impossible to account for experiments at SRI, ENEA, and Energetics with this kind of model

- Problem is with Heyrovsky reaction
- No experimental confirmation of Heyrovsky in Pd (base)
- Qualitative behavior of Heyrvosky inconsistent with observations

Basically, Heyrovsky acts as wall. Pick some loading that you think is Heyrovsky limited, then the resulting model will never get to higher loadings

The problem

So, we have to dispense with Heyrovsky for Pd loading

- Then how to account for lower loading at high J?
- Volmer brings in H/D, one per charge of electrochemical current
- Tafel doesn't care about J
- So if J increases, without Heyrovsky the loading has to increase
- But in the experiment the loading decreases!

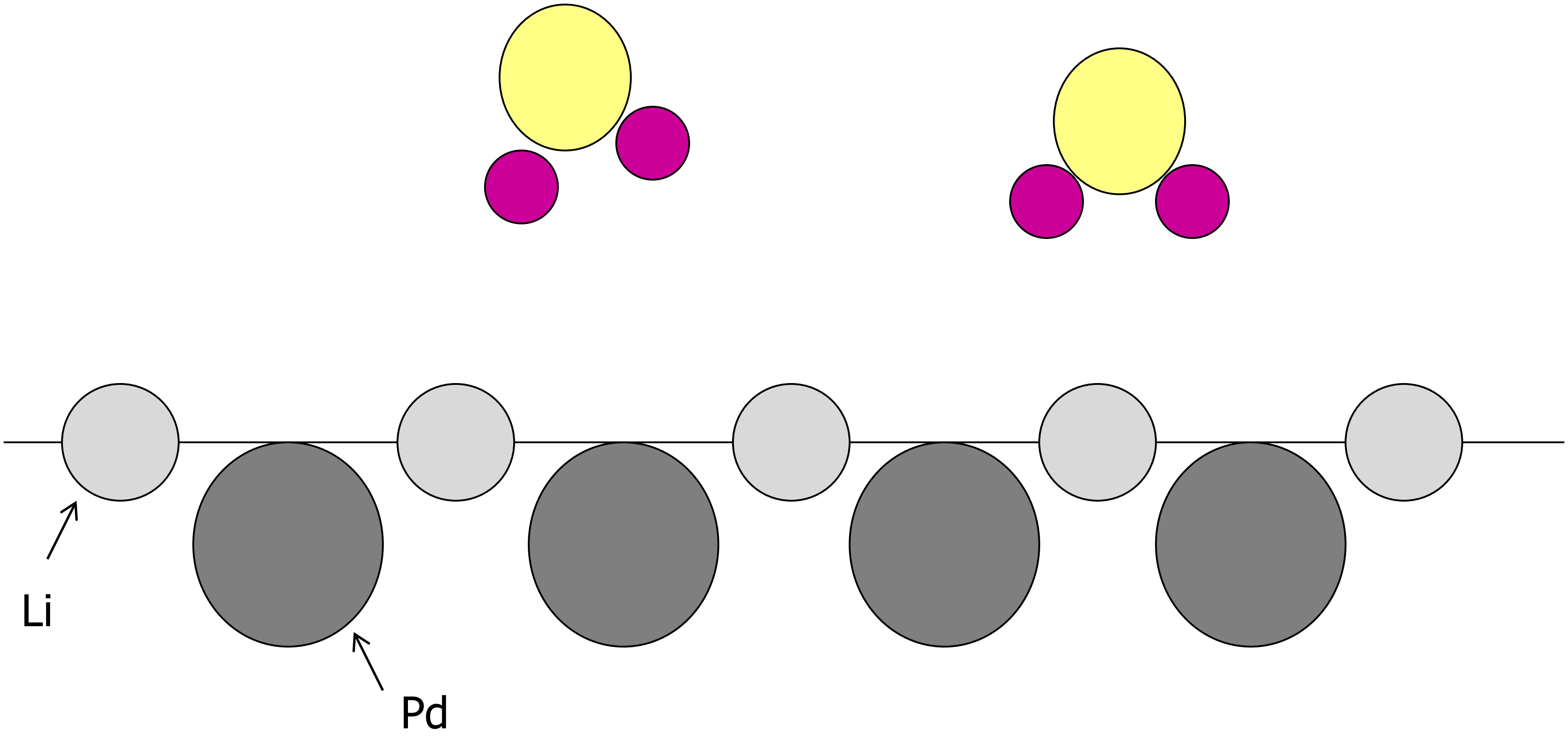
Two-electron transfer reaction

Overall reaction:

$$2D_2O + 2e^- + M \rightarrow 2OD^- + D_2 + M$$

- Reaction does not load or deload (but takes away from Volmer)
- No dependence on chemical potential in PdD
- Does not act as wall

Propose that Li adsorbs and blocks adsorbed D



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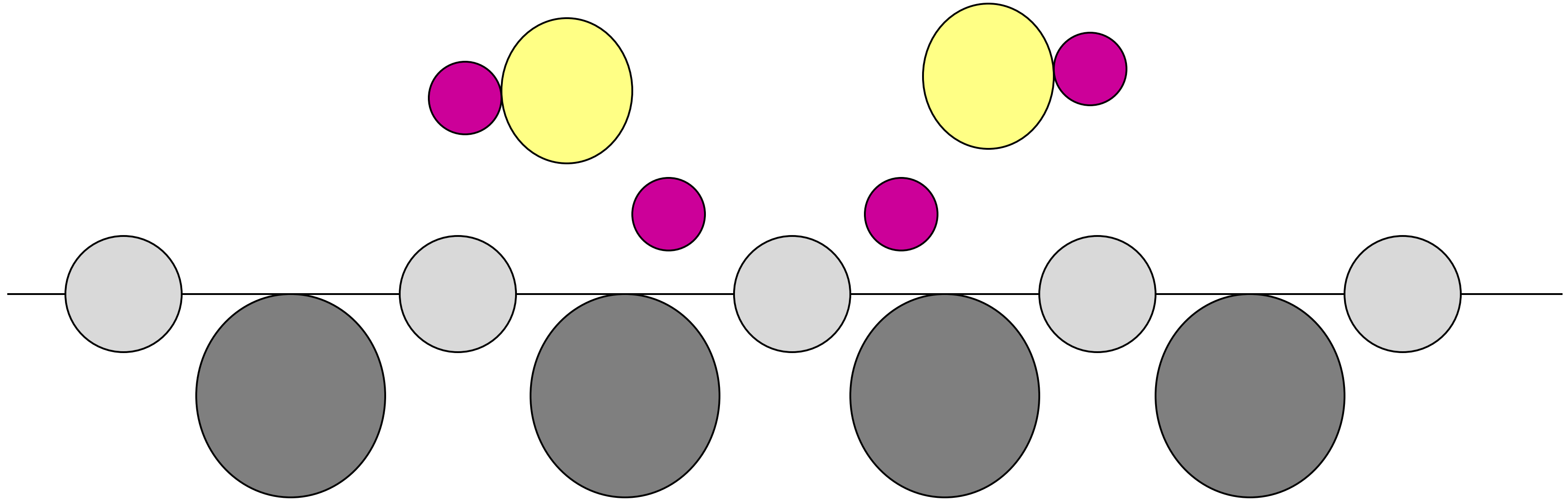

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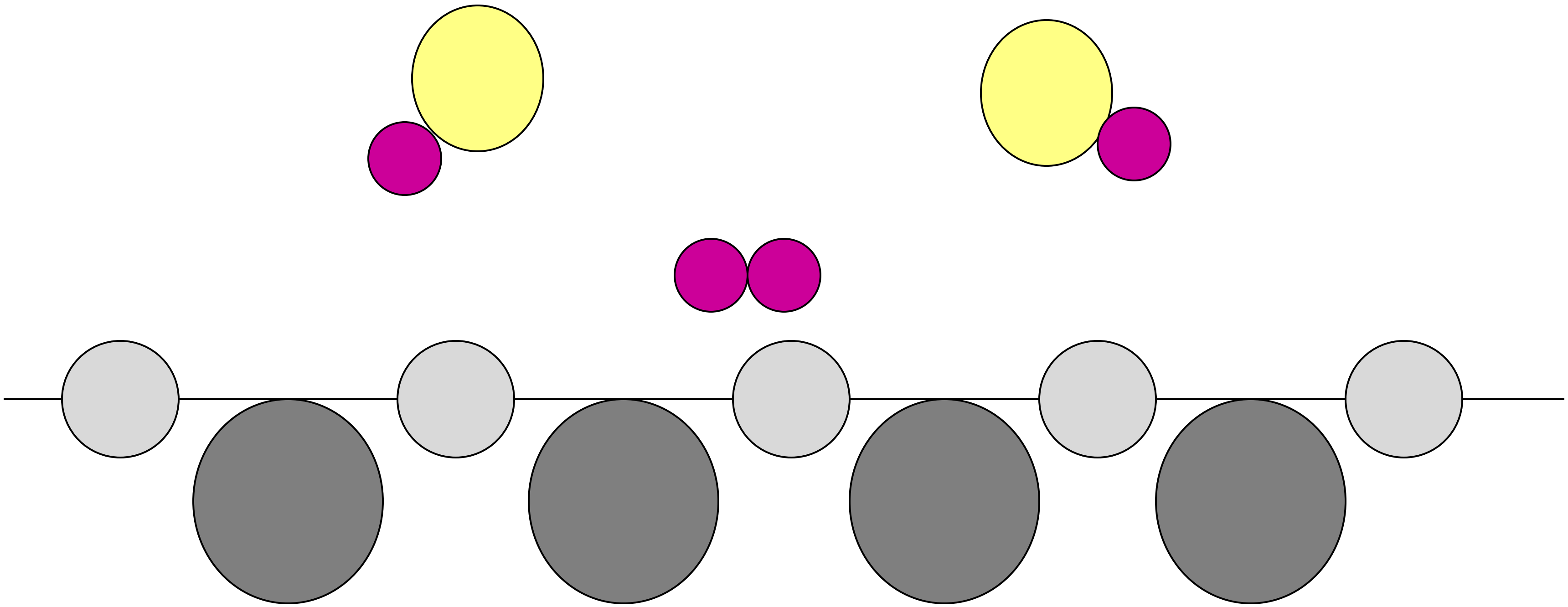


Need model for Li adsorption

Use a modified Frumkin adsorption isotherm:

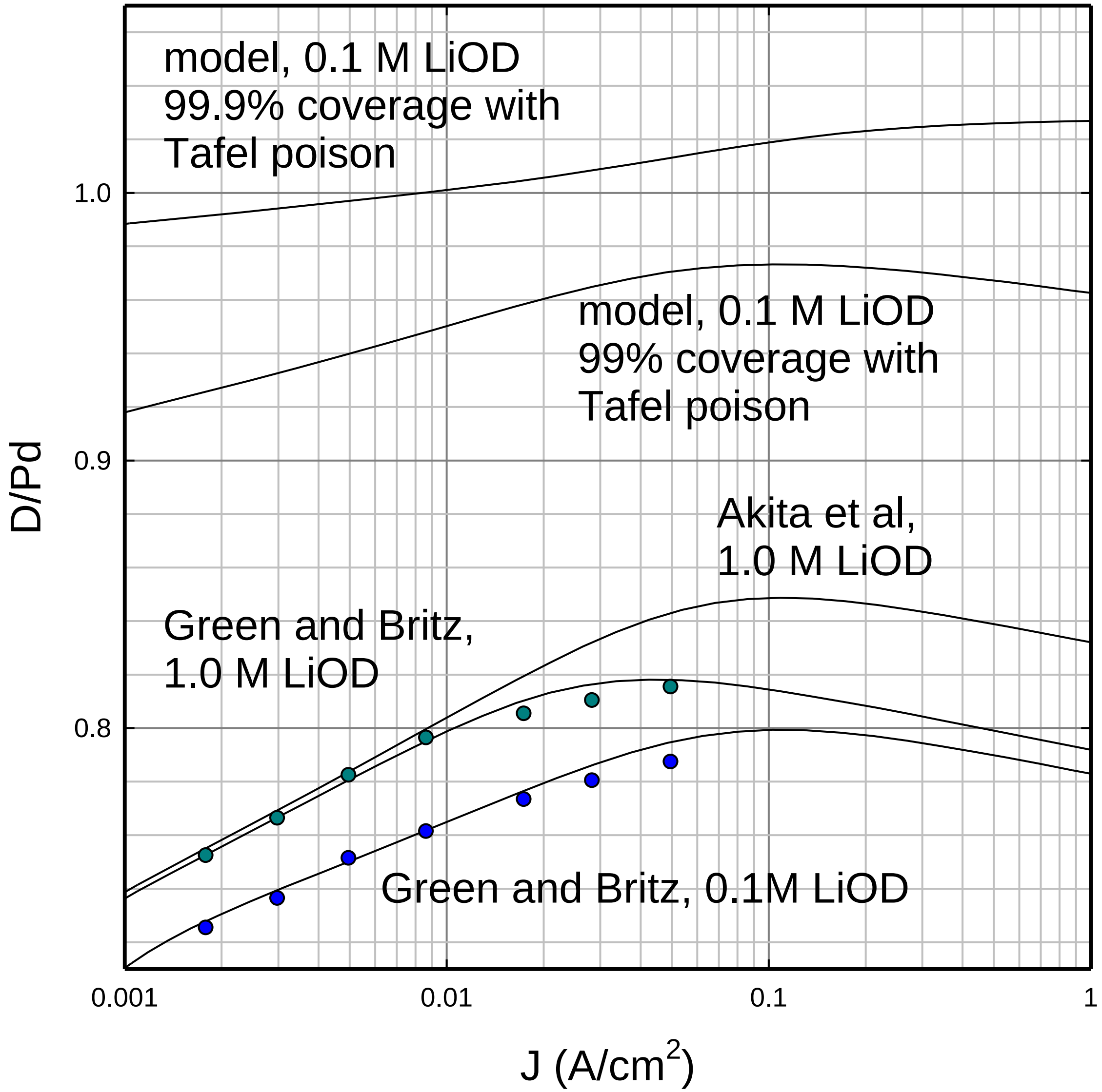
$$\frac{\theta}{1-\theta}e^{u\theta} = \frac{k_+}{k_-}\left[\mathrm{Li}^+\right]e^{-f\eta}$$

and fit to data as best one can

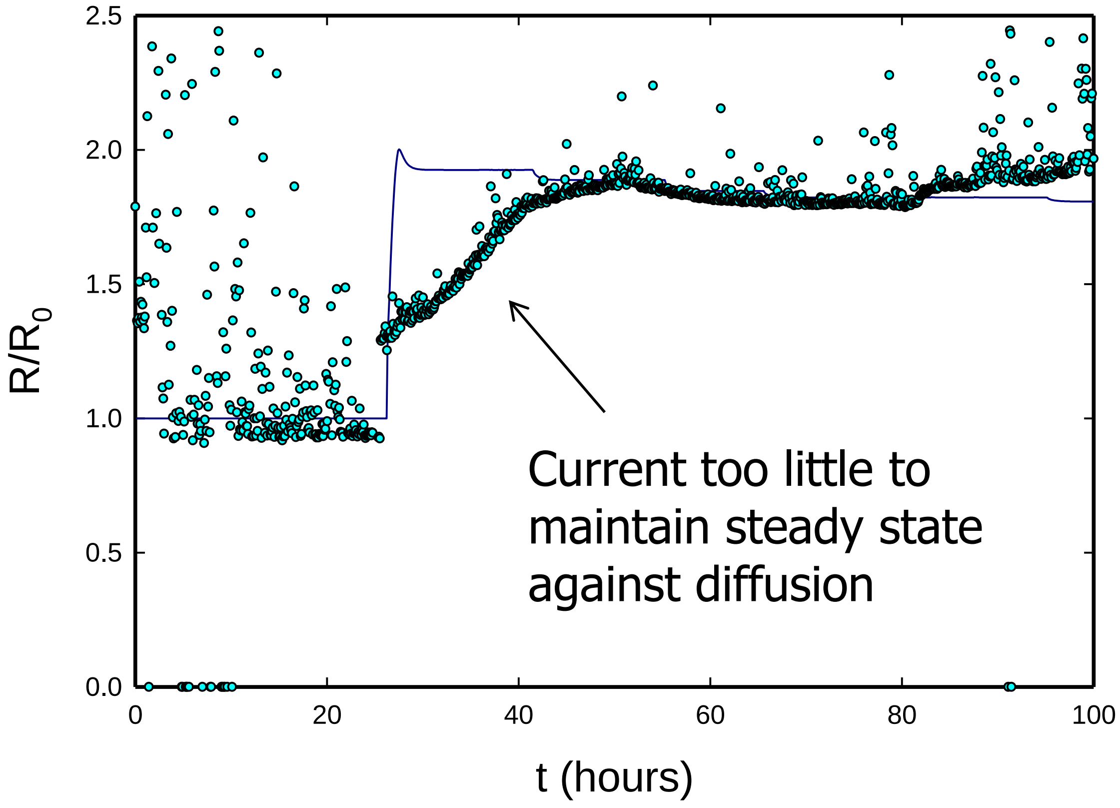
Resulting electrochemical model

The resulting model seems to work pretty well

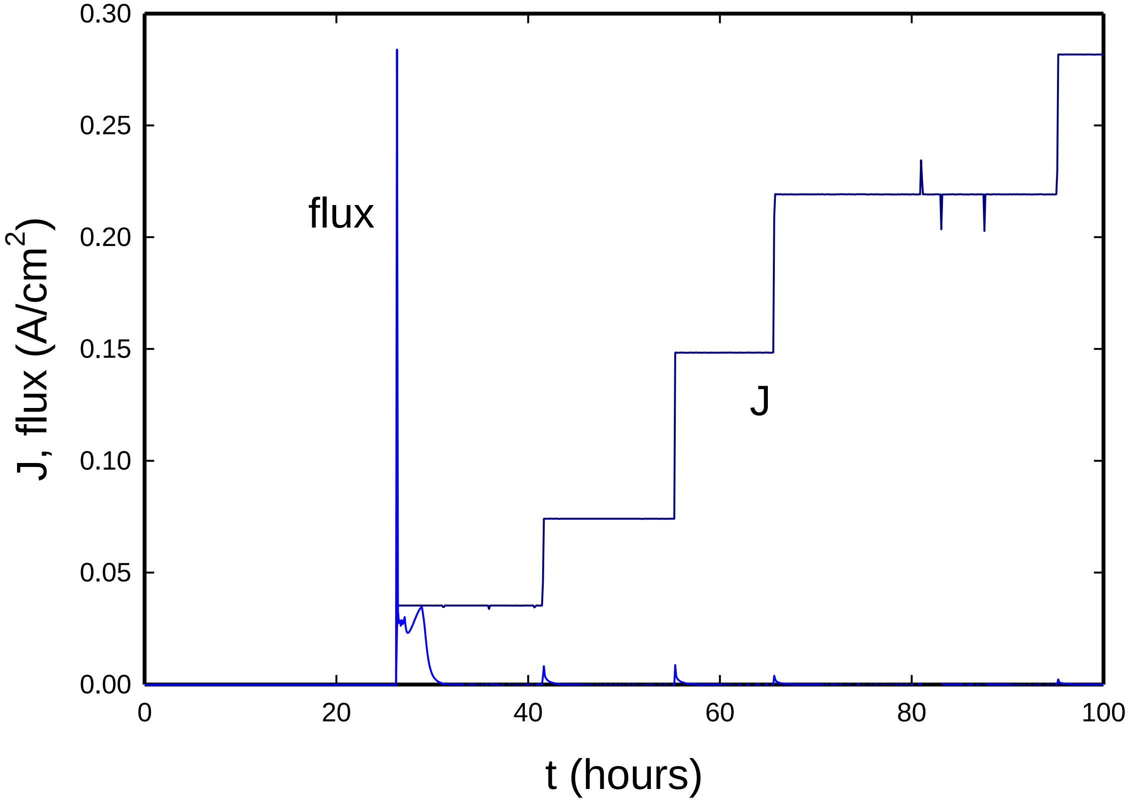
- Fitted to best available data sets in the literature
- No Heyrovsky wall
- Surface lithium consistent with literature
- Can match experimental loading curves
- Only free parameter is cathode-dependent leak rate
- Li plugs leaks


model, 0.1 M LiOD
99.9% coverage with
Tafel poison
model, 0.1 M LiOD
99% coverage with
Tafel poison
Akita et al,
1.0 M LiOD
Green and Britz,
1.0 M LiOD
Green and Britz, 0.1M LiOD
D/Pd
1.0
0.9
0.8
0.001
0.01
0.1
1
J (A/cm2)

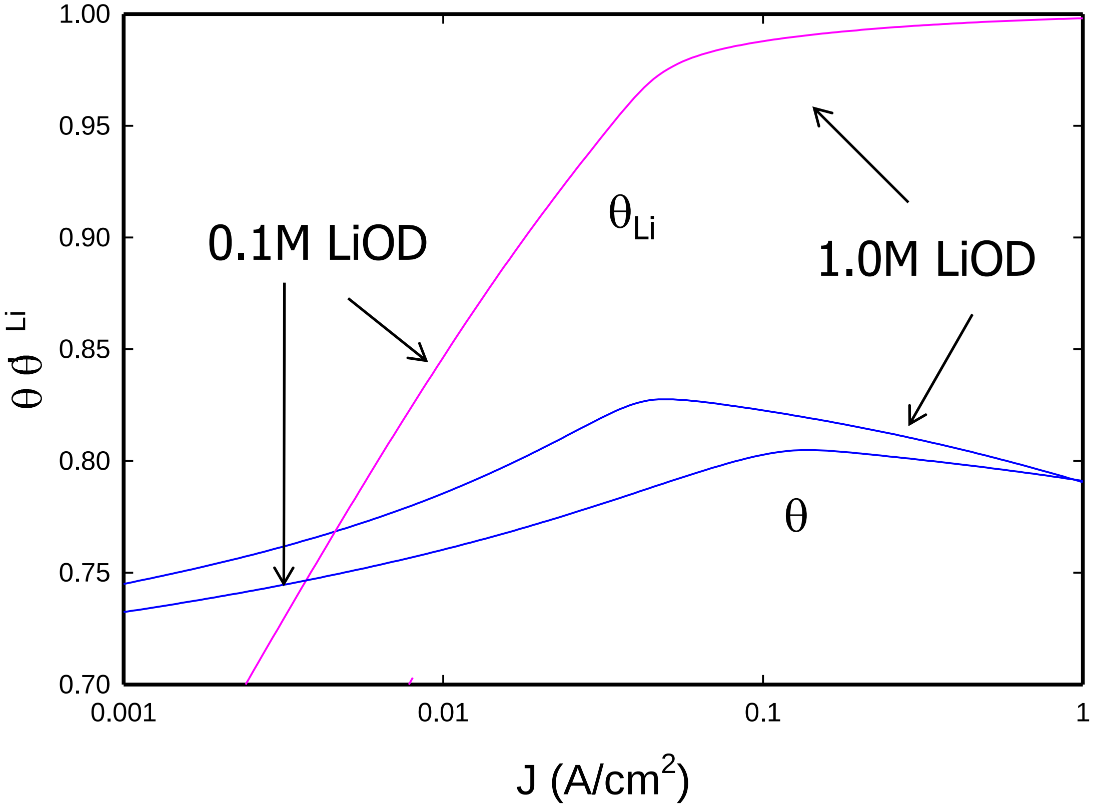
Assume steady state at surface



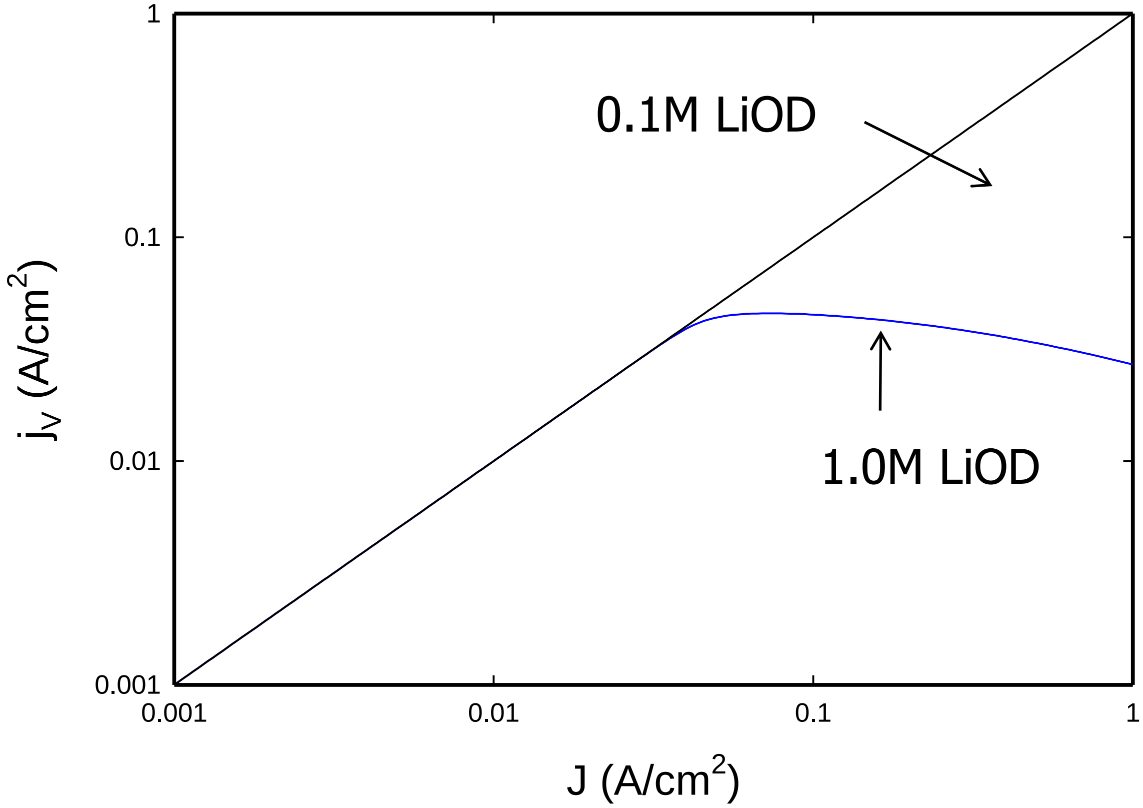
Required flux vs current density



Updated version of model



Volmer current



Summary and conclusions

- What started out to be a simple modeling exercise has turned into textbook rewrite exercise
- Diffusion not understood generally, but a few papers have models that are qualitatively similar
- Electrochemical reaction mechanisms not understood for Pd
- New electrochemical loading model
- Some modeling of SRI DoL cells (in progress)
- Waiting for data from excess heat cells