Supporting Information

Exploring Real-World Applications of Electrochemistry by Constructing a Rechargeable Lithium-Ion Battery

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Demonstration Overview

The following demonstration involves the assembly, charging, and testing of five identical rechargeable lithium-ion coin cells. It is designed to take 15 minutes of class time, plus another 15 minutes of student interaction, discussion, and Q&A. Some post-demonstration questions are recommended to evaluate student response. Pictures of a coin cell battery constructed in this demonstration are shown in Fig. S1 along with pictures of a commercially-available CR2032 coin cell battery.

Note: The traditional definition of anode and cathode change depending whether the battery is being charged or discharged. The convention among battery chemists is to refer to the anode as the electrode that is oxidized (loses electrons) upon discharge, which in this case is the graphite. The cathode is the electrode that is reduced (gains electrons) upon discharge, which in this case is the manganese oxide).

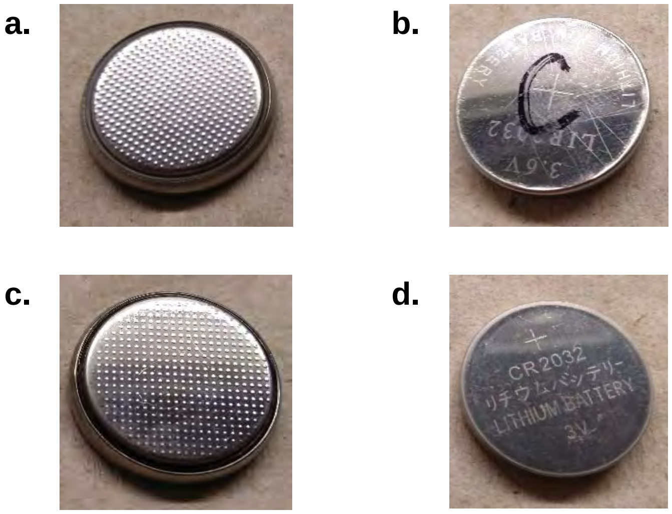

Figure S1. a and **b** pictures of the top and bottom of the coin cell battery described in this demonstration. **c** and **d** a purchased CR2032 battery for comparison.

The battery contains seven components including the cathode and anode caps of the cell case, a stainless steel spring, stainless steel spacer, lithium manganese oxide cathode with steel mesh current collector, glass fiber separator, and a graphite anode with steel mesh current collector (Fig S2). The electrolyte (not shown) comprises 0.1 M lithium trifluoromethanesulfonate (LiO_3SCF_3, lithium triflate) in propylene carbonate solvent. Each of the components and electrolyte can be prepared prior to the demonstration. For the demonstration, the components are assembled in the correct order and the cell case is sealed in a coin cell hydraulic crimper. The battery is then placed in a USB-powered coin cell charger. The battery takes approximately 20 seconds to charge, which is indicated by the light of the charger turning from red to green. The coin cell is then placed into a LED tea candle, which operates for approximately 90 seconds. The charging procedure can be repeated several times.

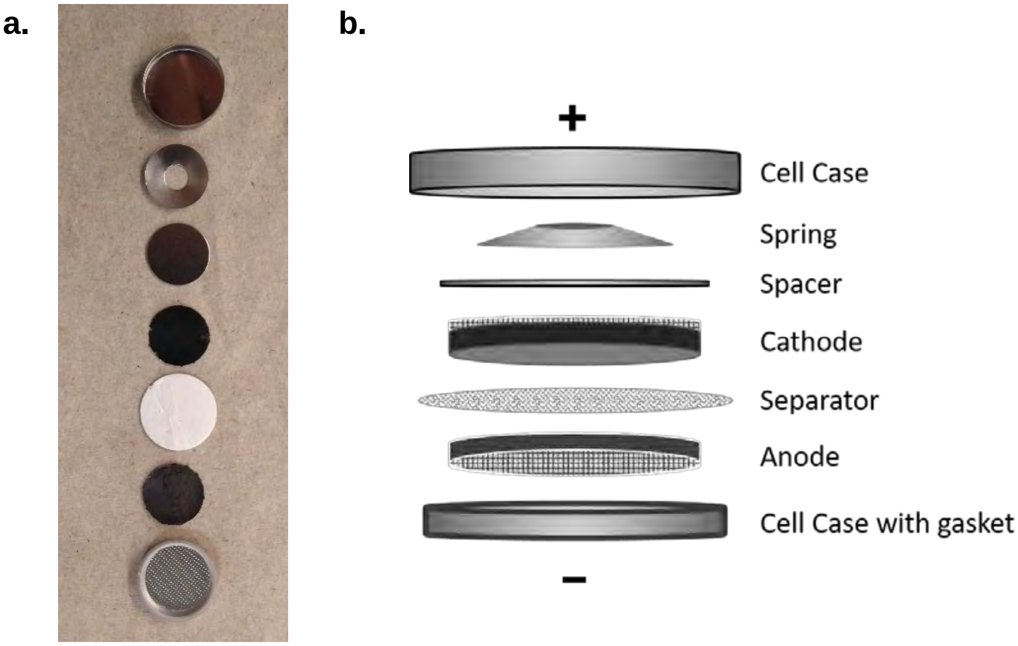

Figure S2. a. Picture of battery components before assembly (top to bottom: cathode cap, spring, spacer, cathode, separator, anode, anode cap with gasket). **b.** Diagram showing the order of assembly, starting with the bottom.

Pre-Demonstration Preparation

The battery components require approximately one hour of preparation time and should be completed the day prior to the demonstration in order to adequately heat and dry the electrodes. Table 1 lists the required materials, equipment and chemicals for the demonstration. The most expensive component is the hydraulic crimping press by a significant margin, but may be available to loan from a local university research lab. The other materials and chemicals are relatively inexpensive and result in a marginal cost of approximately $5 per battery.

Table 1. Required Materials, Equipment, and Chemicals

Equipment	Vendor	Part Number	Cost
Hydraulic Crimper	MTI	MSK-110	$3,398
Multimeter	Amazon	AstroAI Digital	$10.99
Rechargeable USB Charger	Amazon	Zackees Coin Cell Charger	$19.95
Balance			
Glass vials for mixing			
Metal spatula			
Tweezers			
Pipettes			
Scissors			
Hotplate or oven			
Stopwatch			

Materials	**Vendor**	**Part Number**	**Cost**
CR2032 Coin Cell Cases	MTI	EQ-CR2032-CASE-304-LD	$195 per 100
Steel Spring	MTI	EQ-CR20Be-Spring	$40 per 100
Steel Spacer	MTI	EQ-CR20-Spacer-05	$59 per 100
Wire Cloth 200 Mesh	Grainger	3GNX5	$66 per 16 sq. ft.
Glass Fiber Filters	VWR	28297-978	$36.88 per 100
Flameless LED Tea Lights	Amazon	Vivii Battery-powered LED	$12.99 per 36

Chemicals	**Vendor**	**Part Number**	**Cost**
Conductive Graphite Powder	MTI	EQ-Lib-CGP	$60 per 80 g
$LiMn_2O_4$ cathode powder	MTI	EQ-Lib-LMO	$119 PER 200 g
PTFE Liquid binder	MTI	EQ-Lib-PTFE	$190 per 360 g
CF_3SO_3Li Electrolyte	Aldrich	481548-5G	$43 per 5 g
Propylene carbonate, anhydr.	Aldrich	310328-100ML	$56 per 100 mL

Vendor Details:
MTI: MTI Corporation, www.mtixtl.com
Amazon: Amazon.com, Inc., www.amazon.com
Grainger: W.W. Grainger, Inc., www.grainger.com
VWR: VWR International, LLC. www.vwr.com
Aldrich: Millipore Sigma, www.sigmaaldrich.com

Preparation of Current Collectors

Stainless steel mesh current collectors are prepared by cutting stainless steel mesh (#200 threads per inch) into ten squares (two per battery), each square 10 mm by 10 mm, with a pair of scissors.

Preparation of Anode

The anode is composed of an aqueous slurry of graphite and PTFE (i.e. Teflon) that is spread onto a piece of stainless steel mesh and dried overnight. The anode material was made by combining 0.9 g of graphite powder with 0.1 g of PTFE binder in a glass vial. 1–3 mL of water is added in small increments to the anode powder and mixed with a spatula to form a uniform paste with a consistency of toothpaste.

A pea-sized amount of the anode paste is spread on one piece stainless steel mesh current collector (**Figure S3**) with a spatula. The anode is labeled and dried overnight at 150 °C, either in an oven or by placement on a hot plate (**Figure S2**).

Figure S3. Spreading the anode slurry onto the stainless steel mesh current collector.

Figure S1. The electrodes can be dried overnight. Make sure to note which electrodes are the anodes and which are the cathodes.

Preparation of Cathode

The cathode is composed of an aqueous slurry of lithium manganese oxide, graphite powder, and PTFE binder that is spread onto a piece of stainless steel mesh and dried overnight. The cathode material is made by combining 0.6 g of lithium manganese oxide ($LiMn_2O_4$) with 0.3 g of graphite powder and 0.1 g of PTFE binder. 1–3 mL of water is added in small increments to the cathode powder and mixed with a spatula to form a uniform paste with a consistency of toothpaste.

A pea-sized amount of the cathode paste is spread on one piece stainless steel mesh current collector with a spatula. The cathode is labeled and dried overnight at 150 °C, either in an oven or by placing them on a hot plate. Make sure to allow the electrodes to completely cool before beginning the demonstration.

Electrolyte & Separator Preparation

To create the 0.1 M lithium triflate electrolyte solution, 234 mg of lithium trifluormethanesulfonate (LiO_3SCF_3) is dissolved in 15 mL of propylene carbonate. The separator is made by cutting glass microfiber filter paper in circles of 19 mm diameter. 5 mL of electrolyte should be added to the separators and left to soak for at least an hour.

Demonstration

The demonstration consists of the assembly of the battery components according to Figure S2, sealing the battery in a hydraulic crimper, charging the battery in a USB charger, and testing the battery in an LED tea light.

Battery Assembly and Crimping

The anode cap with attached gasket is placed on the benchtop and the anode is placed inside of the anode cap with active material facing up (steel mesh facing down). A few drops of electrolyte should be added into the anode cap. The separator, now soaked with electrolyte, should be carefully removed from the electrolyte and placed on top of the anode with tweezers. Next, the cathode is placed such that the active material faces the separator and the stainless steel current collector faces up. Next, the spacer is placed on top, taking care to make sure that the separator is visible completely around the spacer. A small amount of pressure can be applied to the spacer to compress the above components into the anode cap. The conical spring is the placed on the spacer (wider side down) and a few more drops of electrolyte added over the spring to completely saturate the cell. Finally, the larger cathode cap is placed on top, covering the battery, and all of the components are gently pressed together.

The battery is carefully removed from the benchtop and placed into the crimping die of the hydraulic press, with the anode cap face up. The hydraulic valve is rotated to the lock position and the handle is pumped to raise the coin cell into the die. The handle is manually pumped until a pressure of 500–700 psi is achieved. The hydraulic valve is then rotated to the unlocked position and the battery is removed from the crimping die. The battery is now sealed should be blotted with a towel and rinsed with water to remove any electrolyte that may have leaked.

Charging and Testing the Battery

The battery is then placed into the USB-powered coin cell charger and the charging time recorded with a stopwatch. Charging is complete when the LED light on the charger changes from red to green (Supporting Information video of coin cell assembly). This process should take approximately 15–20 seconds. If the battery does not charge properly, the battery can be put aside to rest for a few minutes; it is possible that additional time is required for the electrolyte to wet the electrodes. Once charged, the battery voltage can be tested with a multimeter. It should read about 3 Volts.

The charged battery is then placed into the battery compartment of the LED tea light. The light is switched on and the total illumination time is recorded with a stopwatch. We have found it is better to use a flickering, dimmable tea candle, as it does not have a sharp cut-off, but fades somewhat over time before the battery is fully discharged. The final battery voltage can be read after the tea light shuts off. It is typically around 1.8 Volts. The process is repeated for several cycles, recording the charge/discharge time and voltages for each cycle.

Disposal

After the demonstration, the battery should be disposed of as hazardous waste or in a battery recycling bin that accepts lithium-ion batteries.

Alternative Materials and Equipment

Other cathode materials might be tested including lithium cobalt oxide ($LiCoO_2$) or NMC ($LiNi_xMn_yCo_zO_2$), which could give different voltages and different capacities. The electrolyte was chosen because lithium triflate does not release hydrofluoric acid upon contact with water or moist air. Propylene carbonate was chosen for its low toxicity, low flammability, and low volatility (boiling point = 242 °C). Stainless steel mesh (SAE 304 steel, 200 wires per inch) is used as the current collector. This mesh size is convenient as it can be cut with ordinary scissors. Thicker or thinner mesh can be used, but wire cutters may be necessary to shape the electrodes. Circles can be cut out instead of squares, as shown above. While this is slightly more difficult, the increased surface area of the circle should increase the capacity by allowing more electrode material to be added. The USB-powered battery charger used was a Zackees LIR2032, which retails for around $20. Any similar such device designed to recharge 2032 batteries should suffice. The batteries should be capable of powering a range of devices, if only for a short time. We chose to use an inexpensive LED tea candle. The candles mimicked a traditional wax candle by flickering. The most expensive component of the demonstration is the hydraulic battery crimper. We are currently investigating cheaper methods to seal the battery.

Quantitative Analysis

Electrochemistry

Note: The traditional definition of anode and cathode change depending whether the battery is being charged or discharged. The convention among battery chemists is to refer to the anode as the electrode that is oxidized (loses electrons) upon discharge, which in this case is the graphite. The cathode is the electrode that is reduced (gains electrons) upon discharge, which in this case is the manganese oxide).

The battery is charged by removing electrons from the $LiMn_2O_4$ cathode (oxidation) and adding them to the graphite anode (reduction). These processes are described by the following redox half reactions:

$$LiMn_2O_4 \xrightleftharpoons[\textit{discharge}]{\textit{charge}} 2\ MnO_2 + Li_{+} + e_{-}$$

$$C_{graphite} + Li_{+} + e_{-} \xrightleftharpoons[\textit{discharge}]{\textit{charge}} LiC_{graphite}$$

As the battery charges, lithium ions leave the $LiMn_2O_4$ and move into the electrolyte, travel through the separator, and become intercalated in the graphite. Upon discharge, the reaction flips. Lithium ions leave the graphite, pass through the separator once again, and intercalate back into the manganese oxide to produce $LiMn_2O_4$. A detailed explanation of lithium-ion battery electrochemistry can be found in an article by Richard S. Treptow[1].

Capacity

After measuring the charging and discharging times with a stopwatch and voltages with the multimeter for several cycles, the data can be used to quantitatively, albeit roughly, estimate the capacity and efficiency of the battery. The battery typically behaves very differently during first charge cycle due to side reactions within the cell. For the following analysis, it is better to use data from the second cycle onward.

The 2032 battery charger should indicate the charging current. If not, the multimeter can be used to measure the current by connecting it in series between the battery and the leads of the LED. This approach can also be used to approximate current draw of the LED tea light. The charge and discharge stopwatch times can be converted to hours and then multiplied by their respective currents to give a capacity in milliamp hours (mAh). An example of this calculation follows. For our unit, the USB-powered 2032 charger is rated to supply 40 mA to the battery. For one of the batteries we tested, it charged for 14 seconds, giving a charging capacity of 560 milliamp-seconds, or 0.156 mAh. The battery was then discharged for 80 seconds at a rate of 6.2 mA, giving a discharge capacity of 0.138 mAh. The ratio of these numbers (0.138/0.156) gives 88.5% coulombic efficiency.

Charging capacity: $$40\,mA\ \times 20\,s\ \times \frac{1\,h}{3600\,s} = 0.156\,mAh$$

Discharging capacity: $$6.2\,mA\ \times 80\,s\ \times \frac{1\,h}{3600\,s} = 0.138\,mAh$$

Next, a simple charge-discharge plot can be constructed using the voltages measured for the battery before and after charging and discharging. The charging curve is made by plotting the voltage before charging and the voltage at the fully charged capacity. The discharge curve is similarly made by plotting the voltage before and after discharge.

If one would like to determine the specific capacity of the batteries, the finished battery should be weighed. The capacity found with the stopwatch can be divided by the battery's mass to determine the specific capacity, in mAh/g.

Before charging, this battery was measured with the multimeter to have a potential of 1.15 V, which rose to 2.87 V after charging. Using the multimeter, the tea-candle was measured to draw an average of 6.2 mA from the 2032 battery. The tea candle remained visibly lit for about 80 seconds, indicating a discharge capacity of about 0.138 mAh. After this discharge, the voltage was measured to be 1.85 V. This data is plotted on the chart below (**Figure S5**).

One can also determine the total energy capacity, in mWh, of the battery. First, charge and discharge the battery three times to calculate an average discharge time. Discharge again for half of the average discharge time, and measure the voltage. This will be the voltage of the battery at approximately 50% state of charge. Multiply this voltage by the mAh capacity found earlier to obtain the energy of the battery. For example, our battery discharged for 80 seconds and maintained a voltage of 2.4 Volts after 40 seconds our energy. Thus we calculate the energy capacity is 0.138 mAh × 2.4 V = 0.331 mWh.

$$0.138\ mAh\ \times 2.4\ V = 0.331\ mWh$$

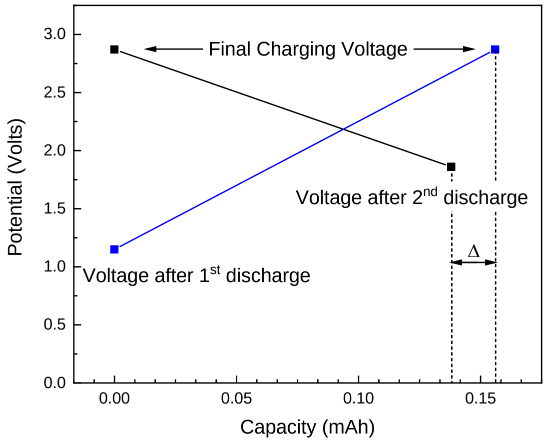

Figure S5. Battery voltage before and after charging. The charging line (blue) shows an upward slope as the voltage increases as the state of charge of the battery increases. The discharge line has a downward slope indicating that the voltage decreases as the battery is discharged. The difference in capacity between the charge and discharge curve indicates the loss of charge upon cycling.

Post-Demonstration Questions

The following questions are provided to provide a basis for discussion and to assess student understanding after the demonstration.

- Describe the movement of electrons and ions at the anode (graphite side) of this lithium-ion battery as it is charged? How does this change when the battery discharges?
  - *When the battery is charged, electrons flow from the charger to the anode. To balance the negative charge of the electrons, lithium ions move from the cathode, through the electrolyte solution and into the graphite anode, where they intercalate between the graphite layers. When the battery is discharged, lithium is released from the carbon, and returns as free ions in the solvent. See the above equations for more details.*
- Describe the movement of electrons and ions at the cathode (lithium manganese oxide side) of this lithium-ion battery as it charges? How does this change when the battery discharges?
  - *As the battery is charged, electrons are removed from the lithium manganese oxide cathode, and to balance the charge the material also loses a positively charged lithium ion to the solution, to create manganese oxide. When the battery is discharged, electrons flow to the cathode and the lithium ions diffuse through solution back to the manganese oxide to create lithium manganese oxide again. See the above equations for more details.*

- What is the purpose of the separator in this battery? How is it different from commercial separators?
    - *The separator prevents electrons from flowing directly between the anode and cathode, but permits lithium ions to move between them. Commercial batteries use a porous plastic separator instead of glass fibers.*
- What is the role of the stainless steel mesh and why is graphite added to the cathode?
    - *The stainless steel mesh acts as a conductive material to collect electrons from the anode and cathode. Graphite is used as a conductor in the cathode to improve the conductivity of manganese oxide. It is very important that the electrons can get into and out of the electrode materials, and these materials help to improve the conductivity of the electrodes.*
- What is the solvent in this battery? How is it different from the solvent in commercial batteries?
    - *A mix of dimethyl carbonate and ethylene carbonate is typically used in commercial lithium-ion batteries. This battery uses propylene carbonate as the solvent. Although propylene carbonate is significantly less flammable, it does degrade in rechargeable lithium ion batteries,*[2] *which can reduce their cycle life.*
- How does this capacity compare to a commercial lithium-ion battery?
    - *The capacity of this battery may be around 0.1–0.2 mAh. The capacity of a commercial rechargeable 2032 battery is around 40 mAh, and the capacity of a commercial non-rechargeable (primary) 2032 is often over 200 mAh.*[3]
- Making the anode and cathode materials thicker is one way to increase the battery capacity. How would you expect thicker electrodes to affect the resistance, voltage, and power of the battery? Hint: Use Ohm's law ($E = I \times R$) and Watt's law ($P = E \times I$).
    - *As the electrodes get thicker, it becomes harder for the electrons and lithium ions to escape or intercalate. This phenomenon is reflected by an increase in resistance of the battery. Ohm's law states that resistance is equal to the voltage divided by the current; Watt's law states that the power is the voltage times the current. Combining these two laws we find that power equals the voltage squared divided by resistance* ($P = E^2/R$)*. Because the voltage* (E) *is fixed by the chemical reactions, an increase in resistance results in a decrease in the power that the battery can discharge.*
- Describe some possible modes of decomposition or side reactions that could occur and how they might be avoided.
    - *When the battery is charged, the lithium on the anode reacts with water and oxygen from the air that was trapped inside the battery when it was assembled. Assembling the battery in a water and oxygen-free environment (nitrogen, argon) would prevent the anode from decomposing. One could also avoid propylene carbonate and use the more flammable dimethyl carbonate to prevent solvent decomposition.*
- What is the current efficiency of this battery? Why is this significant?

- *The current efficiency is determined by dividing the discharge capacity in mAh by the charging capacity in mAh, giving an efficiency expressed as a %. In an ideal battery, this number would equal 100% current efficiency (the same number of the electrons flow during charge and discharge. Deviations from 100% battery indicate that there is some current lost during the charging or discharging process due to side reactions. These side reactions may break down the solvent, corrode the metal casing, or degrade the active materials of the battery. All of these things can lower the total capacity of the battery.*

References

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(2) Dey, A. N.; Sullivan, B. P. The Electrochemical Decomposition of Propylene Carbonate on Graphite. *J. Electrochem. Soc.* **1970**, *117* (2), 222–224. https://doi.org/10.1149/1.2407470.
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