

Chapter 3

Loading Measurements

3.1 Background and Literature Review

Given the fantasy and biasing that exists around studying LENR, Callisto sought to ground their research program in principles of physics and chemistry. Within this framework, one of our primary thrusts was to understand, control, and maximize deuterium loading in palladium and other relevant metals. Regardless of observing any excess heat, we could certainly develop methods for enhancing the fractional loading of hydrogen isotopes. Success depended on accurately measuring the hydrogen loading, exploring methods for increasing this loading, and ultimately optimizing these methods to yield the highest possible fractional loadings near ambient conditions.

The focus of this section is on measurement techniques that can be used to estimate the fractional loading of hydrogen in a metal hydride. The majority of our work was performed on palladium protide (PdH) and palladium deuteride (PdD), although Callisto did investigate a few other metal systems including palladium alloys, nickel, and several rare-earth metals. Not only is palladium considered a model system, but it is also widely believed to be the most relevant material for LENR. Herein, we will emphasize methods and literature that work well for palladium hydride, although these methods can be extended to other metal hydride systems.

We can classify loading measurements as either direct or indirect. In a direct loading measurement, the moles or mass of hydrogen is tracked directly. Typically, direct measurements offer higher measurement accuracy, given there is less error propagation. However, direct methods are typically more constrained, making it hard to apply an arbitrary form factor or in situ to an experiment. In contrast, indirect loading measurements offer more flexibility in experimental design, albeit at the cost of lower certainty.

In an indirect loading measurement, a proxy property is measured and is correlated with hydrogen loading, either using an empirical calibration or a first principles model. Any indirect loading measurement must be motivated by a first principles understanding of the hydrogenation process. Hydrogen atoms occupy octahedral interstitial sites in the face-centered cubic lattice of palladium, leading to its lattice expansion. The absorption of hydrogen into interstitial sites leads to significant alterations in the electronic structure, primarily through interactions between hydrogen atoms' electrons and palladium atoms' electronic states. The interstitial hydrogen atoms contribute their 1s electrons, which interact with the palladium d-band electrons, leading to hybridization and modification of the electronic structure. Additionally, palladium's s and p orbitals (5s and 5p) participate in hybridization, resulting in bonding and anti-bonding states that

affect the density of states at the Fermi level.

Due to the combined effects of electronic band structure changes and mechanical effects of interstitial occupation and atomic displacement, many electrical, mechanical, and optical properties change along a continuum as the fractional loading of hydrogen increases.

The following sections cover various methods used in the literature to measure hydrogen loading in palladium hydride.

3.2 Gravimetric Analysis

Mass loading, or gravimetric analysis, involves measuring the change in mass of the metal before and after hydrogen absorption. By accurately determining the mass difference, the amount of hydrogen absorbed can be quantified as follows:

$$x \text{ in PdH}_x : x = \frac{n_{\text{H}}}{n_{\text{Pd}}} = \frac{\Delta m}{m_{\text{Pd}}} \times \frac{M_{\text{Pd}}}{M_{\text{H}}} \quad (3.1)$$

Where $n_{\text{H,Pd}}$ are moles, m_{Pd} is the mass of palladium, Δm is the mass difference before and after hydrogen absorption, and $M_{\text{H,Pd}}$ are the molar masses.

This technique is straightforward but requires a precise balance and isolation from environmental variables. A modern scale has a typical precision of 100 μg , meaning that for a loading precision of 0.1 %, a minimum mass of palladium of 100 mg is required. Given these requirements, common form factors like wires and thin films may be limited in their use for gravimetric loading measurements due to their relatively small mass. For example, a 500-micron diameter palladium wire that is 30 mm long has a mass of approximately 70 mg, which is below the 100 mg threshold for the desired precision. Similarly, a thin palladium film with a thickness of 100 nm and an area of 1 cm^2 has a mass of about 120 μg , which is significantly less than the required mass for high-precision measurements.

Gravimetric methods are widely applicable to measuring hydrogen uptake in different materials and have been used for decades to characterize hydrogen loading in both elemental and composite systems [116–118]. Besides constraints around form factor, in-situ gravimetric analysis during electrolysis is prohibitive due to impurity depositions and moisture retention [119]. These issues necessitate the use of alternative measurement techniques, such as in-situ resistance or optical measurements to measure fractional hydrogen loading under electrochemical conditions.

3.3 Sievert Isotherm

Another common direct loading measurement is the Sievert method, which relies on measuring the pressure change in a closed system as hydrogen gas is absorbed by the metal [120]. Assuming first-order kinetics, the amount of hydrogen absorbed can be calculated using the ideal gas law and the known volume of the system:

$$x \text{ in PdH}_x : x = \frac{n_{\text{H}}}{n_{\text{Pd}}} = \frac{n_{\text{absorbed}}}{n_{\text{Pd}}} = \frac{1}{n_{\text{Pd}}} \frac{V \Delta p}{RT} \quad (3.2)$$

Where n_{absorbed} is the moles of hydrogen absorbed by the metal, n_{Pd} is the moles of metal, V is the system volume, R is the gas constant, T is the system temperature, and Δp is the pressure change after hydrogen absorption.

However, researchers have shown that the palladium hydride system deviates from this first-order behavior, primarily due to the dissociation of hydrogen being a rate-limiting step and the effects of concentration polarization, where the rate of hydrogen transport through a palladium membrane exceeds its supply from the bulk gas [121, 122]. As a result, a more complex model is required to accurately calculate hydrogen loading based on Sievert isotherms when using a membrane configuration. If bulk palladium is encapsulated in a closed system, the first order behavior captures the mass loading well-enough.

The Sievert method is also useful for characterizing the differences in hydrogen storage capacity between bulk and nanomaterials. For example, it was observed that palladium nanoparticles exhibit modified thermodynamics and kinetics for hydrogen storage compared to bulk palladium, including reduced hysteresis, lower desorption temperatures, and different enthalpy and entropy values [123].

Despite its advantages, the Sievert method has limitations. Sample form factor and reactor design can limit precision. For instance, to achieve 0.1% precision for a 70 mg wire, a pressure gauge with ~ 10 μ bar precision and a range of 10 mbar is required. Such experimental setups are neither accessible nor inexpensive. Similar to the gravimetric method, the Sievert method also improves with increased sample mass. Additionally, the Sievert method is specific to gas-loaded metal hydrides and is not readily translatable to electrolytically loaded metal hydrides due to gas evolution simultaneous with loading and dissolution of gas into the electrolyte.

3.4 Coulometry

Coulometry is an effective electrochemical technique for quantifying hydrogen or deuterium loading in palladium and palladium alloys [124, 125]. This method involves measuring the total charge passed during the oxidative discharge of hydrogen from the palladium, which can then be related to the amount of absorbed hydrogen. The coulometric analysis is based on Faraday’s laws of electrolysis, which states that the amount of a substance altered at an electrode during electrolysis is proportional to the total electric charge passed through the substance. In the context of hydrogen loading, the fractional loading is given by:

$$x \text{ in PdH}_x : x = \frac{Q}{Fn_{\text{Pd}}} \quad (3.3)$$

where Q is the total charge passed during the electrolysis, F is Faraday’s constant (approximately 96,485 C/mol), and n_{Pd} is the number of moles of palladium atoms.

Despite its facile implementation, coulometry does have its limitations. Ideally, a flow cell geometry is used, which mitigates the hydrogen oxidation reaction which convolutes the electron flow and can lead to overestimates in loading [126]. In multi-modal studies that use complementary loading measurements, it was found that the method is most accurate for low fractional loadings [127]. Additionally, the use of additives in the electrolyte can introduce inaccuracies due to the presence of other Faradaic processes. For instance, arsenic salts (extremely relevant to subsequent discussion) can significantly affect the measured loading levels due to concurrent oxidation reactions during discharge [128]. For this reason, early in Callisto’s investigations, it was concluded that coulometry was incompatible with additive-based loading enhancement strategies. As such, the focus shifted to methodologies that did not require a complete understanding of the Faradaic reactions present in an experiment.

3.5 Quartz Crystal Microbalance

Quartz crystal microbalances (QCMs) are another valuable tool for studying hydrogen storage materials, capable of detecting minute mass changes on the order of nanograms, allowing for precise and quantifiable measurements of hydrogen uptake in thin films [129–131]. Not only can QCMs be used to quantify loading in thin film metal hydrides, but they are also versatile and can be adapted for use in different environments including electrochemical cells and gas-loading cells [126, 132]. QCMs provide real-time, sensitive measurements of mass changes associated with hydrogen absorption and desorption in palladium and its alloys, offering insights into the loading processes and material behaviors [133].

QCMs operate by measuring the frequency shift of a quartz crystal resonator as a thin film of palladium absorbs or desorbs hydrogen. The mass change associated with hydrogen uptake or release induces a corresponding shift in the resonant frequency, which can be quantitatively related to the amount of hydrogen absorbed, given by the Sauerbrey equation:

$$\Delta m = -\frac{\Delta f A}{2f_0^2} \sqrt{\frac{\mu_q}{\rho_q}} \quad (3.4)$$

Where Δf is the change in resonant frequency, f_0 is the fundamental frequency of the quartz crystal, A is the area of the crystal, ρ_q is the density of quartz, μ_q is the shear modulus of quartz, and Δm is the mass change.

However, the frequency shift measured by QCMs is not solely due to mass changes but also includes contributions from stress within the palladium film as it expands or contracts during hydrogen absorption and desorption. This complicates the interpretation of data and requires careful analysis to separate mass and stress. Additionally, rough or irregular surfaces may introduce additional frequency shifts unrelated to mass changes, leading to errors in loading estimates. External factors such as temperature fluctuations, pressure variations, and the presence of contaminants can impact QCM measurements as well. These need to be carefully controlled and accounted for during experiments to ensure reliable loading estimates. Given these corrections, one can use the modified Sauerbrey equation to calculate mass change in hydrogen-loaded thin films:

$$\Delta m = -\frac{A}{2f_0^2} \cdot \sqrt{\frac{\mu_q}{\rho_q}} \cdot (\Delta f - C_\sigma \Delta \sigma - C_r \Delta r) \quad (3.5)$$

Where additional terms: C_σ is a system-dependent stress coefficient, $\Delta \sigma$ is the change in stress due to hydrogenation, C_r is a system-dependent roughness coefficient, and Δr is the change in roughness due to hydrogenation.

In addition to providing quantitative loading for thin film metal hydrides, QCMs are particularly useful for investigating isotopic effects, such as differentiating between protium (H) and deuterium (D) absorption in palladium. The mass difference between these isotopes leads to distinct frequency shifts, and deuterium loading resulting in a larger frequency change compared to protium due to its higher atomic mass.

In Callisto's efforts to use QCM measurements to quantify loading in thin film systems, several challenges arose when using chemical enhancement to increase the deuterium loading, including stress corrections, motional resistance corrections, and catastrophic blistering of the film, which led to large errors in the QCM signal. As a result, we did not find QCMs a useful method for measuring loadings over 80% in thin films.

3.6 Macrostrain

The use of strain measurements to quantify hydrogen loading in palladium dates back to the 1800s. This method can be performed using optical strain measurements, strain gauges, or X-ray diffraction techniques [134, 135]. For palladium hydride, the strain induced by hydrogen loading increases linearly with fractional hydrogen loading. Fig. 3.2 a) illustrates various loading-strain relationships reported in the literature, with a broad range in slopes. For this discussion, we will use the following relationship:

$$x \text{ in PdH}_x : x = 17\epsilon = 17 \frac{L - L_0}{L_0}, \quad (3.6)$$

where ϵ is the strain, L is the length and L_0 is the initial length.

As mentioned previously, the strain can be measured with either strain gauges monitoring the macrostrain, or with X-ray diffraction monitoring the lattice expansion.

3.7 Optical Reflectivity

For palladium hydride and other metal hydride systems, the optical properties of the material change continuously with hydrogen uptake [136–139]. This continuum can be leveraged to estimate the fractional hydrogen loading. The most fundamental optical constants that can be calculated are the permittivity coefficients for a material, ϵ_1 and ϵ_2 . However, these require detailed modeling to arrive at accurate numbers [140]. Another complicating factor is that surface roughness on the order of the studied wavelength can influence the optical parameters that are measured. For instance, it has been observed that the substrate material and the evolution of surface roughness of palladium significantly affected its optical response to hydrogen [141]. Due to this, it is challenging to use reflectance-based approaches on bulk metal hydrides.

However, the substrate constraint in a thin film structure allows for more precise control and measurement of the optical response. By monitoring backside reflectance in a thin film device, one can effectively estimate fractional hydrogen loading. Despite roughening at the frontside palladium-electrolyte interface, the backside palladium-substrate interface remains smooth during hydrogen cycling. This methodology, as it applies to thin film metal hydrides, will be discussed in more detail in a section 3.14, as it was critical for Callisto’s investigation into loading enhancers.

3.8 Thermal Desorption Spectroscopy

Thermal desorption spectroscopy (TDS) provides insights into hydrogen content and binding energy by heating the metal hydride and measuring the desorbed hydrogen as a function of temperature. TDS’s ability to produce detailed desorption profiles enables differentiation between various hydrogen trapping sites and the analysis of a variety of metal hydrides [142–146]. Specifically, it can examine differences in binding energies and the amount of surface versus bulk-absorbed hydrogen. Despite its high sensitivity, capable of detecting hydrogen at ~1 wt. ppm, phase transitions, and complex desorption processes may require data modeling for accurate interpretation of results. Additionally, water absorption can significantly affect measurements, necessitating careful handling in an inert atmosphere. Given these experimental constraints, TDS is unsuitable for measuring hydrogen loading in electrolytically loaded metal hydrides.

3.9 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) works by exploiting the magnetic properties of atomic nuclei. When placed in a strong magnetic field, nuclei with a magnetic moment (such as hydrogen) can absorb and re-emit electromagnetic radiation at a characteristic frequency. This frequency is influenced by the local environment of the nuclei, including electronic structure and interactions with neighboring atoms. By analyzing the resulting NMR spectra, information about the hydrogen atom's local environment, such as the number of hydrogen atoms and their local environment can be obtained. This makes NMR a powerful tool for directly probing the proton population inside the metal lattice [147–152]. However, its use is limited to the expensive nature of the measurement equipment.

3.10 Neutron Scattering

Neutron scattering (NS) and small-angle neutron scattering (SANS) are analogous techniques to X-ray scattering methods, used to measure the scattering patterns of neutrons to determine the distribution and quantity of hydrogen within a metal lattice. Despite neutrons' direct interaction with lattice-bound protons, neutron scattering is considered an indirect measurement due to the need for a complex physical model to determine fractional hydrogen loading.

NS measurements in palladium protide and palladium deuteride confirmed that hydrogen atoms occupy octahedral positions in the face-centered cubic (fcc) palladium lattice [153]. Other early NS studies on the thermal motion in palladium hydride showed that hydrogen atoms have isotropic thermal motion within the palladium lattice [154]. Additionally, NS methods are valuable for characterizing the electron and phonon band structures of palladium and palladium hydride, important for understanding the material's thermal response and hypothesizing effective stimulation schemes [155].

While NS and SANS are powerful techniques for characterizing hydrogen loading in palladium hydride, providing deep insight into structural and thermochemical behavior, they are fairly inaccessible as large-scale scientific facilities are required to perform these measurements.

3.11 Resistance-based Loading Measurement

Electrical resistivity is probably the most widely used indirect method to estimate fractional hydrogen loading in palladium hydrides [156–165]. The primary reason for this is the continuous change in electrical resistivity with hydrogen absorption, which allows for facile, in-situ monitoring of hydrogen content. As hydrogen atoms are absorbed into the palladium lattice, they initially act as scattering centers for conduction electrons, leading to an increase in electrical resistivity. This increase continues until about 75% hydrogen loading at room temperature. However, as hydrogen loading continues to increase towards stoichiometric unity (PdH), the resistivity starts to decrease. This decrease at high fractional loading can be attributed to the donation of electrons to the conduction band, where the scattering from hydrogen atoms becomes less effective.

One of the advantages of using electrical resistivity is its capability for in-situ monitoring. This is particularly useful in dynamic systems where hydrogen cycling is critical. Additionally, the method is relatively straightforward to implement in both electrolytic and gas-loading schemes. It involves simple electrical measurements, which can be easily integrated into various experimental setups. Finally, electrical resistance measurements are non-destructive, allowing for continuous monitoring without affecting the sample.

However, the method is not without its challenges. The relationship between hydrogen loading and electrical resistivity is not linear. The resistivity increases with hydrogen uptake until about 75% loading, after which it decreases, leading to a non-linear relationship with two possible loading values for any particular resistance. This double-valued property can complicate the interpretation of the data, particularly near the maximum in the resistivity versus loading curve. There are also discrepancies in the literature regarding the exact mapping between hydrogen loading and resistivity changes. These discrepancies can arise from various factors, including differences in the palladium samples' form factor, the resistance measurement implementation, and experimental conditions such as temperature and reactor cleanliness. Additionally, as hydrogen is absorbed into the palladium lattice, it can induce stress and create defects, which further impact the electrical resistivity. These additional factors need to be considered when interpreting resistance measurements.

To address some of these challenges, Zhang et al. derived an empirical formula based on literature that provides a reasonable mapping between fractional loading and resistivity changes for PdH_x and PdD_x [166]. This formula provides an accurate representation of the relationship. According to Zhang et al., the fractional loading can be described by the following equations:

$$\frac{R_{\text{PdH}_x}}{R_{\text{Pd}}} = 1 + 1.69731x - 5.34162x^2 + 13.4472x^3 - 9.87644x^4, \quad (3.7)$$

$$\frac{R_{\text{PdD}_x}}{R_{\text{Pd}}} = 1 + 1.88402x - 6.94933x^2 + 17.2941x^3 - 12.0073x^4, \quad (3.8)$$

where R_{Pd} is the initial palladium resistance and R_{PdH_x} , R_{PdD_x} are the resistances of palladium protide and palladium deuteride, respectively.

3.11.1 Practical Implications

The resistivity of palladium is $1.05 \cdot 10^{-7} \Omega\cdot\text{m}$. A typical sample, e.g., a 25 mm long, 0.5 mm diameter wire has a resistance of 13.4 m Ω . Samples with larger ratios of cross-sectional area to length, e.g., thicker wires, foils, rods, often have even lower resistances in the m Ω or $\mu\Omega$ range.

In order to measure these low resistances, a four-wire measurement is necessary. The measurement current is introduced into the sample through two leads connected to the ends of the sample, while the voltage difference is measured between the sense leads, which are attached to the sample between the current leads. This way, contact resistances are minimized and resistances within the current leads are excluded from the circuit. Maximum test currents for resistance measurements are often 1 mA (e.g., NI PXIe-4071 digital multimeter), resulting in voltages of a few μV . In order to increase the voltage signal, higher probe currents can be applied using a source measure unit (SMU) instead of a digital multimeter (DMM). Source and sense leads are attached to the sample either through laser welding or through clamping (Fig. 3.1). We found that repeated loading and deloading can affect the robustness of laser welds, but clamping the lead wires (instead of laser welding) is a reliable contacting method in this case.

If resistance measurements are performed in situ, co-conductance through the electrolyte must be considered, but it is significant only for very thin wire samples. For a 25 mm long, 0.5 mm diameter wire sample in 0.5 M LiOH, the electrolyte resistance is $\sim 1000 \times$ the sample resistance.

If the resistance is measured in situ in the presence of an electrochemical bias, crosstalk between these two signals can occur. As the electrochemical current flows through the cathode to different extents before it flows through the electrolyte to the anode, it creates a superimposed voltage gradient within the cathode,

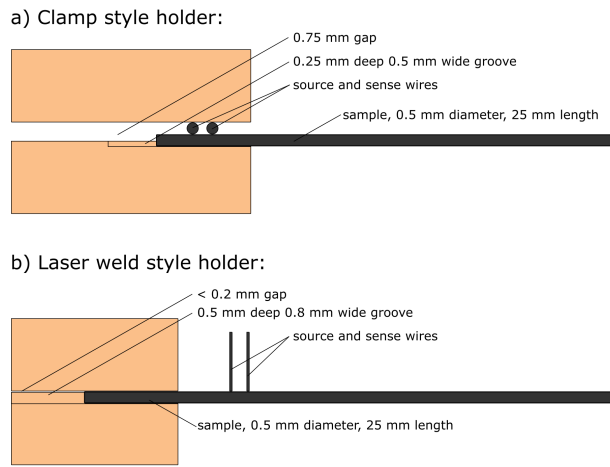


Fig. 3.1: Methods to connect leads (for resistance measurement or electrochemical current) to wire samples: a) clamp style or b) laser weld. In the clamp style holder, the clamps are pressed together using PEEK screws. The source and sense wires are 0.5 mm diameter platinum wires, which are in turn laser-welded to insulated copper leads. In the laser weld style holder, source and sense leads are typically 0.13mm diameter platinum wire coated with PFA (A-M Systems) laser welded directly to the palladium sample. Drawing is not to scale.

depending on the electrochemical current, the electrolyte resistance and the cathode resistance. The variation in electrolyte resistance due to bubbling can cause fluctuations in that superimposed voltage difference, complicating the measurement of the cathode resistance. To disentangle the two potentials, we can apply the resistance measurement probe current using a lock-in amplifier (Zurich Instruments MFLI). It overlays a harmonic reference current on top of the electrochemical current and can demodulate the measured signal to extract the in-phase component, from which the sample resistance can be calculated. For the HTcal (section 2.9.1), we emulated the lock-in principle digitally, taking advantage of the microsecond time resolution of the NI PXIe-4139 source measure unit. To cancel out the potential contribution from the electrochemical current, the resistance probe current follows a square wave with an amplitude of 100 mA centered around 0 mA, i.e. it covers both polarities. Four square waves (each with 10 sampling points) with a period of 1 ms are applied for each resistance measurement (typically 1 Hz).

One thing to note is that strictly speaking only the resistivity ρ is a material property, while the resistance R is the quantity being measured. They are related by

$$R = \rho \frac{L}{A}, \quad (3.9)$$

where L is the length and A is the cross-sectional area. It is frequently observed that the sample changes its geometry upon cycling (loading and deloading). Straight wires can end up curved. More importantly, they tend to become shorter and thicker with the number of loading cycles, decreasing the resistance [167]. This is likely due to the loading gradient (caused by diffusion kinetics) during the initial phase of the loading. With the core experiencing less volumetric strain than the shell, the shell will expand radially more than axially. This should be reversible upon deloading, but in practice we have seen wires remaining bent after deloading

and becoming shorter over several loading cycles, depending on the sample retention and sample geometry. Additionally, repeated loading and deloading can introduce defects into the palladium lattice, increasing the resistance. Both effects mean that after a load-deload cycle the resistance ratio (sample resistance normalized with the initial resistance of the deloaded sample) rarely falls exactly on 1 and is typically suppressed by a few percent. In order to measure the loading for the subsequent cycle, we re-normalize the resistance ratio. We expect slight deviations from the established loading-resistance relationships depending on the microstructure (grain size, defect density caused by cycling or annealing), however these effects have not been quantified.

While often a single loading value is taken to represent the entire sample, in practice we have frequently observed non-uniform loading within a sample. In samples with large cross-sectional area, the diffusion of hydrogen through the palladium lattice considerably slows down the loading and deloading kinetics. Depending on the current, in a >1 mm thick wire it can take more than an hour to achieve uniform loading throughout the cross-section. We have shown that thinner wires load faster than thicker wires. During the loading transient, surface-sensitive and bulk-sensitive methods are expected to yield different loading values.

Similarly, loading gradients along the length of the sample have been identified. This is most pronounced when the ends of the sample are occluded from electrolyte exposure, e.g., due to being mounted into a sample holder. The occluded surface means that this area is not available for Volmer reactions and hydrogen insertion. Hence, the underlying palladium can only load through diffusion from non-occluded parts of the sample. Accordingly, we have measured higher loadings in the center section of a sample compared to the entire sample, which included the occluded areas due to sample clamps. For this experiment, we have attached multiple sense leads (0.13 mm diameter Pt wire coated with PFA, A-M Systems) to various segments of the wire sample by laser welding.

3.12 X-ray Diffraction

X-ray diffraction (XRD) has been extensively used to study hydrogen absorption dynamics and structural changes in palladium [40, 168–172]. The advantages of using XRD-based strain measurements include high precision and the ability to provide detailed information about the crystallographic structure and internal stresses of thin films and low-mass samples. XRD is non-destructive and can be used in-situ to monitor real-time changes during hydrogen cycling. However, there are disadvantages as well. The methodology requires highly controlled conditions and sophisticated equipment, which can limit its accessibility. Despite these limitations, the benefits of XRD in providing detailed, accurate strain measurements make it very useful for estimating hydrogen loading of palladium hydride.

To estimate strain from X-ray diffraction, we must invoke Bragg’s law:

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.10)$$

where n is the order of the reflection, λ is the wavelength of the incident X-ray, d is the spacing between crystal planes with Miller indices hkl , and θ is the angle of incidence. By measuring the shift in the diffraction peak positions ($\Delta\theta$) one can calculate the change in d-spacing (Δd), which directly relates to the strain in the material.

Palladium is typically a polycrystalline material, and so is palladium hydride. With the insertion of hydrogen on the interstitial octahedral sites during loading (gas or electrochemical), the palladium host lattice expands. Due to the inverse relationship between the reciprocal space, represented by the X-ray diffraction pattern, and the real space, the diffraction peaks shift to smaller diffraction angles as the lattice

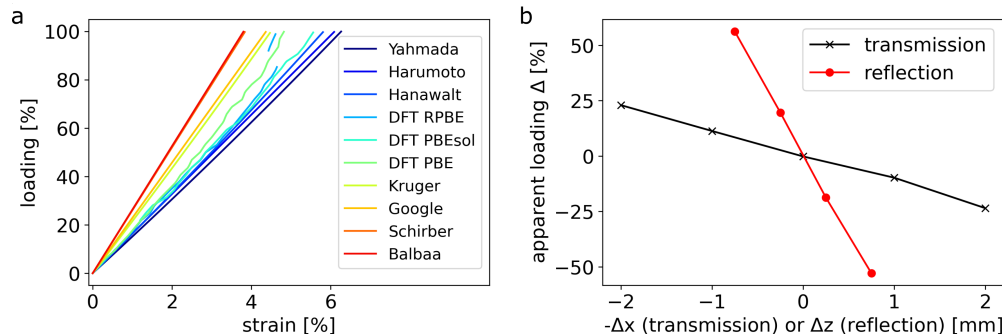


Fig. 3.2: a) Strain-loading relationships reported in the literature by Yahmada [173,174], Harumoto [175,176], Hanawalt [173,177], Kruger [178], Google [179], Schirber [173,180], Balbaa [181] and computed using DFT [182]. b) Effect of sample misalignment due to buckling (in transmission of reflection geometry) on change in apparent loading, resulting from apparent strain from XRD peak shift.

expands during hydrogen loading. Thus, from the shifts in X-ray diffraction peaks (e.g., (111) or (200) peaks), the lattice strain can be computed and hence the degree of loading can be derived qualitatively. The precise relationship between the lattice strain and hydrogen loading however is not known a priori. Various relationships can be found in the literature, sometimes with rather poor agreement (Fig. 3.2 a). This makes XRD an indirect loading measurement method. On the other hand, while the precise relationship between lattice strain and loading is not known, theory and experiments suggest that the relationship is monotonous, i. e., the higher the strain, the higher the loading. Hence, XRD is a useful method to rank the loadings of various palladium hydride samples, e. g. as a function of electrochemical current, loading enhancer or sample preparation.

In order to avoid outgasing of the sample during handling, we designed and built an in-situ XRD apparatus, acquiring diffractograms of palladium hydride while the sample was in electrolyte and electrochemical bias was applied. While these types of in-situ experiments are typically performed at synchrotron X-ray sources, we resorted to a rotating anode laboratory source with molybdenum as anode material. Compared to the more commonly used copper anode, the shorter wavelength of the Mo K α spectral line (0.71 Å vs. 1.54 Å) results in a much longer attenuation length in water (1 cm vs. 1 mm). For the X-ray to interact with the sample, two geometries are common: reflection and transmission (Fig. 3.3). In the reflection geometry, the X-ray hits the sample at an incident angle, which is typically chosen to be the same as the diffraction angle in order to maximize signal (and minimize absorption by electrolyte). This geometry probes the top tens of μm of the sample. The advantage is that wires, foils as well as films can be probed. The downside is that the thickness of the electrolyte layer on top of the sample must be kept to a minimum in order to avoid excessive X-ray attenuation due to the long path length at the incident angle ($\sim 9^\circ$ for (111) peak). Too thin of an electrolyte layer makes it difficult to obtain a uniform electric field around the working electrode and hydrogen bubbles on top of the electrode extending through the electrolyte layer might present an unfavorable deload pathway. In practice, the main difficulty with reflection geometry was that buckling of the sample (palladium foil or wire) during loading led to major diffraction peak shifts, despite keeping the sample under slight tension with a spring mechanism. A theoretical comparison of the effect of sample misalignment (due to buckling) on XRD peak position is shown in Fig. 3.2 b). We considered accounting for the peak shift using crystalline reference materials on the surface of the palladium sample, but determined

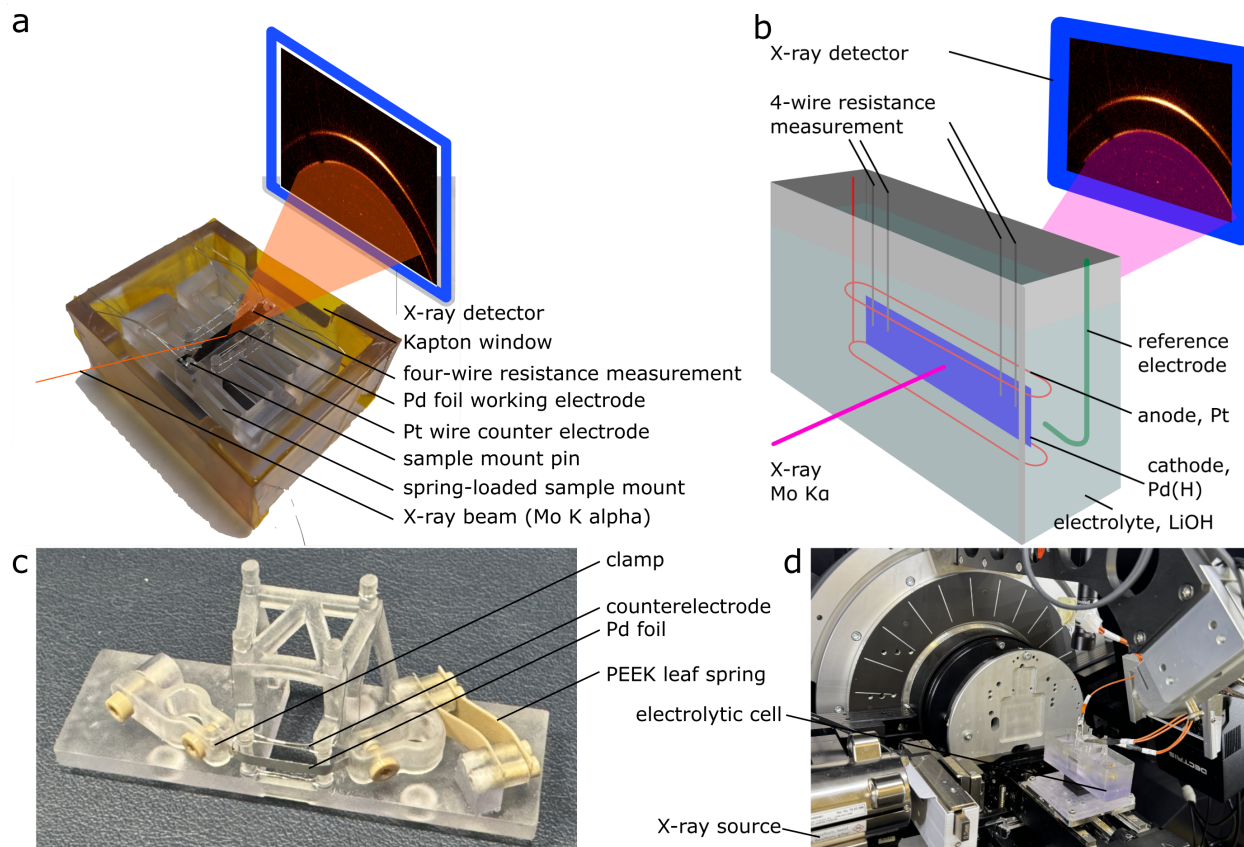


Fig. 3.3: Devices for in-situ XRD during electrochemical loading: a) Schematic of reflection geometry setup; b) Schematic of transmission geometry setup; c) Photograph of transmission geometry setup without vessel; d) Photograph of transmission geometry setup in X-ray diffractometer

that this would alter the loading.

For that reason, we abandoned the reflection geometry and implemented an in-situ vessel with transmission geometry. This geometry limits the choice of samples to foils, typically 50 μm thin, 30 mm long and 3 mm wide. The sample is held under slight tension by PEEK leaf springs, keeping buckling to a minimum (Fig. 3.3). A sophisticated mechanism avoids overconstraining the foil, thus eliminating out-of-plane displacement, keeping the sample-to-detector distance constant. During the in-situ XRD experiment, electrochemical voltage (using a NI PXIe-4138) is applied between the palladium foil and a platinum counterelectrode, made from 0.5 mm wire, at an electrode spacing of 4 mm, submerged in 0.5 M LiOH aqueous electrolyte. The resistance of the palladium foil is measured using a four-wire measurement in the same manner as in the HTcal (i. e., employing a square wave on a precision source measure unit (NI PXIe-4141), see section 2.9.1). The experiments were performed on a Bruker D8 Discover. XRD exposure times were typically 200 s, with about 30 s of dead time between exposures. Data analysis was performed in the Bruker Diffrac.Eva software and Python. An example XRD experiment is illustrated in Fig. 3.4. It shows the transition from the α

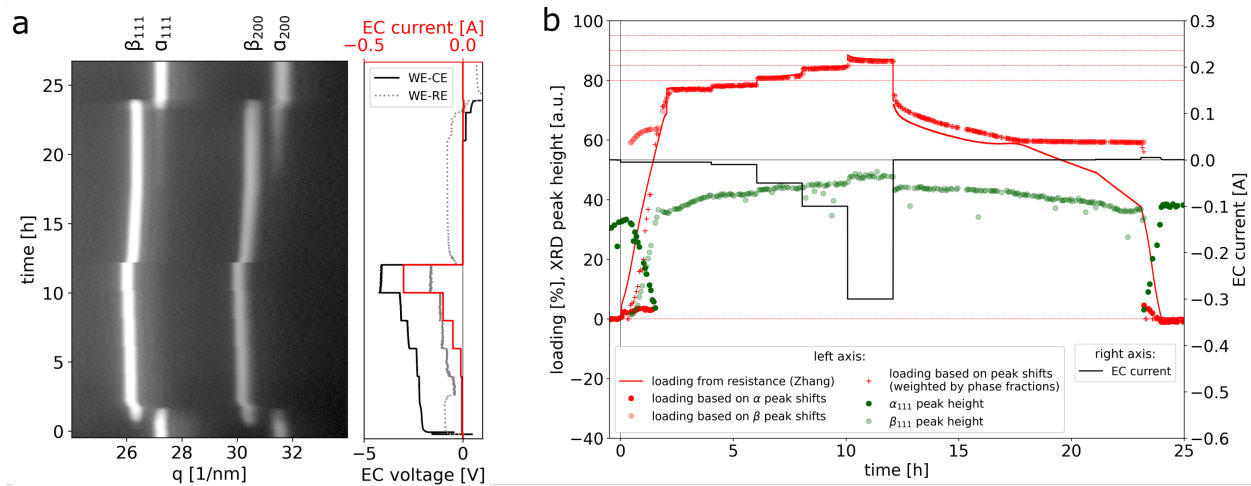


Fig. 3.4: Example of XRD results: a) Waterfall plot (time vs. scattering vector magnitude q) from an in-situ load-deload experiment, assembled from 2D diffractograms. The brightness represents the scattering intensity. The right panel shows the loading conditions (current and voltage). b) Derived quantities (lattice strain, loading from peak shift using DFTsol conversion, loading from resistance ratio using Zhang conversion) from the same experiment.

phase (which barely loads) to the β phase, which starts highly loaded and increases in loading as well as in phase fraction as the loading progresses. Upon cessation of electrochemical bias (~ 12 h), the lattice contracts and, as the bias is reversed, transitions back to the α phase, with some transient co-existence of α and β phases.

3.13 Orphaned Oxygen

Among other methods, the partial loading of deuterium (D) and hydrogen (H) into the palladium (Pd) lattice was calculated by measuring the orphaned oxygen in the headspace of the thermodynamically closed calorimeter. The intercalation of hydrogen into the palladium lattice leads to a non-stoichiometric mixture of oxyhydrogen gas and assuming perfect recombination, the pressure increase upon application of electrolytic current can be used to estimate the hydrogen locked into the Pd lattice. If the headspace volume and the Pd mass are well defined, the moles of orphaned oxygen can be related to the H and D loading using the equation below. This oxygen remains "orphaned" until the sample is deloaded and the hydrogen is made available to recombine with the oxygen.

$$n_{O_2} = \frac{V_{Pd} \rho_{Pd} x}{4M_{Pd}} \quad (3.11)$$

Eq. 3.11 describes how orphaned oxygen can be calculated based on the volume, density, and loading fraction x of the Pd cathode where n_{O_2} are moles of orphaned oxygen, V_{Pd} is the volume of the Pd cathode, ρ_{Pd} is the density of Pd, M_{Pd} is the molar mass of Pd. Once the expected moles of orphaned oxygen are calculated the pressure exerted by the newly produced gas in the head space can be calculated. For example, a 70 mg

Pd wire, in a 60 ml headspace, at 90% H loading, and 30°C yields about 0.289 mmol of n_{O_2} . Using the ideal gas law, the pressure exerted by these moles of oxygen in our 60 ml headspace can be calculated to be 0.120 atm (1.76 psi) of oxygen gas in the headspace.

Of course, this process can be reversed to estimate loading percentages of the Pd cathode, in addition to or in the absence of resistance measurements. In our experiments, this lack of reliable resistance measurement usually occurs in Pd and Pd alloy samples with low aspect ratio as it is challenging to measure resistances less than a milliohm accurately. Pressure increases from orphaned oxygen can be converted to moles of n_{O_2} and plugged into a rearranged version of Equation 3.11 to solve for x . While this is a viable method to approximate loadings in the absence of resistance measurements, the accuracy of the loadings determined by orphaned oxygen calculations can vary between 10 to 20 % from actual loadings when compared to control experiments using four-point resistance measurements. Ultimately, we found that not all observed pressure increases were due to orphaned oxygen. Many times, when the loading could be considered stable, the pressure would fluctuate due to variations in recombination reaction rates. In a few cases, we observed pressure buildup due to inactive recombiners, which sometimes was relieved by abrupt recombination (detonation of oxyhydrogen), resulting in a heat flow spike.

While we've discussed the value of using orphaned oxygen to calculate loading in the absence of electrical resistance data, assumptions regarding our system's Faradaic and recombiner efficiency are made. Firstly, we assume near 100% faradaic efficiency in our system, meaning that all our applied current goes to electrolysis, and we use that assumption to calculate our expected gas production. Of course, this assumption does not always hold true in an aqueous electrochemical environment with metal components despite our best efforts to mitigate side reactions. Secondly, we assume our activated carbon-Pt recombiner packets operate at a constant 100% efficiency, preventing the build up of gases from electrolysis in the headspace. Recombiner efficiency is not always 100% as we have observed large pressure increases after loading equilibrates suggesting that gases produced outside of loading are not being recombined. Given these conditions, without a dedicated mass spectrometer (MS) it is difficult to reliably deconvolute the two gas streams produced from electrolysis and orphaned oxygen from loading.

Another consideration when using orphaned oxygen to calculate H loading is the need for a well-defined system boundary with reliable pressure sensors. Without a sealed vessel, orphaned oxygen would leak from the vessel and there would be no way to accurately measure the production of gas. Simultaneously, it is also necessary to create a fail-safe against over pressurization of the vessel which can lead to dangerous failure of the hardware. In our systems we use back-pressure lines connected to a valve that acts as a pressure relief valve to prevent over pressurization. While in closed systems unintentional leaks must be avoided for accurate measurement, measuring gaseous products in a semi-open system using mass flow meters is a viable and well-established strategy in the field of HER and CO₂ reduction (CO₂ R) [183]. Whether in a fully sealed system using pressure sensors or in a semi-open system with mass flow meters, sensitive and robust hardware are necessary to measure deviations from expected gas production from electrolysis.

As a final note, non-faradaic and unintended faradaic reactions must be considered when using orphaned oxygen as a proxy for loading. Non-faradaic processes leading to other gases being produced could also lead to erroneous measurements in the amount of orphaned oxygen in the head space as other gaseous products can be produced. An example of this would be using additives such as ammonia to enhance loadings, where unintended faradaic electrochemical processes (i.e. electrolysis of ammonia at the cathode) produce nitrogen, hydrogen, and some gaseous ammonia which can severely skew the orphaned oxygen pressure contributions. To avoid this, careful attention to experimental design, specifically the system's composition and reactions pathways, is essential. One way to avoid this is doing proper control experiments and measuring electrolyte change and measuring headspace composition of the gaseous product with gas chromatography.

3.14 Thin Film Reflectance

3.14.1 Theory

The intercalation of hydrogen into palladium and other metals significantly alters their optical properties due to changes in their electronic structure. When hydrogen atoms are absorbed into a metal lattice, they introduce additional electrons, modifying the electronic density of states near the Fermi level. This process leads to a narrowing of the d-band and an increase in s-p hybridization, impacting both interband and intraband transitions. Interband transitions occur when electrons are excited from the valence band to the conduction band, contributing significantly to the absorption spectrum. Intraband transitions, on the other hand, involve the excitation of lower energy electrons within the conduction band to higher energy states in the same band, affecting the material's reflectivity.

The electronic structure of a metal can be described by the density of states (DOS), $g(E)$, which represents the number of electronic states at each energy level that are available to be occupied by electrons. When hydrogen atoms intercalate into the palladium lattice, they introduce additional states and alter the existing ones. This can be modeled as:

$$g(E) = \sum_k \delta(E - E_k) \quad (3.12)$$

where $g(E)$ is the DOS at energy E , E is the energy at which the DOS is being calculated, E_k are the discrete energy levels of the electrons in the system with the index k representing different quantum states, and δ is the Dirac delta function. This function is zero everywhere except at $E = E_k$, where it is infinite, and its integral over all space is equal to one. Essentially, it "picks out" the energy levels E_k and contributes to $g(E)$ only at those specific energies. Therefore, equation (1) represents the sum of Dirac delta functions centered at each energy level E_k , ensuring that the DOS is non-zero only at the discrete energy levels E_k . In other words, it counts the number of states at each energy level.

The DOS plays a crucial role in determining the optical properties of a material, as it influences how electrons interact with photons. The connection between DOS and optical properties can be established through the material's dielectric function or permittivity $\epsilon(\omega)$, which governs the material's response to an external electromagnetic field. The dielectric function $\epsilon(\omega)$ is related to the electronic structure and the transitions between energy states in a material. The real part of the dielectric function $\epsilon_1(\omega)$ and the imaginary part $\epsilon_2(\omega)$ can be derived from the electronic band structure and the DOS. $\epsilon_1(\omega)$ represents the dispersive response of the material, indicating how the phase velocity of light is affected as it propagates through the material, while $\epsilon_2(\omega)$ represents the absorptive response, indicating how much energy from the light is absorbed by the material. The Kramers-Kronig relations express the fact that the real and imaginary parts of a complex function (like the dielectric function) are not independent but are related through integral transforms. These relations are derived from the principle of causality, which states that the response of a system to an external perturbation cannot precede the perturbation itself. This interdependence is characterized as [184]:

$$\epsilon_1(\omega) = 1 + \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon_2(\omega')}{\omega - \omega'} d\omega' \quad (3.13)$$

$$\epsilon_2(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon_1(\omega') - 1}{\omega - \omega'} d\omega' \quad (3.14)$$

$$\epsilon(\omega) = \epsilon_1(\omega) - i\epsilon_2(\omega) \quad (3.15)$$

In palladium hydride, as the hydrogen content increases, the real part of the dielectric function $\epsilon_1(\omega)$ increases in the near-infrared range, while the imaginary part $\epsilon_2(\omega)$ decreases. This makes the material less metallic and more transparent. As a result, one can correlate the change in reflectivity to the fractional loading of hydrogen in the metal lattice. The reflectivity, R , of a material can be related to its permittivity function by:

$$R = \left| \frac{\sqrt{\epsilon(\omega)} - 1}{\sqrt{\epsilon(\omega)} + 1} \right|^2 \quad (3.16)$$

Metals other than palladium may undergo more or less dramatic changes to their optical properties. For example, magnesium, titanium, and certain rare earth metals undergo a more dramatic transformation from a highly lossy metal to an insulator upon full hydrogenation. On the other hand, zirconium shows relatively minor changes in its optical properties with hydrogen intercalation, with only the imaginary part of the dielectric function increasing, indicating a slight increase in absorption.

Given this first principles understanding of the optical response to hydrogen intercalation, Callisto set out to design a measurement apparatus that could be used to quantify the fractional loading of hydrogen in palladium, with the ultimate goal of using this apparatus to rapidly identify and optimize additive-based loading enhancers. Despite this fundamental understanding, to make this measurement work in practice, we needed to calibrate the method against another vetted loading measurement. In subsequent sections, we will highlight how we used both quartz crystal microbalances and x-ray diffraction to arrive at a quantitative mapping between reflectance and fractional hydrogen loading. For the remainder of this section, we will highlight the hardware, the results of the calibrations (not the methods), and several case studies that were investigated using this calibrated reflectance method.

3.14.2 Reflectance Hardware

Callisto leveraged its engineering resources to design and implement custom reflectance-based loading measurements. Over the course of our investigations, we deployed several generations of reflectance hardware. The first generation of hardware used a supercontinuum laser with a wide range of wavelengths. The setup, shown in Fig. 3.5, involved splitting light from the laser with a beam splitter, directing one path to a spectrograph for analysis and the other to reflect off the sample. A detector measured the reflected light, allowing us to probe how reflectivity across the visible and near-IR spectrum changes with loading. An example of the hardware setup used for these measurements is shown in Fig. 3.6, and includes fiber controls and electronics, an active stabilization system with a 6-axis stage, and a MEMS mirror for fine adjustments. The fiber optics system ensures precise delivery and collection of light, while the active MEMS stabilization maintains alignment and minimizes vibrations, crucial for accurate measurements with minimal drift.

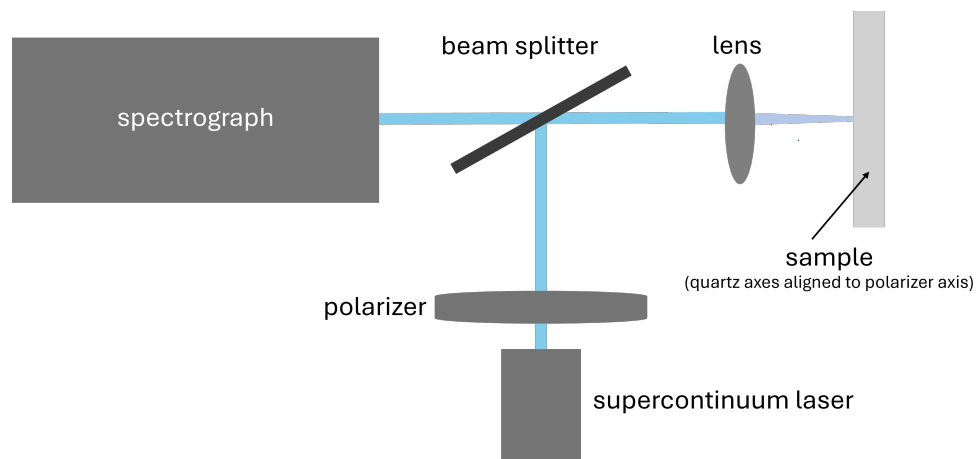


Fig. 3.5: Schematic of first generation reflectance hardware setup using supercontinuum laser.

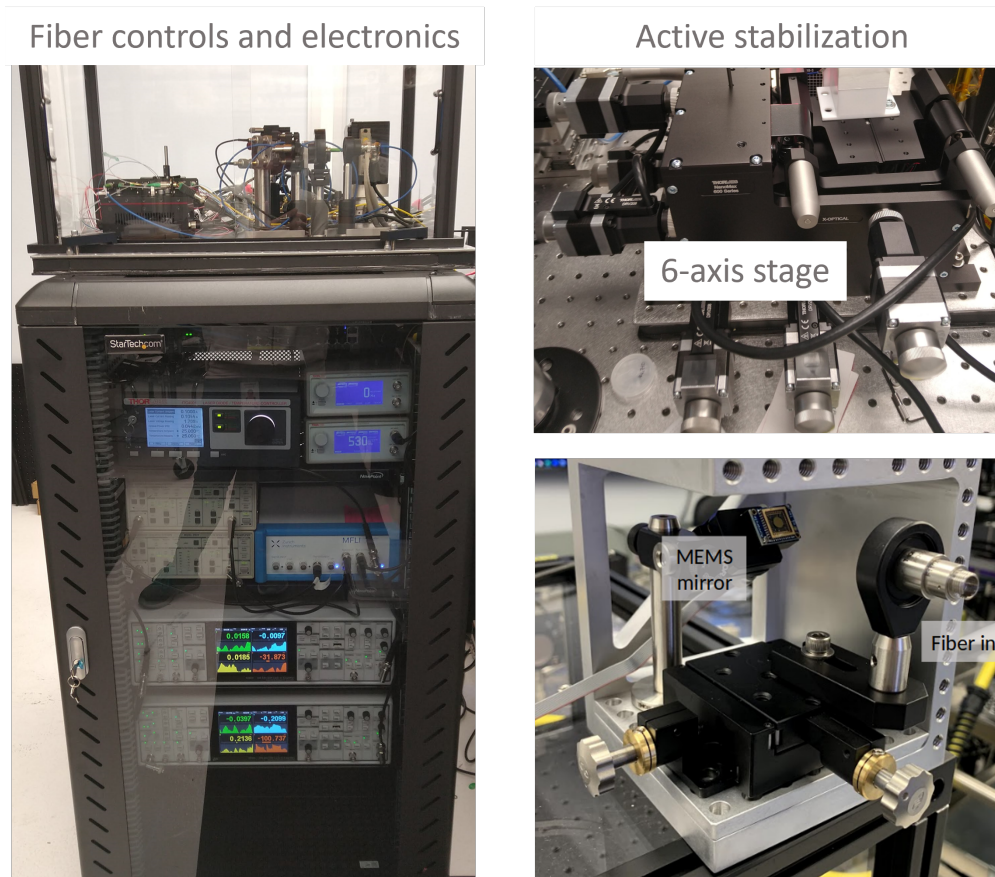


Fig. 3.6: Reflectance hardware.

We used this first-generation apparatus to probe how reflectivity across the visible and near-IR would change with loading, the latter measured by quartz crystal microbalances. An illustrative example of how reflectivity in palladium hydride changes with increasing frequency shift in the QCM is shown in Fig. 3.7 a). Here, we observed the reflectivity decreases roughly monotonically with increasing frequency shift. Additionally, the use of different loading enhancers resulted in further decreases in reflectivity, shown in Figure 3.7 b). These results not only proved our ability to use reflectance to measure loading but also demonstrated that we could use optical methods to rank the performance of different loading enhancers.

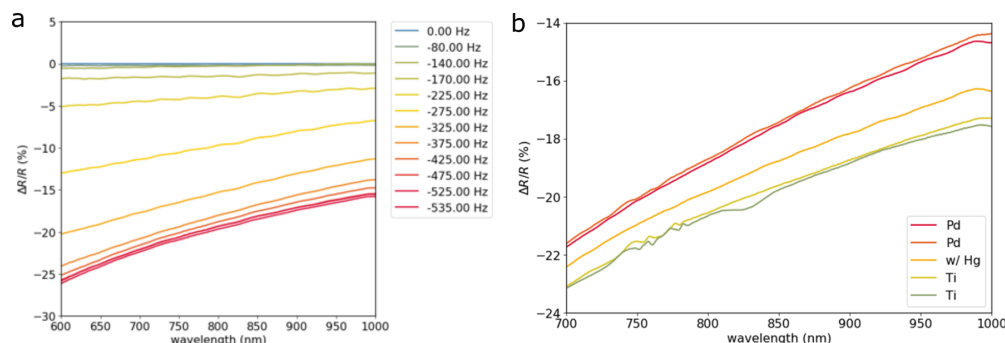


Fig. 3.7: a) Change in reflectance for palladium film as a function of frequency shift in QCM. b) Reflectivity measurements using the first-generation apparatus

With this proof-of-concept in hand, we simplified the measurement design by restricting the laser to a single wavelength. This change allowed us to miniaturize and decrease the cost of the apparatus, so that we could more readily replicate it into multiple setups. We also deployed several 785 nm and 1550 nm reflectance setups, the former showing strong monotonic and linear response to increases in fractional loading while the latter showed non-linear changes to reflectance as the fractional loading approached stoichiometry.

In another iteration of reflectance hardware shown in Figure 3.8, we developed a spatially resolved reflectance setup that allowed us to monitor changes to loading across an entire sample, as opposed to in a single point as in the first generations. This setup included a camera for capturing spatially resolved data, enabling us to observe any non-uniformity in loading that might occur from cell geometry, bubbling, or application of an electric field.

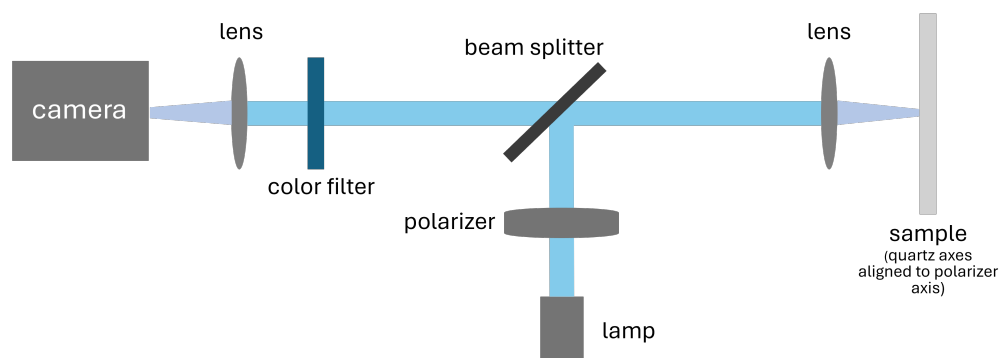


Fig. 3.8: Spatially resolved reflectance hardware setup.

Each of these generations was calibrated against x-ray diffraction measurements to obtain a quantitative mapping between reflectance and fractional hydrogen loading. It should be noted that Callisto's reflectance-based measurements probed the substrate-film interface as opposed to the film-electrolyte interface. Due to the complicating effects of evolving surface roughness with hydrogen cycling, the frontside interface resulted in inconsistent data. The backside interface, however, remained smooth throughout hydrogen cycling and therefore resulted in consistent data, with minimal sample-to-sample variation.

3.14.3 Calibrations

In order to perform calibrations, we implemented simultaneous backside reflectance and x-ray diffraction measurements. A cross-section of the electrolysis cell and its implementation in a diffractometer are shown in Figure 3.9. The cell was designed to retain 1 inch diameter thin film devices which comprised a sapphire substrate, a 5 nm titanium adhesion layer, and palladium thin films with thicknesses between 20 nm and 4000 nm. Two frontside contacts connect the device to a potentiostat, allowing us to pass current between the palladium film and a platinum counter electrode. A 0.5 M LiOH or LiOD solution was used as the electrolyte, and arsenic salt, typically AsCl_3 , was used to achieve nearly stoichiometric loadings.

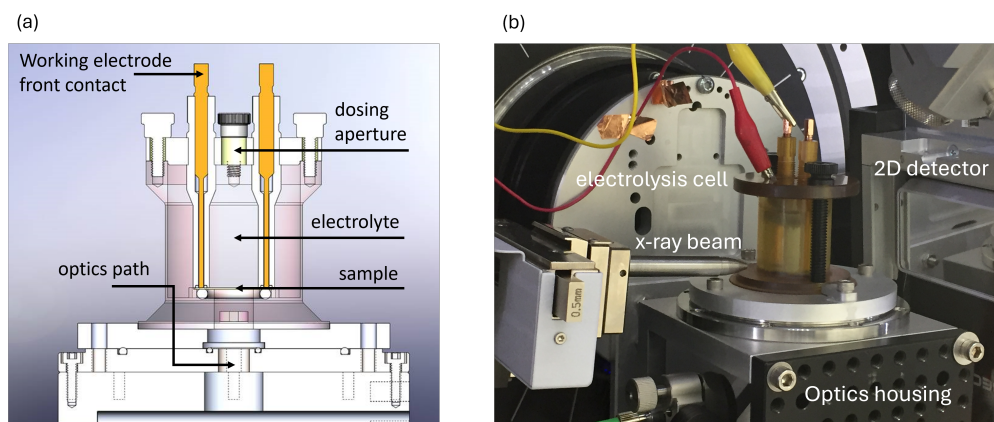


Fig. 3.9: a) Cross-section of the electrolysis cell; b) Implementation in a diffractometer

The x-ray diffraction setup is briefly described here. We used a Bragg-Brentano geometry with Mo K-alpha radiation, which has an energy near 17 keV. A collimated beam with an aperture of 0.5 mm was directed at the sample at an incident angle of $9.1^\circ 2\theta$. A Dectris 500K two-dimensional detector was placed at $9.1^\circ 2\theta$, opposite the beam. We calculated the total volumetric expansion of the thin film from hydrogen intercalating by analyzing both in-plane and out-of-plane diffraction peaks. The film expansion is constrained in-plane by bonding to the substrate, resulting in asymmetric expansion with lower-than-expected in-plane and greater-than-expected out-of-plane expansion. Ignoring this effect could lead to overestimating fractional loading by as much as 10%.

The results of these calibrations are shown in Figure 3.10, which depicts the mapping at both 785 nm and 1550 nm. The calibration for 785 nm demonstrates good linearity from 0 to nearly 100% PdH loading, regardless of isotope. In contrast, we observed a slight discrepancy between PdH and PdD for 1550 nm, although it was within the measurement scatter. We focused on calibrating loadings between 70% and 100% because of its relevance to our LENR research and the challenges in achieving low loadings with electrolytic methods. Using these calibrations, we were able to quickly and robustly probe the loading parameter space.

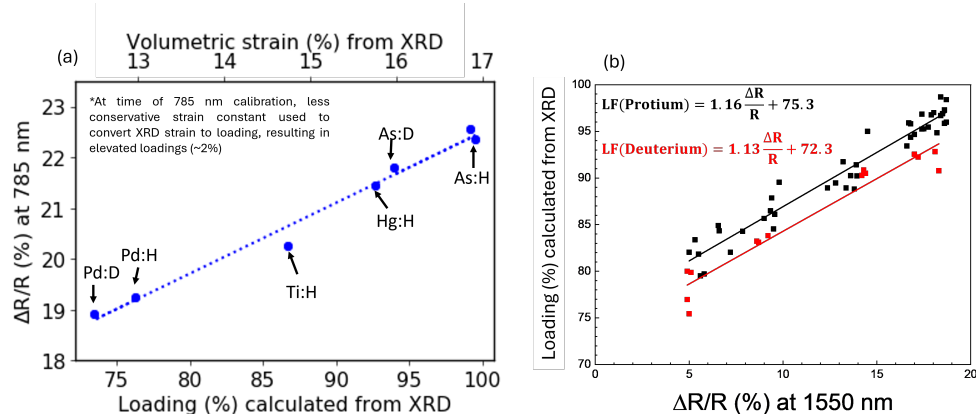


Fig. 3.10: Calibration results at 785 nm (a) and 1550 nm (b)

3.14.4 Some Example Case Studies

In this first case study, we looked at the effect of current density on chemically enhanced (AsCl_3 additive) loadings, with the results shown in Figure 3.11. In this example, we see that there are diminishing returns for applying current densities greater than 20 mA/cm^2 . Conversely, decreasing the current density below 20 mA/cm^2 resulted in a dramatic decrease in loadings. Interestingly, the ideal current density for thin films is not the same as for bulk cathodes, which we found to be around 120 mA/cm^2 . Although there is no strong fundamental reason for this discrepancy between nanoscale and bulk current densities, it is nonetheless important to characterize. If we were to speculate, it may be related to the combined effect of high surface-to-volume ratio and high grain boundary density in thin film cathodes compared to bulk. Essentially, diffusion of protium from the surface into the lattice is much more efficient in the thin film system, requiring a much smaller driving force to intercalate a similar amount of hydrogen.

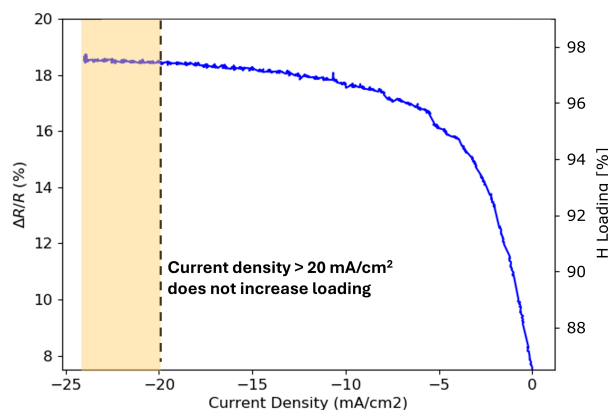


Fig. 3.11: Effect of current density on chemically enhanced (0.5 mM AsCl_3 additive) loadings.

In a second case study, we looked at how different parameters might impact the longevity of chemically

enhanced (0.5 mM AsCl_3 additive) loadings. In Figure 3.12, we examine the effects of current density, film thickness, and electrode spacing. We observed that higher current densities were better for longevity, while performance was largely unimpacted by film thickness and electrode spacing. Because of the facile setup of the measurement and implementation of the loading protocol, we were able to rapidly move through this parameter space.

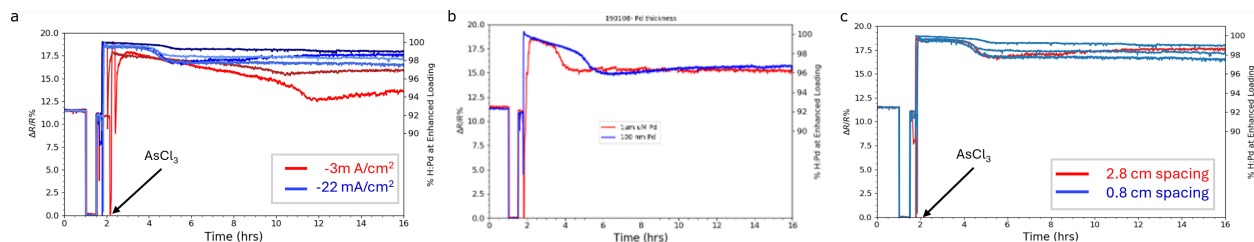


Fig. 3.12: Effects of current density (a), film thickness (b), and electrode spacing (c) on loading longevity.

In a third example, we used the spatially resolved reflectance apparatus to look at the effect of bubbling on thin film cathodes. In Figure 3.13, we observe lower loadings in areas where bubble attachment was prevalent. While it may be intuitive to expect that bubbling is detrimental to loading, we were able to provide direct evidence. When a bubble forms, there is no longer an electrochemical driving force to split water, resulting in the Tafel reaction dominating the reaction landscape. The loss of loading through gaseous recombination lowers the loading both locally and globally. One avenue explored by our companion high-pressure research team was to increase the system pressure, one of the effects being the suppression of bubbles and therefore the suppression of gaseous recombination. A separately submitted report covers this in more detail.

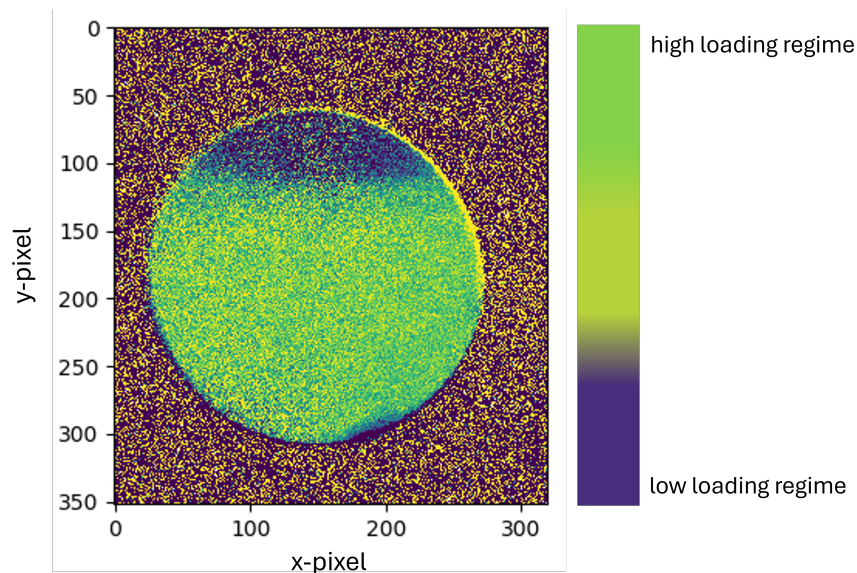


Fig. 3.13: Effect of bubbling on thin film cathodes. The circular thin film Pd cathode was oriented vertically, resulting in bubble accumulation at the top portion of the circle.

In a final case study presented in this report, we used our reflectance-based loading measurement to replicate chemical enhancement observed by another research organization, Coolescence [185]. This study is highlighted in Figure 3.14. In their study, Coolescence used both bismuth and combinations of bismuth and platinum to enhance the hydrogen loading in palladium cathodes. They estimated loadings using coulometry, which has its limitations at high loadings. In our replications, we applied their protocol for chemical enhancement while monitoring the loading via reflectance. One advantage of our methodology is the time-resolved nature of the data stream, whereas coulometry is best used for steady-state estimates. In addition to replicating Coolescence's loadings, we were able to show similar surface compositions following the experiment using energy-dispersive spectroscopy, overviewed in Fig. 3.15. Note that our replication study looked at using their chemistries in palladium deuteride thin films, as opposed to palladium hydride thin films which was the topic of the original study. As such and as expected from isotopic differences, we achieved slightly lower fractional loadings. Despite the admirable performance of their chemistries, our own chemical enhancement strategies proved to be more effective.

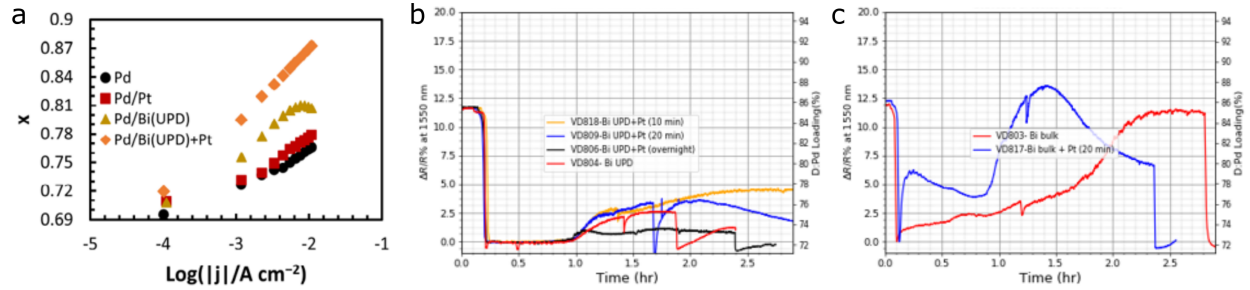


Fig. 3.14: a) x vs. $\log(|j|)$ reproduced from Coolescence [186]; b) Change in reflectance for replicated underpotential deposition; c) Replication of chemical enhancement observed by Coolescence

Atomic %						
	Pre/Post Loading	Pd	Pt	Bi	Pt/Bi	Peak Loading
VD806	Pre	98.6	0.4	1.0	0.4	74%
	Post	98.5	0.5	1.0	0.5	
VD809	Pre	99.2	0.1	0.7	0.14	77%
	Post	98.7	0.2	1.1	0.18	
VD818	Pre	98.8	0.3	0.9	0.33	78%
	Post	98.8	0.2	1.0	0.2	
Coolescence					Pt/Bi	Peak Loading
Pd Bi(UPD)				1.8		80%
Pd Bi(UPD)+Pt				0.13		87%

Fig. 3.15: Surface compositions following Coolescence protocol for chemical enhancement. Coolescence data is from [186]. VD806: Underpotential deposition (UPD) of Bi and Pt (overnight); VD809: UPD of Bi and Pt (20 min); VD818: UPD of Bi and Pt (10 min)

3.14.5 Ranking of Different Additives for Chemically Enhancing Hydrogen Loading

The primary objective for developing the reflectance-based loading measurement was to deploy a high throughput measurement system for ranking different chemical additives and their impact on deuterium loadings in thin film palladium. The idea was that thin films loaded much more rapidly than bulk cathodes, allowing us to proceed through the parameter space much more quickly than using bulk cathodes, which

would take hours to reach steady-state.

In Figure 3.16, we present the most interesting additives that were investigated using our reflectance-based methods. The figure shows the deuterium loading percentage in palladium thin films when different promoters were used. The data points are represented by different symbols to indicate the electrolyte used: blue squares for ${}^6\text{LiOD}$, blue circles for ${}^7\text{LiOD}$, and red diamonds for D_2SO_4 . The x-axis lists the various promoters, while the y-axis shows the D/Pd loading percentage.

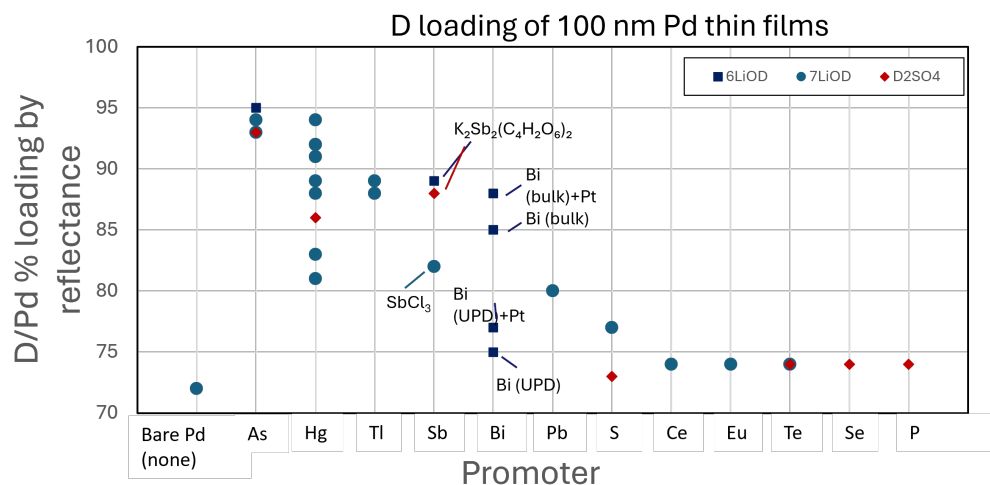


Fig. 3.16: Ranking of different additives for chemically enhancing deuterium loading in palladium thin films.

From the figure, we can observe that arsenic salts yielded the best performance, followed by mercury, thallium, antimony, and bismuth. Of note, the best results with mercury were comparable to arsenic, however, the spread in performance was much more significant. Some additives, such as sulfur, cerium, europium, tellurium, selenium, and phosphorus, did not significantly enhance loading. This comprehensive study allowed us to identify the most effective chemical additives for enhancing deuterium loading in palladium thin films.

Based on these findings, Callisto decided to focus on optimizing arsenic chemistries for both thin film and bulk cathodes to maximize deuterium loadings in our LENR experiments. Many of these additives' performances were corroborated by XRD measurements and QCM measurements, discussed in other sections, providing a robust validation of our reflectance-based ranking system.

3.15 Isotopic Effects

Given the nature of Callisto's research, we were concerned with characterizing the fractional hydrogen loading of both protonated and deuterated palladium lattices. From a first principles perspective, there are fundamental reasons why the driving forces for protium and deuterium uptake are different under identical conditions. The thermodynamic and kinetic requirements for the catalytic dissociation of deuterium gas or electrocatalytic heavy water splitting are greater than for hydrogen gas and light water. As a result, there are higher proton loadings for the same driving forces, as well as selective uptake of protium over deuterium in a mixed environment. Despite a fundamental understanding that palladium protide and palladium deuteride

should have different fractional loadings when everything else is controlled, the exact differences must still be determined empirically.

Regarding direct loading measurements, the isotopic effect is self-evident. For gravimetric analysis, while the molar mass of the isotopes is different, the analysis remains largely the same. The Sievert method's analysis is generally unaffected by isotope, except under ultrahigh pressures (> 1 kbar) where gas behavior deviates from ideality; this condition, however, is beyond the scope of this discussion.

For certain indirect loading measurements, the isotope impact is more pronounced. For example, Zhang et al. provided an empirical mapping between electrical resistance and fractional loading for palladium deuteride, which varied substantially from palladium hydride. This variation is attributed to differences in electron scattering mechanisms, where deuterium causes approximately twice the electron scattering effect compared to hydrogen, significantly affecting electrical resistivity. During our exploration of optical measurements, we determined that there were pronounced isotopic differences in the near-IR spectrum, but less so in the visible spectrum. These findings align with other studies, indicating that the isotopic mass affects the optical phonon excitations differently, leading to variations in the elastic constants and other material properties of PdH, PdD, and PdT [63].

Another critical observation is that protium is preferentially absorbed over deuterium in mixed light and heavy water electrolytes (Fig. 3.17). When adding increasing concentrations of light water to heavy water electrolyte in subsequent load-deload cycles, the loading x as measured by QCM goes down. In isotopically pure LiOD in D_2O , $x = 73\%$. In isotopically pure LiOH in H_2O , $x = 78\%$. Assuming the total loading varies linearly between 73% and 78% with isotopic composition of the electrolyte, the isotopic composition of the hydrogen loaded into the palladium can be computed from the relative mass increase per palladium atom as measured by QCM, $\frac{m_H + m_D}{n_{Pd}}$:

$$\frac{a}{a+b} = 2 - \frac{1}{0.73 + 0.05 f_H} \frac{m_H + m_D}{n_{Pd}}, \quad (3.17)$$

where $\frac{a}{a+b}$ is the fraction of protium in mixed isotope palladium hydride (PdH_aD_b) and $f_H = \frac{V_{H_2O}}{V_{H_2O} + V_{D_2O}}$ is the protium fraction in the mixed isotope electrolyte. The analysis shows that at 3% protium content in the electrolyte, almost 40% of the occupied sites are loaded with protium (Fig. 3.17b). Given that the loading is determined by the kinetic balance of various reactions (see chapter 4) and given that protium reaction kinetics are typically faster than deuterium reaction kinetics [187], the observation of a preferential uptake of protium is not surprising.

One notable consequence of this observation of isotopic poisoning is the need to start with and maintain high isotopic purity in any electrolyte used for LENR experiments. Atmospheric light water can readily contaminate an open-cell experiment, poisoning the heavy water electrolyte at rates up to 1% a day initially. LENR in electrolytic cells was believed by Fleischmann and Pons to be exclusive to PdD, so the presence of PdH may prevent the reaction from initiating (although we admit this is speculation).

These observations underscore the importance of one of Callisto's major efforts: to robustly characterize the difference in isotopic loading behavior under different conditions.

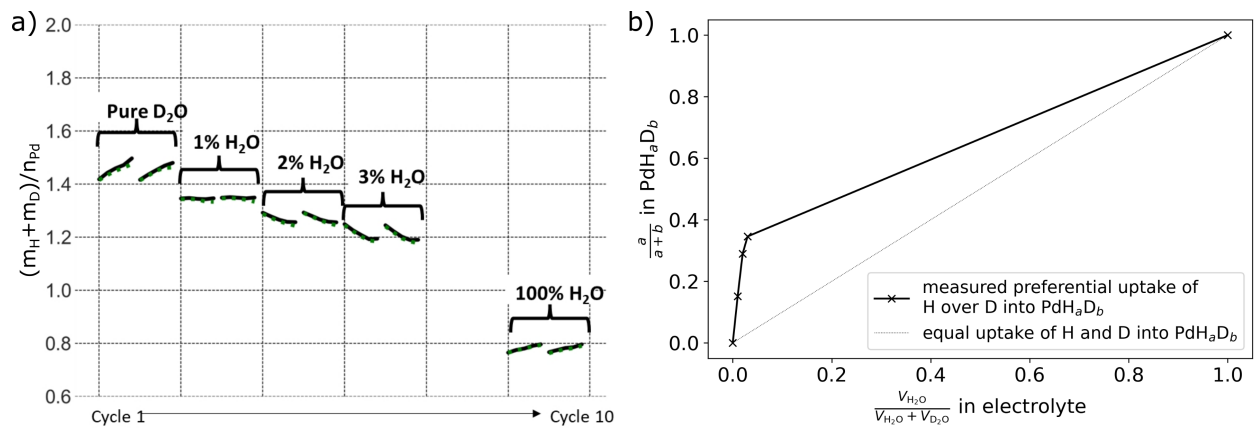


Fig. 3.17: Preferential loading of protium from mixed isotope electrolyte (LiOH in H₂O / LiOD in D₂O). a) QCM measurements showing the decrease in relative mass $\frac{m_H + m_D}{n_{Pd}}$ as light water is added before every other load-deload cycle. b) Fraction of protium in mixed isotope palladium hydride ($\frac{a}{a+b}$ in PdH_aD_b) as function of the protium fraction in the mixed isotope electrolyte, $\frac{V_{H_2O}}{V_{H_2O} + V_{D_2O}}$, acc. to Eq. 3.17.