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High-Power, Low Temperature Li-Metal Battery Cell for Military Vehicle Applications

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ABSTRACT

Cornerstone Research Group (CRG) developed a lithium metal (Li-metal) battery cell for military applications. Utilizing a Li-metal anode, high energy density cathode, and an advanced low-temperature fluorinated electrolyte, the cell was designed and developed to provide high-power and low temperature capabilities. The 1.5 Ah Li-metal pouch cell had a specific energy of 247 Wh/kg and was able to discharge at ultra-low temperatures (-57 °C). Moreover, the Li-metal cell demonstrated extremely high-power by fully discharging at 10 C while maintaining over 70% its initial capacity. To demonstrate the Li-metal cell's utility for military vehicle use, CRG modeled the cell into the 6T battery platform. A novel module housing was designed to evenly apply compression to the Li-metal cells to improve cell performance. Based on these projections, the Li-metal 6T battery could have a capacity of 163 Ah with a specific energy of 179 Wh/kg.

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1. INTRODUCTION

Batteries have become a necessity in the field of battle and are critical to the operations of military vehicles. Hybridization and full electrification of the powertrain can provide enhanced tactical capabilities to military vehicles by increasing the available onboard power, reducing fuel costs, and enabling stealth/silent mode. [1] [2] Moreover, batteries are needed for high-power applications such as starting vehicles and powering advanced directed energy weapons where a large amount of energy is needed for a short period of time. This need for high power/energy batteries for military vehicles is exacerbated in extremely cold applications where current lithium ion batteries (LIBs) are unable to provide high energy and high-power output at low temperatures. This need for advancements is critical when considering the range of challenging environments with artic conditions (e.g., high elevation or high latitudes). Without this reliable energy storage system, key missions that depend on operating electrical equipment/vehicles can be hindered or even fail, jeopardizing missions which can result in loss of life. Therefore, there is a high demand for the development of new advanced cell chemistries which can provide high power output with large capacity, even at extremely low temperatures.

2. BACKGROUND/MOTIVATION

Traditionally, Li-ion cells operating in extremely low temperature environments require integrated heaters to maintain battery temperature above -20 °C for cells to function. Such thermal management systems add complexity and consume valuable energy, mass and volume. The low-end temperature limitations of conventional lithium-ion cells mostly stem from high electrolyte viscosity followed by electrolyte solidification, sluggish electrode kinetics, poor charge transfer across the solid electrolyte interface (SEI), and lithium metal plating on graphite during charging. Batteries which can operate at extremely low temperature could reduce or eliminate the thermal management needs, reduce complexity, and liberate mass budget towards greater energy storage capacity for extended mission duration and capability. However, LIBs which have been specifically designed for low temperature and high-power applications have limited energy density (100-150 Wh/kg), due to very thin material loadings on the anode and cathode. Therefore, opportunity and need exist to advance the state-of-the-art of batteries for future arctic and high-altitude missions by simultaneously extending the lower operational temperature limits while increasing specific energy and power output.

3. CHEMISTRY AND CELL DESIGN

The high-power capability, fast transient response, and high efficiency during charge and discharge at low temperatures make Li-metal cells a viable energy storage choice for military vehicles. Therefore, CRG designed and fabricated a high specific energy (≈250 Wh/kg) Li-metal cell capable of high power (10 C) output and which can operate at extremely low temperature (-50 °C). The cell chemistry utilizes a thin (20 µm) lithium metal anode, high energy density cathode (>200 mAh/g), and an advanced fluorinated electrolyte that has a low freezing point and is nonflammable, Figure 1.

3.1. Lithium Metal Anode

A lithium metal anode was chosen for its high energy density and low temperature capability. In terms of gravimetric capacity (3861 mAh/g) and volumetric capacity (2278 mAh/cm^3), lithium metal has tremendous advantages over other anode materials and can leverage traditional Li-ion cathodes. This option is a readily available material and easy to manufacture. Conventional LIBs use graphite anodes. While they provide excellent cycling at moderate temperatures and low cost, their low specific capacity (350 mAh/g) limits achievable specific energy. Moreover, low temperatures can cause premature cell failure during charging from plating. Similar limitations exist with lithium titanate (LTO), also having low specific capacity (175 mAh/g) and, even more detrimental, high electrode potential (1.55 V vs

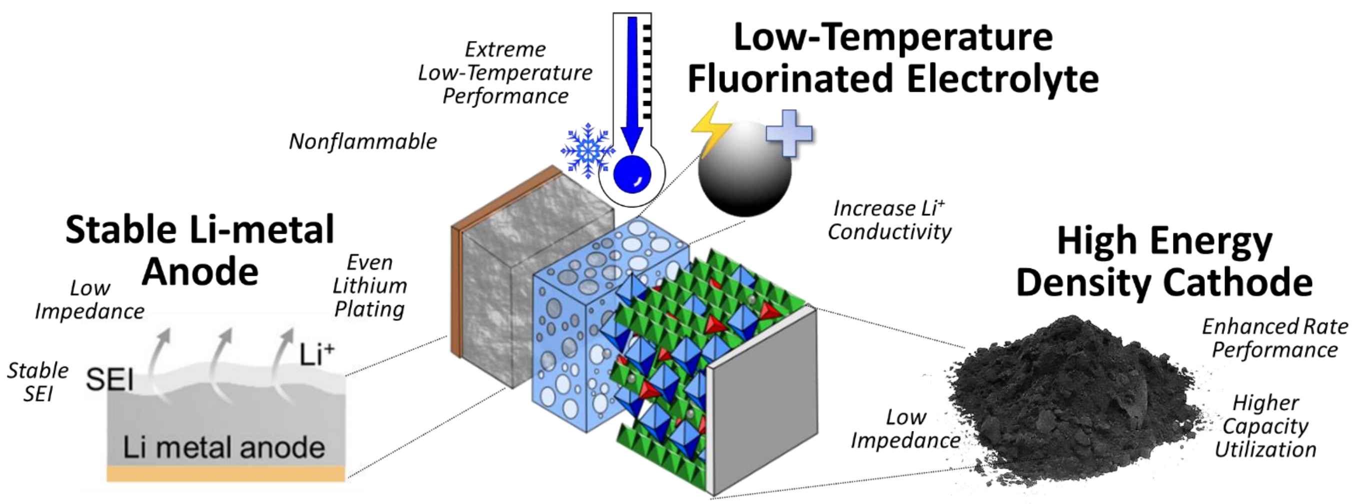


Figure 1: Illustration of the High-Power, Low Temperature Li-Metal Battery Cell for military applications

Li/Li^+) which decreases cell operating voltage. Conversely, silicon (Si) has an extremely high specific capacity (3600 mAh/g), but exhibits 400% volume expansion upon lithiation, resulting in unstable solid-electrolyte interphase (SEI), electrolyte consumption, particle pulverization, and anode disintegration. Moreover, Li-metal demonstrates improved kinetics during charge and discharge at low temperature compared to intercalation (graphite) and alloying (silicon) chemistries. Note, lithium metal does have several disadvantages such as unstable SEI, Li porosity, dendrite growth, and electrolyte consumption which can lead to accelerated cell death. However, CRG has performed extensive research into lithium metal anode chemistries and has developed methods for improving cycle life. Most of these improvements are based on an advanced fluorinated electrolyte.

3.2. Low Temperature Fluorinated Electrolyte

The greatest hurdle limiting Li-metal anodes for low temperature batteries is an inadequate electrolyte. CRG has developed a fully fluorinated electrolyte that solves many of these problems. This advanced fluorinated electrolyte forms a stable SEI, has a high dielectric constant for dissolving lithiated salts, has high voltage stability (>5 V), and has low surface energy for improved wettability which lowers impedance. Fluorinated electrolyte solvents were carefully selected which have extremely low freezing points. When combined with lithiated salts, the fluorinated solvents form an electrolyte with high ionic conductivity even at low temperatures. Moreover, fully fluorinated electrolytes are typically nonflammable and have been shown to increase the safety of Li-metal cells (no smoke or flame when pierced with nail or bullet penetration). [3]

During cell formation, a lithium fluoride (LiF) SEI is formed through fluorine donation from the electrolyte. This LiF SEI is a critical piece to integrate lithium metal anodes into high energy and power dense batteries. LiF intrinsic characteristics such as a large bandgap (13.6 eV), extremely wide electrochemical stability window (>6 V vs Li/Li^+), and low Li adatom surface diffusion energy barrier makes it the perfect SEI, especially for low temperatures operations. [4] [5] Moreover, LiF has high surface energy and a small lattice constant which allows it to plastically deform, suppressing morphological instabilities. [6] Therefore, the fluorinated electrolyte is indeed a critical addition into the cell design and enables the utilization of lithium metal for high energy batteries operating at extremely low temperatures.

3.3. High Energy Density Cathode

The Li-metal cell chemistry is compatible with a variety of different cathodes. For the application of high energy and low temperatures, a high nickel chemistry (NCA) was chosen. While lithium iron phosphate (LFP) potentially has higher power density due to increased discharge kinetics, its low capacity and discharge voltage limit energy density. NCA was utilized as it has extremely high energy density (capacity of >200 mAh/g, and 3.8 V nominal voltage). Additionally, the cathode active material was modified via a scalable wet chemistry technique to create a solid electrolyte coating. This protective coating provides several key benefits. First, the solid electrolyte forms an artificial SEI on the cathode improving the first charge efficiency. Second, it creates a high surface energy layer improving wettability which lowers impedance. Third, the coating forms a protective layer preventing the electrolyte from reacting with the lithiated cathode active material. This not only improves cycle life, but also enhances the safety of the battery.

3.4. Cell Design

CRG utilized the chemistry described previously and created several high capacity pouch cells (~1.5 Ah), Figure 2. The cell was designed to operate at high power and at extremely low temperatures; therefore, the cathodes were cast at low loadings (8.3 mg/cm^2, 1.5 mAh/cm^2) and high porosity (40%). The high porosity of the cathode allows for a less torturous path for ion transport, but increases the amount and weight of the electrolyte (~18% of total cell weight). While modest loading and high porosity drops the energy density (247 Wh/kg, compared to CRG's high energy Li-metal cells >400 Wh/kg), it significantly reduces the impedance of the cells (only 10 Ω-cm). Low impedance is critical for reducing overpotential and increasing active material utilization, especially at low temperatures.

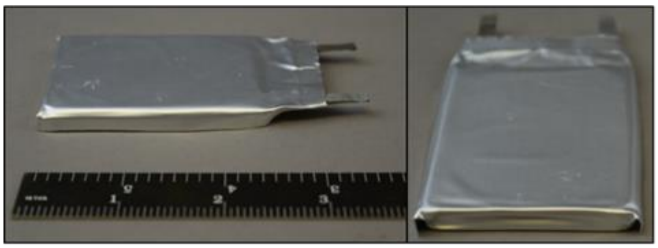


Figure 2: Photo showing the 1.5 Ah High-Power, Low-Temperature Li-Metal Battery Cell

4. PERFORMANCE

4.1. Low Temperature Performance

The high-power, low temperature Li-metal cell demonstrates high energy density even at extremely low temperatures. While conventional lithium ion batteries begin to freeze at -20 °C and have little to no capacity at -30 °C, the Li-metal cells can operate effectively in extremely cold temperatures (-57 °C).

The developed Li-metal pouch cells were tested for their low temperature performance. Charged cells (4.5 V) were placed in an environmental chamber at various low temperatures (-19 to -57 °C). After acclimating for 2 hours, the cells were discharged to 2.5 V at a constant current of C/5. The state of discharge curve can be seen in Figure 3a. NCA has a layered crystal structure; therefore, the discharge voltage is transient from 4.5 V to ~3.5 V. As the temperature of the cell decreases, a small overpotential forms slowly dropping the voltage of the cell. However, at -51 °C, the nominal voltage drops to only ~3.2 V, compared to ~3.8 V at room temperature. At -57 °C the voltage drops from overpotential prevented the cell from fully discharging (36% capacity retention), because the voltage cutoff was set to 2.5 V. If the cell were discharged to 2.0 V, the capacity retention increases to 56%, highlighting the importance of low overpotential.

The Li-metal cells have high cathode active material specific capacity and great utilization even at low temperatures, Figure 3b. At room temperature, the NCA active material had a specific capacity of over 210 mAh/g. As the temperature decreased, the capacity retention remained high and at -43 °C, the NCA still had ≈150 mAh/g. At extremely low temperatures where conventional cells and even most state-of-the-art cells would be frozen, the Li-metal cells have excellent capacity retention, 126 and 76 mAh/g at -51 and -57 °C, respectively.

One other extremely important note to consider is that the cells were discharged at a moderate rate (C/5). CRG believes this discharge rate accurately represents an application of large military vehicle during anti-idle, use of auxiliary electronics, and/or silent watch operations (30-60 amps per 6T). [7] This rate is high enough to cause stress and overpotential on the cell but is not high enough to cause significant self-heating. Higher discharge rates can increase the temperature of the cell due to internal ionic and electronic resistance (joule heating). While beneficial for low temperature performance, it cannot be depended on for military missions. If the cells are discharged at higher rate (>1 C), the voltage and capacity would be artificially high due to self-heating and not accurately represent mission profiles where high discharge rates are not always constant.

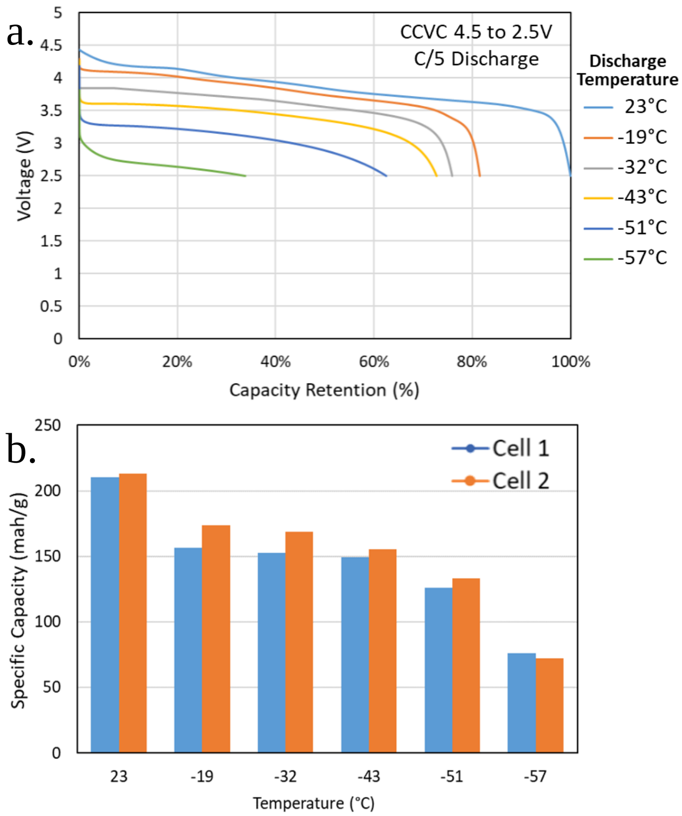


Figure 3: a) State of discharge profiles (voltage vs capacity retention) for cells discharged at different temperature. b) Specific capacity of the cathode active materials at different discharge temperatures.

The energy density of a cell is affected not only by capacity retention at low temperatures, but also the discharge voltage. As the overpotential increases and the capacity decreases, there is an accumulative adverse effect on the energy density. Never-the-less, the Li-metal cells have high energy density across a wide temperature range, Figure 4. The Li-metal cells have an energy density of 247 Wh/kg at room temperature. Note that this energy density is comparable to high energy density lithium ion battery (graphite anode), while high power cells are typically closer to 100-150 Wh/kg. Even at low temperatures, the Li-metal cells retain high energy density, >150 Wh/kg at -43 °C and at extremely cold conditions (-51 and -57 °C) operate close to 100 Wh/kg.

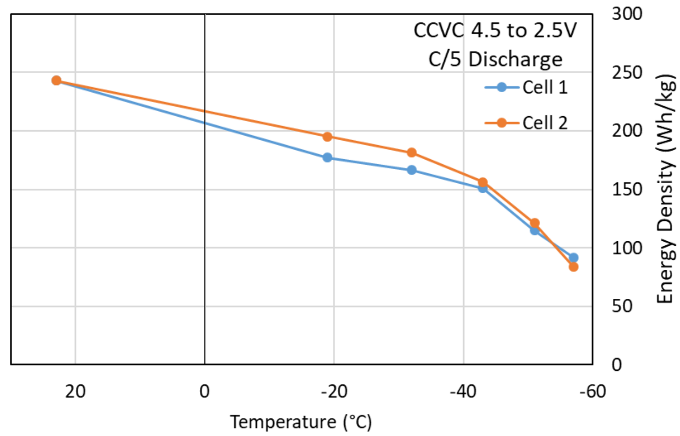


Figure 4: Energy density as a function of temperature.

4.2. Discharge Performance

CRG's Li-metal cells were designed to decrease overpotential which is not only beneficial for extreme low temperatures, but also high charge and discharge rates. The Li-metal cell can fully discharge at high rates while maintaining a significant portion of their initial capacity. At 5 C, the Li-metal cells were able to discharge at 195 Wh/kg (82% of capacity). When discharged at 10 C the cells were able to deliver a specific power of >1.6 kW/kg with over 70% of its initial capacity. After high rate discharge the cells recovered to ~100% initial capacity when discharge at C/5.

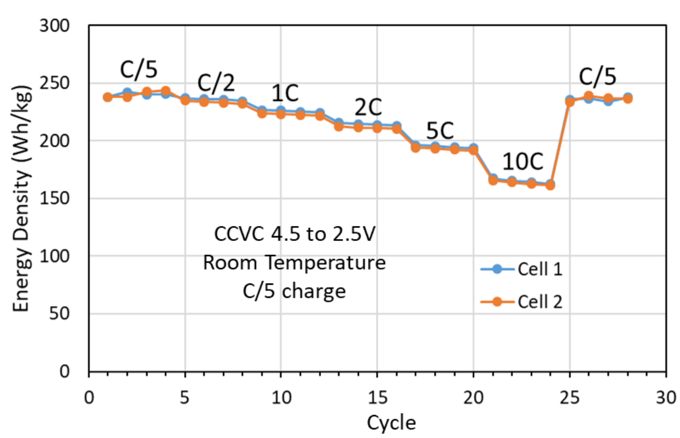


Figure 5: Energy density as a function of discharge rate

5. FUTURE WORK AND APPLICATIONS

The high-power, low temperature Li-metal cell could be utilized in a variety of different applications, but is especially desirable for military vehicles. CRG constructed a computer aided design (CAD) model integrating the Li-metal cell into a 6T battery platform. The 6T is typically used as a vehicle starter battery and used by roughly 95% of military ground vehicles. The military performance specification of rechargeable LIB 6Ts is currently governed by MIL-PRF-32565C. [8]

A cell holder was designed to encase and protect the cell and electrically connect them into a module. An aluminum heat-sink fin covers the cell holder allowing heat to be evenly dissipated across and away from the cell. Fourteen cells were connected (seven in series and two parallel) to form a module (≈24 V). Compression plates with a rubber expansion layer are mounted on each side of the module. These plates are compressed at each corner by threaded rods. Compressing the cells has been shown to increase the cycle life of lithium metal batteries, especially when cycling at high rates and low temperatures, by preventing dendrites and improving plating morphology. [9] [10] Eight of these modules are connected in parallel to form a 6T battery assembly.

Based on the CAD model, CRG estimated the capacity and energy density of the scaled Li-metal pouch cell and full 6T battery assembly, Figure 7. If the Li-metal cell is scaled to a 95 x 105 x 6.9 mm format, the projected capacity would be 10.7 Ah. With a mass of 143 g, the cell would have a specific energy of 264 Wh/kg, which is ~7% greater than the 1.5 Ah cell previously demonstrated due to less inert material mass. If 112 cells were stacked in a 7s16p arrangement, the 6T battery would be filled by roughly 54% cells, with their weight accounting for 16 kg. The additional volume and mass (7.5 kg) would be filled by the module housing materials, electronics, interconnects wiring, and thermal management materials. The Li-metal 6T would have a nominal voltage of 26.6 V and capacity of 163 Ah. At roughly 23.5 kg, the specific energy would be 179 Wh/kg, which is significantly higher than current lithium ion 6T's (~100 Wh/kg). [11] [12] While conventional Li-ion 6T batteries need to discharge at extremely high rates (10-15 C) to achieve the 1100A for starting military vehicles, the higher capacity of the Li-metal 6T reduces the discharge rate to only 6 C. Moreover, the Li-metal cell operates efficiently even in extremely cold environments (< -50 °C), demonstrating its utility for 6T batteries in artic conditions.

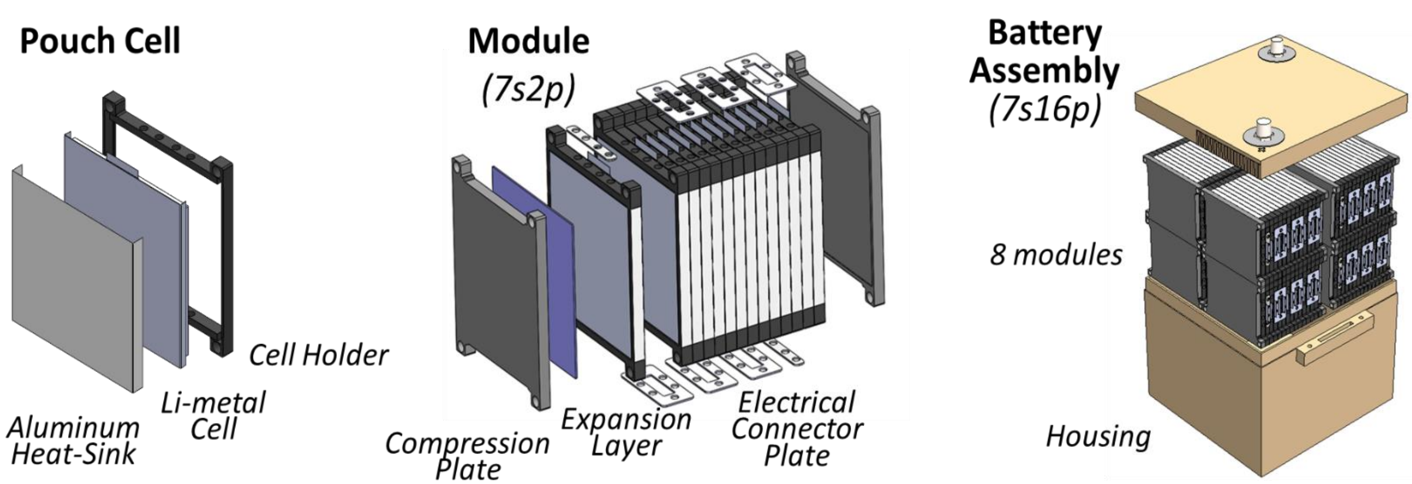
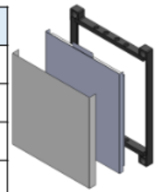


Figure 6: CAD model integrating High-Power Li-metal cell into 6T battery platform

Cell Level		
Voltage	3.8	V
Mass	143	g
Thickness	6.9	mm
Capacity	10.2	Ah
Specific Energy	264	Wh/kg
Battery Assembly Level		
Config (S x P)	7x16	(S x P)
Total Cells	112	Cells
Nom. Voltage	25.9	V
Cell Fill	54%	kg
Cell Mass	16.0	kg
Total Battery Mass	23.5	kg
Capacity	163	Ah
Specific Energy	179	Wh/kg



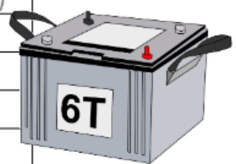


Figure 7: Estimated performance of scaled high-power Li-metal cell and resulting 6T battery

6. CONCLUSION

Batteries have become critically important for military applications, including ground vehicles. However, current LIBs are unable to provide high power and energy density at extremely low temperatures. CRG has designed and developed a high energy (247 Wh/kg) Li-metal pouch cell which can provide high specific power (>1.6 kW/kg at 10C) and can operate at extremely low temperature (< -50 °C). CRG demonstrated the utility of this Li-metal cell for military vehicle applications by developing a CAD model that integrates a scaled pouch cell into a 6T battery platform. This design utilizes a novel module housing that provides compression force to the Li-metal cells to improve cycling performance. The Li-metal 6T battery could have 163 Ah with a specific energy of 179 Wh/kg.

7. References

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