Electrochemistry is becoming more and more a part of the world around us to decrease the dependence on fossil fuels and upscale bio-derived materials and fuels. The focus of our experiments was to gain insight into the effects of catalyst composition and concentration and the selectivity and conversion of electrochemical furfural oxidation. This paper will summarize the work done during the semester and the correlating analysis.

It has been observed that while using a standard platinum working electrode during the process of electrolysis of furfural, the surface of the electrode can accumulate CO (Adv. Energy Mater. 2018). This is called CO poisoning and decreases the available surface area for electrolysis, decreasing the efficiency of the process at lower potentials. As furfural oxidizes, some of the first species to be produced also produce CO, and due to the high binding affinity of CO, can lead to CO poisoning (Adv. Energy Mater. 2018). As a note, CO leaves its binding site at potentials over 1.2V and this limit should never be exceeded to avoid further oxidizing the platinum and degrading the electrode.. Other research in the field has shown promising results using Pt/ATO, as a catalyst applied to the working electrode for various reactions. Preliminary data for Pt/ATO has shown a lower oxidation potential onset for furfural oxidation (Hasse, J et al 2023.

To assess the effects of ATO as a support for platinum, Cyclic Voltammetry (CV) and electrolysis experiments were performed. A carefully crafted standard operating procedure allowed for seamless capturing of CV and electrolysis data in the same experiment. PtATO is prepared as a liquid ink and deposited in varying numbers of aliquots onto conducting carbon flags and dried in a vacuum dryer, yielding different concentrations of catalyst to run CV experiments. The concentrations tested ranged from 0.1mg of PtATO to 1mg. For the furural oxidation a catalyst concentration of 9mg per flag was always used. Once prepared, h-cells are assembled with a platinum mesh counter electrode, a standard Ag/AgCl reference electrode, a Nafion 117 membrane and 15 mL of 0.1 M $HClO_4$ on the counter side and 13 mL on the working side. After assembly, the working cell is bubbled with argon for 10 minutes while a break-in CV is collected. This is done at a faster sweep rate of 150 mV/s per cycle for 30 cycles to effectively clean and prepare the interfaces for electrolysis. At this point the argon is switched from bubbling to blanketing and an area CV is collected at a sweep rate of 20 mV/s for 10 cycles. The under-potential deposition region for hydrogen is measured to quantify the electrochemically active surface area of PtATO.

The working cell is emptied and replaced with the same volume of a furfural and HClO4 solution. The molarity of the furfural solution is 2mM, 10mM, or 50mM for the respective experiments. The working chamber is bubbled for ten minutes after the addition of furfural and then blanked for the entirety of the electrolysis. Electrolysis is run at a potential of 0.9V or 1.2V versus the reference electrode for 6 hours. In addition, experiments on previously used PtATO electrodes and on the thermal effects were conducted by submerging the cell in a heat bath at 50°C.

All the collection of data was performed on Gamry 3000 and BioLogic SP-300. For the collection of physical data, the distribution of products and reactants in the electrolyte, samples were taken from the working and counter cells at time intervals of 30 minutes, 1 hour, 4 hours and 6 hours to track the oxidation progress. Approximately 300 mg of fluid was collected and from that, 20µL was sequestered into its own vile. 980µL of DI water was added to the small sample and 500µL to the original sample creating a diluted and undiluted sample for the working and counter cell at each time interval. These samples were then run through high-pressure liquid chromatography, HPLC, to classify their composition. HPLC utilizes UV-Visible spectroscopy producing a spectra with peaks at wavelengths that can be associated with molecular compounds. For a control, the stock furfural electrolyte solution was also run along with the electrolysis samples through HPLC.

To compare CV data for different process parameters, the CVs from each experiment are overlaid. When these data are superimposed on one another the variance in characteristics can be seen for different catalysts at varying concentrations. **Figure 1** shows the CV's collected in the increasing catalyst concentration experiments. In these CV's it can be seen that at higher concentrations of PtATO and after multiple electrolysis runs the working electrode shows that the Hydrogen underpotential deposition region increases

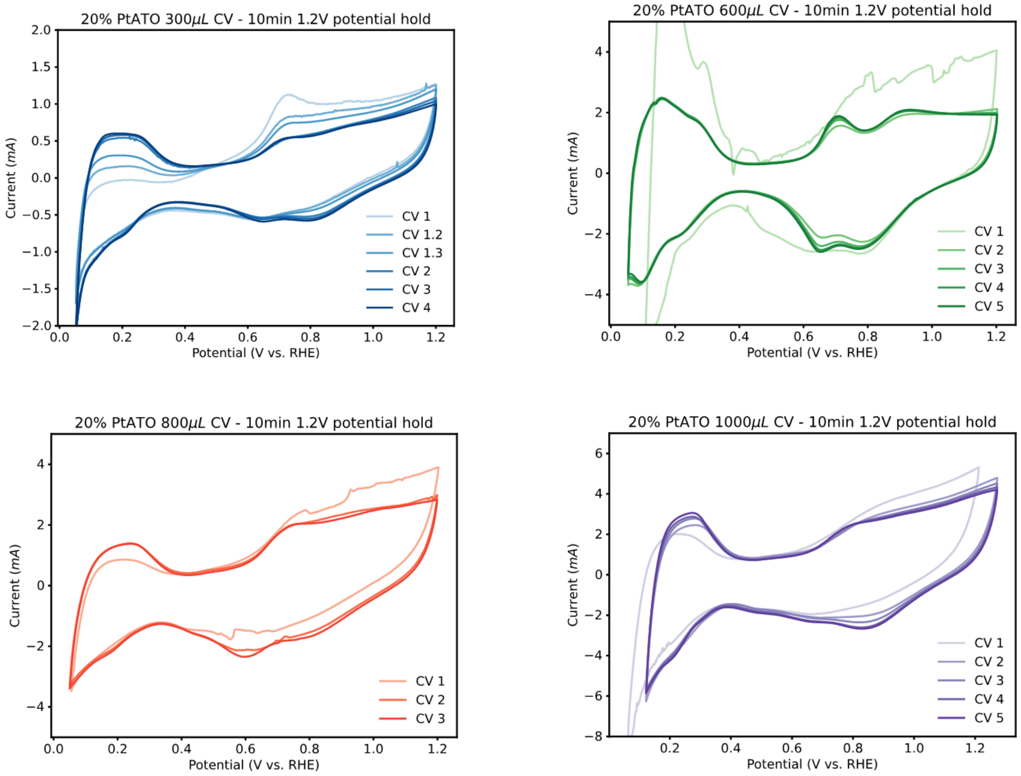

Figure 1: CV's collected for increasing aliquots of PtATO ink deposited on carbon flags.

During the electrolysis, furfural oxidizes into a finite set of products and the associated HPLC wavelengths for these compounds was determined using sets of standards. Products produced in the oxidation of furfural are as follows; Maleic Acid, 5-Hydroxyfuroic Acid, 5-Hydroxy-furan-2(5H)-one, 2(3H)-Furanone, and Furoic Acid (Hasse, J et al n.d.). The area of the peaks is integrated and compared with standards to establish the concentration of each product.

In summary, CV's were collected to quantify the activity of the PtATO catalyst and electrolysis was conducted to determine the selectivity and conversion of furfural, the dependent variables. The independent variables were the concentration of PtATO applied to the working carbon flag electrodes, the potential applied to the cell and the concentration of furfural in the electrolyte. Addressing the CO poisoning that was one of the drivers for experimenting with PtATO, this catalyst produces fewer carboxylates than a standard platinum electrode and can be observed in **Figure 2**. PtATO allows for the onset of electrolysis to occur at a lower potential allowing for fine-tuning of the selectivity of the products, while overcoming carboxylate and CO poisoning. The 50C runs showed an increase in charge passed and overall yield, with selectivites showing a more even product distribution, also in **Figure 2**. Results, **Figure 1**, from rerunning the PtATO flags showed relatively improved overall yields and accepted more current than the first time the flags were run. This led to the idea of pretreating the carbon flags before the addition of the catalyst which proved to better facilitate the reproducibility and standard performance of the catalyst.

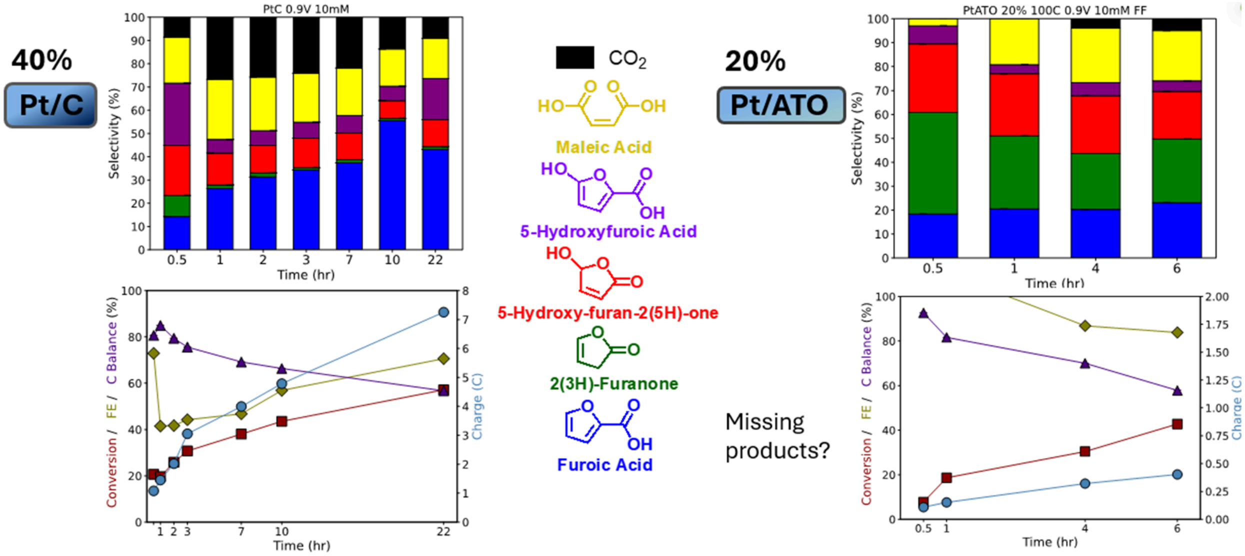

Figure 2: Selectivity results from HPLC analysis of electrolysis samples.

Some insights to gain from these results are that PtATO is a very durable catalyst as seen with the rerun experiments, and I-T curves compared to PtC. Using PtATO as a catalyst exhibited less CO poisoning, higher yields and increased selectivity when compared to a platinum-on-carbon electrode. There was an expectation that mass transport limitations would be reached at the higher concentrations but analysis from the re-run experiment shows that when increasing the concentration of PtATO deposited to the flags there aren't any diminishing returns and that ATO is a durable catalyst.

PtATO indicates promise as a catalyst for electrocatalytic oxidation of furfural. The next steps to investigate would be increasing the concentration of furfural and PtATO to discover if there are upper bounds to the benefits seen in these experiments. Further experiments on the thermal effects should be planned to determine if there is a temperature that shows enhanced performance and less degradation. Finally, changing the pH of the solution will alter the chemistry in the cell and should be investigated.

Reference:

Adv. Energy Mater. 2018, 8, 1701476

Hasse, J. C. & Manyé Ibáñez, M.; Holewinski, A. Impact of Reaction Conditions on the Bulk Electrolysis of Furfural over Platinum electrodes. *ChemCatChem*. 22 September 2023