Individual Cell Testing Evaluation

Quick Overview and Recommendations:

By testing individual cells, our pack will be safer, more reliable, and provide more usable energy. In all the reports I have looked through, there have ALWAYS been outliers that have low capacity, high internal resistance, high self-discharge, etc that will cause issues at some indeterminable point. The major effects (sudden capacity loss) are most likely appear after 100 cycles of the pack, however, minor effects will always be present.

Individual cell testing will take about 2 weeks to complete, and can be done concurrently with module prototyping in order to not push timelines back.

I strongly advise testing individual cells for all parameters that we can fit into our timeline.

If we can get access to a capacity testing machine on campus or from Keysight, that would be amazing. In the reports below, there was rarely a strong correlation between capacity and any other parameter, and there were always outliers in capacity.

The goal of cell testing:

The more data and the more informed we are about the status of our pack, the better, safer, and more reliable our pack will be.

Any imbalances present in the pack at the start will only get worse as the pack is cycled. Within series modules, this variance can be overcome with cell balancing, but within parallel cells there is no way to overcome this. Due to the nature of li-ion cells being a manufactured component, there is always some degree of tolerance from the manufacturer. This page will discuss the parameters that can vary, how they affect pack imbalance, and what testing we should be doing to eliminate it.

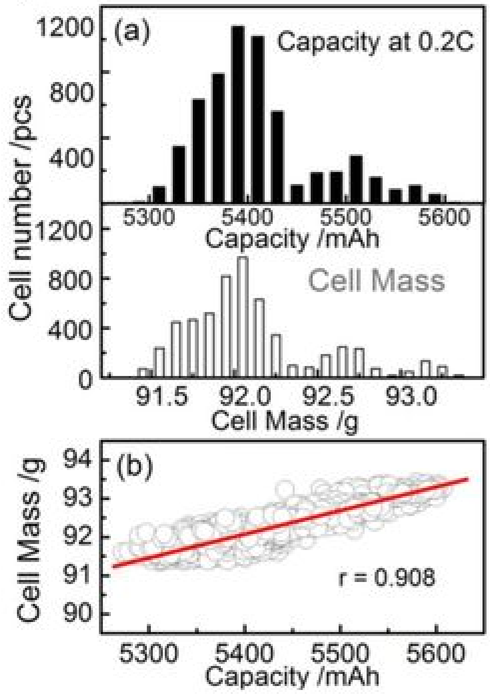
What parameters can be measured, and do they cause pack imbalance?

As-Received OCV - Assuming the cells were manufactured at the same point on the voltage curve, the as-received OCV is an indicator of the amount of self-discharge current of the cell. See the self-discharge method.

Self-Discharge - (https://literature.cdn.keysight.com/litweb/pdf/5992-2517EN.pdf?id=2911018). Keysight has developed a self-discharge measuring unit, which incorporates a super-high precision DC voltage source and a super high precision current measurement device (accurate to the tens of uA). The bucket method described in the document provides a quick (1 hour) test of the self-discharge current. A single cells having a significantly higher self-discharge current will cause the module to have a larger self-discharge current. Over long periods of time (such as sitting idle in the bay for a month), this self discharge current will cause an imbalance in SoC of the cells and lead to decreased pack capacity. Over the course of a week long competition, Self-Discharge will not cause any significant difference in SoC.

Cell Weight - The weight of a cell is an indicator of how much material is inside the cell. According to this paper (https://www.nature.com/articles/srep35051), the weight of a cell correlates loosely with the capacity of the cell, before factory screening occurs, as tested on 5,473 Boston Power Li-ion cells (Swing 5300 5.3Ah). See capacity section for the effect of capacity on imbalance. Another study (https://www.hnei.hawaii.edu/sites/www.hnei.hawaii.edu/files/Initial%20Conditioning%20Characterization%20Test.pdf) did not strictly test the correlation between capacity and rate but, however the capacity ration vs weight was 'barely correlated' with a 'r' value of 0.47.

Figure 1



(**a**) Distributions of cell capacity (0.2 C) and mass of 5473 cells from the same batch, (**b**) the correlation between cell capacity and mass.

Capacity - The difference in capacity between cells in parallel groups causes current spikes in these cells at the end of charge or discharge cycles. In order to maintain a stable cell voltage, the cells will discharge at different rates. This will create different voltage drop across the cells due to IR and thus different OCV. When the current from the pack stops being drawn, then the higher capacity cell with charge the lower capacity cell until the voltage is again equal. This rapid change in current direction and extra cycling on these cells decreases the pack life (https://www.sciencedirect.com/science/article/pii/S0378775316313921?via%3Dihub).

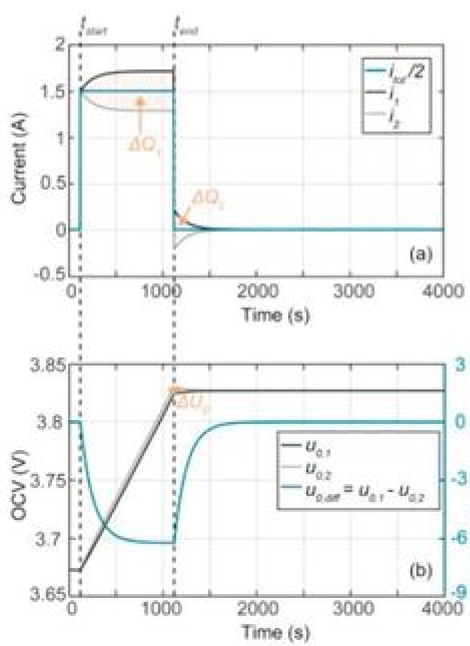


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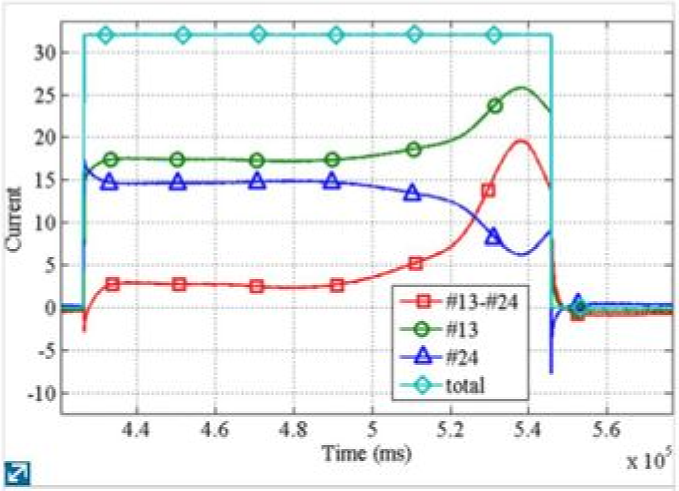
Fig. 5. Simulation results for pulse current applied to ΔC scenario for 1000 s: (a) currents, (b) OCVs and differential OCV.

The above figure is based on simulations, however it shows the reverse charging current well.

Below are the results for a similar report that used cells with mismatched capacity and identical resistance to produce the graph below. It can be noted that the balancing current reaches 8A after a 32A load, for a capacity difference of 33% (https://ieeexplore.ieee.org/document/6872532).



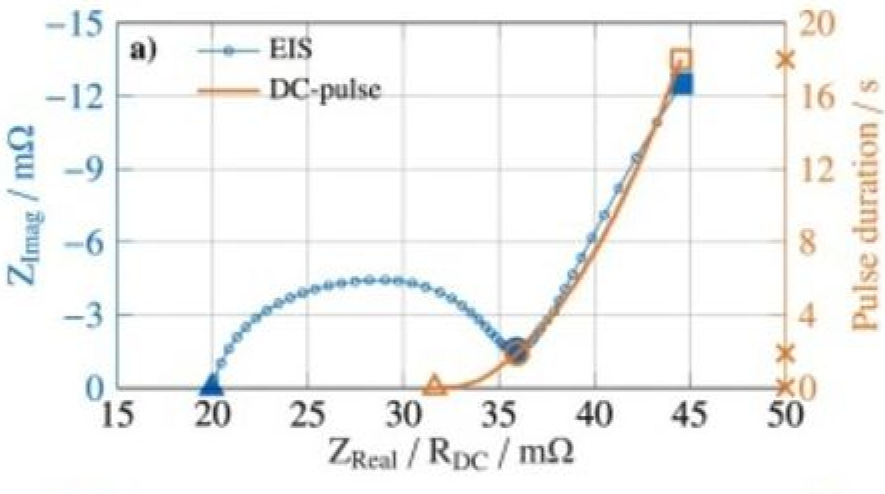
From this graph, we can extrapolate and make a few assumptions of linearity to determine that if there is a maximum of 100mAh (difference between nominal and minimum capacity in LG MJ1 Datasheet) or 3%, the balancing current expected after stopping a 100A load on the pack (4A per cell) would be (8A / 32A) * 4A * (3% / 33%) = **100mA**. This current is very small and well within the specified maximum charge current for these cells, however, it is a quick transition between charge and discharge, changing the direction of motion of the lithium ions very quickly. Also to note, the cell with higher capacity will provide more current to keep the voltages balanced. The current is shared between all cells in the pack, so the increase in discharge current will be very small, likely on the order of 10-50mA. Also to note from this graph is the increase in current from Cell 13 near the end of the discharge cycle. This imbalance is even more severe than that of the charging current, and is expected to be around 100-200mA. While this will not push any cells to their limits, they will age faster than the others, and any defects will show up sooner.

DC Internal Resistance - The DC Internal resistance (DCIR, DCR, Ri, or IR) is modelled as a resistor in series with the cell. Measuring the resistor involves putting a pulse discharge current on the cell, and measuring the voltage drop. This voltage drop is attributed to the series resistance inside the cell. Typical values for DCIR are between 30-80mOhm for a new 18650 cells. For comparison, LiPo cells with high discharge ratings used in RC models typically have a DCIR in the range of 2-10mOhm.

AC Internal Impedance - The internal impedance of a cell is a similar measure to the DC internal resistance except measured with a 1kHz sinusoidal signal applied. This is typically a single point on the EIS measurement curve and is generally not too useful, as there are better methods of determining power loss and voltage drop. More info can be found here: (http://liionbms.com/php/wp_resistance_vs_impedance.php).

Electrochemical Impedance Spectroscopy (EIS) Measurements - For basics of EIS measurements, there is a great explanation here . EIS measurement, by sweeping the frequency of an applied signal across a wide range of frequencies determines the cell impedance at each of these frequency. Complex mathematical algorithms can fit many free parameters to this data, allowing measurement and evaluation of much more complex cell models, involving inductors, capacitors, and resistors to model the AC behaviour. As a research tool, this is a super powerful technique allowing characterization of all cell parameters except capacity. Nyquist plots are used to determine the real component of the series resistance at the zero-crossing point. EIS measurements take a long time to perform, and are not necessarily better than the other methods for our applications.

A comparison of EIS measurement and DC Pulse measurement of resistance is shown below (https://www.sciencedirect.com/science/article/pii/S2352152X18300732#bib0090). I don't claim to understand everything about EIS measurements, but according to this report (https://pdfs.semanticscholar.org/58a9/c593a684fa1a503492383ec807334b4aaaef.pdf?_ga=2.120996168.1162077320.1560615736-269352092.1559077519, page 17) explaining the Nyquist plot (blue) below, the intersection between the semicircle and the Warburg straight line represents the sum of all the internal resistances (the electrolyte, the solid electrolyte interface, and the electron transfer reaction). Notice how the DC IR curve intersects that corner at a pulse time of around 2s. The value obtained for the resistance matches the expected value when compared with calorimetry data in the same report. The cell tested was a Panasonic NCR18650PF.



Initial Characterization Predicted Results

If we do go ahead with individual cell testing, what are the values that are expected, how much variation is expected, and are there outliers that will cause imbalance?

Below is a figure showing DCR and capacity tests for over 20,000 cells measured at beginning of life. The tests were performed on LiFePO4 cells, however the data is a good indication of the variance we should expect as the manufacturing processes are pretty much identical. The key thing to notice here is that while the capacities and DCR measurements at beginning of life follow a normal distribution, with fairly low variance from nominal (5.8% for DCR and 1.3% for capacity), there are **outliers** within the data at the edges of the normal distribution. It is these outlier cells that will cause issues in packs, due to previously mentioned imbalance factors (https://www.sciencedirect.com/science/article/pii/S037877531300116X?via%3Dihub) (blue/yellow graphs).

The second set of graphs show Initial Conditioning and Characterization Tests performed on 100 Panasonic NCR18650B cells, and a similar amount of outliers and standard deviation is noted. The Panasonic cells have been around for a long time. An email from Steve McMullen, ASC Inspector, notes that "Their testing was also with very mature technology Panasonic 18650 3.2AH cells that have been manufactured in the millions if not billions. The newer cells don't have as much credibility. I believe your team is using LG CHEM INR 18650 MJI which is a variant of the technology to trade off Rate for Life and Weight for Capacity, so the cell is already working in realm different than the Panasonics". We should be aware that the MJ1 cells we are using could have more variation than the data from the panasonic NCR18650B and other LiFePO4 tests noted below.(https://www.hnei.hawaii.edu/sites/www.hnei.hawaii.edu/files/Initial%20Conditioning%20Characterization%20Test.pdf - red/blue/black graphs).

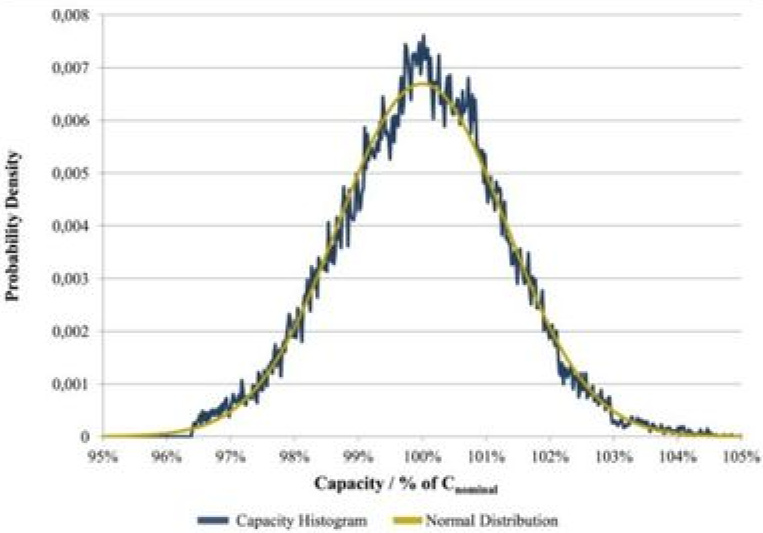


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Fig. 6. Distribution cell capacity at begin of life (σ = 1.3% of nominal capacity, over 20 000 cells measured).

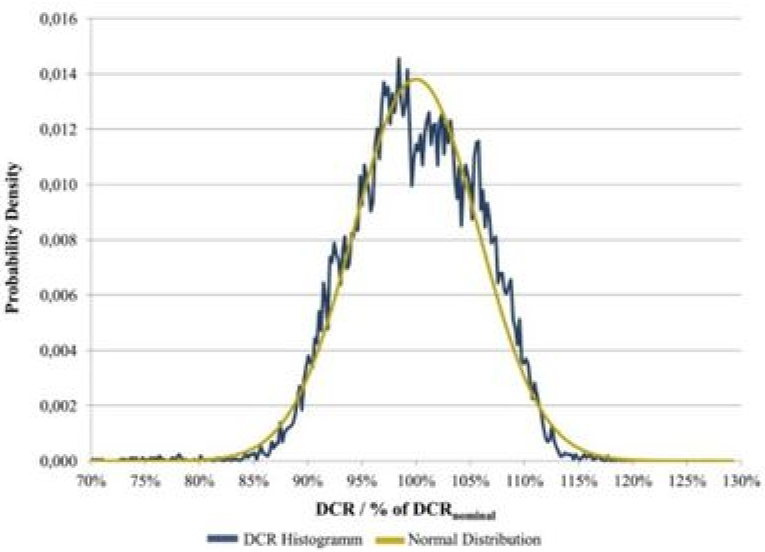

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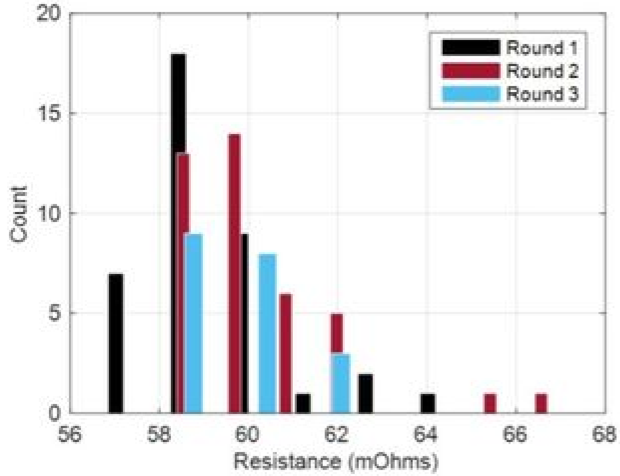
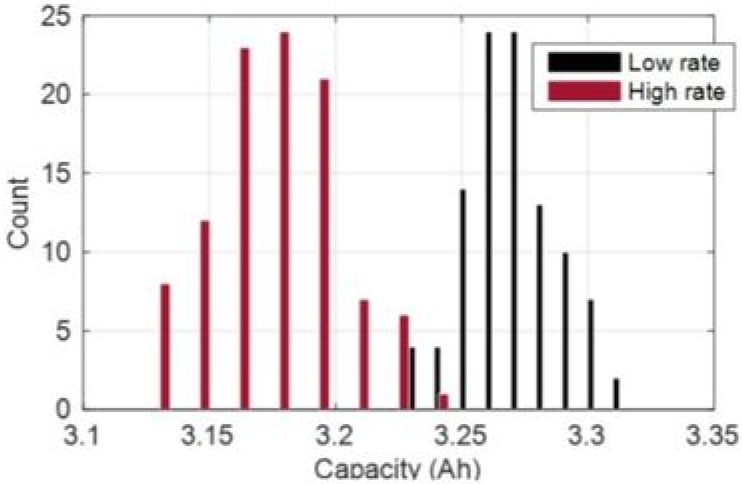
Fig. 7. Distribution DCR at begin of life (σ = 5.8% of nominal DCR, over 20 000 cells measured).



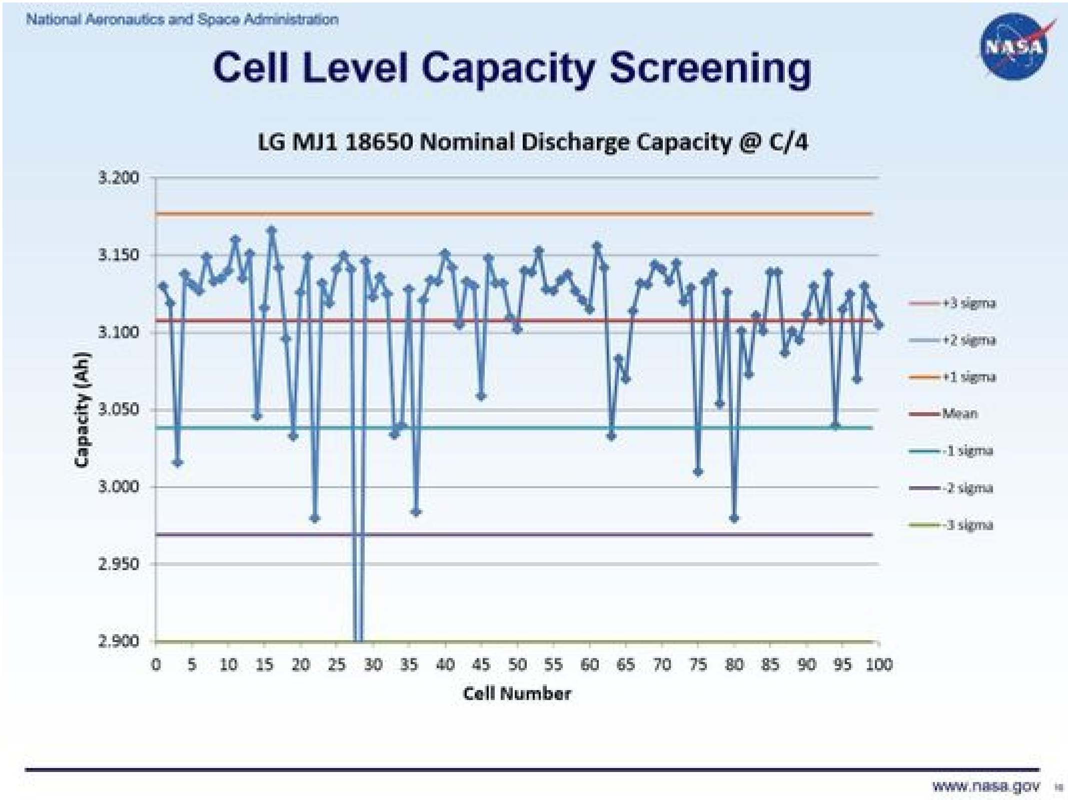


Given a nominal capacity of 3500mAh, results from a capacity assuming a range similar to the graphs above will give 3360-3640mAh, a difference of 280mAh from best to worst cell, 140mAh between the average and worst cells.

This factory tour from EM3EV, an e-Bike battery manufacturer, mentions that they previously used a NEWARE battery testing system to test their cells. They found that 'all cells were within 20mAh of each other', and determined that capacity testing was a waste of time. They generally do a quick voltage test on every cell and discard the low cells. Later in the video he mentions doing 'voltage tests and a few basic tests'. My best guess would be that these basic tests include voltage, weight, and IR. This data should not be taken at the same weight as the reports mentioned above, as it is not verifiable that no other outliers existed.

Also to note from this video, check out the PTC fuses for balance leads and the CNC cell holders that they make.

Results of cell screening on LG MJ1 cells conducted by NASA in 2016 shows 9 cells below 1 standard deviation (0.135Ahr) at C/4 capacity. While the mean capacity of around 3.11Ah is low for LG MJ1 cells (maybe they used a higher cutoff voltage?), it shows what kind of outliers we should expect (https://www.hnei.hawaii.edu/sites/www.hnei.hawaii.edu/files/Initial%20Conditioning%20Characterization%20Test.pdf)(https://www.energytech.org/wp-content/uploads/ET2016Presentations/ET16-4G2DevelopmentofDistributedLithiumIonBatteryforSpaceSuitMiller.pdf).



Why single cell testing is important (comparison against module/pack testing):

1 - A manufacturing error (outlier values of capacity or IR) will be impossible to detect once we put the cells in modules

Once we put the cells in modules, the IR will be extremely low. Finding differences in the IR of the modules due to 1 bad cell will be next to impossible due to small contribution each cell has to the overall Resistance. If we take the internal resistance of each cell to be 50mOhm, then the IR of a 24P module will be 2.08mOhm. If one cell had an IR of 70mOhm (which would cause increased currents during the ends of charge/discharge cycles due to mismatched SOC-OCV curves), the total resistance would be 2.11mOhm. A 100A load connected to the module would produce a voltage drop of 0.208V if all cells were 50mOhm, and 0.211V if one cells was at 60mOhm. While this level of precision if achievable with our multimeters, the same voltage drop (0.211V would occur if all cells had an Ir of 51mOhm).Thus, to determine any imbalances in Ir, individual cell testing must be conducted.

While the capacity of the modules might be able to tell of a faulty cell, if other cells were picked such that the capacity was increased more than the average, the faulty cell could not be detected on a module level.

Self-Discharge is difficult to measure without extremely accurate and precise equipment (which may be available from Keysight). If one cell has an elevated self-discharge current of 20uA while all other cells have a self-discharge current of 10uA, a 24P module made up of 10uA self-discharge cells will have a self-discharge current of 240uA. If one cell in the module has an elevated self-discharge, then the total self-discharge will be 250uA.

2 - The cell life can be prolonged by avoiding exposure of the cells to high charge and discharge currents.

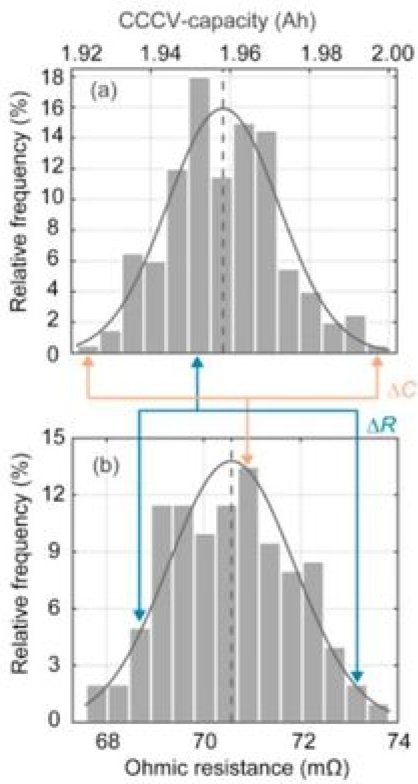
Every cell inside a pack with matched IR will be able to deliver the full energy in the cell due to the change in SOC-OCV curve at higher internal resistance (https://iopscience.iop.org/article/10.1088/1742-6596/795/1/012036/pdf). The higher resistance will cause a larger voltage drop. In order to maintain the same voltage at the bus plate, then internal voltage of the cell must be higher than the others, so there is still more energy left in the cell when the end voltage for the pack is reached.

3 - Once we put the cells inside the modules, they cannot be taken out. This is one of the reasons that we bought additional cells. Detecting a singular bad cell inside a module is possible in some cases, but we would never be able to identify the offending cell and replace it. If all the metrics (except capacity) of the individual cells are tested before being put into modules, we will know that there are no manufacturing defects in the cells.

Effects of an imbalance in parallel connected cells - Why variance is the enemy of battery packs

Some of this may be repeated from the above sections, and the above sections also complement the info contained here.

From the report linked, a cell-cell variation of internal resistance is +/- 15% (https://www.sciencedirect.com/science/article/pii/S2352152X18308156, Table 2), and follows a roughly normal distribution. This matches with results in several other reports, while a +/- 5% variation in capacity is noted from the same table. The Initial Characterization Predicted Results section shows that a variance of 5% IR standard variation should be expected from the normal distribution, and around 1% standard deviation for capacity.



Internal resistance mismatch between cells can lead to sudden capacity losses and a decrease in overall cycle life of around 40% (http://web.mit.edu/bazant/www/papers/pdf/Gogoana_2013_J_Power_Sources.pdf). While we are not concerned with the cycle life of our pack, sudden capacity losses must be avoided. The graph below shows that capacity suddenly drops by roughly 20% around the 100-150 cycle mark. The cells in these tests were LiFePO4 cells, and the internal resistance measured by a 15s 40A pulse, with a distribution shown above from 13.5 - 21.5 mOhm. This is a fairly large spread (50%) or IR and the currents that the pack were tested at are much larger than anything our cells will ever see. A high current test such as this decreases the time that the mismatch effects take to show up as the cells are performing at their peak characteristics.

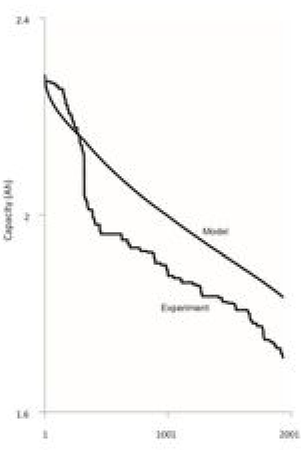


Fig. 8. Experimental and model capacity fade for two cells.

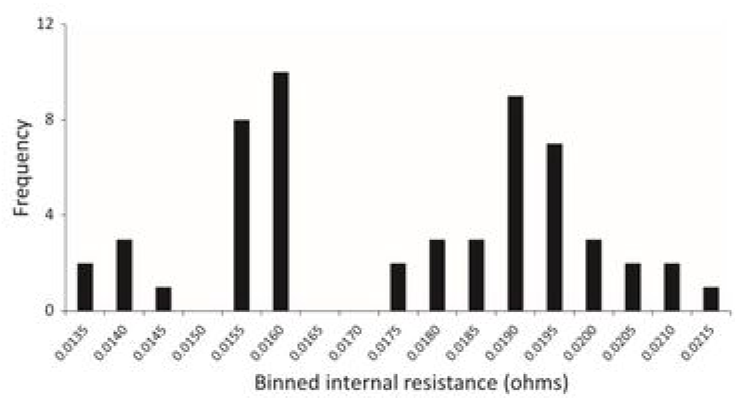


Fig. 1. Internal resistance distribution of cells tested.

The capacity loss shown in the figure happens after around 100 cycles, and is due to the mismatched cells being exposed to large charge/discharge currents as the ends of the charging and discharging cycles due to differing SoC-OCV curves cause by the mismatched resistance.

Internal resistance mismatch causes current mismatch on charge and discharge cycles. The current mismatch creates voltage drop difference and thus a difference in SoC between the cells in parallel groups. Thus there is an SoC mismatch between the cells when current is being drawn, which leads to internal current spikes when the external current flow stops (https://www.sciencedirect.com/science/article/pii/S0378775316313921?via%3Dihub),

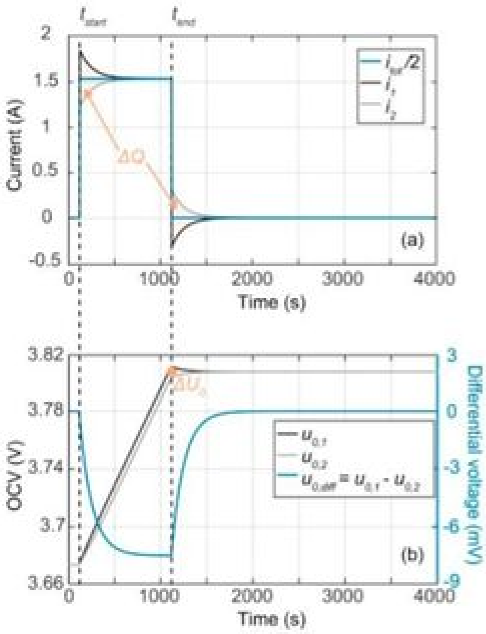


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Fig. 4. Simulation results for pulse current applied to ΔR scenario for 1000 s: (a) currents, (b) OCVs and differential OCV.

A capacity drop in any one of our modules will affect the whole pack. If one cell in one module drops by 10% capacity due a an uncaught cell parameter outlier (IR or capacity), then we lose (3.5Ah * 10% * 3.7 * 36 = 47Wh) 47Wh of energy in our pack. That single cell will then also start to degrade quicker and the module will have to be replaced. Going by the efficiencies of other winning solar cars, 47Wh could add an additional 1-2 Km of range to the car (and avoid headaches from increases in variation after many cycles).

Thoughts on Temperature Variation:

Pack-Variation: As the temperature of a battery pack increases, the self-discharge rate also increases due to the increased rate of the chemical reactions inside the cell. An increase in 10 degrees Celsius will double the amount of self-discharge current. (Keysight link) The self-discharge will still be in the high-uA range (maybe low mA in the worst case), and thus not be an issue in module or pack balancing as the passive balancing circuit will take care of the pack-level variation in self-discharge. Assuming the temperature within the pack is only hotter when we are drawing current, the change in DC Internal Resistance will more than offset the change in self-discharge current.

Module-Variation: Temperature variation within a module, under extreme circumstances, can result in a positive feedback situation (until a certain delta OCV is reached). A decrease in internal resistance of the cell due to an increase in temperature will cause more current to be drawn from that cell, which will lower its OCV. Due to the close proximity of cells within a module, the temperature variation (unless caused by a cell with initially high IR) will be very small ans thus its effects negligible. With temperature variation, the useable capacity of the cell will increase as the internal resistance decreases and thus we have less power loss in the cells due to IR. (Show IR-temp graph and Capacity-Temp Graph)

Conclusions:

Will individual testing give us more range in the low cycle count that we will be running - probably not a significant amount. I imagine 50-100Wh of extra power would be a good estimate.

Will it make our battery **safer**, more **reliable**, **predictable**, **consistent**, and **cause fewer headaches** - definitely. Testing is the only way to ensure that we have a well-built, balanced, and reliable battery pack. An outlier cell inside a module will be detected at the module level. Without individual cell testing, an outlier cell could find its way in to our pack and cause a sudden capacity drop during competition.

How long will testing take? - We will only conduct capacity testing if we can get access to the right cell cycling equipment. The University of Waterloo's logo is on Neware's site, so I am sure we have some high volume cell cycling machines on campus (just have to figure out where they are and if we can use them for a week). Setting up the testing of the other factors (weight, as-received OCV, DCIR, AC impedance), will take a few days, so we can schedule **1 week** for cell test setup. Performing the cell tests will take a day, so we can schedule **2 days**. After all the data is collected, it will take a few days to go through the data and group the cells based on lowest variation.

This testing can happen concurrently with module prototyping, so I do not believe the timelines will be shifted at all. This data and process will also prove to be invaluable when creating future packs.

The last thing we want to happen to our pack is to have our packs be at risk of reduced capacity due to failing cells or to have to replace a module during the middle of competition. Nothing can ever 100% guarantee that a spontaneous internal short can happen inside the packs, however proper testing and handling will significantly reduce the chances.

The more shortcuts we take during testing, we are leaving the bad cells to be discovered once the car is actually being used and depended upon.

MSXII was a good example of taking shortcuts on testing - while I'm sure that replacing a module during ASC was great experience, I don't think that anyone wants to do it again.

Recommendations:

Do as much testing as we can on every single cell. I am not willing to risk a bad cell entering our modules and causing trouble later.

Reports mentioned and used for research in the text:

Self-diacharge: https://literature.cdn.keysight.com/litweb/pdf/5992-2517EN.pdf?id=2911018

5000 Boston Power Cells: https://www.nature.com/articles/srep35051

ICCT on NCR18650B: https://www.hnei.hawaii.edu/sites/www.hnei.hawaii.edu/files/Initial%20Conditioning%20Characterization%20Test.pdf

Capacity Mismatch large cells: https://ieeexplore.ieee.org/document/6872532

Simulations with capacity, resistance mismatch: https://www.sciencedirect.com/science/article/pii/S0378775316313921?via%3Dihub

Resistance and Impedance: http://liionbms.com/php/wp_resistance_vs_impedance.php

EIS Measurement: https://www.sciencedirect.com/science/article/pii/S2352152X18300732#bib0090

EIS Measurement explained well: https://pdfs.semanticscholar.org/58a9/c593a684fa1a503492383ec807334b4aaaef.pdf?_ga=2.120996168.1162077320.1560615736-269352092.1559077519

ICCT on 20,000 LiFePO4: https://www.sciencedirect.com/science/article/pii/S037877531300116X?via%3Dihub

NASA LG MJ1 Cell Screening: https://www.energytech.org/wp-content/uploads/ET2016Presentations/ET16-4G2DevelopmentofDistributedLithiumIonBatteryforSpaceSuitMiller.pdf

More energy available when matched IR: https://iopscience.iop.org/article/10.1088/1742-6596/795/1/012036/pdf

Some ICCT Testing: https://www.sciencedirect.com/science/article/pii/S2352152X18308156

IR 20% imbalance, 40% cycle life loss. sudden capacity loss, ICCT: http://web.mit.edu/bazant/www/papers/pdf/Gogoana_2013_J_Power_Sources.pdf

LG MJ1 Datasheet: https://www.nkon.nl/sk/k/Specification%20INR18650MJ1%2022.08.2014.pdf

Cell Sorting Article: https://www.sciencedirect.com/science/article/pii/S2352152X16300561?via%3Dihub