

Loading

Concept

Callisto has focused on using pressure (generally via D_2 gas) as the tool to achieve very high loadings of deuterium into palladium metal. This, of course, is not the D_2O electrolysis method used by most LENR researchers. Gas loading offers one extraordinary attraction; at a given pressure and temperature, the loading is governed by thermodynamic equilibrium. This makes loading stable, reliable, and reproducible. Experiments at the same pressure and temperature will reach the same loading, every time, and for every researcher. Furthermore, the loading will stay at this equilibrium value, for as long as the pressure and temperature are maintained.

There is, however, one problem with gas loading; reaching high loadings requires extremely large pressures. For example, in order to reach a loading of 90% (often considered the threshold level for LENR), one needs a D_2 pressure of 70 ksi (70,000 psi), and then increasing this to 95% requires almost twice as high a pressure (135 ksi). These pressures are far beyond those commonly available to LENR researchers; while diamond anvil cells are indeed capable of pressures dwarfing these, the price is that their experimental volumes are only fractions of a millimeter in extent.

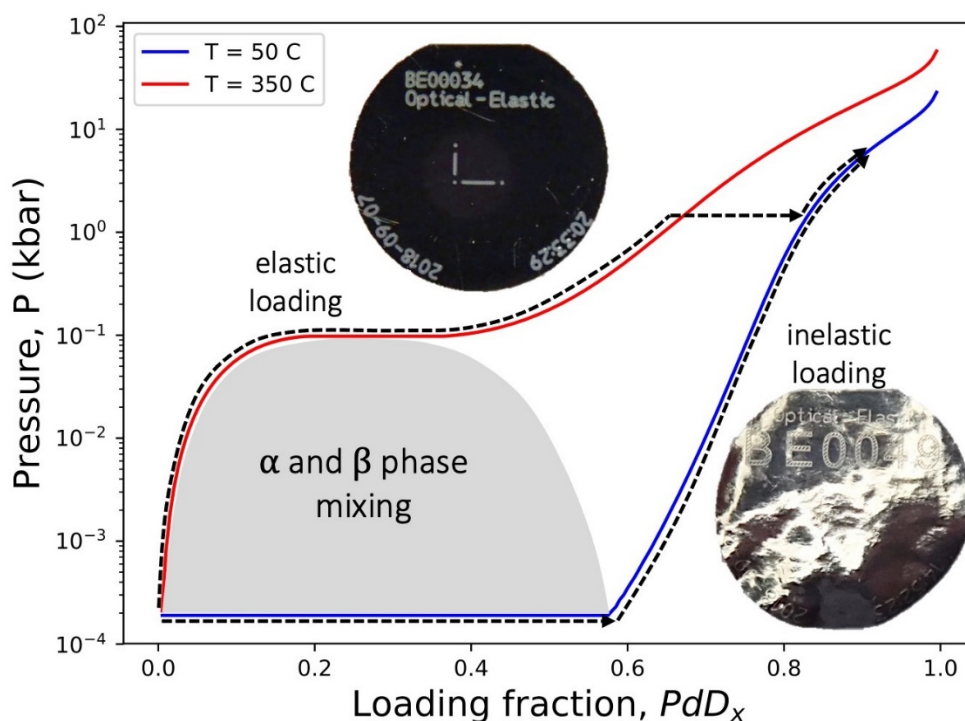
For Callisto to successfully operate gas loaded LENR experiments at loadings above 95%, we had to solve two practical problems. One was to develop the pressure equipment allowing us to field large (centimeter sized) LENR experiments at pressures of 150,000 psi and above. The other challenge was learning how to handle PdD under these conditions; having it survive the internal loading stresses and being able to accurately measure loadings as values approach 100%.

As protons/deuterons load into a metal lattice, material properties change (mechanical, optical, etc.). Furthermore, high fractional loadings (e.g., >90%) are theorized to be necessary for AHE. Hence, carefully characterizing a sample's loading level is essential to investigate AHE. A key challenge is that most loading measurements are proxies for loading i.e., they are indirect measurements that require calibration. However, gas loading has an advantage: since the loading is in thermodynamic equilibrium, it can be calibrated as a function of pressure and temperature. Hence, once we measure the equilibrium loading values with a true mass loading technique, we can calibrate indirect loading measurement techniques, which are more straightforward and enable in-situ, real-time measurements. We developed two true mass loading techniques: the UltraSorb (a form of a Sieverts apparatus) and the MicroSorb (a mass measurement using a microbalance). We leveraged three in-situ, indirect loading measurements: lateral strain, resistance, and reflectance. A nuance to loading (gas or electrolytic) is that the loading protocol matters. Loading deforms the lattice and leads to both nanoscale and macroscopic deformations that obscure loading and AHE diagnostics. Hence, we developed a gas loading protocol that we've termed "elastic loading", which uniformly loads a lattice and mitigates deformations.

Elastic Loading

Metal hydrides swell as they load protons/deuterons. For example, Pd swells up to ~17% volumetrically at full loading. The swelling is often uneven, which distorts the material on both nanoscales and macroscales and convolutes loading and AHE diagnostics. So, our objective is to uniformly load Pd without distortion during swelling. This preserves the surface morphology making it easier to detect AHE damage sites and enables optical loading measurements such as lateral strain and reflectivity. The key insight is to load (and deload) at high temperatures, which we've termed "elastic loading".

At high temperatures, protons/deuterons quickly diffuse through the Pd lattice, ensuring uniform loading throughout the material. At low temperatures, Pd loads more slowly which introduces loading gradients into lattice deforming the material. Pd's lattice constant is 3.89 Å while β -PdH_x and β -PdD_x lattice constants are 4.09 Å and 4.084 Å, respectively⁸. When loading gradients are present, the up to 0.2 Å lattice constant mismatch introduces significant stress into the lattice, which produces deformations. Room-temperature loading passes through the $\alpha - \beta$ phase mixing region, which makes distortions inevitable (**Fig. 1**). We've termed non-uniform loading that passes through the $\alpha - \beta$ phase mixing region "inelastic loading".



⁸ Schirber, J. E.; Morosin, B. "Lattice constants of β - PdH_x and β - PdD_x with x near 1.0." *Phys. Rev. B.* 1975, 12, 117-118.

Fig. 1: Inelastic loading is characterized by non-uniform loading and passage through the $\alpha - \beta$ phase mixing region, which produces nanoscale and macroscopic distortions. As shown, an inelastically loaded Pd foil visibly shows deformations. Elastic loading/deloading follows a high-temperature isotherm which ensures uniform loading and avoids the $\alpha - \beta$ phase mixing region, mitigating nanoscale and macroscopic distortions.

At temperatures above the phase threshold (e.g., 350°C or higher) the free energy no longer has a loading inflection, and so the $\alpha - \beta$ phase transition ceases to exist. The elastic loading protocol exploits this effect, by pre-heating the Pd to 350°C in an inert gas (or at high vacuum) and then slowly ramps the H₂/D₂ pressure up to >1100 psi; loading continues by cooling to room temperature and subsequently increases the pressure to the desired setpoint (e.g., for most AHE experiments, the setpoint was >100 ksi). To deload, the reverse process is followed. As an example, we tracked a Pd sample's surface roughness with a confocal microscope and measured the lateral strain between laser marked fiducials using optical images. We show the lateral strain during the elastic loading process and that the surface roughness remains constant (Fig. 2).

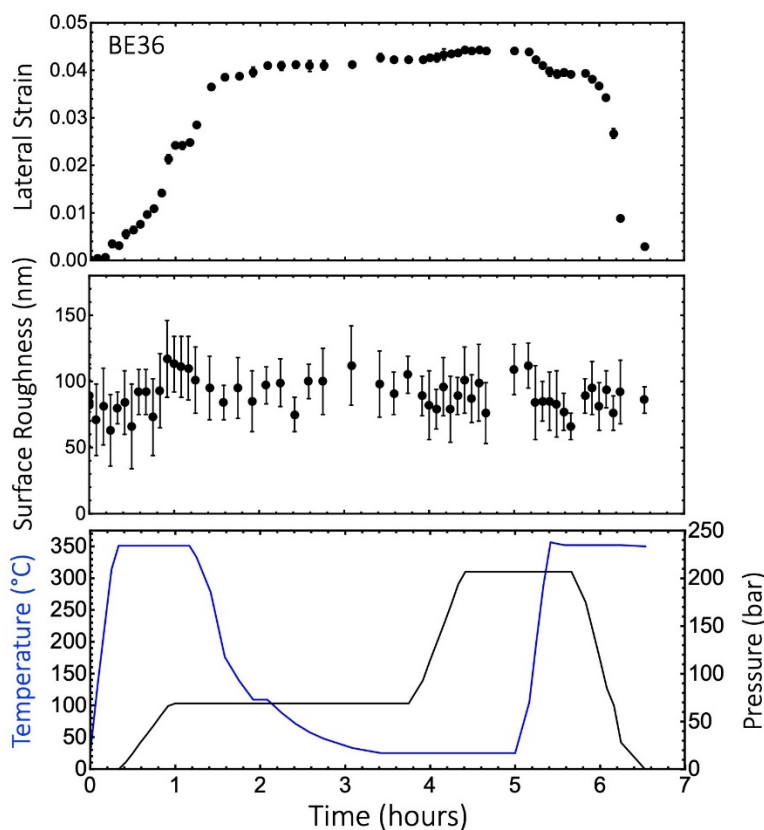


Fig. 2: The elastic loading protocol pre-heats the Pd to 350°C, slowly loads to ~75 bar (~1100 psi), cools to room temperature (~25°C) and then increases pressure the desired setpoint. The deload follows the reverse process. The Pd sample's lateral strain is proportional to the loading and shows the loading and deloading. The surface roughness remains constant during elastic loading and deloading.

While elastic loading mitigates macroscopic deformations, nanoscale distortions may still be present depending on the sample's crystallinity. We developed sample preparation processes (e.g., mechanical polishing, chemical cleaning, ion milling, etc.) that produce pristine Pd surfaces (**Fig. 3**). However, polycrystalline Pd sample surfaces are modified even after elastic loading. Grain boundaries contribute to most of the post-loading surface distortions: intergranular voids and cracks, and grain growth. Terracing is a feature of high loadings (e.g., >90%) and varies with grain orientation (**Fig. 3**). To mitigate grain boundary driven distortions, we moved to Pd single crystals: (100), (110), and (111) orientations. We've shown with XRD (X-Ray Diffraction) that the Pd is in fact single crystal (**Fig. 4**). After elastic loading and deloading, single crystal Pd sample surfaces remain pristine, successfully mitigating distortions driven by grain boundaries (**Fig. 5**).

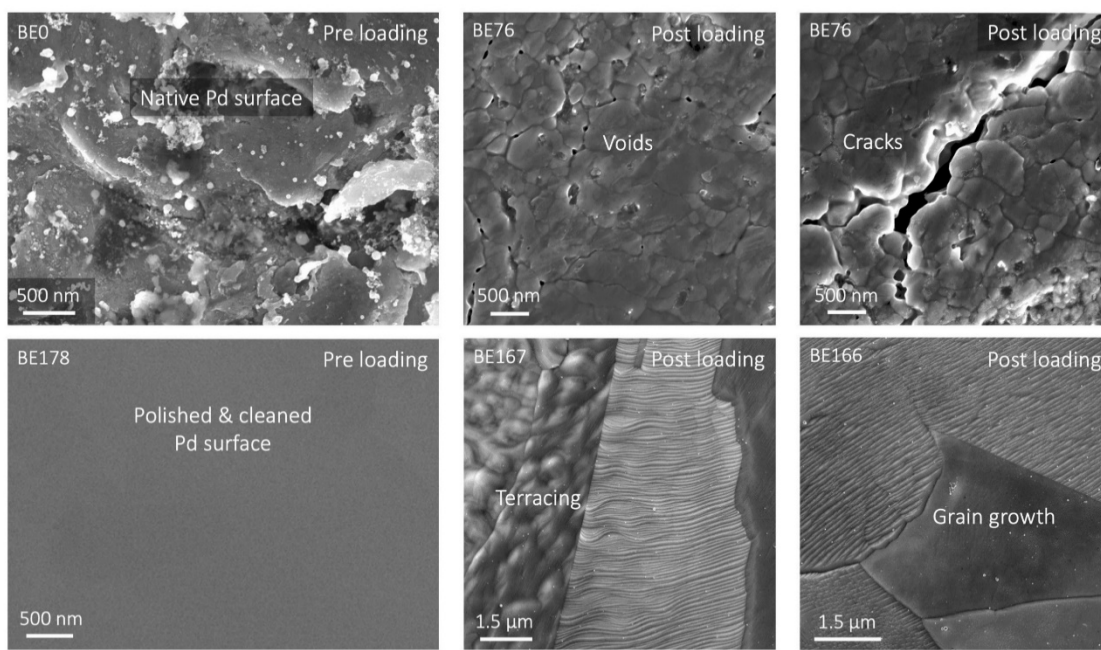


Fig. 3: Native polycrystalline Pd surfaces are rough and full of debris / contamination. After mechanically polishing and chemically cleaning, the Pd surfaces are pristine. Post elastic loading, polycrystalline surfaces are distorted (e.g., intergranular voids and cracks, grain growth, and terracing), primarily due to the presence of grain boundaries.

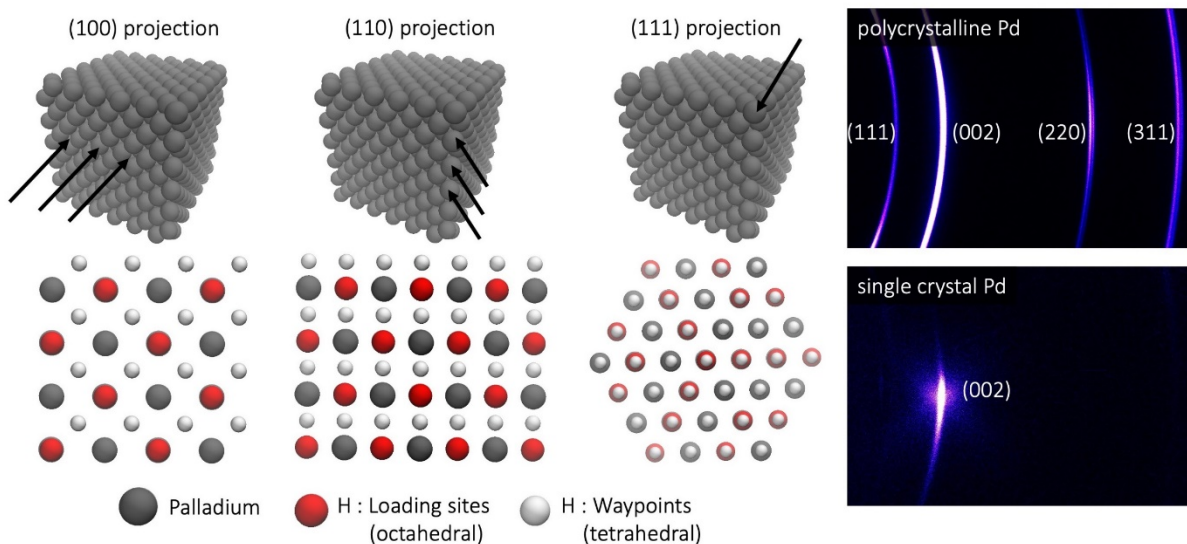


Fig. 4: Pd has an FCC crystal structure, and we show the (100), (110), and (111) orientations in addition to the octahedral and tetrahedral sites. Protons/deuterons load into octahedral sites. We confirm the Pd single crystal orientation using XRD.

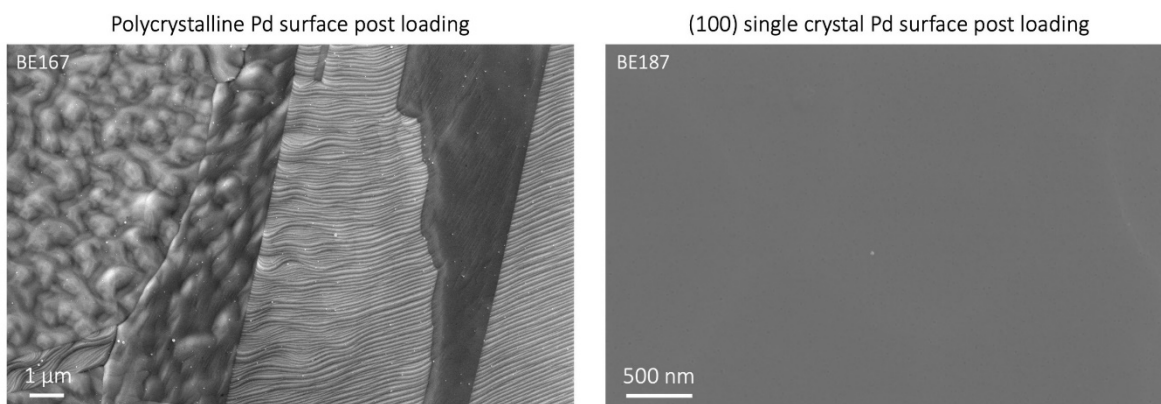


Fig. 5: Single crystal Pd surfaces remain pristine after elastic loading and deloading, successfully mitigating the distortions driven by grain boundaries in polycrystalline Pd.

Measuring Loading

To quantify loading values in metal hydrides, we developed two mass-loading measurement techniques (i.e., a direct measure of loading) and three indirect loading measurement techniques: UltraSorb & MicroSorb (direct measurements), and lateral strain, resistance, and reflectance (indirect measurements). For gas loading, our indirect loading measurements are calibrated as functions of gas pressure and temperature using our direct loading measurements. Once this is done, indirect loading measurements have proven to be very useful, both for convenience, and to monitor changes in loading. However, for determining absolute loading values, they are only as good as the underlying calibrations. So, for instance, indirect measurements based on calibrations

with Pd at room temperature, will not give accurate results for much different temperatures, or for Pd-alloys. In order to measure loading for general temperatures or materials, some form of direct loading measurement is essential.

Measuring Loading : Lateral Strain

A metal hydride swells as it loads protons/deuterons. Moreover, elastic loading of freestanding (i.e., unconstrained) samples ensures the strain is isotropic (i.e., the lateral and vertical strains are equivalent). With sufficient pixel resolution, the lateral strain (and thus loading) can be measured between fiducials on the sample surface using optical images.

Our objective is 1% loading resolution using lateral strain. For Pd, we estimate the volumetric strain Ω at full loading to be $\Omega = 0.17$; literature reports volumetric strains between 0.13-0.19⁹. We assume a linear relationship with loading. This is an approximation: strain is linear w.r.t to loading in α -phase and is linear w.r.t loading with a slightly different scaling in β -phase; however, using a single volumetric strain constant closely approximates the loading and is an accepted approximation in the technical literature. Note: we use a conservative volumetric strain constant (our measurements corroborate those literature which indicate it's closer to $\Omega = 0.16$).

If the sample is free standing (i.e., it's not constrained in any dimension), the strain is isotropic. Given this, we can approximate the loading (Γ) by $\Gamma = 3\varepsilon / \Omega$, where ε is the average measured lateral strain between tracked keypoints. Given our requirement of 1% loading resolution, we must be able to resolve strains of $\varepsilon_{\min} = 0.000567$. By associating our strain resolution $\varepsilon_{\min}$ with our characteristic pixel resolution τ (i.e., $\tau = 1$ for a single pixel), we obtain the minimum required distance $L_{\min}$ between tracked keypoints by using the relation $\tau = L_{\min} \times \varepsilon_{\min}$. So, $L_{\min} = 1765$ pixels at $\tau = 1$ and $\varepsilon_{\min} = 0.000567$.

The required pixel size and field-of-view (FOV) depends on the sample geometry. As an example, a version of our ultra-pressure vessel allowed 4 mm diameter samples. To adequately accommodate the sample strain and tolerances on manufactured parts, the sample diameter was set to 3.65 mm, and the minimum distance between loading fiducials was set to 0.7 mm. This set the required pixel size at 0.4 $\mu\text{m}/\text{pixel}$. To provide an adequate buffer for the strain measurement, we preferred a FOV of at least 1.5 mm x 1.0 mm (**Fig. 6**).

⁹ Peisl, H. "Lattice strains due to hydrogen in metals." *Hydrogen in metals I*. Springer Berlin Heidelberg, 1978. 53-74.

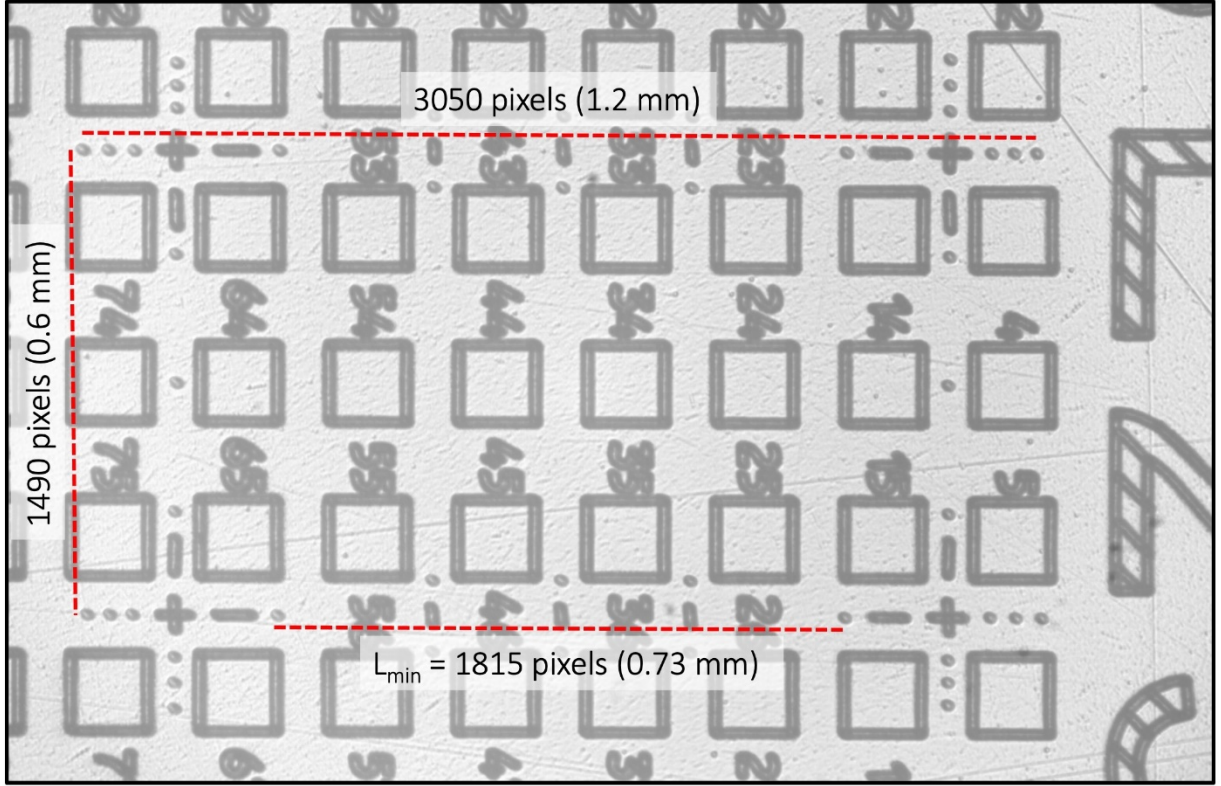


Fig. 6: Example image used for an in-situ strain measurement. The field-of-view is 3840x2484 pixels with 0.4 $\mu\text{m}/\text{pixel}$. The optical path contains three windows between the camera and the sample: camera $\rightarrow$ 0.5mm window $\rightarrow$ 0.5mm window $\rightarrow$ 7.5mm window $\rightarrow$ sample.

To enable lateral strain as a real-time loading diagnostic, we developed a computer vision software package using Python (**Fig. 7**). The measurement requires a source image (i.e., baseline image) of the unloaded Pd at a given pressure and temperature. Typically, the source image is set at 0 psi and the intended experiment temperature (often 25-50°C). At a set frame rate, target images are taken and compared to the source image. The sample surface has fiducials (typically laser-marked or lithographically patterned) that are detected in both the source and target images using the SIFT algorithm¹⁰. We match keypoints using a Brute Force Matcher¹¹ and KNN Matcher. We qualify the matches using a ratio test and RANSAC and filter the qualified matches by a minimum distance requirement (typically 700 pixels) and a minimum keypoints requirement (at least 4 valid matches are required, but we typically track and attempt to match 120 keypoints across each image). With a validated set of matched keypoints between the source and target images, K , we compute the Euclidian distance between each pair of keypoints in the source, $d_{src}(i, j)$, and target, $d_{dst}(i, j)$, images to measure the lateral strain:

¹⁰ https://docs.opencv.org/4.x/d7/d60/classcv_1_1SIFT.html

¹¹ https://docs.opencv.org/4.x/d3/da1/classcv_1_1BFMatcher.html

$$\varepsilon = \frac{1}{N} \sum_{i,j \in K} \frac{d_{dst}(i,j) - d_{src}(i,j)}{d_{src}(i,j)}$$

The in-situ strain tracker is sensitive enough to measure both thermal strain and loading strain (**Fig. 7**).

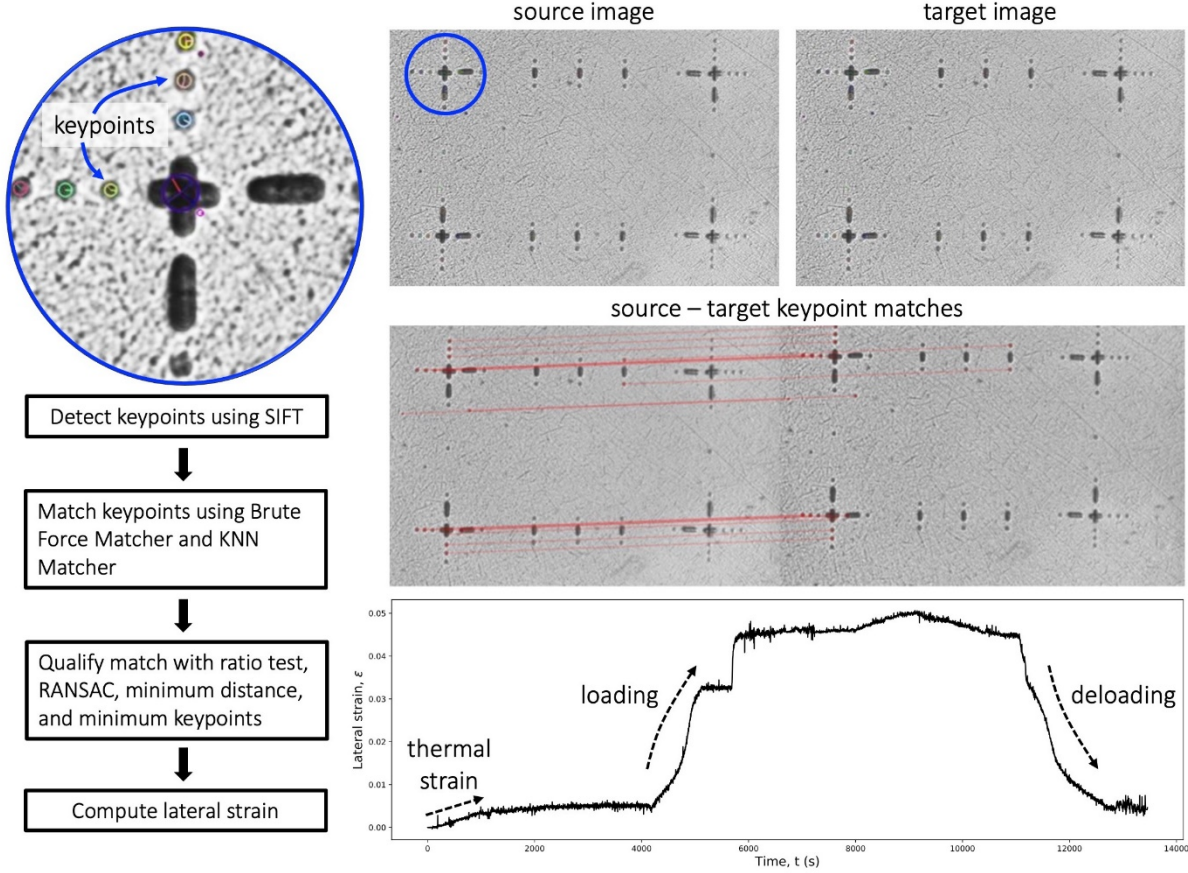


Fig. 7: To measure real-time lateral strain, keypoints are detected and matched between source and target images and strain is subsequently computed between the set of matched keypoints. Both thermal strain and loading strain are measured using this technique. Importantly, this technique relies on elastic loading/deloading to ensure the strain is isotropic.

A caveat to the lateral strain measurements is ensuring the sample surface remains in focus. When the focus drifts, it introduces error into the strain measurement. Both temperature and pressure changes require focus adjustments to avoid drift. As an example, we show a series of discontinuities in strain from focus drifts due to temperature changes (**Fig. 8**). When the focus is consistent between the source and target images, there is no strain error from drift. If the focus begins to drift, it can be re-adjusted, and the measurement will resume accurate strain measurements.

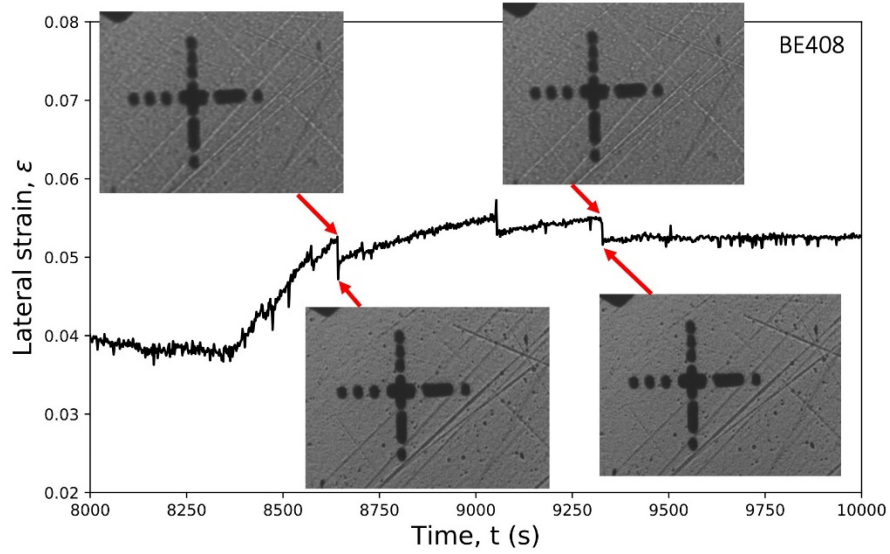


Fig. 8: Drifts in focus introduce error into the lateral strain measurement typically on the order of $\epsilon_{err} = 0.002 - 0.003$. Full loading for Pd produces lateral strains of $\epsilon = 0.057$ (assuming $\Delta V = 0.17$), indicating strain drifts of 0.002-0.003 leads to 3.5-5% loading errors.

We show an example strain measurement of a $\text{Pd}_{0.8}\text{Rh}_{0.2}$ alloy in **Fig. 9**. The lateral strain measures the thermal strain during the pre-heat to 350°C and subsequently measures the loading strain up to 5.7% at 100 ksi, 50°C. At a given pressure and temperature, the strain measurements are repeatable to < 0.0005 strain or $< 1\%$ loading (**Fig. 10**).

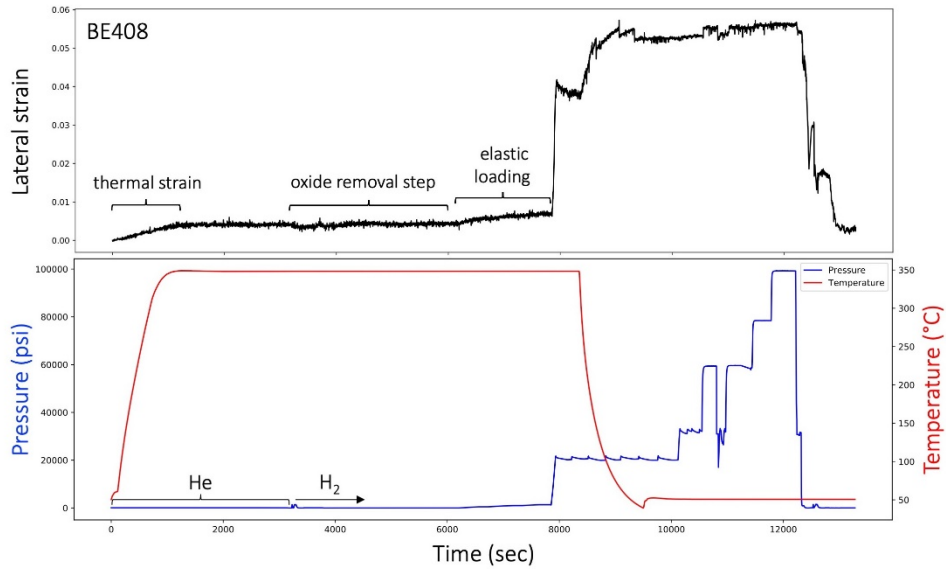


Fig. 9: A typical real-time strain measurement that senses both thermal and loading strains.

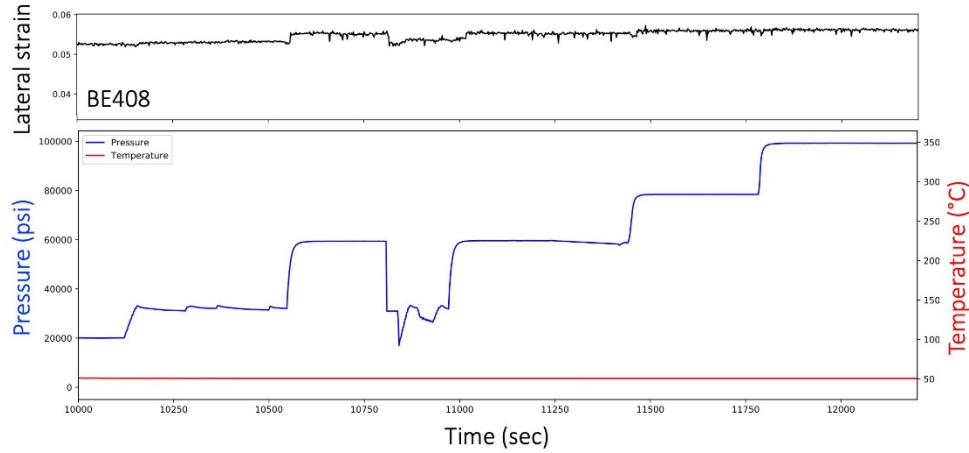


Fig. 10: Lateral strain measurements are repeatable to < 0.0005 strain (or $< 1\%$ loading) at a given pressure and temperature within a given experiment.

The strain measurement is highly reproducible sample-to-sample at a given pressure and temperature. We show several (P,T) points across three different samples in **Table 1**.

Experiment id	Pressure (psi)	Temperature ($^{\circ}\text{C}$)	Lateral strain	Lateral strain std
BE34	3000	25	0.0442	0.000771
BE36	3000	25	0.0441	0.000306
BE50	3000	25	0.0443	0.000693
BE34	3000	350	0.0395	0.00105
BE36	3000	350	0.0393	0.000645
BE50	3000	350	0.0393	0.000533

Table 1: Lateral strain measurements are highly reproducible from sample-to-sample for a given pressure and temperature (i.e., to within 0.0002 strain or 0.35% loading).

Beyond tracking equilibrium loading, the lateral strain measurement is a useful diagnostic for kinetic behavior. For example, we wanted to confirm that cryogenic temperatures kinetically lock-in loading when out of thermodynamic equilibrium. To observe this, we loaded a Pd sample with 150 ksi, -100°C , D_2 gas and subsequently removed the D_2 gas and pulled high vacuum on the sample while remaining at -100°C . We observed no change in lateral strain (i.e., no deloading) for over 16 hours until the sample temperature was raised to 0°C , after which the sample began to deload (**Fig. 11**).

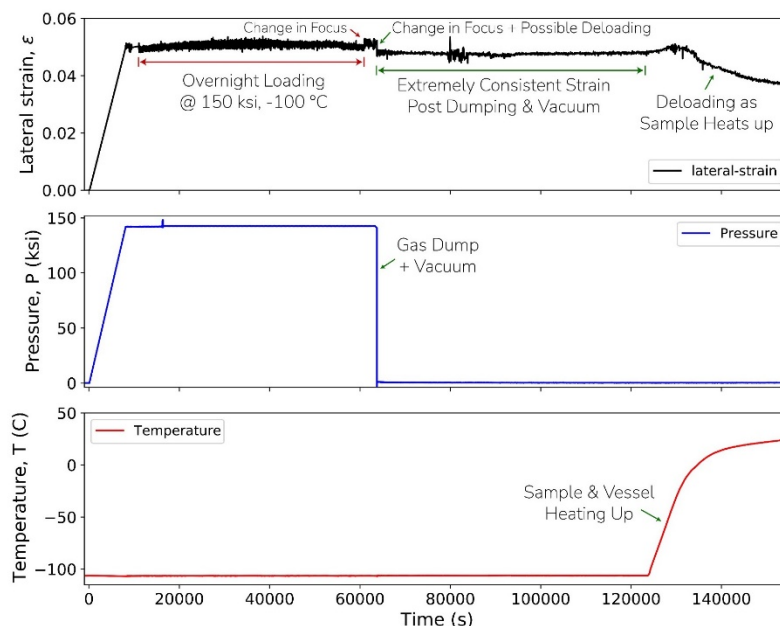


Fig. 11: The lateral strain measurement confirmed that cryogenic temperatures kinetically locks-in loading even when the gas is fully removed.

Measuring Loading : Resistive

The most common loading measurement approach in literature is the resistance ratio. The mapping between resistance ratio and loading is well documented¹² and our measurements generally agree with literature values (**Fig. 12**). However, most of these loading calibrations do not account for the effect pressure has on Pd/H(D). As we approach loadings nearing 1.0 where each 1% increase in loading requires ~100 ksi, the effect of pressure begins to make a difference. We find that the resistance of Pd decreases by ~2% from ambient pressure to 150 ksi, slightly changing our loading calibrations (~0.5% loading). We plot the resistance ratios for PdH_x and PdD_x wires at 25°C in **Fig. 13**. We've mainly used resistance ratio measurements with wire sample geometries.

¹² Zhang, Wu-Shou, Zhao-Fu Zhang, and Zhong-Liang Zhang. "Some problems on the resistance method in the in situ measurement of hydrogen content in palladium electrode." *Journal of Electroanalytical Chemistry* 528.1-2 (2002): 1-17.

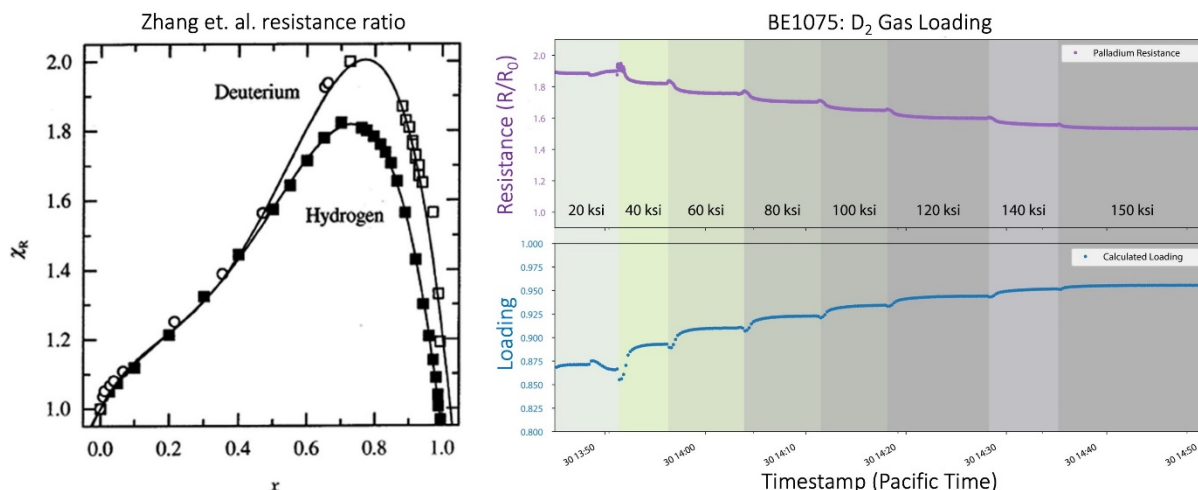


Fig. 12: The most accepted resistance ratio calibration curve from literature (Zhang) and a typical in-situ resistance ratio that we measured in a gas loading experiment with a Pd wire.

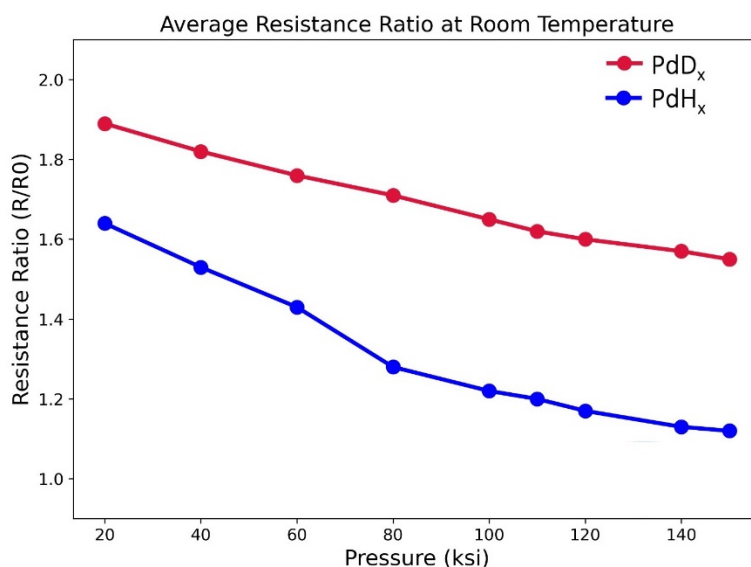


Fig. 13: The resistance ratios for PdH_x and PdD_x wires gas-loaded at 25°C up to 150 ksi.

Measuring Loading : Reflectance

As a Pd sample loads, its reflectance changes. We've found that 532nm wavelength is sensitive to loading: reflectivity changes by 15-20% when Pd loading changes from 0% to ~75% (**Fig. 14**). Importantly, live imaging allows continuous monitoring of non-loading factors that may alter reflectivity data such as beam position, focus, and sample surface. Due to the measurement's sensitivity to beam position, focus, and sample surface, reflectance measurements require thin-film sample geometries. We've attempted measurements in bulk samples, but the results were unreliable.

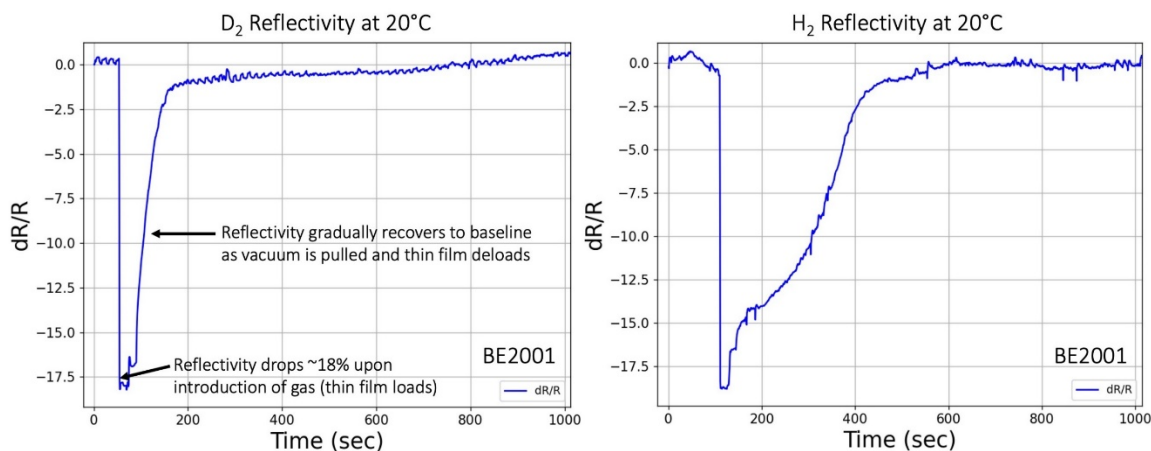


Fig. 14: Typical reflectivity data showing loading and deloading of thin-film Pd for H₂ and D₂ at 20°C. Both gases show loading times on the order of 1s (likely limited by gas flow rate of our apparatus, not intrinsic material properties). D₂ mostly deloads after 100-200s, while H₂ needs ~400s to deload to the same extent.

We've found reflectivity measurements to be a useful diagnostic to characterize deloading rates in thin films, but less useful as an absolute loading measurement. We found that deloading times increase ~1000x from 50°C to -20°C: from ~1 sec to >1000 sec (**Fig. 15**). At -80C, deloading is too slow to resolve at any measurable timescale (reflectivity did not measurably change after ~8 hours). From 20°C to 50°C, H₂ shows slower deloading times than D₂. Below 20°C, the data is less reproducible, but both isotopes show large increases in deloading times as temperature is reduced. Inconsistency could be related to inconsistent vacuum, mechanical shifts, or other factors.

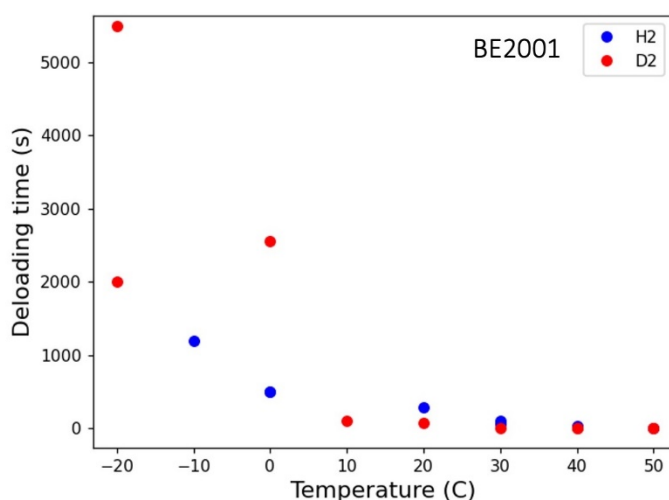


Fig. 15: Comparing D₂ and H₂ deloading kinetics of 20nm Pd thin films.

Beyond characterizing deloading kinetics, reflectivity measurements were a helpful diagnostic when developing purge sequences for our pressure systems. Reflectivity measurements showed that serial-dilution purge cycles at 50psi He were not effective; however, 100psi He cycles

completely deloaded the sample within a reasonable time i.e., we need high enough pressure to force gas through thin BeCu tubes on apparatus (**Fig. 16**). To ensure sufficient headroom, we use 5-7 purges at 1000psi to effectively exchange gas and deload the sample.

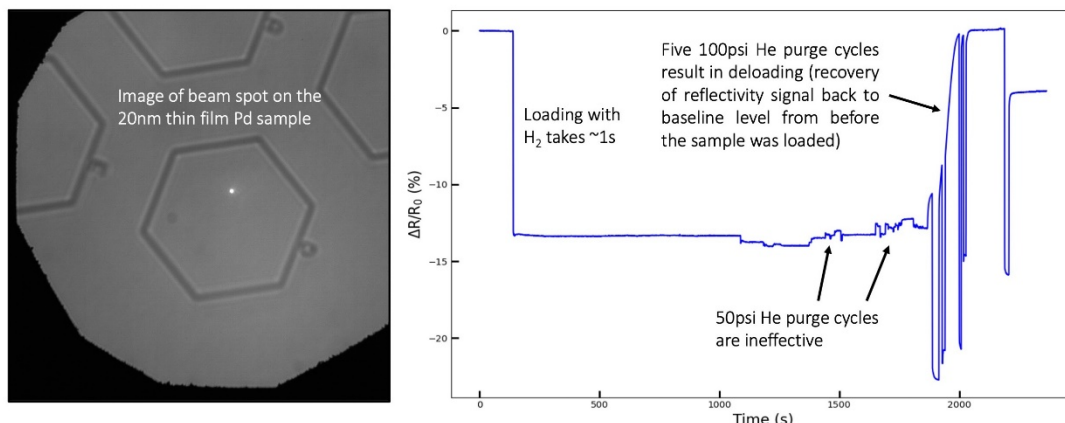


Fig. 16: Reflectivity measurements are used to test purge sequences with Protonpack and Chips panel.

Measuring Loading : Mass (UltraSorb)

To definitively measure mass loadings above 0.85 (i.e., a direct loading measurement with no calibration required), we developed a form of a Sieverts apparatus capable of handling pressures up to 10 kbar called the UltraSorb. The measurement involves a series of inert gas expansions between a pressurization-cell and an expansion-cell. These expansions enable precise volume calibration of the pressurization and expansion cells (**Fig. 17**).

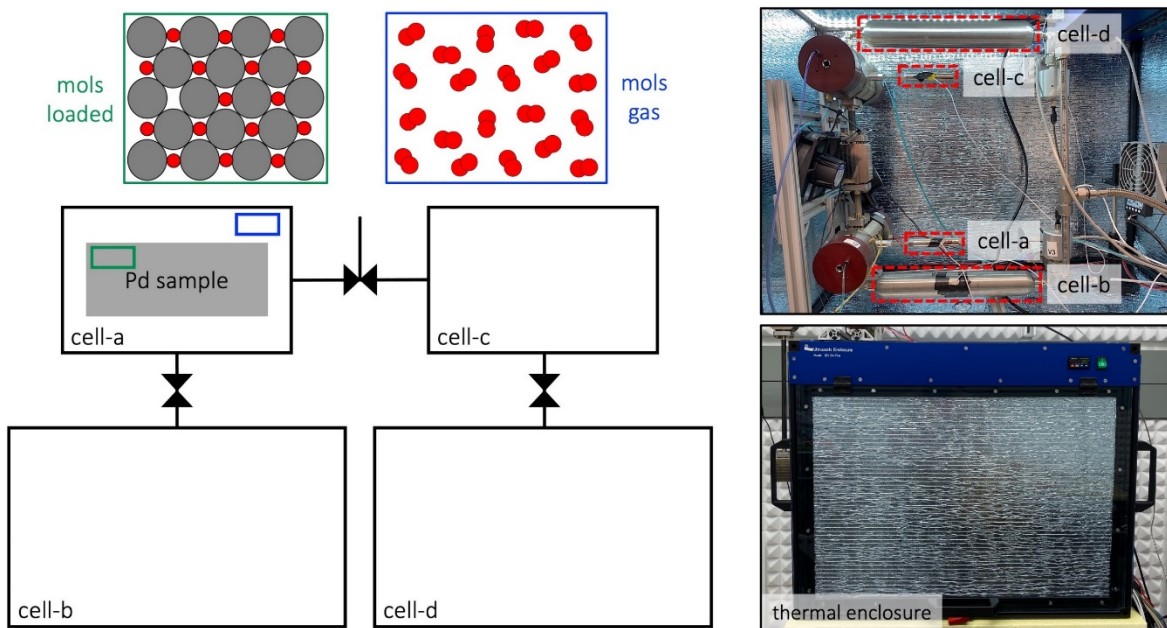
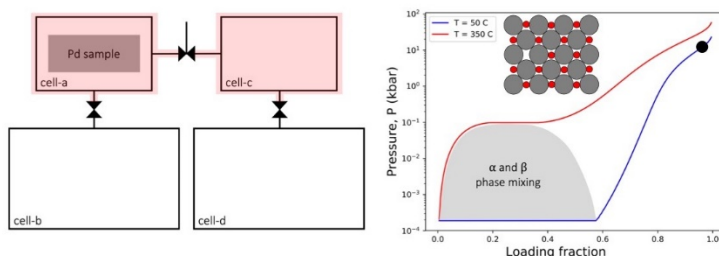


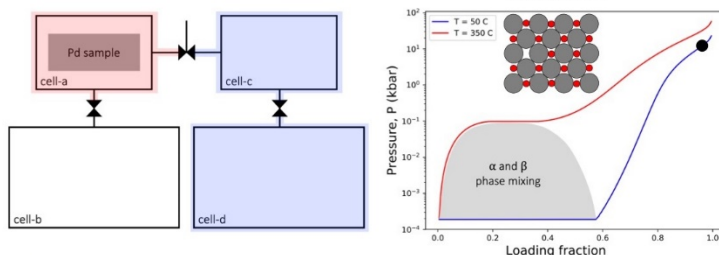
Fig. 17: The UltraSorb apparatus contains a pressurization-cell (cell-a) and an expansion-cell (cell-b) in addition to a gas density calibrator (cell-c & cell-d).

To measure loading at a given hydrogen pressure and temperature, a sample (Pd, Pd-alloy, etc.) is placed in the calibrated pressurization-cell and pressurized with hydrogen. Some hydrogen loads into the sample (mols-loaded) and the remaining hydrogen resides in the free volume around the sample (mols-gas); this sets the initial mols of hydrogen. The key challenge is differentiating the mols-loaded from the mols-gas. The hydrogen is then expanded into the calibrated expansion-cell. We know the expected mols of hydrogen from the free volume in the pressurization-cell, but the expansion-cell also measures excess mols of gas which come from the hydrogen loaded into the sample. Any residual mols of hydrogen in the sample (that did not deload during the initial expansion) can be measured as well by heating the sample and expanding into the calibrated expansion-cell. This overall excess is a direct loading measurement at the pressure and temperature in the pressurization-cell (**Fig. 18**).

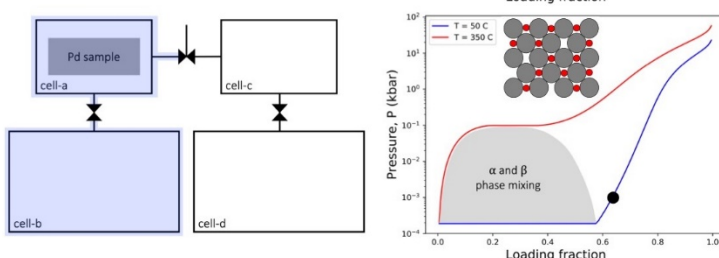
1. Load sample and density-calibrator



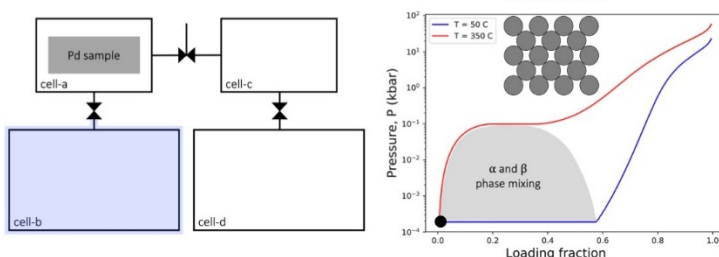
2. Measure gas density



3. Measure excess loading



4. Measure residual loading



high pressure low pressure

Fig. 18: The UltraSorb loading measurement requires calibrated cell volumes. The gas density is measured at the same pressure and temperature as the loaded sample. A high-pressure expansion measures the excess loading above 1 bar and subsequent low-pressure expansions measure the residual loading.

To track the mols of hydrogen in each cell, we must know the cell volume and gas density. Both cell volume and gas density require highly accurate pressure and temperature measurements as well as the gas's equation-of-state (EOS). Hydrogen's EOS is well known at low pressures, but not as well-known at ultra-pressures (e.g., 10 kbar); moreover, pressure transducers can have poor accuracy at ultra-pressures. To bypass the need to accurately measure ultra-pressures, we've designed a density calibrator into our apparatus, which directly measures the gas density at a particular pressure and temperature.

For the hydrogen and deuterium EOS, our codebase used the CoolProp library¹³, which claims to reference the NIST Thermophysical Properties of Fluid Systems database¹⁴. Both CoolProp and NIST reference the Richardson et al. EOS¹⁵ for deuterium. We confirmed the CoolProp library agrees with the NIST database (**Table 2**).

Pressure (psi)	Temperature (°C)	NIST – ρ (g/cm ³)	CoolProp – ρ (g/cm ³)
1000	25	0.010770	0.0107698
10000	25	0.078133	0.0781332
40000	25	0.17010	0.1701044
1000	100	0.0086552	0.0086551
10000	100	0.066204	0.0662041
50000	100	0.17226	0.1722616
1000	200	0.0068675	0.0068674
10000	200	0.055144	0.0551438
60000	200	0.17060	0.1705980

Table 2: The CoolProp library agrees well with the NIST database for the deuterium EOS.

Each loading point at a given pressure and temperature requires five different measurements: (1) expansion-cell volume calibration, (2) pressurization-cell volume calibration, (3) high pressure density calibration, (4) high pressure excess loading, and (5) low pressure residual loading. We define the nomenclature used in the measurements in **Table 3**.

UltraSorb Nomenclature	
V_p	Pressurization-cell volume
$V_{g(p)}$	Free gas volume in the pressurization-cell

¹³ <http://www.coolprop.org/index.html>

¹⁴ <https://webbook.nist.gov/chemistry/fluid/>

¹⁵ Richardson, I.A.; Leachman, J.W.; Lemmon, E.W., "Fundamental Equation of State for Deuterium", J. Phys. Chem. Ref. Data, 2014, 43, 1, 013103.

V_e	Expansion-cell volume
$V_{g(e)}$	Free gas volume in the expansion-cell
V_g	Total free gas volume
V_{cal}	Calibration sample's volume (e.g., Au, Pt, etc.)
ρ_i	Gas density in state- i
V_s	The unloaded sample's volume (e.g., Pd)
e_L	The sample's strain due to loading
e_T	The sample's strain due to thermal expansion
n_g	Mols of gas
M_g	Molar mass of the gas
A	The number of atoms per gas molecule
n_{ex}	Excess mols of gas (molecular) deloaded from the sample in an expansion
$n_{ex(at)}$	Excess mols (atomic) deloaded from the sample in an expansion
$n_{tot(at)}$	Total excess mols (atomic) deloaded from the sample across all expansions
m_s	Unloaded sample mass (e.g., Pd)
M_s	Molar mass of the unloaded sample (e.g., Pd)
n_s	Mols of atoms in the unloaded sample (e.g., Pd)
Γ	The measured loading fraction

Table 3: Nomenclature used in the UltraSorb calculations.

Expansion-cell volume calibration measurement

The expansion-cell volume calibration requires the apparatus to have a small, high-pressure volume (the pressurization-cell) that expands into a much larger, low-pressure expansion volume (the expansion-cell) as well as a high purity noble metal sample (e.g., Au or Pt) that serves as a calibration volume (**Fig. 19**).

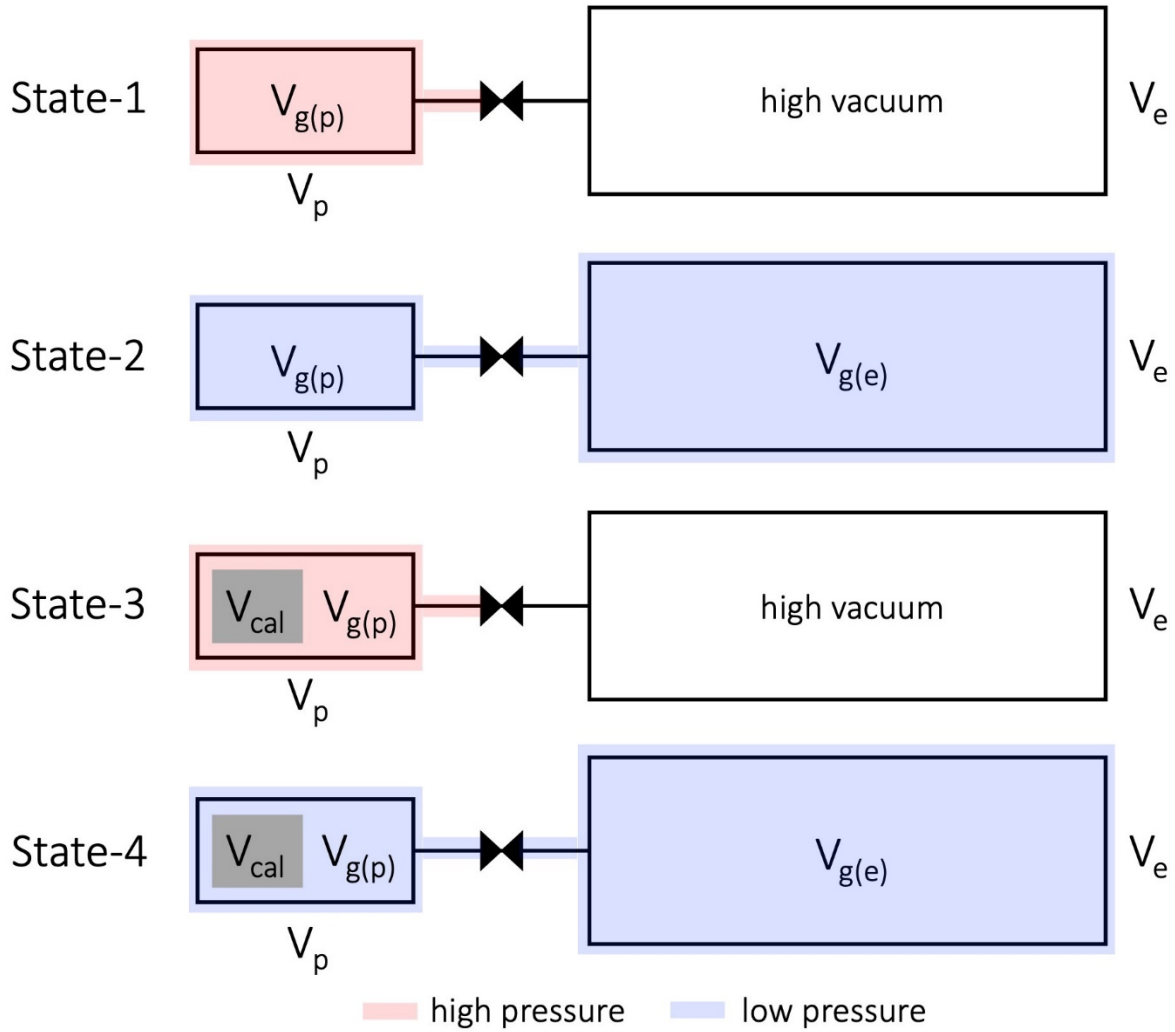


Fig. 19: Expansion-cell volume calibration measurement.

The measurement involves two expansions. The first expansion starts with empty pressurization and expansion cells (i.e., no calibration mass is included in the expansion) and involves two states:

- State-1: add inert gas to the pressurization-cell, while isolated from the expansion-cell at high vacuum.
- State-2: expand the inert gas in the pressurization-cell into the expansion-cell.

The second expansion add the calibration mass to the pressurization-cell and involves two states:

- State-3: add inert gas to the pressurization-cell, while isolated from the expansion cell at high vacuum.
- State-4: expand the inert gas in the pressurization-cell into the expansion-cell.

The expansion-cell volume calibration measurement has the following assumptions:

1. Zero leak requirement (i.e., the mols of inert gas are conserved between states).

2. The vessel strain of the pressurization-cell is negligible at low pressures (the measurements are done at lower pressures to take advantage of high precision and accuracy pressure transducers).
3. The calibration sample is high purity (i.e., > 4N); the sample's volume is the standard used to calibrate the cell volumes; we measure the sample mass to < 1 µg accuracy with a Mettler Toledo Microbalance, but the density is taken from NIST tables and assumes a high-purity sample.
4. The pressurization-cell volume remains constant between the two expansions (i.e., the vessel assembly with and without the calibration sample must be consistent).

Now, we derive the expansion-cell volume expression. Expanding state-1 into state-2 and using mass conservation, we get:

$$\rho_1 \times V_{g(p)} = \rho_2 \times (V_{g(p)} + V_{g(e)})$$

Now, the free gas volumes consume the entire cell-volumes since no calibration sample is present: $V_{g(p)} = V_p$ and $V_{g(e)} = V_e$. Substituting the free gas volumes, we get:

$$\rho_1 \times V_p = \rho_2 \times (V_p + V_e)$$

Expanding state-3 into state-4 and using mass conservation, we get:

$$\rho_3 \times V_{g(p)} = \rho_4 \times (V_{g(p)} + V_{g(e)})$$

Now, the free gas volume consumes the entire expansion-cell (i.e., it's empty), but only a subset of the pressurization-cell, which contains the calibration sample: $V_{g(p)} = V_p - V_{cal}$ and $V_{g(e)} = V_e$. Substituting the free gas volumes, we get:

$$\rho_3 \times (V_p - V_{cal}) = \rho_4 \times (V_p - V_{cal} + V_e)$$

Combining the state-1/state-2 and state-3/state-4 expansions, we get:

$$V_e = V_{cal} \times \frac{(\rho_1 - \rho_2)(\rho_3 - \rho_4)}{\rho_2 \times \rho_3 - \rho_1 \times \rho_4}$$

Pressurization-cell volume calibration measurement

The pressurization-cell volume measurement requires a known expansion-cell volume. This assumes an apparatus with a small, high-pressure volume (the pressurization-cell) that expands

into a larger, low-pressure expansion volume (the expansion-cell). The apparatus may or may not contain a non-loading sample volume that resides in the pressurization-cell (**Fig. 20**).

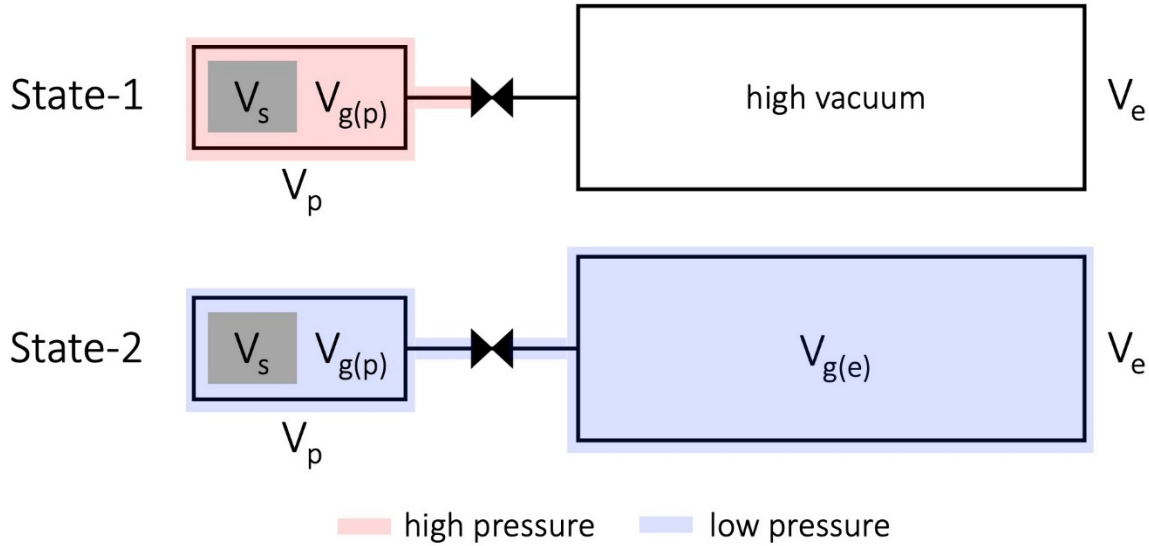


Fig. 20: The pressurization-cell volume calibration measurement.

The measurement has a single expansion:

- State-1: add inert gas to the pressurization-cell (at the target loading measurement pressure to ensure vessel-strain is accounted for), while isolated from the expansion-cell at high vacuum.
- State-2: expand the inert gas in the pressurization-cell into the expansion-cell.

The pressurization-cell volume calibration measurement has the following assumptions:

1. Zero leak requirement (i.e., the mols of inert gas are conserved between states).
2. The expansion-cell volume is known, i.e., it's been calibrated.
3. The sample is high purity such that the density taken from NIST tables is accurate. We measure the sample's mass to $< 1 \mu\text{g}$ accuracy with a Mettler Toledo Microbalance.

Now, we derive the pressurization-cell volume expression. Expanding state-1 into state-2 and using mass conservation, we get:

$$\rho_1 \times V_{g(p)} = \rho_2 \times (V_{g(p)} + V_{g(e)})$$

The free gas volume consumes the entire expansion-cell (i.e., it's empty) and a subset of the pressurization-cell if a sample is involved (the pressurization-cell may or may not contain the sample; so, we include V_s and set to it 0 if no sample is included): $V_{g(p)} = V_p - V_s$ and $V_{g(e)} = V_e$. Substituting for the free gas volumes, we get:

$$\rho_1 \times (V_p - V_s) = \rho_2 \times (V_p - V_s + V_e)$$

Solving for V_p we get:

$$V_p = V_s + V_e \times \frac{\rho_2}{\rho_1 - \rho_2}$$

High pressure density calibration measurement

At high pressures, pressure transducers are often inaccurate, and hydrogen's EOS is not well-known to our desired precision; so, we use our apparatus to directly measure gas density at high pressures. This measurement assumes an apparatus with a small, high-pressure volume (the pressurization-cell) that expands into a larger, low-pressure expansion volume (the expansion-cell). The apparatus may or may not contain a sample volume that resides in the pressurization-cell. Importantly, if the pressurization-cell contains a sample, it must not load hydrogen, e.g., it can be Au, Pt, etc. (**Fig. 21**).

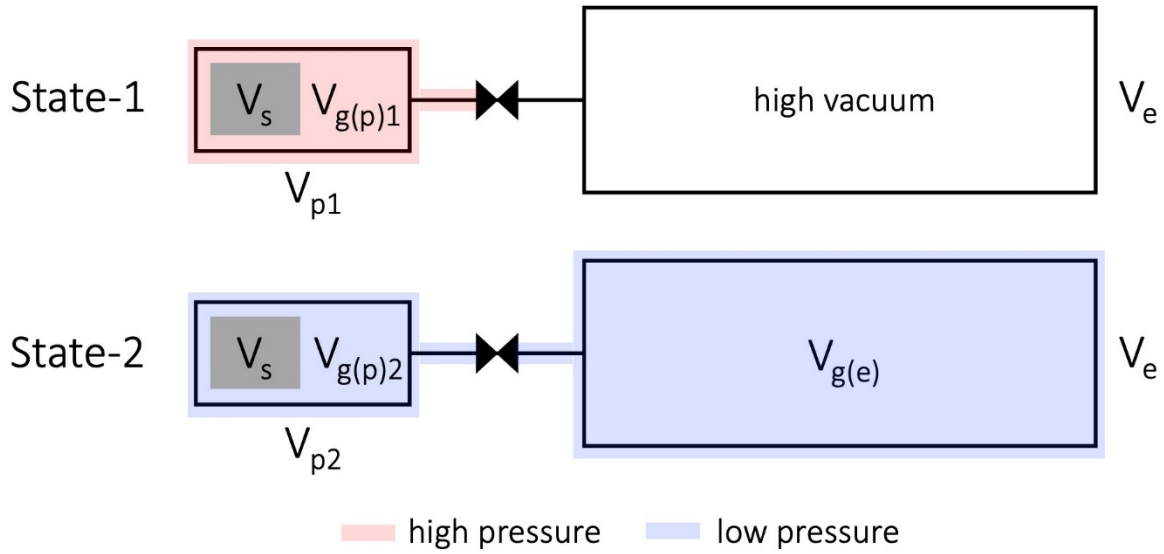


Fig. 21: The high-pressure, gas density calibration measurement.

The measurement has a single expansion:

- State-1: add the measurement gas (e.g., hydrogen) to the pressurization-cell (at matched pressure and temperature to the target loading measurement), while isolated from the expansion-cell at high vacuum.
- State-2: expand the gas in the pressurization-cell into the expansion-cell.

The high-pressure density calibration measurement has the following assumptions:

1. Zero leak requirement (i.e., the mols of gas are conserved between states).

2. The pressurization-cell volume is known, i.e., it's been calibrated.
3. The expansion-cell volume is known, i.e., it's been calibrated.
4. If an inert sample resides in the pressurization-cell, it's high purity such that the density taken from NIST tables is accurate. We measure the sample's mass to < 1 µg accuracy with a Mettler Toledo Microbalance.

Now, we derive the gas density expression. Expanding state-1 into state-2 and using mass conservation, we get:

$$\rho_1 \times V_{g(p)1} = \rho_2 \times (V_{g(p)2} + V_{g(e)})$$

The pressurization-cell strains 1-2% at high pressures, so we must use a V_p that accounts for the vessel strain in state-1 to avoid a significant source of error. Since $V_e \gg V_p$ (i.e., V_e is ~1000x larger than V_p), the expanded volume in state-1 ($V_{g(p)2} + V_{g(e)}$) is nearly all contained in V_e . So, we do not need to account for differences in the pressurization-cell vessel strain between the two states i.e., in state-2, $V_{g2} = V_{p2} - V_s + V_e \approx V_{p1} - V_s + V_e$. This calculation differentiates between V_{p1} and V_{p2} ; however, it's acceptable to set $V_{p1} \approx V_{p2}$ since the error it introduces is well below the measurement resolution.

The free gas volume consumes the entire expansion-cell (i.e., it's empty) and a subset of the pressurization-cell: $V_{g(p)1} = V_{p1} - V_s$, $V_{g(p)2} = V_{p2} - V_s$, and $V_{g(e)} = V_e$. Substituting for the free gas volumes, we get:

$$\rho_1 \times (V_{p1} - V_s) = \rho_2 \times (V_{p2} - V_s + V_e)$$

Solving for the state-1 (i.e., high pressure) gas density, we get:

$$\rho_1 = \rho_2 \times \frac{V_{p2} - V_s + V_e}{V_{p1} - V_s}$$

High pressure excess loading measurement

The excess mols loaded into a sample at high pressures are measured with a single expansion. The measurement assumes an apparatus with a small, high-pressure volume (the pressurization-cell) that contains the sample of interest and a larger, low-pressure volume (the expansion-cell) (**Fig. 22**).

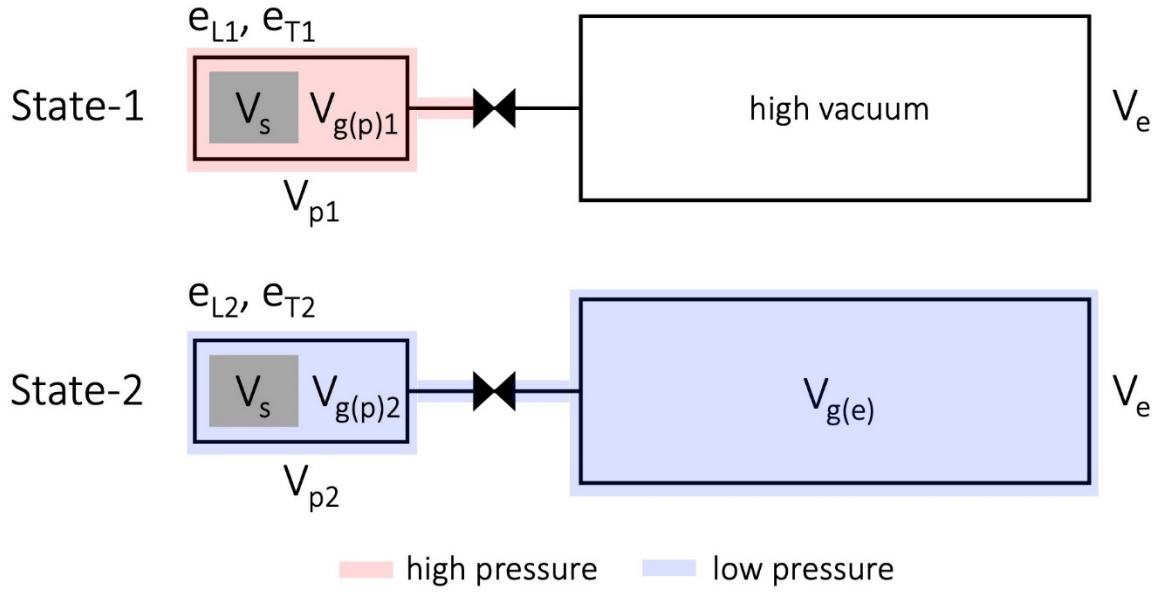


Fig. 22: The high-pressure, excess loading measurement.

The expansion consists of the following:

- State-1: add process gas (e.g., hydrogen) to the pressurization-cell that contains the sample of interest, which is isolated from the expansion-cell at high vacuum.
- State-2: expand the gas in the pressurization-cell into the expansion-cell and wait until the pressure plateaus in the expansion-cell.

The high-pressure excess loading measurement has the following assumptions:

1. Zero leak requirement i.e., the mols of gas are conserved between states.
2. The pressurization-cell volume is known, i.e., it's been calibrated.
3. The expansion-cell volume is known, i.e., it's been calibrated.
4. The gas density in state-1 is known, i.e., it's been calibrated; experimentally, the gas density calibration cell is simultaneously pressurized to the loading measurement cell to ensure the pressure is matched and the cells are held at the same temperature; this ensures the gas density is the same between the two cells.
5. The sample's lattice strain from loading is known, i.e., it's been calibrated.
6. The sample's thermal strain is known.
7. The sample is high purity such that the density taken from NIST tables is accurate. We measure the sample's mass to $< 1 \mu\text{g}$ accuracy with a Mettler Toledo Microbalance.

Now, we derive the excess mols of atoms loaded into the sample. The free gas volume in state-2 is given by:

$$V_{g1} = V_{p1} - V_s \times (1 + e_{L1} + e_{T1})$$

The sample's lattice strain from loading, e_L , is calibrated from our lateral strain measurement technique (**Fig. 23**). We've found that the volumetric strain for $\text{PdH}_x / \text{PdD}_x$ roughly scales as $e_L \approx 0.17 \times \Gamma$, where Γ is the loading fraction. For new materials, loading strain must be calibrated as a function of pressure and temperature as small changes in free gas volume in the pressurization-cell lead to large differences in measured loading. The sample's volumetric thermal strain, e_T , is approximated from the sample's coefficient of thermal expansion (CTE) taken from the NIST tables: $e_T \approx 3 \times \text{CTE}$. Thermal strain is only relevant for high-temperature measurements (e.g., $>100^\circ\text{C}$). It's important to note that the CTE will change as a function of loading, but it's a small effect in most materials (i.e., the error introduced is well below the resolution of the loading measurement).

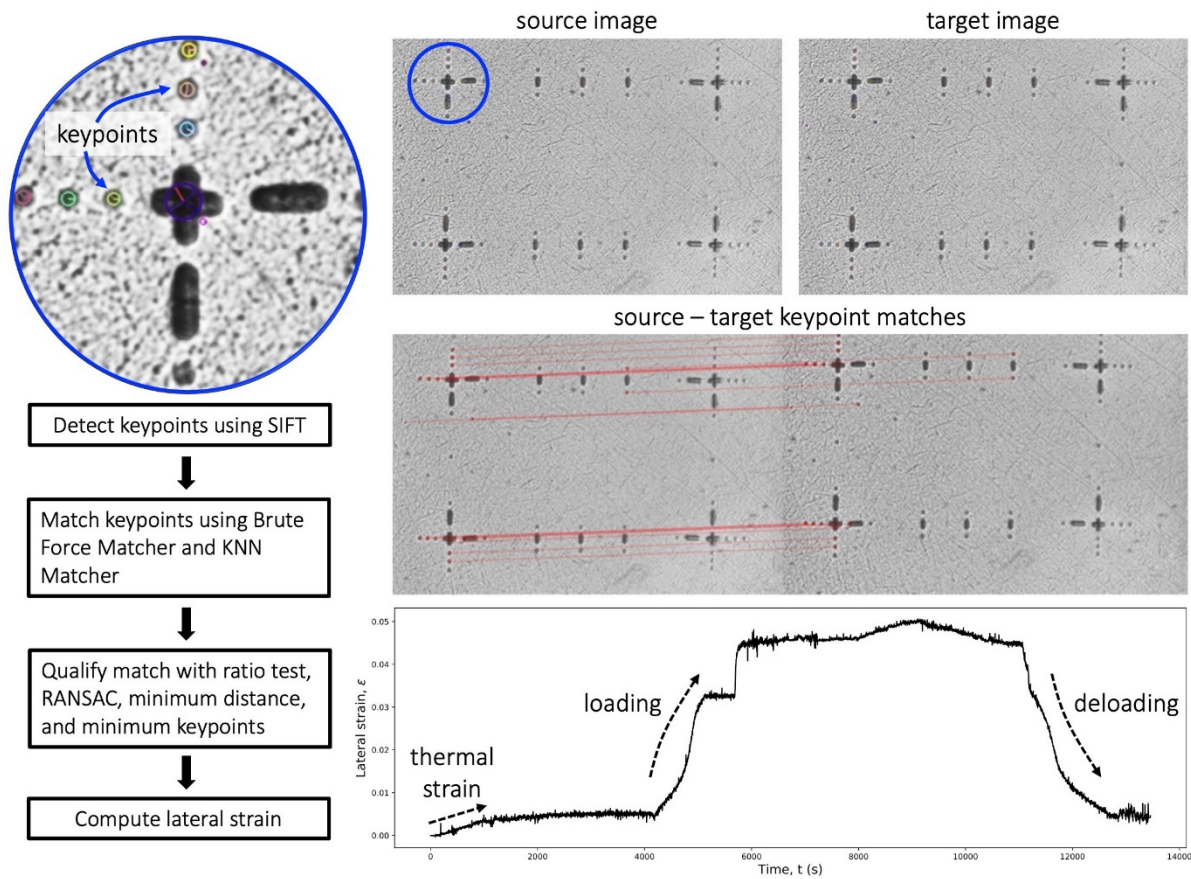


Fig. 23: Our in-situ lateral strain measurement calibrates the volumetric strain of a hydride as a function of pressure and temperature.

The mols of gas is given by $n = \rho V / M$. Substituting, we get:

$$n_{g1} = \frac{\rho_1 \times (V_{p1} - V_s \times (1 + e_{L1} + e_{T1}))}{M_g}$$

Similarly, we can write down the measured mols of gas in state-2 (after the gas from state-1 is expanded into state-2):

$$V_{g2} = V_{p2} - V_s \times (1 + e_{L2} + e_{T2}) + V_e$$

$$n_{g2} = \frac{\rho_2 \times V_{g2}}{M_g}$$

$$n_{g2} = \frac{\rho_2 \times (V_{p2} - V_s \times (1 + e_{L2} + e_{T2}) + V_e)}{M_g}$$

Now, the measured mols of gas in state-2 contains the mols of gas in state-1 (assuming mass conservation) as well as the excess mols of gas that were loaded in the sample in state-1. So, $n_{g2} = n_{g1} + n_{ex1}$. Solving for the excess mols of gas loaded in the sample in state-1, we get $n_{ex1} = n_{g2} - n_{g1}$. To get the excess mols of atoms loaded (versus mols of gas molecules), we multiply by the number of atoms per gas molecule: $n_{ex(at)} = A \times n_{ex}$. Substituting for n_{g1} and n_{g2} , we get:

$$n_{ex(at)} = A \times \left[\frac{\rho_2 \times (V_{p2} - V_s \times (1 + e_{L2} + e_{T2}) + V_e)}{M_g} - \frac{\rho_1 \times (V_{p1} - V_s \times (1 + e_{L1} + e_{T1}))}{M_g} \right]$$

Low pressure residual loading measurement

After expanding the high-pressure state and measuring the excess mols, the sample still has residual loading. For example, a high-pressure expansion generally reduces the pressure from 10 kbar to 1 bar. At 1 bar, 25 °C, PdH_x is still ~70% loaded. To measure the residual loading, the sample is heated (typically to ~200 °C) to deload the sample and is subsequently expanded into the expansion-cell, which is vented between each expansion and brought to high vacuum. The excess mols deloaded from the sample are calculated using the expression for $n_{ex(at)}$ established above. At these low pressures, hydrogen's EOS is accurate, so density-calibration measurements are not required. Furthermore, at low pressures, the pressurization-cell's vessel strain is not relevant. Expansions are continued until there is no observable increase in pressure in the expansion-cell i.e., the sample has fully deloaded. In typical measurement, 3 residual loading measurements are required to fully deload the sample. In summary, the total excess mols (atomic) is expressed by:

$$n_{tot(at)} = \sum_{i=1}^N n_{ex(at)i}$$

where N is the number of expansion cycles.

Loading calculation

To calculate the loading of the sample at the initial pressure and temperature, the total excess mols (atomic) deloaded from the sample is compared to the mols of lattice atoms: $\Gamma = n_{tot(at)}/n_s$. The mols of lattice atoms is given by:

$$n_s = \frac{m_s}{M_s}$$

So, the loading fraction can be expressed by:

$$\Gamma = \frac{M_s}{m_s} \times \sum_{i=1}^N n_{ex(at)i}$$

Example measurement

As an example measurement, we review BE2360, where we measured the PdD_x loading at 135 ksi, 50°C to be 92.6%. We used a 0.17757 cm³ Pt sample and N₂ gas to calibrate the expansion-cell volumes and found them to be 501.65 ± 3.59 cm³ (cell-b) and 493.67 ± 2.20 cm³ (cell-d) (**Table 4, 5, 6**). Using the expansion-cell volumes, we calibrated the pressurization-cell volumes with N₂ gas and found them to be 0.51574 ± 0.002633 cm³ (cell-a) and 0.49806 ± 0.000552 cm³ (cell-c) (**Table 5, 6**). We simultaneously pressurized cell-a and cell-c with ~135 ksi, 50°C D₂ and measured the D₂ gas density to be 0.2337 g/cm³ by expanding cell-c into cell-d (**Table 5, 7**). Finally, we expanded cell-a (containing the loaded PdD_x sample and ~135 ksi, 50°C of D₂) into cell-b to measure the excess loading above ~1 bar. We heated the PdD_x sample to ~200 °C and did three more expansions to measure the residual loading. It's important to note that we wait sufficient time for the sample to deload (i.e., when the pressure in the expansion-cell plateaus) for each expansion to ensure we measure the equilibrium value; depending on the sample thickness, each expansion can require 1-5 hours to equilibrate (**Fig. 24**). The sum of the loadings totaled 92.6% (**Table 5, 8**).

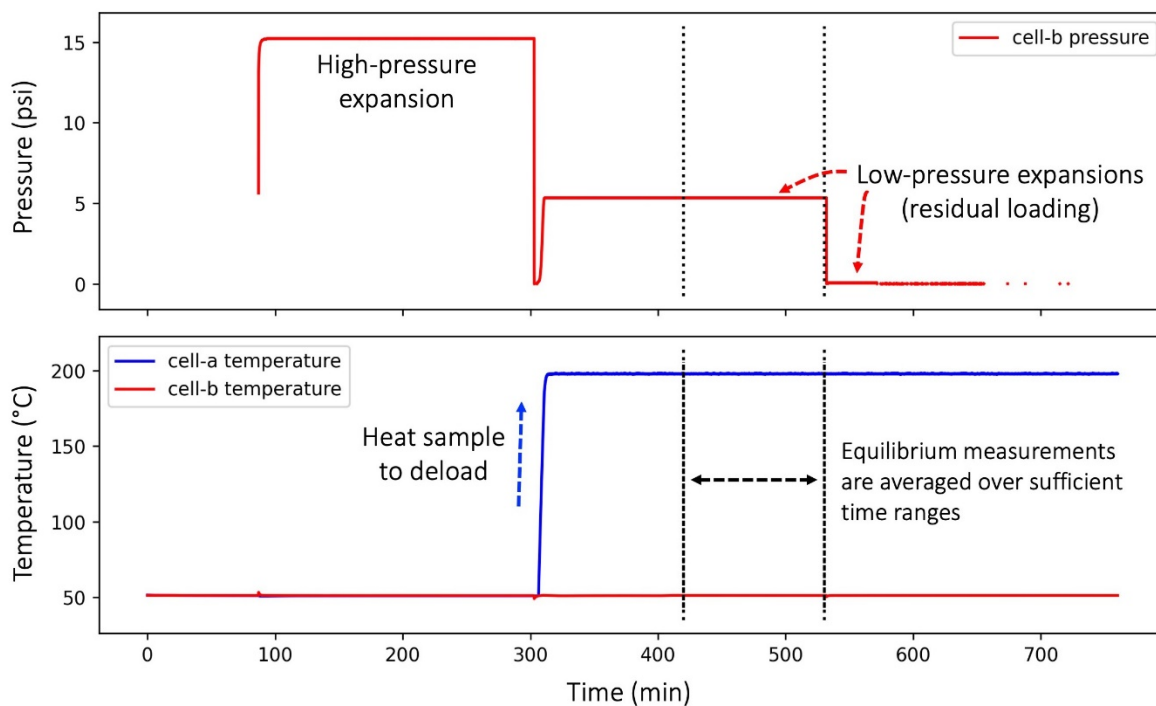


Fig. 24: A loading measurement includes a high-pressure expansion followed by low-pressure expansions while heating to fully deload the sample. Each expansion waits sufficient time for the sample to reach equilibrium and averages over a time range.

Sample id	Material	Mass (g)	Volume (cm ³)
BD1913	Pt	3.8089303	0.17757
BD3917	Pd	2.3122827	0.19237

Table 4: The samples used are a Pt sample for the expansion-cell volume calibrations and the Pd sample for the loading measurement.

Expansion id	Gas	Sample id	Pressurization-cell					Expansion-cell				
			Name	P (psi)	P std (psi)	T (°C)	T std (°C)	Name	P (psi)	P std (psi)	T (°C)	T std (°C)
BE2136-EX1	N ₂	Empty	cell-a	1452.08	5.16	50.47	0.00148	cell-b	1.329	0.0566	50.10	0.00609
BE2136-EX2	N ₂	BD1913	cell-c	1452.08	5.16	50.31	0.000963	cell-d	0.815	0.0611	50.62	0.00562
BE2136-EX3	N ₂	Empty	cell-a	1460.95	5.11	50.43	0.00177	cell-b	1.338	0.0578	50.12	0.00608
BE2136-EX4	N ₂	BD1913	cell-c	1460.95	5.11	50.25	0.000657	cell-d	0.819	0.0622	50.59	0.00425
BE2136-EX5	N ₂	Empty	cell-a	1469.73	4.61	50.42	0.00272	cell-b	1.351	0.0573	50.12	0.006574
BE2136-EX6	N ₂	BD1913	cell-c	1469.73	4.61	50.24	0.000824	cell-d	0.828	0.0619	50.56	0.00568
BE2136-EX7	N ₂	BD1913	cell-a	1446.08	4.01	50.52	0.00139	cell-b	0.822	0.0572	50.19	0.00952
BE2136-EX8	N ₂	Empty	cell-c	1446.08	4.01	50.52	0.000766	cell-d	1.321	0.0617	50.50	0.00995
BE2136-EX9	N ₂	BD1913	cell-a	1467.93	4.58	50.42	0.00156	cell-b	0.839	0.0572	50.22	0.00890
BE2136-EX10	N ₂	Empty	cell-c	1467.93	4.58	50.46	0.00148	cell-d	1.343	0.0619	50.49	0.00339
BE2136-EX11	N ₂	BD1913	cell-a	1468.90	4.89	50.44	0.00178	cell-b	0.837	0.0557	50.23	0.00597
BE2136-EX12	N ₂	Empty	cell-c	1468.90	4.89	50.45	0.000557	cell-d	1.342	0.0600	50.47	0.00265
BE2360-EX1	N ₂	BD3917	cell-a	138613.8	172.17	51.91	0.00915	cell-b	8.497	0.00358	51.80	0.00237

BE2360-EX2	N ₂	BD1913	cell-c	138613.8	172.17	51.71	0.00994	cell-d	8.509	0.00384	50.75	0.0173
BE2360-EX3	N ₂	BD3917	cell-a	138530.1	70.46	51.89	0.00379	cell-b	8.506	0.00364	51.79	0.00267
BE2360-EX4	N ₂	BD1913	cell-c	138048.6	15.66	51.28	0.00386	cell-d	8.484	0.00356	50.63	0.00399
BE2360-EX5	N ₂	BD3917	cell-a	138046.9	32.84	51.88	0.00724	cell-b	8.391	0.00437	51.82	0.00599
BE2360-EX6	N ₂	BD1913	cell-c	138046.9	32.84	51.09	0.0131	cell-d	8.492	0.00431	50.63	0.00335
BE2360-EX7	D ₂	BD1913	cell-c	-	-	50.19	0.00529	cell-d	14.695	0.00436	50.35	0.00732
BE2360-EX8	D ₂	BD3917	cell-a	-	-	51.78	0.00141	cell-b	15.765	0.00421	51.93	0.0113
BE2360-EX9	D ₂	BD3917	cell-a	-	-	197.25	0.309	cell-b	5.347	0.00395	51.51	0.00231
BE2360-EX10	D ₂	BD3917	cell-a	-	-	197.08	0.317	cell-b	0.0606	0.00399	51.49	0.00312
BE2360-EX11	D ₂	BD3917	cell-a	-	-	197.10	0.323	cell-b	0.002	0.00399	51.39	0.00365

Table 5: The expansions table for the volume calibrations, gas density calibration, and loading measurements.

Calibration id	Name	V (cm ³)	V std (cm ³)	P (psi)	P std (psi)	T (°C)	T std (°C)	Expansions
VC8	cell-b	501.65	3.59	0.8326	0.00812	50.21	0.01240	BE2136-EX1 BE2136-EX3 BE2136-EX5 BE2136-EX7 BE2136-EX9 BE2136-EX11
VC9	cell-d	493.67	2.20	0.8205	0.00566	50.59	0.02621	BE2136-EX2 BE2136-EX4 BE2136-EX6 BE2136-EX8 BE2136-EX10 BE2136-EX12
VC24	cell-a	0.51574	0.002633	138396.9	306.02	51.89	0.01732	BE2360-EX1 BE2360-EX3 BE2360-EX5
VC25	cell-c	0.49806	0.000552	138236.4	326.81	51.36	0.31911	BE2360-EX2 BE2360-EX4 BE2360-EX6

Table 6: The volume calibrations table. The pressurization-cell/expansion-cell combinations are cell-a/cell-b and cell-c/cell-d).

Calibration id	Cell	Gas	ρ (g/cm ³)	T (°C)	Expansions	Volume Calibrations
GD11	cell-c	D ₂	0.2337	50.19	BE2360-EX7	VC9, VC25

Table 7: The gas density calibration table.

Experiment id	Sample id	Hydride	P (ksi)	T (°C)	Loading (%)	Expansions	Volume Calibrations	Density Calibration
BE2360	BD3917	PdD _x	135.0	51.78	92.6	BE2360-EX8 BE2360-EX9 BE2360-EX10 BE2360-EX11	VC8, VC24	GD11

Table 8: The loading measurement results table.

Summary of key loading measurements

We primarily focused our UltraSorb loading measurements on PdD_x. Most of our AHE experiments were run between 100 – 150 ksi D₂ at 50°C. We show equilibrium loading values

ranging between 87 – 135 ksi D_2 at 50°C in **Table 9**. A subset of our experiments (specifically, our passive gas-loading Calorimetry campaign) ran at higher temperatures, so we’ve included a loading value at 108 ksi, 100°C D_2 (**Table 9**).

Experiment id	Hydride	Pressure (ksi)	Temperature (°C)	Loading %
BE2260	PdD_x	87.29	51.20	90.7
BE1971	PdD_x	101.71	50.87	91.2
BE2360	PdD_x	135.00	51.78	92.6
BE2192	PdD_x	108.68	99.88	89.4

Table 9: Summary of key UltraSorb experiments.

Measuring Loading: Mass (MicroSorb)

An alternative direct mass loading measurement is to simply weigh the loaded mass with a microbalance. To accomplish this, we developed a microcapsule that retains a sample of interest (generally a metal lattice) and has a weldable gas inlet (**Fig. 25**). After loading a metal lattice at a set pressure and temperature, the microcapsule is in-situ welded shut, which captures the thermodynamic state. The pressure and temperature surrounding the microcapsule can be brought to ambient conditions, enabling the microcapsule to be removed from the pressure system and have its mass measured with a microbalance. By measuring the mass before and after the loading experiment, the mass difference is a direct measurement of the mols of hydrogen/deuterium. Some of the hydrogen mass is from the free gas internal to the capsule, i.e., not loaded into the sample, so it must be properly accounted for. We’ve measured the internal volume of the microcapsules using X-ray tomography with a voxel size of 7 μ m.

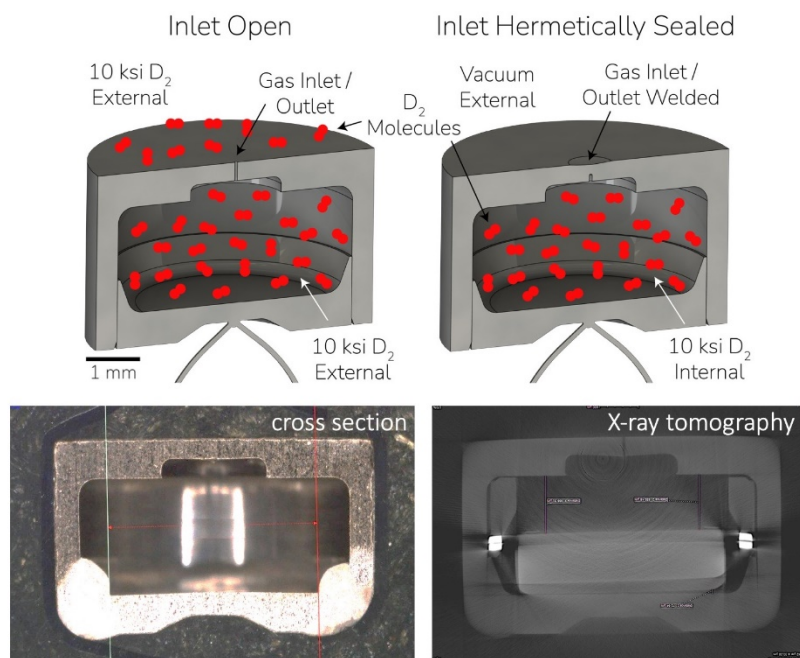


Fig. 25: A microcapsule can be used for a direct-mass loading measurement by incorporating a weldable gas inlet and weighing pre/post the experiment on a microbalance.

Now, let's derive the analytical expressions for the MicroSorb measurement (the nomenclature is given in **Table 10**). The microcapsule contains a sample, retention-spring, and free-gas (**Fig. 26**).

MicroSorb Nomenclature	
V_s	Sample volume
V_r	Retention-spring volume
V_i	Internal capsule volume
V_g	Free gas volume
V_c	Capsule volume (internal volume and wall volume)
ρ_s	Sample density
ρ_r	Retention-spring material's density
ρ_c	Capsule material's density
ρ_g	Gas density
ρ_{air}	Air density
e_s	Sample strain due to loading
m_s	Sample mass
m_r	Retention-spring mass
m_c	Empty capsule mass
m_g	Mass of the free gas
m_{air}	Mass of displaced air
m'	Buoyancy corrected mass
m_{pre}	Mass of entire μ -capsule assembly prior to the experiment
m_{post}	Mass of entire μ -capsule assembly after the experiment
m_{ex}	Excess mass from residual gas and loading
m_l	Mass loaded in the sample
M_l	Molar mass of the atomic species loaded into the sample (atomic species)
M_s	Molar mass of the sample
Γ	Loading fraction

Table 10: MicroSorb nomenclature used in the calculations.

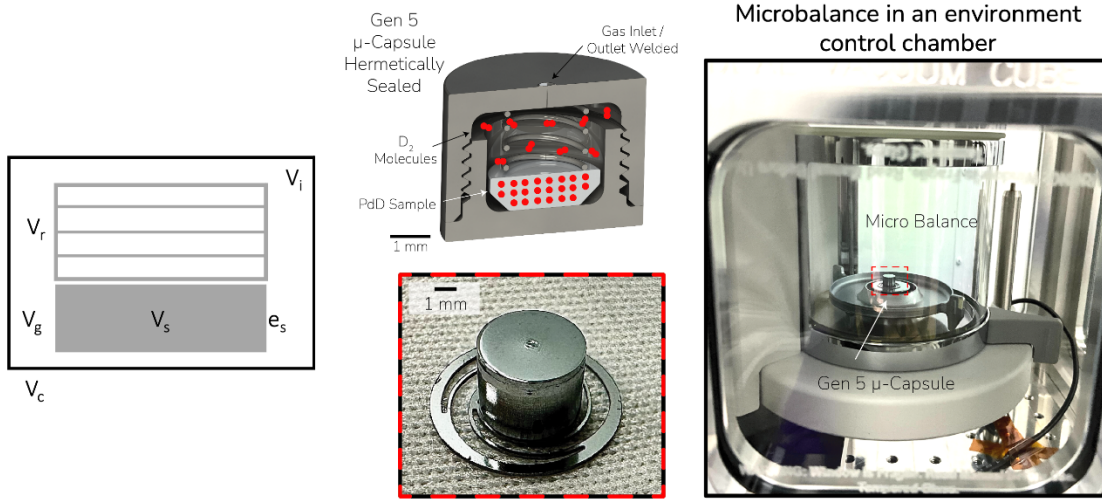


Fig. 26: The MicroSorb capsule contains a sample, retention-spring, and free gas. The capsules are weighed before and after the experiment to determine the loading.

The sample volume is obtained by measuring the unloaded sample mass and referencing the NIST density for the material: $V_s = m_s / \rho_s$. Similarly, the retention-spring's volume is obtained by measuring the spring's mass and referencing the spring's material density: $V_r = m_r / \rho_r$. The internal volume of the microcapsule, V_i , can be measured with X-ray tomography and destructively confirmed by cross sectioning (**Fig. 25**). We've found that the capsules drawing-specification is close to the measured volumes. The sample strains when loaded, e_s , which we've calibrated with lateral-strain measurements. The free gas volume is then given by:

$$V_g = V_i - V_r - V_s \times (1 + e_s)$$

And the mass of the free gas is simply $m_g = \rho_g \times V_g$, where the gas density is obtained from gas's equation-of-state at the measured pressure and temperature. We weigh the full capsule assembly before the experiment, m_{pre} , and can obtain the empty capsule mass:

$$m_c = m_{pre} - m_s - m_r$$

During the experiment, the microcapsules are in-situ hermetically sealed, so we must use buoyancy corrected masses for the sample, spring-retention, and empty microcapsule:

$$m'_s = \frac{m_s}{1 - \rho_{air}/\rho_s}, \quad m'_r = \frac{m_r}{1 - \rho_{air}/\rho_r}, \quad m'_c = \frac{m_c}{1 - \rho_{air}/\rho_c}$$

Now, the capsule volume is the sum of the internal volume and wall volume (we get the wall volume from the buoyancy-corrected empty capsule mass and density of the capsule material):

$$V_c = V_i + \frac{m'_c}{\rho_c}$$

The mass of displaced air is given by:

$$m_{air} = \rho_{air} \times V_c$$

We weigh the entire microcapsule assembly after the experiment, m_{post} , and account for the mass of displaced air:

$$m'_{post} = m_{post} + m_{air}$$

Now, we can calculate the excess mass, which is the difference between the post mass and the buoyancy corrected sample, spring-retention, and empty capsule:

$$m_{ex} = m'_{post} - m'_s - m'_r - m'_c$$

The excess mass is a combination of the loaded mass and residual free mass. So, we calculate the loaded mass by:

$$m_l = m_{ex} - m_g$$

The loading is then computed by comparing the mols of loaded species ($n_l = m_l/M_l$) to the mols of lattice atoms ($n_s = m'_s/M_s$):

$$\Gamma = \frac{n_l}{n_s}$$

As an example measurement, we review BE2983. A Pd sample was placed in a microcapsule and held at (145 ksi, 150°C) D_2 for 20 minutes, (145 ksi, 25°C) for 1 hour, and (145 ksi, -100°C) for 1 hour (note: the sample was 500 μ m thick, so 1 hour at -100°C is not nearly enough time to hit equilibrium loading; nevertheless, we expect to measure a loading >94%, which is the estimated loading at 145 ksi, 25°C). Holding the temperature at -100°C, the pressure was reduced to 20 psi and the microcapsule was in-situ welded shut. The microcapsule was removed from the apparatus and weighed at 20°C. The material densities are given in **Table 11**, volumes in **Table 12**, and masses in **Table 13**. We approximate the volumetric strain from 100% loading to be $e_s = 0.17$. Using the molecular weights of Pd (106.42 g/mol) and D (2.014 g/mol), we converted the masses to mols and found the loading to be $\Gamma = 0.968$.

Component	Density (g/cm ³)
Pd sample	12.023
Retention-spring (WRe3)	19.5
Capsule (MoRe 47.5/52.5)	13.5
Air	0.001025
D ₂ (20 psi, 20°C)	0.0002279

Table 11: Material densities used in the BE2983 MicroSorb measurement.

Component	Volume (cm ³)
Pd sample (V_s)	0.004362
Retention-spring (V_r)	0.000419
Internal capsule (V_i)	0.018567
Free gas (V_g)	0.013044
Capsule (V_c)	0.081720

Table 12: Volumes used in the BE2983 MicroSorb measurement.

Component	Mass (g)	Buoyancy-corrected Mass (g)
Pd sample (m_s)	0.052438	0.052443
Retention-spring (m_r)	0.008179	0.008180
Empty capsule (m_c)	0.852493	0.852569
Free gas (m_g)	2.9734e-6	-
Displaced air (m_{air})	9.8473e-5	-
Full assembly - pre (m_{pre})	0.913110	-
Full assembly - post (m_{post})	0.914057	0.914155
Excess mass (m_{ex})	0.00096341	-
Loaded mass (m_l)	0.00096044	-

Table 13: Masses used in the BE2983 MicroSorb measurement.

Stoichiometric Loading

To fully exhaust the loading-hypothesis for AHE, we needed to confirm stoichiometric (i.e., 100%) loading. We developed two paths to stoichiometric loadings: cryogenic temperatures and high-pressure gas.

Stoichiometric Loading: Cryogenic

Loading increases with decreasing temperature (i.e., it lowers the required pressures to reach high loadings), but the kinetics exponentially decrease with low temperatures. The challenge in reaching stoichiometric loadings at cryogenic temperatures is the slow loading kinetics, i.e., it could take days-weeks to load depending on the sample geometry (surface area and diffusion length). To reduce the time to reach stoichiometry, we ran cryogenic experiments at high-pressure (and added most of the loading at higher temperatures before cooling) and modified the sample geometries (e.g., thin-films, nanoparticles, etc.). We ran typical cryogenic experiments at ~150 ksi,

-100°C, which should be stoichiometric in PdD and PdH (**Fig. 27**). As an example, we show a cryogenic calorimetry experiment run at 130 ksi, -100°C D₂ (PdD_x is in Ch2), where we observed no evidence of AHE (**Fig. 28**).

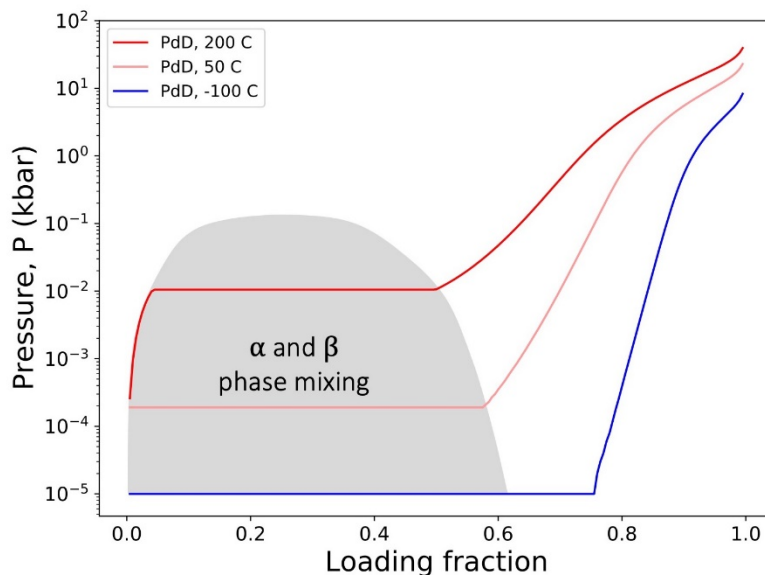


Fig. 27: Stoichiometric loadings can be achieved at 10 kbar, -100°C.

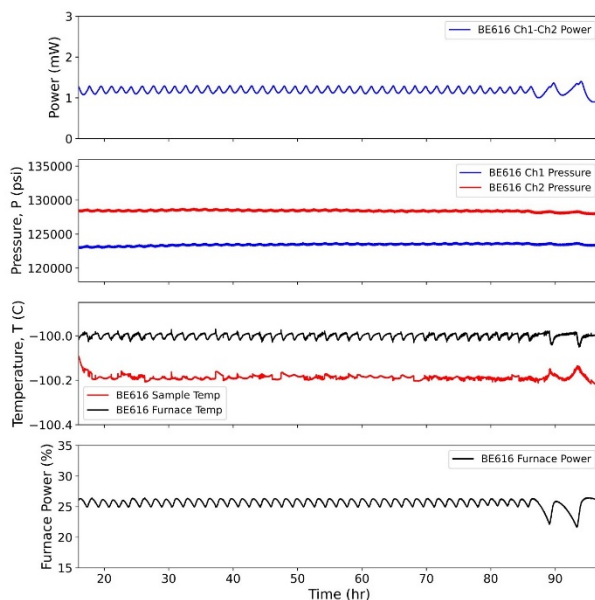


Fig. 28: A passive differential calorimetry experiment ran at 130 ksi, -100°C.

To confirm stoichiometric PdD at 150 ksi, -100°C, we ran a MicroSorb experiment. To reduce the diffusion path and increase surface area, we in-situ modified the Pd sample. Cavities and surface blisters form in metal hydrides when rapidly heated and pushed too far out of equilibrium (i.e., thermal diffusion $\gg$ mass diffusion). The result is the creation of new surfaces in the bulk of the

metal hydride (**Fig. 29**). In BE3270, the in-situ modification decreased the diffusion path of deuterons from $\sim 440 \mu\text{m}$ to $\sim 30 \mu\text{m}$ and increased the surface area. The MicroSorb measurement showed a loading of 99-100%.

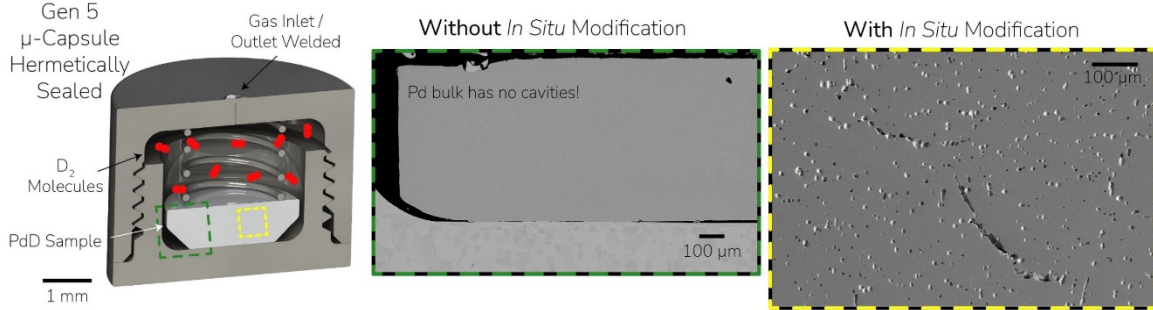


Fig. 29: In BE3270, a MicroSorb experiment in-situ modified a Pd sample to decrease the diffusion path and increase surface area while loading the Pd at 150 ksi, -100°C . The loading was measured at 99-100%.

Stoichiometric Loading: High Pressure Gas

High pressure is a direct method to achieving stoichiometric Pd/D(H) loadings. However, the pressure (at 25°C) above which stoichiometric loadings are guaranteed is not well established. Diamond anvil cells have been used in conjunction with synchrotron x-ray diffraction measurements, but this approach has large error bounds in both loading ($\sim 5\%$) and pressure (~ 100 ksi) (**Fig. 30**).

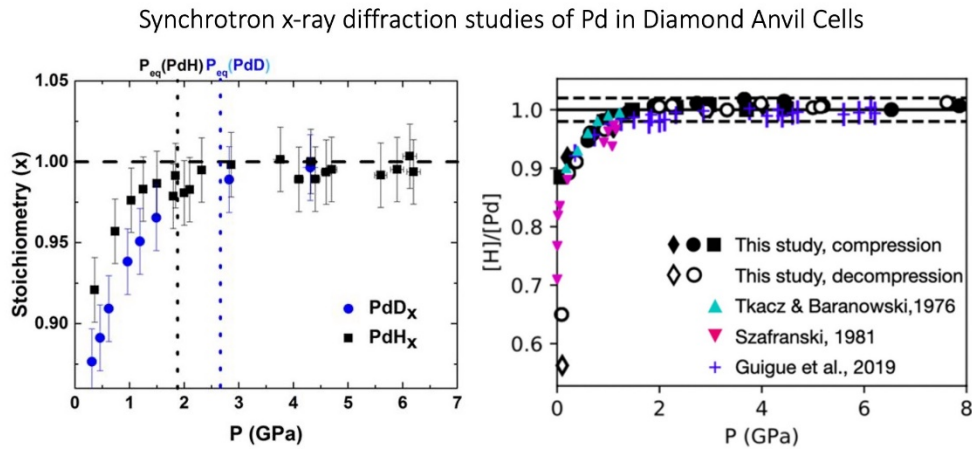


Fig. 30: Synchrotron x-ray diffraction studies of Pd hydrides in Diamond Anvil Cells^{16,17}.

¹⁶ Z. Geballe, et. al, Phys. Rev. B 103, 024515 (2021)

¹⁷ B. Guigue, et. al, J. of Appl. Phys. 127, 075901 (2020)

Electrical resistivity of PdH_x and PdD_x is the most common metric used to quantify loadings in Pd, but the ability to differentiate between 99% and 100% loading is difficult. While the mapping between resistance ratio and loading is well documented and regularly referenced, there is some spread in the resistivity values reported in literature in the last 1-2% of loading, and there are no reports of resistivity measurements past 435 ksi in D_2 (**Fig. 31**). We completed resistive gas measurements up to 550 ksi and have run several controls to decouple the effects of loading and pressure to better determine the pressures required for 100% D/Pd.

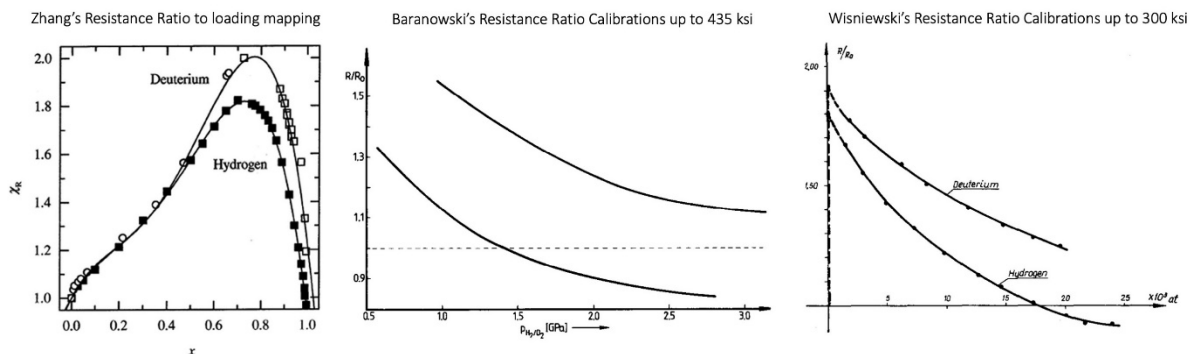


Fig. 31: Resistance ratio calibrations from literature shows spread in the last 1-2% of loading^{18,19,20}.

To confirm stoichiometric PdD/H loadings via resistivity, we look for the point at which the resistance ratio stops changing with increasing pressure. Diamond anvil literature shows that the lattice strain does not change from 2 GPa to 8 GPa, indicating that once the Pd octahedral sites are fully occupied, the lattice does not load further, i.e., 100% loading is the max limit for Pd. However, for PdH we continue to observe decreases in resistivity above 300 ksi; similarly, for PdD we continue to observe decreases in resistivity above 400 ksi and measure R/R_0 values as low as 1.1, 5% lower than the lowest numbers reported in literature (**Fig. 32**).

¹⁸ Z. Zhang, et. al, J. of Elec. Analytical. Chem. 528 (2002)

¹⁹ R. Wisniewski, Review of Scientific Instruments, 41, 3 (1969)

²⁰ B. Baranowski, et. al., J. of the Less-Common Metals, 158 (1990)

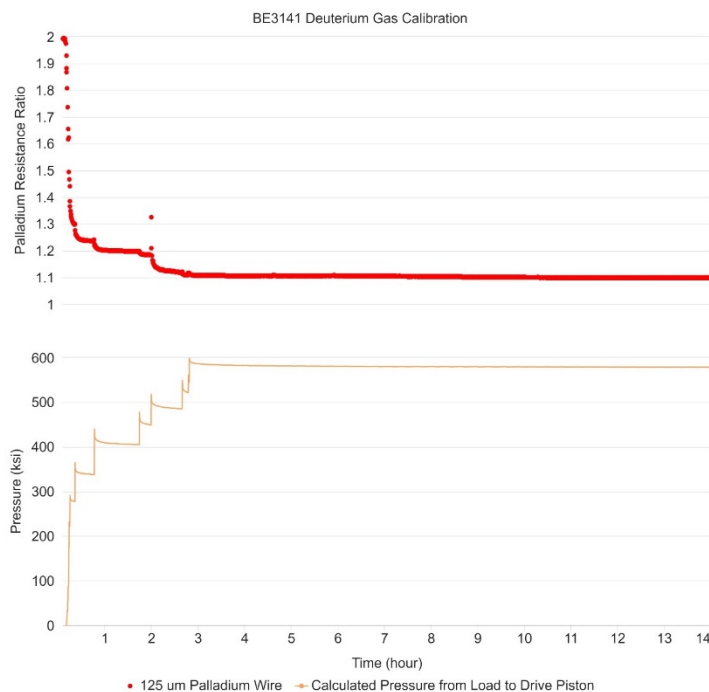


Fig. 32: In BE3141 we ran a resistance ratio calibration of a 125 μm diameter Pd wire up to >550 ksi D_2 at 25°C . The resistance continues to drop with increasing pressure.

To build confidence that we are in-fact reaching stoichiometry with PdH and PdD, we need to decouple the effects of pressure and loading on the resistivity of Pd at >300 ksi pressures. Hence, we performed measurements with only N_2 and with $\text{H}_2/\text{D}_2:\text{N}_2$ gas mixtures. In N_2 , we confirmed pressure effects on Pd resistivity are non-negligible above 150 ksi (**Fig. 33**). To establish stoichiometry, we find the point where R/R_0 converges for the pure gases (H_2/D_2) and gas mixtures ($\text{H}_2/\text{D}_2:\text{N}_2$). For protium, we targeted an 84:16 $\text{H}_2:\text{N}_2$ mixture to reach ~380 ksi of H_2 partial pressure at 450 ksi of total pressure (~70 ksi of N_2 partial pressure). For deuterium, we targeted an 82:18 $\text{D}_2:\text{N}_2$ mixture to reach ~410 ksi of D_2 partial pressure at 500 ksi of total pressure (~90 ksi of N_2 partial pressure).

For PdH we find nearly identical final R/R_0 values in $\text{H}_2:\text{N}_2$ mixtures as we did at ~400 ksi H_2 . This suggests that we are at PdH stoichiometry >330 ksi and that the effect pressure has on resistance is what continues to drive resistivity lower. Similarly, for PdD we find the R/R_0 values in $\text{D}_2:\text{N}_2$ mixtures converge at 500 ksi, indicating that any further decrease in resistance is due to pressure alone, not loading.

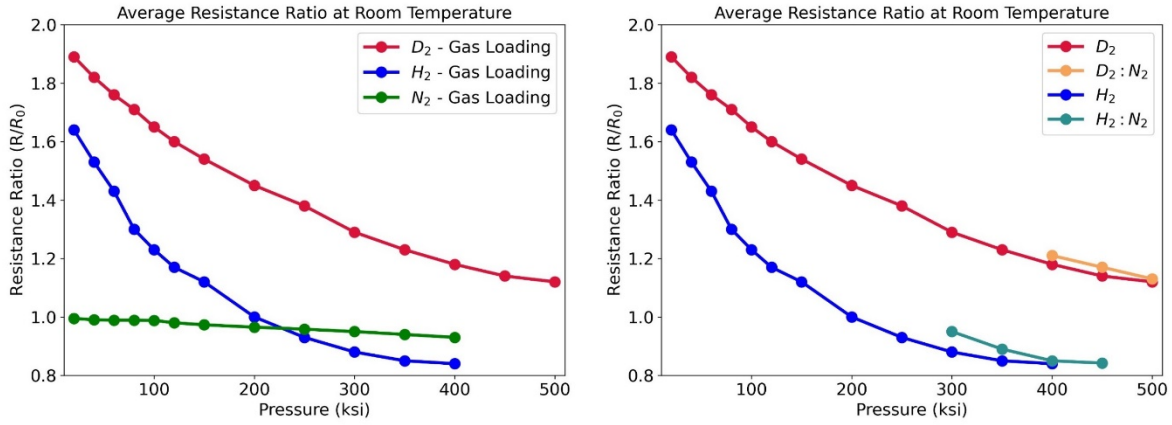


Fig. 33: Pressure effects on resistance are non-negligible at pressures >150 ksi as shown the by N_2 control. To decouple the effects of pressure and loading on the resistivity of Pd, we performed measurements with $H_2/D_2:N_2$ gas mixtures.

Through a combination of hydrogen and deuterium gas mixtures with inert gases, as well as access to sufficiently high pressures, we determined the pressures required to reach stoichiometry. For PdH, stoichiometry is around 330 ksi, higher than the ~ 270 ksi values proposed in literature. For PdD, we find that ~ 400 ksi is not enough, and that pressures >450 ksi are needed. Our gas-mixture calibrations are the first demonstrations to decouple resistance changes from pressure and loading. While the pressures required to reach stoichiometric H/Pd and D/Pd are higher than we anticipated, we are well suited to operate at pressures beyond what is required for stoichiometry to ensure we are studying Pd under unity loading conditions at ambient temperatures.

Hardware

A fundamental hypothesis to exploring the existence/non-existence of AHE is the necessity of high fractional loadings (e.g., 90-100%). From a gas-loading perspective, this requires high-pressure, hydrogen-compatible systems (e.g., >10 kbar H_2/D_2). Commercial systems, which can handle H_2/D_2 at these pressures, do not exist and very few components (pumps, valves, vessels, etc.) are commercially available. So, we put significant effort into building zero-leak high-pressure systems and a facility to support them.

Hardware: Safety

High-pressure hydrogen introduces safety risks: combustible gas, embrittlement (i.e., strong, ductile materials become brittle), shrapnel from pressure failures, etc. To mitigate these risks, we built armored chambers that housed our pressure sources and experimental apparatuses (**Fig. 34**). All pressure failures, combustions, etc. were confined inside the chamber, mitigating any personnel risks; all high-pressure experiments were performed remotely, without humans in the chambers. Nevertheless, we still added isolated air exchange systems and fire suppression systems on each chamber to mitigate the risk of hydrogen fires inside the chambers. It's important to note that our compressed-hydrogen volumes were very small (e.g., < 10 cm³ at high pressures), so the total stored energy was low, and the risk of run-away hydrogen fires was nonexistent. In total, we built a “main” chamber that housed pressure sources and fed pressure into 8 experimental chambers: 5x chambers that fit a full-sized optics table and 3x mini chambers that housed compact experimental apparatuses.

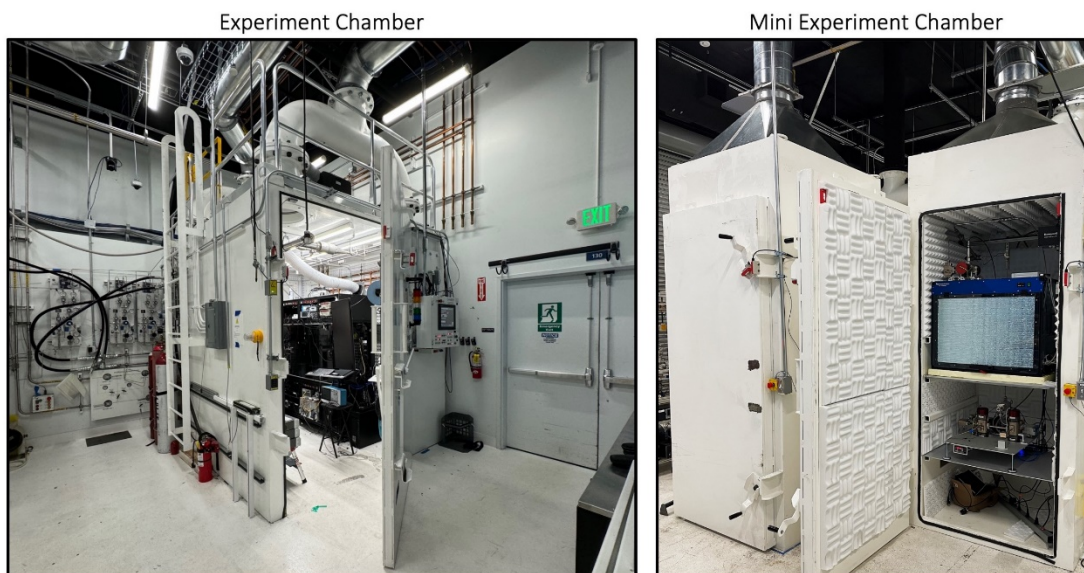


Fig. 34: Armored and vented chambers housed our high-pressure hydrogen sources and experimental apparatuses.

Hardware: Pressure Sources

We developed 4 different pressure sources (**Fig. 35, Table 14**). To start, Powerpack 1 was designed to use vendor-supplied components (e.g. valves and pumps) and had a maximum pressure capability of 100 ksi. We quickly ran into bottlenecks with vendor supplied components as high-pressure requires constant maintenance (e.g., seal stacks wear quickly, sub-components break, etc.) and we had to frequently send parts to vendors for refurbishment. This led to significant down-time. Moreover, vendor-supplied valves and pumps were leaky and Powerpack 1 could only hold high pressure for < 1 min. So, we designed in-house components (valves, pumps, fittings) to increase reliability and enable rapid maintenance, and over the years designed and built 3 different zero-leak systems: Powerpack 2, Screwjack, and Protonpack. Most high-pressure components were made with Toughmet® due to its strength and hydrogen resistance.

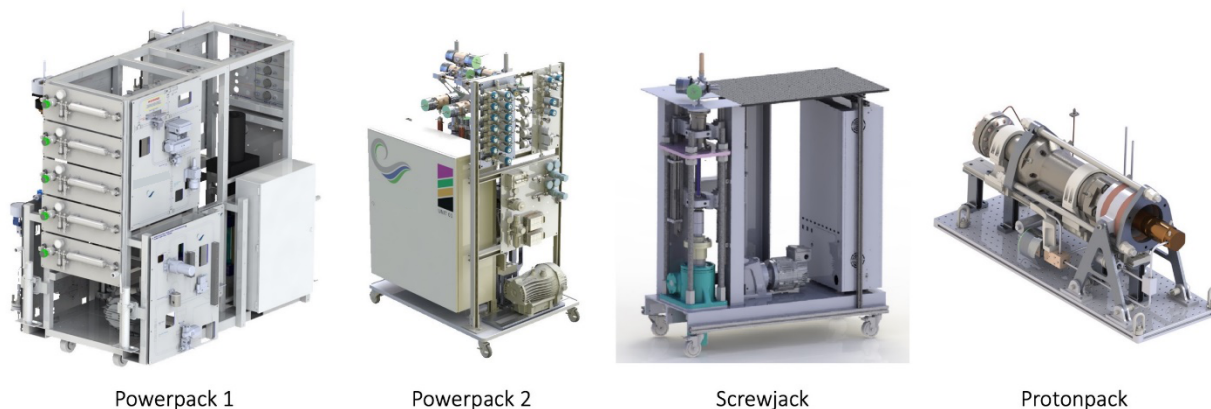


Fig. 35: Pressure sources developed at Callisto.

Source	Pressure Capability	Drive	Media
Powerpack 1	100 ksi	Hydraulic	Gas
Powerpack 2	150 ksi	Hydraulic	Gas
Screwjack	150 ksi	Electric	Gas / Liquid
Protonpack	150 ksi	Pneumatic	Gas

Table 14: High-level specs of the pressure sources developed at Callisto.

Powerpack 2 fully integrated in-house components (discussed more below), was our first zero-leak system, and increased our pressure capability from 100 ksi to 150 ksi. To increase control over a pump's piston position (which is important for liquids as they are highly incompressible i.e., small changes in piston position lead to large pressure changes), we moved to a Screwjack design. The Screwjack utilized our valves and pumps but replaced hydraulic actuation with a screw-jack driven by a motor. The Screwjacks were our most stable and reliable systems. Due to limited facility space and the need for additional experimental apparatuses, we opted to build mini chambers. To decouple the mini chambers from sharing pressure with other chambers, we built a small pressure source, the Protonpack, that fit inside a mini chamber along with an experimental apparatus. It was a pneumatically actuated system that was the most compact, but also the most hazardous due to a lack of control over the piston during leaks.

Our 150 ksi zero-leak valves were essential to all pressure systems and experimental apparatuses (**Fig. 36**). Our valves reduced the number of possible leak paths from 6 (in vendor-supplied valves) to 2 and updated the seal materials to metal rings and Teflon (vendor-supplied valves used metal, elastomers, and even leather). The updated seals achieved zero-leak and increased the cleanliness of our systems, which is important for debris-free AHE experiments. Seals that shed material (such as leather) would often contaminate our samples.

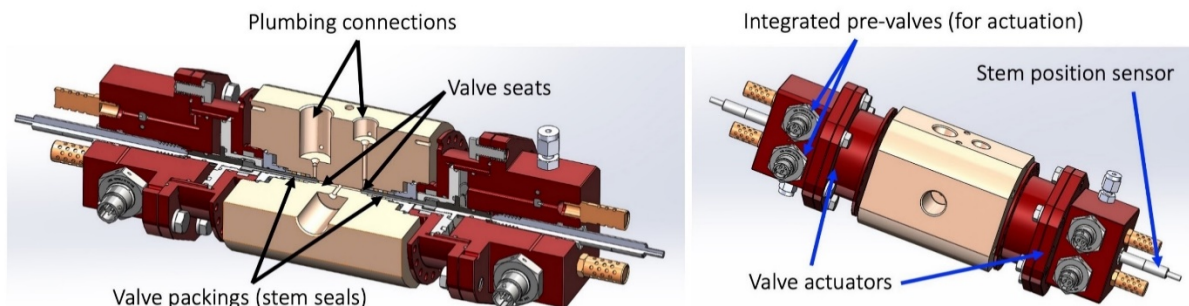


Fig. 36: 150 ksi compatible manifold valve.

We designed and fabricated 150 ksi zero-leak pumps (**Fig. 37**). The pump's seal is a small Teflon ring which is compressed $\sim 10\%$ by a carbide packing ram to a far higher internal stress than the surrounding gas. We found this seal approach much more effective than pressure-energized designs, which require a certain minimum pressure to seal. The linkage to the actuation cylinder is fixed in one degree of freedom but unconstrained in 5 degrees of freedom. This assures alignment of the rod with the seal pack. Pumping is accomplished by a tungsten carbide rod displacing volume inside the Toughmet bore.

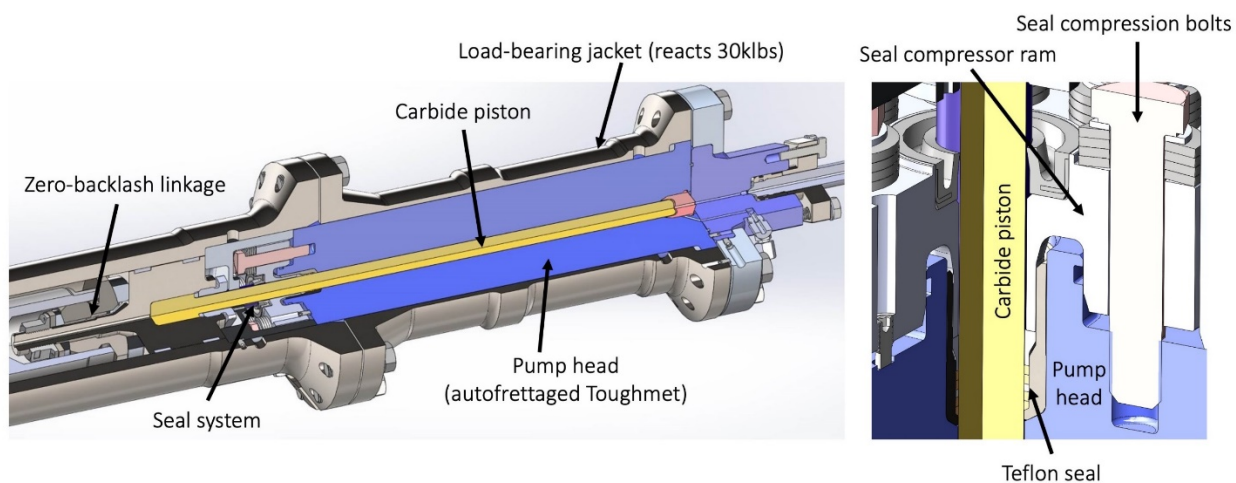


Fig. 37: 150 ksi intensifier (i.e., pump) that was designed and fabricated in-house.

In addition to our 150 ksi pumps, we developed a 20 ksi pump to enable finer control over the pressure from 0-20 ksi (**Fig. 38**). Initially, we used commercial boost pumps which do not give fine pressure control and require an additional pressure regulator. Our 20 ksi pumps use commercial off-the-shelf seals and implement an actuator/pump linkage similar to the 150 ksi pumps.

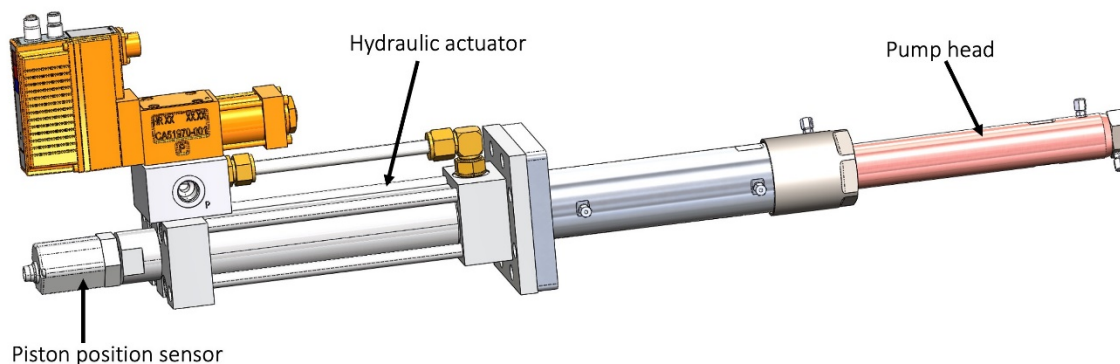


Fig. 38: 20 ksi intensifier (i.e., pump) that was designed and fabricated in-house.

Another highly useful component we developed was a 150 ksi tube fitting (**Fig. 39**). We experienced tube failures (i.e., ruptures) due to torsional stress from commercial fittings (the seat compression is generated by a single gland nut, transmitting torque into the tube). Our fittings removed the torsional stress with a bolted flange design and never led to a tube failure.

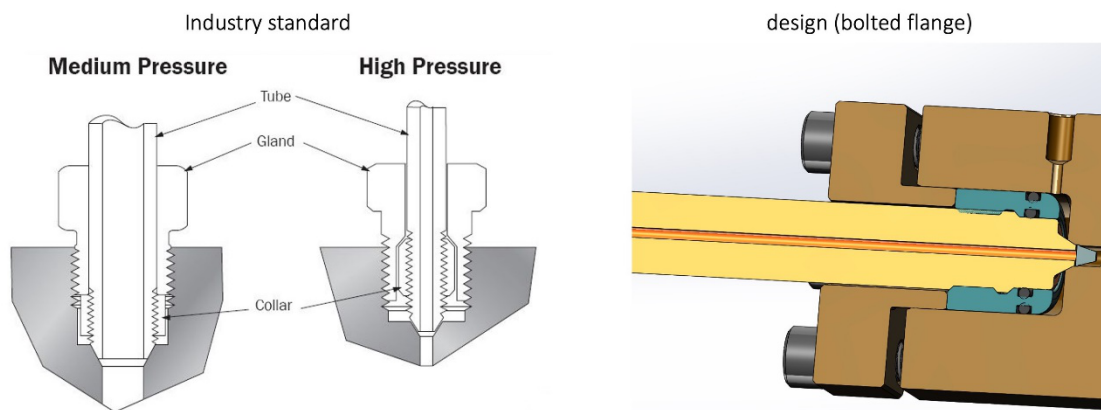


Fig. 39: Commercial fittings generated seat compression with a single gland nut, which transmits torque into the tube. Callisto fittings generate seat compression with bolts and no torque is transmitted into the tube.

Hardware: Pressure Vessels

Pressure vessels are central to high pressure experiments: they house the sample, control the pressure and temperature environment, and enable access for stimulation and in-situ diagnostics. While we developed an array of vessels, the main workhorse was the “Hammerhead” vessel, which evolved into a versatile and modular testbed (**Fig. 40, Table 15**). Depending on the experiment,

various volume, vacuum-level, thermal, optical, and electrical options could be configured to achieve the desired environmental and stimulation conditions.

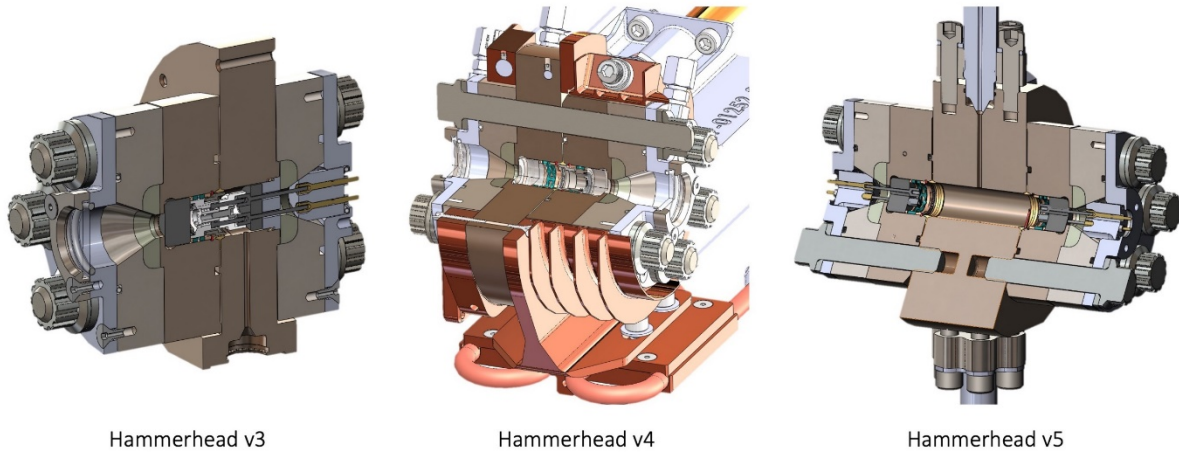


Fig. 40: The Hammerhead vessel served as a versatile testbed, enabling a wide range of pressure and temperatures in addition to providing access to stimulation sources and diagnostics.

Hammerhead	Pressure Range	Temperature Range	Features
v1	1mbar to 10 kbar	25°C to 50°C	• Electrical feedthroughs • Optical port
v2	1mbar to 10 kbar	-120°C to 50°C	• Cryo • Electrical feedthroughs • Optical port
v3	1nbar to 10 kbar	-120°C to 50°C	• Cryo • High vacuum • Electrical feedthroughs • Optical port
v4	1mbar to 10 kbar	-120°C to 350°C	• Cryo + High temperature • Two optical ports
v5	1mbar to 10 kbar	25°C to 50°C	• Corrosion resistant • Large internal volume • Dual electrical feedthroughs

Table 15: The Hammerhead vessel served as a versatile testbed, enabling a wide range of pressure and temperatures in addition to providing access to stimulation sources and diagnostics.

Developing zero-leak 150ksi electrical feedthroughs was a challenge. We initially started with brazing pins to single crystal sapphire windows to take advantage of our optical hardware. However, the brazed sapphire approach was unreliable and often cracked. So, we developed feedthrough pins with a self-energizing seal (**Fig. 41**). Pressure from the test cell pushes against the head of the pin, which transfers force to a ceramic traveling anvil. This type of design improves as sealing pressure increases. Manufacturing the seals requires micromachining of both metallic and ceramic parts, but the pins are easy to assemble and do not require specialized equipment.

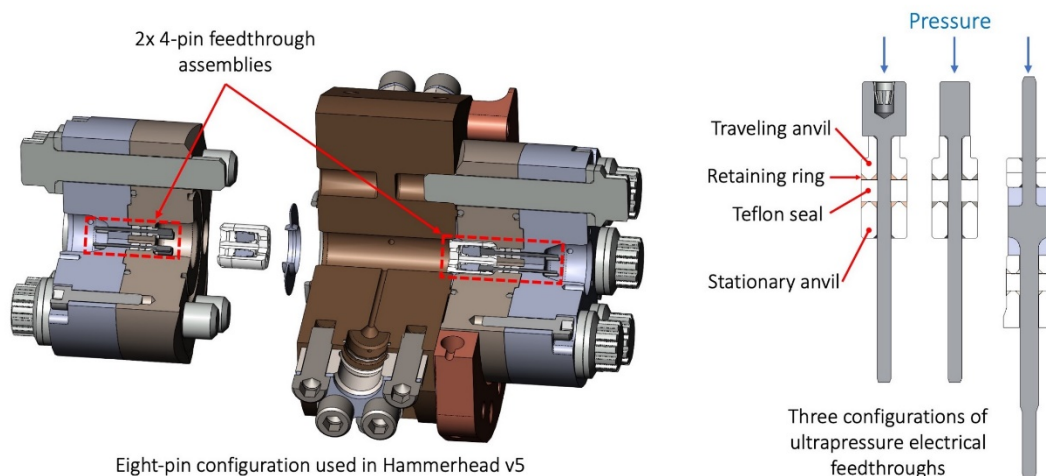


Fig. 41: Zero-leak, 150ksi electrical “pin” feedthroughs take advantage of a self-energizing seal that improves sealing as pressure increases.

Hardware: >300 ksi

While our 150 ksi hardware was effective at studying AHE above 90% loadings, we need much high pressures to hit 100% (stoichiometric loading) at room temperatures. To bypass designing >150 ksi valves, tubing, and fittings, we pursued a combined intensifier-vessel design. Sealing >300 ksi hydrogen gas is notoriously difficult and has only been historically demonstrated by 2 academic groups outside of the diamond anvil cell literature with little-to-no documentation. Hydrogen compatibility significantly reduces the materials we can work with, particularly high strength steels, which were successful in our >300 ksi liquid apparatuses. While Toughmet was our workhorse hydrogen-compatible material at lower pressures, >300 ksi is well beyond Toughmet’s ~140 ksi yield strength. So, we moved to multi-layer vessels to constrain the materials (Fig. 42).

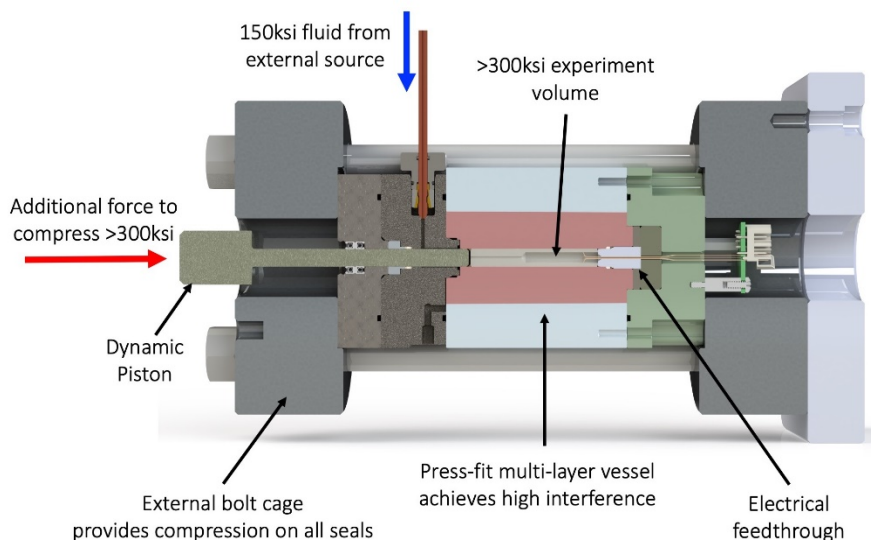


Fig. 42: Multi-layer vessel design for >300 ksi.

By placing a liner under compression with a jacket, the stress of the inside wall can be placed under compression during assembly to decrease the tensile stress during pressurization (**Fig. 43**). The higher the interference between the two layers, the greater the compression. The limit of how much interference one can achieve is determined by the yield strength of the jacket and inner liner. The interference pressure between an internal layer and external layer is given by:

$$p_{int} = \frac{\delta_R}{R \left(\frac{R^2(\nu_i - 1)}{E_i(R^2 - r_i^2)} - \frac{R^2(\nu_o - 1)}{E_o(R^2 - r_o^2)} + \frac{r_i^2(\nu_i + 1)}{E_i(-R^2 + r_i^2)} + \frac{r_o^2(\nu_o + 1)}{E_o(R^2 - r_o^2)} \right)}$$

where E_i is the modulus of elasticity of the internal layer, E_o is the modulus of elasticity of the external layer, ν_i is the Poisson's ratio of the internal layer, ν_o is the Poisson's ratio of the external layer, δ_R is the radial interference, R is the final radius of the interface, r_i is the radius of the internal layer, and r_o is the radius of the external layer.

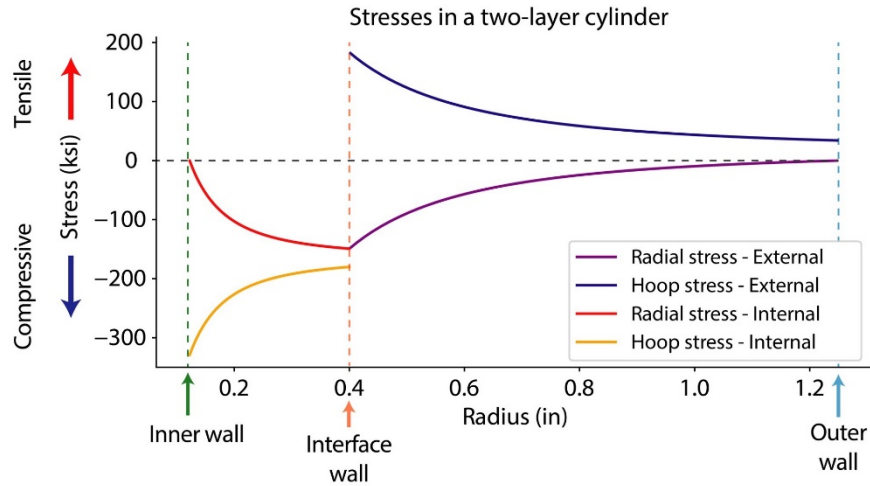


Fig. 43: Stresses in a two-layer cylinder.

To reach pressures >300 ksi, we need to keep the bore from dilating. We began to employ extremely high interference, multi-layer vessels to keep the internal bore under compression. We accomplished this with tapered fits (instead of thermal fits) because of the ability to achieve significantly larger interferences. While extremely stiff materials like Tungsten Carbide make ideal jacket materials, they are extremely poor under tension. We employ 3-layer designs to keep the carbide contained as an intermediate layer. A Toughmet inner sleeve (which mitigates hydrogen embrittlement) is pressed into the Tungsten-Carbide/Steel composite jacket, achieving theoretical interference pressures >250 ksi (**Fig. 44**). This is beyond the elastic regime, collapsing the inner liner. Aside from the ability to use carbides and ceramics as the vessel material or a significantly larger footprint, this is as radially constrained as we can get. The vessel is honed to the correct diameter, but the material properties are ambiguous in this plastic regime. With the

bore under large amounts of compression from the high interference jackets, we can now seal directly along the bore of the vessel with a simple anti-extrusion ring and PTFE liners (**Fig. 45**). The seal engages with the piston only after filling with >100 ksi gas, removing most of the compressibility of the gas. The seal translates along the bore of the vessel as the piston is driven deeper to achieve higher pressures. This is only possible with minimal bore dilation.

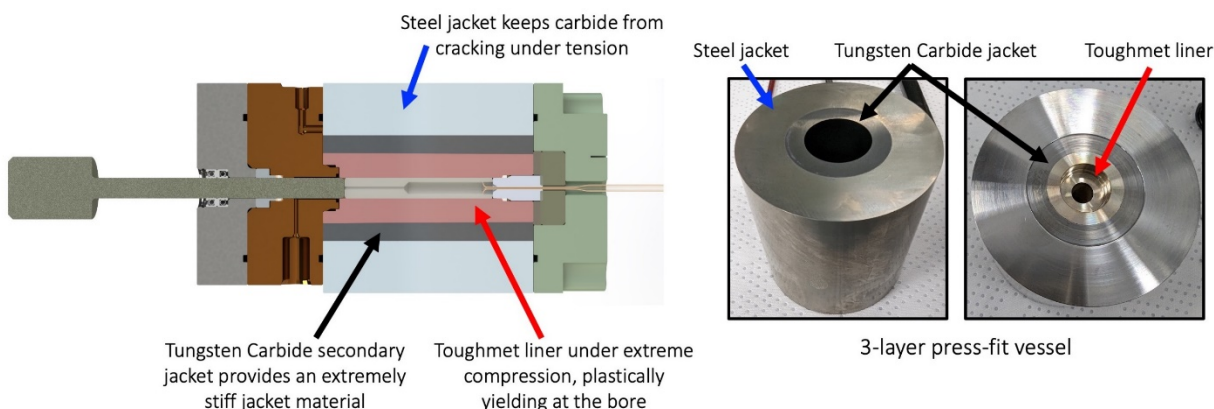


Fig. 44: A 3-layer press-fit vessel utilizes a steel jacket to keep a Tungsten Carbide jacket from cracking, which in turn keeps a Toughmet liner under extreme compression.

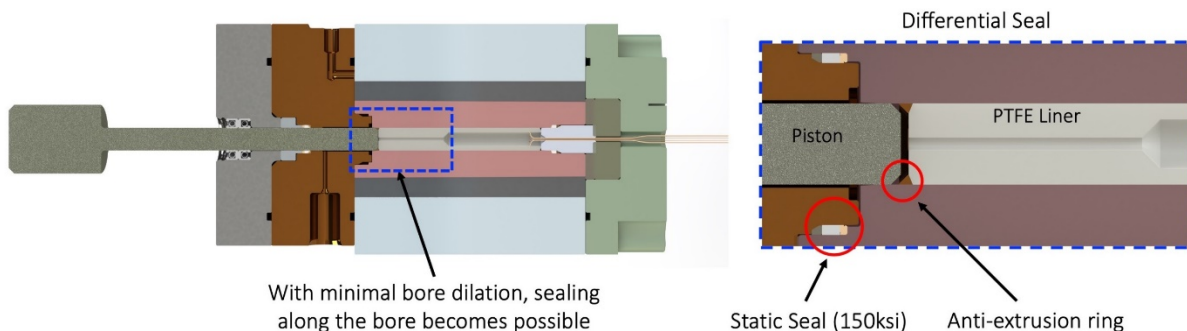


Fig. 45: With the bore under compression, the seal is directly along the bore of the vessel with an anti-extrusion ring and PTFE liner.

With 3-layer vessels, we could consistently reach ~350-400 ksi pressures. At pressures >400 ksi, the innermost liners significantly dilate, and the seals extrude into the gap between the piston and liner. To address this, we began to sequentially autofrettage the vessels to higher pressures. This got us to 450 ksi. Eventually, we ran into limits of radial compression and autofrettage. At >450 ksi, we consistently observed that liners grow axially. With axial compression >200 ksi, we constrain the material in all dimensions and our limitation now becomes the strength of our piston. Using the highest strength grade carbides for pistons, we could access pressures near 600 ksi, operating well past the elastic regime. These are the highest pressures reached with hydrogen outside of diamond anvil cells, pushing past Baranowski's limits.

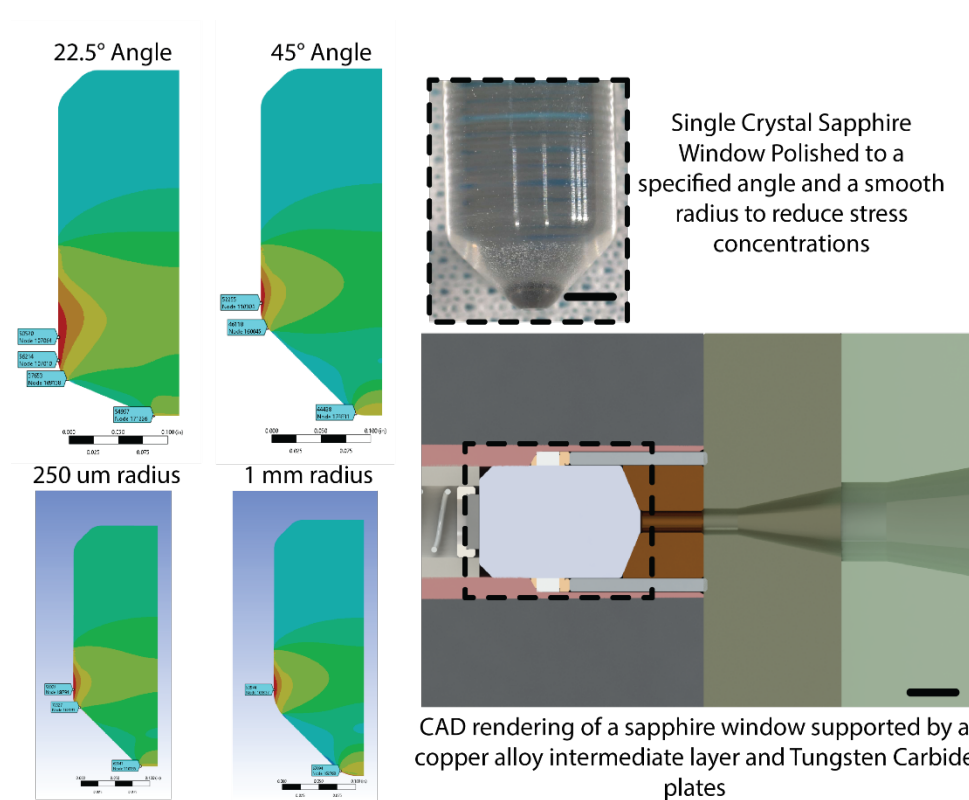


Fig 46: Single crystal sapphire window designed to take advantage of a cone, distributing the load over a larger area. Black scale bar shown is 2 mm. We used FEA modeling to determine the optimal angle and radius of curvature to reduce stress concentrations at the edges. The images shown compare the simulated stresses at 450 ksi of gas pressure

To contain gas pressures >300 ksi, several strategies are employed to keep any material from experiencing stresses above its limit. For example, by pre-stressing the innermost layers through interference fits, we decrease the partial pressure that layer is exposed to. However, the electrical and optical ports into the vessel are exposed to the full pressure differential, as they provide access from atmospheric conditions to the pressure inside the vessel. These are typically the weak links in pressure vessels and where material choice is most limited.

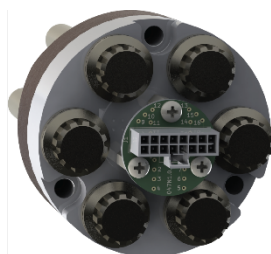
Optical Access > 300 ksi:

For optical access into the pressure vessels, we utilized single-crystal sapphire and silicon carbide windows. Aside from diamond, these are the best material candidates that are optically transparent. However, even single-crystal sapphire and silicon carbide contain minor defects that serve as crack initiation points, particularly at edges, leading to a significant reduction in the operable pressure. To overcome this limitation, we investigated a variety of geometries to find which ones are most resilient to pre-existing cracks.

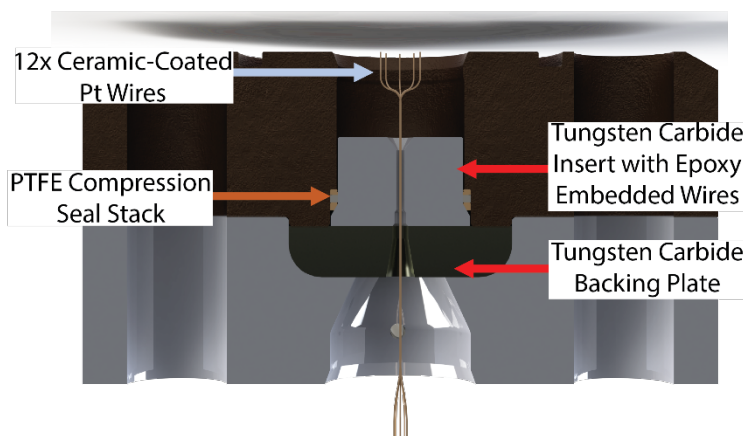
Our most successful design was to use a 45-degree cone on the low-pressure side of the optical window. A grinding process was developed to achieve a desired geometry, and diamond polishing

was used to remove any defects that were introduced in the grinding step. The process of adding an angle to the optical window removed the defects already present in the window as well as distributed the load over more surface area. A copper alloy intermediate layer matches the angle on the sapphire and serves as an intermediate layer between the tungsten carbide backing layer and the brittle sapphire windows. Behind the sapphire window, we found that a softer material, like copper, served a critical role in ensuring that the load distributed as evenly as possible to the sapphire. Stiff (e.g. tungsten carbide) intermediate layers were tested with angles matching the sapphire windows, but typically ended in crack propagation at pressures >300 ksi, while softer materials (e.g. copper alloys) could consistently operate at pressures > 450 ksi. The aperture of the copper intermediate layer and tungsten carbide backing flange was limited to ~2 mm for 7 mm sapphire windows for operation at 450 ksi. A low ratio of unsupported / supported area is needed to prevent the sapphire window from experiencing extreme tensile stresses.

Electrical Access > 300 ksi:



Feedthrough PCB Assembly CAD rendering



Similar to the optical window port, electrical feedthroughs experience the full pressure differential (>300 ksi to atmosphere). Tungsten carbide (WC) inserts were used with a PTFE-compression seal stack around the periphery. In short, a thin PTFE ring is compressed between the WC insert and the vessel wall, and opposing copper-alloy rings are used to prevent the extrusion of the PTFE at elevated pressures. An 800 μm hole is drilled into the WC insert, where 12 ceramic-coated Pt microwires (125 μm diameter) are embedded with an epoxy and aluminum oxide encapsulant (50 nm Al_2O_3 nanopowder mixed with Stycast 2850FT). These electrical feedthroughs were stable up the highest pressures we've tested, providing electrical access at pressures >500 ksi.

Measuring hydrogen pressures >300 ksi is non-trivial. Intuitively, one can calculate the pressure p by $p = F/A$, where F is the applied force and A is the area the force is applied to. However, this method includes the frictional forces from sealing. We attempted to measure the vessel strain at the outer diameter; however, due to operating in the plastic regime, it's difficult to measure accurate results >300 ksi. Resistive manganin sensors are often utilized to infer pressure at different temperatures, given its resistivity is temperature-insensitive and pressure-sensitive. However, it's well documented that the pressure response of manganin resistive sensors becomes highly non-linear past 400 ksi^{21,22}. Through a combination of these approaches, we can determine the minimum bound of pressure and find that the most accurate pressure data is calculated from the force to drive the piston into the high-pressure area minus the friction of the seals along the bore (**Fig. 47**). To bound the impact of seal friction, we move the piston forward and backward equal amounts around our pressure setpoint. When the piston moves forward/backwards, the friction acts in the positive/negative direction, respectively.

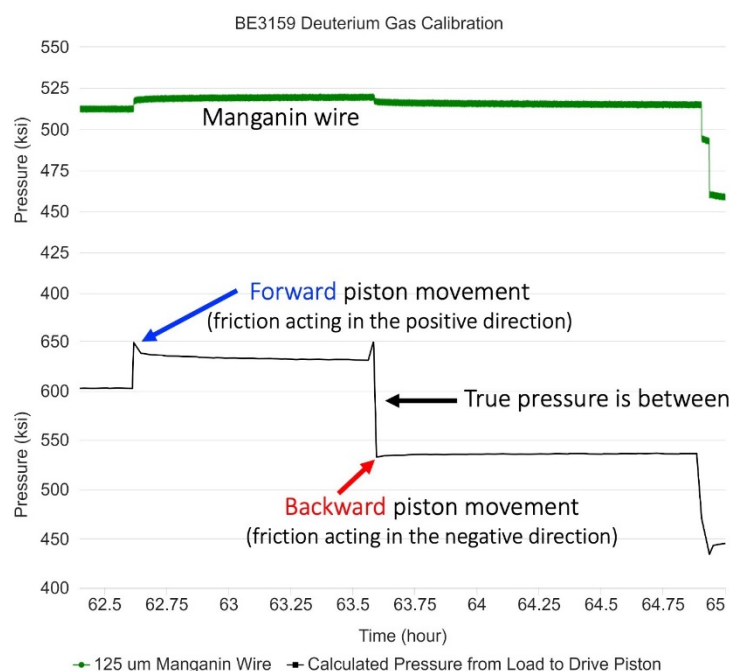


Fig. 47: Pressure measurements >300 ksi using a Manganin wire and load to drive the piston; forward & backward piston movements around the pressure setpoint bound the impact of seal friction on the load.

Hardware: Machine Shop

Due to our hardware quantity, exotic materials, and tight tolerances (e.g., 0.001 inch), fully outsourcing our parts to external machine shops became prohibitive in time. For example, vendors

²¹ L. Xiang, et. al., Rev. of Sci. Instr. 91, 095103 (2020)

²² R. Zeto et. al., J. of Appl. Phys. 50, 5 (1968)

often quote 6-8 week lead times for a single, tight-tolerance part with non-standard materials. Given the number of iterations required to achieve our record-setting hydrogen pressures (for large volume), we built an in-house machine shop to accelerate our cycle-times (**Fig. 48**). As an example, during our >300 ksi hardware project, our machine shop enabled >15 unique design iterations, made thousands of match-fit parts, and performed hundreds of part modifications over the course of about 4 months. If completely outsourced, the >300 ksi hardware project would have taken 5-10 years assuming a 4-8 week cycle time.



Fig. 48: Our in-house machine shop significantly accelerated our design-build-test-learn cycle-time.