Chapter 5

Surface Preparation Methods

5.1 Cleaning Protocol

During our investigations, we discovered the impact that sample surface character has on loading and the consequent need for rigorous sample preparation. We developed a multi-step cleaning process for ridding the samples and hardware of contaminants. Samples were cleaned by a 10-minute sonication bath in laboratory detergent water, DI water, acetone, IPA, and a final Radio Corporation of America (RCA) clean. While all these solvents are widely used in literature, the final RCA clean, which removes surface organic contaminants, has shown a strong correlation to a decreased spread in loadings. We posit that this increased consistency in loadings is due to the lack of residual surface organic compounds which could block active sites for H adsorption and intercalation. The exact mechanism of this organic-electrolyte reaction is currently unknown.

5.2 Electropolishing and Centerless Grinding

Another surface characteristic that we found to significantly impact sample loading is the surface roughness. A common method used to refine material surfaces is electropolishing. Electropolishing is an electrochemical process in which the surface roughness of a metal sample of interest is decreased or "polished" by applying a positive bias and dissolving a thin layer of surface metal ions into solution. The sample acts as the positive anode, the counter electrode is generally stainless steel, and the electrolyte is usually comprised of sulfuric and phosphoric acid mixture, which both conducts electrical current and dissolves the metal ions released from the surface. By electropolishing our samples in acidic media, the Pd surface was removed of any debris, cracks, and trenches. Additionally, we observed the exposure of grain boundaries of the sample after an optimal time of electropolishing (~30 min.). These features can influence the conformal coating formed during electrolysis and its robustness, specifically, how long Pd cathodes maintain enhanced loading. Figure 5.1 depicts the change in surface character as a function of electropolishing time using SEM. The figure also shows electrochemical loading data for first cycle loading percentage (red) and normalized resistance (grey) in 0.5M LiOD as a function of time for unpolished and polished Pd wires, respectively. We can observe from the figure that as the polishing time for samples increased, the rough surface features decreased until we reach a point where local anisotropy led to pit formation as observed in the 45-minute polish. It is important to note that a 25mM $NaAsO_2$ loading enhancer was introduced to all samples after 2.5 hours of

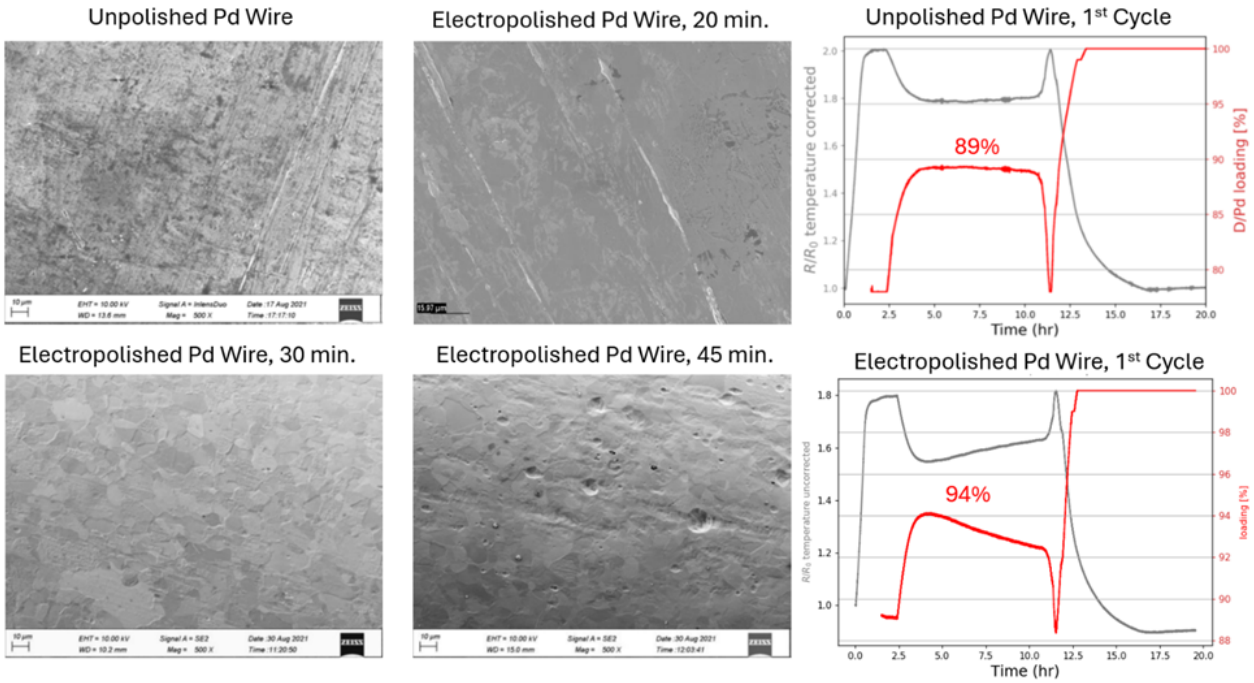

Fig. 5.1: Scanning electron microscopy (SEM) images comparing unpolished Pd wires to electropolished wires exposed to various electropolishing times (20, 30, and 45 minutes). Right panels show electrochemical loading data in 0.5 M LiOD electrolyte for unpolished Pd wires (top) and 45 min. electropolished Pd wires (bottom) after being dosed with 25mM NaAsO2 enhancer. (Data came from slide 196 in cumulative summary deck in 08/2021)

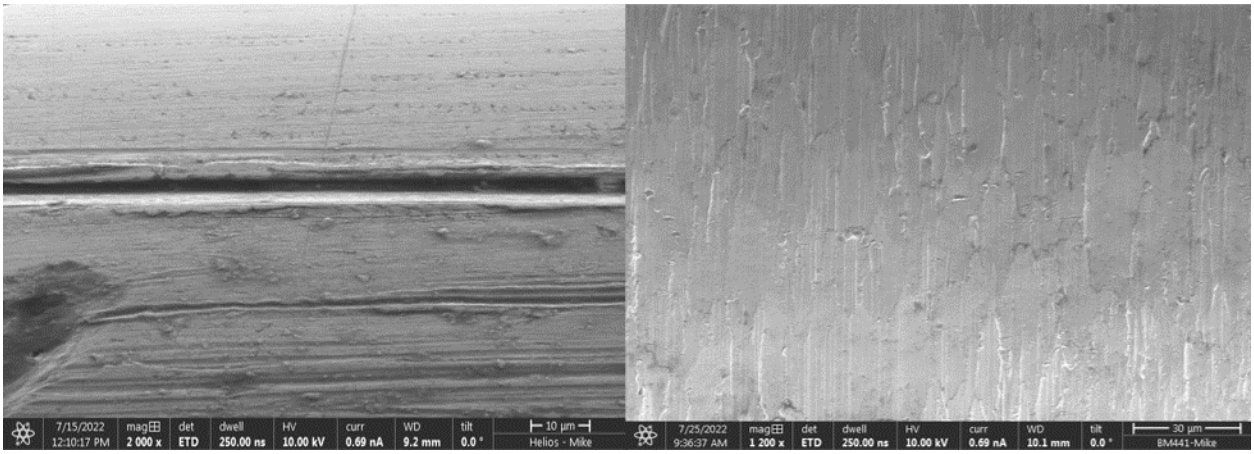

Fig. 5.2: SEM images comparing untreated Pd wire with longitudinal crack surface defect (left) to a Pd wire after centerless grinding treatment. (Data came from slide 1897 in cumulative slide deck)

unenhanced loading. This loading enhancement strategy is discussed at length in the following section. The grain boundaries can be clearly seen after the 30min polishing. The panels to the right show representative effects on loading of the total surface preparation procedure on unpolished and polished wires respectively. There is a clear increase in peak loading, 89% unpolished compared to 94% polished, upon Arsenic (As) enhancement when samples receive the exact same treatment outside of electropolishing. This study shows the large impact that surface pretreatment can have on an electrochemical study where deuterium loading is thought to be a vital parameter.

Despite positive outcomes of the electropolishing, the inability to efficiently produce these high-quality samples in large batches onsite became gating. SEM pre-imaging uncovered that the major source of the variability in loading performance and longevity was the presence of longitudinal cracks along many of the Pd wire samples. This longitudinal crack was found to be a weak point in the interfacial coating formed on the electrode surface that normally acts as a Tafel inhibitor and ultimately leads to longer loading longevities. We determined that the ideal Pd sample for obtaining high loadings would be devoid of these longitudinal cracks but also be mass produced unlike with electropolishing. It was determined that the best course of action was to outsource samples for centerless grinding and then post-treat samples onsite. Centerless grinding is a process in which the removal of the outer layer of a material is achieved by rotation against a coarse grinding wheel. Figure 5.2 illustrates this finding as well as before and after SEM images showing the removal of the longitudinal surface crack. Ultimately, we found that centerless grinding was effective in removing surface defects that lead to loading failure; although, it was not as efficient in exposing grain boundaries as electropolishing. Regardless, centerless grinding allowed for more consistent loadings across our samples and large-batch sample preparation facilitating higher experimental output.