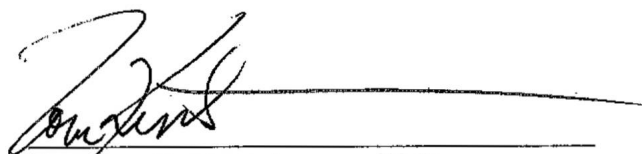


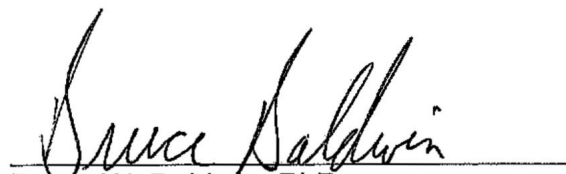
**The Chemistry of Alkaline Batteries:
Investigating Why Dead Batteries Bounce and Using
This Phenomenon for Chemical Education**

By
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Senior Research Thesis
Spring 2016



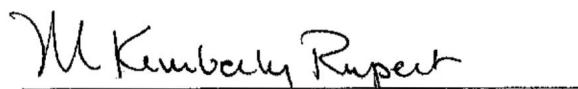
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Some of the information in this thesis can be found in the following publication:

Experiments To Illustrate the Chemistry and Bouncing Ability of Fresh and Spent Zinc–Manganese Oxide Alkaline Batteries

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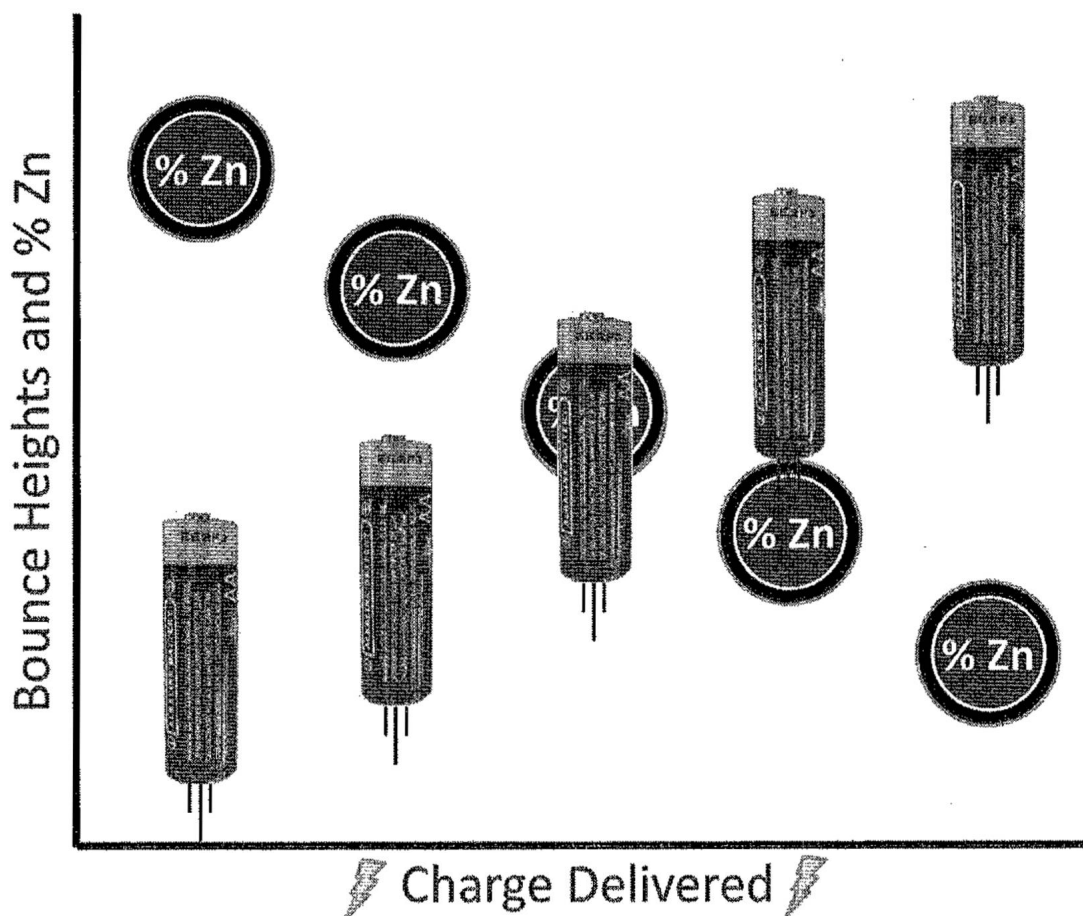
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Graphical Abstract:



Graphical Abstract: This figure represents that AA alkaline batteries bounce higher as they are discharged. The percentage of zinc also decreases as batteries are discharged, which is likely to be the cause for the increase in bounce height.

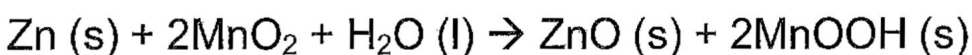
Chapter 1: Introduction

Recently, an unexplained phenomenon was discovered to be useful for testing the life of an AA alkaline battery: dead batteries bounce higher than fresh batteries¹. More precisely, the coefficient of restitution (COR) increases as alkaline batteries are discharged. COR relates to the bounce height of alkaline batteries in the following formula, where h_1 is the height at which a battery is dropped and h_2 is the bounce height¹³:

$$COR = \sqrt{\frac{h_2}{h_1}}$$

Equation 1. The COR of an object can be found using the equation above, where h_2 is the rebound height and h_1 is the height from which the object was dropped.

This knowledge is quite useful because it provides a fast, inexpensive way to test the life of a battery. Since a chemical reaction occurs within the alkaline cell, chemistry may be able to explain why the batteries bounce higher as they are discharged (Scheme 1).



Scheme 1. The overall chemical reaction that occurs within an alkaline battery^{1,2,3}.

Based on this chemical reaction, three hypotheses were formed to explain the bouncing phenomenon: (1) the loss of water increases the bounce heights of alkaline batteries, (2) the formation of zinc oxide increases the bounce heights of alkaline batteries, and (3) the formation of MnOOH increases the bounce heights of alkaline batteries.

In addition to testing these hypotheses, this work was developed into a series of laboratory experiments and/or chemical demonstrations for high school and early undergraduate students. Alkaline batteries can serve as a unique platform to introduce oxidation/reduction chemistry and tie together concepts such as chemical equations, gas laws, and stoichiometry. Coupled with the unique bouncing effect, the chemistry of alkaline batteries may provide an engaging learning experience for high school and early undergraduate students. Therefore, the possibility of using alkaline batteries as a laboratory experiment or chemical demonstration was investigated as well.

Chapter 2: Discharging Batteries with the MicroLAB Resistive Load Module

In order to measure the charge delivered from AA Duracell alkaline batteries, a MicroLAB Resistive Load Module (RLM) was used (Figure 1). The RLM is capable of measuring current and time as batteries are discharged (Figure 2). This allows for the calculation of charge delivered by integrating the curve in the current versus time graph (Equation 2).

$$q = \int I dt$$

Equation 2. Charge in coulombs can be calculated using the equation above, where q is the charge in coulombs, I is the current in amperes, and the current is integrated with respect to time.

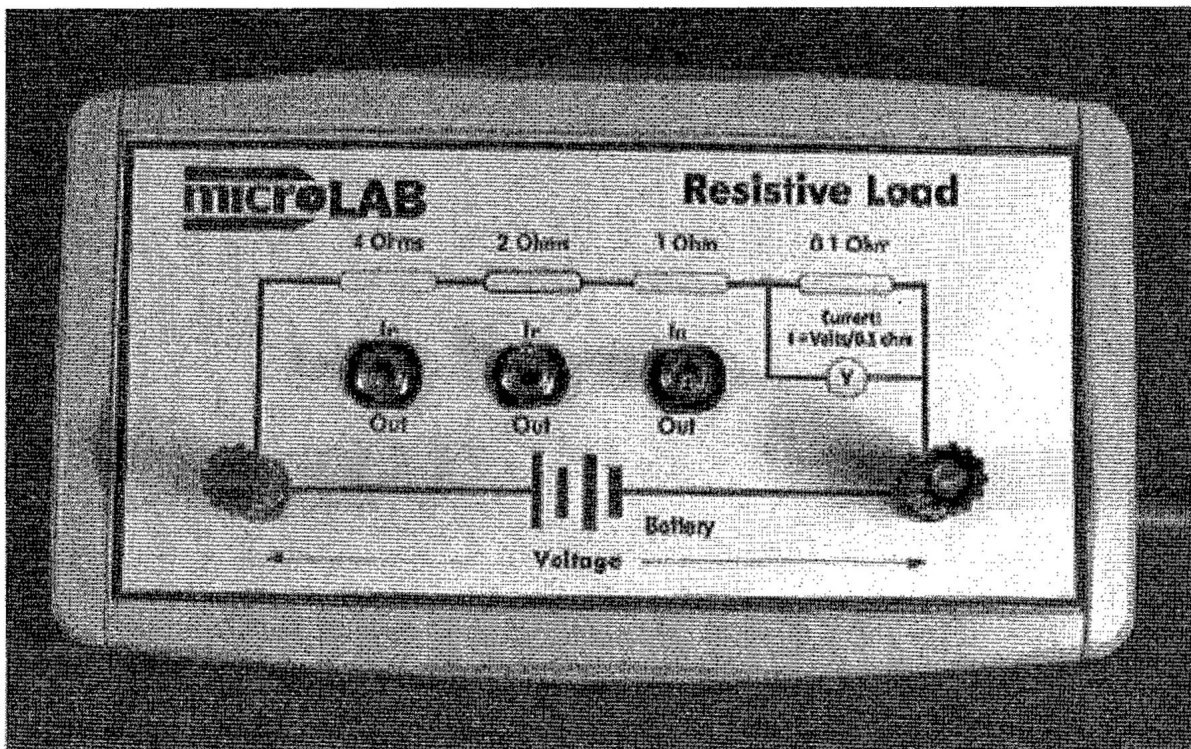


Figure 1. A picture of the MicroLAB Resistive Load module that was used to discharge alkaline batteries.

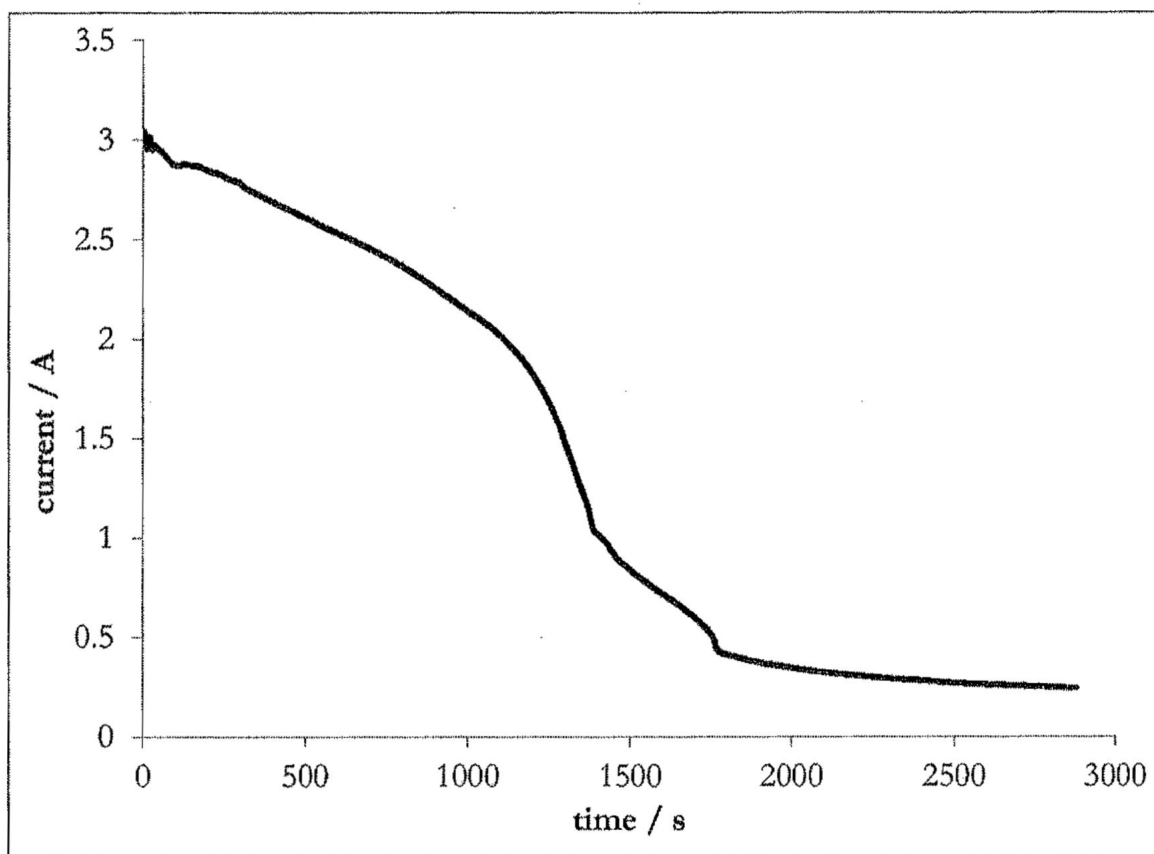


Figure 2. The current versus time output of the MicroLAB Resistive Load Module for a AA Duracell alkaline battery. The area under the curve represents the total amount of charge delivered, which was equal to 3900 coulombs in this case.

For all of the following experiments, AA Duracell alkaline batteries were used and discharged to the desired extent using the RLM. However, an ammeter could be substituted for the RLM or time spent powering a flashlight could be measured to obtain partially drained batteries. The RLM was connected to a computer that runs MicroLAB and a battery holder was connected to the RLM to allow for the discharge to occur. An experiment was created in the MicroLAB program so that current was measured on the Y-axis and time was measured on the X-axis. The experiment was started and a battery was immediately inserted into the battery holder to begin discharging. When the battery had finished discharging, the plot of current and time was integrated to

determine the total amount of charge delivered. In order to fully discharge a battery, this process was repeated several times with the same battery after allowing the battery to cool down for at least an hour.

Chapter 3: Measuring the Bounce Heights as Charge is Delivered

In order to confirm that alkaline batteries bounce higher than fresh batteries, a method was developed to measure the bounce heights of alkaline batteries as they are discharged. Using a slow-motion camera application from an iPhone 5s, batteries were dropped from 60 cm and their rebound height was recorded. Upon reviewing the slow-motion video, the greatest height that the lowest part of the battery achieved after the initial contact with the ground was determined. It was important to drop the batteries onto the same surface each time because the expected bounce height values could change if the surface they were dropped onto was altered. This experiment was performed six times for batteries that had discharged near 0, 1000, 2000, 2900, 3700, 5000, and 7000 coulombs. Dropping the batteries through a PVC tube was helpful to ensure the battery would strike flat on the negative terminal end. If the battery did not strike the ground flat on the negative terminal, the measurement was discarded. A significant rotational motion after the bounce often indicated that the battery had not struck the ground flat on the negative terminal. The results indicated a linear relationship between COR and charge delivered (Figure 3). This is different from the sigmoidal relationship that had been previously determined¹. After the batteries had delivered 50% of their charge, the bounce heights kept increasing as charge was delivered. This result may be due to the faster method of discharging the batteries or the increased height from which the batteries were dropped.

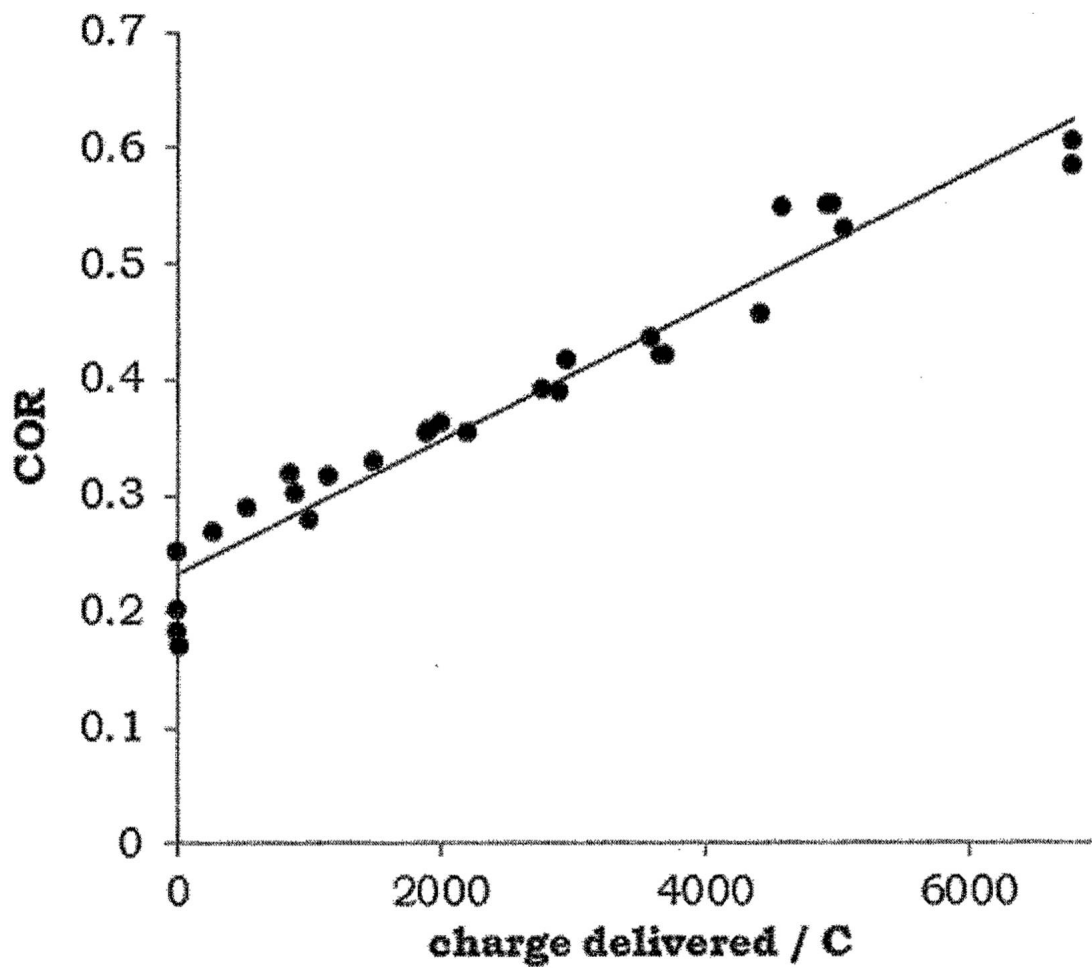


Figure 3. The bounce heights of alkaline batteries increase as charge is delivered.

Chapter 4: Does the Loss of Water Increases the COR of Alkaline Batteries?

The first hypothesis tested was that the loss of water contributed to the increased COR of discharged alkaline batteries. An educational analogy to explain this hypothesis is that a raw egg does not bounce when dropped, but a hard-boiled egg does. The presence of liquid in the raw egg allows for the kinetic energy of motion to be easily dispersed throughout the fluid when the egg strikes the surface. This leaves little energy for rebound. On the other hand, the hard-boiled egg contains little fluid and the kinetic energy of motion is not damped as in the raw egg. Here, the fresh battery parallels the raw egg while the dead battery, with little to no water remaining, is like the hard-boiled egg.

To test this hypothesis, AA Duracell batteries were discharged with a MicroLAB Resistive Load module. Next, the batteries were cut open and the mass of the anode was weighed on a watch glass. The wet anodic material was heated at 100 °C overnight in an oven to evaporate any water in the sample. After cooling to room temperature, the anodic material was weighed again to determine percent mass loss due to water evaporation. The results were unclear because the data did not fit very well to a linear relationship ($r^2 = 0.7031$) (Figure 4). In fact, a logarithmic fit provided an r^2 value greater than 0.9. This suggests that the water loss data do not correlate with the increase in COR as alkaline batteries are discharged.

These results were less than satisfying because the evidence does not fully support or refute “the loss of water hypothesis” and the precision of the collected data was low. To

further explore the loss of water observed in alkaline batteries, Fourier Transform Infrared Spectroscopy was employed to gain insight into the amount of water in the anode of a fresh and dead battery. By comparing the peaks around 3400 cm^{-1} in the IR spectra, the batteries appear to lose water content as they are discharged (Figure 5). There may be a correlation between water loss and COR of alkaline batteries, but the impact of water loss on the COR of alkaline batteries remains unclear.

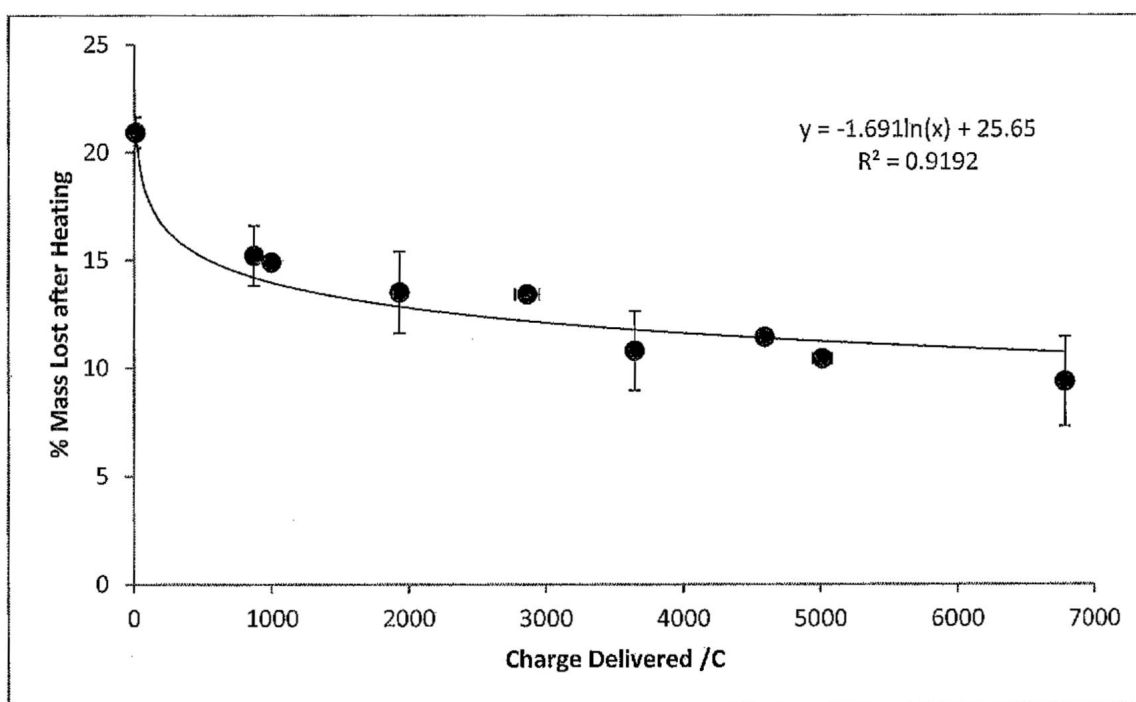


Figure 4. The percent mass lost from the anode material of AA Duracell alkaline batteries after heating in an oven at $100\text{ }^{\circ}\text{C}$ overnight versus charge delivered.

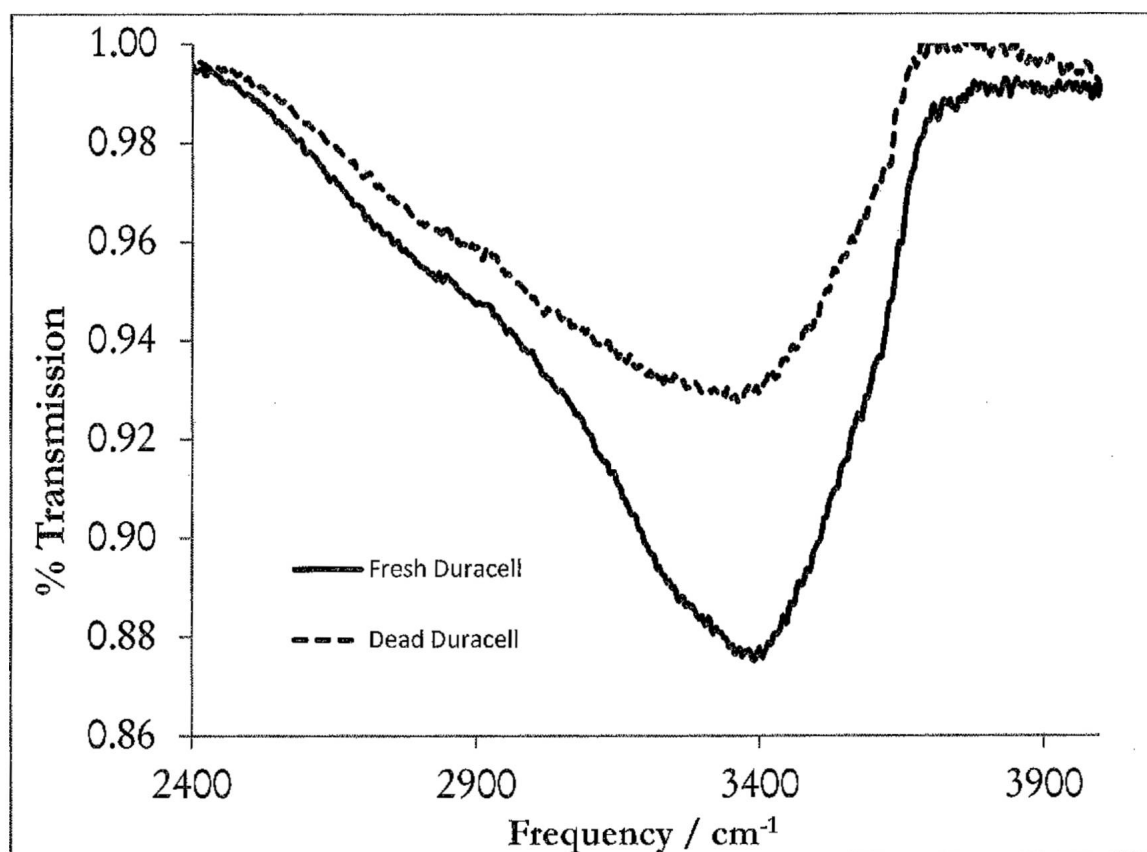


Figure 5. FTIR spectra of the anodes of a fresh AA Duracell alkaline battery versus a dead AA Duracell alkaline battery (baseline corrected).

Chapter 5: The Formation of ZnO Increases the COR of Alkaline Batteries

The second hypothesis that was tested is that the formation of zinc oxide increases the COR of alkaline batteries. The bulk modulus of zinc oxide is 127% greater than that of zinc¹ (Table 1). As the reaction progresses, this change should naturally increase the COR of an alkaline battery because materials with higher bulk moduli demonstrate higher bouncing ability. For example, ZnO has been added to golf balls in order to increase their bouncing capabilities^{3,4}. Here, the pressure of a tennis ball can be used as an analogy to explain the bouncing effect. A pressurized tennis ball, similar to a

dead alkaline battery, has a high COR. As an alkaline battery is discharged, it is metaphorically like adding pressure to a tennis ball and thereby increasing its bounce.

Material	Density /g cm ⁻³	Bulk Modulus /Gpa
Diamond	3.51	443
Steel	7.9	200
ZnO	5.06	134
MnO ₂	4.37	119
MnOOH	4.14	96
Glass	2.6	65
Zn	7.05	59
Water	1.00	2.15

Table 1. Bulk modulus and density properties of selected materials are reported^{1, 14-18}.

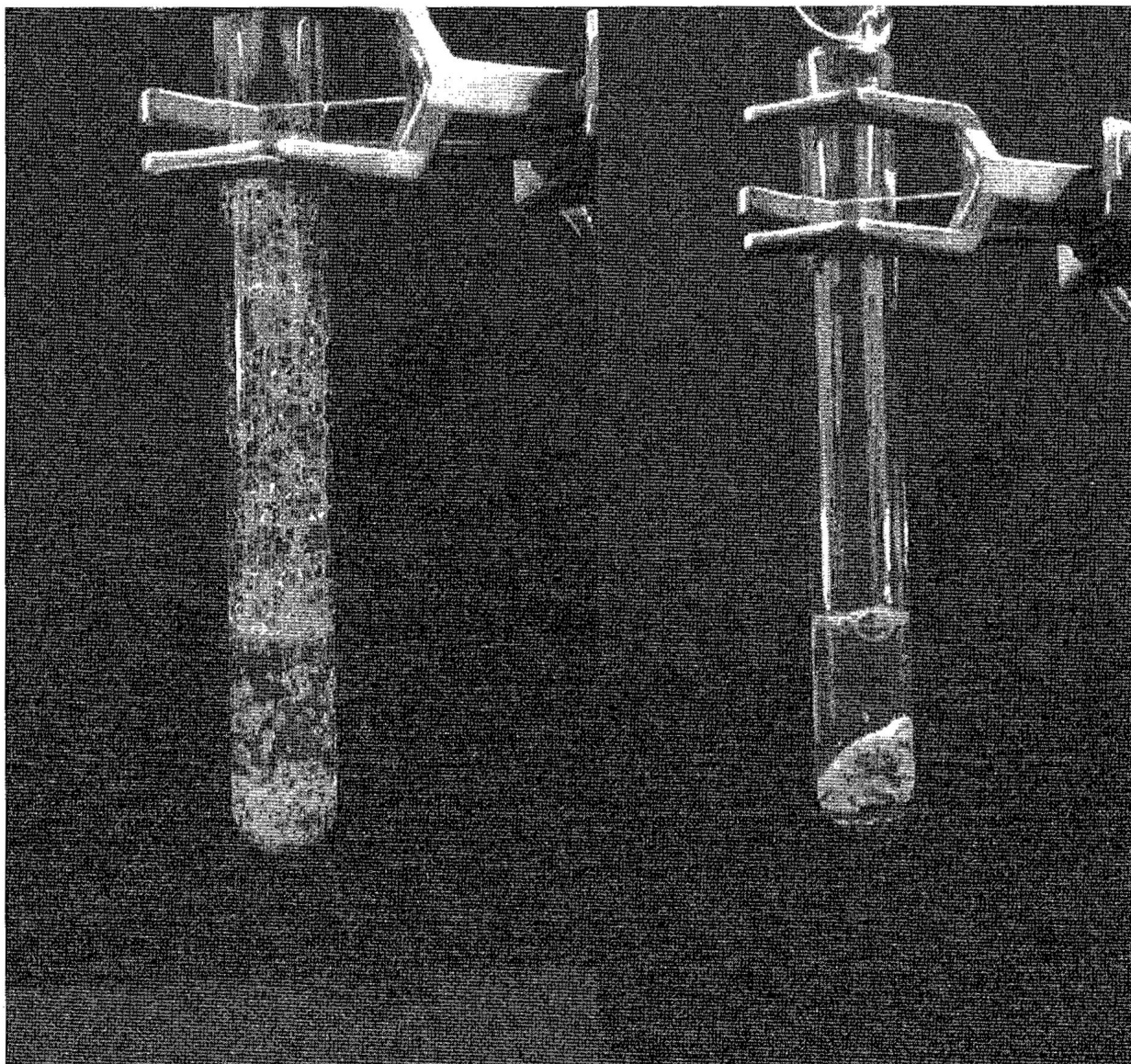


Figure 6. Hydrochloric acid produces hydrogen gas when reacted with zinc (left), but produces no gas when added to zinc oxide (right) (Schemes 2 and 3).



Schemes 2 and 3. The addition of hydrochloric acid to zinc produces a gas while it does not produce a gas when added to zinc oxide.

To test for the percentage of zinc in the anode of alkaline batteries, hydrochloric acid was added in excess to a determined mass of anodic material (Figure 6) (Schemes 2 and 3). The amount of hydrogen gas collected from the reaction with the anodic material was used to determine mass of zinc that had been present in the sample. Next, the mass percentage of zinc in the anodic material can be calculated. To ensure an accurate calculation, it was important to correct for the pressure of water and record the temperature and pressure in the laboratory. As this experiment was performed, a linear decrease in the percentage of zinc was observed as charge was delivered from alkaline batteries (Figure 7).

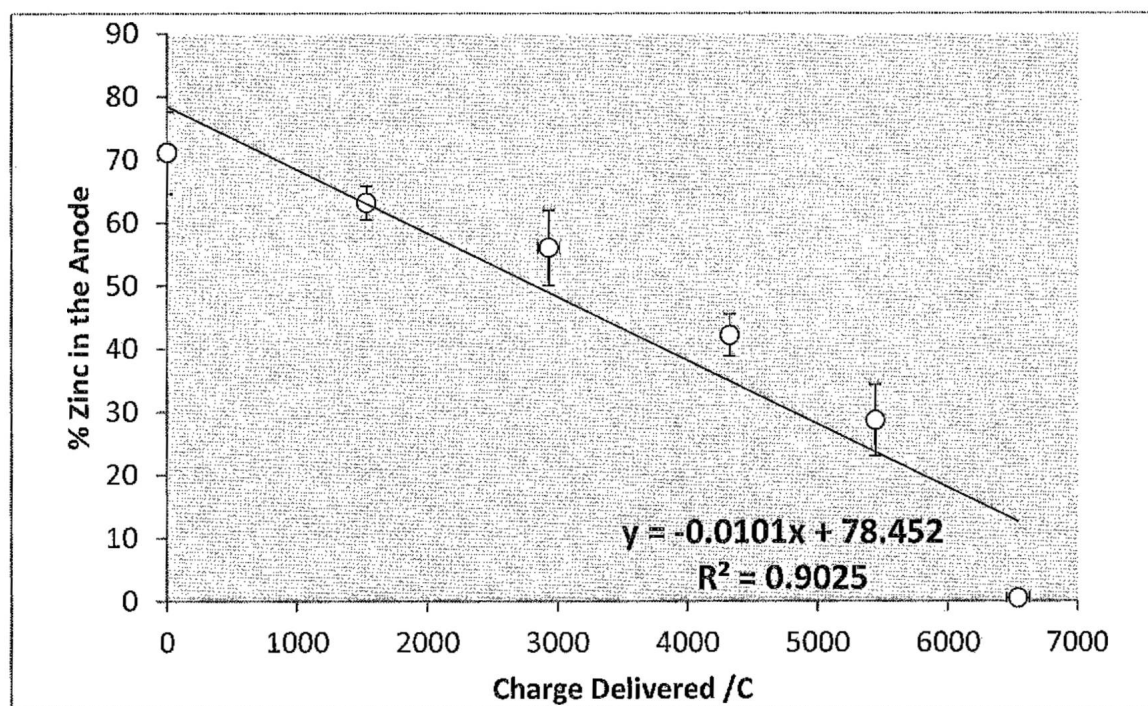


Figure 7. The percentage of zinc in the anode of AA Duracell alkaline batteries decreases as charge is delivered.

This procedure started with cutting the AA Duracell alkaline batteries in half with a PVC cutter so that the positive and negative terminals were separated (Figure 8). It was important to wear gloves and goggles during this step because the inner contents of the

battery can stain hands and surfaces. Then, a small portion of the anode was carefully weighed in a side-armed flask. A stopper and tubing that appropriately fit the side-armed Erlenmeyer flask were obtained. The tubing was connected to the flask and a water trough. In the water trough, an inverted 100 mL graduated cylinder was filled with water and fixed above the end of the tubing. This allowed for the gas to be collected in the graduated cylinder. An excess of hydrochloric acid was added to the flask and the stopper was quickly placed in the mouth of the flask. When the volume of gas collected had not increased within two minutes, the final volume of collected gas and the water level on the graduated cylinder were recorded. Additionally, the temperature and pressure of the laboratory were recorded. The moles of hydrogen gas produced, which correspond to the moles of zinc present in the sample, could then be calculated. This allowed for the determination of percentage of zinc in the anode based on mass.

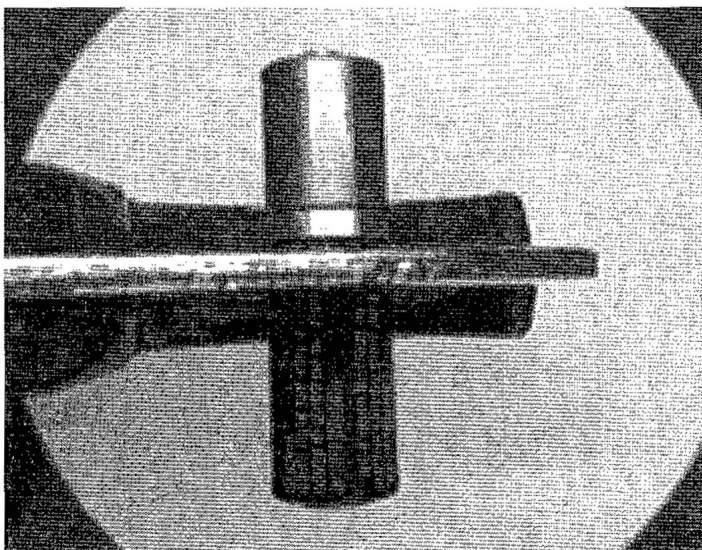


Figure 8. AA alkaline batteries were cut in half using PVC cutters.

To demonstrate the qualitative differences between the anode of fresh and spent batteries, this procedure could be modified. Two test tubes could be fixed side-by-side.

A portion of fresh battery anode could be placed in left test tube while an equal by weight portion of dead battery anode could be placed in the right test tube. Then, equal volumes of hydrochloric acid could be added to the test tubes at the same time (Figure 6). The amount of bubbling can be observed to qualitatively show that there is much more zinc present in the anode of the fresh battery. Additionally, a flame test could be performed to demonstrate the chemical properties of hydrogen gas.

Chapter 6: Does the Reduction of Mn IV to III Increases the COR of Alkaline Batteries?

The third hypothesis that was investigated dealt with the chemical changes at the cathode of alkaline batteries. The bulk modulus argument used in the second hypothesis cannot be applied here because the bulk modulus of MnOOH is less than MnO_2 ¹ (Table 1). Yet, experiments to illustrate the chemical differences in cathode material between fresh and spent batteries can enhance student understanding of the chemistry behind alkaline cells. Interestingly enough, MnO_2 and MnOOH can catalyze the decoloration of methylene blue in the presence of hydrogen peroxide. This reaction occurs significantly faster with MnO_2 and can be used as an excellent demonstration because the color change can differentiate between the manganese species (Figure 9).

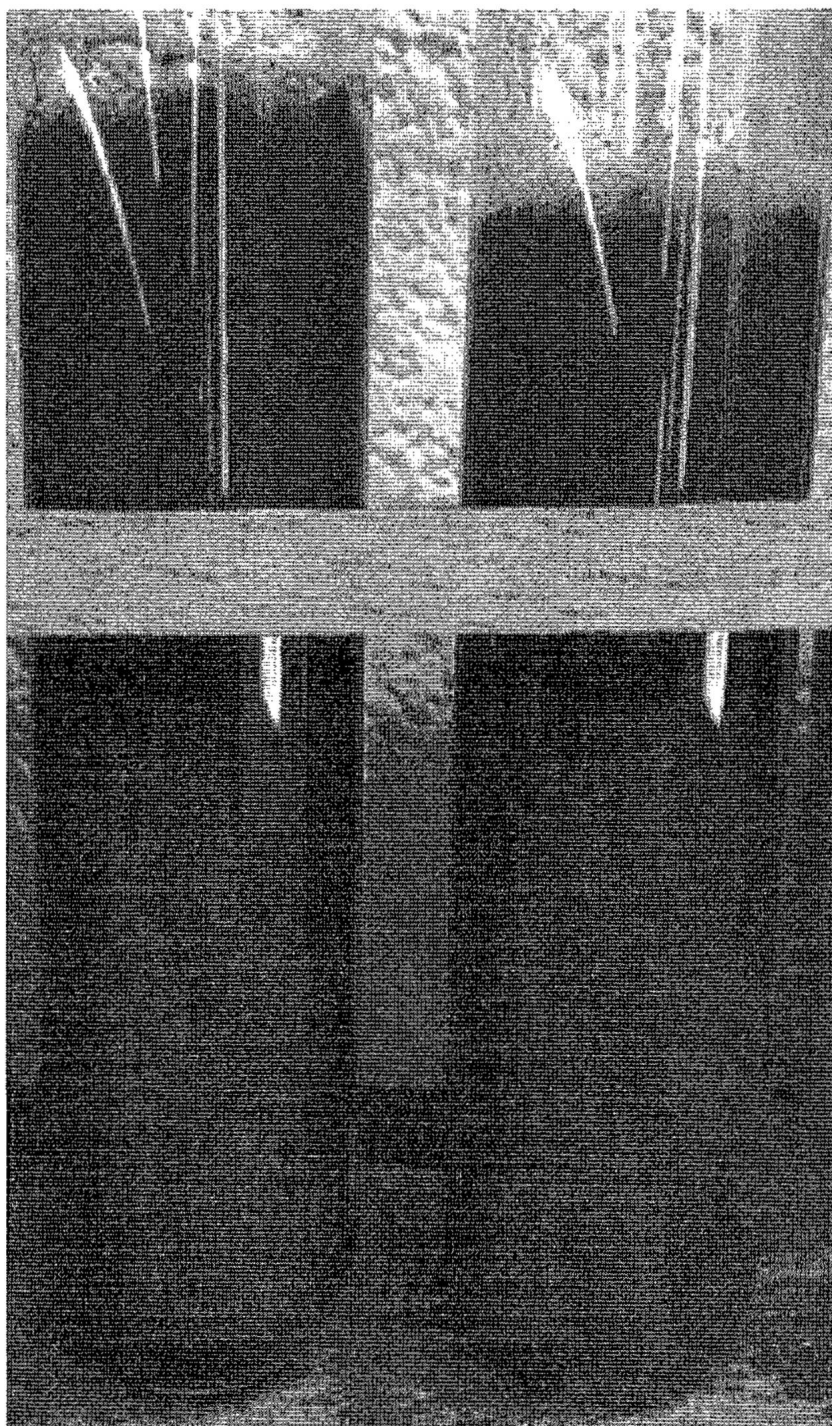


Figure 9. MnO_2 from the cathode of a fresh AA Duracell alkaline battery on the left is able to decolorize methylene blue in the presence of H_2O_2 at a much faster rate than the reduced manganese species present in the dead AA Duracell alkaline battery cathode material on the right.

Even though the chemical changes in the cathode are unlikely to influence the COR of alkaline batteries, this simple test can be performed to demonstrate the differences between the cathode of a fresh and dead battery. The AA Duracell alkaline batteries were cut open with a PVC cutter just as the batteries had been cut open to analyze the anode. Gloves and goggles, again, were important for this step and the remainder of the experiment. Equal portions of cathode material from the dead and fresh AA Duracell alkaline batteries were weighed separately into small containers. About 3 milliliters of deionized water was added to each container and the contents were gently swirled by hand several times.

Three drops of methylene blue were added to a test tube containing 15 milliliters of 3% hydrogen peroxide. Another test tube was prepared in the same way and the test tubes were fixed side-by-side. Simultaneously, the mixture of cathode material from the fresh battery was added to the test tube on the left while the solution of cathode material from the dead battery was added to the test tube on the right. Within one to two minutes, the methylene blue in the test tube on the left had decolorized while the blue color persisted in the test tube on the right.

Chapter 7: Replacing the Anode of Alkaline Batteries

Upon investigating each hypothesis, the idea that zinc oxide formation increases the COR of alkaline batteries has the greatest support. The loss of water might play a minimal role in the increase in COR of alkaline batteries as they are discharged.

However, the logarithmic fit to the loss of water data suggests there is not a correlation between water loss and COR as alkaline batteries are discharged. Lastly, the bulk modulus argument does not support that chemical changes in the cathode increase COR. As these positions were evaluated in more detail, a new experiment was proposed: what would happen if the anode of a dead battery was replaced with that of a fresh battery? A decrease in COR would be expected if the changes in bounce height are centered on the chemical composition of the anode rather than the cathode.

Here, AA Duracell alkaline batteries were completely discharged with MicroLAB. These batteries recorded an average COR of 0.565. The batteries were carefully sawed in half, re-sealed with tape, and new COR values were calculated to be 0.364. Then, the batteries were re-opened and the entire anode was replaced with anodic material from a fresh battery. After replacing the anode, the COR dropped down to about 0.248 (Figure 9).

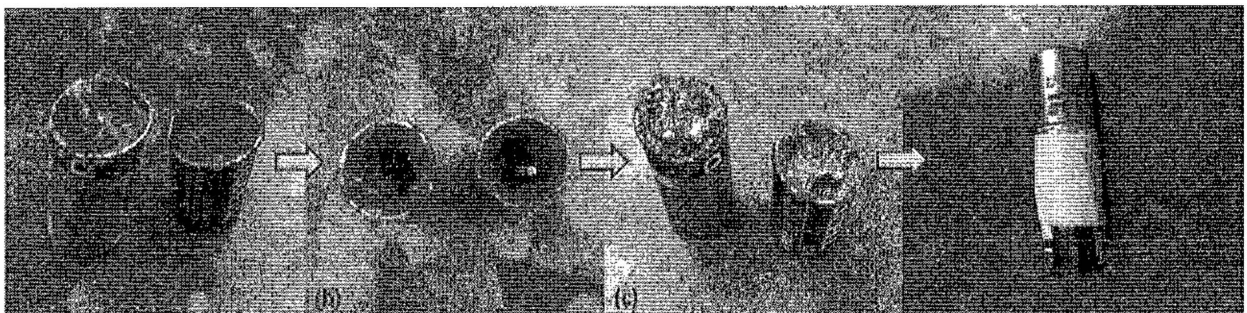


Figure 9. (a) Spent AA Duracell batteries were sawed in half, (b) the anode was scooped out, (c) anodic material from a fresh battery was used to replace it, (d) and the battery was taped back together. Bounce height measurements were taken before step (a), after step (a), and after step (d).

When the anode of a dead battery was replaced with that of a fresh battery, a 31% decrease in COR was observed. This further supports that chemical changes in the anode of alkaline batteries are responsible for the increases in COR as the batteries are discharged. Since cathode material and spent anode material are difficult to remove, the opposite experiments were not performed. Future experiments could include packing water, Zn, ZnO, MnO₂, MnOOH, fresh AA Duracell alkaline battery anode material, fresh AA Duracell alkaline battery cathode material, spent AA Duracell alkaline battery anode material, and spent AA Duracell alkaline battery cathode material into a plastic ball and comparing the differences in COR as the material inside the ball changes. Moreover, this experiment could be repeated using fresh AA Duracell alkaline battery anode material that had been dried in an oven at 100 °C overnight to test for the impact of water on COR heights.

Chapter 8: Conclusions

After determining that COR increases as alkaline batteries are discharged and investigating several hypotheses, the formation of zinc oxide in the anode of alkaline batteries appears to be the most responsible for the increase in COR. The bulk modulus increases significantly as zinc is converted to zinc oxide. A linear decrease in the mass percentage of zinc was observed as the alkaline batteries were discharged, which correlates to the linear increase in COR as the batteries are discharged. The loss of water as alkaline batteries are discharged may play a role in increasing the COR. FTIR analysis indicated that the spent alkaline batteries had less water present in the anode than fresh batteries. The percentage of mass lost after heating as the alkaline batteries were discharged remains relatively unclear. Lastly, the chemical composition of the cathode is unlikely to play a significant role in the increase in COR as alkaline batteries are discharged because the bulk modulus does not change significantly and a battery with fresh anode material but dead cathode material maintained a very low COR.

These experiments could be used to educate high school and early undergraduate students as well. Students can perform tests for the bounce heights and calculate the COR of AA alkaline batteries. Additionally, they can test for the mass percentage of zinc in the anode. Prior to performing these experiments, the instructor may desire to discharge AA alkaline batteries to various extents and label them appropriately. The instructor should also use the PVC cutter to cut open the batteries after the students have finished performing the bounce tests.

These experiments could also be used as a demonstration while introducing oxidation and reduction reactions to students. The instructor could cut open a fresh and completely spent AA Duracell alkaline battery to show the students what the inside of a battery looks like. After explaining the oxidation and reduction reactions at work within alkaline cells, the instructor could demonstrate and explain that the alkaline batteries increase in COR as they are discharged. Students could perform a few in-class calculations while the instructor sets up the anode and cathode demonstrations. Finally, the instructor could end the lecture with a qualitative demonstration of the chemical differences between fresh and spent alkaline batteries in the anode, then the cathode. If desired, the instructor could remind the students of the properties of gases by performing a flame test on the hydrogen gas produced in the anode demonstration and a glowing splint test on the oxygen gas produced in the cathode demonstration.

The science behind AA alkaline batteries tangibly connects chemistry to everyday life while reinforcing concepts such as oxidation, reduction, chemical equations, and gas laws. Physical concepts such as the bulk modulus are integrated into this learning activity as well. Since oxidation and reduction reactions are often covered late in chemistry curriculum, students should have the prior background knowledge of chemical equations and gas laws that enhance the understanding of alkaline batteries. This offers an excellent opportunity to calculate the mass percentage of zinc in the anode of a battery. Moreover, these experiments appeal to visual, auditory, and hands-on learning styles.

The costs of these experiments are fairly inexpensive and most of the necessary components can be purchased at a grocery store. Students are capable of completing

these experiments in the laboratory under the supervision of an instructor. The safety of these experiments, however, can be maximized by allowing students to measure bounce heights while the instructor performs the remaining portions as a demonstration. Therefore, the "bouncing battery breakdown" is an excellent experiment or demonstration for high school and early undergraduate chemistry courses.

An industrial application of this research could be a battery life tester. This would only suffice for alkaline batteries, but nevertheless could become a fairly reliable product to test the remaining life of a battery. Since most people do not need a battery life tester, the price of such a device would need to be fairly inexpensive for any success in the market. Luckily, dropping a battery is an inexpensive method to determine the amount of charge that it has delivered. This is a possible future direction for this research outside from investigating other brands of alkaline batteries (figure 10).

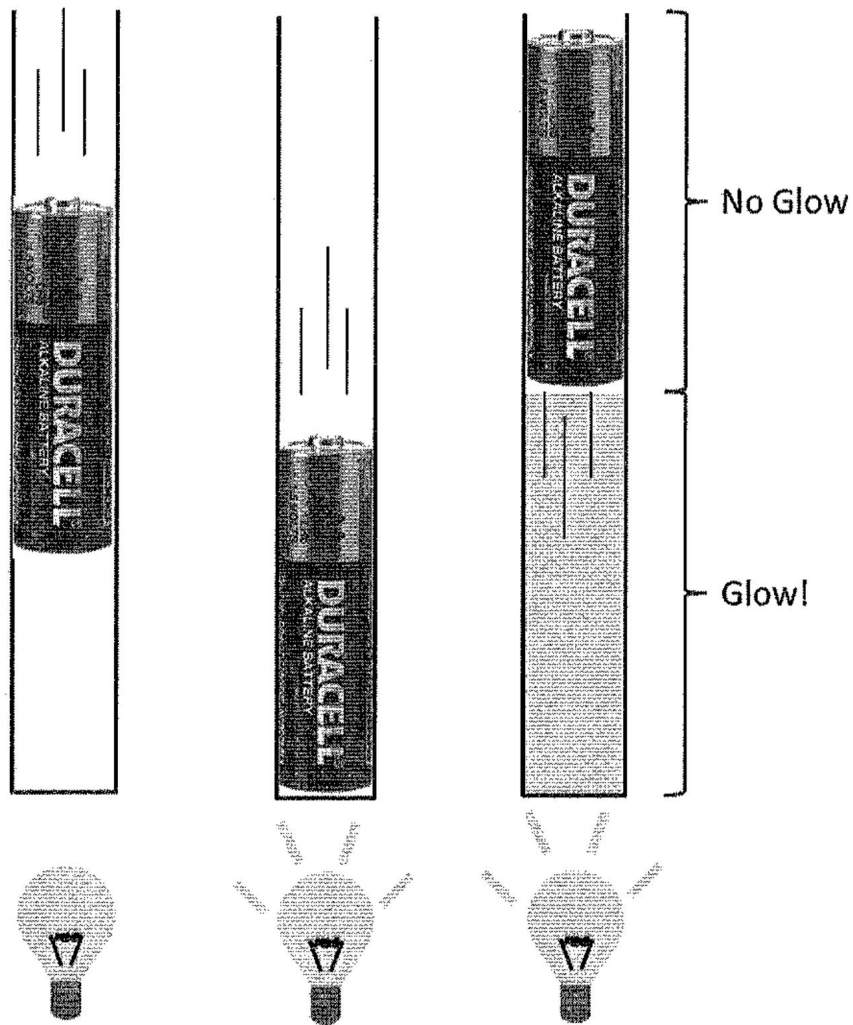


Figure 10. A proposed idea for a relatively inexpensive battery tester is depicted. The battery would be dropped through a tube when the light switch is off. Then, as the battery hits the ground, the light would be activated. Glow-in-the-dark material on the side of the clear tube would begin to glow up until the highest point that the battery reaches because the battery will block light from reaching the material above the battery.

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