Chemistry: Challenges and Solutions
<u>Unit 11: The Metallic World</u>
<u>Electrochemistry and Coordination Compounds</u>
Hosted by Cathy Drennan

[Tease]

Metals are the sturdy materials that help build skyscrapers.
They also play a crucial role in electrochemistry, which is the transfer of electrons in chemical reactions. One way we take advantage of this transfer is to power batteries.

CATHY DRENNAN: It's very hard to do some of this chemistry without a metal. You put a metal in there and then the chemistry can go.

Central to this chemistry of metals are reactions that involve oxidation and reduction, or redox for short. In these reactions, one species loses electrons while another gains electrons.

CATHY DRENNAN: Some redox reactions in the body require that our diet contain vitamins and trace metals. Vitamin B12 and B9, for example, are important for reducing the risk of heart disease and birth defects.

HOPE RICCIOTTI: Where these chemical reactions are occurring, that's where it all begins. And so a simple vitamin can prevent what is a devastating birth defect.

Studying redox reactions in batteries and in the body helps us understand that the metallic world and electrochemistry provide us energy and benefits to our health.

[Title: Unit 11 – The Metallic World]

CATHY DRENNAN: This red solution has trace amount of metal ions in it. These metal ions are important for making chemical reactions go and those chemical reactions are important in human health. My name is Cathy Drennan, and I'm a professor at the Massachusetts Institute of Technology, and studying metal ions is my life's work. We're interested in these reactions, these oxidation-reduction reactions that are so important in the human body.

An oxidation-reduction reaction, also known as a redox reaction, involves a transfer of electrons, where one species gains electrons and one loses electrons. Oxidation is the loss of electrons, and reduction is the gain of electrons.

Metals in the middle part of the periodic table are called transition metals and they can exist as ions with a variety of different charges. This flexibility is exploited in oxidation-reduction reactions that occur in the human body

And it's the same oxidation-reduction reactions that occur to power batteries, batteries that are in your cell phone, in a flashlight, or that power robots.

[SEGMENT 1: Powered by Redox]

ARCHIE: Hello I'm Archie. I run on batteries.

Archie is a PR-2 robot programmed by a team at Worcester Polytechnic Institute.

DMITRY BERENSON: We create robots to do things that are helpful to people in the real world. For people that are elderly or have disabilities, tasks like getting something out of the refrigerator or making the bed, those tasks are actually very hard. And so we're hopeful that in the future, robots can be tools for those people to be more independent in their homes.

In real life scenarios, Archie needs to be able to get around, without being plugged in. So it runs on batteries.

DMITRY BERENSON: Any time the robot moves or interacts with the world, it requires energy. And Archie can get that energy from the batteries in its base.

But how do these batteries work? The batteries provide energy through a spontaneous chemical reaction called oxidation-reduction, or redox, which involves a transfer of electrons. During this process, one substance must gain electrons, which we call reduction, while another loses electrons, which we call oxidation. This movement of electrons creates an electric current which can power a device.

ARCHIE: Oxidation-reduction reactions are what power my batteries.

Before we actually learn about how redox reactions power Archie's batteries, let's look at a redox reaction of a metal in a solution.

[SEGMENT 2: DEMO – Oxidation-Reduction Reaction]

DANIEL ROSENBERG: Let's do a redox reaction. So I have this zinc metal in copper sulfate, plus two copper, and we are going to move some electrons. In this reaction, when the copper ions come in contact with the zinc, zinc gives up its electrons to the copper. Because zinc loses two of its electrons, it becomes ionized, plus two, and these ions move into the solution. At the same time, because the copper ions gain two electrons, they become neutral, copper metal, and deposit on the surface of the zinc. I extract the zinc. We can see that there's a darker coppery layer on top of the metal. In this reaction, zinc loses electrons, which is the oxidation; and copper gains electrons, which is the reduction. And that is a redox reaction.

But how can we take advantage of this transfer of electrons to power a battery? Batteries use two separate, or half-reactions, to convert a spontaneous redox reaction into electricity.

[SEGMENT 3: DEMO – Redox: Creating an Electric Current]

DANIEL ROSENBERG: So we're going to do the same redox reaction as we did before, only this time we're going to separate the oxidation side of zinc going from zinc metal to zinc ions, and the reduction side where copper ions turn into copper metal. Why do we do this? So that we can grab the electrons that we will transfer via this wire from the zinc metal to the copper solution. What you're about to see is exactly like the oxidation-reduction reactions that happen inside of a battery. So the oxidation: zinc metal goes to zinc ions, leaving behind electrons in the metal. The reduction side: copper ions go to copper metal, and they do that when they have electrons available to change their copper plus two to copper zero metallic state. And in order to get those electrons from this zinc electrode to the copper electrode, I'm going to connect them with a wire. So now we have the same redox reaction as we had when we just put zinc into a copper solution, except here the zinc is oxidizing into solution leaving behind electrons, which flow on the wire to the copper electrode, where they reduce the copper ions. So the zinc is dissolving and the copper metal is plating out on the copper electrode.

But this is only going to work for a little while because the zinc solution is going to get too positive and the copper solution is going to get too negative. And so in order to balance out the solutions, we have a salt bridge. The salt bridge is really just a tube full of salt water and when I place it into the solutions that allows for positive and negative ions to move and balance out the charge of the solutions. So now we have a complete circuit. And I know that electrons are flowing, but if we want to know how much work we can do with those electrons, we can connect these two half-cells to a voltmeter. And the voltmeter is going to tell us the pressure at which the electrons are being pushed out of the zinc and over to the copper. And so when I connect these two, we should see a voltage of a little bit more than one volt, which we do. So what we essentially did is to trick a redox reaction into lending us electrons, just like we do inside any battery.

[SEGMENT 4: Vitamin B12]

Metals allow for redox reactions, and we can take advantage of this transfer of electrons to provide energy, just as in a battery. But metals also contribute to important redox reactions inside our bodies.

Cathy Drennan: There are many metals inside the human body. It's an inorganic playground of metals. All throughout the human body there's oxidation-reduction reactions going on as you are transforming the food that you eat to turn it into energy. Oxidation-reduction is important from your head to your toe, which means that we are just one big battery.

CATHY DRENNAN: Welcome to my lab. Come on in.

Cathy Drennan and her team study vitamins with trace metals to understand how these redox reactions drive chemistry within the human body. Vitamins are molecules found in food that your body needs to carry out certain reactions. One vitamin they are focused on is B12.

CATHY DRENNAN: B12 is found in meat and fish, and is an essential vitamin. B12, along with vitamin B9, can help reduce the risk of heart disease and promote cell replication.

So my favorite vitamin is vitamin B12. And it's important for all sorts of different human health aspects. And it's really this elaborate, beautiful molecule. And it's capable of doing amazing chemistry.

In the center of B12 is the trace metal cobalt, which is essential for the proper functioning of the vitamin. Cobalt exists in three different oxidation states in the body: plus one, plus two and plus three. The oxidation state of an atom is the number of electrons that have either been gained or lost from its neutral state. The amount of positive charge, or oxidation number, of the cobalt atom will determine how B12 interacts within the body.

CATHY DRENNAN: Different oxidation states have different properties. They can do different chemistries. So knowing what state your vitamin is in is very important in thinking about what chemistry it is going to be able to do.

To study B12 at the molecular level, the team grows crystals of proteins that contain B12.

CATHY DRENNAN: To avoid oxygen from the environment changing the oxidation state of the metal, an anaerobic chamber can be used.

ELIZABETH WITTENBORN: This is an anaerobic chamber. It's an oxygen-free environment where we can study proteins that have metal ions in them without the metal ions being oxidized by oxygen.

Once the crystals have grown, the team uses X-ray crystallography to learn more about the structure of their vitamin B12 proteins. A pin with a crystal of the B12 protein is placed on a machine that will fire X-rays to reveal the electron density of each and every atom.

ELIZABETH WITTENBORN: What the electron density shows is where there are a large number of electrons in the molecule, and so that's the blue that we see here on the screen. And wherever there are a large number of electrons that correlates to where the atoms are. And so that tells us that the cobalt is there because it's very large and electron-dense relative to the atoms around it and so that causes the large ball of electron density. So this tells us there is actually a metal ion present in the protein but it doesn't tell us anything about the oxidation state.

CATHY DRENNAN: Oh, that looks great.

In addition to spectra data, the oxidation state of cobalt can be determined simply by color.

CATHY DRENNAN: Telling the oxidation state of the cobalt within the B12 is actually pretty easy because of the color.

NOZOMI ANDO: So this is a photo of a protein crystal. So here's a protein crystal, and the protein has vitamin B12, which has cobalt, and the cobalt is in roughly in the plus one oxidation state. And you can tell this because the color is kind of greenish.

CATHY DRENNAN: And then the cob plus two state is much of an orangey color. In the cob three state, it's this sort of brilliant sort of red color. And so we can just look at it either with a naked eye or you can look at crystals under a microscope. But often you have the protein concentrated enough, you can just hold it up and go, cob two.

While the cobalt atom in B12 can exist in three different oxidation states in the body, two of them are important for a reaction that involves folic acid, or vitamin B9. They are cobalt plus one and plus three. In the cobalt plus one state, B12 is highly reactive. It performs the difficult task of converting a type of folic acid, called methyltetrahydrofolate, into a form the body can use. In the reaction, B12 breaks the bond of the folic acid, removing the methyl group, CH_3, which then attaches to the cobalt atom, changing its oxidation state from plus one to plus three. With the methyl group removed, folic acid is in a state known as tetrahydrofolate, a version of the vitamin that helps promote cell replication.

CATHY DRENNAN: It is really hard to just pull that methyl group off the folic acid, but when you have vitamin B12 in that super-reactive cob plus one state, it can do it. And if you don't have it in that state, the methyl group stays stuck on your folic acid and the folic acid is not useful. And that is a real problem for human health.

CATHY DRENNAN: Once cobalt is converted to the plus three state, B12 performs another important function. It reacts with an amino acid called homocysteine to produce another amino acid called methionine. Methionine is essential for making proteins in the body. In converting homocysteine to methionine, the methyl group is transferred such that two electrons are left behind with the B12, reducing the cobalt from the plus three to the plus one state. Homocysteine forms a new bond with this methyl group using two of its electrons, and the amino acid methionine is generated. This redox reaction decreases homocysteine levels and increases methionine, both crucial for human health.

CATHY DRENNAN**:** Do you want a high level of homocysteine or do you want your homocysteine converted to methionine? High homocysteine levels are correlated with heart disease. And it is, in fact, a better correlation than other things like cholesterol. So people should be asking, "What is my homocysteine level?" and maybe thinking about what they are eating, what their diet is and are they really getting enough of vitamin B12 and folic acid to make sure that their homocysteine levels are low.

These two separate redox reactions continue to cycle spontaneously. And crucial to the cycle is the cobalt atom, with its changing oxidation states.

CATHY DRENNAN: When you put a metal like that into a biological system, those metals allow for incredible transformations of one molecule to another molecule. And it's very hard to do some of this chemistry without a metal. You put a metal in there and then the chemistry can go.

[SEGMENT 5: Folic Acid in Fetal Development]

Redox reactions that occur in our bodies when we eat foods with vitamin B12 are studied down to the atomic scale in the lab. The results of this research lend insight into a public health study on the positive effects of vitamin B9. B9, or folic acid, is found in leafy greens and is an important ingredient for your body to make new cells, which is especially critical in the earliest weeks of life.

HOPE RICCIOTTI: Folic acid or folate is a B vitamin that is naturally occurring in food, but people often take it as a supplement. And it's probably the single most important nutrient that I end up talking about to my patients of childbearing age. And that's because there was an enormous discovery a couple of decades ago when we found out that adequate amounts of folate or folic acid in the diet could substantially reduce the risk of neural tube defects – devastating birth defects, for which there's no good treatment. A simple vitamin supplement can make an incredible difference in one of the most common birth defects we see.

Folic acid is an integral part of the cycle of redox reactions involving cobalt, the trace metal found in vitamin B12. It is this redox reaction that lends

insight into why B9 has been linked to a decrease in birth defects. But to take part in these important redox reactions folic acid has to be in the diet of the mother even before she realizes she is pregnant. This is because the neural tube forms very soon after conception.

HOPE RICCIOTTI: The neural tube is the tube that ultimately goes on to form the spinal cord and the brain. And it starts out as a disc, and that disc undergoes a folding to create a tube at about four weeks after conception. And defects in the seam of that tube are what ultimately can become neural tube defects.

Because the neural tube forms so early, it is essential to have folic acid in your diet in the very first weeks of pregnancy and even before pregnancy, since many are not planned.

HOPE RICCIOTTI: The average person in the United States doesn't plan their pregnancy. Half of pregnancies in the United States are unplanned. It doesn't mean unwanted, it just means unplanned. And so unless you're really planning ahead, you won't know to get the folic acid in time, and half of our patients are not planning ahead. So we have to sneak folic acid or folate into them without their noticing. And so the U.S. government, since 1998 started fortifying grain products in the United States with folic acid. And there has been a significant decrease in the number of neural tube defects that we've seen since that time. So it's been an enormous public health success story.

CATHY DRENNAN: You have to get an electron in, and we have to get an electron out.

To understand how folic acid can have such an influence on our health, we must turn to chemistry.

SQUIRE BOOKER: To really appreciate the need for folic acid, requires the understanding of the detailed mechanisms by which folic acid is used in the cell.

CATHY DRENNAN: Folic acid takes part in a redox reaction with the trace metal cobalt in vitamin B12. A form of folic acid, called methyltetrahydrofolate, reacts with the cobalt plus one atom in B12 and contributes its methyl group. The methyl group moves through its cycle until it is attached to homocysteine to generate methionine. Through an additional reaction, methionine is converted to S-adenosyl methionine, a molecule that is essential for numerous reactions in the body including formation and maintenance of the spinal column.

SQUIRE BOOKER: So I think everyone appreciates that folic acid is essential. We get folic acid basically as methyltetrahydrofolate. But in order for it to be useful for other biochemical processes, we need to remove the methyl group.

CATHY DRENNAN: An additional issue that must be considered when understanding the chemistry of B12, is that when we ingest it, the cobalt atom is in the plus two oxidation state, which is not reactive with folate. The cob two state, is sadly non-reactive in this particular form. If it is cob two it is not going to be able to do the chemistry you want. But you can fix it. You can reduce it.

To reduce the cobalt atom from the plus two to the plus one state requires a non-spontaneous reaction. In other words, energy must be supplied to the system to drive the reaction forward. The electron needed to reduce the cobalt of B12 comes from a protein called flavodoxin, which contains another B vitamin that is derived from riboflavin or vitamin B2. Flavodoxin gives up an electron, becoming oxidized, while at the same time, reducing the cobalt atom from plus two to plus one. Because the reduction of B12 by flavodoxin is non-spontaneous, energy must be supplied to the system for the electron to move from the flavodoxin to B12. In the body, that energy comes from a high-energy molecule. Once the cobalt of B12 is in the plus one state, it is ready to react with folic acid, and start the chain of reactions that helps create a healthy brain and spine.

HOPE RICCIOTTI: It's one of the most extraordinary stories when you think about it. Vitamins can prevent what is a devastating birth defect. Something that, you know, all the technology and all of the medicine and surgery in the world can't fix or prevent. But simply taking a vitamin supplement, or fortifying the food line, that's a very simple intervention with a huge impact on human health.

CATHY DRENNAN: So in an oxidation-reduction reaction sometimes the process by which one element gives off an electron and another one takes it, it can be spontaneous. You just put these guys near each other and they say, "Hey you want an electron?" The other one grabs it. Everybody's happy. Other times, it's non-spontaneous. The things that you have mixed together, they don't really want to transfer electrons to each other. And sometimes you might not care about it, but if you want that reaction to go, you need to apply energy to drive that reaction forward.

[SEGMENT 6: DEMO – Non-Spontaneous Redox Reaction]

DANIEL ROSENBERG: Hi, today we are going to make a non-spontaneous reduction-oxidation reaction, and that sounds complicated, but really what we're going to do is we are going to put zinc on this drywall screw. The way we're going to do that is with a zinc electrode in a zinc solution of zinc plus two ions. And when we place iron into a zinc solution nothing happens. In order to make a non-spontaneous reaction happen, we have to add energy. And in this case we're adding energy with this DC power supply. When I attach the electrodes and I place the iron screw into the solution, the zinc metal clings to the iron and forms a coating. So what have we done? At the zinc electrode, zinc metal loses electrons to form zinc plus two ions that go into solution. And that is an oxidation reaction. At the negative terminal, the zinc plus two is drawn to the electrons that we're putting onto the screw. Zinc plus two gains electrons to form zinc metal on this iron screw. And that is a reduction reaction. And now when I remove the screw from the solution we can see that instead of the black iron color that we started with, we have this sort of light grey zinc layer. And that's not just a decorative coating. Zinc metal coating on an iron screw is called galvanizing and it is one way that you can make iron objects resistant to rust. And this is all because we did a non-spontaneous reduction-oxidation reaction.

[SEGMENT 7: Hair, Highlights and Redox]

CATHY DRENNAN: The ability for transition metals to exist in several different oxidation states makes them ideal candidates for redox reactions. But not all redox reactions involve transition metals or metals of any kind.

So today I'm doing a different kind of chemistry. I'm not in my laboratory. Today I'm in a salon in downtown Boston. And I'm having my hair highlighted. And when you highlight your hair, or bleach your hair, you're putting chemicals in your hair. One of these chemicals is hydrogen peroxide, and it's causing a redox reaction. In my hair there's a small molecule called melanin and it is responsible for my hair's color. Changing the oxidation state of melanin will change the color of my hair. In one half-reaction, the hydrogen peroxide or H_2O_2 is gaining electrons and is being reduced. And in the other half-reaction, the melanin molecules lose electrons and are being oxidized. And that will make my hair lighter, as you'll see in a few minutes. Hair, like anything that has color, absorbs some light and reflects the rest of the light.

For white hair, no light is being absorbed. All of the colors of the visible spectrum are being reflected, so it appears white. With black hair, all of the colors of the visible spectrum are being absorbed, and no colors are reflected, so it appears black. After the melanin molecules in my hair are oxidized through bleaching, they only absorb the highest energy visible light, mainly violet. The rest of the light is reflected. Our brains interpret this color as the middle of the spectrum of what is being reflected. Thus my hair looks yellow or blond.

And you can see the results of oxidation of my hair. So who says chemistry can't be fun?

[WRAP-UP]

CATHY DRENNAN: So there you have it. Redox reactions are everywhere. Whether you're turning on your flashlight or coloring your hair. Redox reactions are also why vitamin B12 and folic acid keep us healthy. As a mom and a scientist, remember to eat your greens!

[END]