

CHEMISTRY

Electrochemistry and Galvanic Cells

NGSS HIGH SCHOOL LESSON PLAN

What is electrochemistry? How is electrochemistry related to solar cells? This lesson is designed to help teachers educate students about the chemistry of solar energy.

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Image (cover): In a single replacement reaction, one element in a compound is displaced by another element: A + BC \rightarrow C + BA

Image Credit: Don Farrall/ Getty Images

Before You Start

1. What do I know about electrochemistry?

Evaluate what you know about electrochemistry and galvanic cells with this short assessment. Pre-lab Assessment

- 1. What is electrochemistry?
 - a. the study of the sun
 - b. the study of the movement of electrons
- 2. Balance the following redox half-reactions:
 - a. $Cr_2O_7^{2-} \rightarrow Cr^{3+}$
 - b. $SO_2 \rightarrow HSO_4^-$
 - c. What is the net reaction of (a) and (b)?
- 3. Mark the following statements as true or false.
 - a. In our dye-sensitized solar cells, triiodide is reduced at the counter electrode.
 - b. <u>Galvanic</u> cells require energy to run. A common example is a battery.
 - c. Less active metals are more easily <u>oxidized</u> than more active metals.

Assessment key:

- 1. B, electrochemistry is the study of how and why electrons move in plants, chemicals, people and much more.
- 2. Remember that equations with extra hydrogen or oxygen atoms can be balanced by adding hydrogen ions (H⁺) and water (H₂O).
 - a. $Cr_2O_7^{2-} + 14 H^+ + 6 e^- \rightarrow 2 Cr^{3+} + 7 H_2O$
 - b. $SO_2 + 2 H_2O \rightarrow HSO_4^- + 3 H^+ + 2 e^-$
 - c. $Cr_2O_7^{2-} + 3 SO_2 + 5 H^+ \rightleftharpoons 2 Cr^{3+} + 3 HSO_4^- + H_2O$

3a. True, triiodide, half of the electrolyte couple, is reduced at the counter electrode. Iodide, the product of this reduction is then oxidized in the presence of the blackberry juice dye.

3b. False, <u>electrolytic</u> cells require energy to run; however, batteries *are* <u>galvanic</u> cells.

3c. False, less active metals are more easily <u>reduced</u> than more active metals.

How did you do? Identify the material you need to review from the questions you missed and continue on to #2.

2. How does electrochemistry relate to solar energy?

Now that you've identified what you need to review, take some time to read through the background information on the next few pages. This information along with the information provided in the accompanying prelab handouts should serve to fill in any knowledge gaps you may have identified in #1. Once you are done, continue on to #3.

- c. the study of electrical circuits
- d. All of the above
- e. None of the above





3. Identify 3-4 learning objectives that connect the background information to the standards.

After reading through the five next generation science standards on page 6, what would you like your students to learn from this lab? To help prompt your thoughts, we've provided example objectives using language directly from the NGSS table.

Example objectives:

Students should be able to:

- construct and revise an explanation for the outcome of a simple chemical reaction based on knowledge of the patterns of chemical properties
- apply scientific principles and evidence to provide an explanation about the effects of changing concentration of the reacting particles on the rate at which a reaction occurs
- refine a solution to a complex real-world problem, based on scientific knowledge, student-generated sources of evidence, prioritized criteria, and tradeoff considerations

What objectives would you like your students to be able to complete?

4. Read through the demonstration procedure.

Any questions or concerns? Contact a Caltech scientist! We've happy to answer questions and clarify instructions as necessary.

5. Assess what you have learned.

At the end of this demonstration, your students (and you too!) should be able to fulfill all the objectives listed above in #3 along with any alternative or additional objectives you have identified from the NGSS standards. We have suggested some questions to assess what your students have learned. Feel free to use these questions or write your own.

What is electrochemistry?

As the name may suggest, electrochemistry deals with the chemistry of electrons: where electrons are and how they can move. Electrochemistry is the study of electron movement as it relates to chemical reactions. From photosynthesis to a rusting ship, electrochemical processes can be found at every level of life (Figure 1).

In particular, electrochemistry is critical to the development of solar cells. In order to understand how to generate electricity or chemical fuels -- the two possible products of solar energy conversion by solar cell -- we need to be able to track the electrons and how they are interacting with their environment.



Figure 1. The formation of rust on an old ship is an electrochemical process that forms iron oxide.

Redox reactions: the building blocks of electrochemistry

In the field of electrochemistry, one of the basic reactions is the oxidation–reduction, or *redox*, reaction. An oxidation–reduction reaction involves the transfer of one or more electrons from one species to another. The substance that loses electrons is *oxidized*; the substance that gains electrons is *reduced*.

Redox half-reactions

The electrons needed to reduce a compound must come from somewhere. Thus, all reduction reactions must occur with a corresponding oxidation. Because these reactions occur in pairs, it is often useful to consider each redox reaction in two parts, called *half reactions*. Added together, these two half reactions make up the overall oxidation—reduction redox reaction:

$$\begin{array}{ccc} A^{+} + e^{-} & \rightarrow & A & \text{reduction} \\ \hline B & \rightarrow & B^{+} + e^{-} & \text{oxidation} \\ \hline A^{+} + B & \rightarrow & A + B^{+} & \text{overall reaction} \end{array}$$

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The electrochemistry of solar cells

How does electrochemistry relate to solar cells? When we think about solar cells, we will start talking about *photoelectrochemistry*, the movement of electrons induced by light energy. While studying the movement of electrons in any part of our dye-sensitized solar cell is considered electrochemistry, we will focus on one aspect of this process: the regeneration of our dye, anthocyanin from blackberry juice, by an *electrolyte redox couple* (Figure 2).

The electrolyte redox couple, iodide/triiodide (written as I^{-}/I_{3}^{-}), moves electrons from the *counter electrode* to the dye, after the electrons have been used to do work in the load. At the counter electrode, electrons

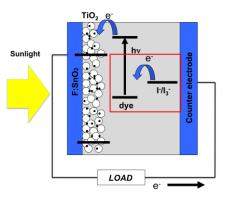


Figure 2. In this dye-sensitized solar cell, the redox couple Γ/I_3^- regenerates the anthocyanin dye.

are being removed from the electrode and into solution; thus, the species in solution that can most easily accept electrons will be reduced at the counter electrode. In this case, that species is the triiodide which will be reduced to iodide ($I_3^- + 2 e^- \rightarrow 3 I^-$). Once the iodide encounters a *dye cation* (Dye⁺), the dye cation is reduced and the iodide is oxidized back to triiodide ($3 I^- \rightarrow I_3^- + 2 e^-$).

Single replacement reactions

How do we determine what species in a reaction will be oxidized or reduced? One common example of a redox reaction is the single replacement, a reaction between a metal salt (such as NaCl) and an elemental metal (such as Mg). For these types of reactions, an **activity series** of metals is used to determine whether a particular reaction occurs. When a metal is higher on the activity series, it is considered more active; that is, it is easier for this metal to

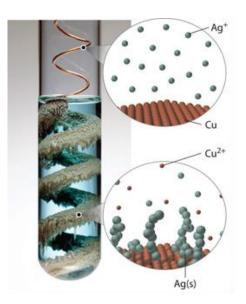


Figure 3. One example of a singlereplacement reaction can be seen here. Solid silver particles form on a copper wire dipped in a silver nitrate solution as copper ions form in solution, since the copper is easier to oxidize than the silver.

What are the two half reactions for this process? For copper (Cu) to Cu^{2+} : Cu (s) $\rightarrow Cu^{2+}$ (aq) + 2 e⁻ For Ag⁺ to silver (Ag): Ag⁺ (aq) + e⁻ \rightarrow Ag (s)

Write out the net reaction here. Remember to balance compounds and charge (i.e. number of electrons!).

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lose electrons, or be oxidized. Thus, in the single replacement reaction, the metal in a selected salt is reduced by an elemental metal that is more active, or higher on the activity series (Figure 3). An activity series reference table is shown below:

TABLE 4.4 Activity Series of Metals in Aqueous Solution			
Metal	Oxidation Reaction		
Lithium	$Li \longrightarrow Li^+ +$	e-	
Potassium	$K \longrightarrow K^+ +$	e-	
Barium	Ba → Ba²+ +	2e-	
Calcium	$Ca \longrightarrow Ca^{2+} +$	2e-	
Sodium	$Na \longrightarrow Na^+ +$	e-	$\langle \rangle$
Magnesium	$Mg \longrightarrow Mg^{2+} +$	2e-	
Aluminum	$AI \longrightarrow AI^{3+} +$	3e-	of oxidation increases
Manganese	$Mn \longrightarrow Mn^{2+} +$	2e-	8
Zinc	$Zn \longrightarrow Zn^{2+} +$	2e-	15
Chromium	$Cr \longrightarrow Cr^{3+} +$	3e-	
Iron	Fe → Fe²+ +	2e-	110
Cobalt	$Co \longrightarrow Co^{2+} +$	2e-	Ida
Nickel	Ni → Ni²+ +	2e-	8
Tin	$Sn \longrightarrow Sn^{2+} +$	2e-	님
Lead	$Pb \longrightarrow Pb^{2+} +$	2e-	356
Hydrogen	$H_2 \longrightarrow 2H^+ +$	2e-	Щ
Copper	$Cu \longrightarrow Cu^{2+} +$	2e-	
Silver	$Ag \longrightarrow Ag^+ +$	e-	
Mercury	Hg → Hg²+ +	2e-	
Platinum	Pt → Pt²+ +		
Gold	Au → Au ³⁺ +	3e-	

The activity series to the left shows which metals are more easily oxidized. That is, lithium is the most easily oxidized – the most active – metal in this series.

Which species is the most easily reduced – the least active -- in this activity series?

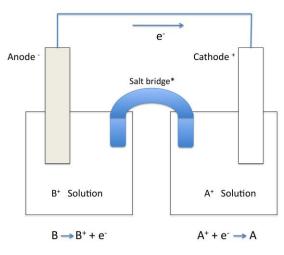
Galvanic cells

A galvanic cell is an electrochemical device that can produce electrical energy from spontaneous single-replacement redox reactions. A spontaneous reaction is a reaction that occurs without the input of additional energy. All electrochemical cells have two electrodes, a cathode and an anode. Solution species are always reduced at the cathode, and oxidized at the anode. In galvanic cells the cathode is then charged positive, as it is giving up electrons to reduce solution species, and the anode negative, as it is accepting electrons to oxidize solution species. When two different metals are used, the identity of which is the anode and which is the cathode is determined by their relative position in the activity series. The electrode containing the metal that is higher in the series – a metal that is more easily oxidized -- is the anode. Conversely, the electrode containing the less active metal – a metal that is more easily reduced – is the cathode.



The basic procedure

In this experiment you will construct a series of galvanic cells using metals and metal salt solutions. Each cell will consist of two half cells, each containing a metal electrode and its corresponding ion in solution (e.g. a piece of copper in a Cu²⁺ solution). Pairs of half cells will be connected together by a salt bridge which will supply inert cations and anions to each of the half cells, providing a pathway for ion flow (see diagram below). By examining your results you will be able to place four metals in order of activity, which should correspond to the actual reactivity of the metals.



*Salt bridge allows ions to flow between half-cells to maintain neutrality



Next Generation Science Standards

- HS-PS1-2. Construct and revise an explanation for the outcome of a simple chemical reaction based on the outermost electron states of atoms, trends in the periodic table, and knowledge of the patterns of chemical properties. [Clarification Statement: Examples of chemical reactions could include the reaction of sodium and chlorine, of carbon and oxygen, or of carbon and hydrogen.] [Assessment Boundary: Assessment is limited to chemical reactions involving main group elements and combustion reactions.]
- HS-PS1-4. Develop a model to illustrate that the release or absorption of energy from a chemical reaction system depends upon the changes in total bond energy. [Clarification Statement: Emphasis is on the idea that a chemical reaction is a system that affects the energy change. Examples of models could include molecular-level drawings and diagrams of reactions, graphs showing the relative energies of reactants and products, and representations showing energy is conserved.] [Assessment Boundary: Assessment does not include calculating the total bond energy changes during a chemical reaction from the bond energies of reactants and products.]
- HS-PS1-5. Apply scientific principles and evidence to provide an explanation about the effects of changing the temperature or concentration of the reacting particles on the rate at which a reaction occurs. [Clarification Statement: Emphasis is on student reasoning that focuses on the number and energy of collisions between molecules.] [Assessment Boundary: Assessment is limited to simple reactions in which there are only two reactants; evidence from temperature, concentration, and rate data; and qualitative relationships between rate and temperature.]
- HS-PS1-6. Refine the design of a chemical system by specifying a change in conditions that would produce increased amounts of products at equilibrium.* [Clarification Statement: Emphasis is on the application of Le Chatelier's Principle and on refining designs of chemical reaction systems, including descriptions of the connection between changes made at the macroscopic level and what happens at the molecular level. Examples of designs could include different ways to increase product formation including adding reactants or removing products.] [Assessment Boundary: Assessment is limited to specifying the change in only one variable at a time. Assessment does not include calculating equilibrium constants and concentrations.]



Science and Engineering Practices

Constructing Explanations and Designing Solutions

Constructing explanations and designing solutions in 9–12 builds on K–8 experiences and progresses to explanations and designs that are supported by multiple and independent student-generated sources of evidence consistent with scientific ideas, principles, and theories.

- Apply scientific principles and evidence to provide an explanation of phenomena and solve design problems, taking into account possible unanticipated effects. (HS-PS1-5)
- Construct and revise an explanation based on valid and reliable evidence obtained from a variety of sources (including students' own investigations, models, theories, simulations, peer review) and the assumption that theories and laws that describe the natural world operate today as they did in the past and will continue to do so in the future. (HS-PS1-2)
- Refine a solution to a complex realworld problem, based on scientific knowledge, student-generated sources of evidence, prioritized criteria, and tradeoff considerations. (HS-PS1-6)

Disciplinary Core Ideas

PS1.A: Structure and Properties of Path Matter

• The periodic table orders elements horizontally by the number of protons in the atom's nucleus and places those with similar chemical properties in columns. The repeating patterns of this table reflect patterns of outer electron states. (HS-PS1-1) (*Note: This Disciplinary Core Idea is also* addressed by HS-PS1-1.)

PS1.B: Chemical Reactions

- Chemical processes, their rates, and whether or not energy is stored or released can be understood in terms of the collisions of molecules and the rearrangements of atoms into new molecules, with consequent changes in the sum of all bond energies in the set of molecules that are matched by changes in kinetic energy. (HS-PS1-4),(HS-PS1-5)
- The fact that atoms are conserved, together with knowledge of the chemical properties of the elements involved, can be used to describe and predict chemical reactions. (HS-PS1-2),(HS-PS1-7)

ETS1.C: Optimizing the Design Solution

 Criteria may need to be broken down into simpler ones that can be approached systematically, and decisions about the priority of certain criteria over others (trade-offs) may be needed. (secondary to HS-PS1-6)

Crosscutting Concepts

Patterns

Different patterns may be observed at each of the scales at which a system is studied and can provide evidence for causality in explanations of phenomena. (HS-PS1-2),(HS-PS1-5)



HS-ETS1-3. Evaluate a solution to a complex real-world problem based on prioritized criteria and tradeoffs that account for a range of constraints, including cost, safety, reliability, and aesthetics as well as possible social, cultural, and environmental impacts.

Science and Engineering Practices	Disciplinary Core Ideas	Crosscutting Concepts
 Constructing Explanations and Designing Solutions Constructing explanations and designing solutions in 9–12 builds on K–8 experiences and progresses to explanations and designs that are supported by multiple and independent student-generated sources of evidence consistent with scientific ideas, principles and theories. Evaluate a solution to a complex real- world problem, based on scientific knowledge, student-generated sources of evidence, prioritized criteria, and tradeoff considerations. 	runge of oonotrunte, moruanty	Connections to Engineering, Technology, and Applications of Science Influence of Science, Engineering, and Technology on Society and the Natural World • New technologies can have deep impacts on society and the environment, including some that were not anticipated. Analysis of costs and benefits is a critical aspect of decisions about technology.



Procedure

<u>SAFETY NOTE</u>: Prudent lab safety practices are required in performing this lab. The solutions contain heavy metal ions and care should be taken in their handling. Put on your goggles! Avoid ingesting the chemicals by properly washing your hands after the experiment and using gloves if possible. Students should follow safe lab procedure and treat the NaCl solution with equal respect. When "food" is used in lab it is a chemical and absolutely not for eating!

Materials

For each group of 2-4:

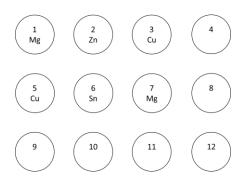
- Well plate with at least 6 wells
- 1 each Zinc, Copper, Magnesium, & Tin strips
- 0.1 M Zinc sulfate, Copper sulfate, Magnesium sulfate & Tin chloride solutions*
- At least 6 thin 2-5" long pieces of filter paper (several extra are a good idea!)
- Saturated NaCl solution in cup
- Tweezers
- 2 Alligator clips
- Multimeter

*To make each solution ZnSO₄ (~0.1M as 0.58g/20mL) CuSO₄ (~0.1M as 0.50g/20mL) MgSO₄ (~0.1M as 0.49g/20mL) SnCl₂ (~0.1M as 0.45g/20mL)



Creating an activity series

1. Fill the wells about halfway full with the appropriate metal ion solution as shown in the arrangement below:









2. Be sure to know which metal strip is which. Writing the names down on a paper and placing the metals back where they belong is a good method to not mix them up. If any of the pieces of metal have a coating or discoloration on them, light sanding can clean them up.



3. Place the thin filter paper strips into the cup of NaCl solution so that they become saturated with liquid. These will be the "salt bridges". Each paper can only be used once and sometimes mistakes occur. Be sure to have a few extras.





4. Select two metals to be tested (see student data table below), and place one end of the salt bridge in the well of one metal, and the other end of the salt bridge in the well of the other metal. Be sure that each end is touching the solution. Tweezers can help for this step but are not necessary as the NaCl solution is harmless. One person in the group will need to hold the bridge there as a teammate completes the next steps.





- 5. Attach one alligator clip to the strip of one of the metals chosen and another alligator clip to a strip of the other metal. Then connect the loose ends of the alligator clips to the red and black leads of the multimeter. Be sure to note which metal is clipped to the red lead and which to the black (alligator clip color does not matter, only the multimeter lead color matters).
- 6. Immerse the metal strips into their corresponding metal ion solutions along with the salt bridge. Be sure both strips and both ends of the bridge are in the liquid. Then read the voltage off of the multimeter (multimeter should be set at 20 in the DCV rang to read Volts). Be sure to only place a metal strip into a well of the same metal (ie zinc only in zinc sulfate, copper only in copper sulfate) otherwise the foreign metal ions in solution will start plating out onto the metal strip compromising the strip's efficacy and the voltage reading.





What happens if you switch the connections? Try switching which lead the alligator clips are connected to and record your observations. (i.e. If the red lead was connected to the red alligator clip, connect the red lead to the black alligator clip, and vice verse)



- 7. Once the voltage of that metal combination has been recorded, remove the strips from the wells and the alligator clips and place them back on the paper with their names. Remove the salt bridge from the wells and discard it. Never reuse a salt bridge or your metal solutions and all future readings will be compromised.
- 8. When finished testing all possible combinations, throw away the salt bridges, and pour the solutions down the drain. If possible, rinse the metal strips in water and dry them off to prevent oxidation before the next class uses the materials.





Potentials (V) of all possible combinations

black / red	Cu	Mg	Sn	Zn
Cu				
Mg				
Sn				
Zn				

Note: Results across the gray diagonal should be the opposite sign of each other.

Possible Inquiry Extensions:

- Submerge the strips in larger volume of the solution. Does that affect cell voltage or current? Record any change in voltage in the table below.
- Dilute the well with water and test whether the electrolyte concentration affects the cell voltage or current. Record any change in voltage in the table below.

black / red	Cu	Mg	Sn	Zn
Cu				
Mg				
Sn				
Zn				



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Review questions

1. Which cell produced the highest (positive) voltage? Lowest (positive) voltage?

How does this relate to the difference in "activity?" Which metal of the two cells listed above is more active?

Deduce from your data the next easiest to reduce, the next, and so on. In this way you can build the activity series of single replacement reactions for these four metals/cations.

2. Examine your data. Was there a metal which was oxidized by each of the others (i.e. an anode in a cell producing a <u>positive</u> voltage with all other metals)?

Compare the voltages for the cells above and arrange the metals in order, from most easily oxidized (most "active") to least.

- 3. What happens when a metal combination is switched between the red and black electrodes? Why does that occur?
- 4. Why is the salt bridge necessary?
- 5. Draw a diagram for a cell of your choice. Write the anode and cathode reactions.



Optional Analysis

How do we evaluate whether or not students can successfully fulfill the objectives we set out at the beginning of the lesson? Here are some sample assessment activities based on our example objectives.

Example objectives:

Students should be able to:

1. <u>Construct</u> and <u>revise</u> an explanation for the outcome of a simple chemical reaction based on knowledge of the patterns of chemical properties.

After constructing the activity series for the experiment, students should be able to answer basic questions about reactivity and redox. These questions are covered in the review questions.

2. <u>Apply</u> scientific principles and evidence to provide an explanation about the effects of changing concentration of the reacting particles on the rate at which a reaction occurs.

Discuss as a class the expected effect of changing concentration on a redox cell. After testing the hypotheses, let students change the concentration of the reactants. Ask them to explain what they observe. Were their hypotheses correct?

3. <u>Refine</u> a solution to a complex real-world problem, based on scientific knowledge, studentgenerated sources of evidence, prioritized criteria, and tradeoff considerations.

Have your students work through the Applying Your Knowledge worksheet. This worksheet will guide them through designing battery and subsequently refining their design.



Applying Your Knowledge

Batteries are a common example of galvanic cells that we use every day. Using what you've learned about redox, let's design a battery.

- 1. What makes a good battery: a large voltage difference or small voltage difference? Explain your choice.
- 2. Draw out the galvanic cell for the couple from your experiment that would make the best battery. Remember to draw the salt bridge!

Unlike in this experiment, modern batteries are typically *dry cell* batteries. That is, instead being immersed in solution, the metals are surrounded by dry or moist materials that can still transfer electrons as quickly as a solution. This is what a modern battery looks like.

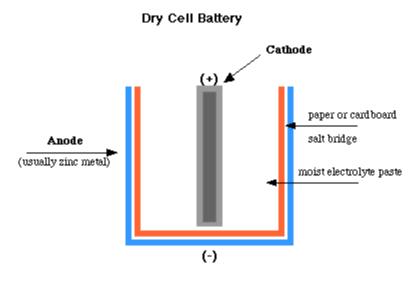


Image from http://makahiki.kcc.hawaii.edu/chem/everyday_battery_fig1.gif

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 Two common dry cell batteries are Cd/Ni batteries, one of the first rechargeable batteries, and Zn/MnO batteries. Given the information below, write out the net reaction for each type of dry cell battery. What potential difference (V) does each type produce?

Reduction half-reaction	Potential (V)
$Cd(OH)_2 + 2 e^- \rightarrow Cd + 2 OH^-$	- 0.86
2 NiO(OH) + 2 H ₂ O + 2 e ⁻ → Ni(OH) ₂ + 2 OH ⁻	+0.49
$Zn^{2+} + 2e^{-} \rightarrow Zn$	- 0.76
$2 \text{ MnO}_2 + 2 \text{ e}^- + 2 \text{ NH}_4\text{Cl} \rightarrow \text{Mn}_2\text{O}_3 + 2 \text{ NH}_3 + \text{H}_2\text{O} + 2 \text{ Cl}^-$	+0.50

4. Is the potential from your cell in #2 greater than, less than, or equal to the potentials you calculated in #3? Why don't we use this couple from #2 in modern batteries? Think about the materials you're using (Where are they in the periodic table? How common are they?). Also, consider safety concerns (Are any of these compounds dangerous?).

5. With the answer to #4 in mind, how would you make a better battery?

6. Using what you have learned about redox couples, explain the chemical process to recharge a Cd/Ni battery. (Hint: Remember that batteries are galvanic cells. If we want to reverse the reactions, we need to add energy to the system.)