THE COMMERCIALIZATION OF LITHIUM BATTERY TECHNOLOGY

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INTRODUCTION

Last year, lithium battery recalls reached an unprecedented level, with mostly all the computer laptop manufacturers initiating significant programs to replace specific production runs of batteries. Even syndicated cartoons and Internet blogs poked fun at the safety problem. From the R&D days to last year's recalls - the journey has been a bumpy ride for the end-user.

In the history of the battery industry, one could dub 2006 as the "Year of Lithium Battery Recalls." This paper will briefly cover lithium-anode battery commercialization from the early R&D days to various present day applications. It will trace the use of lithium technology as an emerging power source technology in the 70's and 80's. In the 90's, lithium batteries gained much wider usage and became an enabling technology in many applications. Lithium technology replaced a variety of water-based battery systems. However, using lithium technology also surfaced some unique safety related incidents beyond its predecessor water-based chemical systems. Although we believe we can engineer systems to mitigate the safety risk, we are periodically reminded that these lithium systems are very different than the power systems they replaced. It has been said very often that we don't learn well from history.[i] In my experience, the safe use of lithium battery technology is achievable, even though the commercial roadmap has been bumpy (speed bumps) when using lithium technology in new applications.[ii]

THE BATTERY INDUSTRY AND MOORE'S LAW

Before we review some lithium battery safety issues, let's first focus on a few perceptions of the battery industry. There have been many advances in power source technology since World War II. We would not have been able to land on the moon and return the astronauts safely to earth without advancements in battery systems. The "real" advancements in batteries technology are not in the newspapers or the six o'clock news. But when a battery catches on fire or explodes, that incident will surely make the headlines.

Some system designers compare the battery industry to the semiconductor industry from a technology maturity point of view. They compare the advances in both industries and expect Moore's Law to govern in the energy conversion arena. Unfortunately, that is not true. These two technology bases are very different. The battery industry has been around for about 200+ years. Its product produces DC power while it consumes materials. With chemical batteries, the key process is an electrochemical reaction that generates electrical power to an external circuit. In comparison, the semiconductor industry produces a variety of "solid-state circuits" that use electrical power. These two industries are essential partners. But their advances do not parallel. The science and engineering principles applied to their respective end products are different. Battery design, development, and production manufacturing use a different set of materials, different design principles, and different production processes. Moore's Law can not apply. In reality, Moore Law is not a "scientific law" at all.[iii] Tuomi says it is an empirical observation, cleverly formulated.

Can I really say that some of these lithium-ion fires and explosions follow Murphy's Law[iv], No, I cannot! Murphy's Law is also not a law at all. So, what empirical observation can I make about the Battery Industry with its inherent and reoccurring problems.

The Realities and Complexities of Manufacturing Chemical Batteries

Chemical batteries are enabling technology in portable electronic equipment. Their runtime is limited. Some designs are rechargeable. However, there is a performance tradeoff to engineer a rechargeable chemical battery. There has been significant amount of time and money spent on design, development, and production engineering from government and commercial ventures. Although very good work has been done, the final production product can vary from batch-to-batch runs and even within a single production run on an automated line the service hour capacities are not gaussian distributed. The industry has traditionally had problems with sealing batteries. Haven't we all seen that "white fuzz" on our alkaline flashlight batteries or, with lead-acid, the "blue-green fuzz."

Battery manufacturers have had raw materials problems that vary in purity levels and contamination issues.
These materials are inherently toxic or corrosive or flammable, and some electrolytes lose properties over time. In addition, the "real" laws of science have theoretical limits. As soon as a cell is manufactured, it starts to self-discharge, and its performance is highly dependent on actual use, which might not be really what the cell was originally designed for. Battery manufacturers tend to design a particular cell for a specific application. Once that design is in production, and is readily available other uses are found but not for that specific size. Sometimes the scale-up or scale-down in size is non-linear. So performance variation is not consistent within a family of sizes. More importantly to Lithium developments is the demand to increase energy density. The result is that the manufacturer will cram more material into the enclosure and reduce the thickness of the separator. For example the Sony's Lithium-ion cell 18650, used in many recalled laptop batteries, followed that trend. Does anyone remember the half-gram transportation rule? This cell qualified under that rule in 1991 but it does not today.

The Personality of Chemical Batteries

In my opinion, the best description of the nature of chemical batteries can be found in Per Bro and Sam Levy's book entitled, *"Quality and Reliability Methods for Primary Batteries."* They claimed that **"batteries are unique……living, dynamic systems that respond to their environment….not observed by with other electrical components."** My extension is that like living things, they have a quality much like our human personalities. We are inherently different. Some of us have the ability to perform at high levels, while others can't. We also have a tendency for "thermal runaway" if someone pushes the wrong button.

The early history of lithium battery developments focused on understanding the science and engineering the best designs. Some safety issues in those early use cases and the repetitive shipping transportation problems illustrated a unique hazard level associated with lithium. We know that lithium is hazardous. We also recognize that other materials used in other electrochemical batteries are hazardous. We also had experience with non-lithium systems having safety problems. So why can't we do better with deploying lithium batteries safely? It seems that we have to re-learn those lessons again.

Lithium - The Mystery Metal

Nehemiah Margalit, a research chemist, maintained that the development of lithium anode technology opened a new dimension to battery research, the selection of cell voltage.[v] The product of voltage and capacity determined the energy content of these new systems. There have been over 200 different lithium couples investigated over the past four decades. About two dozen systems made the cut into some markets. However, there have only been about one dozen couples used in sustaining applications for one reason or another. In the early days, researchers looked at replacing the standard 1.5 volt cells with some advanced lithium systems like Li/Copper Sulfide and Li/Iron Sulfide (which can be found today in Walmart stores). Table 1 shows the half cell potential of lithium verses other traditional anode metals.

Table 1 -Anode Material Comparisons[vi]

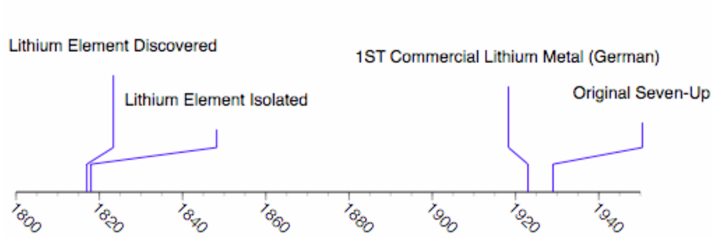
Material	Standard Potential (V)	Density (g/cm)	Electrochemical Equivalents (Ah/g)
Li	-3.01	0.54	3.86
Mg	-2.71	1.74	2.2
Al	-1.66	2.69	2.98
Zn	-0.76	7.14	0.96
Fe	-0.44	7.85	0.82
Cd	-0.4	8.65	0.48
Pb	-0.13	11.34	0.26
	-0.13	11.34	0.26

The higher 3+ voltage primary lithium cells were developed for the Department of Defense (DoD) and NASA space requirements. Even Detroit understood the potential advantage of Lithium and also started IR&D battery programs before the Clean Air Act.[vii]

As an element, lithium was discovered in the early 1800's. Lithium salts are one of the first commodities that gained usage in the marketplace. Lithium metal and lithium alloy metals followed in the marketplace. There is some indication in the literature that Lewis pioneered using lithium as an anode material, but I could not confirm that. The initial limited availability of lithium metal did not make it attractive to use as an anode material in lithium batteries. The increase in production of lithium did not occur until after World War II for military weapons programs.

Timeline 1 shows key milestones of lithium as a material in the commercial sector.

Timeline 1 – Lithium the Element



LITHIUM ION AND THE RECALLS OF 2000

Some battery technologists will tell you that with the high usage rate of lithium-ion batteries in cell phones, digital cameras and laptops, there were bound to be safety issues. A one-in-million failure rate triggered a recall of almost six million lithium-ion packs used in laptops. Seems like a low probability event. Sony, the maker of the 18650 lithium-ion cells built battery pack, said that microscopic nickel particles may have lead to a short circuit within the cell. A soft short will only cause an elevated self-discharge. Little heat is generated because the discharge current is low. If, however, enough microscopic nickel particles converge on one spot, a major electrical short can develop and a sizable current will flow between the positive and negative plates. This causes the temperature to rise, leading to a thermal runaway, also referred to "venting with flame." Lithium-ion cells with cobalt cathodes (same as the recalled laptop batteries) should never rise above 130°C (265°F). At 150°C (302°F), the cell becomes thermally unstable, a condition that can lead to a thermal runaway, in which flaming gases are vented. During a thermal runaway, the high heat of the failing cell can propagate to the next cell, causing it to become thermally unstable as well. In some cases, a chain reaction occurs in which each cell disintegrates at its own timetable. A pack can get destroyed within a few short seconds or linger on for several hours as each cell is consumed one-by-one. To increase safety, packs are fitted with dividers to protect the failing cell from spreading to neighboring cells. [viii]

Lithium-Ion Innovation

The invention of an intercalation battery electrode technology is a landmark solid-state chemistry achievement. This really made possible the "rechargeability" of lithium (lithium-ion). Lithium and lithium alloys are not good reversible electrodes. Credit goes to the inventors of this technology. Dr. John Goodenough, while at Sony, invented the specific lithium-ion "cobalt" system and Dr. M. Stanley Whittingham researched the basic intercalation mechanism of lithium.

Lithium-ion Battery Goes Commercial

Since the cell was introduced in 1991 in the marketplace, its evolution has been remarkable. The numbers being made in a production mode are very impressive. For the past decade, the lithium-ion cell's energy density content doubled. This was what the OEMs wanted. However, did this increase lead to a cell design that traded-off safety levels? One fact not widely known is that Sony had a fire at their battery plant in 1995, which suspended production. Battery plant fires also occurred at other lithium battery companies in the US in the 70's and 80's. It appears that there is no single source collecting these data. I know that this is a relationship stretch. I maintain that if you have problems making something, that those problems are early indictors of the potential level of hazard that can exist in the final product.

IEEE Standard

The Battcon attendees are very familiar with the IEEE Standards. There are many. We all know the benefits of standardization. From a commercial advantage it makes a product more sellable and its value increases. However, I am not so sure the IEEE Standard 1625 made any difference with respect to the Sony cell safety hazard. The standard appears to be weak in areas that should have addressed manufacturing process variability. I believe that the specific IEEE Standard 1625 needs to be revised since there is now the recall "field use" history.

IPC – A New Standard Effort

Below is the press release of a new effort to establish a quality standard to be used by the battery manufacturers:

IPC OEM CRITICAL COMPONENTS COMMITTEE TO DEVELOP STANDARDIZATION FOR MANUFACTURING LITHIUM ION BATTERIES

Bannockburn, Ill., August 16, 2006 –IPC – Association Connecting Electronics Industries has announced that its OEM Critical Components Committee, which includes representatives from Dell Inc., Lenovo and other major computer manufacturers, will hold a technical summit meeting in mid–September in San Jose, Calif. to begin development of standards for the manufacture of lithium ion batteries for portable and handheld electronics.

"Without a doubt, standardization can and will address the issue of operation and safety called into question by the use of lithium ion batteries. While the Committee had identified lithium ion batteries as the next product for standardization, we are going to accelerate our activities now," said John Grosso, chairman of the IPC OEM Critical Components Committee and director of supplier engineering and quality, sub-tier and critical components, Dell Inc.

The IPC Committee, according to Grosso, will identify any current standards related to lithium ion batteries with the goal of standardizing design, performance and safety requirements for these batteries.

"The IPC Committee has been very active in identifying and working to standardize components vital to the function of products in the computer and telecommunications industry," according to Anthony Hilvers, IPC vice president of industry programs. He added that the committee has recently completed a standard for fans for electronics applications and is also working on standardizing performance parameters for power conversion devices for electronic products.

About IPC IPC (www.ipc.org) is a global trade association based in Bannockburn, Ill., dedicated to the competitive excellence and financial success of its 2,400 member companies which represent all facets of the electronic interconnection industry, including design, printed circuit board manufacturing and electronics assembly. IPC is a leading source for industry standards, training, market research and public policy advocacy and supports programs to meet the needs of an estimated $3.4 trillion global electronics industry. IPC maintains additional offices in Taos, N.M.; Arlington, Va.; Garden Grove, Calif.; Stockholm, Sweden; and Shanghai, China.

This same effort was tried before, with limited success, by the US government in the early days of primary lithium battery developments.

LITHIUM BATTERIES - THE EARLY R&D DAYS

Non-Government R&D

In the early 60's, some companies had IR&D programs to look at lithium as an anode material in "high-energy" density batteries. The early heart pacemaker devices were powered using zinc-mercury cells. There were shorting problems and limited service life. The market wanted longer service life and greater reliability. The lithium promise for medical implantable devices had a fair number of battery companies competing for that market. Although there were a variety of lithium-couples under research and development for the medical market, the Lithium-Iodine system quickly won the race powering heart pacemakers. As we all know, Dr. Wilson Greatbatch pioneered that pacemaker industry first with zinc-mercury batteries (1956). Throughout the 70's, the lithium-iodine development efforts improved the reliability replacing the mercury cells. Today, that specific market sector is commercialized and sustained by these solid-state lithium systems.
I consider this a true business success story. A small company in Baltimore, Maryland called Catalyst Research discovered this couple (U.S.P. 3,674,562) in the late 60's while researching new methods of manufacturing electrochemical batteries in situ.[ix]

US Government R&D

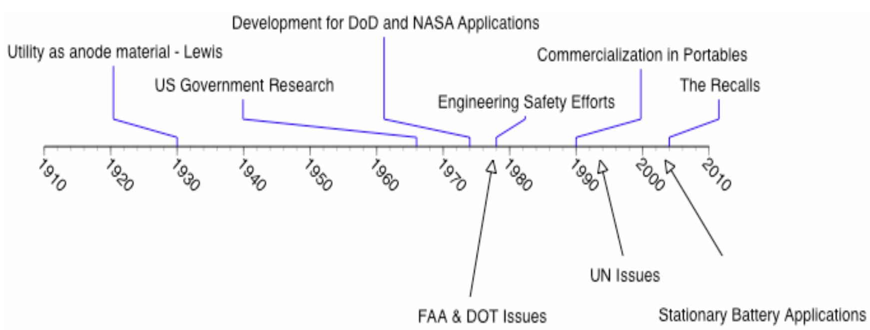
In the early 70's, the Power Sources Division of the US Army Electronics Command (ECOM), Fort Monmouth, New Jersey sponsored primary lithium battery developments. They recognized the lithium promise of high voltage, high energy density lithium-anode batteries could give to the next generation soldier mobile communication equipment. Like most battery developments, there were a variety of electrochemical couples that competed with one or two finally making it into the military stockpiles. For soldier communication, the BA-5590, lithium-sulfur dioxide system was used during the 80s and 90s. These lithium batteries served the military well in the Gulf War. It was also recognized during the 70s that "safety" was an issue. Some explosions and fires occurred during initial testing. In addition, the US Army's lithium battery developments had to deal with the environmental impact and transportation shipping issues that surfaced in the mid-70s. The major thrust of safety related efforts focused on the cell design and user abuse conditions. DoD only gave battery manufacturers a specification for the final battery package, allowing each supplier freedom to design abuse resistance in their specific cell designs. Designs with the anode limited, cathode limited, and balanced designs were evaluated. In some other lithium couples, the cell case polarity would be considered a design trade-off issue. Even the container's polarity became an issue in studies with case positive, case negative, or case neutral designs. The chemical reaction processes and products of the reaction were also investigated, including parasitic reactions.

The priority issues in safety testing were the identification of user or environmental abuse conditions. Educating the user and the equipment designers on proper handling, proper battery pack design, proper shipping, etc., resulted in a number of safety manuals being issued by DoD. Mostly all of the Department of Energy (DOE) and its Federally Funded R&D Centers (National Labs, i.e. Sandia) contributed advancement in understanding lithium battery design and safety limits.

Aircraft Fires and the Search for a "Safer" Design

The Federal Aviation Administration (FAA), within the Department of Transportation, was one of the first government organization to be confronted with lithium battery safety issues. In the early 70's, some battery manufacturers courted the aircraft Emergency Locator Transmitters (ELT) market, because the lithium-sulfur dioxide battery was able to handle the new FAA low temperature operating specification for ELTs. This specification was in response to the tragic loss of Congressmen Hale Boggs (D-LA) and Nick Begich (D-AK) in the Alaskan wilderness on October 16, 1972. A massive search effort failed to locate them. The result was a U.S. law mandating that all aircraft carry an emergency locator transmitter[x]. Unfortunately, this occurred before most of the US army's safety work on electrochemical balanced designs. The FAA at one time recorded about 500 safety related incidents in US civil aircraft. The Commercial Airlines also experienced some fire and venting of gases. Fortunately none occurred in flight. As a result of these safety incidents, FAA convened a study group and later issued the Technical Standard Order C97 (which evolved into TSO-C142 in 2000). The TSO (order) established battery design standards, and safety testing qualification requirements. The Office of Hazardous Materials (OHM), responsible for transportation regulations, quickly learned of the FAA's ELT problem. OHM notified each lithium battery manufacturer that they must request to be a party to a special exemption for shipping before they could resume transport in commerce. This was the birth of DOT-E-7052, which I call the longest running exemption in DOT history with the most parties to an exemption. DOT-E-7052 established packaging standards and required warning labels and placard standards. As the exemption matured, OHM added some testing requirements. In the early 90's, DOT-E-7052 was incorporated into the packaging performance tests of the UN international shipping regulations. The half-gram rule which allowed any lithium battery to be shipped unregulated survived the UN transition.

Timeline 2 – Lithium Batteries



During the late 70's, Underwriters Laboratories would also join the ranks of companies looking at the safety issue with lithium batteries in the Public Interest. They would establish UL 1642 Standard and recognize some manufacturers in their recognized components program. Under this program, UL would visit battery companies to inspect the quality of manufacturing.

Navy Lithium Battery Safety Program

The Navy took a very serious approach to safety in the late 70's with lithium batteries. They centralized the approval process for all Navy lithium battery procurements under NAVSEAINST 9310 (1979), essentially leading to the establishment of a process for the development, testing, qualification and approval of all lithium batteries for use by the Navy and the Marines. The Navy claims that they have the best safety track record[xi]. The Navy's Lithium Battery Safety program was a result of early indications of safety related accidents - seven personal injuries were reported during the period 1976 through 1983, including one death.[xii] The stated goal of the Navy program is to minimize risk to personnel and platforms while allowing the use of lithium batteries to advance military capabilities. The latest version of the Navy's Instruction document is NAVSEAINST 9310.1c. The Army issued Mil-PRF-49471 to deal with non-rechargeables and Mil-PRF-32052 to deal with rechargeables. About two years ago, the Navy and the Army worked out joint certifications[xiii] for lithium battery safety testing, since a large number of batteries overlap in similar equipment.

Lithium Battery Safety Working Group

To deal with the Federal Government's Lithium Battery Safety issues, DoD and other Federal Agencies established a technical working group called the Lithium Battery Safety Working Group.[xiv] This working group met regularly during the 80's and 90's. The group shared pertinent information and continues to meet today on field use experience and testing results of newer lithium chemistries.

NASA Man Space Mission Requirements

Batteries for space missions are custom designed and fabricated to meet mission requirements.[xv] It is for this reason that the National Aeronautics and Space Administration (NASA) has been very successful on safety. Some experiments in space were conducted using commercial off-the-shelf batteries, but those were rare. Throughout NASA's 50 year track record, they developed a unique methodology to design and engineer reliable and safe battery supplies. NASA has been known for "multi-level" redundancy. No single point failures allowed. As a fellow battery colleague once said – "Hubble had problems – but the battery worked".[xvi] NASA power requirements for man-space mission required a high level of reliability in batteries. Their approach was to issue a specification to the battery manufacturers very early in the development phase of a cell. When NASA felt that a specific battery would reach the qualification stage, they would re-issue the specification with a requirement that the manufacturer use an "approved" Manufacturing Document Control (MCD)[xvii] in the building of cells for actual use. Their approach for the MCD comes very close to the IPC effort.[xviii] NASA also sponsored and hosted annual battery workshops. These workshops provided an opportunity to exchange information on a variety of topics on battery developments for NASA, and views regarding perceived trends in technology. In 1980 I was asked to chair a panel discussion on lithium safety at the Goddard Space Flight Center Battery Workshop. We dealt with some legal issues of product liability, workers compensation, and hazardous warning labels. What also surfaced were issues of heat management with larger cell sizes, an avalanche effect of cells in battery packs, the observation that more energy packed per unit volume will raise the magnitude of the safety incident, and the battery industry in a perpetual development phase. Essential in one panel member's opinion, "batteries are never out of the development phase" and into a production phase.[xix]

MARKET DRIVERS FOR BATTERY INDUSTRY

The Department of Commerce did a study (working paper 05-01) under the auspices of the Advanced Technology Program (NIST) on Li-ion manufacturing. The results of this study are only published on the Internet.[xx] I highly recommend you read this paper, because it captures the US Battery Industry's R&D and production status. It details the "actual" market drivers, which have an important affect on products available to those markets. Safety maturity from designs through high volume production of chemical based energy conversion devices are indirectly related to these market drivers. It also illuminates the cost of manufacturing and decisions that "big" battery companies have to make for the commercial and government markets. With the assumption that future battery and other technologies may be expected to experience commercialization pathways similar to the Li-ion case, this study sought answers to the following questions:

- Why are there no large volume producers of rechargeable Li-ion batteries in the United States?
- What are the factors affecting the introduction of new technology into the marketplace?
- What are the implications of the findings for other developing technologies, for example, fuel cells, displays, and other electronic components?

As future requirements for Lithium-ion technology expand, we will see some large scale manufacturing activity based in the US in the near-term future.

Battery Pack Configurations, Standards, and Qualification Testing

I have selected a number of papers that warrant comment from previous Battcon and Intelec conferences. The Table 2 lists these papers noting key points in those papers that relate to safety.

Table 2 Presentations

Paper Title	Conference	Key Points
The Shape of Batteries to Come	Battcon 2006	System Designs for the Future
Low cost, convenient, battery health assessment: Who needs it?	Battcon 2006	Health Assessment
Intelligent Battery Charging: An Alternate solution to you battery woes	Battcon 2006	Battery charging
Advanced System Management for Stationary Standby Batteries	Battcon 2006	A new Paradigm – State of Health all the Time
Building and Fire Code Requirements for Stationary Storage Battery systems	Battcon 2006	Lithium-ion batteries added to Code
Lies, Damned Lies and Statistics: The Statistical Treatment of Battery Failures	Battcon 2004	No mention of quad-redundancy
Parallel Strings – Parallel Universes	Battcon 2002	Misinformation in the Battery Industry
A New Approach to Qualification of Lithium-based Battery Systems	Intelec	Special Case for Qualification on two Grounds and Each Cell measured

SUMMARY

Lithium batteries have had commercial success in many applications and consumer products. I fully expect lithium batteries to find applications in the Stationary Battery arena. The manufacturers are interested in your application area and will work together with you to provide the systems you need - trouble free. I believe that if we learn from our past experience and respect the potential safety hazard level of lithium batteries, we can benefit from the advantages and lower the risk of damage to property and human life. Table 2 lists a few papers I maintain are very important in setting a tone for safe deployment of these systems. I know that there have been some pilot or demonstrations with these systems. I don’t believe that there have been any safety related problems with those deployments. However, I caution us all to evaluate the potential hazard and design systems with that in mind. Today’s technology advances in sensors and state-of-health indictors allow us to monitor these battery systems all the time. Reliability is part of the safety equation. Well-crafted qualification tests will surely yield better results. The battery manufacturers do know how to make the products, but the end-user really understands the performance domain of the batteries. This conference and a few others are excellent forums to exchange information.

Electrical shorts are just one abuse condition for a chemical battery. It is easy to understand the external short. The internal short is subtle. You might not be able to detect it until it is too late. Electrical shorts have traditionally been a problem for all chemical batteries, except solid-state system designed for very low current drains. These shorts potentially discharge batteries before there calculated end-of-life. They have started fires. And in some cases even ignited hydrogen gas explosions. The incorporation of safety testing into the qualification test matrix will enhance the safety envelope for use.

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[i] McDowall, J, *"Is History Repeating?,"* proceedings of Battcon, 2004.
[ii] McDowall, *"Life in the city,"* proceedings of Battcon, 2006
[iii] Tuomi, I, "The lives and Death of Moore's Law," http://www.firstmonday.org/issues/issue7_11/tuomi/index.html
[iv] http://en.wikipedia.org/wiki/Murphy's_law
[v] Gabano, J.P, *"Lithium Batteries,"* p183, Academic Press, London, 1983
[vi] Linden, D, *"Handbook of Batteries and Fuel Cells",* p1-8, McGraw-Hill, New York, 1983
[vii] Camp Market Report, *"The Government Battery and the Fuel Cell Market,"* Frost and Sullivan, 1972
[viii] http://www.powerpulse.net/techPaper.php?paperID=131&page=2
[ix] Alan Schneider, co-inventor U.S. 3,674,562, private communication.
[x] http://en.wikipedia.org/wiki/Emergency_locator_transmitter#History
[xi] http://www.safetycenter.navy.mil/presentations/conferences/amsc/2004/sourcefile/lithium.ppt
[xii] ibid.
[xiii] Winchester c. and Kernan,d., *"Lithium Battery Safety, Good Batteries, Gone Bad,"* proceedings of the Joint Service Power Expo, 2005
[xiv] I co-authored the original charter
[xv] http://trs-new.jpl.nasa.gov/dspace/bitstream/2014/12059/1/02-0885.pdf
[xvi] Methlie, G.J., private communication.
[xvii] Goddard Space Flight Center, *"Specification for AeroSpace Nickel-Cadmium Storage Cells"*, S-761-P-6, para. 3.2.1 MCD, March 1971
[xviii] "Sealed-cell Nickel-Cadmium Battery Applications Manual, " NASA Reference Publication 1052, pp 234-243, December 1979.
[xix] Panel Discussion, *"Safety- Whose Responsibility?",* pp 119-139, proceedings of the GSFC Battery Workshop 1980
[xx] http://www.atp.nist.gov/eao/wp05-01/chapt1.htm