The reproducibility of coin cell data for NMC111, LFP and Sa1520

Iaroslav Kovalchuk
ikovalch@umich.edu

October 18, 2022

Abstract

Our research team focuses on the end of the life behavior of lithium-ion batteries. Using nine coin cell batteries that were produced in at the University of Michigan Battery Lab, we hope to improve models that would accurately estimate battery's life expectancy. In this paper, I will be focusing on reproducibility of data as we run more and more experiments on the fresh coin cells. Three of the cells are produced using NMC111, 3 use LFP and 3 contain graphite. We charge and discharge them numerous times and get the voltage vs time and current vs time graphs. We generally used 3 programs: Preconditioning charged and discharged the battery 3 times, HPPC(Hybrid Pulse Power Characterization) applies pulses of current. Using parsers to extract the exact data we need, we plotyed the a resistance vs time graph. Afterward, we could research the correspondence of resistance and the number of cycles.

1 Introduction

Nowadays lithium-ion batteries play essential roles in almost any aspect of our lives. Most electronic gadgets run on these batteries and a deep understanding of them would allow engineers to optimize the technology and improve all of the gadgets at once. A few important metrics that every battery has include capacity, resistance, optimal voltage, and gravimetric energy density of the materials Reproducibility of such metrics is an extremely important question for our study since objective comparison of results for different materials is only possible if all other factors were held constant.

Numerous researches are conducted all around the globe. Questions include the difference between coin cells, and pouch cells, characterization of newly formed batteries, the impact of the formation protocol on the lifetime and capacity of the cell, the increase of battery's performance, protocols for lithium-ion cells production, and characteristics that matter the most. More research is done with different non-lithium materials and some teams focus on the variety of protocols that help conduct more knowledge about the cells.

Measurements on full lithium-ion batteries would give signals from both the cathode and anode, making it difficult to separate the effect from each electrode. In order to separate the materials, we created special coin cell batteries. Coin cells were produced using NMC111, LFP, or graphite as a working electrode and lithium metal as a counter electrode. These special coin cells would allow us to separate cathode and anode characteristics and have two sets of values for each part of the battery. In addition, it allows to compare different materials within the same conditions.

The usage of pure lithium in coin cells has some disadvantages. Firstly, lithium has a relatively low Coulombic efficiency. Because of the reactivity of lithium, unwanted reactions are more likely to appear within the cell. It means that such batteries would have a shorter life cycle and more unstable overall behavior. Secondly, lithium metal is expected to have dendritic growth. To begin, it is possible for the growing branches to simply break which would make them electrochemically isolated. In addition, such a case would expose some of the pure lithium without SEI on the surface. This would increase the chances to have an unwanted reaction between unprotected lithium and electrolyte. Moreover, if there would be no break in the branch, there is a possibility of it reaching the working electrode which would lead to a short circuit and instant discharge that would create a lot of excess heat. Lastly, pure lithium contracts and expands as lithium ions enter and leave the material. So surface area of lithium

in the charged and discharged batteries is different exposing a new lithium surface without the formed SEI on it.

The first few charging and discharging cycles are really important for the battery and even are key for the battery's life expectancy. In addition, the more battery is used the more the cathode and anode would expand and contract. It lets liquid electrolyte insert deeper into the material, therefore, increasing the surface between cathode/anode and electrolyte. It would increase the overall capacity of the coin cell. It is important since if such a process occurs, it would be hard to compare the results between an older and a younger battery since even though the material might still be the same, their characteristics are slightly different.

2 Experimental

The coin cells were built and characterized at the University of Michigan battery lab. The cell consists of a stainless steel top with a donut-like spring between it and an aluminum spacer. Then the counter electrode which is a shim of lithium metal is added. It is about 16mm in diameter and 750 µm thick. Then comes the polymeric separator with the ability to let lithium ions pass, but not the electrons. It is 19mm in diameter and is soaked in electrolyte on both sides. Then the working electrode is placed: either NMC111, LFP, or graphite. The active material is about 14mm in diameter, 60 µm thick and is coated on the aluminum foil. Both aluminum and copper current collectors collect electrons from the working and counter electrodes. Calculated theoretical capacities for the NMC111, LFP, and graphite cells were 2.0, 2.9, and 4.6 mAh, respectively.

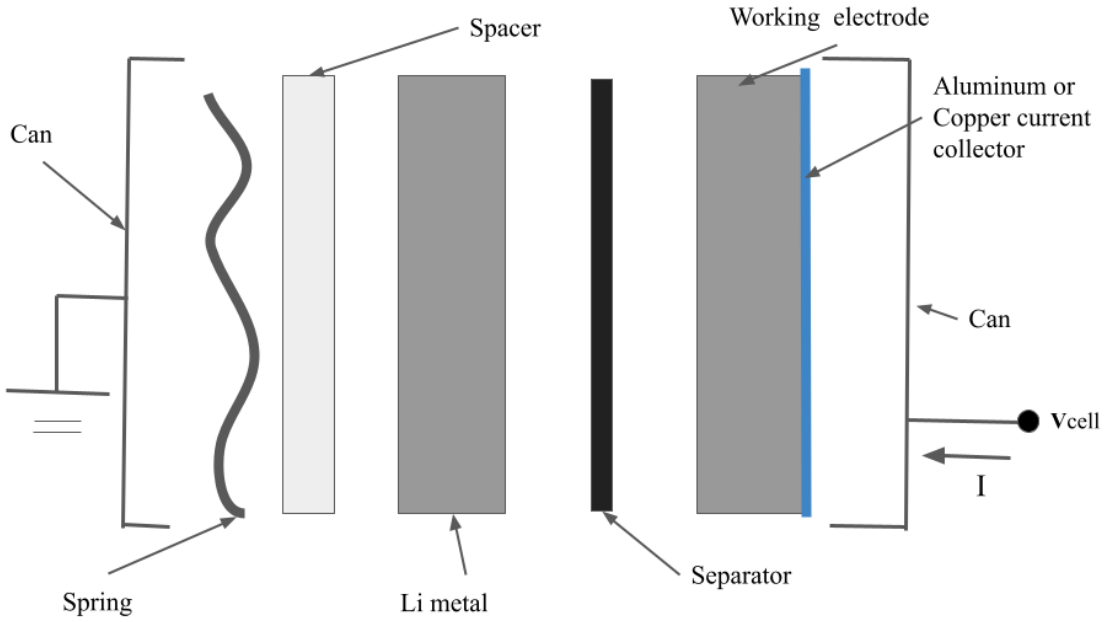

Figure 1: Figure 1 demonstrates the structure of the coin cell batteries that were built.

Using Biologic potentiostat, we were running two different tests on these batteries:

The first test was a preconditioning protocol. It consisted of the 3 cycles in which the battery is being charged and discharged at the C/5 rate. That test helped us measure the capacities of each coin cell and form SEI.

The second protocol is Hybrid Pulse Power Characterization (HPPC). In this program, we charge the battery and then gradually discharge it. What is interesting about it is that there are current drops to C/5 discharge for 10 seconds. It leads to the voltage dropping down faster in a parabolic shape. As the current drop ends voltage curve comes back to the smoother discharge curve. During such a drop we are able to measure the resistance of the cell by dividing the difference in voltage at the first and the last moments of the drop by the current applied.

Lastly, it is important to note that since the last 3 cells are made with graphite the definition of charging 'flipped' since graphite still plays the role of the working electrode in our cell batteries, however in full cells we consider it a counter electrode.

Cell #	Material in Cell	Voltage (V)	Capacity (mAh)	Type of Holder	Channel	PreCondition	HPPC	C-50
1	NMC111	1.784	1.94		2	1	1	
2	NMC111	2.078	1.99	A	2	2	3	1
3	NMC111	2.010	2.02	B	4	2		
4	LFP	3.029	2.93	A	4	1		
5	LFP	2.871	2.96		4	3		
6	LFP	3.029	2.77		4	2	2	3
7	Sa1520	2.820	4.66	A	7	4	2	3
8	Sa1520	2.980	4.49		8	2	1	2
9	Sa1520	2.984	4.59			1		

Figure 2: Figure 2 demonstrates the log of the tests we ran on each of 9 batteries and their recorded characteristics like material, voltage and capacity. The numbers in the last rows indicate number of tests ran.

3 Results

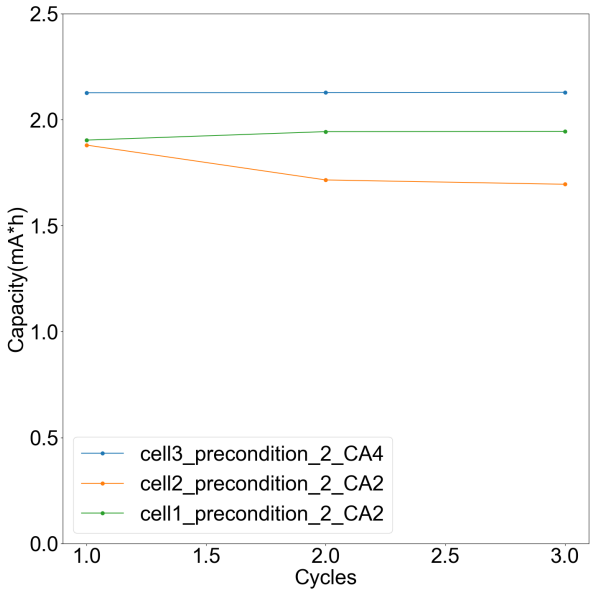

Figure 3: Cell-to-cell variability with NMC111 during preconditioning. Figure 3 compares the same material(NMC111) and the same Preconditioning program(2). The 3 cells run shows the greatest difference in capacity of 0.4 mAh. The capacity is unstable.

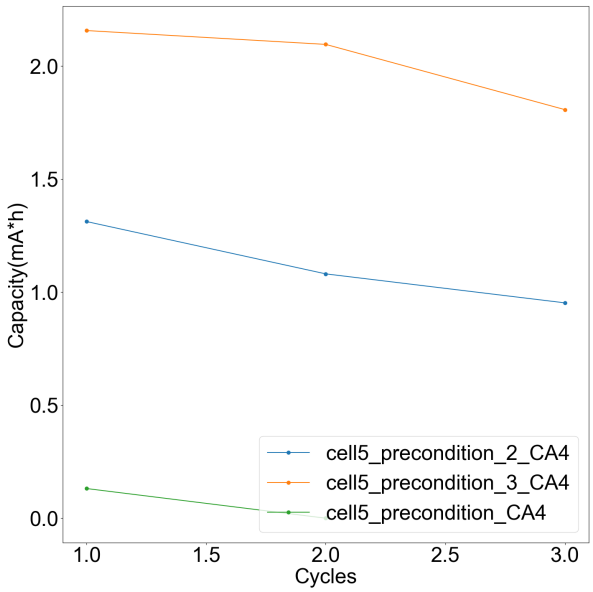

Figure 4: Capacity vs Cycles. Figure 4 compares the same LFP cell along 3 Preconditioning protocols. Data suits our hypothesis and we can see how the capacity of the coin cell 5 increases as we continue to run programs. The 3 cells run shows the greatest difference in capacity of 0.6 mAh. The capacity is unstable.

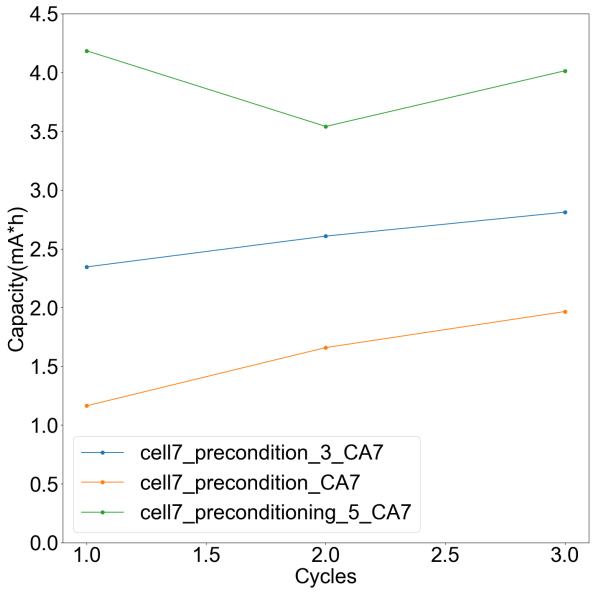

Figure 5: Capacity vs Cycles. Figure 5 compares the same graphite cell along 3 Preconditioning protocols. The 3 cells run shows the greatest difference in capacity of 3 mAh between the first and last Preconditioning programs. The capacity is incredibly unstable.

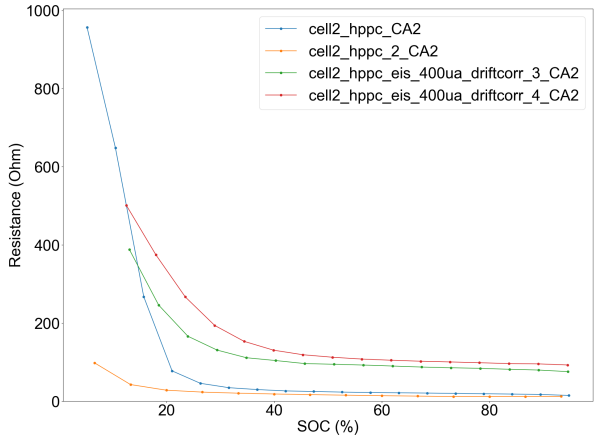

Figure 6: Resistance vs SOC for the same NMC111 cell along 4 HPPC protocols. Overall trend shows that resistance increases as more test are run, but the shape of resistance curve is consistent.

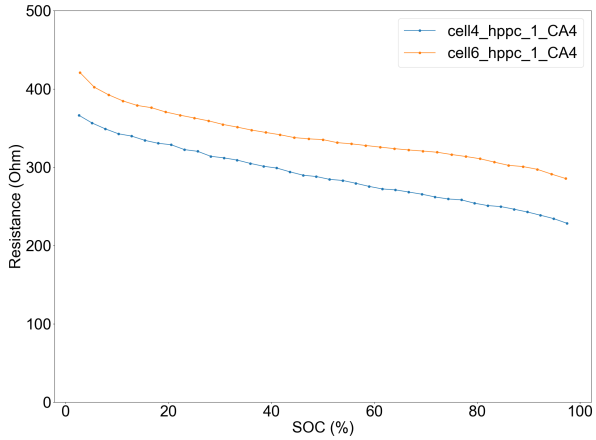

Figure 7: Resistance vs SOC. Figure 7 compares different LFP cells along the same first HPPC protocol. Some variation is present, but overall graphs are very consistent.

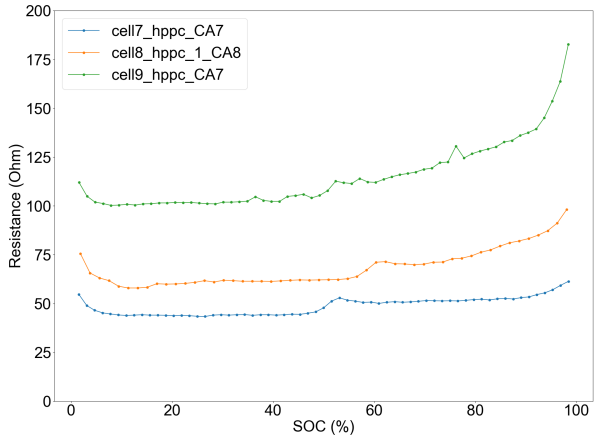

Figure 8: Resistance vs SOC. Figure 8 compares different graphite cells along the same first HPPC protocol. Cell 9 shows some deviation from the expected curve however overall shape is still consistent and the trend is clear.

4 Discussion

During the first few cycles, the Solid Electrolyte Interphase is formed and the proper coating of both anode and cathode could prolong the life of the battery greatly by excluding all of the unwanted reactions between electrolyte and electrodes. It is formed with certain reactions between electrode and electrolyte. In the short run, it is expected that the capacity decreases a little bit as some of the electrode material is used during the reaction. On the other side, in the long run, it is expected to see the absence of changes in the cell's capacity. However, our results indicate the fact that there are changes in the cells' capacity. In particular, every cell showed an increase in capacity as more and more protocols are being run. However only graphite showed the increase in capacity within one protocol.

There are multiple reasons for both increases and decreases in capacity. Firstly, graphite is an extremely porous material that has a lot of layers. Considering the fact that during the charging and discharging process materials expand and contract, it seems reasonable to assume that liquid electrolyte gets a chance to enter deeper and deeper inside the working electrode increasing the surface area and therefore the capacity of the coin cell. Secondly, for all cells the counter electrode was lithium, and lithium is known to expand and contract greater than other materials therefore it is one of the reasons for all three types of cells to demonstrate the increase in the capacity as more and more protocols were run.

In addition, we can see that the capacities of the coin cells with graphite are way greater compared to the capacities of NMC111 and LFP. It is the case due to the higher theoretic capacity of the material:372 mAh/g compared to 160 mAh/g for NMC111 and 170mAh/g for LFP. Graphite has an exceptional energy density due to its structure: it can place a lot of Lithium-ion between its layers.

Overall, a quite big variation of capacities can be observed from the same types of cells. Another possible reason for that can be the slight misalignment between working and counter electrodes. Our cells are created by humans which increases the chance of misalignment between the cathode and anode. Even a slight deviation in the electrode's position can decrease the surface area between the counter electrode and working electrode and lead to the lack of electrolyte on a part of the electrode shim and therefore create that part electrochemically isolated.

Furthermore, The resistance graphs predominantly show higher resistance at lower SOCs and lowest resistance towards the 100%. It can be interfered that it is harder for cathodes to give out lithium while all of it is stored in the cathode. As some of the lithium ions leave the working electrode, after 40% SOC, NMC111 seems to hit an asymptote and the resistance does not change. In comparison, LFP displays a much smoother change in resistance over the whole discharge process. Only for graphite, the trend is opposite, so for our example of the anode, it is easy for graphite to give our lithium ions when there is a lot of it. In the end, however, we can see an increasing resistance trend so it is hard to transfer the last bits of lithium-ion to the counter electrode.

5 Conclusions

While a lot of research is conducted on batteries and coin cells, specifically. The reproducibility of such data is rarely investigated. By testing 9 coin cells with 3 different materials, our team was able to record valuable data. Using the preconditioning protocol we had a chance to compare and contrast the capacities of coin cells and with HPPC protocol, resistance data was extracted. This data shows that capacities vary a lot and it seems reasonable to say that batteries' capacity improves as we run more and more protocols. On the other hand, resistance graphs were more consistent and with even small deviation, each material had its own shape that was consistent no matter throughout all the test.

Certainly, it is clear that careful management is necessary while working with coin cells: the data can be reasonably compared only if exactly the same sequence of protocols was run on the cell and if researchers keep track of the time. Due to the usage of the more unstable lithium, the cells are more unstable and the data can variate greatly

In the future, our team plans to implement electrochemical impedance spectroscopy to dive deeper in the processes of the coin cells. That way we would be able to point out specific processes that affect our batteries and possibly change the way we assemble them, in order to get more stable results.

References