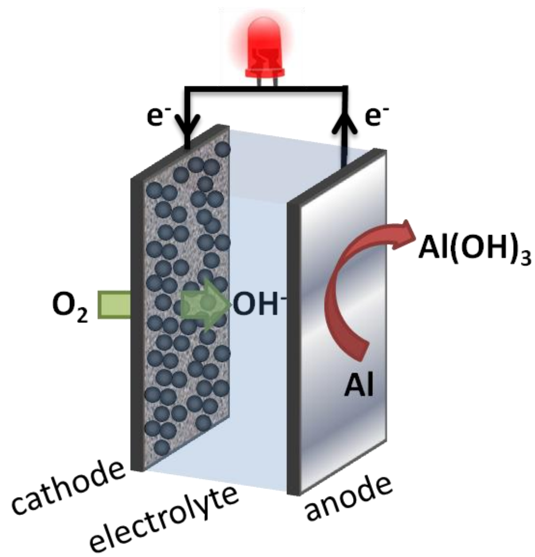
Aluminum/Air Battery Experiment

Josephine Cunningham, Martha Gross, Pauline Han, Watchareeya Keveevivitchai, Siyang Liu, Tyler Mefford, Daniel Redman, Benjamin Weaver, Kevin Yee, & Veronica Augustyn

The SciBridge Project
Texas Materials Institute
The University of Texas at Austin



Overview

Students prepare aluminum/air (Al/air) batteries which convert chemical energy into electrical energy, and use this energy to power three different color LEDs. Students will fabricate electrodes, assemble batteries, take electrical measurements, and understand how LEDs work.

Outline

Teacher Pre-Lab (1 hour): prepare carbon ink, prepare electrolyte, cut Ni foam, organize supplies
Student Procedure (1 hour): prepare carbon cathode, cut separators, cut aluminum foil, assemble batteries, take electrical measurements, power LEDs
Teacher Post-Lab (30 min): neutralize hazardous waste, store reusable supplies

Acknowledgement

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1. Background

Metal/air batteries are a class of energy conversion (chemical to electrical) devices that exhibit very high energy densities by harnessing the chemical energy associated with the reduction of oxygen (from air) and the oxidation of a metal. While the cathode in all metal/air batteries is oxygen, the anode metal can vary and is typically either zinc or aluminum. In this lab, you will make aluminum (Al)/air batteries.

The three major components of Al/air batteries are the anode (Al foil), electrolyte (potassium hydroxide in water), and cathode (air). The air cathode is composed of a conductive and porous nickel foam, a carbon catalyst, and a hydrophobic polymer glue. The conductive and porous nickel foam is used to transfer electrons to the oxygen gas at the interface. It has to be porous to allow the air to flow through to the interface. The carbon catalyst is utilized to lower the energy barrier for the oxygen reduction. Here we use a high surface area carbon black called acetylene black made by combustion of petroleum by-products. The hydrophobic polymer glue is utilized to stick the carbon to the nickel foam as well as to allow the oxygen gas to come in. Here we use PTFE (polytetrafluoroethylene), a fluoropolymer also known as Teflon®. The oxygen reduction reaction therefore occurs at a triple-phase boundary (solid - carbon catalyst, liquid - electrolyte, and gas - oxygen) and so the air cathode must be able to provide this type of architecture along with efficient electron transport.

In order to understand the device being built, first we will review the basic electrochemistry taking place. Electrochemistry is the coupling of electric current with chemical reactions. Electrochemical reactions can be either spontaneous or non-spontaneous. Spontaneous electrochemical reactions are also called galvanic cells, and these are the reactions that we harness in primary (non-rechargeable) batteries like Al/air which are energy *conversion* devices. Non-spontaneous electrochemical reactions are called electrolytic cells. Secondary (rechargeable) batteries like Li-ion utilize both galvanic and electrolytic electrochemical reactions making them energy *storage* devices.

2. Battery Electrochemistry

The balanced half cell and full cell chemical conversion reactions occurring in the Al/air battery are:

$$\text{anode: } 4Al_{(s)} + 12OH^-_{(l)} \rightarrow 4Al(OH)_{3,\,(s)} + 12e^- \qquad E^\circ = -2.31\text{ V}$$

$$\text{cathode: } 3O_{2,\,(g)} + 12e^- + 6H_2O_{(l)} \rightarrow 12OH^-_{(l)} \qquad E^\circ = 0.40\text{ V}$$

$$\text{total: } 4Al_{(s)} + 3O_{2,\,(g)} + 6H_2O_{(l)} \rightarrow 4Al(OH)_{3,\,(s)} \qquad E^\circ_{cell} = 2.71\text{ V}$$

The standard potential at room temperature, E°, is calculated directly from the Gibbs free energy of the reaction (ΔG°_{rxn}):

$$\Delta G^\circ_{rxn} = \Delta G^\circ_{products} - \Delta G^\circ_{reactants}$$

$$\Delta G^\circ_{rxn} = -nFE^\circ$$

where *n* is the number of electrons transferred and F is the Faraday constant (96,485 C/mol). So that the ΔG°_{rxn} doesn't have to be calculated each time, E° values are typically tabulated in tables of standard potentials versus a reference like the standard hydrogen electrode (SHE):

Half Reaction	E° (*vs*. SHE)
$4Al_{(s)} + 12OH^-_{(l)} \rightarrow 4Al(OH)_{3,(s)} + 12e^-$	-2.31
$2H^+ + 2e^- \leftrightarrow H_{2,(g)}$	0
$O_{2,(g)} + 4e^- + 2H_2O_{(l)} \rightarrow 4OH^-_{(l)}$	0.40

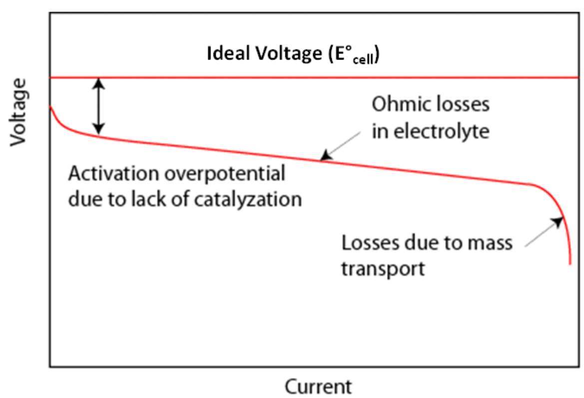
To calculate the potential of the cell:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

For the Al/air battery then:

$$E^\circ_{cell} = E^\circ_{air\ cathode} - E^\circ_{Al\ anode}$$
$$E^\circ_{cell} = 0.40 - (-2.31) = 2.71$$

The cell voltage that students will measure for a single cell will be lower than 2.71 V, approximately 1 to 1.3 V, depending on how good the battery is. The difference between the theoretical (E°_{cell}) and actual voltage is due to battery polarization - different types of processes that add resistance and decrease the voltage, as shown below:



There are three major types of polarization processes: (1) activation polarization, associated with the energy barrier for electron transfer, (2) ohmic polarization, associated with the resistance of all the components of the battery, and (3) mass transport polarization, associated with the diffusion of reactants and products at the electrode interface. In the Al/air battery, activation polarization mostly comes from the cathode oxygen reduction reaction and that is why we need the carbon catalyst. The ohmic polarization comes from all of the components. The mass transport polarization comes from oxygen gas diffusion, hydroxide diffusion, and aluminum hydroxide diffusion.

An important metric of batteries is their energy density, or amount of energy stored per unit mass or volume, typically calculated by the weight of the electrode materials. Comparing the energy density of metal air batteries is tricky because sometimes the mass of the air cathode is included, and sometimes it isn't. Below we calculate the energy density of an Al/air battery based on the weight of aluminum only. First, we calculate the capacity, Q, associated with the oxidation of aluminum from the anode equation:

$$\frac{12\ e-}{4\ Al} \times \frac{1.602x10^{-19}\ C}{1\ e-} \times \frac{6.02\times10^{23}\ Al}{1\ mol\ Al} \times \frac{1\ mol\ Al}{26.98\ g\ Al} = 10724\ C/g$$

Second, we calculate the energy density (*ED*) of the battery in Wh/kg using the cell voltage of 2.71 V:

$$ED = Q \times V$$
$$ED = 10724\frac{C}{g} \times 2.71V$$
$$ED = 8072\ Wh/kg$$

Al/air batteries exhibit a very high theoretical energy density making them useful for different applications. However, if we consider the mass of the inactive air cathode components (nickel foam, carbon catalyst, polymer binder), the energy density will decrease by as much as 70%.

3. Applications & Research Directions

The high theoretical energy density of Al/air batteries make them attractive for different applications. The biggest competitor to Al/air batteries are Zn/air batteries which offer a lower energy density (1,300 Wh/kg) but also lower cost. Major issues with the battery are that the aluminum anode is significantly more expensive than the zinc anode. Al/air batteries can be recharged in two different ways: (1) mechanically, by opening up the cell and replacing the Al anode and recycling the $Al(OH)_3$ and (2) electrochemically, by reversing the anode and cathode reactions. Mechanical charging is not ideal but there are companies commercializing this technology. Electrochemical charging would be ideal, but suffers from large inefficiencies due to the energy barrier associated with converting $Al(OH)_3$ to Al and OH^- to O_2 (the oxygen evolution reaction). However, the large theoretical energy density (more than 10X of Li-ion batteries), non-toxic materials, and good safety motivates researchers to identify catalysts and anode architectures to enable rechargeable Al/air batteries.

4. Light-Emitting Diodes (LEDs)

LEDs are solid state semiconductor lighting devices that are essentially the opposite of solar cells. Whereas a solar cell is a semiconductor p-n junction connected in reverse, a LED is a p-n junction biased in the forward direction and the recombination of electrons and holes at the interface generate light. The generation of light by LEDs is highly efficient, making them interesting for lighting applications. The color or wavelength of the light emitted is dependent upon the bandgap of the semiconductor. In this lab, you will use red, green, and blue LEDs. The table below gives the characteristics of each of LED:

Color	Wavelength (nm)	Band Gap (eV)	Semiconductor
red	660	1.88	AlGaAs/GaAs
green	565	2.20	GaP
blue	468	2.65	InGaN

The wavelength of light emitted by the LED (λ) is inversely proportional to its band gap, E_g:

$$E_g = hc/\lambda$$

where h is Planck's constant (4.136×10^{-15} eV s) and c is the speed of light (3×10^{8} m/s).

In 2014, the Physics Nobel Prize was awarded for the invention of the blue LED. This invention was important and very challenging. Red LEDs were developed in the early 1960s, green LEDs in the early 1970s, but it wasn't until 1993 that the first brilliant blue LED based on InGaN was developed by Shuji Nakamure (the Nobel prize winner). The reason it took longer to develop blue LEDs was due to the challenge of growing good quality single crystals of GaN. The invention of the blue LED led to the development of white LEDs (which are blue LEDs coated in different phosphors) in 1995, which are needed for highly efficient lighting to replace fluorescent and incandescent light bulbs. The energy savings of LED lighting are very significant - the U.S. Department of Energy estimates that a complete switch to LED lighting in the United States could save $250 billion, reduce the electricity consumption of lighting by half, and reduce 1,800 million metric tons of CO_2 emission. Two major challenges for LED lighting research are to improve the efficiency of phosphor-based white LEDs and cost.

Al/Air Battery Supply List

Item	Quantity in Kit	Quantity per Group
Acetylene black	4 g	Varies
30% PTFE aqueous dispersion	2 mL	Varies
Stir bars	20	1
Vials for ink	20	Varies
Ni foam	~2000 cm^2	3 ea - 1 x 3 cm^2 pieces
Plastic pipettes	~80	1
Celgard separator	~4000 cm^2	3 ea - ~ 2 x 3 cm^2 pieces
Al foil	Excess	3 ea - ~ 1 x 3 cm^2 pieces
Glass plates	20	1
Binder clips	60	3
Red LED	20	1
Green LED	20	1
Blue LED	10	Share 1 per 2 groups
Multimeter	5	Share among groups
Kim wipes	3 boxes	Share among groups
Gloves, small	40	Varies
Gloves, medium	40	Varies
Gloves, large	40	Varies
Plastic bottle for KOH electrolyte	4	Share among groups

Al/Air Supplies Provided by the Instructor

Item	Quantity per Group
Scissors	shared
6 M potassium hydroxide (KOH)	shared
Hot plate	shared

Teacher Pre-Lab (1 hour)

The Pre-Lab procedure is based on a typical classroom of 40 students divided into 20 groups. If your classroom size is bigger or smaller, please adjust accordingly.

1. Each carbon ink can be shared between 4 student groups. You will need to make a total of 5 inks. Each ink is made by the following procedure:
   - Put 1 stir bar in the vial
   - Add 200 mg of acetylene black into the vial using the plastic scoop
   - Add 10 mL of ethanol to the vial
   - Add 100 μL (0.1 mL) of the PTFE dispersion to the vial
   - Stir the ink at medium speed for ~30 minutes before use

2. Prepare 400 mL of 6 M KOH (potassium hydroxide) in water as the electrolyte:

$$6\ M\ KOH \times 0.4\ L\ solution = 2.4\ mol\ KOH$$
$$2.4\ mol\ KOH \times \frac{56.1056\ g\ KOH}{1\ mol} = 134.6534\ g\ KOH$$

   To make 6 M KOH, add 400 mL of water to 134.6534 g of KOH and stir until the KOH dissolves. The glassware will get warm as the KOH dissolves. **<u>**Caution: KOH is very corrosive! Protect eyes and skin when working by wearing safety glasses, long sleeves, pants, and gloves.**</u>**

3. Divide the 400 mL of KOH into each of the 4 plastic vials which can hold 100 mL of electrolyte, and are to be shared among the groups.

4. Each group will need 3 Ni foam pieces. Cut 60 - 1 x 3 cm^2 pieces of Ni foam. **Be careful when measuring the Ni foam - it is the most expensive component of the kit! Measure twice - cut once!**

5. Organize the supplies around the classroom:
   - scissors
   - 4 bottles of potassium hydroxide
   - 5 carbon inks
   - 5 hot plates
   - central location for Ni foam, plastic pipettes, Celgard separator, Al foil, glass plates, LEDs, binder clips

Student Al/Air Battery Procedure

In this experiment, you will build an aluminum/air (Al/air) battery and then use this battery to light different color LED lights. Read the procedure carefully before beginning, ask the instructor if you have any questions, and **be sure to wear long sleeves, pants, gloves and safety glasses**!

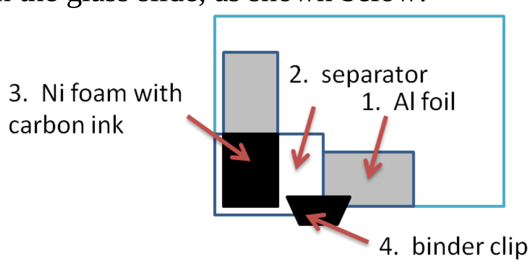
Tear off the **Results Worksheet** on the back and use it to record your observations.

1. Prepare the air cathode:
    a. Take three pieces of the 1 x 3 cm^2 Ni foam.
    b. Using the plastic dropper, drop a few drops of the carbon ink to cover one half of the Ni foam. Repeat for the other two pieces of Ni foam.
    c. When you finish, put the Ni foams on a glass plate and put the glass plate on a heat plate at ~ 70°C for ~5-10 minutes to evaporate the ethanol solvent.

2. Cut three 2 x 3 cm^2 pieces of the Celgard separator. The Celgard has to keep the Ni foam from touching the aluminum foil. If you run out of Celgard, you can try fiber paper or even Kim wipes as the separator.

3. Cut three 1 x 3 cm^2 pieces of aluminum foil. The aluminum foil should be smaller than the separator in width.

4. Assemble the 1st battery on the glass slide, as shown below:

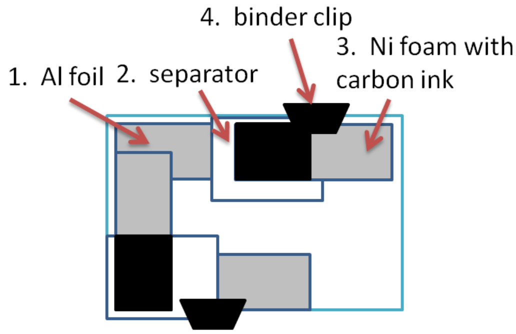


5. Once assembled, add a few drops of 6 M KOH electrolyte to the separator; allow the separator to absorb the electrolyte. ****Caution: KOH is very corrosive!****

6. Measure the potential between the Ni foam and the Al foil and record in Table 1 of the Results Worksheet.

7. Next, try to see if the red, green, or blue LEDs will light up when connected between the Ni foam and the Al foil. Circle which LEDs you were able to light up in Table 1 of the Results Worksheet. **Remember, LEDs will not light if connected in reverse. Flip the LED around if you're unsure which way the LED is connected.**

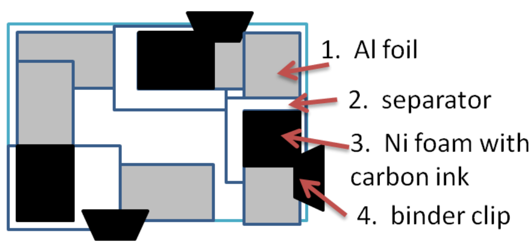
8. Assemble the 2nd battery in series with the first on the glass slide, as shown below:



9. Once assembled, add a few drops of 6 M KOH electrolyte to the separator of the 2nd battery; allow the separator to absorb the electrolyte.

10. Measure the potential between the Al foil of the 1st battery and the Ni foam of the 2nd battery, and record it in Table 1 of the Results Worksheet. Next, try to see if the red, green, or blue LEDs will light up when connected between the Al foil of the 1st battery and the Ni foam of the 2nd battery. Circle which LEDs you were able to light up in Table 1 of the Results Worksheet.

11. Assemble the 3rd battery in series with the other two batteries on the glass slide, as shown below:



12. Add a few drops of 6 M KOH electrolyte to the separator of the 3rd battery.

13. Measure the potential between the Al foil of the 1st battery and the Ni foam of the 3rd battery, and record it in Table 1 of the Results Worksheet. Next, try to see if the red, green, or blue LEDs will light up when connected between the Al foil of the 1st battery and the Ni foam of the 3rd battery. Circle which LEDs you were able to light up in Table 1 of the Results Worksheet.

14. If your battery is able to light up a red LED, measure how long it keeps the red LED lit. Write down your observations about what you see happening at the Al foil, and what happens to the Al foil when the LED stops being lit in the Results Worksheet.

15. When you finish working with your battery, rinse the aluminum foil, nickel foam, and separator then throw away the aluminum and separator. The Ni foam can be reused. Wipe the LED and multi-meter wires with a tissue soaked in water and dry.

Teacher Post-Lab (30 min)

1. If you have leftover potassium hydroxide electrolyte that you will not use again, you can neutralize the electrolyte by adding a strong acid like hydrochloric acid:

$$KOH + HCl \rightarrow KCl + H_2O$$

Calculate the volume of HCl needed with the following (M = molarity, V = volume):

$$M_{KOH}V_{KOH} = M_{HCl}V_{HCl}$$

ex. To 100 mL of 6 M potassium hydroxide, add 50 mL of 12 M (37%) concentrated hydrochloric acid. Test the pH before and after to ensure complete neutralization. Neutralized electrolyte (pH = 7) is not hazardous and can be safely disposed down the sink.

2. The following items are reusable supplies:

Item	**Quantity in Kit**	**Quantity per Group**
Stir bars	20	1
Vials for ink	20	Varies
Ni foam	~2000 cm^2	3 ea - 1 x 3 cm^2 pieces
Glass plates	20	1
Binder clips	60	3
Red LED	20	1
Green LED	20	1
Blue LED	10	Share 1 per 2 groups
Multimeter	5	Share among groups
Plastic bottle for KOH electrolyte	4	Share among groups

3. The following items are provided in excess and can be used for further experiments:

Item	**Quantity in Kit**	**Quantity per Group**
Acetylene black	4 g	Varies
30% PTFE aqueous dispersion	2 mL	Varies
Plastic pipettes	~80	1
Celgard separator	~4000 cm^2	3 ea - ~ 2 x 3 cm^2 pieces
Al foil	Excess	3 ea - ~ 1 x 3 cm^2 pieces
Binder clips	60	3

Al/Air Battery Experiment
Student Results Worksheet

Table 1. Al/Air Battery Performance

# of Batteries in Series	Potential (V)	LED lit up (circle which apply)
1		R G B
2		R G B
3		R G B

1. What do you see happening on the battery when the LED is lit up?

____

____

2. What do you see happening on the battery when the LED is no longer lit up?

____

____

3. How long does your battery keep the red LED lit?

____

____

4. (a) Balance the chemical reactions happening on the anode, cathode, and the total reaction and (b) indicate the phase of the different components (e.g. Al, s = Aluminum, solid):

anode: __Al__ + __OH^-__ → __$Al(OH)_3$__ + __e^-

cathode: __O_2__ + __H_2O__ + __e^- → __OH^-__

sum: __Al__ + __O_2__ + __H_2O__ → __$Al(OH)_3$__

5. The anode half reaction has a voltage of 2.31 V *vs.* SHE (Standard Hydrogen Electrode) while the cathode half reaction has a voltage of 0.41 V *vs.* SHE. What is the theoretical voltage of the battery?
E°_{cell} = _________ V

6. Why is the voltage for your 1 battery in series (see Table 1) lower than the theoretical voltage?

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