Design Considerations for Lithium-ion Cells
Part I: Cell Components

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1. Introduction

Development of lithium-ion battery systems, a relatively new technology in comparison to conventional rechargeable battery systems, has encompassed an extensive number of design considerations. These considerations are based primarily on safety, performance and cost. In this paper we will discuss the design considerations for lithium-ion cells at a cell component level. In a future paper we will expand our discussion to cell assembly considerations including electrode and cell design and manufacturing.

1.1 Background

Lithium-ion batteries have rapidly become the rechargeable battery of choice for many applications, including portable computers, cellular and personal phones, video cameras, minidisk players and portable data terminals. Performance and safety are the two important design considerations however, cost and availability have been two critical factors slowing the introduction of lithium-ion batteries into a broader range of applications. In this paper we will investigate the issues involved in the design of lithium-ion cells. Through innovative design and material choices, the cost of lithium-ion cells can be reduced and the performance improved while maintaining a high level of safety. Cost reduction and increased availability will lead to the proliferation of lithium-ion batteries in applications that use conventional rechargeable batteries today.

1.2 Description of the Technology

Lithium-ion cells evolved from earlier lithium metal battery technology. Primary (or single-use) lithium metal batteries were first used in the 1970s'[1]. In

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[1] Linden, D., Handbook of Batteries, McGraw-Hill, 2nd Ed., 1994, Chap. 14: Lithium Cells.

the 1980s secondary (or rechargeable) lithium metal batteries were commercialized.[2] While primary lithium metal cells continue to be used in both commercial and military applications requiring high energy[3], most secondary lithium metal battery manufacturers stopped production after safety issues arose. The problem in the rechargeable cells was related to the reactive, high surface area electroplated lithium metal formed in the charging process.[4,5] Lithium intercalation at the anode is a safer alternative to the electroplating in lithium metal rechargeable cells.[6] The move to a dual intercalation system, sometimes referred to as rocking chair technology[7], was the natural transition as many lithium metal cells already used intercalation cathodes. In 1990 Sony introduced the first commercial lithium-ion product.[8]

In addition to safety, lithium intercalation also has a number of performance advantages over electroplating. Intercalation is the reversible insertion and de-insertion of metal ions into a host material. Minimal structural changes to the host during insertion result in a very reversible, high cycle life product vastly superior to electroplated lithium metal anodes. Electroplated lithium metal anodes are prone to dendrite growth which can ultimately short the cells and reduce the cycle life. Intercalation allows fast charging, a requirement for many applications. Lower charge rates on the order of 10 to 20 hours are required to achieve uniform plating of lithium in metal cells compared to lithium-ions 1 to 3 hour fast charging. Intercalation anodes provide both safety and performance advantages in lithium batteries.

Many materials can intercalate lithium ions. The chart shown in Figure 1

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[2] Laman, F.C. and K. Brandt, J. Power Sources, **24**, 195 (1988).

[3] Manufacturers include: Alliant Techsystems, BlueStar, Duracell, Eagle-Picher, Eveready, Gould, Matsushita, PCI, SAFT America, Ultralife

[4] Wilkinson, D.P., J.R. Dahn, U. von Sacken, and D.T. Fouchard, Paper 53 presented at the Electrochemical Society Meeting, Seattle, WA, Oct 14-19, 1990. Also U. von Sacken and J.R. Dahn, Paper 54, *ibid.*

[5] Note: Tadiran continues to promote a rechargeable lithium metal battery assembled in a AA cell form factor, however safety in widespread use has yet to be demonstrated.

[6] Dahn, J.R., U. von Sacken, M.W. Juzkow and H. Al-Janaby, J. Electrochem. Soc., **138** (1991) p. 2207.

[7] Auborn, J.J. and Y.L. Barberio, J. Electrochem. Soc., **134** (1987) p. 638.

[8] Naguara, T. and K. Tazawa, Prog. Batteries Sol. Cells, **9** (1990) p. 20.

lists some of the choices available for designing intercalation systems.[9] Many factors must be considered when choosing both positive and negative host materials, such as reversibility, specific and volumetric capacity, and voltage (for electrolyte stability and determining overall cell voltage).

Todays lithium-ion cells are designed with high voltage cathodes and carbon anodes. A number of cathode materials are either commercially available or under intensive development including $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. All of these compounds intercalate lithium between 3.6 and 4.6 volts versus the Li/Li^+ potential. Anode materials currently in use include both graphitic and non-graphitic carbons. More detail on these intercalation materials will be given in Section 3.

2. Design Considerations

Considerations in the design of lithium-ion batteries fall into three categories: safety, performance and cost. We will discuss the implications and relative importance of each of these design factors.

Of these design considerations, safety should never be compromised. Stricter product liability and environmental regulations make it more difficult to introduce new battery technologies in todays market. It is unlikely that lead-acid or nickel-cadmium batteries would have been accepted into the market if only introduced in the last five years. Consider that thousands of safety incidents causing injury are reported every year for lead-acid batteries resulting from sulfuric acid spills, explosion of the hydrogen and oxygen gas generated and the release of toxic gases such as arsine and stibine. Consider introducing a battery today that contained hazardous materials of the nature of cadmium or lead. Imagine if lithium-ion batteries had the safety record of lead-acid batteries or toxicity level of cadmium or lead. It is clear that lithium-ion battery systems must be designed with a higher level of safety and environmental emphasis than existing conventional battery systems.

Lithium-ion technology is in its infancy with respect to performance and cost reduction. Despite the early stage of its development, the performance of

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[9] Dahn, J.R., Tutorial at Power96, October 13-16, 1996, Santa Clara.

lithium-ion cells has been outstanding providing significant benefits over conventional batteries. As a result of its superior performance and the strong demand for a better rechargeable battery, cost reduction had previously been given a low priority. This situation has changed recently due to conventional battery performance improvements and cell oversupply.

3. Design Considerations of Cell Components

3.1 Introduction

The proper choice or design of each cell component is made on the basis of safety, performance and cost. In this section, we will evaluate the design considerations for each of the critical lithium-ion cell components: electrolyte, cathode, anode, separator and hardware. In section 4, we will expand our discussion for these components and the interactions between them with respect to safety considerations.

3.2 Electrolyte

The important electrolyte performance criteria include voltage window of electrochemical stability, ability to passivate the reactive anode surface, temperature range, and conductivity. Safety, in particular thermal stability, and cost must also be considered. The solvent system and lithium salt are discussed with respect to these criteria.

No one solvent has been found to possess all of the necessary requirements for a lithium-ion battery, therefore combinations of solvents are typically chosen. The non-aqueous solvents used in lithium-ion battery systems must have a wide voltage window of electrochemical stability ($\geq 4.5V$). While it is likely that no solvent is thermodynamically stable in the presence of lithium or lithiated carbon, the formation of a compact solid-electrolyte interface (SEI) layer can effectively stop further decomposition of the solvents. Both propylene carbonate (PC) and ethylene carbonate (EC) have been used in commercial lithium-ion cells because of their excellent passivating nature to form a Li^+ conductive film on the anode. The use of PC is generally limited to non-graphitic anode systems. EC is a solid at room temperature and therefore requires the use of a co-solvent(s) to decrease the electrolyte viscosity and increase the conductivity. The co-solvents generally used are di-carbonates. Some propionates and acetates have been used for improved low temperature performance.[10] The most widely used co-solvents include dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). Solvent systems containing EC and one or more di-carbonate co-solvents will provide the necessary performance required for a lithium-ion cell.

In selecting a lithium salt for lithium-ion cells, the most important considerations are 1) safety, related to the thermal stability under abusive conditions and toxicity, 2) stability over a wide potential range, and 3) cost. Suitable choices are limited. Perfluorinated inorganic ions are preferred because of their high electrochemical stability. $LiPF_6$ and $LiBF_4$ salts are currently used in most commercial lithium-ion cells. Their selection is primarily due to their good performance and stabilizing characteristics on both the SEI film and the cathode current collector. However, dry $LiPF_6$ and $LiBF_4$ salts decompose at low temperature (approximately 150°C) and are reactive with trace water, making handling and purification difficult. Most alternative salts have one or more problems which make their use undesirable. The problems include a limited oxidative stability (e.g. $LiSO_3CF_3$, $LiClO_4$), corrosion of the aluminum current collector (e.g. $LiN(SO_2CF_3)_2$), potential toxicity (e.g. $LiAsF_6$), low conductivity (e.g. $LiSO_3CF_3$), potential explosions at high concentrations of salt (e.g. $LiClO_4$) and high cost (e.g. $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_3)_2$, $LiC(SO_2CF_3)_3$).

3.3 Cathode Material

While a large number of lithium containing transition metal oxides have been studied as potential high voltage cathodes, almost all lithium-ion cells commercially available today use lithium cobaltite ($LiCoO_2$). The reasons for its preference include ease of manufacture, good electrochemical performance and safety. Lower cost and higher performance are two motivations behind the intense development of alternative cathode materials now underway.

Figure 2 shows the discharge of a Lithium/$LiCoO_2$ coin cell. The cell

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[10] Mayer, S.T., H.C. Yoon, C. Bragg and J.H. Lee, The Thirteenth International Seminar on Primary and Secondary Battery Technology and Application, March 4-7, 1996, Boca Raton, Florida.

was first charged at an approximate rate of 17.1 mA/g until a voltage of 4.2V was reached, at which point the potential was held constant until the cell finished charging, for a total charge time of 12 hours. This current was chosen to correspond to a rate of removal of one lithium for two cobalt atoms over a period of 8 hours. The same current was used for discharge. On discharge, the potential initially dropped at a decreasing rate until a plateau was reached at about 3.85V versus Li. As the reinsertion of lithium in the compound reached its maximum value, the potential dropped rapidly. The reversible discharge capacity of lithium was about 140 mAh/g, which was attained at 4.2V versus Li. While charging to a higher voltage can lead to the extraction of more lithium, such a process is not completely reversible, and can lead to rapid capacity degradation with cycling. In addition, the compound becomes progressively more unstable with removal of lithium beyond about 140 mAh/g leading to increased self discharge rates as well as some safety concerns (see below). $LiCoO_2$ cathodes when cycled to 4.2V versus Li will provide their optimum performance, based on capacity and cycle life, and safety.

While $LiCoO_2$ has been generally found to be adequate, there are two major problems with its use. The first is that the specific capacity of 140 mAh/g is relatively low when compared to the carbon anode of 372 mAh/g. Cathode performance will be discussed in detail later. Second, cobalt is expensive. In fact, $LiCoO_2$ can contribute up to 40% of the material cost of a lithium-ion cell as shown in figure 3. Alternative cathode materials, including $LiNiO_2$ and $LiMn_2O_4$, are now being investigated to reduce the overall cell cost. The cost of nickel is about one-quarter that of cobalt. The cost of $LiMn_2O_4$ is largely driven by its manufacturing costs as manganese is readily available and inexpensive. In full scale production $LiMn_2O_4$ has the potential to be the lowest cost of the three cathode choices.

The discharge curves of the two lower cost alternatives to $LiCoO_2$ are also shown in figure 2. $LiNiO_2$ is isostructural with $LiCoO_2$; both are layered compounds with repeating layers of metal, oxygen and lithium. $LiMn_2O_4$ has a spinel structure with three dimensional tunnels in which lithium can be inserted. The discharge capacity of $LiNiO_2$ at 180 mAh/g is greater than $LiCoO_2$ at 140 mAh/g. Furthermore, the average discharge voltage is only slightly less (3.85 versus 3.92V), therefore $LiNiO_2$ cells will generally have higher energy than

$LiCoO_2$ cells. Unfortunately, there are a number of problems with the use of $LiNiO_2$ despite its desirable high discharge capacity. First is the poor capacity retention when charged and discharged at full depth of discharge. A second problem is the relatively slow kinetics of $LiNiO_2$, particularly near the end of discharge. Third is the difficult and complicated synthesis where only a relatively few precursors can be used and the reaction must be carried out under an oxygen atmosphere within a narrow temperature range. Fourth and foremost, $LiNiO_2$ has a high irreversible capacity loss on first charge adding to the difficulty in insuring safe cell operation under all conditions (see further discussion below).

A tremendous amount of effort has gone into developing a high capacity lithiated manganese spinel cathode material. The theoretical capacity of $LiMn_2O_4$ is 147 mAh/g, but this value has never been obtained in practice. Reversible capacities of 110 to 125 mAh/g are typical. The observed value is found to depend on a number of factors which include 1) the amount of lithium precursor used, 2) the temperature and time of heating, 3) the rate of cooling, and 4) the amount of impurities in the product. Often it is observed that materials with the highest capacities exhibit the highest degree of capacity fade. For example, we have found that the addition of 5% excess lithium carbonate to a Li_2CO_3 / MnO_2 reaction mix reduces the capacity from 120 mAh/g to about 110 mAh/g, but the lower capacity material cycles significantly better as shown in figure 4. In addition to the lower cost of the material itself, $LiMn_2O_4$ is significantly more resistant to conditions which arise from abuse or charger malfunction (see safety discussion below) and therefore offers a further potential savings in the cost of cell design components required for abuse safety. The lower cycle life and high self discharge, particularly at high temperatures, however are significant drawbacks. It is believed that some manganese is dissolved into the electrolyte as Mn^{+3} during repeated cycling, and is also responsible for the higher self discharge rate compared to $LiCoO_2$. Perhaps more important is the fact that the capacity density (mAh/cc) of this spinel oxide is much lower than the alternative layered-compounds. The density of $LiNiO_2$ and $LiCoO_2$ are similar (approximately 4.9 g/cc), but $LiMn_2O_4$ is about 30% smaller. While the reversible capacity densities of $LiCoO_2$ and graphite are comparable (686 and 818 mAh/cc respectively), $LiMn_2O_4$ is significantly less (412 mAh/cc).

Performance improvements in $LiMn_2O_4$ could lead to its wide usage as a low cost cathode material in the future.

3.4 Anode Material

As mentioned previously, during the 1970s and 80s most of the work on rechargeable lithium batteries centered on using lithium metal anodes and various intercalation compounds as positives. The major performance and safety limitations revolved around the efficiency of the lithium electroplating process, and the morphology of the plated material. Acceptable cycling characteristics could be obtained with certain electrolyte solvents using a 3-4 fold excess of lithium metal in the cell. However, the morphology of the electrodeposited lithium is more porous and less uniform than the original material. Furthermore, lithium is thermodynamically unstable with virtually all solvents and reacts to form a surface film each time a new surface is generated by the electroplating process. The surface film forming reaction is exothermic. One can now understand why this newly introduced, high surface area lithium can produce a safety problem. It is possible for the electroplated lithium to penetrate the separator, causing an internal short circuit. A soft short will lead to poor charge efficiency and premature cell failure. A hard short could lead to fire and/or explosion. Lithium metal anodes have both poor cycling and safety characteristics.

The electrochemical intercalation of lithium into graphite (or less ordered carbon) has been known since the late 1970s,[11] but the application of carbon intercalation compound in a lithium-ion battery didnt occur until 15 years later. The specific capacity of Li and carbon are 3.86 and 0.372 Ah/g, respectively. The capacity densities of Li and carbon are 1.97 and 0.818 Ah/cc, respectively. The volumetric value for carbon drops to 70% or about 0.57 Ah/cc as it is used as a powder. Secondary lithium metal batteries however, require a 3-4 fold excess of lithium to achieve reasonable cycle lives as they lose 1% lithium per cycle in a best case situation. Despite the lower theoretical energy of carbon as an anode compared to lithium metal, in practice the energy differences are small. Another factor is that the electrolyte solvents that allow the best lithium cycling, cannot withstand the high working voltages (above 3.5V). In lithium-ion cells,

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[11] Gabano, J.P., editor, Lithium Batteries, Academic Press, 1983, pg. 24

all three major cell components were changed: anode, electrolyte and cathode. Freed of the requirement of high lithium plating efficiency, electrolytes capable of operation at high potentials were introduced, thereby allowing the introduction of higher voltage (> 4V) cathodes, increasing the energy of the system. The result is a cell with a slightly lower specific energy, similar energy density and better performance and safety than lithium metal batteries.

The first commercial lithium-ion cells used a non-graphitic carbon anode. The reason for this choice is largely historical, and is related to the selection of solvents. It was well known that attempts to intercalate lithium into graphite using propylene carbonate (PC) solvent resulted in massive exfoliation of the electrode. While the exact mechanism for this phenomena is unknown, it is probable that a reduction product of the PC is entering the graphite layer planes and forcing the layers apart. This phenomena was not observed in non-graphitic (less ordered) carbons, and therefore it was believed that only non-graphitic carbon materials were capable of highly efficient lithium intercalation. Yet non-graphitic carbons have a number of disadvantages compared to graphite. The intercalation voltage in non-graphitic carbons is significantly higher and the capacity is generally less than that of graphite. Furthermore, the true density of graphite is 20-40% higher than non-graphitic carbon. The use of graphite over a non-graphitic carbon therefore, can yield a higher capacity density. A number of attempts were made to circumvent the exfoliation problem (e.g. coating graphite with a carbon coke). It is now known that electrolytes containing EC as the primary solvent can be used in lithium-ion cells containing graphite anodes without exhibiting exfoliation during lithium intercalation.

The amount of lithium that will intercalate in the carbon depends on a number of factors. These include the choice of carbon precursor, pyrolysis temperature, pyrolysis atmosphere, particle size, as well as electrode manufacturing parameters such as binder type and amount, additives, etc. In addition, the amount of excess capacity irreversibly consumed during the first charge of the anode is generally dependent on a larger number of process related variables. Irreversible capacity loss is associated with the formation of a solid-electrolyte interface (SEI) layer or film on the carbon anode surface, similar to that found on lithium metal anodes. To insure excellent safety and cycling performance, a solvent must be selected that reacts to provide a uniform, thin, stable SEI layer which allow easy migration of lithium ions, but is impervious to solvent molecules. Ethylene carbonate (EC) is an excellent primary solvent because its reduction products are highly effective in passivating the surface from further reaction. Examples of a SEI formation reaction involving EC are:

$$\mathrm{EC} + 2\ \mathrm{Li}^+ + 2e^-\ (\mathrm{carbon}) \rightarrow \mathrm{Li_2CO_3} + \mathrm{C_2H_4}$$
$$\mathrm{EC} + 2\ \mathrm{Li}^+ + 2e^-\ (\mathrm{carbon}) \rightarrow \mathrm{LiOC_2H_4OLi} + \mathrm{CO}$$

Both Li_2CO_3 and $LiOC_2H_4OLi$ have limited solubility in the electrolyte, and are incorporated into the surface film. Additional reaction products, such as LiF, are also present in the SEI film due to some limited reduction of the fluorinated salt. Carbons with high surface area generally have higher first cycle irreversible capacity losses. In addition, high surface area carbons can be unsafe under abusive conditions (see discussion below).

3.5 Balancing the Cathode and Anode

Obtaining a proper cathode to anode balance will result in the optimum performance for a lithium-ion cell. The mass of the anode and cathode must be balanced in such a way that the amount of capacity supplied to the anode from the cathode on the first charge does not exceed the sum of the reversible and irreversible capacity. Too little cathode capacity can result in an under utilized anode and poor cycle performance, therefore when designing a lithium-ion cell, excess cathode capacity must be supplied to accommodate the irreversible capacity loss of the carbon. Too large a cathode capacity however, can lead to lithium plating on the anode. Materials with low irreversible capacity loss and high reversible capacity are preferred to optimize cell capacity.

Table 1 lists the typical 1st charge and discharge capacities for a few types of anodes and cathodes, derived from half-cells using a lithium reference electrode. These capacity values are used to calculate out balancing. The cathode material half-cells were cycled between 2.5 and 4.2V versus Li. The anode material half-cells were cycle between 0.05V and 3 V versus Li. When calculating cell balance one must include the lithium from the cathode that is consumed in the anode SEI formation process. Cells can be designed to be either cathode or anode limited, depending on the cell chemistry. One disadvantage of anode limited cells is a phenomena that results on over discharge. Because the cathode has excess capacity, on over discharge the voltage of the negative electrode increases, approaching that of the cathode. If the anode potential exceeds about 3 V versus Li at the end of discharge, the copper current collector of the anode may corrode. The correct balance is dependent on the cell chemistry.

Table 1. First Charge and Discharge Capacities of some Cathode and Anode Materials

Material	1st Charge Capacity (mAh/g)	1st Discharge Capacity (mAh/g)	Charge/ Discharge Ratio
$LiCoO_2$	148	140	1.057
$LiNiO_2$	220	180	1.23
$LiMn_2O_4$	120	115	1.043
Synthetic Graphite	380	320	1.19
Pitch Derived Carbon	356	270	1.32

3.6 Separator

Choosing the right separator previously involved a choice between polyethylene and polypropylene microporous separators. Recently, a trilayer laminate containing both materials was developed by Hoechst-Celanese.[12] Polypropylene separator provides good mechanical stability at temperatures as high as 165°C. High density polyethylene separators melt as low as 130°C. When a cell is externally shorted, the high current flowing through the cell raises the internal cell temperature. Polyethylene separator will melt earlier than polypropylene and has been shown to stop the current flow by restricting electrolyte movement through the melted pores. However, concern has arisen for mechanical abuse tests where the structural stability of the polyethylene separator fails and the electrodes can come into direct contact creating very high short circuit currents leading to internal hot spots. Laminated separators consisting of the lower melting point polyethylene and the mechanically stable polypropylene have been designed to provide the best of both worlds. It is up to the cell

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[12] Spotnitz, R., The Twelfth International Seminar on Primary and Secondary Battery Technology and Application, March 1996, Deerfield Beach, Florida.

designer to choose between the added safety of the laminate separator and its higher cost.

3.7 Hardware

The hardware components include the header or cap, can, current collectors and tabs. Some of these components, such as the header and negative current collector can be designed to increase intrinsic cell safety. The materials must be chosen carefully based on the electrochemical potential that each will be exposed to.

Lithium-ion cell headers have been designed to include different safety features, including external short circuit, overcharge and thermal abuse protection. Three components provide these functions including the PTC device or switch, electrical disconnect mechanism and rupture vent.

A PTC (positive thermal coefficient) device is routinely designed into lithium-ion cell headers to provide a resettable external short circuit protection device as an alternative to the nonresettable separator shutdown. The high current flow during an external short circuit flowing through the PTC device will heat the device, causing the impedance to increase at least two orders of magnitude. The current flow is slowed to a normal, safe discharge rate. When the high current is removed, the PTC drops back to its lower impedance setting.

Overcharge is the Achilles Heel of lithium-ion cells and therefore must be protected on an individual cell basis. Overcharging lithium-ion cells (except those containing $LiMn_2O_4$) can lead to venting with fire unless a protective device is included in the cell. A common design used by most manufacturers is a pressure actuated electrical disconnect. On overcharge, the cathode material breaks down releasing oxygen, lithium metal is plated on the anode after the carbon is fully lithiated and the resulting pressure is used to permanently move a dome shaped diaphragm and break an electrical contact between the cathode current collector and the positive cap of the header. This action is permanent and not resettable but protects the cell without venting or leakage.

The third protective device designed into most lithium-ion cell headers is a rupture vent to protect the cell from explosion when exposed to excessive heat or thermal abuse. If a cell is placed in a fire or in a hot oven above 130°C, it is important for the pressure generated in the cell to be released in a controlled manner through a safety vent. Without this rupture vent, the cell could explode, blowing the header off as a projectile.

4. Safety and Abuse Testing

4.1 Testing Programs

Safety testing programs have been born out of adversity. Lithium fires in early lithium metal cells forced government and industry to generate regulations for the safe transport of lithium batteries. The U.S. Department of Transport prepared a series of regulations and tests for lithium batteries.[13] While these tests are legal requirements for air shipping cells, the most thorough safety testing program was developed by Underwriters Laboratories and a group of industry experts. The UL1642 Safety Standard for Lithium Batteries is a comprehensive set of mechanical, electrical and environmental tests designed originally for lithium metal batteries but adopted by lithium-ion battery manufacturers as the industry standard to pass. Passing the tests in UL1642 provides UL recognition for their lithium-ion products, similar to the UL recognition granted to most electrical devices. A new standard document is currently being drafted by a group of industry experts in the IEC (International Electrotechnical Commission) Secondary Battery Group. The intent of this standard is to incorporate and update all existing lithium battery testing standards into one comprehensive safety program. This IEC document also specifies cell designation and performance tests.

Two levels of testing exist: safety and abuse. Safety testing can be described as situations that might occur during intended use. Abuse testing are more severe and include foreseeable misuse of the batteries. We have reviewed both programs and combined the critical safety and abuse tests as presented in Table 2 and 3.

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[13] U.S. Department of Transportation Code of Federal Regulations, CFR49. U.S. Government Printing Office, Washington, D.C.; Exemption E-7052, Department of Transportation, Washington, D.C.

Table 2. Safety Tests

Category	Test	Result
Electric	IEC Continuous Charge (28 days)	No Leakage
Mechanical	IEC/UL Vibration	No Leakage
Environmental	IEC High Temperature Storage (75°C)	< 0.1% Weight Loss
	IEC Thermal Shock (75°C/-20°C/20°C)	< 0.1% Weight Loss

Table 3. Abuse Tests

Category	Test	Result
Electric	UL Short Circuit (60°C)	No leakage, fire or explosion (Max temperature = 90°C)
	IEC/UL Forced Discharge	No leakage, fire or explosion
	IEC Overcharge	No leakage, fire or explosion
	IEC High Rate Charge	No leakage, fire or explosion
	IEC Internal Short Circuit Test (Crush)	No fire or explosion
Mechanical	UL 6 foot Drop; 10 times onto concrete	No fire or explosion
Environmental	UL 150°C Heating	No fire or explosion
	UL Incineration	No explosion

Although the common safety testing programs include testing of thermal aged, thermal shocked and electrically cycled cells, lithium-ion cells are most vulnerable to thermal abuse when they are new and freshly charged. At this stage, the passivation layer in the cells is not fully formed and is more vulnerable to break down.

The desired test result depends on the severity of the test. In general, safety or intended use tests stipulate no cell leakage, venting, fire or explosion. The more severe abuse or foreseeable misuse tests typically stipulate no fire or explosion, however PolyStors lithium-ion cell results shown in Table 3 exceed these requirements for many tests. Note: cell leakage is acceptable, particularly when the cell and more specifically the header, is mechanically deformed. An exception to the no fire requirement is the incineration test where the cell is burned with a propane torch. The UL requirement for the incineration test is for the cell to not ignite a piece of cheesecloth 3 feet away and not to emit projectiles or explode. Lithium-ion cells should be designed to pass both Underwriters Laboratories 1642 Standard and the proposed IEC Standard for Secondary Lithium Cells.

Designing safety into a lithium-ion cell means that one considers the thermal stability of the system first and foremost. Most safety and abuse tests have been designed to simulate different scenarios, such as dropping a cell or crushing a cell in a garbage compactor, electrical shorting or overcharging, or putting a cell into an oven or fire. These mechanical, electrical and thermal tests have one common outcome, they all have the potential for overheating the cell. If a safety or abuse test does not cause internal cell heating, the cell will be safe. All of the more difficult tests either cause cell heating either by internal or external shorting of the electrodes or by an external source of heat. Cells must therefore be designed to withstand either internal or external heating.

4.2 Overcharge Condition

Figure 5 shows the charge (including overcharge) curves for $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. The voltage of $LiMn_2O_4$ rises quickly above 4.2V, as it has very limited charge capacity beyond that potential. Lithium cobaltite shows a steady increase in potential until around 200 mAh, where it exhibits a plateau before exhausting the available lithium. $LiNiO_2$ exhibits a large capacity plateau centered at 4.2V. Small fluctuations in the charger voltages therefore, can result in large changes in released lithium in lithium-ion cells containing a $LiNiO_2$ cathode. Such voltage fluctuations will not only cause lithium plating on the anode, but further increase in the oxidation state of an already unstable compound.

4.3 Thermal Stability

Thermal management is an integral consideration in design of a safe lithium-ion cell. For example, if the temperature of a cell at the beginning of overcharge is unusually high then as the cell is overcharged and heat is produced the decomposition of the oxide and the reaction of electrolyte with anode lithium could lead to a runaway reaction (because the rate of these reaction increase substantially with temperature). Charging a cell in a hot environment (e.g. near hot circuit components) can cause problems. Also, as the cell size (diameter) increases, the surface to volume ratio of the cell is reduced. The amount of heat generated increases more rapidly with diameter than the ability to remove the heat. For this reason, a prismatic cell design is favored for large cells.

It is known that $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ have varying degrees of thermal stability in their delithiated forms.[14] For example, the layered compound $Li_{0.5}NiO_2$ (oxidation state 3.5) is transformed to the spinel $LiNi_2O_4$ on heating to above 200°C. This transformation is accompanied by little mass loss or heat generation. In contrast, at higher degrees of delithiation (e.g. $Li_{0.3}NiO_2$ which is formed at 4.2V charge) the transformation to spinel is also accompanied by significant oxygen evolution and heat generation. One possible reaction that could occur from the typical charge state is:

$$10\ Li_{0.3}NiO_2 \rightarrow 3\ LiNi_2O_4 + 4\ NiO + 2\ O_2 + \text{Heat}$$

Of all of the cathodes, $LiNiO_2$ has the lowest thermal stability when fully charged.

Highly delithiated $LiCoO_2$ does not undergo a transformation to spinel form but rather decomposes to layered $LiCoO_2$ and stable Co_3O_4 at about 245°C. Some oxygen and heat is also released along with this reaction. Under normal operations, the maximum removal of lithium from $LiCoO_2$ is about ½LiCo, corresponding to an oxidation state of 3.5. In uncontrolled overcharge, the cobalt oxidation state of $Li_{1-x}CoO_2$ continues to increase. If the charger

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[14] Dahn, J.R., E.W. Fuller, M. Obrovac and U. von Sacken, Solid State Ionics **69** (1994) p.265-270.

continues to supply current at a voltage above 4.75V, all of the lithium is removed and electrochemical oxidation of the electrolyte begins. Note that the carbon is nearly fully intercalated at the normal state of charge, and overcharging adds additional lithium to the anode which the carbon can not absorb, resulting in the formation of electroplated lithium on the carbon anode. During normal operation and the early stage of overcharge of a lithium-ion cell, lithium which is removed from the electrolyte at the anode is replenished from de-intercalated lithium from the cathode. However, at the end of overcharge, the oxidation of the electrolyte doesnt produce any ionic lithium (or any other ionic species). Therefore, at the end of overcharge, the electrolyte becomes depleted of ionic lithium, and its conductivity decreases. As the impedance of the electrolyte increases, but the current supplied remains constant, cell heating can occur. Another source of cell heating is the high overpotential (irreversibility) of the electrolyte oxidation process. As the cells temperature increases, the rate of decomposition of the delithiated cathode increases, increasing the gas pressure within the cell and further increasing the cell temperature. Another source of pressure buildup is the formation of gases during the oxidation of the electrolyte. The temperature increase in overcharge is typically about 25-40°C for an ICR-18650 cell. The current path to the cell must be interrupted at this point. If it is not, the cell temperature continues to increase and can reach a point where the heat generated (from the decomposition of the delithiated cathode, and the reaction of anode materials with the electrolyte) may exceed the cells ability to remove heat from the cell, and fire and/or explosion can result.

Lithium manganese oxide spinel ($LiMn_2O_4$) is generally considered a safer compound than either of the layered Co or Ni compounds because the completely delithiated compound decomposes from the λ-MnO_2 (the structure of the delithiated analog) to ε-MnO_2. This structural rearrangement releases little energy and no oxygen. Beyond this temperature the material can decompose to Mn_2O_3 releasing oxygen, but only at temperature of over 400°C. Furthermore, overcharging a $LiMn_2O_4$ cell doesnt result in a significant amount of lithium plating on the anode because no further lithium is available from the parent cathode.

Another critical abuse condition is high temperature exposure (see UL 150°C Heating Test in Table 3). For cells using fully charged $LiCoO_2$ or

$LiMn_2O_4$ cells (cathode state $Li_{0.5}CoO_2$ and λ-MnO_2) only a small amount of heat is released from the cathode during high temperature (150°C) exposure. Significantly more heat is produced from $Li_{0.3}NiO_2$ under the same conditions. The selection of a carbon material and electrolyte is very critical because around 130°C an exothermic reaction occurs with lithiated carbon and electrolyte. This reaction depends on the type of carbon used, and has been shown to increase with carbon surface area for a given type of carbon.[15] Furthermore, the extent of the reaction is also dependent on the selection of solvents and salt. The exact nature of the reaction is unknown, but is believed to be similar to the SEI film formation reaction that occurs at ambient temperature. As the temperature is increased, some solvent may penetrate the SEI film, or the film may become cracked or porous (e.g. due to differences in thermal expansion coefficients of the film and carbon). The exposure of electrolyte to the hot lithiated surface causes a chemical reaction and the release of heat, further increasing the cell temperature. If the newly reacted material forms a film that insufficiently passivates the surface, or the rate of heat produced exceeds that which can be removed, thermal runaway can result. Careful selection of material components, thermal design, and testing are required.

5. Summary

Many of the design considerations for lithium-ion cells involve tradeoffs between performance and/or safety. When designing lithium-ion cells, safety should never be compromised, in fact cells should be designed with safety as the first priority. Performance and cost considerations should be viewed of secondary importance to safety issues.

Lithium-ion cell technology is in its infancy. We have already seen many improvements since their introduction, including new cathode, anode and electrolyte materials, and one should expect to see many more. Current commercial lithium-ion cells have been shown to have good performance and safety but at a price premium in comparison to conventional rechargeable

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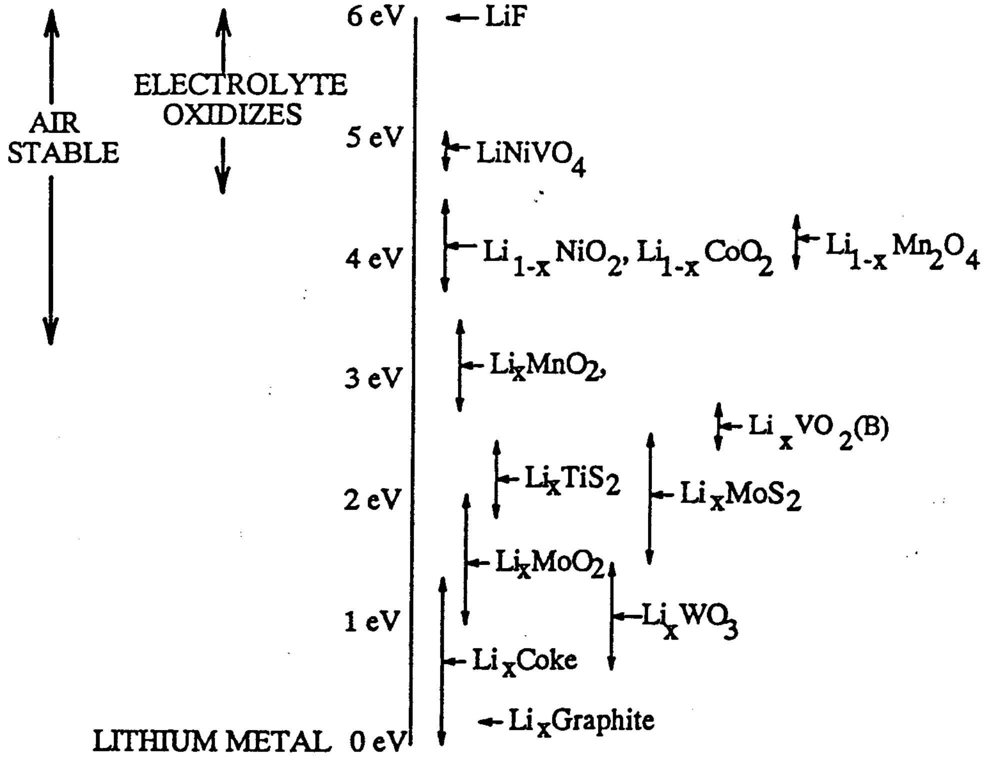
[15] von Sacken, U., E. Nodwell, A. Sundher and J.R. Dahn, Solid State Ionics **69** (1994) p.284-290.

systems. Increased competition will require new developments to both improve performance and lower cost without compromising safety.

Lithium Intercalation Compounds



BINDING ENERGY OF Li IN VARIOUS COMPOUNDS

Figure 1

Dahn, J.R., Tutorial at Power 96, October 13, 1996, Santa Clara, CA

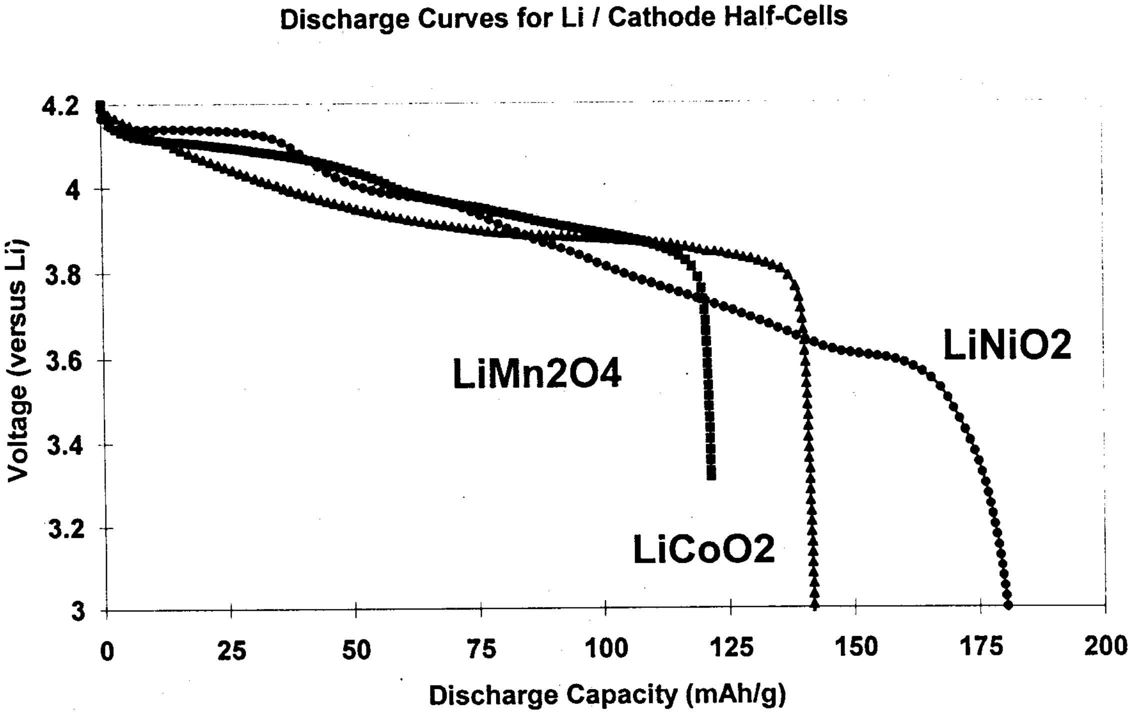


Figure 2

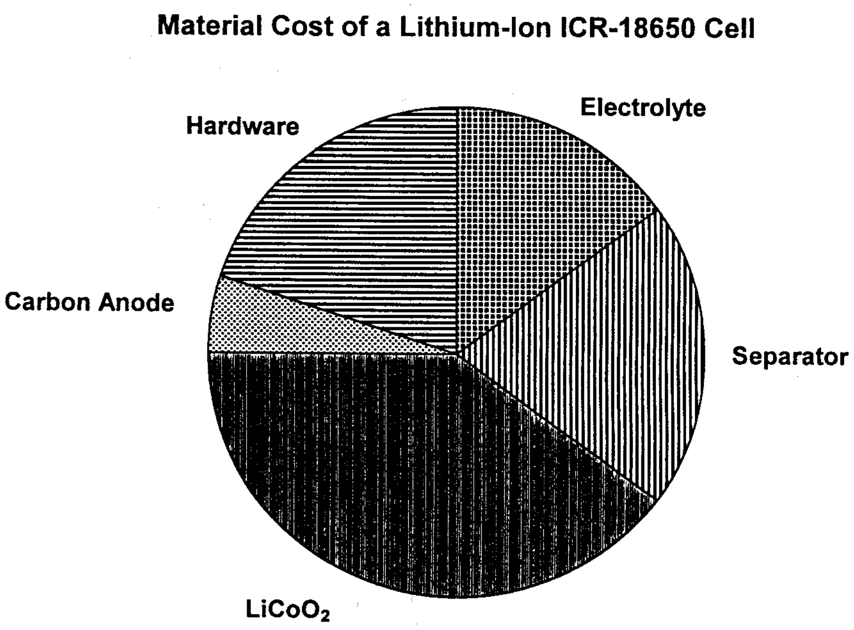


Figure 3

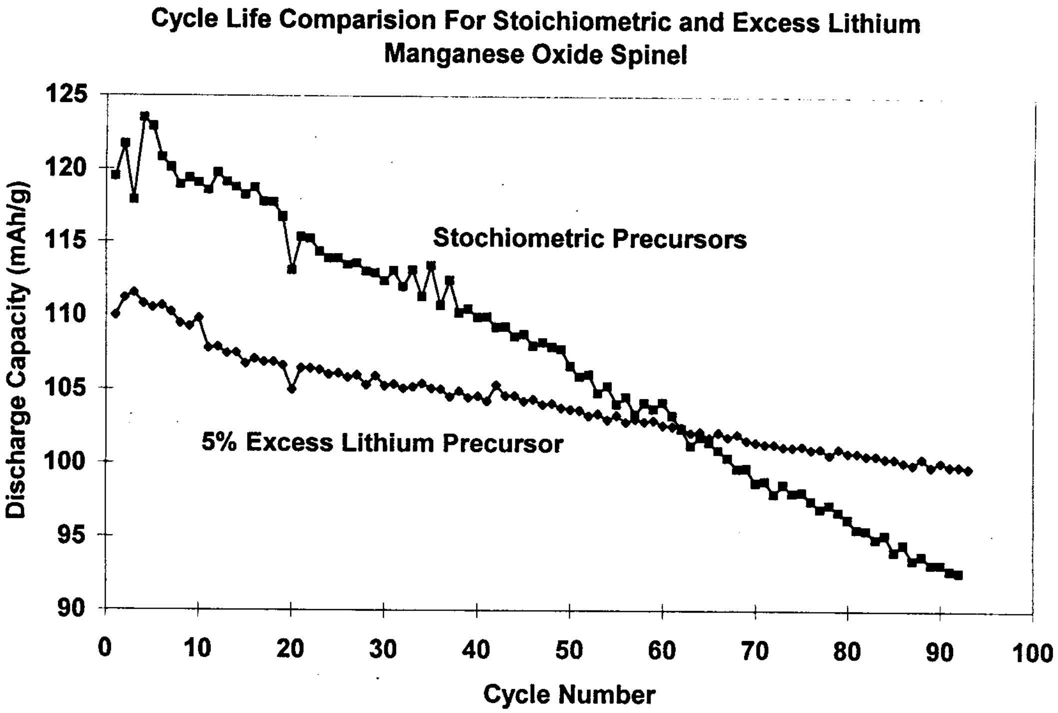


Figure 4

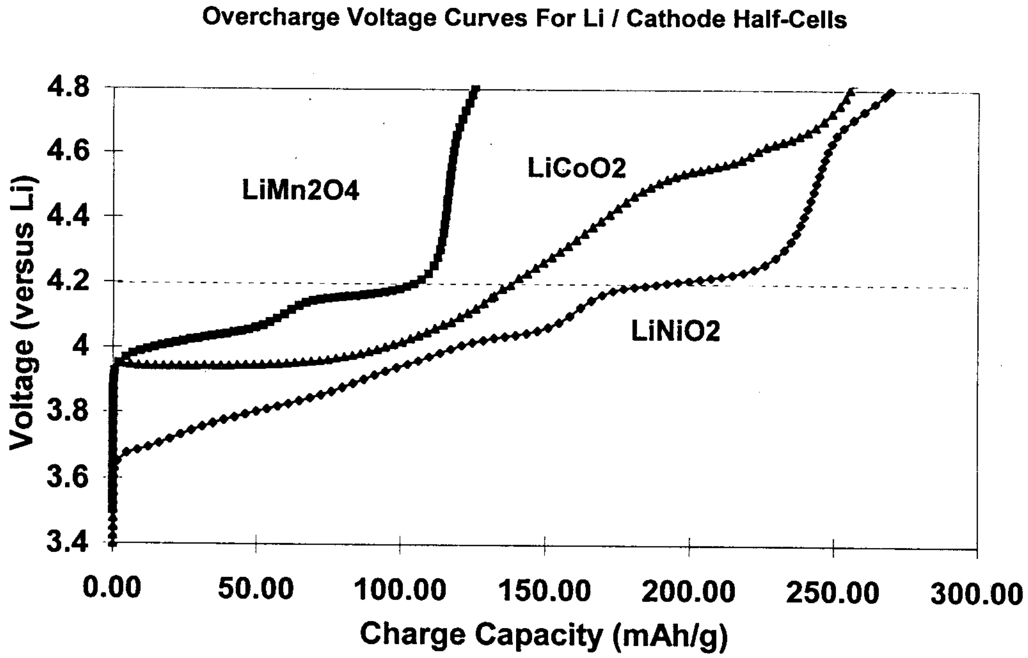


Figure 5