

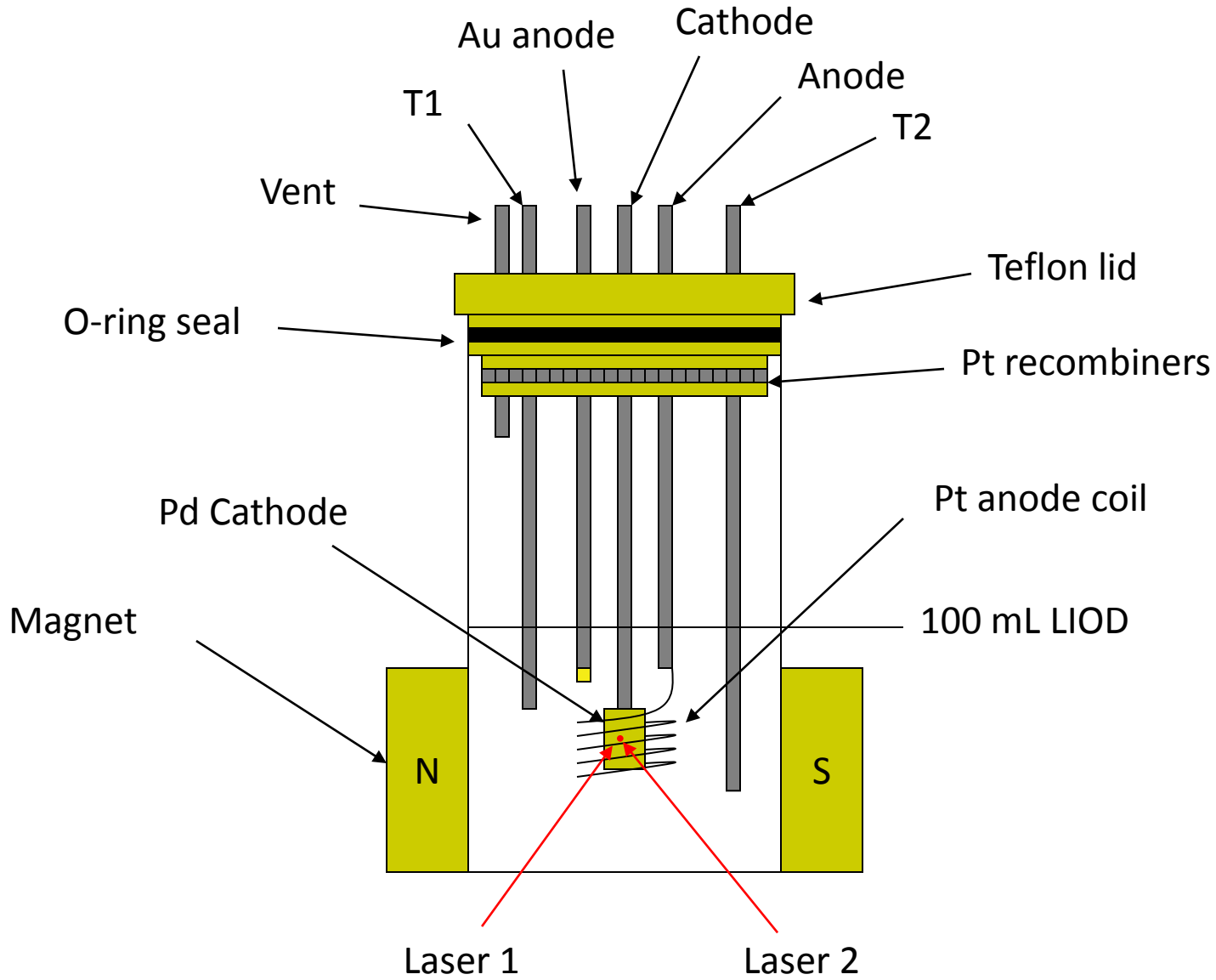
Progress on two-laser experiments

Peter Hagelstein, Dennis Letts,
and Dennis Cravens

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

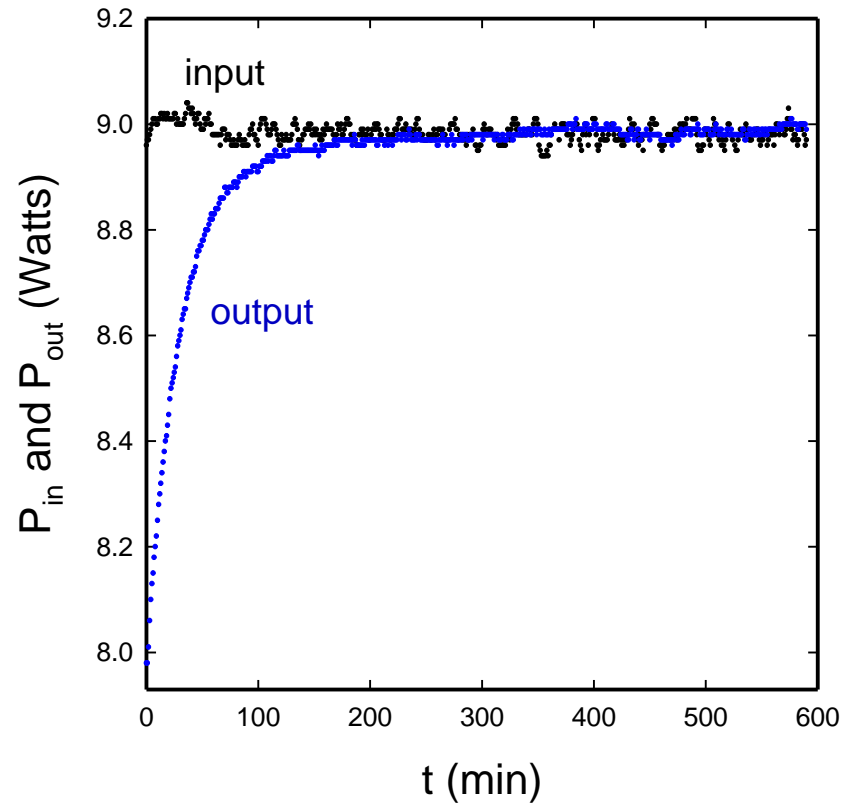


- In previous years Letts and Cravens showed that a laser could trigger excess heat
- Hope was that two lasers might trigger excess heat
- If so, then could study the dependence of excess heat on the difference frequency
- Possible method to see whether optical phonons involved

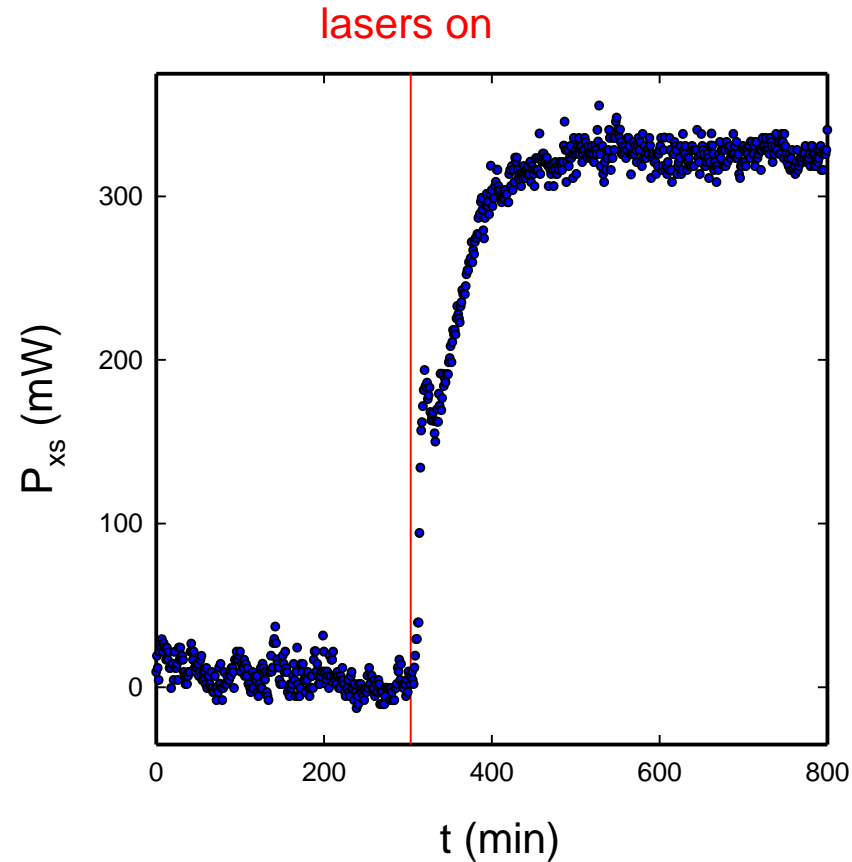


Schematic of experimental set-up

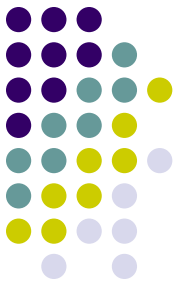
Power balance assuming $P_{th} = K \Delta T$, and $P_{in} = I(V - V_0)$



Lasers stimulate excess heat

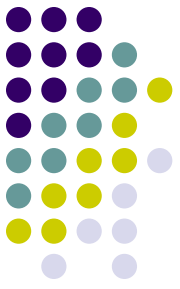


Big response seen at “sweet spots”, little response at other difference frequencies

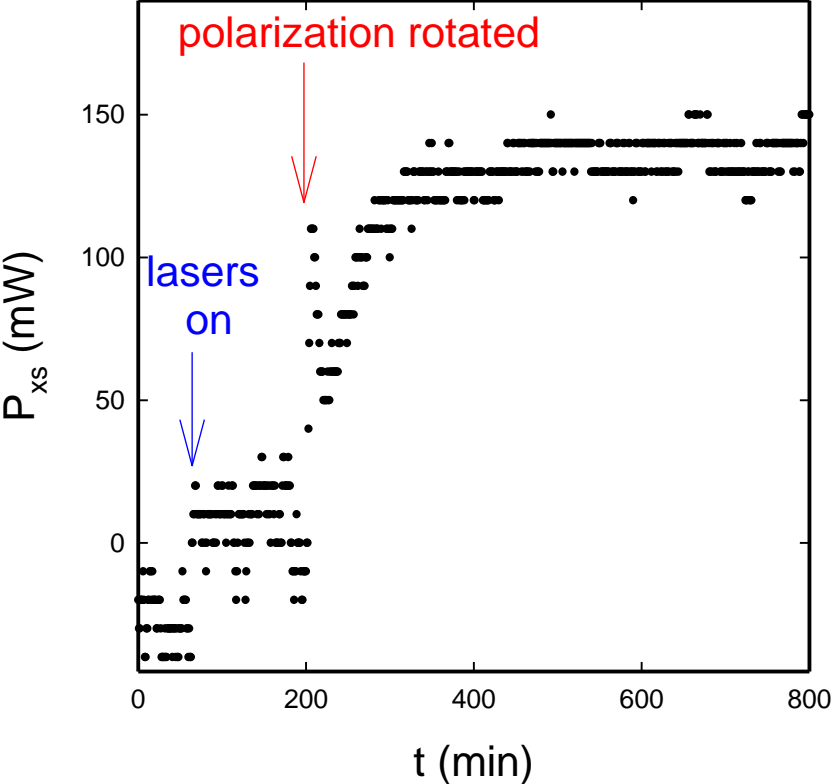


Excess power responds to two laser stimulation:

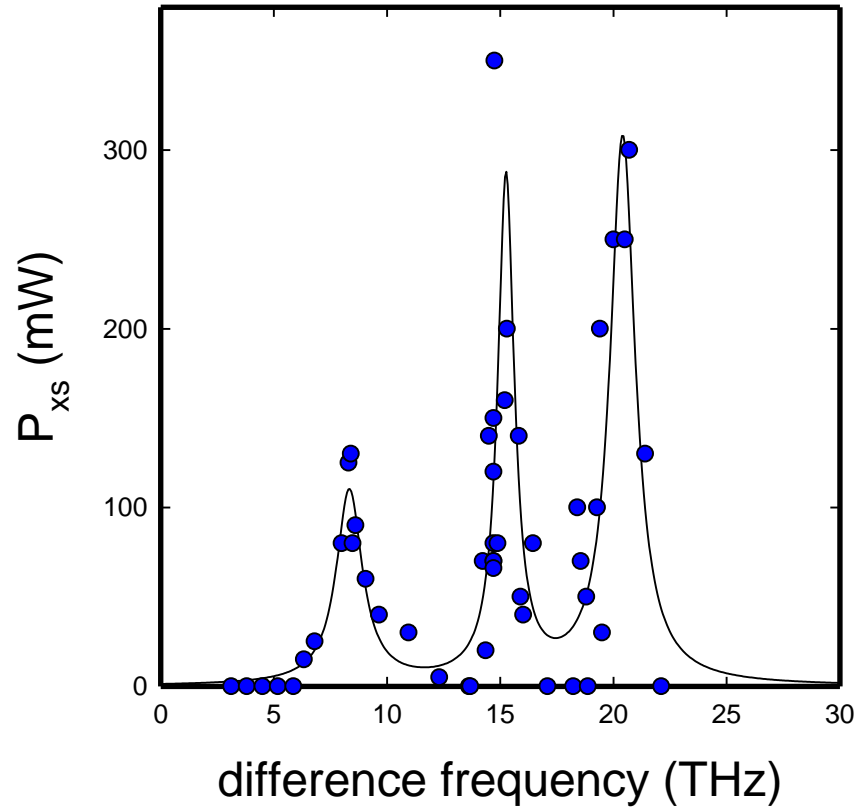
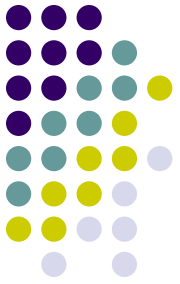
- p polarization required for both lasers
- Overlap of beams required
- Lasers at different frequencies
- Response only at specific difference frequencies



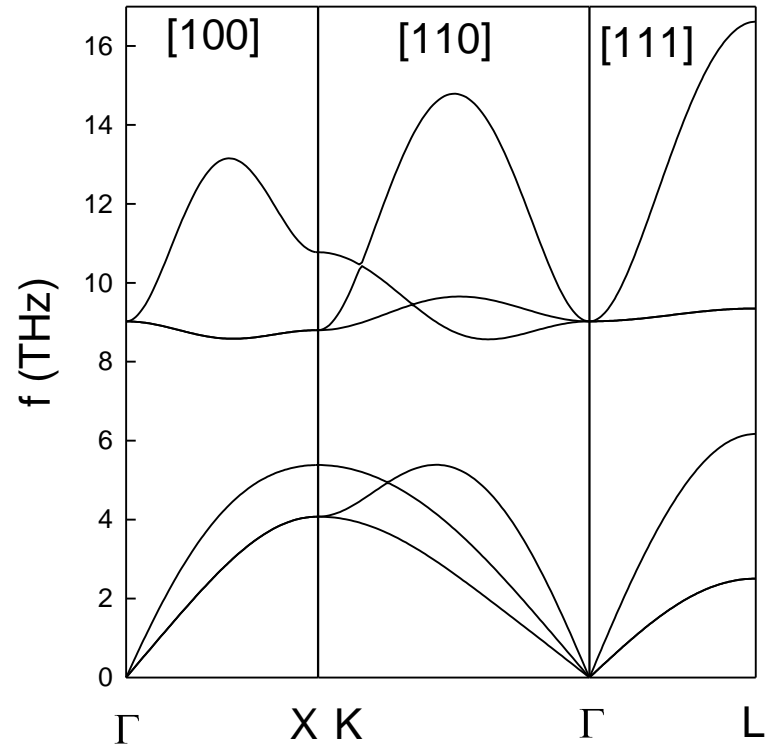
Aligning the polarization leads to excess power



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 $\text{PdD}_{0.75}\text{H}_{0.25}$ give L-point mode at 19.7 THz
- Results implicate optical phonons in these experiments



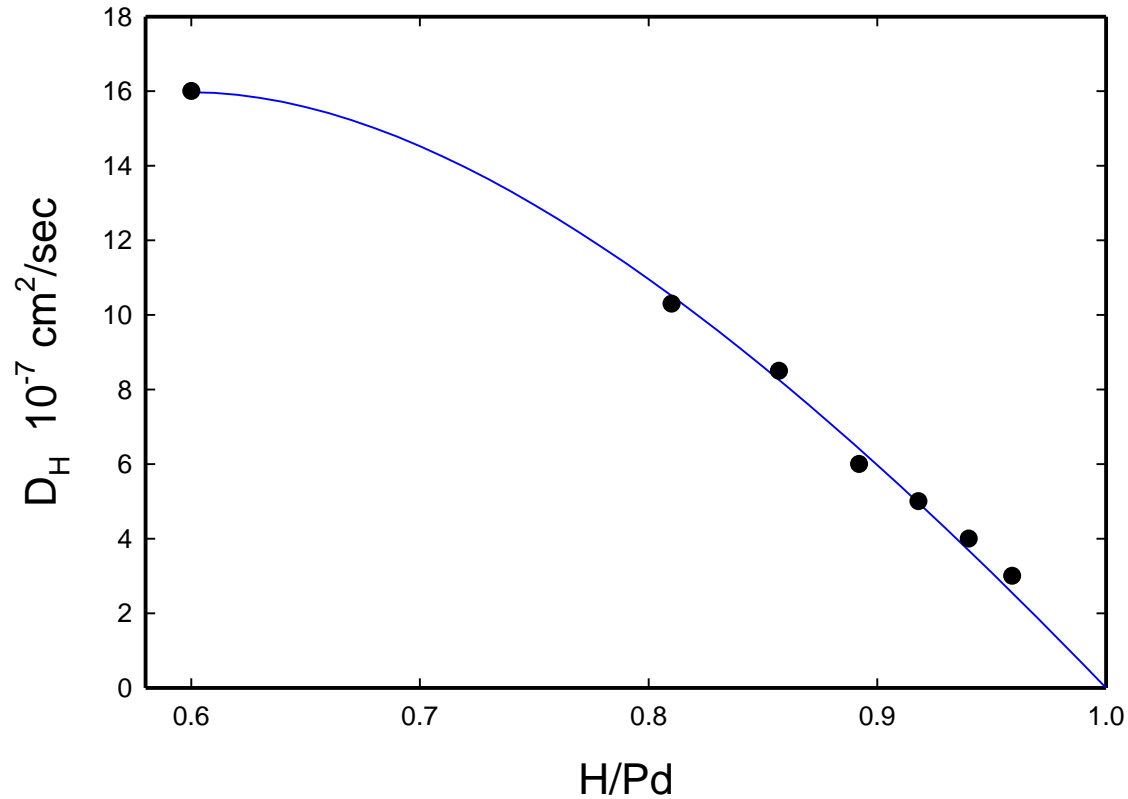
Modeling the SRI loading experiments

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¹Research Laboratory of Electronics
Massachusetts Institute of Technology

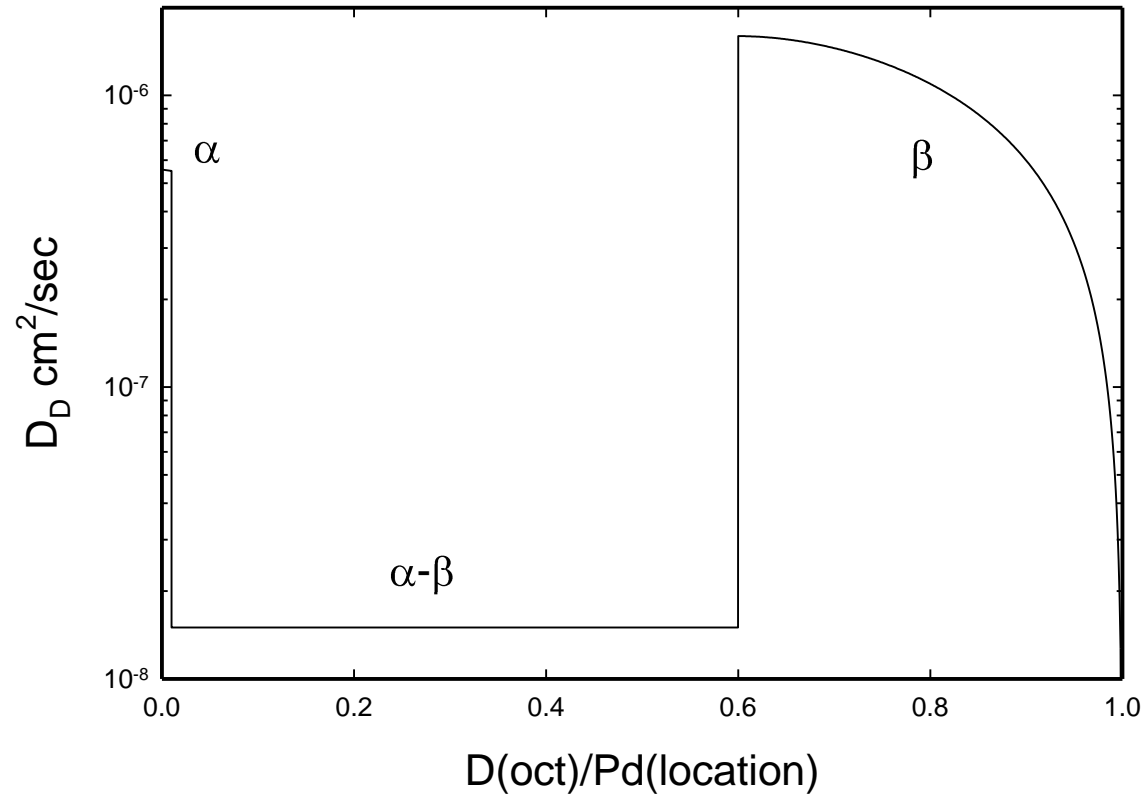
²SRI International, Menlo Park, CA

Diffusion coefficient at high loading

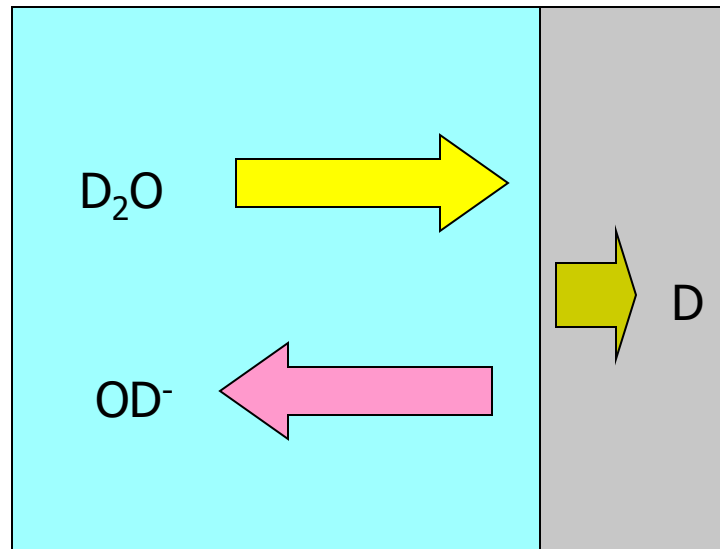


Fit to Baranowski data, and also other experimental data at beta phase boundary

Our diffusion model



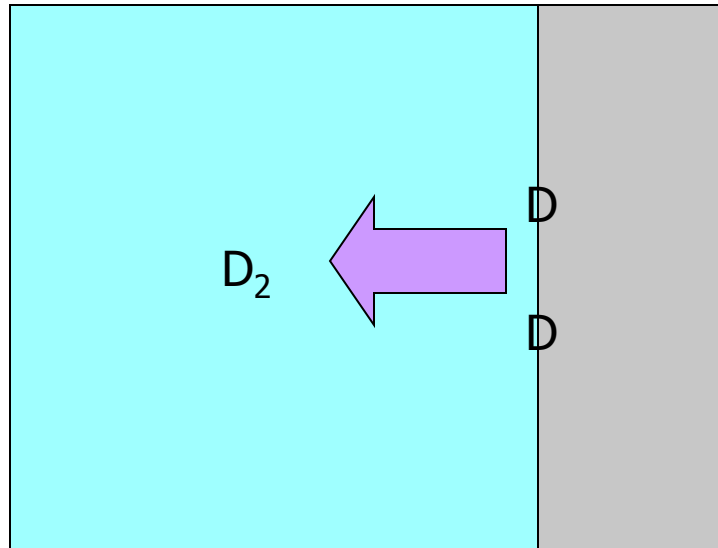
Loading deuterium into Pd



M. Volmer

Electrochemical current density J loads 1 D per charge.

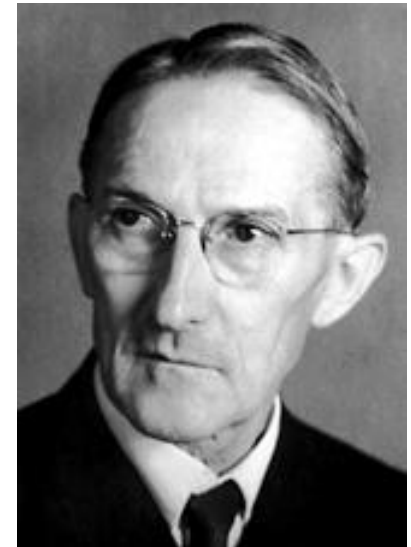
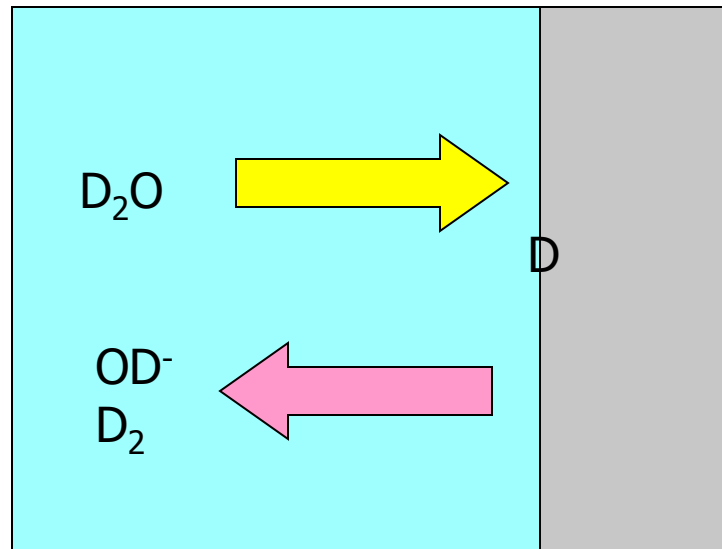
Deuterium loss from PdD



J Tafel

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

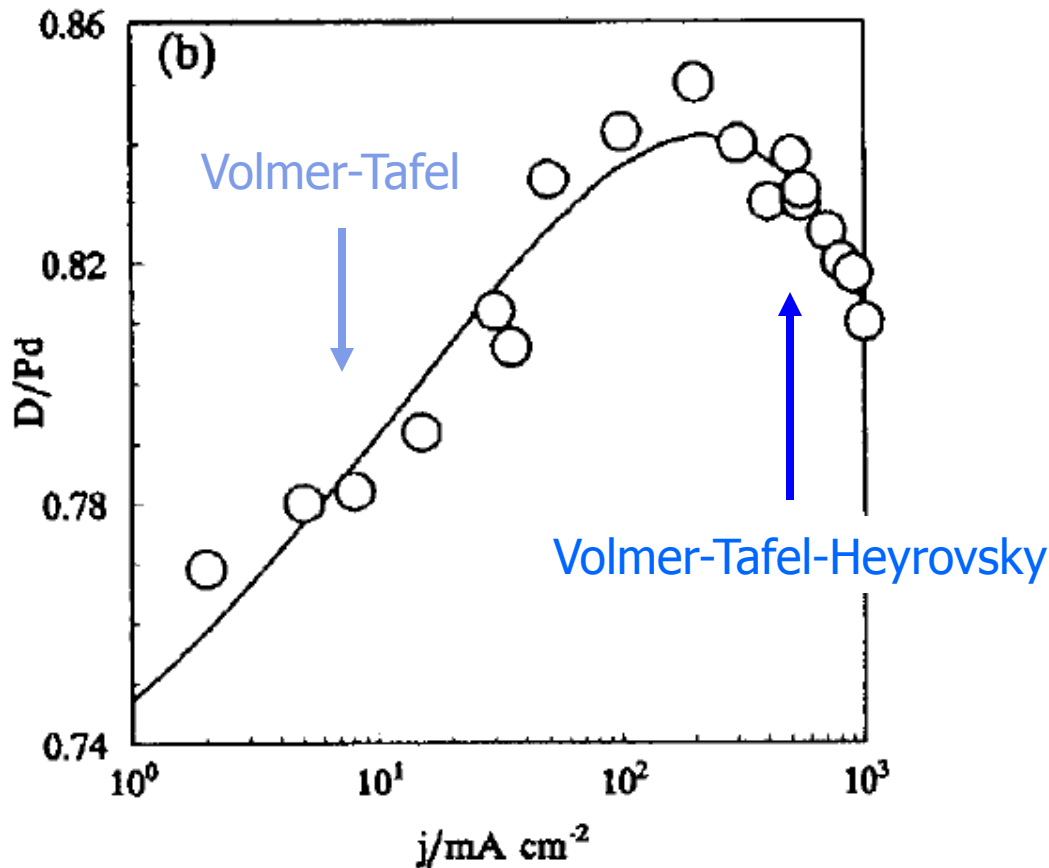
An additional pathway?



J Heyrovsky

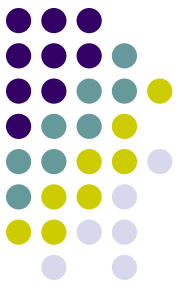
If the chemical potential of deuterium is high, then the electrochemical current density J contains a part that deloads deuterium

Explanation for loss of loading



Data of Akita et al,
ICCF4 (1994)

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



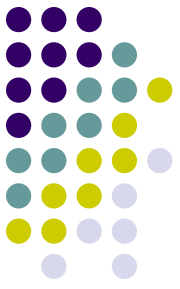
Why are the models broken?

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 Heyrovsky 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

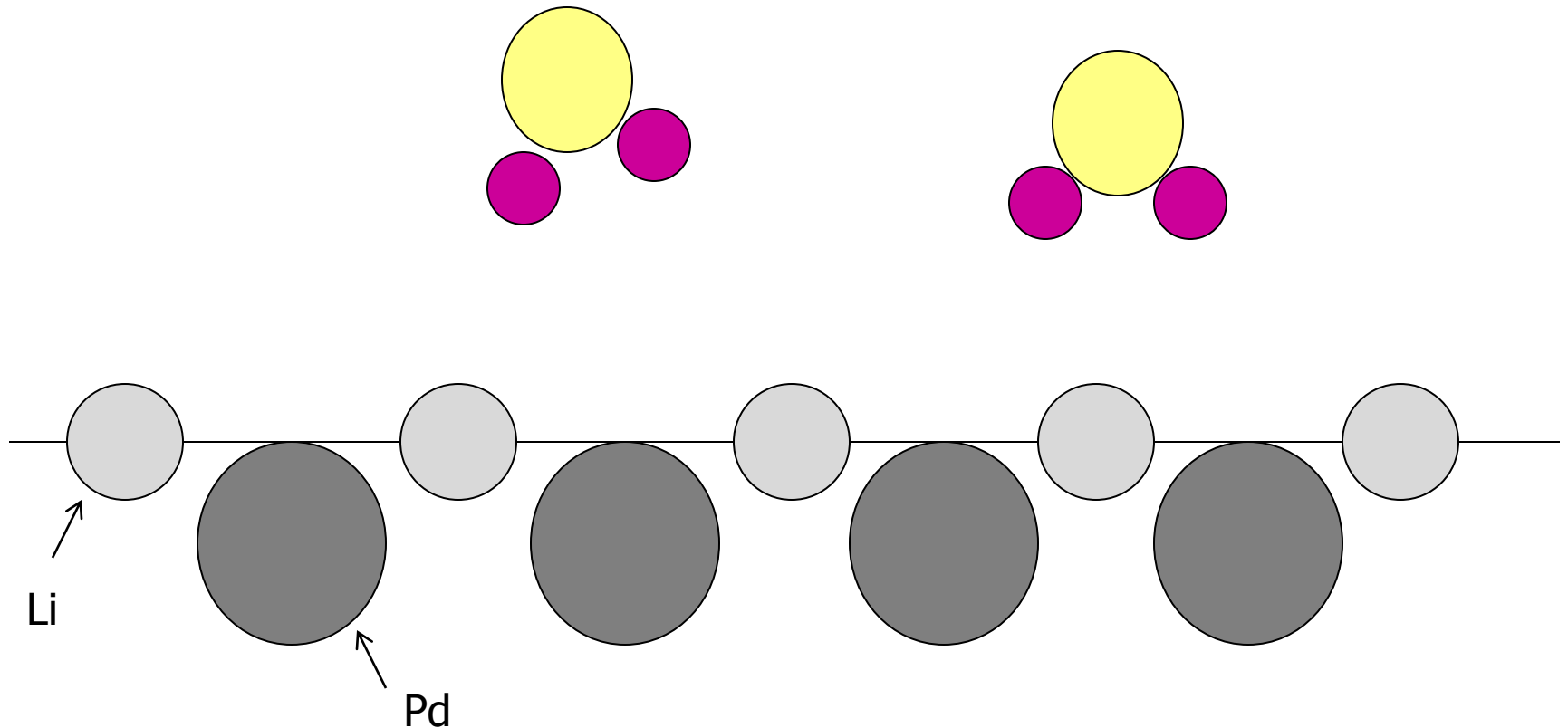


Overall reaction:

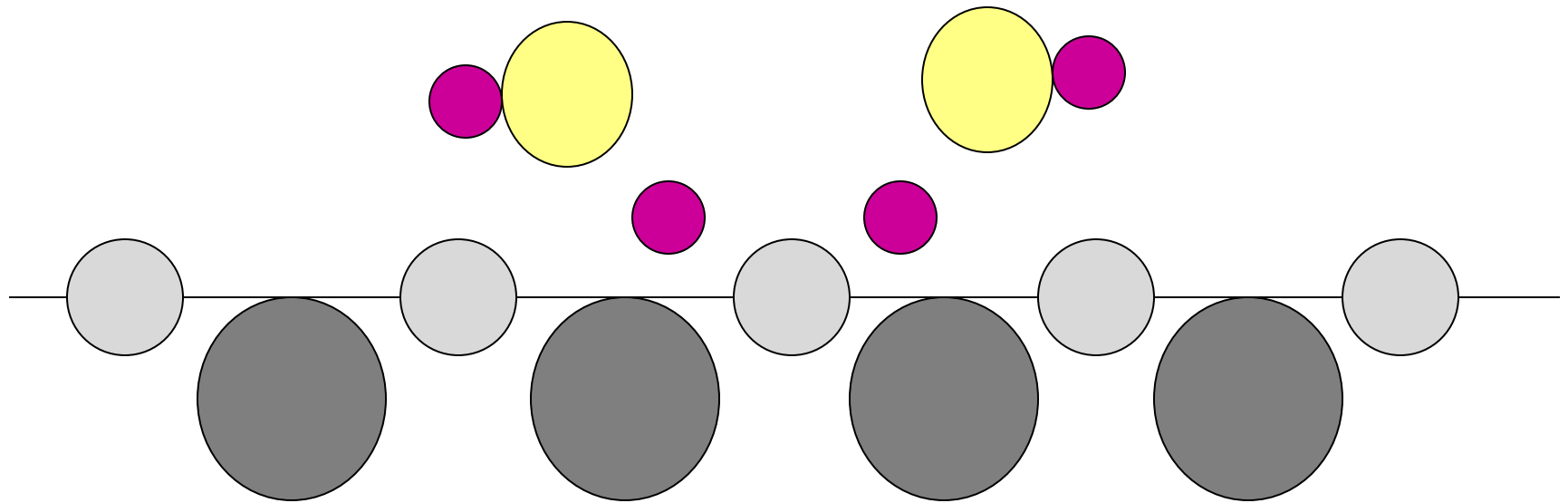


- Reaction does not load or deload (but takes away from Volmer)
- No dependence on chemical potential in PdD
- Does not act as wall

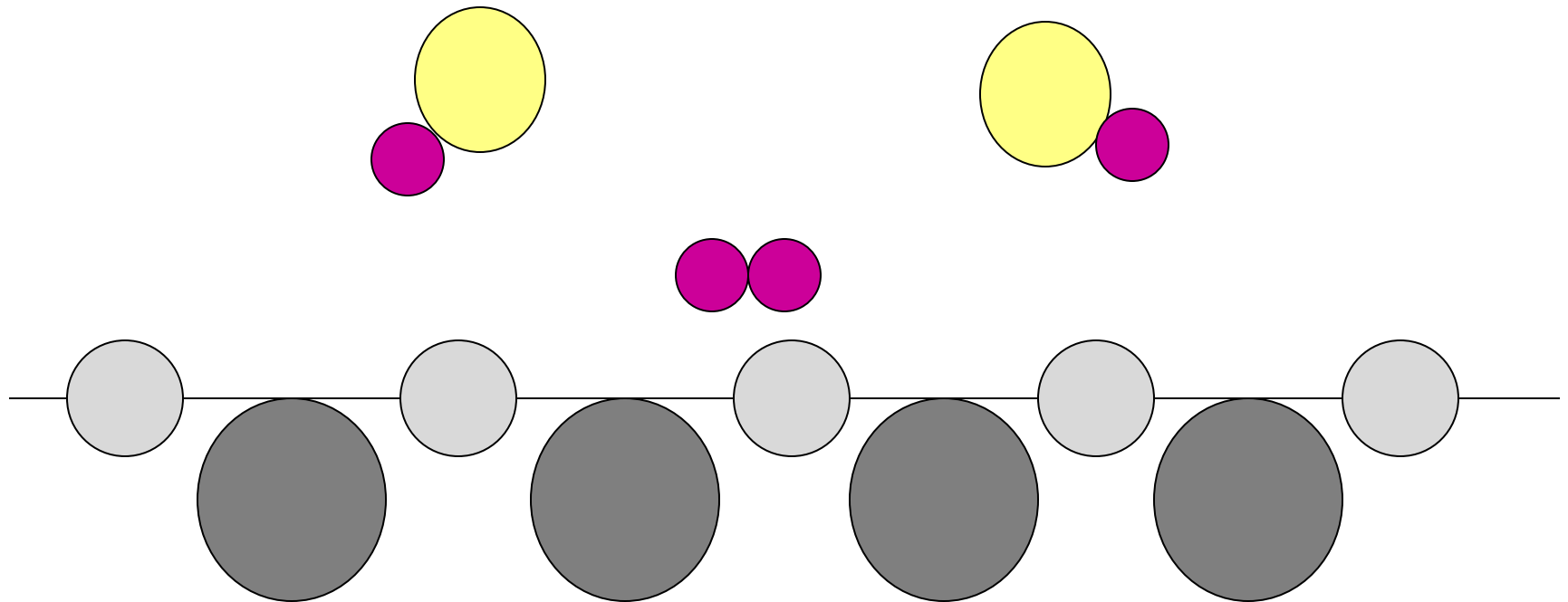
Propose that Li adsorbs and blocks adsorbed D



Propose that Li adsorbs and blocks adsorbed D



Propose that Li adsorbs and blocks adsorbed D



Need model for Li adsorption

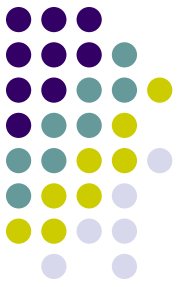


Use a modified Frumkin adsorption isotherm:

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

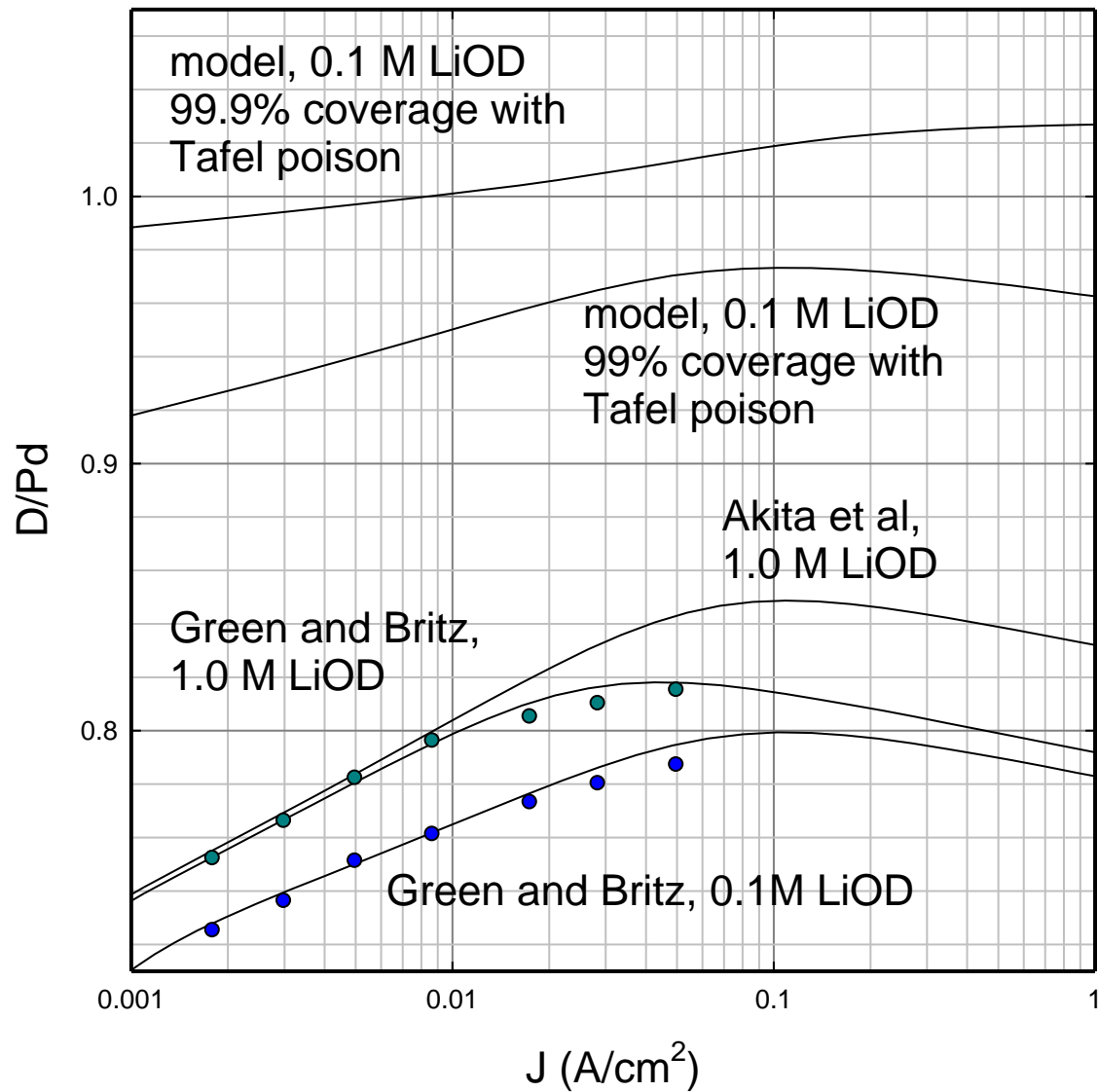
and fit to data as best one can

Resulting electrochemical model

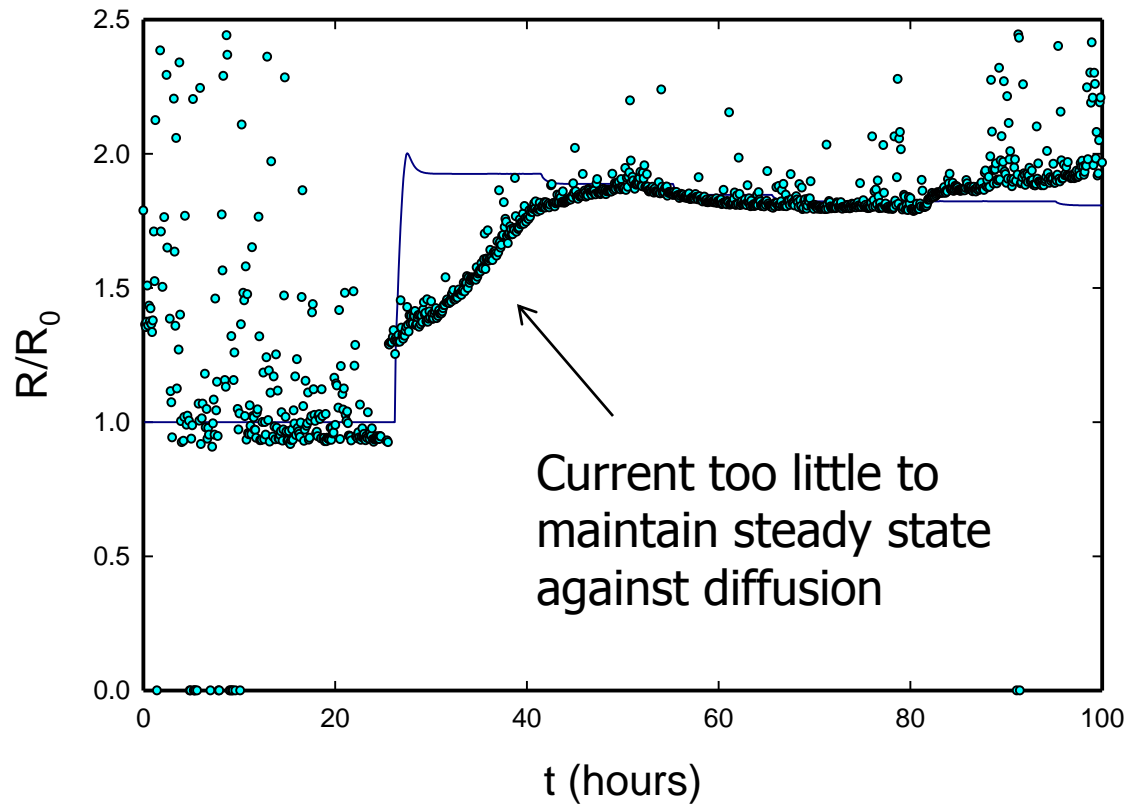


The resulting model seems to work pretty well

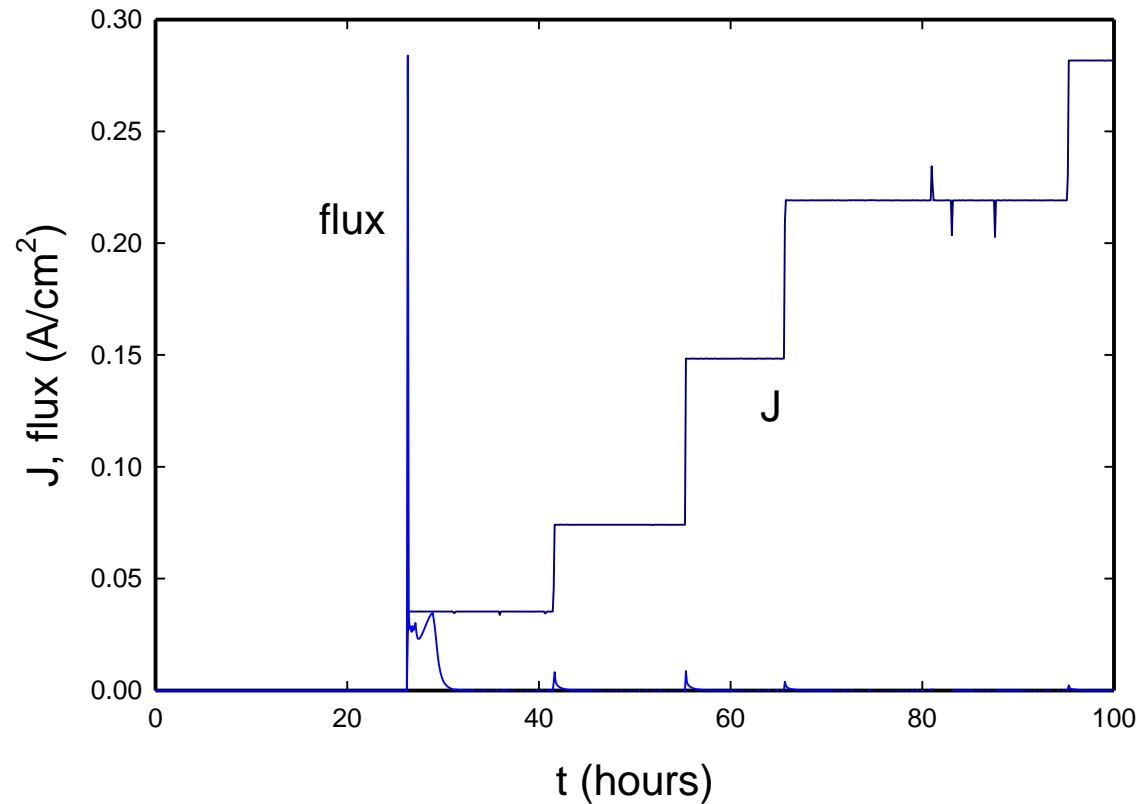
- Fitted to best available data sets in the literature
- No Heyrovsky wall
- Surface lithium consistent with literature
- Can match experimental loading curves
- Only free parameter is cathode-dependent leak rate
- Li plugs leaks



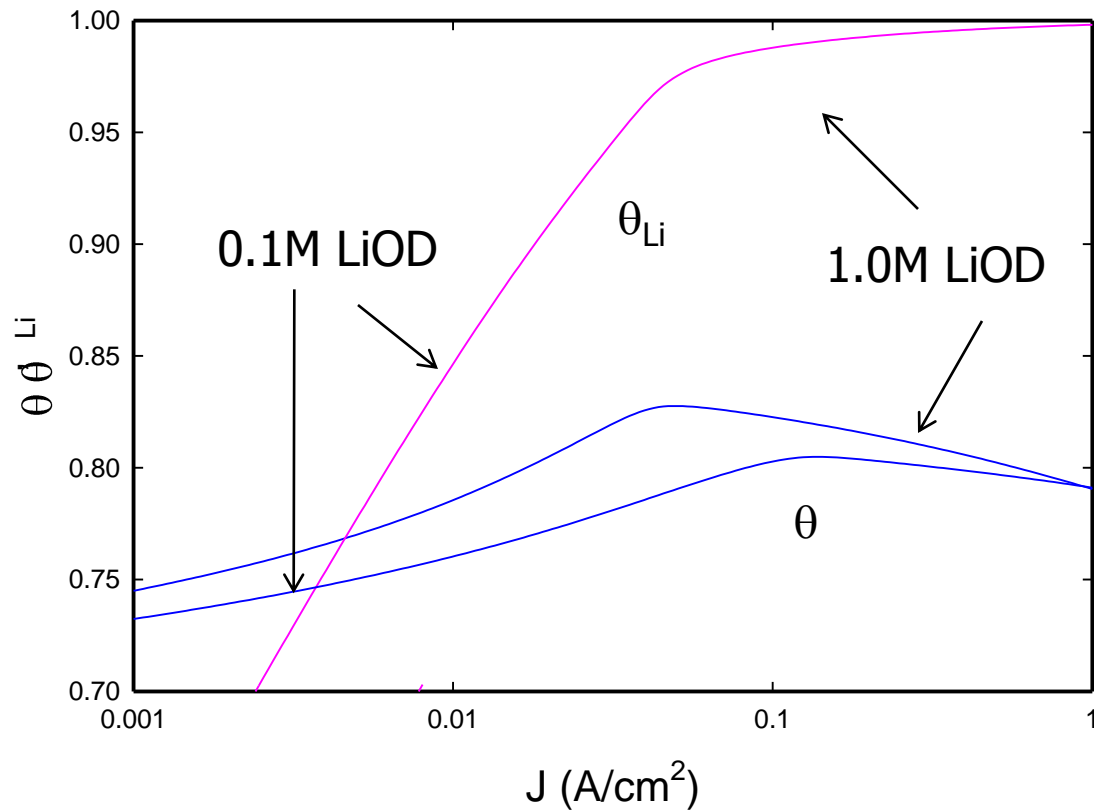
Assume steady state at surface



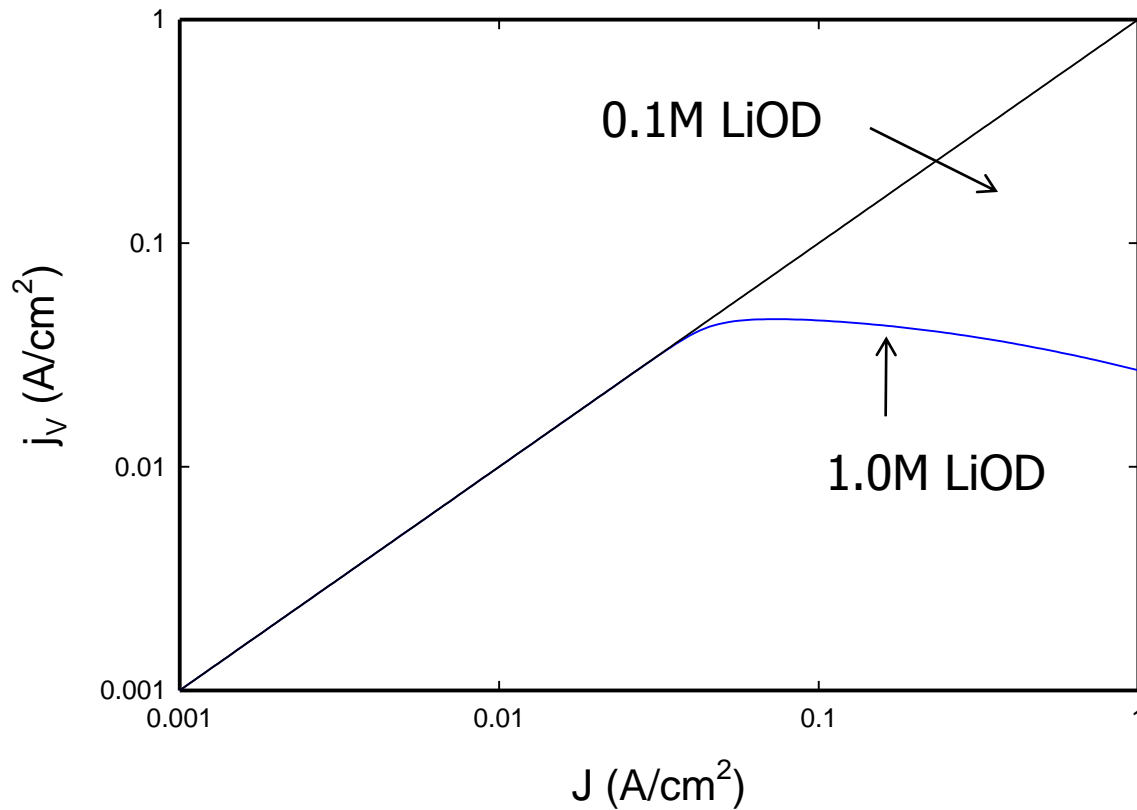
Required flux vs current density



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