# **ABSTRACT**

Performance analysis of different generation of LFPC cells….. (to be added)

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# **Abbreviations**

|  |  |
| --- | --- |
| BOL | Beginning of life |
| DOD | Depth of discharge |
| ECU | Extended check-up |
| EFC | Equivalent full cycle |
| EOL | End of life |
| SCU | Short check-up |
| SOC | State of charge |
| SOH | State of health |
| SPICY | Silicon and polyanionic chemistries and architectures of Li-ion cell for high energy battery |

# Introduction

Lithium ion batteries have taken the most significant role in present day energy storage technologies and systems, primarily due to their high energy density and high specific energy. Invented by the American physicist Professor John Goodenough in 1980 as a new type of battery in which the lithium (Li) could migrate through the battery from one electrode to the other as a Li+ ion (Alarco and Talbot 2015), it was first commercially introduced as a product by Sony Corporation (Blomgren 2016). The simple basis of these batteries is that a compound of lithium with a transition metal - such as nickel, manganese, cobalt, iron - and oxygen forms the cathode, whereas, graphite is the anode (Alarco and Talbot 2015).

In terms of chemistry, Li-ion cells have an advantage over other technologies due to variety of reasons. Due to its lowest reduction potential of all elements, Li-ion cells have the highest available cell potential. Further, because of being one of the lightest element and having one of the smallest radii, Li-based batteries have high gravimetric and volumetric capacity and power density. (Nitta et al. 2015, 2015) Therefore, despite disadvantages like high costs and possible high temperature development, the above advantages make it very desirable for many commercial and research-related activities. This prompts for further studies and experiments to improve safety and reducing the costs of Li-ion batteries.

The **Table 1** shows a comparison of Li-ion based batteries with others with different cathode materials.

**Table 1. Comparison of Li-ion with other cathode materials in a battery**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Cathode | Li-ion | Pb-acid | Ni-Cd | Ni-MH |
| Cycle life | 500-1000 | 200-500 | 500 | 500 |
|  |  |  |  |  |
| Working potential (V) | 3.6 | 1.0 | 1.2 | 1.2 |
|  |  |  |  |  |
| Specific energy (Wh/kg) | 100 | 30 | 60 | 70 |
|  |  |  |  |  |
| Specific energy (Wh/L) | 240 | 100 | 155 | 190 |

Source:*(Soylu 2011)*

Currently, Li-ion technologies are used in a variety of applications, especially in portable electronics, hybrid/electric vehicles and power tools. The high energy efficiency of Li-ion batteries may also allow their use in various electric grid applications, including improving the quality of energy harvested from wind, solar, geo-thermal and other renewable sources, thus contributing to their more widespread use and building an energy-sustainable economy. (Nitta et al. 2015)

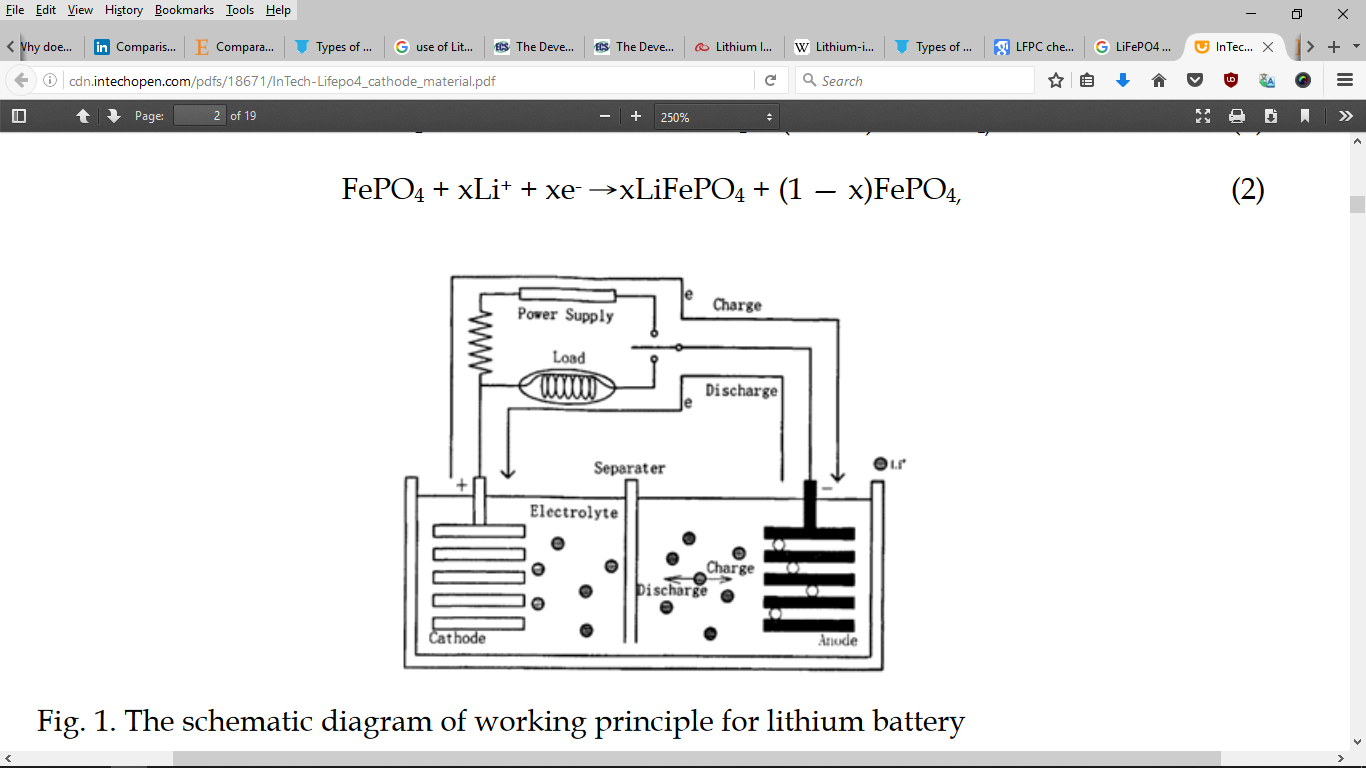
Because of Li’s ability to form compounds with a variety of transition metals and oxygen, different types of Li battery technologies are available. **Table 2** shows some typical properties and their applications of the most commonly used types of Li-ion batteries:

**Table 2. Typrical properties and applications of some main types of Li-ion cells**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Li-Cobalt  (LCO) | Li-Manganese  (LMO) | Li-Nickel Manganese Cobalt (LNMC) | Li-Iron Phosphate (LFP) |
| Specific energy  (Wh/kg) | 150-200 | 100-150 | 150-220 | 90-120 |
|  |  |  |  |  |
| Nominal  voltage (V) | 3.6 | 3.7 | 3.7 | 3.3 |
|  |  |  |  |  |
| Cycle life | 500-1000 | 300-700 | 1000-2000 | 1000-2000 |
|  |  |  |  |  |
| Cost (USD/kWh) | - | - | 420 | 580 |
|  |  |  |  |  |
| Application | Mobile phones, tablets, laptops, cameras | Power tools, medical devices, electric powertrains | E-bikes, medical devices, EVs, industrial | Portable and stationary needing high load currents and endurance |

Source: *http://batteryuniversity.com/learn/article/types\_of\_lithium\_ion*

Despite disadvantages like low electrical conductivity and slow Li-solid state diffusion and therefore, low specific energy and low capacity (Eftekhari 2017), LFPC is one of the safest Li-ion technologies and forms the basis of our studies in this work. It consists of LiFePO4 as the cathode along with a graphitic carbon electrode in a metallic current collector grid as the anode. The following figure shows a schematic of the ion-transport inside an LFPC cell.



**Figure 1. Schematic of the ion-electron transport in a Li-ion based cell** **(Soylu 2011)**

The above figure shows the direction of electron flow in charging and discharging conditions. **……Equation 1** shows the extraction of Li-ion to charge the cathode, while **……Equation 2** shows the reverse process.

LiFePO4 – x Li1+ - x e- 🡪 x FePO4 + (1-x) LiFePO4

**……Equation 1** **(Soylu 2011)**

FePO4 + x Li1+ + x e- 🡪 x LiFePO4 + (1-x) FePO4

**……Equation 2** **(Soylu 2011)**

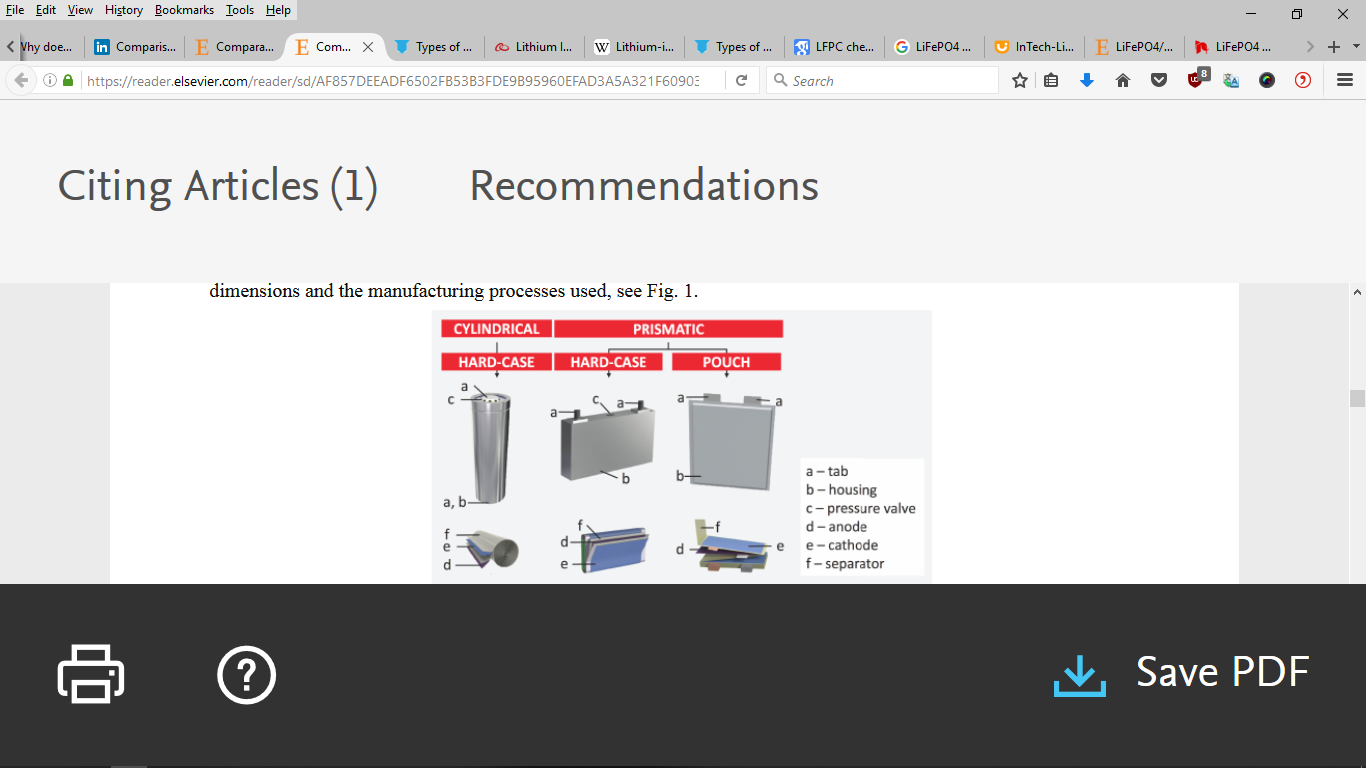
Apart from the electrode configuration, Li-ion cells can be divided into different types based on their geometry or the types of packaging of the electrodes with each other. The LiFePO4-C are generally available in three main geometries: *cylindrical*, *prismatic* and *pouch* type.

Cylindrical geometry is the most common packaging technique for both primary and secondary cells. *“It has the main advantages of ease of manufacture and good mechanical stability. The tubular cylinder can withstand high internal pressures without deforming. Even though the cylindrical cell does not fully utilize the space by creating air cavities on side-by-side placement, the most common cylindrical cell dimension, the 18650, has a higher energy density than a prismatic/pouch Li-ion cell. The higher energy density of the cylindrical cell compensates for its less ideal stacking abilities and the empty space can always be used for cooling to improve thermal management. This cell design allows for added safety features that are not possible with other formats. It cycles well, offers a long calendar life and is low cost, but it has less than ideal packaging density. The cylindrical cell is commonly used for portable applications.*” (include reference of the webpage using Citavi Picker <http://batteryuniversity.com/learn/article/types_of_battery_cells>).

*“Prismatic cells are encased in aluminum or steel for stability. Jelly-rolled or stacked, the cell is space-efficient but can be costlier to manufacture than the cylindrical cell. The prismatic cell improves space utilization and allows flexible design but it can be more expensive to manufacture, less efficient in thermal management and have a shorter cycle life than the cylindrical design.” (same reference as cylindrical cells above)*

*“The pouch cell offers a simple, flexible and lightweight solution to battery design. Some stack pressure is recommended but allowance for swelling must be made. The pouch cells can deliver high load currents but it performs best under light loading conditions and with moderate charging.* *It is cost-effective but exposure to humidity and high temperature can shorten life. Adding a light stack pressure prolongs longevity by preventing delamination. Swelling of 8–10 percent over 500 cycles must be considered with some cell designs.” (same reference as cylindrical cells above)*

**Figure 2** below shows diagrammatically the different geometries of Li-ion cells



**Figure 2. Diagrammatic representation of types of Li-ion packaging geometries** **(Schröder et al. 2017)**

The **Table 3** below shows a comparison between the cell geometries with respect to their advantages, disadvantages and their applications.

**Table 3. Comparison of cell packaging geometries**

|  |  |  |  |
| --- | --- | --- | --- |
|  | Cylindrical | Prismatic | Pouch |
| Advantages | Ease of manufacture  Good mechanical stability  Withstand high internal pressure without deforming  Lower cost (watt per hour)  Long calendar life and cycling ability  Higher energy density | Thin profile (effective use of space)  Light weight  Allows flexible design  Encased in metal or steel for stability | Similar to prismatic cell except no need for metallic casing  Most efficient use of space  Light weight |
| Disadvantages | Notable space between cells (less space efficiency)  Heavy  Low packaging density due to space cavities | More expensive to manufacture  Difficult and less efficient in thermal management  Shorter cycle life  Deformation in high pressure situations  Higher cost (watt per hour) | Provision for swelling must be made  Similar to prismatic cells |
| Applications | Power tools, medical instruments, laptops and E-bike | Mobiles phones, tablets and low-profile laptops  Electric powertrains in hybrid and electric vehicles, electric buses, trucks, solar/wind storage UPS | Portable applications like drones and hobby gadgets  Energy storage systems (ESS) |

Source: *https://www.slideshare.net/AnmolJaggi/comparison-between-different-li-ion-cells-type*

In this work, a study has been done on the experiments done on various generations of LFPC cells. The different generations indicate different modifications done on either of the electrodes to improve the capacity and energy density of LFPC and then, analyzing the experiments results to determine the performance changes for the different packaging geometries of the cells.

# Experimental Setup

The collaborative research project, SPICY (acronym for Silicon and polyanionic chemistries and architectures of Li-ion cell for high energy battery) aims at development of new generation of Li-ion batteries with respect to performance, safety, costs, recyclability and lifetime. It particularly involves performance improvement of LiFePO­4 based on LFPC cells. “LiFePO4 is well known as a safer and more durable cathode material. Unfortunately, its energy density is low due to the electrochemical potential of Fe. One objective of SPICY will be to bind metals having a higher potential than Fe, allowing an increase of the material potential, and thus a higher energy.” (SPICY Innovative Battery 2015)

“One of the main objectives in SPICY is to work on the family of polyanionic phosphates bound to metals. This active material allows higher potentials resulting in an increased energy density and reduced battery weight.” (TUM-Institute for Electrical Energy Storage Technology, SPICY Homepage 2018)

For the thorough comparison of Li-ion cells, cells of different geometries have been manufactured. This gives the opportunity to compare the performance capabilities of the three geometries for same materials and conditions of the cells. Literature on comparison of cell packaging geometries for cells of same chemical composition and size is limited and therefore, it has an elevated scope for research.

In this chapter, the experimental setup is discussed. In the first part, the cell geometry, size and chemical composition of the cathodes and anodes are mentioned. The second part describes the test performed on the cells which are used in scope of this thesis work.

* 1. Cell chemistry

To have a common comparison standard between the cell packaging geometries, the chemistry for the anode, cathode, electrolyte and separator were chosen to be the same. All cells have been manufactured have the same material for the electrodes, i.e., LiFePO4 as the cathode and graphite as the anode. Both the materials of the electrodes are from the same batch of raw materials for all the cells (Include SPICY Deliverable 5.6).

The separator, as already discussed, isolates the two electrodes and is a membrane that allows transfer of ions from cathode to anode on charge (reverse on discharge). The small current passing through the separator constitutes the self-discharge and gradually reduces the cell capacity. The separator used for the cell manufacture is a tri-layers Celgard 2325 grade. This type of tri-layered poly-olefin separator consists of 1 polyethylene (PE) layer sandwiched between two layers of polypropylene (PP), and is the most commonly used separator type. This is because of their chemical inertia and the safety feature the combination of PP-PE-PP offers. In the case of overheating, the PE layer melts, losing its porosity (i.e., mechanically blocking the Li+ ion movement), while the PP layer prevents large dimensional changes until its own melting, thus preventing short-circuits. The Cellgard 2325 has a thickness of 27 µm and an air permeability defined by a Gurley number of 570s. (Kirchhöfer et al. 2014) Gurley number is defined as the number of seconds required for 100 cubic centimeters (1 deciliter) of air to pass through 1.0 square inch of a given material at a pressure differential of 4.88 inches of water (0.176 psi) (ISO 5636-5:2003). (Hutten 2007)

The composition of the electrolyte solution strongly influences the temperature dependence of the capacity. This is related to the quality of the passivation of the graphite electrodes in the various solutions and to the transport properties of the passivating surface films that cover the graphite particles (Yaakov et al. 2010). For the cells manufactured by SPICY, the electrolyte solution used is a blend of ethylene carbonate (EC), propylene carbonate (PC) and di-methyl carbonate (DMC) in volume proportion 1:1:3, respectively, with 1M of LiPF6 and 2% weight of vinylene carbonate (VC). (Include SPICY Deliverable 5.6)

* 1. Cell geometry and size

The three packaging geometries (cylindrical, prismatic and pouch) were assembled in different ways, which are mentioned in the SPICY Deliverable 5.6.

Jelly roll manufacturing was used to wind together the electrodes and separator in cylindrical and flat cores ***for cylindrical and prismatic cells***, respectively. While the cylindrical cores are basically rolls of electrodes with separators within them, for the prismatic cells, the cores resemble layers placed into a Z-shape.

Next, the cells are welded together complete with the placing the current collectors and finally welding the top cap. The electrolyte is filled using different holders through the aperture at the top cap. It is necessary to ensure that the electrolyte solution covers every pore in the internal structure and the separator membrane. After this step, the cells are conditioned outside the dry room.

The ***pouch cells*** were manufactured separately. The process lacked a standardized equipment and therefore, needed a lot of workforce and manual job initially. In the first step, the electrodes and the separators were cut into layers using a cutting press and stacked into layers of 38 anodes, 76 separators and 37 cathodes. The terminals were drawn out and tabs were welded on them. The stacks thus formed were wrapped in two half-aluminium shells and heat sealed. The pouch cells were filled with the electrolyte solution in a glove box and the remaining side was welded. Then the cells were conditioned outside the dry room and the trapped gas bubbles in the structure were degassed as the last step.

|  |  |
| --- | --- |
|  |  |
| (a) | (b) |

**Figure 3. Packaging geometries of the cells manufactured (a) Prismatic (L), Cylindrical (R), (b) Pouch (Source: SPICY Deliverable 5.6)**

The post manufacturing specifications of the cells are reported further in this subsection. The cell specifications of each geometry are mentioned in the following **Table 4**:

**Table 4. Cell specification for cells of different geometries (Source: SPICY Deliverables 5.6)**

|  |  |  |  |
| --- | --- | --- | --- |
|  | Cylindrical | Prismatic | Pouch |
| Lower Voltage limit (V) | 2.5 | 2.5 | 2.5 |
| Upper Voltage limit (V) | 3.6 | 3.6 | 3.6 |
| Maximum charge current (A) | 50 | 4 | 50 |
| Maximum discharge current (A) | 100[[1]](#footnote-1) | 4\*\*\*[[2]](#footnote-2) | 100[[3]](#footnote-3) |
| Temperature operation range (°C) | [-10, +55][[4]](#footnote-4) | [0, +45] | [-10, +55]\*\*[[5]](#footnote-5) |

The weight contribution of all the different components and the materials used to manufacture them are shown in **Table 5**. A clear difference is noticed in the cells with soft packaging, i.e. the pouch cells, due to softer casing.

**Table 5. Weight contribution of different components of a cell characterised by cell packaging geometry (SOURCE: SPICY Deliverable 5.6)**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Weight (g)** | **Cylindrical (wound)** | **Prismatic (wound)** | **Pouch (soft casing)** | **Material** |
| **Electrode collector** | 26.78 | 26.78 | 24.49 | Al |
| 55.53 | 55.53 | 48.59 | Cu |
| Component total | **82.31** | **82.31** | **73.08** |  |
| **Electrode coating** | 73.9 | 73.9 | 71.10 | C |
| 5.93 | 5.93 | 5.63 | Li |
| 43.94 | 43.94 | 41.69 | Fe |
| 76.43 | 76.43 | 72.51 | PO4 |
| 9.15 | 9.15 | 6.12 | Binder |
| Component total | **209.35** | **209.35** | **197.05** |  |
| **Electrolyte** | 11.74 | 11.74 | 11.10 | LiPF6 |
| 87.40 | 87.80 | 82.90 | Carbonate |
| Component total | **99.14** | **99.54** | **94** |  |
| **Separator** | 11.30 | 11.30 | 10.45 | Polypropylene |
| **Mechanical parts (packaging, collectors, core, etc.)** | 46.54 | 85.19 | 7.70 | Al |
| 5.06 | 31.41 | 3.80 | Polypropylene |
| 20.88 | 22.04 | 6.01 | Cu |
| 0.18 | 0.26 | 0.20 | Ni |
|  |  | 1.50 | Polyamid |
|  |  | 0.37 | Other |
| Component total | **72.66** | **138.9** | **19.21** |  |
| **Total cell weight** | **475** | **542** | **394** |  |

The weight results are documented as expected because of the hard cover being replaced by aluminum foil in the pouch cells, the packaging component and the overall cell weighs less. In the case of the prismatic cell, it requires more packaging than a cylindrical cell because of the higher surface area, as can be seen from the reception test data given in **Table 6**. The cells delivered were subjected to reception test and the data obtained are documented in the table:

**Table 6. Cell geometry and reception test specifications (Source: Spicy\_Reception\_test\_report\_GEN0\_September 2016\_FZJ)**

|  |  |  |  |
| --- | --- | --- | --- |
|  | Cylindrical | Prismatic | Pouch |
| Energy density (Wh/kg)[[6]](#footnote-6) | 108.61 | 94.25 | 121.77 |
| Capacity (Ah) | 16.099 | 15.963 | 14.889 |
| Weight (g)[[7]](#footnote-7) | 474.32 | 541.98 | 391.25 |
| Height (mm) | 125 | 125 | - |
| Curved Surface area (mm2) | 19625[[8]](#footnote-8) | 31250[[9]](#footnote-9) | - |
| Nominal voltage (V) | 3.2 | 3.2 | 3.2[[10]](#footnote-10) |

Cycle Life Tests involve testing of the cells at different charging/discharging rates at different conditions of temperature over different states of health (SOH) or ageing time. In the cycle tests, the equivalent cycle numbers reached are kept in track over the ageing of the cells.

In both calendar life and cycle life tests, two kinds of checks are given – short check-up (SCU) and extended check-up (ECU). The extended check-ups (ECUs) involve the measurements of capacity evolution, pulse power (using DST tests), open circuit voltages (OCV) and internal resistances.

The third test done on the cells was the Electrochemical Impedance Spectroscopy (EIS). EIS helps in determining the ageing characteristics of the cell. In this test, a small sinusoidal current is applied to the cell at a fixed frequency and the impedance response is measured. The same is done for different frequencies and a Nyquist diagram is plotted. Theoretically, it gives information about the ions mobility in the batteries. (Rusling Research Group 2015)

# Results and discussions

## Generation 0 of LFPC

Generation 0 of LiFePO4-C cells involved testing the three different geometries of the commercial and most widely available LFPC cells to determine the status quo. These cells have a cathode made of regular grade graphite with no structural modifications. The anodes are non-doped LiFePO4.

In this section, the major characteristics and comparison between the three main geometries of the cells (cylindrical, prismatic and pouch) is done using the data obtained from the life-cycling tests done on each of them for cells stored in similar conditions of current rates and temperatures. All the cells in this test are rated at 16 Ah and are stored at 0.3C (current rating). For ease of study and data representation, all the data values for the same geometry and same test conditions are averaged out.

### Performance of different geometries at 100% State of Health

Before comparing the effects of ageing on the three geometries, first their performances are compared at 100% State of Health (i.e. initial storage stage, or first cycling test after reception).

#### Cell storage conditions and reception test specifications

The reception test specifications of the 16Ah cells are given in **Table 5**:

The cell energy density was calculated using the formula:

**….Equation 3**

where *E* is the energy density (Wh/kg), *Q* is the capacity of the cell at 1C (in Ah), *V* is the nominal voltage (V) and *m* is the mass of the cell (in kg).

The difference in capacities of the cell geometries are minimal with pouch cell having the least capacities. On the other hand, the energy density of pouch cells seems to be significantly higher. This is expected because in a pouch cell, the cathode, separators and anode are stacked instead of wound, as can be seen in **Figure 2**. This approach increases packaging density to the maximum and saves weight, thus increasing energy density of the cell. The packaging density when grouping cylindrical cells is low due to their round shape, and the cell case is comparatively heavy. (Maiser 2014) It is interesting note here is the significantly low value of energy density for the prismatic cell. This could be because despite having a better packaging than cylindrical cells, it has a metallic/steel support for stability, as opposed to pouch cells, and this might increase their overall mass.

#### Internal resistance at 100% SOH for different cell geometries

The unaged cells were subjected to charging and discharging current pulses of 30s each, and the internal resistance developed was calculated at three instants each after 0.5s, 10s and 30s. This internal resistance data was calculated over different State of Charge (SOC) of the cycling process. The resulting data comparison between the different cell geometries at the same conditions is represented in **Figure 3** and **Figure 4**.

It can be seen from the figures that the internal resistance values for cylindrical and prismatic geometries are almost identical in most cases, though the values for pouch cells are much lower. It is interesting to note that there is a sharp drop in internal resistance value at the start of the charging pulse (around 0-10% SOC). A similar phenomenon is observed for pouch cells in the reverse direction in the case of the discharge pulse. While in most cases, the internal resistance values of prismatic and cylindrical are higher than pouch, at the end of the discharge cycle, there is a sharp increase in the internal resistance curve for the pouch cell to reach values quite higher than prismatic and cylinder.

It is also notable from **Figure 3** (charging pulse at 0.3C and 5°C) that there is a characteristic decrease in the value of internal resistance when approaching an SOC of 70% in all geometries at the instants 10s and 30s (though it is negligible at 0.5s). Similarly, from **Figure 4** (discharging pulse at 0.3C and 5°C), during the discharge process, there is sudden peak of internal resistance around the 70% SOC mark for all geometries.

It can be easily concluded from the figures that in general the internal resistances of cylindrical and prismatic cells are higher as expected, at very low SOC values, this parameter value is higher for the pouch cells. Since development of internal resistances is directly related to capacity losses, cylindrical and prismatic cells have higher capacity losses in general. But if pouch cells are used at a lower SOC for longer period of times, this might lead to steeper capacity losses for it.

|  |
| --- |
| C:\Users\AYUSHSENGUPTA\AppData\Local\Microsoft\Windows\INetCache\Content.Word\ires_lowtemp_charging.jpg  **Figure 4. Internal resistance comparison at 100% (0.3C, 5°C and charging pulse)** |
| C:\Users\AYUSHSENGUPTA\AppData\Local\Microsoft\Windows\INetCache\Content.Word\ires_lowtemp_discharging.jpg  **Figure 5. Internal resistance comparison at 100% (0.3C, 5°C and discharging pulse)** |

**Table 6** below enumerates the values of internal resistance at the SOC values of 5%, 50% and 95%.It can be seen that neglecting the sudden surges in internal resistance in pouch cells around the early SOC regions, the internal resistance follows the general trend of: prismatic >= cylindrical > pouch.

**Table 7. Internal resistance of selected SOC stages for a charging pulse for all geometries.**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Geometry | 5% (in mOhm) | | | 50% (in mOhm) | | | 95% (in mOhm) | | |
| Pulse instant | 0.5s | 10s | 30s | 0.5s | 10s | 30s | 0.5s | 10s | 30s |
| **Charging pulse for cells at *5°C/0.3C*** | | | | | | | | | |
| Cylindrical | 3.241 | 4.682 | 5.845 | 3.343 | 5.026 | 6.626 | 3.196 | 4.995 | 8.059 |
|  |  |  |  |  |  |  |  |  |  |
| Prismatic | 3.411 | 4.773 | 5.929 | 3.486 | 5.197 | 6.727 | 3.349 | 5.183 | 8.367 |
|  |  |  |  |  |  |  |  |  |  |
| Pouch | 1.972 | 3.806 | 5.122 | 2.017 | 3.756 | 5.214 | 1.779 | 3.743 | 5.155 |
| **Discharging pulse for cells at *5°C/0.3C*** | | | | | | | | | |
| Cylindrical | 3.741 | 7.299 | 12.294 | 3.381 | 4.686 | 5.909 | 3.225 | 4.455 | 5.530 |
|  |  |  |  |  |  |  |  |  |  |
| Prismatic | 3.792 | 6.538 | 9.616 | 3.516 | 4.764 | 5.927 | 3.411 | 4.558 | 5.582 |
|  |  |  |  |  |  |  |  |  |  |
| Pouch | 2.142 | 7.278 | 16.19 | 1.72 | 3.085 | 4.242 | 1.697 | 2.940 | 3.906 |

#### 

#### Temperature developed over cycling

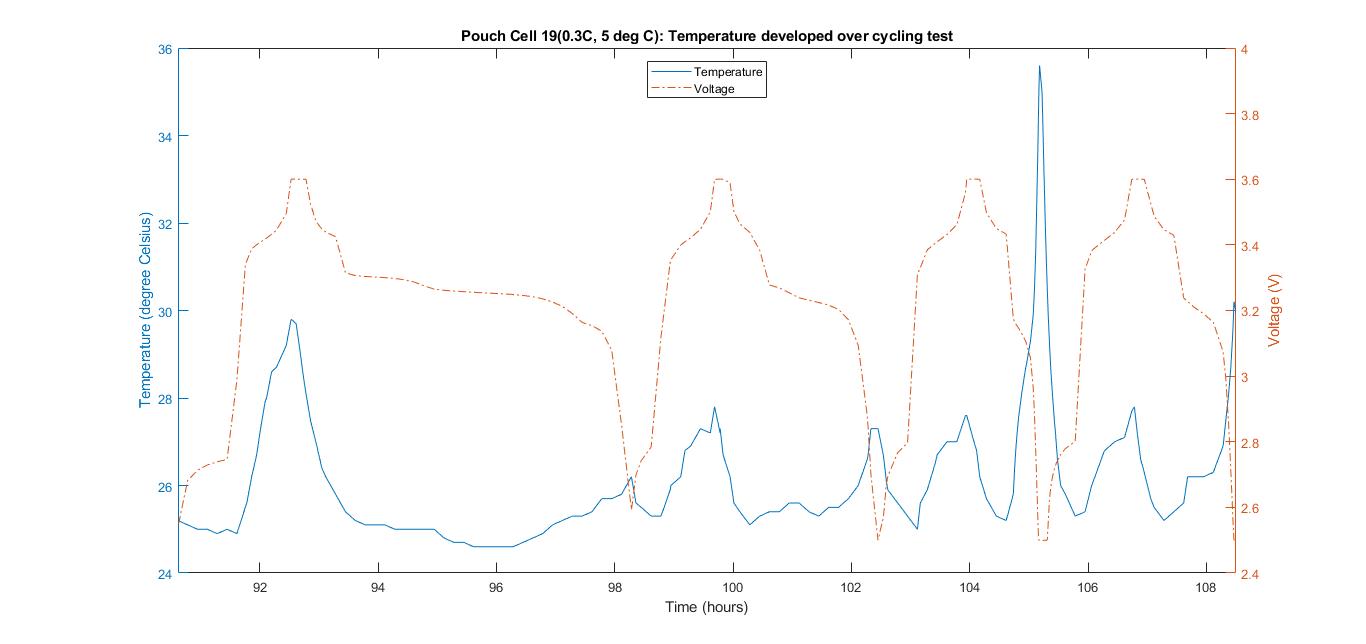
One of the major safety issues in commercial Li-ion batteries especially in EV and HEV is associated with the temperature developed over the cycling period. Therefore, it becomes an important parameter for cell performance evaluation. Data for temperature developed in an unaged cell during the first cycling was obtained from the first extended checkup (ECU). Due to lack of data, temperature profiles were only plotted for cylindrical, prismatic and pouch cells stored at 0.3C and 5°C.

|  |
| --- |
| C:\Users\AYUSHSENGUPTA\AppData\Local\Microsoft\Windows\INetCache\Content.Word\CYL_Cell19_Temp.jpg |
|  |

**Figure 6. Temperature developed during the first extended check-up (ECU) of a cylindrical cell stored at 0.3C and 5°C**

|  |
| --- |
|  |
| C:\Users\AYUSHSENGUPTA\AppData\Local\Microsoft\Windows\INetCache\Content.Word\PRISM_Cell20_Temp.jpg |

**Figure 7. Temperature developed during the first extended check-up (ECU) of a prismatic cell stored at 0.3C and 5°C**



**Figure 8.Temperature developed during the first extended check-up (ECU) of a pouch cell stored at 0.3C and 5°C**

A study of **Figure 5** (Cylindrical cells), **Figure 6** (Prismatic cells) and **Figure 7** (Pouch cells) shows a similar trend. After the cycling involving discharge with a rate 1C or the third cycle, there is a sudden increase in the temperature developed in the cells. The temperature peak is the highest at the 2C discharge. A further look at the curves show that the temperature peak in prismatic and cylindrical geometries are higher than the pouch geometry. This is a reasonable conclusion since the problems with thermal management and a lack of proper passage for waste heat in prismatic cells are well known. This mostly because of the higher mechanical stresses. (Eric Maiser 2014) This leads to the temperatures building inside especially when subjected to rapid discharging currents. A cylindrical cell has the least surface area for heat dissipation (Zhao et al. 2016), which explains the higher temperatures developed in it.

The following table shows a comparison of temperature difference developed in all the cells during the different stages of first 1C charge and 0.5C, 1C and 2C discharge.

**Table 8. Temperature difference developed at different stages of ECU and charge/discharge cycles for all geometries**

|  |  |  |  |
| --- | --- | --- | --- |
| Cell Type | First 1C Charge  (°C or K) | 1C discharge  (°C or K) | 2C discharge  (°C or K) |
|  |  |  |  |
| Cylindrical | 4.14 | 1.83 | 10.19 |
|  |  |  |  |
| Prismatic | 2 | 1.34 | 10.51 |
|  |  |  |  |
| Pouch | 4.8 | 2.5 | 10.30 |
|  |  |  |  |

**Table 7** shows that while temperature change in pouch cell at 1C charge and 1C discharge are comparatively higher, the increase is almost similar in the three geometries at 2C discharge. Thin electrodes can enhance the fluency of ion diffusion and improve the electrochemical reactions which helps high rate discharges and long term performances due to the mild temperature variation (Zhao et al. 2016), which might also indicate the lower temperature developed in pouch cells and no rapid increase in temperature at 2C.

### Ageing effects on cells of different geometries

Having done a comparison of the different geometries of Generation 0 LFPC cells at beginning of life (BOL) or at 100% SOH, the next part involves observing the effects of ageing of different geometries. In this section, the tests are restricted to the discharging and charging pulse tests for different aged cells and for ease of data representation, only one aged state along with the unaged state are used, that is, the first extended check-up (ECU) at 100% SOH and the second extended check-up (ECU) after certain ageing time.

#### Ageing characteristics over equivalent full cycle (EFC)

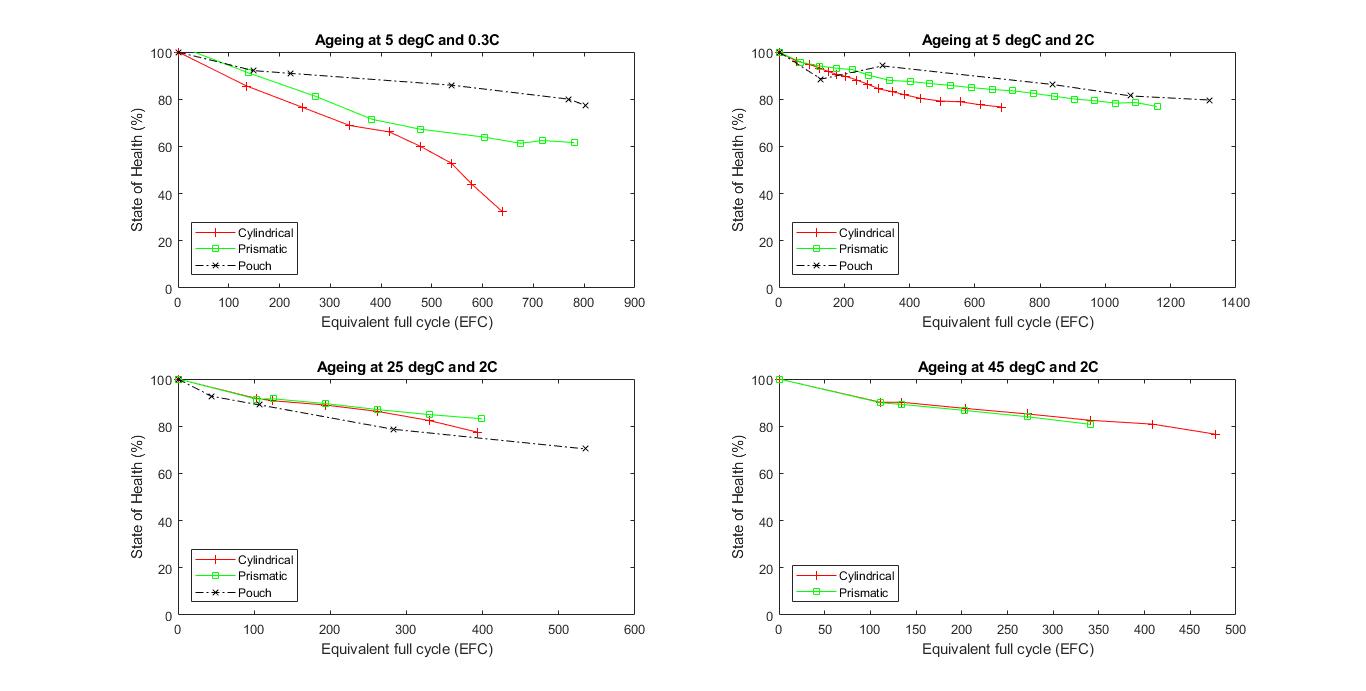
The capability of a cell to achieve multiple equivalent full cycle number before it reaches end of life (EOL i.e. around 70-80% SOH) is essential to determine its usability. Because of reducing net capacity of the cell over ageing time, the term equivalent full cycle is used instead of total cycle number.

The equivalent full cycles is calculated using the following formula:

….Equation 4, (Svens et al. 2015)

Here, *Neq* = equivalent full cycles, *Wtot* = accumulated energy throughput for the cycled cell, *Unom* = specified nominal battery voltage, *Qinit* = measured initial battery capacity.

**Figure 8** shows the equivalent number of cycles for each geometry of cell for different cell conditions over the ageing period as shown by the State of Health (SOH) (NOTE: Pouch cell data for 45°C and 2C were not available).



**Figure 9. Ageing of different cell geometries over equivalent cycle numbers obtained.**

For cylindrical cells, it is observed that an increase in C-rate of cycling reduces the capacity drop of the cell while the number of equivalent full cycles almost remain. Further, an increase in temperature has marginal change on the number of equivalent full cycles (marginal decrease at 25°C from 5°C and marginal increase at 45°C from 25°C), whereas the capacity loss remains almost the same.

For prismatic cells, an increase in C-rate of cycling increases significantly the equivalent full cycles and reduces the capacity deterioration as well. But an increase in temperature from 5°C to 25°C significantly brings down the number of equivalent full cycles, while the capacity deterioration almost remains the same. There is a further decrease in equivalent full cycles when the temperature is increased to 45°C, while the capacity deterioration is almost unchanged.

The pouch geometry shows a low capacity deterioration in all conditions of temperature and C-rate, and it also does not undergo a big change. It also has a higher number of equivalent full cycles in all cases as compared to cylindrical and prismatic geometries. An increase in C-rate has a significant increase in the equivalent full cycles, though it drops down when the temperature is increased from 5°C to 25°C.

In conclusion, it can be inferred from these results that for cylindrical geometry goes through improvement in number of cycles and less deterioration in capacity by an increase in C-rate of cycling. For the prismatic packaging, C-rate has significant improvement in cycles numbers and its life as well, while an increase in temperature has a negative impact on cycles. Pouch cells have the best ageing performance under the given conditions with respect to cylindrical and pouch cells. It has a good life in all conditions but goes through a loss of cycles at elevated temperatures.

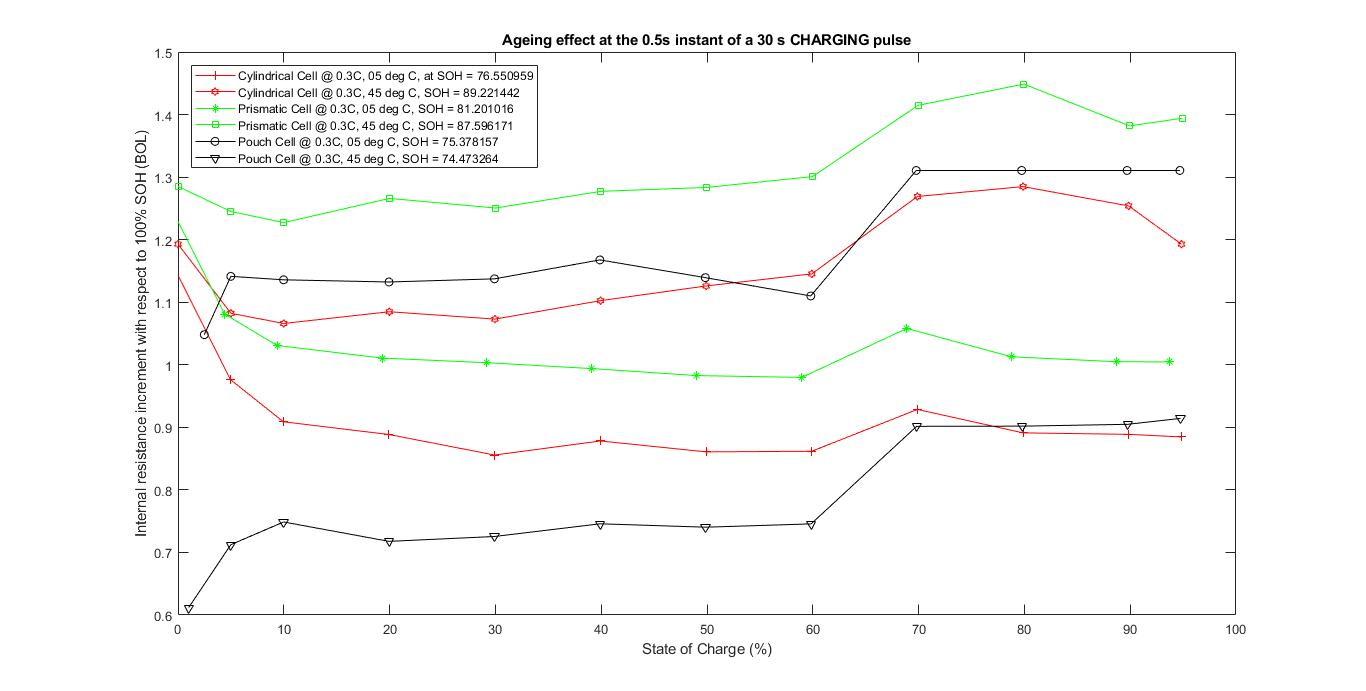
#### Change in internal resistance by ageing (during a charging/discharging pulse)

Ageing leads to an increase in internal resistance and higher the resistance increase higher is the capacity loss of the cell/ Therefore, it is more interesting to note the incremental change in internal resistance over ageing period on the different cell geometries. This section analyzed the incremental change in internal resistance during charging and discharging. The plots with the absolute values of internal resistances can be found in **APPENDIX**

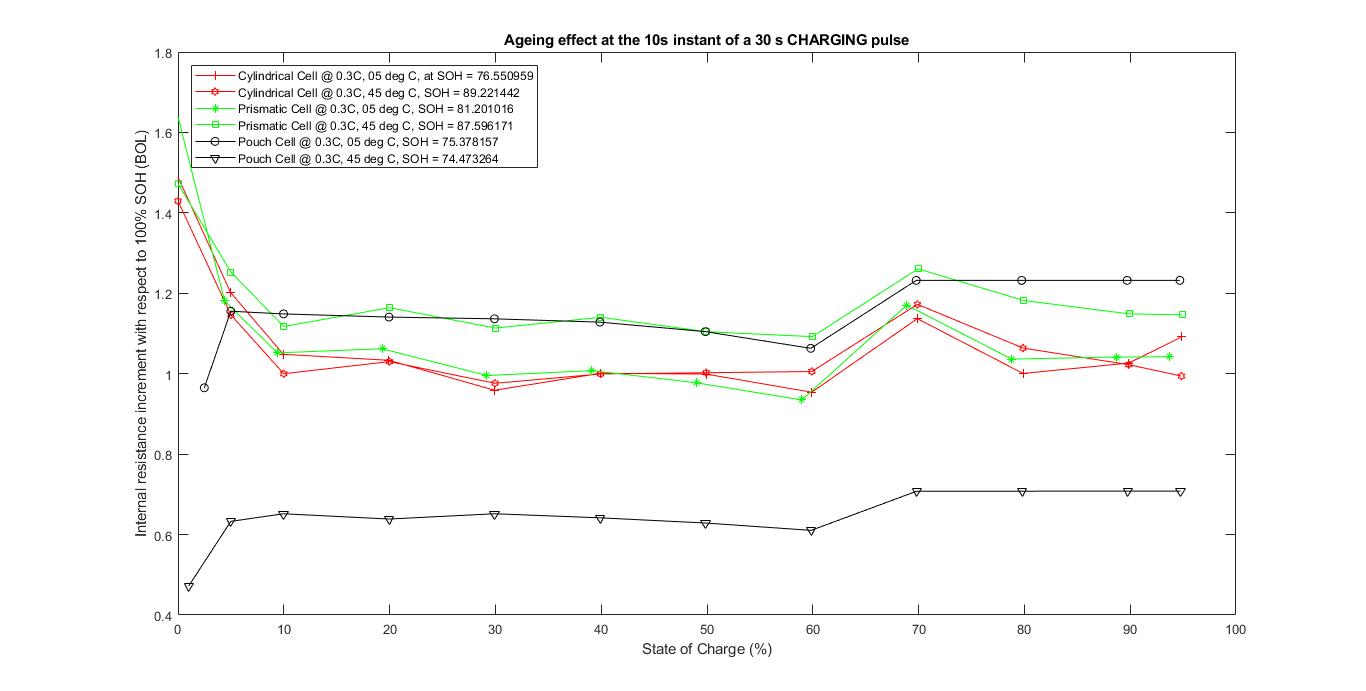
**Figure 9**, **Figure 10** and **Figure 11** show the incremental change in internal resistance of a cell during a 30s charging pulse at different instants of 0.5s, 10s and 30s, compared over different geometries stored at different temperatures. The incremental change is calculated by taking the ratio of the internal resistance of the cell at an aged stage with respect to the internal resistance at 100% State of Health (SOH) or unaged stage.

A very first observation shows that a pouch cell at elevated temperatures (45°C) shows a positive change, that is a reduction in the internal resistance value (ratio less than 1) at all time instants of measurement. Whereas a prismatic cell at the same temperature shows the highest increase in internal resistance value at almost all measurement, though the difference is negligible compared to the other geometries. **Table 8** shows that the increment is highest for the prismatic cell stored at 45°C with a value of 1.394, while the pouch cell at 45°C shows a maximum decrease of almost by half.

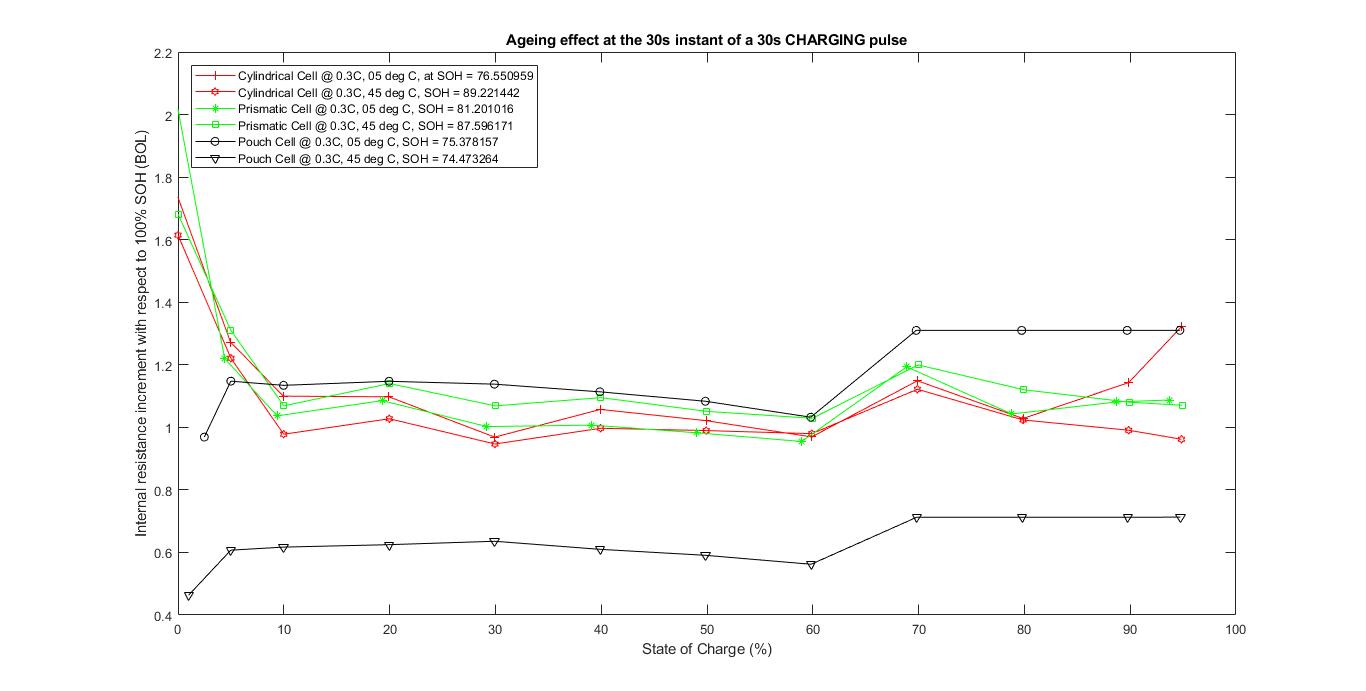
However, on comparing the absolute values, it can also be seen that the internal resistance values for pouch cells under most conditions are the least.



**Figure 10. Incremental internal resistance (compared to 100% SOH) at the 0.5s instant of a 30s charging pulse.**



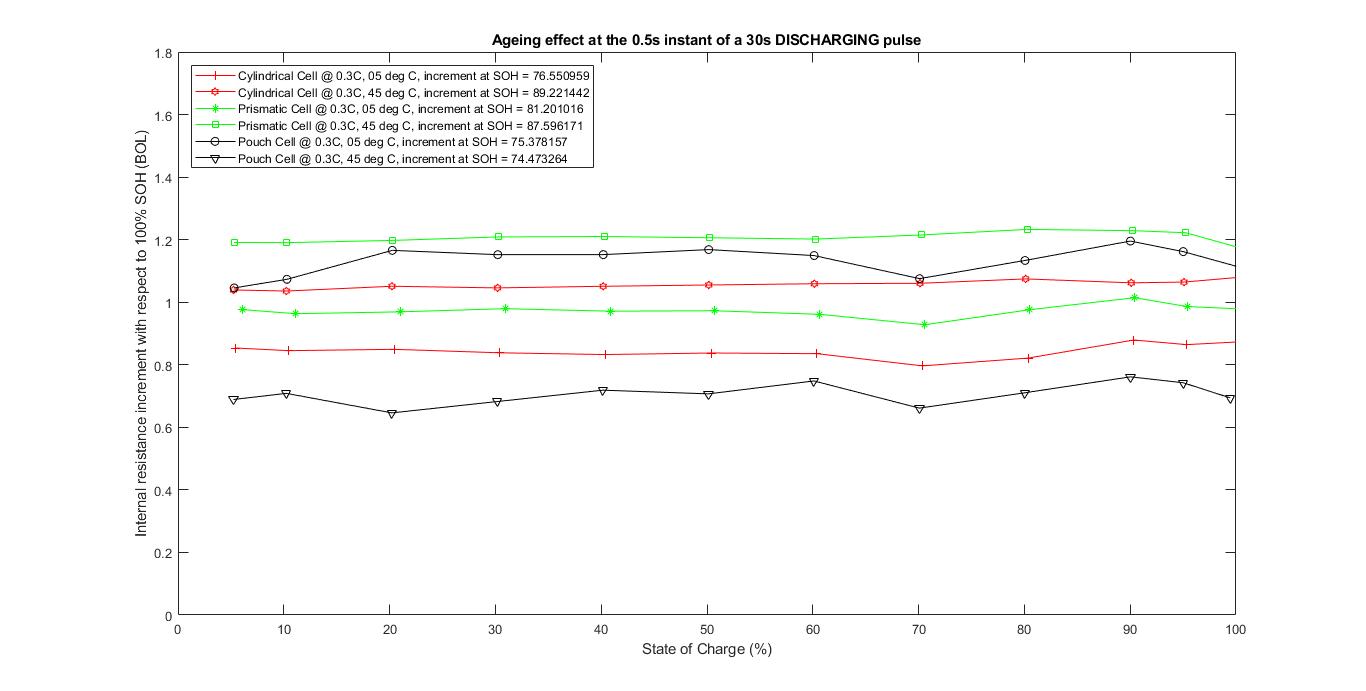
**Figure 11. Incremental internal resistance (compared to 100% SOH) at the 10s instant of a 30s charging pulse.**



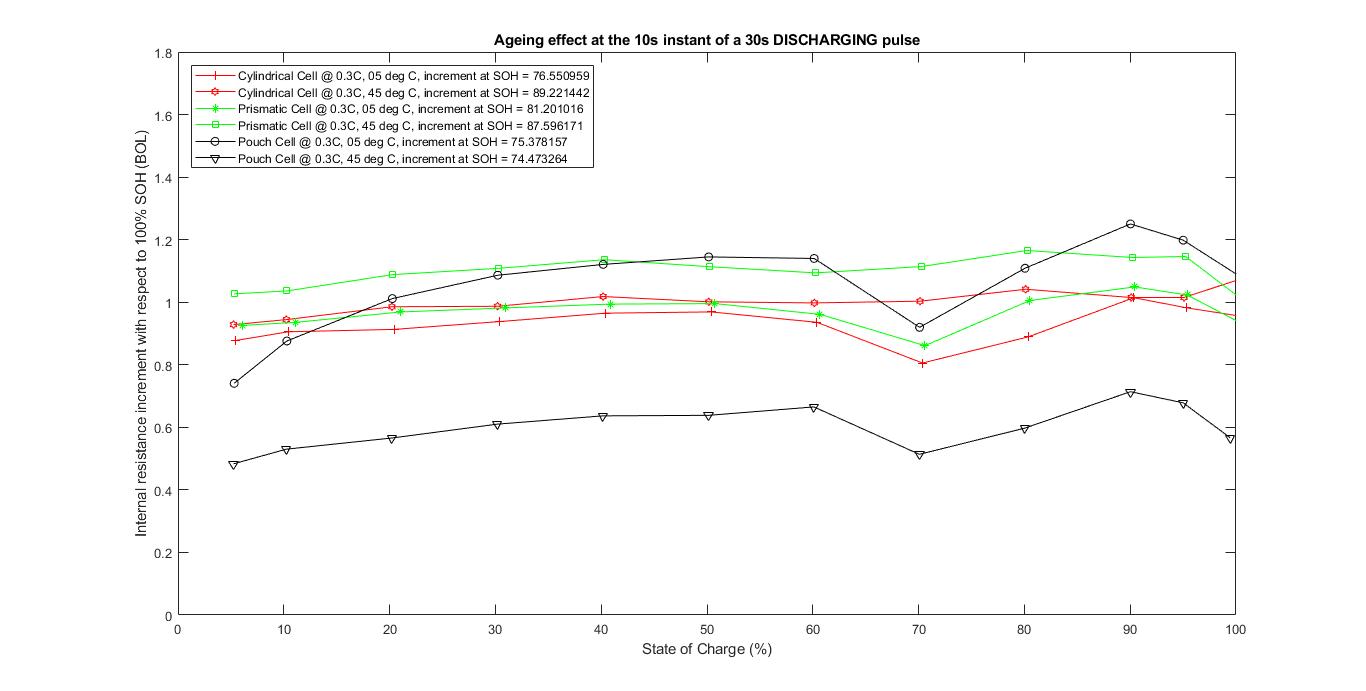
**Figure 12. Incremental internal resistance (compared to 100% SOH) at the 30s instant of a 30s charging pulse.**

**Figure 13**, **Figure 14** and **Figure 14** show the incremental change in internal resistance of a cell during a 30s discharging pulse at different instants of 0.5s, 10s and 30s, compared over different geometries stored at different temperatures.

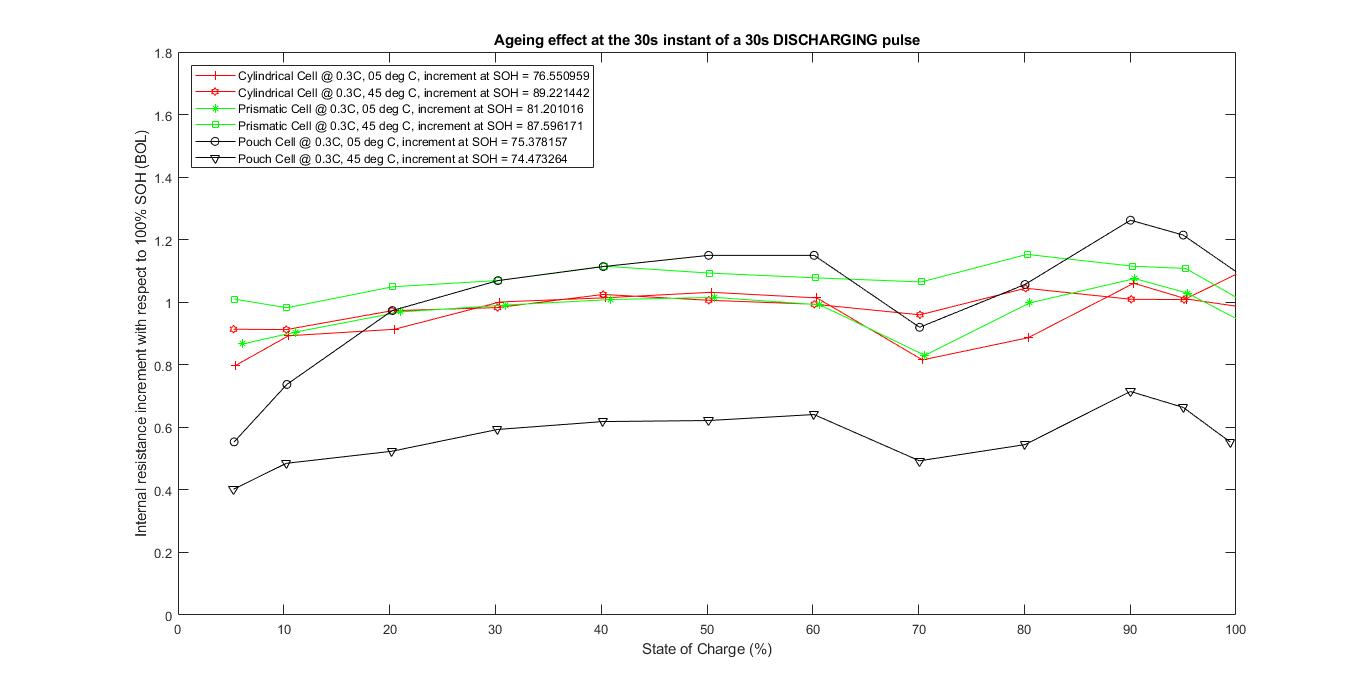
For the discharge pulses, the internal resistances increase by less magnitude than in the case of charging pulse (max increase is 1.222) but the pouch cell at elevated temperatures shows a peculiar trend under a discharge pulse. At 45°C, the internal resistance value in the case of pouch cells shows a constant decrease as compared to the case at 100% SOH with a value up to almost 40% of the unaged cells. This can perhaps be explained by the results from the last section where the ageing of the pouch cells did not suffer by an increase in temperature or increase in C-rate. Therefore it brings a further stability to the functioning of the pouch type cells.



**Figure 13. Incremental internal resistance (compared to 100% SOH) at the 0.5s instant of a 30s discharging pulse.**



**Figure 14. Incremental internal resistance (compared to 100% SOH) at the 10s instant of a 30s discharging pulse.**



**Figure 15. Incremental internal resistance (compared to 100% SOH) at the 30s instant of a 30s discharging pulse.**

From the sections in page number 10 and page number 11, it can be inferred that the ageing of the cells can predicted based on internal resistance increment values and the effect of temperature and cycling on the equivalent cycle number and capacity drop. That is, a decrease in internal resistance in a 30s charge/discharge test may indicate a gradual deterioration or decay of the cell life as can be seen in the case of pouch cells

*NOTE: In* ***Table 8*** *and* ***Table 9****, the shaded rows refer to the increment ratio of the internal resistance, while the unshaded rows are the absolute values of internal resistance at the aged SOH mentioned with the geometry column. Cyl = Cylindrical, Pri = Prismatic, Po = Pouch*

**Table 9. Changing in internal resistance due to ageing (for charging pulses)**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | 5% | | | 50% | | | 95% | | |
| Pulse | 0.5s | 10s | 30s | 0.5s | 10s | 30s | 0.5s | 10s | 30s |
| **Charging pulse for cells at *5°C/0.3C*** | | | | | | | | | |
| Cyl  76.6% | 3.110 | 5.685 | 7.433 | 2.874 | 5.020 | 6.767 | 2.824 | 5.449 | 10.65 |
| *0.976* | ***1.146*** | ***1.273*** | *0.861* | ***1.002*** | ***1.021*** | *0.885* | *0.994* | ***1.325*** |
| Pri  81.2% | 3.630 | 5.580 | 6.980 | 3.426 | 5.08 | 6.610 | 3.370 | 5.450 | 9.110 |
| ***1.081*** | ***1.252*** | ***1.196*** | *0.983* | ***1.104*** | *0.979* | ***1.005*** | ***1.146*** | ***1.087*** |
| Po  75.4% | 2.244 | 4.393 | 5.867 | 2.296 | 4.149 | 5.649 | 2.325 | 4.608 | 6.750 |
| ***1.141*** | *0.633* | ***1.147*** | ***1.139*** | *0.629* | ***1.083*** | ***1.311*** | *0.708* | ***1.310*** |
| **Charging pulse for cells at 4*5°C/0.3C*** | | | | | | | | | |
| Cy  89.2% | 2.877 | 4.666 | 6.125 | 2.820 | 4.325 | 5.804 | 2.657 | 4.193 | 6.544 |
| ***1.082*** | ***1.202*** | ***1.221*** | ***1.126*** | *0.999* | *0.990* | ***1.193*** | ***1.091*** | *0.962* |
| Pri  87.6% | 3.742 | 5.442 | 6.847 | 3.670 | 5.036 | 6.352 | 3.574 | 5.078 | 7.331 |
| ***1.245*** | ***1.172*** | ***1.310*** | ***1.284*** | *0.977* | ***1.051*** | ***1.394*** | ***1.042*** | ***1.071*** |
| Po  74.5% | 1.497 | 2.497 | 3.333 | 1.627 | 2.476 | 3.190 | 1.708 | 2.768 | 3.809 |
| *0.712* | *1.155* | *0.607* | *0.740* | *1.105* | *0.591* | *0.914* | *1.232* | *0.713* |

**Table 10. Changing in internal resistance due to ageing (for discharging pulses)**

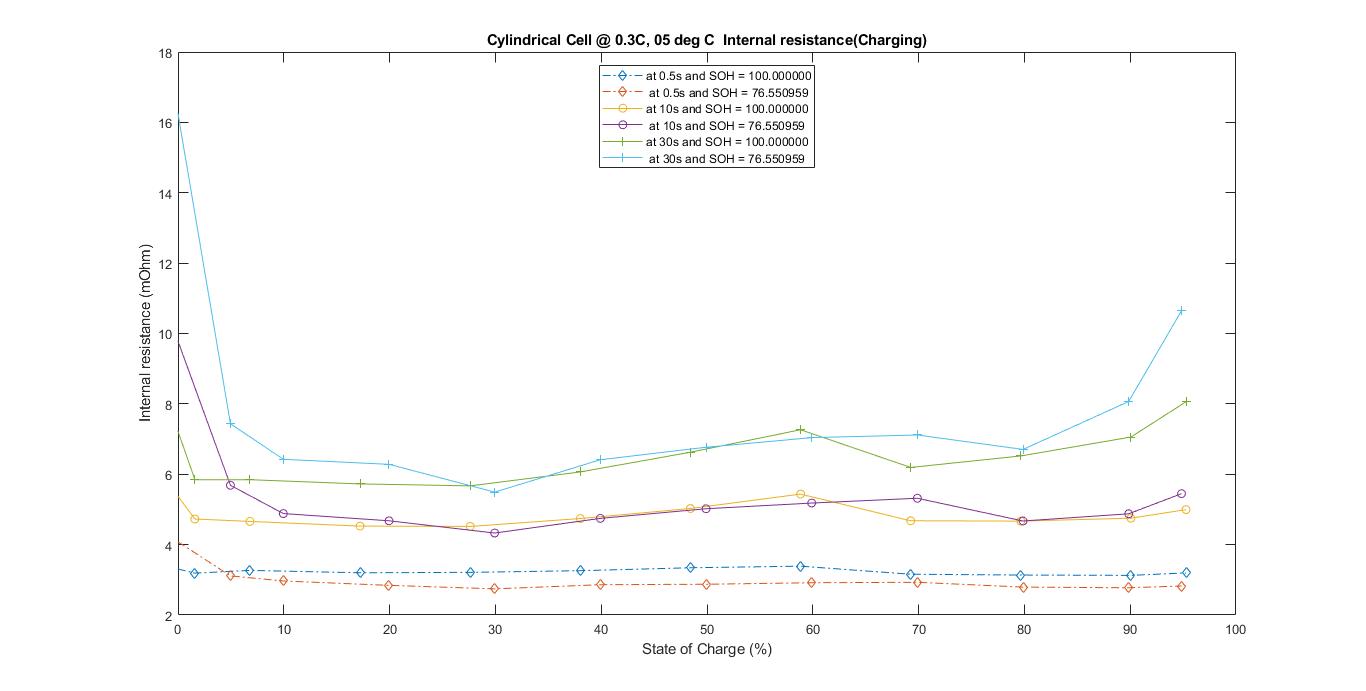
|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | 5% | | | 50% | | | 95% | | |
| Pulse | 0.5s | 10s | 30s | 0.5s | 10s | 30s | 0.5s | 10s | 30s |
| **Discharging pulse for cells at *5°C/0.3C*** | | | | | | | | | |
| Cyl  76.55% | 3.247 | 6.767 | 10.741 | 2.830 | 4.541 | 6.096 | 2.792 | 4.385 | 5.598 |
| *0.853* | *0.877* | *0.798* | *0.837* | *0.965* | ***1.031*** | *0.864* | *0.982* | ***1.010*** |
| Pri  81.20% | 3.731 | 6.722 | 10.211 | 3.420 | 4.744 | 6.019 | 3.364 | 4.664 | 5.746 |
| *0.976* | *0.926* | *0.866* | *0.972* | *0.994* | ***1.015*** | *0.986* | ***1.023*** | ***1.029*** |
| Po  75.38% | 2.150 | 4.720 | 7.070 | 2.010 | 3.532 | 4.878 | 1.972 | 3.524 | 4.745 |
| ***1.045*** | *0.740* | *0.553* | ***1.168*** | ***1.120*** | ***1.149*** | ***1.161*** | ***1.198*** | ***1.214*** |
| **Discharging pulse for cells at 4*5°C/0.3C*** | | | | | | | | | |
| Cy  89.22% | 3.029 | 5.641 | 8.909 | 2.748 | 3.991 | 5.221 | 2.701 | 3.858 | 4.901 |
| ***1.039*** | *0.928* | *0.913* | ***1.055*** | ***1.018*** | ***1.006*** | ***1.064*** | ***1.015*** | ***1.008*** |
| Pri  87.60% | 3.890 | 6.387 | 9.567 | 3.630 | 4.802 | 5.927 | 3.564 | 4.649 | 5.591 |
| ***1.190*** | ***1.026*** | ***1.009*** | ***1.206*** | ***1.136*** | ***1.093*** | ***1.222*** | ***1.146*** | ***1.108*** |
| Po  74.47% | 1.392 | 2.648 | 4.112 | 1.307 | 2.030 | 2.700 | 1.325 | 2.040 | 2.643 |
| *0.689* | *0.483* | *0.402* | *0.707* | *0.636* | *0.621* | *0.742* | *0.678* | *0.663* |

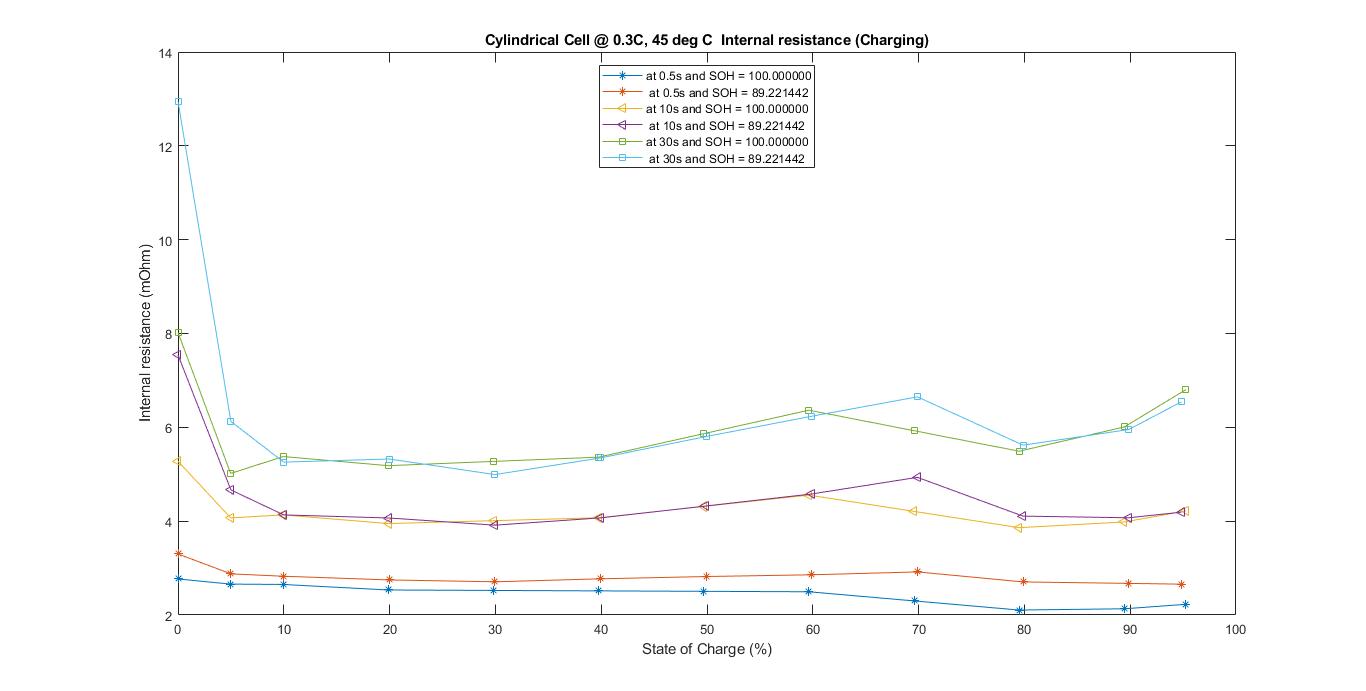
# Bibliography

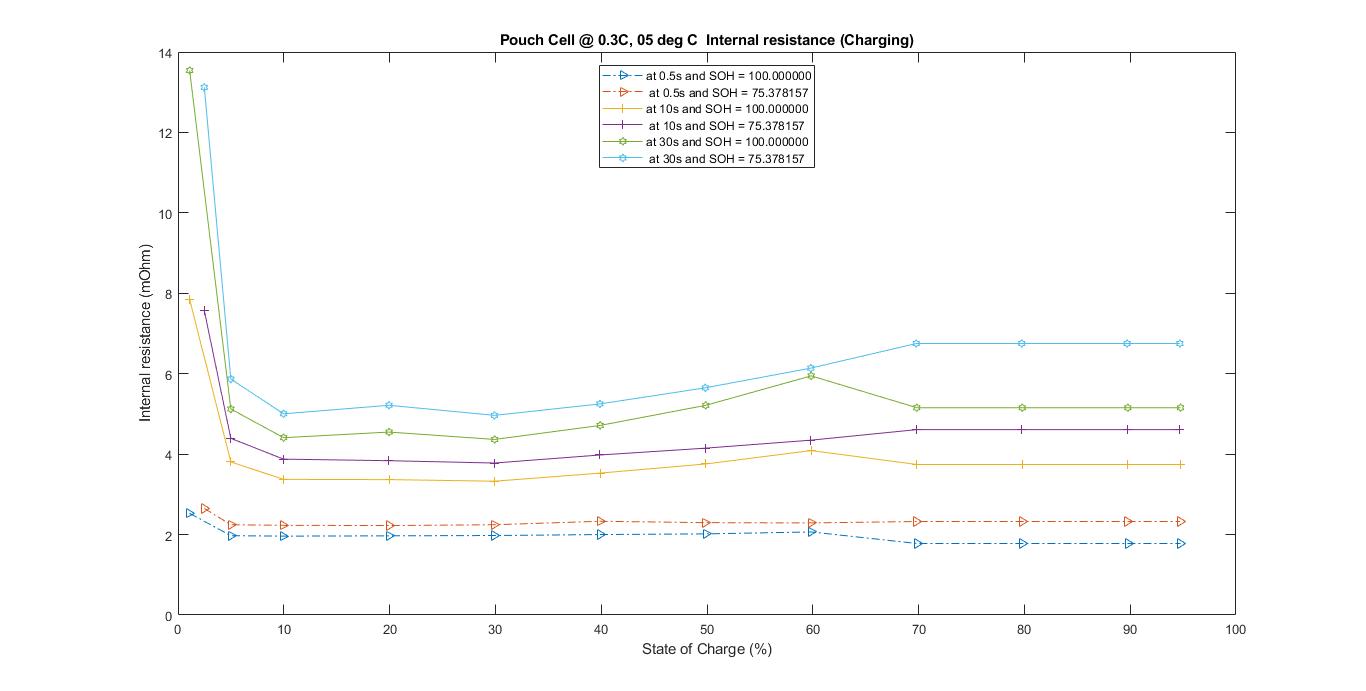
**There are no sources in the current document.**

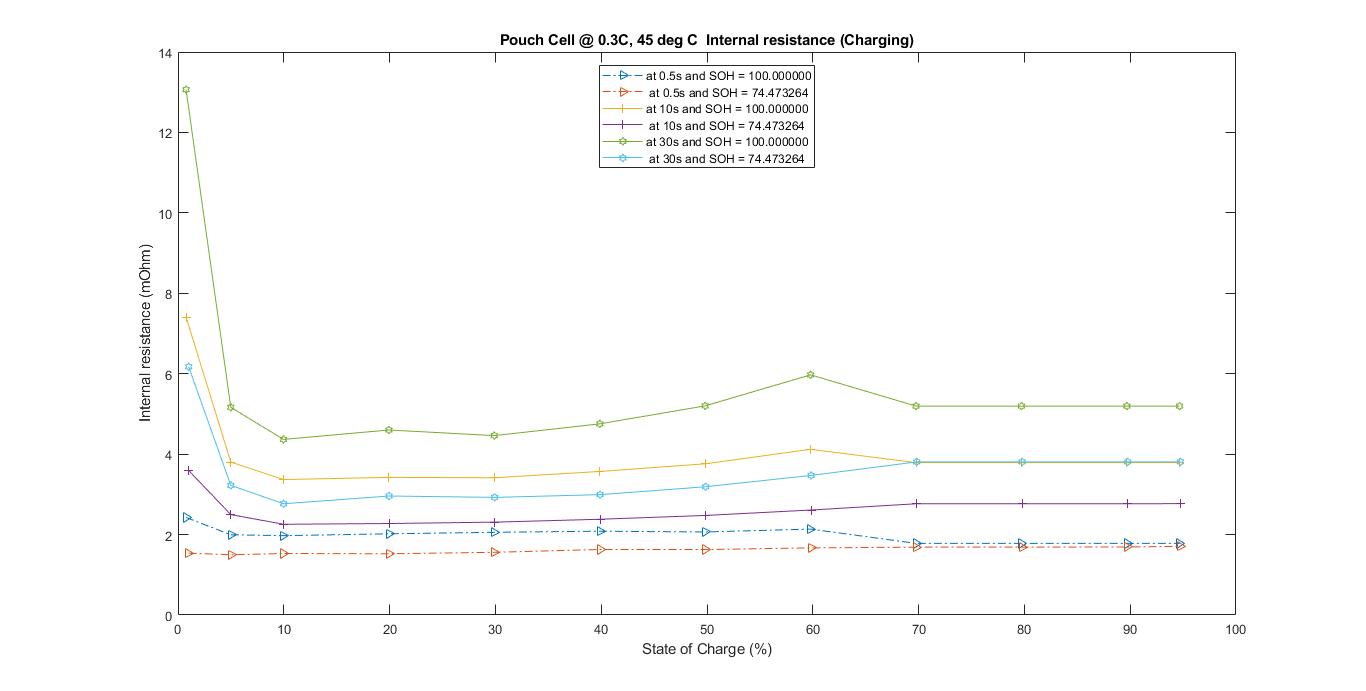
# **APPENDIX**

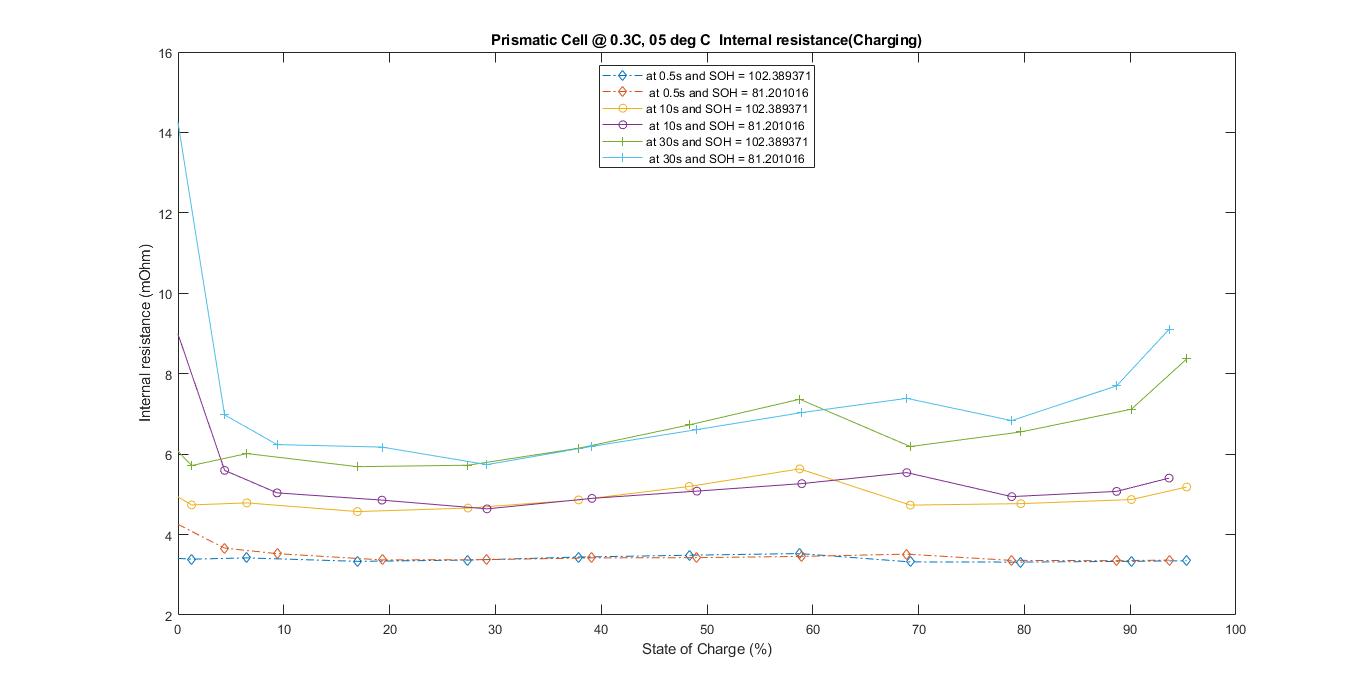
#### *A1.* Internal resistance curves for two different SOH values for charging pulses

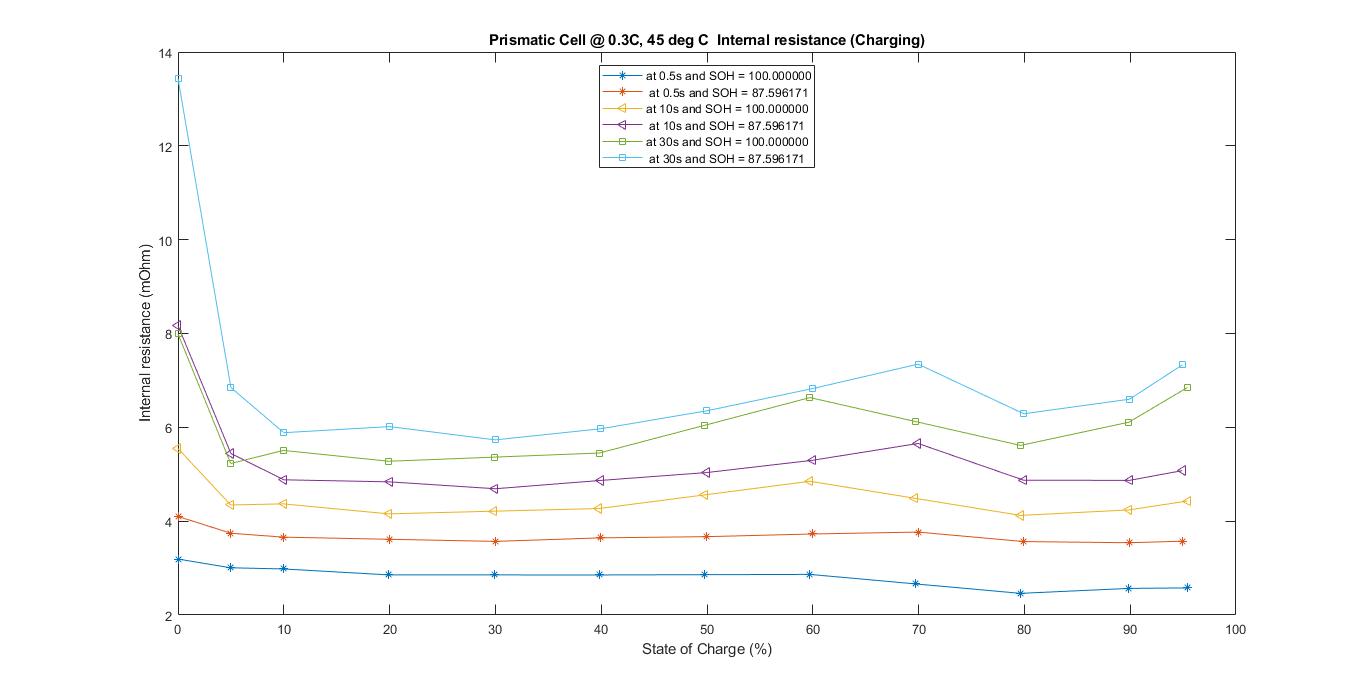




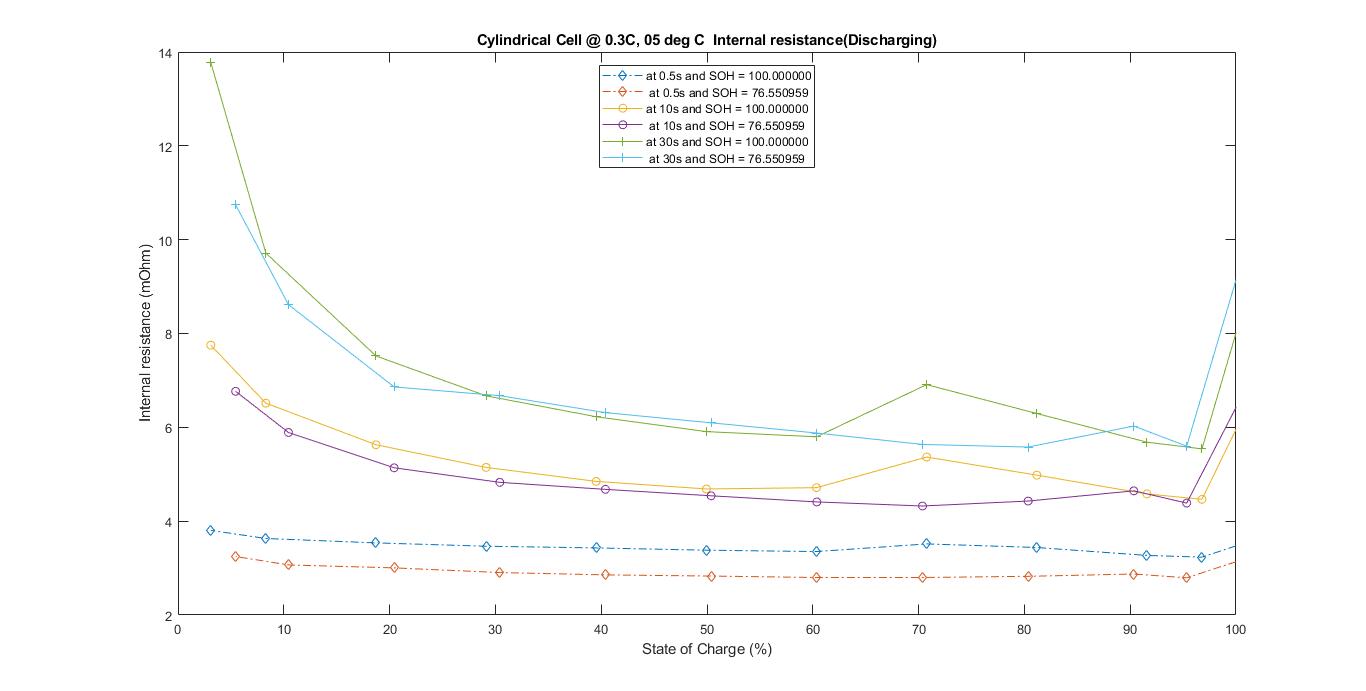


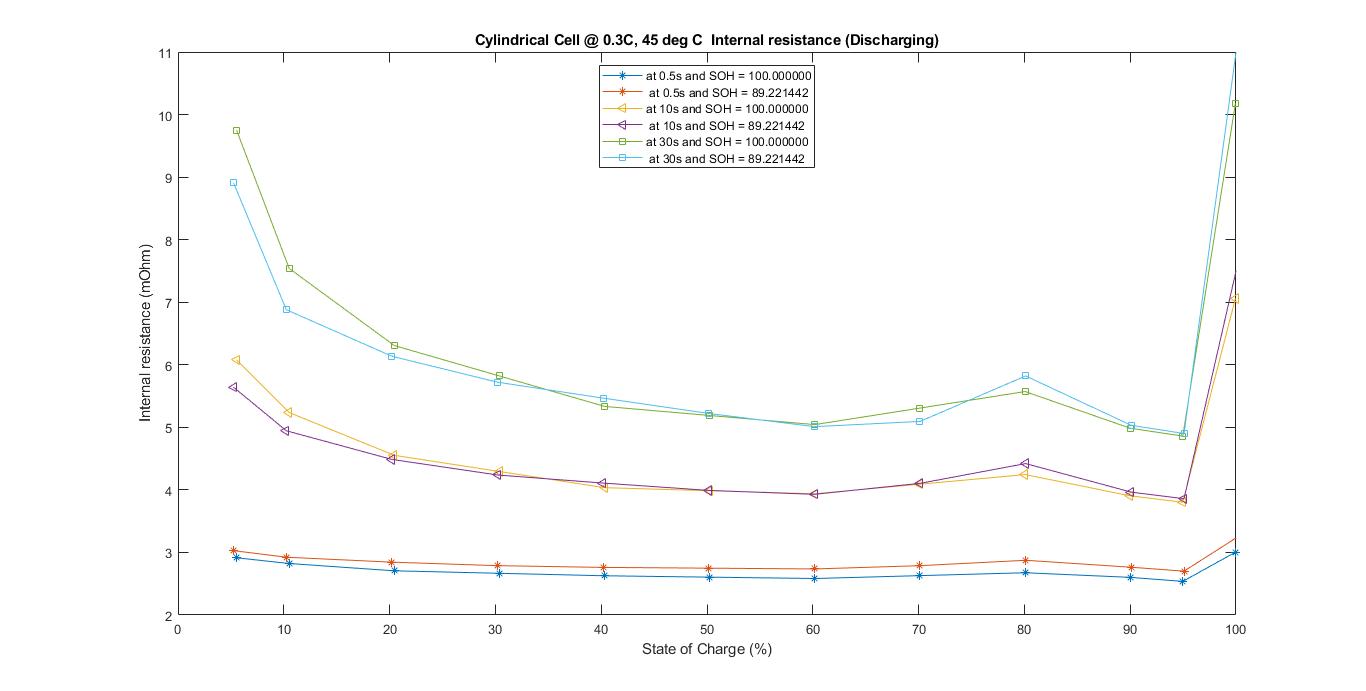


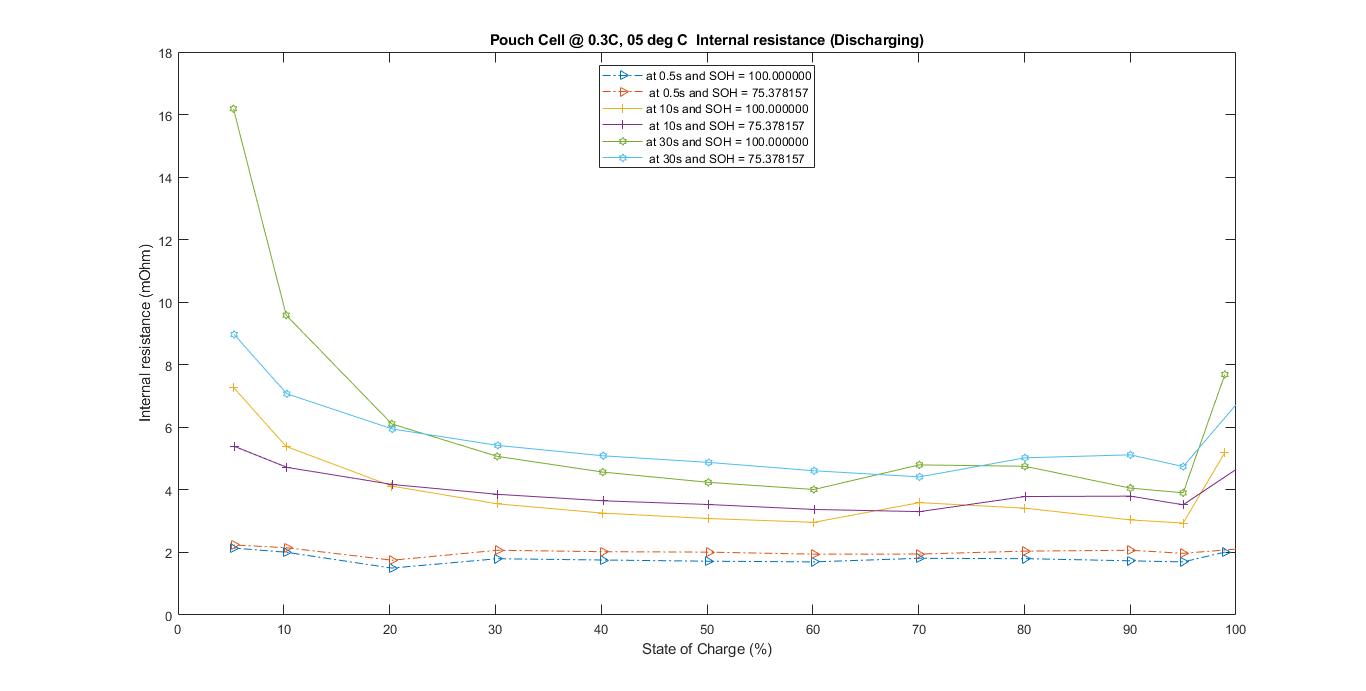


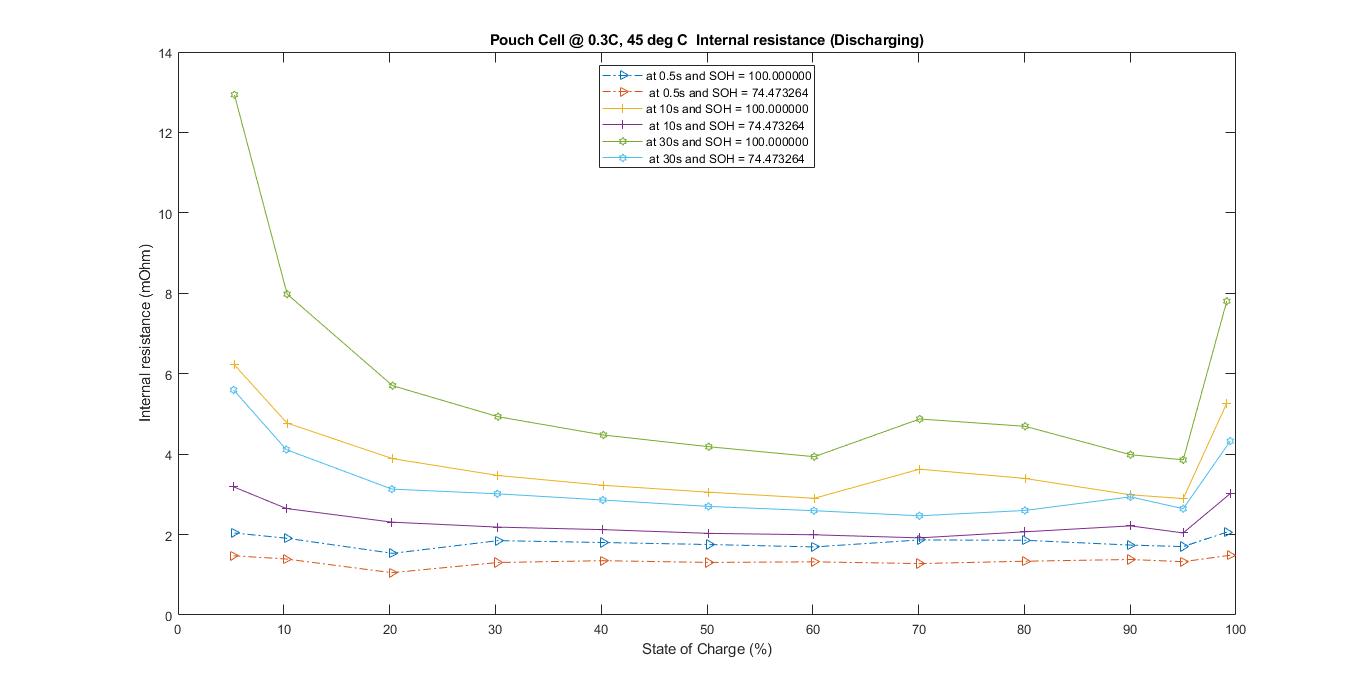


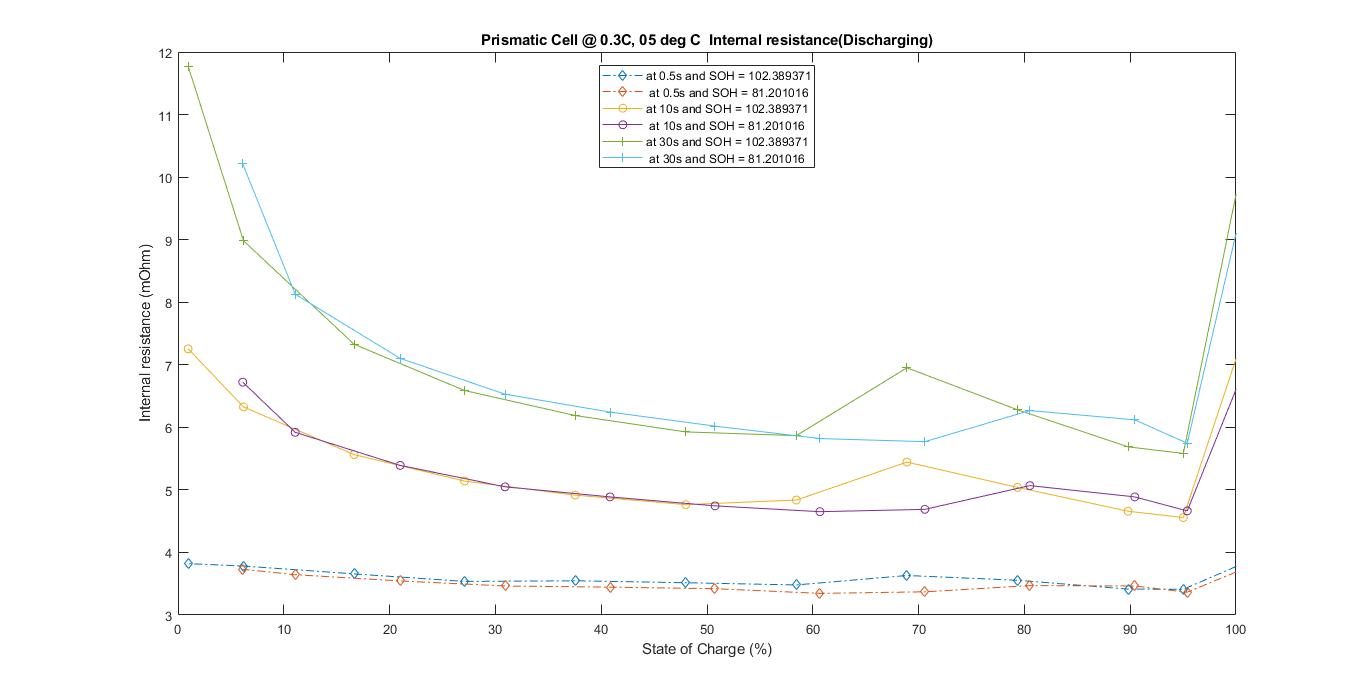
#### A2. Internal resistance curves for two different SOH values for charging pulses

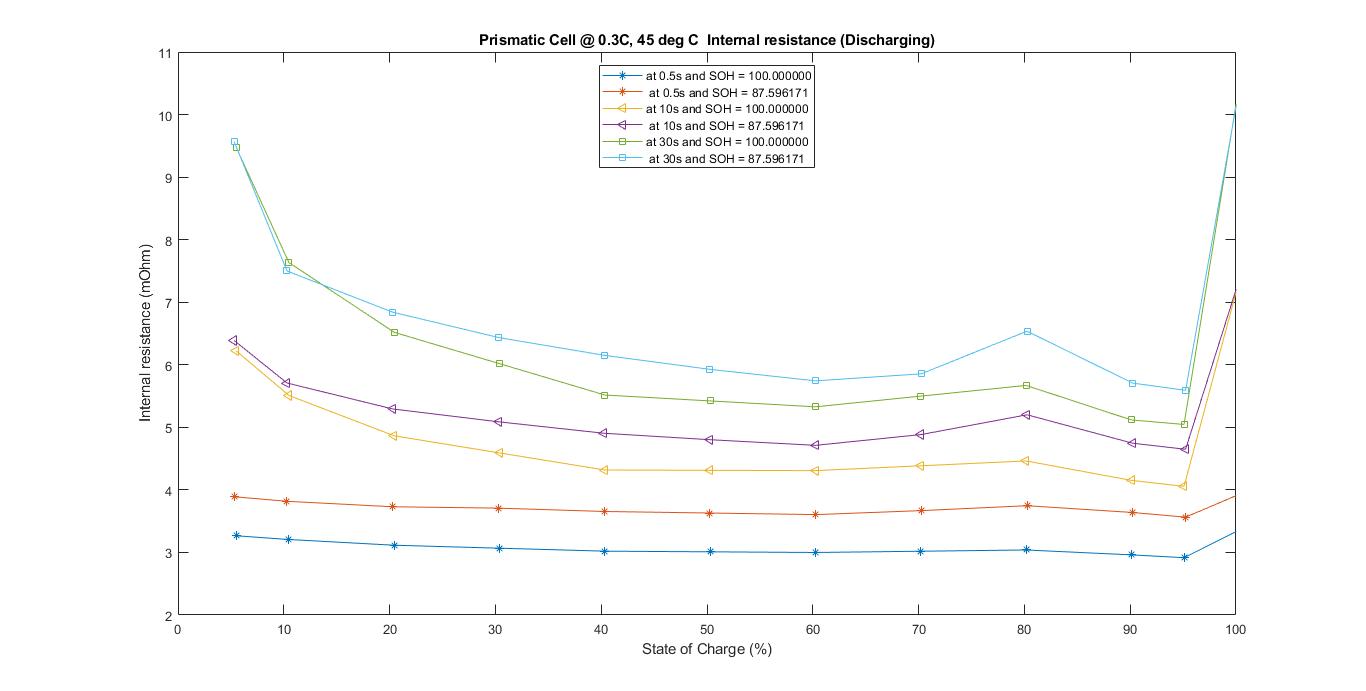












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1. for a 30s pulse [↑](#footnote-ref-1)
2. normal cycling, rate tests upto 12A [↑](#footnote-ref-2)
3. for a 30s pulse [↑](#footnote-ref-3)
4. for charging [+5, +55] [↑](#footnote-ref-4)
5. for charging [+5, +55] [↑](#footnote-ref-5)
6. Energy density, , where *Q* = Capacity, *Vnom* = nominal voltage, *m* = mass

   [↑](#footnote-ref-6)
7. the weight differs from value in **Table 4** because the reception test results mentioned refer only to the cells chosen to be tested within the scope of this work. [↑](#footnote-ref-7)
8. Curved surface area of cylindrical cell = [↑](#footnote-ref-8)
9. Curved surface area of prismatic cell, considered to be cuboidal = [↑](#footnote-ref-9)
10. The nominal voltage for pouch could not be found from the data but for uniformity it has been assumed to be almost equal to prismatic and cylindrical. [↑](#footnote-ref-10)