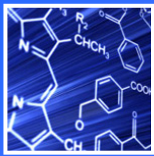


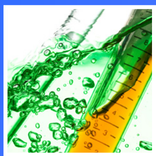


NEI Corporation

Lithium Titanate Based Batteries for High Rate and High Cycle Life Applications

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Introduction

In general, the demand for smaller and lighter batteries has been growing drastically during the last decade. Conventional lead acid batteries have been in use since 1860 in stationary applications. Lead acid batteries are still widely used due to their low cost, matured state of development and ruggedness compared to other battery technologies. However, lead acid batteries (both flooded and VRLA) are heavier and bulkier. They also do not cycle well to meet some of the demanding new application needs.

Nickel-cadmium batteries have been used in deep cycle applications. They are smaller and lighter compared to lead acid batteries. Large batteries have to have large amounts of free electrolyte within the battery. Like flooded lead acid batteries, NiCad batteries have to be maintained periodically. NiCad batteries also have memory effect, which results in lower usable capacity over a period of time. They were also the choice of batteries for portable applications like cameras and other portable devices. However, the use of these batteries has been reduced significantly due to environmental concerns related to the use of cadmium. Many countries, including the United States, have banned cadmium recycling.

To address these issues, Nickel Metal Hydride (NiMH) batteries became an alternative solution for portable applications. NiMH battery technology was not successful in large stationary applications due to the high cost of nickel and patent limitations related to this technology. Another disadvantage with NiMH batteries is the high self discharge rate. Though NiMH batteries are lighter and smaller compared to lead acid batteries, lithium ion batteries appear to be much more promising. Also, the recharge times for all these battery technologies are several hours. This can be very inconvenient in applications that require quick charge, such as in electric vehicles. For specific applications where the availability of grid power is limited, the need for high cycle life batteries with quick charge capability is becoming more and more critical. If a battery does not cycle well in an application where cycling performance is important, the customer is left with two choices: either replace the batteries often or use alternate sources of power, such as diesel engines. However, both of these options are expensive.

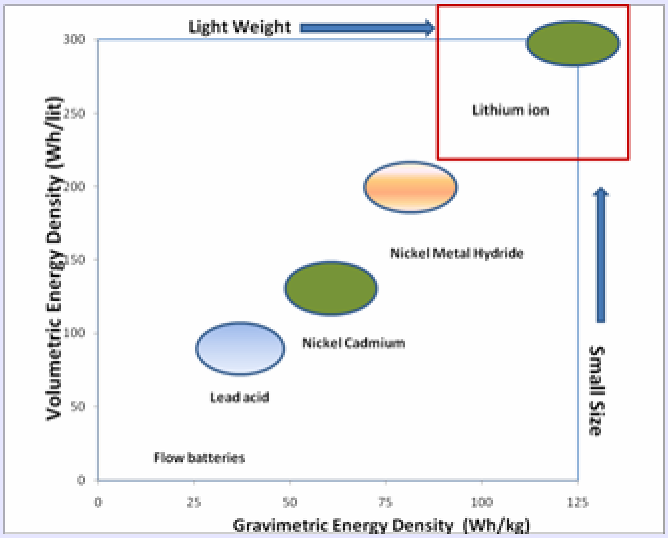
Lithium batteries were first proposed in 1976 [1] and have been widely used in portable applications since the early 1990s. In recent years, the high price of oil has provided the incentive for researchers to look into new battery technologies for use in electric vehicle applications. Among lithium batteries there are three different categories, namely: lithium metal, lithium polymer and lithium ion.

Lithium ion does not have a defined unique chemistry like lead acid, nickel metal hydride or Nickel Cadmium batteries. It has a number of different possible combinations, providing a number of possibilities to a variety of application requirements. A lithium ion cell has three main components: positive electrode (cathode), negative electrode (anode) and separator. This has both advantages and disadvantages. On the one hand, various cathode and anode materials provide flexibility to design batteries for specific application needs, but on the other hand the large number of possible chemistries creates confusion to the customers until a particular chemistry is fully developed and successfully tested in the field.

The different options available for each of these components (and their benefits and disadvantages) are described in detail below. The battery's electrical and performance characteristics like voltage, capacity, energy density, rate capability, cycle life, and calendar life will change as one chooses different materials for anode, cathode, electrolyte and separator. As will be shown later, there is no one particular combination of these cell components that can meet every requirement in all applications. One has to choose and modify the cell components to meet the application needs. In addition, one can also change the cathode and anode material composition, particle size and morphology to achieve a specific battery performance.

Figure 1 shows the range of different battery technologies compared in terms of volumetric energy density (Wh/l) and gravimetric energy density (Wh/kg). As can be observed in Figure 1, lithium batteries are much smaller and lighter compared to all other technologies. The red box shows the range of new lithium battery technologies with unique battery performance. In sharp contrast to lithium batteries, flow batteries are the most bulky among all the energy storage technologies.

Figure 1

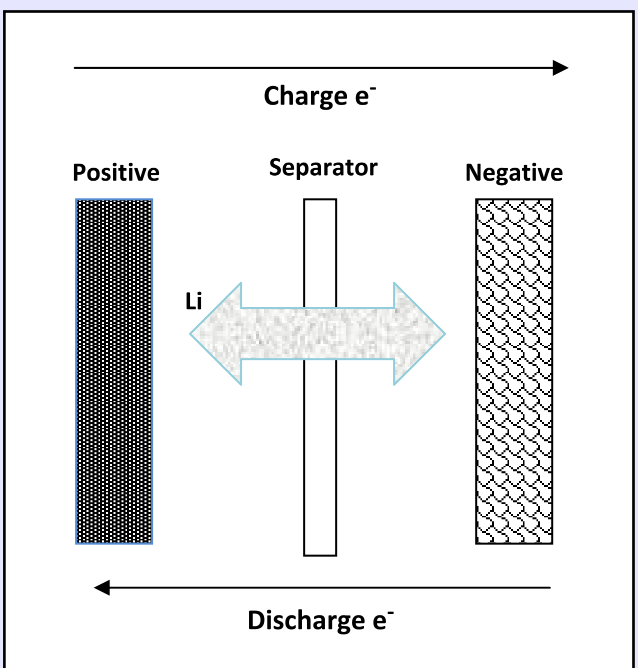


Principle of operation

Figure 2 shows the basic principle of operation of a lithium ion cell. Also, the following two equations show the charge and discharge reactions in a lithium ion battery. There are a number of material choices available for both cathode and anode materials, which will be discussed later. When the battery is charged, the lithium ions in the cathode material (lithium compound) migrate via a separator in between the layers of carbon material that form the anode and charge current flows. Similarly, when the battery is discharged, the lithium ions in the carbon material that form the anode migrate via a separator to the cathode material and discharge current flows.

Figure 2

Cobalt type: Charging	**Cobalt type: Discharging**
LiCoO2+Cn ---> Li1-XCoO2+CnLix	Li1-XCoO2+CnLix ---> LiCoO2+Cn
Manganese type: Charging	**Manganese type: Discharging**
LiMn2O4+Cn ---> Li1-XMn2O4+CnLix	Li1-XMn2O4+CnLix ---> LiMn2O4+Cn



Cathode Materials

A number of different cathode materials have been evaluated since 1990. The available materials include Lithium cobalt oxide (LC), Lithium Nickel Cobalt Aluminum Oxide (NCA), Lithium Manganese Spinel (LiMn2O4), Lithium Nickel Cobalt Manganese oxide (NCM) and Olivine based materials, such as Lithium Iron Phosphate (LFP).

The first commercial lithium batteries used lithium as the anode. However, the poor cycle life and safety issues associated with the use of metallic lithium forced scientists to look for alternative anode materials. LiCoO2 cathode, in conjunction with carbon as negative electrode, was introduced in the early 1990s [1,2]. Until recently, LiCoO2 was predominantly used in portable lithium batteries like laptops and cellular phones. The cycle life of the batteries with LiCoO2 was between 500 – 700, depending upon the manufacturer and the cell design. Over the years, batteries with LiCoO2 cathode also had safety related incidents and the cost of LiCoO2 has increased over time. Due to these reasons, it became necessary to identify new cathode materials. Lithiated manganese oxide, also known as ‘spinel’ due to its spinel crystal structure, yielded a similar energy density as LiCoO2, but with a much lower cycle life.

Other mixed metal oxides based upon nickel oxide (LiNiO2) were also explored. Two such materials were lithium nickel cobalt aluminum oxide (NCA) and lithium nickel manganese cobalt oxide (NMC). NCA has slightly lower voltage and hence better safety characteristics, compared to LiCoO2-based cells. On the other hand, NCA has much better cycle life. NMC has slightly lower cycle life compared to NCA and has similar safety characteristics. Even within these mixed metal oxides, variations in the ratios of the cations have also been studied.

Although there was some improvement in the safety due to the use of mixed metal oxides, it was still necessary to further improve the safety features of the positive electrode. Lithiated iron phosphate (LiFePO4) was the solution for the safety issues associated with the positive electrode. Lithium iron phosphate is also known as LFP for short in the battery industry. LFP gave reasonable calendar life and excellent cycling characteristics when operated at moderate temperatures. The energy density of LFP-based materials was much lower than LiCoO2 or mixed metal oxides, but the high rate capability of LFP-based batteries made them attractive for applications in power tools. Table 1 shows the list of cathode materials used in lithium ion batteries along with their advantages and limitations when used with carbon as the anode material.

Anode Materials

To date, carbon has been the most commonly used anode material in a lithium ion cell. One of the synthetic materials used is Meso Carbon MicroBeads (MCMB). MCMB has a high energy density: 350 plus mAh/g. This material has good performance, but is expensive. Modified natural graphite, on the other hand, is less expensive than MCMB and many varieties are available. Amorphous carbon gives good power, but has a lower energy density than graphite. Although hard carbons are good for high rate capability, they give lower capacity: ~200 mAh/g. Much research is still ongoing with single and multi-walled nanotubes and graphemes; however they seem expensive at this time for commercial use.

Table 1

Material	Chemical formula	Advantages	Disadvantages
Lithium Cobalt	$LiCoO_2$	High energy density, Reasonably good cycle life	Safety and cost
Lithium Nickel Cobalt Aluminum Oxide (NCA)	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	High Capacity 180 mAh/g, Reasonably good cycle life, Slightly better safety than lithium cobalt oxide	Safety
Lithium Nickel Manganese Cobalt Oxide (NMC)	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	High Capacity, 200 mAh/g, Reasonably good calendar life. Cycle life is less than NCA. Safety slightly better than lithium cobalt.	Energy density
Lithium Manganese Oxide	$LiMn_2O_4$	High power, high voltage, lower cost and improved abuse tolerance	Calendar life when used with graphite, low capacity, 125 mAh/g.
Lithium Iron Phosphate (LFP)	$LiFePO_4$	Better safety, high rate capability, good cycle life at normal temperatures	Poor energy density, Low operating voltage, 3.4V, low capacity, 134mAh/g

Lithium titanate ($Li_4Ti_5O_{12}$, referred to as LTO in the battery industry) is a promising anode material for certain niche applications that require high rate capability and long cycle life. LTO offers advantages in terms of power and chemical stability, but LTO-based batteries have lower voltage: 2.5V vs. $LiCoO_2$ and 1.9V vs. LFP. Nevertheless, the lower operating voltage brings significant advantages in terms of safety. Further, these batteries can be charged fast. Data shows that these batteries can be safely charged at rates higher than 10C. This means the battery can be charged in less than 10 minutes. The LTO-based batteries also have a wider operating temperature range and a recharge efficiency exceeding 98%. Although the energy density of LTO-based batteries is low compared to other lithium ion batteries, it is still higher than lead acid and NiCad batteries. There are numerous applications where lead acid batteries and NiCad batteries are used in conjunction with generators. The volumetric change during charge and discharge is very small compared to carbon and results provide much longer cycle life. LTO based batteries provide much better low temperature performance compared to carbon based batteries. The large cycle life and high rate capability of LTO-based batteries also brings unique advantages in applications where the reliability of the grid is poor. When the grid power is available, the batteries can be charged quickly and discharged slowly. This will save a significant amount of cost in terms of diesel and frequent replacements of VRLA batteries. For electric vehicles, the fast recharge capability makes a huge difference in recharge time compared to other chemistries: 10 minutes for LTO-based batteries compared to 8 hours for certain chemistries.

Toshiba has already introduced LTO-based batteries for electric bike applications. Utilities often have peak problems associated with demand and production. Often, they do not produce sufficient power to meet the peak demand, while they can produce much more than what is needed during off-peak hours. Building power plants just to meet the peak demands can be expensive. Batteries in this application, however, often do not require high energy density. LTO-based lithium batteries will be a suitable technology for this application. Also, the lower charge voltage provides an option for new aqueous based electrolytes, which brings unique advantages in float charge applications.

Tin and silicon-based alloys and intermetallic materials are also being explored by a number of researchers; however, there are a number of challenges that need to be overcome before implementing these intermetallics in commercial applications.

Electrolytes

Since the cell voltage of lithium cells is higher than the potential at which aqueous solutions electrolyze, one has to use non-aqueous electrolytes in lithium ion batteries. There are a number of liquid organic solvent options available for use as lithium ion battery electrolytes. Mixtures of dimethyl carbonate (DMC)[4], ethylene carbonate (EC), diethyl carbonate (DEC), and ethylmethyl carbonate (EMC) with dissolved lithium hexafluorophosphate ($LiPF_6$) are among the most commonly used electrolytes. The ratio of each component in the mixture is often optimized by each cell manufacturer. The above described electrolyte normally works well at room temperatures. However, under abuse conditions, such as overcharge or higher operating temperatures, decomposition reactions can occur.

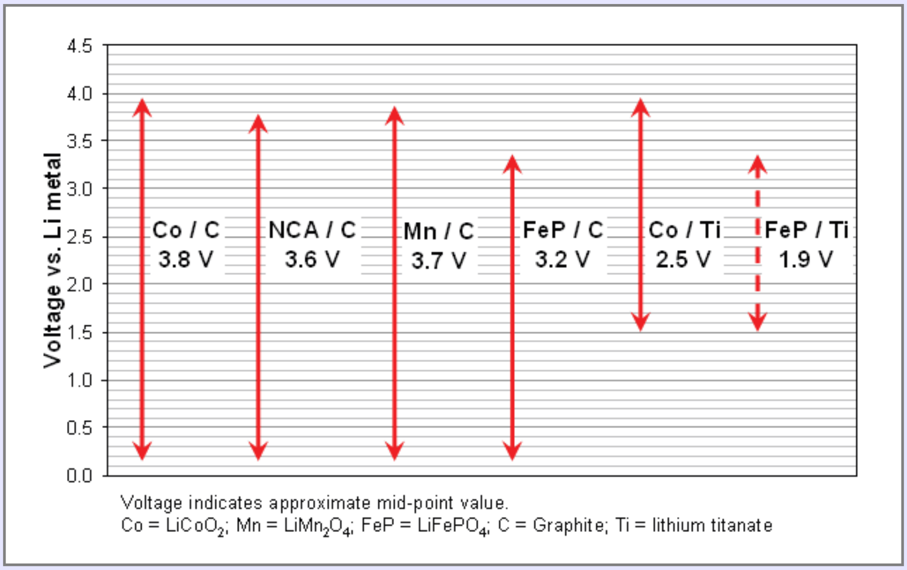
Conducting solid polymer electrolytes can replace solvent-based electrolytes. They offer greater advantage when used with a lithium metal anode. Some of the challenges relate to the degree of conductivity at low temperatures. Ionic liquids offer advantages in stability at higher voltages and have better abuse tolerance, but they are still in the early stages of development.

Container/Cell Design

Lithium batteries come in both cylindrical and flat pack (prismatic) designs. A metal can (spiral wind) is one of the most common designs and has a limited number of parts (one anode, one cathode and one separator). The strength provided by the metal cylinder is an added advantage. 18650 cylindrical cells are the most widely used lithium ion cells. These are being used in laptops and many other portable devices. However, challenges exist in winding large electrodes for large format cells. Also, the challenge relating to attaching tabs for high power cell design still remains. Larger cylindrical cells have issues with uniform heat dissipation. During high rate discharge, the core of the cells becomes hotter than the outside. The higher temperature makes the inner part of the battery age faster, which results in the premature loss of capacity for the entire cell.

The flat/prismatic stack design is most commonly used in lithium polymer cells. This design offers advantages in building large, high power cells and provides a means to dissipate heat efficiently so the cells age uniformly. Also, when a large number of cells are packed for a specific application then this design provides much better safety characteristics. This design, however, has its own challenges: an external support structure is needed for the electrode stack. Further, single sided tab design cells have issues with uniform current density and impedance.

Figure 3



Courtesy: Jim McDowall [5]

Cell Characteristics

The active materials discussed above for cathode and anode materials can each be combined to form an electrochemical cell. Each cell will yield different characteristics, depending upon the combination of the particular cathode and anode. Figure 3 shows the voltage range for some popular cathode and anode material combinations. For example, the highest voltage of the lithium cell is obtained from a cell made from LiCoO2 and carbon anode (3.8V). Similarly, for the lithium cell with LFP as cathode and LTO as anode, the voltage was only 1.9V, which is even lower than that of a lead acid cell. The larger voltage cells bring higher energy and power densities, while the lower voltage cells have better safety features. The lower voltage cells will of course have lower energy and power densities.

Given that the LTO anode material operates at a higher voltage (less negative), the overall cell voltage is lower and hence the overheating problem with respect to solid electrolyte interface (SEI) is eliminated. Also, the higher negative voltage of LTO allows them to be recharged at a higher rate, sometimes as little as five minutes. Due to this higher negative voltage, the overall cell voltage is lower and hence the energy and power densities are also lower. The cycle life for these batteries has been reported to be more than 10,000 at 80% depth of discharge. Due to the low energy and power density, these batteries are not attractive for traditional portable applications. However, the long cycle life, safety, and fast charge and discharge capabilities of LTO cells bring unique values to applications where these attributes are critical. These applications include: telecom, data center UPS, aerospace, sensors, renewable energy, and the Smart Grid.

Charge balance requirements

Aqueous systems like VRLA and NiCad are charged about 100 mV above the open circuit voltage of the cell. The electrochemistry in these systems is largely regulated by side reactions involving water. These systems can typically tolerate moderate levels of overcharging. The excess charge current is consumed by the above mentioned side reactions. Lithium systems are not aqueous and the side reactions are absent. All of the applied charge is going to charge the batteries, therefore the charging is efficient. However, it lacks the regulating mechanism supplied by the side reactions, and must be provided electronically. The variation of state of charge among the cells in a battery pack can affect the battery discharge capacity. It is essential to keep the cell voltages close to each other. Also, one needs to avoid over charging the cell. The external cell balancing function will bring the voltage of the cells close to each other.

Like any other energy storage system, there are issues related to safety that need to be addressed. The two main safety issues related to lithium ion batteries are overcharging and overheating. Also, all the situations relating to the application like temperature, operating voltage window, and heat dissipation should be considered into the battery pack design. Since lithium ion batteries have to have electronic battery management system, it provides the opportunity to add "smartness" into the battery system. The functions include state of charge, discharge history, battery diagnostic capability, reserve time prediction, remote battery monitoring and alarm capability. Due to its low voltage of operation the lithium titanate based batteries offer much safer operating parameters.

Summary

Lithium batteries provide a variety of design choices to meet a variety of application needs. No single chemistry will meet all the application needs. A number of different cathode, anode, and electrolyte materials offer both advantages and disadvantages. Using Lithium Titanate as an anode material offers excellent recharge capability, safety, and exceptionally large cycle life. In spite of its lower energy density, it offers exceptional advantages over other chemistries in numerous applications.

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