

Final Report

1. Name of Grantee: **A123Systems, Inc.**
DOE Award No.: DE-EE0003513
Project Title: Lithium Ion Cell Development for Photovoltaic Energy Storage Applications
Project Director: Susan Babinec
Reporting Period: August 9, 2010 to February 8, 2012
2. Project Objectives & Percent Completion:
Objective 1: anode development – new low cost material: 100% completed
Objective 2: new & existing anodes at loading higher than baseline: 100% completed
Objective 3: anode development – aqueous binder processing: 100% completed
Objective 4: high voltage nanophosphateTM – electrolyte development: 100% completed
Objective 5: regular and high voltage nanophosphateTM thick electrode development: 100% complete
Objective 6: Low cost nanocomposite separator proof of suitability on high loading anodes (including new anodes) and cathodes: 100% completed

3. Executive Summary

The overall project goal is to reduce the cost of home and neighborhood photovoltaic storage systems by reducing the single largest cost component – the energy storage cells.

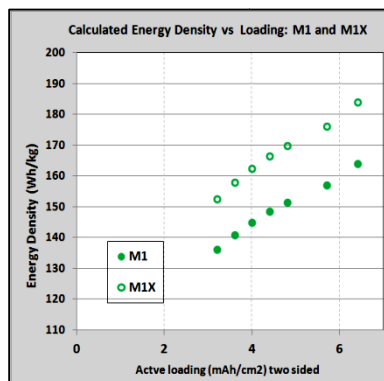
Solar power is accepted as an environmentally advantaged renewable power source. Its deployment in small communities and integrated into the grid, requires a safe, reliable and low cost energy storage system. The incumbent technology of lead acid cells is large, toxic to produce and dispose of, and offer limited life even with significant maintenance. The ideal PV storage battery would have the safety and low cost of lead acid but the performance of lithium ion chemistry. Present lithium ion batteries have the desired performance but cost and safety remain the two key implementation barriers. *The purpose of this project is to develop new lithium ion cells that can meet PVES cost and safety requirements using A123Systems phosphate-based cathode chemistries in commercial PHEV cell formats.* The cost target is a cell design for a home or neighborhood scale at <\$25/kWh.

This DOE program is the continuation and expansion of an initial MPSC (Michigan Public Service Commission) program towards this goal. This program further pushes the initial limits of some aspects of the original program – even lower cost anode and cathode actives implemented at even higher electrode loadings, and as well explores new avenues of cost reduction via new materials – specifically our higher voltage cathode (see detail in Appendix A1).

The challenge in our materials development is to achieve parity in the performance metrics of cycle life and high temperature storage, and to produce quality materials at the production scale. Our new cathode material, M1X, has a higher voltage and so requires

electrolyte reformulation to meet the high temperature storage requirements. The challenge of thick electrode systems is to maintain adequate adhesion and cycle life. The composite separator has been proven in systems having standard loading electrodes; the challenge with this material will be to maintain proven performance when this composite is coated onto a thicker electrode; as well the high temperature storage must meet application requirements. One continuing program challenge was the lack of specific performance variables for this PV application and so the low power requirements of PHEV/EV transportation markets were again used.

ease in cell energy increases; increasing adjacent transportation medium, while for PV cost reduction via these materials. From this there is a significant energy density increase for M1X cathode (average increase of this chemistry is 15% at electrode loading.



Technical Targets – Cost, Energy Density and Safety:

- Develop and evaluate anode powders which are significantly lower in cost than existing (target is 70% cost reduction)
- Develop thick loaded anodes – up to 2.0X baseline - using low cost aqueous binders, with both standard and low cost anode actives.
- Optimize M1X for chemical stability and production readiness.
- Develop electrolyte formulations which enable M1X cells to meet performance targets.
- Develop thick M1 and M1X based electrodes - up to 2.0X of baseline.
- Implement the nanocomposite separator (NCS) in a cell having thick electrodes. Demonstrate high temperature (55°C) stability.

Table 1 summarizes the major program accomplishments. Significant progress was made on all goals, and the majority were fully met, with the exception of demonstration of cycle life of NCS coated thick electrodes. As a result of this program many barriers to commercialization of low cost high energy cells is now possible. Our models predict that a cell with the features in Table 1, executed at ~60 Ah capacity cell (to further the cost down) would be safe and offer energy density of ~163 Wh/Kg and 185 Wh/kg for M1 and M1X chemistries, respectively.

Our original economic model indicates that these systems can meet the cost target of \$25/KWh; however, this we will not expand on this topic beyond provision of this estimate since there are several caveats which will need reworking when further technical information becomes available. Specifically, precision can be gained in understanding the relationship between coating costs of high loaded electrodes in an optimized coating line (existing lines are optimized for baseline loading) and further experience is gained with our new low cost synthesis for both

our proprietary anode active and our low cost/high quality cathode M1 and M1X powders which are optimized for high loaded electrodes.

Table 1: Technical Accomplishments

Objective	Accomplishments
1	<ul style="list-style-type: none"> Production scale demonstration of an anode active which is 70% cost reduction in comparison to our starting point. This material provides targeted high temperature storage and cycle life at parity with high cost material.
2/3	<ul style="list-style-type: none"> Performance of natural anodes with aqueous binders at 1.75X and 2.0X proven at the pilot scale. This binder provides superior adhesion in comparison to the industry standard PVDF binder
4	<ul style="list-style-type: none"> M1X proven resistant to Mn leaching; stability of this material is as good as our pure iron phosphate active which is commercial. Demonstrated production capabilities for M1 and M1X with 30% and 50% cost reductions, respectively. M1X electrolyte formulations enable it to provide excellent high temperature one month/70°C stability (78% and 88%% capacity retention and recovery, respectively) and improved low temperature performance; there is not a PV low temperature performance target yet. The RT cycle life of M1X is very similar to M1 out to 3500 cycles at 1C/2C. In accelerated tests at 35°C it provided > 1200 cycles.
5	<ul style="list-style-type: none"> Determined appropriate powder PSD and manufacturing approach for low cost/high quality actives for electrode loadings > 1.5X. 1.75X loadings for both M1 and M1X can meet cycle life using PVDF binders; but not at 2.0X due to adhesion issues with the PVDF-based anode. Cycle life tests are in progress at 2.0X loading for both M1 and M1X electrodes with anodes having aqueous binders which pass adhesion tests.
6	<ul style="list-style-type: none"> The nanocomposite separator has been reformulated to improve 55°C high temperature storage performance. At 35um thickness NCS can significantly improve nail penetration performance in a mixed metal oxide 26650 cell. Cycle life did not meet the target; cells had soft shorts due to NCS imperfections.

Future Activities: Low cost/high quality active materials development activities preceded the electrode development; as such, we feel that the cycle life performance which was the final task is not yet optimized. Future activities should focus on further optimizing the electrode microstructures and cell balancing in order to improve this, especially at 2.0X loading. Similarly, NCS related tasks were not as extensively probed as they could have been due to the need for optimized electrodes as a precursor. We note, however, that NCS is not anticipated to be required for this M1X cell chemistry. Recommended future activities:

- Conduct full safety tests of 55 Ah M1X cells with natural graphite/aqueous binders

- Determine the lower limit NCS thickness for abuse of the above cell, if needed
- Optimize full cells for cycle life at 2.0X loading.
- Evaluate the economics of coating thicker electrodes in an optimized coating line

4. DETAILED TECHNICAL RESULTS: This program has five primary technical targets; Table 2 summarizes these results.

Table 2: Summary of program major technical goals and results

PARAMETER	OBJECTIVE	RESULT	COMMENT
ANODE: Low Cost produced by A123Systems	70% cost reduction and parity in all performance parameters	Target Met	-All performance parameters and cost estimates meet and/or exceed existing anode which is commercial natural graphite. -Successfully scaled new material to > 150kg.
ANODE ELECTRODE High loading of Anode Aqueous Anode Binder	Develop formulation and process technology for electrode loadings up to 1.75X to 2X baseline	Targets Met	-Fully meet 1.75X and 2.0X for energy, wet & dry adhesion and calendar life. -Acceptable accelerated cycle life at 1.75X in a full cell -Cycle life testing at 2.0X with optimized anodes is in progress.
HIGH VOLTAGE CATHODE STABILITY	Develop electrolyte formulation(s) which enable M1X cells to pass photovoltaic & automotive metrics	TARGETS MET ¹	-Low temperature energy is close to the automotive target (not PV target). -High temperature capacity retention and low gassing are fully met -Low power cycle life is met.
CATHODE ELECTRODE: Up to 2.0X loading low cost M1 and M1X	Develop powder synthesis, electrode formulation and process technology for electrode loadings up to 1.75x to 2X baseline	TARGETS PARTIALLY MET	-Low cost powder PSD fine tuned for high loaded electrodes. -Both M1 and M1X electrodes had uniform coating and passed adhesion tests. -Low power cycle life tests in full cells are still in progress.

<p>LOW COST SEPARATOR - NCS:</p> <p>High Temperature Storage and Safety</p>	<p>Improve High Temperature Storage and prove cycle life and safety of new formulation</p>	<p>TARGET PARTIALLY MET</p>	<p>-High temperature storage nearly matches cells with traditional polyolefin separator.</p> <p>-Safety of metal oxides cells passes with ~35um of NCS – minimal NCS thickness will be > 12um NCS - needs further testing.</p> <p>- Cycle life in 1.75X and 2.0X cells with 35um NCS failed due to shorting – root cause is imperfections in the NCS coating.</p>
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1: One single electrolyte formulation does not meet all the different requirements.

Objective 1: Anode Development – New Low Cost Material: 100% completed

Objective 1 is the development of new proprietary anode powders which are significantly lower cost than current commercial natural graphite (“CNG”) powders and to demonstrate a scalable manufacturing process. A123 has successfully met this objective and presently is evaluating this material for next generation products in our long term roadmap. The specific targets and results are summarized in Table 3.

Table 3: Summary of Results for Objective 1:

TARGET	RESULT	COMMENT
70% cost reduction vs. the commercial natural graphite which was in use at program start	Target Met	<ul style="list-style-type: none"> - Cost analysis, inclusive of raw materials, shipping, processing, and yield, indicates approximately 60% of comparable CNGs. - Successfully scaled to 120-150 kg.
Particle size distribution (PSD) typical of commercial anode powders	Target Met	-A123’s graphite PSD is similar to the CNGs - Figure 1. CNG powders typically average 10-20 μm.
First cycle discharge / charge efficiency >90%.	Target Met	-First cycle efficiency is 94% in the coin cell test (Li metal counter electrode) which is somewhat better than the 90% target – Figure 2.
Parity energy, cycle life, and high temperature storage in comparison to CNG	Target Met	<ul style="list-style-type: none"> - A very <i>slight</i> increase in watt hours was obtained in a 6C, 23°C discharge of cells made with A123 low cost graphite vs a standard CNG, as shown in Figure 3. - 35°C accelerated cycle life, in 1C charge/1C discharge of full cells (nanophosphate cathode) with pilot scale powder shows <i>better performance</i> than CNG powder - Figure 4. - 55°C storage evaluated in 63450 cells (~650 mAh) shows retained capacity parity after 12 weeks; however, DCR is 5-7% higher for A123’s pilot scale graphite in comparison to CNG. For low power PV applications this is not expected to be a concern – Figures 5a, 5b.

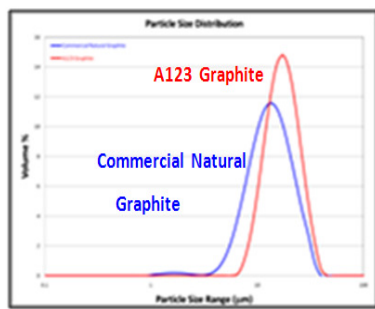


Figure 1: Particle size distribution of A123 Low Cost Natural Graphite vs. CNG

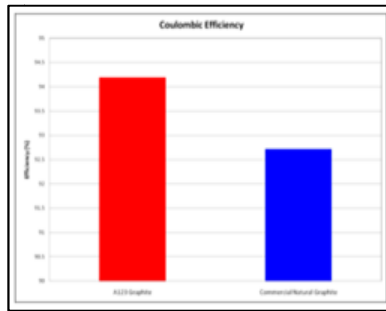
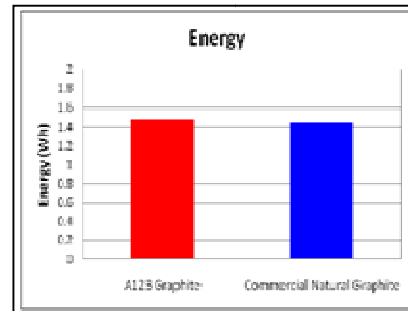
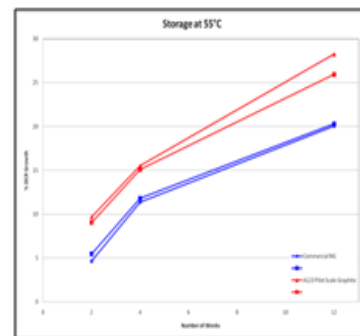
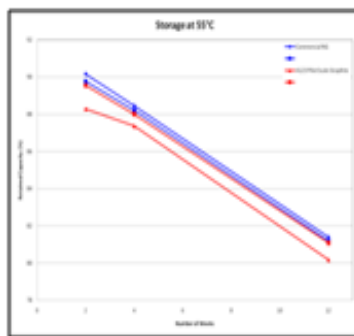
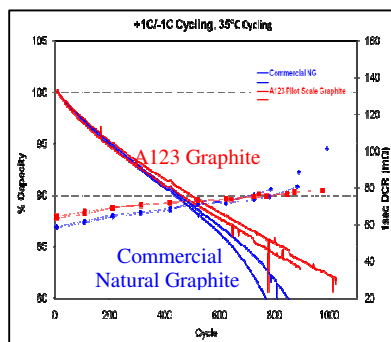


Figure 2: 1st cycle efficiency of A123 anode is better than that of comparable CNG



(discharge Wh) A123 Graphite is equal to or higher than Commercial Natural Graphite



growth (b)

Objectives 2/3: Anode electrode development - new A123 low cost and CNG at loadings beyond baseline, using aqueous binders: 100% complete

Objective 2 for high loaded anodes and objective 3 for aqueous anode binders were combined for reporting as they are developed concurrently: the goal is to develop formulation and process technology for anode electrodes using aqueous binders at electrode loadings up to 2X baseline. A123 has successfully met these objectives.

Lower cost natural graphite uniquely requires aqueous binders and so this technology is critical for their implementation. In addition, aqueous binders also improve the abuse tolerance of high energy systems which is important since safety concerns increase with cell capacity/higher loaded electrodes. Thick anodes with the traditional PVDF binders are primarily used for comparative purposes.

The typical electrode/cell challenges of rate capability, cycle life and calendar life are further negatively impacted in electrode designs with increased active material loading; therefore, these remain the key evaluation metrics. The requirements for the 1.75X and 2X electrodes of this objective are below:

- Adhesion: Pass dry and wet adhesion tests
- Parity or acceptable performance vs. higher cost CNG for:
 - Energy
 - Rate map
 - Cycle life
 - Calendar life
- Full Cell evaluations:
 - *Practical limitations* - Full cell evaluations of thick anodes require thick cathodes. Unfortunately, *optimized* cathodes were not available during the majority of this program; powders optimized for thick cathodes were concurrently under development and unavailable until very near the program end.
 - *Approach to address practical limitation:* In the spirit of gaining some insight, albeit without optimal conditions, thick anode evaluations were primarily run in half cell coin cells and in full cells with sub-optimal cathodes at 1.75X throughout this objective (2.0X available only at program end). The final proof of full cells at loadings up to 2.0X was not possible until program end – this is reported after the section on thick cathodes.

The summary in Table 4 shows that **A123 has successfully developed formulations and processing technology to prepare higher loaded electrodes with a low cost aqueous binder.**

Table 4: Summary of Results for Objectives 2/3:

TARGET	RESULT	COMMENT
Adhesion: Pass dry and wet adhesion	Targets Met	- 2.0X loading with aqueous binders, but not with traditional PVDF binder, passes both dry and hot electrolyte adhesion tests. - Figure 6 shows the dry adhesion results. -Figure 7 shows the difference between the hot electrolyte test of electrodes made with the two different binders – PVDF and aqueous.
Energy parity and Rate	Targets Met	-Half cell/coin cell energy for A123 graphite with aqueous binders up to 2.0X loadings matched that of baseline loading with commercial natural graphites. (Table 5) -The coin cell rate map at 2.0X is in Figure 8. -The full cell energy at 1.75X is equal – Figure 9.

Cycle Life	Performance acceptable	-1.75X only was evaluated in this early stage of the program. 35°C accelerated 1C/1C cycling of cells with A123 anode and non-optimal cathode have > ~1200 cycles to 80% retention vs. ~100 cycles for cell with CNG - Figure 10.
High Temperature Storage (55°C)	Target Met	-DCR, recovered capacity and retained capacity are at parity with CNG (Figure 11)

Requirement 1 - Dry and Wet Adhesion

- **DRY:** Sufficient dry adhesion of the electrode to the metal substrate is important for high yield manufacturing (no spalling during stamping) and long cyclelife and calendar life. To improve the dry adhesion of the aqueous anode, optimization of the formulation, mixing and coating process were performed. Adjustments to mixing time, mixing shear rate, and the various zones of oven drying temperatures improved the dry adhesion by over 100%, to an acceptable for efficient electrode processing (see Figure 6).
- **WET:** Coating adhesion after soaking in hot electrolyte has also been evaluated - optimized formulation and processing conditions produce electrodes at both 1.75X and 2.0X that consistently pass the wet hot electrolyte adhesion test.

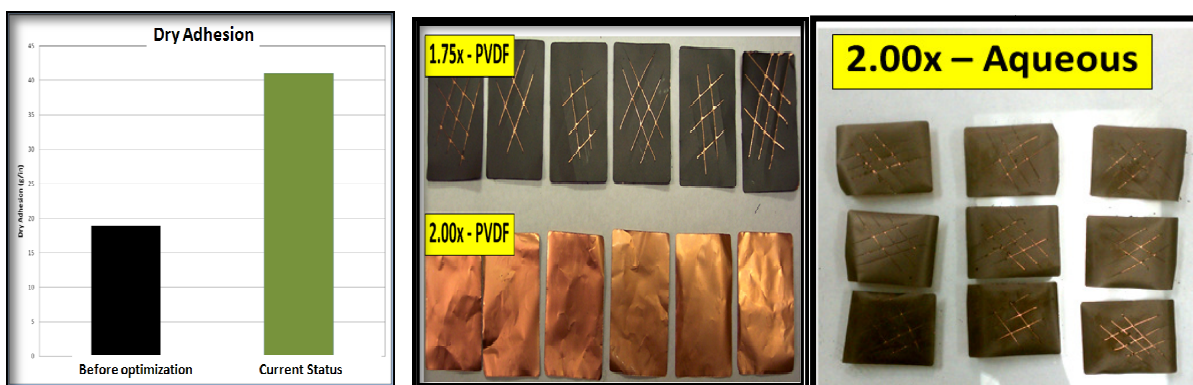


Figure 6: Improvement in dry adhesion of thick aqueous anodes after optimization

ditions resulted , with aqueous √DF binder.

Requirement 2 – Energy

- Aqueous anode electrodes were made up to 2X normal loading with A123’s low cost natural graphite and new formulation, with a small scale coater. Coin half cells were used to assess capacity, efficiency, and impedance. Table 5 shows that the anodes with

2X loading provided parity capacity with 1X loading, Figure 8 shows that full cells (1.75X/non optimized cathodes) would achieve the expected volumetric energy advantage with heavier electrode loading. Figure 9 is the half cell coin cell rate map, showing that the 2.0X loading meets the target of > 80% capacity retention up to and beyond rates of 1C.

Loading	Reversible Capacity (mAh/g)
1.0x	349.8
1.8x	351.3
2x	350.5

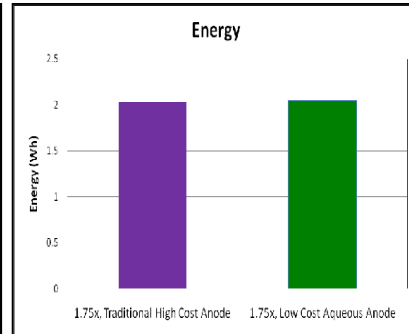
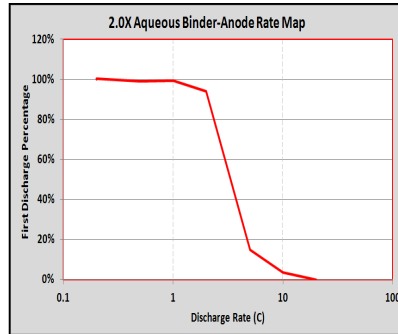
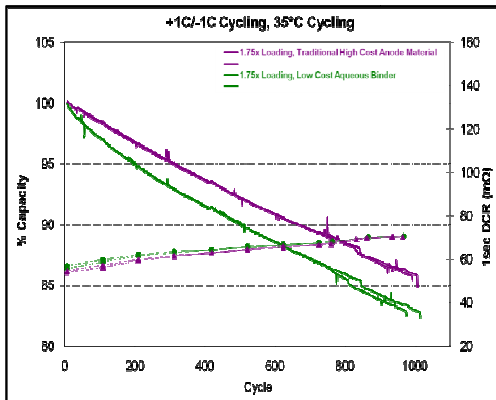


Table 5: Capacity of aqueous anode at increasing electrode loading graphites

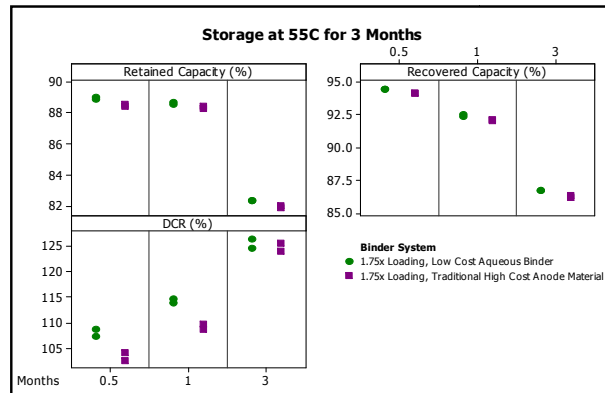
Figure 8: Coin cell rate map of the optimized formulation at 2.0X

energy at binders s. CNG natural

- **CYCLELIFE:** Figure 10 shows that 63450 cells with thick aqueous anodes and higher cost synthetic anodes, both with non-optimal cathodes, show slightly less projected cycle life, and comparable DCR growth after 1000 1C/1C cycles.
- **CALENDAR LIFE:** Figure 11 shows results for cells with 1.75X electrodes, and non-optimal cathodes that were stored at 55°C for three months. The low cost aqueous anodes demonstrated parity storage performance when compared to CNG; this was achieved through improvements to both the anode material and also the electrolyte.



full cell at binders for



testing of higher

Objective 4: High Voltage Nanophosphate – Electrolyte Development: 100% completed

“M1X” is the code name for our high-voltage Nanophosphate cathode, which was initiated as an internally funded program. The critical gap in M1X implementation is high temperature storage and cycle life, which are rooted in electrolyte issues due to the higher voltage. *The goal of objective 4 is to develop electrolyte formulations which enable M1X cells to satisfy the following A123 internal requirements which are critical to automotive applications. Unfortunately PV requirements are not available at this time:*

- 70% of rated RT energy at temperatures down to -30°C – this relates primarily to cold-cranking in transportation applications.
- 75% capacity retention and 85% capacity recovery after one month at temperatures up to 70°C
- Parity cycle life to standard nanophosphate material
- Minimal gas evolution, especially during high-temperature storage and cycling
- Optimize processes and procedures to assembly large-capacity M1x that exhibit the 4 characteristics listed above

A key component of success in this task was the initial refinement of M1X powder synthesis in order to reduce the amount of Mn and Fe which solubilizes at high temperatures. Once this optimized composition was available, successful demonstrations across all of the above requirements were met, *but not by one single common electrolyte formulation.* This result relates to the challenge in bridging requirements at very low (-30 °C) and very high (+75 °C) temperatures, as the fundamental design characteristics for these temperatures are opposing. As a result, selections have been made which maximize performance across the various targets. **If the very low temperatures cold cranking transportation target is omitted, as may be the case for PV, then objective 4 is met.** These are summarized in Table 6.

Table 6: Summary of Results for Objective 4:

TARGET	RESULT	COMMENT	VALUE FOR THE SINGLE OVERALL BEST ELECTROLYTE (“TWJ00731”)*
<p>Low Temperature Energy:</p> <p>70% of RT energy at -30°C</p>	Target Met	Figure 12: actual values were 94% of the target	30%
<p>High Temperature Capacity</p> <p>75% of retained and 85% recovered capacity after one month at 70°C</p>	Target Met	Figure 13: 11 of the 20 formulations passed both retained and recovered capacity metric; of these, two also passed the above low temperature requirement	<p>PASS:</p> <p>78% Retained</p> <p>88% Recovered</p>

<p>Low Power Cycle Life parity with standard A123 Nanophosphate™</p>	<p>Target Nearly Met</p>	<p>-Figure 14: 4 formulations can provide targeted cycle life in 45°C accelerated test; one of these also meets the high temperature storage test. -Figure 15: 1 formulation matches the RT cycling of our standard Nanophosphate™ cell.</p>	<p>Near Parity In RT cycling</p>
<p>Gassing; Minimize gas evolution in high temperature storage</p>	<p>Target Met</p>	<p>-Figure 16 shows that 5 formulations pass</p>	<p>PASS: 1 ml vs. internal A123 target of 2ml</p>

*Analysis was conducted to determine which *one formulation* came closest to an acceptable *overall balance* across all core criteria, for down-selection into the large format cell build – this is formulation “TWJ00371” . If cold-cranking is not required, as might be the case for PV applications, then there are more candidates and a full pass across all metrics is possible.

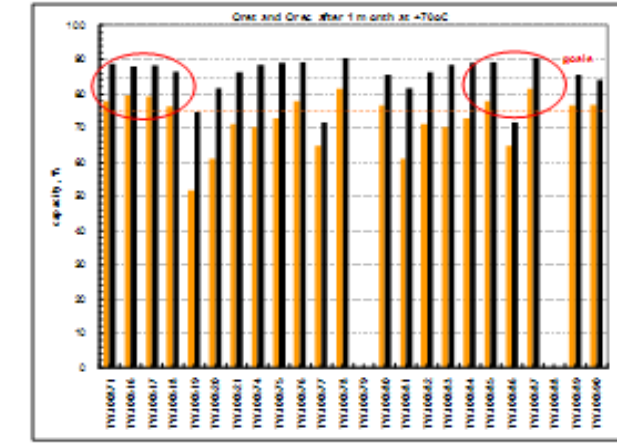
Over twenty electrolyte formulations covering a range of solvents and additives to enable low temperature performance and high temperature storage were evaluated with M1x cathodes in small prismatic cells in order to meet requirements 1 and 2:

Requirement 1- Provide 70% of rated energy at -30°C

- The greatest performance challenge is the -30°C performance as this temperature is near the freezing point of many common electrolyte formulations. Even if the electrolyte is not fully frozen it will still have very low viscosity and a majority fraction of salt will have dropped out of solution - both of these greatly reduce electrolyte Li⁺ conductivity which impacts the ability to meet other performance targets. Nevertheless, two formulations did come close to (~ 94% of) the 70% capacity target (see the circled formulations in Figure 12) and we indicate this as “success”. No formulation *exactly* achieved the 70% of rated capacity at this temperature.

Requirement 2 – Provide 75% of retained capacity and 85% recovered capacity after one month at 70°C

- Figure 13 shows that 11 of the 20 formulations survived on month of 70°C storage for both retained and recovered capacity. (The lighter bar is retained capacity, and the dark bar is recovered capacity.)
- Two formulations which passed the low temperature testing also achieved *recovered* capacity target, but did not achieve 75% *retained* capacity. *Often recovered capacity is a more critical and meaningful metric* since it represents irreversible losses, and so *the performance of these two formulations is very close to fully successful.*

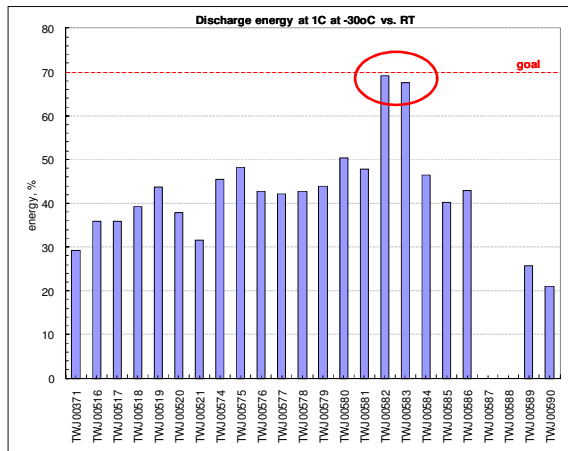


-30°C, for electrolyte

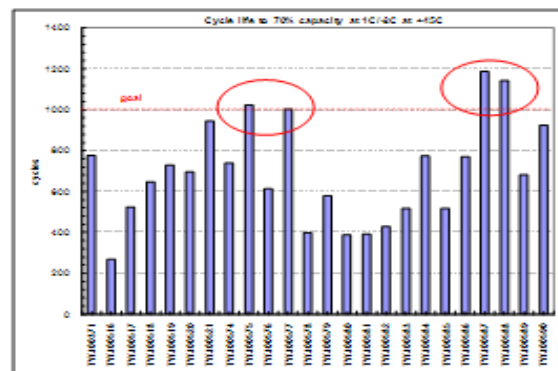
recovered 1 Month at 70°C, and Alternative

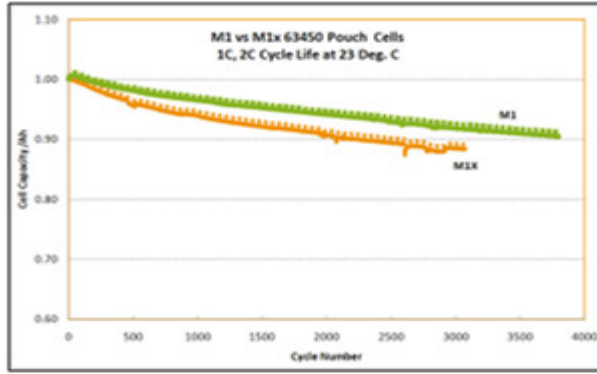
Requirement 3 – Provide parity cycle life to standard A123 Nanophosphate™ material, using M1x cathodes and the modified electrolyte

- Four different electrolyte formulations met or exceeded the low power (1C/2C) target of 1000 cycles to 70% capacity, at 45°C – see Figure 14. Of these four, one nearly matches the cycle life performance of our standard Nanophosphate cell – see Figure 15.



- Only one of these four formulations (TWJ00585) achieved the retained / recovered capacity target, and none met the low temperature energy target.





, to 70%

te™ cathode,

Requirement 4 – Minimize gas evolution during high temperature storage and cycling

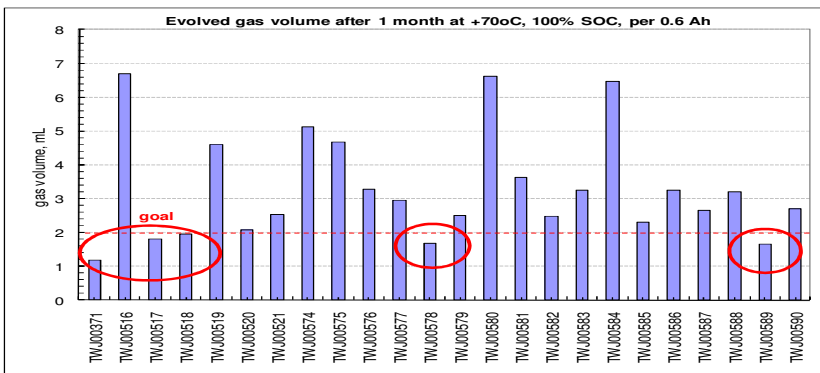
- Figure 16 shows that five of the 24 formulations met our A123 internal target for evolved gas volume of 2ml/0.6 Ah cell capacity after one month at 70°C. Even more formulations were quite close to the target, therefore, this criteria does not severely limit selection of the best overall electrolyte option.

: Evolved Gas
Following 1 Month
70°C, 100%
target set by
nl under these

Requirement 5 – Demonstrate above achievements in large capacity cell with M1x cathodes

- A preliminary trial of large format cells using A123’s high voltage nanophosphate cathode and selected electrolyte was initiated, however the coating technology for thick

electrodes was not yet developed sufficiently to assure successful electrode build.



Objective 5: Both iron and high voltage nanophosphate thick electrode development:

100% complete

The goal of this objective is to develop both the usual iron (“M1”) and high voltage (“M1X”) cathodes at 1.75X to 2.0X loading vs. usual baseline; this requires production of appropriate high quality/low cost cathode active powders. A123 met this target.

As with anodes, higher cathode loadings reduce cell cost by dilution of the inactive material's cost (current collectors, tabs and packaging). *Thick cathodes are often more challenging than anodes since the lower charge capacity of cathode actives vs. anode actives (~150 mAh/g for the cathode active and ~ 320 mAh/g for the anode active) translates into about double the thickness for a cathode.* Thicker electrodes typically have higher stress than thinner, which can result in adhesion issues which manifest in a variety of manufacturing defects. For example, adhesion issues can lead to coating spalling at the edges during electrode cutting/stamping.

In the early stages of this research it became clear that the PSD is an important element in controlling mechanical stress for successful thick electrode coating. Preliminary coating runs showed that the desired PSD did not naturally arise in our low cost synthesis process and so gaining access to appropriate powder PSD via deliberate fine tuning became part of this development program. This required collaboration with our M1 and M1X synthesis team. Figure 17 illustrates the overall electrode development concepts that were used for successful high loadings of both M1 and M1X cathode actives.

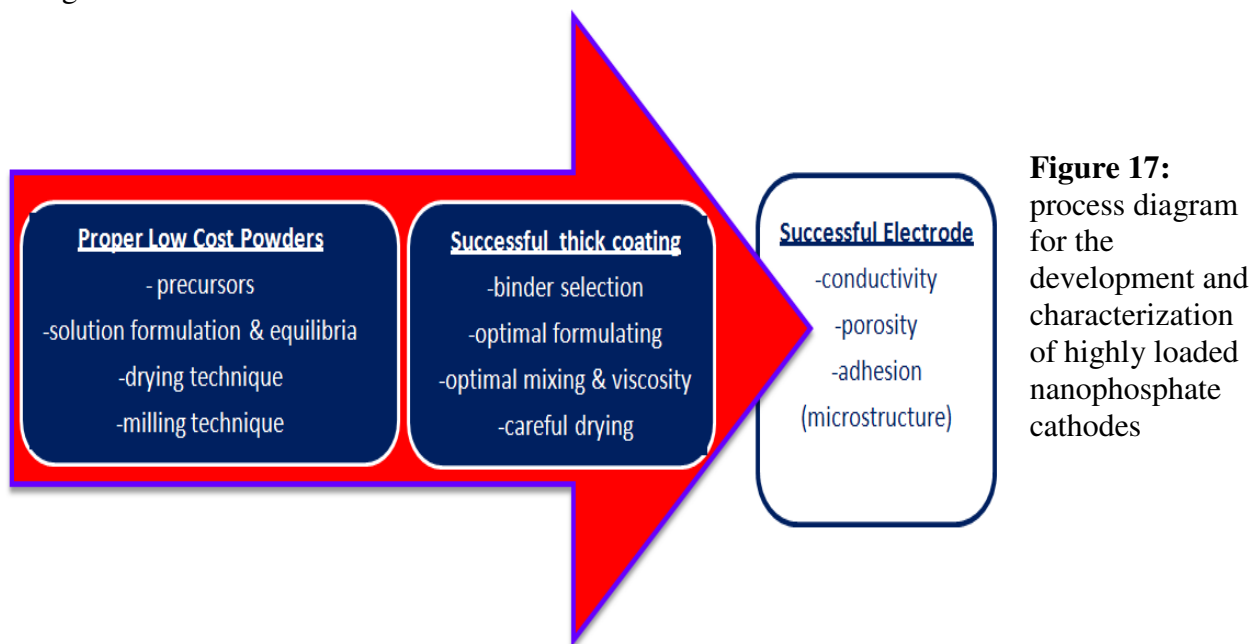


Figure 17: process diagram for the development and characterization of highly loaded nanophosphate cathodes

Table 7 summarizes the subtasks of objective 5, which are based on concepts in Figure 17 above. There are two levels of material evaluations – those of the cathode films and those of the cathodes matched with anodes in full cells. To complete the program successfully, full cells need to pass cyclife tests; these evaluations were not begun until program end as both anode and cathode active *materials* developments were a significant effort prior to thick *anode and cathode* electrode technology development for production. To summarize the approach:

- Initial *full cell* tests at program start used the available anodes which were those prepared with traditional PVDF binders - these more successful at 1.75X vs. 2.0X. The root cause of poor cell cyclife at 2.0X is believed to be poor anode adhesion - Figure 7 shows that the 2.0X electrode did not pass adhesion tests.
- In the subsequent round of full cell builds, the 2.0X loaded anodes had *aqueous binders* which did (in contrast to the initial PVDF attempt) pass the hot electrolyte

adhesion tests. *These cells were prepared at the end of the program and are still on test (cycling).*

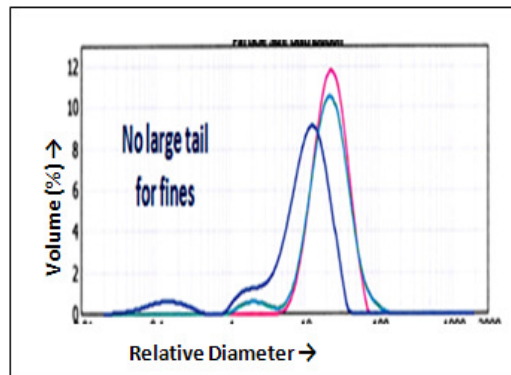
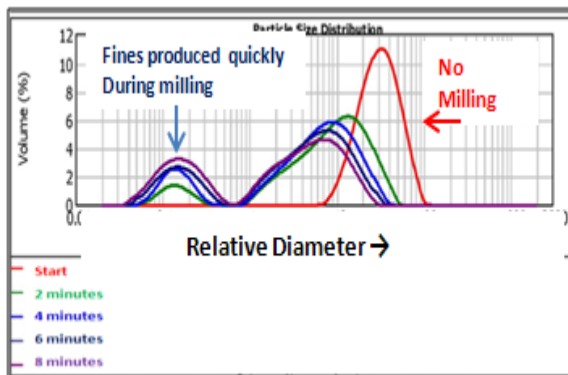
Table 7: Summary of results for Objective 5:

TARGET	RESULT	COMMENT
<p>Low Cost Powders</p> <p>Develop low cost manufacturing processes for both M1 and M1X powders which are acceptable in thick electrodes</p>	<p><i>TARGET MET FOR BOTH M1 AND M1X</i></p>	<p>- The manufacturing cost reduction effort is a major program funded by NIST – TIP and the synthesis was developed in that program:</p> <ul style="list-style-type: none"> - 35% cost reduction for M1 - 50% cost reduction for M1X <p>- In this DOE program we fine-tuned the synthesis and milling parameters in order to optimize the PSD for thick electrodes. There is no cost modification of the (estimated manufacturing) for this step.</p>
<p>Thick Electrodes</p> <p>Develop coating technology for electrodes up to 1.75X and 2.0X vs. baseline thickness</p>	<p><i>TARGET MET FOR BOTH M1 AND M1X</i></p>	<p>M1: both 1.75X and 2.0X electrodes had uniform distribution across the web and passed adhesion tests.</p> <p>M1X: both 1.75X and 2.0X electrodes had uniform distribution across the web and passed adhesion tests.</p>
<p>Performance</p> <p>Parity to baseline for high temperature storage and cycle life</p>	<p><i>TARGETS PARTIALLY MET</i></p>	<p>High Temperature Storage: <i>met at 1.0X loading – not tested for higher loadings;</i></p> <p>Cycle Life:</p> <ol style="list-style-type: none"> 1. <i>Initial results generated with non-optimal PVDF binder based anodes and this was acceptable at 1.75X but problematic at 2.0X loading.</i> 2. <i>New cells made with optimized anodes have passed initial formation tests and are cycling – full 1200 cycles will be completed in July</i>

POWDER: As per Figure 17, the start of low cost thick electrodes is a low cost/high quality powder. The production of low cost nanophosphate powders is a major A123 effort which is presently funded by a National Institute of Standards and Technology - Technology Innovation Program (NIST/TIP) program (Cooperative Agreement No. 70NANB10H008). All cathode actives evaluated in this program were produced by the NIST effort. The cost reductions are achieved through improvements in raw materials, formulating and process parameters. In addition, there was a significant effort devoted to establishing a globally secure raw materials supply. The US based pilot line came on stream as a research tool in Q2/Q3 2011.

The PSD fine tuning efforts for these low cost powders for thick electrodes, 1.75X and 2.0X, however were activities uniquely associated with this DOE program; particle size fine tuning was affected by details in synthesis and drying. Figures 18a and 18b illustrate the general

concepts for PSD acceptability, which is that the powder should neither have excessive fines or too large a D90. In practice there is a coupling of the powder density and the power and milling time to achieve the desired distribution with any particular powder. The routes to this for M1 and MIX were quite different.



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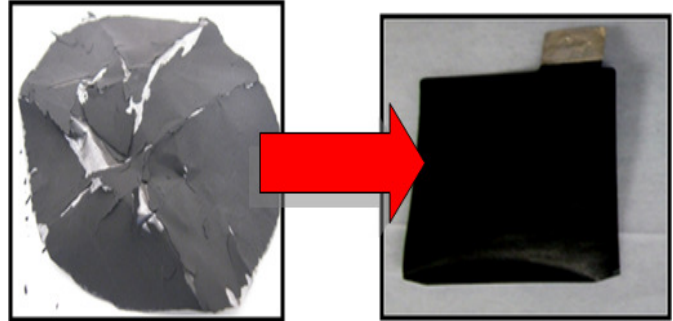
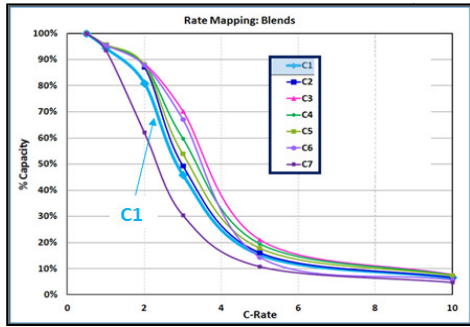
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Table 8: Details of characterizations of optimized highly loaded M1 and MIX electrodes

METRIC	M1		MIX		COMMENT
	1.75X	2.0X	1.75X	2.0X	
DISPERSION	PASS	PASS	PASS	PASS	SEM
RATE: > 80% capacity at 1C	PASS	PASS	PASS	PASS	½ cell coin cell
MANDREL	PASS	FAIL	PASS		Not needed for prismatic
TAPE ADHESION	PASS	PASS	PASS	PASS	Binder choice significantly effects adhesion
WET ADHESION	PASS	PASS on dull side – shiny side had some buckling	PASS	PASS	
CROSS-WEB UNIFORMITY	PASS	PASS	PASS	PASS	Relates to slurry stability & viscosity vs. shear
RESISTANCE	-	0.35 Ω	2.2 Ω	0.70 Ω	

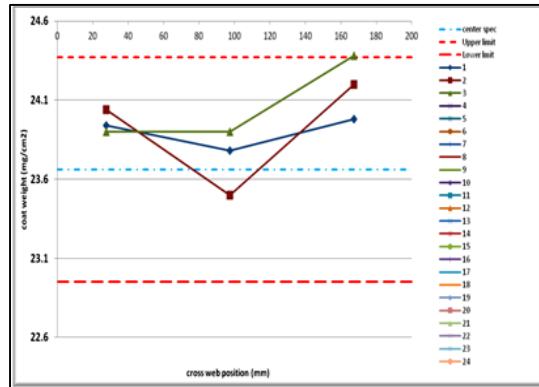
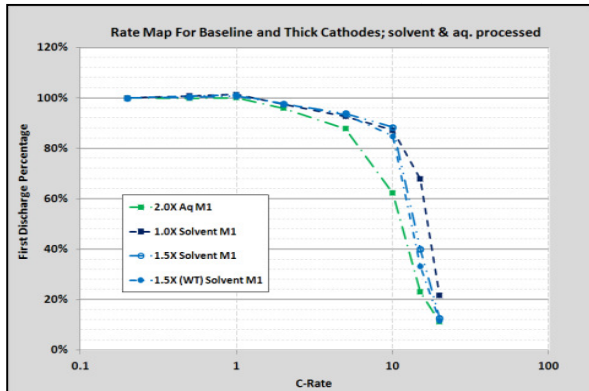
M1 High Loaded Electrodes: At program start the PSD of our existing solvent based commercial A123 powders used in 1.25X loaded electrodes for PHEV cells was used as the hypothesized PSD for higher loaded/low cost-high quality cathodes. For preliminary evaluations of thick aqueous anodes at 1.75X loading – electrodes from the high cost solvent based processes were used (successfully). For the cathode development portion of the program, using *new low cost* powders tuned to a PSD similar to solvent based process; eight formulations which explored carbon choices, ratios and total content were prepared by hand draw-down; the first pass evaluation criteria are formation capacity and rate behavior in coin half cells and dry/hot electrolyte adhesion. All formation capacities were similar; rate behaviors were more varied but all, excluding one, met the criteria for > 80% capacity retention at 1C – Figure 19 shows the

range of behaviors. Formula “C1” was chosen from this group since it is similar to those which have been successfully scaled up in pilot runs at lower electrode loadings, and it too scaled successfully. Figures 20a,b show the dry adhesion results with the low cost powder prepared on the pilot line before optimization and then with the optimized “C1 formulation. Figure 21 shows the coin cell rate maps for optimized M1 as a function of loading; the rate does not begin to drop off until about 2.0X, and all electrode loadings pass the rate metric of 80% capacity retention at 1C. Figure 22 shows the uniformity of C1 coating thickness across the web, which indicates excellent slurry stability.



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art, 1.75A M1X electrodes were prepared using the higher cos/solvent process power, as these were the only powders available and we wanted to begin range finding the correct PSD. From this effort it was determined that a similar PSD to that of M1 would be required.

When *low cost*/high quality M1X became available, six combinations of powder synthesis and milling conditions were tested in order to determine the best approach to provide the above hypothesized powder target PSD. Next, five composite formulations for electrodes were

prepared with this optimized M1X powder; all formulations used the binder which was found to be optimal for thick M1 electrode adhesion (figure 20) – the variations in the formulation design space were primarily the types and combinations of various conductive carbons. Figure 23A provides the coin cell rate map of this optimized formulation which shows that both loadings meet and exceed the target of 80% capacity retention at 1C; Figure 23 B shows the excellent uniformity of the coated roll of this material.

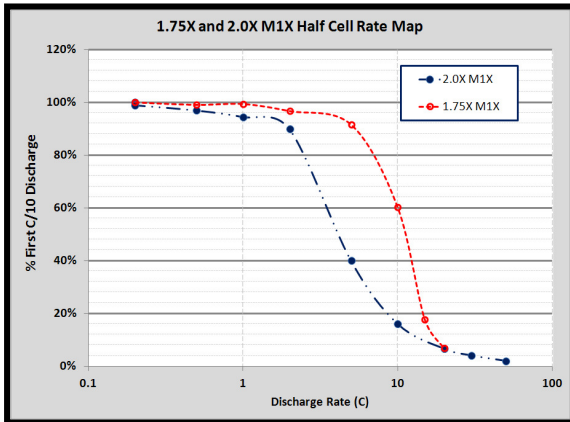
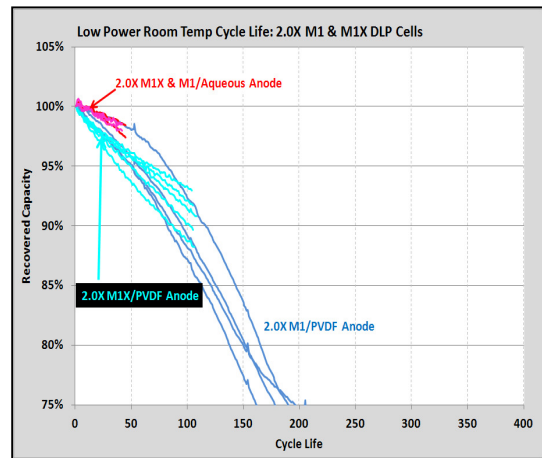
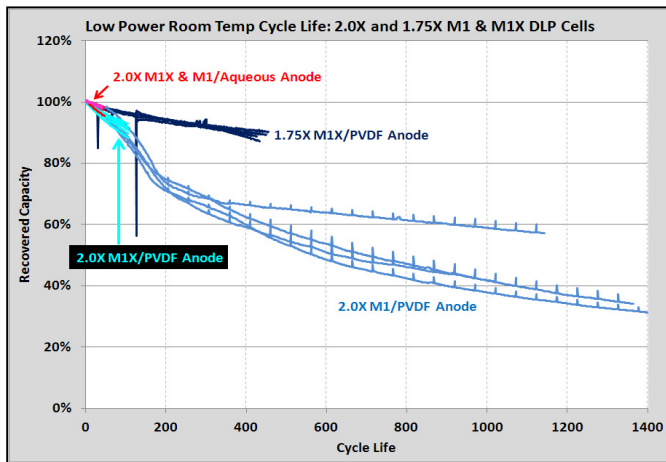


Figure 23A: M1X coin cell rate map shows 1.75X and 2.0X are both > 80% capacity at 1C – which is the target



Figure 23B: the pilot coated 6” film of 2.0X M1X had excellent uniformity

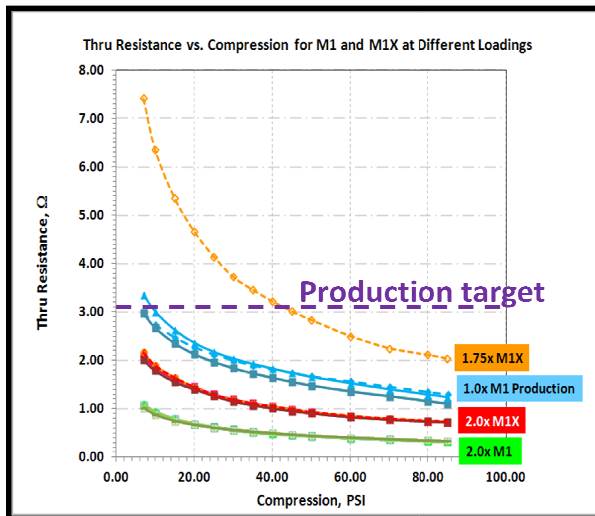
Figure 24 is the final full cell evaluations of highly loaded cathodes with anodes prepared with natural graphite with both PVDF and aqueous binders. There is a significant issue with the 2.0X loaded system with PVDF anodes – an adhesion issue is believed to be the root cause (Figure 7). The cells with anodes/aqueous binders continue to cycle beyond the end of this program.



Figures 24A, B: A - Full cell evaluations of M1 and M1X (both 1.7X and 2.0X) with natural graphite anodes with both types of binders. The adhesion of the 2.0X anodes with PVDF binder was poor (Figure 7) and resulted in poor cycle life. B – Transitioning to aqueous anode binders improves cycle performance.

Summary of low power cycle life evaluations of full cells: Figure 25 is a plot of electrode resistance vs. applied pressure for both M1 and M1X electrodes which are considered to be the best effort in this program – the asymptotic value is reported in the table. Total resistance includes both material and interfacial resistances – increase applied pressure reduces contact resistance to the point which the measurement ultimately represents the resistance of the bulk material. The production target for PHEV electrodes is 3 ohms, and so this value was used as the preliminary requirement for these highly loaded electrodes ((although ultimately a target would need to be set for PV applications). The high loaded cathodes meet the resistance targets. Table 9 summarizes the cycle life performance for this DOE and the prior MPSC programs. The cycle life drops at higher loadings, which is anticipated.

Much of this program's efforts were focused on production of low cost/high quality energy storage materials, and once these were developed the next step was technology development for the production of thick electrodes. The thick electrodes do show promise (all at 1.75X met the cycle life target) despite the relatively low percentage of program effort devoted to their development. Future studies should be devoted to further optimizing the thick electrode work which has been proven feasible with these materials.



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Table 9: Cycle life performance for different loadings and different anode and cathode actives – during both the initial MPSC and this Program – 63450 and double layer pouch cells

Electrode Loading	ANODE: (type graphite & type binder)		Cathode	Separator	1C/2C Cycling at Room Temperature	
	Type Graphite	Type Binder			% Initial capacity at 1200	Cycles to 80% Capacity

					cycles	
1.0X	High Cost Synthetic	PVDF	High Cost M1	Commercial PO separator	97%	>5500
			High Cost M1X		97%	>7,000
1.0X	Low Cost Natural	PVDF	High Cost M1		91%	2800
1.25X					86%	2650
1.5X					87%	2800
					NCS Gen 2	84%
1.75X	Low Cost Natural	PVDF	M1X	Commercial	80%	1200
		Aqueous	M1	PO separator	>80% ¹	>1200 ¹
2.0X		PVDF	M1	Commercial	40%-60%	~200
			M1X	NCS Gen2	-	100
		Aqueous	M1	Commercial	-	~300
			M1X	PO separator	TBD	TBD
					TBD	TBD

1: a 35°C accelerated test; room temperature result would be higher / TBD: cycling continues
2.2.7 Objective 6: Low cost nanocomposite separator proof of viability when coated on high loading anodes (including new anodes) and cathodes: 100% completed

Background on A123Systems Low Cost Separator – A123Systems has been developing an inorganic nanocomposite separator (“NCS”); it has the potential to be *very low cost* and as well to improve the safety of cells under abuse conditions. The NCS abuse resistance is due to its high mechanical durability at temperatures up to and beyond 200°C; this contrasts polyolefin separators that melt at ~130°C and allow contact of the cathode to the anode which insights a dangerous exotherm. Safety is increasingly important as cell capacities increase (for example 20 Ah → 60Ah cell), which is part of the low cost design concept.

Previous USABC and TARDEC programs focused on establishing material designs for cycle life and conductivity, with slot die coating onto electrodes as the manufacturing approach. The performance metrics were met successfully and the two development tasks remaining for this program were: 1) *High temperature storage* using Gen2 NCS was found to be less than cells with traditional polyolefin separators and this must be improved, and 2) *abuse performance* in a cell must be characterized and optimized to achieve the desired safety enhancement. The safety characterization will include NCS used both as the only separator and as a heat resistant layer (HRL). In the former design the NCS will be > 20μ thick while the latter will be a ~10μ layer used in combination with a traditional separator.

Table 10: Summary of targets and results for objective 6

TARGET	RESULT	COMMENT
<p><i>High Temperature Storage:</i></p> <p>Similar to standard polyolefin separator cells</p>	<p><i>TARGET MET</i></p>	<p>- A PV application specific high temperature storage target was not available – used traditional separator performance as target – this may be greater than what will be needed.</p> <p>-Gen2.5NCS is the new formulation which significantly improves upon Gen2 NCS. After 26 weeks at 55°C, the cell with 20um of NCS would have ~77% recovered capacity. This is slightly less than PO separator cell.</p>
<p>Cycle Life:</p> <p>1C/2C room temperature cycling of cells with 1.75X and 2.0X loading</p>	<p><i>TARGET NOT MET</i></p>	<p>-Cells having 25um of NCS as the only separator did not form, due to electrical shorts.</p> <p>-Root cause analysis showed that the slot-die coating had fish-eye holes –the hypothesis is that cathode debris filled these and caused the shorting.</p> <p>-This shorting issue <i>is believed to be particular to the circumstances of this build, and not a fundamental flaw in the NCS cell concept when applied to thick electrodes.</i></p>

<p>Safety:</p> <p>Determine NCS thickness required to pass all abuse tests.</p>	<p><i>TARGET PARTIALLY MET</i></p>	<p>- Thick M1 and M1X high capacity cells are expected to pass all abuse tests. M1 cells at capacities up to 45 Ah did not need NCS to pass abuse tests.</p> <p>Therefore, NCS efficacy evaluated with highly reactive 26650 cylindrical cells with metal oxide cathodes; 30-35um NCS will enable pass of all safety tests. At 12um, some but not all abuse tests will be passed.</p> <p>-Further evaluations of the lower limit of NCS effectiveness vs. thickness were conducted - the most difficult to pass test is nail penetration and > 12um Gen2 will be needed for this; further delineation requires the specific cell final design.</p>
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High temperature storage (HTS): NCS Gen2 met performance requirements for automotive applications with the exception of 55°C high temperature performance. Improvement of HTS therefore was the first step of integration of this material into the thick electrode cells. (see Appendix A2)

Reformulations to improve high temperature storage focused on changes and modifications to the inorganic material and binder content/composition as well as cell handling. High temperature screening in this program was conducted with double layer pouch cells in which the outer electrode is an anode coated with 40μ of the particular type of NCS (electrode is bare on the outer side) and the inner electrode is a double sided cathode with no NCS coating; PHEV electrodes at 1.0X loading were used. This high NCS thickness is intended to amplify the loss signal relative to smaller thicknesses and present a worst-case scenario; 40μ were used here in this screen while typical cells will have 20-30μ. In commercial cells with thinner NCS the loss in capacity would be expected to lower (anticipate it would scale with the NCS thickness after normalizing to the usual polyolefin separator cell). Figure 26 shows the performance of the best candidates in this screen. The best result is an A123 proprietary modification of Gen2 NCS. Polyolefin baseline and the “Gen 2.5 NCS” capacities after 28 weeks storage are 81% and 72%, respectively. Gen 2.5 normalized for standard thickness would be 77%.

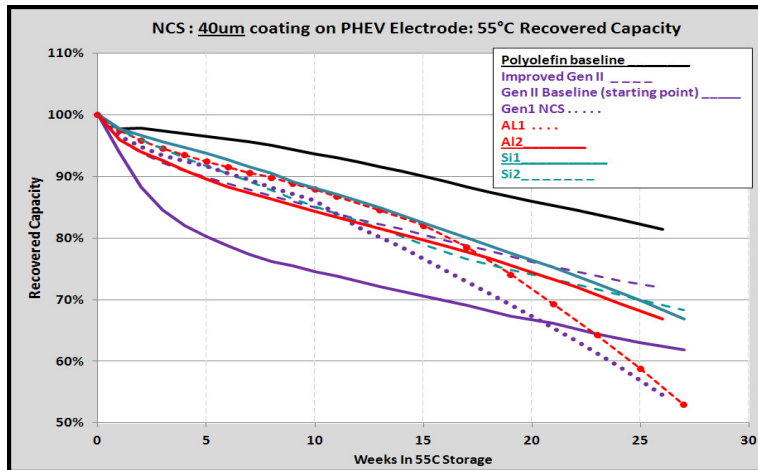


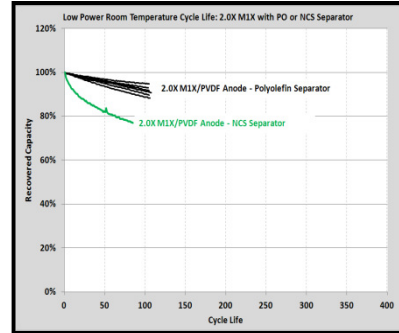
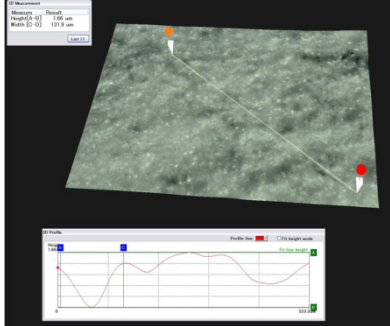
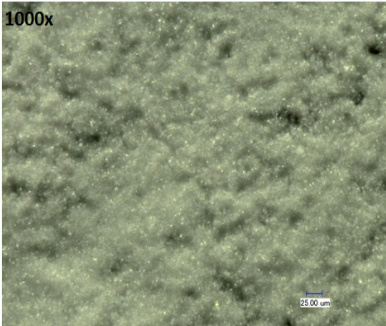
Figure 26: Gen2.5 candidates optimized for 55°C storage: the test is run on double the expected NCS cell thickness to enhance signal. The best result is an A123 proprietary modification of Gen2 NCS. Polyolefin baseline and the Gen 2.5 NCS capacities after 28 weeks storage are 81% and 72%, respectively. Gen 2.5 normalized for standard thickness would be 77%.

Small cell performance evaluations: Initial Gen2.5 deposition, as previously reported, was via spray coating on the 1.75X anode and MIX cathode. Optical micrographs showed that the coverage was uniform, of low surface roughness and without cracks. Thus the basic proof of concept, that thicker electrodes can fundamentally be coated effectively, was completed. The next step of a commercial slot die coating process was run with the Gen 2.5 NCS coated onto only the anode, due to limited available quantities of thick cathode. (Limited quantities of low cost M1 and MIX powder were available.) The decision was made to not coat the NCS on these cathodes due to the risk associated with development the NCS slot die coating process on this “new substrate”.

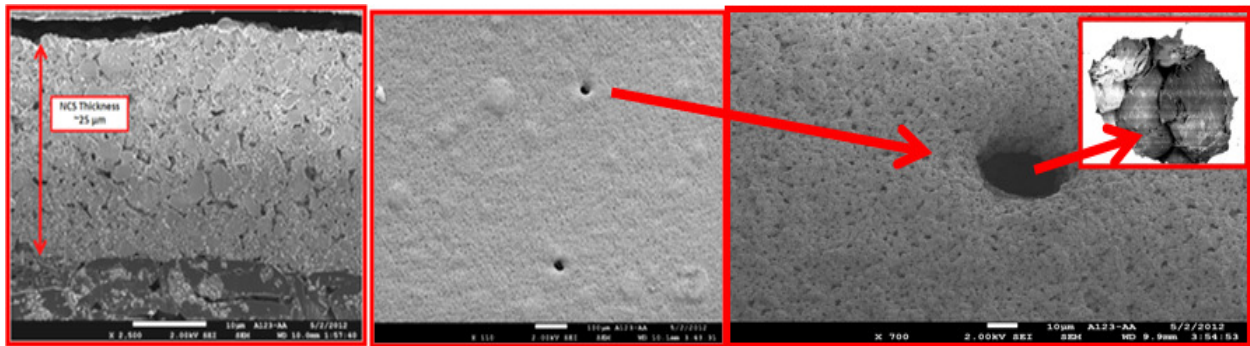
NCS cells were prepared from slot die coated 25um of Gen2.5 NCS on thick anodes – which were in this case 1.75X and 2.0X PVDF/natural graphite. The coating process appeared to proceed as expected and high magnification (1000X) optical microscopy showed a uniform film, as is typically the case – see Figure 27. However, with one exception, all of these cells failed to form due to shorting (cell open circuit potentials greater than about 100 mv were not achieved).

An extensive root cause investigation was conducted, including optical and SEM microscopy and EDS on tear-down samples and samples as prepared. This analysis showed a not-inconsequential number of fish-eye holes of diameter 10-30um in the NCS surface – see figure 28; these are not detectable with optical microscopy. Adjustment of SEM focal point shows that the natural graphite anode can be seen at the bottom of these holes which is in contrast to previous coating runs on thinner electrodes in which the fish-eye holes did not go through the depth of the NCS. Additionally there was some cathode debris on the NCS surface, as evidenced by Mn and Fe elemental signatures in the EDS. The failure hypothesis is that cathode debris filled the holes and shorted the anode to the cathode. NCS coatings have always had a certain density of these fish-eyes, but in thinner electrodes the electrode cohesion is better and there is less debris available to cross the gap and short the two electrodes together. As well, the typical NCS cell design calls for NCS coating of *both electrodes* so that a flaw in one NCS layer is (likely) compensated by an insulating adjacent layer on the opposite electrode. This was not possible with this build since materials supply issues did not allow coating of both electrodes. Thus, cell shorting in this first thick electrode build is believed to be particular to the circumstances of this build, and not a fundamental flaw in the NCS cell concept when applied to

thick electrodes. Future studies would coat NCS on both the anode and the cathode, improve thick electrode cohesion, and SEM inspect (rather than optical) for fish-eyes prior to cell building. Future runs would also include anodes with aqueous binder instead of the PVDF binder which was used in this case; these have improved adhesion/cohesion.



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NCS Abuse performance tests: In our initial evaluations it was determined that 20 Ahr cells with M1/graphite do not need NCS to pass abuse tests. The cell capacity was next increased to 45 Ah and there was still no reactivity issue in overcharge, 150°C and 300°C hotbox, and nail penetration safety. Therefore, it is anticipated that there will not be any major safety concerns in high capacity cells with M1 chemistry. MIX cells will need to be evaluated at these high capacities, once more material becomes available.

Therefore, evaluations which *focus on the effectiveness of NCS* in significant abuse situations were transitioned to the more reactive chemistry of mixed nickel oxide cathode and graphite

anode in a 26650. In these preliminary evaluations, 35μ but not 8μ of NCS enabled full pass of nail penetration, overcharge, and 150°C and 300°C hotbox tests (Appendix A3).

The second round of tests probed the lower limit of NCS thickness, since the upper limit (35um) was shown to be fully affective. Towards this objective, 8 and 12 micron coatings (applied to the cathode) with three different NCS designs were evaluated for nail penetration, 150°C hotbox and 5V overcharge in 63450 cells with metal oxide cathodes. These two thicknesses can be combined with traditional free standing commercial separators while keeping the *total* separator *thickness* at an acceptable level. In this way, abuse resistance can be implemented immediately while bypassing the significant development task of developing a manufacturing process for an NCS-only cell. (We estimate that about 30 microns total separator is acceptable and a typical PO separator is 17- 20 um thick, which leaves about 10um NCS).

The abuse results are provided below in Tables 10A, B, along with the code for reaction severity rating (“Eucar” number).

- Nail penetration results were sporadic with 8μ coating, and definitely improved with 12μ. However, full success will require more than 12μ – Figure 29A.
- For the 5V overcharge test, 8μ is sufficient – Figure 29B.
- For 150°C hotbox, the best and most consistent behavior requires 12μ of coating. Figure 29C has the plots of volt/current/temperature during this test and this shows that there is a significant time during which the voltage (pink curve in these plots) drops but the cell does not short for those cells with NCS. Shorting occurs quickly in traditional cells.

8.0 OPERATION	
The lot qualification testing is broken down into two categories:	
8.1	Performance testing (8.1.1 – 8.1.9)
8.2	Safety abuse testing (8.2.1 – 8.2.10)
The outcome of the safety abuse tests are given a numerical score, based on the results:	
Code	Definition
0	No change
1	Leak, vent, ACR>20mΩ, capacity<80% initial, or OCV change>10%
2	Smoke (more than a wisp)
3	Spark (more than just one spark)
4	Temperature > 150 °C
5	Jelly roll ejection (length of JR outside of can greater than 50mm)
6	Sustained flame (more than one second)
7	Explosion
8	Explosion where battery parts penetrate aluminum vice screen by breaking holes in that screen (Note: powder or similar small particles that exit through the normal openings of the screen/mesh is not considered 'penetrating the screen')

Table 10A; Eucar code

Test	Gen1 NCS		Gen2 NCS		Baseline 3.1 Ah (11.7 mΩ)
	8um 2.8Ah (12.5 mΩ)	12um 2.8Ah (13.2 mΩ)	8um 2.8Ah (12.0 mΩ)	12um 2.8 Ah (12.4 mΩ)	
Nail pen (test 4)	1=4	3= 4	1=4	1=3	2=6
	1-5	1=6	1=6 (2 tested)	2=4	2=7
	2=6			1=6	
150°C Hotbox (test 2)	Vent-5	Vent-4	Vent-4	Vent-4	Vent-1
			Vent-5		
Overcharge (test 2)	Vent-1	Vent-1	Vent-1	Vent-1	Vent-1

Table 10B: Summary of abuse results for thinner layers of NCS with two different designs- Gen1 and Gen2.



Figure 29A: cells after nail penetration test

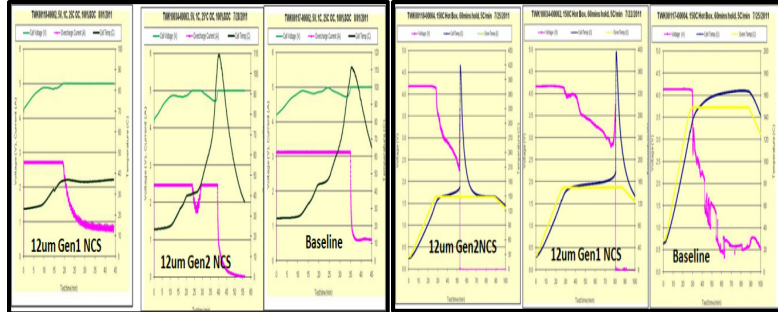


Figure 29B: Volt / current temperature profiles for the 5V Overcharge test

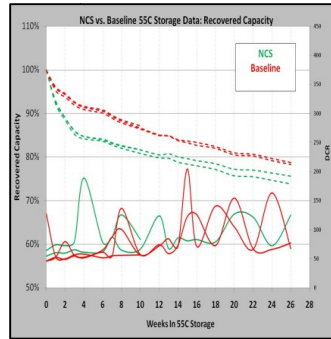
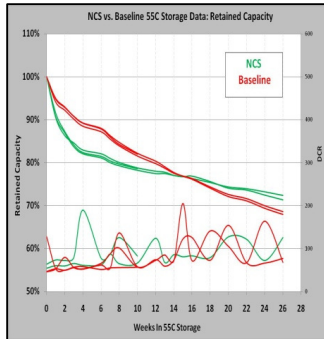
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APPENDIX

A1: Summary of Objectives spanning the original MPSC and this DOE program

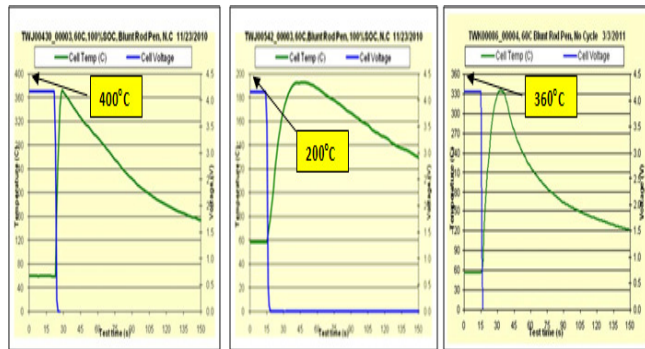
TECHNICAL GOALS & APPROACH: <i>Large format low cost lithium ion battery for PV and Other Low Power Applications</i>				
Objective	Metric(s) MPSC → DOE	Design Variable	Approach Program 1 (MPSC)	Approach Program 2 (DOE)
Low Cost	\$0.30/Wh → \$0.25/Wh	Cathode	Reduce Fe phosphate cathode active cost to <\$20/kg	Increase cathode energy density: FePhosphte → FeMnPhosphate Reduce FeMnPhosphate cost relative to start of program
		Anode	Reduce active cost 50%: synthetic → natural graphite	Reduce active cost: manufacture A123 proprietary low cost natural graphite
		Reduce relative passive materials cost by increasing amount of energy storage material	Increase electrode loading by 50% vs. baseline	Further increase loading to 75% to 100% vs. baseline
		Increase energy content of chemistry	None	Increase cathode energy density: FePhosphte → FeMnPhosphate
Energy Density	>120 Wh/kg → >150 Wh/kg	Cell Design & Cell Chemistry	Increase electrode loading by 50% vs. baseline	Increase electrode to 75-100%
				Increase cathode energy
				Increase cell capacity to > 20 Ah
Safety	No flame or short in standard abuse tests (Nail pen)	Flammable electrolytes	Nanophosphates do not liberate O ₂ to support combustion – not a problem	
		Reactive cathode material	Nanophosphates are much less reactive than traditional chemistry with metal oxides	
		Li dendrite shorts	Nanophosphate has no excess lithium, unlike metal oxides, and so cannot readily plate lithium	

A2. NCS Gen2 high temperature storage background – NCS which met all other performance metrics had lower recovered and retained capacity in comparison to polyolefin baseline. In this DOE program the improvement in storage was addressed. Below is the starting point for Gen 2.0 performance in 63450 cells with PHEV electrodes (1.0X loading).



Separator	% Retained Capacity after 26 weeks	% Recovered Capacity after 26 weeks
NCS Gen 2	72.0%	74.9%
Polyolefin	68.6%	78.4%

A3. Initial NCS cell abuse tests on metal oxide cells – A123 Nanophosphate™ cells are very safe and do not provide enough signal for effective abuse testing. As such, a screening for NCS was run in a 26650 cylindrical cell with a nickel-based metal oxide cathode and a graphite anode; this is a highly. The plots below show the temperature response with varying amounts of Gen 2.0 NC, the table summarizes the performance across all abuse evaluations. These results show that a thickness between 8um and 35um Gen2 NCS is required in order to pass all abuse tests for this cell. This is an approximation of what would be needed in another cell design.



Test	No NCS (3.7Ah, 11mΩ)	35 μm Gen2 NCS: no additional separator (2.6Ah, 12mΩ)	8μm Gen2 NCS + Polyolefin Separator (3.4Ah, 13mΩ)
Nail pen	Fire (6)	No fire (4)	Fire (6)
150°C Hobbox	Vented (1)	Fire (6)	Vented (1)
“300°C” Hobbox	Fire (6)	Fire (6)	Fire (6)
Overcharge	Vented (1)	Vented (1)	Vented (1)