Final Technical Report (FTR)

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Executive Summary

Being able to refill a cars gas tank when low on fuel is incredibly convenient and is a lacking feature for battery elective vehicles. New High-Energy & Safe Battery Technology with Extreme Fast Charging Capability for Automotive Applications was a research project designed to help correct this lacking feature by developing automotive sized Li-ion battery cells and demonstrating their ability to charge in under 10-minutes. To address the technical challenges Microvast, a cell manufacturer, was joined by Argonne National Labs, battery technology innovator, and BMW, a renown OEM, worked together to define and validate materials and cells for this project.

By projects end, Microvast had successfully built and demonstrated a 240 Wh/kg, 35 Ah pouch cell that was capable of over 800 10-minute charge, full discharge cycles. From the outset of the project the plan was to use large amp-hour cells (ie automotive relevant sizes) to ensure the project findings and outcomes were most relevant for electric vehicle applications. The manufacture of cells was done using test manufacturing lines at Microvast and BMW that closely resemble the procedures of a Li-ion battery cell factory.

To achieve the fast charge performance the project relied on advanced materials developed by Microvast and Argonne National Labs. The cell incorporated Microvast’s thermally stable separator and Argonne invented, Microvast scaled full concentration gradient (FCG) cathode to improve the cells safety at the material level. The FCG cathode was also further developed in the project to boost energy delivered and improve the materials durability to abusive conditions such as fast charge. The FCG, as a designer cathode, is well suited to customization that improves performance compared to NMC or NCA cathodes that are typically being used in electric vehicle battery designs today.

This project provides benefit to the United States public in a number of ways:

- Advancing fast charge technology makes electric vehicles even more attractive compared to traditional gasoline powered cars, which reduces greenhouse gas emissions and is more compatible with renewable energy sources like wind and solar compared to imported oils.
- For commercial & fleet vehicles fast charge is attractive because it allows strategic charging during off peak hours and allows more up-time for vehicle operation, which translates to improved energy efficiency and lower greenhouse gas emissions.
- The research advances general knowledge on battery science, which is an emerging market that has traditionally been dominated by Asian companies. For the United States to become self-reliant on batteries advanced materials and component production trials like those done in this study are necessary.

Overall, this project accomplished the development of materials and cells for high energy fast charging battery cells, as was proposed in the statement of project objectives agreed to during project selection.

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Summary of Project

Objectives

The objective of the project is to research, develop, design, fabricate, and demonstrate high energy XFC cells capable of a 10-minute fast charge protocol at ≥6 C charging rate (1 C Discharge, > 180 Wh/kg delivered energy), cost of ≤$150/KWh, and 500 cycles with <20% fade in specific energy.

Overview of Work Plan

Microvast received input from BMW regarding the cell requirements, then the project team worked to to test cells with existing cathode, anode, electrolyte and separator (220Wh/kg capable) to baseline the fast charge performance during budget period 1. During budget period 1 Microvast and Argonne worked on developing a new high-energy redox couple comprising a varying slope, full concentration gradient cathode and a new electrolyte additive to reduce impedance rise on the anode, especially during fast charge, to achieve higher energy densities. These new materials will be used in conjunction with existing anode, carbon, and high thermal stability separator technologies to develop XFC cells. The project team worked during budget period 2 will focus on refining the technology, understanding the failure modes, and generating a new higher energy XFC cell. All generations of XFC cell developed during the project were < 15Ah and used prismatic and pouch designs, with the final deliverable pouch cell being about 35Ah in capacity, and providing 240Wh/kg at C/3.

Project Task and Gantt Chart

Task 1.1 – Build Gen1 Cells: Using the existing state of the full concentration gradient material, in conjunction high quality artificial graphite the project team built pouch and prismatic cells > 15Ah in size to baseline the XFC performance of the same electrode in different cell formats.

Task 1.2 – Gen2 R&D: Laboratory development of FCG-VS cathode and LiDFOB electroltye additive for use in the Li-ion XFC cell. These materials are incorporated into the Gen2 XFC cell electrodes to try and boost the Wh/kg by 20 Wh/kg at C/3 compared to Gen1. The cells were built as pouch and prismatic cells.

Go/NoGo: At end of project period 1 9 XFC cells were delivered to a DOE national lab for independent testing.

Task 2.1 – Gen2 Analysis and Diagnostics: Teardown of used XFC cells made by the project were characterized to study the status of the anode electrode interface, and to identify how the electrode materials were holding up to XFC cycling.

Task 2.2 – Gen3 R&D: Scale-up of the final version of project materials was conducted for the FCG-VS and LiDFOB electrolyte additive. The project materials were used to build a Li-ion pouch cell. The original plan was to increase Gen 3 by 20 Wh/kg compared to Gen 2, but the inability of Gen 2 to meet the cycle requirements led the project team to make some adjustments; maintaining the energy density of Gen 2 and electing to only pursue pouch cell format.

Final Deliverable: 18 pouch cells, 240 Wh/kg at C/3 and 35Ah in capacity were delivered to a DOE national lab for independent testing.

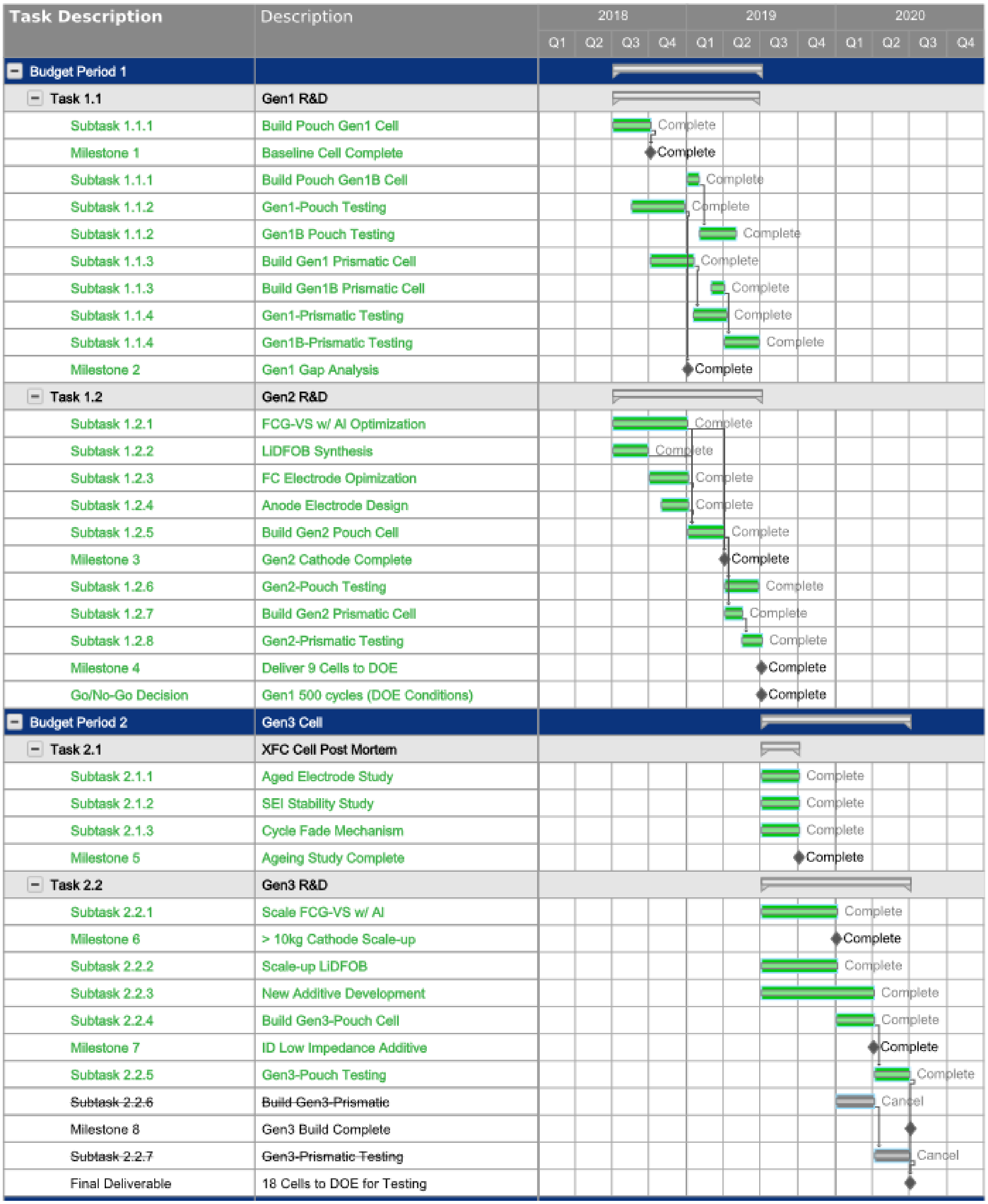
Special Requirements: The extreme fast charge testing performance needed to meet the following criteria:

1. The cells charging time is limited to 10-minutes when doing XFC testing. The procedure within those 10-minutes has no requirements.
2. The beginning of life 10-minute charge must deliver > 180 Wh/kg when discharged at C/3.
3. The end of life 10-minute charge must deliver > 144 Wh/kg when discharged at C/3.
4. The XFC cycle tests will be done at 10-minute charge and 1C discharge; with periodic reference performance tests.

Project Milestones

Table 1 The milestone table used for project.

Milestone	Target End Date	Description (And TRL Rating)	Milestone Progress
Gen1 Build Complete	10/3/2018	At the start of project, a baseline cell will be designed by project partners. **Gen1 TRL4 to TRL5**	Complete
Gen1 Analysis Complete	1/3/2019	The final analysis on Gen1 cell will be complete, and the technology gap will be known to aid additional cell development	Complete
Gen2 FCG-VS Optimized	4/3/2019	The cathode material process for use in Gen2 cells is complete **Gen2 TRL3 to TRL4**	Complete
Deliver 9 cells to DOE	7/3/2019	Upon completion of budget period one 9 cells (Gen1 or Gen2) will be delivered to the DOE for cycle testing	Complete
Go/No Go Decision Point	Go/No Go	Gen-1 cells PASS 500 cycles 6C charge*/1C discharge cycle requirements (see FOA for * details) **Gen1 TRL5 to TRL6**	Complete, PASS
Ageing Study Complete	10/3/2019	The findings of spent cell diagnostics are done for Gen2 cell **Gen2 TRL4 to TRL5**	Complete
>10 kg Cathode Scale-up	1/3/2020	The designed cathode is scaled to at least 10kg **TRL4 to TRL5**	Complete
Low impedance Additive	4/3/2020	The new additive designed to limit impedance rise in the cell is determined	Complete
Gen3 Build Complete	7/3/2020	The final Gen3 pouch and can cells completed **Gen3 TRL4 to TRL5**	Complete, delivered to DOE



Task Description	Description	
Budget Period 1		
Task 1.1	Gen1 R&D	
Subtask 1.1.1	Build Pouch Gen1 Cell	Complete
Milestone 1	Baseline Cell Complete	Complete
Subtask 1.1.1	Build Pouch Gen1B Cell	Complete
Subtask 1.1.2	Gen1-Pouch Testing	Complete
Subtask 1.1.2	Gen1B Pouch Testing	Complete
Subtask 1.1.3	Build Gen1 Prismatic Cell	Complete
Subtask 1.1.3	Build Gen1B Prismatic Cell	Complete
Subtask 1.1.4	Gen1-Prismatic Testing	Complete
Subtask 1.1.4	Gen1B-Prismatic Testing	Complete
Milestone 2	Gen1 Gap Analysis	Complete
Task 1.2	Gen2 R&D	
Subtask 1.2.1	FCG-VS w/ AI Optimization	Complete
Subtask 1.2.2	LiDFOB Synthesis	Complete
Subtask 1.2.3	FC Electrode Opimization	Complete
Subtask 1.2.4	Anode Electrode Design	Complete
Subtask 1.2.5	Build Gen2 Pouch Cell	Complete
Milestone 3	Gen2 Cathode Complete	Complete
Subtask 1.2.6	Gen2-Pouch Testing	Complete
Subtask 1.2.7	Build Gen2 Prismatic Cell	Complete
Subtask 1.2.8	Gen2-Prismatic Testing	Complete
Milestone 4	Deliver 9 Cells to DOE	Complete
Go/No-Go Decision	Gen1 500 cycles (DOE Conditions)	Complete
Budget Period 2	Gen3 Cell	
Task 2.1	XFC Cell Post Mortem	
Subtask 2.1.1	Aged Electrode Study	Complete
Subtask 2.1.2	SEI Stability Study	Complete
Subtask 2.1.3	Cycle Fade Mechanism	Complete
Milestone 5	Ageing Study Complete	Complete
Task 2.2	Gen3 R&D	
Subtask 2.2.1	Scale FCG-VS w/ AI	Complete
Milestone 6	> 10kg Cathode Scale-up	Complete
Subtask 2.2.2	Scale-up LiDFOB	Complete
Subtask 2.2.3	New Additive Development	Complete
Subtask 2.2.4	Build Gen3-Pouch Cell	Complete
Milestone 7	ID Low Impedance Additive	Complete
Subtask 2.2.5	Gen3-Pouch Testing	Complete
~~Subtask 2.2.6~~	~~Build Gen3-Prismatic~~	Cancel
Milestone 8	Gen3 Build Complete	
~~Subtask 2.2.7~~	~~Gen3-Prismatic Testing~~	Cancel
Final Deliverable	18 Cells to DOE for Testing	

Figure 1 Gantt Chart for Project

Overview of Technical Approach

Since Microvast's inception in 2006, the company's mission has been to develop battery systems focused on the 3 key battery criteria viewed as essential for electric vehicle technology: **Safety, Fast Charging, and Long Life**. The plan for this project was to develop XFC cell technology while maintaining those three design principles.

Using Automotive Size Li-ion Battery Cells: As a Li-ion battery grows in format new challenges for safety and fast charge performance are expected. These challenges often relate to the difficulty in diffusing or distributing heat in the Li-ion cell when high currents from fast charging or hotspots related to shorts or other defects are present in the cell. To ensure the project focused on relevant challenges for XFC cycling, the team agreed that XFC evaluations would be done using automotive size pouch or prismatic cells. The electrodes for the Li-ion batteries were prepared by Microvast; and then the pouch cells were built by Microvast and the Prismatic cells were constructed by BMW.

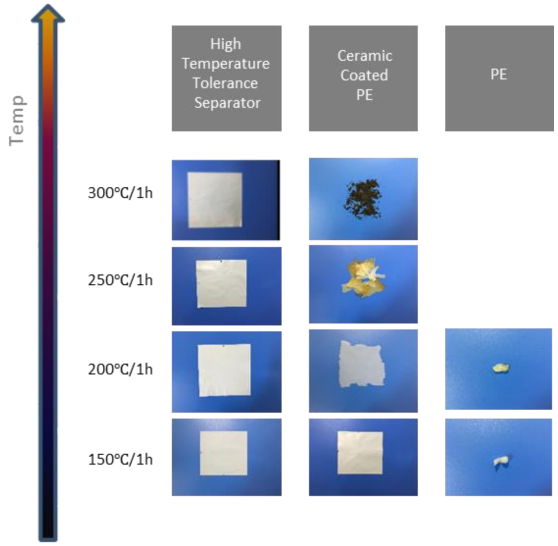


Figure 2 Microvast Aramid separator compared to PE and ceramic coated PE while heated to $300^{0}C$

Intrinsically Safer Materials: Cell safety is a major concern for automotive size Li-ion batteries, because larger amounts of stored energy are enclosed within the cell casing. While there are engineering controls that can be applied to a Li-ion cell in an automotive setting, the root cause for many unwanted safety issues occurs at the cell's material level. Knowing this, Microvast has worked to develop intrinsically safer cell component materials for use in fast charge batteries. While not developed as part of this project, Microvast's Aramid separator was used, which provides exceptional thermal stability (see Figure 2) without compromising fast charge performance. This separator pairs well with the full concentration gradient variable slope (FCG-VS) material that was developed during the project, and is conceptualized for a single cathode particle in Figure 3). FCG cathodes have been previously reported to provide improved safety because their design places more stable transition metal compositions at the particle surface while protecting more energetic compositions inside the materials core [1, 2, 3, 4]. With the FCG-VS the thermal decomposition is slowed and delayed, while the separator maintains its shape until the cathode is de-energized during a thermal event.

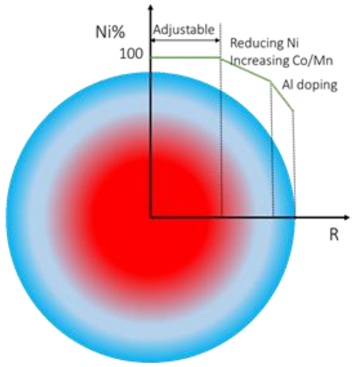


Figure 3 Schematic of full concentration gradient variable slope (FCG-VS) cathode particle design

Materials to Enhance Fast Charge: Li-ion battery fast charge performance is influenced by kinetic and diffusion characteristics of the cell and the component materials. On the cathode side, the FCG material is known to have a unique, radially oriented crystal morphology that makes the 2-D Li layers in the cathode crystal perpendicular to the secondary particle surface. By orienting the crystal planes in this manner the rates for intercalation and deintercalation are improved, which is beneficial for fast charging. In addition, the performance of the electrolyte and how it interacts to form the solid-electrolyte interface (SEI) is critically important. In this project the team worked on formulations that contained LiDFOB additive because its decomposition helps form a more stable SEI. A more stable SEI means lower resistance, and with lower resistance there is less overpotential, meaning the fast charge performance can be improved. As the overall cells energy density is increased having a way to reduce the overpotential thru materials becomes increasingly important, since the thicker electrodes create diffusional overpotentials that result in Li-plating and worse capacity utilization during fast charging.

Plan Adjustments During Project: As a research and development effort, the best laid plans sometimes require adjustment as new information and understanding are produced during the work. For this Extreme Fast Charge work the bulk of our hypothesis and planning remained intact throughout the project, but there were some changes worth noting.

- Originally the project plan was intended to be three generations of XFC cells , with each generation increasing in energy density during C/3 grading. During the course of the project, it was found that the Generation 2 build was lacking in performance, so the project team decided to remain at the same 240 Wh/kg target energy density for Gen3 as well. This counter measure was outlined as a risk control in the project concept paper and initial proposal.
- For Generation 3 the project team decided to only focus on pouch cell XFC batteries. Between Generation 2 and 3 the team was interested in changing the electrode format from a jelly roll to stacked electrodes in the hard can cell [NOTE: the pouch was always stacked], however the manufacturing the electrode at Microvast and sending to BMW proved not possible due to new physical dimensions. Instead of manufacturing hard can cells for Generation 3, Microvast delivered pouch cells to BMW for fast charge protocol testing instead.
- The original project planning listed the use of mesoporous carbon micro beads (MCMB) as a component in the anode electrode to boost fast charge performance. During the project, however, only artificial graphite was necessary; which the project team considered to be a positive change in plan since the material cost, and hence the cell cost, is lower.
- The original timeline for project was set to run for 2 years. However, a no cost extension was needed to complete the final Generation 3 work. This delay was partially due to COVID 19.

Results and Discussion

To facilitate the reporting of project findings the results section will be broken into three categories: 1) Material Development, 2) Post-Cycle Studies, and 3) Extreme Fast Charge Cell Performance. In actuality the work was often being done in parallel on the three topics, and broken down as budget period 1 and 2 in the Gantt chart.

Material Development:

Gen1 Cell FCG

The FCG cathode used in the cell was prepared with a Ni70Mn30 core and grew to a Ni50Mn30Co20 surface during the precursor preparation. The precursor material was mixed with LiOH and calcined under a mixed air & oxygen protocol to get the final material, which has a tap density near 2.15 g/cc and a 177 mAh/g C/10 capacity in the voltage window 2.7-4.3V when tested in a half cell. The final material SEM is shown below.

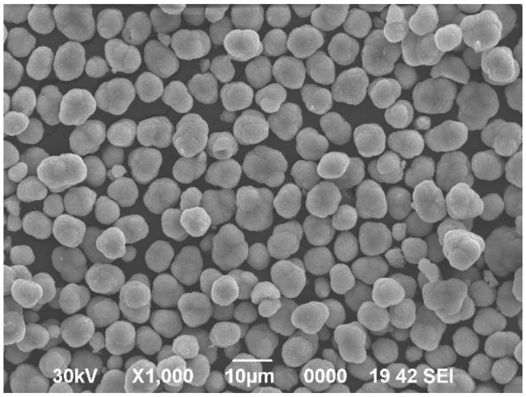


Figure 4 SEM of FCG linear particles used in the Gen1a electrode.

ANL also studied some 631 FCG provided by Microvast (Figure 4), since that was the composition selected for use in the Gen1a cell. Using a TiO2 coating technique, the particles were modified to contain some Ti. This was an innovative strategy hypothesized to make FCG-VS surface more stable, since the Ti is unable to diffuse throughout the particle during calcination. Performance of the coated and uncoated material is shown in half cell tests in Figure 5.

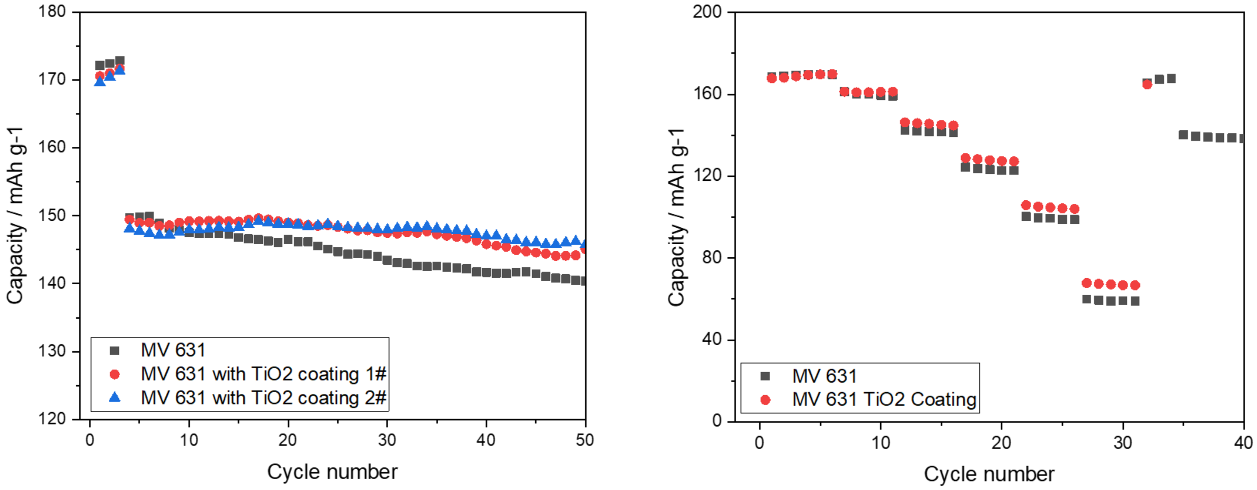


Figure 5: Modification of a Microvast prepared 631FCG material with some Ti coating. It is hypothesized that the coating, once calcined, introduced a new sharp gradient slope into the particle. The Ti addition improves the rate performance, and maybe the capacity retention, of the material.

Gen2 and Gen3 Cell FCG-VS Development

The FCG-VS material is intended to be a high capacity cathode that shows improved stability and performance over NMC cathodes. The reason a varied slope material is necessary to make a higher nickel composition is that it has better stability and safety then a uniform NMC composition. Using co-precipitation reactors are ANL and MV, a control NMC and FCG cathode with Ni85% was synthesized. To better understand the differences of materials with and without a gradient, a number of characterizations were undertaken on these materials. The SEM of the precursor and final material for Ni85% NMC collected after 24 and 48 hrs as well as the FCG Ni85% material is shown in Figure 6. Both materials show good tap density after being calcined.

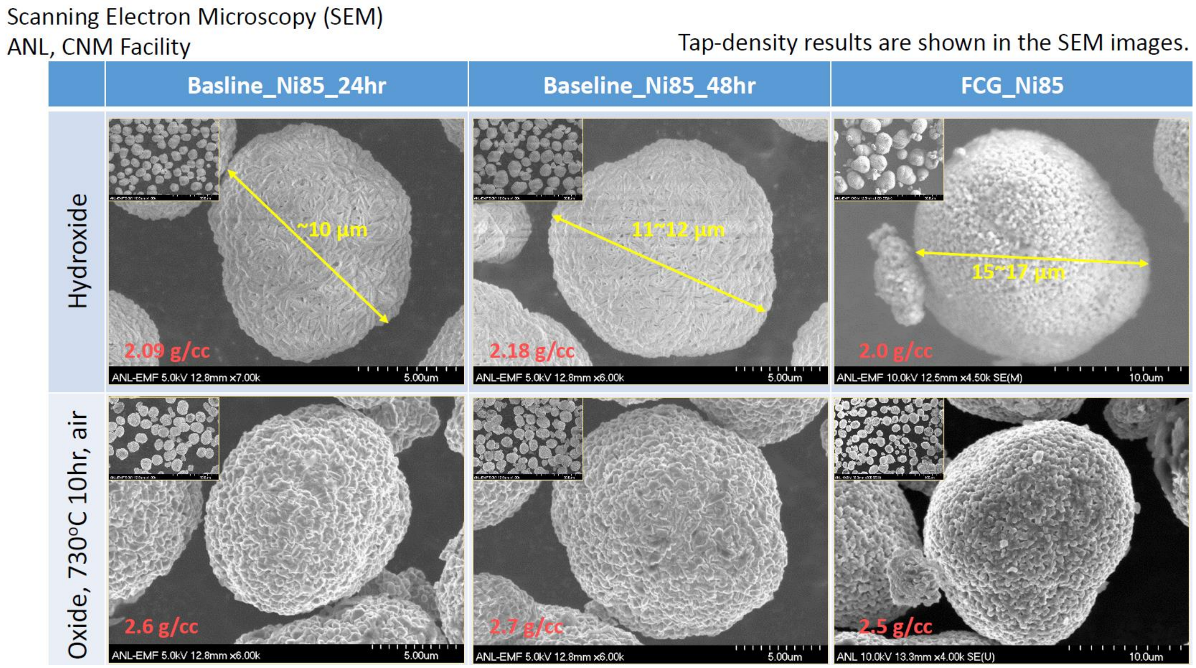


Figure 6: SEM of the precursor and final cathode material for NMC and FCG Ni85. The tap density is shown in red, and the SEM inset shows a zoomed out view of the particles

The battery half cell performance of these NMC and FCG Ni85% samples was tested for rate and cycle performance (Figure 7). The FCG material has better capacity and rate performance then the NMC material. To understand the differences in cycle performance additional characterizations were done.

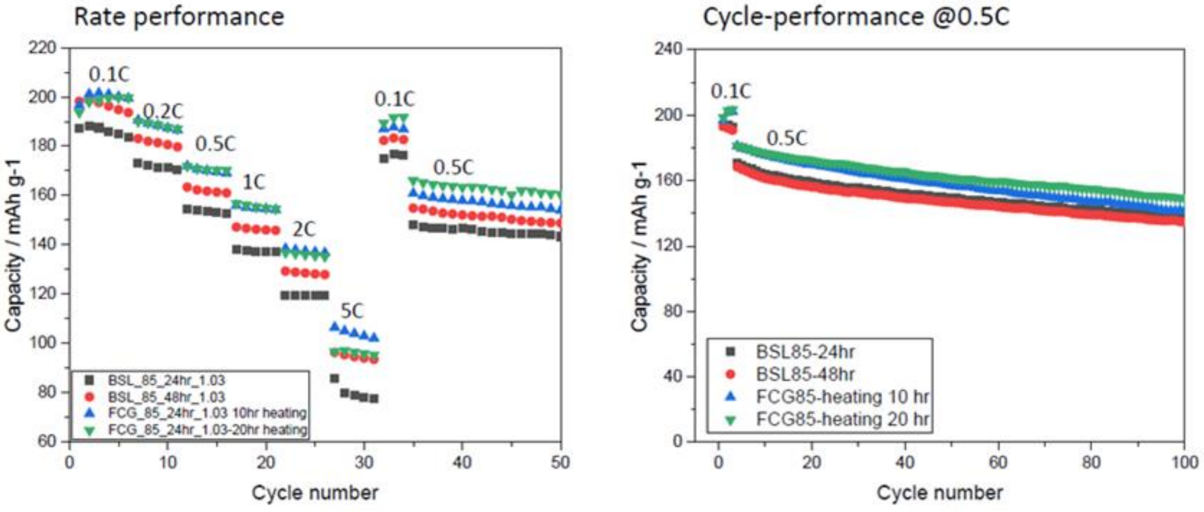
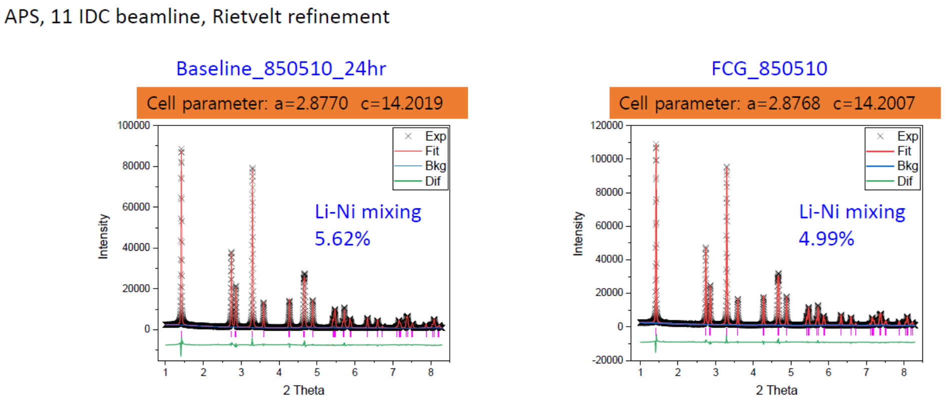


Figure 7: The rate and cycle performance of the FCG and NMC Ni85% cathode materials prepared for the project. The rate and capacity are better for the FCG material.

The final materials of Ni85% NMC and FCG were further compared using advanced characterization at the Advanced Photon Source (APS). First, x-ray diffraction was collected and then analyzed via reitveld refinement (Figure 8). From the refinement the degree of Li-Ni mixing, which is an indication of the disorder in the crystal lattice and has been shown in past papers to correlate with material rate performance, was determined. The FCG material has a slightly lower Li-Ni mixing, which could help explain the improved rate performance.



Element	Occupancy
Li1	0.9438
Ni1	0.7938
Mn	0.05
Co	0.1
Li2	0.0562
Ni2	0.0562
O1	1.000

Element	Occupancy
Li1	0.9501
Ni1	0.8001
Mn	0.05
Co	0.1
Li2	0.0499
Ni2	0.0499
O1	1.000

Figure 8: The reitveld refinement of NMC and FCG cathode particles with Ni85%. The occupancy from the refinement is shown below the XRD pattern

During the transmission x-ray microscopy elemental mapping of the FCG particle is also possible and shows a weak gradient from the core to the surface of the material (Figure 10a)). In addition, a FIB cross section of the FCG particle was done (Figure 10b)) at Peking University and elemental mapping was collected to visualize the Ni and Mn gradient (Figure 10c) & 10d)). From the image Mn is particularly present at the particle interface, which is important for material stability since interfacial degradation is the initiator for impedance rise and thermal decomposition.

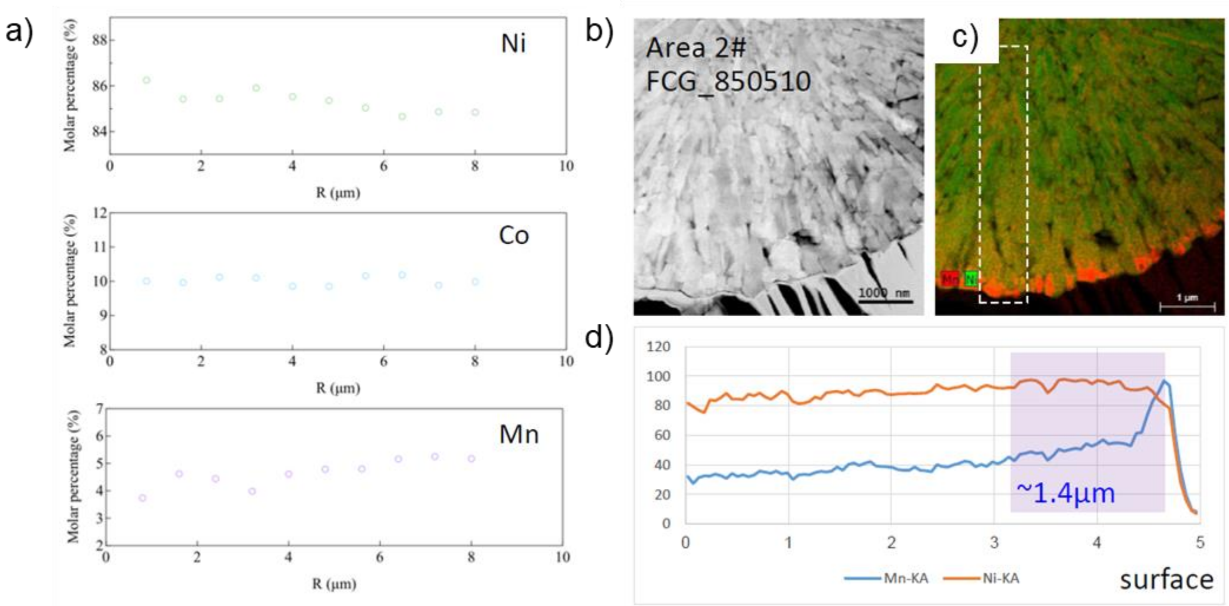


Figure 9: a) The percentage of Ni-Mn-Co from the interior to exterior of particle analyzed by TXM. b) FIB cross section of the FCG Ni85% particle. c) The elemental mapping of Ni and Mn on a cross sectioned particle, showing a higher concentration of Mn at the particle surface. d) The signal intensity of Ni and Mn from a line scan within the white dashed box of c).

In addition to the gradient of Ni-Mn in the FCG, the particle can be further improved by the adding a doping/coating "gradient" near the surface of the material. The FCG Ni85% material was treated with Al, Ti and B treatments. The confirmation that the Al and Ti elements were on the particles was proved with EDS mapping from SEM collected at CNM (Figure 11).

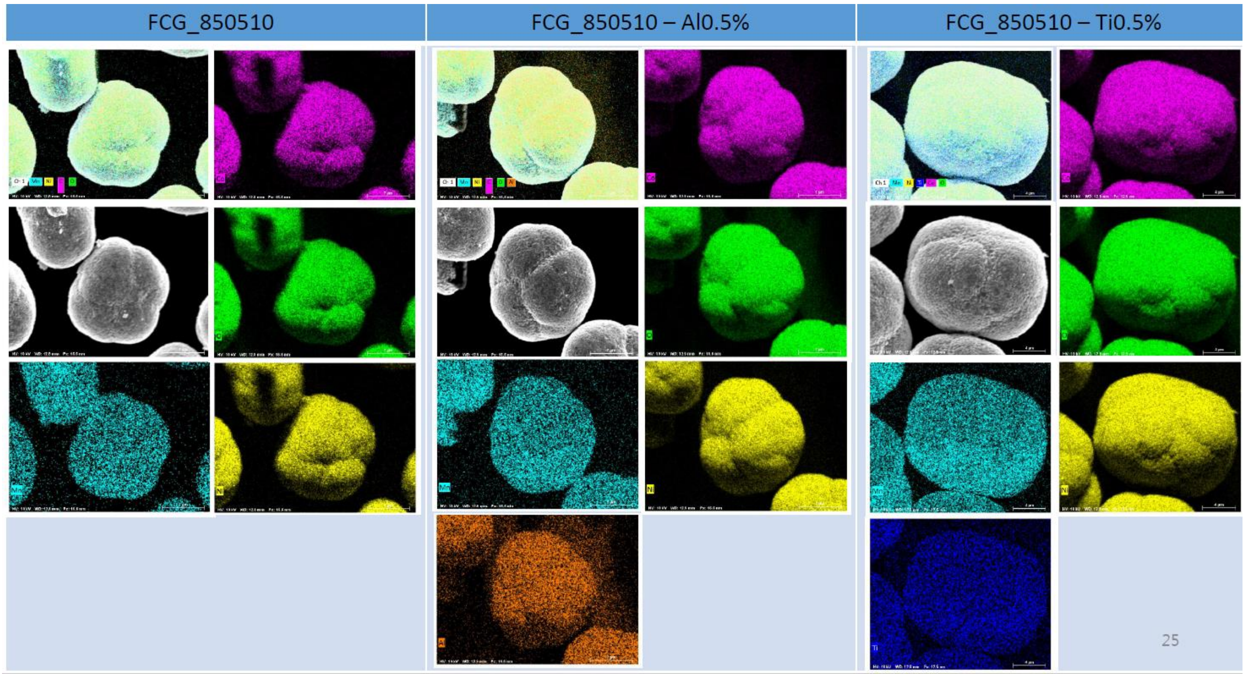


Figure 10: SEM-EDS elemental mapping of FCG Ni85% untreated, and after a Al or Ti treatment.

Variable slope FCG was prepared with an average Ni composition of 82.5% Ni/Ni:Mn:Co in 100 kg batches, based on the confirmation last report that materials can be made with some gradient preference for Al at the material surface. 4 batches were prepared, three with Al and one w/o as a control for full cell testing. The three batches with Al have very small differences in their processing so we could explore the impact of those processing variables on performance. In Figure 20 the 0.33C cycle data for ~5.8AH cells tested at room temperature is shown. After about 300 cycles the cells are showing good retention. Microvast also tested the materials under 1C conditions (Figure 21), with a reference cycle at 0.33C + HPPC collected periodically to align with USABC test manual reporting methods. The results of those reference cycles are reported in Table 2. After about 700 cycles all the samples show greater than 90% capacity retention during the reference cycle.

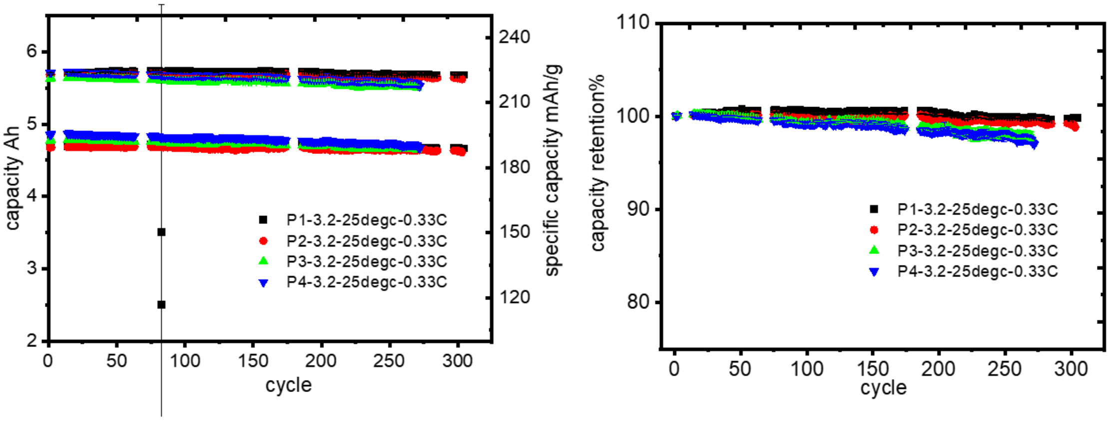


Figure 11 Small pouch cell (~5.8AH) cycling at 0.33C, 25^{0}C results for FCG-VS w/ Al material cathode.

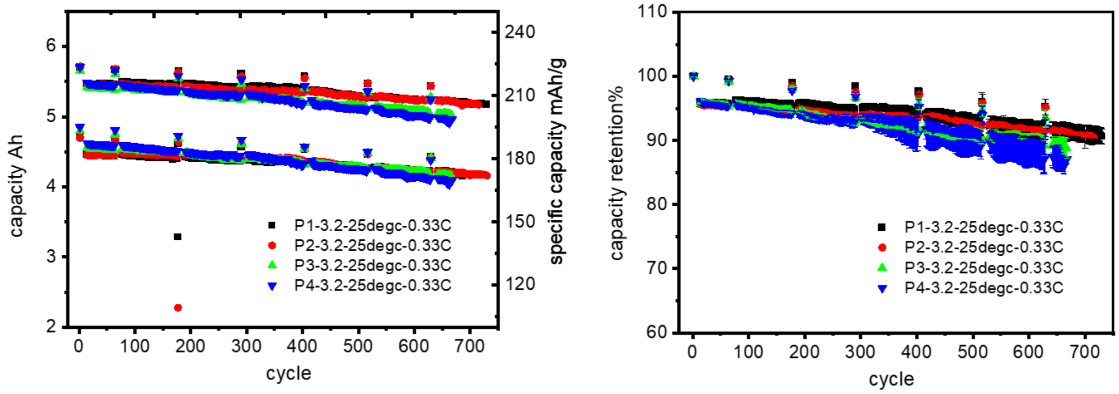


Figure 12 Small pouch cell (~5.8AH) cycling at 1C, 25^{0}C result for FCG-VS w/ Al cathode. Error bars are included to show variation between cell duplicates.

Table 2 Cell property table at the reference performance cycle (RPTX) for the ~5.8AH FCG-VS w/ Al cells tested at 25^{0}C at rate 0.33C and 1C.

	T1-4-1C								**T1-4-0.33C**			
	RPT1	RPT50	RPT100	RPT200	RPT300	RPT400	RPT500	RPT600	RPT1	RPT50	RPT100	RPT200
Cycle Number	2	65	178	291	404	517	630	743	2	63	174	285
Capacity (AH)	5.72	5.69	5.67	5.63	5.57	5.43	5.39	5.34	5.71	5.73	5.73	5.68
Retention %	100.00	99.48	99.02	98.38	97.33	94.85	94.26	93.28	100.00	100.34	100.35	99.57
Wh/kg	227.12	226.19	225.12	223.53	220.97	215.09	213.58	211.12	226.46	227.31	227.21	225.28
80% DOD Discharge Power (W/kg)	1960.13	2166.26	2256.02	2236.75	2139.01	1876.60	1796.84	1589.55	1942.84	2125.86	2176.21	2120.05
80% DOD Regen Power (W/kg)	3065.50	3510.31	3768.80	3792.11	3757.63	3471.12	3433.79	3186.18	3037.05	3420.58	3597.92	3564.72
Average dV (Vch-Vdis)	0.0953	0.0873	0.0838	0.0860	0.0879	0.0951	0.0987	0.1042	0.0973	0.0888	0.0875	0.0912

LiDFOB & New Electrolyte Additive Work

Argonne National Labs settled upon a synthesis method for high purity LiDFOB. The purified salt was added to the ANL standard electrolyte at different concentrations to determine its minimum loading level for stable performance (Figure 22 & 23) These electrochemical tests were done in coin cells.

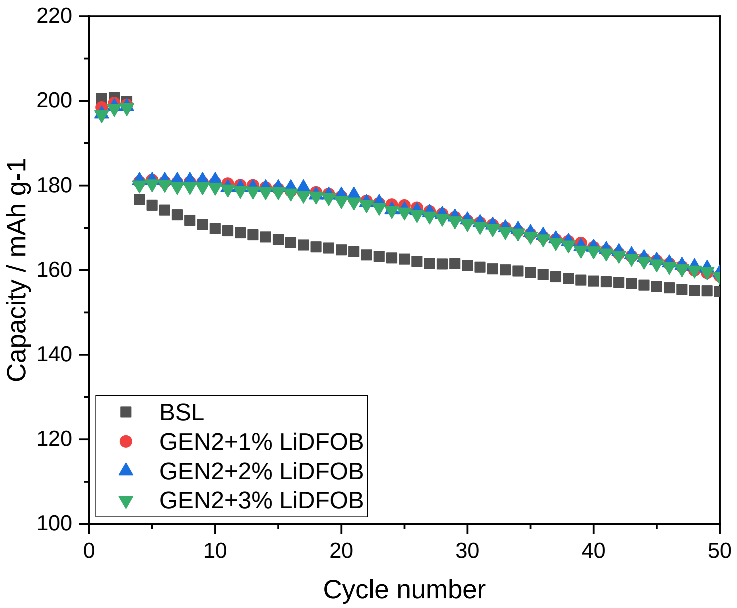


Figure 13: Cycle performance of Ni85 cathode material using the baseline electrolyte (BSL) and the BSL+LiDFOB at various percent.

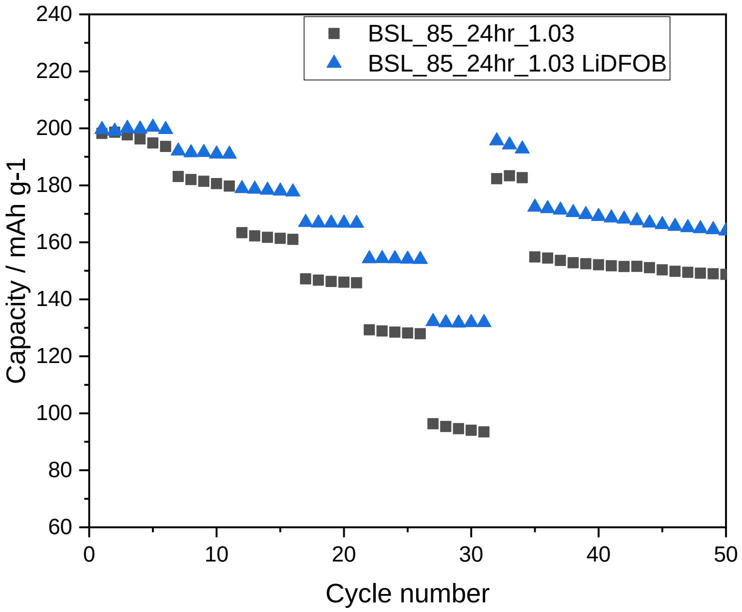


Figure 14: A comparison of the rate performance capacity for baseline electrolyte versus electrolyte with LiDFOB.

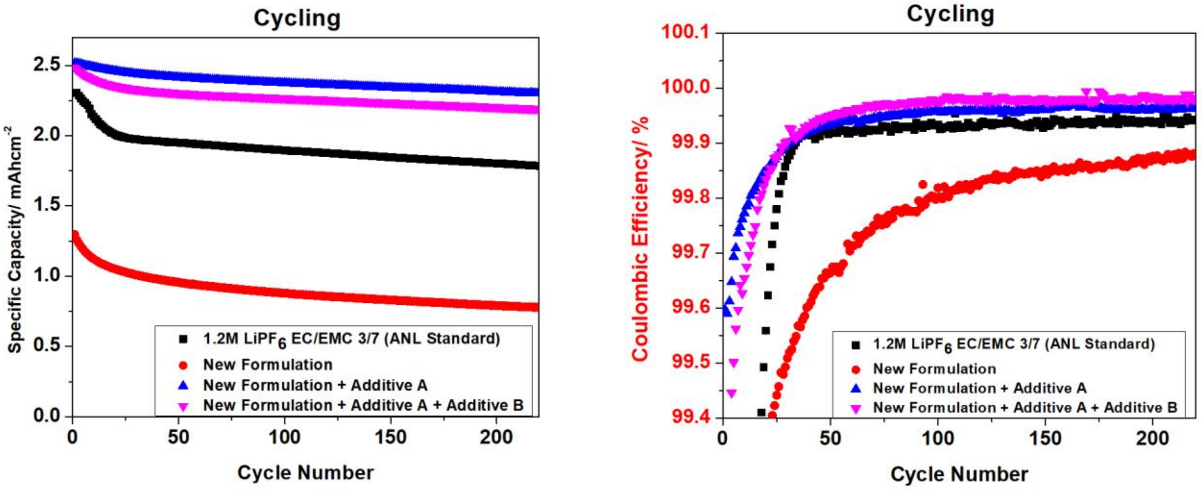


Figure 15 FCG cell test at 50oC and 1C rate. Left: specific capacity retention. Right: Coulombic efficiency of the corresponding cells.

ANL standard electrolyte (1.2M $LiPF_6$ EC/EMC 3/7, Tomiyama) was employed as the baseline electrolyte for the development of new electrolyte/additive. To evaluate the fast charging capability of the electrolytes, FCG/graphite cells were tested at 50 ^oC with a 1C rate after 5 cycles of formation at C/10 rate. The specific capacity of the baseline cell dropped from 2.3 to around 1.9 mAh/cm^2 within the first 30 cycles and the Coulombic efficiency of the cell stabilized at around 99.91% after 30 cycles. In an attempt to improve the charging capacity and retention of the FCG/graphite cell, a new formulation comprising of multiple lithium salts and carbonates were introduced. However, the electrochemical performance of the cell using the new formulation slipped significantly compared to the baseline cell with only half of the capacity retained and Coulombic efficiency of the cell dropped. To solve the problem, a new additive A was introduced to the new formulation (Figure 24). There exists a synergistic effect between the new formulation and additive A, leading to the increase of not only the fast charging capability, but also the retention rate, as well as the Coulombic efficiency ($\geq$ 99.95%) of the FCG/graphite cell. The Coulombic efficiency of the FCG/graphite cell can be furthered enhanced with the introduction of additive B. In summary, an electrolyte system with a new formulation with a new additive A, which demonstrated significant improvement on fast charging capability and capacity retention, was successfully developed.

XFC Large Ah Cells

Pre Gen1 Baseline Cell

To start the project a pre-Gen1 cell comprising a 190 Wh/kg NMC cathode and graphite anode was assembled by Microvast and cycled with 6C (i.e. 10 minute) fast charge, and 1C discharge for > 500 cycles. The purpose of the testing was to get a baseline assessment for the technical challenges of the project, and to identify any key issues that must be considered while assembling the Gen1 cell.

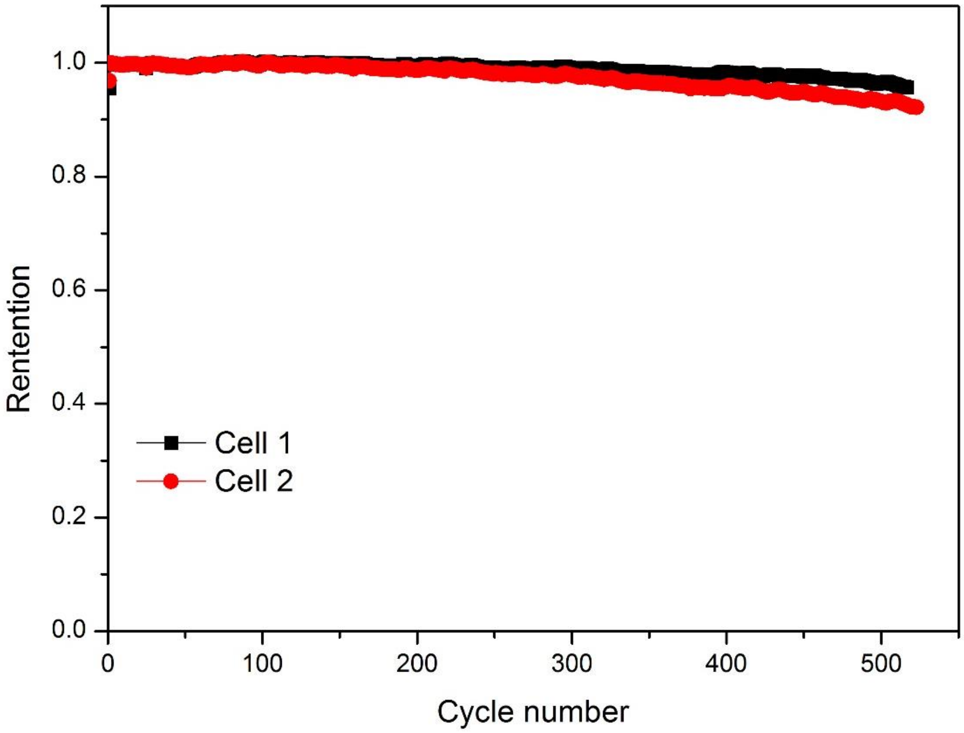


Figure 16: The capacity retention of two 190 Wh/kg, 15AH cells cycled using 6C charge, 1C discharge.

Gen1 XFC Cell Development

Post the preliminary cell test Microvast and BMW communicated to determine the electrode design, transfer of materials, and necessary changes to ensure electrodes can be incorporated into BMW's prismatic cell assembly line. For reference, Microvast uses pouch cells, so the assembly and electrode configurations are different. The cells were graded for their energy density using a 0.33 CC/ 0.33 CD cycling procedure from 2.7-4.25 V to get a 210 Wh/kg cell capacity. This is a little lower then originally planned, due to a cell format change at the last minute from Microvast's MpCO format to Microvast's VDA format because the VDA size is more compatible with the jelly-roll coating sizes needed for BMW. The VDA cell allows the same electrode casting to be tested in the VDA and jelly-roll format. The areal capacity of the cathode electrode is ~2.3 mAh/cm^2, and the cells have an n/p ratio of 1.13.

Two of the Gen1 pouch cells were cycled using a traditional 1CCCV/1CD cycling protocol to check that the cell electrodes would be stable and high quality under normal cycling conditions (Figure 26). The cells showed stable and consistent cycling performance (~100% retention) after 375 cycles under room temperature testing conditions. The electrolyte used in these cells was Microvast's commercial formula.

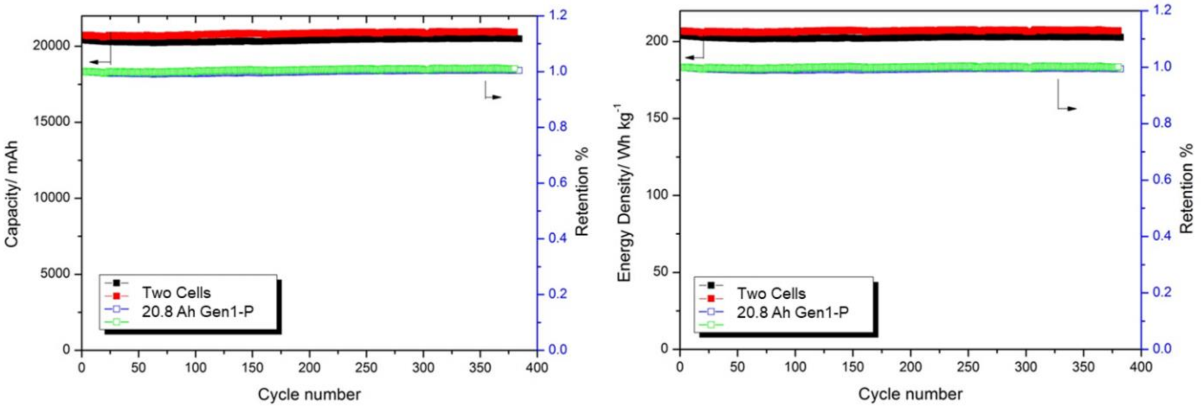


Figure 17 - Cycle capacity and retention plots at 1C charge and discharge for Gen1 pouch cells to confirm normal condition electrode integrity.

Another two cells were tested under XFC conditions as laid out in the FOA. These two cells were tested using the full voltage window (2.7-4.25V) and a 6CCCV/1CD cycling protocol (Figure 27). The 6CCCV cut-off has two end conditions, one by minimum current and another if the cycle time reaches 10 minutes. Per suggestion of the DOE program manager a 6C/0.33C energy density check was done at near cycle 140, and resulted in a 185 Wh/kg energy density. The cell was already cycling, which is why the first 6C/0.33C check was done near cycle 140. Over 500 cycles were performed on the two cells using the XFC test conditions. Around cycle 350-400 cell fade started to occur, which can be obviously seen by the bend in the cycling data. After 500 cycles the cells were near 80% capacity retention, with the two cells having a 6C/0.33C end-of-cycling energy density of 150 and 140 wh/kg, respectively.

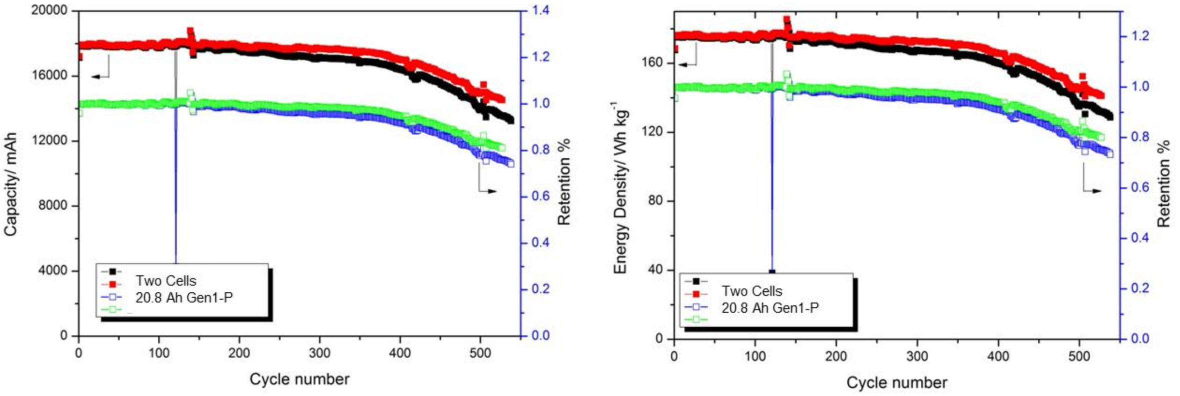


Figure 18: Gen1 pouch cells tested under an XFC protocol (10 minute charge, 1C discharge). The cells were tested at room temperature from 2.8-4.25V.

The cell performance cycling had lower retention thru 500 cycles versus the preliminary trial done using Microvast's 190 Wh/kg baseline cell.

Prismatic hard can cells built by BMW had some challenges during assembly, so a second Gen1B batch was prepared and underwent a variety of tests including pulse power, cycle aging and calendar aging.

Cycling behavior of Gen1B hard can cells is shown in Figure 29. Cells were cycled at C/3, 1C and 6C charging rates with C/3, 1C and 1C discharge rates respectively (all for constant current part of CCCV cycle). Every 50 cycles, a low rate capacity check cycle was used to evaluate degradation. Initial cell capacities averaged 22.5Ah for these samples. Low C/3 and 1C cycling demonstrated fairly good capacity retention over 300 and 500+ cycles respectively (>95%). There is effectively no difference in the degradation rate at these two rates so we accept that 1C charge/discharge cycling is an adequate baseline for comparison against fast charging behavior. Capacity retention for cells cycled at 6C charge rates was ~72% at 500 cycles which is consistent with the rate of degradation in pouch cells using the same electrodes, reported previously. Note that the voltage range applied in cycling (2.8-4.2V) was slightly restricted versus that used to evaluate pouch cells of a similar capacity. Deviations among cells are greater at higher lifetimes representing a difference in rate of capacity loss.

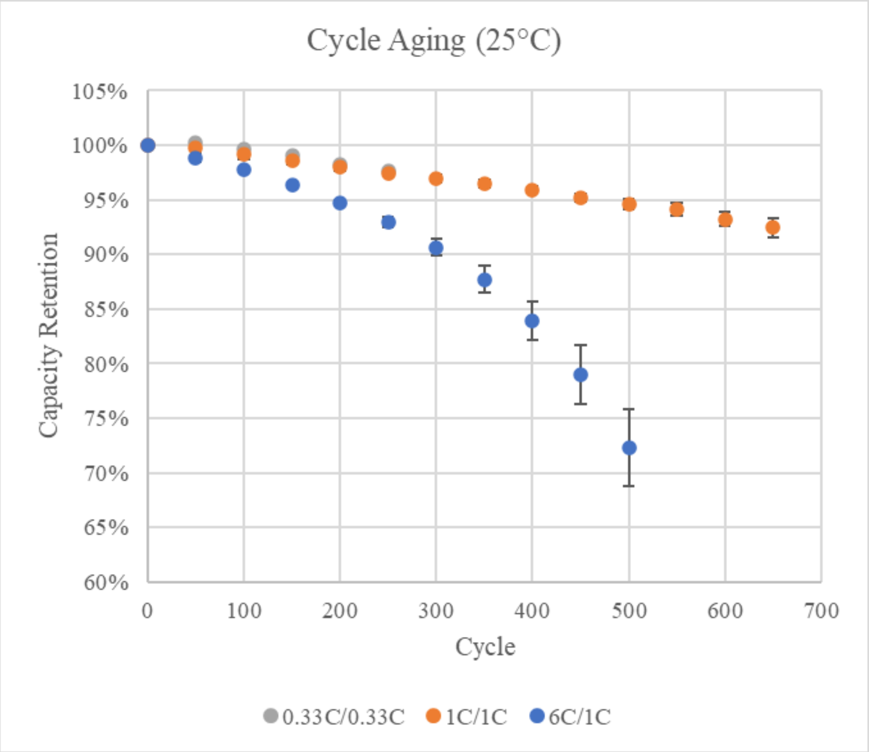


Figure 19 Cycle aging tests at 25°C. Average capacity retention for three cell replicates per condition with one standard deviation error bar. Capacity checks shown every 50 cycles at C/3 rate (or C/10 rate for normal C/3 cycling). Average initial capacity per cell was 22.5Ah for the cycled range of 2.8-4.2V.

Three hard can cells were subjected to a calendar aging protocol where cells were stored at 60°C and the voltage and capacity were checked with a standard slow cycle every 30 days. The choice of 60°C represents an extreme temperature for automotive applications, but is a standard benchmark for evaluating cell performance within BMW. This temperature may also be achieved in certain conditions related to fast charging. Figure 30 demonstrates that after 30 days at elevated temperature 87% of capacity remains. Thereafter capacity loss due to thermal degradation slows and retained capacity reaches 82% after 90 days.

In addition to the data above, hard can prismatic cells were also subjected to drop and short testing to establish their baseline safety. In the drop test, cells were dropped from a height of 150cm onto the tabs. Cell resistance was measured before and after, establishing that no internal faults resulted from the test. Short testing resulted in an expected increase in cell temperatures. For some cells, after reaching a high internal pressure, the pressure burst membrane was activated. All hard can prismatic cells were deemed to be functioning properly.

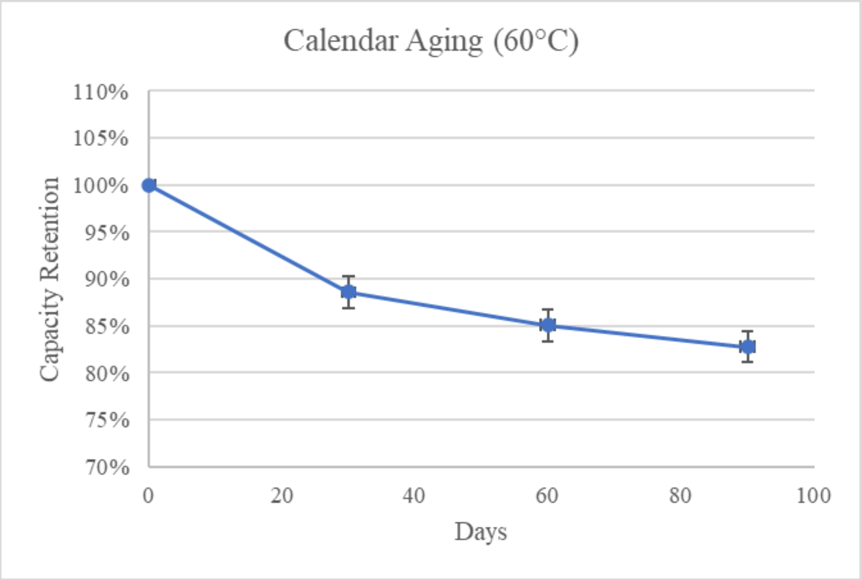


Figure 20 Calendar aging tests at 60°C. Cells were charged to 4.2V then stored for 30 days. Capacity checks after every 30 days were conducted at a C/3 charge and discharge rate.

We also note that temperature measured at the negative pole of Gen1B cells under 6C conditions increases 11-13°C from the 25°C controlled chamber temperature. This is true for both discharge and charge at fast rates. Peak temperatures correspond to the end of discharge (low SOC) or the end of charge (high SOC). Thus, it was reasonable to conclude that the rate of heat dissipation should be considered in further cell optimization.

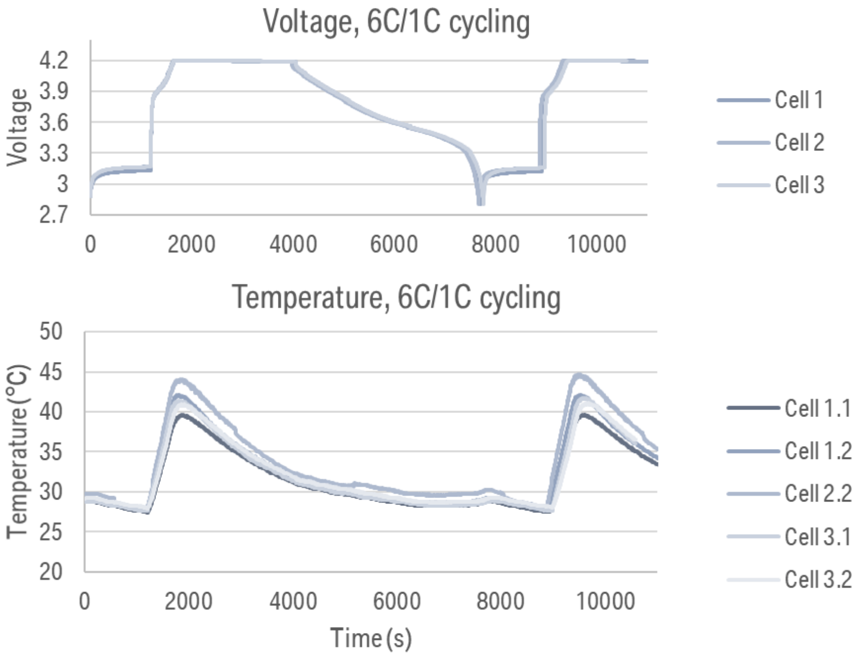


Figure 21 Representative voltage and temperature profiles for Gen1B cells during cycling at the 6CCCV/1CCD condition. Cells were instrumented with thermocouples in two locations (top of can and negative terminal) to measure the temperature change.

The temperature response of cells charged at the 6C rate was analyzed. Figure 32 illustrates the voltage and temperature profile of three cells (sensors at 1 or 2 locations each). It is clear that temperature ramps rapidly following the onset of 6C charging and peaks shortly after the switch from constant current to constant voltage charging at 4.2 V. In this cycling condition, rest periods between cycles are 20 min, allowing cells to cool to ~26-27°C. Temperature increases vary depending on the sensor location, but the negative pole regularly exhibits the highest temperature. Changes of +12-17°C are observed across these cells regardless of aging.

The rate of charging was also extracted from this data, demonstrating that charging from 0 to 70% SOC could be achieved in 7 min 17 s for one cell (comprising the entire constant current phase). After 10 min, including a portion of the constant voltage phase, 85% SOC was reached. Full charging was reached after 48 min.

Deliverable Budget Period 1 Gen1 Cell

Following the results of the Gen1 cell finding in pouch and prismatic design, a new cell batch for the end of budget period 1 delivery to a DOE National Lab was prepared. The cell design used an FCG 622 cathode, same as Gen1B, but the press density was increased following the prismatic feedback. After grading the cell at 1C from 2.7-4.25V the pouch cell capacity was ~20.8 AH and the energy density is ~215 Wh/kg. To make sure the cell build worked correctly for the XFC cells a quick test, where the cells were charged at 1C and 5C respectively were completed to check the anode for any obvious signs of plating or imperfections. 5C was used because the tester available was unable to supply the current needed for 6C. A representative photo for the quick check test is shown in Figure 33, and as the photos show there was not obvious damage or plating on any of the electrodes in the cell.

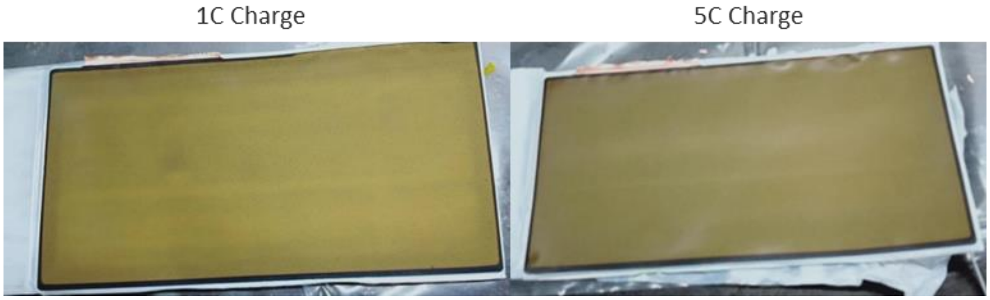


Figure 22: Images of anode after quick check of cells charge stability. Cells were opened after grading plus one cycle at the listed charge rate.

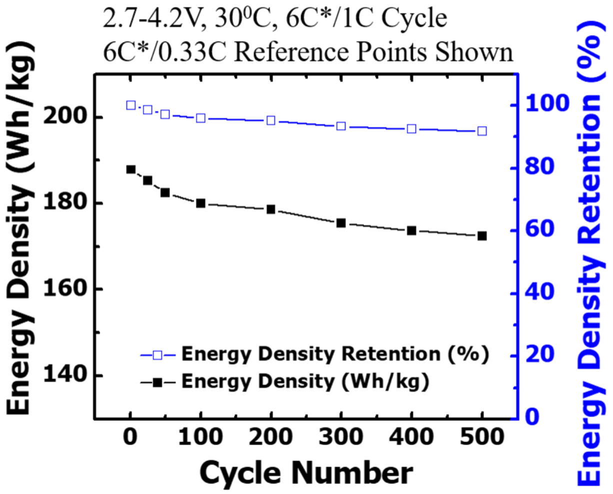
Another cell in the batch was tested to determine the impact of voltage window range on XFC discharge energy density at 0.33C after a XFC 10-minute 6CCCV charge. During the test a cell was cycled at the smaller voltage window, and then the window was increased until the full state of charge 2.7-4.25 range was tested. The voltage window test results for the cell are provided in Table 4.

Table 3: The capacity and energy density of pouch cell built for Milestone 4 at various cut-off voltages for XFC 10-minute CCCV charging.

Cut Off Voltage	Capacity (AH)	Energy Density (Wh/kg)
4.25	19.00	197.2
4.2	18.17	188.1
4.15	17.45	180.0
4.1	16.80	172.7
4.05	16.11	165.0

Based on the cut off voltage test, it was decided that 4.2V would be used, which corresponds to about 95% SOC. An upper cut-off voltage of 4.15V is boarder line for the 180 Wh/kg starting energy density, so we elected to choose a condition slightly higher in case some of the cells energy density deviation ended up slightly lower.

The cell batch intended for delivery to the DOE National Labs completed 500 6C*/1C cycles with periodic reference cycles (6C*/0.33C cycle followed by HPPC) as shown in Figure 35. The cells tested in Orlando were placed inside an environmental chamber at 30^0C; so there is some active cooling that occurs during the cycling in response to the heat rise that occurs during fast charge. It is clearly seen that the cells started above 180 Wh/kg, as required by the FOA, and finished above 80% retention / > 140Wh/kg as outlined in the FOA. The higher states of charge show good stability after fast charge, suggesting the FCG cathode used in Generation 1 is stable to the high current conditions being experienced within the cell.



RPT	Capacity (Ah)	Energy Density (Wh/kg)	Energy Density Retention
1	18.33	187.85	100
25	18.09	185.35	98.67
50	17.82	182.44	97.12
100	17.61	180.09	95.87
200	17.47	178.60	95.08
300	17.18	175.36	93.35
400	17.03	173.72	92.48
500	16.90	172.41	91.78

Figure 23 (left) Energy density and retention thru 500 cycles on Gen1 delivered cell from 2.7-4.2V at 30^{0}C. The points shown are 10-minute charge & C/3 discharge reference points taken between 10-minute charge / 1C cycles. (right) Table of the capacity, energy and retention at each RPT cycle..

Gen2 XFC Cell Development

Following the completion of Gen1, and a successful Go/No-Go from the deliverable cell at 215 Wh/kg the project team advanced the energy density goal.

Electrodes were prepared for Generation 2 using a Ni83% cathode material and an artificial graphite anode. The cathode material did not have a high-quality gradient after calcination, but the electrochemistry was known to be good for the sample.

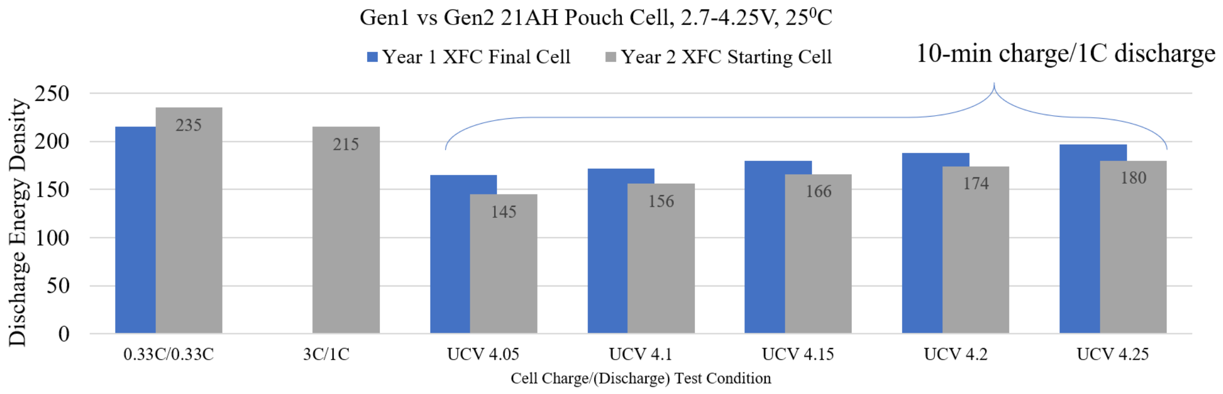


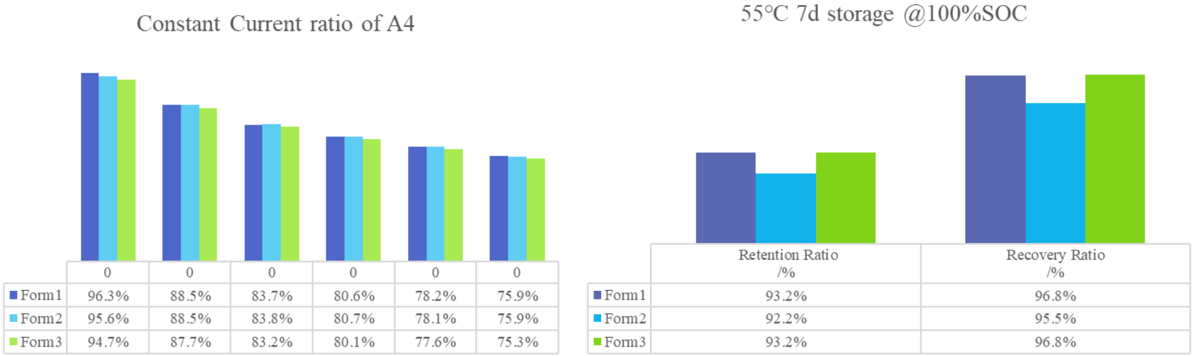
Figure 24 Comparison of the deliverable Generation 1 cell to Generation 2 pouch cell for energy density under graded (1C/1C) and XFC conditions with varied Vmax.

To determine the upper cut-off voltage, and compare how fast charge is different in the higher energy density Gen2 cell the delivered energy after charging at 10-minutes was conducted, and is shown in Figure 36 with the C/3 graded value as a reference. As expected, with the higher energy density of the cell the rate performance became more difficult.

The Gen2 pouch cells that were tested under 10-minute charge conditions show a fast fade in performance before reaching a stabilized capacity (Figure 37). Interestingly, the maximum temperature recorded during cycling seems to peak at a similar cycle number to the roll over failure observed in the cell. Overall, it seems the cycling conditions were too challenging for XFC, and adjustments are needed going forward in cell design and possibly cell strategy to meet the final objectives.

Gen3 XFC Cell Development

Given the status of the Gen2 system, particularly in regards to XFC performance the project team implemented a risk control option outlined during project proposal, and did not advance the cells energy density. Hence, Gen3 is targeting the same objective of Gen2, a 240 Wh/kg cell pouch cell. However, to create a different outcome some choices were made to help the Gen3 system. 1) Only pouch cells would be the focus; and no more prismatic trials would be conducted. This helped focus the development work on only one system. 2) The materials used in the Gen3 cell were re-evaluated, and an improved electrolyte formulation + better quality FCG-VS was sought for the cell.



	0	0	0	0	0	0
■ Form1	96.3%	88.5%	83.7%	80.6%	78.2%	75.9%
■ Form2	95.6%	88.5%	83.8%	80.7%	78.1%	75.9%
■ Form3	94.7%	87.7%	83.2%	80.1%	77.6%	75.3%

	Retention Ratio /%	Recovery Ratio /%
■ Form1	93.2%	96.8%
■ Form2	92.2%	95.5%
■ Form3	93.2%	96.8%

Figure 25 Testing various electrolyte formulations for Gen3 XFC pouch cells via rate performance and storage ability.

In Figure 42 the evaluation of 3 electrolyte formulations considered are compared at various c-rates and after a 55^{0}C storage test. All three electrolyte formulations were fairly similar in rate performance from C/3 to 6C conditions (though Form 1 & 2 were slightly better), so the storage performance was the main decider in formulation selection. In that test Form 1 and 3 are significantly better, so Form 1 was chosen for Gen3 due to the good rate performance and storage performance.

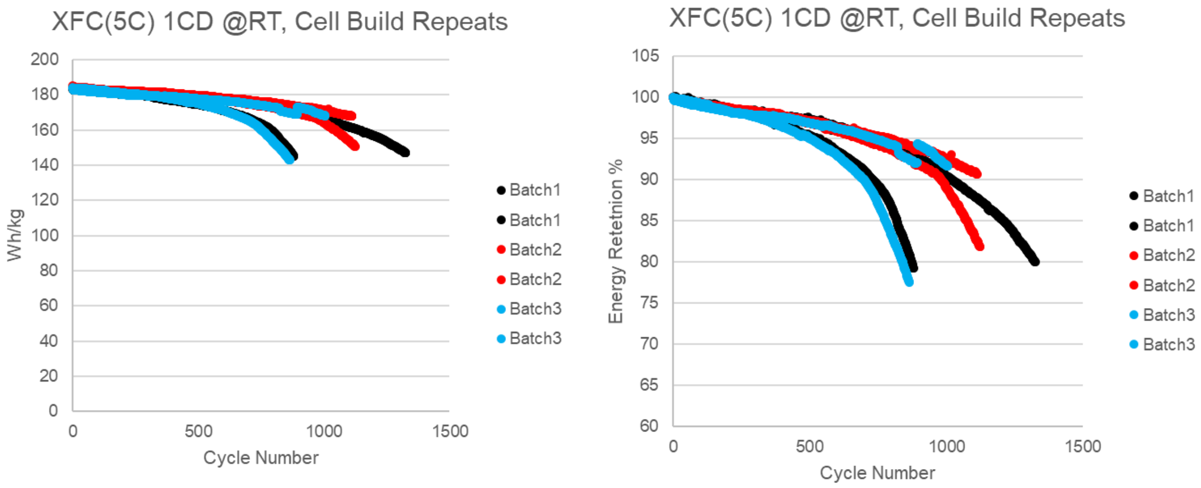


Figure 26 – Capacity and retention plots for 240 Wh/kg XFC cell being charged in 10-minutes at 5CCCV, and discharged at 1CD. The 1CD is > 180 Wh/kg at beginning of life.

Table 4 Comparison duplicate batches of XFC Gen3 pouch cell for eneryg density and temperature rise

NO.	Test Condition	Voltage range	Energy Density @1C10min Wh/Kg	Energy Density @0.33C0.33D Wh/Kg	Temperature Rise °C
Gen3 1st Batch	5C1D CCCV 10min Cutoff	2.7-4.2	184	241	10
Gen3 2nd Batch	5C1D CCCV 10min Cutoff	2.7-4.2	185	244	10
Gen3 3rd Batch	5C1D CCCV 10min Cutoff	2.7-4.2	183	243	10

After some trials with >230 Wh/kg cells the Gen3 pouch cell was further optimized to deliver > 240 Wh/kg during a room temperature static capacity test. This cell was the design selected for delivery to the National Labs and BMW for end of project testing. In order to make enough cell for internal testing, and the deliveries 3 pilot cell runs were conducted at Microvast, and the comparison of each batch XFC cycling and beginning of life metrics is shown in Figure 44 and Table 7, respectively. The 10-minute charge XFC cycling is able to deliver at least 800 cycles (worst batch cells), and in some cells provided close to 1,400 cycles. The deviation at later cycling is a technical challenge that requires additional work, but for the FOA requirements of 500 cycles it appears the deviation and stability is quite good.

The beginning of life temperature rise during XFC cycling is ~10^0C for Gen3. It is believed by the project team that controlling the peak temperature is very important for cycle life, since higher temperatures are responsible for accelerating the kinetics of side reactions, and the prior Gen1 and Gen2 testing in pouch cand prismatic design showed worse performance as the temperature peaked.

Using the projects final versions of cathode and electrolyte were thought to help improve this results some, and a new artificial graphite material was selected for the Gen3 cell as well.

Post-Analysis Studies on XFC Cells

After XFC cycling of the XFC Gen1 deliverable cell the cycled cell was moved to an Ar filled glovebox and dismantled inside to ensure atmospheric protection to the electrode surfaces. There was some small deformation of the pouch cell packaging from the swelling and contraction that occurs as the inlet chamber to the glovebox was purged to remove air. The electrodes inside the pouch cell were still wet after XFC cycling. From the project team data, there does seem to be a correlation in the observation of wet electrodes and improved fast charge performance. Exact cause is unknown, but two possible reasons are 1) a wet electrode signifies stable interfaces have formed between the electrode materials and the electrolyte; or 2) as the electrode dries out the available pathways for Li-ions to move from cathode to anode is reduced, which in turn creates a higher local current density that exacerbates Li-plating.

Conclusions

The “New High-Energy & Safe Battery Technology with Extreme Fast Charging Capability for Automotive Applications” has successfully proven that a 240 Wh/kg XFC pouch cell is viable for automotive cells when advanced materials such as low impedance electrolyte additives, Microvast’s Full Concentration Gradient (FCG) and High Thermal Stability Aramid Separator are used in the preparation of the pouch cell electrode. For the materials it appears that optimizing the interface is of critical importance for boosting cycle and calendar aging in future cells.

The project successfully demonstrated a 10-minute charge on a 240 Wh/kg, 35Ah pouch cell can retain 88% retention thru 850 cycles while meeting the starting XFC condition of > 180 Wh/kg fast charge energy storage. This result in testing (done on 6 cells, from different production batches) is 22% higher than energy density and up to 165% higher in cycle life compared to the 500 cycle objectives for this project.

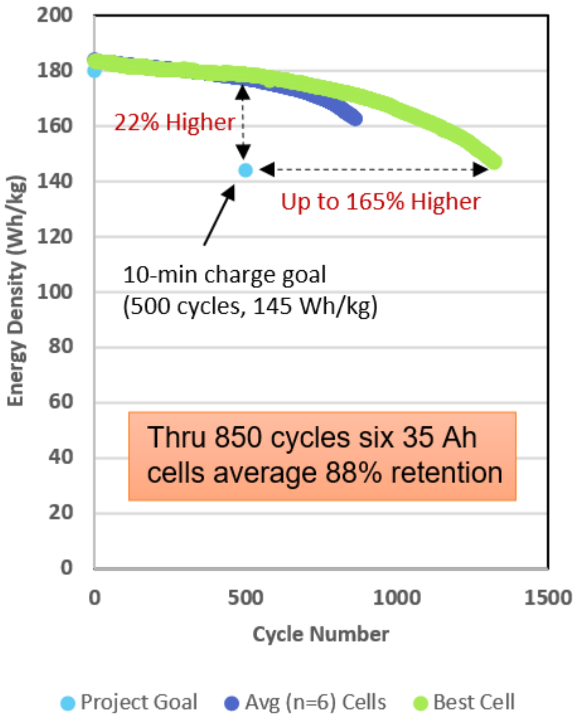


Figure 27 The energy density versus cycle number of tested 10-minute charge / 1-hour discharge Li-ion cells. The project energy density goals, average for 6-duplicate cells and the best cell tested is shown.

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