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A Survey of Low-Temperature Operational Boundaries of Navy and Marine Corps Lithium and Lithium-Ion Batteries

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EXECUTIVE SUMMARY

The U.S. Navy and Marine Corps have identified a strategic interest to operate lithium-ion batteries in cold climate regions as well as undersea and high altitude environments. The environmental operating envelope is expanded towards low temperatures pushing the boundaries of safe operation of lithium and lithium-ion batteries. While low-temperature discharge data is widely reported by battery manufactures for lithium and lithium-ion chemistries, there is a lack of data regarding the low-temperature recharging capability of lithium-ion batteries. This report presents the need to understand and identify the lower threshold temperatures for safe, reliable recharging of lithium-ion batteries to provide repeatable discharge capacities, a critical need for the U.S. Navy and Marine Corps to execute their mission. There is also a need to develop robust low temperature recharging characterization tools, including in-situ techniques, diagnostics and post-mortem studies. The development of advanced materials and improved pulse recharging protocols could further support the Warfighter with high performance, safe lithium and lithium-ion batteries.

INTRODUCTION

The U.S. Navy and Marine Corps depend on lithium (Li) and lithium-ion (Li-ion) batteries as mission-enabling power sources for the modern warfighter. With superior weight-normalized energy and power compared to its nickel-metal hydride and lead-acid predecessors, in conjunction with low self-discharge rates and no memory effects, Li-based batteries are currently the U.S. Navy and Marine Corps top choice for telecommunications and personal portable power devices, and are being pursued aggressively for larger systems such as vehicle propulsion and advanced high energy directed weaponry. Despite such advantages, the poor low-temperature performance of Li-batteries is a concern, especially considering the U.S. strategic interests in regions of cold climate, as covered by USNORTHCOM, USEUCOM, and USPACOM.¹

The operation of Li-based batteries at low temperatures commonly leads to three problems:^{2,3,4} discharge capacity fade (*i.e.*, less energy available), decreased power, and increased risk of thermal runaway and fires upon charging (for secondary battery systems). In general, the discharge capacity fade at low temperatures results from: (i) low electrolyte conductivity ($\sim 350\%$ decrease when cooling standard electrolytes from $+25^{\circ}\text{C} \rightarrow -20^{\circ}\text{C}$); (ii) slower mass transport of lithium ions (cooling from $0^{\circ}\text{C} \rightarrow -20^{\circ}\text{C}$ decreases the Li^+ diffusivity); and (iii) sluggish charge-transfer kinetics at the active electrodes. These low-temperature limitations are exacerbated during the recharge cycle where Li-ion cells that typically use graphite anodes undergo Li-ion insertion at potentials close to that of the Li/Li^+ redox potential. As the temperature is lowered and lithium transport and reaction kinetics at the graphite anode become slower, lithium metal plating becomes more dominant than lithium-ion insertion, and metallic lithium dendrites (needle-like whiskers) begin to form (Figure 1). Subsequent cycling can lead to internal short circuits where dendrites pierce the separator of the cell leading to thermal runaway and the risk of a catastrophic event.

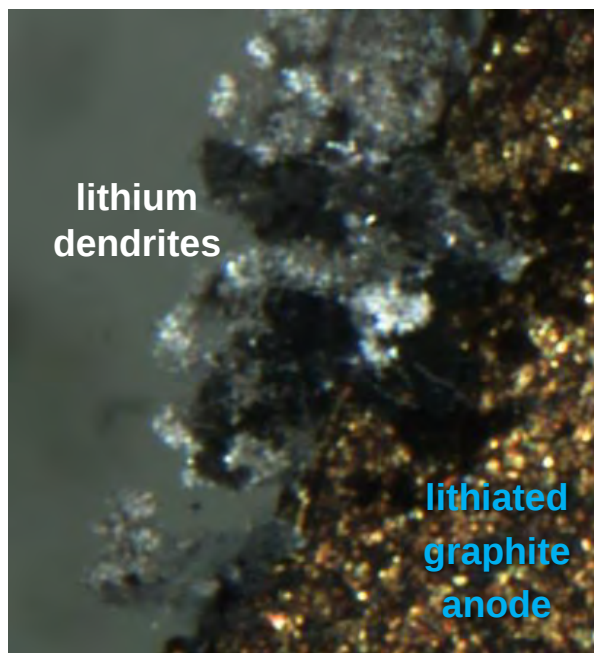


Figure 1. Micrograph of lithium dendrites formed on the edge of a commercial Li-ion battery graphite anode.

The low temperature performance of Li-based batteries will vary based on the individual cell chemistries as well as the identities of the electrolyte: solvent, salt, and chemical additives. Table 1 shows several Li and Li-ion chemistries. The half-cell electrochemical reactions are provided in the Appendix for reference.

Primary batteries utilize metallic lithium as the anode material and are non-rechargeable. Attempts to recharge non-rechargeable chemistries such as Li-SO₂ and Li-MnO₂ can form dendrites after only a few cycles, leading to a rapid temperature increase and eventual short-circuiting of the cell which could lead to catastrophic thermal runaway. This behavior is exacerbated at lower temperatures as the lithium-ion diffusivity decreases and lithium plating begins to occur at points of high current density. In comparison, secondary or rechargeable classes of batteries use two complementary electrode materials that undergo Li-ion insertion/intercalation reactions at different electrochemical potentials. When charged at near-ambient temperatures (> 15°C), the potential of Li-ion intercalation into the anode (typically graphite) is above that for lithium plating. The ability of Li-ion batteries to reversibly intercalate ions is the characteristic that makes them rechargeable (secondary).

The present report summarizes the key properties and performance metrics, particularly at low-temperature conditions, for the following military battery systems: the non-rechargeable BA-5590 and BA-5390, the rechargeable BB-2590, 28 V LBB for ITAS (improved target acquisition system) and GREENS (Ground Renewable Expeditionary Energy System) HEDBS (high energy density battery system) batteries. The chemistry of each battery system is shown in Table 1.

Table 1. Overview of batteries surveyed for this report

Model Number	Manufacturer	Chemistry	Operation	Performance Specification
BA-5590	Saft	Li-SO ₂	Primary	MIL PRF 49471
BA-5390	Saft; Ultralife	Li-MnO ₂	Primary	MIL-PRF 32383
BB-2590	Saft; Ultralife; Patco; BrenTronics	Li ₆ -CoO ₂	Secondary	MIL-PRF 32052
28 V LBB	Saft	LiC ₆ -NiCoAlO ₂	Secondary	Saft standard specification
HEDB	UEC Electronics	LiC ₆ -LiFePO ₄	Secondary	UEC Electronics specification

LITHIUM PRIMARY BATTERIES

BA-5590 — Li|SO₂ Battery

The non-rechargeable BA-5590 battery manufactured by Saft is designed to meet military performance specification MIL-PRF-49471 (Current Rev. 30 Nov 2000). Lithium-sulfur dioxide batteries are known for their high specific energy (up to 250 Wh·kg⁻¹), nominal cell voltage of ~2.8 V, very low self-discharge rate, and wide operating temperature range. The BA-5590 batteries produced by Saft are available in two models; (i) the standard capacity “BA-5590 B/U” and (ii) its high-capacity counterpart, the aptly named “BA-5590 High Capacity.” The BA-5590 B/U uses ten Saft LO 26 SX Li-SO₂ D-cells, with two groups of five cells in series, each cell with a nominal capacity of 7.75 Ah at 21°C and a 2 A discharge current. The high capacity model uses ten LO 26 SXC D-cells, each with a nominal capacity of 9.2 Ah in the same configuration. The general specifications for both cells are given in Table 2.

Table 2. Operating specifications for Saft BA-5590 batteries

Model	Nominal Voltage		Capacity		Operating temperature	Storage temperature
	Series Mode	Parallel Mode	Series Mode	Parallel Mode		
BA-5590 B/U	27 V	13.5 V	7.5 Ah	15 Ah	−40°C to +71°C	−40°C to +71°C (rec. max: +35°C)
BA-5590 High Capacity	27 V	13.5 V	9.1 Ah	18.2 Ah	−40°C to +71°C	−40°C to +71°C (rec. max: +35°C)

The nominal voltage and the capacity can be used to calculate the specific energy of the two Saft BA-5590 batteries as 203 and 246 Wh·kg^{−1} for the standard and high-capacity versions, respectively. A hallmark of the BA-5590 is the wide operating temperatures, from +71°C down to −40°C. An overlay of typical discharge curves for temperatures spanning this window is given in Figure 2 below.

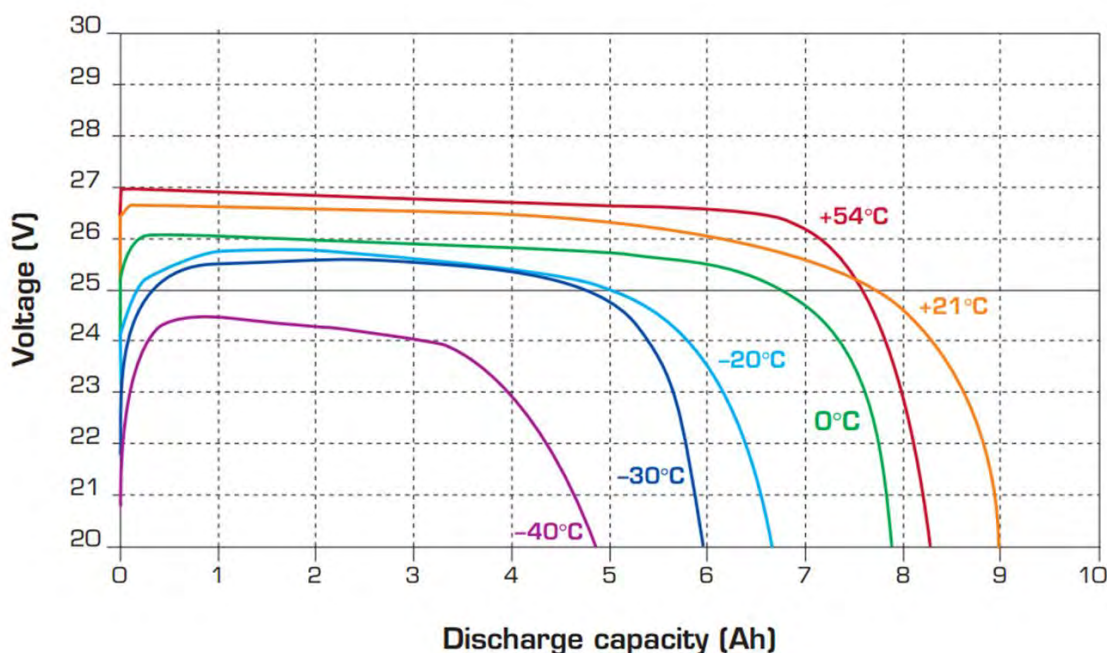


Figure 2. Typical discharge curves of the Saft BA-5590 at various temperatures, operating at 2 A in 24 V series mode (high capacity version shown) (Ref: <http://www.saftbatteries.com>)

From the curves in Figure 2, it is apparent that the capacity of the BA-5590 battery declines dramatically when discharged at temperatures less than 0°C. At −40°C, the capacity falls to <60% of the nominal capacity at the optimal operating temperature of +21°C and the discharge voltage falls from 27 V to ~24.25 V. The D-size Li-SO₂ cells that comprise the BA-5590 batteries use acetonitrile as the solvent and lithium bromide as the electrolyte salt. Electrolyte conductivity decreases when approaching these temperatures, leading to the lowered discharge voltage observed.

As of September 2012, the BA-5590 was the main battery supply for telecommunications equipment for the U.S. Marine Corps, with more than 350,000 batteries up to that time. During Operation Desert Storm in 2003, the energy requirements of the U.S. military were so demanding that the Marines alone were

discharging >3,000 Saft BA-5590 batteries per day, prompting Navy Capt. Clark Driscoll to declare that “We literally [came] within days of running out of these batteries.” Ultimately, the unexpectedly high demand of the BA-5590 prompted the U.S. Navy and Marine Corps to seek out longer lifetime primary batteries and rechargeable Li-ion batteries to avoid this problem in the future. In the Marine Corps’ “Guide to Employing Renewable Energy and Efficient Technologies” briefing,⁵ it was highlighted that “[i]ncreased operational tempo and unexpected production shortfalls have severely reduced the availability of high demand, high-use batteries.”

BA-5390 — Li|MnO₂ Battery

The non-rechargeable BA-5390 battery was a first step in alleviating some of the operational lifetime and energy density concerns of the BA-5590. The limitations of the BA-5590 described above led many manufacturers, including Ultralife, to discontinue that technology and transition to the BA-5390. The current BA-5390 available from Saft and Ultralife is designed based on the individual manufacturers’ specification, but were originally derived from the military performance specification MIL-PRF 32383 (Current Rev. 16 Jun 2011) for non-rechargeable Li–MnO₂ batteries. Lithium-manganese oxide batteries are known for their high specific energy (up to 280 Wh·kg^{−1}; higher than Li–SO₂), nominal cell voltage of ~2.8 V, very low self-discharge rate, and wide operating temperature.

The BA-5390 batteries produced by Saft come in two models: (i) the “BA-5390/U” and (ii) the “BA-5390/U” with an onboard state-of-charge indicator—the performance specifications of the two are identical. The Ultralife version has the standard model number BA-5390A/U. The BA-5390 for both manufacturers use ten Li–MnO₂ D-cells (Saft LM 33550 and Ultralife UHR-CR34610), with two groups of five cells in series, each cell with a nominal capacity of 13 Ah and 11.1 Ah, respectively. The general specifications for the available cells are given in Table 3.

Table 3. Operating specifications for Saft and Ultralife BA-5390 batteries

Model	Nominal Voltage		Capacity		Operating temperature	Storage temperature
	Series Mode	Parallel Mode	Series Mode	Parallel Mode		
Saft BA-5390/U	27 V	13.5 V	12.4 Ah	24.8 Ah	−40°C to +71°C	−40°C to +71°C (rec. max: +35°C)
Ultralife BA-5390A/U	27 V	13.5 V	11.1 Ah	22.2 Ah	−30°C to +72°C	−40°C to +90°C

The nominal voltage and the capacity can be used to calculate specific energy of the Saft BA-5390/U and Ultralife BA-5390A/U as 237 and 225 Wh kg^{−1}, respectively, representing >15% increase in specific energy compared to their BA-5590 analogs. A hallmark of the BA-5390 system is not only its wide operating temperatures, from +71°C down to −30/−40°C, but its ability to maintain a high depth-of-discharge, even when discharging at those temperatures. An overlay of typical discharge curves for temperatures spanning this window is given in Figure 3.

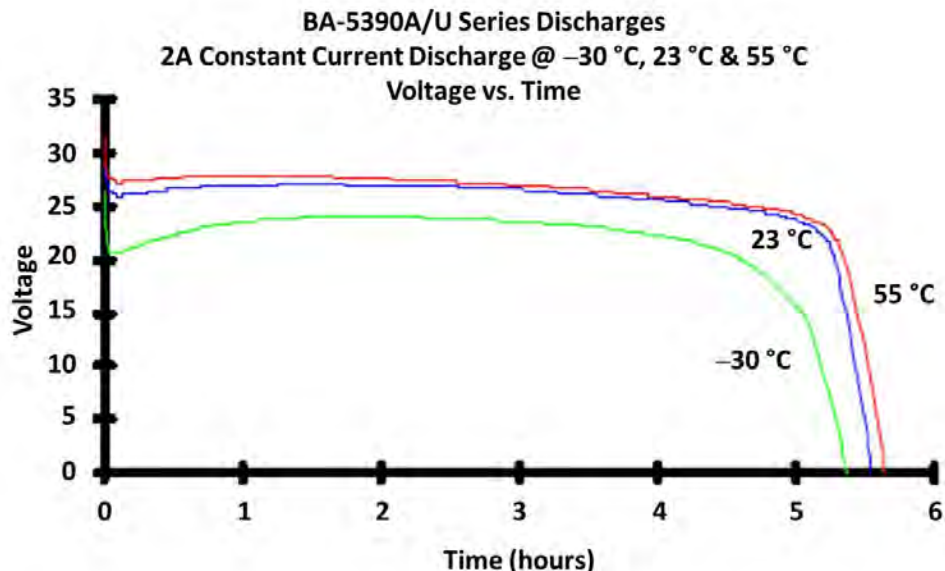


Figure 3. Typical discharge curves of the Ultralife BA-5390 at various temperatures, operating at 2 A in 24 V series mode (Ref: <http://www.ultralifecorporation.com>)

From the curves in Figure 3, it is apparent that the capacity of the BA-5390 is sustained, even when discharging throughout the temperature range of -30°C to $+55^{\circ}\text{C}$. At -30°C , the capacity only falls $\sim 5\%$ from its initial value at room temperature. Contrast these specifications with that of the BA-5590, for which the capacity drops $>25\%$ when discharging at -30°C . However, as observed in the BA-5590, average voltage is lower when discharging at these low temperatures

The Li-MnO_2 D-size cells use tetrahydrofuran (THF), propylene carbonate (PC), and 1,2-dimethoxyethane (DME) as the solvent mixture and lithium perchlorate as the electrolyte salt. As with other electrolytes, the conductivity of this specific electrolyte composition decreases at lower temperatures, although less so than for the electrolyte composition in the BA-5590. In the absence of THF, mixtures of PC and DME become more viscous and conductivity falls dramatically at lower temperatures. As the volume-percent of THF is optimized, the viscosity and conductivity of LiClO_4 -containing solutions can decrease (less THF) and increase (more THF), respectively.⁶

The enhanced capacity of the BA-5390 relative to the BA-5590, spanning the entire temperature range of -40°C to $+70^{\circ}\text{C}$, is the driving force behind the replacement in the field by the former and Ultralife's discontinuation of the latter. The impact of temperature on the discharge of the two primary batteries are given in Figure 4.

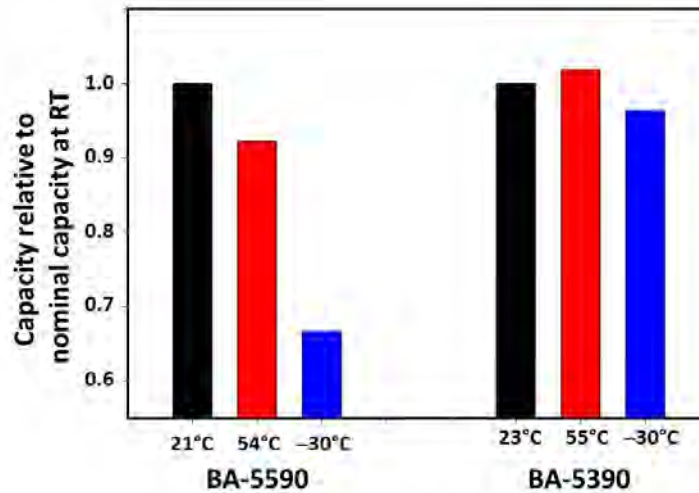


Figure 4. Relative capacities of the BA-5590 vs BA-5390 at elevated and reduced temperatures (compared to their rating at room temperature; 21°C for BA-5590 and 23°C for BA-5390).

For mission-specific telecommunications and personal power applications, both of these primary batteries may still have some utility, but as energy demands have continued to increase, it is apparent that non-rechargeable batteries are not suitable as the sole go-to power source for the U.S. Navy and Marine Corps. Specifically, in the Marine Corps’ “Guide to Employing Renewable Energy and Efficient Technologies” briefing, it was further established that “[u]nits cannot continue to rely on primary batteries as the sole source of power for their communications equipment.”

LITHIUM-ION BATTERIES

BB-2590 — $\text{LiC}_6|\text{CoO}_2$ Battery

While the BA-5390 extended mission lifetime beyond that achievable using the BA-5590, both suffer from the same problem—they are non-rechargeable batteries and any attempts to recharge them would likely cause rapid dendritic growth, thermal runaway, and pose the risk for catastrophic failure. Lithium-ion batteries, replace the lithium metal anode with a graphite (C_6) anode that intercalates/de-intercalates Li-ions supplied from the cathode and electrolyte as the battery cycles. Over the past two decades, the commercial success of Li-ion batteries has continued to grow and eventually led several manufacturers to introduce the BB-2590 Li-ion for U.S. Navy and Marine Corps applications according to military performance specification MIL-PRF 32052 (Current Rev. 6 Oct 2000) for rechargeable Li-ion batteries.

The benefits of Li-ion batteries beyond their cyclability include the possibility for high specific energy (up to $250 \text{ Wh}\cdot\text{kg}^{-1}$), high cell voltage (around 3.7 V), and low self-discharge rate. The BB-2590 batteries are produced by several manufacturers, including Saft, Ultralife, Patco, and BrenTronics, each with subtle variations in their specifications. In general, the BB-2590 contains ICR-18650-sized cells; a principal manufacturer for these individual cells is E-One Moli Energy Corp. Each manufacturer’s battery is comprised of 24 18650-size cell, with three sets of eight cells in series (8S3P). Performance specifications for the available batteries are given in Tables 4 & 5 for the discharge and charge operations, respectively.

Table 4. Discharge specifications for commercial BB-2590 LiC₆/CoO₂ batteries

Model	Nominal Voltage		Capacity		Discharge temperature	Storage temperature
	Series Mode	Parallel Mode	Series Mode	Parallel Mode		
Saft BB-2590/U SMBus	28.8 V	14.4 V	7.8 Ah	15.6 Ah	−30°C to +60°C	−30°C to +50°C
Saft BB-2590HC/U SMBus	29.2 V	14.6 V	9.6 Ah	19.2 Ah	−30°C to +60°C	−30°C to +50°C
Ultralife BB-2590/U SMBus	29.6 V	14.8 V	7.8 Ah	15.6 Ah	−32°C to +60°C	−32°C to +60°C
Patco BB-2590/U SMB 7.2	29.6 V	14.8 V	7.2 Ah	14.4 Ah	−20°C to +70°C	−20°C to +50°C
Patco BB-2590/U SMB 8.7	28.8 V	14.4 V	8.7 Ah	17.4 Ah	−30°C to +70°C	−20°C to +50°C
BrenTronics BT-70791CX	28.8 V	14.4 V	7.5 Ah – 9.9 Ah	15.0 – 19.8 Ah	−20°C [†] to +60°C	−40°C to +40°C
BrenTronics BT-70791JM	28.8 V	14.4 V	6.0 Ah	12.0 Ah	−40°C to +60°C	−40°C to +40°C

[†]The BrenTronics BT-70791CE operates between −30°C to +60°C

Table 5. Charge specifications for commercial BB-2590 LiC₆/CoO₂ batteries

Model	charging method	maximum charging rate (A)	charging temperature
Saft BB-2590/U SMBus	CC/CV [†]	8 A (parallel) 4 A (series)	0°C to +45°C
Saft BB-2590HC/U SMBus	CC/CV	8 A (parallel) 4 A (series)	0°C to +45°C
Ultralife BB-2590/U SMBus	CC/CV 3.0 A to 16.8 V; Hold at 16.8 V until $i < 300$ mA	4.8 A	0°C to +45°C
Patco BB-2590/U SMB 7.2	CV constant 16.8 V until $i < 100$ mA	3.0 A	0°C to +45°C
Patco BB-2590/U SMB 8.7	CV constant 16.8 V until $i < 100$ mA	3.0 A	0°C to +45°C
BrenTronics BT-70791XX	proprietary chargers ^{††}		

[†]CC = constant current; CV = constant voltage

^{††}The BrenTronics BT-70791XX batteries use proprietary chargers and charging specifications are not listed. However, the nuances of the charging profile are not expected to differ greatly from the requirements of MIL-PRF-32052 and the charging temperature is not expected to differ from the previous manufacturers.

The nominal voltage and the capacity can be used to calculate the average specific energy of commercial BB-2590s as $165 \pm 26 \text{ Wh}\cdot\text{kg}^{-1}$ with the highest specific energy achieved in the BrenTronics BT-70791CG at $210 \text{ Wh}\cdot\text{kg}^{-1}$. The low-temperature discharge performance varies slightly among the manufacturers, with the best performing example being the BrenTronics BT-70791JM, the only one capable of discharge at -40°C . The Materials Safety Data Sheet for the BrenTronics 2590/U BT-70791XX batteries list the electrolyte for all models as a combination of linear and cyclic carbonic solvents, the ratios of which will ultimately determine the low-temperature performance. The MSDS for 18650-sized cells from E-One Moli Energy Corp highlights the organic electrolyte combination to be LiPF_6 in dimethyl carbonate/ethylene carbonate/propylene carbonate. The ratio of these three solvents is variable among models and can impart better low-temperature performance.⁶ An overlay of typical discharge curves for temperatures spanning the -32°C to $+60^\circ\text{C}$ window is given in Figure 5.

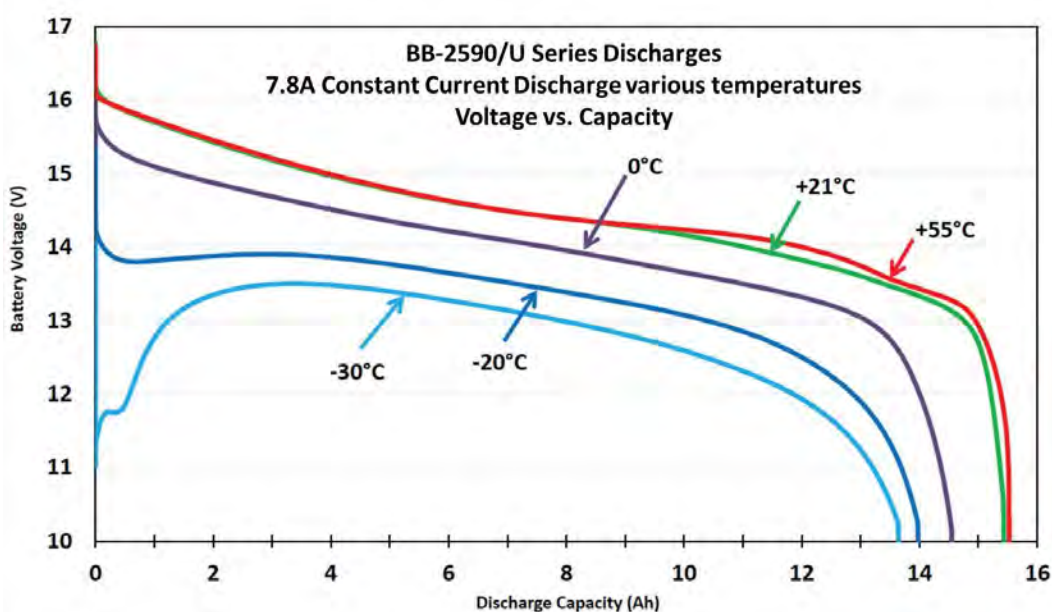


Figure 5. Battery voltage as a function of discharge capacities for the Saft BB-2590/U at elevated and reduced temperatures. (Ref: <http://www.saftbatteries.com>)

From the curves in Figure 5, it is apparent that the capacity of the BB-2590 is reasonably consistent when discharging across a broad temperature range (-30°C to $+55^\circ\text{C}$), albeit with a modest decreased discharge voltage and corresponding specific energy. At -30°C , the capacity only falls $\sim 13\%$ of its initial amount at room temperature. As stated above, the Li_6CoO_2 18650-size cells that comprise the BB-2590 batteries use a combination of organic carbonates and lithium perchlorate as the electrolyte, which maintains a reasonable conductivity, even to -30°C .⁷

The temperatures discussed thus far for the BB-2590 solely apply to the discharge process. Because this is a rechargeable battery, low-temperature charging must also be addressed. It is a well-established problem that low-temperature charging results in Li metal plating *onto*, rather than Li^+ insertion *into*, the graphite anode, leading to the following problems: a) the battery does not recover all of the prior discharge capacity upon subsequent charging, and b) dendrites begin to form and grow, posing the risk for shorting and catastrophic failure. In Table 5, the charging specifications generally employ a constant-voltage (CV) or a constant-current/constant-voltage (CC/CV) charging profile to avoid overcharging at the high voltages incurred during recharge. Biphenyl and propane sulfone are additives included in some formulations; these

are present to protect the cell against overcharge and high-temperature cycling, but they are electrochemically unstable and their effect decreases with increasing cycle number.⁸ The various BB-2590 battery manufactures are also in agreement that charging should not be attempted under 0°C. While the individual manufacturers do not portend to include charging curves for a BB-2590 battery below 0°C, studies of individual LiCoO₂ cells similar to those in this report have been reported previously (Figure 6).⁹

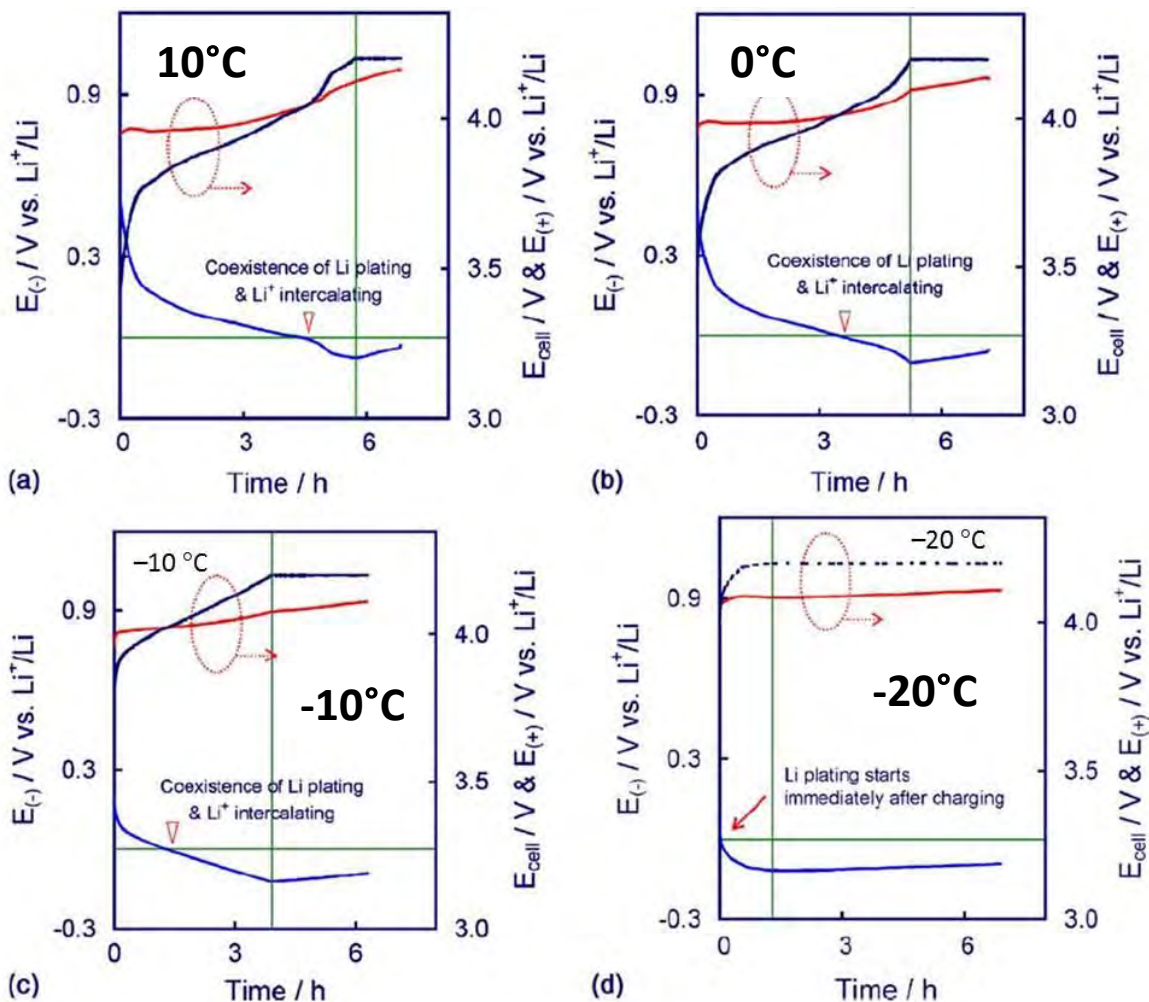


Figure 6. Correlation of the cell voltage (red curve – right y-axis), cathode potential (black curve – right y-axis), and anode potential (blue curve – left y-axis) with charging time for a 32 mAh MCMB|LiCoO₂ cell charging at a) 10°C b) 0°C c) –10°C and d) –20°C (reprinted from reference 9).

As the temperature of the cell decreases, the cell voltage falls, both as a consequence of the increased cell resistance and Li⁺ diffusivity. However, the thermodynamic potential for lithium plating is unchanged. The authors of this study conclude that for low-temperature charging, the potential of the graphite anode must stay sufficiently positive of 0 V versus Li⁺/Li, but because of the high overpotential of graphite and a decreased ionic conductivity, lithium plating is kinetically preferred, even at temperatures as high as 10°C, with a complete absence of Li⁺ insertion at –20°C.

The storage temperature of rechargeable Li-ion batteries is also a consideration because of the increased prevalence of self-discharge at higher temperatures. The military specification MIF-PRF-32052/1 requires that 87% of nominal capacity of the BB-2590 be maintained when storing them at 50°C for 7 days. Manufacturer specifications suggest that storing these batteries at extreme cold temperatures poses no problems and, in accordance with the military requirements, they can be stored up to about 50°C. Independent testing of BrenTronics' BB-2590 has revealed that storing them at temperatures over 50°C leads to a permanent loss in capacity, as detrimental as 65% when stored at 80°C for only seven days.¹⁰

28 V LBB for ITAS — $\text{LiC}_6\text{Ni}_x\text{Co}_y\text{Al}_z\text{O}_2$ Battery

The BB-2590 is the gold standard for rechargeable Li-ion batteries for routine field use in the U.S. Navy and Marine Corps. However, some applications have more challenging operating specifications, as in Raytheon's Improved Target Acquisition System (ITAS), where the demand for high-power output demands, structural robustness, longer-term storage, and low-maintenance operation, necessitate development of other specialized batteries. In 2009, The Raytheon Company awarded a \$13.5 million dollar contract to Saft to provide the 28 V Li-ion battery box (LBB) that the ITAS requires.

The Saft 28 V LBB that powers the ITAS is comprised of individual VL 52E cells with $\text{LiC}_6\text{-NiCoAlO}_2$ chemistry. The ITAS is comprised of 16 of these large-type Li-ion cells, with two sets of eight cells in series (8S2P). The general specifications for the ITAS LBB are given in Table 6.

Table 6. Specifications for the (left) Saft VL 52E cell and (right) 28 V LBB for the ITAS

28 V LBB Cell Characteristics	Specification	Battery Characteristics	Specification
Nominal voltage	3.6 V	Nominal voltage	28.8 V
Capacity at +25 °C	52 Ah	Capacity @ +54 °C +21 °C −32 °C	>80 Ah >80 Ah >70 Ah
Maximum discharge rate	52 A	Maximum discharge rate	30 A
Maximum charge rate	C/7	Maximum charge rate	10 A
charge temperature	5°C to +35°C	mass	29 kg
discharge temperature	−25°C to +55°C	number of cells	16

The nominal voltage and the capacity can be used to calculate the average specific energy of the Saft 28 V LBB batteries, $\sim 80 \text{ Wh}\cdot\text{kg}^{-1}$, a marked decrease in the specific energy when compared to the BB-2590 above. However, this shortfall is a small price to pay for higher current output, higher power, structural integrity, and longer lifetime for the applications that the ITAS requires, namely to power the tube-launched, optically tracked, wire-guided (TOW) missile.

Low-temperature discharge performance of the LBB is similar to that observed in the BB-2590, maintaining >85% of its nominal capacity when discharging as low as -32°C . A sample set of experiments on the individual component cells (Saft VL 52E) is given in Figure 7, which are a demonstration of exhaustive discharges at these temperatures. It is noteworthy that the explanation for a long, stable lifetime of the Saft 28 V LBB is the limit of the depth-of-discharge when packaged in the 28 V LBB ITAS system.¹¹ The Materials Safety Data Sheet for all Saft Li-ion batteries is the same: lithiated metal compounds (in this case nickel cobalt aluminum oxide), organic electrolyte, graphite, copper, aluminum, and remainder packaging materials. The Saft VLE cells (VL XXE) contain carbonate electrolytes with LiPF_6 , which will run into the same low-temperature limits as the BB-2590/U. Likewise, whenever graphite is the active anode material, low-temperature recharge is not expected to be successful at temperatures $<10^{\circ}\text{C}$.

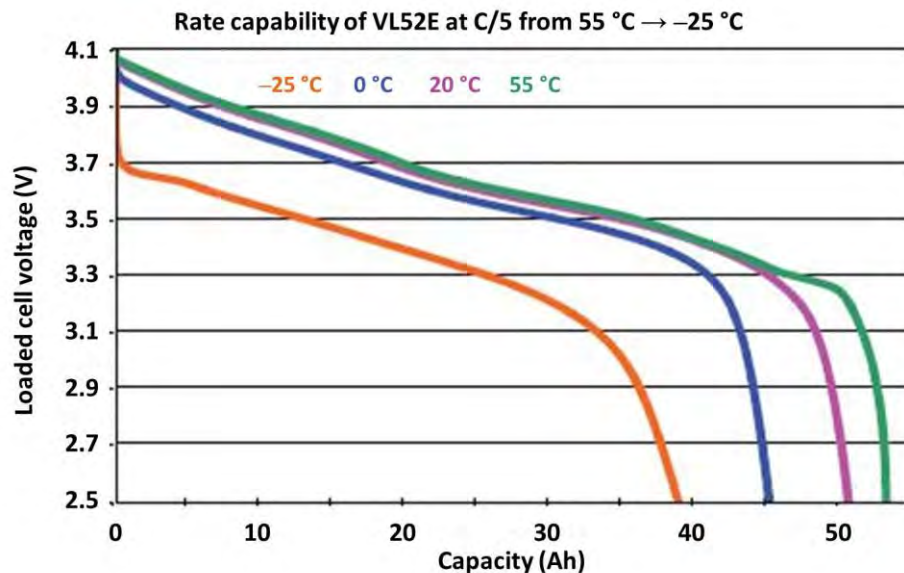


Figure 7. Battery voltage as a function of discharge capacities for the Saft VL 52E, an example of an individual cell that makes up the 28 V LBB ITAS battery. (Ref: <http://www.saftbatteries.com>)

Manufacturer's experiments on individual VL 52E cells has also provided information on their self-discharge and preferred storage conditions. A benefit of the Li-ion with NCA cathodes is their ability to be stored at 100% state of charge, therefore not requiring an initial charge step prior to use. Storage for 10 years at 10°C and 30°C has led to a capacity loss of 0.5% and 1.2% per year, respectively. However, storage at 60°C leads to a capacity loss >13% per year, still a marked improvement over the BB-2590, which drops by 65% after storage at 50°C for only seven days. Storage at the lower bounds of the operating temperature range is therefore preferred, so long as the operator brings the temperature of the cell back up $>10^{\circ}\text{C}$ before attempting any recharge processes.

HEDB for GREENS — $\text{LiC}_6\text{-FePO}_4$ Battery

The final technology surveyed in this report is the High Energy Density Battery system for the Ground Renewable Expeditionary Energy Network System (GREENS). The GREENS project was initiated in 2009 as a means to harness solar energy using photovoltaic cells, store the energy in Li-ion batteries, and then

use that power for in-field demand. The primary manufacturer of the HEDB system for GREENS is UEC Electronics.

The Li-ion batteries on board the GREENS use the lithium-iron-phosphate (LiFePO_4) cathode chemistry paired with graphite anodes. The individual cells used are model number LFP26650EV manufactured by K2 Electronics. The HEDB is comprised of 32 of these LiFePO_4 cells, with four sets of eight cells in series (8S4P). The general specifications for the HEDB and its components cells are given in Table 7.

Table 7. Specifications for the (left) K2 LFP 26650EV cell and (right) HEDBS for the GREENS

LFP26650EV Cell Characteristic	Specification	Battery Characteristic	Specification
Nominal voltage	3.2 V	Nominal voltage	25.6 V
Capacity at +25 °C	3.2 Ah	Capacity	51 Ah
Maximum discharge rate	20 A (6C) [†]	Maximum discharge rate	40 A
Maximum charge rate	C/7	discharge temperature	−20°C to +65°C
discharge temperature	−20°C to +65°C	mass	18 kg
		number of cells	32

[†]While 6C is achievable, the manufacturers recommend continuous discharge to stay below 3.2 A for long-term stability.

From the table above, the nominal voltage and the capacity can be used to calculate the average specific energy of the UEC HEDB system as $\sim 72 \text{ Wh}\cdot\text{kg}^{-1}$, a marked decrease in specific energy relative to other batteries in this report. However, the application-specific benefit of providing silent and renewable energy harvested from the sun justifies the lower specific energy.

The low-temperature discharge performance of the cells that comprise the HEDB maintains $>80\%$ of its nominal capacity when discharging as low as -20°C , but with the caveat that maintenance is only achieved when discharging at much lower rates (Figure 8). For the KFP26650EV cells, a discharge current of $\sim 0.16 \text{ A}$ is required to achieve the nominal capacity of the C/5 rate of $\sim 3 \text{ A}$.¹²

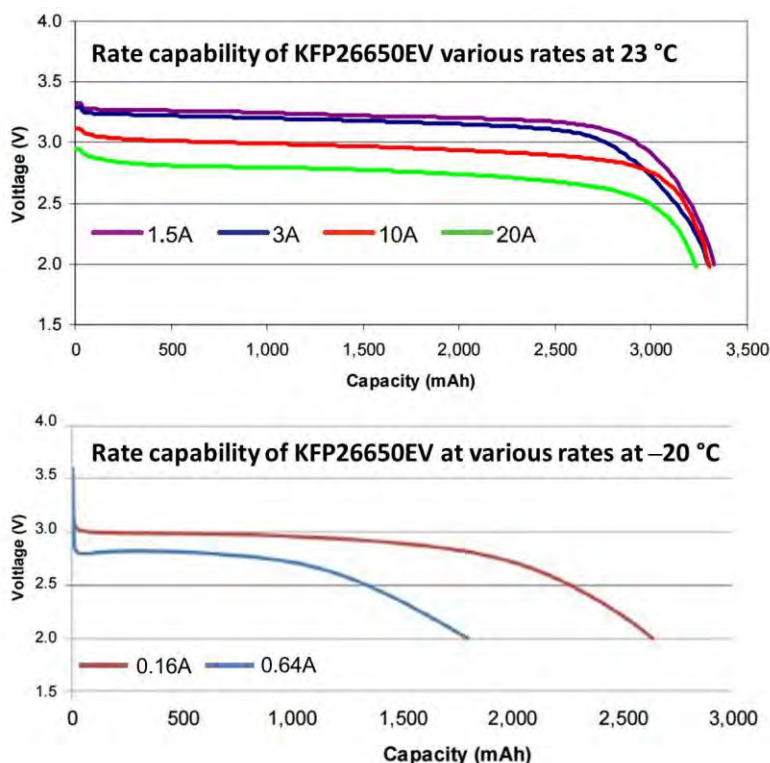


Figure 8. Battery voltage as a function of discharge capacities of the KFP26650EV at (top) +23°C and (bottom) -20°C. (Ref: <http://www.k2battery.com> & personal correspondence)

The Materials Safety Data Sheet for the K2 KFP26650EV shows lithium iron phosphate, a graphite anode, and an electrolyte mixture of lithium hexafluorophosphate in ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate as components of the cell. As noted above, cells that use graphite anodes are not expected to show successful recharging at temperatures $<10^{\circ}\text{C}$.

A benefit of LiFePO_4 cathodes is their ability to be stored at 100% state of charge, and therefore not requiring an initial charge step prior to use; they also maintain higher specific capacity at higher temperatures. Solid-state lithium ionic conductivity is higher in the FePO_4 case, compared to other battery technologies in this report. However, storage at reasonable temperatures, $<30^{\circ}\text{C}$ is expected to optimize battery lifetime and minimize self-discharge.

SUMMARY AND FUTURE OPPORTUNITIES

The low-temperature performance of the most common Li-based batteries for the U.S. Navy and Marine Corps depends mainly on whether or not the batteries are intended to be recharged. Non-rechargeable (primary) batteries use a sacrificial lithium metal as the anode material, and thus the limits of low-temperature discharge depend on the limits of Li^+ diffusivity and electrolyte conductivity at those temperatures. The subtle variation of these properties in the components of the non-rechargeable batteries surveyed in this report reveal that the BA-5390 exceeds the BA-5590 in terms of retention of capacity at low-temperatures (ca. -30°C).

The U.S. Military, aside from some niche applications, is moving beyond non-rechargeable lithium metal batteries in favor of Li-ion batteries, so not only is low-temperature discharge a concern, but so is the subsequent low-temperature recharge (perhaps more so). The common denominator in all of the rechargeable (secondary) batteries highlighted in this report is that they all use graphite as the anode insertion material. During low-temperature ($<10^{\circ}\text{C}$) recharge, the voltage required for Li-ion insertion falls below that required for lithium plating at the graphite. This leads to metallic regions on the anode, dendrite growth and ultimately the loss of discharge capacity. These drawbacks not only dramatically hinder long-term stability of rechargeable batteries, but also are a primary cause for catastrophic damage; when the dendrites grow long enough to short-circuit the battery, thermal runaway and fires are difficult to avoid. Low-temperature recharging data are difficult to obtain. More data is required with repeated charges at low temperatures to more accurately mimic anticipated field conditions. Additionally, the ability to gain fundamental insights into battery operation and safety by observing electrode operation through advanced characterization techniques will inform U.S. Navy and Marine Corps energy stakeholders of actual low-temperature recharge limitations and identify more accurate low end temperature boundaries for safe and reliable lithium battery operation.

The ranking of the capacity retention at low-temperature discharge can be summarized as BB-2590 > LBB for ITAS > HEDB for GREENS, but this fails to take into account the many benefits of the LBB and HEDB in their specific applications. Ranking these three batteries in terms of low-temperature recharge would not be prudent, because they all suffer from the same limitations when using graphite anodes.

There are options for other technologies to meet the demand for low-temperature cyclability (both discharge and recharge). For example, with a planned launch date of 2015, Saft began manufacturing the XcelionTM battery, which is a 60 Ah, 26.4 V LiFePO₄ system that incorporates on-board heaters that are automatically engaged to achieve optimal charging, allowing recharge down to -40°C (see www.saftbatteries.com). Achieving this comes at the expense of a balance of plant that drives the specific energy down to 79 Wh kg^{-1} , but allows an application space previously unrealized. Another recent breakthrough is the use of lithium titanate as the anode material in lieu of graphite.¹³ The voltage of lithium insertion into titanate is considerably less than that in graphite, so dendrite formation is effectively eliminated, although high current recharging rates could nucleate lithium dendrites; however, that also comes with the drawback of an overall lower cell voltage, perhaps a small price to pay for low-temperature recharge without the safety hazards of modern lithium-ion. Also, cell heating and warming strategies have been explored to maintain a safe cell temperature to ensure dendrite-free recharging. Perhaps most promising is the development of informed pulse charging schemes unique to a cell's chemistry and form factor. These tailorable protocols provide optimal lithium-ion transport to the surface of the anode during a charge pulse while allowing for ionic diffusion through the anode during the short rest, no current portion of the pulse.

APPENDIX

Half-cell electrochemical reactions are provided for the various cell chemistries listed in the present report.

1. Li-SO₂ cell:
 - Anode: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$ 1a
 - Cathode: $\text{SO}_2 + \text{e}^- \rightarrow \text{S}_2\text{O}_4^-$ 1b
2. Li-MnO₂ cell:
 - Anode: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$ 2a
 - Cathode: $\text{MnO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiMnO}_2$ 2b
3. Li-CoO₂ cell:
 - Anode: $\text{LiC}_6 \rightarrow \text{Li}^+ + \text{e}^- + \text{C}_6$ 3a
 - Cathode: $\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^- \rightarrow \text{LiCoO}_2$ 3b
4. Li-NiCoAlO₂ cell:
 - Anode: $\text{LiC}_6 \rightarrow \text{Li}^+ + \text{e}^- + \text{C}_6$ 4a
 - Cathode: $\text{Li}_{1-x}\text{NiCoAlO}_2 + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li NiCoAlO}_2$ 4b
5. LiFePO₄ cell:
 - Anode: $\text{LiC}_6 \rightarrow \text{Li}^+ + \text{e}^- + \text{C}_6$ 5a
 - Cathode: $\text{FePO}_4 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiFePO}_4$ 5b

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