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NMP-free Lithium Ion for Sustainable Manufacturing in Silent-Watch Applications

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ABSTRACT

PPG formulates N-methyl pyrrolidone free (NMP-free) cathodes for Li-ion batteries capable of delivering sufficient power for automotive starting, lighting and ignition (SLI) as well as adequate charge capacity for powering auxiliary electronics. In this paper, NMP-free energy cathodes and power cathodes were formulated using developmental binders, and refinement of carbon/binder ratio and slurry mix procedure. Learnings from the energy and power cathode development were conceptually combined in the formulation of capacity enhanced power cathodes. These cathodes were evaluated electrochemically via power capability and rate capability testing in battery coin cells, as well as in 0.5 Ah multilayer pouch cells. Carbon content was found to be a critical factor in attaining high cold crank performance. This work represents significant steps toward potential commercialization of NMP-free cathode coated foil for Li-ion batteries.

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1. INTRODUCTION

Vehicle electrification is a high priority for the United States Department of Defense as an approach to mitigate fossil fuel costs, improve logistical efficiency and reduce noise during silent watch and silent mobility missions.¹⁻³ In collaboration with the Ground Vehicle Systems Center (GVSC), the National Center for Manufacturing Sciences

(NCMS), and Navitas, PPG initiated a project to develop cathode coatings that deliver both high energy density and high power using PPG’s NMP-free binder technology. The purpose of the project is to utilize PPG’s NMP-free binders, in combination with its expertise in coatings technology, to develop cathode coating formulations that reduce cost, provide manufacturing efficiency and improve the performance of lithium ion cells utilized in the ‘6T’ battery module for military vehicles. The design and

Table 1. Description 6T tests and pass/fail criteria for individual cells

Test	Description	Pass/Fail Criteria
Cold Crank, -40 °C	Charge 4.2 V, Discharge @ 4C 30 sec	$V_{cell} \geq 2.06V$
Cold Crank, -18 °C	Charge 4.2 V, Discharge @ 12C 30 sec	$V_{cell} \geq 2.06V$
Cycle Life, 38 °C	Charge/Discharge 1C/1C x 1000	$\geq 80\%$ retention
Cycle Life, 50 °C	Charge/Discharge 1C/1C x 500	$\geq 80\%$ retention
Elevated Temperature Storage Test, 60 °C, 28 days	Charge 4.2 V, Store 60 °C 28 days, monitor V weekly	$V_{cell} \geq 3.8V$

performance requirements for the 6T module are provided in MIL-PRF-32565. Cold crank, cycle life and elevated temperature storage tests in the 6T MIL-SPEC have been adapted for testing individual (i.e. pouch) cells and the corresponding test criteria are provided below in Table 1.

NMP-free binders are expected to reduce manufacturing cost versus PVDF-NMP binders extensively utilized in lithium ion batteries. PPG’s binder system has higher solids, higher lower explosive limit (LEL) and lower toxicity compared to PVDF-NMP binders. Furthermore, optimization of coating characteristics is expected to provide a performance boost in comparison with a traditional cathode system. In order to meet 6T cold crank requirements and boost energy density, one cathode formulation was tailored for high energy density, while another cathode formulation was engineered for delivering high power. These formulations correspond to different operation modes in military vehicles – a high power cathode will supply charge at a rate and duration needed for starting the engine, while the high energy density cathode will supply enough charge to

power the vehicle electronics for ‘Silent Watch’ operation.

PPG set individual tasks toward achieving NMP-free Li-ion electrodes for ‘Silent Watch’ operation, including (1) exploration and formulation of high energy and high power Li-ion cathode electrodes using NMP-free solvent & binder systems, (2) coating design to deliver 6T specifications in Li-ion batteries, and (3) cell testing of experimental NMP-free coatings in single-sided full cell pouch cell format

2. NMC CATHODE FORMULATION

PPG formulated cathodes utilizing $LiNi_{0.5}Mn_{0.3}Co_{0.2}$ (NMC 532) supplied by Navitas. To address the need to deliver high power for cold crank as well as adequate energy density for potential silent watch/silent mobility applications in 6T batteries, PPG developed cathodes formulated for power and energy density. For power cathode formulation, areas of focus included optimization of active material loading, carbon selection, carbon / binder ratio and mix procedure with the principal goal of maximizing rate and power capabilities as substitutes for cold crank performance. Exploratory development of binders and additives were primary areas of focus for energy cathode development.

2.1. Energy-dense Cathode

Energy cathode development focused on cathodes with between 90 wt% and 96 wt% active material. A formulation higher in active material content was needed to ensure sufficient energy density for a 6T battery. In addition, various binder and carbon-to-binder ratios were optimized for maximum power performance for 6T specifications.

In PPG’s research on the energy cathode, the binder to carbon ratio was kept at 1 to 1, and focus was primarily on porosity, binder development, and wt% active material.

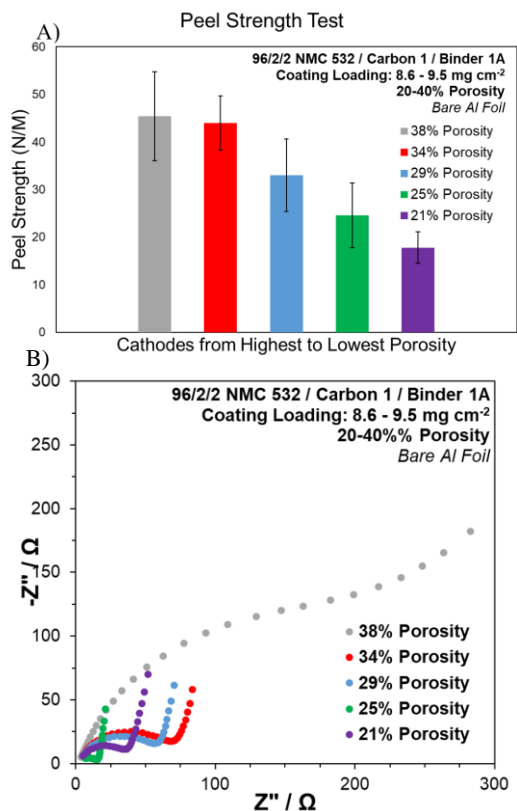


Figure 1. (A) Peel strength as a function of porosity (error = 1σ); (B) cell resistance as a function of porosity.

Binder 1A–B and Binder 5–9 were tested internally at PPG in half-cell coin cells, with the most promising binders being down-selected for double-layer pouch (DLP) cells.

Data from the porosity study are shown in Figure 1A. As porosity decreased, peel strength decreased at a linear rate. As peel strength decreases as a function of porosity, cell resistance decreases as well (Figure 1B). From both the peel strength and impedance data, an ideal porosity range is determined to be between 25% and 30% porosity for the energy cathode

The binder development was performed to increase capacity retention of the cathodes to be in line with PVDF–NMP cathodes by screening different binder types and varying active material loadings. The test was a rate ladder from 0.1C to 1.6C followed by 50 1C cycles. In Figure 2A, cathodes formulated

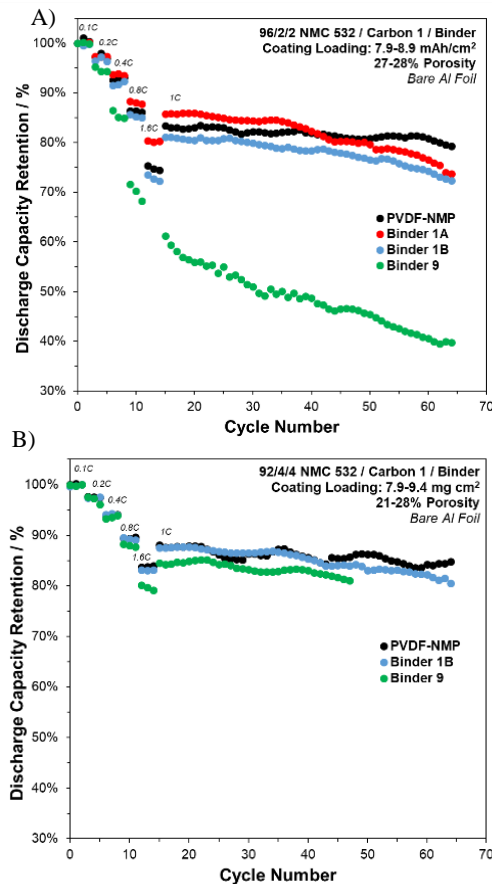


Figure 2. Discharge capacity retention of Binders 1A, 1B, and 9, and PVDF–NMP in a (A) 96/2/2, (B) 94/3/3, and (C) 92/4/4 NMC 532 / Carbon 1 / Binder formulation.

with Binder 1A and 1B at 96% active material loading have similar capacity retention as the PVDF–NMP control, but cathodes containing Binder 9 have only 40% capacity retention after 50 1C cycles. Additionally, in Figure 2B, cathodes formulated at 92% active material loading with both Binder 1B and Binder 9 have similar capacity retention after the 50 1C cycles. From these results, the indication is that the 96/2/2 and 92/4/4 formulations with Binder 1A and 1B show promise to pass the 6T cycle life requirements, while Binder 9 was dismissed as a candidate for further study due to expected long-term cycle life issues presented from poor overall performance at

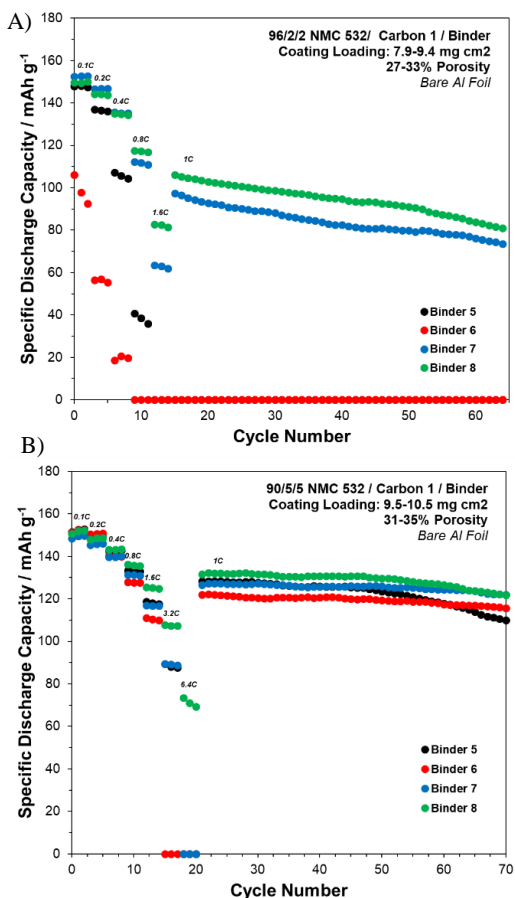


Figure 3. Binders 5–8 in a (A) 96/2/2 and (B) 90/5/5 NMC 532 / Carbon 1 / Binder formulation

low binder and 1.6C discharge testing compared to Binder 1A and 1B.

As shown in Figure 3A, cathodes formulated with additional binder offsets (Binders 5–8) have poor specific discharge capacities in the high energy formulation of 96/2/2. Cathodes with Binder 7 and Binder 8 did not fail during the 1C cycling, so cathodes formulated using these binders were sent to Navitas for testing in DLP cells. In Figure 3B, cathodes formulated for higher power at 90 wt-% active material loading containing Binders 5–8 all have expected specific discharge capacities for the 1C cycling, but the Binder 8 cathode is the only binder that handles 6.4C. In general, cathodes formulated with Binders 5–7 all fail at high C-rates, which may be from the slight differences in coating weights. As coating

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Table 2. 6T DLP cell test results for energy cathodes

Formula	Cold Crank		Cycle Life		ETS 60 °C 28 d
	-40 °C	-18 °C	38 °C	50 °C	
96/2/2 NMC532 / C1 / B7	Red	Red	Red	Red	Green
96/2/2 NMC532 / C1 / B8	Red	Red	Red	Red	Green
96/2/2 NMC532 / C1 / PVDF	Green	Green	Red	Green	Green
96/2/2 NMC532 / C1 / B1A	Red	Red	Red	Green	Green
96/2/2 NMC532 / C1 / B1B	Green	Green	Red	Green	Green
92/4/4 NMC532 / C1 / B1B	Red	Red	Green	Green	Green

weight increases so does the areal capacity, and high areal capacities have C-rate limitations in half-cell coin cells.

In Table 2, a high-level summary of various cathode formulations in DLP cell format paired with proprietary Navitas anode formulations is presented, showing promise for 96/2/2 NMC 532 / Carbon 1 / Binder 1A. Specifically, this cathode formulation passes all 6T testing except 38 °C cycle life testing. Another promising cathode is the 92/4/4 NMC 532 / Carbon 1 / Binder 1B as this cathode passes all cycle life requirements.

2.2. Power-dense Cathode

For the power cathode, a formulation richer in carbon than the baseline formulation calculated from the specifications provided by Navitas was rationalized as a good starting point. Higher conductivity is required to enable faster charge/discharge kinetics, and therefore higher carbon content is necessary. Additionally, maintaining carbon/binder ratio of 1/1 was a desirable balance between a binder-rich cathode ($C/B \approx 0.75$) having good adhesion but lower conductivity, and carbon-rich cathode ($C/B \approx 1.33$) having high conductivity but lower adhesion. Binder 7 was selected based on internal evaluation of rheological characteristics and electrical

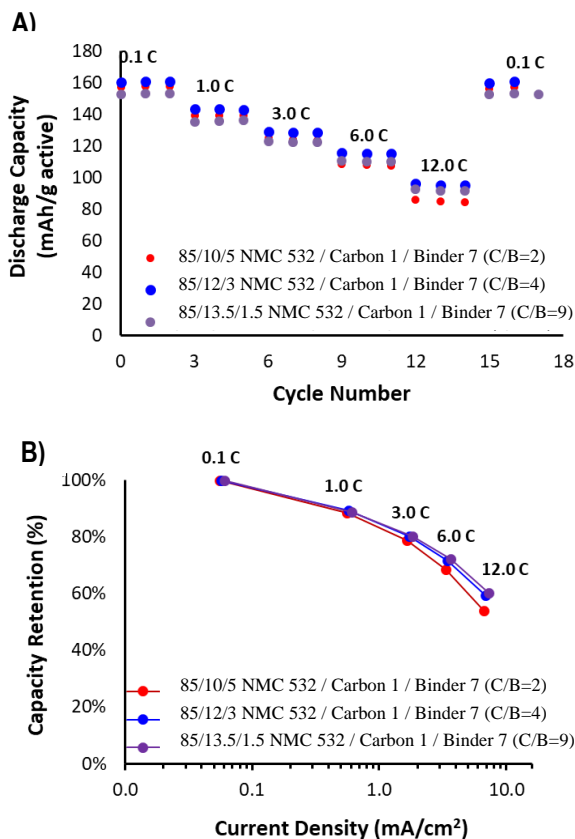


Figure 4. Half-cell coin cell testing: A) Discharge capacity of power cathodes with varying C/B ratios plotted against cycle number; B) Capacity retention of power cathodes plotted against current density

impedance of corresponding cathodes. Therefore, 85/7.5/7.5 NMC 532 / Carbon / Binder 7 was chosen as the candidate for the power cathode.

The strategy to refine the power cathode formulation was to perform a series of studies focused on optimizing parameters rationally expected to affect power performance, such as carbon/binder ratio, binder composition and mix procedure. Capacity retention at high (6C, 12C) discharge rates was utilized as the optimization metric. This refinement work culminated in the development of a capacity-enhanced power cathode as a route to an NMP-free 6T cathode.

Carbon 1 was utilized as the conductive additive and NMC 532 was maintained at 85

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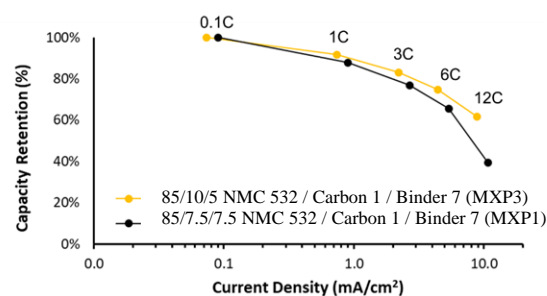


Figure 5. Rate capability of half-cell coin cells assembled with 85/7.5/7.5 NMC 532 / Carbon 1 / Binder 7 cathode prepared using Mix Procedure 1 versus 85/10/5 NMC 532 / Carbon 1 / Binder 7 prepared using Mix Procedure 3.

wt%. Cathode slurries were prepared with carbon/binder (C/B) ratio incrementally increased from C/B = 1 (85/7.5/7.5) to C/B = 2 (85/10/5), to C/B = 4 (85/12/3), and to C/B = 9 (85/13.5/1.5). Cathodes were coated on Armor En' Safe 121 carbon-coated foil at a loading of 0.49 – 0.5 mAh/cm², and calendared to 29 – 32% porosity. Rate capability was tested from 0.1C to 12C. C-rates were converted to current density to account for differences in experimental coating loadings between samples.

As shown in Figure 4A and 4B, capacity retention slightly increases as C/B ratio increases from C/B = 2 (85/10/5) to C/B = 4 (85/12/3). However, no further improvement was observed as carbon was further increased to C/B = 9. Further formulation work was performed at C/B = 2 and C/B = 4.

Formulation optimization for mixing was also explored for using the 85/7.5/7.5 formulation to optimize proper dispersion of materials in the coating. In effect, modifying the slurry preparation using formulation mix procedure MXP3 achieves a higher capacity retention at high C-rates compared to our initial formulation mix procedure MXP1 (~60% vs ~40% at 12C), as shown in Figure 5.

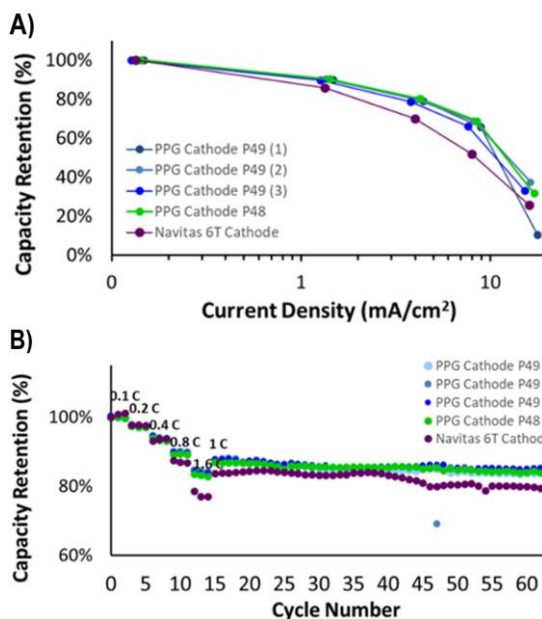


Figure 6. A) Rate capability and B) Cycle life of half-cell coin cells assembled with capacity-enhanced power cathode P48/P49 and Navitas 6T cathode.

3. Coating Design

The learnings from the previous studies discussed previously on C/B ratio, binder selection and mix procedure were applied in the formulation of a capacity-enhanced power cathode. To boost capacity, the wt-% active was increased from 85 wt% to 90 wt%. Combining this with C/B ratio = 2 and Binder 7 yielded the cathode formulation 90/6.7/3.3 NMC 532 / Carbon 1 / Binder 7 prepared via formulation procedure MXP3. This cathode formulation is denoted as PPG Cathode P48.

As shown in Figure 6, when coated to an areal capacity of 1.42 mAh/cm² and calendared to 21% porosity, the rate capability of PPG Cathode P48 was higher than the Navitas 6T cathode. Additionally, consistent performance was also observed when binder and slurry were prepared under dry conditions (PPG Cathode P49). These data indicated that PPG Cathode P48 would

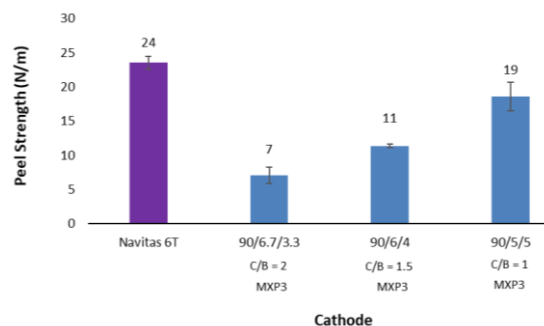


Figure 7. Cathode peel strength as a function of Carbon/Binder (C/B) ratio with 90 wt-% NMC 532 (error = 1σ).

perform well under 6T testing. However, during further evaluation, the adhesion of PPG Cathodes P48/P49 was found to be unacceptably low. This was evidenced by cathode cracking and delamination during electrode punches performed on samples supplied to Navitas. A follow-up study was performed where peel strength was measured as C/B ratio was incrementally reduced in capacity-enhanced power cathodes formulated at 90% NMC 532 with Carbon 1 and Binder 7. As shown in Figure 7, the peel strength significantly improved as C/B ratio was reduced from 2 (90/6.7/3.3) to 1 (90/5/5). Additionally, the peel strength at 90/5/5 was comparable to the Navitas 6T cathode.

For PPG, a key deliverable for this project is cathode coated foil supplied to Navitas for assembly and testing of large pouch cells under 6T conditions. To prepare 3 Ah pouch cells, a pilot-scale coating trial was performed. The scaled-up formulation for this coating trial was 90/5/5 NMC 532 / Carbon 1 / Binder 7 prepared using MXP1, MXP3, and MXP3.1 to determine whether the additive used in MXP3.1 could improve cycle life.

The pilot-scale cathode coating trial was performed. In preparation for the trial, 5.0 kg of 90/5/5 NMC 532 / Carbon 1 / Binder 7 cathode slurry at 53 wt% solids was prepared via pilot-scale variant of MXP3. Slurries prepped via MXP1 were prepared on-site at

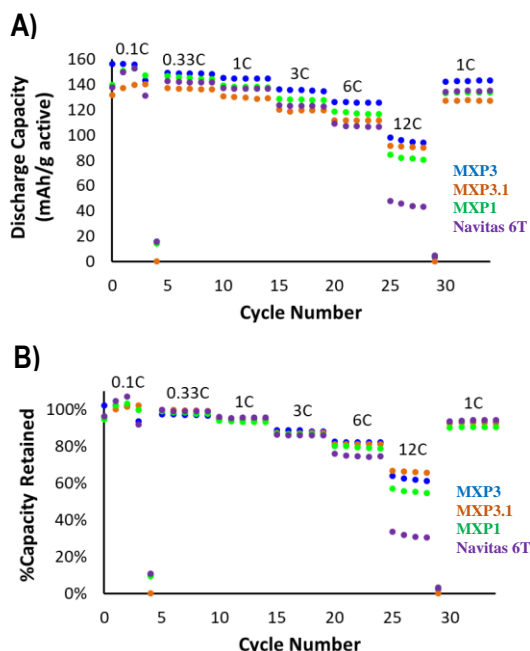


Figure 8. A) Discharge capacity and B) Capacity retention of full-cell coin cells assembled from PPG capacity-enhanced power cathodes prepared via Mix Procedure 1 (MXP1), Mix Procedure 3 (MXP3) and Mix Procedure 3 + Additive MX (MXP3 + MX) and Navitas 6T cathode, all paired with Navitas 6T anode.

the pilot-scale trial. Cathode coatings were applied to the 200mm-wide primer area of the En’ Safe 121 current collector foil using a reverse comma coater. The wet coatings were cured in 55 °C and 135 °C oven zones at a line speed of 1 m/min. The second side was likewise coated and cured. All three cathode slurries were coated at loadings of 8.05 mg/cm² and areal capacities of 1.35 mA/cm² (first charge, theoretical). All cathodes were

calendared to 30% porosity at room temperature. The cured electrodes were dried in a vacuum oven overnight at 60 °C and then transferred to a dry room (dew point <40 °C) for storage.

Rate capability and cycle life testing were performed on Li-ion coin cell and multi-layer pouch cell batteries (MLPs) assembled from the capacity-enhanced power cathodes coated during the pilot-scale trial. Full-cell coin cells were assembled and tested from punch-outs of each capacity-enhanced power cathode coating and paired with Navitas’ 6T anode. SEI formation was performed via 5 cycles of 0.1C/0.1C charge/discharge, followed by asymmetric rate ladder of 5 cycles of 1C charge/0.33, 1C, 3C, 6C, and 12 C discharge rates. As shown in Figure 8, at 12C all PPG capacity-enhanced power cathodes exhibited capacity retentions of 55% - 63%, significantly higher than that of the Navitas 6T cathode with 32% capacity retention.

In addition to rate capability testing, Peak power testing was performed in accordance with USABC Peak Power Test. Testing parameters were adapted to be relevant to 6T cold crank testing. Prior to testing, full cell coin cells were subjected to formation at 5 cycles of 0.1C/0.1C charge/discharge. Afterwards, the experimental capacities were averaged and recorded. The full cell coin cells were then fully charged at 0.33C to 4.2 V, then allowed to rest for 1 hour. Afterwards, the cells were continuously

Table 3. Summary of cold crank, cycle life and elevated temperature storage testing of pouch cells assembled using preliminary PPG NMP-free power cathodes supplied to Navitas. Green = PASS, Yellow = provisional PASS, Orange = BORDERLINE, Red = FAIL.

Cathode type	Composition	Areal Capacity / mAh/cm ²	Cold Crank		Cycle Life		ETS 60 °C 28 d
			-40 °C	-18 °C	38 °C	50 °C	
PPG, Power	90/5/5 NMC 532 / C1 / B7, MXP 1	1.35	Yellow	Green	Green	Green	Green
	90/5/5 NMC 532 / C1 / B7, MXP 3	1.35	Yellow	Green	Green	Red	Green
	90/5/5 NMC 532 / C1 / B7, MXP 3.1	1.35	Yellow	Green	Green	Orange	Green
Navitas 6T	90 – 92% NMC 532	1.39 – 1.47	Markets 6T Li-ion batteries				

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discharged in 10 increments comprising a high current discharge pulse (6C discharge for 30 sec) and base current discharge (0.1C discharge for 30 min). For the high current discharge, the voltage limit was set to 2.06V, the same voltage limit established by Navitas in pouch cell cold crank testing. The voltage limit was set to 3.0 V for the base current discharge increments.

For each high current discharge pulse, the discharge resistance, $R_{\text{discharge}}$, was calculated by Equation 1.

$$R_{\text{discharge}} = \frac{\Delta V}{\Delta I} = \left| \frac{V_{t1} - V_{t0}}{I_{t1} - I_{t0}} \right| \quad (1)$$

Where V_{t1} is the voltage before pulse, V_{t0} is the voltage at the end of the pulse, I_{t1} is the current before fast discharge, and I_{t0} is the current at the end of the pulse. Next, the open circuit voltage, $V_{\text{IR, free}}$, was estimated using Equation 2.

$$V_{\text{IR, free}} = V_{t0} + I_{t0} R_{\text{discharge}} \quad (2)$$

Lastly, the power delivered by the cell, P_1 , was calculated as function of the difference between the open circuit voltage and the minimum voltage during the pulse, as expressed in Equation 3.

$$P_1 = \frac{V_{\text{min}}(V_{\text{IR, free}} - V_{\text{min}})}{R_{\text{discharge}}} \quad (3)$$

Further, power delivered in each pulse was normalized to the mass of the cathode coating in the cell. As seen in the rate capability data (Figure 9), the PPG capacity-enhanced power cathodes out-perform the Navitas 6T cathode across the entire depth of discharge range. The gap in performance is especially apparent at low depths of discharge. This may be beneficial in situations where the battery needs to provide starting and lighting power after extended use in a critical situation, where the opportunity to recharge the battery has been unexpectedly delayed.

Taken collectively, the data prompted PPG to supply Navitas with samples of the capacity-enhanced power cathodes for testing. Navitas assembled DLPs with PPG capacity-enhanced power cathode samples matched with Navitas 6T proprietary anode and tested DLPs under 6T conditions. A detailed review of the pouch cell testing data are provided therein. The data are graphically summarized in tabular form (see Table 3). The test results indicate that batteries assembled with PPG capacity-enhanced power cathodes will likely meet 6T performance requirements. The DLPs passed cold crank testing at -18 °C; however, analysis of data from -40 °C cold crank test is more nuanced. During the 30 sec pulse at 4C, the cell voltage falls to approx. 1.7 V, which is below the 2.06 V minimum. However, Navitas provided a supplemental data (Figure 10) that documents historical cold crank performance of its cells at cell sizes ranging from 0.05 ~ 0.1 Ah (SLP, DLP) to 3 Ah, 10 Ah and 45 Ah cells. The data show that for 0.05 Ah cells, the voltage drops to approximately 1.8 V during 30 sec 4C discharge at -40 °C. However, as the cell size is increased to 3 Ah, 10 Ah and 45 Ah, final voltages are 2.3, 2.4 and 2.6 V, respectively. We believe this phenomenon is due to internal heating within the larger format cells, as heat generated during discharge is less efficiently removed in larger cells compared to smaller format cells, thereby reducing resistance to Li ion diffusion and mitigating

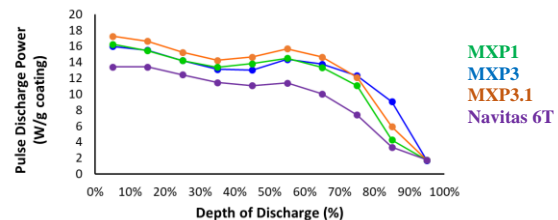


Figure 9. Power capability of full-cell coin cells assembled using PPG capacity-enhanced power cathodes coated at pilot-scale, and Navitas 6T cathode all paired with Navitas 6T anode.

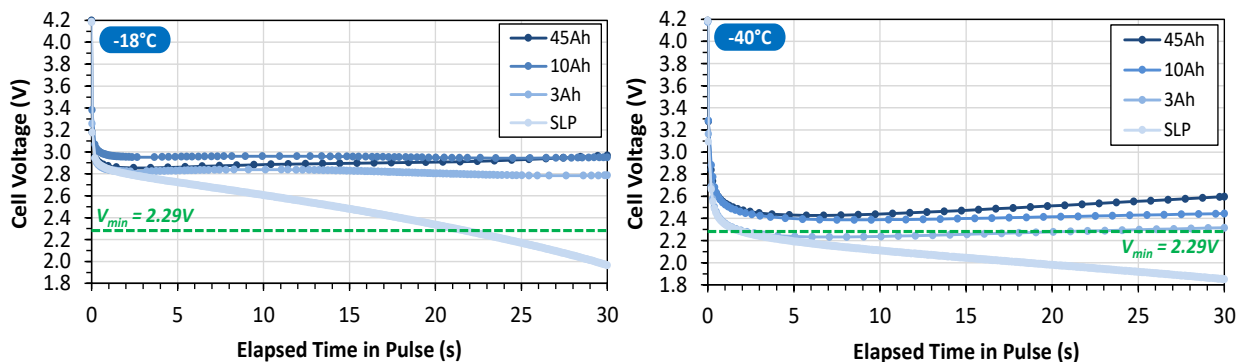


Figure 10. Relationship of cold crank response to cell size (Navitas NMC “Baseline”).

voltage drop at low temperatures. The difference between the voltage after 30 sec discharge for the 45 Ah cell and the 0.05 Ah cell is 0.8 V. Assuming that a comparable increase would be observed in a 45 Ah cell assembled using PPG capacity-enhanced power cathodes, the voltage after 30 sec 4C discharge at $-40\text{ }^{\circ}\text{C}$ may be reasonably expected to be 2.5 V, which is above the minimum. So for the cold crank performance at $-40\text{ }^{\circ}\text{C}$, the PPG capacity-enhanced power cathodes are assigned a ‘provisional’ pass when analyzed in the context of historical Navitas 6T cells. Cells passed cycle life tests at $38\text{ }^{\circ}\text{C}$; however, only cells assembled using cathode formulated using MXP1 passed cycle life testing at $50\text{ }^{\circ}\text{C}$. In the elevated temperature storage (ETS) test, all DLP cells with PPG capacity-enhanced power cathodes surpassed the even high end range of Navitas 6T electrodes.

Overall, these data prove that the capacity-enhanced power cathode concept was an effective strategy to delivering a cathode that exhibits performance in-line with the 6T specifications using PPG’s NMP-free binder technology.

4. Multi-layer Pouch Cell Testing

4.1. Cell Build & Cycling Parameters

All cells were assembled as ~ 0.1 Ah double-layer pouch (DLP) cells (single sided

anode/double sided cathode/single sided anode) to reduce electrode curling issues. Apart from the PPG cathodes, the balance of the test cell bill of materials are standard materials selected for the production Navitas 6T cell (laminable separator, low-temperature power optimized electrolyte). Anode is custom coated by Navitas, as coat weight is adjusted to match with the coat weight of the PPG cathode samples.

DLP cell cold crank testing was completed using constant-current / constant-voltage (CCCV) charging at room temperatures, then stabilizing the cells at the specified temperature ($-18\text{ }^{\circ}\text{C}$, $-40\text{ }^{\circ}\text{C}$) for a minimum of 4 hours, then subjecting the cells to the appropriate discharge pulse current (12C rate at $-18\text{ }^{\circ}\text{C}$, 4C rate at $-40\text{ }^{\circ}\text{C}$) for 30 seconds. The test is considered successful if the cell voltage does not polarize below a V_{\min} of 2.06V during the pulse. In practice, the voltage response of small cells will violate V_{\min} (generally near the end of the pulse) but still be considered successful as the voltage of cells under test tends to stabilize due to self-heating as cell size increases (thermal mass increases). As discussed previously, Navitas has studied the relationship of cell size and performance; this data is shown in Figure 10. SLP or DLP cells that show high degrees of polarization in cold crank, including those that fall to the system limit (generally 1.2 V) do not correct successfully with self-heating when built as larger cells.

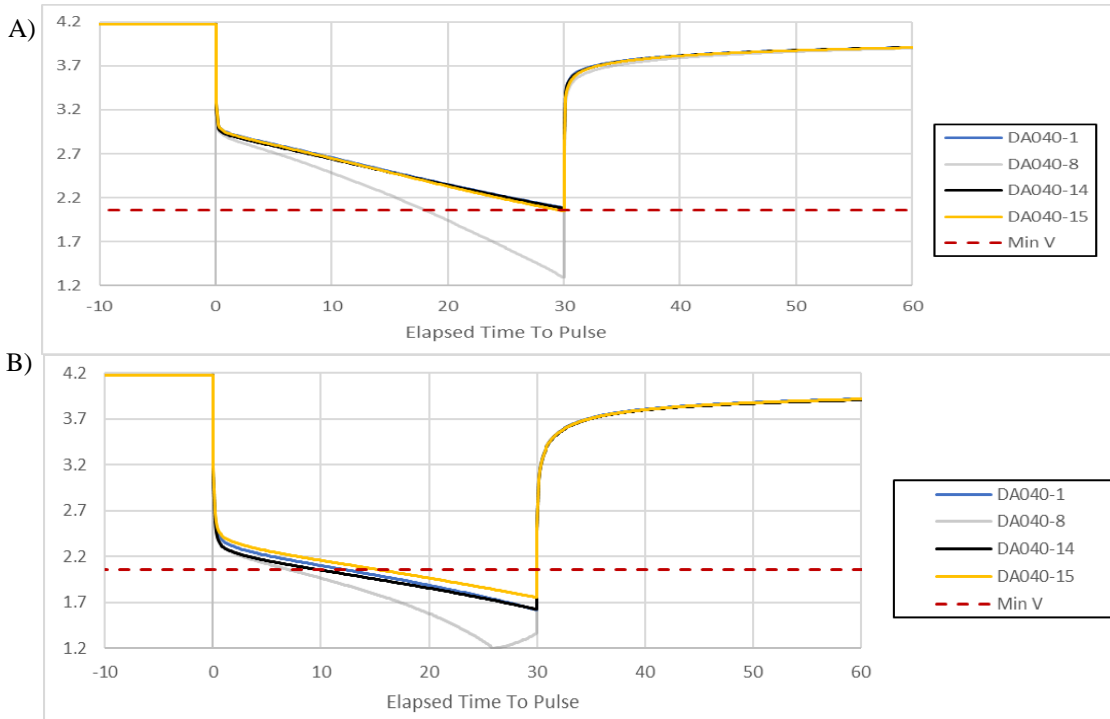


Figure 11. Cold crank voltage profile [DA040] at (A) -18 °C and (B) -40 °C in DLP cell format, measuring voltage of the cell as a function of time during cold crank.

The rate capability of DLP cells was measured by repetitively CCCV charging cells at low rate (C/2), then discharging at increasing rates. 6T-type DLP cells are discharged at 0.1C, 0.2C, 0.5C, 1C, 2C, 5C, 10C, and 15C rates. All DLP cell cycling was conducted at 1C charge (CCCV charging), 1C discharge at the specified soak temperature, with V_{max} equal to 4.2V, and V_{min} equal to 3.0V. For reference, 6T battery cycle life goals are 1000 cycles at 38 °C to 70% retention and 500 cycles at 50 °C to 75% retention. DLP cells were subjected to a capacity and direct current resistance (DCR) test ending in full charge, then set at 60 °C for 28 days. Cell voltage is measured every 7 days during the elevated temperature exposure. Following exposure, cells are cooled to room temperature, then subjected to the capacity and DCR test. Capacity loss, DCR gain, and self-discharge behaviors as a result of the exposure are determined.

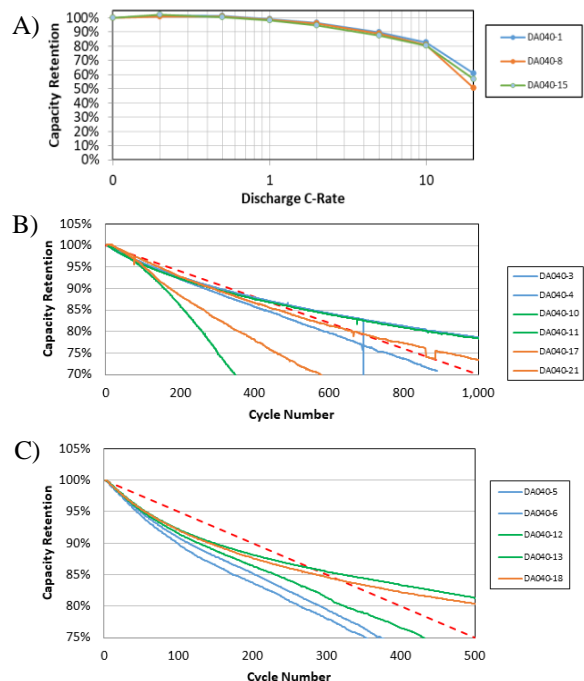


Figure 12. (a) Capacity retention versus discharge rate, and capacity retention versus cycle number at (b) 38 °C and (c) 50 °C for [DA040] samples in DLP cell format.

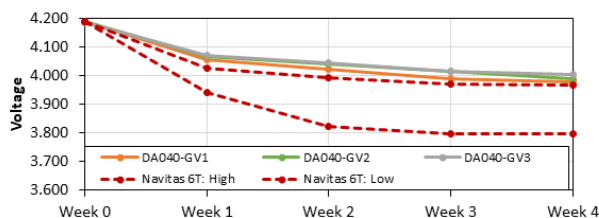


Figure 13. Elevated temperature storage measurements over time, measuring cell voltage for self-discharge at 60 °C for [DA040] samples in DLP cell format.

4.2. PPG vs Navitas: Roll-to-Roll Cold-Crank & Cycle Life Testing

Navitas received a set of roll to roll coatings at 8.00 +/- .02 mg/cm² [DA040]. The build contains 3 sets of cells evaluating the roll to roll films received by Navitas. Cells 1-7 include films from the MXP3 set, cells 8-14 from MXP3.1, and cells 15-21 from MXP1.

Results from [DA040] samples for cold crank testing at -18 °C and -40 °C are shown in Figure 11A and 11B, respectively. In this case, cells underperformed versus the goal at -40 °C, though compared to each other similarly compared to the -18 °C test.

Rate capability from [DA040] at 38 °C are shown in Figures 12A. In addition, cycle life data for these samples are shown in Figures 12B and 12C. In all cases, the samples performed similarly in rate capability and were all capable of discharge beyond 10C rate. With regard to cycle life, cells from each of the roll to roll coating groups surpassed the 38 °C cycling goal. As for high-temperature cycling data, shown in Figure 12C, cells from the MXP3.1 and MXP1 coating sections surpassed the 50 °C cycling goal, while cells from the MXP3 coating section delivered around 350 cycles.

Finally, testing for elevated temperature storage (ETS) showed all cells within the 6T specifications for self-discharged cell voltage over 4 weeks at 60 °C (Figure 13) based on historical upper and lower voltage bounds from baseline Navitas cells.

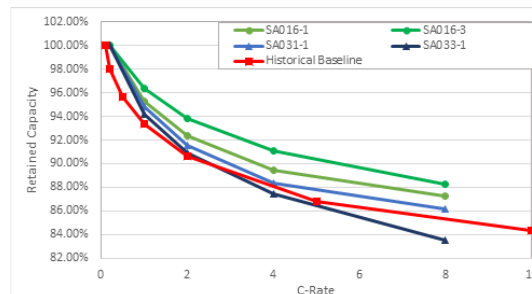


Figure 14. Rate capability of 3Ah pouch cells submitted by PPG with optimized formulation versus Navitas historical 6T cells.

4.3. Final deliverable: PPG Cell Pilot Testing Results

Navitas received an additional roll of PPG NMP-free cathode for larger cell builds. The specifications of the roll were a formulation of 90/5/5 NMC 532 / Carbon 1 / Binder 7 using mixing procedure MXP1, and total coating loading of 8.00 ± 0.02 mg/cm². Cells were then produced from both PPG-supplied foils and Navitas control foils using PVDF-NMP as the binder system, each with 8 x 3Ah cell builds. All cells were produced with the same stack count of cathodes and anodes. The difference in cell capacities can be attributable to differences in electrode coat weight between PPG and Navitas-coated cathodes. The final cell builds were produced using a total of 3 separate cathode coatings: one PPG NMP-free cathode and two Navitas coated cathodes. These cathode coating runs are distinguished by cell number, with PPG cathodes designated SA016, and two Navitas Pilot coated cathodes at 8.54 and 8.46 mg/cm² designated as SA031 and SA033, respectively. Rate capability was performed on two PPG NMP-free cells and two Navitas baseline cells in order to verify performance. The results of these tests are summarized in Figure 14 along with historical 3Ah 6T baseline cells. The delivery cells perform largely in line with the historical baseline cells and show promising performance for 6T battery or a similar application.

5. Conclusions & Benefits

PPG prepared NMP-free cathodes tailored for use in Li-ion batteries designed for automotive starting, lighting and ignition in military vehicles in accordance with 6T specifications. Cathodes designed to provide high energy density were formulated for exploratory binder development. Cathodes formulated for high power were formulated to elucidate the compositional bounds, material selection and mixing considerations necessary for achieving cold crank testing. Refinement of active loading, carbon/binder ratio and mix procedure afforded developmental cathodes, which were evaluated by rate capability and peak power testing in coin cells. Cathodes that exhibited favorable performance were supplied to Navitas for assembly of pouch cells, and evaluated under 6T-relevant test protocols.

The learnings from the formulation efforts described herein culminated in the development of a capacity-enhanced power cathode, with a composition of 90/5/5 NMC 532 / Carbon 1 / Binder 7. The cathode composition was prepared in a pilot-scale formulation using MXP1 and MXP3, and the respective slurries were coated on carbon-coated aluminum foil at 1.2 mAh/cm² (reversible capacity basis). Pouch cell testing revealed that the capacity-enhanced power cathode prepared via MXP1 exhibited performance that was in-line with 6T requirements. PPG supplied its final deliverable of 20 m cathode coated foil, and Navitas subsequently provided the final deliverable of 3 Ah pouch cells to GVSC.

PPG's Li-ion battery binder system described herein can generate significant benefits over traditional PVDF in NMP binder systems tested to meet or exceed 6T specifications, including a 40% reduction in solvent compared to viscosity-matched

cathode slurries formulated with PVDF-NMP binder, a reduced solvent demand to enable increased line speed, and pouch cell assemblies using PPG's capacity-enhanced power cathode aligned with historical 6T batteries developed by Navitas.

6. Acknowledgments & Disclosures

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7. REFERENCES

- [1] L. M. Toomey, Energy Storage Branch Chief, "U.S. Army Combat Capabilities Development Command – Ground Vehicle Systems Center, Combat Vehicle Energy Storage," CCDC GVSC, Presentation, 2020, CALSTART 202 Webinar Series, High-Efficiency Truck Users Forum
- [2] L. M. Toomey, Energy Storage Branch Chief, "U.S. Army's Ground Vehicle Energy Storage," U.S. Army TARDEC, Presentation, 2014, ARPA-E RANGE Kickoff 2014.
- [3] MIL-PRF-32565, "Performance specification Battery, Rechargeable, Sealed, 6T Lithium-Ion," Department of Defense, 2016