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Over 40 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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Developing catalytic pathways for the valorization of biomass-based platform molecules via electrochemical reduction and oxidation reactions

By

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Chapter 1. An introduction to electrochemistry and biomass valorization for a non-scientist

1.1 Introduction

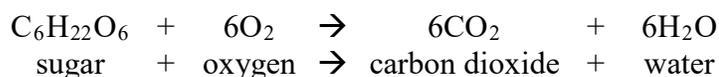
“What are the building blocks of our universe?” is a complicated question and if you ask a biologist, a chemist, and a physicist, you may receive four different answers. From my perspective, matter is composed of atoms which themselves are made of subatomic particles: protons, neutrons, and electrons. As a chemist, I seek to study how these particles interact with each other and with energy. The field of chemistry is immensely broad, ranging from research in the minute scale of the subatomic particles themselves, to the kiloton scale of industrial chemical production. My research presented herein falls somewhere in the middle, specifically on *developing catalytic pathways for the valorization of biomass-based platform molecules via electrochemical reduction and oxidation reactions*. Even as a chemist, I don’t always (and often don’t) understand the full meaning and impact of the titles of chemical research beyond my specific field of study at first glance. When this happens, I try to break it down to smaller parts, smile and nod, and hope by the end of a paper or presentation I collected enough context-clues to take away the key points. For this title, my main points are *electrochemistry* and *catalysis*, and then putting the two together to utilize *biomass*, which I will discuss below.

1.2 Electrochemistry

First, what are electrochemical reactions and electrochemistry? *Electro-* probably means electricity or electrons, and *-chemistry* probably means chemistry. Luckily it’s as simple as that in this instance. As an electrochemist, I study the flow of electrons in chemical reduction and oxidation reactions. To keep the two types of reactions straight I still often use the mnemonic I originally learned in high school: **OIL RIG** “**O**xidation **I**s **L**oss (of electrons), **R**eduction **I**s **G**ain (of electrons).” Or depending on the teacher others may have learned **LEO** the lion says

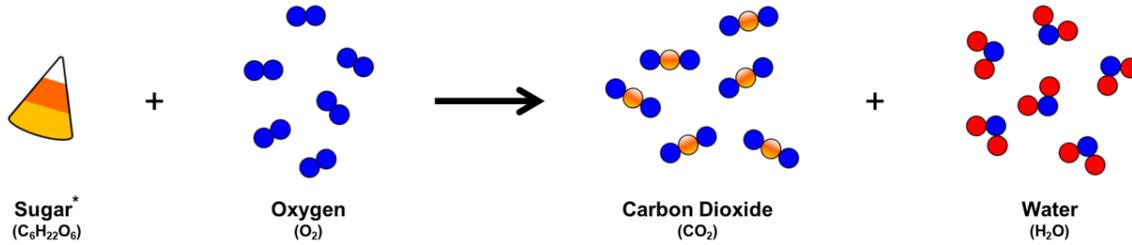
GER “Loss of Electrons is **O**xidation, **G**ain of Electrons is **R**eduction.” (I learned OIL RIG originally so I’ll arbitrarily claim it as the superior of the two).

Oxidation and reduction reactions are incredibly important as they are involved in many aspects of life, from bodily processes to the manufacture of goods. The first key thing to remember is that an oxidation reaction is always tied to a reduction reaction. If something is oxidized, and loses electrons, then something must be reduced, and gain electrons. A common reaction that is occurring in the cells of my body as I write this chapter is the result of stress eating sugar (Figure 1.1).

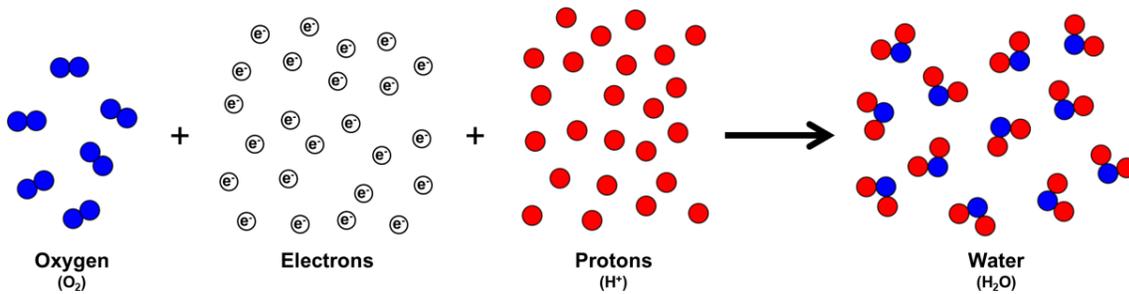


Overall, the cells of my body absorb and make use of the ample supply of protons, water, and sugar sloshing around in my stomach and the end result is the sugar I eat is oxidized (loses electrons) and oxygen I breathe is reduced (gains electrons). Through this reaction energy is released which my body can use to accomplish everyday tasks.

Overall reaction:



Reduction half-reaction:



Oxidation half-reaction:

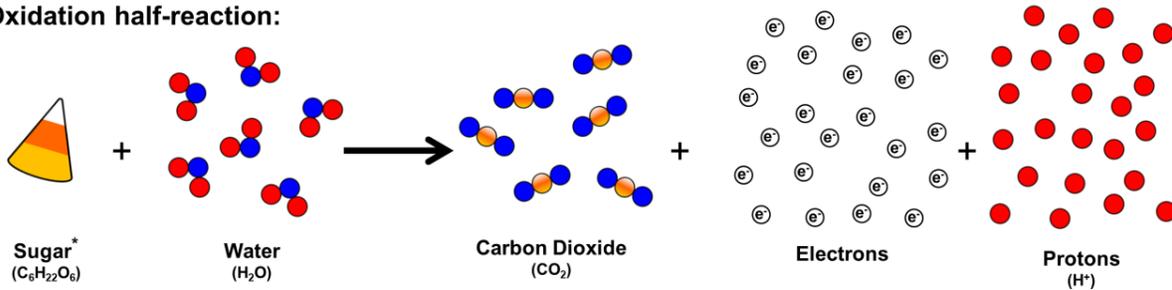


Figure 1.1. Overall balanced reduction-oxidation reaction of sugar (chemical formula: C₆H₂₂O₆) and oxygen (O₂) reacting to form carbon dioxide (CO₂) and water (H₂O), as well as the two balanced half-reactions that add together to make the overall reaction. *IMPORTANT NOTE: the representation of sugar as candy corn is not a statement that I frequently eat candy corn, I just found it an easy candy-shape to draw.

To study reduction and oxidation reactions, I make use of an electrochemical cell, which is composed of two electrodes, an anode and a cathode, submerged in a liquid solution with an electrolyte (Figure 1.2). An electrode is a material that allows electrons to flow through the electrochemical cell. Whether an electrode is the anode or cathode depends on the direction electrons are flowing in the electrochemical cell. To remember which electrode is which I again use a high school mnemonic: **A**node **O**xidation (both start with vowels) and **C**athode **R**eduction (both start with consonants). So **O**xidation reactions happen at the **A**node (electrons leave the cell), and **R**eduction reactions happen at the **C**athode (electrons enter the cell). (All of these mnemonics I use show that even now I can still use some concepts that were initially introduced even as far back as high school. I don't use "mitochondria are the powerhouse of the cell" in my research, but I am sure you can find that in a biochemistry or biology thesis somewhere).

To complete the electrical circuit I connect the anode and cathode by wires to a device called a potentiostat. The potentiostat gives me the ability to apply an electric potential (voltage) and then record the resulting direction and amount of electrons flowing in the circuit (electric current). Electric potential can be compared to a more intuitive gravitational potential; a ball will roll down a hill due to gravitational potential energy, and electrons will likewise flow due to an electrical potential (Figure 1.3).

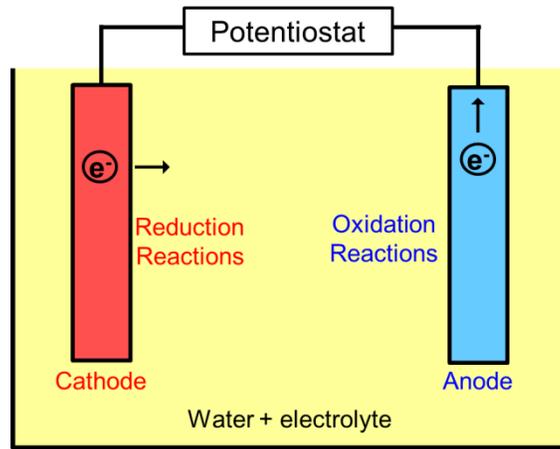


Figure 1.2. Schematic of an electrochemical cell. e^- represent electrons

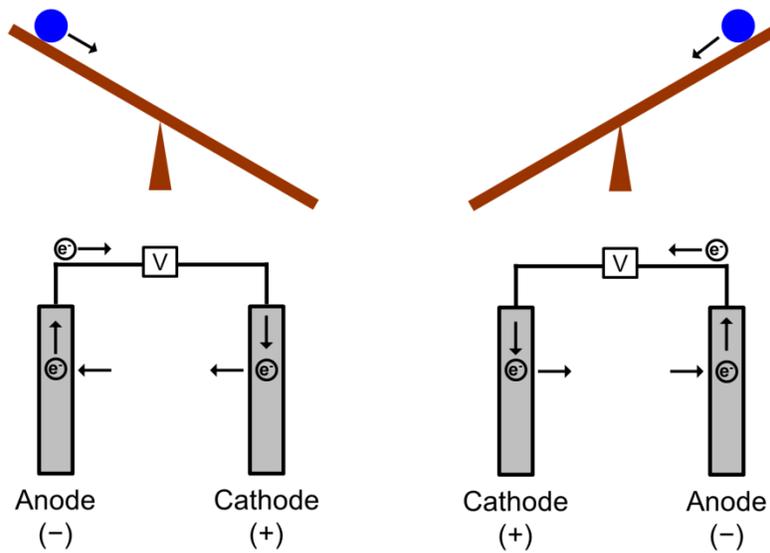


Figure 1.3 Schematic representation of an electrochemical cell in comparison to a ball rolling down a slope. On the left, the ball rolls down the slope due to gravitational potential energy, electrons flow from the anode to the cathode due to an applied electrical potential. On the right, the slope is reversed so the ball rolls in the opposite direction, likewise reversing the applied electrical potential causes the electrons to flow in the opposite direction.

An example of a useful reduction-oxidation reaction that makes use of an electrochemical cell is (Figure 1.4):

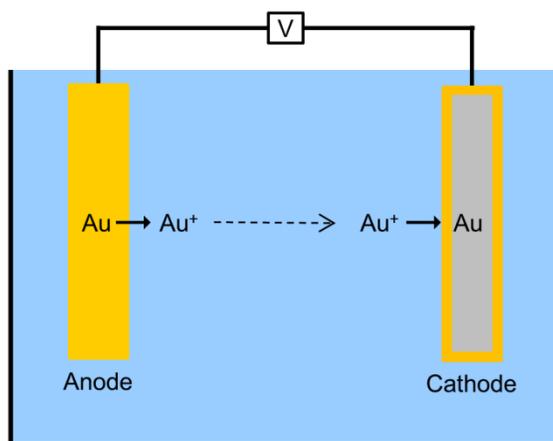
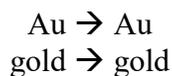


Figure 1.4. Schematic of an electrochemical cell where the anode is gold metal (Au) that is oxidized to soluble gold ions (Au^+). The gold ions travel through the solution to the surface of the cathode where they are reduced back to solid gold metal.

At first glance, turning gold into gold does not appear to be very useful. However, this reaction does have useful applications. First we can again break the overall reaction into two half reactions. In the oxidation reaction solid gold metal is oxidized to gold ions, which can dissolve in solution. In the reduction reaction dissolved gold ions are reduced back to solid gold metal.

Still, turning gold into gold may not be obviously useful or exciting and far from fabled alchemists trying to turn lead into gold. The key here is that in an electrochemical cell I can control where gold is dissolving (oxidation, anode) and where gold is being made solid (reduction, cathode) by applying the proper electric potential. For example, I can take a block of gold as my anode and connect it to a copper necklace as my cathode. In this configuration, gold from the solid block dissolves, travels through the solution, and is then plated onto the copper necklace as solid gold. In other words, I can take a worthless, shapeless block of gold and turn it into a gold-plated necklace (well a block of gold isn't quite worthless, but you know what I mean, it's harder to wear).

The above two reactions, sugar oxidation and gold plating, show the versatility of studying electrochemistry. I can study processes (e.g. oxidizing sugar to release energy) and I can make materials (e.g. reducing metal ions to make solid metal). I can also combine the two by making a material that is *catalytic* for a desirable process.

1.3 Catalysis

Catalysts increase the speed at which a chemical reaction will happen. Back to the rolling a ball down a slope analogy, imagine the slope has a bump in the middle (Figure 1.5). This time, instead of just rolling the ball once, you're repeatedly rolling balls down the slope. Depending on the size of the bump, the ball may easily pass every time (Figure 1.5a), it may get stuck some of the time depending on how hard you roll it (Figure 1.5b), or it may be simply impossible for the ball to roll down (Figure 1.5c).

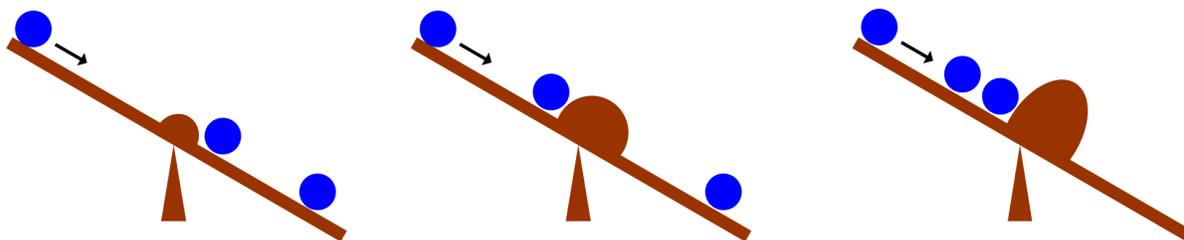


Figure 1.5. Rolling a ball down a slope with an obstacle in the middle. Depending on the size of the obstacle, balls may (left) pass with no problem, (middle) some can pass while others will be halted, (right) no ball can pass.

Chemical reactions work in a similar way and, in fact, chemical reaction profiles are even drawn in a similar way to the ball analogy (Figure 1.6). Chemical X may be able to convert to chemical Y spontaneously because it is energetically favorable overall (rolling down a hill) but there is an activation energy (a bump that takes some effort to pass) that affects the speed at which the conversion happens. A catalyst can increase the speed that X converts to Y by providing a route that has a lower activation energy so less energy is needed to “lift” over the activation energy.

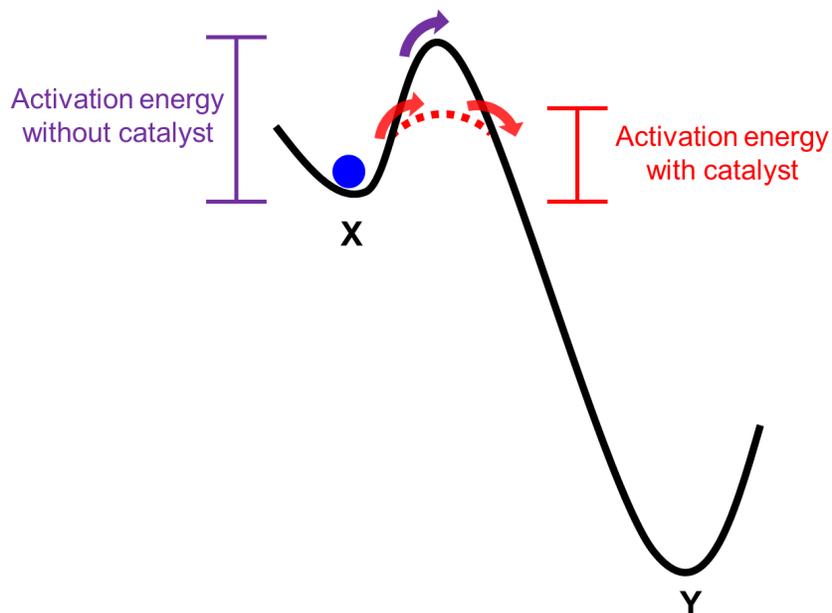


Figure 1.6. Reaction profile of chemical X converting to chemical Y. Activation energy is required to pass a barrier before the chemical X can be converted. The purple path shows the reaction without a catalyst. The red path shows that introducing a catalyst to the system can provide an alternate route that does not require as much energy, thus speeding the reaction.

I use electrochemistry described in the previous section to both make catalysts and to drive the catalysts I make to perform desirable oxidation and reduction reactions. The electrochemical synthesis is very similar to the gold electroplating example. I take a soluble precursor and then electrochemically reduce or oxidize it to make a solid catalyst material. Through electrochemical synthesis I can make a variety of metals, metal oxides, and composite materials all of which have different catalytic abilities for different chemical reactions.

With my catalysts made, I use electrochemistry to drive the catalysts to perform desirable oxidation or reduction reactions by applying an electric potential. Okay, so we have covered *electrochemistry* and *catalysis*, but what does this have to do with *biomass*?

1.4 Biomass Valorization

Finally, by *biomass valorization* I intend to increase the value of biomass, specifically plant-based biomass waste (e.g. the inedible parts of food crops), by converting it into useful chemicals via electrochemical catalysis. The goal is that by using biomass as a source for the production of industrially and commercially useful chemicals, our dependence on fossil fuels can be reduced.

Currently fossil fuels (e.g. coal, oil, natural gas) are used to produce a tremendous amount of products including fuels, plastics, pharmaceuticals, etc. Our dependence on fossil fuels has some problems. First, fossil fuels are finite. Exactly how much fossil fuel is available to us is difficult to quantify, as new drilling and mining techniques occasionally open access to previously inaccessible sources. However, fossil fuel deposits take millions of years to form, so there is no question that our sources of it are ultimately limited. Secondly, fossil fuel use results in the release of carbon dioxide into the atmosphere that was originally sequestered in Earth's crust. This released carbon dioxide can lead to a variety of environmental problems including climate change and ocean acidification.

In contrast, plant-based biomass is renewable. Instead of waiting millions of years for new fossil fuel, we only need to wait the growing season of the plant. Also the problem of releasing sequestered carbon dioxide into the atmosphere is eliminated. Of course a car or plane with a combustion engine will generate carbon dioxide regardless of whether the gasoline is derived from fossil fuels or biomass. The difference is if the fuel is derived from biomass this

represents a closed loop in the carbon dioxide cycle. Any carbon dioxide produced from biomass can be reincorporated into biomass by photosynthesis, so there is no net change in the amount of atmospheric carbon dioxide.

In order to not compete with human food sources, the biomass I seek to convert to valuable chemicals is derived from lignocellulosic biomass. Cellulose is the main component of the cell walls of plants and lignin is what makes plants woody or rigid. Lignocellulosic biomass represents the largest store of organic carbon on earth and is inedible to humans. This makes lignocellulosic biomass a rich raw-material source to manufacture valuable products. For example, we can grow and eat corn as normal but then use the inedible cob, husk, and stalk to produce useful chemicals. Figure 1.7 shows the chemical structure of cellulose. The brackets indicate that cellulose is made up of a very long chain of repeating units. Both lignin and cellulose are large structures, so I instead work with smaller “platform molecules.” Platform molecules are small, simpler molecules derived from lignin and cellulose that serve as platforms to generate useful chemicals. (Other research groups work on the process of breaking down lignin and cellulose into various platform molecules).

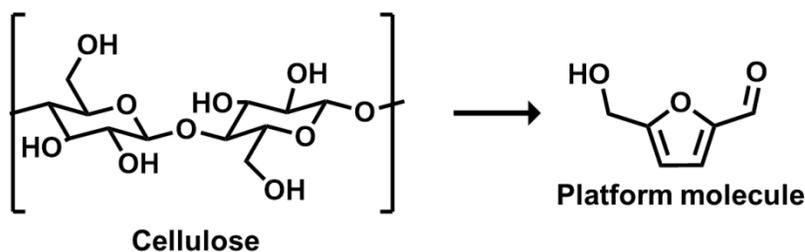


Figure 1.7. Cellulose is a large chain of repeating units that are used in the cell walls of plants that can be broken down into smaller platform molecules.

To tie everything together, my research involves the development of catalytic materials and conditions to electrochemically convert biomass-derived platform molecules into useful chemicals. One platform chemical I use is 5-hydroxymethylfurfural (HMF), which is a platform molecule that has recently generated a tremendous amount of research. Both reduction and oxidation of HMF can lead to very useful chemicals (Figure 1.8). Electrochemical reduction of HMF can result in 2,5-dimethylfuran (DMF). DMF can be used as a fuel that has a similar energy content to gasoline so can be used in combustion engines. Electrochemical oxidation of HMF can result in 2,5-furandicarboxylic acid (FDCA). FDCA can be used to make PEF plastics which have similar properties to those found in PET plastic (e.g. soda bottles). In other words this biomass-derived platform molecule, HMF, can (among other uses) be used to make both fuels and plastics to replace fossil fuel-derived counterparts.

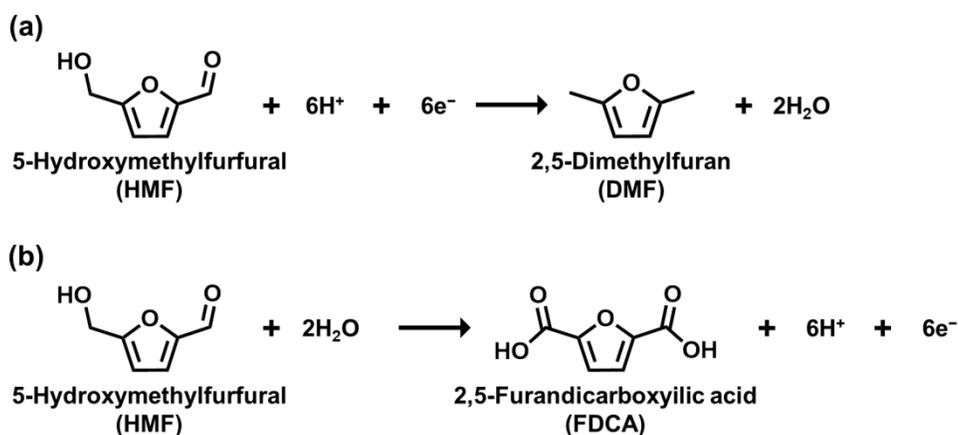


Figure 1.8. Balanced electrochemical half-reactions of (a) reduction of HMF to DMF which can be used as a fuel and (b) oxidation of HMF to FDCA which can be used to make plastics.

1.5 Conclusion

In summary, my research involves using electrochemistry to both make catalysts and then use said catalysts to drive useful reduction and oxidation reactions. Specifically, I aimed to develop ways to convert biomass-derived platform molecules into useful products to replace fossil fuel-derived products. All of the electrochemical methods I employed involve very benign conditions including the use of water, atmospheric pressure, and ambient or slightly elevated temperature. These safe features make scaling of electrochemical biomass conversion into industrial and commercial scales safe and relatively straightforward. In my lab benchtop-scale research my catalysts are on the scale of centimeters and my solutions on the scale of milliliters. To increase the scale I need only find a bigger beaker, replace milliliters with liters and my centimeter catalyst with a meter one, and so on and so forth until I reach an industrial scale.

During my graduate research, I have explored a variety of different starting platform molecules, catalytic materials for anodes and cathodes, and reaction conditions to generate a variety of different industrially and commercially useful chemicals. My research is just one piece of the larger picture that will continue even after I graduate. Other chemists in my research group as well as groups across the world will continue to research this topic. Further research will lead to finding new and better pathways to utilize biomass which will result in new ways to make the various chemicals and products we rely on in a renewable fashion.