Practical Applications of Inorganic Chemistry: Modern Materials

In our previous experiments you explored the chemical reactions of selected inorganic cations and anions, determined the optimum structure for some simple inorganic molecules and polyatomic ions, and studied the structure of a variety of solid-state inorganic materials. In this experiment we turn our attention to exploring some practical applications of the reactivity of and the structure of inorganic compounds. You will work through the various portions of this experiment in an order to be shared with you in lab.

Pre-lab Assignment

Read through the lab to familiarize yourself with the procedure for each station, paying particular attention to the safety precautions.

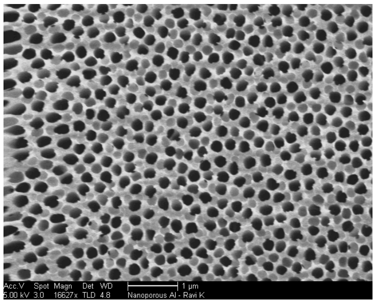
Station 1. Anodization of Aluminum

If we pass an electric current between two metal electrodes suspended in an aqueous solution of dissolved ions, we can break up water molecules into hydrogen and oxygen gases, a process we call electrolysis. The chemical equation describing this reaction is

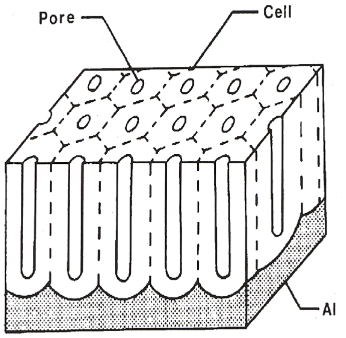
$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

with H_2 forming at the cathode (the electrode where reduction takes place) and O_2 forming at the anode (where oxidation takes place). If the electrodes are relatively inert metals, such as platinum, then bubbles of H_2 and O_2 form at the electrodes. If the anode is a more reactive metal, however, the oxygen that forms during electrolysis reacts with the metal and no bubbles of O_2 are seen. For example, if we use aluminum as the anode, then the O_2 reacts with Al to form a layer of aluminum oxide (alumina or Al_3O_2) that protects the metal from further oxidation. We call this process anodization.

The aluminum oxide coating produced through anodization is extremely hard and durable, and possesses a unique structure (see photo and figure below). The coating consists of a base layer of aluminum covered with a porous layer of aluminum oxide that extends down into the base layer. The pores are extremely uniform, and regularly arranged in a honeycomb-like hexagonal grid pattern.



Scanning Electron Microscope (SEM) image of the anodic aluminum layer showing the uniformity of the pore structure. (Picture from Deb Simon)



Pore structure of idealized anodized aluminum oxide layer. (Diagram from the Electrochemical Society)

We can take advantage of this porous structure to permanently color the surface of the anodized metal by immersing it in a solution of dye, allowing the dye molecules to enter into the pores, and then immersing it in a sealing bath, which hydrates the crystalline structure and permanently locks the dye within the layer.

Working with a partner, you will anodize two bars of aluminum. If there are an uneven number of students, then the lone person will anodize two bars. At the station you will find the items shown in the photo below and an electrolysis station.

Cleaning the Aluminum

Cleaning is crucial as every mark will show up in the finished product. Wash your hands before handling the aluminum and handle the bars by the edges only.

Wash the bar using the soap at the sink and the small scrubber-sponges; scrub the bar well and rinse thoroughly.

After cleaning the aluminum, hook the bar on the small end of the long aluminum hook and immerse it in the test tube of NaOH for approximately two minutes to remove any surface coating of Al_2O_3. The bar should have a smooth matte finish; if it does not, return it to the NaOH for another minute or two.

When the NaOH rinse is complete, dunk the Al into a bath of HNO_3 to neutralize the base and then into a DI water bath to remove the excess acid. Rinse the bar well with DI water. Do not rub the bar with your fingers while rinsing. Finally, handling only by the edges, lay the aluminum bars on a dry Kimwipe.

Setting Up the Electrolysis Cell

The electrolyte for this step is a solution of the alum you prepared in Experiment 2 and sulfuric acid. If needed, add electrolyte to the 400-mL beaker so that there is at least 300 mL of electrolyte. Place the beaker of electrolyte in the center of the water bath that is sitting on the stir plate. Add the plastic grid and a stir bar to the beaker.

> ***Caution: The electrolyte contains sulfuric acid (H_2SO_4), which is a strong acid; do not get it on yourself!***

Check and adjust the level of the water in the water bath; it should be about even with the level of the acid in the beaker. The basin of water will serve to moderate the heat produced by the reaction.

Setting Up the Cathode

> ***Caution: The power supply must remain OFF and unplugged until your instructor indicates that it is safe to plug it in and turn it on. Before continuing, ensure that the power supply is unplugged and that the I/O switch is in the off ("O") position.***

Clip the BLACK lead (connected to the "–" terminal on the power supply) to the very top right hand corner of the cathode (the Al plate provided at the station). Place the cathode as far back in the beaker as possible and make sure the plastic grid is in front of the cathode.

Setting Up the Anode

Handling them only by the edges, clip an Al bar to each of the two alligator clips and attach them to the RED lead. Make sure that the tops of the bars are even with each other and that they do not touch each other.

Gently but firmly clamp the RED lead in the fingers of the micro-clamp on the ring stand so that the bars are submerged. Do NOT let the alligator clips touch the acid; they should be about ¼ – ½ inch above the acid. Readjust the bars if they are crooked.

Be sure that the bars as close to the front of the beaker as possible (as far from the cathode as you can and on the other side of the plastic grid), and that neither the bars or the clips are touching the beaker's walls.

Running the Electrolytic Cell

Turn on the stir plate. The stir bar might bump into the Al bars or the plastic grid, but it should be fairly smooth-running. Before proceeding further, ask your instructor to approve your set-up.

Instructor's initials:________________

Plug in the power supply, flip the I/O switch to "I" to turn on the power, and start the timer immediately.

You want the cell to pull a current of 0.6–0.7 amps, but you will not achieve this immediately. Because the current drawn by the cell will vary with time (it changes as the coating builds up), you will need to adjust the voltage knob to bring the current into the proper range.

Adjust the upper knob to set the voltage to approximately 10 volts and after 2-3 minutes, increase the voltage until you are pulling a current of 0.6–0.7 amps, but keep the voltage below 17. If needed, you may adjust the amp knob as well. It may take several minutes before you arrive at 0.6–0.7 amps. Be patient! Keep adjusting the knobs. Most of your run will be at approximately 16 volts and approximately 0.7 amps.

> ***Caution: Do not put your head over the cell and take a deep breath because the reaction is producing H_2 gas!***

Monitor the set-up throughout the run and adjust the knobs if the voltage or current becomes too high or too low. If bubbles of hydrogen gas stops forming at the cathode, call the instructor.

Turn off the power after 20 minutes.

Removing the Bars

> ***Caution: Unplug the power supply before continuing!***

Unfasten the red lead wire from the finger clamp and, holding the bars over a beaker or the sink, rinse the bars well with DI water. Holding by the edges only, gently unclip each bar and hook it onto the small end of a long hook. Rinse the bars under fast running COLD tap water. Rinse both sides thoroughly, but DO NOT RUB.

In your notebook, be sure to describe reactions and the changes of color and/or texture that occur as the anodization proceeds. Describe the texture/color of the metal surface formed.

Dyeing and Sealing the Aluminum

When you finish the anodization reaction, you may choose to mask a part of your aluminum bar using a Sharpie Paint pen so that it is not colored by the dye. If you do, be careful to let the piece dry and do not touch other parts of the bar when using the pens. Allow the ink to dry thoroughly before continuing.

Take your aluminum bars to one of the dyeing stations. Check the temperature of the dye. Do not use a dye solution unless its temperature is between 60–65°C. If necessary, cool the dye by pouring into an empty beaker. If it is too hot, it will seal the piece before the color can enter the pores of the Al_2O_3.

Immerse the piece in the dye bath for 2–5 minutes; longer times give darker, more uniform colors. To check color intensity, take the piece out, rinse it off, and check the color. Put it back if you want a darker color. When the color reaches a desired shade, rinse the bar well with deionized H_2O. Do not rub the metal.

Immerse the rinsed piece in the sealing bath (80 °C) for 5 minutes, and then rinse well under cold tap water.

While your pieces are dyeing, remove everything from your beaker of electrolyte, rinse all the pieces off, and lay them on the towel in front of your station. Dispose of the electrolyte in the waste bottle in the hood if you are the last group of the day.

When you have finished dyeing your piece of Al, take it to the hood. Remove the ink mask by dunking it in acetone.

In your notebook, describe the durability of the layer of color created by this process.

Checking Conductivity

Turn the multimeter to the **Ω** setting; this will measure resistance (the higher the resistance, the lower the conductivity). Place both leads on the anodized portion of your aluminum bar and note the results. Place both leads on the bare metal and note the results.

In your notebook, record your results and explain the difference in conductivity.

Split Rings and Engraving

If you want to put initials on your bar, you can use the letters provided. They are a bit crude and you will probably want to line them up using a straight edge, such as a ruler. Take a split ring and enjoy your new keychain!

Station 2. Anodization of Niobium Wire

Niobium (Nb) is a light gray reactive metal that forms a variety of surface colors when anodized. When undergoing anodization, niobium metal forms a layer of niobium oxide. Although the oxide is colorless, the metal's surface appears brightly colored due to the interference of light by a thin film, the same process responsible for the bright colors seen when you look at a soap bubble.

The thickness of the oxide coating, and thus the resulting color due to interference, depends on the voltage used during electrolysis. Niobium is a popular metal for jewelry because is easy to fashion into various shapes, forms a broad range of colors when anodized, and is modest in price. It is also hypoallergenic and can be worn by those sensitive to other metals, such as copper and nickel.

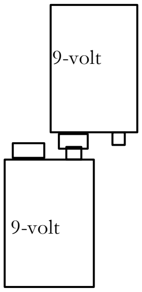
To anodize niobium we will use a set of 9-volt batteries as a source of current, combining them in series to obtain voltages from 9 volts to 81 volts. These voltages are not dangerous, although it is possible to receive an unpleasant electric shock if you do not follow these safety precautions:

> ***Handle only the plastic; do not touch any metal parts that are connected to the batteries. Plastic is an insulator, which means that the electric current will not travel through plastic.***
>
> ***Keep your hands dry as dry skin does not conduct electricity as well as wet skin.***

Complete the circuit using only one hand. For electrical current to flow, a circuit is required. Using one hand makes it difficult for you to become part of a circuit.

Obtain a 3.5-inch long piece of 22 gauge Nb wire. Clean the wire with soap, water, and a paper towel. Wipe the surface of the wire with alcohol on a Kimwipe to remove any fingerprints. Obtain a beaker filled with electrolyte solution (sodium borate in water). Use a stainless steel scoopula as the cathode and connect it to the negative terminal of a single 9-volt battery. Suspend the cathode in the beaker of electrolyte (do not allow the clip to touch the electrolyte) and clip it to the side of the beaker. Connect the Nb wire to the positive terminal (the anode) of the battery and submerge the wire into the electrolyte solution as far as it will go without submerging the clip holding the wire and without allowing the wire to touch the stainless steel cathode. You are now passing 9 volts of electricity through the wire and coating the wire with a thin layer of niobium oxide. Leave the wire in the solution for about 30 seconds. Remove the wire, wipe it off with a Kimwipe, and observe and note the color of the oxide film.

Connect a second battery in series with the first battery (see the diagram on the right), which will allow you to pass 18 volts through the wire). Attach the batteries open "–" terminal to the stainless steel cathode and its open "+" terminal to the Nb wire anode. Lower the wire into the electrolyte leaving approximately ¼–in of the previously anodized section of wire above the level of the electrolyte. Allow the wire to anodize for 30–60 seconds. Remove the wire, wipe off, and note the color produced.



Add a third battery to provide 27 volts. Lower the wire into the electrolyte solution, but leave approximately ¼–in of the previously anodized section of wire above the level of the electrolyte. Allow the wire to anodize for 30–60 seconds. Remove the wire, wipe off, and note the color produced. Now you have a wire with three different colors — one produce by 9 volts, one by 18 volts, and one by 27 volts — as well as the original gray color of the unanodized wire.

Continue to anodize your Nb wire by connecting it to 4, 5, 6, 7, 8, and 9 batteries, providing voltages from 36 volts to 81 volts. Be sure to leave approximately ¼–in of the previously anodized section of wire above the level of the electrolyte each time you change the voltage. When you are done you will have a wire with nine different anodized colors on it.

Now that you know what voltage will produce a particular color, you can obtain one or more pieces of Nb wire (up to a total amount of 1 ft. per person), anodize them to produce your desired color or colors, and form them into some type of jewelry. Because Nb wire is ductile, it is easy to bend and form them into a desired shape prior to anodization. Alternatively, you can make a small wire sculpture. Ear wires are also available to attach to your jewelry. You can use the provided beads, or some of your own, to augment your creation.

In your notebook, answer the following questions: (1) What change in color do you observe as you increase the voltage? (2) Is there a pattern to this change? (3) What is the chemical formula for niobium oxide? (4) Is the formation of niobium oxide an oxidation or a reduction reaction? (5) Write a balanced equation for the reaction producing niobium oxide at the anode and a balanced equation for the overall reaction. (6) What is the texture of the metal surface? (7) How durable is the layer of color created by this process?

Station 3: Superconductivity

One of the interesting properties of a superconductor, and the easiest to demonstrate, is the Meissner effect. When cooled below a critical temperature, T_c, a superconductor becomes so strongly diamagnetic that it will repel a magnet!

> ***Caution: Liquid nitrogen is extremely cold and can result in severe frostbite! Always wear safety glasses and thermal gloves when handling. Do not touch anything that has been immersed in liquid nitrogen until it has warmed up to room temperature. Always use the provided tweezers to place things into and to remove things from liquid nitrogen. Some of the metals that make up superconductors are toxic. Do not handle the superconductors with your hands.***

Using tweezers, place the superconductor disc in a Styrofoam dish. Carefully pour liquid nitrogen into the dish until the liquid is about ¼–inch deep and completely covers the superconductor. The nitrogen will boil around the disc, so wait until the boiling stops before proceeding. After ensuring that the disc is completely (and just) covered by the liquid nitrogen, use the tweezers to pick up the rare earth magnet and attempt to balance it on top of the superconductor disc. Try to set the magnet spinning with your tweezers (this models a frictionless magnetic bearing!).

In your notebook, answer the following questions: (1) Why did the liquid nitrogen boil when you added it to the dish? (2) When the liquid nitrogen boils off, the magnet stays levitated for a while longer. Why is this? (3) What are some possible applications of the Meissner effect?

Examine the unit cell for this superconductor It obviously is a much more complicated unit cell than the models you examined in the previous experiment. The colors representing each element are as follows: oxygen is colorless, copper is blue, barium is green, and yttrium is yellow. To help you investigate its structure, feel free to move the balls in the model up and down if it helps you better see the interior ions. In your notebook, answer the following questions about this unit cell: (1) What kind of hole does yttrium occupy? (2) How many nearest neighbors do the copper ions have? (3) The formula for this compound is $YBa_2Cu_3O_7$. Can you prove this based on your analysis of the unit cell? Show your work. (4) What can you conclude about the oxidation states of copper in this compound?

Station 4: Paramagnetism, Diamagnetism, and Ferromagnetism

You probably are familiar with ferromagnets—the ubiquitous "refrigerator magnets" that we encounter everyday—but you likely are unaware of why they are magnetic. In a normal paramagnetic compound, the spins of the unpaired electrons are oriented in random directions unless a magnetic field is present to align them. Ferromagnetism arises when these unpaired electrons interact with one another so that they are more or less permanently lined up even after the magnetic field is removed (hence the name "permanent magnet"). One of the interesting properties of paramagnetic (and ferromagnetic substances) is that they are attracted to a magnet, while diamagnetic substances are repelled by them. We can take advantage of this property to determine whether a compound is paramagnetic or diamagnetic.

Obtain gelatin capsules containing the following substances: MnO_2, Mn_2O_3, $KMnO_4$, and Fe. Draw a line on a piece of paper and place the capsules along the line. Approach each capsule with a large cow magnet and record what happens (i.e. the gelatin capsule moves a little, moves a lot, or shows no perceptible movement).

In your notebook, answer the following questions: (1) How many unpaired electrons would you predict that each of the metals has based on the oxidation states of manganese? (2) What relationship do you observe between the attraction of the compounds to the magnet and the compound's number of unpaired electrons?

Station 5: Ferrofluids

A ferrofluid is a liquid in which tiny ferromagnetic particles are suspended. Because of its make up, a ferrofluid can be controlled using an applied magnetic field. Use the magnets provided to investigate the properties of the ferrofluid in the sealed vial (note: do not attempt to open the vial). The spikes are due to the magnetic particles in the fluid lining up along the magnetic force lines of the applied magnetic field. Record your observations in your notebook.

As strange as ferrofluids may seem, they are more than just a novelty item. Ferrofluid inks are used in the printing of dollar bills to make them more difficult to counterfeit. Hang a dollar bill halfway off the lab bench, holding it in place with the palm of your hand. With your other hand, take a strong "cow magnet" and approach the end of the bill hanging off the bench very closely (end on) to an inked spot on the bottom of the dollar bill and pull the magnet very slightly downward. Watch very closely and record your observations! (Note: this is subtle but very cool!)

Station 6: Nitinol Memory Wire

Nitinol wire is an alloy of nickel and tin with a chemical formula of NiTi. The unit cell for nitinol is a simple cubic lattice of nickel atoms with titanium atoms occupying 100% of the lattice's cubic holes. Below 50°C, nitinol adopts a slightly distorted cubic structure in which the cubic lattice has interior angles slightly greater than and slightly less than 90°. At temperatures above 50°C, nitinol reverts spontaneously to its normal cubic structure in which all interior angles are 90°.

Obtain a piece of nitinol wire and bend it into a shape of your choosing. You may wish to use the available pliers to help you in fashioning your shape. Heat a beaker of water to boiling and immerse the shaped wire in the water. Record your observations.

Write Up

The write up for this lab is completed entirely in your lab notebook. Be sure to record data and observations for each station and to answer the questions associated with each station. Turn in a copy of your lab notebook pages at the beginning of our next lab.