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Polarized D^+/Pd-D_2O System: Hot Spots and "Mini-Explosions"

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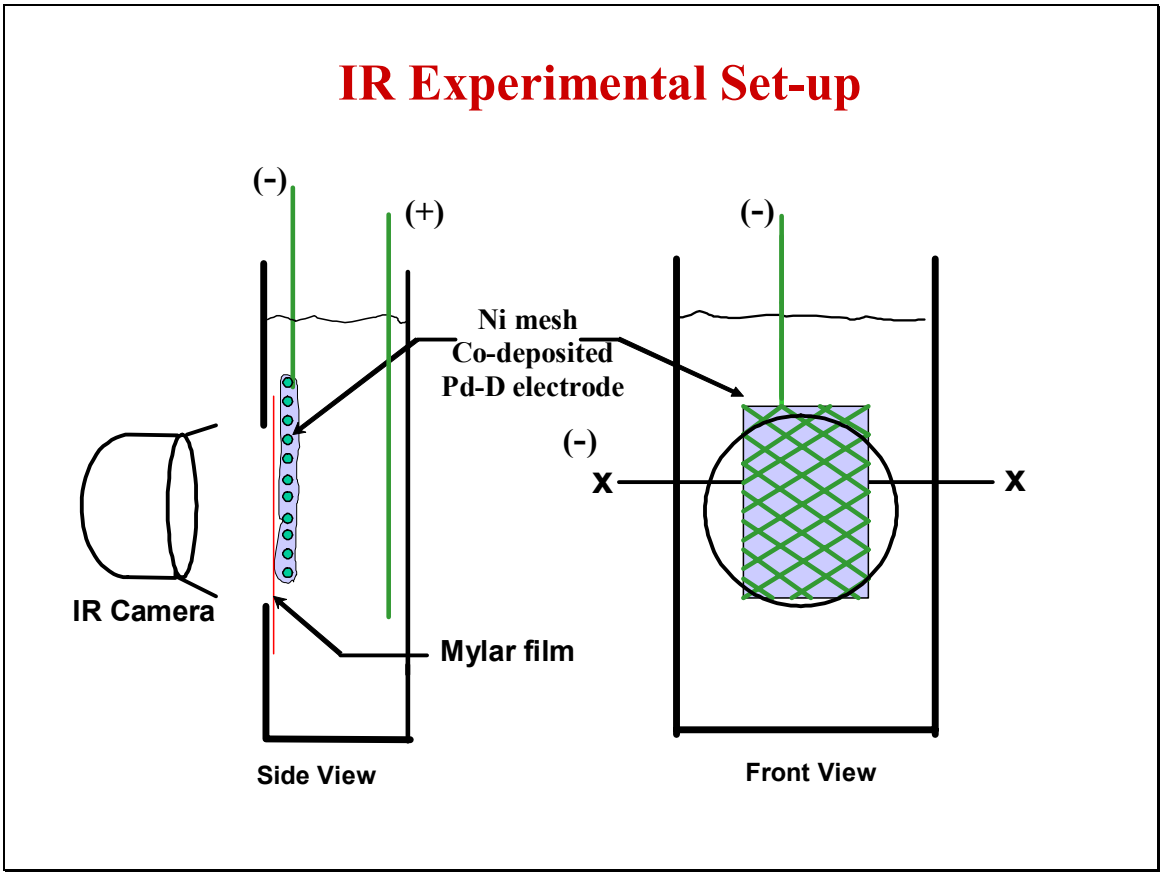
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Electrode preparation using co-deposition

- Advantages:
  - Deposits Pd in the presence of evolving D_2
  - Short loading times—measurable effects within minutes
  - Extremely high repeatability
  - Maximizes experimental controls
  - Experimental flexibility
    - Multiple electrode surfaces possible
    - Multiple electrode geometries possible

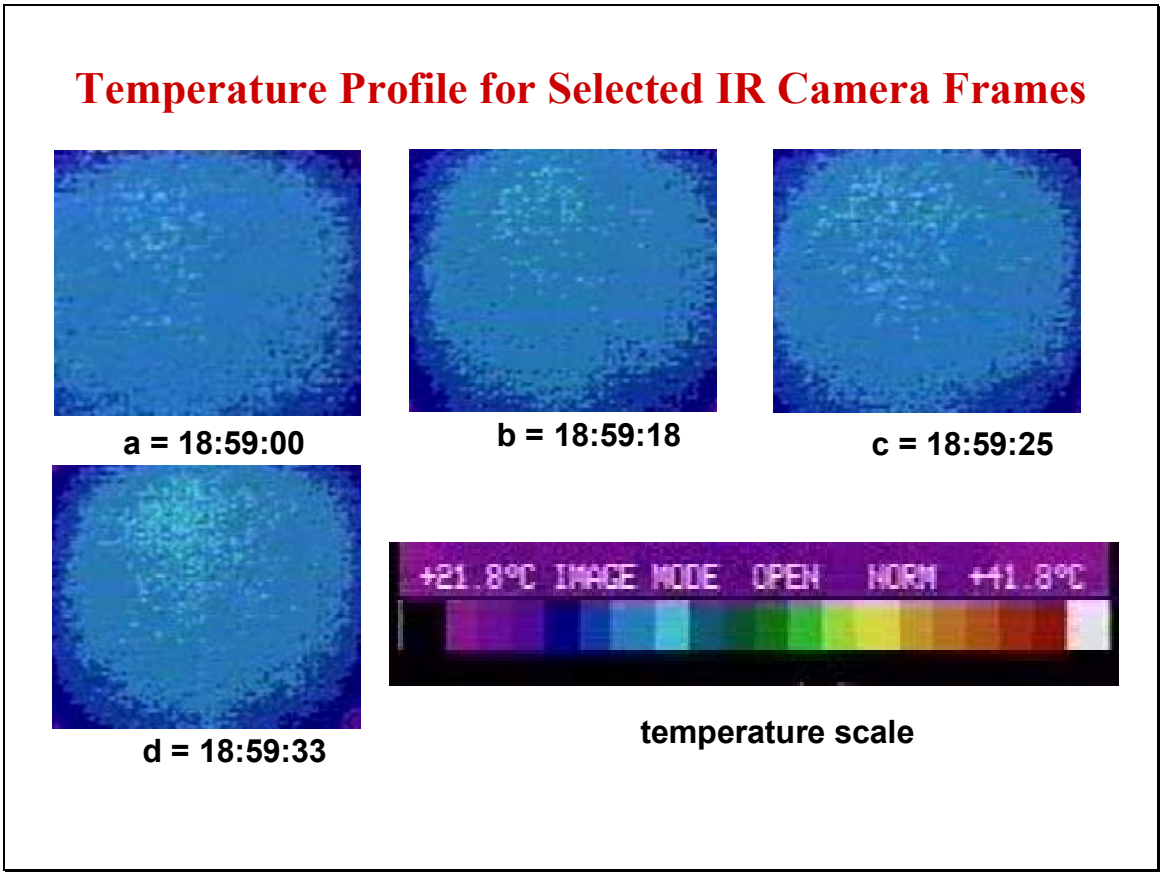
By way of background, we have pioneered the use of co-deposition as the means to prepare the electrode to investigate the F-P effect and have conducted several hundred experiments using this basic technique over the past 13+ years. The Pd is co-deposited on an electrode surface, that does not absorb deuterium, in the presence of evolving D_2 from a solution of $PdCl_2$ in heavy water. This technique offers several advantages including high D loading simultaneous with the formation of the Pd lattice resulting in observable effects within minutes. In addition to extremely high repeatability, we have considerable control over the formation of the Pd electrode and the flexibility to co-deposit onto different electrode surfaces and electrode and cell geometries.

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This experimental set up is an example of the flexibility that co-deposition provides. In this case, we co-deposited onto a Ni mesh that was physically placed close to a mylar film, covering a hole in the cell wall. An IR camera was positioned to focus on the electrode and recordings were made during and after the co-deposition process to monitor the temperature of the electrode and the surrounding solution. These tests were conducted with the help of the late Prof. M. Simnad, from UCSD, and Dr. Todd Evans, from GA Inc, who provided the IR camera.

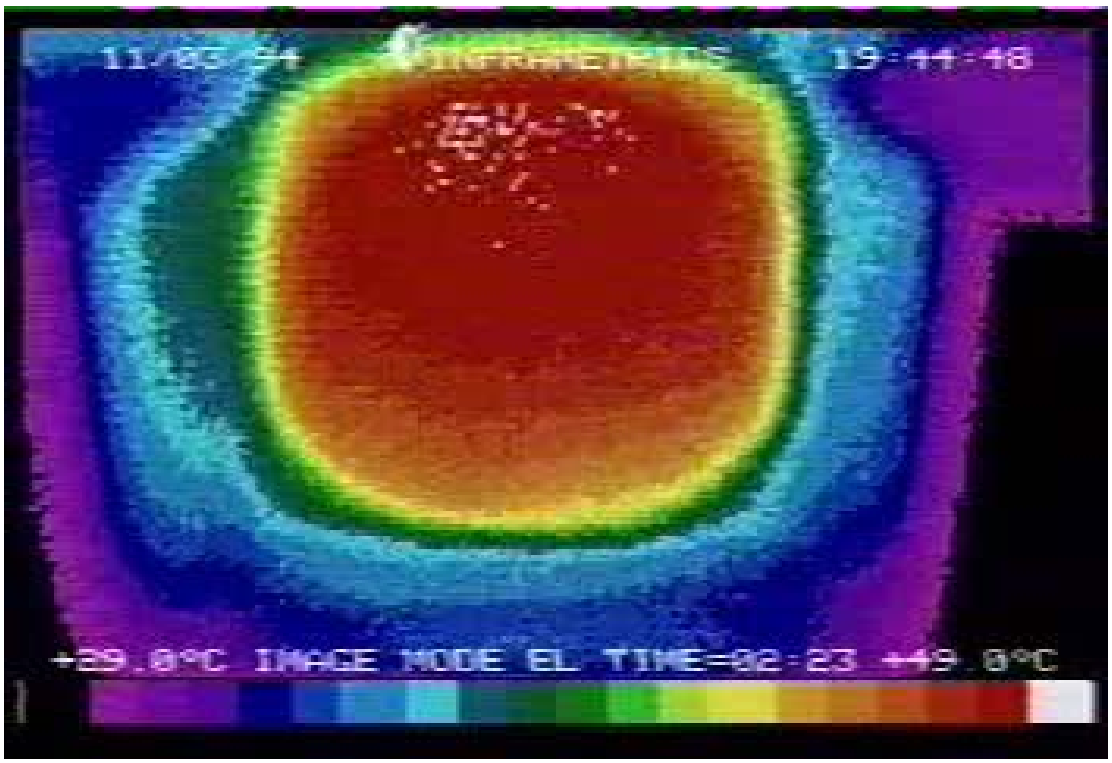
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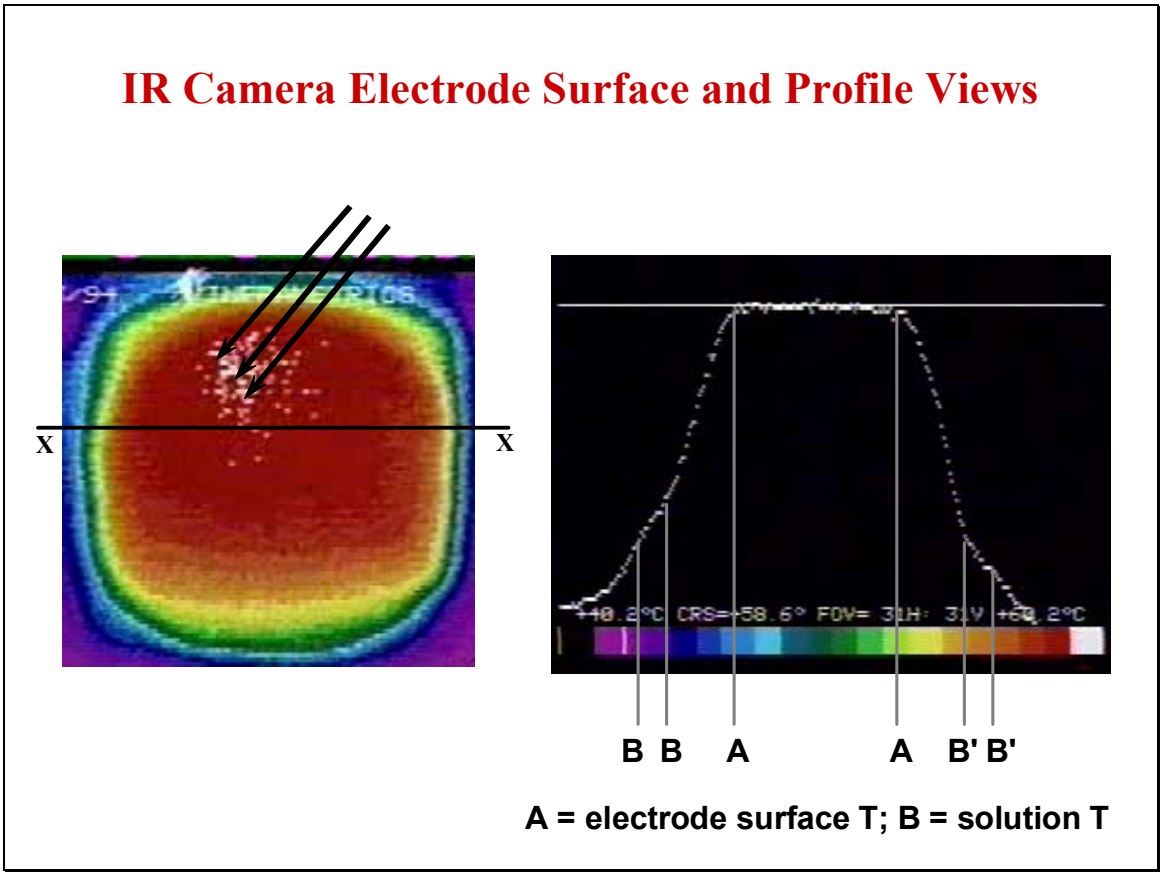
This viewgraph shows a few frames from the IR camera. I would like to point out several interesting features. In the upper left, several different temperatures are represented by the colors with the lighter blue being hotter. Toward the edge of the electrode, the temperatures are lower. Also, these frames "freeze" the action which is actually very dynamic with flashes of the light blue that decays back to the surrounding temperature. Over time, the flashes become more frequent and tend to cluster in an area with the average temperature of that area becoming hotter than the surrounding areas. Over time, the entire electrode surface reaches the hotter temperature and the process repeats itself with flashes of colors representing hotter temperatures starting to show up. The 4 frames shown here represent about 33 seconds of activity and it is clearly evident that the electrode is heating up.

The next viewgraph is a short video clip which shows the hot spots, initially in a small area of the electrode that over about 1.5 minutes expands to cover a significant portion of the electrode's surface.

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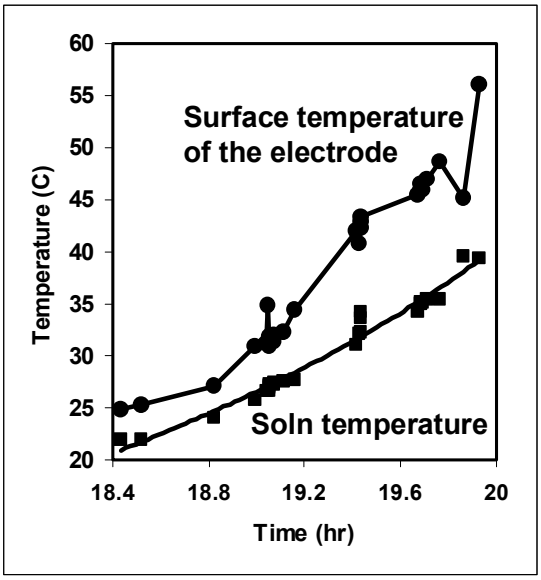
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This viewgraph clearly shows flashes of heat and the temperature profile across the face of the electrode and into the solution.

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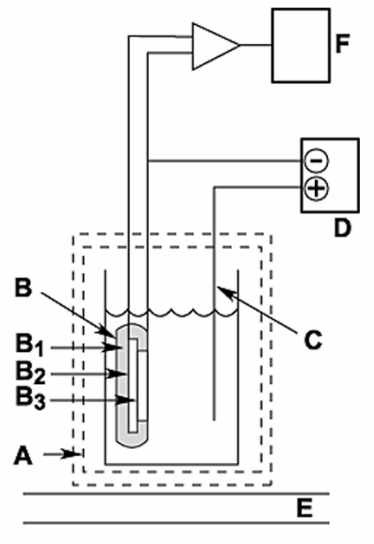
Temperature vs Time Profile



A plot of the temperature variation between the electrode surface and the surrounding solution shows that the ΔT increases over time, reaching in excess of 10^{o} C.

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Piezoelectric Electrode Experimental Set-up

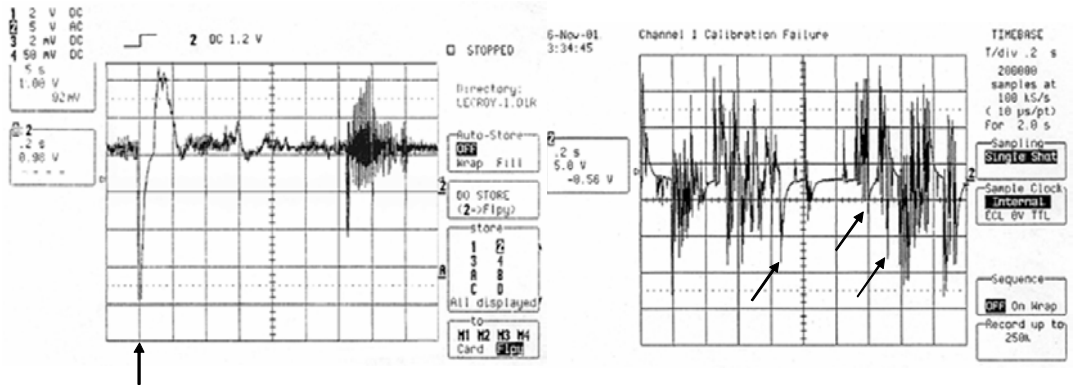


A – Faraday cage
B – negative electrode assembly (B_1 – insulating material; B_2 – piezoelectric substrate; B_3 – Pd/D film)
C – positive electrode
D – potentiostat/galvanostat
E – shock absorbing material
F – oscilloscope (LeCroy digital) with computerized data logging
E – laboratory bench

The flashes observed in the IR experiments suggest "mini-explosions" so we designed an experimental set-up to see if we could record these events using a piezoelectric sensor. Again, the co-deposition approach made this possible. A piezoelectric transducer was coated with epoxy as an insulation layer except for approximately 1 sq cm on the front on which an electrically conducting material (Ag) was deposited. This became the cathode onto which Pd was co-deposited from the PdCl in a deuterated water solution. The experimental setup and instrumentation is shown.

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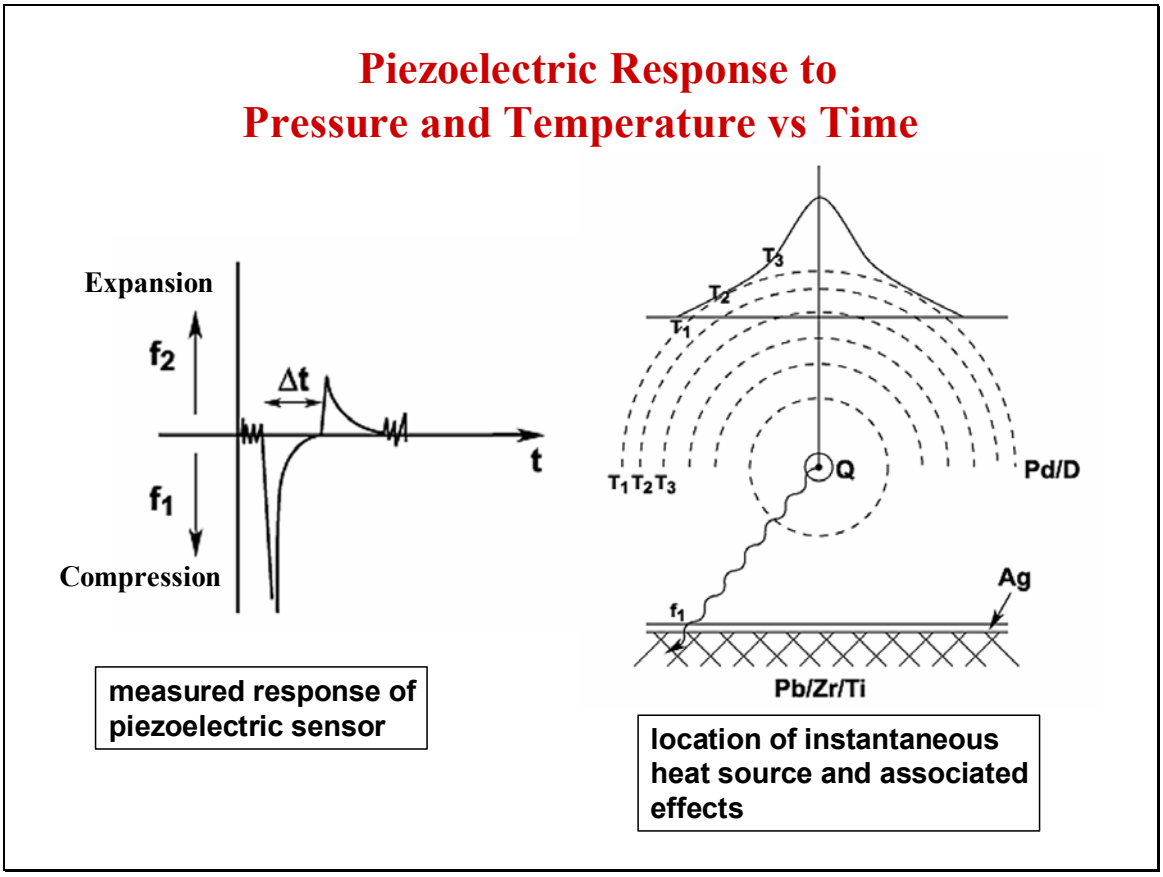
Piezoelectric Response to Pressure and Temperature vs Time



Isolated event **Expanded series of events**

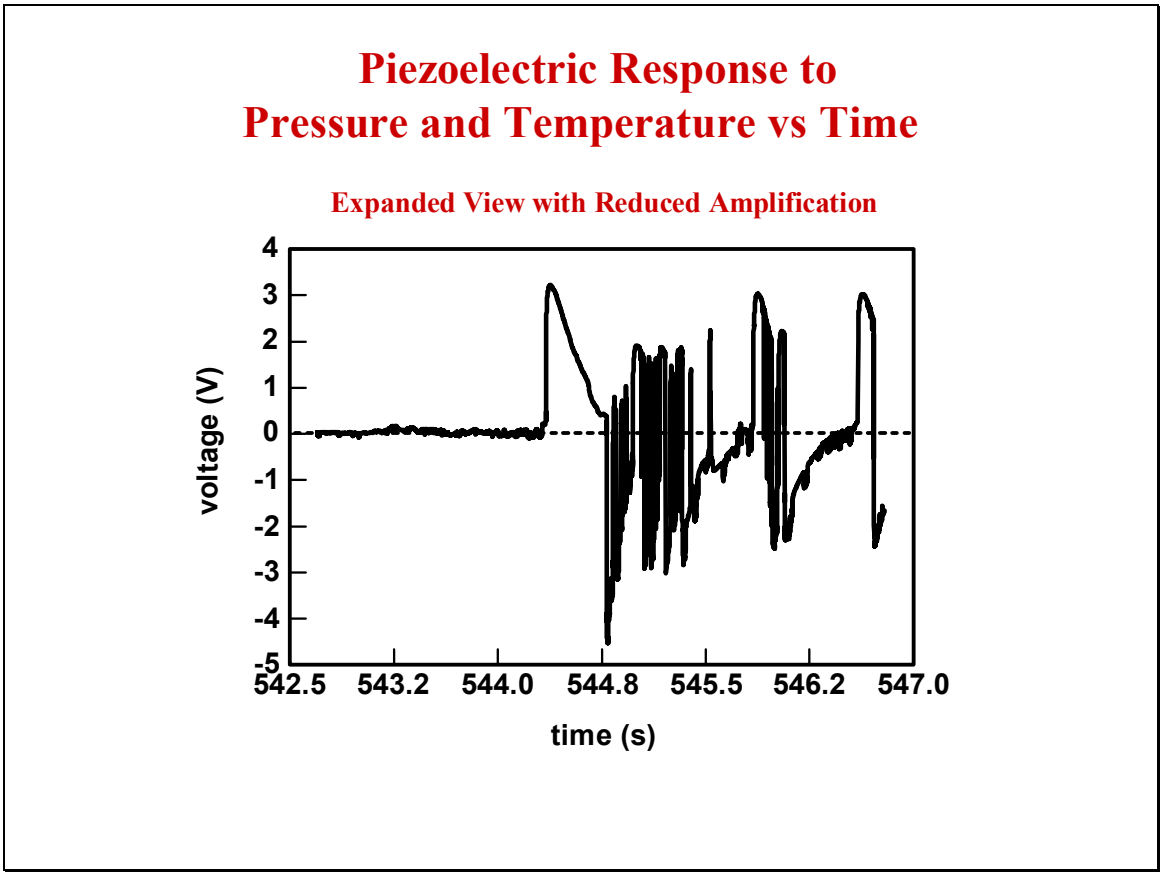
Here are a couple of plots of data recorded from the piezoelectric experiment. The plot on the left clearly shows continuous stream of events, including a large isolated event and a cluster of larger events. The plot of the right expands the time scale to show the characteristic shape that the events produce. Typically, there is a sharp spike down followed by a broader but smaller upward spike which decays back to equilibrium.

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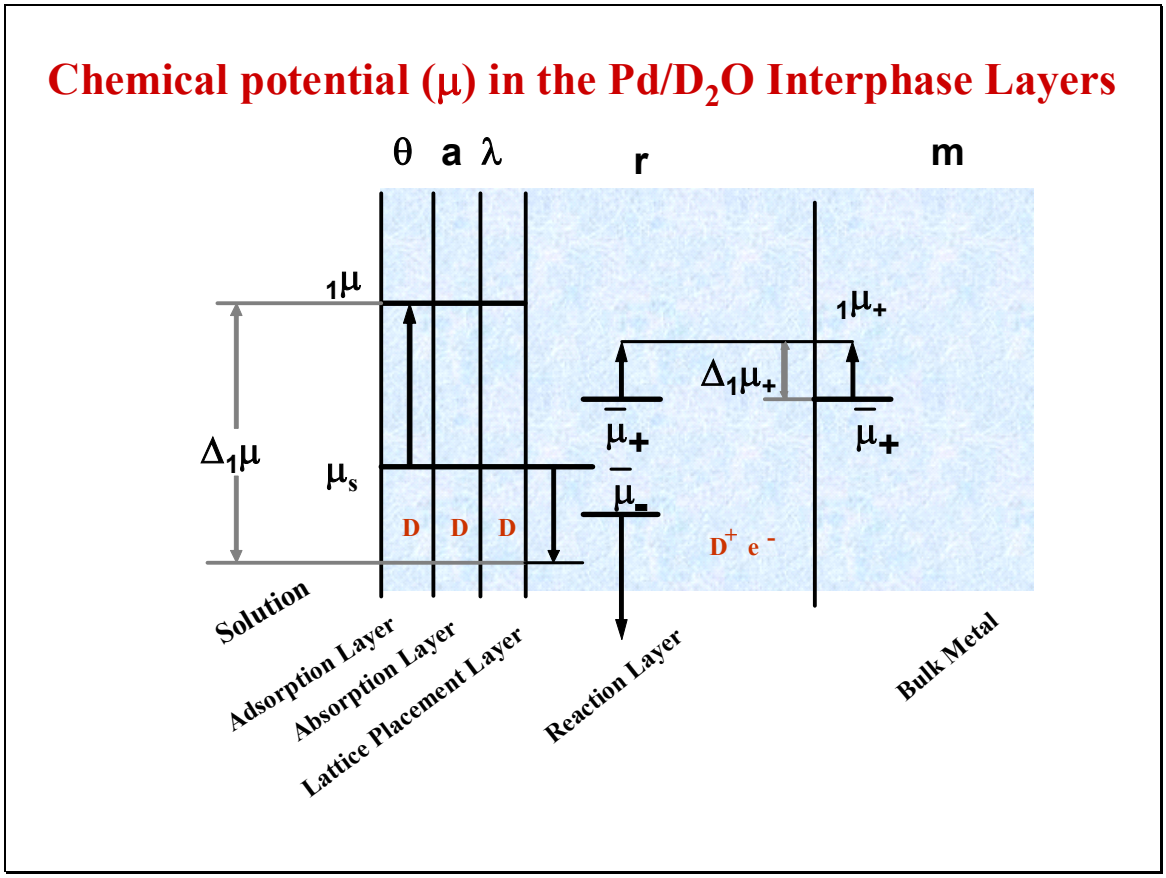
Here, we illustrate one typical response of the piezoelectric sensor. The sharp spike down is a result of compression on the sensor and the swing above the line is caused by expansion. These signals are representative of an initial pressure wave impinging on the sensor which causes compression, followed by a localized increase in temperature which causes expansion. The diagram on the right suggests an explanation which is consistent with the observed measurements. The pressure wave propagates at the speed of sound through the metal. Heat propagation is much slower. It's also worthwhile to note that these observed responses continued after the current to the cell was turned off which is consistent with "heat after death" reports that others have seen. Although it was observed that the frequency and intensity of the events decayed with time, a few events were still observed after 3 days.

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This plot is included to show that we also observed short intermittent periods of much larger activity. The scale on the left is now in volts. The small signals shown to the left, occurring between 543 and 544 seconds are representative of the signal amplitude which the previous graphs have shown at much larger scale. The large signals starting shortly after 544 seconds are 3 to 5 orders of magnitude larger. We only observed these a few times during the experiment when the solution temperature was approaching 90^{o} C. We have no explanation, at this time, for these observations which only lasted a few seconds and ended as quickly as they began.

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These experiments suggest that the events are the result of clusters of $D^+ \cdot e^-$ complexes. Chemical reactions can explain the formation of such complexes. The blue represents a section through the electrode with several layers shown where the layers are identified by the processes that occur rather than specific physical depth. Starting on the left, with the reduction of D^+ to D as it contacts the adsorption layer. Next, it moves inside the absorbed layer inside the contact surface and then incorporated in the lattice placement layer. At this point, dissociation occurs, leaving D^+ and e^-. The chemical potential is the driving force for all of these processes. At this stationary state, i.e. no net flow of matter but flow of energy is permitted, assures the equality of the chemical potential μ_s in all the layers. If the chemical potential is increased by increasing the over potential, and assuming fast processes in the first three layers, a gradient is created in the reaction layer that promotes the influx of deuterium followed by dissociation to form D^+ and

aggregates of $D^{+}\cdot e^{-}$ complexes. Formation of these clusters is a necessary condition to initiate the Fleischmann-Pons effect.

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Conclusions

- The electrode/electrolyte interphase is viewed as an assembly of a set of homogeneous layers defined by processes
- The ionization (dissociation) of D in the Pd lattice is a chemical reaction (mass action law and chemical potential obeyed, etc)
- The s-electrons play a dominant role in both the high values of $\bar{\mu}_{+}$ as well as in the forming of $[D^{+}_{m}\cdot e^{-}_{n}]$ complexes