High-Nickel Cathode / Graphite Anode Cells for Diverse DoD Applications

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Abstract: *CAMX Power has developed the CAM-7® cathode material platform that combines high specific energy with high rate capability. In this paper, we present data on the performance of CAM-7/graphite cells for DoD applications. We demonstrate CAM-7/graphite cells with high specific energy capable of superior performance, relative to COTS cells, at -40°C. We demonstrate life of the CAM-7/graphite cell chemistry in different form-factor cells including 18650 and soft pouch cells.*

Keywords: lithium ion, CAM-7; 18650 cells; pouch cells;

Introduction

Owing to its high energy content, Li-ion technology is attractive for many DoD applications including Rifleman Radios and Conformal Wearable Batteries. However, commercial off the shelf (COTS) cells frequently cannot meet all of the DoD specific operational requirements for energy and power capability across a broad range of operating conditions. The specific energy, energy density, and power capability of Li-ion cells are largely determined by the properties of the cathode active material used. Historically, lithium cobalt oxide (LCO) cathode paired with graphite anode has been the material of choice for high energy density cells. Continued questions around cobalt availability and cost volatility have forced displacement of LCO with lithium nickel cobalt aluminum oxide (NCA) and lithium nickel cobalt manganese oxide (NCM) platforms. However, even COTS cells containing NCA or NCM cannot meet all of the performance targets needed for DoD platforms. Higher nickel-content (hence higher energy) versions of NCA/NCM are in development now but suffer from poor cycle life. Furthermore, the rapid growth of electric drive vehicles (EDVs), which require large Li-ion batteries, is placing unprecedented strain on the supply of NCA and NCM materials. This trend is of particular concern to DoD, given that DoD batteries present a small fraction of the total global battery supply-chain and are not the focus of the major materials and battery producers.

We present an alternative high-nickel cathode material platform developed at CAMX Power, CAM-7, which is attractive for DoD Li-ion batteries not only because of its technical performance, but also because it can be produced in the US. CAM-7 is a dopant stabilized $LiNiO_2$-based cathode material that combines high capacity, high average discharge voltage, excellent rate capability, and long life. Discharge capacity for different CAM-7 compositions and their rate capability are shown in Table 1. CAM-7 can provide very high energy density when paired with graphite anode. The projected cell-level specific energy and energy density of CAM-7 compared to that of other commercial off-the-shelf cathode materials is shown in Figure 1.

Table 1. CAM-7 cathode materials platform combines high discharge capacity with high rate capability. Coin cell measurements with Li-metal anode, ~10mg/cm², 4.3-3.0V.

Cathode Material	Ni (mol %)	1st Cycle C/20 (mAh/g)		Discharge Rate Capability (mAh/g)		
		CHG	DCH	C/5	1C	5C
CAM-7.3	88	235	218	210	196	179
CAM-7.4	88	228	213	202	187	168
NCM-811	80	223	204	192	180	155
NCA	81	219	181	176	169	135
NCM-622	60	199	183	174	160	131

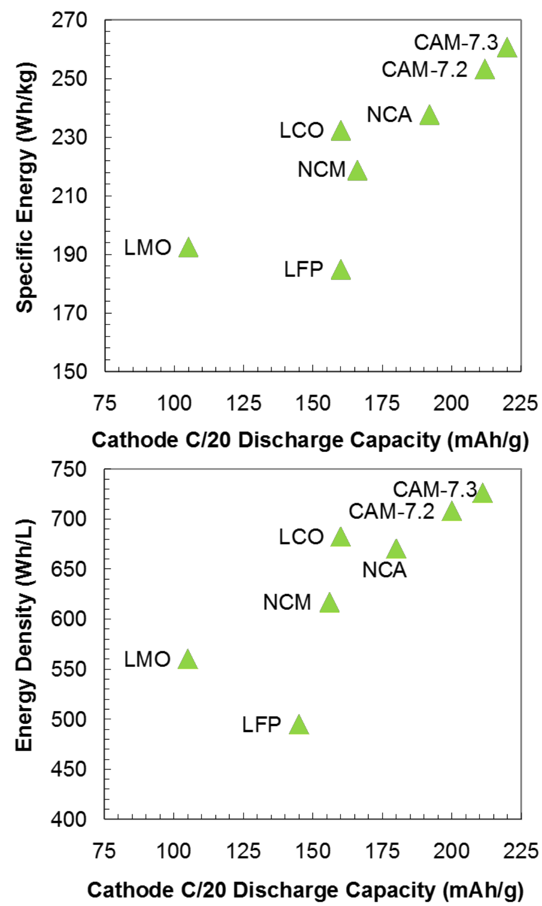

Figure 1. Comparison of the estimated cell-level specific energy (top) and energy density (bottom) of CAM-7 cathode materials with commercial off-the-shelf cathode materials in identically designed 18650 cells with graphite anode. LFP is $LiFePO_4$ and LMO is $LiMn_2O_4$.

Figure 2. Photograph of a 50 MT/y pilot plant for our CAM-7 cathode material located in Rowley outside of Boston MA.

CAM-7 Production

The synthesis of CAM-7 material has been scaled-up to pilot level. CAMX Power owns and operates a 50 MT/y pilot plant specifically designed for the production of CAM-7 cathode material (Figure 2). The plant can be easily upgraded to 300 MT/y with the addition of one piece of equipment. Following more than a decade of development, this material platform was recently licensed to both BASF and Johnson Matthey for scaled-up production primarily for the burgeoning EDV market. CAMX Power is continuing to develop advanced versions of this material targeting simultaneous achievement of higher capacity and longer life.

Cycle Life of CAM-7/Graphite Cells

CAM-7 is engineered to simultaneously offer high power capability as well as high energy and long life. Figure 3 shows representative cycle life data in two different cell formats – 18650 cells (plot on the bottom) and pouch cells (plot on the top) – at 45°C for full depth-of-discharge cycling (4.2V – 2.7V). Historically, it has not been possible to implement high-nickel cathode materials in laminate pouch cells because of unacceptable levels of swelling (gassing) when the cells were operated at high temperature. Recently, we have implemented CAM-7/graphite in pouch cells with excellent cycle life (as shown in Figure 3) and very low gassing.

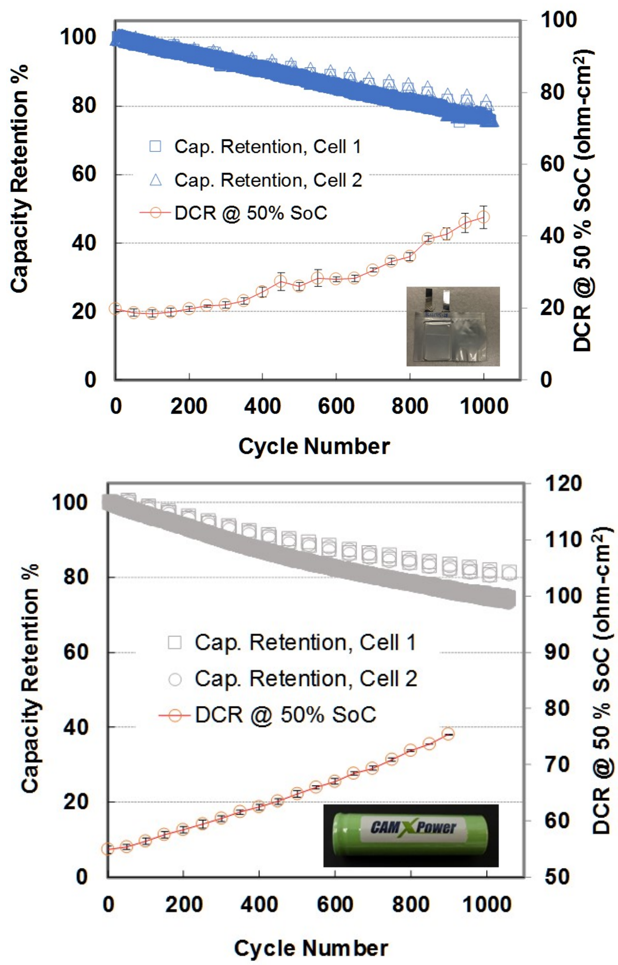

Figure 3. Demonstration of long life during cycle life testing at 45°C in pouch (top) and 18650 (bottom) cells containing CAM-7.3 high capacity cathode and graphite anode. 2.7-4.2V 1C-1C for pouch and 2.7-4.2V C/2-1C for 18650 cell cycling.

High-energy Cells with Excellent Low Temperature Performance

Specifically of interest to DoD is the development of high-specific energy cells that are capable of broad temperature range operation. As part of a program for U.S. Army, we developed a CAM-7/graphite cell chemistry and electrolyte combination capable of achieving high specific energy, long life, and excellent discharge performance even at -40ºC. The discharge voltage curves for 18650 cells fabricated at CAMX Power are shown in Figure 4. The inset table in Figure 4 shows the measured specific energy and energy density both at the cell level and at the jelly roll level. These 18650 cells delivered 247Wh/kg (cell level) and 290Wh/kg (jelly roll level) at C/20 rate. Moreover, during continuous constant power discharge (1.15W, based on the Rifleman radio performance requirement), CAMX Power CAM-7/Graphite 18650 cells with high specific energy were able to deliver substantially more energy that commercial off the shelf (COTS) 2.9Ah 18650 cells (Figure 5). Note that further improvements in cell specific energy can be achieved for this cell chemistry by utilization of state-of-the-art 18650 cell hardware that is slightly lighter and bigger (~18mm vs. ~17.3mm inner diameter vs. CAMX cans) and contains more active material, while reducing the relative mass of inactive components. Moreover, by implementing more recent grades of CAM-7 cathode that have higher capacity than the material used in these 18650s, even higher energy densities can be obtained.

These CAM-7/graphite 18650 cells were also independently evaluated at the Army Research Laboratory (ARL), as part of a Phase II SBIR program, with the results summarized in an ARL report[i]. The rate capabilities of these cells at room temperature and at -20°C are shown in Figure 6. This ARL report concluded (for DoD use) *that these cells were ideal for applications where cycle life is imperative, even in extreme conditions.*

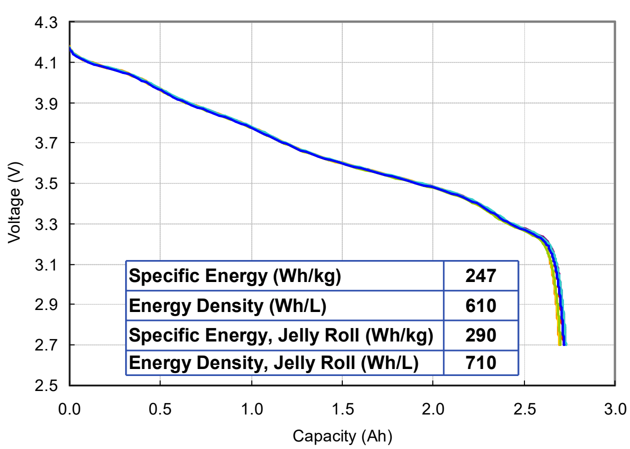

Figure 4. Discharge curves for CAM-7/graphite 18650 cells designed for very high specific energy. The cells were charged to 4.2 V and discharged to 2.7 V.

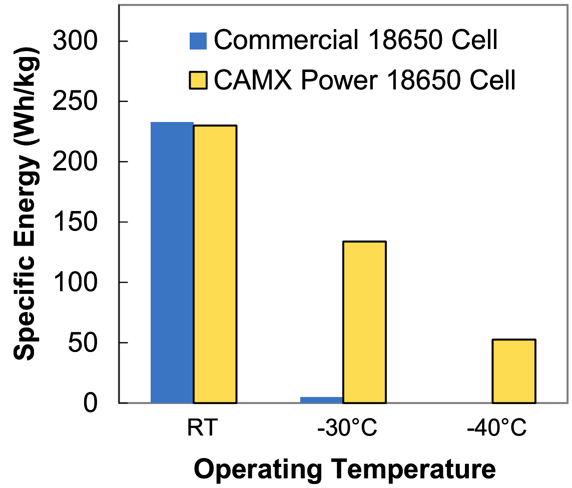

Figure 5. Comparison of delivered specific energy at different temperatures of COTS 2.9Ah 18650 cells with CAM-7/graphite high-energy 18650 cells. 4.2 V – 2.7 V discharge at 1.15W (power required for Rifleman radios).

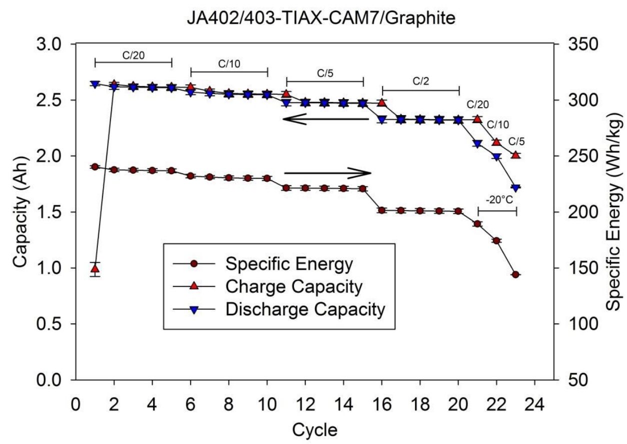

Figure 6. Measurements by ARL on CAM-7/graphite high-energy 18650 cells delivered to ARL as part of a Phase II SBIR project. Figure reproduced from ref. i. Room temperature (25°C, cycles 1–20) and low-temperature (–20°C, cycles 21–23) rate cycling of high energy 18650 cells.

CAM-7/Graphite Cells with Excellent Pulse Power Capability

Some applications, like hybrid (HEV) or plugin hybrid electric vehicle (PHEV) batteries require not only high specific energy, but also pulse power capability for acceleration or regenerative breaking that can be supported across a wide state-of-charge (SOC) range. Typically, lithium metal oxide cathode materials that suffer from high impedance at low states of charge can substantially reduce the operating SOC range and thus the 'available energy', requiring over-sizing the battery to meet power requirements. Because of its high rate capability, CAM-7 cathode material can support high rate pulse power discharge even at low SOCs.

We have implemented CAM-7 with a graphite anode in 18650 cells with low electrode loadings (~2mAh/cm²) that target PHEV operation. Using the hybrid pulse power characterization (HPPC) test developed by DOE, we measured the 1s and 10s discharge resistance during a constant current pulse for a batch of these 18650 cells. Data in Figure 7 show that these cells have low pulse resistance (DCR) suggesting high power capability over a wide range of state-of-charge, even down to 10%.

These cells also have excellent life, as demonstrated both during storage (Figure 8) and during cycling (Figure 9). Figure 8 shows that during storage at 4.1V at 45°C for a year, we observed only a minor decrease in capacity with little change in resistance measured at 50% SOC. Figure 9 shows that these cells maintain 80% of their capacity after 2000 cycles at room temperature across the full SOC range (2.7-4.2V).

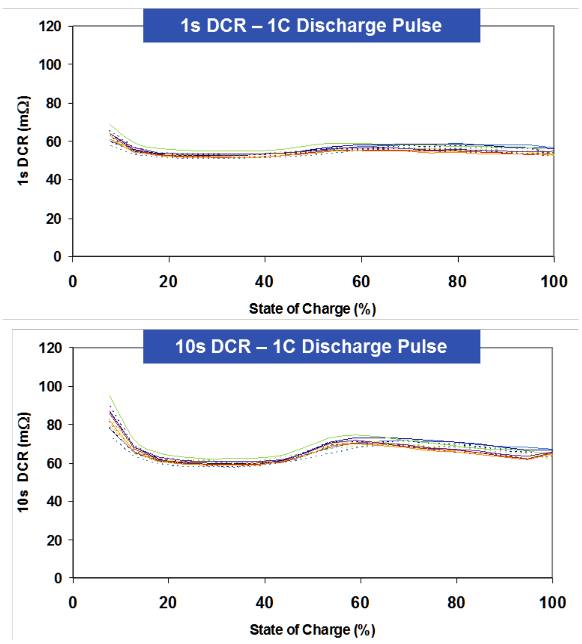

Figure 7. Discharge pulse power rate capability for a batch of CAM-7/Graphite 18650 cells designed for PHEV applications. Value for 1s (top) and 10s (bottom) direct current resistance shown as a function of SOC.

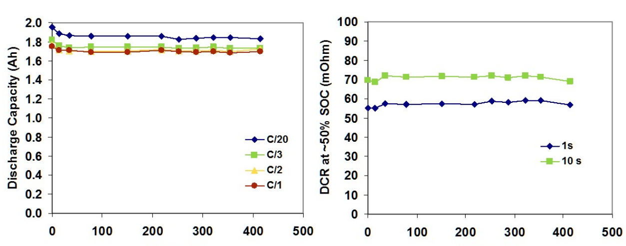

Figure 8. Capacity retention (left) and impedance rise (right) during storage of the CAM-7/ graphite 18650 cells at 4.1V at 45°C.

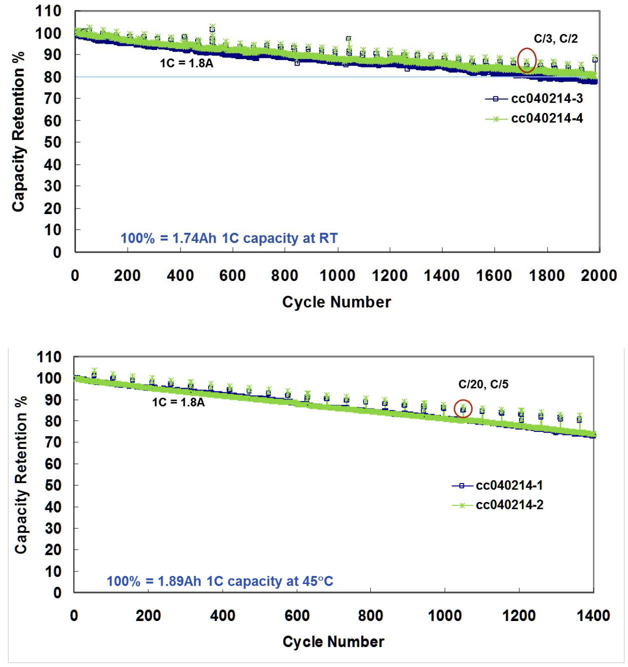

Figure 9. Cycle life of CAM-7/graphite 18650 cells designed for PHEV application. Cycling conditions: C/2 charge – 1C discharge 4.2 – 2.7V at room temperature (top) and at 45°C (bottom).

Summary

This paper demonstrates the versatility of the high energy and high power CAM-7 cathode material when implemented with graphite anode in cells designed for different end use scenarios. We show how long life can be achieved both in 18650 and in pouch cells during elevated temperature cycling. We show superior performance of this cell chemistry when combined with low-temperature-capable electrolytes for high specific energy delivery at -40°C. We also demonstrate excellent storage and cycle life for CAM-7/Graphite 18650 cells designed for applications that require pulse power capability over a wide range of SOC.

Acknowledgements

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References

[i] Allen JL, Allen JL, Delp SA, Jow TR. (2014). Evaluation of TIAX High Energy CAM-7/Graphite Lithium-Ion Batteries at High & Low Temperatures, U.S. Army Research Laboratory.