High-Pressure Electrochemistry

Executive Summary

This report presents a comprehensive analysis of experimental research conducted in the field of high-pressure electrochemistry, focusing on achieving high loadings at elevated temperatures. The study spans various experiments, from explorations in supercritical water environments to high-pressure, ambient-temperature conditions, and includes substantial hardware developments to accommodate these unique experimental settings. The primary objective of this research is to facilitate higher loadings at elevated temperatures than what could be achieved with gas-loading alone.

The initial hypothesis centered on using supercritical water as a medium for electrochemical loading, aiming to maintain a uniform, bubble-free electrochemical loading environment at high temperatures. However, achieving measurable H/Pd loading levels at temperatures >200°C proved to be challenging, and we could not measure stable loading in a supercritical water environment. We then focused on exploring the potential symbiotic relationship between high-pressure and electrochemical loading driving forces and found that we could achieve higher loadings than what could be achieved with gas pressure alone under equivalent conditions. We also found that high-pressure electrochemical (HPE) loading could maintain near-unity loading conditions indefinitely but found no evidence of LENR. We found that the highly non-equilibrium nature of HPE would produce blisters within the Pd lattice, as well as heat-producing chemical reactions, but these observations were non-isotopic and chemical in nature.

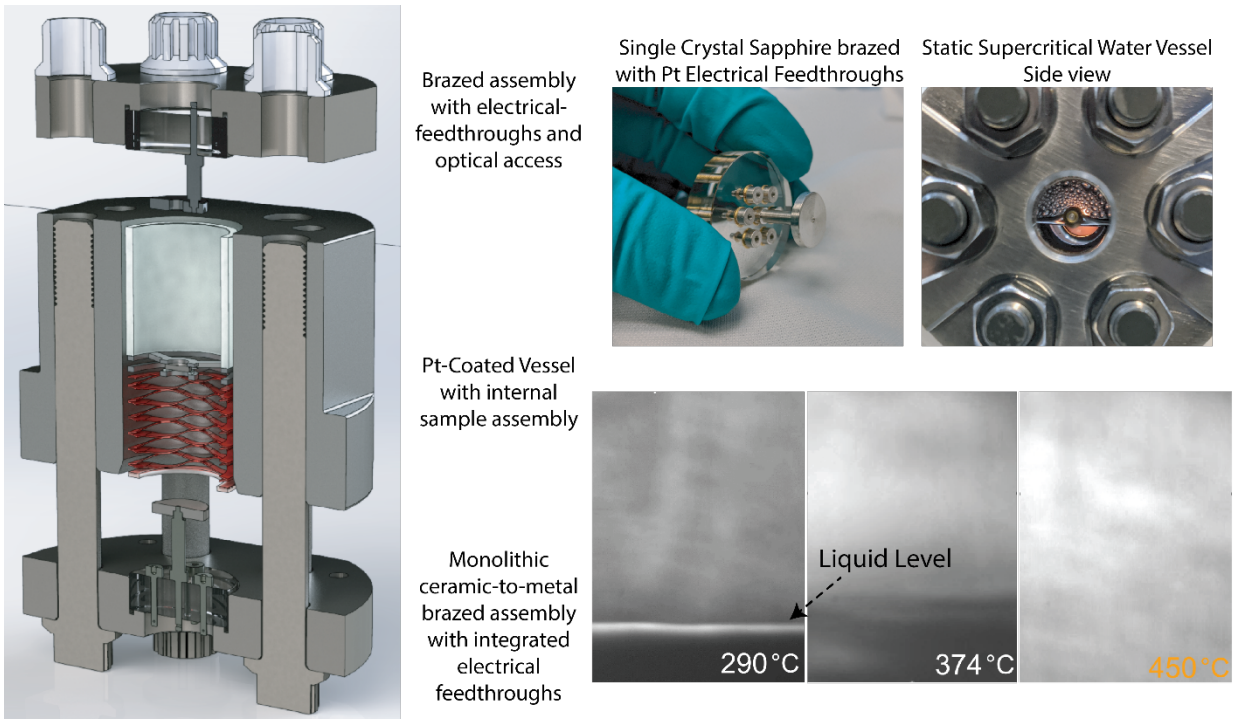

Figure 1: A high pressure, corrosion resistant vessel was used to test in supercritical water conditions. Because of the need to operate at pressures above 10 ksi and 374°C with corrosive liquids, material choice was limited. Seals and electrical and optical access were custom designed to meet these requirements. The three panels in the lower right are optical images of the water/electrolyte in the vessel at 3 different temperatures (i.e., below, at, and above the critical point).

Experimental Concept

The goal with high pressure electrochemical loading is to achieve high Pd loadings at elevated temperatures to test if this was a possible route to LENR. Since electrolytic loading doesn't work well at high temperatures, we aimed to explore if high-pressure may offer a way around this. To accomplish this goal, we proposed electrochemical loading under supercritical conditions. The supercritical regime is defined as beyond the critical point (> 374 °C and > 3200 psi for water) and is essentially a form of gas, that, above 374 °C, will never liquify. From electrolytic loading, the fugacity comes from an electrochemical potential, not ultra-pressure, and in a supercritical electrolyte.

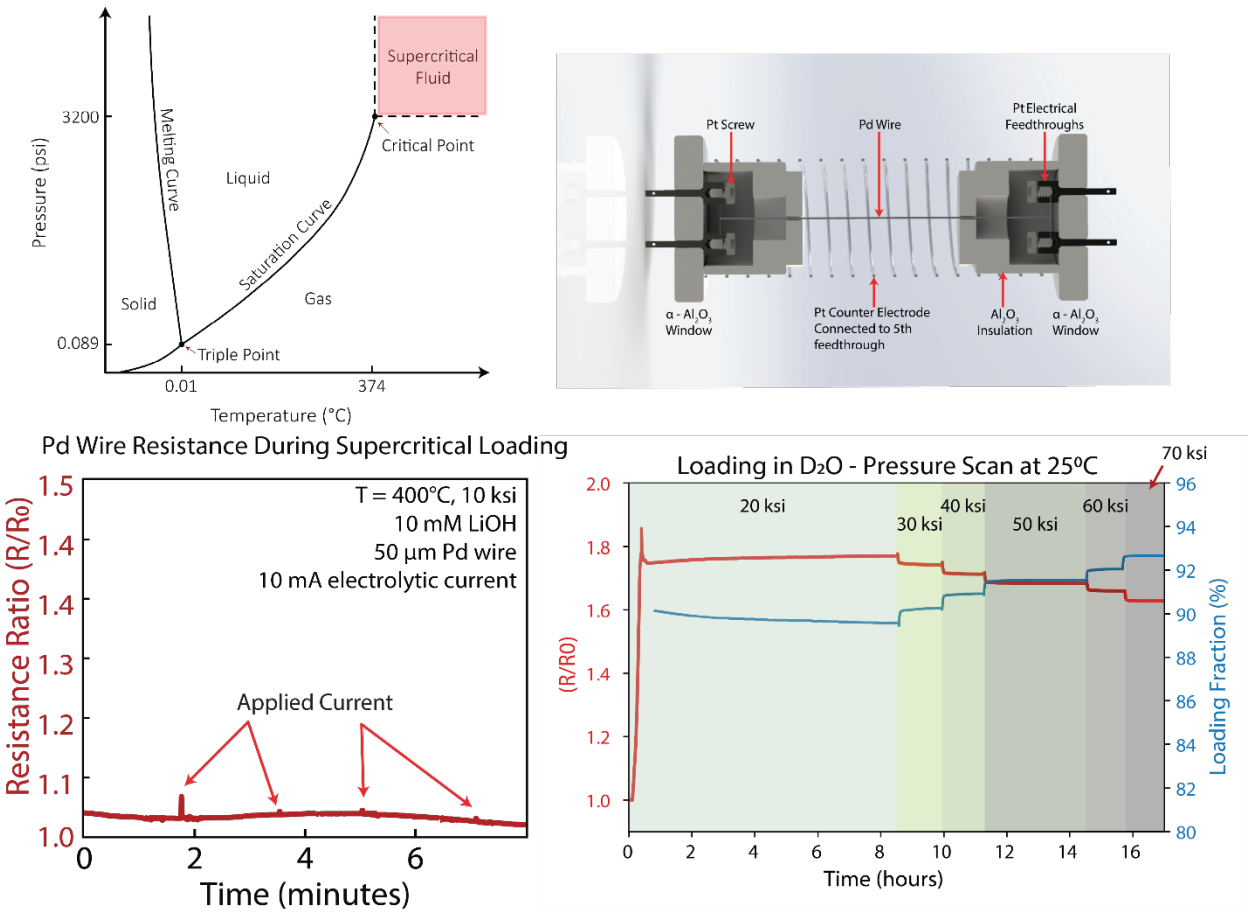

Figure 2: To operate in the supercritical regime with water-based electrolytes, temperatures >374°C and pressures >3200 psi are held in a corrosion-resistant pressure vessel. Using 4-wire resistivity measurements, we could not detect stable resistance changes that would suggest we were loading Pd. In contrast, when electrochemically loading Pd at increasing pressures, higher and higher Pd loadings are observed. These loading levels are higher than gas loadings at equivalent pressures.

Experiments were conducted in various settings, including high pressure vessels with water/electrolyte mixtures and intensifiers for generating pressure, similar to ones described in the Hardware section. These setups allowed for the exploration of ultra-high pressures and temperatures and their effects on electrochemical loading. To work in these high temperature, high pressure, corrosive environments, we had to make a few key hardware improvements, including creating high pressure seals compatible with high temperatures, preventing oxidation, and most importantly, corrosion mitigation. We found that supercritical water, especially when combined with electrolytes, became an extremely corrosive environment that required a lot of engineering to keep in control.

Figure 1 shows the high pressure, corrosion resistant vessel that was designed to operate in supercritical water conditions. Inconel 718 was the primary material used for the vessel body because of its high temperature stability and corrosion resistance, and all parts were coated with 50 nm Cr and 1000 nm of Pt to further reduce corrosion. Seals and electrical and optical access

were custom designed to meet these requirements. We brazed Pt electrical feedthroughs into single crystal sapphire windows with Au to maintain both optical and electrical access into the vessels. The use of Au, Pt and sapphire was critical to mitigate corrosion and survive the high temperature environment. Post-experiment analysis showed no significant contaminants on Pd sample surfaces.

The high-pressure vessel was filled with a water/electrolyte mixture in a N_2 glovebox (to remove the presence of oxygen) and sealed shut. The vessel is heated up to 450°C and the water level is monitored with a camera on the optical window. Sample images are shown in Figure 1, where the water line is clearly visible at temperatures <374°C and disappears as the temperature is increased above this point. Once temperature is dropped below the critical point, the water reliquefies, and the water line is optically visible.

In these environments, we tested 50-250 μm diameter Pd wires, spot welded to 4 Pt wires for resistivity measurements and in between a Pt counter electrode. Current densities ~ -50 - 150 mA/cm^2 between the Pd and Pt electrodes were applied, and we found that we could not observe stable resistance changes when loading in supercritical water. 0.1M H_2SO_4 and 0.1M LiOH/LiOD electrolytes were tested with identical results (several dozen tests done with varying concentrations and electrolytes, but these were the best candidates). A plot of an example measurement, wherein we measure the resistance of a palladium wire as we apply an electrochemical bias, is shown in Figure 2. We found that while we may observe small transients in the resistance of the Pd wire, possibly indicating small amounts of loading, they weren't stable and were within the noise of temperature fluctuations of a few degrees.

We confirmed that this was not an artifact of being in a supercritical environment, and we observed the same behavior in the liquid phase at high temperatures, between 250 to 350°C, confirming that this was a challenge with electrochemical loading at high temperatures. This left us to ask the question, at what temperatures can we sustain high loadings. Our hope was to find that with the assistance of pressure, we can overcome some of the difficulty in maintaining high electrolytic loadings at elevated temperatures.

HPE in the Liquid Phase

HPE : Up to 110 ksi with water electrolytes

This section is focused on understanding the effect pressure has on electrolytic loading at room temperature conditions. When performing these experiments, we quickly found that while we had significant experience with high-pressure gas systems, corrosion from electrolytes presented some new challenges. Primarily, corrosion from electrolytes would damage our pressure generating hardware. After a few uses, valves are rendered useless due to corrosion from electrolytes, and our high-pressure seals would wear out at a significantly faster rate. In addition, the hydrogen

generated from high-pressure electrolysis made hydrogen embrittlement a key limitation in material choice. Figure 3 is an image of an Inconel 718 high-pressure tube that ruptured due to hydrogen embrittlement. While we took advantage of copper superalloys (e.g., Toughmet

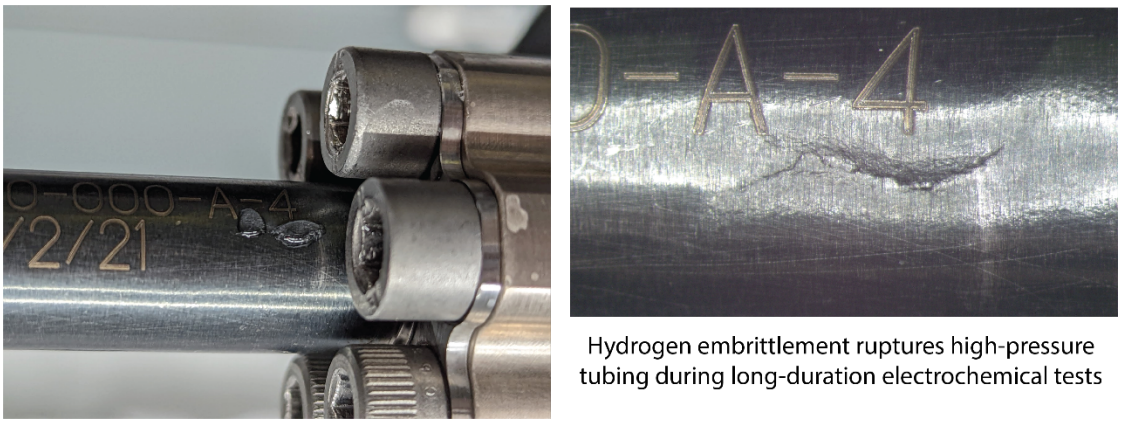

Figure 3: Inconel 718 is the material of choice for high pressure vessels and tubing to withstand corrosive liquids, but the hydrogen generated from long-duration electrochemical loading leads to hydrogen embrittlement.

TS160U) in our gas-based hardware to avoid hydrogen embrittlement, in electrolytic usage copper contamination would build up on Pd surfaces and inhibit Pd loading. We explored a variety of coatings and found that sputtered Pt helped mitigate corrosion, but no coating was robust enough to withstand these conditions for more than 2-3 tests.

To limit the effects of corrosion, we developed a 1-to-1 ratio fluid separator capable of translating pressure from our existing pressure-generating equipment without exposing our valves and intensifiers to corrosive electrolytes (Figure 4). Using spring-energized seals, a fluid separator piston is housed in a smooth (Ra < 4 μ–inch), Pt-coated Inconel 718 bore. As one side is pressurized, the spring-energized seals translate the piston, compressing the electrolyte volume and translating the pressure between the inert and electrolyte fluids without any exchange of liquid. This significantly decreases the surface area exposed to corrosive electrolytes, leading to cleaner electrochemical systems, and further abstracting away the difficulty with working with corrosive fluids. The fluid separator assisted in focusing our corrosion mitigation measures to just the high-pressure vessel and not any of the pressure generation hardware. Sputter coating a 1 μm thick Pt layer inside the high-pressure vessel proved to be sufficient to limit corrosion in HPE tests and resulted in clean working electrode surfaces following electrochemical loading, even after week-long experiments. There are no signs of Cu, Fe, or Zn which are usually common contaminants on electrolytically loaded samples, as seen in Figure 5.

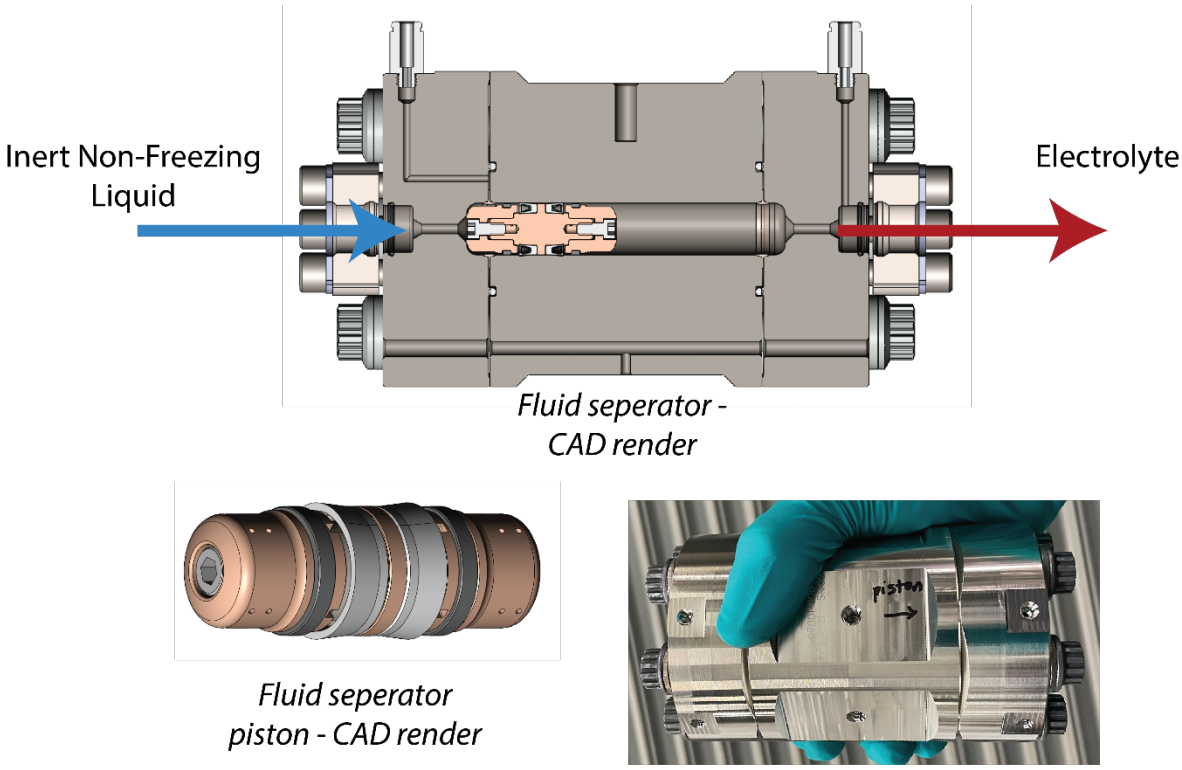

Figure 4: An ultra-high pressure fluid separator was designed to protect ultra-high pressure generation equipment from corrosive electrolytes, minimizing the amount of hardware that needed to meet strict corrosion-resistance requirements. A fluid separator piston is housed in a smooth (Ra < 4), Pt-coated Inconel 718 bore. As one side is pressurized, the spring-energized seals translate the piston, compressing the electrolyte volume and translating the pressure between the inert and electrolyte fluids without any exchange of liquid.

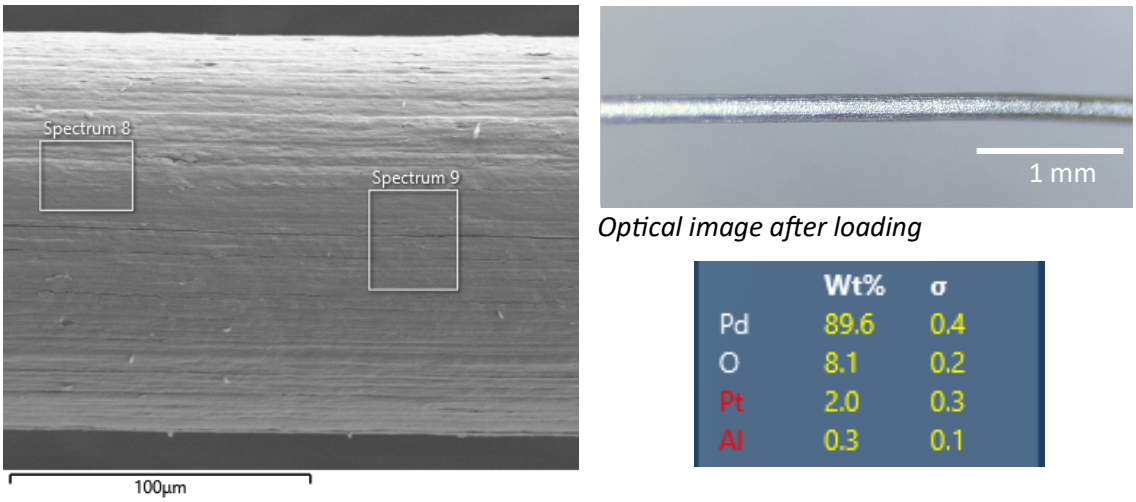

Figure 5: SEM/EDS analysis of 125 µm Pd wire loaded in high-pressure e-chem apparatus for over a week.

With the hardware improvements we made, we were able to test electrolytic loading at pressures

up to 110 ksi. Testing was done on bulk Pd wires and foils with no additives and 0.1 – 0.5M LiOD in D_2O electrolytes. Inside the pressure vessel, the resistance of Pd is measured through 4-wire resistance measurements as the proxy for loading, and a thin Platinum wire coiled around the Palladium cathode provides a measurement of the average temperature of the electrolyte near the Palladium cathode. External to the vessel, the temperature of all the key components is monitored up and downstream of the test vessel. In Figure 6 is a sample experimental HPE data stream from a light water test. We find that as we apply the electrochemical potential, as seen in the 2nd and 3rd plots, Pd begins to load as seen in the first subplot. After about an hour, Pd reaches a loading of 98-99%, and this loading remains extremely stable during the duration of the test. On the bottom two subplots, the temperature of a few components in the system is shown along with pressure data.

At pressures up to 110 ksi, we found that we could reach loadings of 99% and 97% with light and heavy water, respectively, without the use of loading enhancers. These results are fundamentally new - there are no loading enhancers used, and we reached loadings that are extremely rare in the electrochemical loading field, which previously has been nearly impossible without loading enhancers. If we turn off the electrochemical potential, the Pd sample immediately begins to deload, demonstrating that this is fundamentally different than typical gas phase experiments. Pressure alone is not leading to loading. More notably, these loadings are extremely stable and could be sustained for as long as the experiments are run, largely due to some of the work to control for contamination in the test systems, such as platinum coating all wetted materials past the fluid separator.

As a reference point, the loadings achieved at 110 ksi with HPE loading were equivalent to what is measured with 200 ksi of gas pressure loading. We propose two primary explanations for why an increase in electrolytic loading of bare Pd with increasing pressures is observed. The first is the reduction of bubbles with pressure. In normal electrolysis, bubbles are present at the electrode surfaces and are known to act as local deloading sites and create large concentration gradients. With high pressures, bubble size is significantly reduced, and the solubility of gas is increased, which further mitigates bubble formation. In addition, the local availability of hydrogen/deuterium at the Pd surface determines electrolytic loading. It's possible that the increased partial pressure of dissolved H_2/D_2 in the electrolyte has an additive effect on loading, or affects the relative reaction rates of Volmer-Tafel/Volmer-Heyrovsky processes.

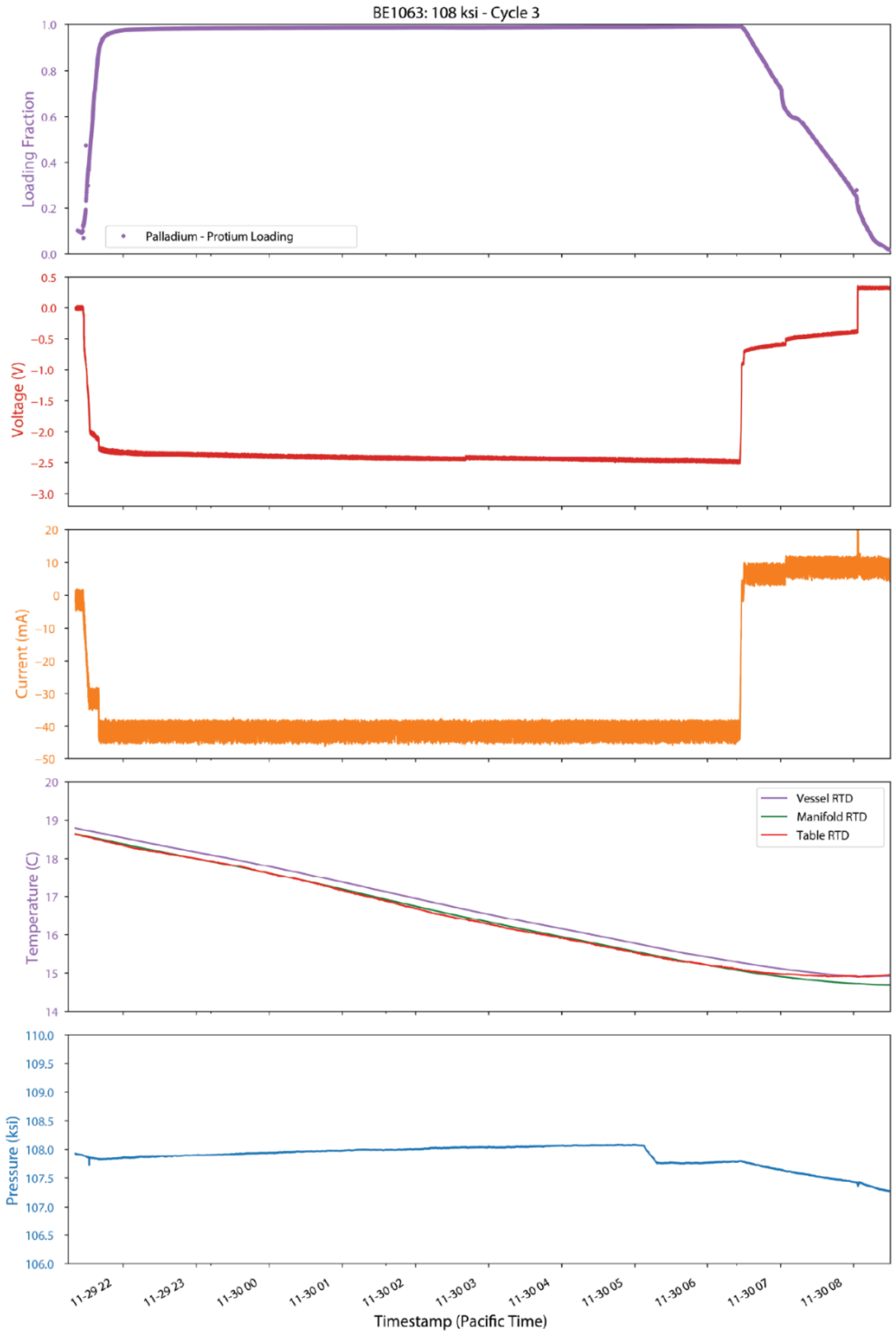

Figure 6 Data from a representative H/Pd electrochemical loading test. Loading is measured through 4-wire resistivity, and the electrochemical voltage and current are shown in the second and third subplots. Temperature is recorded in various points across the high-pressure electrochemical setup, along with pressure (fourth and fifth subplots). This is a sample loading cycle of a 250 µm Pd wire at >100 ksi. At high pressures, high loadings are sustained nearly indefinitely (days) with no measurable fluctuations.

HPE : Above 110 ksi with alternative electrolytes:

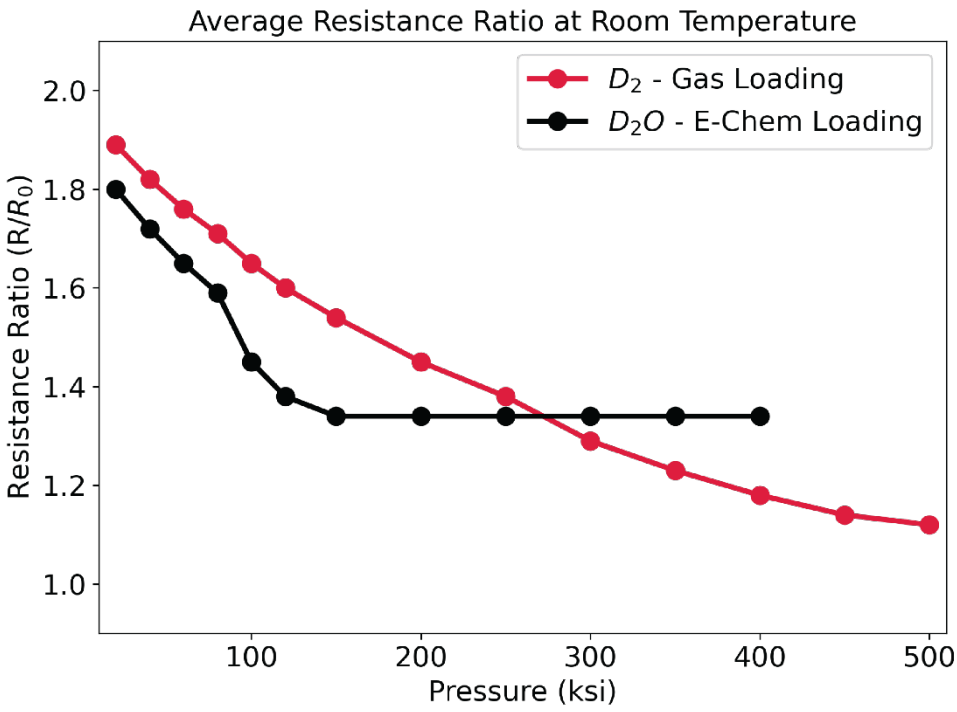

Figure 7 High pressure electrochemical loading summary. The average resistance ratio of all of our experiments in gas and HPE setups is plotted as a function of the maximum pressure tested. Resistance ratio is the primary metric used to estimate Pd loading fraction in these experiments.

As we pushed to higher pressures, we began to run into the high pressure freezing of water-based electrolytes at around 110 ksi. Water-based electrolytes undergo solidification/clathrate formation above 110 ksi at room temperature. Essentially, once we passed the freezing point of the water-based electrolyte, the loading would become extremely unstable, likely due to changes in the electrical properties of electrolytes during freezing. This effect takes attempting to push the pressure knob further with solid electrolytes alone off-the-table, and we needed to figure out a way to remain liquid. Pressure-induced freezing limits how much we can continue to push pressure using water-based electrolytes at room temperature. Initially, we tested increasing the temperature of LiOD in D_2O electrolytes up to 120°C to test if this would bypass any phase changes from occurring, but found that high-pressure solidification still occurred at temperatures up to these temperatures. This meant that temperature alone wasn't going to get us around high-pressure solidification.

Dilute methanol in water has been reported in literature to bypass freezing up to 300 ksi, and we were able to empirically confirm that this was viable up to 220 ksi. Past 220 ksi, 5-20% deuterated methanol (CD_3OD) in LiOD/D_2O electrolytes also solidified, likely due to phase separation of the water from the methanol and so acidic electrolytes had to be used. We tested with acidic electrolytes which are typically used for cryogenic loading, primarily, 1M deuterated hydrochloric acid (DCl) in deuterated methanol (CD_3OD) and 10% deuterated sulfuric acid (D_2SO_4, 96-98 wt. % in D_2O) in deuterated ethanol (CD_3CD_2OD). We found that these electrolytes were stable up to the maximum pressures we tested with HPE, 400 ksi.

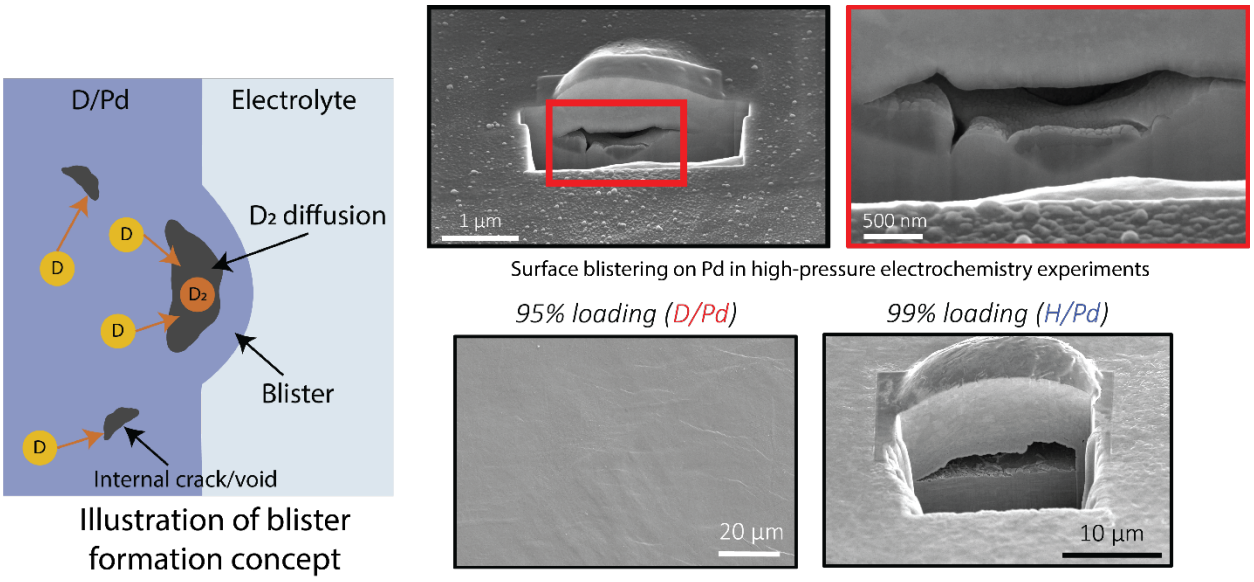

Figure 8 Blistering is observed on electrochemically loaded targets only when loadings >97% are reached. While their origin is unknown, blisters 1-30 µm in size are observed in both D/Pd and H/Pd, and no isotopic contrast is observed. We believe that the highly non-equilibrium nature of electrochemically loaded Pd is what leads to these significant blisters.

Figure 7 is a meta-summary of all HPE loading experiments in heavy water, compared to gas loading with D_2. Here, the measured resistance ratio as a function of the pressure is directly compared between gas and electrochemical loading experiments at identical pressures. We have not been able to find that HPE loaded bulk samples can get above 98% D/Pd loading with increasing pressures. Simply testing electrolytes that don't immediately solidify at 400 ksi didn't yield higher loadings than what was observed at 110-150 ksi. We believe that pressure-assisted electrochemical loading reaches a point of diminishing returns near 98% D/Pd loading. HPE can be very beneficial when pressure capabilities are limited, but at high enough pressures, there is little to no benefit to loading with HPE than with gas. For D/Pd, this cross-over happens at ~275 ksi.

HPE : Surface blistering in highly loaded HPE samples

One of the interesting features we consistently observed with HPE loaded samples is blister formation, particularly in experiments where Pd reached loadings above 97%. Post-experiment characterization of the palladium surfaces from our near-stoichiometric loading experiments revealed that the Pd surface would form microscopic blisters throughout the sample. These blisters vary in size, between 300 nm to 10 µm. Figure 8 is a SEM image of palladium foils tested in HPE. A slice of these blisters can be taken using focused-ion beam milling, where a thin protective platinum film is locally deposited on the area of interest, and local milling cuts the area in the middle of one of these blisters. On the top two images, we can see that these blisters are several hundred nanometers deep into the bulk, sometimes up to a micron, and we can confirm that there's a cavity behind where the blister is on the surface.

As a reference point, on the bottom right is an image of a palladium surface from a light water test that reached near-unity loadings and formed blisters, in comparison to an experiment that only reached 95% loadings. Through extensive cross-sectioning, we can isolate that these features are in close-proximity to some form of lattice distortion, many times from an impurity. There was a large amount of stochasticity in the presence of blistering and the density and size of these blistered surfaces, particularly with palladium hydride. We performed focused tests with our ultra-sensitive calorimeters to search for any meaningful evidence of heat production. Those results are discussed in more detail in the Calorimetry section. In short, no evidence of heat production was found for experiments that formed blistered Pd surfaces in comparison to those that didn't.

Table 1 is a summary of the experiments we ran with samples of different morphologies across both isotopes. In short, we observe blister formation in bulk-Pd of varying thicknesses and surface treatments, both polished and roughened. There are several reports in literature of blisters forming in metals from hydrogen and deuterium gas. These blisters are typically found in metals such as Be, Cu, Al when they're exposed to large fluxes of H_2 or D_2 plasma. It's proposed that these blisters form when protons or deuterons are introduced into the metal, in that case by irradiation with hydrogen or deuterium plasma, and segregate into defect sites where they recombine and form a blister, instead of diffusing to the surface. While HPE conditions are different than these reports, they both share similarities in that the Pd lattice is in a highly non-equilibrium state.

Table 1 Summary of completed HPE experiments at > 150 ksi.

Sample Type	Isotope	Number of Experiments	Peak Loading %	Blistering?
Wire	D_2O	1	98	1/1
Wire	H_2O	2	98/99	0/2
Polished Foil	D_2O	19	97/98	17/19
Polished Foil	H_2O	10	99	0/10
Roughened Foil	D_2O	1	98	1/1
Roughened Foil	H_2O	5	99	4/5
Single Crystal Slug	D_2O	2	R/R_0 is not reliable	0/2

HPE Loaded Thin Films

So far, we've discussed work done on bulk Pd. However, most of our AHE-diagnostics in Callisto are reliant on thin-film Pd to achieve the highest levels of sensitivity. While the resistivity of H/Pd and D/Pd as a function of loading is well-understood in bulk, thin-film measurements have never been done in literature to the best of our knowledge. In gas loading, we found that thin-film resistivity matched up with bulk Pd very well. Figure 9 plots the resistivity of thin films in gas as a function of pressure in comparison to bulk. While the exact magnitudes of resistivity are offset, they both follow the same trend, and a clear point of diminishing returns with increasing pressures is observed. We attribute minor variations in resistivity to the changes in geometry, as well as the role that constrained films might have, but overall, the trends are the same between bulk and thin films.

However, in HPE loaded thin films, we found that thin films of varying thicknesses become significantly more conductive as they load, reaching resistivity values well below their initial starting point. Additionally, the low resistivity values are reached at relatively moderate pressures as low as 70 ksi. To the right of Figure 9 is an example HPE experiment with a 20 nm Pd thin film, where pressure is increased from 70 ksi to 220 ksi and the resistivity is relatively unaffected. While this suggests that additional pressure has little effect on the loading of thin-films, it's unclear what loading the Pd thin-film is at. It's also worth noting that at ambient pressures, this does not happen. Resistivity stays above its starting value throughout the loading cycle. Table 2 is a summary of the lowest resistivity values of thin-films and at what pressures those are reached, where it's clear that increasing pressures don't enhance loading for HPE loaded thin films past 50 ksi. Regardless of what loading thin films are at, we don't observe any evidence of damage to the thin films that would suggest any relevance for LENR.

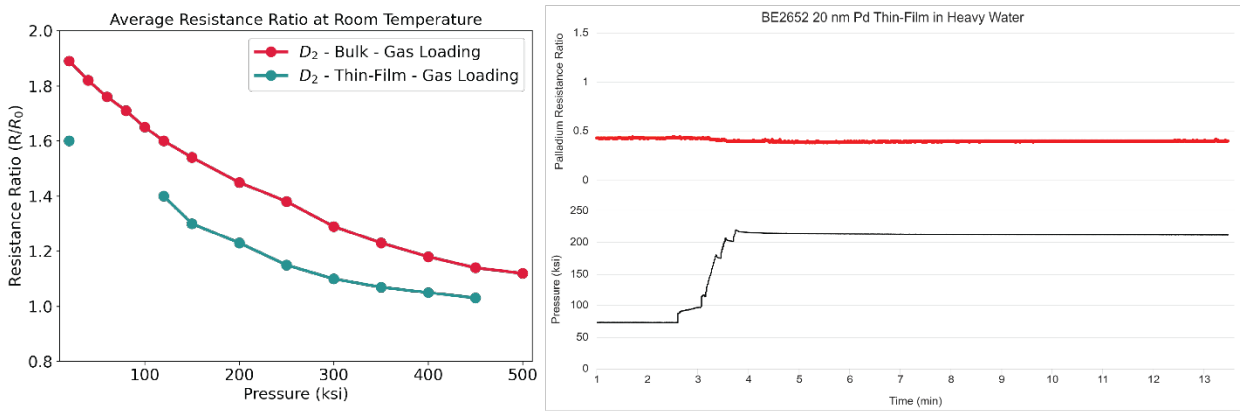

Figure 9 The resistivity of Pd thin films between 20-200 nm thick were measured with both gas and electrochemical loading as a function of pressure. Gas-loaded thin-films exhibited resistivities different in magnitude than gas-loaded bulk Pd, but the trends were consistent. HPE loaded thin films, however, displayed resistivity values significantly lower than bulk Pd. In addition, HPE loaded thin-films showed no signs of continued decreases in resistance past 80 ksi, while gas-loaded thin-films continue to show decreasing resistance at pressures up to 400 ksi.

Table 2 The range of resistivity ratios of thin films between 20-200 nm thickness are shown below under various testing conditions.

Resistivity Ratios of Thin-Films			
	Isotope	Min R/R_0	Pressures tested
Gas	H_2	0.88	400 ksi
HPE	H_2O	0.4	50-220 ksi
Gas	D_2	1.03	450 ksi
HPE	D_2O	0.4	50-400ksi

Conclusion

As far as we know, we're the only ones that have ever done electrochemistry at 10-20 kbar pressures, even outside of the context of loading Palladium. The occurrence of high energy events (discussed in more detail in the Calorimetry section) is sporadic, and we believe them to be chemical in origin, but we don't know mechanistically how they emerge. However, these are electrochemical phenomena and do not suggest any relevance for LENR. The potential symbiotic relationship between electrolytic and pressure loading warrants deeper exploration. Understanding this relationship could lead to more effective methods for achieving high loadings at elevated temperatures. It's unclear if there remains any benefit to performing bulk high pressure electrochemical loading if there is already access to pressures high enough to reach stoichiometry with gas, but electrochemistry may be its own form of stimulation. With electrochemically loaded thin films, we find that they become significantly more conductive than they began. This has never been reported on before and is potentially interesting, but we do not have reason to believe that this behavior is relevant for LENR.