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Advanced Deposition Methods for Bipolar Battery Active Materials

Improving High-Rate Performance & Cycle Life

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BACKGROUND

Paste to grid adhesion in lead acid batteries is a vital factor in determining not only formation efficiency, but also initial performance, high-rate performance and cycle life.

A standard monopolar grid has an open grid pattern through which the active material can flow, envelop and connect to both itself and to the grid wires. In this way, both adhesion and cohesion of the paste play a role in the strength of the connection to the grid.

Other factors including wire shape, surface roughness of the lead, the paste temperature, formula, additives, the cure and others all have influence as well.

Bipolar electrodes, by their nature, have a disadvantage as far as active material connection. Because there is no way for the paste to go through, connection quality is solely based on the condition of the surface lead, the paste formula and conditions, and the application method.

Gridtential Energy has tested methods ranging from pre-cured slab placement to hand application to a most recent method of vibratory application.

Testing adhesion quality is a challenge for bipole electrodes as the drop test does not always result in consistent data. We have examined internal resistance as the indicator of the quality of the connection of the active material to the bipolar electrode surface.

INTERNAL RESISTANCE MEASUREMENTS

$$R= (V2-V1)/(I2-I1)$$

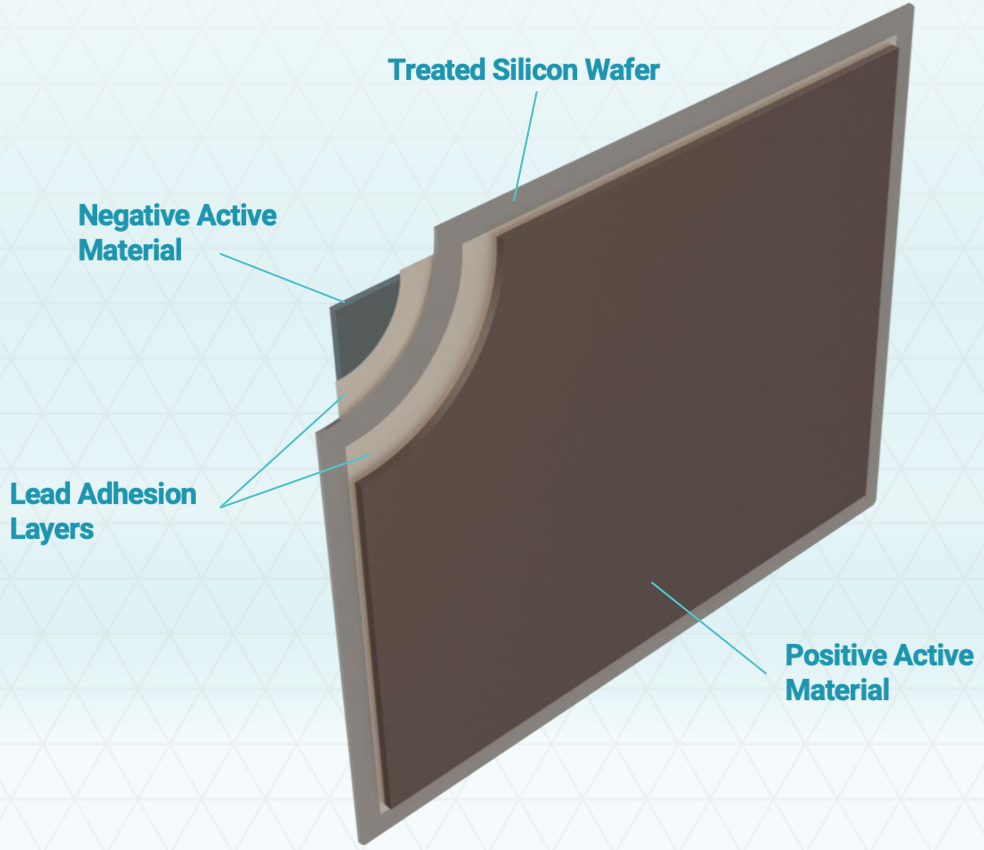
For this study, internal resistance is calculated at intervals throughout formation, performance tests and cycling.

The internal resistance is calculated using the formula R= (V2-V1)/(I2-I1) where *t=<0.01 sec and V1 and I1 are at rest*

Insignificant rest periods were inserted into the formation profile to collect resistance data

Data collection during performance and DCA testing as well as cycling were taken from exiting data collected by the testing circuits.

SILICON JOULE BIPOLE



Each Bipole consists of

Proprietary treated Silicon wafer (~900um thick)

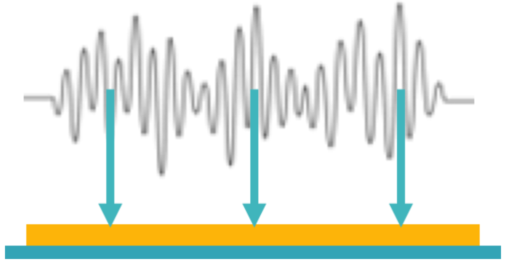
Electrodeposited high-purity Pb Adhesion layers on both sides (<300um)

Positive Active Material (PAM) **and Negative Active Material** (NAM) applied to opposing sides

Bipoles measured 146mm x 178mm for this experiment

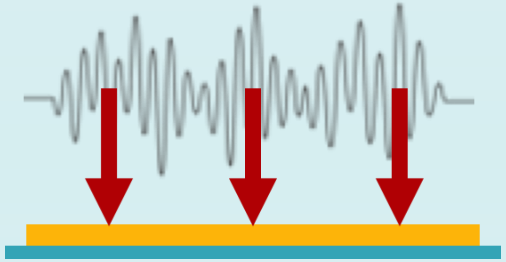
Active material pasted to ~2mm thick on both sides

VARIABLE PASTE APPLICATION DESCRIPTIONS



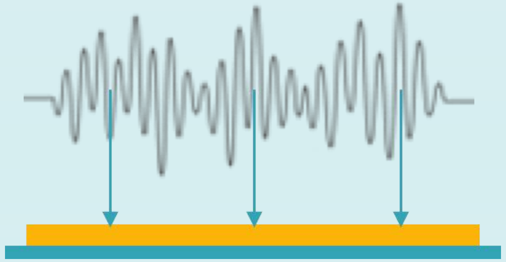
Standard

This is the control method of application used by **Gridtential Energy**.



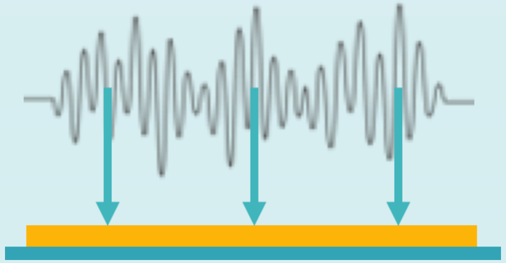
Increased Force

More work was applied to the paste to attempt to improve intimacy and adhesion at the paste-wafer interface. The goal was to maximize the surface are of contact. The hope was this would result in lower resistance and higher performance.



Decreased Force

A gentler application method was used to reduce the surface area of contact. It was expected that higher resistance shorter cycle life would result.



Chemistry Change

The standard application method was used in conjunction with an additive meant to increase pH in the mix and therefore increase the ionic activity at the paste-bipole interface. The hope was to see a stronger adhesion layer and lower resistance.

PASTE FORMULAS

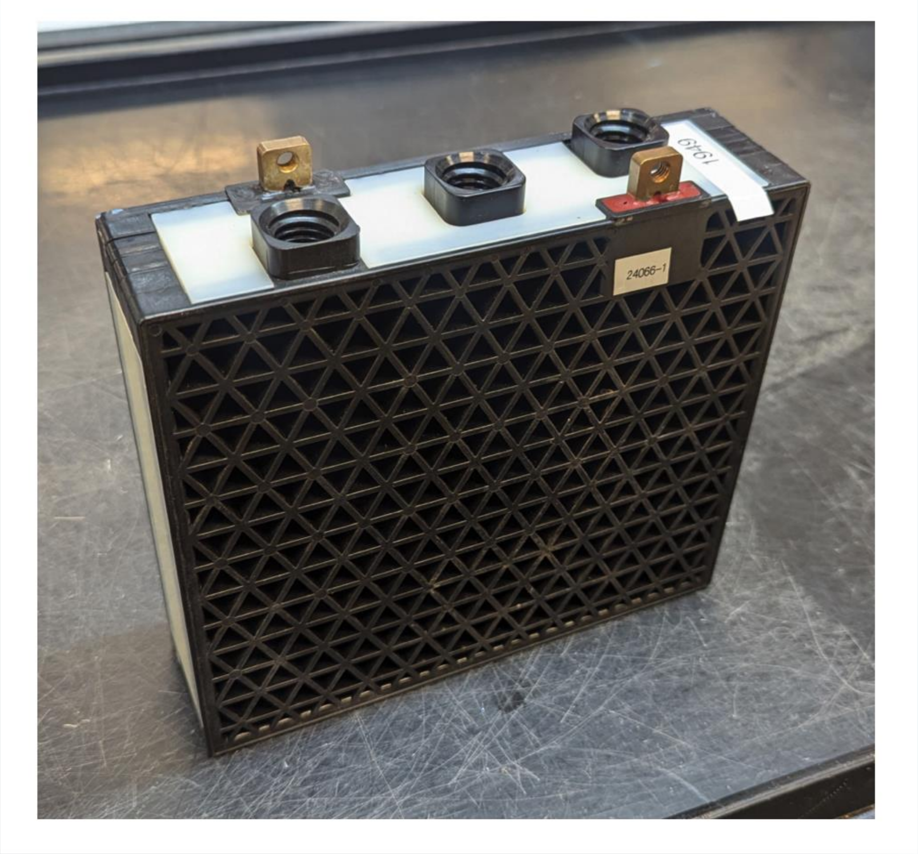
Standard, **Increased Force**, and **Decreased Force variables**

- used the same PAM paste formula
- contain the Hammond Group additive SureCure140

All variables

- were cured with a high humidity phase of 95%RH at 54oC and dried at 60oC
- achieved tetrabasic crystal morphology (4BS)
- contain control Advanced Negative Active Material (NAM)

BATTERY DESCRIPTION AND TESTS PERFORMED



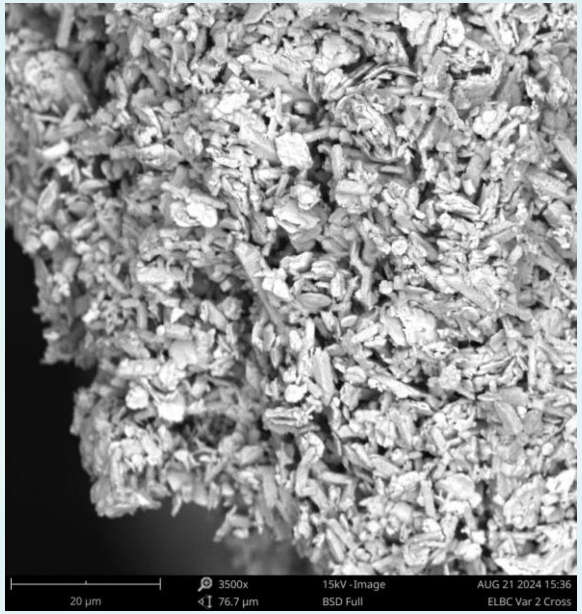
All variables

- used to build 6-volt Silicon Joule U1E batteries with a 2-Hour Capacity of 10 Amp hours
- formed using the same profile

All batteries

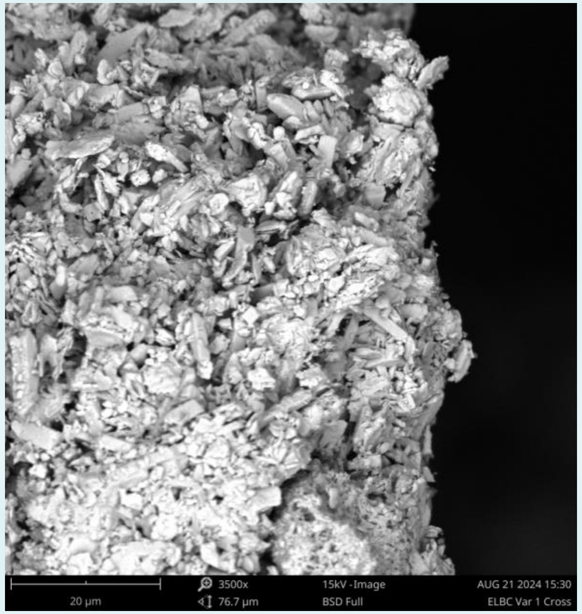
- tested using the DCA Pre-Cycle test (RC,RC, 20-hour DCH, Ic, Id)
- cycled according to the BCIS06 cycling profile

POSITIVE ACTIVE MATERIAL COMPARISON



Standard
(BET = 0.5681 m2/g)

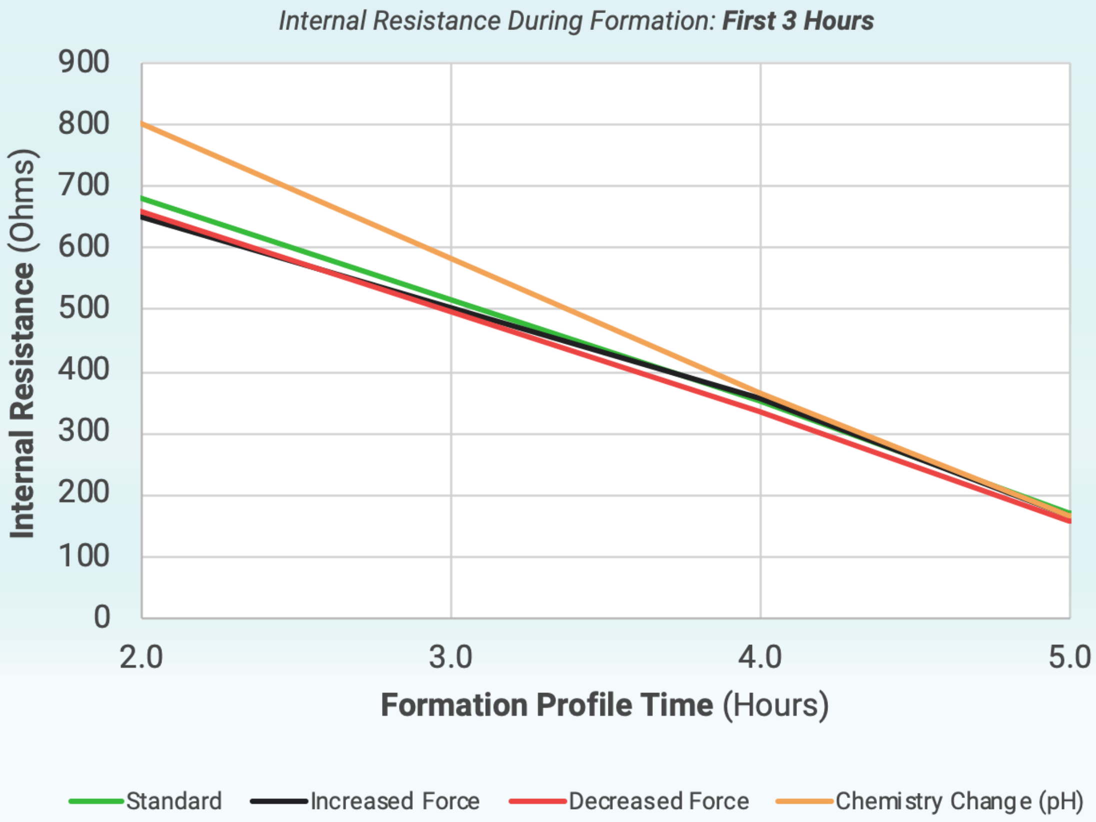
Increased Force
(BET = 0.4986 m2/g)



Decreased Force
(BET = 0.5563 m2/g)

Chemistry Change (pH)
(BET = 0.5664 m2/g)

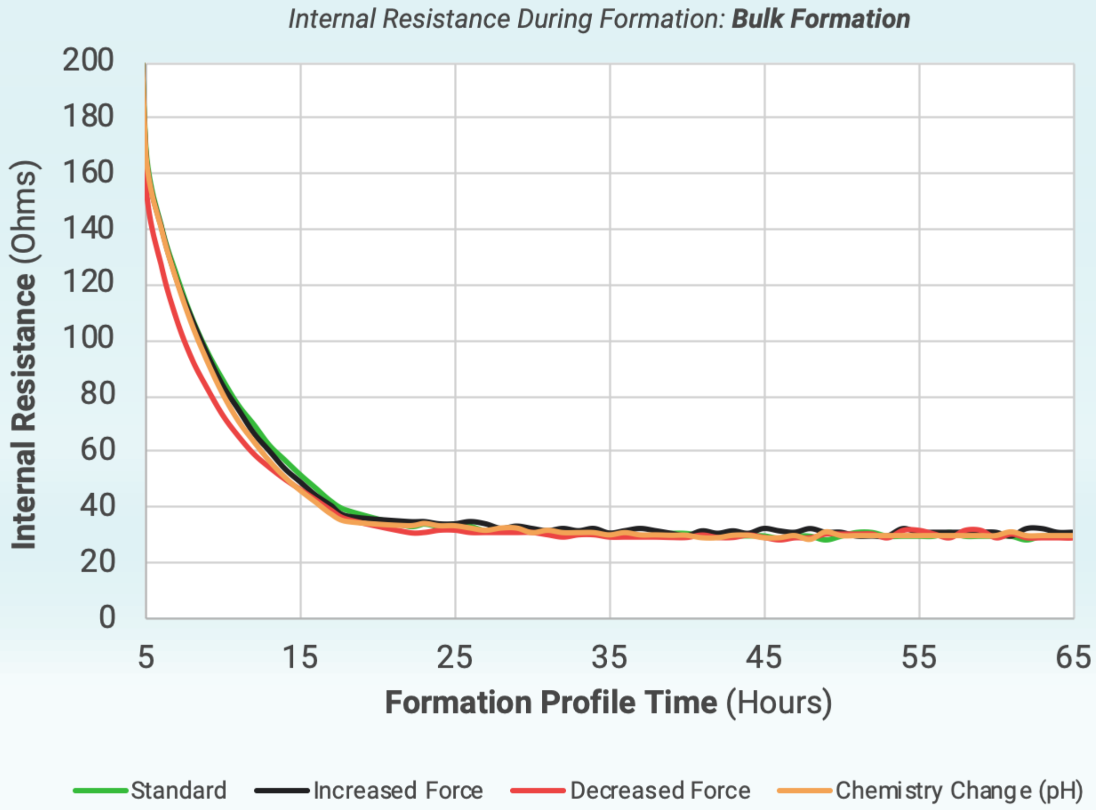
FORMATION RESISTANCE SUMMARY: FIRST HOURS



The three variables with identical paste showed very similar early formation resistance.

The Chemistry Change variable was different from the others in that it did not contain SureCure140. SureCure140 has shown the early formation benefit of reduced resistance.

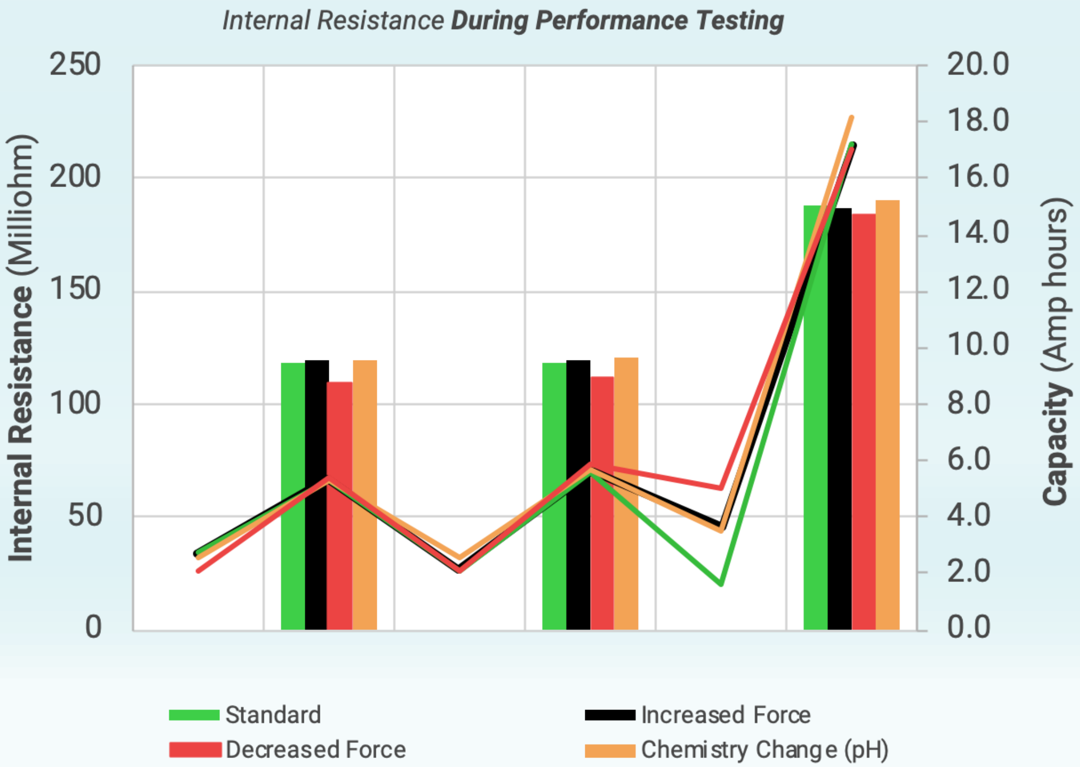
FORMATION RESISTANCE SUMMARY: BULK



After the first 4 hours, the resistance of all variables became similar and insignificantly different.

All variables ended formation with an average resistance around 30 milliohms.

INITIAL PERFORMANCE



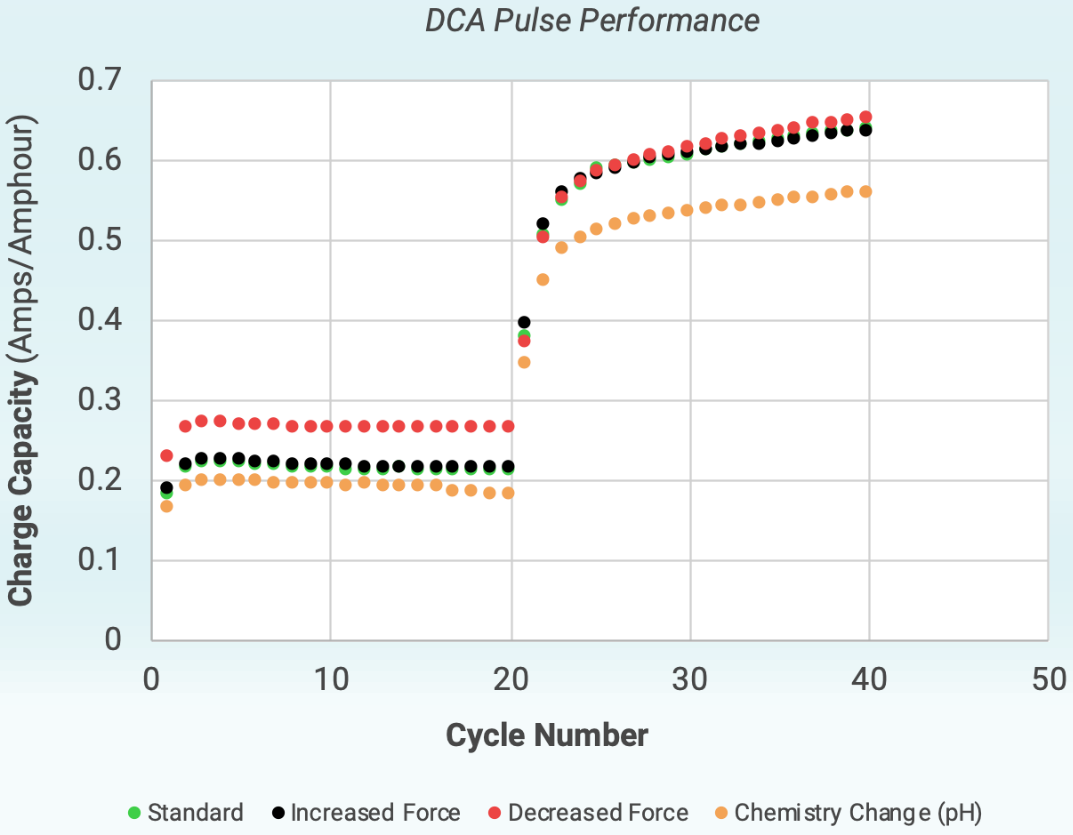
After formation, the batteries were tested according to EN50324-6:2015 Section 7.3 (excluding DCR_{SS} part)

The Internal resistance measurement was taken at the top of charge and the bottom of discharge

The Decreased Force batteries show lower capacity, and higher resistance during the reserve capacity tests

The Chemistry Change variable shows good capacity but higher resistance

DCA PERFORMANCE



The highest performer for charge capacity was the Decreased Force variable during the charge history portion of the test

The lowest performer on all charge capacity tests was the Chemistry Change Variable

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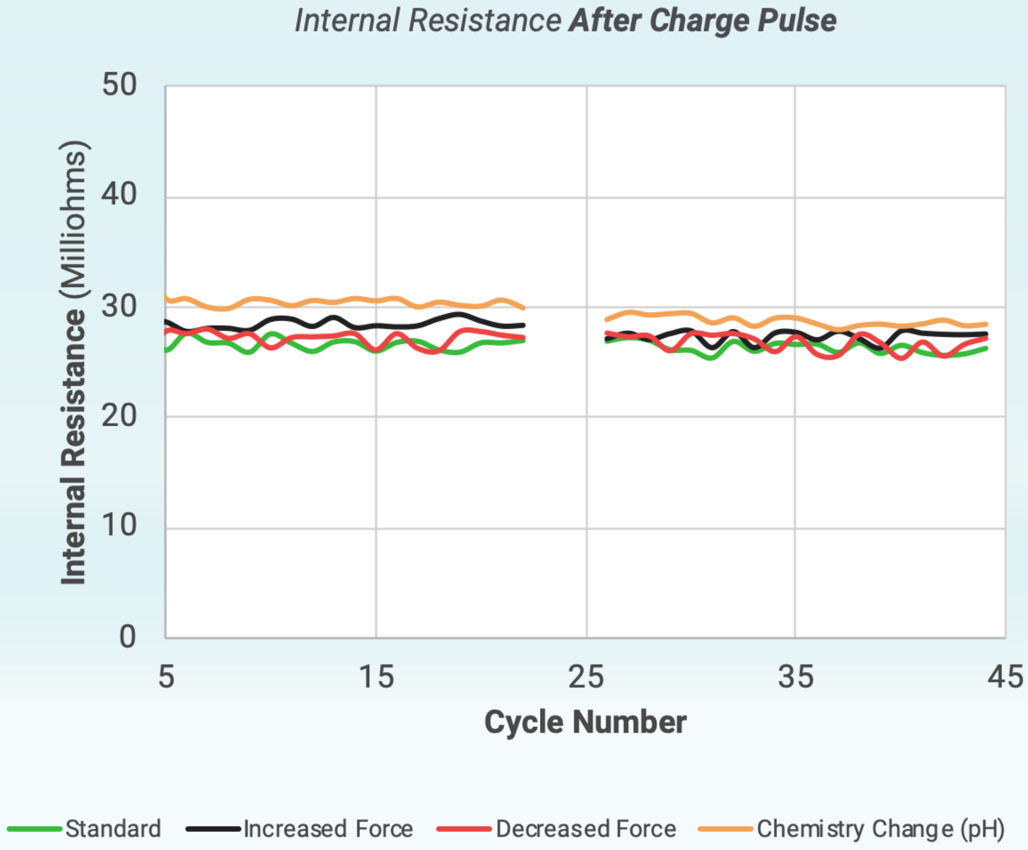
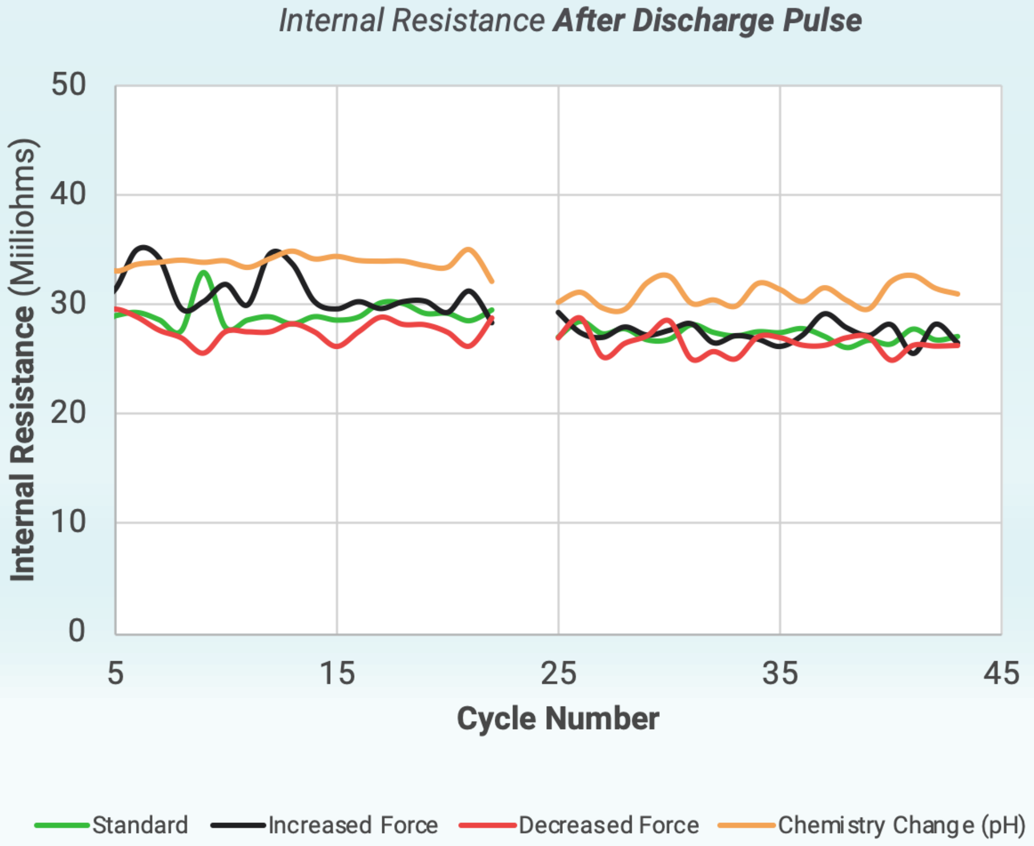
DCA PERFORMANCE





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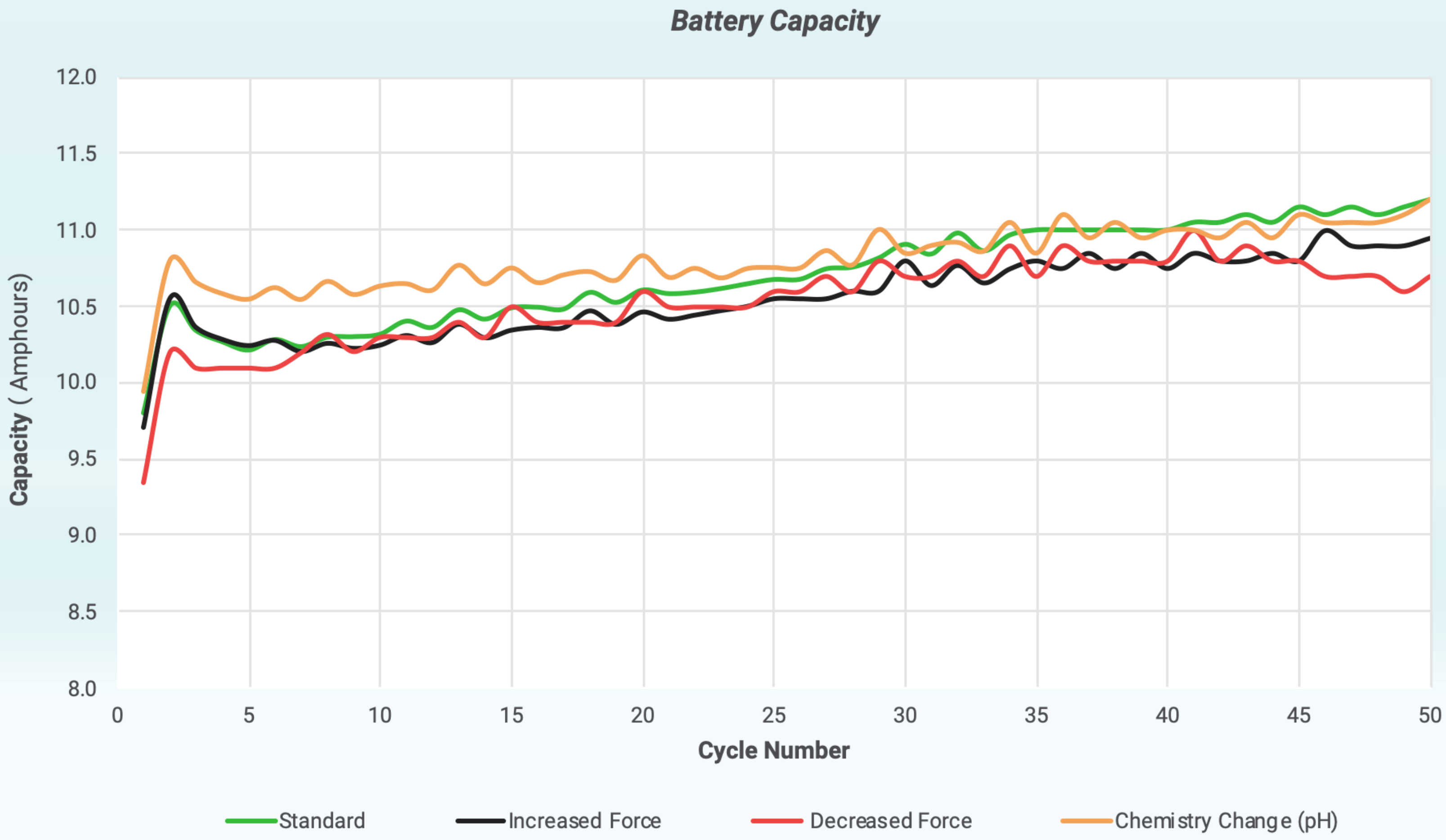
BCIS06 CYCLING



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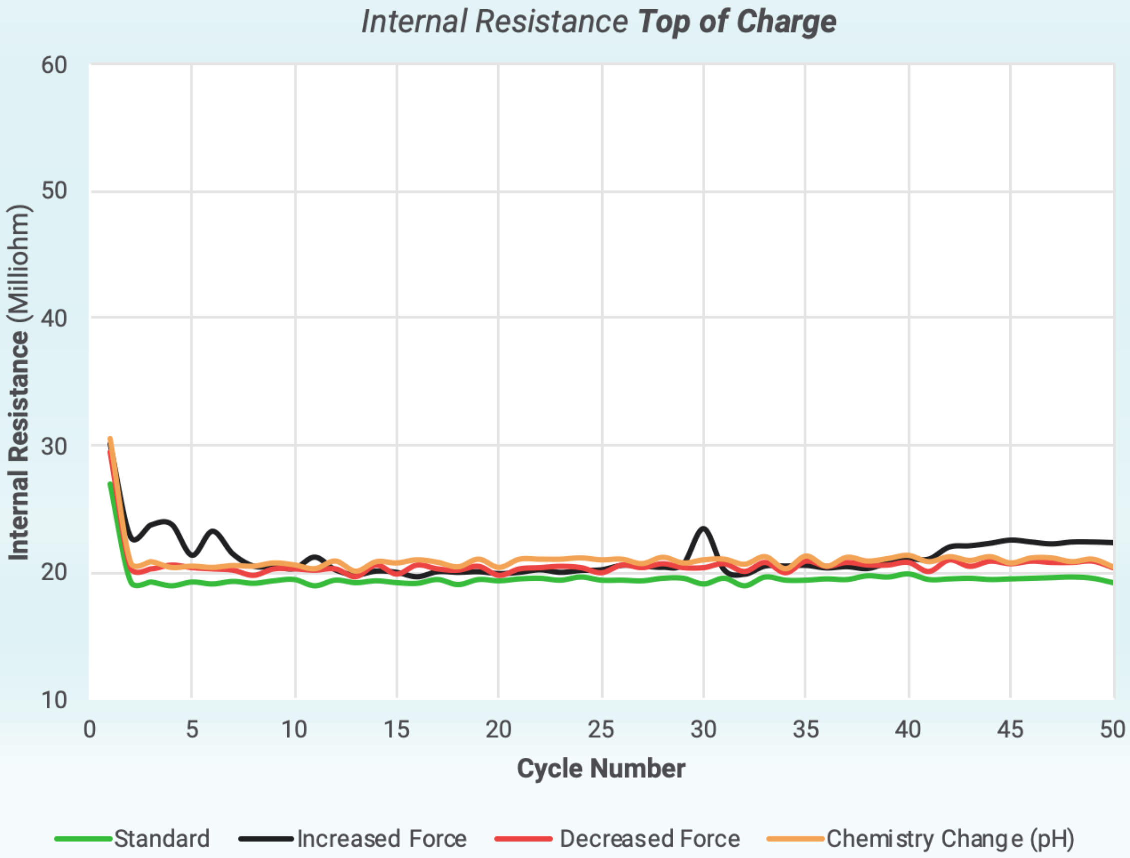
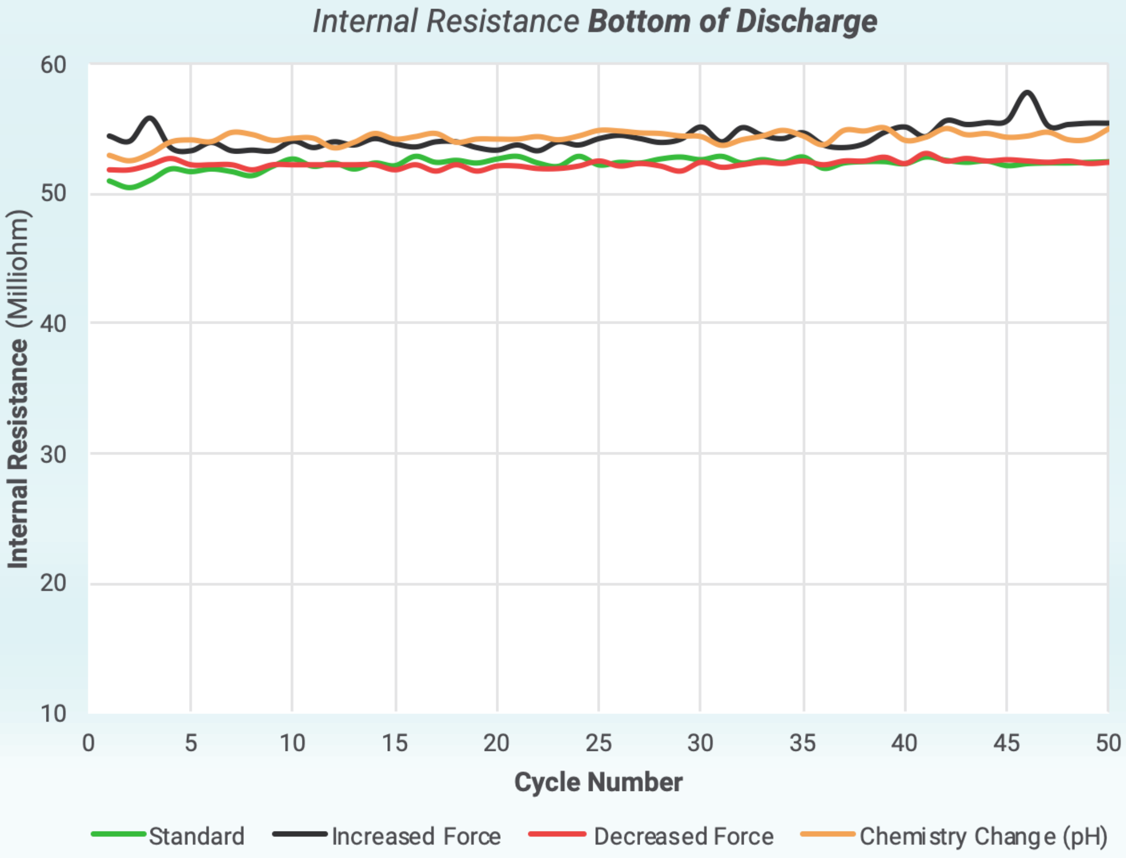
BCIS06 CYCLING





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CONCLUSIONS

- **The use of internal resistance** as an indicator for high-rate performance and cycle life may be a useful tool during development and design of advanced battery technology

- **Too little work** and **too much work** during the pasting process can affect the quality of the interface of the paste with the lead surface

- **Changing the pH of the paste formula** caused an initial boost in out of box performance, but caused a higher resistance and poor high-rate performance

- **There was less difference in the data than expected,** likely because bipolar batteries already rely on high separator compression. For future testing we would recommend decreasing AGM compression to apply more stress to the paste-bipole interface.

THANK YOU

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