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

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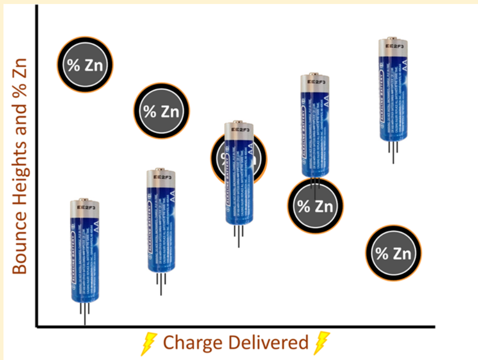
Supporting Information

ABSTRACT: Why do dead batteries bounce considerably higher than fresh batteries? This phenomenon has a chemical explanation that can be used to teach students about the chemistry of alkaline Zn/MnO_2 cells. Batteries discharged to various extents can be tested for bounciness and conversion of Zn to ZnO. These measurements allow students to connect the chemistry that powers these batteries with the increased bouncing effect. The experiments can be presented as a teacher-led demonstration or hands-on laboratory for students.



KEYWORDS: *General Public, Elementary/Middle School Science, High School/Introductory Chemistry, First Year Undergraduate/General, Demonstrations, Inorganic Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Electrochemistry, Electrolytic/Galvanic Cells/Potentials, Introductory Physics*

■ INTRODUCTION

There is an easy way to check if an alkaline battery is fresh or spent: drop the battery so that it lands upright and its negative terminal strikes flat on a hard surface.[1] If the battery does not bounce, it is fresh. If it rebounds significantly, it is time to replace it. This simple test has gained a surprising amount of popularity, mostly through online videos that describe how to carry it out.[2]

■ BACKGROUND

The bouncing ability of a battery or any other object is often measured using the coefficient of restitution (COR). The COR of an object is found by comparing the velocity of an object both before (v_1) and after (v_2) striking a hard, flat surface:[3]

$$\mathrm{COR} = \frac{v_2}{v_1} \tag{1}$$

A straightforward measurement of COR can be made by finding the rebound height, h_2, of an object dropped from a height h_1, and using eq 2[3]

$$\mathrm{COR} = \sqrt{\frac{h_2}{h_1}} \tag{2}$$

Because a battery bounces higher when discharged, the COR of an alkaline battery increases as its charge is depleted. A knowledge of alkaline battery chemistry aids in the appreciation of how this transformation takes place. The chemical reaction that powers alkaline batteries can be written as[1,4–6]

$$\begin{aligned} &Zn(s) + 2MnO_2(s) + H_2O(l) \\ &\quad \rightarrow ZnO(s) + 2MnOOH(s) \end{aligned} \tag{3}$$

In this spontaneous oxidation–reduction reaction, Zn is oxidized to ZnO and MnO_2 is reduced to MnOOH. During the reaction, electrons are transferred from Zn to MnO_2, converting Zn to ZnO and MnO_2 to MnOOH. The Zn and MnO_2 are isolated in separate compartments so that eq 3 does not occur when the battery is not in use. Otherwise, batteries would continuously run and burn out even when not connected to a device. Zn is sealed in the inner portion of an alkaline battery, and the MnO_2 surrounds the inner core of Zn. These two reactants are separated by a porous membrane (Figure 1).

The portion of the battery that houses the Zn (and ZnO product) is called the anode compartment, whereas the portion of the battery that contains the MnO_2 (and MnOOH product) is called the cathode compartment. When these sections are separated from one another, no reaction occurs. When the battery is placed in an electrical device and the device is turned on, electrical contact is made between the two sections. As a result, electrons spontaneously move from the anode compart-

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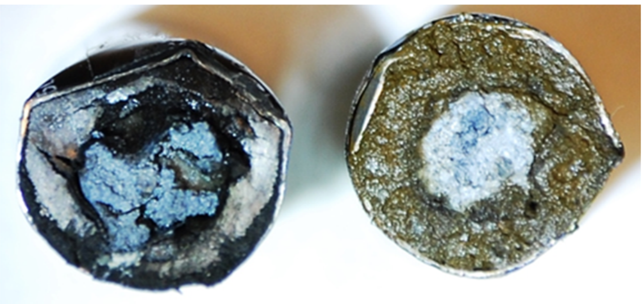

Figure 1. Cross-sectional view of a fresh (left) and spent (right) Duracell alkaline battery. The inner (anode) portion contains Zn, ZnO, or both in KOH electrolyte in a gel; the outer (cathode) portion contains MnO_2, MnOOH, or both in conductive carbon. The anode and cathode are separated by a porous membrane.

ment to the cathode compartment. The half reactions that occur as a result of this electron flow are[1,4,6]

$$Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^- \quad (4)$$

$$2MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow 2MnOOH(s) + 2OH^-(aq) \quad (5)$$

Other reduced manganese species (e.g., Mn_2O_3 and Mn_3O_4) are reported to form in the cathode of alkaline batteries,[1,4−8] thus the chemistry that occurs at the cathode is not completely understood. The standard reduction potentials of MnO_2 to MnOOH and ZnO to Zn are +0.21 V and −1.26 V, respectively.[9,10] Therefore, the cell potential for the overall reaction occurring in the alkaline cell (eq 3) is +1.47 V.

Facile measurements can be performed to show how chemical changes are related to the increased ability of batteries to bounce as they are discharged. These measurements can be conducted as a teacher-led demonstration or by students in the laboratory. First, the COR and extent of conversion of Zn to ZnO is determined in batteries discharged to various extents. Simple battery bounce tests suffice for COR measurements. Observing the extent of conversion of Zn to ZnO is possible because only the former releases gas when treated with HCl

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g) \quad (6)$$

$$ZnO(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(l) \quad (7)$$

Thus, the anode portion of fresh batteries is expected to release more gas than anodic material from dead batteries upon treatment with HCl. By comparing the COR results with the extent of Zn to ZnO conversion, it can be hypothesized that the chemical conversion of Zn to ZnO might be responsible for the increased bounce in dead batteries.

■ EXPERIMENTAL SET UP

Discharging of Batteries

All experiments were conducted with Duracell AA batteries. Batteries were discharged to different extents using a resistive load module (RLM, Figure 2). To do so, fresh out of the package batteries were connected to the RLM, which was set so that only R1 was in the circuit. Current and time delivered by each battery was recorded with a MicroLab Model 522 data acquisition system, and the total charge delivered was determined by integrating the resulting current vs time curve (Figure 3). It should be noted that the RLM is not required to carry out this experiment. Both fresh and spent batteries are easily obtained and performing the tests described herein suffices to differentiate between the chemistries of these two batteries types. If it is wished to quantify the extent to which batteries are drained without the RLM, current and time can be recorded while batteries are discharged when connected to an ammeter (see laboratory sheet in Supporting Information).

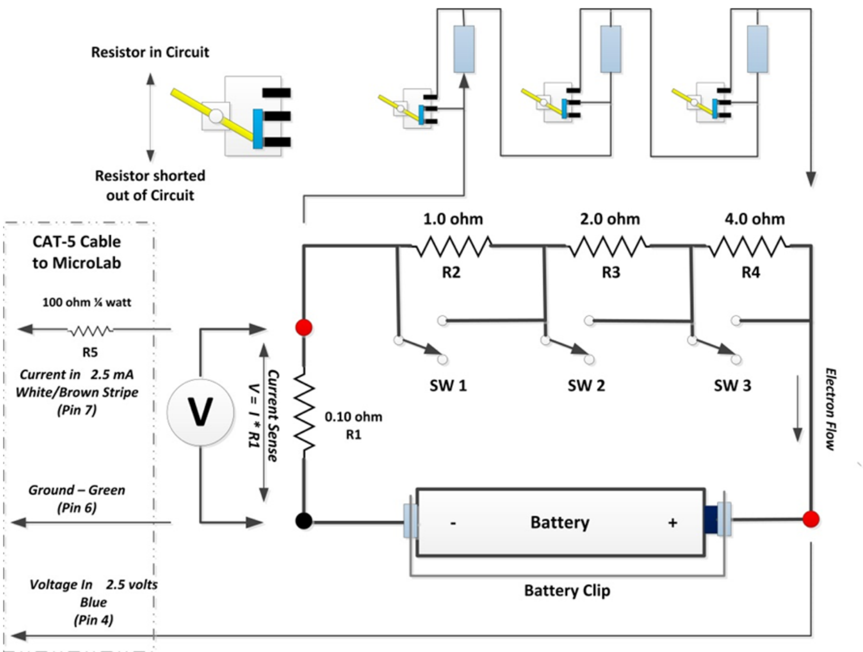

Figure 2. Circuit diagram of the resistive load module. The module included a set of four resistors, three of which could be switched in or out to provide variable resistance. The current through the circuit was determined by measuring the voltage drop across resistor R1. See Supporting Information for more details.

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J. Chem. Educ. XXXX, XXX, XXX−XXX

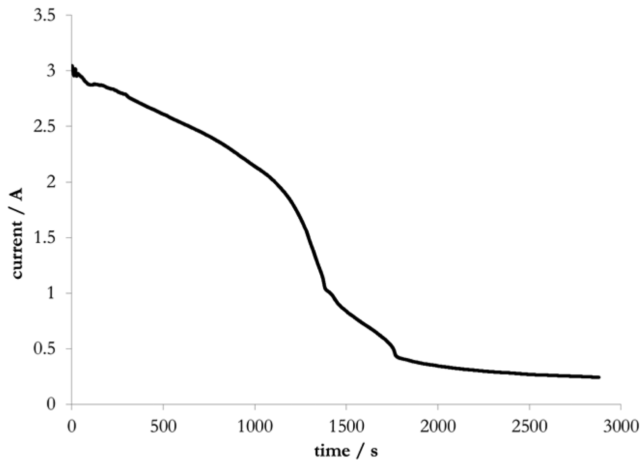

Figure 3. Current vs time observed for a Duracell AA alkaline battery that was almost completely drained using the MicroLab RLM.

COR of Batteries

Bounce heights were determined by using a free cell phone application to capture slow-motion videos of batteries dropped from 60 cm onto a flat, hard surface. Videos were analyzed to determine the maximum height achieved after the first bounce. A meter stick was used as a reference point, and bounce height was taken as the maximum height the lowest point of the battery reached after initial contact with the ground (Figure 4).

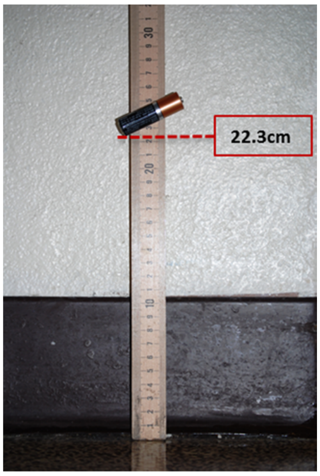

Figure 4. Measurement of battery bounce height.

The average of six bounce height measurements was calculated for each battery. Only trials in which the battery was observed to strike flat on contact were recorded. The COR was determined using the measured bounce heights and eq 2.

Extent of Zn to ZnO Conversion

After the COR tests, the batteries were cut open. The anodic portion of the battery was carefully removed and precisely weighed. The % Zn remaining in the sample was quantified by treating the sample with an excess of 3 M HCl and measuring H_2 gas production as described by Burgstahler.[11] Conversion of H_2 produced to Zn remaining in the anode was done using eq 6.

■ HAZARDS

The experiments described herein are only intended for zinc−MnO_2 alkaline batteries. Do not attempt to cut open any other type of batteries; the contents may be hazardous. The inner contents of alkaline batteries contain concentrated, strong base. Wear goggles and gloves when cutting open a battery and using its contents. Do not allow batteries to become hot when connected to the RLM or ammeter. Periodically remove batteries from the discharging unit and allow them to cool when discharging. Only cut open batteries that have been cooled to room temperature. Avoid contact with the solution of hydrochloric acid, which is corrosive. Inhalation of vapor may cause respiratory irritation. Use caution when performing reactions that generate hydrogen gas; keep materials away from sparks and flame.

■ RESULTS

Batteries were discharged to various extents and the charge delivered, COR, and % Zn remaining in the anode was determined for each battery as described in the Experimental Set Up. As expected, the COR was found to increase with the amount of charge drained from each battery (Figure 5). The linear increase in COR observed differs slightly from the sigmoidal increase observed in a previous study.[1] As argued previously,[1] this difference is likely due to the different physical properties that arise in batteries discharged at different rates.[4]

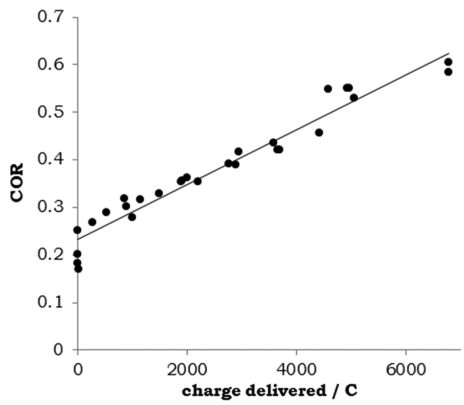

Figure 5. COR for Duracell AA alkaline batteries discharged to varying extents. R^2 = 0.95 for the linear fit (data pooled from several student trials).

Consistent with the results displayed in Figure 5, the % of Zn remaining in the anode was found to decrease in a linear fashion (Figure 6). Taken together (Figures 5 and 6) these results allowed students to suggest that the conversion of Zn to ZnO as batteries are discharged might contribute to the increased bounciness of batteries.

■ DISCUSSION

X-ray diffraction measurements conducted on material collected from alkaline batteries discharged to various extents indicate that the conversion of Zn to ZnO is largely responsible for the increased COR of discharged batteries.[1] This hypothesis is consistent with a comparison of the bulk modulus of the various materials contained within batteries (Table 1). Materials composed of substances with a high bulk modulus generally have a higher COR than those with a low bulk modulus. Thus, it is expected that the formation of ZnO and

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J. Chem. Educ. XXXX, XXX, XXX−XXX

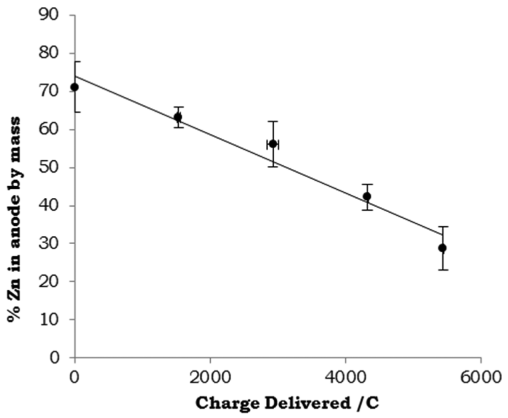

Figure 6. Percent Zn remaining in the anode for Duracell AA alkaline batteries discharged to varying extents. $R^2 = 0.96$ for the linear fit (data pooled from several student trials).

Table 1. Bulk Modulus of Materials Found in Alkaline Batteries[a]

Material	Bulk Modulus/GPa
ZnO	134
Zn	59
MnO_2	119
MnOOH	96

[a]See ref 1.

concomitant consumption of Zn would increase the bounciness of batteries because the bulk modulus of the former is well over twice as high as that of the latter. In fact, ZnO has been added to golf balls to increase their COR.[12]

Quantifying the conversion of Zn to ZnO using HCl is relatively quick and straightforward. Indeed, the acid test for Zn can be used in an in-class demonstration to qualitatively show that a drained battery contains less Zn and more ZnO than a fresh one (Figure 7). Pairing this demonstration with COR tests on a fresh vs spent battery provides a nice lesson that ties together many concepts such as chemical reactivity, material properties, and electrochemistry.

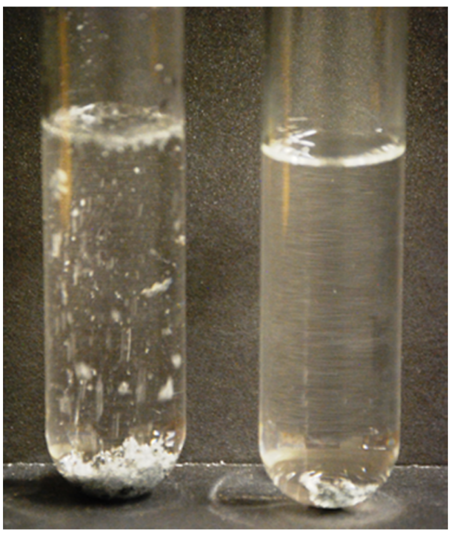

Figure 7. HCl (3 M) added to anodic material from a (left) fresh and (right) spent Duracell alkaline battery. The substantially greater bubbling observed in the former is indicative of a much higher Zn content in the fresh battery.

Although conversion of MnO_2 to MnOOH (or other reduced Mn species) is likely not responsible[1] for the battery bouncing effect, students nevertheless find it interesting to observe differences in the chemical properties of the cathode in fresh and spent batteries. To do so, a small amount (~0.02 g, enough to cover the tip of a microspatula) of cathode material is obtained separately from fresh and spent batteries. This material is mixed with 3 mL of water in separate test tubes. The contents of each test tube are agitated to break apart and evenly disperse particles. Differences in color are immediately noted between the fresh (black) and drained (brown) cathode material, suggesting differences in chemical composition. This material also differs in its ability to catalyze the decomposition of methylene blue in the presence of H_2O_2. To see this, two separate test tubes are filled with 20−25 mL of 3% H_2O_2. To each test tube, 3 drops of 0.2 wt % methylene blue are added. For the test, the separate cathode/water mixtures are added to the separate H_2O_2/methylene blue mixtures. The blue color immediately disappears and rapid effervescence from H_2O_2 decomposition occurs in the test tube treated with fresh cathode material; the blue color persists and gentler bubbling is observed in the other test tube (Figure 8). These observations are consistent with a previous study[13] that reports that MnO_2 catalyzes the decomposition of methylene blue by H_2O_2 more quickly than reduced manganese species. Thus, this test is useful as a qualitative measure of the extent of reduction of cathode material in alkaline batteries.

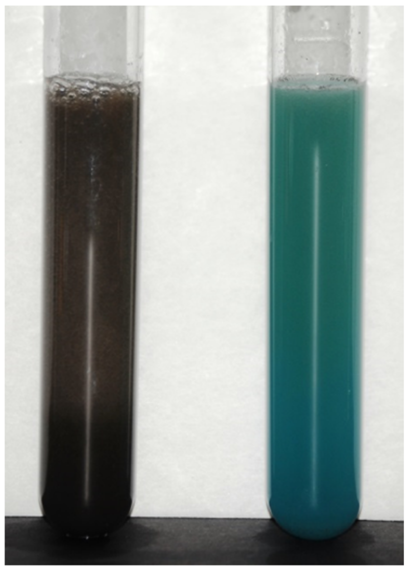

Figure 8. Material from the cathode of a fresh (left) and spent (right) Duracell alkaline battery added to a mixture of methylene blue and H_2O_2. Strong effervescence and rapid discoloration of methylene blue catalyzed by fresh cathode indicates the presence of MnO_2 rather than reduced Mn species.

■ CONCLUSION

These activities and demonstrations provide fast, fun and easy ways to experience the chemistry of batteries. Simultaneous tests of the COR and % Zn in the anode material of fresh and dead batteries allows students to understand how the chemical reaction that powers alkaline batteries ultimately causes them to

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J. Chem. Educ. XXXX, XXX, XXX−XXX

bounce higher as they are used. The experiments can be presented as an in-class demonstration or laboratory activity. By making either qualitative observations or quantitative measurements, these activities can be tailored to suit the level of student involvement desired.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00796.

Procedure for discharging batteries using an ammeter, sample student laboratory sheet, more information on fresh vs spent cathode experiment, and description of the resistive load module. (PDF)

Procedure for discharging batteries using an ammeter, sample student laboratory sheet, more information on fresh vs spent cathode experiment, and description of the resistive load module. (DOCX)

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Notes

The authors declare no competing financial interest.

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