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At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison chemistry Ph.D. candidates.

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The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Development of antimony-containing catalysts and semiconductors for (photo)electrochemical fuel production

By

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Chapter One: What can be done with antimony?

1.1 Introduction

The planet Earth is an incredible place. It is the only known planet that can sustain life as we know it and has a tremendous amount of diversity in its living organic creatures and non-living geological features. However, this diversity is relatively delicate and the rapid growth of humanity has caused unintended side effects upon the environment of the wonderful blue marble we call home. As these environmental effects of human expansion become more and more prevalent, there are many people who seek to live a more sustainable and less environmentally taxing lifestyle by taking actions like recycling, using less wasteful products, driving electric cars, etc. For me, the desire to contribute to a more sustainable future has led me down the path of scientific research, in particular to the field of materials development for use in renewable energy applications. The primary goal of scientific research is to help people understand the past, live safely in the present, and protect the future. This illustrates the importance of sharing what scientists actually discover and that everyone should be able to understand the work done by scientists. I, therefore, appreciate the assistance and directive of the Wisconsin Initiative for Science Literacy at the University of Wisconsin-Madison during the writing of this chapter meant for non-scientific audiences.

Before we get into how the element antimony fits into my research, let us first check out the element itself. Looking at the periodic table, we find antimony in a relatively quiet neighborhood, with a few well-known neighbors like lead and tin, in the lower right region of the table (**Figure 1**). We can notice that the chemical symbol for antimony (Sb) does not follow the typical method of naming that we see in other elements like carbon (C) and hydrogen (H) that use the first (or first two) letter(s) of their full names as their chemical symbol shorthand. The letters "Sb" actually originate from the Latin name for antimony, "stibium." Several other elements have this method of naming including more well-known elements like iron (Fe, ferrum), lead (Pb, plumbum), and gold (Au, aurum). Therefore, so we don’t have to spell out “antimony” every time I want to mention the element, I will use the shorthand “Sb” instead.

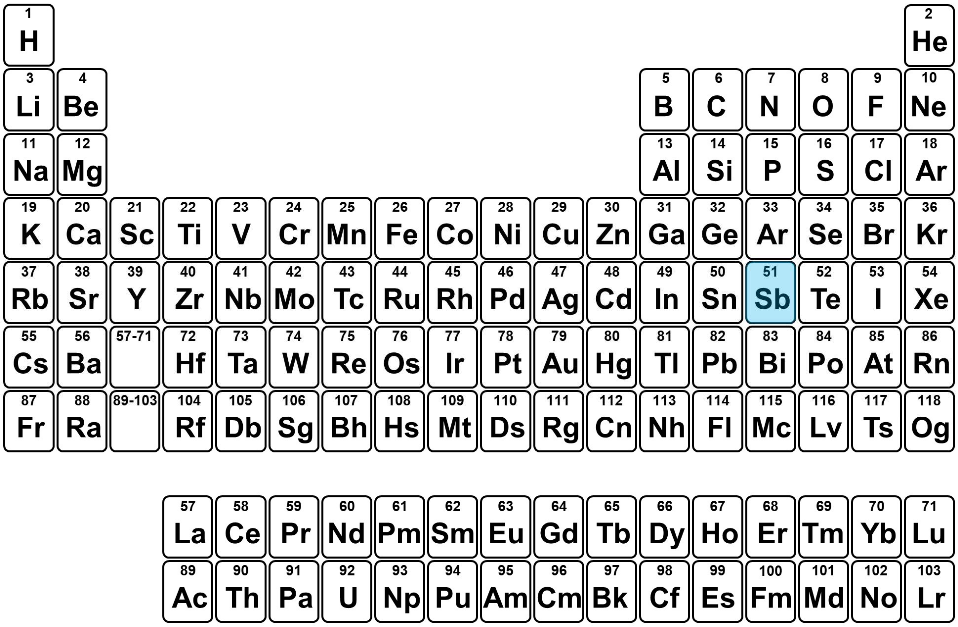

Figure 1. The periodic table of elements with antimony (Sb) highlighted in blue.

Sb as a pure element is a semi-metal, meaning it acts somewhere between a metal, like iron, and a non-metal, like sulfur. It can conduct electricity like a metal, but also melts and evaporates at relatively low temperatures like a non-metal. This gives it unique properties but also makes it more challenging to work with as you cannot treat it wholly as a metal or wholly as a non-metal. This is part of the reason Sb is relatively unexplored as a material or part of a material for modern applications. That doesn’t mean it isn’t used for some things though! It has a few relatively niche uses including as an alloy with lead in lead acid batteries in cars and as a part of flame retardants in clothing, children’s toys, and car seat covers.

Because of this relative obscurity, I didn’t even think about Sb when I entered graduate school. By happenstance, as a second-year graduate student in 2016, I worked on a project using

Sb, although this initial project did not develop enough to be included within my thesis. However, I was intrigued by this element I had heard almost nothing about and wondered what else I could do with it. Over the next couple of years and working with my research advisor, Professor Kyoung-Shin Choi, we developed a series of projects to investigate Sb and Sb-containing compounds for a variety of renewable energy applications. This thesis is the result of that work.

The primary tool I used to synthesize and investigate the Sb materials in the following sections was electrochemistry. Electrochemistry can be thought of as chemistry that is done with electricity, and you likely come into contact with a material made by it or one that uses it many times a day! For example, when someone says "chrome-plating" for their tire rims, what they are referring to is the process of electrochemically plating chromium (the shiny metal) onto the tire-rim to protect it. Many important metals for our modern society, like copper and aluminum, are purified using electrochemistry and every single battery in a laptop, phone, pacemaker, and hearing aid relies upon electrochemistry to function.

The heart of electrochemistry is the electrochemical cell which contains several important components that are required for the cell to function (**Figure 2**), kind of like how an animal or plant cell has several parts that are required for them to function. Every electrochemical cell contains two electrodes, an anode and cathode. These electrodes sit inside a conductive solution composed of water and ions dissolved in the water. Having some ions in solution is important, because pure water by itself is actually not conductive! Many cells also contain a third electrode, called a reference electrode, that is used to measure the voltage at our anode or cathode electrodes, but it itself doesn't participate in any reactions. All of these electrodes are hooked up to a device called a potentiostat labelled P. The potentiostat can control the current or voltage at our electrodes and measure the response from our electrochemical cell.

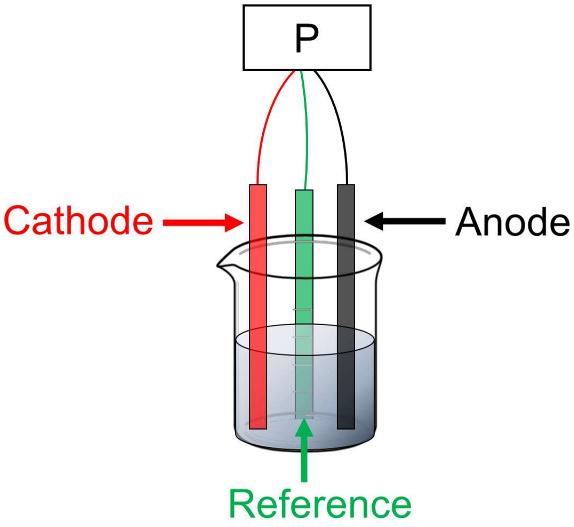

Figure 2. A model electrochemical cell with the three electrodes (cathode, anode, reference) hooked up to a potentiostat (P) while immersed in a water solution containing dissolved ions.

Having the two electrodes (anode and cathode) immersed in a conductive solution is important because electrochemistry is all about moving charges, i.e. electrons, from one place to another, in this case moving electrons from the anode to the cathode. This means that at the anode we are doing oxidation, or the removal of electrons from something in solution (or water itself). Electrons are negatively charged, so by removing them from our target compound (or water) we are making our target compound more positive, i.e. more “oxidized”. These electrons then travel to the cathode where they reduce a compound (or water) dissolved in solution. Because we are adding electrons that means this compound is now more negative, i.e. more “reduced.” A common mnemonic to remember this is OIL RIG “**O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain,” where oxidation is loss of electrons and reduction is gain of electrons.

Thinking back to the example of chrome-plating, the un-plated car rim is used as a cathode in a water solution containing dissolved chromium ions. Using a stainless steel anode, water is oxidized into oxygen gas producing electrons. The electrons are then sent to the un-plated rim cathode to reduce the positively charged chromium ions to neutrally charged chromium metal.

This metal uniformly coats the rim and leaves a nice shiny layer on the surface! While more complicated analysis can be done to understand what might be happening in greater detail at the different electrodes, the simple dual process of oxidation and reduction defines all electrochemical experiments.

Now that a basic understanding of electrochemistry has been developed, we can return to the work I have done with antimony (Sb). There are three primary fields of renewable energy materials that I investigated, which will be overviewed in the following three sections. Each section is a little bit different and will therefore contain introductions to their respective field of study and explanations on the different terminology used within each section. Section 1.2 describes the work I have done on developing Sb-containing oxide materials for water oxidation in acidic solutions. Section 1.3 is about how I developed a method to create quaternary Sb-containing metal oxides to split water using sunlight. Section 1.4 explores the results of using Sb and bismuth (Bi) to produce ammonia from nitrogen gas.

1.2 Antimony oxides for water oxidation in acid

This section contains a brief summary of the work I have done for chapters two and three of my thesis. Specifically, it focuses on developing acid stable electrodes for water oxidation. "Acid stable electrodes" means that the electrodes (cathode or anode) are stable and do not corrode in acid. When you think of corrosion in acid, think about how your stomach acid is full of hydrochloric acid that dissolves your food. The electrodes I made can resist being dissolved in those kinds of harsh conditions. As mentioned in the chrome plating example above, "water oxidation" is performed by oxidizing water at our anode. This final process produces the fully oxidized form of water, oxygen gas (O_2). The air we breathe is already 21% oxygen gas, so what is the point of making more? To answer that concern, think about hydrogen fueled cars, which use hydrogen gas (H_2) to produce energy to run the car. Well, to make that hydrogen we needed to reduce water (add in electrons) at a cathode. But those electrons had to come from somewhere right? That somewhere is the reaction happening at the anode, the oxidation of something. And when we are reducing water at the cathode, the easiest reaction to perform at the anode is the oxidation of water!

So we are oxidizing water at the anode in acid to make hydrogen gas at the cathode. Making hydrogen gas is relatively easy in acidic solutions as there are a number of stable and active materials that can reduce water in these conditions. However, making a stable anode to use for water oxidation in acid is not easy as many elements, compounds, and materials are not stable under such harsh conditions. The only materials that are stable are rare and expensive noble metals like iridium and ruthenium. This is where Sb comes in. Antimony oxide (Sb_2O_5) is one of the very few compounds that is stable under the oxidizing, acidic conditions used in this type of electrochemical cell. Antimony oxide is so inert that it cannot even oxidize water when used as the anode! It needs some help by combining it with another element that is able to oxidize water but is not stable on its own in acid, such as cobalt (Co) or manganese (Mn). These ternary (containing three elements) compounds, cobalt antimony oxide ($CoSb_2O_6$) and manganese antimony oxide ($MnSb_2O_6$), oxidized water and showed stable performance for 24 hours in a solution more acidic than your stomach acid! Considering most compounds dissolve in a couple of minutes or hours, lasting for 24 hours is an incredible result.

Figure 3 is the keystone figure to show the stability for these two ternary compounds. On the bottom axis (x-axis) is time in hours, on the left axis (y-axis) is the potential in volts we are measuring at our anode. This potential or voltage can be thought of as, but not directly related to, how much energy we need to put into the system to oxidize water at the anode. If the electrodes were corroding over time and then eventually had completely dissolved, the lines would spike up to a really high value. The system would then shut off because the electrochemical cell wouldn't have an anode to produce electrons for the cathode. The flat lines indicate the electrodes are still there and able to oxidize water.

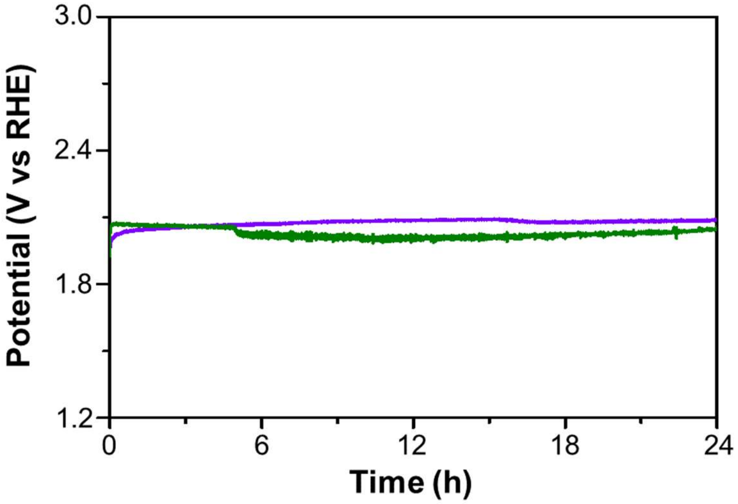

Figure 3. A voltage over time plot of $CoSb_2O_6$ (purple) and $MnSb_2O_6$ (green) performing water oxidation in sulfuric acid.

These two materials are not perfect though. While both $CoSb_2O_6$ and $MnSb_2O_6$ are able to oxidize water for 24 hours, they both have too high of a potential to oxidize water in order to compete with the rare and expensive noble metals. The $MnSb_2O_6$ also slowly dissolves over time and if we ran the experiment in **Figure 3** longer, it would eventually show that big spike in voltage and then shut off. That doesn't mean this discovery isn't important though! The work done on ternary materials containing Sb is an important milestone in developing new and interesting materials to oxidize water in acidic conditions. It can lead to new discoveries that may one day be able to replace the expensive noble metals with abundant, inexpensive catalysts that might contain a little bit of antimony oxide for that extra stability it can provide!

1.3 Antimony oxides and sunlight to split water

This section describes the work I have done in chapter 4 on developing quaternary metal oxides containing antimony (Sb) and bismuth (Bi) to use as photoelectrochemical electrodes. As before, let's break this down into bite sized chunks. "Quaternary metal oxides" means that we are forming metal oxides, which are compounds that contain both oxygen and metal elements, containing four different elements within them. "Containing Sb and Bi" means that two of those elements are antimony (Sb) and bismuth (Bi). These quaternary metal oxides are being used as "photoelectrochemical electrodes." Breaking that into three parts we see photo- meaning "light", electro- meaning "electricity" and chemical meaning "a compound" generally. These quaternary metal oxides are being used to absorb light, to convert that light into electricity (like a solar panel), which is then used to create a chemical compound directly at the surface of the electrode. This chemical compound is usually hydrogen, which is made by reducing water at our cathode, or oxygen, which is made by oxidizing water at our anode. What makes a photoelectrochemical (PEC) electrode different from a regular electrode, such as the $CoSb_2O_6$ described in section 1.2, is that a PEC electrode uses sunlight directly to create hydrogen gas or oxygen gas, instead of relying upon a powerplant to provide electricity.

There are *many* compounds and materials out there being investigated for use as PEC electrodes and they all have varying levels of success. A lot of work is going into trying to optimize known materials to improve their performance and stability, but researchers are also investigating brand new materials to use as PEC electrodes. This is inherently challenging as many of the binary metal oxides, which are composed of one metal and oxygen, have been extensively investigated. A large portion of the possible ternary metal oxides (two metals and oxygen) also have cursory results reported. For this reason, I chose to investigate even more complex compounds containing three metals and oxygen, i.e. quaternary metal oxides.

To help understand the complexity of synthesizing a quaternary material, think about mixing colors while painting a picture. In this analogy, a color is like a metal and the little bit of water you add to help the paint flow is oxygen. If you just add water to one of the colors, you are making a binary oxide, so just one metal and oxygen. Now what if you combined two colors, say red and blue to create purple, in this case you are making a ternary metal oxide. You need the exact same amount of red and blue with some water to create a perfect purple, otherwise you will have some excess blue or excess red which doesn’t make that perfect purple. What if you wanted to create the perfect brown (quaternary) by adding in yellow to the purple. Now you need the exact right combination of yellow, red, and blue paints. If you add in a little extra red and blue, it might form some purple (ternary) or maybe the red and blue (binaries) will stay separate. Or if you add in some extra yellow it might form some yellow spots mixed in the brown paint. You can see where this is going. Without very careful care, a material can contain a lot of different impurities and be a big mixture instead of one homogeneous compound. One of the most important parts of doing good science is being able to make observations and draw conclusions using a pure material, because those little impurities could have a big effect!

To make a homogeneous pure quaternary compound I developed a method of first depositing Sb and Bi together using electrochemistry. I applied a negative potential to reduce (adding electrons to) dissolved metal ions at a cathode creating the perfect one to one mixture of Sb and Bi on top of an inert glass slide as a thin film. Think of it like mixing blue and red first in a perfect manner to create flawless purple. To add in the third metal (the yellow paint), I placed a solution that contains the dissolved metal ions of our third metal on top of the Sb and Bi and then heated it up really hot (over 600 °C). The solvent evaporated leaving behind the third metal which then mixed with the Bi and Sb while it was really hot. Oxygen was also able to join the party from the surrounding air. Once the film cooled down, I washed away any remaining residue from the solution on top using a soaking solution that depended on which of the quaternary materials I was making. After this washing step, the desired quaternary metal oxide phase was successfully synthesized!

Figure 4. The quaternary phase $Cu_2Bi_3Sb_3O_{14}$ on a glass slide after removal of excess residue from the heating process.

Figure 4 shows an example of one of the synthesized quaternary compounds on a glass slide. This particular compound is copper bismuth antimony oxide ($Cu_2Bi_3Sb_3O_{14}$) and was the material I investigated the most as a PEC electrode. Its performance was not close to that of state of the art PEC electrodes unfortunately, but being able to make such a complex material in a relatively easy manner is still an important development towards finding the perfect brown color, or no wait, finding the perfect PEC electrode to split water!

1.4 Antimony and bismuth for ammonia synthesis

Here we are going to deviate slightly from the work I have described thus far. The two sections above have dealt with Sb combined with oxygen to form a metal oxide with some other elements thrown in. For this section, which describes chapter five of my thesis, the work has been done using Sb as an element and not as an oxide. This is different in that we are going to be really looking at what Sb is like by itself, or combined with another metal, instead of being combined with oxygen. But before we dive into the results of this work, I would first like to describe why ammonia (NH_3) is important.

Ammonia is made up of one nitrogen (N) atom and three hydrogen (H) atoms, so it is a relatively simple molecule. However, the only reliable source of naturally occurring NH_3 is from specialized bacteria that live in soil and on plant roots. These bacteria use powerful (but relatively slow) enzymes that can break the strong triple bond between the two nitrogen atoms in nitrogen gas (N_2) from Earth's atmosphere. This process is relatively efficient and is how a vast majority of life on earth obtains the critical nitrogen needed to make proteins and membranes. However, it was too slow for the growing number of humans on the planet one hundred years ago. Therefore, in the early 1900's, two chemists developed a process to artificially synthesize NH_3 using very high temperatures and very high pressures. This artificial synthesis method is called the Haber-Bosch process after the two scientists that developed it. The NH_3 produced via this process is used to make fertilizers for our food, plastics for our foam mattresses and clothing, cleaners for our houses, etc.

While this has been great for humanity, it has been quite taxing on the environment. The hydrogen we need to combine with nitrogen to make NH_3 comes from natural gas, a limited fossil fuel. This process releases almost two tons of CO_2 for every ton of NH_3 made, contributing a significant portion of the CO_2 emissions humans produce every year. The Haber-Bosch process also requires really high temperatures and pressures which can be quite dangerous and necessitates complex systems to produce this simple molecule safely. However, electrochemistry provides us with a safer and more sustainable solution! By applying a reducing potential at a cathode (remember this is where we add in electrons), we can break apart the strong triple bond in N_2 gas and then use hydrogen from water to create NH_3. This can all be done at room temperature, atmospheric pressure, and doesn't need large complex machinery to make it all work.

So why isn't it already all over the place? The difficulty with electrochemically producing NH_3 lies in an issue with selectivity. When we apply a reducing potential to our cathode in water with N_2 gas dissolved inside, NH_3 is produced but we also produce hydrogen gas (H_2)! NH_3 is the target molecule for our electrochemical cell but it has to compete with the production of H_2 at the cathode in water. This is difficult because H_2 is easier to make than NH_3 as it is a simpler molecule. Expensive noble metals like gold and palladium have shown interesting properties to improve the selectivity towards NH_3. However, they are expensive for a reason, they are very scarce and not a suitable electrode material for a future sustainable process. This requires investigating other elements to use as our cathode for NH_3 production.

Looking at the periodic table (**Figure 1**), there are a lot of elements and relatively limited work done on a vast majority of them for making NH_3 electrochemically. One that has been investigated semi-recently is bismuth (Bi), another semi-metal right below Sb on the periodic table. This had me thinking, what about Sb? It is right above Bi, it is also a semi-metal and has similar properties to Bi. This curiosity prompted a collaboration with Dr. Youn Jeong Jang, a postdoctoral scholar in our research group who has extensive knowledge in the field of NH_3 synthesis. We therefore worked together to develop and investigate Bi and Sb containing materials to use as cathodes for electrochemically making NH_3.

Figure 5 highlights the results we obtained for Sb alone, Bi alone, and then Sb and Bi combined. The bottom axis is looking at potential, or volts, so like in section 1.2 it is related to the energy we put into the system. The more negative the number, the more reducing potential we are applying to our cathode to reduce nitrogen to NH_3. The left axis is the efficiency of the reaction, which is telling of how selective our electrodes are for producing NH_3. The higher the number, the more selective the electrode is. Now, the results for Bi and Sb alone are not very interesting, both show relatively low efficiency and thus low selectivity. This is not too surprising as again, H_2 production is just so much easier than NH_3 production. However, by combining the two, we see a significant enhancement in the efficiency that is greater than either Bi or Sb alone.

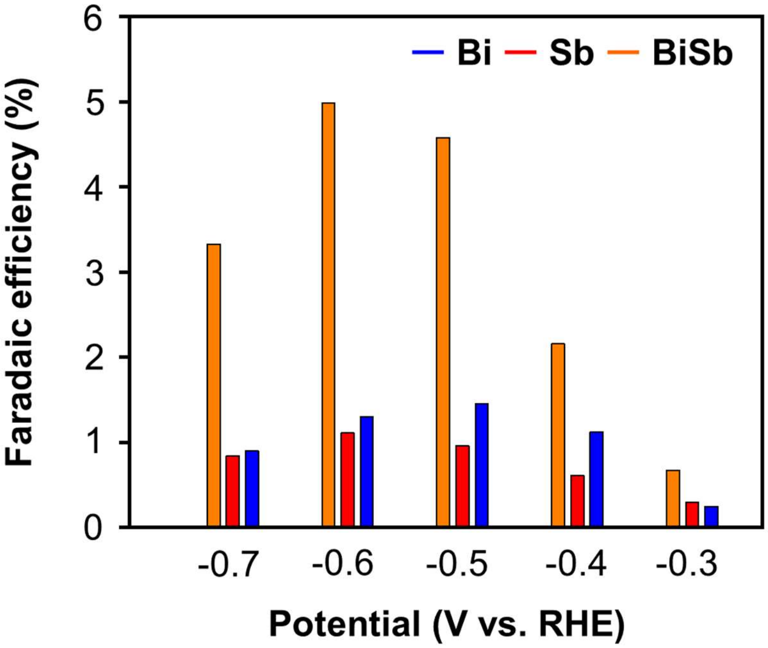

Figure 5. The efficiency (related to selectivity) of ammonia production at different potentials for Bi (blue), Sb (red), and BiSb (orange).

While the overall efficiency is still low for the BiSb combination, it still provides us with new knowledge about making NH_3. Something unique is happening by putting the two elements together that wasn't happening when they were separate. What is happening at the atomic level here? What interesting new information could we learn by exploring this further? Could we use this to make a better material? That is my favorite part about science; finding one new discovery opens the door to a number of new questions that lead to new discoveries and new questions. It is a chain reaction of learning and knowledge. While we have not yet fully elucidated the mechanism behind this fascinating discovery, we will be continuing to search for answers, because that is what scientists do!