

Advances in the Energy and Power Density of Lithium-ion Batteries for Undersea Applications

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ABSTRACT

With its demonstrated high Energy and Power Densities, long Cycle and Calendar Life, and proven reliability, Lithium-ion Technology is making its way into a number of Manned and Unmanned Undersea Applications. These applications are typically divided into two categories, the High Energy systems – such as UUVs and long range submersibles; and High Power systems – such as electric propulsion torpedoes and targets. Lithium-ion technology is flexible enough that it can be optimized for either of these performance zones.

Yardney Technical Products has already supplied batteries for fielded applications of both types. The 1.2MWh Lithium-ion battery, one of the world's largest, provides high energy storage for the Advanced SEAL Delivery System (ASDS), and high power batteries have been supplied to power electric torpedoes. Continuing research and development efforts have been focused on establishing the Next Generation chemistries and designs to support further increases in capability. High Energy systems have been developed that deliver >210Wh/kg at the cell level. High Power cells are supporting 15C continuous discharge rates and delivering >8000W/kg. These advances in cell design and chemistry take advantage of not only new active materials, but also improved binders, separators, and electrolyte additives.

Improvements to battery safety must also be made, as evidenced by some of the recent events with commercial consumer electronics batteries. This issue, combined with the high temperature performance limitations of commercial chemistries, has resulted in several automotive manufacturers delaying the introduction of Lithium-ion batteries into Hybrid and Electric Vehicles. It is also noted that the transition to large format Li-Ion batteries continues with the Chinese presently building 10,000Ah Li-Ion cells for submarines and buses. Replacement of a 300V/8000Ah Lead Acid battery on a submarine with a Lithium-ion version would reduce mass by over 80,000lb and volume by up to 1000ft³.

Safety aspects of these battery designs need to be addressed at the Cell, Battery and System levels as each of these three areas individually impacts the safety

and performance of High Energy and High Power Lithium-ion batteries.

INTRODUCTION

As undersea applications continue to grow in power and energy consumption the battery often becomes an enabling technology. Some recent events aside, Lithium-ion technology offers an efficient, mass and volume minimized solution for such needs. Lithium-ion technology has demonstrated excellent performance in a host of commercial, military and aerospace applications. Lithium-ion cells and batteries can be designed to support the High Energy needs of applications such as Unmanned Underwater Vehicles (UUV) that typically operate for hours, or even days, away from a power generation or charging source. High Energy Lithium-ion cells have been demonstrated in large format, high capacity, designs that provide high reliability and efficiency in packaging to meet system-level energy densities. High Power applications, such as torpedoes and targets, benefit from the excellent rate capability, even at low temperatures, and high efficiency (thus less power lost to waste heat) that Lithium-ion technologies can offer. These higher rate applications utilize either single-string, or multi-string battery designs to help distribute the current loads.

Yardney Technical Products has delivered battery systems for both types of applications, and continues to develop and improve the technology to support even more applications. Recent improvements have focused on reducing cell impedance for improved rate capability and reduced power fade, increased cycle life, and enhanced cell and battery designs for specific application needs. Yardney continues to advance the technology and demonstrate the applicability to a number of undersea applications.

MANNED AND UNMANNED UNDERWATER VEHICLES.

ADVANCED SEAL DELIVERY SYSTEM – The Advanced Seal Delivery System is a manned submersible consisting of an 8-ton, 300V, 1.2MWh Li-Ion battery. This battery was delivered over 3 years ago and represented one of the largest fielded Lithium-ion

batteries in a Navy application. Figure 1 shows an oft-used picture of the battery just to convey its size for those not familiar with the program. The powering of a manned submersible has demonstrated the viability of such batteries, quantified cost savings while the three years of feedback from field service allows for enhancements to subsequent generations.

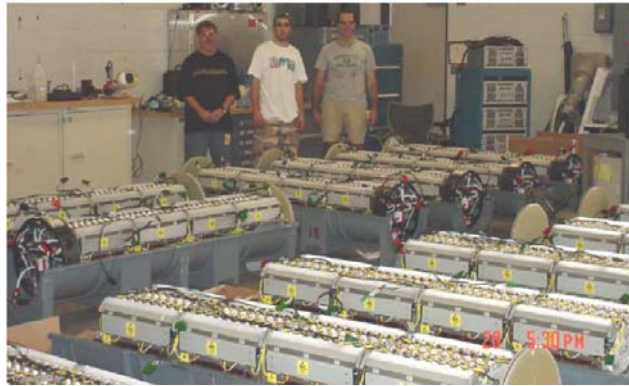


Figure 1: Several of the 14 1/2-Strings at Navy Base During a Field Review

One of the most striking features was that the battery changed the way the vessel is used by not having to fully recharge the battery and allowing relatively rapid recharges. The preceding Ag-Zn battery required greater than one day to charge, followed by a prolonged cooling period. The vessel was used more often with both full and partial recharges. A significant next generation enhancement was the desire to develop a cell equalization capability that did not require the battery to be fully charged for balancing to operate efficiently. In addition, the reduction of heat generation during equalization is desirable due to the limited thermal dissipation common with many UUVs.

LIGHT WEIGHT TORPEDO- For a High Power application, Yardney is working with the Navy on the joint development effort of a 360V, 75kW battery for the Light Weight Torpedo (Figure 2). Although a high rate application, this effort has many of the same design concerns as the lower rate ASDS and many other UUVs. Specifically, the accumulation and dissipation of heat needs to be addressed in both battery design and material selection. As a high rate application this battery typically discharges in 5-15 minutes, limiting the ability of the battery to dissipate any heat generated from the discharge. In addition, the size and shape of this battery do not make it a good candidate for the improved thermal design utilized in ASDS in which every cell is uniformly heat sunk to the outer wall (Figure 3).¹

Battery Management Electronics, developed by the Navy, do provide the opportunity to equalize the battery cells at any State of Charge, and provide rapid feedback on battery temperatures, currents and all cell voltages during all stages of battery charging and discharging. Such information is critical in the proper care and maintenance of a large Lithium-ion system.

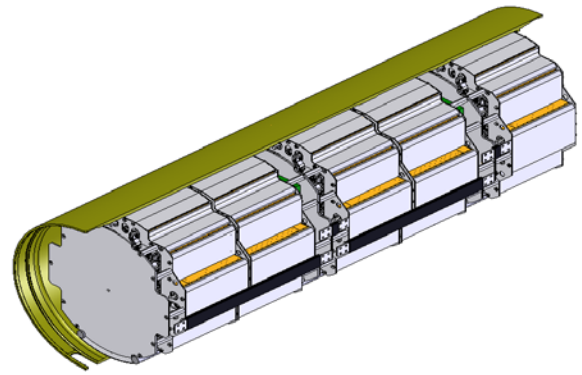


Figure 2: Lt Wt Torpedo Battery.

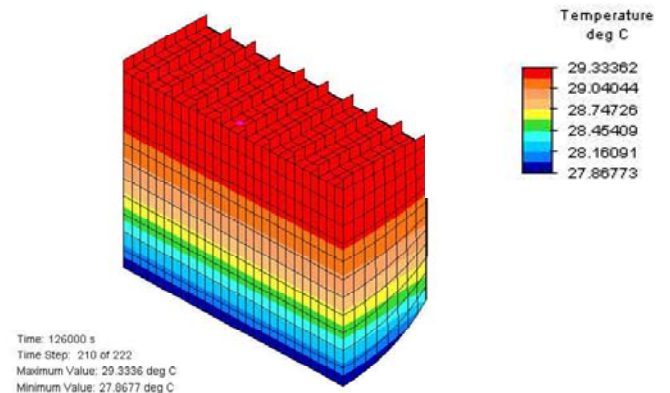


Figure 3: ASDS Thermal Model.

MATERIAL DEVELOPMENT FOR HIGH ENERGY AND HIGH POWER APPLICATIONS

Though these two applications have very different uses, the commonality is the need for stability at higher temperatures and high states of charge. Both applications are sensitive to energy density and require materials at a high Technology Readiness Level. In both instances mixed metal oxides such as LiNiCoO_2 and LiNiCoAlO_2 are the best candidates. Table 1 shows a comparison of the several possible replacements.

Table 1: Energy Comparison for Various Cathodes.

	Specific Capacity mAh/g	Averag Discharg Voltage	Normalized LiNiCo_2 Energy
LiNiCo_2	178	3.650	100%
LiMn_2O_4	135	3.810	79%
LiNiCoMnO_2	147	3.840	87%
LiFePO_4	152	3.300	77%

This table shows that with the voltage limits imposed due to buss limitations, no other mature material matches the cell energy density of LiNiCoO_2 . It is noted

that as material is being considered to replace a fielded and qualified design, the physical changes (e.g. reducing the number of cells) that are beneficial to higher voltage systems are not practical.

For the torpedo application, the need for high energy density remains but is tempered by high power requirements. Chemical improvements to the design come from developing and utilizing materials with lower impedance. Material selection, binder type and amount, and selection of conductive diluents can reduce a cell's impedance without drastically impacting the overall energy density. Referring to Figure 4, Lot 1, Lot 2 and Lot 3 all utilize the same cathode but against different anodes. The comparison between Lot 2 and Lot 3 indicates that Lot 3 has 8.4% lower impedance. Lot 3 and Lot 4 use the same anode but different cathodes at the same loading. Here the difference corresponds to 6.2% lower impedance. For a 400V system operating at 15C or higher, with an average discharge voltage suppressed to 3.35V, the cathode change corresponds to a 600W reduction in heat generation. It is noted that the p-value for comparison of the means is below 0.05 for any two Lots. An analysis of the deviations within each lot found that the Lot 2 anode had a 96.8% likelihood of exhibiting a narrower range of cell resistances. This could possibly be attributed to improved processability.

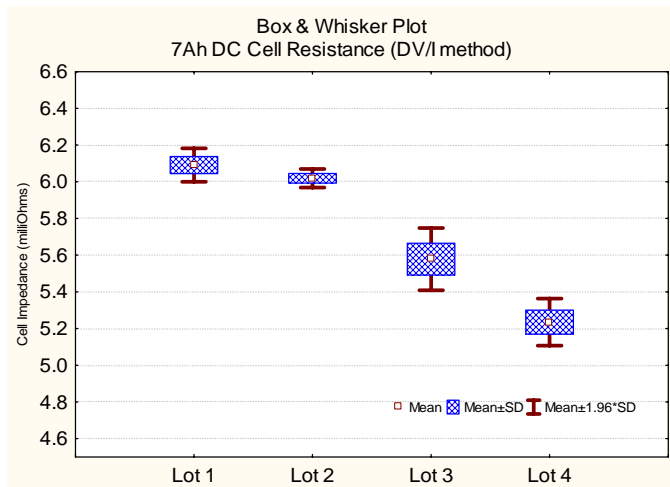


Figure 4: Lower Impedance of the cell chemistries based on active material selection.

High rate capability can be enhanced through the use of electrolyte additives as well. In addition to improving high temperature stability, enabling cells and batteries to perform well after prolonged exposure to temperatures as high as 70°C, such additives can reduce the impedance of the system. Such additives have been shown to increase rate capability and reduce power fade on high rate cycling. Figure 5 shows the high rate performance of 25Ah cells discharged at a constant 15C (375A) rate, with and without the electrolyte additives. Additional high-rate life cycle testing of these cells is currently on going to demonstrate the life capabilities and reduced power fade of this chemistry.

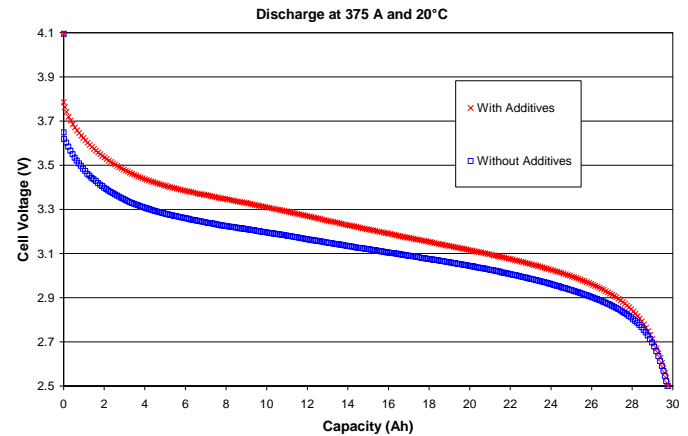


Figure 5: High Rate (15C) discharge of cells With Additives (top line) and Without (bottom line).

In addition to the high rate and high energy applications discussed above, the material qualification is addressing the needs of various UUVs. In these applications the end device must survive underwater explosion (UNDEX) events which impart both chemical safety and physical safety requirements. Cell and battery design and construction play a key role in surviving such events.

LARGE CELL AND BATTERY DESIGN CONSIDERATIONS

Large, high capacity, batteries have been used extensively in undersea applications. They typically have been satisfied by extremely large Lead/Acid cells, but as power and energy demands continue to increase, Lithium-ion cells and batteries offer a significantly reduced mass and volume solution. Historically such large systems have not been comprised of large series/parallel arrays of smaller cells, and with good reason. Primarily overall system safety and reliability can be enhanced by being able to truly monitor individual cell voltages, ensure equal utilization of all cells, and reduction in the number of piece parts. Placing a higher impedance cell in parallel with a normal, or "good cell", can lead to excessive heat generation, especially during high rate discharges. Multiple smaller cells present reliability issues with many more intercell connections to fail, potentially more terminals to leak, and more difficulty in packaging and ruggidizing the Battery design. There are of course disadvantages, as larger cells tend to be more specialized and have higher initial costs, they tend to be from specific vendors, reducing competition, and they can have larger safety issues – although recent incidents with even small laptop batteries have shown that failures can propagate in a small cell battery design and yield catastrophic results.

Several design considerations come into play when developing any large capacity system, Lithium-ion cells

and batteries are suitable for such applications, but must be appropriately designed and managed. For High Power applications, the ultimate cell size is limited by Thermal and Heat Dissipation concerns. Simple thermal analysis of three different cell designs demonstrates how the thermal management of such systems can be achieved. The three designs, shown in Figure 6, are variations on a 55Ah capacity cell. Thermal modeling shows how these cells dissipate the heat generated, due to internal resistance and self-heating, from an 8,250 Amp, 7.5 second pulse, Figure 7. The cell's ability to dissipate heat is a function of geometry, and larger cells become impractical at certain designs, thus the final cell design options are limited. Power distribution buss work can also be a limiting factor as distribution of high currents can allow for smaller individual cables vs. a single string with full current carrying capability.

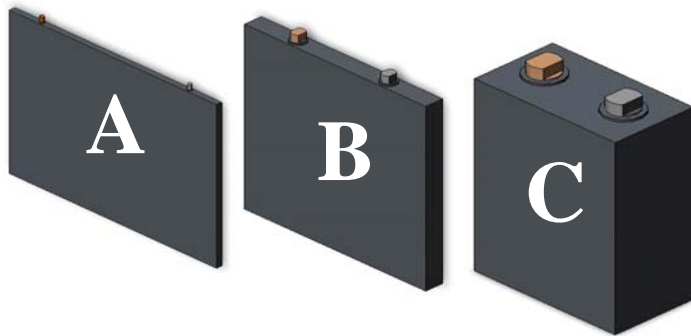


Figure 6: 55Ah cell designs for Thermal Dissipation study, all cells yield the same theoretical nameplate capacity

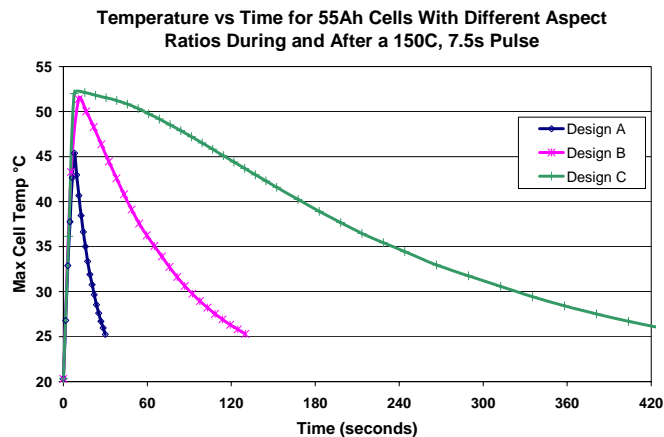


Figure 7: Thermal analysis results for 55Ah cells with different aspect ratios.

High Energy systems, typically low rate applications, are not typically subjected to the same thermal design limitations as the High Power designs. Lithium-ion technology typically operates with a 95% to 97% Energy Efficiency, so with 5 hour or greater discharges, the cells and batteries will dissipate the heat generated almost immediately. This means that the cells for these types of applications have almost no natural limitation on cell

size, and in fact manufacturing and handling concerns become predominate in designing such systems.

System safety must, however, always be a primary concern in designing such systems. Cell voltages, temperatures, and even currents (on multi-string batteries) should be consistently, and frequently, monitored and maintained within prescribed limits. Battery Management Electronics are typically responsible for monitoring and controlling the charge, and perhaps discharge, modes of the battery. They are typically designed to limit maximum cell voltage and deviation, and abort operation if temperatures get out of range. These systems should also interface with the application system, at least at the charger and/or power distribution levels to ensure that unsafe demands are not made on the batteries and to provide backup to any internal protections. Communications and data recording features provide additional information in case out of bounds events are encountered, or as a means of providing details for Battery State of Health assessments.

HYBRIDIZED DESIGNS

Many unmanned applications have extreme power and temperature requirements, such as an engine start at -40°C, that while power intensive do not require a large portion of the battery's energy. These requirements are often in conjunction with a desire for a long run time at a nominal temperature. Unfortunately, the design and chemistry changes needed to support low temperature and high rate requirements result in overall reduction in battery capacity. Hybrid battery (and even cell) designs are a potential solution to this problem. Combining a High Power cell, to support the high rate need, with a High Energy cell, providing longer run time, yields a system that can operate effectively over all ranges of the performance profile. To demonstrate the viability of this concept YTP placed a High Power cell in parallel with a medium power UUV cell and demonstrated performance at -30°C. The High Power cell has only approximately 8% of the capacity of the UUV cell; however it provides a high rate capability that far exceeds the High Energy cell on its own.

Figure 8 shows the combined performance of the stand alone High Energy cell and prototype hybrid system. In this hybrid testing the cells are externally connected in parallel. The cells were discharged at a net C/2 rate at -30°C. A reduction in cell impedance of 25% was observed for the 8% increase in capacity. The impact on the nominal rate and temperature discharges for the hybrid system would be a capacity reduction of 9%. Reducing the impedance of the cell by 25% for a low temperature discharge with a non-hybrid system would reduce the capacity available for nominal rate and temperature discharges by about 15%. The benefit to the hybrid increases as the temperature decreases and rates increase. Further, the lower rate portion of the system would be modified to be a higher energy, lower rate design to take full advantage of the high power

section in parallel.

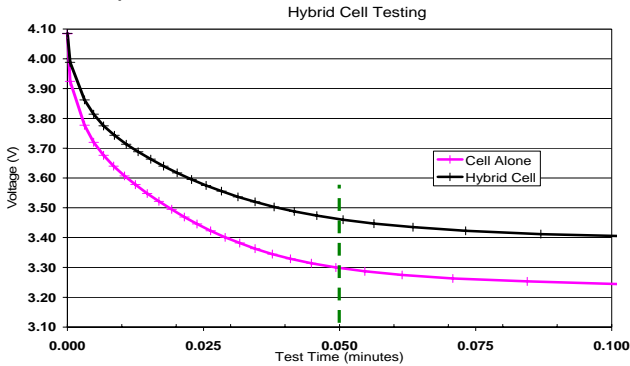


Figure 8: Testing of Prototype-Hybrid Li-Ion Cell

OTHER UNMANNED APPLICATIONS (UNMANNED MARTIAN VEHICLES)

Yardney's fifth and sixth Li-Ion batteries landed on Mars on May 25th, 2008. The first four batteries were the two 10Ah, 28V batteries on each of two Mars Exploration Rovers that landed in January 2004. These Li-Ion batteries continue to operate after over 5 years on Mars. Yardney's seventh and eighth Mars batteries are presently undergoing qualification to provide power to the 2009 Mars Science Laboratory (MSL).² The MSL has two 28V, 23Ah Li-Ion batteries in isolated parallel. Figure 9 shows a picture of the qualification battery being prepared for electrical and environmental testing. Figure 10 shows one of the extensive thermal models undertaken. This low temperature analysis shows the limited atmosphere causes most of the heat to be lost through the titanium bipods, power cables and by radiation.



Figure 9: 28V, 26Ah Mars Science Laboratory Qualification Battery.

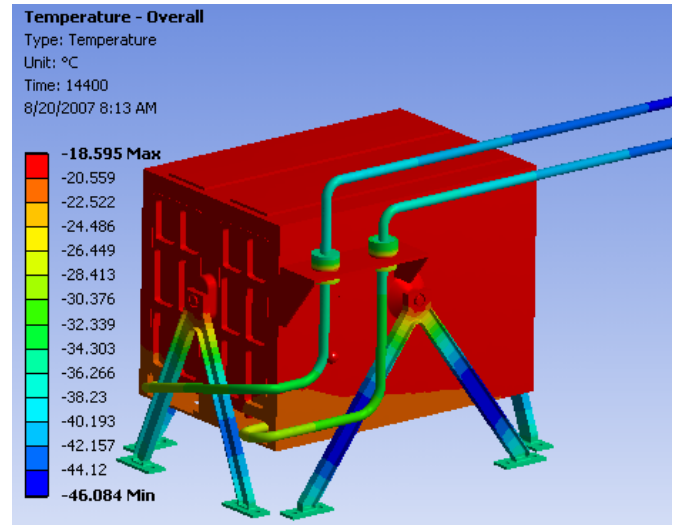


Figure 10: Cold Day Thermal Analysis to Determine Heater Sizing

CONCLUSION

High Energy and High Power undersea applications will continue to benefit from the capabilities of Lithium-ion technologies. Such applications benefit from the energy density, efficiency, and flexibility of the technology. Large format, high capacity, cells and batteries are best when specifically designed for the application, with appropriate performance, thermal, and safety concerns in place and well understood. Continued development of such systems for all types of manned and unmanned applications will provide robust systems under the sea, and beyond the stars.

ACKNOWLEDGMENTS

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