LAB103

Construction of a Lithium-Ion Battery

Table of Contents

Nomenclature ***2***
Abstract ***3***
Introduction ***3***
Stages of the experiment ***4***
Fabrication of the Electrodes **5**
Assembly of the battery components **7**
Charging and test performance **8**
Data analysis ***11***
Battery 1 ..... **11**
Battery 2 ..... **13**
Comparison between B_1 and B_2 ..... **15**
Conclusion and afterthoughts ***16***
Is there any better alternative to a Lithium-Ion Battery? **16**
Bibliography ***18***

Nomenclature

$\bar{X}$	Mean value of a series of data for quantity X
X^*	Theoretical value for quantity X
$\sigma(X)$	Standard deviation of a series of data for quantity X
i	Index of a cycle for battery CR2025
j	Index of a cycle for battery CR2032
B_1 or Battery 1	Battery CR2025
B_2 or Battery 2	Battery CR2032
u(X)	Uncertainty of quantity X
$u_{99\%}(X)$	Enlarged uncertainty of quantity X
z(X)	z-score for quantity X
I	Charge current in mA
I'	Discharge current in mA
m	Mass of the concerned battery in g
τ_{charge}	Time for the battery to charge in s
$\tau_{discharge}$	Time for the battery to discharge in s
γ_k	Coulombic efficiency for battery k (k=1 or k=2)
Q	Charge capacity in mAh
Q’	Discharge capacity in mAh
Q_s	Specific charge capacity in $mAh.g^{-1}$
Q'_s	Specific discharge capacity in $mAh.g^{-1}$
X<<Y	X can be neglected when compared to Y
U	Battery voltage during the charge in V
U’	Battery voltage during the discharge in V
R_V	Voltmeter’s resistance in Ω
R_A	Ammeter’s resistance in Ω

Abstract

During our first laboratory session which took place on Wednesday, September 28th, 2022, from 2:15 to 6:15 PM in the chemistry department, we, Vlad-Ștefănuț Radu and Peter Sayegh, followed a specific procedure to build a pair of Lithium-Ion based Batteries. Our goal was to estimate their capacity by doing a series of different measurements and calculations, their capacity and voltage amongst others. We will be presenting the steps which guided us and the data we collected before analyzing and interpreting the latter in our report.

Introduction

From smartphones and laptops to bicycles and cars, the various tools that we use on a daily basis run on electricity as energy, the electrochemical reactions involved being contained in galvanic cells or, as they are widely known, batteries.

The prototype of the battery was invented around the end of the 18th century, and batteries have evolved over more than 200 years since then, in order to fulfill the demands of a constantly evolving world. Modern batteries represent a means to store energy in an environmentally responsible way, facilitating society's attempt to move away from fossil fuels, one of the most employed batteries being the Lithium-Ion Battery.

Due to its small size and its large electrochemical potential, lithium easily gives away electrons from its atomic structure in order to attain noble gas configuration, which results in high cell voltages and high energy density, which stand to show the efficiency of such batteries. When thinking of the benefits of using such batteries, it comes as no surprise that the 2019 Nobel Prize in Chemistry[1] was awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino for their groundbreaking work in developing Lithium-Ion Batteries, their studies laying the foundations for a fossil-free world.

Knowing that lithium would make a good anode due to its electropositivity, the researchers tried to find efficient materials to store lithium ions in the cathode. However, lithium's reactivity with water or oxygen, for instance, means that batteries in which lithium metal is present in large quantities are not viable, therefore, the solution they found was to use laminar structures as electrodes materials, allowing the storage and stabilization of the small lithium atom, eliminating pure lithium from the battery entirely. By using graphite as the anode and Lithium Manganese Oxide as the cathode, they managed to obtain a compact and reliable battery. It is of no wonder that even such a battery has its flaws, since there is a limited number

of times that a Lithium-Ion Battery can be replenished before it deteriorates and can no longer hold a charge, but it cannot be denied the fact that they represent a force for good.

Part of our activity was to construct two such Lithium-Ion Batteries, our work having involved fabricating the electrodes, assembling the battery components and assessing their capacity by calculating their Coulombic efficiency. The main goal of our study was to explore the technology behind such batteries, accumulating new theoretical and practical notions. We were mainly interested in testing the battery's performance, measuring different parameters, such as the voltage, the charging and discharging current and the time to charge and discharge the batteries.

In the next section, we describe the stages of the experiment. It will be followed by the "Data analysis" section, where the gathered data is analyzed, the report ending with a short presentation of our conclusions.

Stages of the experiment

Our experiment involved three main steps:

- Fabrication of the Electrodes;
- Assembly of the battery components;
- Charging and test performance.

For a better understanding of the materials chosen and the steps of the process, in Figure 1, a diagram of a Lithium-Ion Battery has been realized.

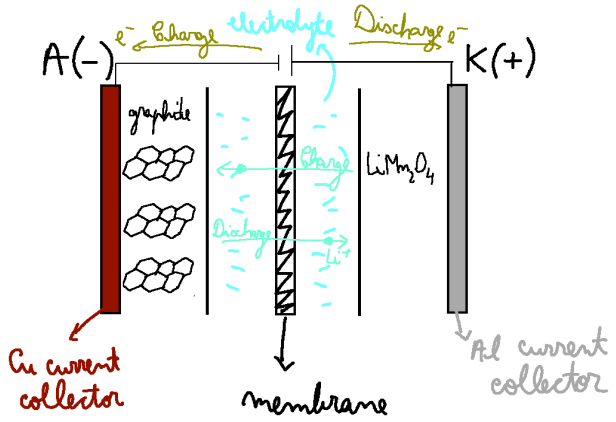


Figure 1: The Diagram of a Lithium-Ion Battery

The anode consists of a copper foil used as a current collector and graphite. Taking into account the laminar structure of graphite, the storage of the small-sized lithium atoms in its structure is allowed (Figure 2), reducing its reactivity by preventing the reactions with oxygen in the air or water and making the battery safer. For the cathode, an aluminum foil is used as a current collector together with Lithium Manganese Oxide ($LiMn_2O_4$), a mixed oxide with a spinel structure[2].

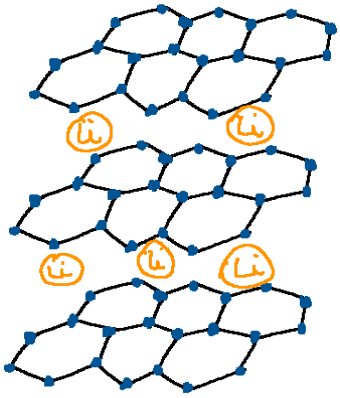


Figure 2: The structure of graphite, allowing the storage of lithium atoms

Both electrodes are immersed in an electrolyte solution and are separated by a permeable membrane that allows the transfer of ions between electrodes.

As the battery is charging, lithium ions in the electrolyte solution gain electrons (reduction), the resulting lithium being stored between the graphite layers (anode). The electrons are produced by the cathode (oxidation) such that the electroneutrality principle is respected. At discharge, the reverse reactions occur, the anode releasing electrons (oxidation), the reduction reaction taking place at the cathode.

One could argue that due to the fact that such a battery could run infinite time since the reactions are reversible, but, in practice, factors such as side reactions or volumetric expansion reduce its lifetime.

It should be mentioned that, for the experiment, instead of a copper and an aluminum foil as current collectors, we used a stainless steel micro mesh.

Fabrication of the Electrodes

By cutting the ***stainless steel micro mesh*** into four 10 mm x 10 mm squares with ***a pair of scissors*** so that they could fit into the battery case, we obtained the current collectors.

The electrode materials used (***graphite*** for the anode and ***Lithium Manganese Oxide*** for the cathode) were powdered materials, therefore we had to give them the required mechanical stability in order to spread the graphite anode and the Lithium Manganese Oxide cathode over the current collectors by mixing them with ***PTFE Binder (Polytetrafluoroethylene)***.

To do so, we combined 0.9 g of graphite powder with 0.1 g of polymer in ***a clean vial glass***, adding a few drops of ***distilled water*** with ***a clean pipette*** to create an aqueous slurry and then mixed with ***a spatula*** until the paste gained the consistency of a toothpaste. Thus, we prepared the anode material.

Then, the same process was repeated for the cathode material, mixing 0.6 g of Lithium Manganese Oxide with 0.3 g of graphite (to increase the conductivity) and 0.1 g of polymer, adding a few drops of distilled water to facilitate the fabrication of the electrode by spreading the paste over the current collectors. All weights were determined with a scale. Since the polymer was liquid, another ***clean pipette*** was used to add it to the mixture.

After checking the consistency of the mixtures, we spread them with another ***clean spatula*** over the corresponding square made by cutting the stainless steel mesh (Figure 3). Taking into account the fact that any presence of water would have drastically dropped the performance of the battery, we dried the electrodes in the oven for about 45 minutes, at 150°C.

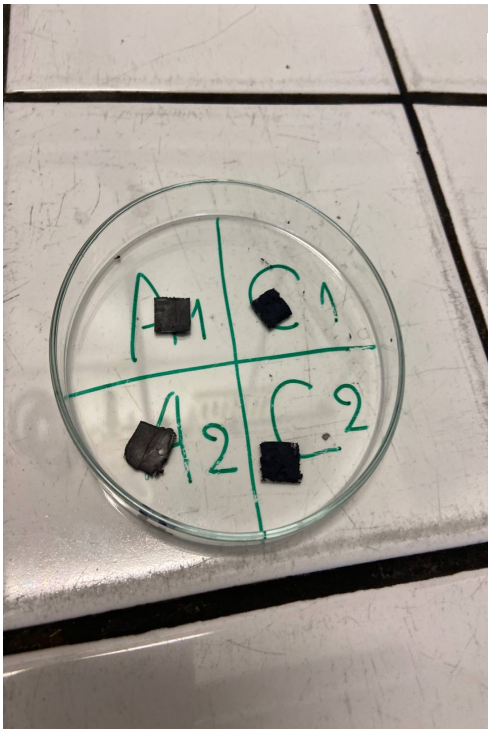


Figure 3: The four Electrodes

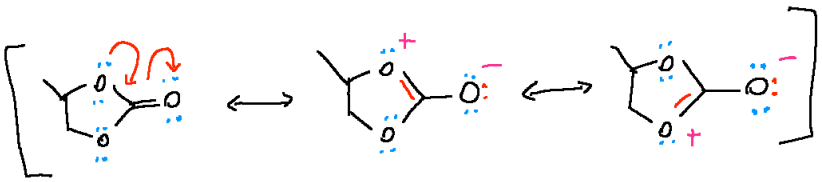


Figure 4: Resonance structures of propylene carbonate, showing it is a polar, aprotic solvent

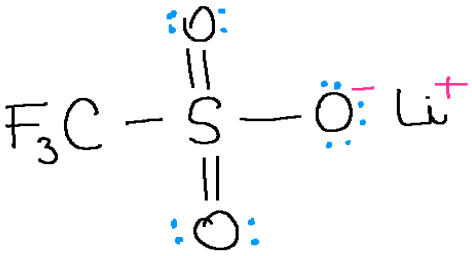


Figure 5: The structure of the lithium salt

Since we wanted to avoid protic solvents for safety reasons, we used as ***electrolyte*** a 0.1 moles/liter ***solution of lithium trifluoromethanesulfonate in propylene carbonate***. The advantage of using propylene carbonate as a solvent is that it is a polar solvent, yet aprotic, dissolving the lithium salt, but preventing dangerous reactions (Figure 4 and Figure 5).

In order to have no shortcuts, the two electrodes had to be physically separated, but allow the transfer of ions, therefore we used ***a microfiber filter paper of 19 mm diameter*** as a permeable membrane. Before using it, the membrane had been soaked for an hour into the electrolyte solution, to make it easier for the ions to move between the anode and the cathode.

Assembly of the battery components

After the electrodes stayed long enough in the oven to lose all the water, we were ready to assemble the battery components. Two batteries were made, one by using ***a CR2025 case*** and one using ***a CR2032 case***.

To do so, we put the components one over the other in the following order: the cell case with gasket, the anode with the steel mesh facing down (with a few drops of electrolyte added into the anode cap), the membrane (using a pair of tweezers in order to avoid any impurities reaching the glass fiber paper), the cathode with the steel mesh facing up, a conical spring and a spacer (to ensure that the battery is compact and there is no deformation), as can be seen in Figure 6.

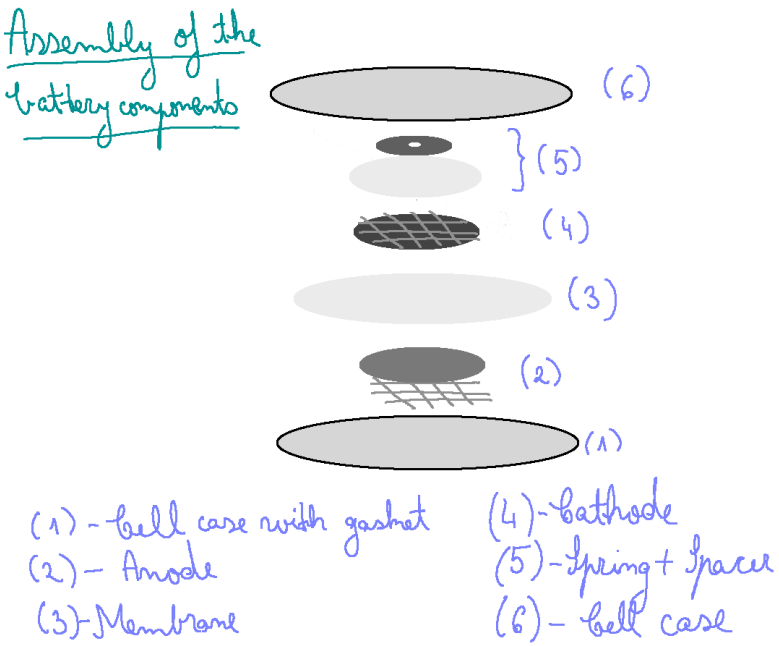


Figure 6: Assembly of the battery components

Having made sure that the membrane covers all the bottom cell, we closed the cell with the cathode cap, not before adding a few drops of electrolyte solution to saturate the cell (Figure 7).

Then, to properly seal the battery, we compressed it with a hydraulic press (Figure 8).

This procedure was applied to both batteries, in the end obtaining two batteries (Figure 9). What followed next was assessing the capacity of both batteries.

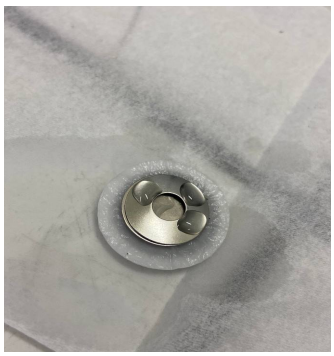


Figure 7: Saturating the cell

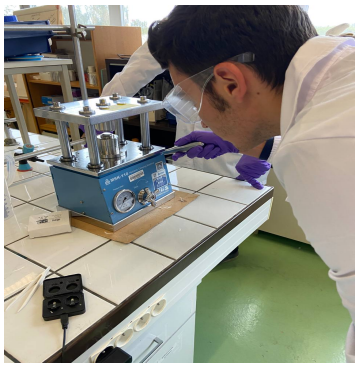


Figure 8: Sealing the battery with a hydraulic press



Figure 9: The two batteries assembled

Charging and test performance

We then had to charge the batteries and test their performance, using ***an USB charger***, ***a battery LED gadget*** to discharge the batteries, ***cables*** to realize the circuits and ***a multimeter*** to measure the charging/discharge current and the voltage after each cycle.

For the sake of simplicity, the CR2025 battery was denoted as Battery 1, and the CR2032 battery as Battery 2. When presenting the steps followed, we will talk only about one battery, but it should be remembered that the same procedure was applied to both batteries.

Since pure lithium metal was not used, there was no energy stored in the battery, thus we first had to charge it with the USB powered coin cell charger. The LED light indicated when the battery was fully charged, as it went from red to green and then it turned off. Keeping in mind that the first cycle is a bit dodgy due to the fact that it is then that most side reactions happen, no measurement was performed for it, because the data would not have been relevant. Therefore, we discharged the battery connecting it to the light bulb. As the light was switched on (Figure 10), it meant that our battery worked. Hence, we waited for it to fully discharge and then ran four cycles to determine relevant parameters, such as charging/discharge current, time of charge/discharge, voltage and calculate its Coulombic efficiency.

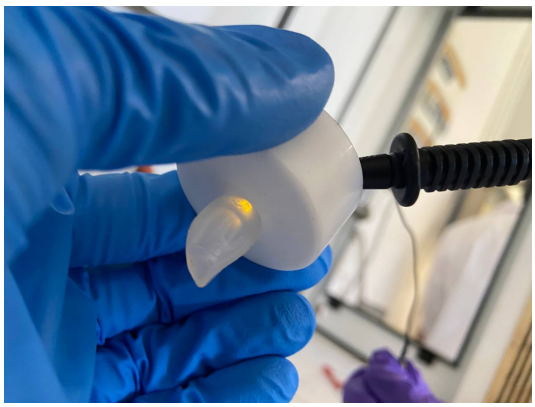


Figure 10: Discharging the battery

For each charge-discharge cycle, the next procedure was repeated: first, we charged the battery, but since we also had to use the multimeter to measure the charging current (the mA scale), we connected it in series with the USB charger, using the addition wire we had in the box, as can be observed in Figure 11. Afterwards, when the charger's LED light turned off, meaning that the battery was fully charged, we recorded the time of charge with a stopwatch.

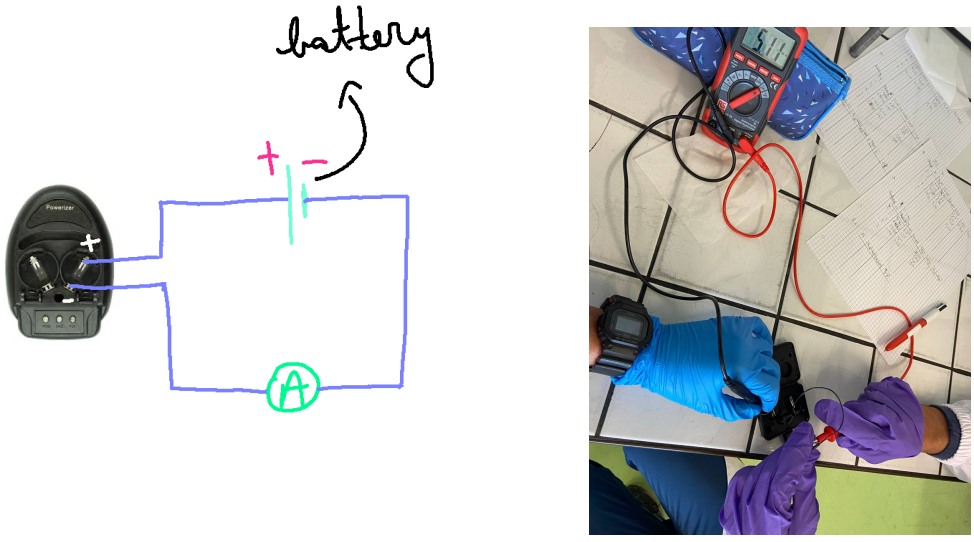


Figure 11: The charging circuit

In order to measure the voltage, we switched the multimeter to voltmeter mode, and connected it to the battery (Figure 12).

To discharge the battery and be able to gather the needed data (discharge current and time of discharge), we realized the circuit in Figure 13, one of us monitoring the multimeter for the discharge current, and the other watching the LED gadget to see when the light switched off so that we could also find the time of discharge (Figure 14).

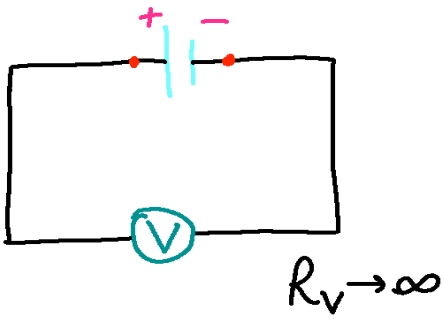


Figure 12: Measuring the voltage

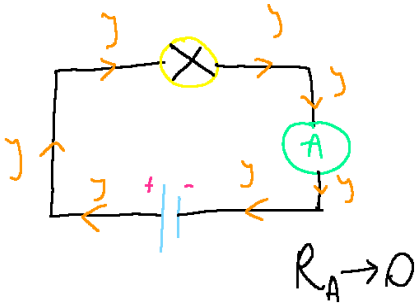


Figure 13: The discharge circuit

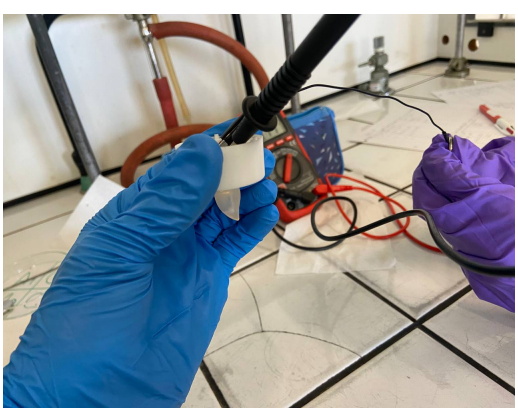




Figure 14: Monitoring the discharge current and the light bulb

Once again, after fully discharged, we measured the final battery voltage, the circuit being similar to the one in Figure 12.

After running four charge-discharge cycles for both batteries, we were able to compute the charge capacity and the discharge capacity, the ratio between the discharge and the charge capacity wielding the Coulombic efficiency, an important parameter when it comes to describing a battery's performance.

In the end, we measured the total weight of both batteries with a scale, determining their specific capacities. Then, to verify the accuracy of our experiments and the efficiency of our batteries, we compared the results with the standard values of a commercial Lithium-Ion Battery.

Data analysis

Battery 1

i	τ_{charge} (s)	I(mA)	Q(mAh)	Qs(mAh/g)	U(V)	$u_{99\%}$(Qs)
1	19.61	10.35	0.05638	0.01812	2.37	0.00001324117
2	31.10	10.75	0.09287	0.02984	2.63	0.00000272076
3	34.74	10.85	0.1047	0.03364	2.64	0.00001202356
4	32.10	10.91	0.09728	0.03126	2.76	0.00001110455
AVERAGE	29.39	10.715	0.08781	0.02822	2.6	0.00000977251
STANDARD DEVIATION	6.69674	0.25212	0.021514	0.006913	0.1643167673	0.000004781919663
MEDIAN	31.60	10.8	0.09507	0.03055	2.635	0.00001156405
ERROR MARGIN	7.565	0.25	0.024162	0.007764	0.135	0.000004651395657

Figure 15: Results for Battery 1's charge

For the sake of simplicity, the current was considered constant with respect to time, but in practice, we noticed that during charging, the current was decreasing at a slow rate as the charger's LED light was red whereas when it turned green, it experienced a sudden fall. As far as discharge is concerned, the current decreased steadily in time (Figure 16).

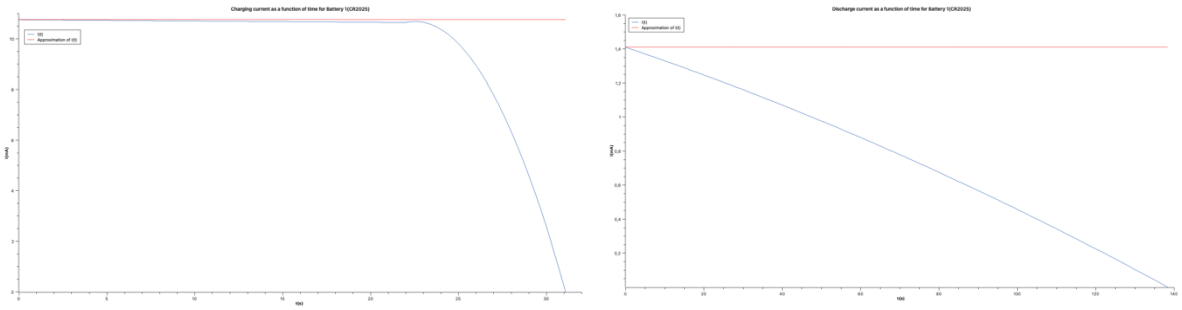


Figure 16: Charging and discharge current as a function of time for B_1

Given our experimental results values, we can notice that the standard deviation and the error margin are low compared to the actual values. Moreover, the mean and the median values are close enough to the values in the series (Figure 15).

The mean value for the specific capacity we get for battery 1 is: $\overline{Q_s} = 0{,}02822\, mAh.g^{-1}$ keeping four significant digits.

Following are several values for the charging capacity of commercial Li-ion batteries that could be found on the Internet:

- 285 mAh.g^{-1} according to Science Direct[3];
- 285 mAh.g^{-1} according to IOP Science[4];
- 286 mAh.g^{-1} according to OSTI[5];
- 290 mAh.g^{-1} according to International Journal of ELECTROCHEMICAL SCIENCE[6].

From there we can compute the mean of these 4 values and their standard deviation:

$$\overline{Q_s^*} = 286.5 \text{ mAh}.g^{-1}, \qquad \sigma(Q_s^*) = 2.380 \text{ mAh}.g^{-1}$$

We will consider the mean value for our calculations and compute the z-score in order to compare our experimental mean capacity value to the theoretical data we found on the Internet:

$$z(Q_s) = \left|\frac{\overline{Q_s} - \overline{Q_s^*}}{u(Q_s)}\right|$$

Knowing that $u(Q_s) = \overline{Q_s}\sqrt{(\frac{\partial Q_s}{\partial I}u(I))^2 + (\frac{\partial Q_s}{\partial m}u(m))^2 + (\frac{\partial Q_s}{\partial \tau_{charge}}u(\tau_{charge}))^2}$ and

Since $Q_s = \frac{I \cdot \tau_{charge}}{m}$, where m=3.112 g (measured on an electric scale)

Therefore, $u(Q_s) = \overline{Q_s}\sqrt{(\frac{u(I)}{I})^2 + (\frac{u(m)}{m})^2 + (\frac{u(\tau_{charge})}{\tau_{charge}})^2}$.

In order to have a confidence level of 99%, we multiply our uncertainty by a factor of 3:

$$u_{99\%}(Q_s) = 3\overline{Q_s} \cdot \sqrt{(\frac{u(I)}{I})^2 + (\frac{u(m)}{m})^2 + (\frac{u(\tau_{charge})}{\tau_{charge}})^2}$$

One could read on the electric scale that its tolerance is t= $\pm 1\, mg$. Thus, u(m)=$\frac{0.001g}{\sqrt{6}} = 0.4\, mg$.

Since we did not have any indication about the multimeter's tolerance and values of current were given with 2 digits after the comma, one can infer that:

u(I)=$\frac{0.01\, mA}{2} = 5\, \mu A$

Similarly, time was measured using the chronometer mode of one of us' watch for which we had no indication on the tolerance and its precision was to the hundredth of a second.

Hence, u(τ_{charge}) = $\frac{0.01\, s}{2} = 5\, ms$.

Then, we have several values for I and τ_{charge} so we will compute the uncertainty for each series of measurements and then consider the mean of uncertainties.

Using a spreadsheet software, we found $\overline{u_{99\%}(Q_s)} = 0.00001$ mAh.g^{-1} keeping one significant digit.

Then, z(Q_s)= $\left|\frac{0.02822-286.5}{0.00001}\right|$ =2.864 ·10^7.

Notice hence that z>>2. This means that our experimental value is far from theoretical capacity. This can be caused by several factors:

- Uncertainty related to the measurement instruments (e. g. scale, multimeter, …) ;
- Impurities on the used materials even after cleaning;
- Contacts with external matter;
- Insufficient time in the oven;
- Experimental errors during either the measures or the assembly.

We can also add the high value of the z-score is also caused by a very low uncertainty (which is actually a good sign since it translates a coherence in our measurements even when the uncertainty is enlarged).

Battery 2

j	τ_{charge}(s)	I(mA)	Q(mAh)	U(V)	$u_{99\%}$(Q)
1	40.74	9.72	0.11000	2.27	0.0000001697
2	24.18	9.87	0.06629	2.48	0.00000003363
3	28.40	9.30	0.0734	2.33	0.0000001126
4	21.26	10.34	0.06106	2.4	0.0000001127
AVERAGE	28.645	9.8075	0.07768	2.37	0.0000001071
STANDARD DEVIATION	8.5795	0.4292	0.02213	0.0906	0.0000000559
MEDIAN	26.29	9.795	0.06983	2.365	0.000000112
ERROR MARGIN	9.74	0.52	0.02447	0.105	0.0000000680

Figure 17: Results for Battery 2's charge

As can be observed in Figure 18, the current varied in almost a similar way to B_1, for both charge and discharge.

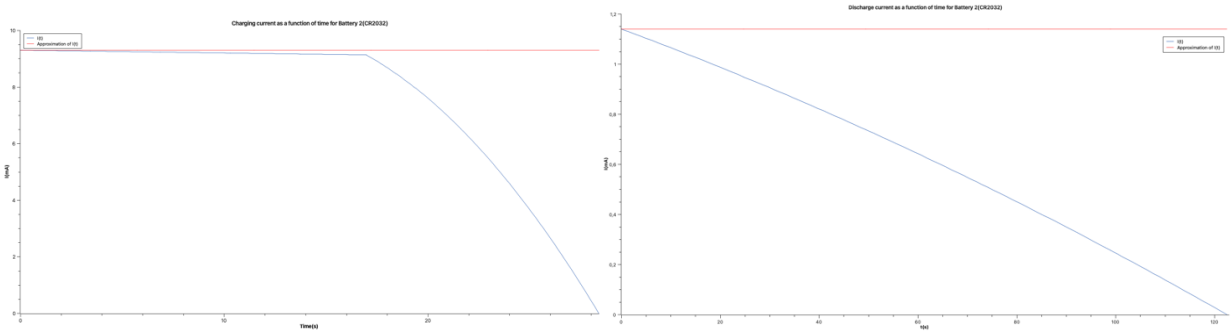


Figure 18: Charging and discharge current as a function of time for B_2

As for battery 1, the series of measures are not spread out which translates the cohesion of our values amongst each other (Figure 17).

The mean value for the capacity we get for battery 2 is: $\bar{Q} = 0.0777\, mAh$ keeping four significant digits.

This time, we are going to compare are average charging capacity (in mAh) to theoretical values we can find on the Internet (instead of the specific capacity) for CR2032-type commercial batteries:

- Energizer[7]: 235 mAh;
- Chinese CR2032 on Stack Exchange[8]: 220 mAh;
- According to Arrow[9]: 225 mAh;
- According to Farnell[10]: 210 mAh.

From there we can compute the mean of these 4 values and their standard deviation:

$$\overline{Q^*} = 225.5 \text{ mAh}, \sigma(Q^*) = 9.014 \text{ mAh}$$

Once again, we will compute the z-score to compare our values to the theoretical capacity we found on the Internet:

$$z(Q) = \left| \frac{\overline{Q^*} - \bar{Q}}{u(Q)} \right|$$

Knowing that $u(Q) = \bar{Q}\sqrt{(\frac{\partial Q}{\partial I}u(I))^2 + (\frac{\partial Q}{\partial \tau_{charge}}u(\tau_{charge}))^2}$ and

Since $Q = I \cdot \tau_{charge}$

Therefore, $u(Q) = \bar{Q}\sqrt{(\frac{u(I)}{I})^2 + (\frac{u(\tau_{charge})}{\tau_{charge}})^2}$.

In order to have a confidence level of 99%, we multiply our uncertainty by a factor of 3 as well:

$$u_{99\%}(Q) = 3\bar{Q} \cdot \sqrt{(\frac{u(I)}{I})^2 + (\frac{u(\tau_{charge})}{\tau_{charge}})^2}$$

u(I) and u(τ_{charge}) are the same as for battery 1 since same instruments were used.

Using a spreadsheet software, we found $\overline{u_{99\%}(Q)} = 0.0000001$ mAh keeping one significant digit.

Then, z(Q)= $\left|\frac{0.07768-225.5}{0.0000001}\right|$ = 2.254·10^9.

Notice hence again that z>>2. This means that our experimental value is far from theoretical capacity. This can be caused by the same factors mentioned for battery 1.

Comparison between B_1 and B_2

Battery 1

i	Q(mAh)	Q'(mAh)	γ_1
1	0.05638	0.05421	96.16%
2	0.09287	0.07024	75.63%
3	0.10470	0.05739	54.81%
4	0.09728	0.05420	55.71%

Battery 2

j	Q(mAh)	Q'(mAh)	γ_2
1	0.06106	0.04583	75.04%
2	0.06629	0.03878	58.50%
3	0.07337	0.04207	57.34%
4	0.11000	0.04725	42.95%

Figure 19: Comparison of Coulombic efficiency for both batteries

Looking to our table sheets and to Figure 19, we notice that our mean coulombic efficiency for B_1 is $\overline{\gamma_1} = 70.58\%$ and for B_2 it is equal to $\overline{\gamma_2} = 58.46\%$.

Hence, B_2 does not perform as efficiently as B_1 does. We could expect that result since we used more water to build battery 2's anode which explains the decrease in Coulombic efficiency.

Conclusion and afterthoughts

During the cycles, after fully charging the battery, taking it out from the USB charger and then putting it there once again, what we noticed was that the charger's LED light turned red, indicating that the battery discharged in the meantime.

This apparently strange phenomenon could be related to the side reactions occurring inside the battery, affecting its performance, the yield of the reactions generating the energy decreasing.

Apart from that, one could argue that the electrodes should have stayed longer in the oven in order to lose all the water, since any traces of water in the battery cause significant drops in its performance. In addition, as the number of cycles increased, the efficiency decreased, because such a battery cannot be run infinite times.

Since B_1 performed better than B_2, as it could be observed in the previous section, one can be more cautious while preparing the electrodes, in that carefulness is required when measuring the quantities of each substance added in the mixture. Thus, for the second battery, the anode material had more water, whereas for the first battery, more graphite was added to compensate for the water surplus, which might explain the difference in results.

The instruments used, such as the spatulas and the pipettes, were checked beforehand to be clean in order to prevent any impurity from reaching the sample. Moreover, in order to avoid external contact, all the samples were kept on a tissue, to ensure the proper conditions for fabricating the electodes.

However, the gloves should have been changed more frequently, as that might have had a negative influence on the performance.

Is there any better alternative to a Lithium-Ion Battery?

In the current evolution of batteries, the most promising long-term solution seems to be the rechargeable lightweight Lithium-Ion Battery. Such batteries also hold a promise for the storage of electricity from solar cells. Their weight is 1/3 of a lead-acid battery, yet they can pack more energy and have a much longer lifetime. In Figure 20, one can observe how different common batteries compare to one another when it comes to their specific energy density per unit volume and per unit mass.

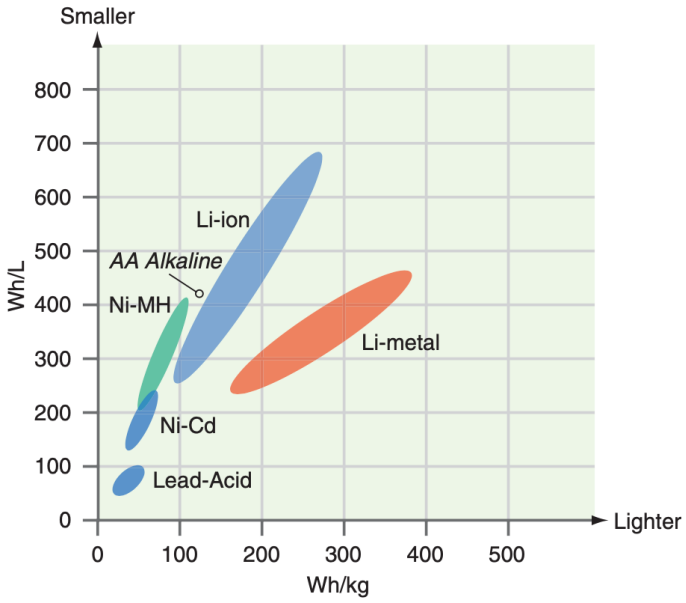


Figure 20: A number of different batteries are classified with their specific energy density per unit volume and per unit mass[11]

It can be observed that Lithium-Ion Batteries have a high energy density per unit volume and a high energy density per unit mass, explaining why such batteries have such a wide range of usage, from cellphones to electric vehicles.

On the other hand, there exist opposing voices, since several problems regarding lithium extraction appeared. More than half of lithium is gathered using brine extraction from deep inside the earth, especially in South America, and the rest is still mined traditionally from rock. Both methods have caused environmental damage to areas around lithium processing operations. What is more, once Lithium-Ion Batteries are used up in electronics, they are often disposed of improperly by consumers.

Yet, there is no denying that Lithium-Ion Batteries represent a force for good, changing our lives for the better.

In the end, this experiment gave us the opportunity to develop essential practical skills and understand what research work entails, raising our interest in chemistry, especially as far as galvanic cells are concerned given the rising integration of technology in virtually every aspect of our lives.

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