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CAM-7/LTO LITHIUM-ION CELLS FOR BATTERIES WITH HIGH CHARGE/DISCHARGE PERFORMANCE AT EXTREME LOW TEMPERATURE

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ABSTRACT

TIAX is developing laminated prismatic lithium-ion (Li-ion) cell technology capable of rapid charging at low temperature (to -50 °C) to replace current lead-acid vehicle batteries. The novel cells are based on TIAX's high energy, high power CAM-7 cathode material, high rate capability lithium titanate (LTO) anode material, and novel electrolyte formulation, and target cell-level energy content greater than 90 Wh/kg and 250 Wh/l. CAM-7 cathode material promises significant boost in power and run time of Li-Ion batteries for a wide range of DoD applications, and is now being commercialized by a separate company, CAMX Power, which is scaling up production in a 50 metric ton per year plant installed in Massachusetts.

INTRODUCTION

Military applications can require rechargeable batteries to operate in extreme environments with temperatures as low as -50 °C or as high as 70 °C. These temperature extremes extend beyond those to which current commercial Li-ion technology is constrained, and are a major hindrance to replacement of current lead-acid vehicle battery technologies with much lighter, more compact Li-ion batteries. Prismatic laminate type lithium-ion rechargeable cells are of particular interest to the military because of their potential for dual-use application in both military and commercial automotive vehicles.

Operational temperature limitations of Li-ion batteries are related to the electrolytes and materials they use. At low temperatures, performance is hampered by low electrolyte conductivity and poor electrochemical kinetics associated with ion-desolvation processes [1]. Low-temperature charge acceptance capability is particularly poor because the graphitic carbon anodes used in Li-ion cells are particularly prone to plating lithium metal when charged at low temperature: a condition giving rise to rapid fade and serious safety concerns. At high temperatures, Li-ion battery lifetime is compromised by thermal instability of the electrolytes and of electrode surface films they form, and by the electrolytes' reactivity with the charged electrode materials; in particular by decomposition reactions at the graphitic carbon anode [2]. Furthermore, the high-temperature decomposition reactions of Li-ion electrolytes result in the formation of non-condensable gaseous products. This gassing results in swelling of prismatic pouch cells thereby limiting their use, although they are otherwise very advantageous for their light weight and flexible form factor.

Accordingly, in a TARDEC-sponsored program, TIAX is developing low-temperature-capable, laminated prismatic lithium-ion cell technology employing TIAX's high energy, high power CAM-7 cathode material, high rate capability lithium titanate (LTO) anode material, and novel electrolyte formulation. CAM-7 provides the highest energy content and rate capability (Figure 1) of any market-ready cathode material, and therefore minimizes the cost to cell energy content incurred by use of high rate charging-capable LTO anode. Commercially available nanostructured LTO is used for its high rate capability and its high potential vs. Li, enabling it to be lithiated at high rate and low temperature without plating lithium metal. Novel electrolyte provides outstanding performance at low temperatures and suppresses electrolyte gassing in foil laminate-packaged cell designs.

CELL CHEMISTRY

CAM-7 Cathode Material

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 uniquely high combined energy content and power capability offered by this class of materials.

Figure 1 illustrates CAM-7's exceptional combination of energy and power. At low rates, the discharge capacity exceeds 200 mAh/g, with an average discharge voltage exceeding 3.85 V (in half cells with Li metal anode). In addition, CAM-7 supports excellent high power and high rate discharge capacities as illustrated by delivery of > 120 mAh/g discharge capacity at a rate of 100 C when measured using electrodes with low enough loading to reduce electrolyte-imposed rate limitations.

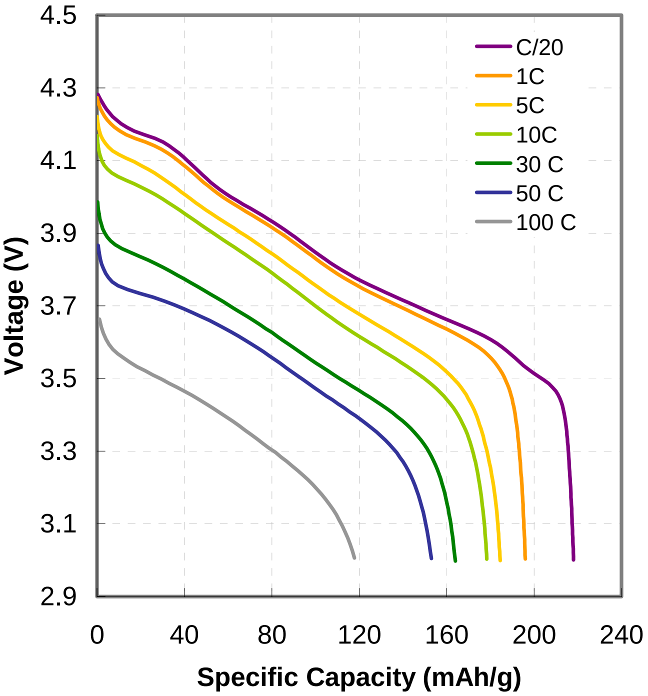

Figure 1: Capacity and rate capability of CAM-7 measured on a low loading (~2 mg/cm^2) electrode in a coin cell with a lithium metal anode. The cell was charged in CCCV mode to 4.3 V, and discharged at different rates.

CAM-7 also delivers outstanding low-temperature performance. Figure 2 shows a comparison of the discharge performance of CAM-7 relative to commercially available cathode materials at -20ºC. CAM-7 provides higher discharge capacity at a higher average discharge voltage compared to commercially available NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) and NCM ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$).

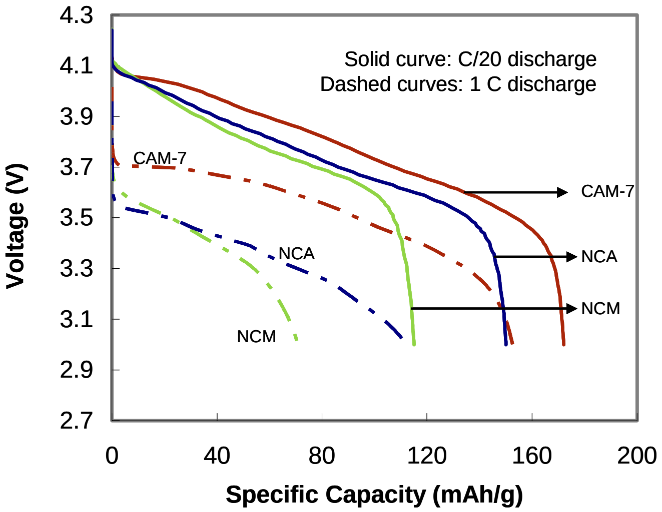

Figure 2: Comparison of discharge voltage profiles of CAM-7 with competing cathode materials at -20ºC, measured for 10-11 mg/cm^2 electrodes in coin cells with lithium metal anode. The cells were charged to 4.2 V at RT, equilibrated at -20ºC, and discharged at different C-rates.

CAM-7 has low levels of gas generation, facilitating its use in prismatic and laminate-packaging cell formats. CAM-7 evolves less gas than either commercial NCA or LCO ($LiCoO_2$) as shown by Figure 3, which compares results for gas evolution tests of charged cathode in contact with electrolyte.

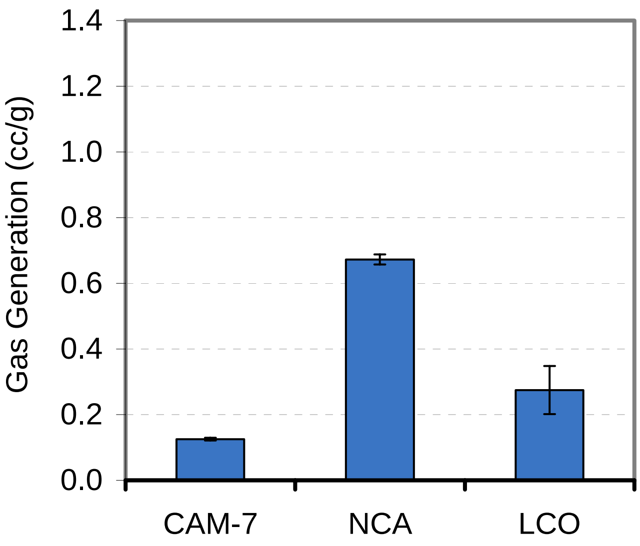

Figure 3: Comparison of gas generated from charged active materials in contact with all-carbonate-solvent electrolyte.

CAM-7 is produced by a readily scaleable solid-state synthesis process. A separate company, CAMX Power, has been established to produce and commercialize CAM-7, and has installed and is operating a 50 t/y plant for producing CAM-7 in Massachusetts, shown in Figure 4.

Figure 4: Panoramic view in 50 t/y CAM-7 production plant in Massachusetts.

LTO Anode Material

Graphitic carbon Li-ion anode active material can not be lithiated during high rate charging or at low temperatures, without plating Li metal. This is because the potential of the graphite anode is too close to that of metallic Li. $Li_4Ti_5O_{12}$ or LTO anode material was initially noted for its negligible volume change during electrochemical cycling, being designated a "zero strain material,"[3] and giving it exceptional cycling stability. Nano-structured LTO is capable of very high rate capability 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 enables it to be charged at high rates without danger of Li plating, as illustrated by Figure 5 which shows half cell lithiation profiles for commercially sourced nanostructured LTO made into very low loading 0.07 mAh/cm^2 electrodes at TIAX.

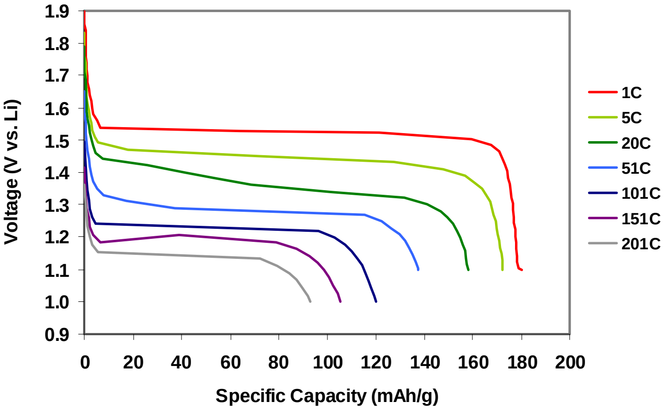

Figure 5: Half cell lithiation profiles for LTO electrodes.

Although LTO has very attractive attributes with respect to stability and charging rate capability, its low capacity and high potential impose significant sacrifice of Li-ion cell energy. However, LTO remains the only truly commercially available Li-ion anode alternative to carbon materials and is the only material capable of being charged at very low temperatures. Therefore, the use of a cathode material with the highest possible energy content (CAM-7) together with suitable high rate capability helps offset the loss of cell-level energy content that comes with use of LTO.

Low-Temperature-Capable Electrolyte

Current commercial Li-ion electrolyte compositions consist almost exclusively of $LiPF_6$ salt in mixtures of cyclic ethylene carbonate (EC) with various linear carbonates, having emerged as providing the best overall balance of properties for Li-ion batteries in consumer electronics [4]. EC provides the high Li^+ ion solvating power by virtue of its high dielectric constant, while the linear carbonates reduce the electrolyte viscosity (thus raising conductivity) and lower the freezing point. However cells with these electrolytes generally do not have acceptable life at temperatures above 60 °C or acceptable performance below -20 °C because the thermal instability of $LiPF_6$ is deleterious at high temperatures, while the high freezing point and viscosity of EC, as well as its high activation energy for lithium ion desolvation, is deleterious at low temperature.

Reducing the electrolyte EC content, and replacing linear carbonates with alternative higher dielectric constant, low viscosity, low freezing point cosolvents has been shown to greatly improve Li-ion low-temperature performance [5]. A comparison of the properties of exemplary alternative cosolvents to those of standard carbonate solvents is shown in Table 1. Cosolvents such as nitriles or esters can offer a better combination of high polarity with low viscosity and extended liquid temperature range than linear carbonates do.

Solvent	Abb.	Molecular Formula	Melting Point (^{o}C)	Dielectric constant (20 ^{o}C)	Viscosity (cp @ 25 °C)
Ethylene Carbonate	**EC**	$C_3H_4O_3$	38	90 (40 °C)	1.86 (40 °C)
Diethyl Carbonate	**DEC**	$C_5H_{10}O_3$	-43	2.8	0.75
Dimethyl Carbonate	**DMC**	$C_3H_6O_3$	4	3.1	0.59
Ethyl Methyl Carbonate	**EMC**	$C_4H_8O_3$	-55	2.9	0.65
Butyronitrile	**BN**	C_3H_7CN	-112	20.7	0.52
Methyl Acetate	**MA**	CH_3CO_2 CH_3	-99	6.7	0.37
Methyl Butyrate	**MB**	$C_3H_7CO_2$ CH_3	-85	5.6	0.58

Table 1: Comparison of electrolyte solvent physical properties.

CELL PERFORMANCE

Coin Cells

Coin cell experiments demonstrate that excellent low-temperature performance is achieved by the CAM-7/LTO/low-temperature electrolyte system. Figure 6 shows rate dependence of charge and discharge curves for a low loading CAM-7/LTO coin cell with TIAX electrolyte at -47 °C. Even using a standard (normal for ambient-temperature use) charge termination voltage of 2.75 V (corresponding to cathode potential of 4.3 V vs. Li), ~50% of full charge capacity (that full charge capacity being ~200 mAh/g CAM-7) is obtained in 1 hour, and almost 30% of charge capacity is obtained in 20 minutes at -47 °C, while much more capacity can be obtained if the voltage limit is raised. Almost 20% of the cell's intrinsic energy content can be delivered in 6 minutes for discharge to 1.4 V at -47 °C.

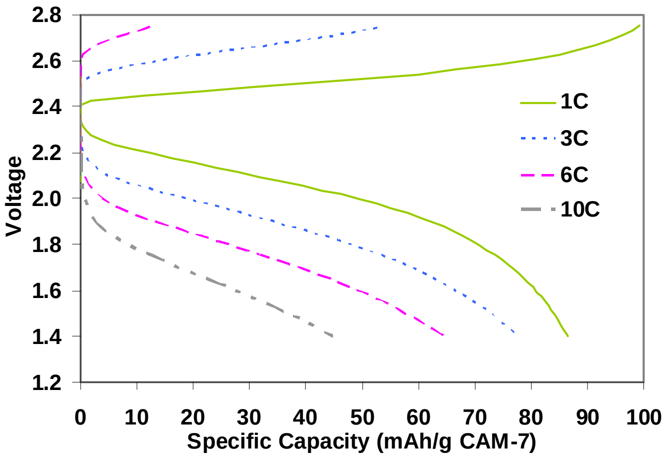

Figure 6: Rate dependence of -47 °C constant current charge and discharge (1C = 200 mA/g CAM-7) for 0.4 mAh/cm^2 CAM-7/LTO cells built with TIAX low-temperature electrolyte.

Figure 7 compares the -47 °C capacities of cells prepared with the TIAX electrolyte to those of cells that are identical except for being built with conventional all-carbonate EDE electrolyte. The conventional electrolyte does not sustain practical performance levels at -47 °C, while the TIAX electrolyte clearly does.

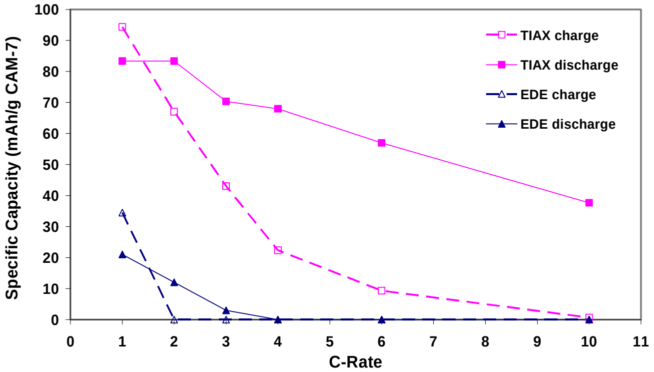

Figure 7: -47 °C rate capability (1C = 200 mA/g CAM-7) of CAM-7/LTO cells built with TIAX and conventional EDE electrolytes and cycled between 2.75 V and 1.4 V.

The TIAX low-temperature electrolyte formulation does reduce high-temperature cycle life; however, the relative benefit to low-temperature performance outweighs the impact on elevated temperature life. This can be seen by comparing the difference between data in Figure 7 for performance of standard carbonate (EDE) and TIAX electrolyte cells at -47 °C to the difference between data for capacity retention at 70 °C of cells made with both electrolytes, shown in Figure 8. We are optimizing the electrolyte composition further to obtain the most favorable combination of high-temperature cycle life and low-temperature performance.

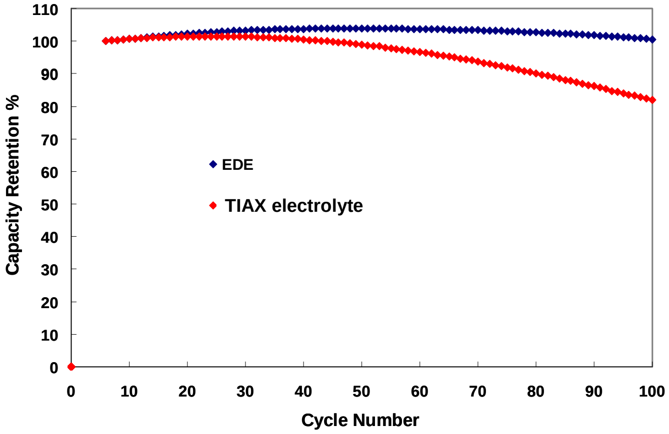

Figure 8: Capacity retention for 70 °C 2C/2C (1C=200 mA/g CAM-7) cycling of CAM-7/LTO (1.1 mAh/cm^2 electrode loading) Li-ion cells with EDE and TIAX electrolytes.

Laminate-Packaged Cells

Initial laminate-packaged prismatic cells have demonstrated that the CAM-7/LTO/nitrile-cosolvent electrolyte system is compatible with implementation in laminated packaging and form factors. Although these initial cells did not perform as well as coin cells, they nevertheless performed well enough to distinguish between electrolytes. Figure 9 shows low-temperature

C/20 discharge curves for CAM-7/LTO laminate cells built with TIAX and EDE electrolytes.

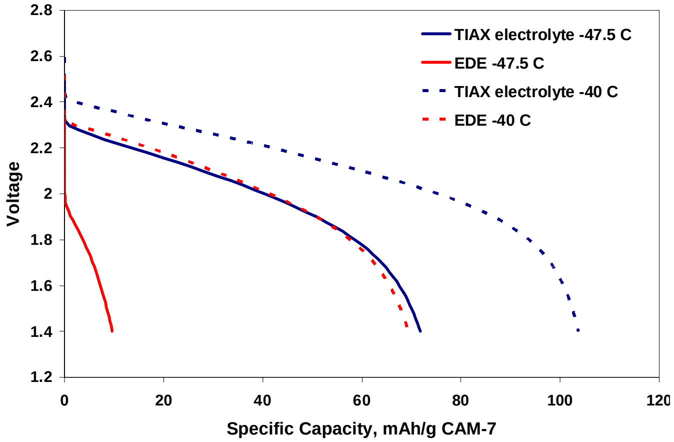

Figure 9: C/20 discharges at -40 °C and -47 °C for 0.75 mAh/cm^2 CAM-7/LTO laminate cells made with TIAX and EDE electrolytes.

Gassing experiments have demonstrated that the TIAX electrolyte has less elevated-temperature gas evolution than conventional electrolyte, a very desirable attribute for laminate-packaged cell designs. Figure 10 compares gassing results for samples of TIAX and EDE electrolytes stored at 85 °C, showing that the TIAX electrolyte evolves little if any gas, while EDE gas evolution increases with storage time.

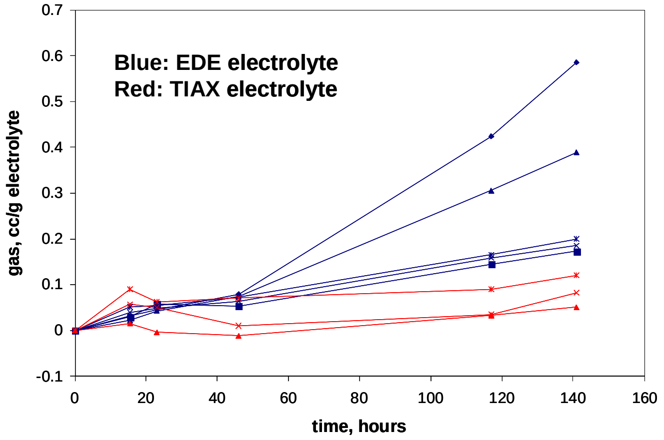

Figure 10: Volume of gas evolved dependence on time stored at 85 °C for samples of EDE and TIAX electrolytes.

TIAX is currently developing cell design and assembly techniques that will yield laminate cells with performance comparable to that already demonstrated in coin cells. The principle challenge in doing so will be to obtain similar performance in higher loading cells. Design models show that laminate cells can achieve energy content in excess of 90 Wh/kg and 250 Wh/l, as summarized by table 2.

loading (mAh/cm^2)	**0.5**	**1.0**	**1.5**	**2.0**
loading (mg/cm^2)	**2.5**	**5**	**7.5**	**10**
specific energy (Wh/kg)	63	87	100	108
energy density (Wh/l)	182	248	282	303

Table 1: Calculated dependence of laminate cell energy content metrics on electrode loading.

We will seek to demonstrate achievement of superior performance at temperatures down to -50 °C in laminate cells having at least 1 mAh/cm^2 electrode loading. Doing so will require further electrolyte optimization, possibly entailing some tradeoff of elevated temperature cycling stability for low-temperature performance.

ACKNOWLEDGEMENTS

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REFERENCES

[1]Kang Xu, “Charge-Transfer” Process at Graphite/ Electrolyte Interface and the Solvation Sheath Structure of Li$^+$ in Nonaqueous Electrolytes,” Journal of the Electrochemical Society, Vol. 154, no. 3, pp. A162-A167, 2007.

[2]Michel Broussely in “Advances in Lithium-Ion Batteries,” W. van Schalwijk and B. Scrosati, eds., Chapter 13, Kluwer Academic/Plenum, 2002.

[3]Tsutomu Ohzuku, Atsushi Ueda, and Norihiro Yamamota, “Zero-Strain Insertion Material of $Li[Li_{1/3}Ti_{5/3}]O_4$ for Rechargeable Lithium Cells,” Journal of the Electrochemical Society, Vol. 142, no. 5, pp. 1431-1435, 1995.

[4] Kang Xu, “Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries,” Chemical Reviews, Vol. 104, pp. 4303-4417, 2004.

[5]M.C. Smart, B.V. Ratnakumar, K.B. Chin and L.D. Whitcanack, “Lithium-Ion Electrolytes Containing Ester Cosolvents for Improved Low Temperature Performance,” Journal of the Electrochemical Society, Vol. 157, pp. A1361-A1374, 2010.