DESIGN AND PERFORMANCE OF LITHIUM ION CELLS FOR UNDERWATER ENERGY STORAGE AND POWER DELIVERY

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ABSTRACT

Li-Ion cell and battery technology has matured to the extent that it can be found in applications ranging from a few MilliAmpHours to more than a MegaWattHour. The technology has also advanced from its original low rate incarnation, supporting laptop computers, to designs specialized for high energy, high rate or low temperature. The present state-of-the-art designs support continuous discharge rates in excess of 100C and pulse rates exceeding 300C, leading to specific powers surpassing 10kW/kg. In applications such as the B2 Stealth Bomber, the operating temperature for the battery ranges from -40°C to 85°C. In contrast to applications such as the NASA's twin Mars Exploration Rovers where the batteries have allowed a planned 90 day mission to be extended to more than 1200 days and counting, despite low temperatures and high levels of ionizing radiation. Furthermore, Li-Ion cells, originally offered only in a ~1.1Ah – 18650 format (cylindrical cell that is 18mm in diameter 65 mm long), can now be found in capacities from 1mAh to 400Ah, or higher. The smaller cells are already being used in rechargeable human implantable medical devices and are being evaluated for rechargeable micro sensors. The medium sized cells (5Ah to 50Ah) are used primarily for military and aerospace applications such as: the Mars Exploration Rovers, the Mars Phoenix Lander, the B2 Stealth Bomber, a Lightweight Electric Torpedo, satellites and numerous Unmanned Underwater Vehicles (UUVs). The largest cells (200Ah and greater) have found a niche as the main energy storage systems primarily for naval applications such as the 8-ton, 1.2 MegaWattHour Li-Ion battery for the Advanced Seal Delivery System (ASDS), which the Office of Naval Research (ONR) has given a Technology Readiness Level 9 (TRL 9) designation, the Seal Delivery Vehicle (SDV) and various large format (30" diameter and larger) UUVs.

This customization of the cell size, shape and chemistry has been critical in the ability of Li-Ion to adapt to a wide range of applications. However, the ongoing safety issue with Li-Ion laptop computer batteries brings into question the safety of Li-Ion technology in military applications. This issue is further complicated by the widening gap between the needs of commercial and military markets leading to the replacement of premium raw materials with lower cost, inferior materials. This paper addresses the state-of-the-art of Li-Ion technology in both cell and chemistry design, including an analysis of available cathode and anode materials, while reviewing the enhancements to safety and energy density on the horizon. The paper also reviews battery safety from the chemistry cell and battery design standpoint. Finally, since Li-Ion battery technology, as a stand alone system, will not meet the energy requirements of all platforms, a review of Li-Ion technology as part of a hybrid system (e.g. Diesel/Li-Ion or Fuel Cell/Li-Ion) is discussed.

Since its accepted commercial inception in 1991 by SONY Inc., Li-Ion cells and batteries have undergone significant advancements. Initially offered in a ~1.1 Ah – 18650 format, this same size cell can now contain nearly 3 times the energy. Early Li-Ion cells found their home mostly in consumer electronic devices and toys. Today, Li-Ion cells are found in a multitude of varying applications; nearly every laptop, satellite, space craft, UUV, submarine, aircraft and more.

There have been many safety related concerns with Li-Ion over the years.

Technology has progressed so much that rechargeable Li-Ion cells are replacing many non-rechargeable, bulky medical batteries which allows entire devices to be implanted. The progression of Yardney's rechargeable Li-Ion medical cells can be seen in Figure 1.

There are three major types of secondary rechargeable batteries; Li-Ion, Nickel Cadmium and Nickel Metal Hydride. Li-Ion cells have many advantages over these other rechargeable cells. Most importantly, these cells store energy in the form of Lithium Ions. Lithium is the third lightest element and the lightest of all metals. Therefore, these cells are lighter, sometimes much lighter than their counterparts of the same energy. Lithium also has the greatest electrochemical reduction potential which makes it ideal for use in cells and batteries. The high cell voltage means that fewer cells need to be added in series to reach a certain battery voltage, leading to a lighter battery than the other major rechargeable battery technologies. Li-Ion cells do not suffer from the so-called "memory-effect", where discharging to levels less than full discharge and then charging leads to losses in energy capacity, like the Ni-Cd batteries. Micro-cycles and low Depths of Discharge have zero ill effects on the cell capacity or energy, making it the ideal chemistry for satellites and micro-sensors. All chemical batteries have what is known as self-discharge. Self discharge is a result of chemical reactions taking place within the cell leading to losses of the stored energy even without a load applied to the cell. Li-Ion cells have the lowest self-discharge rate (see Table 1) of the three leading rechargeable battery chemistries, making them ideal candidates for applications requiring batteries being stored off-line without access to a charger. NASA's twin Mars Exploration Rovers are a good example, where the batteries had to be stored on the craft's power buss getting power solely from solar arrays for the seven month cruise duration. A cell with higher self discharge rates may have required larger solar panels adding mass - which comes at an extremely high cost. It costs in excess of $50,000 to send one pound of mass to Mars, reducing the allowable scientific instrument payload.

Chemsitry	Ni-Cd	Ni-MH	Li-Ion
Self-Discharge per Month	15-20	20-30	5-10

Table 1. Self Discharge Rates of the three Rechargeable Cell Chemistries

The miniature Li-ion cells offer an affordable method for distributing remote sensors with long durations and, if needed, high power capability. Such systems can be recharged through solar power or by wave action as has been demonstrated by the University of Rhode Island. The batteries are also comparable in power capability (W/l and W/kg) to ultracapacitors and thus offer improved energy density, excellent self discharge and power. Figure 2 shows the state-of-the-art Li-Ion battery technology rate

Figure 1. Progression of Yardney's Various Rechargeable Li-Ion Cells

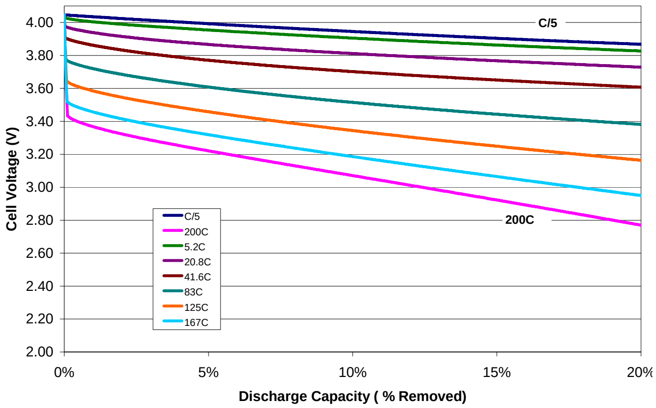

Figure 2. Li-Ion Rate Capability

capability. With the ability to support 200C pulses, several seconds in duration, power outputs exceeding 30kW/L are achievable for larger cells.

Today, Li-Ion cells come in a variety of formats, styles and chemistries. Typical Li-ion batteries have a positive electrode of aluminum, coated with a lithium compound such as lithium cobalt dioxide, lithium-nickel dioxide or lithium-manganese dioxide. The negative electrode is generally comprised of copper, coated with carbon (i.e. graphite or coke), while the electrolyte is a lithium salt such as lithium phosphorus hexafluoride, dissolved in an organic solvent mixture such as ethylene carbonate and di-methyl carbonate.

The majority of the cell formats are still based on the initial design of a 3 component wound core consisting of the cathode, anode and separator material tightly wrapped around one another. These bundles are then typically placed in a cylindrical, aluminum can and filled with electrolyte. There are also various safety design features that are incorporated into the cell design. This type of cell offers the advantage of high output production lines and low cost. It comes with disadvantages such as the difficulty in scaling up these wound cells into extremely large formats due to difficulty in obtaining lengthy, continuous, defect free rolls of separator, cathode and anode materials.

Figure 3. Yardney's NCP350 has a Capacity of Nearly 400 Ah and 1400 Wh

An alternative to the spirally wound, cylindrical cell is the “true” prismatic cell. Prismatic cells have the same base components as their cylindrical cousins. Yet they are typically manufactured with multiple positive and negative electrode plates stacked on top of one another with separator sheets between them. The advantage to this is that the manufacturer is no longer limited in cell size due to difficulties in processing capabilities handling extensive lengths of material. This type of cell design opens the door to innumerable shapes and geometries, efficient utilization of pre-defined volumes and envelopes. Yardney’s Sea Division has looked extensively into various cell geometries in order to maximize the utilized volume in various diameter tubes as would be typical in many UUV and other submersible crafts. The 1.2 MegaWattHour, 8-ton battery for the Advanced Seal Delivery System which uses Yardney’s NCP350 (see Figure 3) is one example of where the ability to create any shape

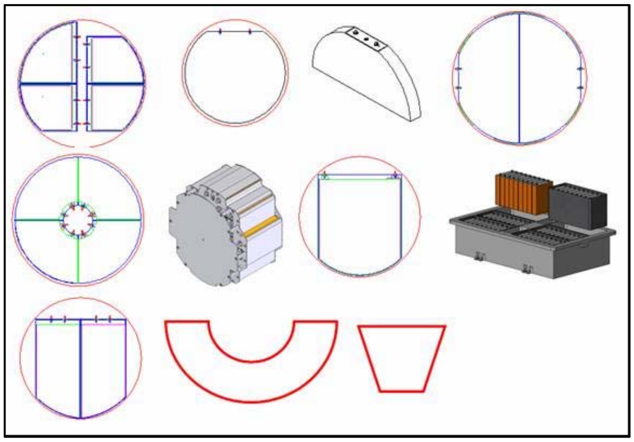

Figure 4. Various Cell Geometries Considered for UUVs

cell allows customization of these parts to efficiently fill available volumes. Figure 4 shows some of the other design options studied to fulfill the Navy's specifications. All of these design options are valid, prismatic cell designs. Broad trade-studies were performed prior to making the final selection. The cells not selected were excluded for various reasons. Certain cell and battery pack designs spawned from these cells left little room for the control and monitoring electronics. Some simply would fill up the tube lengthwise without being able to meet the energy requirements. Others would easily meet the length and energy requirements however they would be accompanied with project mass penalties or did not possess suitable paths for heat removal.

The final design of the ASDS battery was chosen for its safety, redundancy, modularity and simplicity. This battery is the sole source of power for the crewed vehicle. For such a critical and massive battery, it was important to keep the number of components to a minimum in order to maintain high overall system reliability. The large cells were essential to this progression. Fewer cells allowed us to create simple repeatable modules with simpler electronics having a small power consumption footprint, and fewer intercell connections which add to a battery's total impedence. This unnecessary heat generation reduces overall system efficiency and voltage at the load. Despite the use of the large format, 400 Ah cells, the entire battery system still utilized 1008 of these cells. The system was broken down into identical 9-cell modules dubbed Lowest Replaceable Units (LRUs). Alternatively, it would have required 150,000 of the modern 2.4 Ah – 18650s cells to create a battery of comparable energy, greatly increasing system complexity and reducing overall reliability. Battery management software and safety also benefit from the large format cells through keeping overall monitoring scan duration to a minimum. This leaves valuable processing time for the system to quickly communicate information to the host computer architecture and make important safety decisions based on the data. Li-Ion batteries typically do not respond well to overcharge. Although individual small cells may behave more benignly during an overcharge test, once packed into a battery, the mutual heating and PTC failure increase the catastrophic failure potential. As a result, the electronics system incorporated into this battery monitors the voltage of every cell in order to thwart any overcharge condition. The monitoring system includes various action steps based upon the level of cell overcharge detected (green, yellow and red) warning the operator of the increasing risk. If detected, the system will initially attempt to reduce the charge current to zero. The ASDS, being a manned system, next instructs the operator to terminate the charge manually. The third level of safety has the electronics automatically opening the charging contactors breaking the circuit.

No rechargeable battery is 100% efficient. Essentially, this means all batteries are going to self-heat while charging and discharging because of their inherent electrical and electrochemical impedence and thermodynamic properties. Although Li-Ion cells are extremely efficient, >98% energy efficiency, at lower than 1C rates extremely large format cells and high discharging rates can still generate a considerable amount of energy going to heat. The ability for a cell to exude heat to its surroundings via conduction is an important safety and performance design concern for high rate applications. Thermal management is one of the key concerns in designing a battery with high reliability and long cycle life. It is not merely average battery temperature that is of importance but also the temperature gradient between battery modules and cells. Li-Ion cells can degrade more rapidly when exposed to high temperature for an extended period of time. Battery temperature also affects the ability to provide discharge power and energy as well as charge acceptance.

These effects accompanied by existing cell to cell temperature variations in a battery can lead to electrically unbalanced battery packs, reducing the batteries overall performance. High temperature in a battery compartment has the potential to negatively influence temperature sensitive devices and subsystems located in proximity to the battery thus decreasing the reliability or life of the entire system.

Evaluation of the battery design for the Navy's ASDS involved sound engineering practices. The approach included finite element thermal analysis of heat transfer and fluid flow as well as thermal imaging techniques on a prototype battery system. In submersible systems where weight is a key requirement it was imperative to incorporate passive thermal management techniques into the design in order eliminate the need for heavy active cooling systems and components which not only add weight but take away from the systems overall energy. The thermal conductivity of the cell core is anisotropic. The cell simply cannot move heat equally well in all directions. Since the positive and negative electrodes are coated metal substrates, it is easy to move heat in directions parallel to the plates within the plate substrate itself. The coatings do not transfer heat nearly as well as the metal, producing a much lower thermal conductivity in the direction perpendicular to the plates, through the coatings. This is nearly an order of magnitude less than that of the parallel directions. The final battery design uses the true prismatic NCP350 which conforms to the bottom of the battery tube, creating an excellent path for heat flow that is nearly identical for each cell in the battery. This feature minimizes cell to cell temperature gradients extending battery life and increasing battery performance. Figure 5 depicts the thermal analysis of one of the 9-Cell repeating modules during normal operating conditions and clearly shows the negligible cell-to-cell thermal gradient as well as a minimal temperature variation within a cell. It is easy to see the uniform heat transfer path through the bottom of the cell removing heat from sensitive electronics, into the battery bottle and out into the sea water as quickly as possible. The ability to remove heat in conjunction with the fact that Li-Ion cells do not "outgas" during charge/discharge provide UUVs and other submersible crafts with the ability to charge within a pressure hull. This offers the crafts extended mission durations and reduced mission turn around.

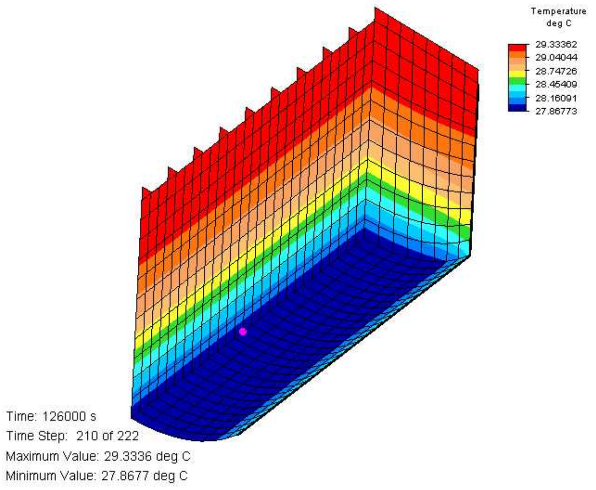

Figure 5. Thermal Analysis of ASDS LRU Under Normal Operating Conditions

Aside from analyzing the physical design characteristics of Li-Ion cells and batteries, Yardney has performed extensive research and testing on various chemistries suitable for typical manned and unmanned submersible vehicles. Figure 6 compares Li-Ion technology to other battery technologies under consideration for UUVs. Li-Ion is divided into three separate sections which correspond to the combination of the highest usage rate and temperature at which that rate will be required. The "HP" bubble relates to the highest power systems, those capable of a continuous discharge exceeding 20C and pulse rates exceeding 100C. A 4 kWh cell can provide a little over 5 horse power for one hour. At 20C this is equivalent to 100 hp for approximately 3 minutes allowing for a significant sprint capability. The "Typical Military" bubble corresponds to the general performance window

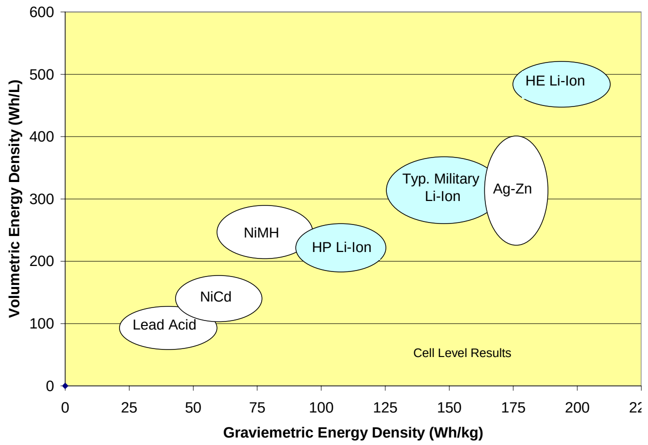

Figure 6. Battery Technology Energy Densities

of fielded military systems. Typically these systems are compatible with performance down to -40°C and discharge rates from 3C-7C, though not both concurrently. The “HE” bubble corresponds to system where discharge rates are 1C or lower and the temperature is no colder than -20°C. The separate performances are a result of anode and electrolyte diffusion limitation but, in theory, the chemistry does allow for any value between the windows to be achieved. While values approaching 200Wh/kg are more familiar the most striking feature is the demonstrated achievement of over 525Wh/L in militarized systems. The specific energy and energy density values given for Li-Ion can thus vary by well over a factor of 2, depending on use.

Further complicating the true performance of Li-Ion multiple chemistries exist. To sort out performance characteristics, each chemistry was used to design a 1400Wh Li-Ion cell. Cell width was varied to account for the volume changes needed to maintain 1400Wh for each design. The results are shown in Figure 7. The difference in performance between $LiNiCoAlO_2$ and $LiNiCoMnO_2$ is sufficient enough so that LiNiCoMnO2 would not have met the ASDS energy requirements. An initial view of the performance of $LiNiCoAlO_2$ calls into question why the other materials are used. This is countered by the fact that the prevalence of $LiNiCoAlO_2$ in cells in decreasing while other materials are increasing. The two factors driving this change are safety and cost. This cost is derived by the amount of Nickel and Cobalt in the powder. The $LiNiCoMnO_2$ has a slightly less reactive event on abuse tests but is still very susceptible to cell to cell event propagation. The $LiMn_2O_4$ materials have significantly less violent reactions with cell to cell propagation in question. The amount of chemical energy stored to deliver the electrochemical power is markedly lower in the Iron Phosphate materials (Figure 7) and the Oxygen is not readily available during the overcharge event. It should be noted, however, that once a thermal runaway reaction begins the level of energy (heat) liberated to support the reaction is much higher than is depicted Figure 7. Thus, the LiFePO4 system does not undergo cell to cell event propagation and is more forgiving to abuse conditions.

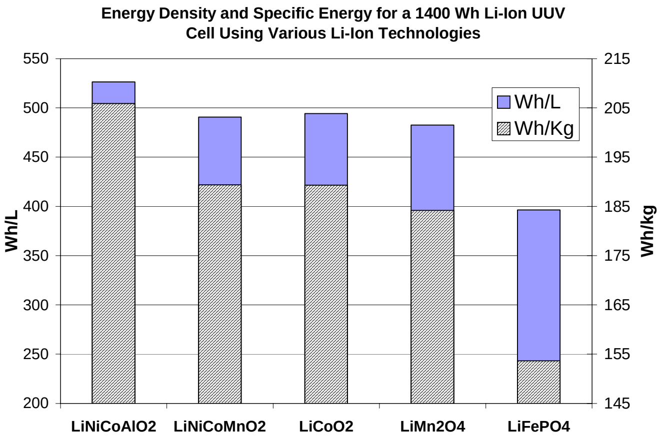

Figure 7. Various Li-Ion Energy Densities

The evaluation of alternate technologies is needed because the best Li-Ion technologies can meet only the lowest end of the energy density goals for many applications and missions. While this paper does not intend to concentrate on the specifics of alternate fuel sources, it is important to note that many of the larger UUV systems under design are planning to utilize either diesel engines or fuel cells as methods to recharge the batteries. Space is often at a premium in UUVs. Figure 8 compares the space needed for energy storage. This figure is

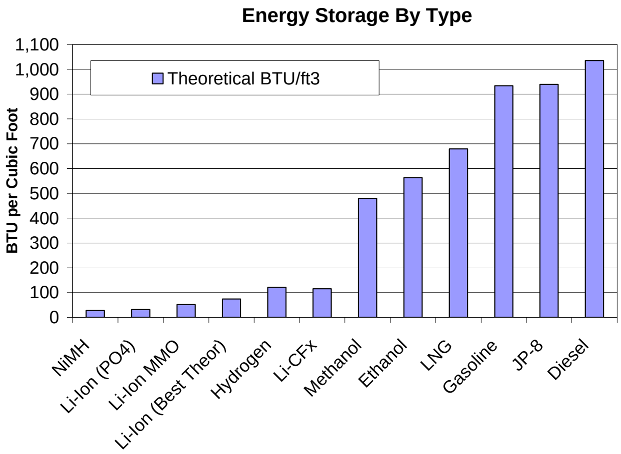

Figure 8. Theoretical Energy Storage per Cubic Foot of Various Fuel Systems

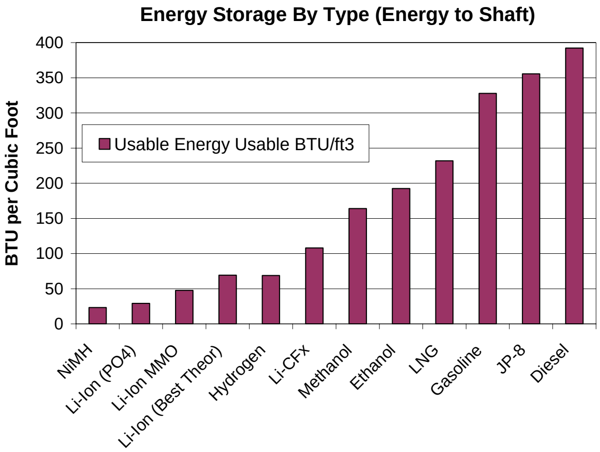

Figure 9. Delivered Energy Storage per Cubic Foot of Various Fuel Systems

for the energy storage system only and not for the fuel cell, engine, intake and exhaust piping, cooling and other components that are required. At present, high energy fuels store 20 times the energy. Figure 9 takes into account the energy that would be available "at the propeller" from the various systems by adding in energy conversion losses. The efficiency results in this figure assume the UUVs are primarily driven by an electric motor. Ultimately, the organic systems remain over 800% more volumetrically efficient. This is sufficient to overcome the volume requirement for the engine or fuel cell, if air breathing is assumed. Though if Oxygen storage is required (e.g. for underwater operation) the volumetric balance and gravimetric balance shifts dramatically.

Another option meeting mission energy requirements takes advantage of the fact that the energy systems are designed around mission profiles. Some devices have energy requirements following a traditional bell-curve distribution probability such that the maximum energy requirement is only required for a small fraction of the proposed mission profiles. One possibility is to utilize primary (non-rechargeable) batteries to bolster energy storage for the small portion of missions requiring the maximum energy density. The Lithium Carbon Monoflouride (LiCFx), at up to 750Wh/kg and over 1150Wh/L could be a good fit for low rate energy usage. This type of "boost" battery can be attached as an external pod. The safety characteristics of any Lithium primary system must be fully appreciated before such an option is considered, especially since some systems (e.g. Thionyl Chloride) can create very violent failure modes and dispel toxic components. When the more violent failure reactions are combined with cell chemistries prone to failure from overheating or crushing, the rate of event propagation from cell to cell can be exceedingly fast, leaving no time to react to the event. The cell or battery design should, at a minimum, contain features to limit the rate of propagation.

In one sense, the energetic abuse failures of high energy density battery systems can be explained by looking at the heat capacity of the batteries; Cp=0.08Wh/(lbm-°F). Traditional Li-Ion at 200Wh/kg (or 91Wh/lb) having an internal short, where all electrochemical energy goes into the cell itself, results in a Cp dictated temperature rise of over 1100°F. At elevated temperatures, the cell cases either melt or rupture, releasing highly compressed and flammable components. This problem is worsened in Lithium systems of higher energy densities. The only mitigating factor sometimes being lower electrochemical reaction rates that allow for the heat to be dissipated fast enough preventing instantaneous cell disassembly.

Li-Ion technology has advanced greatly during its existence. These advancements provide Li-Ion batteries with characteristics ideal for UUV technology. High energy and power densities afford UUVs the luxury of increased mission times and speeds. Li-Ion batteries, with the capability of charging in a pressure hull, high reliability and low maintenance requirements, are an ideal solution for UUV power and energy storage.