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Design and Testing of Flexible Lithium-Ion Batteries

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Abstract

The goal of this disquisition is to delineate the development of a material and casing suitable for flexible lithium-ion rechargeable batteries. Development of these cells is driven by increasing interest in portable and flexible electronics. The goal is to implement them into items such as smart cards, wearable electronics, novelty packages, flexible displays, and transdermal drug delivery patches. To accomplish this task, several individual cathode compounds were explored that used different compositions of lithium cobalt oxide and other compounds. These cells were tested in a generic and easily manufactural cell casing. After the catholyte compound testing was completed the best compounds were cycled numerous times to determine the degradation of the cells energy capacity. From our testing, it was determined that the best composition in terms of achieving the closet to theoretical capacity consistent of:

- Lithium oxide
- Conductive additive
- Lithium salt electrolyte

However, after cycling this composition, severe degradation of its energy capacity was observed after only twelve cycles, with complete loss of capacity occurring at only 30 cycles. Thus, we concluded that the concept of the flexible material tested does have merit; however, in future work, the severe degradation issue must be addressed.

Introduction

Prior to beginning work on developing the cathode and casing design for the flexible lithium ion cells, the general history and theory surrounding lithium ion technology and batteries was explored.

Battery Basics

A functioning battery has eight key requirements:

1. High Specific Energy
2. High Specific Power
3. Affordable Price
4. Long life
5. Safety
6. Wide Operating Range
7. Low Toxicity
8. Fast Charging

Together, these critical aspects describe what is known as the "Octagon Battery." A useful octagon battery must possess these parameters in a balanced manner; however, it is impossible to satisfy all criteria. There will be trade-offs. For instance, one can achieve extremely high specific energy with some battery technologies, but they are prohibitively expensive, sometimes even dangerous to use. Alternatively, one could have a battery that lasts a long time with low self-discharge and many cycles to failure; however, it would have a lower power output relative to other cells. These features must be balanced to achieve commercial success and efficiently perform the task that they are given. Current lithium-ion technology fulfills all the critical requirements of the octagon battery. [1]

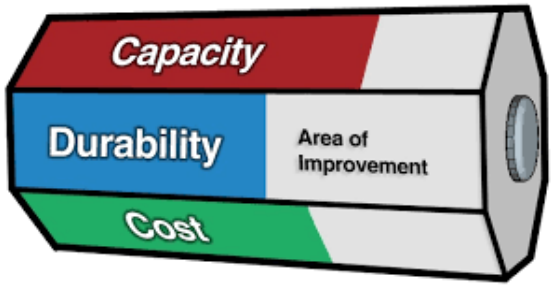


Figure 1: Visual Depiction of Octagon Battery Concept [1]

Lithium cells have high specific energy, they can deliver high current loads for extended periods. Specific energy is a measure used to define the capacity of a cell in weight, usually displayed in ampere-hours per kilogram (Ah/kg). Lithium ion cells are also capable of outputting high specific power, although at the detriment of specific energy. This reflects the loading capability of a cell: the amount of current a battery can deliver, usually displayed in watts per kilogram (W/kg). Together with specific energy, these two measures allow one to paint a picture of the performance of a battery. One could say that specific energy is akin to the size of a container while specific power is the size of the containers opening. [3]

There are three additional quantities of note for batteries: capacity measured in ampere-hours, cell nominal voltage, and C-rate. While capacity is measured using specific energy, it is more useful to rate it in terms of ampere-hours for a set type of cell. [3]

Cell voltage is usually reported nominally as an average between the max charging voltage and end of discharge voltage. The voltage behavior of a cell is influenced by several factors: current load, internal resistance, rate of charge or discharge, and temperature all play a role. Voltage curves are also utilized to determine the viability of a battery chemistry.

The desire is to have a gradually decreasing voltage within the usable discharge range of a battery. [7]

C-rate is a measure of the speed at which a cell can charge or discharge. A high C-rate corresponds to a quick charge/discharge time, while a low C-rate is equivalent to a long charge/discharge time. Typically, batteries are rated at 1C, meaning a one ampere-hour rated cell should be able to provide one amp for one hour. C-rate is also important for battery testing as a battery analyzer will discharge a fully charged cell. [6]

Batteries are typically composed of several building blocks that serve as its basic structure. These are the anode, cathode, electrolyte and separator. The anode acts as the electrode which releases electrons during a discharge cycle and is always considered to have negative potential. This is because a battery intakes and stores energy while also being able to release that energy. Thus, the designation does not change when charging or discharging. The focus of our examination, the cathode, is the electrode that absorbs. For cells to have proper operation, a permeable boundary layer is added between the anode and cathode. It allows lithium ions to flow through the battery while preventing the metallic components from touching and thereby shorting the cell. This ion flow is facilitated by the addition of an electrolyte, a solution which acts as an activator for the transfer of ions between the anode and cathode. [2]

Lithium Ion Theory

The general structure of a lithium-ion cells is delineated in the following table. [2]

Table 1: General makeup of a Lithium-ion cell during charge and discharge cycles [3]

	Cathode (copper foil)	Anode (aluminum foil)	Electrolyte
Material	Metal oxides derived from cobalt, nickel, manganese, iron, or aluminum	Generally Carbon based	Lithium salt in an organic solvent
Full Charge	Metal oxide with intercalation structure	Lithium Ions migrated to anode	
Discharge	Lithium ions move back to cathode	Mainly carbon	

Lithium ion batteries function on the principle of oxidation or reduction reactions where electrons are transferred between two different species. [5] This transfer, as stated earlier, is enabled by ion flow through the separator layer between the anode and cathode layer. In the case of lithium ion cells the reaction is written as:

$$Li^{+} + e^{-}\ LiCo_2 = Li_2O + CoO$$

This reaction can go either way, making the cells rechargeable. [4] The following figure provides a visual depiction of this process:

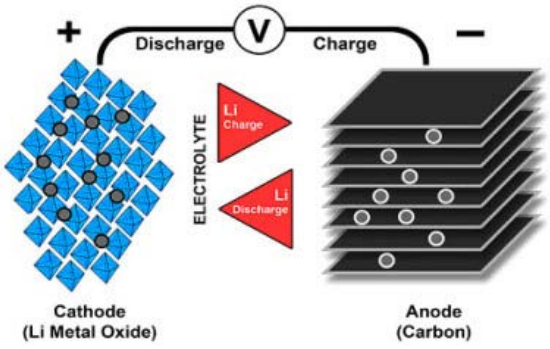


Figure 2: Depiction of Ion transport occurring in Lithium-ion batteries [1]

Regarding the principles of the octagon battery, lithium ion technology excels in several areas:

- Highest specific energy of all commercial battery chemistries [8]
- No memory effect [8]
- Environmentally friendly due to lithium's recyclability [8]
- Long life with proper care and extended shelf-life while being maintenance free [9]
- Low internal resistance allowing for high voltage outputs [9]
- Reasonably short charge times compared with other chemistries [9]
- Low self-discharge [9]

However, there are several limitations or trade-offs that come with this stellar performance:

- Deep discharging reduces life [8]
- Protection circuit needed to avert cell explosion (boom) from thermal runaway [9]
- Degrades when left in high temperatures or high voltages for extended periods [9]
- Transportation of large quantities regulated due to safety concerns [9]

Though lithium ion batteries do possess potentially dangerous flaws (as evidenced recently by some of the product fires of Samsung phones), their superior engineering functions still makes them the best base currently on market for flexible battery technology.

Design

In the more common, non-flexible lithium-ion batteries, the cathode and anode layers, along with the various other components needed to make a battery, are loaded into a rigid metal casing. One variant, referred to as the "Cylindrical Lithium-Ion Battery," is displayed below [10]:

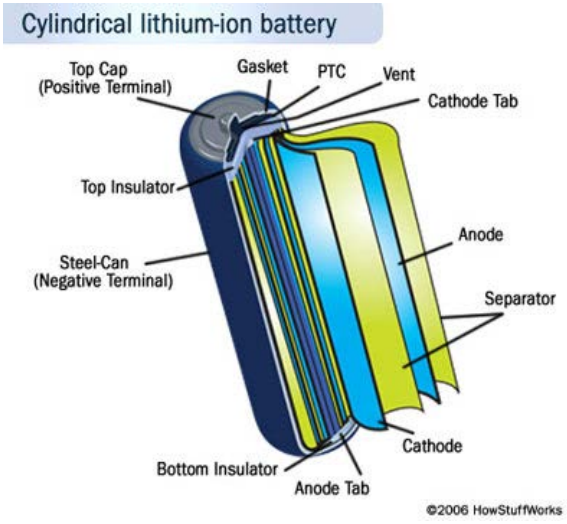


Figure 3: Cylindrical Lithium-Ion Battery [10]

Though these batteries do function well, satisfying the eight conditions of the octagon battery, certain niche applications require batteries of a different sort. Malleable electronics, for example, cannot work without often bulky, separate power sources, making them impractical on the mass market. Wearable consumer products are a great example of this

technology, ranging from on-body health monitors to flexible smartphones and more. It's easy to see how inconvenient batteries lacking flexibility are with these kinds of products.

Unlike rigid lithium-ion batteries, the main type of flexible battery uses binds its lithium oxide cathode components with a polymer to make it solid. Though this produces a battery that is both flexible and safe (since it does not use volatile liquid electrolytes), it possesses several critical flaws inherent to its design.

For one, the capacity of these batteries are limited by the size of the cathode and anode layers. This may sound trivial, but consider the cylindrical battery described earlier: in that cell design, if one wanted to increase the capacity of the battery, they would simply add extra anode and cathode layers; only a nominally larger diameter casing would be necessary to accommodate them. Since thin film batteries cannot be made significantly thicker without sacrificing flexibility, either their outer dimensions need to be expanded -increasing the size and decreasing amount of applications they can be used in- or the materials inside the casing must be improved (a slow, difficult research process). Secondly, lithium ions diffuse more slowly through solid electrolytes than through liquid ones, further limiting the potential capacity growth of thin film batteries [12].

These shortcomings are what motivated the exploration of the new flexible battery type described in this paper. Rather than base the cell on a solid, polymer bound electrolyte-Lithium oxide layer, a fine lithium based powder was dissolved in a liquid electrolyte solution.

This change eliminates the primary issues present in current bendable battery technology. Battery capacity is no longer only dependent on size; rather, only more dissolved compound needs to be added to the cell to increase its capacity. The lithium-ion flow issue associated with the solid cathode layer is also eliminated since this cell uses a liquid electrolyte solution.

Unfortunately, for reasons of confidentiality, little more can be said about the battery design. However, the rest of this paper will explore the results achieved from the testing of this new flexible cell type.

Method

The construction of this battery is much like that of a sandwich. First, the bottom layer of the casing was placed on a flat surface, followed by the addition of the first current collector, separator, and second current collector components. Finally, the top half of the casing was added and connected to the rest of the layers with a heat seaming device. One side was left open so that the active material, anode, and electrolyte could be added in a controlled, non-reactive environment.

Once constructed, the batteries were tested using the Alternative Energy Lab's Battery Analyzer. This system slowly charged (using a conservative C-rate) and then discharged the battery, principally monitoring voltage across the battery and current flow through the battery. The data returned from these tests were used to generate the various plots shown in the results section below.

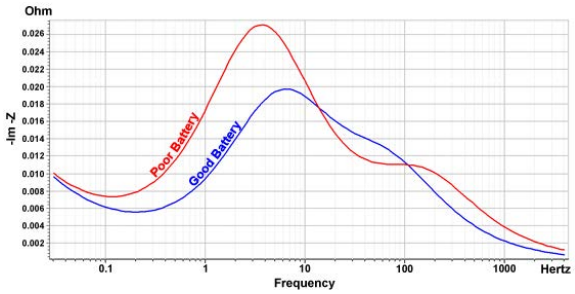
The determination of whether a battery could be labelled "functional" was based on the charge/discharge plots generated by the testing apparatus. Two primary criteria had to be satisfied: stability and magnitude.

For example: properly working batteries do not charge nor discharge instantly. It is a process which takes not insubstantial amounts of time to complete (sometimes on the order of days), and no unusual jumps in the

charge/discharge profiles should appear during testing. Figure four, shown in the appendix, highlights this point. These curves describe the function of a good battery, in the case of the former, and a failed battery, in the case of the latter. Note the rapid discharge in the graph of the bad cell: this is not just an undesirable result, but one which indicates something fundamentally wrong with the battery.

Magnitude, the second criteria, corresponds to what kind of capacity the batteries have. Some cells made throughout this project had charge and discharge curves that indicated they were functional; however, many in this group had trivial capacities, not infrequently multiple orders of magnitude lower than those described in the results section, qualifying them as failures.

A second method by which to determine a battery's quality is to relate the frequency of the battery to its impedance. Lithium ion batteries, flexible included, are dependent on the ability of electrons to flow through the system. Old, damaged, or otherwise used batteries have decreased capacities, and this change can be noted in monitored in plots like the one below [11]:



Though this method was not used for our tests, it is another possible way of testing batteries, particularly since it is well suited to faster testing times.

Originally, seventeen compositions were considered for this battery. Early testing indicated that one composition was particularly promising, referred to as composition three. It appeared to produce the smoothest, most realistic charge/discharge curves, as well as the highest magnitude capacities. Though it is possible that other compositions potentially had even better performance, time constraints prevented complete testing of the entire set of compositions. Fortunately, the changes between the various compounds were mostly in terms of the relative quantity of each component; the lithium oxide base quantity was not changed, only the additives used to make it function better. Of all those tested, composition three appeared to have the best balance of properties.

Results

Based on the experimental results, it was determined that the most viable composition is number three. A summation of the results obtained for the best battery of our chosen composition is shown in the table below.

Table 2: Summation of results for best battery of chosen composition from one cycle

Theoretical capacity	76.05 mAh
Discharge Capacity Percent of Theoretical Capacity	25.9%
Specific Discharge Capacity	25.9 Ah/kg
Specific Discharge Capacity Percent of Specific Charge capacity	32.78%

Figure 6, located in the appendix, displays a comparison of the specific discharge energy versus test apparatus cycle count. While all the composition's energy storage potential decayed rapidly, composition three had the best

initial specific discharge energy, prompting testing to focus on it.

To accomplish this, a test cell was run for 100 cycles with the intent of studying its capacity degradation. The results of this are shown in figure 7, located in the appendix. From the graph, there appears to be a design fault somewhere since cell degradation occurs rapidly, with the test cell losing more than 70% of its initial discharge capacity in only 10 cycles. This is an unacceptable rate of degradation for a functional battery and raises some concerns as to why this may be occurring. This is a problem that was systemic throughout our testing procedure, as only 5 of the 70 or more experimental cells manufactured were deemed satisfactory.

To correct this, we tried several different cell casing styles, as well as procedural changes; however, none seemed to yield promising results. It is believed that there were systemic issues in the procedure of manufacturing a cell that lead to its failure and that even if a cell was completed without damaging it, the method of heat seaming was not effective at creating an airtight seal. It was dolly noted that many of the cells would leak while being tested. Thus, upon cycling of the battery the internal compounds would breakdown due to their interaction with the air. A further issue noted during the construction and was that the anode used was exhibiting corrosion. It is believed this oxidation lead to the numerous failures of test cells. The oxide layer inhibited ion flow, thus causing charge and discharge cycles to be at best sporadic and at worst impossible.

Conclusions and Recommendations

We concede that the final results appear underwhelming. However, most of the battery limitations can be attributed not to failure of the concept itself, but rather to process restrictions imposed by other limitations. While we experienced numerous issues in our testing due to experimental complications, the fact that even a few cells show promise indicates that the powder based cell concept is viable. With initial testing and refinement, it is believed that the preferential properties of our concept could be refined into a cell capable of outperforming current thin-film offerings. While the results presented previously do not indicate this battery is ready for manufacture, they do little to discourage further research into this battery type; rather, they encourage it.

Our test results indicate that our chosen composition has the potential to perform at a significant percentage of its theoretical capacity even with its process limitations- thereby validating the objective of this project: to demonstrate the viability of dissolved powder cathodes in flexible battery applications. Ion transfer functioned properly, although inconsistently, and with careful material control and new case designs, we believe that the issues our group experienced could be easily mitigated.

Thus, we propose a few changes to the cell manufacturing process, as well as a case redesign that reduces the chance of air contamination and adds several interesting features.

First the manufacturing issues. The largest problem with process during this project related to poor material handling. Open air is a non-ideal environment in which to handle highly reactive materials, but we were afforded with

little choice due to the difficulty of preparing the cathode in the argon chamber. Further, the chamber appeared to have been contaminated with air and water vapor, a problem only discovered once various parts began to oxidize inside the chamber. Since anode oxidation appeared to be one of the biggest causes of battery failure, this was a major issue which, without better filtering and monitoring systems, was hard to correct.

In addition, cross-contamination of compounds and other materials likely occurred throughout the battery construction process. Most, if not all of it, was completed by hand, and it was a challenge to precisely and consistently produce compounds and casings to fit the design specifications.

A last problem was related to the heat generated during various steps of the manufacturing process. The electrolyte used to facilitate ion transfer was extremely volatile, and it appears a not insignificant amount was lost in many batteries.

Most of these issues could be easily eliminated in a more well equipped lab. A larger argon chamber would have allowed for better material management, and better storage containers would have reduced the potential for cross contamination. The heat problem was addressed in the design the new casing, a description of which follows.

Rather than use additional aluminum layers as the case, a thin adhesive layer would be added to both the aluminum and copper battery layers, allowing them to function as both current collectors and protective casings. The image shown at the end of this section is a digital rendering of this new casing design:

As stated above, this has numerous benefits. For one, this eliminates the need for heat seaming the outer edges of the casing, a large source of error in the case design due to both air leakage from poor seams and the resulting electrolyte evaporation and escape. Secondly, it reduces the number of components required to produce a complete cell, making both cheaper and easier to produce.

Finally, it gives the batteries an interesting additional property: series stacking. Since the copper and aluminum function as both current collectors and casings, additional capacity can be achieved by simply layering cells on top of one another. Though this is not a property exclusive to bendable batteries, it still provides consumers with additional design flexibility.

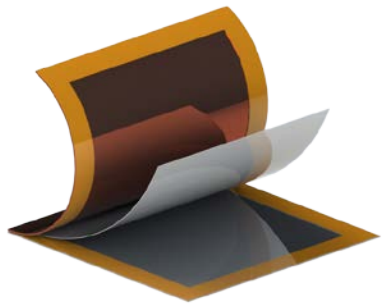


Figure 5: New cell casing concept with revealed layers

This cell design, though presently flawed, has the potential to not just become a functional battery, but a product superior in performance and functionality to those currently commercially available. Implementation of some of the suggested design changes, in addition to further refinement of the battery materials, will likely result in significant performance advantage over what current testing shows possible. The work completed over the duration of this project provides the base for such further development and the eventual commercialization of the final product.

Acknowledgements

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Appendix

Figures and Tables

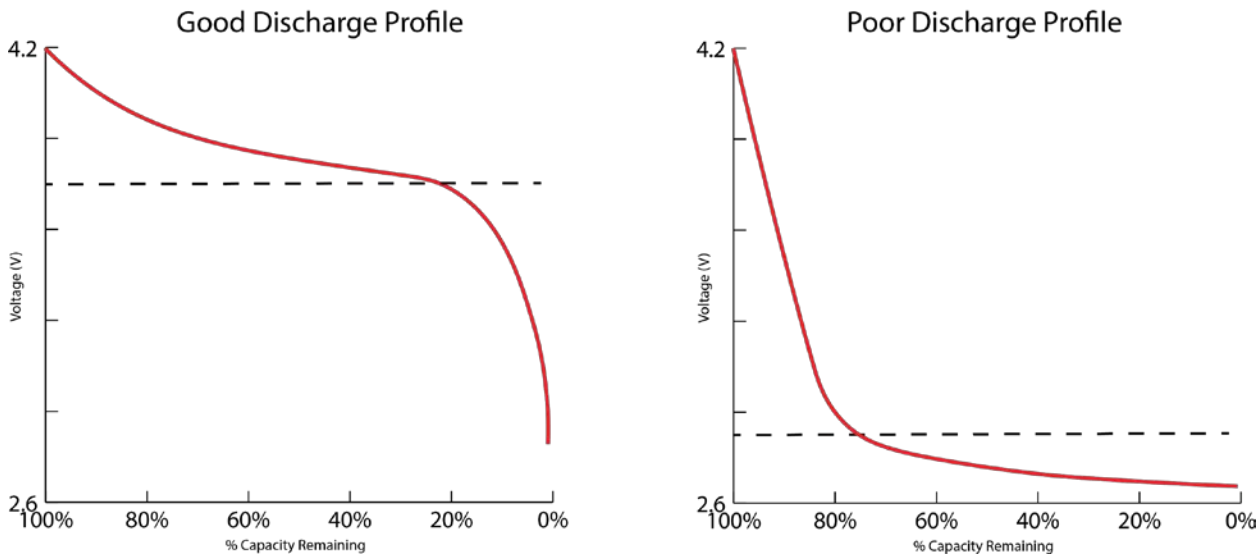

Figure 4: Battery discharge curves

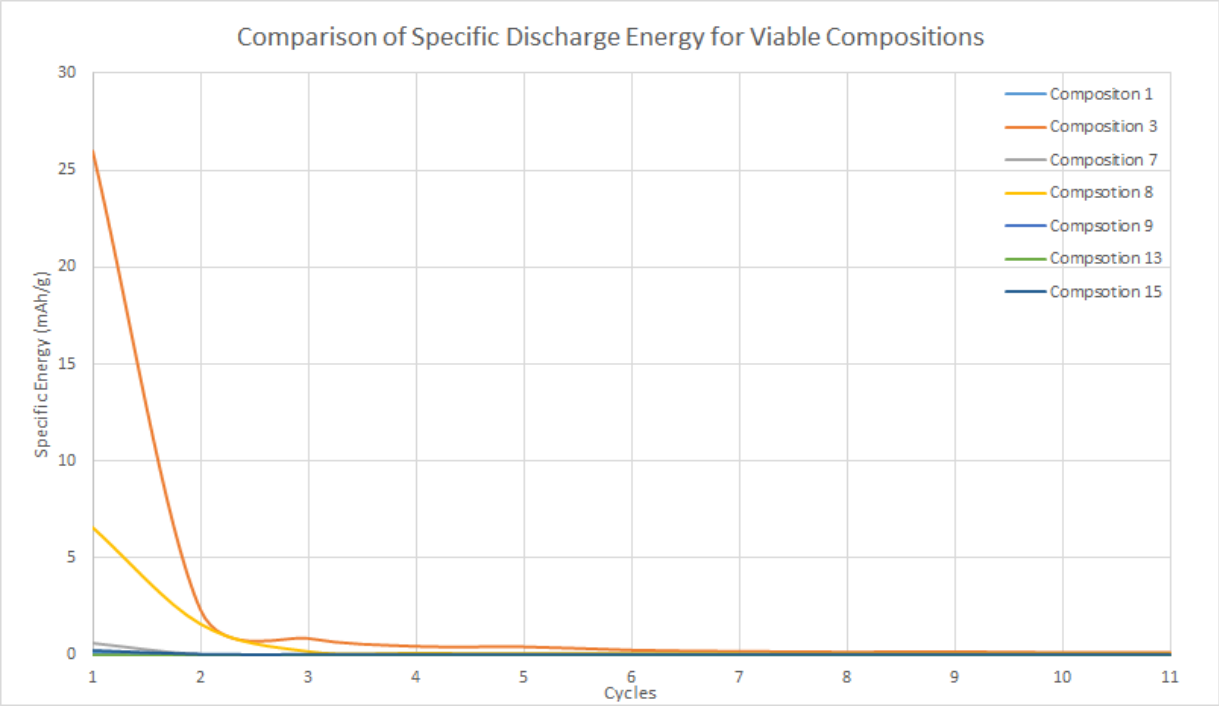

Figure 6: Potential capacities of various compositions

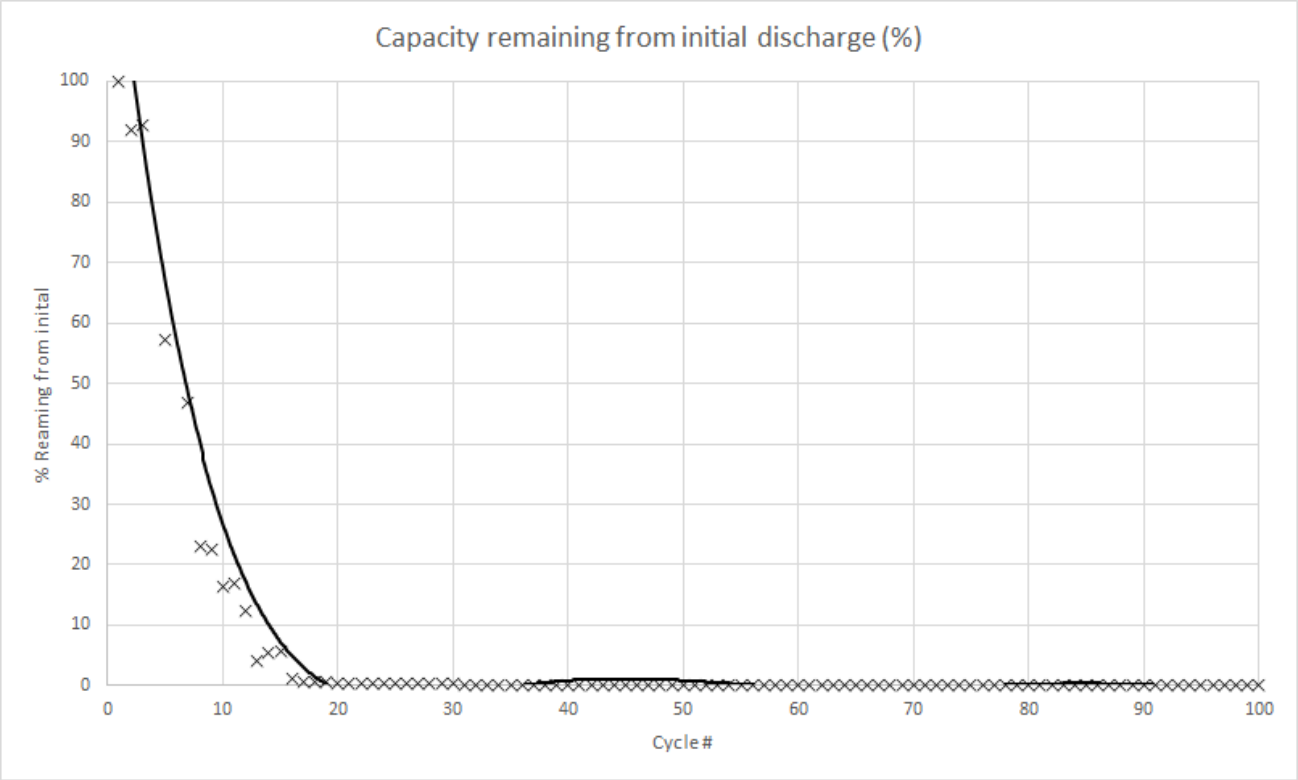

Figure 7: Composition 3 cycle testing showing degradation of capacity