Spectro-electrochemistry using X-ray absorption spectroscopy on a tabletop X-ray machine

Silicone microwires is a promising material for solar-driven hydrogen production via water splitting. To engineer efficient catalysts for their surface coatings, we must study their electronic and oxidation states in real time under in situ conditions. X-ray Absorption Spectroscopy (XAS) specifically X-ray Absorption Near Edge Structure (XANES) is an ideal tool for this task.

In XANES measurements the photons interact with the inner electrons of a target element where the core electron absorb photons and are excited to a unoccupied electronic state. When a photon is absorbed by the inner most shell then this is called the K-edge. XANES focuses on the first main peak in a XAS spectrum called the whiteline where changes in electronic state and oxidation state can be observed. For titanium the K-edge is at 5 keV. As attenuation for matter increases with lower X-ray energies in accordance with Beer-Lamberts law. This makes water and air absorption a challenge for titanium measurements.

To better understand how to mange these low energy X-ray conditions before introducing a liquid setup we collaborated with a researcher called Hang Yin to preform transmission measurements on lanthanum samples which has a similar energy for its L-edge. These samples where pressed into pellets where we encountered problems with microscopic cracks called "pin-holes" leading to long attenuation times where a single measurement took 20 hours. While no change dependent on impurities was observed it proved valuable for learning about our setup.

From the lanthanum measurements as well as our understanding of soft X-ray measurements we made a 3d-printable XAS-SEC cell which is inspired by the design made by Paparoni et al. Where the use of a screw design to adjust the distance between the window and the sample. Several iterations of the cell was made to test the seals and material used.

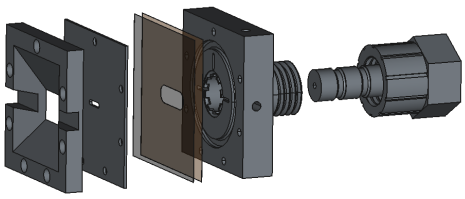
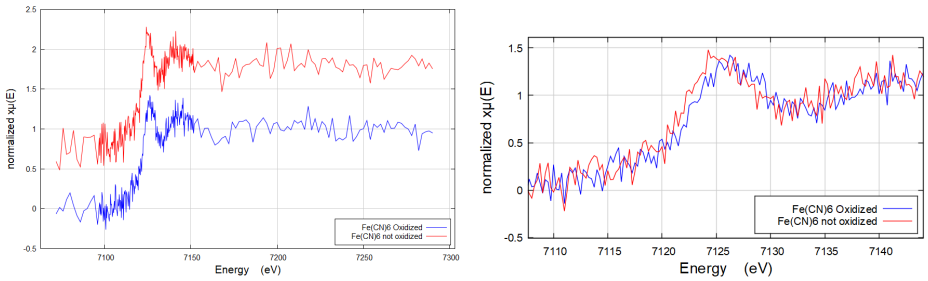


Figure 1: Custom build XAS-Cell with a internal screw mechanism allows us to adjust the sample's position.

To test the cell potassium ferricyanide was dissolved in water and pumped trough the cell. To check the electrochemical components a cyclic voltammetry measurements was preformed. Our potentiostat was not able to measure the current during the entire cyclic voltammetry measurements which limited the potentioal that could be applied during the XAS-SEC measurement. During the XAS-SEC two different potentials was applied to the solutions which oxidized or reduced the sample which caused a $\sim$1 eV shift in the spectrum. This shows that the sample has been oxidized and reduced successfully and we where able to measure this change in our XAS setup.



(a) XAS (b) Main peak shift

Figure 2: XAS measurement of ferricyanide, (a) shows the entire spectrum of both the oxidized and nonoxidized measurement offset by 0.6 xμ(E) to show both specrum and (b) both spectrum overlaped to show the 1 eV shift in energy at the first main peak.

The prototype cell demonstrated the concept, future iterations will focus on solving minor leaks encountered while measuring and integrate a potentiostat that can handle larger currents. Once optemized the cell can be used to measure iron and titanum coated silicone microwires.