# The Salty Science of the Aluminum-Air Battery

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**F**ruit batteries and saltwater batteries are excellent ways to explore simple circuits in the classroom. These are examples of air batteries<sup>1</sup> in which metal reacts with oxygen in the air in order to generate free electrons, which flow through an external circuit and do work. Students are typically told that the salt or fruit water acts as an electrolyte to bring electrons from the anode to the cathode. That's true, but it leaves the battery as a black box. Physics teachers often don't have the background to explain the chemistry behind these batteries. We've written this paper to explore the electrochemistry behind an air battery using copper cathode, aluminum anode, and saltwater.

Activities using batteries are useful in part because students are often familiar with voltage *drops* across a circuit (as in serial resistors) but have fewer opportunities to experience serial voltage *gains*. This activity can also be used in discussions of alternative energy and provide a framework for discussing fuel cells.

## **Materials and Construction**

The construction of this cell is borrowed largely from the Exploratorium's *Square Wheels*<sup>2</sup> book. For full details on construction, please visit http://www. exo.net/pauld/saltwater.

You will need:

- 1. copper (partly stripped copper cord or a pipe from the hardware store), 10 cm long
- 2. aluminum foil, 10 cm by 10 cm
- 3. table salt, water, and cups

- 4. five alligator clip leads
- 5. light emitting diode (LED) or a 12-V dc mini buzzer (try RadioShack #273-065 or #273-075)

Mix about 20 g of salt with 400 ml of warm water. The amounts are not that important, but this will give you a solution that is about 5% salt by weight. Fold the aluminum foil in half and then in half again lengthwise to give you a long paddle. Strip the insulation off both ends of the copper wire, leaving a short section of insulation in the middle to hold the strands together. Separate the strands of one end so it looks like a broom.

Using the alligator clip leads, clip the aluminum foil to one side of a cup. Clip the wire strands of the "broom handle" part of the copper wire to the other side of the cup so the spread "broom" section is inside the cup. This is now one "cell" in your battery. More cups can be connected in series to this one, with the alligator clip lead attached to the copper electrode of one cup connecting to the aluminum electrode of the next cup.

Connect the final two leads to a multimeter, LED, or piezoelectric buzzer. Fill the cups with the saltwater solution. What happens?

# To Do and Notice

The multimeter should register a current, and the LED should glow dimly. If the LED does not glow, try reversing the leads of the LED in the circuit—it's a diode and will only allow current to pass in one direction. In a crowded and well-lit classroom, the piezoelectric buzzer may provide a more impressive result, buzzing when the final cup is filled. Students may investigate what happens to the brightness of the LED and the current when they add/remove cups or touch the electrodes together. How does the current change when they add the LED into the circuit? They can also measure the voltage and current produced by cells individually and the circuit as a whole to investigate Kirchoff's laws and calculate the power produced by the circuit.

## What's Going On?

Each cup is a simple electrochemical cell with operating voltage of about ~0.5 V and current of ~1 mA. When the saltwater cells are put in series, they act like a voltaic pile; the individual voltages add together so that four in series have a voltage of ~2 V. The LED lights (or the buzzer sounds) only when its threshold voltage has been reached (around 1-2 V). The minimum number of cups is generally around four. Touching the copper and aluminum together will short out the cell, and the LED will not light.

When the buzzer is added into the circuit, the current through the cells will drop because the overall resistance has been increased. This current drop can be used to calculate the resistance of the circuit itself, without the LED, leading to a discussion of real batteries and internal resistance.

Note that in order to measure current and voltage across a resistor, you must measure them simultaneously. Thus, you will need two multimeters.

## **Electrochemistry Explorations**

In addition to the physics of circuits, students will readily discover that there is much to be explored in the electrochemistry of the cell.

- Do you notice anything happening at the electrodes?
- What happens if we stir the solution or add salt?
- What happens to the current if we add a little bleach?
- What if we add vinegar, baking soda, or fruit juice?
- What do we notice if we let the circuit sit overnight or for several days?
- What if we use aluminum for both electrodes?



Fig. 1. Electron flow in the saltwater cell.<sup>3</sup>

#### How does the cell work?

The standard "black box" answer is that copper is more electronegative than aluminum and wins the tug-of-war for electrons. This, however, ignores the important role of dissolved oxygen,  $O_2$ . In the external circuit, the flow of electrons is from the aluminum  $\rightarrow$  LED  $\rightarrow$  copper  $\rightarrow$  dissolved oxygen (the opposite direction from the conventional current). But inside the solution, electrons carried by the ions must flow from copper (cathode)  $\rightarrow$  aluminum (anode) in order to complete the circuit and replenish the electrons lost by aluminum (see Fig. 1). How does this happen, and what is the role of the salt? We explain this below.

It's nice to remark that the electrons are gaining potential energy (through a series of chemical reactions) as they travel from the copper to the aluminum electrode within the solution. This enables them to do work on the external circuit and power the LED.

Any two dissimilar metals would work as electrodes. Carbon is often used, and a recent publication outlines the construction of a powerful aluminum/ carbon battery.<sup>4</sup> The salt acts as a conductor, carrying charge through the solution. Anything could serve as a conductor, such as vinegar, fruit, dill pickles, or the human body<sup>5</sup> although generally the higher the conductivity, the greater the current.

Inside this cell, copper serves as a source of electrons (the cathode). It simply passes on electrons from the external circuit, after they've flowed through the LED. Oxygen (dissolved in the water) is *reduced*<sup>6</sup> by those electrons:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, E^0 = 0.82 \text{ V}.^7$$
 (1)

This forms hydroxide (OH<sup>-</sup>) in the region near the electrode. You will notice that the current drops over time. Over time, the narrow region of solution near the copper runs out of oxygen; stirring can help revive the cell by bringing fresh oxygen into this area. The cell current decreases over long periods of time because the metals become coated with oxides and other byproducts. The voltage, however, remains constant as it's affected primarily by the electronegativity of the metals, which does not change.

At the anode, the aluminum foil is oxidized—it gives up electrons:

Al + 3OH<sup>-</sup> → Al(OH)<sub>3(S)</sub> + 3
$$e^{-}$$
,  $E^{0}$  = 2.30 V.<sup>8</sup> (2)

The aluminum and hydroxide are consumed by this reaction to produce aluminum hydroxide,  $Al(OH)_{3(S)}$ , a white precipitate of  $Al^{3+}$ . Similarly, soda cans and aluminum boats are eaten away by saltwater in the ocean, producing  $Al^{3+}$ . If the aluminum foil is left in the cell overnight, it gets thinner (as it is oxidized) and coated with white aluminum hydroxide.

But the hydroxide ions in Eq. (2) are not those created in Eq. (1)—that's where the salt is important. Sodium (Na<sup>+</sup>) ions must flow to the left to neutralize the OH<sup>-</sup> ions produced at the copper electrode (see Fig. 1). Similarly, the chlorine (Cl<sup>-</sup>) ions move to the right to replace the OH<sup>-</sup> used up in Eq. (2) (the OH<sup>-</sup> comes from free OH<sup>-</sup> ions already present in the water). The net result is electrons moving to the right from copper to aluminum—that's the only role of the salt! If this didn't happen, the reaction would only run for a short time and then fizzle out as charge built up at the electrodes.

Combining Eqs. (1) and (2) stoichiometrically gives the following equation for the cell reaction:

Al 
$$+\frac{3}{4}O_2 + \frac{3}{2}H_2O \rightarrow Al(OH)_{3(S)}, E_{net}^0 = 3.12 \text{ V}.^{1}(3)$$

This reaction summarizes the basic chemistry of the

cell at neutral pH 7. Notice that the copper doesn't actually participate in the cell chemistry—electrons simply pass through it, allowing the reduction of oxygen.

Many students ask why the electrons travel from copper to aluminum within the saltwater solution, especially when copper is more electronegative. Why don't the reactions go the other way around? One could easily write a series of half-reactions for the oxidation of copper instead—in fact, when the copper is left to sit in air, it will turn reddish due to the formation of cuprous oxide  $(Cu_20)$ . So, it can (and is) easily oxidized. However, when the copper is assembled into the battery cell, the oxidation of aluminum  $(E_{net}^0)$ = 3.12 V) by oxygen is more energetically favorable than the oxidation of copper metal to  $Cu_20 (E_{net}^0 =$ 1.18 V) or to  $Cu^{2+}(E_{net}^{0} = 0.48 \text{ V})$ , so it's aluminum that is primarily oxidized instead. Some of the copper may also be oxidized—you may see red ( $Cu_20$ ) and black (CuO) deposits on the copper.

## **Going Further...**

## **Bubbly stuff**

You may notice small bubbles on the aluminum metal during cell operation. This is hydrogen gas. This comes from an additional corrosion reaction that consumes the aluminum but doesn't contribute to the current:

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = -0.41 \text{ V.}^9$$
 (4)

So in addition to Eq. (3), an equation for the nonproductive corrosion of aluminum can be written.<sup>10</sup>

#### **Adding salt**

The current does not depend strongly on the concentration of salt, despite the increased conductivity for stronger salt solutions. The conductivity of saltwater is at a maximum for a 12% solution by weight. We use 2–5% weight solutions, but even trace amounts of salt will do. Try it with tap water—it will work, but the current will be low. Increasing the amount of salt increases the conductivity, but the rate of reaction is limited by the amount of oxygen in the solution.

### Adding vinegar

Actually, a cell made entirely of vinegar water (acetic acid) will work just fine since the H<sup>+</sup> and ace-

tate<sup>-</sup> ions from the dissociation of the weak acid make the solution conductive. A squirt of vinegar to your saltwater cell will make the LED glow brighter. But don't be fooled—stirring the solution does the same thing. Upon settling, the performance of the vinegar/ salt cell is generally comparable to that of the saltwater cell alone.

However, you'll probably find that vinegar/salt cells maintain their current for a *longer* time than saltwater cells. If you leave a vinegar/salt cell overnight, the surface of the copper will not be coated with a reddish oxide but stays shiny and clean. The acetate in vinegar tends to dissolve the cuprous oxide coating as it forms by forming a complex with the Cu(I). This allows better contact with the solution and thus better electron transfer over time.

Additional details about the role of vinegar in the cell can be found at http://www.exo.net/pauld/ saltwater.

#### Adding bleach

You will find you'll get a much more stable and powerful cell if you add a teaspoon of bleach to the saltwater (or to plain water) with current and voltage around 10 mA and 1 V, respectively, with only the multimeter in the circuit. So a bleach-powered cell produces about 20 times as much power! Why is that?

When bleach is added, the battery is no longer an air battery; instead of oxygen from the air, sodium hypochorite (NaOCl), the major constitutent in bleach, and hypochorous acid (HOCl), a minor constituent, are reduced. The full equations for this cell can be found online. This cell potential (3.93 V) is quite a bit higher than the 3.12 V for the saltwater battery [Eq. (3)]. So this reaction proceeds more rapidly, generating more electrons per unit time and thus greater current. We also observed a higher voltage. Another indication that the reaction proceeds more rapidly for the bleach battery is the striking abundance of white fluffy particulate as the cell is left over time—this is Al(OH)<sub>3(S)</sub>.

Additional details about the role of bleach in the cell can be found at http://www.exo.net/pauld/ saltwater.

In conclusion, the saltwater aluminum/air battery is a rich activity combining elements of chemistry and physics. Understanding some of the chemistry behind the cell can help physics teachers to answer their students' questions.

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- 10.  $Al + 3H_2O \rightarrow Al(OH)_3 + \frac{3}{2}H_2$   $E^0 = 1.89$  V.

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