Chapter 6

Conditions Reportedly Amenable to AHE

As previously discussed, there are many commonalities across studies done in the LENR field that build a framework for the conditions purportedly beneficial to observing an AHE event. Chiefly among these conditions is the purported need to have a highly loaded Pd sample. While the exact threshold of "highly-loaded" is not explicitly established, it is commonly accepted that $\geq 90\%$ deuterium loading is necessary to foster an environment conducive to AHE. Parameters that purportedly have influence on deuterium loading include current density, temperature, formation of a coating from the unintentional deposition of trace elements from the electrolyte onto the sample (dubbed in our work as "Coating X"), and additives that lead to loading enhancement. In the following sections we will discuss our experimental findings on each of these conditions' effect on loading and relevant conclusions that can be drawn.

6.1 Effects of Current Density on Hydrogen Loading

Many notable works in the field from authors like Fleischmann and Pons, McKubre, the U.S. Navy, Google [26, 93, 106, 110], and the like have all applied a negative bias to the Pd cathode in a heavy-water electrolyte to load it with deuterium. This intercalation occurs via the surface adsorbed hydrogen atom proceeding through the well-established Volmer-Heyrovsky-Tafel mechanism for hydrogen evolution reaction (HER) in alkaline media. As previously described in the introduction, these three steps can be described by the following:

$$\text{Volmer} : H_2O + Pd_{surface} + e^- \rightarrow Pd_{surface}H_{adsorbed} + OH^- \tag{6.1}$$

$$\text{Heyrovsky} : H_2O + Pd_{surface}H_{adsorbed} + e^- \rightarrow Pd_{surface} + OH^- + H_2 \tag{6.2}$$

$$\text{Tafel} : 2Pd_{surface}H_{adsorbed} \rightarrow 2Pd_{surface} + H_{2(g)} \tag{6.3}$$

$$\text{Intercalation} : 2Pd_{surface}H_{adsorbed} \leftrightarrow 2PdH_{bulk} \tag{6.4}$$

The first three descriptors can be combined to describe two reaction pathways. We also pose a third pathway of "intercalation". 1) Volmer-Heyrovsky (V-H) proceeds via an initial surface adsorbed hydrogen ($H_{adsorbed}$) produced at the Volmer step followed by an interaction of the adsorbed H with a water molecule

causing disassociation from the surface and formation of H_2 gas and a hydroxide ion, 2) Volmer-Tafel (V-T) proceeds after two surface adsorbed H produced in the Volmer step come into close proximity and recombine, leaving the surface as H_2 gas, and 3) Intercalation proceeds as surface adsorbed H produced in the Volmer step enters the bulk of the Pd crystal lattice. While all of these pathways play a role in the intercalation of D into Pd, literature as well our independent studies confirm that HER on Pd proceeds predominately via the V-T pathway. We also found that the Volmer step is the kinetically limiting step in the range of 1 to $50\,mA/cm^2$ using our own Tafel analysis measurement.

In alkaline media, the short surface residence time of $H_{adsorbed}$ is also an issue at low current densities because adsorbed species experience competing reaction pathways: V-T, V-H (though not relevant here), and intercalation. This causes the V-T pathway to be a parasitic reaction in loading procedures as it directly impacts the ability of $H_{adsorbed}$ to be incorporated into the Pd lattice. We will discuss in later sections strategies used to inhibit the V-T pathway leading to higher H loadings in our Pd samples. As we increase the current density we also increase the rate of the HER reaction, leading to more surface coverage with $H_{adsorbed}$ atoms. This increase in $H_{adsorbed}$ surface coverage and current density allows for higher rates of intercalation. However, higher current density also leads to high rates of bubbling as O_2 and H_2 gas leave the surface of the Pd cathode. If these bubbles stay on the surface, particularly H_2 gas from V-T, then catalytically active sites can be blocked inhibiting further HER and ultimately limiting available $H_{adsorbed}$ for intercalation. If current densities are too high they can also have negative effects on the sample integrity (e.g. crack formation) as well as unwanted reactions on the electrical contacts.

Another consideration when running high currents to load Pd in aqueous environment is the inevitable presence of unwanted ions in solution from electrolyte impurities, counter electrode and hardware degradation, etc. Over the course of long duration experiments at high currents, ions such as Cu, Fe, and Zn can leach from hardware and other sources. This ion leaching is especially true for the Pt counter electrode which is oppositely biased in our experiments. Based on Pourbaix diagrams, the negative potentials at which most experiments are carried out overlap with plating potentials for these leached ions in solution, causing them to co-plate as metallic deposits on the Pd surface during intercalation. While this plating can lead to blocked active sites given high ionic concentrations, the formation of an over-layer of metal constituents can be controlled and lead to a beneficial coating, coined "Coating-X", that acts as a V-T inhibitor and increases residence time of $H_{adsorbed}$ and by extension, H loading. We will discuss in later sections how we strategically selected for "Coating X" and leveraged it as a V-T inhibitor.

In addition to the the current density, the duration of current application is also vital to achieve highly loaded samples. Pd samples must load for some optimal time in order to achieve an optimal H/Pd ratio. This optimum ratio is indicated by a stabilization in the resistance measurements of the sample upon current application and introduction of loading enhancements. The time to reach this fully loaded state varies from sample to sample based on form factor, size, and current density. For example, larger bulk palladium samples at low current density would take far longer to reach high loadings compared to a thin Pd foil at high current densities.

6.2 Effects of Temperature on Hydrogen Loading

Temperature is an important parameter regarding AHE because it plays such a vital role in aqueous electrochemical systems in general. The main limiting factor in carrying out electrolysis reactions in aqueous environments is staying within the stability window (i.e., freezing and boiling point) of the electrolyte. In most cases that window will be between 0° C and 100° C, as water will make up the majority of the solution.

Temperature increase can affect the rate of electrolysis by increasing the thermal energy and conductivity of the solution helping ions to reach the Pd surface more readily [225]. While increased temperature can be beneficial, it is important to consider that once power is input into the system for electrolysis the electrolyte temperature can increase tens of degrees Celsius over the duration of the loading period. This is a vital consideration when designing an AHE experiment above room temperature as the electrolyte could readily reach boiling point and depletion long before an AHE event could be observed. Despite operating near boiling point resulting in the loss of electrolyte, there are some studies that purposefully investigated AHE reactions in this temperature regime.

We performed several studies below room temperature that showed increased peak and longevities of loadings when compared to room temperature experiments under the same conditions. We will discuss these low temperature experiments in detail in the loading enhancement section as we investigated the synergistic effects of loading enhancements and low temperatures. Regardless, operating near and below 0 °C necessitates careful experimental design and additives to prevent freezing and avoid lowering electrolyte conductivity to an unacceptably low value. To address this, we added antifreeze agents such as methanol, ethylene glycol, and ammonia to the electrolyte when carrying out studies below 0 °C. These antifreeze agents did present a challenge for closed cell calorimetry, as they can electrochemically split into H_2, N_2, NH_3 and CO_2. All of these gases can accumulate in the headspace and increase the pressure, and in most cases are not recombinable. Consequently, our studies below 0 °C were carried out in open cells and our closed cell experiments were carried out slightly above 0° C, where antifreeze additives were not required. Ultimately, we found that in conjunction with loading enhancers, temperatures near 0 °C had a direct positive effect on the maximum and longevity of loadings which allows the conditions purportedly amenable to AHE to persist longer and increase the likelihood of an event.

6.3 Effect of "Coating X" Formation on Hydrogen Loading

Many studies in the field have observed the reduction of metallic ionic impurities from the electrolyte, either intentional or not, onto the surface of the Pd cathode after experimentation. While this surface deposition being vital to AHE is not explicitly called out by any one researcher, we were interested in its commonality across multiple works in the field. Letts and Cravens' work claimed excess heat after intentionally electrodepositing gold on the Pd cathode surface in the presence of a 700 gauss magnetic field and laser stimulation [226]. As described earlier, when applying negative currents to load samples in aqueous environments there is often a co-deposition on the cathode surface based on the ions plating potential on their Pourbaix diagrams. This electrodeposited coating's thickness varies based on the amount of current applied, the duration of the current application, and the concentration of ions (and their ionic activity) in solution. Each of these factors increases the amount of deposition, with increasing current affecting the rate of deposition. As observed in many electrochemical systems, this over-layer essentially becomes the new catalytically active surface interfacing with our electrolyte once it reaches a certain surface coverage and thickness. An example is in Pd-hydride systems used in HER where the formation of surface PdH_x changes the surface energetics of the pure Pd and weakens the H adsorption on the surface leading to increased reaction rates for HER [227]. In our own studies we began to consistently observe the recurring presence of certain elements on the surfaces of highly loaded samples.

We have coined this interfacial layer formed in our experiments "Coating X", as its composition varies slightly (similar to the variable "x") but the constituents remain largely unchanged. Electron dispersive X-ray spectroscopy (EDS) determined the common constituents of this surface overlayer to be Cu, Fe, Zn,

	$Log(J_{0,Volmer})$		$Log(J_{0,Tafel})$	
	Log(A/cm²)			
	Bare Pd	As-Enhanced	Bare Pd	As-Enhanced
Tidepool	-4.7	-5.1	**-3.3**	**-6.9**
Coolescence	-5.1	N/A	-3.0	N/A

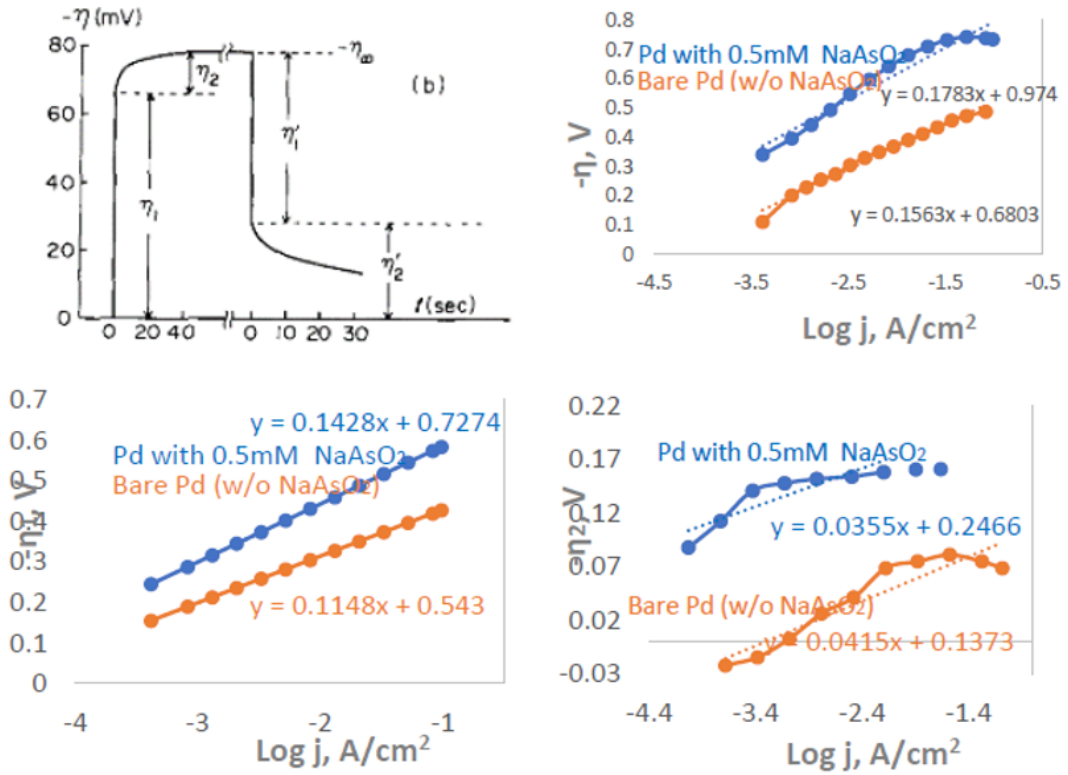

Fig. 6.1: Summary data comparing the effect of arsenic (As) additive on the Volmer and Tafel reaction rates with bare Pd and published data from Coolescence as references. The Tafel plots for the data are also included comparing the results of bare Pd to Pd with a 0.5 mM $NaAsO_2$ additive.

and Pt from the counter electrode. Sources of the Cu, Fe, and Zn have been determined to stem from electrolyte salt impurities and at times, a degradation of cell hardware in solution over time. These ions are usually found in relatively low concentrations in the electrolyte – less than a few ppm – and deposit onto the cathode over long time frames with high loading currents. The presence of Pt ions in solution is a much more complex problem to deal with as they stem from the Pt counter electrode in solution and their ionic concentration is much higher since they are exposed to an oxidizing potential. We found that over the course of long duration experiments Pt ions tend to electrodeposit on the Pd cathode surface, blocking active sites for intercalation and ultimately negatively impacting loading. This is especially the case for experiments that are cycled multiple times as the Pt ion concentration is allowed to continuously build up. We investigated how much this unwanted deposition impacted loading and how we could mitigate its formation by implementing a membrane compartment comprised of semi-permeable membranes housing the Pd cathode. This compartment allowed electrolyte to flow through the membranes to reach the Pd surface but prevented the Pt ions from reaching the cathode. Results showed a noticeable decrease in Pt deposition on the Pd surface and higher peak loadings by 2 - 4%. Unfortunately, these high loading results were not consistent and the experimental setup was tedious compared to the benefit.

These observations of "Coating X"'s natural occurrence during the formation of PdH_x and its recurrence across multiple works in the field, inspired us to create our own tailored overlayer. The hypothesis was that this overlayer acted similarly to PdH_x formation on pure Pd in changing the surface energetics as previously described. However, unlike in published HER studies where the goal was to increase the rate of V-T or V-H to facilitate increased H_2 production, our goal was to inhibit or "poison" these pathways to increase surface residence time of the $H_{adsorbed}$ atoms to increase loading of the Pd lattice. As previously established, our main loss of the $H_{adsorbed}$ atom produced in the Volmer step (1) was via the V-T reaction pathway. To this end, we began to screen additives that could suppress the the V-T pathway by monitoring changes in resistance in order to achieve the highest increase in peak D loadings. The results of this investigation are shown in Figure 6.2 and will be discussed in the following sections on loading enhancers.

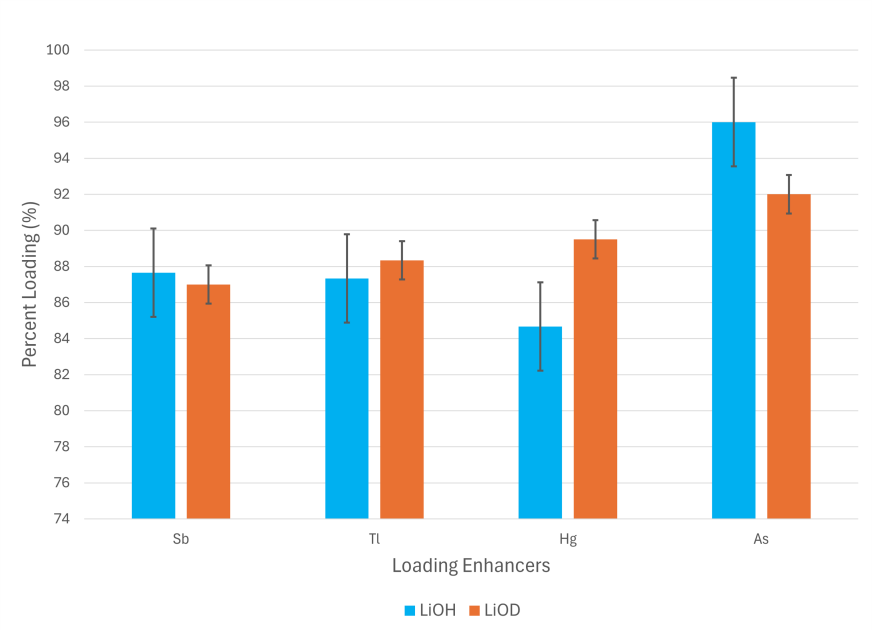

Fig. 6.2: Peak loadings of of various additives achieved in 0.5 M LiOH (blue) and 0.5 M LiOD (orange), respectively. Additives were delivered in 2 mL doses of 25 mM concentrations of the Sb, Tl, Hg, and As in LiOH or LiOD after loading plateau was reached, usually after 20 minutes of loading. Samples were 0.5 mm diameter and 30 mm long Pd wires. Current was a constant 50 mA.

6.4 Effect of Loading Enhancers on Hydrogen Loading

As mentioned above, we carried out various studies probing the best additives to increase the hydrogen (and in particular deuterium) loading in palladium cathodes. In a first screening, we vapor-deposited 100 nm layers of Hg, Ti, Ni or Pb onto Pd thin films. Neither resulted in a consistent loading enhancement effect. We thus dosed the additive to the electrolyte instead. Figure 6.2 shows the elemental salts (Sb, Tl, Hg, and As) that we added to the electrolyte at 25 mM concentration in 2 ml doses (yielding a final concentration of 0.83 mM in solution) and their corresponding peak loadings achieved. Arsenic (As) was determined to yield the best and most consistent results regarding loading enhancement, consistently achieving 92 to 98 % H/Pd loadings. These values are based on the resistance data and calculated using the Zhang formula. We observed that these higher loadings usually occurred on the second loading cycle (i. e., loading and deloading before loading again) which is likely due to some nano-structure preconditioning of the Pd surface. Figure 6.1 shows arsenic's effect on the suppression of V-T compared to bare Pd and its relatively small effect on the rate of the Volmer reaction. During these studies we discovered that As dosing had an optimal time frame during loading – within the first 20 minutes of loading for 0.5 mm Pd wires – to observe its loading enhancing benefit. This is likely because too much Coating X would be allowed to form if too much time elapsed during loading before introducing As into the system.

While As showed promise as the best "Tafel poison", the longevity of this inhibition only lasted for two to three hours on average. This lack of longevity led to a search for strategies to increase the duration of the V-T inhibition and by extension, the longevity of D loading in our Pd samples to trigger an AHE event. As seen in 6.2, other additives' effects on loading were investigated and some showed promise; however, they were plagued by other issues that excluded them from use in our experiments. For example, Mercury (Hg) enhancers showed largely varying range of enhancement as well as displaying an aggressive coating formation that often coated the Pt contacts to our Pd sample leading to errors in current application and improper loadings.

One trend that we did observe across nearly all of our studies is that the protium-loaded samples tended to load higher than their deuterium counterparts. This held true for nearly all studied enhancers except Hg which had the inverse relationship but also inconsistently exhibited the high loading behavior. It is well documented that the rate of the Volmer and Tafel reactions are higher in HER than in DER due to electrolytic H/D separation factors [228, 229]. This explains why H samples load quicker than D and evidences the apparently isotopically unique peak loading difference, as D is more easily disassociated from the catalytic surface compared to H. This could also be compounded by steric hindrance due to the difference in the size of H and D atoms. In a later section we discuss As enhancement experiments and the optimization of its loading enhancement in detail.

6.5 Electromigration

Several researchers, most notably McKubre [101] and Staker [105, 230], have claimed that the application of a current along the length of the palladium hydride cathode wire is beneficial or critical to observing AHE. This current is often referred to as *electromigration current* or *axial current*.

The underlying assumption is typically that the current causes an electric field along the wire, which in turn affects the distribution of hydrogen ions within the wire. Staker proposed a theory according to which the axial current causes a gradient in deuterium ion concentration along the wire, with one end of the wire having a concentration as high as 5 x compared to the other end of the wire (0.5 mm diameter, 25 mm

length wire, 3 A electromigration current) [105]. Upon closer inspection, the proposed model is based on assumptions that do not hold. Most critically, the highly loaded palladium hydride cannot be considered a dilute regime (in terms of interstitial site occupancy) and thus the equations presented by Staker are not applicable [231]. In a recent paper published in an Elsevier journal, Staker reiterates the claim that electromigration enhances loading, even above stoichiometry, but does not provide any data to back up the claim [230].

Apart from the electric field exerted due to the axial voltage, ions also interact with the electrons through momentum transfer. This process is referred to as *electromigration*, and the force of the electrons is likened to an *electron wind*. It can lead to a net transport of metal ions in an electric conductor, particularly at defects, e. g., grain boundaries, where charge symmetry is broken. Typically, these processes are slow and occur over weeks to months. Unlike material transport due to electromigration in thin-film integrated circuits, palladium hydride has the added complexity of other transport processes occurring in parallel. Hydrogen diffusion in the bulk as well as loading and deloading processes at the surface must be accounted for. Both of these processes typically occur at much higher rates than hydrogen transport through electromigration, thus likely swamping any potential effect from electromigration.

McKubre applied an axial current (up to 7 A) in some of his experiments. He noted that "During times when axial current is passing both loading information and calorimetry were seriously inaccurate: Calorimetry was poor because the axial input power was not measured at the calorimeter boundary. Loading measurements were inaccurate because the actual temperature of the cathode could not be determined. [...] During the axial current experiment the scatter in the excess power measurement increased to ±150 mW, but averaged to 0 W." [101]. The relationship between axial current and excess power remains unclear. However, McKubre's comments illustrate that the added complexity from additional power sources (for applying axial current in addition to electrochemical current) can introduce calorimetry errors. In particular, the high axial currents (compared to typical EC currents) can cause parasitic resistive losses if the wires are not dimensioned properly, generating ohmic heating. Parasitic losses scale with the square of the current for a given wire resistance. This additional ohmic heating can cause calorimetry errors if the voltage sense points are not positioned properly or if the calorimeter has different sensitivities depending on the location of the heat sources within the calorimeter.

To our knowledge, there is no experimental data in the literature showing any effect of axial current on loading in an electrochemically loaded palladium wire. For that reason, we performed our own experiments. We measured the local resistance in an electrolytically loaded Pd cathode wire near the ends of the wire with and without application of an axial current, as well as with different polarities of axial current. We found no significant difference in local resistance (hence in loading) as a function of axial current (Fig. 6.3). However, we did notice a temperature effect, with 3 A axial current typically elevating the wire temperature between 5 K and 10 K (for a 25 mm long, 0.5 mm diameter wire), depending on loading.

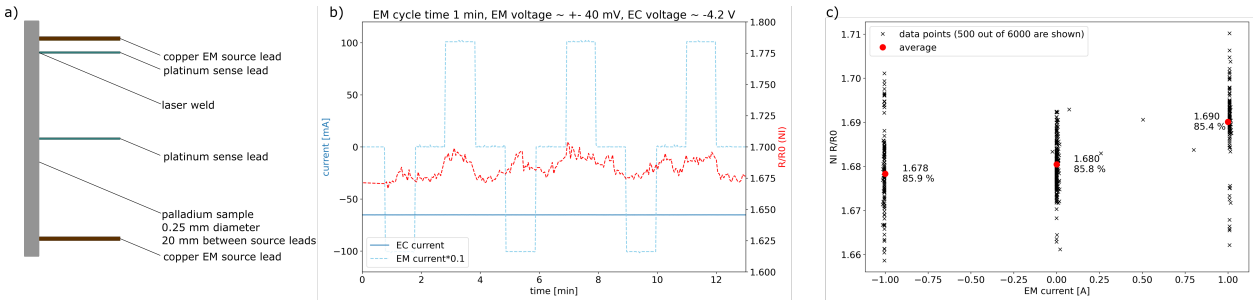

Fig. 6.3: Local loading measurement (by resistance) under axial current. a) Device setup to measure resistance in a palladium wire sample between the platinum sense leads. Depending on the polarity of the axial current, the segment of sample under test will be closer to the positive or negative polarity of the axial current. b) Example dataset showing the measured resistance ratio (compared to the resistance of the deloaded sample) while the axial current is varied between [1, 0, -1] A. c) Statistics of 6000 resistance ratio data points, showing no significant effect of axial current magnitude or polarity on resistance ratio.