

NDnano Summer Undergraduate Research 2022 Project Summary

1. Student name & home university:

Bennett Schmitt – University of Notre Dame

2. ND faculty name & department:

Dr. Adam Jaffe – Chemistry & Biochemistry

3. Summer project title:

Electrochemical Analysis of Hybrid Bronzes

4. Briefly describe new skills you acquired during your summer research:

This summer, I learned an immense amount about solid-state chemistry. Not only did I gain a great amount of insight into the chemical concepts relating to solid-state materials, but I also was exposed to several analytical techniques used to investigate these materials. This summer, I have become familiar with characterization techniques such as Powder X-Ray Diffraction (PXRD) and Single Crystal X-Ray Diffraction (SCXRD), as well as with electrochemical techniques such as cyclic voltammetry which allows one to investigate the redox behavior of materials of interest.

5. Briefly share a practical application/end use of your research:

The novel material platform, known as hybrid bronzes, that the Jaffe Lab is working to synthesize and study has the potential to address modern energy challenges through applications in energy-related technologies such as catalysis, energy storage, electrochromics, and more.

6. 50- to 75-word abstract of your project:

“Bronzes”, aptly named for their lustrous surfaces resulting from high concentrations of free electrons, are inorganic metal oxides exhibiting high chemical and thermal stability, as well as tunable electronic properties. However, this class of materials often requires energy-intensive synthetic routes and lacks post-synthetic tunability. Conversely, molecular species offer fine synthetic control, while lacking the structural and electronic properties seen in bronzes. Thus, the combination of inorganic metal oxides and organic species allows for the synthesis of a novel material platform, known as “hybrid bronzes”, that combines the advantageous properties of each. This work focuses on the electrochemical analysis of these bronzes and hybrid bronzes to investigate their redox behavior with the intention of informing future implementation efforts in clean-energy technologies.

7. References for papers, posters, or presentations of your research:

[1] Glemser, O.; Lutz, G. *Z. Anorg. Allg. Chem.* **1951**, 264, 17.

[2] Elgrishi, N; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. *J. Chem. Educ.* **2018** 95 (2), 197-206

One-page project summary that describes problem, project goal and your activities / results:

The modern world faces an extreme energy crisis that demands immediate action if we hope to avoid catastrophic and irreversible changes to our planet. One interesting class of materials that has the potential to address these energy-related challenges through avenues such as catalysis and energy storage is known as “bronzes”. Bronzes are inorganic metal oxides of the general formula A_xMO_y , where “A” is a cation (typically monovalent) and “M” is a transition metal capable of achieving different oxidation states. The values of “x” and “y” in these bronzes depend on the level of reduction. In this project, we have primarily focused on molybdenum trioxide, MoO_3 , which can undergo varying levels of reduction to create four types of hydrogen molybdenum bronzes of the formula H_xMoO_3 (Figure 1). These bronzes exhibit desirable chemical and thermal stability, as well as interesting electronic properties.

However, these crystalline metal oxides often require energy-intensive synthetic routes and lack post-synthetic tunability. On the other hand, molecular species exhibit fine synthetic control, but lack the structural and electronic properties seen in bronzes.

In the Jaffe Lab, we are focused on developing a novel material platform we call “hybrid bronzes” by combining these inorganic metal oxides and organic species to take advantage of the

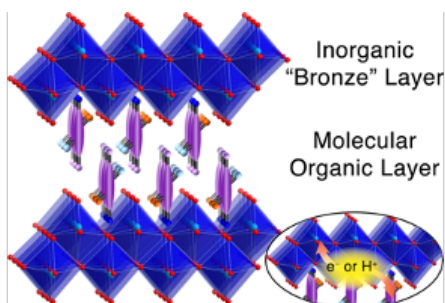


Figure 2. Visualization of a “hybrid bronze”.

beneficial attributes offered by each (Figure 2). There are two synthetic avenues through which we work to create these materials: intercalation and templation. Intercalation involves the insertion of molecular species in between the inorganic layers of bronzes without changing the crystal structure. Templation requires the bonds of the crystal layers to be broken and reformed with the organic species acting as the structure-directing group. These organic-inorganic hybrids proffer applications in clean energy technology, and, specifically, their potential to aid in intermolecular electron transfer—which is a challenge associated with isolated organic species—could allow for additional functionality at organic sites.

This research focuses on the electrochemical analysis of these bronzes and hybrid bronzes. A primary technique used for this electrochemical investigation is known as cyclic voltammetry, which allows one to scan electrochemical potentials and record the current response of a system. The electrochemical cell employed in this project consisted of three electrodes: a working electrode, where the sample of interest was deposited; a reference electrode, which offered a stable redox couple allowing for measurement of the potential applied at the working electrode; and a counter electrode, which completed the circuit. Scanning potentials across this cell allowed us to identify redox couples exhibited by our materials, as well as to explore the reversibility of these electrochemical changes. Through repeated cycling and peak analysis of redox couples, we were able to associate an irreversible reduction at ca. -0.2 V vs. Ag/AgCl seen in MoO_3 and $H_{0.33}MoO_3$ with a restructuring of the crystal layers (Figure 3). We were also able to connect two different redox couples with the electrochemical conversions between Types II and III and Types III and IV.

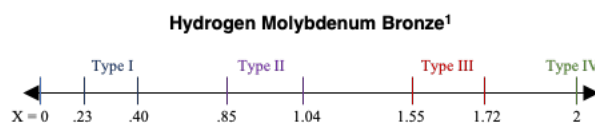


Figure 1. Schematic of reduction thresholds for the four types of molybdenum bronzes.

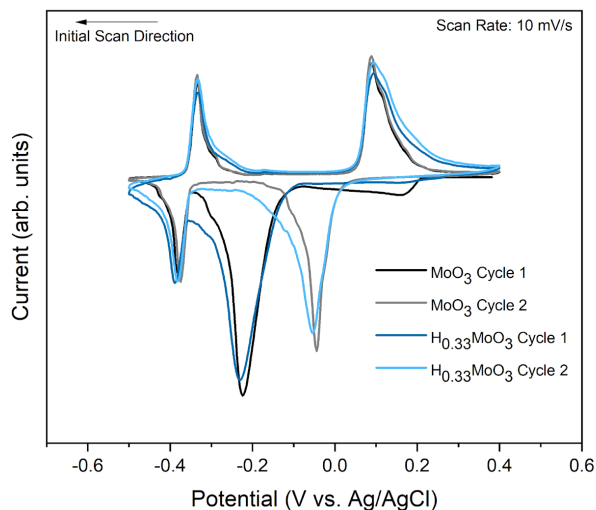


Figure 3. Overlay of CVs of MoO_3 and Type I.

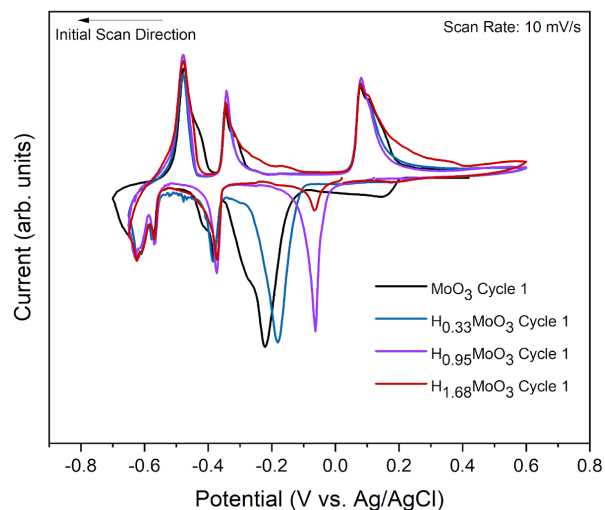


Figure 4. Overlay of CVs of MoO_3 and Types I-III.

Electrochemical analysis was also performed on two materials templated with 4,4'-bipyridine, $\text{MoO}_3(\text{bipy})_{0.5}$ and $\text{H}_{0.33}\text{MoO}_3(\text{bipy})_{0.5}$ (Figures 5 and 6). Cyclic voltammograms (CVs) of these materials exhibited irreversible behavior like that seen in MoO_3 and $\text{H}_{0.33}\text{MoO}_3$. It was previously believed that the irreversible behavior seen in MoO_3 and $\text{H}_{0.33}\text{MoO}_3$ was caused by insertion of protons into the molybdenum oxide bilayer. However, these bipyridine-templated materials lack this bilayer, so further investigation is required to determine the cause of this irreversible behavior. Moving forward, more hybrid materials incorporated with redox-active ligands will be studied, along with the conductivity of these materials in the hope of informing future implementation efforts in clean-energy technologies.

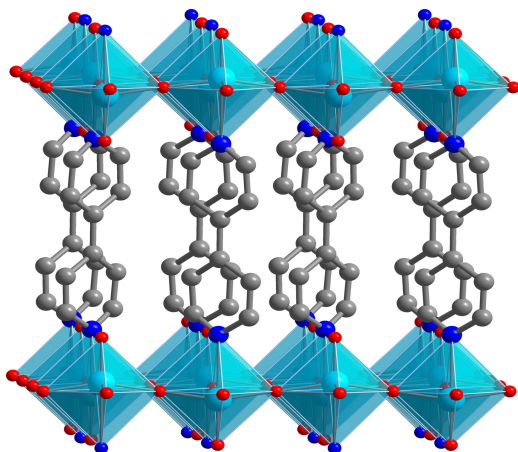


Figure 5. Crystal structure of $\text{MoO}_3(\text{bipy})_{0.5}$

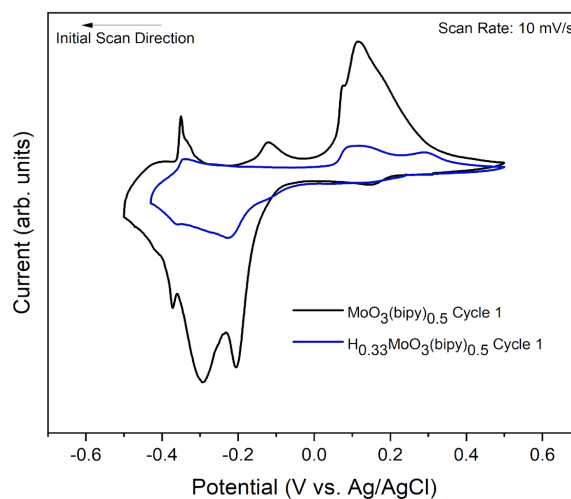


Figure 6. Overlay of CVs of bipyridine-templated materials.