2017 NDIA GROUND VEHICLE SYSTEMS ENGINEERING AND TECHNOLOGY SYMPOSIUM
POWER & MOBILITY (P&M) TECHNICAL SESSION
AUGUST 8-10, 2017 – NOVI, MICHIGAN

CAM-7®/LTO Lithium-Ion Cells for Logistically Robust 6T Vehicle Batteries

David Ofer
Daniel Kaplan
Mark Menard
Celine Yang
Sharon Dalton-Castor
Chris McCoy
Brian Barnett
Suresh Sriramulu

CAMX Power LLC
35 Hartwell Avenue, Lexington, MA 02421

ABSTRACT

CAMX Power is developing Li-ion pouch cells and batteries based on its proprietary CAM-7® cathode material and commercially available lithium titanate (LTO) anode material to provide high power, high charging rate capability, long life, safety and configurational flexibility in military vehicle batteries. The CAM-7®/LTO technology can be discharged to 0 V with no loss in performance, has excellent tolerance for cell voltage reversal and cell overcharge as well as having excellent elevated-temperature storage stability, making it ideally suited for batteries that can be logistically managed with little or no maintenance or environmental controls. These same properties make CAM-7®/LTO technology well-suited for implementing in damage-tolerant, minimally managed, batteries that are structurally distributed and integrated in military vehicles.

INTRODUCTION

Lithium-ion batteries employing CAMX Power's proprietary cathode material CAM-7® (now licensed to BASF and Johnson Matthey) combined with lithium titanate (LTO) anodes offer unique advantages that can be critically enabling for various vehicular and energy storage applications. Among these advantages are their ability to be charged very rapidly and at very low temperatures (even at -50ºC), tolerance for discharge and storage at 0 V, and their very high stability, safety and long life. CAMX Power is developing CAM-7® cathode, LTO anode pouch cells for 6T vehicle batteries with twice the specific energy and over 10 times the cycle life of lead-acid batteries. This same cell chemistry is being adapted for structurally integrated vehicle batteries, for start-stop vehicle batteries, and for large-scale stationary storage batteries. Besides their high capacity and rate capability, these cells have additional attributes that make them especially well-suited for providing long-lived, robust batteries. These cells are very safe and have high tolerance for overcharge and overdischarge, and thus will enable 6T batteries that can be logistically managed in a completely de-energized condition (i.e., at 0 V) with little or no environmental controls. These same robust attributes make the CAM-7®/LTO cell technology ideally suited for minimally managed, damage-tolerant, structurally integrated vehicle batteries that would greatly add to the electrical energy storage capability of military vehicles and extend their mission capabilities

PROPERTIES OF CAM-7®/LTO CELLS

CAM-7® is a $LiNiO_2$-class cathode material stabilized by innovative dopants to resolve the historical long-term stability concerns that have prevented exploitation of the high energy and power capability offered by this class of materials. CAM-7 has been developed by CAMX Power and its predecessor, TIAX over 15+ years.

$Li_4Ti_5O_{12}$ or LTO anode material was initially noted for its negligible volume change during electrochemical cycling [1], which gives it exceptional cycling stability. Nano-structured LTO is capable of very high rate capability as well, and can be lithiated (charged) very rapidly, at least in part because at its high potential (~1.55 V vs. Li), passivating film (SEI) does not form on its surface. Therefore, high surface area (nano) LTO can be used without incurring high 1st cycle irreversible capacity loss, and the lack of an SEI and its associated impedance enhances LTO rate capability. LTO's high potential further enables it to be charged at high rates without danger of Li metal plating.

CAM-7® and nanostructured LTO can therefore be combined to yield cells with exceptional rate capability for both charge and discharge. Figure 1 illustrates this high rate capability, showing constant power charge and discharge voltage characteristics for a small pouch cell made with low-loading electrodes to minimize electrolyte-based rate limitations and emphasize active materials characteristics. The cell was cycled between 2.59 V and 1.31 V, corresponding to the per-cell voltage range of an 11-series-cell 6T battery operated between 28.5 V and 14.4 V.

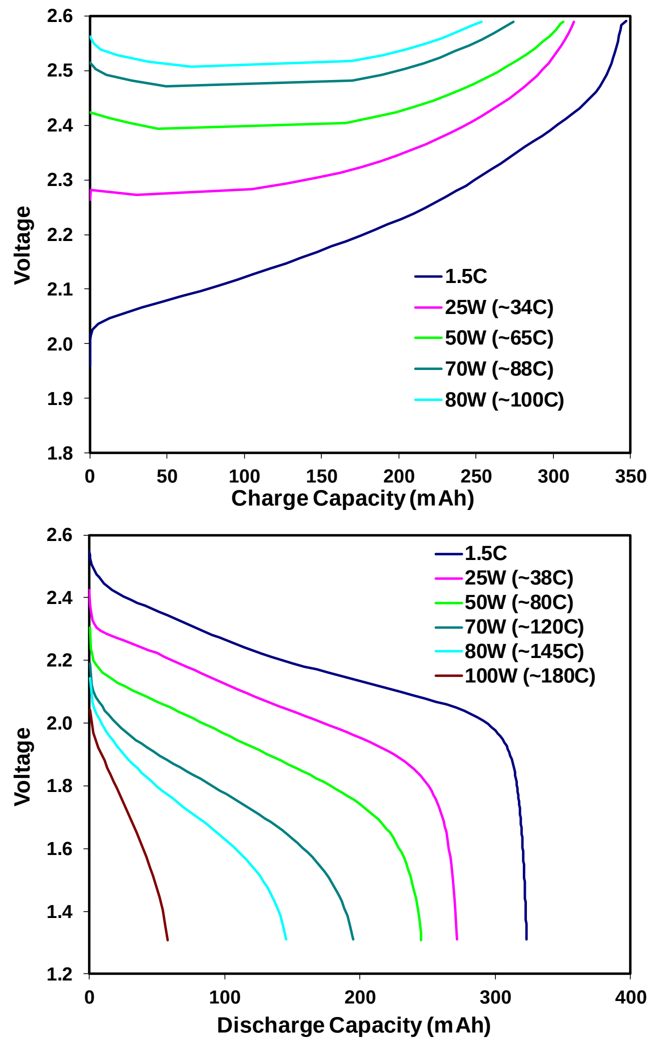

Figure 1: Continuous constant power charge (top) and discharge (bottom) characteristics of a 320 mAh, 0.5 mAh/cm^2 loading CAM-7®/LTO pouch cell at ambient temperature.

The CAM-7®/LTO cell chemistry can employ electrolyte formulations that provide special performance advantages, but that are otherwise unsuitable for conventional Li-ion cell chemistries using low-potential anodes. Use of such novel electrolytes enable CAM-7®/LTO cells to achieve outstanding low-temperature performance, as illustrated by Figure 2, which shows relatively high rate constant current charge and discharge performance for a pouch cell at -50 °C.

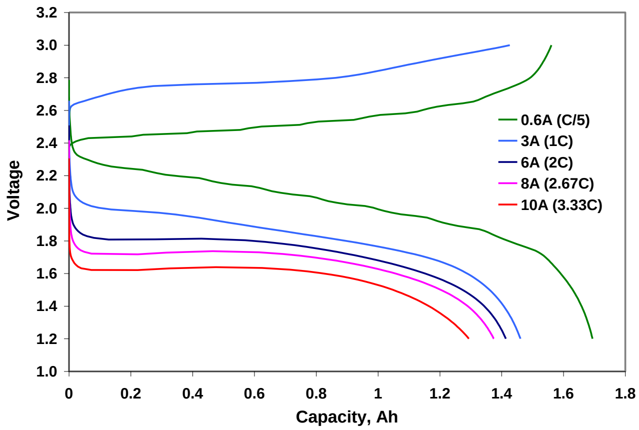

Figure 2: Constant current charge and discharge characteristics of a 3 Ah, 1.7 mAh/cm^2 loading CAM-7®/LTO pouch cell at -50 °C.

CAM-7®/LTO pouch cells have excellent elevated-temperature stability. Figure 3 shows discharge capacity vs. cycle number for 10C/10C cycling of CAM-7®/LTO pouch cells at 45 °C between voltage limits for operation in a 6-series-cell start-stop vehicle battery, and a photograph of a cell after 1,000 full charge-discharge cycles showing that it did not gas or swell at all.

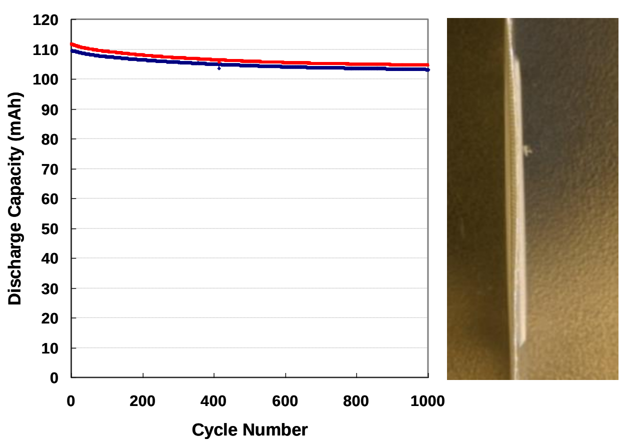

Figure 3: Left: Discharge capacity of 2 unfixtured 120 mAh CAM-7®/LTO pouch cells cycled 1000 times between 2.43 V and 1.2 V at 10C/10C rate at 45 °C. Right: Side-on photograph of one cell after 45 °C cycling.

CAMX Power has found that despite the reputation of LTO-anode cells for gassing [2], there is no gassing problem if adequately purified active materials and electrolyte are used in suitable cell designs.

CAM-7®/LTO cells have extremely long cycle life at ambient temperatures with excellent retention of low impedance characteristics, as shown in Figure 4.

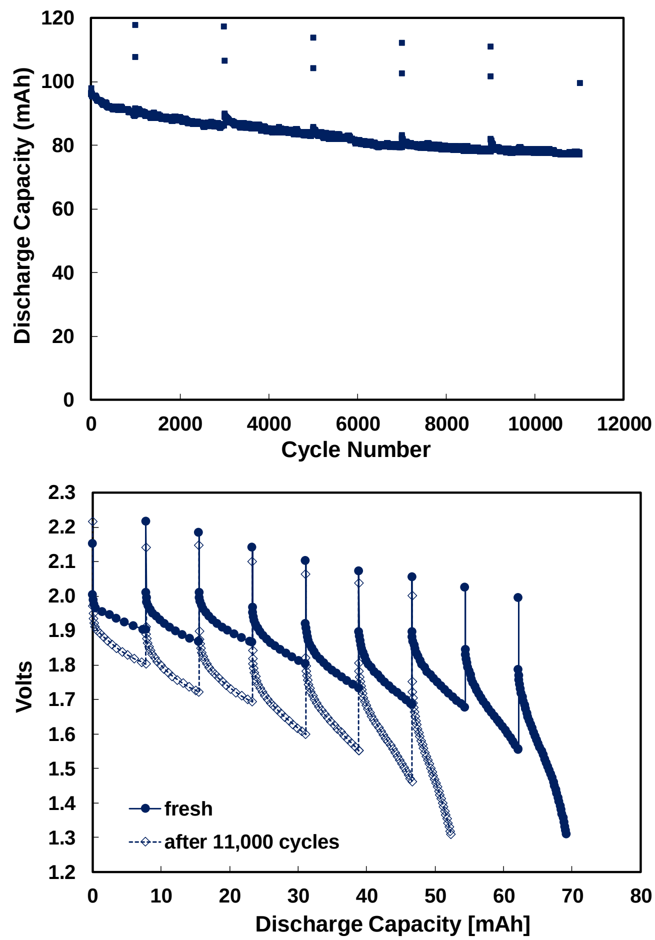

Figure 4: Top: Discharge capacity of an unfixtured 120 mAh CAM-7®/LTO pouch cell 10C/10C cycled between 2.59 V and 1.31 V at ambient temperature, with C/5 and 1C cycles at 2,000 cycle intervals. Bottom: Capacity and voltage for repeated 0.93A, 30 sec. pulsing of the cell to 1.31V cutoff with 30 min. rest between pulses at -18 °C.

The low-temperature pulse capability of the cell before and after 11,000 cycles, as shown in Figure 4, demonstrates its excellent retention of cold cranking performance at 0.93A current which is scaled to correspond to the 600A requirement of the Li-ion 6T draft specification [3]. Note that cold cranking performance targets are especially difficult to achieve, and even slight increase in cell impedance can make it difficult to complete cold cranking pulses. Therefore, only slight change in the cold crank performance even after 1000 cycles at 45C is indicative of very low impedance increase of the cell.

The safety of the CAM-7®/LTO pouch cell technology has been demonstrated in nail penetration tests. Figure 5 shows voltage and temperature results for nail penetration testing of a charged 2.7 Ah cell.

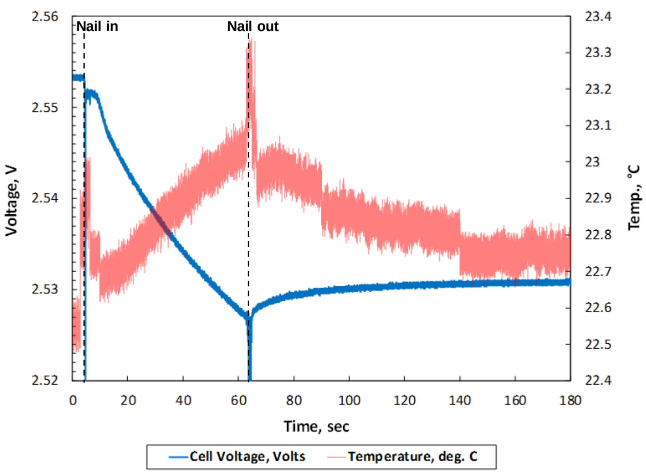

Figure 5: Voltage and surface temperature of a charged (2.65 V) 2.7 Ah CAM-7®/LTO pouch cell during penetration by a blunt 2 mm diameter nail at 1 cm/sec.

The Figure 5 data show that the short circuit induced by the nail penetration event has relatively high resistance and poses little or no safety threat, a display of abuse tolerance that makes the technology very attractive for implementation in large military batteries.

The majority of CAM-7®/LTO cell development efforts to date have been directed towards the 6T battery application. Although current standard 6T military vehicle batteries employ lead-acid chemistry, the need for longer run times in Silent Watch missions, together with the need for longer cycle life for batteries deep-cycled in those missions, is driving the development of Li-ion 6T batteries. However, there are safety concerns around Li-ion batteries, particularly with respect to transportation of military vehicles aboard Navy vessels. Therefore, although it has lower energy density than conventional graphite-anode cell chemistry, CAM-7®/LTO chemistry may prove to be more readily implemented in 6T batteries than the conventional chemistry, both because of the LTO-based cell chemistry's greater safety in the charged state, and because CAM-7®/LTO cells can be completely de-energized (discharged to 0 V) for logistical operations, as described further below.

6 Ah, 15 V CAM-7®/LTO MODULE

A 6-series-cell, 6 Ah module was made from CAM-7®/LTO pouch cells to test against scaled requirements for a Li-ion 6T battery per the Li-ion 6T draft specification, and was cycled between 15.55 V and 7.86 V, corresponding to the per-cell voltage of an 11-series-cell 6T. Figure 6 shows the opened module case prior to final assembly.

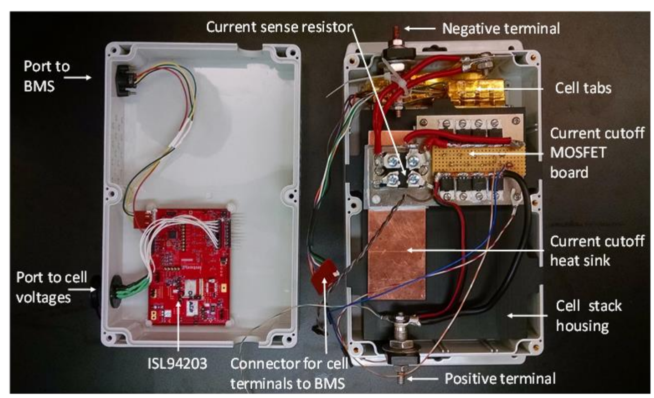

Figure 6: Photograph of 6-series-cell, 6 Ah module.

Figure 7 shows the module's charge and discharge characteristics at ambient temperature, and demonstrates its high rate capability.

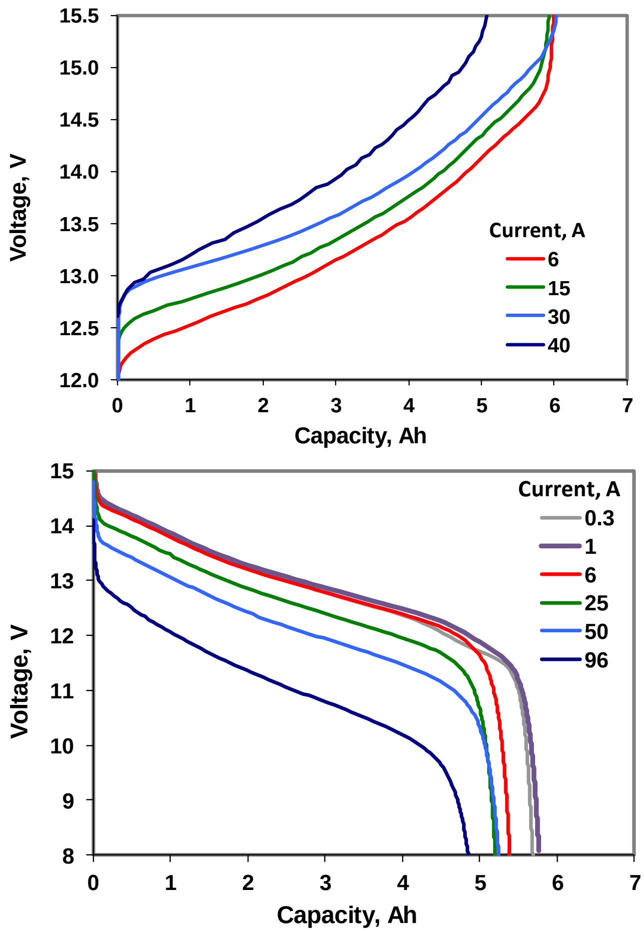

Figure 7: Constant current charge (top) and discharge (bottom) characteristics of 6-series-cell, 6 Ah module.

The module was also tested against the low-temperature pulse performance requirements of the Li-ion 6T draft specification, with the results shown in Figure 8. At -18 °C, the module delivered 600 A-scaled pulse discharge performance as required for Types 1 and 2 batteries by the draft Li-ion 6T specification, and delivered 1100 A-scaled pulse performance at -11 °C. At -40 °C, the module delivered 400 A-scaled pulse performance as the draft specification requires for Type 3 batteries.

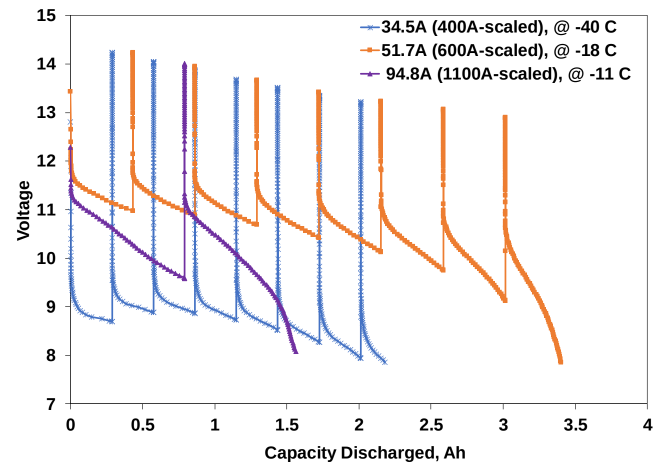

Figure 8: 600 A-scaled, 1100 A-scaled and 400 A-scaled 30 sec. pulse capacity delivered by 6 Ah module at -18 °C, -11 °C and -40 °C, respectively.

This module demonstrated that the CAM-7®/LTO technology is ready for demonstration and testing in full-scale prototype 6T batteries. A 6T battery having 62% of its volume occupied by 18.6 kg of cells based on the design used in the module would be expected to have 66 Ah capacity and 1600 Wh energy, and fill all the Li-ion 6T draft specification's requirements for Type 1 and Type 2 batteries.

CAM-7®/LTO CELLS FOR LOGISTICALLY ROBUST 6T BATTERIES

Unlike conventional Li-ion cells, CAM-7®/LTO cells can be discharged to 0 V and below (cell voltage reversal), which can enable batteries to be logistically managed in a completely de-energized condition in which they require no maintenance and present no electrical or thermal hazards. Furthermore, the thermal stability of CAM-7®/LTO cells is excellent when they are in the 0 V condition, as shown in Figure 9, suggesting that batteries employing them could be logistically managed with little or no environmental controls.

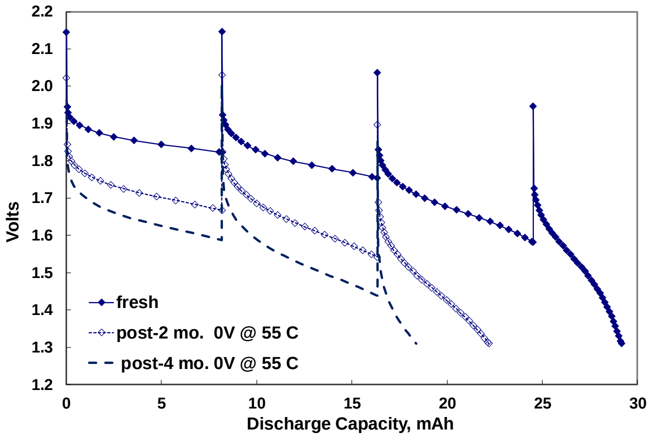

Figure 9: Repeated 0.93A, 30 sec. pulsing of an unfixtured 50 mAh CAM-7®/LTO pouch cell to 1.31V cutoff with 30 minutes rest between pulses at -18 °C, when the cell was fresh, after 2 months storage in 0 V condition at 55 °C, and after 4 months storage in 0V condition at 55 °C.

Figure 9 shows that even after extended exposure at 55 °C (131 °F), cells in the 0 V condition suffer only modest performance loss under the most demanding test conditions (low temperature and high rate approaching 20C).

When batteries having multiple series-connected cells are discharged to 0 V, and/or when they are stored for extended periods with no or minimal maintenance or environmental controls, cell-to-cell imbalances and their effects can become magnified. Because cells in a battery are never completely identical, discharge of a series-cell-configured battery to 0 V in the absence of cell balancing hardware will necessarily force one or more cells into some degree of voltage reversal. Likewise, extended storage of a battery with little or no maintenance is likely to increase impedance and capacity imbalances between cells, increasing the tendency for overcharge of some cells when the battery is recharged. Therefore, tolerance for both voltage reversal and overcharge are important attributes for cells to provide a logistically robust battery. These attributes have been demonstrated for CAM-7®/LTO pouch cells.

Figure 10 shows that CAM-7®/LTO pouch cells have excellent tolerance for both reversal and overcharge.

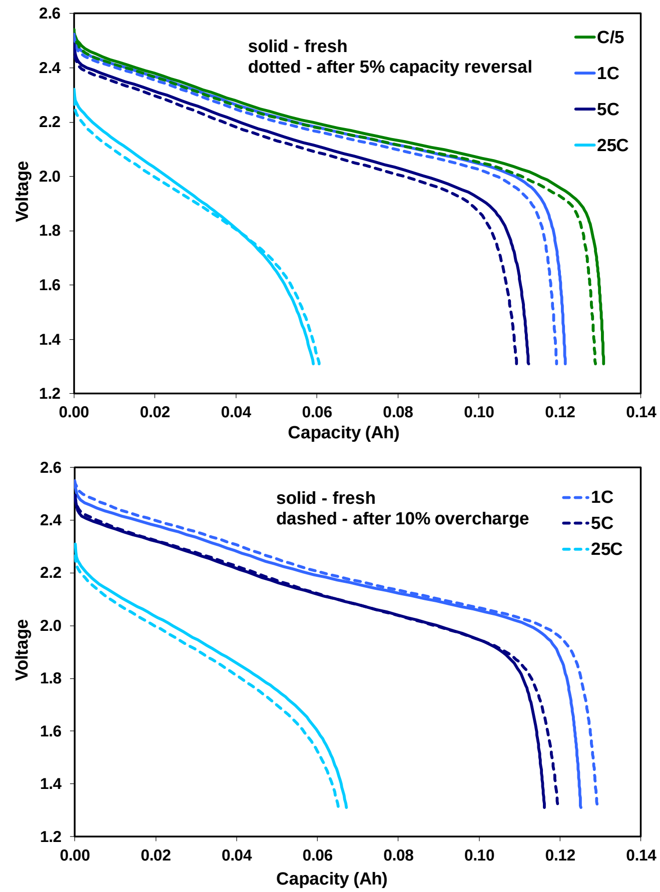

Figure 10: Constant current discharge at ambient temperature of unfixtured 130 mAh pouch cells before and after (top) 5% capacity reversal, and (bottom) 10% overcharge.

The reversed cell in Figure 10 was discharged from 0 V until 5% of its capacity passed, with its voltage dropping to -3.5 V. The overcharged cell was charged from 2.59 V until 10% of its capacity passed, with its voltage rising to 3.5 V.

The CAM-7®/LTO cell technology's tolerance for overcharge and reversal can also enable development of damage-tolerant, structurally integrated military vehicle batteries.

CAM-7®/LTO CELLS FOR STRUCTURALLY INTEGRATED BATTERIES

The energy storage capacities and resulting mission capabilities of current military vehicles could be substantially increased if unfilled spaces in a vehicle's structure, such as those beneath external armor, were filled with batteries. However, implementation of such a distributed, structurally integrated battery on or beneath the surface of a military vehicle poses the unique challenges of essentially uncontrolled exposure to external environmental conditions and the high probability of incurring damage in battle or other operations.

With respect to environmental exposure, batteries on the surface of a vehicle must be particularly tolerant of high temperatures, which ordinarily will rapidly degrade Li-ion cells. The CAM-7®/LTO cell chemistry and design can be tailored for enhanced elevated-temperature tolerance, particularly if high-rate performance requirements are relaxed. This is illustrated by Figure 11, which shows the impacts of cell design (configuration) and electrolyte composition on performance retention of CAM-7®/LTO cells undergoing extreme high-temperature exposure.

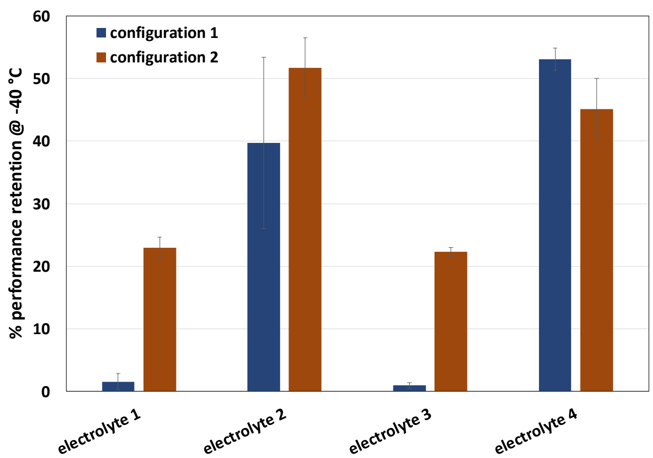

Figure 11: Retention of 1C, 30 sec. duration pulse discharge performance at -40 °C by un-fixtured 130 mAh CAM-7®/LTO pouch cells after storage in charged state at 78 °C (172 °F) for 40 days.

With respect to damage tolerance, batteries distributed on the surface of a vehicle must incorporate redundancy and/or maintain function with some level of damage/disablement to individual cells. Furthermore, current-carrying elements and battery management elements can be more critically vulnerable than cells themselves, and therefore current collection should be as distributed as possible, current cutoff requirements should be minimized, and battery management should be minimized.

CAM-7®/LTO pouch cells in relatively small (e.g., $\leq$10 Ah) series-contacted strings that interface directly with the 28.5 V vehicle bus voltage are well-suited for operation under the above constraints for a structurally integrated vehicle battery. Such an 11-series-cell string could function well with as many as 3 cells hard-shorted by battle damage, as shown by Table 1.

Table 1. Individual cell voltages of an 11-series -cell string charged to 28.5 V.

# of cells shorted	Remaining cells' charge V
0	2.591
1	2.850
2	3.167
3	3.563
4	4.071

With up to 3 cells shorted, voltages of remaining cells will not significantly exceed the 3.5 V value for which high tolerance is demonstrated in Figure 10 data. If individual cells in such a series string are soft-shorted, they can be subject to reversal stress, in addition to the remaining cells being overcharged, but CAM-7®/LTO cell strings will also tolerate some amount of this type of damage.

Implementation of CAM-7®/LTO structurally integrated vehicle batteries could result in an order of magnitude increase in a vehicle's electrical energy storage capacity. For example, the estimated area behind the selected non-hinged armor pieces of an M1100 HMMWV shown in Figure 12 is up to ~7 m^2. At an estimated 2-3 cm thickness of space available beneath the armor, this area could provide over 140 liters of volume available for a 20+ kWh battery, as compared to the approximately 2 kWh expected for a CAM-7®/LTO 6T battery.

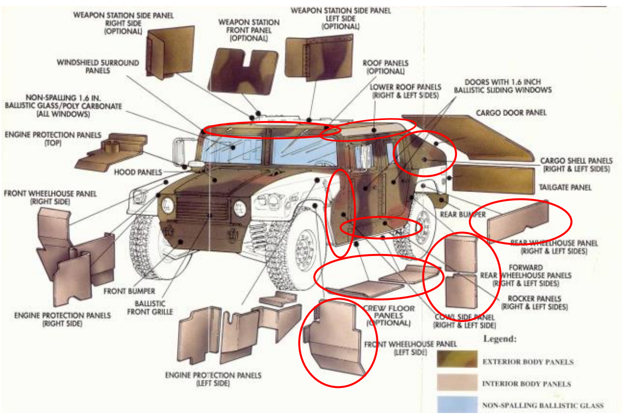

Figure 12: Selected non-hinged armor of an M1100 HMMWV that might accommodate a structural battery.

ACKNOWLEDGEMENTS

This material is based upon work supported by US Army (TARDEC) SBIR Phase II contract # W56HZV-12-C-0065, US Navy (NAVFAC) SBIR Phase II contract # N39430-14-C-1506, US Defense Logistics Agency SBIR Phase I contract # HQ0147-15-C-8003 and US Army (TARDEC) SBIR Phase I contract # W56HZV-16-C-0143.

Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the above funding agencies.

REFERENCES

[1] T. Ohzuku, A. Ueda, N. Yamamoto, Journal of the Electrochemical Society, Vol. 142, no. 5, pp. 1431-1435, 1995.

[2] a) M. He, E. Castel, A. Laumann, G. Nuspl, P. Novak, E. J. Berg, Journal of the Electrochemical Society, Vol. 162, p. A870, 2015. b) C. R. Fell, L. Sun, P. B. Hallac, B. Metz, B. Siska, Journal of the Electrochemical Society, Vol. 162, p. A1916, 2015.

[3] "Performance Specification: Battery, Rechargeable, Sealed, 6T Lithium-Ion", MIL-PRF-32565A Draft.