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Advanced Nonflammable Battery

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ABSTRACT

As military vehicles expand in mission roles and in offensive and defensive weaponry, there is an ever-increasing demand for greater energy storage. Moreover, with the technological breakthroughs in Direct Energy Weapons and Active Protective Systems (e.g., high-energy laser and high-power microwave systems, especially for prevention of UAVs), there is a commensurate need for increased energy density military power supplies to provide electrification to these Next Generation Combat Vehicles (Lynx, Griffin III, and CV-90). Current lithium-ion batteries for vehicles (e.g., 6T) have limited energy density (~100 Wh/kg), which are not sufficient for the high energy and power needs of military vehicles. Additionally, they typically use carbonate electrolytes which are extremely flammable. To address these issues, CRG developed a high specific energy (>225 Wh/kg) lithium ion battery (LIB) pouch cell that could be integrated into current military vehicle battery formats. This cell utilizes a high capacity graphite anode, a thermally safe cathode with high energy density, and a non-flammable temperature/voltage stable electrolyte. The developed cell is an improvement over the current safety and operational performance of military vehicle batteries.

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1. INTRODUCTION

As military vehicles become more dependent on electrical energy to power drive trains, increase fuel efficiency, power advanced directed energy weapons, and provide energy for stealth mode, there is a growing demand for a safe, high energy battery. Without this reliable energy system, key missions that depend on operating electrical equipment such as communications, sensors, jammers, weapons, and control systems can be hindered or even fail, jeopardizing missions which can result in loss of life.

To effectively power the drive trains and systems being developed for Next Generation Combat Vehicles (Lynx, Griffin III, and CV-90), the energy density and safety of lithium ion batteries (LIBs) needs to be improved. Conventional LIBs use highly flammable, volatile electrolytes (comprised of organic carbonate esters and toxic lithium salts) that can react violently if punctured, shorted, overheated, or if they contain a defect from assembly.

To reduce the risks associated with LIBs, CRG developed a high energy LIB which is inherently safe at the cell level. The nonflammable LIB offers tremendous potential to meet or exceed the multifaceted performance requirements of next generation military vehicles. These advantages include high energy density, high rate performance, wide operation temperature range, long cycle life, and most importantly, an inherently safe cell chemistry. CRG is actively working to transition this cell technology to advanced applications of interest for the US military and consumer markets.

2. BACKGROUND/MOTIVATION

Due to their higher energy content, large capacity Li-ion battery packs pose a significant safety risk. Most LIB cells utilize organic solvent-based electrolytes which are highly flammable [e.g., ethylene carbonate (EC) and dimethyl carbonate (DMC)]. Additionally, high energy density cathodes, such as NMC811, LCO, and NCA, have low onset thermal runaway temperature (~175 °C). Any deviations in the metastability of the electrochemical cell can lead to catastrophic “runaway”. This results in a direct chemical reaction between the cathode and anode which can ignite the flammable, volatile electrolyte. Large-format batteries, which increase the stored energy per cell, exacerbate this issue.

Following commercial practice to mitigate the risk, safety requirements are imposed at the cell, module, section, and enclosure levels. Relevant commercial standards include SAE J2289 [1], J2344 [2], and J2910 [3] which provide electric vehicle safety guidelines and best practices. The unique nature of military operation requires safety testing (6T battery, MIL-PRF-32565 [4]), similar to SAE J2464 [5] abuse procedures and response characterization. These tests include internal and external short, overcharge, crush, and nail penetration. The abuse response is characterized in terms of hazard severity levels (HSL) from 0 (no effect) to 7 (explosion).

To lower the safety risk associated with high energy LIB cells, they are often packaged within energy storage systems (ESS). As shown in Figure 1 it is acceptable to use high energetic cells that have HSL 7, as long as the enclosure is able to contain and sustain an HSL of ≤ 4 (venting) for ≥ 30 minutes after an abusive incident (objective).

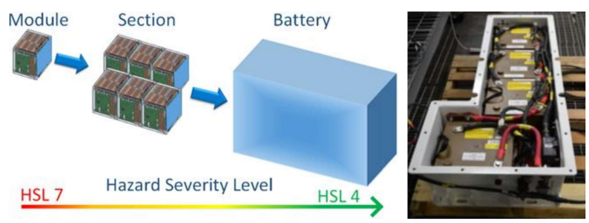

Figure 1: Integration of module in section and battery enclosure, with decreasing hazard severity level (HSL); example of enclosure with top removed

ESS include pressure venting, thermal management, thick protective cases, and charge/discharge limits to contain the potential failure of LIBs. Figure 2 shows an example of a battery enclosure with a vent connection point for restricting the exothermic combustion of the failed battery and routing the outgases.

Figure 2: HSL7 battery (100% SOC) without and with a battery box, respectively

Unfortunately, these ESS features add significant weight to the battery and decrease its energy density. Moreover, these systems need to be extremely over engineered to contain the worst-case scenario of catastrophic battery failure. LIBs are prone to complex failure modes when used for advanced military applications, which can confound even the best fail-safe designs. Therefore, there is a need for a high energy and power dense LIB that is inherently safe at the cell level. Central to a safe LIB cell is the use of a non-flammable, high performance electrolyte that can mitigate or eliminate the risk of combustion during failure. Additionally, the complete cell chemistry should be designed in order to prevent thermal runaway.

3. NONFLAMMABLE LIB CELL DESIGN

At the heart of the safe cell is a high performance, nonflammable electrolyte. As can be seen in Figure 3, conventional carbonate-based electrolyte (EC/DMC) readily catches fire when an ignition source is present. Conversely, the nonflammable electrolyte is flame retardant and inherently resistant to catching fire. Even when a butane torch is applied for 1 second directly to the electrolyte, it immediately self-extinguishes when the ignition source is removed.

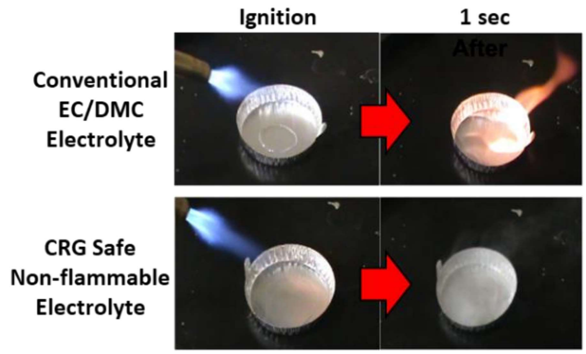

Figure 3: Flame test of conventional electrolyte and the nonflammable electrolyte

The nonflammable electrolyte not only improves the safety of a LIB cell, but also enhances its performance. CRG designed this safe electrolyte to have high ionic conductivity across a wide temperature range, Figure 4. While most carbonate-based electrolytes freeze around -20 °C, the nonflammable electrolyte stays liquid and ionically conductive even at extremely low temperatures (-40 °C).

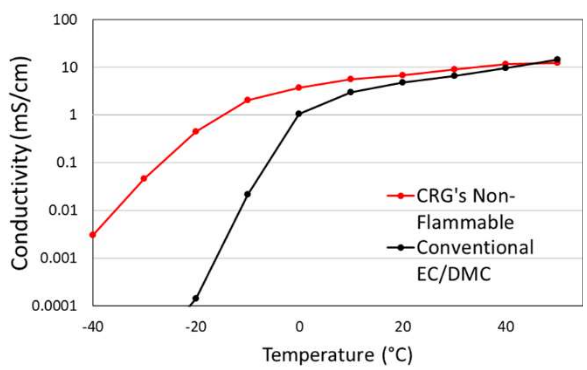

Figure 4: Ionic conductivity of conventional electrolyte and the nonflammable electrolyte

CRG is not only improving the safety of the LIB cell through a nonflammable electrolyte, but also by examining the full cell design. The nonflammable LIB cell (Figure 5) utilizes a high energy cathode that is thermally stable, a high capacity graphite anode, and the non-flammable high-performance electrolyte. CRG is improving the thermal stability of high energy cathode materials by modifying the active material composition and incorporating protective coatings. These improvements help prevent the cathode from decomposing and going into thermal runaway by increasing the onset temperature and decreasing the reaction enthalpy. CRG is also utilizing a state-of-the-art separator. The ceramic coated separator improves the physical barrier between electrodes and reduces micro-shorting. Additionally, the multilayered structure of the separator possesses a thermal shutdown mechanism to ionically isolate the anode and cathode at elevated temperatures.

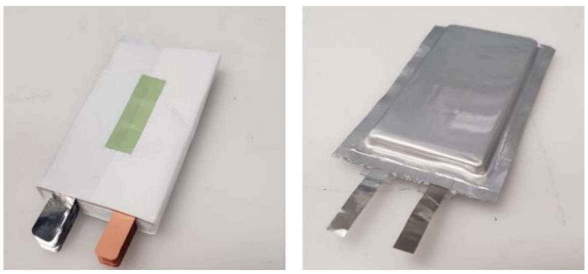

Figure 5: Jelly-roll and packaged nonflammable cell

4. SAFETY PERFORMANCE

The nonflammable LIB cell has improved safety performance meeting or exceeding current requirements for integration into military battery modules such as 6T (MIL-PRF-32565C). CRG has developed a series of in-house tests to characterize and demonstrate the safety performance of the cells. These tests were based on the SAE J2464 (surface vehicle recommended practice).

4.1. Nail Penetration

Cells with conventional (EC/DMC) electrolyte were compared to the nonflammable electrolyte by nail penetration testing. In short, a 2 mm diameter nail was pierced completely through the face of the pouch cells, Figure 6. As the nail passes through the cell, it causes internal shorting between the anode and cathode, releasing the energy stored in the cell at extremely high discharge rates. This energy release causes high temperatures, which can cause the electrolyte to ignite and go into thermal runaway (>500 °C) as seen with the conventional electrolyte. Conversely, the nonflammable electrolyte remains safe even while shorting internally from the nail penetration (drop in voltage from 4.2 V to < 1 V). Note that the high discharge rate causes the cell temperature to increase to ~60 °C, but the cell remained extremely safe and inert throughout the full test. CRG believes the nonflammable cell has an HSL of ≤ 3 (minor cell venting, less than 5% change in mass).

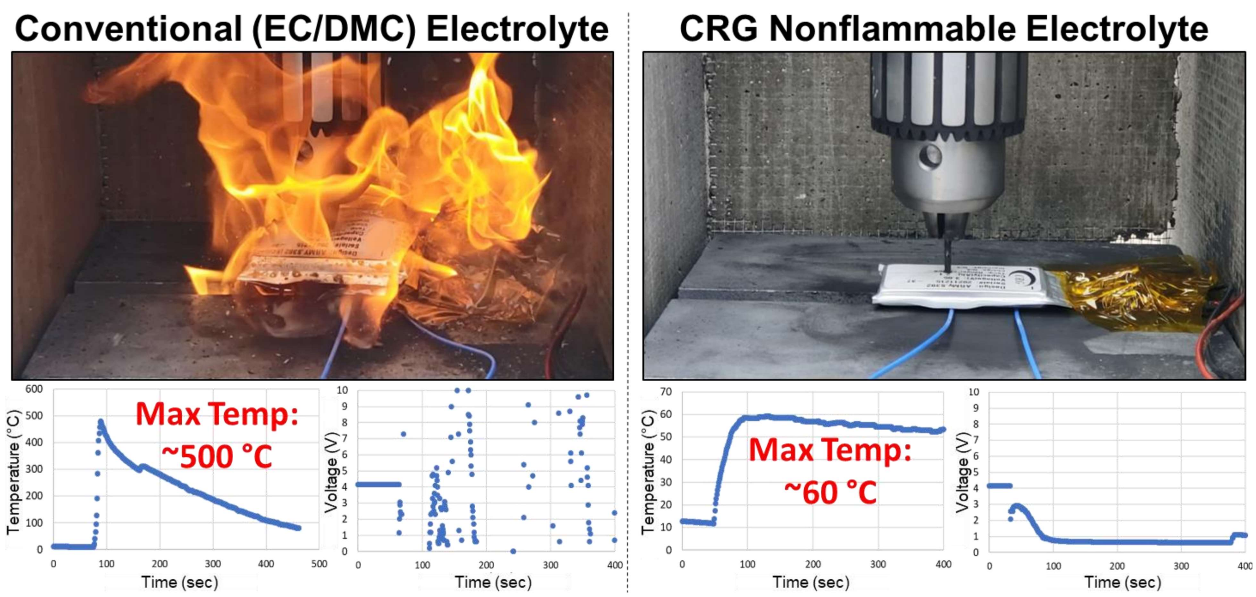

Figure 6: Nail penetration test: cells with conventional electrolyte versus the nonflammable electrolyte with corresponding cell temperature rise and voltage change

4.2. Crush

To assess the stability of the cells and potential of internal short due to perpendicular pressure, the safety of the cells was characterized through a crush test. A 5 mm diameter rod was pressed with over 1000 lbs into the side of the pouch cells and held for over 5 minutes. During this test, the cell temperature and open circuit potential (OCP) were measured. Both the conventional electrolyte cell and the nonflammable cell remained stable throughout the entire test with no increase in temperature or drop in voltage. After the pressure was released, a small deformation of ~5-10% was observed into the pouch cells. By using safe components such as the ceramic coated separator, both cells remained safe. Based on these results, CRG believes the cell have an HSL $\leq$ 0 (No effect or loss of function).

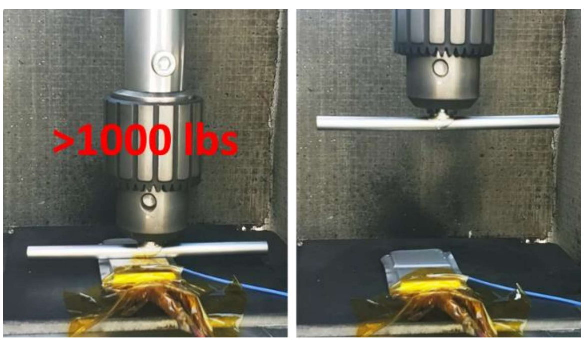

Figure 7: Rod crush test, the nonflammable cell

4.3. External Short-Circuit

CRG tested the pouch cells in two short circuit experiments. First, a hard-short circuit was performed by connecting the cell to an electrically conductive copper switch (< 100 mΩ). During this test, the high discharge rate of the battery causes the leads of the tab to immediately melt (<1 sec), effectively acting as a fuse. Neither the conventional electrolyte cell nor the nonflammable cell had any rise in temperature. Second, a soft-short was performed in which the resistance of the short was slightly increased (~1 Ω). During this process, the cell tabs glowed hot red, but did not melt. CRG estimates that the cells discharge around 30 A. During this soft-short circuit, the high rate discharge caused the temperatures of both the conventional electrolyte cell and the nonflammable electrolyte cell to increase to ~70 °C. The short was maintained for 5 minutes, during which the cell began to slowly cool. Based on these results, CRG believes the cells have an HSL $\leq$ 2 (damage, but no hazard) for the hard-short and HSL $\leq$ 0 (no effect or loss of function) for the soft-short.

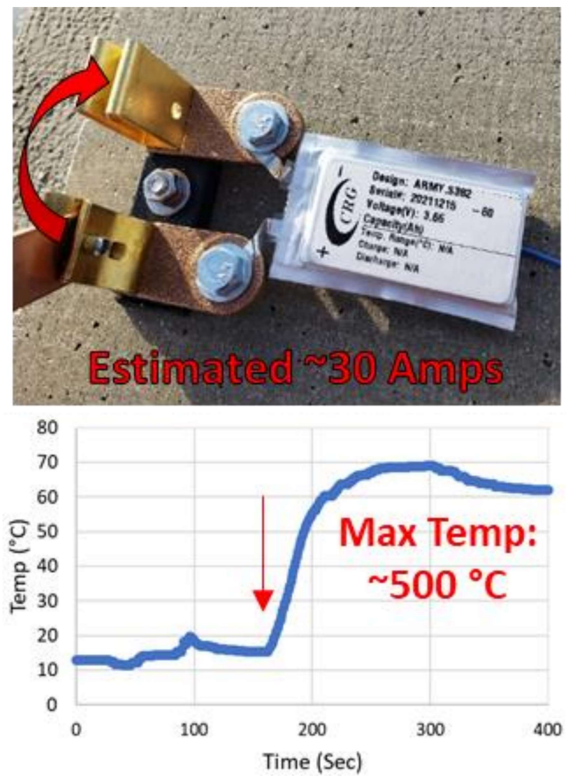

Figure 8: External short test, the nonflammable cell

4.4. Ballistic Penetration

As the cells are being developed for the military's use, a ballistic penetration test was performed to evaluate the cell's safety. CRG conducted the ballistic penetration safety test on 2.3 Ah cells after they were formed and fully charge (4.2 V). A round (7.62 x 39 mm) was fired from 25 m with a muzzle velocity of 2400 fps. The bullet fully penetrated each of the cells and the plywood backing material. CRG recorded if a flame was present, if and when the electrolyte extinguished the flame, and the max temperature of the cell. The conventional EC/DMC electrolyte (which is very flammable) immediately erupted in flames and continued burning until all the electrolyte was consumed (~30 seconds). During this time, the cell went into thermal runaway and increased to >500 °C (measured with infrared thermometer). On the other hand, the non-flammable battery cells had no flames or smoke observed, or they were immediately extinguished by the nonflammable electrolyte. The ballistic impact of the cells did cause internal shorting, releasing the energy of the cell and causing the temperature to rise in the range of 50-70 °C. Based on these results, CRG believes the nonflammable cell has an HSL ≤ 3 (minor leaking < 5%, no smoke or flame).

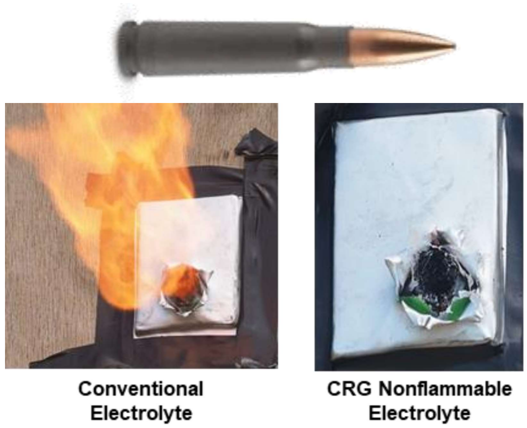

Figure 9: Ballistic penetration test, cells with conventional electrolyte versus the nonflammable electrolyte

To expand upon these results, CRG tested the safety and nonflammability of the cells using incendiary tipped rounds, Figure 10. The armor piercing rounds (762x54r) were fired from 20 m with a muzzle velocity of 2600 fps. The bullet fully penetrated each of the cells and the plywood backing material. Similar to standard ammunition rounds, the cells had no smoke or flames observed, or they were immediately extinguished by the nonflammable electrolyte. The cell temperature increased to 50-70 °C but remained safe without combustion or explosion. Based on these results, CRG believes the nonflammable cell has an HSL ≤ 3 (minor leaking < 5%, no smoke or flame).

Figure 10: Incendiary tipped ballistic penetration test of the nonflammable cells

4.5. Accelerating Rate Calorimetry

Accelerating rate calorimetry (ARC) testing was performed on a commercial 21700 cell and the nonflammable cell at 100% state of charge (SOC). The ARC was operated using a heat-wait-search mode to determine the temperature onset of self-heating. To start the ARC was ramped up to 60 °C. The ARC then heats the batteries in discrete intervals and monitors the response from the cell. This process continues to heat the cell until the temperature increases past the threshold. The ARC then engages in an exothermal mode in which it maintains an adiabatic state by closely matching the temperature of the cell. Figure 11 shows a comparison of the exothermic temperature rate change of the cells versus the cell temperature. The commercial 21700 cells go into thermal runaway (>50 °C/min) around 195 °C. Conversely, the nonflammable LIB cells have better thermal stability with the onset temperature of thermal runaway being roughly 20 °C higher (~215 °C).

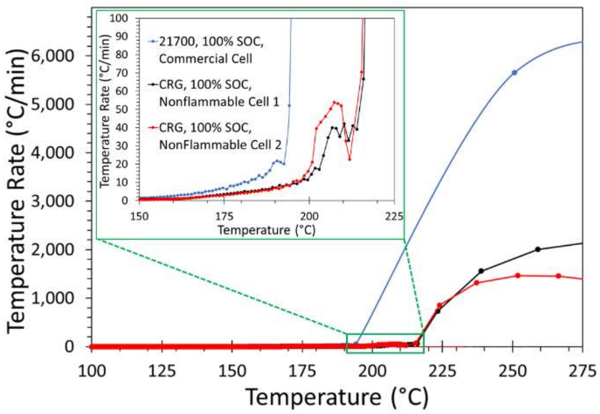

Figure 11: ARC testing, thermal runaway temperature of commercial 21700 (blue) vs the nonflammable cells (red and black)

5. ELECTROCHEMICAL PERFORMANCE

The nonflammable LIB cell not only has excellent safety, but also has outstanding electrochemical performance. The following section highlights the cell performance.

5.1. Capacity, Cycle Life, Energy and Power Density

The nonflammable LIB cell is a 2.3 Ah pouch cell with an energy density of 236 Wh/kg when charging and discharging between 4.2-2.5 V (3.65 V nominal). Figure 12 demonstrates the excellent cycle life of the nonflammable cell. The cycles consist of C/5 (0.46 A) charging and discharging with over 350 cycles. CRG projects the nonflammable cells will achieve over 1000 cycles with >80% capacity retention.

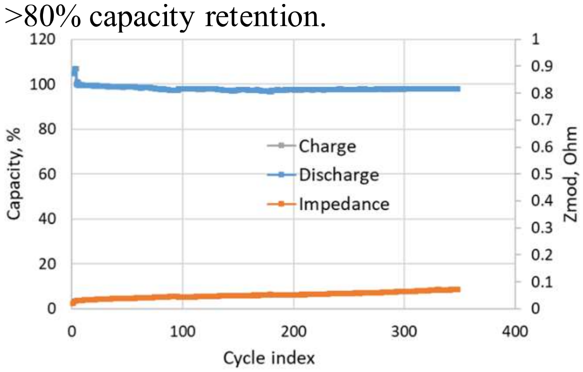

Figure 12: Cycle life of the nonflammable cell

5.2. Discharge Rate

CRG developed the nonflammable battery to have high energy density. However, the cells can also be discharged at modest C-rates while maintaining capacity. Figure 13 shows the rate capability of the nonflammable cell (C/20-2C). After formation, the cell is able to achieve greater than 200 mAh/g (cathode active material capacity). At 1C discharge, the cell is able to maintain > 83% initial capacity and at 2C the capacity retention is 72% (339 W/kg). CRG also tested the nonflammable cell by discharging it at 4C for 30 seconds and 30 seconds off repeatedly. Even at this slightly higher pulsed discharged rate, the cell maintained about 55% capacity.

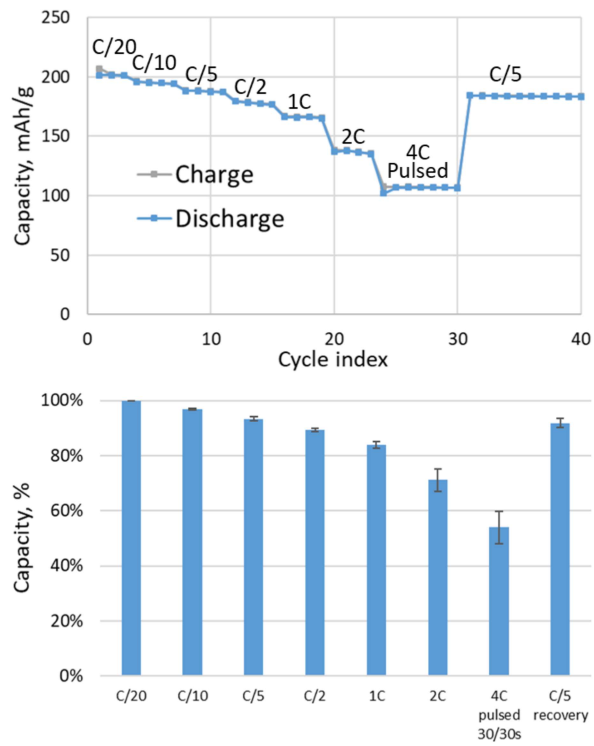

Figure 13: Rate ladder and corresponding capacity retention of the nonflammable cell

5.3. Temperature Performance

CRG also designed the nonflammable electrolyte to be stable and ionically conductive across a wide temperature range. Figure 14 compares pouch cell made with conventional EC/DMC electrolyte to identical pouch cells made with the nonflammable electrolyte. The cells were charged at C/5 at room temperature and then discharged at C/5 at temperatures between 55 °C to -40 °C. As the temperature increases above room temperature, both cells have a slight increase in performance. This increase in capacity (~5% at 55 °C) is due to the ionic conductivity of the electrolytes increasing. At lower temperatures the nonflammable electrolyte cell significantly outperforms the conventional electrolyte cell. At -20 °C EC/DMC becomes extremely viscous and impedes the flow of lithium ions resulting in a drop of capacity (~42% retention). At -30 °C, the conventional electrolyte is completely frozen and refuses to discharge. On the other hand, the nonflammable electrolyte has great low temperature performance. At -20 °C, the nonflammable LIB cells retain close to 80% initial capacity. Even at extremely low temperatures of -40 °C, CRG's cell is able to effectively discharge.

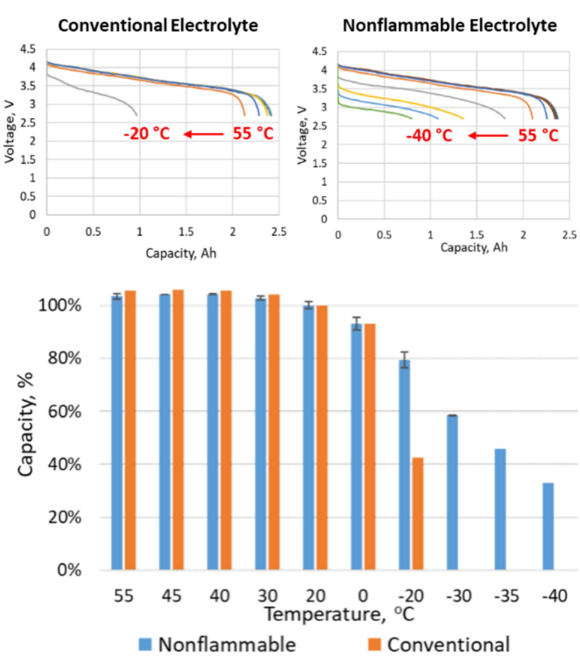

Figure 14: Temperature extreme performance of the nonflammable cell

6. CONCLUSION

Using a battery cell that is inherently safer removes the need for bulky, heavy, and over-engineered ESS. The nonflammable LIB cell provides this energy storage solution and can improve the safety and energy density of military vehicle batteries, Figure 15. CRG successfully demonstrated a non-flammable, high specific energy (2.3 Ah, 236 Wh/kg), and specific power (339 W/kg at 2C) LIB that can be used for military vehicles. The safety and nonflammability of the cell were demonstrated with both nail/ballistic penetration events, crushing, and hard and soft shorting. Through all of the abuse testing, CRG demonstrated an HSL $\leq$ 4. The cells have excellent cycle life (projected over 1000 cycles with >80% capacity retention), good rate performance (~72% at 2C discharge), and operate effectively across an extremely wide temperature range (-40 °C to 55 °C).

Specifications	
Size	70 x 45 x 6.7 mm
Weight	36.1 g
Cell Type/Packaging	Pouch
Capacity	2.3 Ah
Voltage Range	2.7 - 4.2 V
Nominal Voltage	3.65 V
Sp. Energy at C/20	236 Wh/kg
Cycle Life	>1000 cycles (est.)
Operating Temperature	-40 °C to 55 °C
Max Continuous Discharge	2C
Max Pulsed Discharge (30 sec)	10C
Max Charging Current	C/2
Safety Risk (Internal Assessment)	Low (SAE J2464 $\leq$ 4)

Figure 15: Nonflammable cell metrics

7. REFERENCES

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