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The study's authors conducted a review of various battery chemistries, including information on basic electrochemistry and the critical parameters that drive battery design and sizing. The authors examined the performance, life cycle, and safety of lead-acid, lead-carbon, nickel cadmium, nickel metal hydride, bipolar nickel metal hydride, nickel super capacitor, molten sodium metal-halide, and lithium-ion technologies. The authors worked with Class I railroad operators to identify load profiles for long haul locomotives, and then they modeled the performance of a battery system to determine its ability to absorb locomotive regenerative braking loads, provide supplemental locomotive energy, and comply with required life expectancies. Validated models were used to predict the life of a battery system with specific input parameters and operating environments, and the authors focused on the regenerative braking energy that could be recovered as well as the traction loads provided to the main generator by the battery. The study authors also examined cost, noting the system cost of a battery system with an expected operational life of 7 years or more, including the projected cost for various rechargeable battery technologies. A discussion of the potential safety hazards and recycling information for each type of battery chemistry was also included.

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Battery technologies, hybrid diesel-electric locomotives, lead-acid, lead-carbon, nickel cadmium, nickel metal hydride, bipolar nickel metal hydride, nickel super capacitor, molten sodium metal-halide, lithium-ion

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				=	1.1 short tons
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1 pint (pt)	=	0.47 liter (l)			
1 quart (qt)	=	0.96 liter (l)			
1 gallon (gal)	=	3.8 liters (l)			
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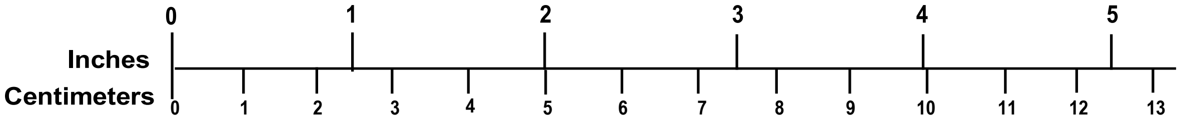

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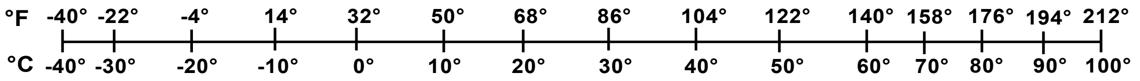

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Executive Summary

The electrification of the transportation sector, and specifically electrification of freight movement, is moving forward as advanced battery technology continues to evolve. Improved energy and power density of batteries, better battery safety, and lower battery costs have helped accelerate the deployment and use of hybrid-electric and all electric vehicles for both passenger and goods movement sectors across the country. All-electric locomotives have been in operation for decades in the subway and light rail passenger carrying sectors, but the freight sector continues to rely on diesel-electric locomotives. Due to the high infrastructure cost of electrifying the freight rail network, recent attention has been focused on the development of Hybrid Diesel-Electric Battery (HDEB) locomotives and battery electric switcher locomotives.

As battery technology advances, an HDEB locomotive for long haul duty may become possible. This study reviews various battery chemistries, including information on the performance, life cycle, and safety of each technology.

The study was conducted from March 24, 2014, to December 31, 2015, by Saft America, Inc. in Valdosta, GA. The study authors and Class I railroad operators identified load profiles for long haul locomotives, and then this information was used to model the performance of a battery system and determine the battery's ability to absorb locomotive regenerative braking, provide supplemental locomotive energy, and comply with required life expectancies. Given the complexity and size of any locomotive battery system needed in terms of the voltage and number of batteries, a battery management system is required regardless of which technology is used to ensure individual batteries or cells do not go into thermal runaway.

Validated models predicted the life of a battery system, given specific input parameters and operating environments, with a focus on the regenerative braking energy that could be recovered and the traction loads provided to the main generator by the battery. The study also included a discussion of cost, emphasizing the system cost of a battery system with an expected operational life of 7 years or more, including the projected cost for various rechargeable battery technologies.

The authors found that lithium-ion (Li-ion) battery systems would be the best solution to meet the needs of an HDEB locomotive application. This includes the ability to absorb up to 63.3% of the regenerative braking loads and provide up to 23.1% of the traction loads for a given route. This study took into account the need for a high voltage system with sufficient recharge capabilities to accept and absorb the regenerative braking energy produced by the locomotive, the high power requirements to support the traction loads, and the modeling results for the load profiles reviewed.

Within the family of Li-ion batteries, the iron phosphate and titanate chemistries seem to be the best options, given the ability of these chemistries to accept high levels of regenerative braking energy, high cycle life, long calendar life, lower life-cycle cost, and increased safety within the family of Li-ion chemistries.

A development of a demonstration project is recommended, which would allow researchers to continue optimizing the battery system, determine the best system design, and demonstrate the specific benefits of a HDEB locomotive for use in Class I railroad service.

1. Introduction

1.1 Background

Tomorrow's locomotives may be able to transport goods across the nation while also being more fuel efficient, polluting less, and operating more quietly in sensitive areas. The full deployment of advanced rechargeable battery technology could make this possible.

The diesel-electric (DE) locomotive has issues such as air pollution, noise pollution, fuel costs, and extensive periodic maintenance requirements. It also has lower energy efficiencies than all-electric locomotives; the DE accelerative force is low in medium and high speed areas, which leads to low running performance; and diesel generator units are poorly utilized, mostly operating below the optimal specific fuel consumption region. Also, the DE locomotive has the following problems:

- Diesel-electric locomotives use a large number of machine parts, which leads to a large volume of maintenance work;
- The oversized diesel generator's requirements increase the cost of the unit and lead to space constraints for the locomotive, which has an impact on its fuel economy.

To conserve additional energy, DE locomotives have been subject to weight-reductions, efficiency improvements, and regenerative braking. However, regenerative braking energy must be stored before it can be utilized for traction or supplemental loads. Also, energy efficiency for DE locomotives is believed to be approximately 30% lower than that of electric locomotives.

Given the need to reduce fuel consumption and meet air quality standards, the railroad industry is under pressure to invest in cleaner, energy efficient locomotives. Hybrid Diesel-Electric Battery (HDEB) technology can improve locomotive engine efficiency, even beyond current Tier 4 engine standards. In certain non-attainment regions, incentives are being provided to commuter railroads to upgrade locomotive engines to Tier 4. Hybrid technology could be another option for non-attainment regions seeking to improve air quality, and it is likely to be supported through similar incentives.

DE locomotives are powered by large diesel engines, which supply current to electric motors. High rail yard emissions frequently come from locomotives that line up a train, because these locomotives are often left idling and operate inefficiently because they have to start and stop often. New locomotives with multiple engines, called gensets, provide locomotives with the power they need and have the ability to shut off engines (and therefore reduce emissions) when not needed. While genset locomotives provide some fuel savings, the next evolution is a diesel-electric battery locomotive that utilizes stored energy.

Furthermore, diesel locomotives emit nitrogen oxides, carbon monoxide and fine particles (soot), which are public health risks. In this matter, diesel locomotives may perform worse than steam locomotives. Scientists have concluded that the annual emissions of nitrogen oxide—which is a major ingredient in smog, acid rain, and soot—will be nearly twice the level that was originally estimated for 2030. As a result, diesel locomotives would release more than 800,000 tons of nitrogen oxide and 25,000 tons of soot every year within a quarter of a century, in contrast to the EPA's previous projections of 480,000 tons of nitrogen dioxide and 12,000 tons of soot.[1] Diesel locomotive pollution has been of particular concern for the city of Chicago. The Chicago Tribune reported that diesel soot from locomotives leaving Chicago was at levels hundreds of times above the level normally found on Chicago streets.[2] Residents of neighborhoods near railroads are often exposed to diesel emissions at levels several times higher than those of the national average for urban areas, which creates environmental justice issues.

Electrification of Freight Transportation

Climate change continues to act as a driving force on different aspects of the environment and community. Due to extensive research done on climate variability, we are better able to understand, predict, and witness extreme weather events, rising temperatures, and subsequent resource shortages that occur as the climate begins to shift to a new equilibrium. Both policymakers and the scientific community have shifted their focus to methods that mitigate the impacts of climate change. This includes greater utilization of technologies to electrify the freight transportation sector, including hybridization of diesel-electric locomotives to HDEB.[3] There are three primary advantages of a HDEB: lower fuel consumption, increased engine maintenance interval, and fewer emissions. The result is a locomotive with lower, more efficient, energy consumption and a reduction of greenhouse gas emissions.

According to a 2012 report from Pike Research, diesel-electric locomotives are a key segment of the global transportation industry, with more than 4,000 diesel locomotives sold each year. The sector has opportunities to improve fuel efficiency and enhance environmental control, and these opportunities could be transferred to other modes of freight transportation.[4] The Pike Research report also provides a comprehensive analysis of battery technologies, regenerative braking for locomotives, and a description of how batteries can be used to reduce emissions and improve the efficiency of locomotives. The report includes a detailed description of battery storage capacity needs. In recent years, hybrid vehicles have been developed in the automotive and railway industries. Hybrid vehicles, in general, operate on two energy sources, typically combining rechargeable batteries with an on-board internal combustion engine and electrical drives.

In the automotive industry, hybrid vehicles have been the most successful. A hybrid passenger vehicle can rely solely on a battery to drive an electric motor in low-power conditions and switch to a gasoline engine in high-power conditions or when the battery charge is low. In addition, the battery can be recharged by both the gasoline engine and a regenerative braking system. These and other features allow hybrid vehicles to achieve relatively low levels of fuel consumption and generate lower carbon emissions.

The railway industry has moved towards more environmentally friendly locomotive designs. While all-electric locomotives have been operating for decades—typically as subway or light-rail passenger carriers—usually they are supplied with a continuous supply of power through an electric “third rail” or overhead cables. Unfortunately, the vast majority of railroads do not support third rails or overhead cables, and the costs of converting existing railroads are prohibitively high. Therefore, recent innovations have been focusing on HDEB locomotives. Although there has not been a consistent definition of the term “hybrid,” existing HDEB locomotives seem to be based on traditional diesel-electric locomotive platforms and include one or more energy storage mechanisms to receive excess energy from the diesel engine, regenerative braking, or both.

Among the most notable hybrid locomotives are those developed by East Japan Railway Company (or “JR East”), General Electric (GE), and Railpower Technologies. JR East's hybrid locomotive (2003 test design) included two 65-kilowatt fuel cells and six hydrogen tanks under the floor, with a lithium-ion (Li-ion) battery on the roof. The JR East test train was capable of 60 mph with a range of 30-60 miles between refills. The GE hybrid locomotive was essentially a diesel-electric locomotive redesigned to capture the energy dissipated during braking and store it in a series of molten salt batteries. The stored energy could be later used on demand to reduce fuel consumption (reportedly by up to 15%). Rail Power’s hybrid locomotives included switchers known as “Green Goats” and “Genset” type locomotives. The Green Goat hybrid switchers were each powered by a small generator and a large bank of batteries. The Genset locomotives were powered by two or four smaller diesel engines, which achieved part of their fuel savings and efficiency by turning the diesel engines on as needed and were shut down during low-power or idle conditions.

1.2 Battery Definitions and Terminologies

These terms are used throughout the report and provide a foundation for the discussion of the benefits and limitations of various battery technologies for use in a HDEB locomotive.

Cell - An electro-chemical device that supplies the energy from an internal electrochemical reaction to an external electric circuit.

Battery Pack - One or more cells that are connected, either in parallel or in series, to obtain a required current/voltage capability. For example, hybrid and all electric vehicles have a high voltage battery pack that consists of individual modules and cells organized in series and parallel. A cell is the smallest packaged form that a battery can take and it is generally on the order of one to six volts. A module consists of several cells generally connected in either series or parallel. A battery pack consists of modules that are connected together, again either in series or parallel.

Cell Impedance – The internal resistance in a cell that limits the amount of peak current that can be delivered. The resistance within the battery is different for charging and discharging, and is also dependent on the battery's state of charge. As internal resistance increases, the battery efficiency decreases and thermal stability is reduced as more of the charging energy is converted into heat. The impedance remains relatively constant during most of the discharge.

Rate and Amp-hour (Ah) – The capacity of a battery (or cell) is its most important figure of merit: it is defined as the amount of current that a battery can deliver for one hour before the battery voltage reaches the end-of-life point. When batteries are discussed, discharge current is often expressed as a "C"-rate in order to normalize against battery capacity, which is often very different between batteries. Charge and discharge currents are typically expressed in fractions or multiples of the "C" rates. A C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. A 1C rate means that the discharge current will discharge the entire battery in 1 hour. For a battery with a capacity of 100 Amp-hours, this equates to a discharge current of 100 Amps. A 5C rate for this battery would be 500 Amps, and a C/2 rate would be 50 Amps. C-rate describes the discharge power. A 1C rate is the discharge power to discharge the entire battery in 1 hour.

Open-circuit voltage (OCV) – The voltage between the battery terminals with no load applied. The open-circuit voltage depends on the battery state of charge and it increases with the state of charge.

The nominal or mid-point voltage (MPV) - The voltage of the cell, and the voltage that is measured when the battery has discharged ~50% of its total energy.

There are two main parameters that influence the terminal voltage of a battery, the ambient temperature and the rate of discharge of the battery. In battery hybrid traction systems, deep discharging of the battery reduces battery life and increases chances of failure of the system. This can be improved by maintaining the battery's state of charge above a specified threshold level. However, this solution will increase the battery size and weight of the overall system.

Specific Energy (Wh/Kg) – Also known as the gravimetric energy density of a battery. It is a measure of how much energy a battery contains in comparison to its mass. Specific energy is a characteristic of the battery chemistry and packaging. Along with the energy consumption of the application, specific energy is used to determine the battery weight needed to achieve a given electric range.

Specific Power (W/Kg) - The maximum available power per unit mass. Specific power is a characteristic of the battery chemistry and packaging. It determines the battery weight that is required to achieve a given performance target.

Energy Density (Wh/l) – Also known as the volumetric energy density of a battery. This term measures how much energy a battery contains in comparison to its volume. Along with the energy consumption of the vehicle, it determines the battery size required to achieve a given electric range.

Power Density (W/l) – This is the maximum available power per unit volume. It determines the battery size required to achieve a given performance target.

Maximum Continuous Discharge Current – The maximum current is the drain rate that a battery can be discharged continuously. This limit is usually defined by the battery manufacturer in order to prevent excessive discharge rates that would damage the battery or reduce its capacity. Along with the maximum continuous power of the motor, this measure defines the top sustainable speed and acceleration of the vehicle.

Maximum Discharge Pulse Current –The maximum current at which the battery can be discharged for extended pulse duration up to 30 seconds. This limit is usually defined by the battery manufacturer in order to prevent excessive discharge rates that would damage the battery.

State of Charge (SOC, %) – This is an expression of the present battery capacity as a percentage of maximum capacity. SOC is generally calculated using current integration to determine the change in battery capacity over time.

Depth of Discharge (DOD, %) – The percentage of battery capacity that has been discharged expressed as a percentage of maximum capacity. A discharge to at least 80 % DOD is referred to as a deep discharge, while a discharge of less than 25% DOD is considered a shallow discharge.

Float Voltage – The voltage at which the battery is maintained after being charge to 100 percent SOC to maintain that capacity by compensating for self-discharge of the battery.

1.3 Objectives

While questions remain regarding the optimal battery for locomotive applications, currently there is a significant amount of information about the energy densities, charge and discharge characteristics, life cycle costs, safety considerations, and maintenance needs of various battery chemistries. Electrical load profiles of locomotives are also available and can be analyzed to determine the optimal battery chemistry for specific locomotive applications. In addition to understanding the energy requirements of an HDEB locomotive, there are unique safety considerations for the locomotive environment, such as intense shock and vibration loadings, and crashworthiness of systems. Further, life cycle costs of battery systems, including maintenance and inspection needs, must be considered to optimize a battery for use in an HDEB locomotive.

The railroad industry has shown interest in hybrid diesel-electric locomotives, yet there remains uncertainty regarding the costs and benefits of various battery technologies for hybrid locomotives. This report attempts to compare battery chemistries on a standardized basis to identify the most likely chemistries for different load profiles, which were derived from railroad route information.

Advanced battery technology is in widespread use in many industrial applications around the world with many different chemistries, including silver-zinc, lead-carbon, sodium-nickel, nickel cadmium (NiCd), nickel-metal-hydride (NiMH), supercapacitors, lithium-iron-phosphate (Li-FePO4), lithium-nickel-manganese-cobalt (Li-NMC), and lithium-manganese-oxide (LMO). From military and commercial vehicles, to aircraft and railroad back-up power, to megawatt sized grid connected systems for capturing regenerative braking of commuter trains and providing frequency regulation to the grid, advanced batteries can be found in numerous ruggedized applications with extremely high power and energy requirements. The use of batteries for passenger rail vehicles, however, has yet to be demonstrated. The knowledge exists to develop a prototype ruggedized battery system, yet such a system has not been demonstrated. This report will help identify the battery chemistries with the greatest potential for a given locomotive application and enable the development of a prototype system with a greater chance of success and commercialized for broad application.

1.4 Overall Approach

This report examined different production battery chemistries and identified their benefits, limitations, and risks. In order to estimate the approximate physical characteristics of several battery systems, industry experts were polled and load profiles obtained. One of the technologies was modeled using empirical data that allow performance and life predictions for a given set of assumptions.

1.5 Scope

The paper discusses a variety of industrialized rechargeable battery chemistries and briefly describes each technology's cell designs, performance, health hazard identification, and recycling. The profiles provided as part of this paper were used to establish estimates for the battery system's physical performance characteristics and "life of battery" expectations. Due to modeling limitations, not all the chemistries could be analyzed for performance. Where possible, technologies were compared between each other to provide better understandings of their benefits and limitations. As there are currently no commercially available performance models that can predict battery performance throughout the life of the battery system, the report based its results on available literature and information from industry experts.

To provide insight into some of the critical parameters of electrochemical systems, this report also discusses various topics that affect performance and life characteristics.

1.6 Organization of the Report

The report provides insight into the basics for battery design and critical parameters that dictate the overall size of a battery system for use in a HDEB locomotive. It also reviews the majority of industrialized and commercially available battery technologies then addresses the benefits, limitations, and risks associated with each.

To better inform the reader, each technology is given a load profile, which is used in conjunction with a performance model to predict battery performance and its life expectancy. The relative costs of each industrialized and commercially battery technology were addressed, and battery-specific rail safety issues were examined for each technology.

2. Battery Design and Sizing Parameters

2.1 Rechargeable Battery Electrochemical Behavior

A battery converts chemical energy into electric energy by transferring electrons from one material to another through an electric circuit. This transfer results in the oxidation of a reducing agent (the anode) and the reduction of an oxidizer (the cathode), which is also known as oxidation-reduction or REDOX. The term “oxidation” means that a material is losing electrons; the term “reduction” means that the material is gaining electrons.

A cell is the basic building block of all batteries. It consists of two electrodes (an anode and a cathode), electrolyte, a separator between the anode and cathode, and a container to hold the assembly. The design can be defined by whether the cell used is recombinant. For vented NiCd and Pb-acid systems, a gas barrier or membrane prevents the recombination of gases, which means that the water must be periodically replenished.

2.1.1 Anode

An anode is the negative electrode or the reducing electrode. It is also known as the fuel electrode. The anode gives up its electrons to the external circuit and is oxidized in the process. Anodes are made from materials with very few electrons in their valence shell. Almost all anodes are made from either metals or compounds that include metals, although newer technologies often use intercalation materials.

2.1.2 Cathode

The cathode, or the positive electrode, is also known as the oxidizing electrode. It is designed to accept electrons from the external circuit and the cathode is reduced in the process. Cathodes are made from materials that have nearly full valence shells. Cathodes are typically made from compounds that include oxygen, chlorine, or both.

2.1.3 Electrolyte

The electrolyte is an ionic conductor. While the electrons are passing through the external circuit, the electrode materials inside the cell are changing into ions. In order to sustain the flow of electrons, the newly formed ions have to pass between the electrodes through the electrolyte. Electrolytes are typically either acids or bases (alkaline), although newer technologies often use organic solvent and salt solutions. Acids, bases, and salt solutions are good ionic conductors.

2.1.4 Separator

The separator, which has its porous structure, serves as insulation between the anode and cathode while allowing ionic transport between the electrodes.

2.1.5 Electrochemical Action

The cell will discharge after the anode is connected to the cathode through an external circuit. Once it discharges, REDOX occurs. The anode material loses electrons (oxidation) and the cathode material gains electrons (reduction). If a voltage is applied to a rechargeable battery in the reverse direction (from discharge), REDOX proceeds in the opposite direction. In a battery, REDOX occurs only at the surface of the electrodes.

When a cell discharges, electrons begin to flow from the anode to the cathode through an electric circuit. Ions form on both electrodes and flow through the electrolyte to react with one another and form new stable compounds. In most practical batteries, the discharge product forms on the surface of the cathode.

Cell Charge begins the process of electrons flowing from the cathode to the anode, induced by an external power source. The discharge product separates out into ions that travel through the electrolyte and the original electrode materials return to their starting points.

Figure 1 details the charge-discharge process.

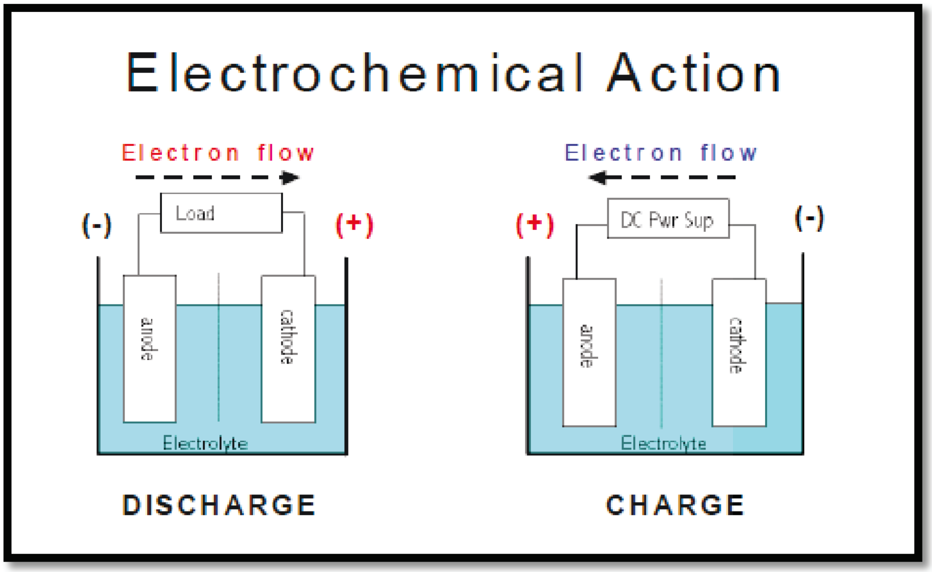


Figure 1 Charge-Discharge Process [5, 6, 7]

The potential (battery voltage) is an "absolute" value, which is determined by the total value between the voltage reactions of the positive and negative electrodes versus a standard reference electrode. In the case of lithium sulfur dioxide (primary battery) potential, the voltage reaction of sulfur dioxide has a zero-volt potential and a voltage potential for the lithium reactions of -3.01V. This result is an absolute value difference of 3.01 volts. For a secondary cell (rechargeable) such as NiCd, it isn't as obvious. The voltage reaction for the positive electrode is +0.49V and the negative electrode is -0.81V. The cell potential is the absolute difference between positive and negative electrodes, +0.49V – (–0.81V) = 1.30V.

2.2 Critical Influences on Battery Systems

As stated above, a rechargeable battery is an energy storage device that converts chemical energy into electrical energy and vice versa. This section discusses the terminology used to describe, classify, and address the critical parameters that influence the sizing of a battery for a specific application, including the variables that characterize battery operating conditions and the manufacturer's specifications for nominal and maximum characteristics of a battery.

Many different measurements can play major roles in sizing batteries. Commonly mentioned electrical variables include maximum discharge rate, cycling rate, high current pulse rate, and Depth of Discharge (DOD). Operating environmental conditions, such as storage and operating temperature conditions should be considered as well. Individual battery variability in the areas of individual cell impedance and cell capacity (Ah) are also critical factors. In addition, the charge-recharge cycling parameters have a significant impact on battery capacity.

The report utilizes information from a locomotive duty cycle and used it to determine the required voltage, power, and energy for a battery. In addition to these operational requirements, other elements that factor into the battery design are the minimum, maximum, and average operating temperature, the target lifetime, the desired cycle life, and cost.

2.2.1 Determining the Number of Cells

The required system voltage directly correlates to the required number of cells to bus in series, also known as a string, see equation below.

$$\frac{System\ Voltage}{Cell\ voltage} = \#\ of\ Cells\ in\ Series = \#\ of\ Cells\ in\ a\ String$$

Since cell voltage is an intrinsic property for a particular chemistry, the minimum quantity of cells in series for a particular voltage requirement is fixed. For example, if the locomotive requires a 270 volt battery this would require 129 lead-acid cells with a nominal voltage of 2.105 V/cell. In the standard naming format, it would be called a "129S system." In contrast, a battery with lithium iron phosphate, a lithium-ion chemistry with a nominal cell voltage of 3.2V, would require only 85 cells to reach the same voltage and would be called an "85S system." The required system voltage is critical to sizing the rest of the battery.

Example 1: 270V/2.105V = 128.3 Cells → 129 Cells required →129S

Example 2: 270V/3.2V = 84.4 Cells → 85 Cells required → 85S

Next, the battery capacity requirement must be met by the system. To calculate the battery's capacity, the cell capacity is multiplied by the number of cells or strings in parallel. A cell's capacity depends upon the amount of active material within it. To provide additional capacity for a particular chemistry, either the physical dimensions of the cell or the density of the active material will have to be increased.

$$\frac{\text{Battery Capacity (Ah)}}{\text{Cell Capacity(Ah)}} = \text{\# of Parallel Strings}$$

For example, if the battery requires 100 Ah and each cell has 20 Ah of capacity, the battery will have to have 5 strings in parallel to meet the required capacity and would be known as a 5P system. On the other hand if 50 Ah cells are available then only 2 strings would be needed.

Example 3: 100Ah/20Ah = 5 Parallel Strings → 5P

Example 4: 100Ah/50Ah = 2 Parallel Strings → 2P

Increasing the capacity of a cell to reduce the number of strings will also substantially reduce the quantity of bussing material and labor required to connect the cells. This will characteristically result in a simplified internal design with less electronics required for balancing and fewer components that can fail.

Rechargeable battery technologies, depending on the application, have to fulfill the following characteristics:

- Provide a fast response
- Small in weight and size
- Acceptance of high peak power
- Handling high rate power requirements
- Accepting regenerative braking energy
- Capable to withstand a wide range of temperature acceptance for storage and performance

2.2.2 *Power and Energy*

Rechargeable battery requirements for HDEB locomotive applications are contingent on the platform, performance, hybrid configuration, drive cycle, operating strategy, all-electric range capability, and level of electric performance on various drive cycles.

The analysis process included defining platforms (mass, aerodynamic, and rolling resistance); performance targets (acceleration, top speed, grade); the desired equivalent electric range; the operating strategy; and the usable state of charge (SOC) window.

For such analysis, a Ragone chart (as shown in Figure 2) is an excellent tool used for performance comparison of various energy-storing devices. The values of energy density (in Wh/kg) are plotted versus power density (in W/kg). Both axes are logarithmic, which allows comparing performances of very different devices (for example, extremely high and extremely low power). Conceptually, the vertical axis describes how much energy is available, while the horizontal axis shows how quickly that energy can be delivered, otherwise known as power, per unit mass. A point in a Ragone chart thus represents the amount of time during which the energy (per mass) on the Y-axis can be delivered at the power (per mass) on the X-axis, and the time (in hours) is given as the ratio between the energy and the power densities.

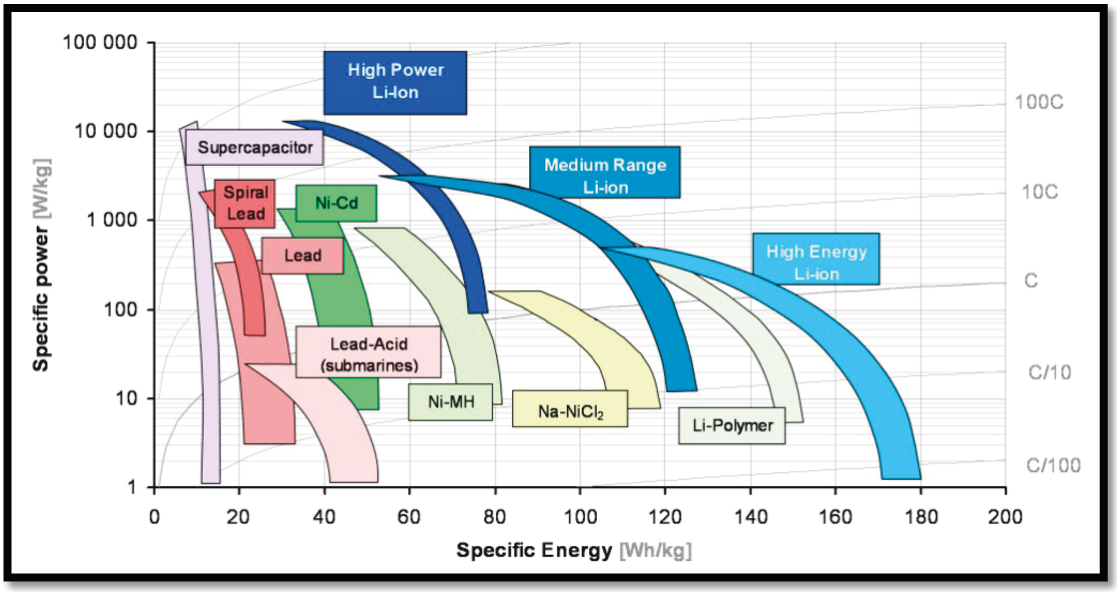


Figure 2 Battery Chemistry Comparison

Increasing the cell capacity does bring about great improvements and simplifies the system level, but if the cells become too large in capacity, safety may become a greater issue. When an individual cell contains a greater quantity of energy and that energy is rapidly released by a single event, the result is typically an event with increased hazard.

Additional key parameters are the power requirement and the operating temperature range. The application's power needs are determined by identifying the maximum continuous and the peak pulse currents. Every cell has an internal resistance (also called impedance), which is correlated to the overall cell design. This includes the current carrying material, cross-sectional area of conductance, separator thickness, loading of the electrode, electrolyte, cell temperature, and both the positive and negative electrode chemistry and architecture. Impedance is measured and observed as the voltage drop while under load as seen in equation below.

$$\text{Impedance} = \frac{\text{Change in Voltage}}{\text{Change in Current}}$$

When the temperature decreases, there is a decrease in the impedance of the electron conduction. However, the diffusion rate of ions is significantly decreased through the active material and through the electrolyte, which produces an overall larger initial voltage drop under a given load and results in increased impedance. When temperature increases the current collector impedance increases, while the impedance corresponding to the ion diffusion decreases. The temperature interactions of the electrode and electrolyte system are typically more significant than those of the current collector.

$$\text{Current Collector (T)} \ll \text{Electrode/Electrolyte(T)}$$

To compensate for difficult conditions (such as high current at low temperature), there are a number of elements that can be optimized. These improvements are usually made by increasing the ionic diffusion rate or reducing the diffusion distance from one electrode to the other.[8]

2.2.3 Temperature Environment

The environmental temperature affects the performance of all electrochemical technologies. Many of the effects are similar across battery chemistries. Specific information on the unique impacts of temperature on certain battery technologies is provided within Section 3.

As noted previously in the discussion of impedance, cold temperature affects battery performance (power and energy) because of poor ion transport. This naturally varies with each technology, with the impact of cold temperatures increasing as temperatures get lower. A typical example of NiMH cold temperature performance can be observed in Figure 3. There is always a cold temperature at which the battery will not operate. Many times, heaters are utilized to permit the battery to satisfy load requirements at cold temperatures. Some lithium-ion technologies must limit charging at cold temperature to ensure battery life and safety. Other battery technologies require higher input voltages to permit the battery to charge at cold temperature.

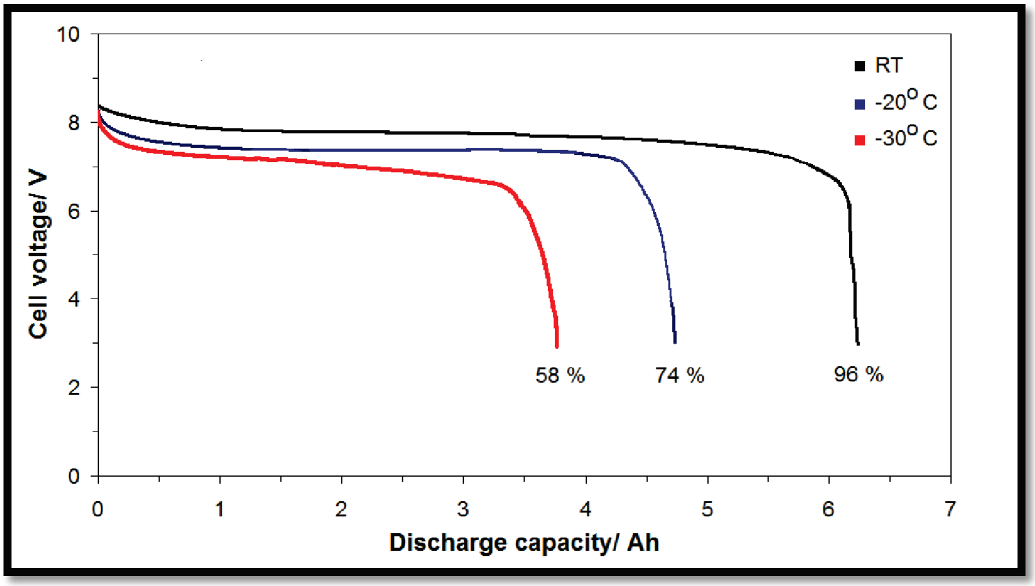


Figure 3 Typical NiMH Performance

At higher temperatures, the impedance of the battery is lower leading to higher discharge performance. Many times, a discharge is not permitted to occur above a maximum temperature or else a thermal runaway situation could occur. Most aqueous technologies have issues accepting charge at high temperature, as the majority of the current supports electrolysis and the production of hydrogen and oxygen. At elevated temperatures lead and nickel based electrodes have issues with charge efficiencies. All technologies, with the exception of molten sodium metal-halide batteries, have issues with active materials going into solution or enabling unwanted reactions to occur faster.

2.2.4 Cycle Life

The cycle life is defined as the number of times a battery can be charged and discharged. For rechargeable batteries, the cycle life is significantly affected by multiple factors, including temperature, design materials, charge and discharge current, excessive charge/discharge, and storage. Also, how a battery is used by an application can have dramatic effects on the life of the battery. Previously, we discussed the impacts of temperature on battery performance. In this section, we will discuss the key factors related to DOD and charge, which are two critical parameters that influence rechargeable battery cycle life.

The cycle life of a battery is significantly increased as the DOD is reduced. The effect of DOD on Valve-Regulated Lead-Acid) VRLA from 30% to 100% is shown in Figure 4, with cycle life increasing to greater than 1,000 cycles at 30% DOD.

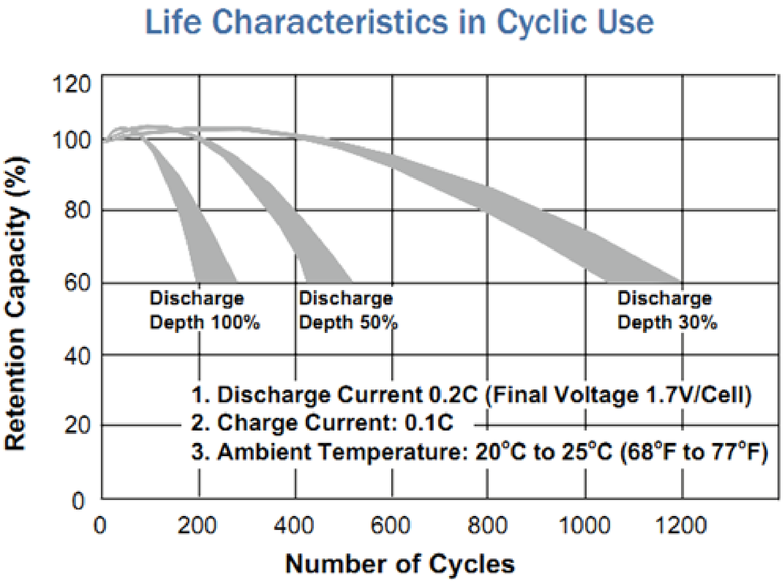


Figure 4 VRLA Cycle Life (Typical)

NiMH batteries show a linear relationship (Figure 5) between cycle life and DOD, with cycle life increasing constantly as DOD is reduced.

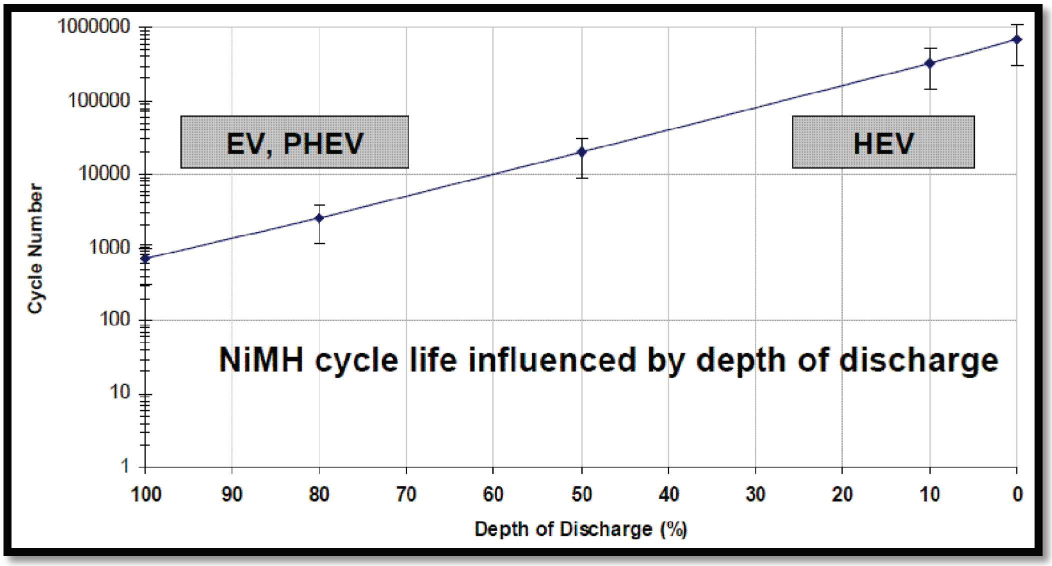


Figure 5 NiMH Cycle Life DOD

As with other battery chemistries, the cycle life of lithium-ion batteries is impacted by DOD. A typical example can be seen in the following chart (Figure 6), which shows the rate of power degradation for three different DOD scenarios in a lithium-ion battery. Deep cycling a lithium-ion battery to an 80% DOD level results in premature End of Life (EOL) for the battery, whereas cycling a battery at a lower DOD level (such as 60% or 70%) maintains a linear degradation in battery power that continues beyond 4,000 cycles.

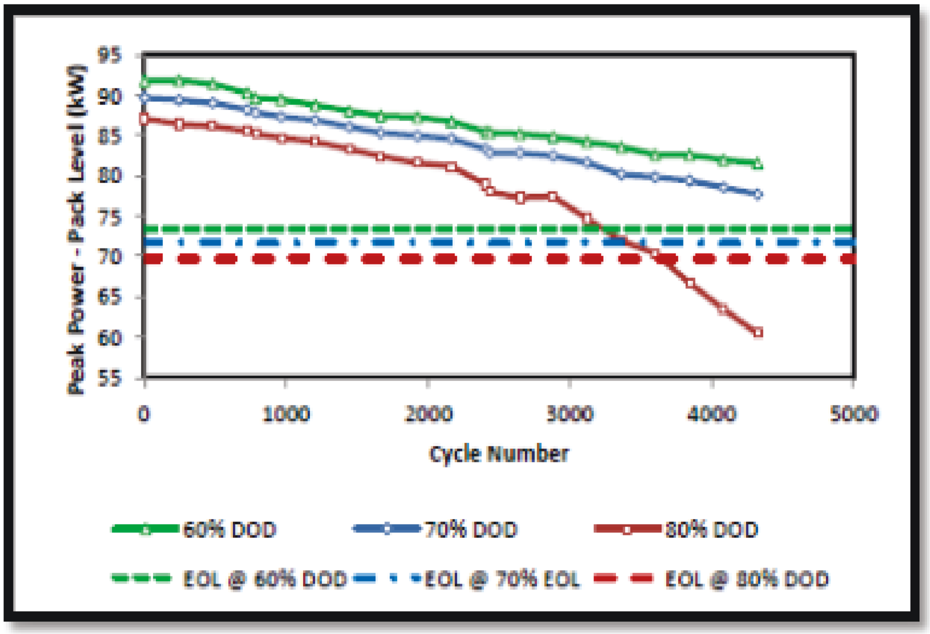


Figure 6 Li-ion Cycle Life

Another influence on cycle life is the charge. The charge has two components: rate and voltage. If the rate is too high for a technology, the cycle life is reduced. In general, aqueous lead and nickel technologies can handle high charge rates better than some sealed battery technologies. As seen in the charge voltage curves for Li-ion in Figure 7, increasing the charge voltage leads to both a reduction in cycle life and capacity.

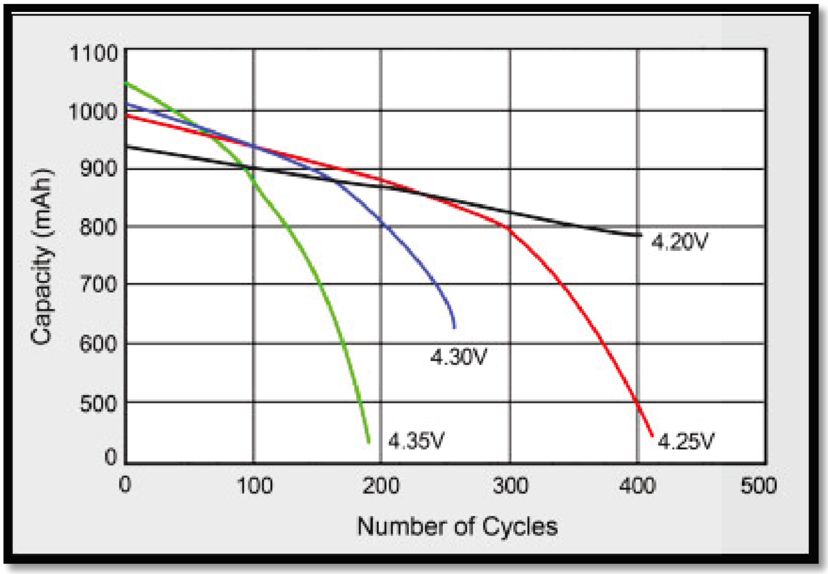


Figure 7 Li-ion Charge Voltage Influences on Cycle Life

2.2.5 *Calendar Life*

A battery's calendar life is the time period that a battery can be left at a set temperature and state of charge before it meets the manufacturer's EOL requirements. One of the key influences on calendar life is self-discharge, which occurs in all batteries and determines the "shelf life" of a battery. Table 1 shows typical self-discharge rates for several battery chemistries, though the exact values will vary with each manufacturer.[9]

Table 1 Self-Discharge

CELL TYPE	**Pb Acid**	**NiCd**	**NiMH**	**Li Ion**
SELF-DISCHARGE @20°C (% per Month)	4-6	10-15	20-25	2-5

In general, lithium-ion batteries display the lowest level of self-discharge, while NiCd and NiMH are fairly similar. NiCd batteries typically demonstrate a lower self-discharge rate than NiMH, but advances in NiMH manufacturing technology have reduced self-discharge rates. It is important to note that self-discharge is highly dependent on temperature, increasing as the battery temperature is increased. Also, to be noted for NiMH batteries is that the self-discharge rate is extremely non-linear. For example, a NiMH battery that loses 30% of its charge in a month may lose 15% to 20% in the first few days.

2.2.6 *Cell Aging*

Aging refers to the gradual loss of a battery's rated electrical performance over time. After a battery is produced it undergoes a number of irreversible chemical reactions that cause its internal resistance to increase and/or its capacity to decrease. There are a number of different physical and chemical processes of the various battery chemistries that are responsible for aging. Battery usage and storage conditions largely determine the rate of aging and the dominant aging mechanism. The life of any battery chemistry, in terms of aging, is determined by a combination of sudden failure events and gradual battery deterioration, leading to gradual loss of performance, and eventually to the end of service life (EOL).

3. Battery Technology

In this report, the performance and life-cycle characteristics for multiple production-level battery technologies have been developed for an HDEB locomotive application. It also includes information on the potential safety hazards of the various battery chemistries and provides recycling information for each type of battery. Appendix A includes a summary of each technology.

3.1 VRLA (Valve-Regulated Lead-Acid) batteries

Valve-Regulated Lead-Acid or VRLA, which includes Gel and Absorbed Glass Mat (AGM) battery designs, can be substituted in virtually any flooded lead-acid battery application combined with a well-regulated charging system. The unique features and benefits of VRLA batteries provide an ideal solution for many applications where traditional flooded batteries cannot deliver the best results.

The electrolyte in AGM batteries is completely absorbed by separators consisting of matted glass fibers. As a result, these batteries are spill proof and, if tipped, do not leak acid like a flooded design. The glass mats in AGM batteries are wrapped around the positive plate, which can prevent damage from vibration and extend cycling. In specific applications, AGM battery designs have over twice the cycle life of a conventional flooded product.

A VRLA battery utilizes a pressure-relief valve system to achieve a recombination process, in which the oxygen that is normally produced on the positive plate is absorbed by the negative plate. This suppresses the production of hydrogen at the negative plate. Water is produced instead and the moisture is retained within the battery. It never needs watering, and the VRLA battery should never be opened because the battery would be exposed to excess oxygen from the air.

Flooded electrolyte batteries do not have pressure-relief valves and therefore, do not work on the recombination principle. Instead, flooded designs utilize a vent to allow gas to escape. The batteries contain liquid electrolyte that can spill and cause corrosion if tipped or punctured. They can only be installed “upright.” Due to sulfation, flooded batteries lose capacity and become permanently damaged if left in a discharged condition for any length of time. Designs that require water maintenance are especially vulnerable. Flooded batteries also can be permanently damaged if active material shedding within the battery causes it to be continually over-discharged.

Both the Green Goat and the first generation NS 999, two locomotives powered by VRLA batteries, face a fundamental battery problem known as negative electrode sulfation. During discharge, a lead-acid battery’s electrodes are partially dissolved and lead sulfate ($PbSO_4$) is created. During charging, the bulk of the lead sulfate gets dissociated and re-deposited on the electrodes. In practice complete dissociation of lead sulfate never happens. Instead, a portion of the lead sulfate is deposited on the negative electrode in the form of hard crystals. As the number of cycles increases, so does the level of crystallization. As this process continues, the crystal buildup becomes extreme within the cell and the battery fails.

$$Pb + PbO_2 + 2HSO_4^- + 2H^+ \Rightarrow 2PbSO_4 + 2H_2O$$

Locomotive applications place strong demands on Pb–acid batteries for improved charge-acceptance and cyclability under partial state-of-charge conditions. Generally reported failure modes for VRLA batteries include:

- Sulfation at the negative plate (Pb)
- Corrosion
  1. Negative top lead

2. Positive grid

- Dry-out: Water Loss
- Thermal Runaway: Heat generation

In failure modes for Pb-acid batteries, the number and the position of $PbSO_4$ molecules depends on the reaction speed, which is linked to the discharge current value. $PbSO_4$ molecules are poor conductors, which means the battery capacitance value is lower with small currents. The higher the current, the lower the amperes hours (Ah) furnished by the battery.

The battery structure degrades when it encounters high discharge currents, which causes higher operating temperatures. This scenario also leads to higher Root Mean Square (RMS) currents, which increases grid corrosion and leads to considerably shorter battery life, and increased gassing within the battery leads to separator dry out and eventual cell failure.

Heat generation in a VRLA battery can exceed the rate at which the heat can be dissipated into the environment, leading to thermal runaway. Should this condition continue for an extended period, the VRLA battery temperature could increase until ultimately the cell will dry-out and the container, if plastic, may soften (100°C), rupture, and then melt (160°C).

High Temperature Operation – In general, a stationary VRLA battery kept at a constant state of charge (float life) will undergo a 50% reduction in life for every 8°C (14.4°F) increases in temperature above optimum 25°C. The following chart (Figure 8) provides a reasonable service life expectancy for a VRLA battery at various operating temperatures.

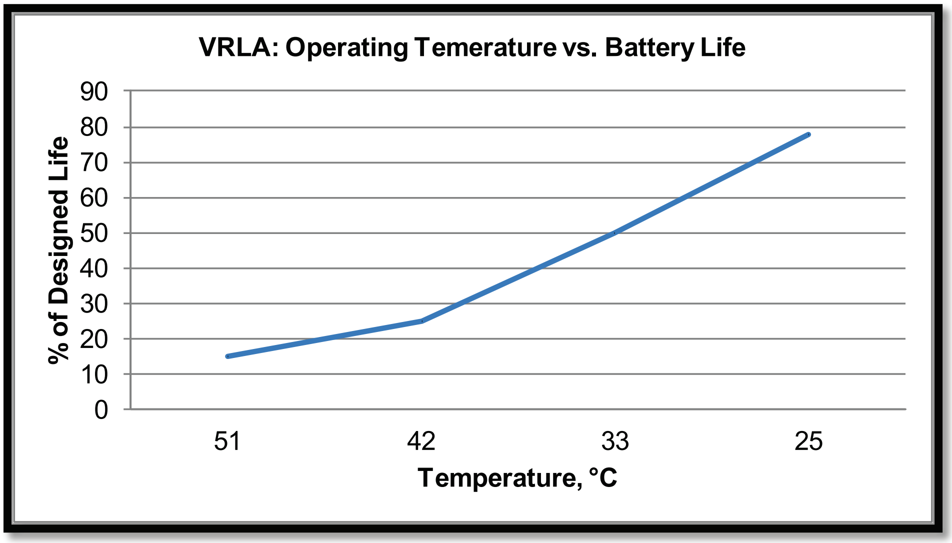


Figure 8 Service Life Expectancy for VRLA (Typical)[10]

There are other factors that impact the VRLA battery life outside of operating temperature. For example, installing batteries in unventilated cabinets can lead to higher internal temperature and premature failure.

As noted above, calendar life for a battery is the time period that a battery can be left at a set temperature and state of charge before it meets the manufacturer's End of Life requirements. For VRLA batteries, design, quality of materials, process, quality control, cycling profile, environmental conditions, and charging regimen are factors that impact calendar life.

VRLA batteries are rated for a certain number of deep discharges and shallow discharges. The load during discharge, length of discharge, rate of recharge and recharge time are all factors that affect VRLA battery life expectancy. Manufacturers rarely publish specific data on the number of discharges that a battery is rated for; however, VRLA batteries are typically designed for 2-3 deep discharges (i.e. 80%) per year and several hundred shallow discharges (i.e. less than 25%) per year.

A string of VRLA batteries can be replaced one battery at a time as defects are discovered, or an entire string can be replaced at once. The replacement method depends on the age and condition of the battery string, the ambient temperature, and the number of deep discharges to which the string has been subjected. If the string has been well maintained and is in good condition, it is acceptable to replace a single battery.

Cell aging in VRLA leads to:

- Anodic corrosion (of grids, plate-lugs, straps or posts)
- Positive active mass degradation and loss of adherence to the grid (shedding, sludging)
- Irreversible formation of lead sulfate in the active mass (crystallization, sulfation)
- Short-circuits
- Loss of water or “dry-out”

Aging mechanisms are often inter-dependent. For example, corroded grids cause increased resistance to current flow, which impedes the charging of certain parts of the active mass and in turn causes sulfation. Active mass degradation may lead to short-circuits. Sulfation may have been caused by a loss of water, and so forth. The different aging processes occur at different rates depending on how the battery is used (or misused). Over-charge will accelerate corrosion and water loss, while depth-of-discharge during cycling accelerates positive active mass degradation.

Some aging mechanisms occur only when the battery is misused. For example, short-circuits across the separators usually occur only after (excessively) deep discharge, due to the formation of metallic lead dendrites. Stationary batteries, operated under float-charge conditions, will typically age as the positive grids corrode. On the other hand, batteries that are subject to cycling regimes age as the structure of the positive active mass degrades. Starter batteries usually age by grid corrosion as the process occurs during normal passenger car use. However, starter batteries of city buses, which are subject to numerous shallow discharge cycles, may age (prematurely) due to positive active mass degradation. Valve-regulated batteries often fail as a result of negative active mass sulfation, or water loss. Temperature has a strong influence on aging. Figure 9 is a semi-log plot of the projected life of a 7.2Ah, Valve-Regulated Lead Acid (VRLA) battery versus temperature. It shows the impact on battery life versus the battery temperature.

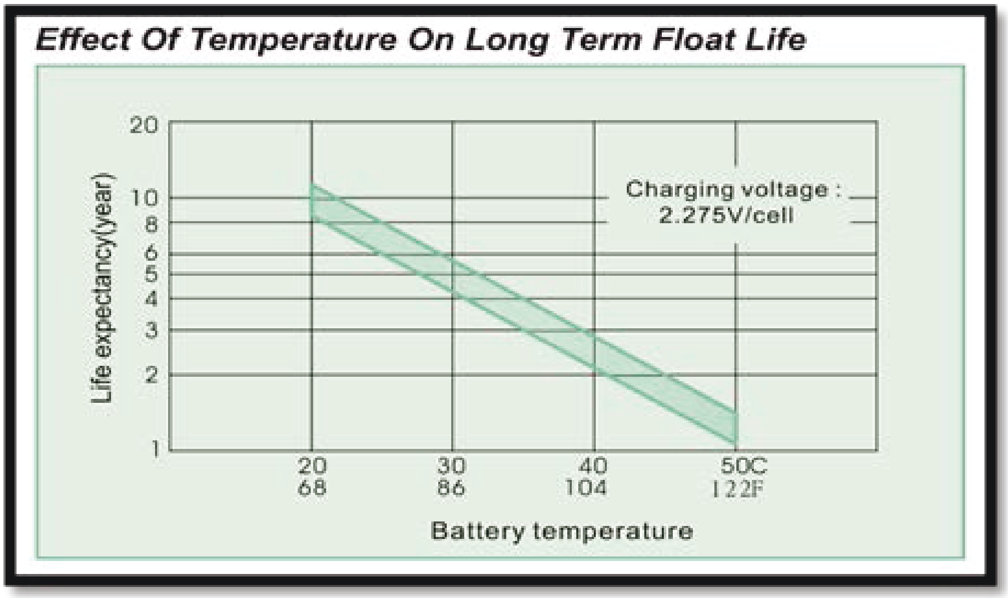


Figure 9 Temperature Effect on VRLA Float Voltage Life

Aging also depends on acid concentration. In general, very low acid concentrations, which prevail in the discharged state, are harmful to the grids. On the other hand, at very high acid concentrations, service life also decreases, in particular due to higher rates of self-discharge, gas evolution, and the increased danger of sulfation of the active material.

If a new battery is inserted into a string of older degraded batteries, the life of the new battery and the life of the older ones can be shortened. The older batteries will have a higher internal resistance, which causes them to recharge to a high voltage level. The new battery will have a lower internal resistance and will recharge to a lower voltage. The end result will be a prematurely aged entire battery string.

An HDEB application with multiple series and parallel configurations would require a battery management system, which would ensure cell/battery balance and prevent severe over and under voltage.

Table 2 provides a summary of benefits, limitation risks for VRLA Pb-Acid technology and Table 3 lists the ones for VRLA Pb-Acid with Absorbed Glass Mat (AGM).

Table 2 VRLA Pb-Acid Summary

Benefits	Limitations / Risks
• Exhibit low self-discharge • Fully recyclable with many recyclers • Low cost compared to other technologies due to large production volumes and low cost raw materials • Safety valve/flame arrested • Mature technology, high volume production capacity at low cost fully established • High volume recycling and collection systems in place in North America & Europe	• Does not tolerate being left completely discharged during storage; must be charged to prevent permanent damage • Environmentally unfriendly • Limited performance at higher rates and lower temperature extremes due diffusion rate of the acid ions • Low cycle life relative to other battery types • Deep discharges severely curtail battery life. Typically, battery capacity degrades quickly unless a starter battery or a minimal depth of discharge used

Benefits	Limitations / Risks
• Simple installation • Higher weight per kW to help in traction • Recombination reaction to minimize the escape of H_2 and O_2 and water consumption • Low maintenance • Simple charge algorithm – constant voltage float charging	• Water is consumed during corrosion of the positive electrode grids (current collecting supports) • Slower to recharge than other battery types leads to poor handling of Brake Energy Regeneration (BER) and Integrated Stop-Start (ISS) • Transportation restrictions on flooded lead acid • When failure mechanism (sudden death) occurs - Grid/plate corrosion sulfation limits the capacity, rate, and cycle life, which ultimately leads to loss of physical and electrical contact • Grid/plate corrosion increases with prolonged exposure to high temperatures. Calendar life highly influenced by temperature • Poor low temperature performance compared to most Long-term usage of lead in industrial applications and other battery technologies is jeopardized by EU REACH regulations. • Battery management would be required to ensure the cells/modules are not allowed to be reversed.

Table 3 VRLA with Absorbed Glass Mat (AGM) Summary

Benefits	Limitations / Risks
• Exhibit low self-discharge • Fully recyclable with many recyclers • Low cost compared to other technologies due to large production volumes and low cost raw materials • Safety valve/flame arrested • Mature Technology • Recombination reaction to minimize the escape of H_2 and O_2 and water consumption • Low maintenance • Simple charge algorithm – constant voltage float charging • Highly compressible mats that provide padded protection around plates to absorb shock and vibration • Wider operational temperature range than other SLA batteries • Improved high power applications	• Cannot be completely discharged during storage; must be boost charged to prevent permanent damage • Environmentally unfriendly • Prolong high temperature exposure increases grid/plate corrosion. • Limited performance at higher rates and lower temperature extremes due diffusion rate of the acid ions • Thermal runaway can occur with improper charging • Relatively low cycle life to other battery technologies • Water is consumed during corrosion of the positive electrode grids (current collecting supports) • Slow recharging leads to poor handling of Brake Energy Regeneration (BER) and Integrated Stop-Start (ISS) • When failure mechanism (sudden death) occurs, grid/plate corrosion sulfation limits capacity, rate, and cycle life. Ultimately, loss of physical and electrical contact occurs

Benefits	Limitations / Risks
• Better cyclic life and charge acceptance compared to other SLA technologies • No transportation restrictions	• Grid/plate corrosion is increased with prolong high temperature exposure. • EU REACH regulations restrict the use of lead and its compounds, which jeopardizes the long-term usage of lead in batteries. • Battery management is needed to ensure that the cells/modules cannot be reversed.

3.1.1 Health Hazard Identification of VRLA batteries

Batteries are safe, but precautions are needed when handling damaged cells and lead acid systems that allow access to lead and sulfuric acid.

Lead is a toxic metal that enters the body through the lungs (lead dust) or ingestion (touching the mouth with lead-contaminated hands). Acid and lead particulates can contaminate the soil and become airborne when dry. Children and pregnant women are most vulnerable to lead exposure. Excessive lead in the bloodstream can affect a child's growth, cause brain damage, harm kidneys, impair hearing and cause behavioral problems. In adults, lead can cause memory loss and lower the ability to concentrate, as well as harm the reproductive system. Lead is also known to cause high blood pressure, nerve disorders, and muscle and joint pain.

The sulfuric acid in a lead acid battery is highly corrosive and is potentially more harmful than acids used in other battery systems. Eye contact can cause permanent blindness; swallowing damages internal organs and can lead to death. First aid treatment calls for flushing the skin for 10 to 15 minutes with large amounts of water to cool the affected tissues and to prevent secondary damage. Immediately remove contaminated clothing and thoroughly wash the underlying skin. Always wear protective equipment when handling sulfuric acid.

Lead acid batteries produce some hydrogen gas while charging, but the amount is minimal if they are charged correctly. Hydrogen gas is explosive and one would need a concentration of 4% to create an explosion, and this level would only occur if large lead acid batteries are charged in a sealed room.

Over-charging a lead acid battery can produce hydrogen sulfide. The gas is colorless, very poisonous, flammable, and has the odor of rotten eggs. Hydrogen sulfide also occurs naturally when organic matter breaks down in swamps and sewers; it is present in volcanic gases, natural gas, and some sources of well water. Being heavier than air, the hydrogen sulfide accumulates at the bottom of poorly ventilated spaces. Although noticeable at first, the sense of smell deadens and potential victims may be unaware of its presence. As a simple guideline, hydrogen sulfide becomes harmful to human life if the odor is noticeable. Precautions include turning off the battery charger, venting the area, and staying outdoors until the odor disappears.

Current limiting must be applied to protect the battery when a VRLA is charged with over-voltage. The limit must be set to the lowest practical setting and the battery voltage and temperature must be observed during charging. In case of rupture, leaking electrolyte or any other exposure to the electrolyte, the affected area should be flushed with water immediately. If eye exposure occurs, flush with water for 15 minutes and consult a physician immediately. Approved gloves should be worn when touching electrolyte, lead, and cadmium. On exposure to skin, flush with water immediately.

Table 4 Pb-Acid Composition Information on Ingredients

Components	CAS Number*	Amount % by weight	OSHA PEL** (mg/m³)
Lead/Lead Oxide /Lead Sulfate	7439-92-1	60-90	0.05 (Lead)
Calcium (lead calcium alloy)	7440-70-2	<0.1	Not Established
Tin	7440-31-5	<0.5	Not Established
Arsenic (inorganic)	7440-38-2	<0.1	0.01
Sulfuric Acid (Battery Electrolyte)	7664-93-9	10-30	1.0
Inert Ingredients	N/A	<6	N/A

* The CAS number is a unique identifier established by the Chemical Abstracts Service
** OSHA Permissible Exposure Limit

3.2 Lead-Carbon Technology

Carbon additives have a pronounced effect on reducing negative-plate sulfation in traditional Lead acid batteries. Carbon additives promote a significant improvement in cyclability and charge-acceptance for both VRLA and flooded Lead acid batteries. However, other properties, such as high rate discharge and water loss can be negatively impacted by the amount of carbon addition. There is strong evidence that decreased high-rate discharge and higher water loss in Lead acid batteries with Carbon additives are due to partial adsorption of lingosulfonate on the carbon surface. This could limit the availability of lignosulfonate on the surface of the lead in the negative active-mass. The presence of lignosulfonate at the lead surface is considered critical for the formation of a porous layer of lead sulfate during high-rate discharge. When the overall concentration of lignosulfonate in the negative plate paste is appropriately adjusted, high-rate discharge performance and water loss can both be restored to an acceptable level.

Unlike using carbon as an additive, a proprietary PbC® technology described as a "multi-celled asymmetrically supercapacitive lead-acid-carbon hybrid battery" is technically classified as an asymmetric ultra-capacitor. Like a lead-acid battery, this PbC® battery consists of a series of cells. While the negative electrodes in typical Lead acid batteries are simple sponge lead plates, PbC® negative electrodes are five-layer assemblies that consist of a carbon electrode, a corrosion barrier, a current collector, a second corrosion barrier and a second carbon electrode. These electrode assemblies are then sandwiched together with conventional separators and positive electrodes to make the battery, which is filled with sulfuric acid electrolyte, sealed and connected in series to the other cells.

Most Lead acid batteries designed for deep discharge (80% or greater) applications can only survive 500 cycles under deep discharge operating conditions. Lead Carbon batteries have the following performance advantages:

- Faster recharge rates than VRLA
- Greater charge acceptance than VRLA
- Longer cycle lives in deep discharge applications (500 versus 2000) for deep cycle VRLA
- Reduced level of maintenance than VRLA

Due to its unique architecture, the Lead Carbon battery does not experience negative electrode sulfation. It also offers significantly higher charge and discharge currents than a conventional lead-acid battery. In a shallow cycling environment like the Green Goat, prototype Lead Carbon batteries have demonstrated the ability to withstand tens of thousands of cycles without degradation seen in traditional lead-acid batteries.

There is very limited information available for calendar life and aging of PbC® battery systems. The following provides a comparison between VRLA and Carbon enhanced Pb-Acid batteries in the areas of cycling and power capabilities.

Based on Axion's PbC® internal lab testing at 100% DOD with seven hours as the cycling time (Charge-Discharge), results indicate that the cycle life of PbC® system is four times better than conventional VRLA technology.

Test results from PbCultracell, detailed in the charts below (Figure 10), show the power performance (a) and cycling performance of a PbCultracell in comparison with a VRLA battery (b). The cycling tests were carried out with a discharge at $2.5C_5$ A for 30 seconds and a charge at a constant voltage of 2.5 with maximum current of $2.5C_5$ A for 31 seconds. There are two-rest times of 6.8 seconds between discharge and charge or charge and discharge. The cells were subjected repetitively to this profile at 40 °C until the voltage of each cell reached 1.77 V, which is considered to be the EOL for the cell.

The results show the discharge and charge behavior of a PbCultracell in comparison with a conventional lead-acid battery. A total of 50% and 60% improvement in the discharge and charge power, respectively, was achieved over traditional Pb-Acid technology. The results indicated that the PbCultracell can be operated at a wider depth-of- discharge window, but still can provide and receive similar power levels to that of the conventional VRLA battery. Figure 10 (b) shows the cycling performance of a PbCultracell, in comparison with a conventional lead-carbon cell. The ultracell with negative plates doped with carbon black and graphite completed 4,000 cycles, approximately 2.7 times longer than conventional lead-acid batteries. In comparison, the PbCultracell achieved approximately 17,000 cycles under a light charge/discharge cycle.

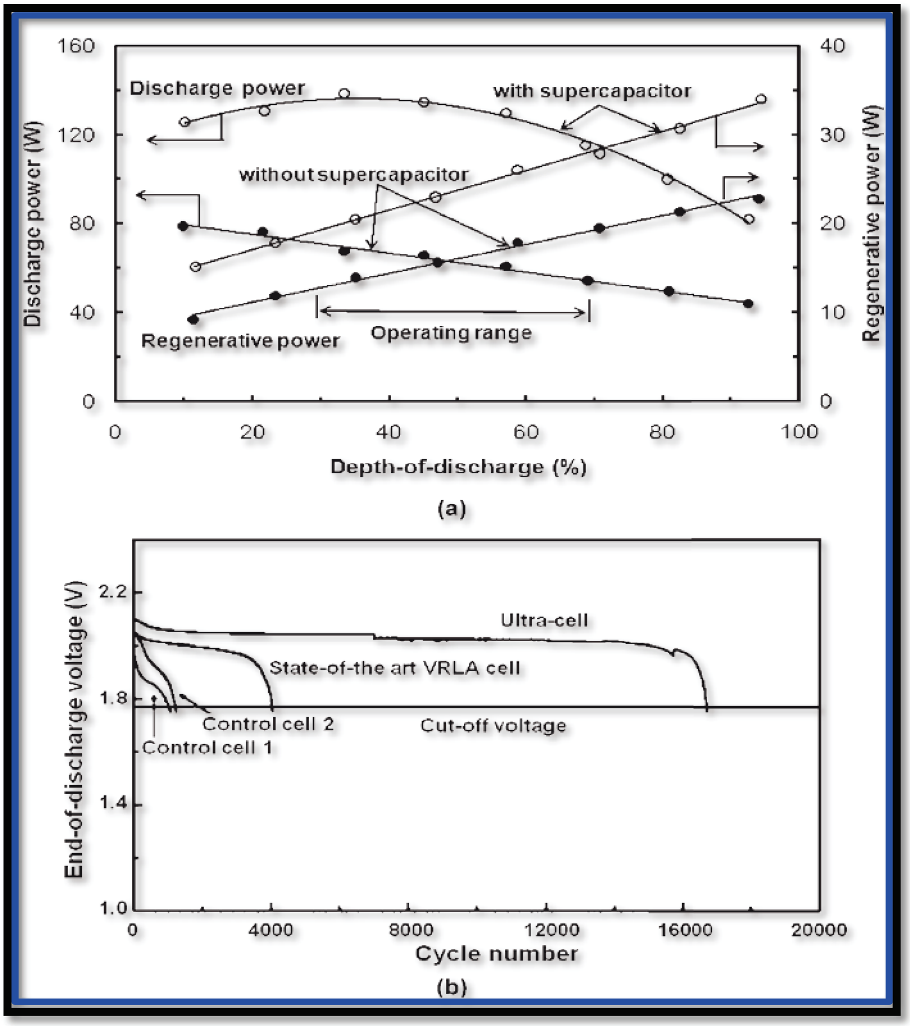


Figure 10 Pb-Carbon and SRLA Life Cycle Comparison

Based on Sandia National Lab testing, Carbon enhanced VRLA batteries were shown to (1) degrade during higher operating temperature (~10 to 15°C above ambient), (2) exhibit reduced Pulse Power Capability, and a reduced number of Partial State of Charge (PSOC) cycles versus traditional VRLA batteries in terms of the cell aging process. Similar data for Axion PbC® batteries is not publically available.

Cycling performance of Pb-C Hybrid is given in the following table. Based on published data, it shows significant longer cycling performance than the control VRLA batteries. More importantly, side-by-side testing has demonstrated that the Pb-C Hybrid chemistry cycle life is comparable, or superior, to that of NiMH cells.

Table 5 Cycling Performance Comparison [11]

Test Profile	Units	Battery Type		
		General VRLA	NiMH Cell	Pb-C Hybrid
Charge at 3C rate to 2.5V, Discharge to 1.75V (Micro HEV Simulation)	Cycles	11000-13000	72000	75000
Charge at 2C rate to 2.83V, Discharge to 1.83V (Micro HEV Simulation)	Cycles	4200	-	18000
Idling-Stop Cycle-Life test (SBA-S-0101, Micro HEV Simulation)	Cycles	15000	-	75000
42V-Profile (Mild HEV Application)	Cycles	17500	-	166000
EUCAR Profile (Medium HEV Simulation)	Cycles	34000-72000	180000	340000 220000
RHOLAB Profile (Medium HEV Simulation)	Cycles	150-180	-	750-1100

Table 6 provides a summary of benefits and limitations / risks for VRLA Pb-Acid technology and Table 7 lists the information for Pb-Carbon Battery / Capacitor Hybrid.

Table 6 Pb Carbon (Carbon as additives) Summary

Benefits	Limitations / Risks
• Advantages of increased surface area of the negative active material (NAM): ○ Low Current Density ○ Low Polarization ○ Improves charge acceptance and efficiency • Highly compressible mats that provides padded protection around plates to absorb shock and vibration • Sulfation process is significantly reduced (Carbon appears to enhance nucleation and retard recrystallization of lead sulfate) • Improve battery cycle life dramatically to other Pb-acid technologies • Require minimal modification of existing industrial-scale manufacturing processes • Offer a potential low-cost, high-performance energy storage solution • Mature technology • Fully recyclable access to many recyclers • Simple installation Best cycle life of traditional Pb-acid	• Researchers do not yet fully understand the characteristics of carbon that are beneficial or detrimental to lead-acid batteries • Battery management system may be required • Low energy density performance to most other battery technologies • Failure mechanism (sudden death) - Grid/plate corrosion; ultimately loss of physical and electrical contact • Not suited to absorb large amounts of regenerative energy. • Higher cost as compared to other Pb-Acid technologies due to manufacturing process • Failure mechanism (sudden death) - Grid/plate corrosion sulfation (less than other Pb acid technologies) - results in limiting the capacity, rate, and cycle life; ultimately loss of physical and electrical contact

Table 7 Pb-Carbon Battery / Capacitor Hybrid Summary

Benefits	Limitations / Risks
• High cycle Life • Unlike other Pb-acid technology, can be cycled at partial SOC's • Lighter weight than other Pb-acid technologies yet the available energy is much less • Improved high power capability compared to other Pb-acid technologies • Fully recyclable • Low maintenance compared to other Pb-acid other Pb-acid technologies • Good power over wide temperature range (-20°C to +50°C) • Virtual elimination of sulfation • Fast recharge capability • Handle the regenerative energy • Minimal negative electrode corrosion (sulfation process) • Charge Profile Characteristics o Forces balancing multiple battery strings and internal cells o Simplifies SOC electronics	• Low specific energy as compared to other battery technologies with the exception of Ni-Cap. • Require BMS at system level • Failure mechanism (sudden death) - Positive Grid/plate corrosion - results in limiting the capacity, rate, and cycle life; ultimately loss of physical and electrical contact.

3.2.1 Health Hazard Identification of Pb-C batteries

The addition of Carbon does not significantly change the composition of the battery from a health hazard perspective, see section 3.1.1

3.2.2 Recycling Pb-C batteries

The addition of Carbon does not significantly change the recycling process, which is similar to VRLA batteries, see section 3.1.2.

3.2.3 Recycling VRLA batteries

Recycling of conventional lead acid and Lead carbon (PbC®) battery

Lead acid battery technology led to the success of early battery recycling efforts and today 99 percent of all lead-acid batteries are recycled. Almost any retailer that sells lead-acid batteries collects used batteries for recycling, as required by most state laws. Reclaimers crush batteries into nickel-sized pieces and separate the plastic components. They send the plastic to a reprocessor for manufacture into new plastic products and deliver purified lead to battery manufacturers and other industries. A typical lead-acid battery contains 60 to 80 percent recycled lead and plastic. [12, 13] The recycling process is simple, as 70 percent of the battery's weight is reusable lead. As a result, over 50 percent of the lead supply comes from recycled batteries.

Lead carbon technology uses a standard lead acid battery positive electrode and a new proprietary carbon negative electrode to replace the standard lead negative electrode in a lead acid battery. The same manufacturing process is used for a Lead carbon battery as a conventional lead acid battery. In addition, the new Lead carbon battery uses the same plastic housing, cover, separator, acid, and other materials that are standard in conventional lead acid battery construction.[14, 15]

The lead-acid battery is a recyclable product, whether it is of an automotive, traction, or standby design. The product benefits from the traditional lead metallurgy that has been developed for both primary (mines) and secondary (recycling) smelting. Secondary smelting accounts for 60% of total lead production in Europe and produce the most reusable metal. In secondary smelters, scrapped batteries are crushed and smelted. The polypropylene from the boxes is recycled to produce secondary plastic for battery, automotive, or other miscellaneous uses. The lead metal is refined to be re-used in the battery industry. The acid is either neutralized or converted into a marketable sulfate compound.

The recycling of lead contributes to the sustainability of lead acid batteries and brings many advantages both to industry and society at large, in areas such as energy consumption, carbon emissions, resource conservation and costs. When used batteries are taken to recycling centers they are treated under strict environmental procedures by a combination of mechanical and flotation processes, to separate them into their component parts (plastic, lead and sulfuric acid).[16]

The battery is broken apart in a hammer mill; a machine that hammers the battery into pieces. The broken battery pieces are then placed into a vat, where the lead and heavy materials fall to the bottom and the plastic floats. At this point, the polypropylene pieces are scooped away and the liquids are decanted, leaving the lead and heavy metals. Each of the materials goes into a different recycling "stream".

Polypropylene pieces are washed, blown dry, and sent to a plastic recycler where the pieces are melted together into an almost liquid state. The molten plastic is put through an extruder that produces small plastic pellets of a uniform size. The pellets are sold to a manufacturer of battery cases and the process begins again.[16]

Lead grids, lead oxide, and other lead parts are cleaned and heated within smelting furnaces. The molten melted lead is then poured into ingot molds. After a few minutes, the impurities float to the top of the still molten lead in the ingot molds. These impurities are scraped away and the ingots are left to cool. When the ingots are cool, they are removed from the molds and sent to battery manufacturers, where they are re-melted and used in the production of new batteries.

Old battery acid can be handled in two ways: 1) The acid is neutralized with an industrial compound similar to household baking soda. [16] Neutralization turns the acid into water, which is then treated, cleaned, and then tested in a waste water treatment plant to be sure it meets clean water standards. 2) The acid is processed and converted to sodium sulfate, an odorless white powder that is used in laundry detergent, glass, and textile manufacturing.

The lead-acid battery recycling structure has been proven to be efficient and highly successful, with no other battery chemistry able to reach the recycling rate of lead-acid batteries.

3.3 Nickel Cadmium Batteries (NiCd)

Active materials in nickel-cadmium cells are nickel oxyhydroxide (NiOOH) in the charged positive plate and sponge cadmium (Cd) in the charged negative plate. The electrolyte is an aqueous potassium hydroxide (KOH) solution in concentration of 20-34 percent by weight pure KOH. The basic electrochemical reaction (Discharge and Charge) is[17, 18]:

$$2NiOOH + Cd + 2H_20 \leftrightarrow 2Ni(OH) + Cd(OH)_2$$

There are two basic cell types: vented and recombinant. Vented cells have a flooded electrolyte, and the hydrogen and oxygen gases generated during charging are vented from the cell container. Recombinant cells have a starved electrolyte, and the oxygen generated from the positive electrode during charging diffuses to the negative electrode where it recombines to form cadmium hydroxide by the following reaction:

$$Cd + H_2O + \frac{1}{2} O_2 \rightarrow Cd(OH)_2$$

The recombination reaction suppresses hydrogen evolution at the negative electrode, thereby allowing the cell to be sealed. Unlike valve-regulated lead-acid cells, recombinant nickel-cadmium cells are sealed with a high-pressure vent that releases only during abusive conditions. Thus, these cells remain sealed under normal charging conditions. However, provisions for gas escape must still be provided when designing battery cases since abnormal conditions may be encountered (e.g., a charger failure that causes an over current condition).

The construction of nickel-cadmium cells varies significantly, depending on the manufacturer.[17, 18] In general, cells feature alternating positive and negative plates with interleaved separator layers, a potassium hydroxide (KOH) electrolyte of approximately 25% concentration by weight, and a prismatic cell container with the cell terminals extending through the cover. The positive plate is impregnated with nickel hydroxide and the negative plate is impregnated with cadmium hydroxide. The plates differ according to manufacturer with respect to the type of substrate, type of plaque, impregnation process, formation process, and termination technique. The most common plate structure is made of nickel powder sintered onto a substrate of perforated nickel foil or woven screens. Cell containers typically are made of nylon, polyamide, or steel. One main difference between vented cells and sealed (recombinant) NiCd cells is the type of separator. Vented cells use a gas barrier layer to prevent gases from diffusing between adjacent plates. Recombinant cells feature a porous separator system that permits gas diffusion between plates.

In long life cells a large excess of electrolyte is contained in cell cases over the plates reducing maintenance for water addition to a 2-year interval, depending upon the amount of overcharge and the operating temperature. Flooded cells of this type have low internal gas recombination rates. Their covers therefore contain spring loaded pressure relief vents that release when the pressure reaches between 2 and 10 psi to relieve excess hydrogen and oxygen formed during overcharge.

The cell voltage of a NiCd cell is the result of the electrochemical potentials of the nickel and the cadmium active materials with the electrolyte, which is equal to a nominal voltage of 1.2 V. State of charge of a NiCd cell on an open circuit slowly self-discharges. As shown in Figure 11, the capacity of NiCd batteries is significantly affected by temperature.

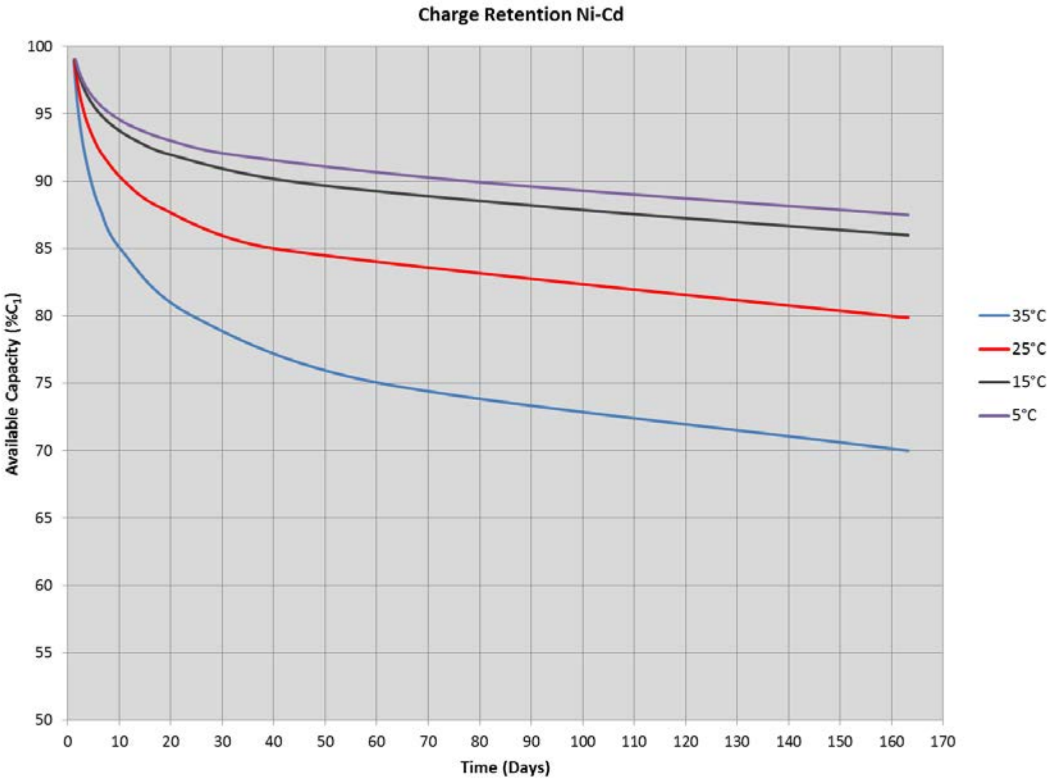


Figure 11 NiCd Storage Charge Retention

The internal resistance of a NiCd cell is very difficult to measure and to define since it varies with temperature, state of discharge, and cell type and size. This is common with all electrochemical devices, with thinner electrodes providing more power while reducing the overall capacity, and thicker electrodes provide less power while increasing the overall capacity.

The variations in ambient temperature and their influence on the cell performance have to be taken into consideration when sizing and choosing a NiCd battery. Low ambient temperature conditions reduce the cell performance, while high temperature environments do not significantly impact NiCd performance. The effect of low temperatures increases with higher rates of discharge.[19] The values can be found in Figure 12.

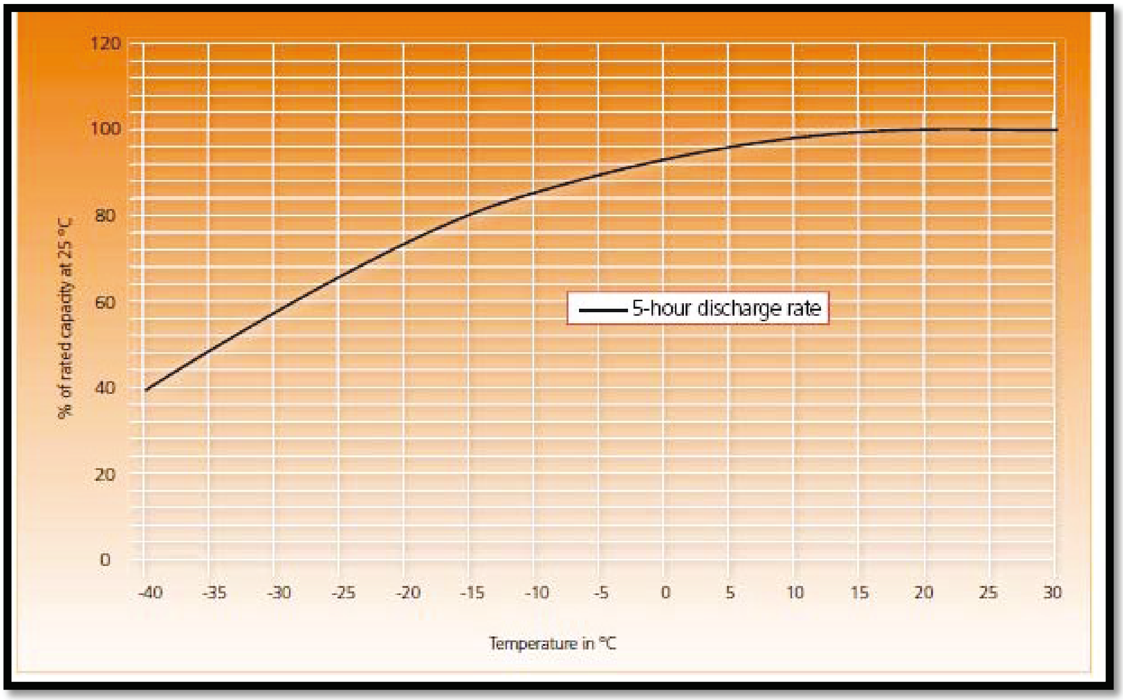


Figure 12 NiCd Capacity Availability Based On Temperature

NiCd battery technology is designed to obtain a very high number of cycles. As with other battery chemistries, DOD plays an important role in NiCd cycle life. The less deeply a battery is discharged the greater the number of cycles it is able to provide before being unable to achieve the minimum design limit. The graph shown in Figure 13 provides typical values for the effect of DOD on the available cycle life.

Figure 13 Cycle Life Vs DOD @20°C

The only impact on the calendar life of NiCd batteries is temperature. If the temperature is maintained within standard conditions, the battery may be stored in a discharged state for up to 10 years. As a result, many NiCd batteries are stored in the shorted, discharged state.

NiCd battery cells age when the active materials are no longer available to participate in the cell reactions shown above. If a NiCd battery has vents, it can regain most of the capacity it had during the previous maintenance interval after the battery's water has been replenished and it has been deep cycled. However, each time this sequence is performed on the overall battery the capacity is slightly reduced, limiting the number of times a NiCd battery can be replenished. Since cadmium is slightly soluble in the electrolyte, the metal forms dendrites on the surface of the negative electrode. If the growth continues to the positive electrode, then the cell develops a short and must be replaced.

Table 8 provides a summary of benefits, limitations, and risks for NiCd technology.

Table 8 NiCd Summary

Benefits	Limitations / Risks
• Good cycle life • Long storage life – recoverable capacity loss. • Rapid charge capability • Mature technology • Good low temperature discharge performance • Simple installation • Low maintenance • High cycle life • Fully recyclable • Simple charge algorithm – constant voltage float charging.	• Low volumetric and gravimetric energy density compared to Li-ion • Environmentally unfriendly • Failure mechanism - Dendrite Growth • Raw material cost more expensive than most other battery technologies. • EU REACH regulations jeopardize long-term usage of Cd in industrial application. • Battery management would be required to ensure the cells/modules are not allowed to be reversed.

3.3.1 Health Hazard Identification of NiCd batteries[20,21,22,23]

Exposure to the contents will not occur unless the battery leaks, is exposed to high temperatures, or is mechanically, physically, or electrically abused. A damaged battery will release concentrated potassium and sodium hydroxides, which are caustic and extremely corrosive. (Reference Table 9)

Table 9 NiCd Composition Information on Ingredients[24,25]

Components	CAS Number	%	OSHA PEL (mg/m^3)
Cadmium	7440-43-9	11-26	**0.005 TWA**
Cadmium Hydroxide	21041-95-2	11-26	**0.005 TWA**
Nickel Powder	7440-02-0	8-17	**1 TWA**
Nickel Hydroxide	12054-48-7	5-12	**1 TWA**

Components	CAS Number	%	OSHA PEL (mg/m³)
Potassium Hydroxide	1310-58-3	<3	**2 Ceiling**
Nylon	N/A	<2	**N/A**
Steel	N/A	12-13	**N/A**
Other	**N/A**	**<1**	**N/A**

During normal use, hazardous constituents are contained inside cell casings (which are inside the battery case). However; if a battery is in a fire, cadmium fumes and other hazardous combustion byproducts may be emitted. Inhaling cadmium dust or fumes may lead to dry throat, respiratory irritation, headache, nausea, vomiting, chest pain, extreme restlessness and irritability, as well as pneumonitis and bronchopneumonia. In the case of high concentration exposures (e.g. above 1 to 5mg/m³ during an eight hour period) death may occur within several days of exposure.

Both cadmium and nickel have been identified by the National Toxicology Program (NTP) as human carcinogens:

- Nickel was listed as a known human carcinogen in the Tenth Report on Carcinogens in 2002.[26]
- *Cadmium* – It was listed as a known human carcinogen in the Ninth Report of Carcinogens in 2000.[27] The U.S. EPA has classified cadmium as a "B1" probable human carcinogen, and the International Agency for Research on Cancer (IARC) has recommended that cadmium be listed as a "2A" probable human carcinogen and the American Conference of Government Industrial Hygienists (ACGIH) has proposed listing cadmium as an A2 carcinogen.

3.3.2 Recycling NiCd Batteries

INMETCO is one of the facilities in North America that recycles the large industrial cells that railroads, electric utilities, the military, and telecommunication companies use for back-up power. It also recycles small nickel-cadmium cells that are used in transceivers, portable power tools and appliances, medical equipment and emergency lighting systems. INMETCO uses the nickel and iron recovered from NiCd batteries to make stainless steel.

Cadmium vaporizes at a relatively low temperature (767˚C) in contrast to the other NiCd battery components nickel (2730˚C) and iron (3000˚C). Once it vaporizes, cadmium vapors go into a condenser, which cools the vapors to produce liquid cadmium. Next, the liquid is poured into molds to create metal sticks, balls, or ingots or dripped into a distilled or deionized water bath to create pellets that are 99.95 percent pure. The cadmium is eventually processed into high purity cadmium for reuse in battery manufacturing and other applications. The electrolyte recovered from NiCd batteries is used to control pH during wastewater treatment.

3.4 Nickel Metal Hydride Batteries (NiMH)

A basic NiMH cell consists of a metal hydride (MH) anode and a nickel hydroxide cathode in a high conductivity aqueous potassium hydroxide electrolyte. This chemistry provides a cell potential of 1.2V with an overall discharge reaction which can be written:

$$MH + NiOOH \rightarrow M + Ni(OH)_2$$

The negative electrode reaction occurring in a NiMH cell is:

$$H_2O + M + e^- \rightleftharpoons OH^- + MH$$

The charge reaction is read left-to-right and the discharge reaction is read right-to-left. On the positive electrode, nickel oxy-hydroxide, NiO(OH), is formed:

$$Ni(OH)_2 + OH^- \rightleftharpoons NiO(OH) + H_2O + e^-$$

The metal M in the negative electrode of a NiMH cell is an inter-metallic compound. Many different compounds have been developed for this application, but those in current use fall into two classes:

- *AB5* is the most common compound, and it is a combination of A (a rare earth mixture of lanthanum, cerium, neodymium, praseodymium) and B (nickel, cobalt, Manganese, and/or Aluminum).
- *AB2* compounds are higher capacity negative electrode materials, where A represents titanium and/or vanadium and B represents zirconium or nickel that has been modified with chromium, cobalt, iron, and/or manganese.

When overcharged at low rates, oxygen produced at the positive electrode passes through the separator and recombines at the surface of the negative electrode. Hydrogen evolution is suppressed and the charging energy is converted to heat. This process allows NiMH cells to remain sealed in normal operation and to be maintenance-free.

Nickel metal hydride (NiMH) batteries are constructed in a variety of shapes and sizes, from small button cells to large format prismatic cells that can contain up to 250 Ah. Whereas smaller cells routinely use the cell case as an electrical contact, prismatic cells (see Figure 14) utilize individual terminals that are electrically insulated from the welded lid/case assembly. The lid also features a re-sealable safety vent.

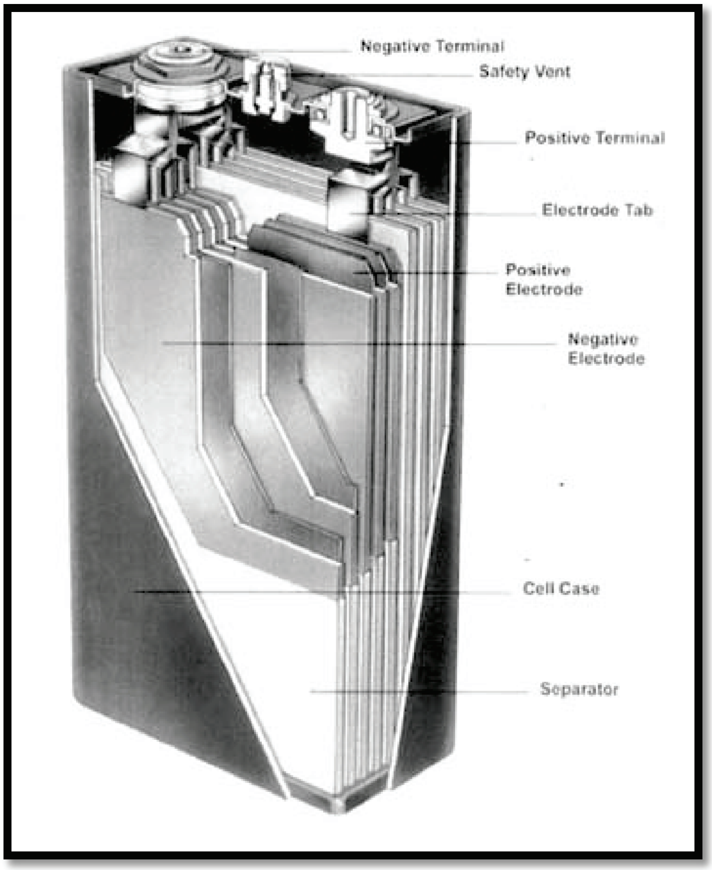


Figure 14 NiMH Cell Construction

NiMH batteries have a relatively low internal resistance (IR) given the large surface area of the electrodes, the wound construction, and the enhanced contacts. The low battery IR allows NiMH batteries to have excellent high rate performance. During discharge, the battery IR will stay relatively constant until near end of life where it will rise sharply.[28]

The graph below describes the calculated IR ($\Delta V \div \Delta I$) during a 750 mA continuous discharge with a 10 mA pulse every 6 minutes. The IR of NiMH batteries will increase with age and use, resulting in a lower voltage during discharge and a higher voltage during charge. IR is also increased as you cycle the battery based on age and use.

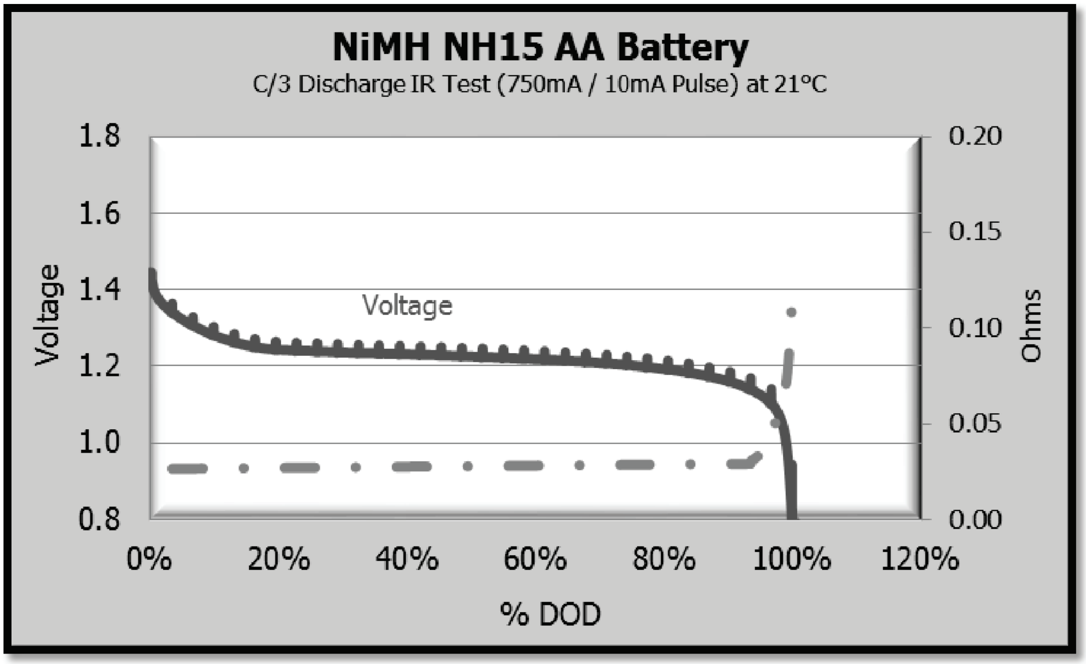


Figure 15 NiMH Calculated Resistance Changes

NREL conducted Hybrid Pulse Power Characterization (HPPC) tests per the Partnership for Next Generation Vehicle (PNGV) Battery Test Manual to obtain power performance of an automotive NiMH module at various SOC and temperatures (0°C, 25°C, and 40°C). The regenerative power performance of the NiMH battery is shown in Figure 17. Discharge power capability of the NiMH battery pack is around 20 kW at 50% SOC with regenerative capability of 14.5 kW at 25°C. The power capability increases with higher temperatures and decreases at lower temperatures. As a result, active thermal management improves power capability of NiMH batteries at lower temperatures.

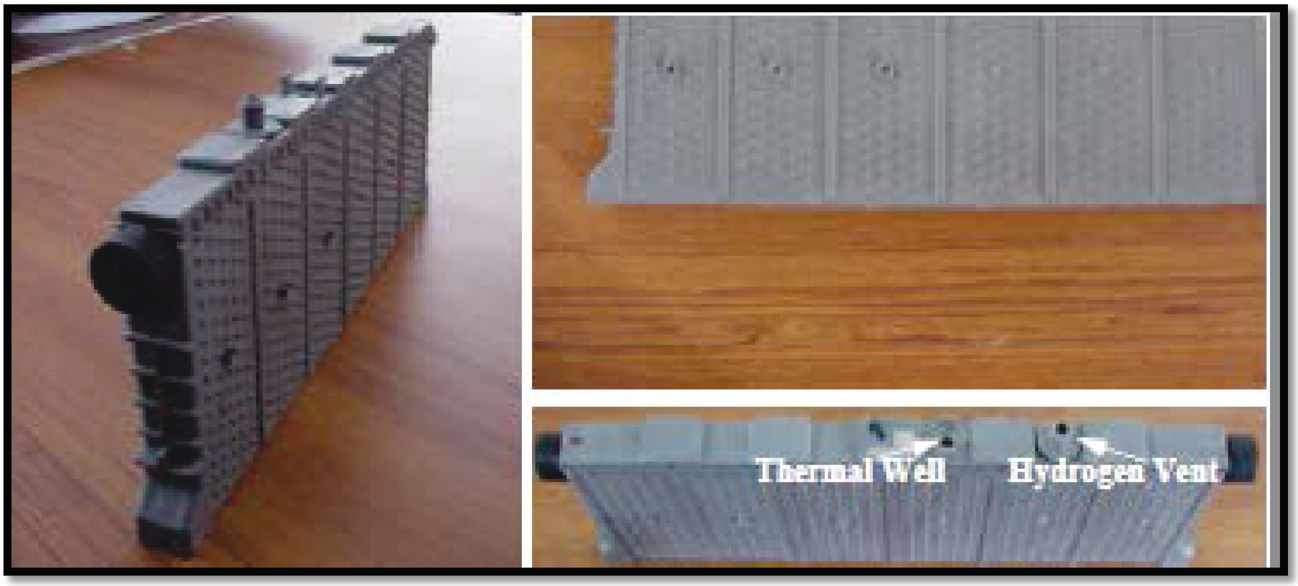


Figure 16 Automotive NiMH Module

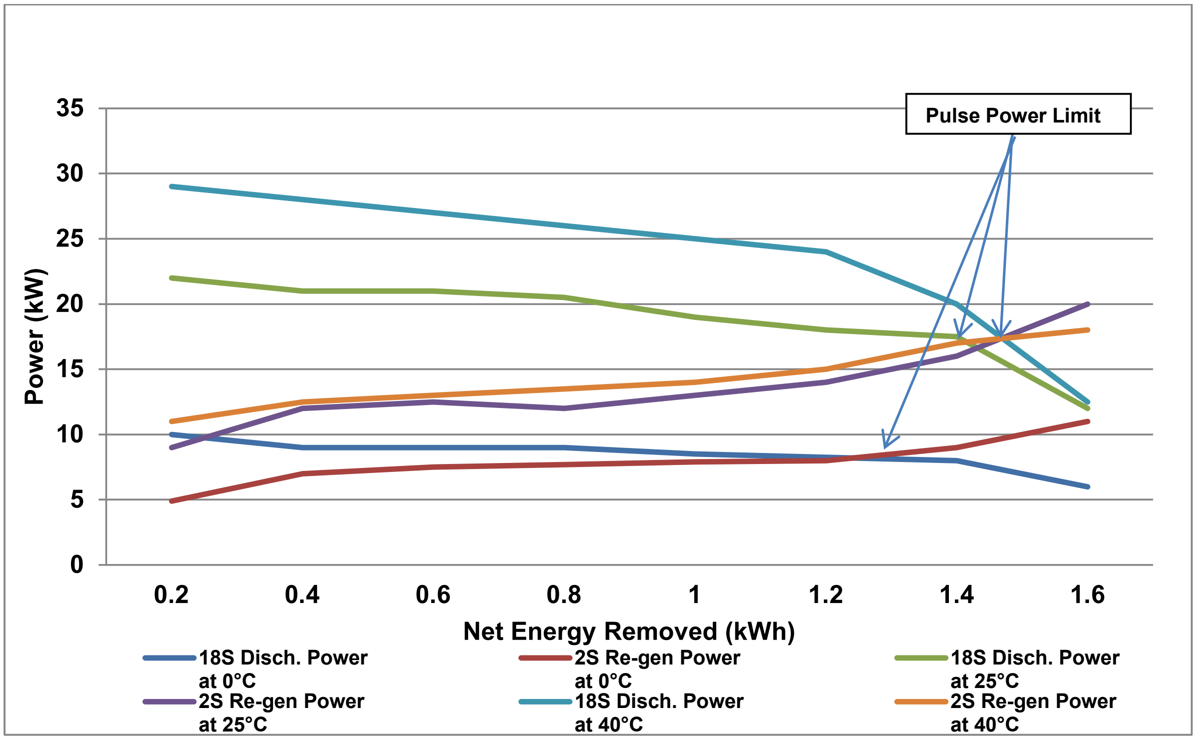


Figure 17 HPPC Characterization Testing at Various Temperatures

Many factors can affect NiMH cycle life. Some of them lead to gas generation within the battery, which can cause the activation of the safety vent and subsequent permanent deterioration of the battery. Under ideal conditions, up to one thousand cycles can be obtained with NiMH batteries. However, in real world use, extreme temperature, overcharging, discharging, rate of charge/discharge, cell balance, and the Depth of Discharge (DOD), among other factors, have a negative impact on the total number of cycles from a NiMH battery. The semi logarithmic chart in Figure 18 shows that NiMH batteries demonstrate reasonably attractive cycle life at all discharge depths.

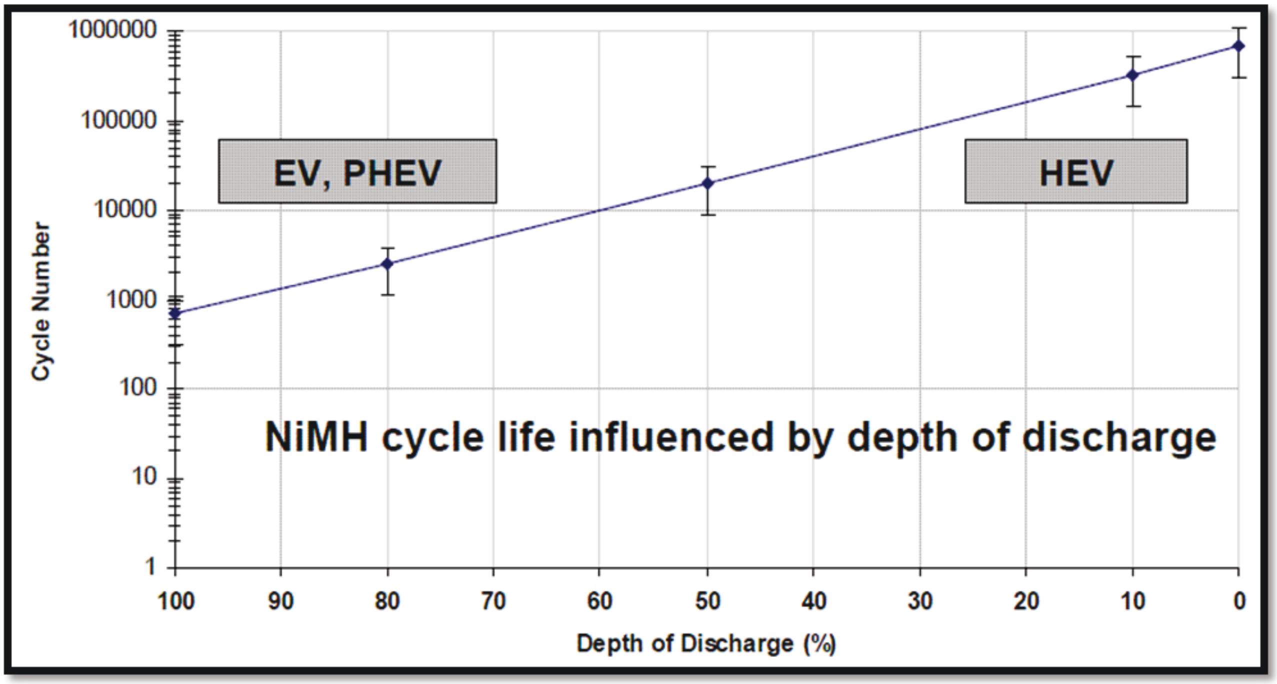


Figure 18 NiMH Cycle Life vs. Discharge Depth[29]

Since NiMH batteries are historically used in Hybrid Electric Vehicle (HEV) applications, there is a significant amount of information regarding calendar life of NiMH batteries used in HEV applications. Typically, the NiMH battery is fully charged initially, and then the vehicle is operated in a charge depleting mode until the charge reaches a predetermined low state-of-charge, after which the vehicle will be operated in charge-sustaining mode. This type of operational environment places additional stress on the battery, and as a result, the calendar life is reduced. The actual calendar life of NiMH is not known accurately (estimated to be less than 6 years) and there is always a risk for reduced calendar life. Also, the performance of NiMH batteries deteriorates with the degradation of the electrochemical constituents. As noted above, extreme temperatures, overcharging, discharging, rate of charge/discharge, and the Depth of Discharge (DOD) of battery cycles are the most important factors that can degrade NiMH batteries.

Memory effects in NiMH battery systems can significantly reduce usable power, because the usable SOC window of operation is reduced to a charge/discharge SOC window that is significantly smaller than the original 100% capability of the battery. As a result, a battery charger must be used to ensure adequate charging, while minimizing overcharging. For NiMH batteries, controlling overcharge exposure, time and charge rate is the key to enhancing battery life. Factors influencing the aging of NiHM batteries include:

- Degree of over charge
- Exposure to high temperature
- Battery Reversal – making the battery voltage negative instead of positive.
- Prolonged storage under load

Abrupt failures, such as mechanical events resulting in the battery shorting or going open-circuit, are relatively rare and are randomly distributed in NiMH batteries. Batteries can degrade in two ways:

- Oxidation of the negative active material that increases battery internal resistance resulting in reduction of available voltage from the battery (mid-point voltage depression). This also affects the balance between electrodes within the battery and may possibly result in reduced gas recombination, increased pressure, and ultimately, battery venting.

- Deterioration of the positive active material results in less active material being available for reaction with the consequent loss of capacity.

Of all the battery technologies, NiMH technology costs are driven by the fact that taxes are being placed on rare earth elements by source countries such as China. Table 1 provides an overview of the eight main areas of application, lists some exemplary products and the amount of rare earth oxides (REO) used in an application in metric tons per annum (tpa) in 2008. During this time NiMH batteries used 12,098 tpa of rare earth oxides.[30]

Table 10 provides a summary of benefits and limitations / risks for NiMH technology.

Table 10 NiMH Summary

Benefits	Limitations / Risks
• Higher capacity than NiCd batteries • Sealed construction and no maintenance required • Cadmium free (Environmentally friendly) • Rapid discharge capability • Long cycle life • Matured technology • Moderate cost • No regulatory control for transportation • Long storage life - recoverable capacity loss • Mature technology • Maintenance free • Fully recyclable	• Lower power capability than NiCd batteries • High self-discharge • Performance degrades if stored/operated at high temperatures • More expensive than NiCd • Raw material cost more expensive than most other battery technologies. • Deep discharge at high current reduces the service life • Battery & thermal management system required • Significantly reduced life due to high temperature exposure • Complex charge algorithm needed; tight charge voltage and current control • Materials controlled/restricted by countries with rare earth metals could limit support/availability;

3.4.1 Health Hazard Identification of NiMH batteries

NiMH cells do not contain cadmium, mercury or lead. The chemicals and metals in this product are contained in a sealed can. Exposure to the contents will not occur unless the battery leaks, is exposed to high temperatures or is mechanically, physically, or electrically abused. A damaged battery will release concentrated potassium and sodium hydroxides, which are caustic. Anticipated potential leakage of potassium and sodium hydroxides is 1-2 grams.

The positive electrode of a NiMH cell is made of nickel-hydroxide, as in many other nickel based batteries including NiCd. The negative electrode is a metal hydride electrode, which contain different metals that can store hydrogen. The NiMH uses an aqueous potassium hydroxide (KOH) electrolyte (Refer to Table 11).

Table 11 NiMH: Composition/Information on Ingredients

Chemical Name	CAS Number	Amount %	OSHA PEL (mg/m³)
Nickel-Cobalt-Manganese- Al Alloy	7440-02-0 7440-48-4 7439-96-5 7429-90-5	20-40	1.0 0.1 5.0 15
Nickel-Cobalt- Zinc Alloy	7440-02-0 7440-48-4 7440-66-6	15-25	1.0 0.1 None Established
Nickel	7440-02-0	5-15	1.0
Potassium Hydroxide (35%)	1310-58-3	1-5	2.0 (ACGIH)
Sodium Hydroxide	1310-73-2	1-5	2.0
Lithium Hydroxide	1310-65-2	1-5	1.0 (WEELs)

The health concerns for nickel hydroxide are the same as noted above for NiCd (Section 3.3.1). In addition, potassium hydroxide, which is in higher concentration in NiMH batteries, is extremely corrosive.

In general, the health and safety hazards associated with NiMH batteries are small. The electrode materials of the NiMH system are not toxic by nature which helps minimize the health and safety hazards of the cells and batteries.

3.4.2 Recycling NiMH Batteries

Nickel-metal-hydride batteries contain nickel and KOH electrolyte, which are considered semi-toxic.[31] NiMH batteries contain several components, including rare earth elements (REE), nickel, cobalt, and steel, each of which has value as recycled materials.[32] Based on Öko-Institut (OKO) Institute data, Figure 19 describes the major components by percent weight in a typical NiMH battery:[33]

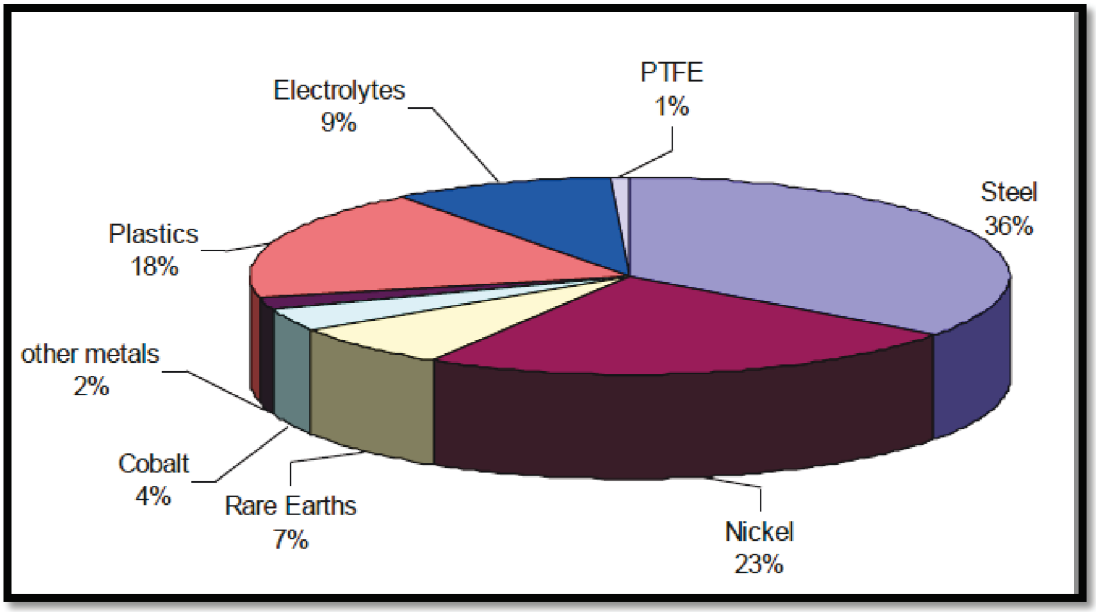


Figure 19 NiMH Major Components

INMETCO (mentioned in Section 3.3.2) also recycles NiMH cells and batteries by recovering the nickel and steel for making stainless steel. There are several hydrometallurgical recycling processes capable of recycling and recovering metals from spent NiMH batteries. In some processes, hydrochloric acid is used to leach the batteries and recover rare earth elements (REEs) by solvent extraction. Nickel, rare earths, cobalt alloy, and nickel hydroxide are selectively recovered as high purity metals and can be used again for production of new NiMH batteries. A closed loop recycling process for the NiMH batteries was developed by Muller and Friedrich. The $CaOCaF_2$ slag was proposed to recover the REEs from NiMH batteries.[34] Similar high temperature process for recycling of Li-ion and NiMH batteries are also practiced by Umicore in reasonably good size volume.[35]

3.5 Bipolar Nickel Metal Hydride Batteries

The nickel metal hydride (NiMH) battery has had the desirable power density, energy density, and life capabilities that would be needed in an advanced battery for transportation systems. However, present battery cost is higher than desired, limiting the full potential of this battery's use in the transportation sector. As a result, the bipolar packaging design concept is being explored to reduce cost and improve the power capability of NiMH batteries.

Bipolar battery design differs from conventionally available designs in that it results in a smaller and lighter battery for transportation applications. US developer G4 Synergetics has developed an 'ultra-high-power' bipolar nickel metal hydride (NiMH) rechargeable battery. G4's NiMH design is primarily for power-dependent applications, rather than high energy applications, which is the design target for most commercial cells. The batteries have a low internal resistance, which enables them to deliver extremely high power. The reduced internal resistance translates into less heat generation during charge and discharge, and allows G4 batteries to be charged more quickly – typically in five minutes – than conventional NiMH battery constructions.[36]

Conventional NiMH battery designs include cylindrical and prismatic types as shown in Figure 20 below.

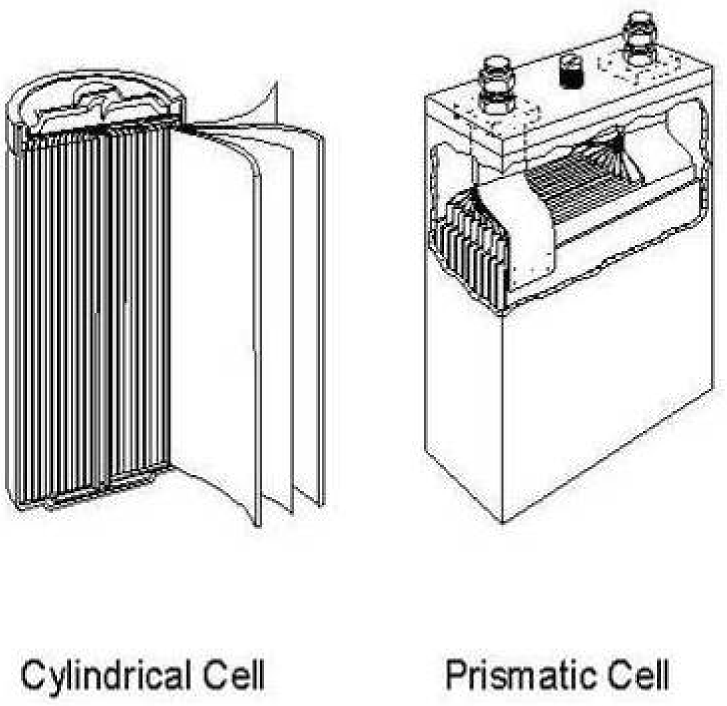


Figure 20 Conventional Nickel Metal Hydride (NiMH) battery designs

The active material in the negative electrode is metal hydride (MH), a special type of inter-metallic alloy that is capable of chemically absorbing and desorbing hydrogen. The most widely used MH in NiMH today is the AB5 alloy with a $CaCu_5$ crystal structure, where A is a mixture of La, Ce, Pr, and Nd, and B is composed of Ni, Co, Mn, and Al. The active material in the positive electrode is $Ni(OH)_2$, which is the same chemical used in the Ni–Fe and Ni–Cd rechargeable batteries.

The separator is typically made from grafted polyethylene (PE)/polypropylene (PP) non-woven fabric. The commonly used electrolyte is a 30 weight % of KOH aqueous solution.

A bipolar battery is one in which both a positive and a negative electrode are in contact with a conductive partition.[37] As shown in Figure 21, a bipolar battery's most attractive attributes involve the reduction of the current path through the electrodes, as well as potentially simplified battery manufacturing. The reduced current path leads to a design that has lower internal resistance, with the capability of supplying much higher power levels. However, most bipolar rechargeable battery designs suffer from electrolyte leakage and a need to manage gas pressure within the cells.

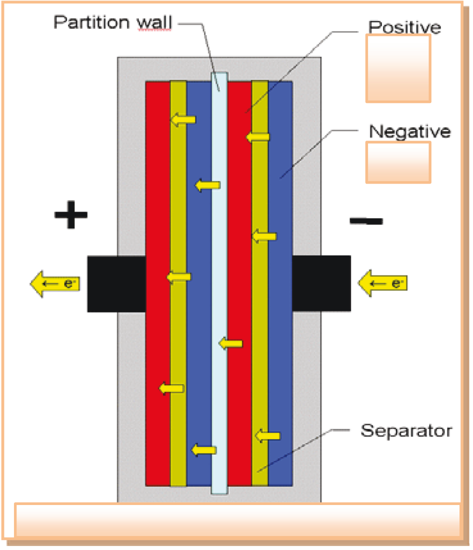


Figure 21 Bipolar Design[38, 37]

In order to handle the pressure and reduce the potential for leakage in a bipolar cell design, Electro Energy Inc (EEI) developed a wafer cell. The EEI design consists of a plastic film, a sealant which serves to prevent electrolyte creep, and a metal foil that conducts the current. When held in compression, this configuration effectively eliminates cell leakage concerns.

Figure 22 provides EEI schematic cutaway of the bipolar wafer cell (Source EEI):

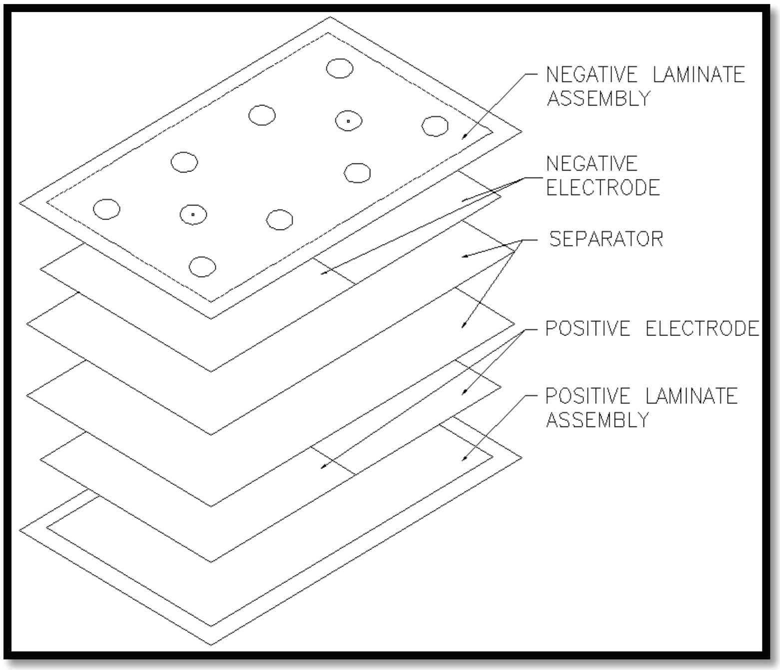


Figure 22 EEI Bipolar Wafer Schematic Cutaway[37, 38, 39]

Individual flat wafer cells are constructed with contact faces, one positive electrode, a separator, and one negative electrode. The contact faces are sealed around the perimeter of the cell. In order to build multi-cell batteries, a series connection of cells is created (a set of identical cells stacked on top of each other, positive-to-negative). To complete the battery, current collecting contact sheets are placed on the end cells and the entire stack is held in compression. The major advantages of the bipolar wafer cell design are the elimination of a number of cell components, the use of lower cost materials, and simpler manufacturing techniques when compared to conventional cylindrical and prismatic designs.

To keep the control system tractable, groups of cells are monitored as stacks, ranging from 24-48 V (20-40 series- connected cells). If any cell within the group generates significant amounts of gas pressure, it expands. The deflection of the stack can be sensed by normally-closed spring-loaded switches or by small load cells placed within the battery. The outputs from these switches are used as inputs to the battery control system.

The combination of the wafer cell design coupled with cell pressure sensing ability solves the fundamental issues in secondary bipolar battery designs. This unique approach eliminates the hardware for inter-cell connections. The result is a battery that can be packaged in a much lower volume, at a lower cost, than a conventional battery having similar energy. As a result, the bipolar battery can be a drop-in replacement for existing batteries of various chemistries. According to Mark Kohler, G4's Project Manager, the company has made a completely new high-power rechargeable NiMH cell architecture that has a very high rate charge acceptance and superior thermal management. He believes that the new design is disruptive and transformational technology.

The bipolar NiMH battery contains similar electrolytes as other NiMH batteries; therefore, the impact of temperature will be similar. Figure 23 illustrates typical discharge curves for Bipolar NiMH batteries.[40]

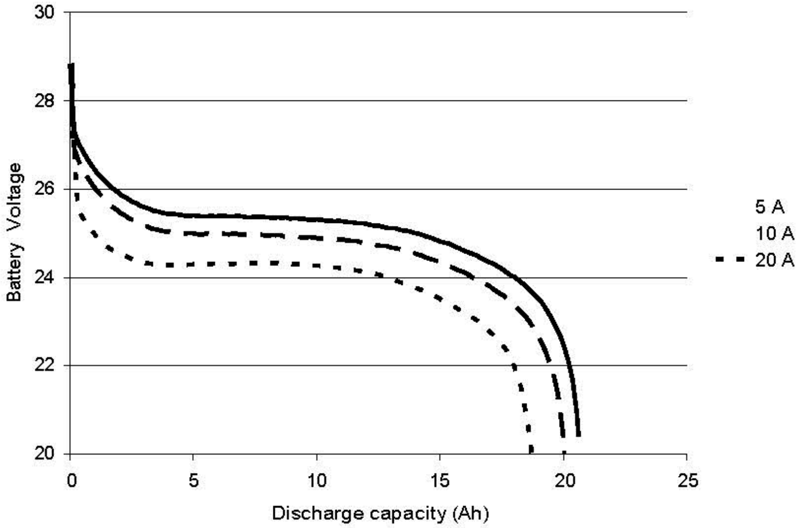


Figure 23 Bipolar Performance Characteristics[39]

Actual cycle life, calendar life and aging information for Bipolar NiMH batteries is not readily available in the public domain, as there has been a lot of work done at the cell level and in the development of modules, but not in large battery formats.

Table 12 provides a summary of benefits, limitations, and risks for Bipolar Nickel Metal Hydride technology.

Table 12 Bipolar Nickel Metal Hydride Summary

Benefits	Limitations / Risks
- Efficient packing - Reduction of collector losses - Higher power and capacity than NiCd and other NiMH batteries - Sealed construction and no maintenance required - Cadmium free (Environmentally friendly) - Rapid charge/discharge capability - Long cycle life - Matured technology - Moderate cost - No regulatory control for transportation - Long storage life - recoverable capacity loss - Mature technology - Maintenance Free - Fully recyclable	- Electrolyte Leakage - Dealing with gas pressure. - Lower power capability than NiCd batteries - High self-discharge - Performance degrades if stored/operated at high temperatures - More expensive than NiCd and other NiMH batteries. - Raw material cost more expensive than most other battery technologies. - Deep discharge at high current reduces the service life - Battery & thermal management system required - Significantly reduced life due to high temperature exposure - Complex charge algorithm needed; tight charge voltage and current control - Materials controlled/restricted by countries with rare earth metals could limit support/availability;

3.5.1 *Health Hazard Identification of Bipolar NiMH batteries*

The materials are identical / similar to NiMH batteries (See Section 3.4.1).

3.5.2 *Recycling Bipolar NiMH Batteries*

The materials are identical / similar to NiMH batteries (See Section 3.4.2).

3.6 Nickel supercapacitor

Nickel capacitors are a type of electrochemical double layer capacitor, also known as a super capacitor (or an ultracapacitor). Super capacitors store their electrical energy at the interface between a conductive surface and an electrolyte within a cell. The charge is stored within an electrode matrix by electrons with a complementary surface charge by ions from the electrolyte. These charges are then subsequently removed during discharge. There is no chemical reaction taking place so a super capacitor can discharge quickly compared to a battery. This produces a tremendous power capacity. Also, super capacitors have remarkable stability and can charge and discharge hundreds of thousands of times. A super capacitor delivers energy electrostatically vs electrochemically and therefore has much longer cycle life. However, the energy storage capability of these devices is limited by the surface area of the electrode (as can be seen in the following formula):

$$C = \frac{\varepsilon A}{d}$$

Where, C is the capacitance, A is the area of the conducting plate surface, d is the distance between the plates and ε is the permittivity of the material.

To take advantage of the storage mechanism, supercapacitors therefore use materials that have a very large surface area and very small distance between the plates (or layers, when referring to a double layer capacitor). This formula holds true for both traditional capacitors and supercapacitors and we can see that performance can be increased via increasing the surface area of the material and reducing the distance between the plates. In a supercapacitor, the plates can be thought of as the electrochemical double layer mentioned. The overall energy can be described by the formula:

$$E = \frac{1}{2} CV^2$$

Where, E = Energy, C = Capacitance and V = Voltage

As there is no intercalation of ions into the electrodes, the energy storage capabilities of super capacitors are significantly lower than a battery. Targeted approaches to increasing the energy include identifying materials that give increased capacitance and electrolytes that give a wider voltage range. Figure 24 is a Ragone plot which compares energy and power density between some of the different energy storage devices:

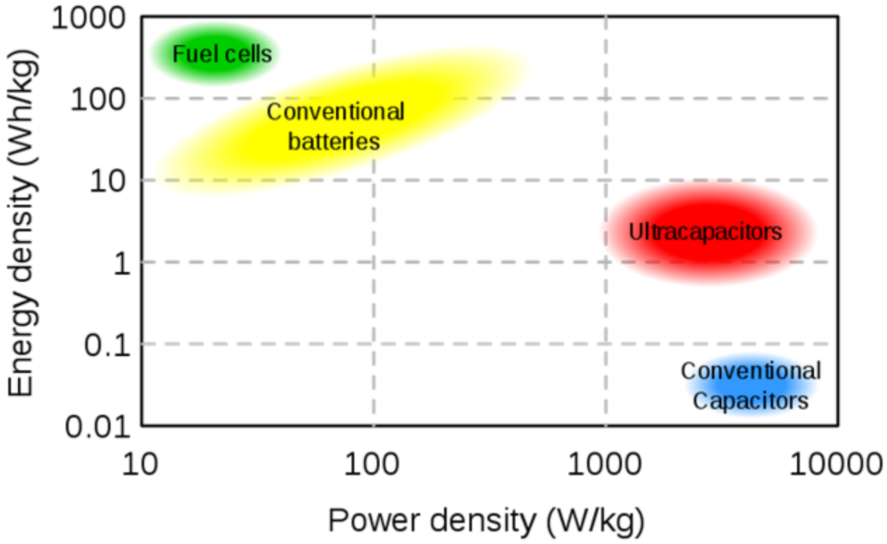


Figure 24 Ragone Charge including Ultracapacitors and Conventional Capacitors

Hybrid nickel super capacitors utilize an asymmetric aqueous electrolyte design and an activated carbon negative electrode to achieve a large surface area. They also utilize a positive electrode of nickel oxy-hydroxide that is similar to the type developed for nickel-cadmium (NiCd) batteries. The electrodes are separated by a porous separator, again similar to battery technology. As a result, this hybrid asymmetric device has a power capability that is comparable to a traditional super capacitor yet with greater energy storage ability due to an increase in the voltage and the ability to access the full capacitance potential of the activated carbon. The electrolyte used is potassium hydroxide, KOH, in water and its concentration can be tailored to give optimum electrical and temperature performance. The open circuit potential of a Nickel supercapacitor cell is typically around 1.45 V and this can normally be discharged to approximately 0.3 V, giving a very wide voltage window. A schematic of the structure of an individual supercapacitor plate-pair is given in Figure 25.

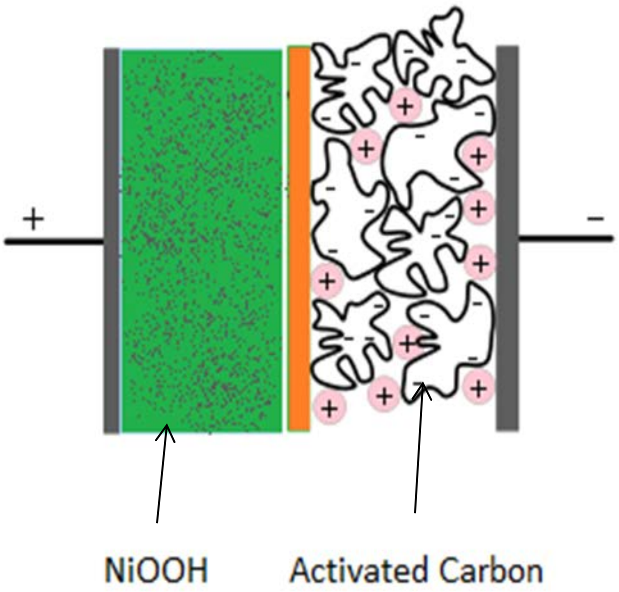


Figure 25 Nickel Capacitor Schematic

The electrolyte acts as an ion source as well as enabling the ions to flow. As noted previously, capacitance is maintained to very low temperatures, due to the lack of intercalation into the carbon, as can be seen in Figure 26. As colder temperatures restrict ion flow, the resistance will start to increase. In spite of this, the supercapacitors can maintain performance capabilities down to less than -40°C, whereas most battery systems will struggle to provide any current or energy below -20°C.

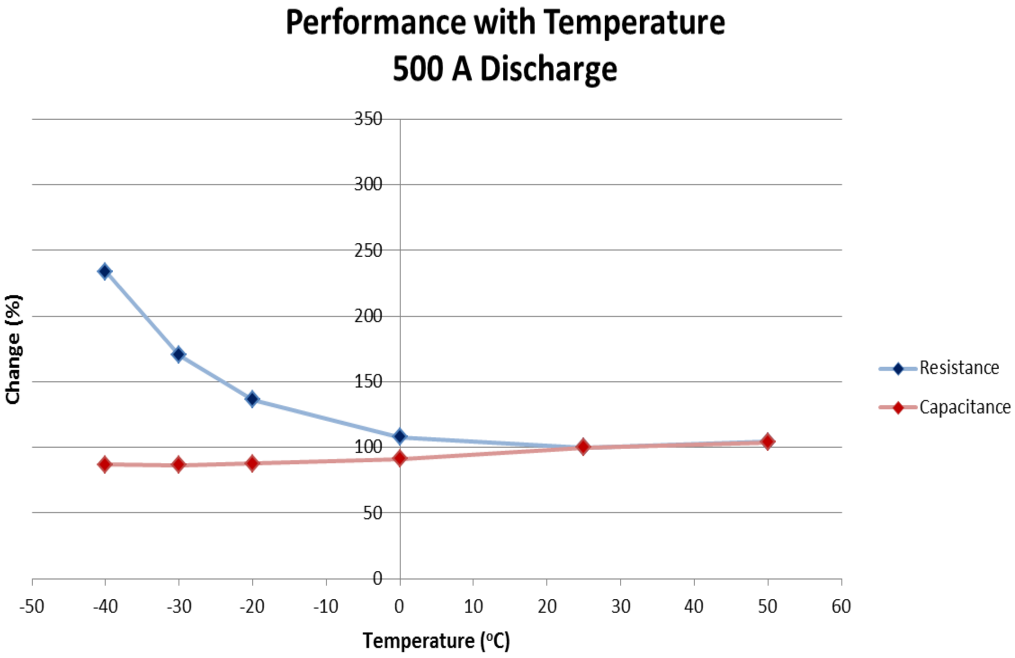


Figure 26 Nickel Supercapacitor Typical Performance

A key performance parameter of super capacitors is cycle life. Typically, batteries will have a cycle life in the order of thousands of cycles. In contrast, asymmetric nickel super capacitors have been able to demonstrate cycle lives of over 100,000 cycles (Figure 27). This is particularly important in many applications where batteries need to be changed frequently. If a supercapacitor can be used in place of a battery, it can enable non-maintenance over the life of a product in which it is used.

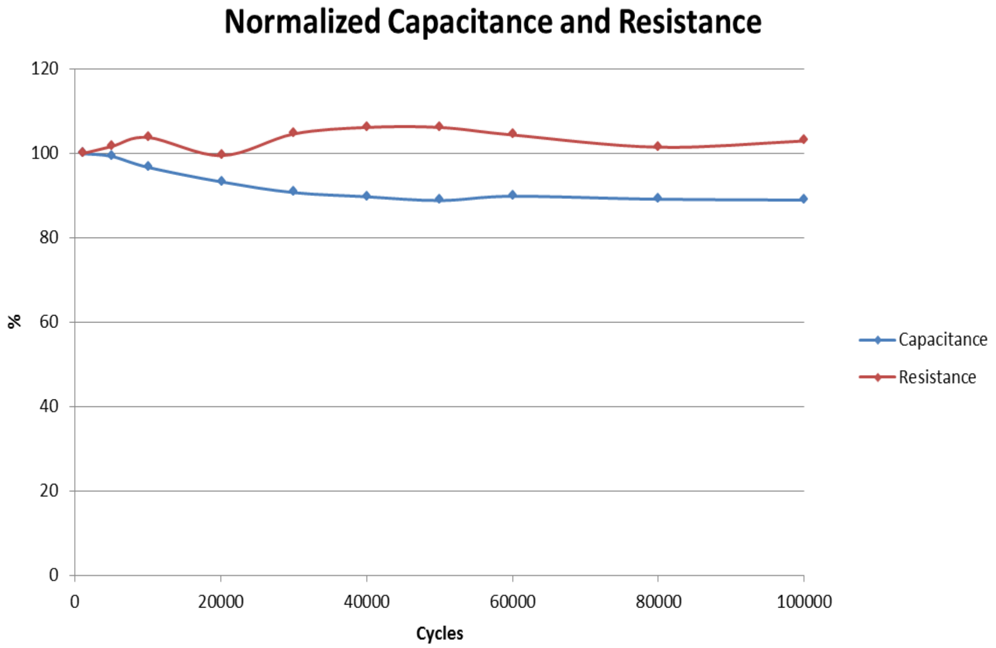


Figure 27 Ni Supercapacitor Normalized Capacitance and Resistance

The performance characteristics mentioned above lend themselves to the typical applications of Super capacitors for engine starting. Super capacitors have the capability to be sized for almost any type of engine. They can also discharge over a wide range of currents with the capability of thousands of amps for short durations. Super capacitors may also provide smaller currents (<100 A) for more extended periods (> 1 minute). The charging time for a super capacitor is quite short (< 2 minutes) and can be charged from any source including a battery that itself has a very small amount of charge remaining. A picture of a full module can be seen in Figure 28. Super capacitors have a very low self-discharge rate and can maintain voltage for years without re-charge. It also does not require balancing electronics or maintenance while in operation, giving great reliability and guaranteed functionality.

Figure 28 Nickel SuperCap

Nickel capacitors are similar to NiCd batteries, with the exception that capacitors should not be over-discharged. This over-discharge of nickel capacitors causes partial deactivation on the positive electrodes that will reduce performance. As with all battery technologies, excessive heating during operation will cause performance issues for nickel capacitors.

Table 13 provides a summary of benefits and limitations / risks for Ni super capacitor technology.

Table 13 Ni Supercapacitor Summary

Benefits	Limitations / Risks
• High specific power and efficiency • Efficient and fast charge acceptance • Low resistance • Quick response • No balancing electronics • Excellent calendar life and cycle life • High specific power even at low temperature ○ Good low temperature performance -40C • No maintenance • Produce no hazard substances	• Low specific energy (Wh/Kg) • Very low energy storage density leading to very high capital costs for large scale applications • High self-discharge • Quick voltage variation • High cost/unit energy • Typical run time: 1 Second to 1 Minute • Heavier and bulkier than conventional batteries • Low voltage cells leading to larger system for higher voltages • Vertical orientation only • Failure mechanism – gradual capacitance loss and resistance growth

3.6.1 Health Hazard Identification of Ni Supercapacitor

Since sealed nickel capacitors only contain trace levels of cadmium and the hazardous components within the carbon are minimal, they are more environmentally and toxicologically benign than NiCd batteries.

Table 14 Nickel Supercapacitor Composition Information on Ingredients

Components	CAS Number	%	OSHA PEL (mg/m³)
Nickel Powder	7440-02-0	< 17	**1**
Nickel Hydroxide	12054-48-7	< 12	**1**
Carbon	7440-44-0	< 10	**3.5 (Carbon Black)**
Potassium Hydroxide	1310-58-3	< 7	**2 Ceiling**
Glass Nylon Composite	N/A	< 10	**N/A**
Steel	N/A	< 30	**N/A**
Other	**N/A**	**< 20**	**N/A**

3.6.2 Recycling Ni Supercapacitor

Given the information in Section 3.6.1, nickel capacitors can easily be recycled with NiCd batteries (Section 3.3.2).

As noted previously, INMETCO is one of the facilities in North America that recycles nickel-based industrial cells, batteries, and capacitors. INMETCO uses the nickel and steel recovered from nickel capacitors to make stainless steel. The electrolyte contained in Ni supercapacitors is used for pH control during the water treatment process.

3.7 Molten Sodium Metal-Halide Batteries - $Na/NiCl_2$

Molten sodium metal-halide battery technology was first developed by the Zeolite Battery Research Africa (ZEBRA®) project in Pretoria, South Africa during the1970s. The ZEBRA® title is also stands for Zero Emission Battery Research Activities. $Na/NiCl_2$ is the technical term for this battery.

Molten sodium metal-halide batteries contain a liquid sodium anode separated from the positive electrode by a ceramic electrolyte called Beta-Alumina, specifically β”-Al_2O_3. The positive electrode consists of transition metal chlorides ($NiCl_2/FeCl_2$) and excess metals (Ni/Fe) which are impregnated with a liquid $NaAlCl_4$ electrolyte. The power density of this battery is 150 W/kg, which makes it an efficient device for powering electric vehicles. In addition to the high energy density and high power density, the abundant and low cost primary elements (Na, Al, Cl, and Fe) used in its fabrication make the ZEBRA® battery very attractive.[41] Further, the ZEBRA® battery has long life and deep discharge cycling ability, which allows it to withstand at least 1000, 100% DOD charge/discharge cycles.

Figure 29 is a schematic of the sodium ion transport through the cell during discharge, while Figure 30 is a representative cross sectional diagram of a sodium-metal halide cell ($Na/NiCl_2$). During manufacture the cathode compartment is filled with Nickel metal (Ni), Sodium Chloride salt (NaCl), other additives, and a liquid electrolyte; there is no elemental sodium involved in the manufacturing process. Reversible (Charge/Discharge) cell reaction is described below:

$$2NaCl + Ni \leftrightarrow 2Na + NiCl_2$$

$$\overset{\text{Charged}}{NiCl_2 + 2Na} \overset{200°–400°C}{\Leftrightarrow} \overset{\text{Discharged}}{Ni + 2NaCl} \qquad Eo = 2.58\ V\ @\ 300°C$$

The cell reaction requires an electrolyte that conducts sodium ions: ß"alumina is used for this purpose. When the sodium battery is first charged, sodium ions from the NaCl in the cathode travel through the liquid electrolyte and the Beta-Alumina (ß" alumina) ceramic Solid Electrolyte (BASE) separator. The BASE separator is an electrical insulation and the conductor of sodium ions at high temperature. When the cell is charged, the anode is filled with liquid sodium. The process is reversed during discharge, with sodium ions traveling through the BASE separator to re-form NaCl in the cathode. Refer to Figure 29 for a schematic representation.

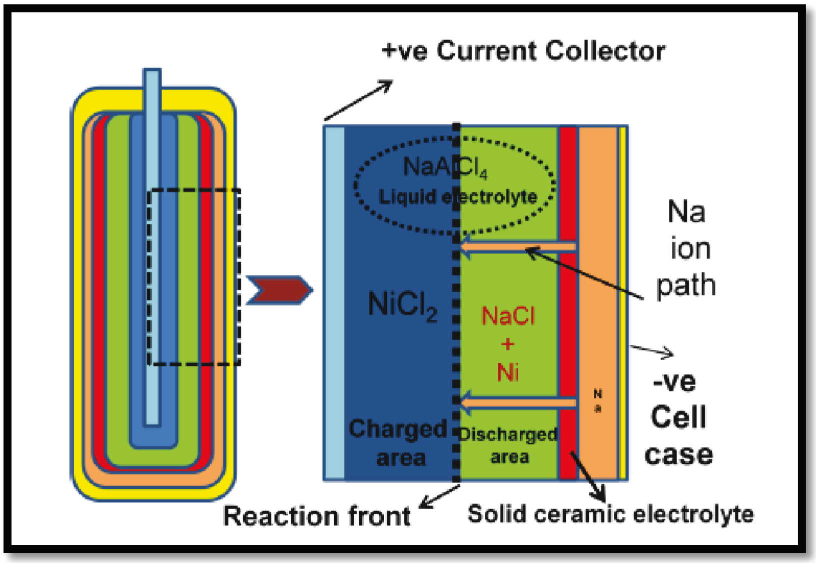


Figure 29 Schematic Representation of Na-NiCl₂ Discharge Reaction

The ZEBRA® cell is enclosed in a steel case that is coated with nickel. The thickness of the steel case is about 0.3 mm. As the steel case is in direct contact with sodium metal, it should be resistant to both the liquid sodium metal and air. Moreover, it must be leak free to prevent sodium loss.

A cross-section of the cell is shown below.

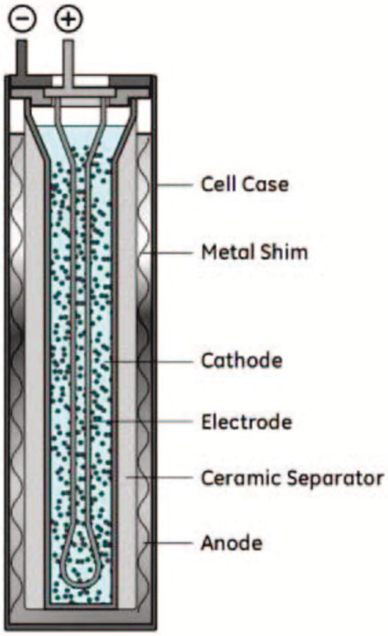


Figure 30 Cross-Sectional View of ZEBRA® cell

The cell contains steel metal foil wicks in close contact with the β”-Al_2O_3 surface in which the liquid Na is drawn up along the electrolyte by capillarity action. The role of these wicks is to decrease the contribution of the negative electrode to the overall cell resistance by maintaining a high surface area on the anode side, especially when the sodium level is low (discharged state); they also make good electronic contact with the ceramic tube during initial charging.

Both $NiCl_2$ and $NaAlCl_4$ salts are hygroscopic and difficult to handle. Therefore, the standard practice is loading the cells in the discharged state (i.e., by adding a granulated mixture of nickel powder and NaCl to the cell) and filling the voids with liquid electrolyte.

While the Ni backbone provides radial conductivity inside the cathode, the hairpin-shaped Ni current collector, which has a highly porous carbon felt sheet in between the pieces of Ni, provides the necessary vertical conduction. The carbon felt keeps the upper part of the cathode wetted by $NaAlCl_4$.

The open-circuit voltage of this cell chemistry is about 2.5V, while operating at an internal temperature in a range of approximately 250° to approximately 350°C (both cell and battery). Depending on the application, the ZEBRA® Battery may discharge as low as about 1.7V per cell. The nominal recharge voltage is about 2.7V per cell.

Each ZEBRA® cell is enclosed in a stable steel case that also serves as the negative pole of the cell. The ß" alumina ceramic electrolyte-separator divides the cell into a chamber for the positive electrode and another chamber for the negative electrode.

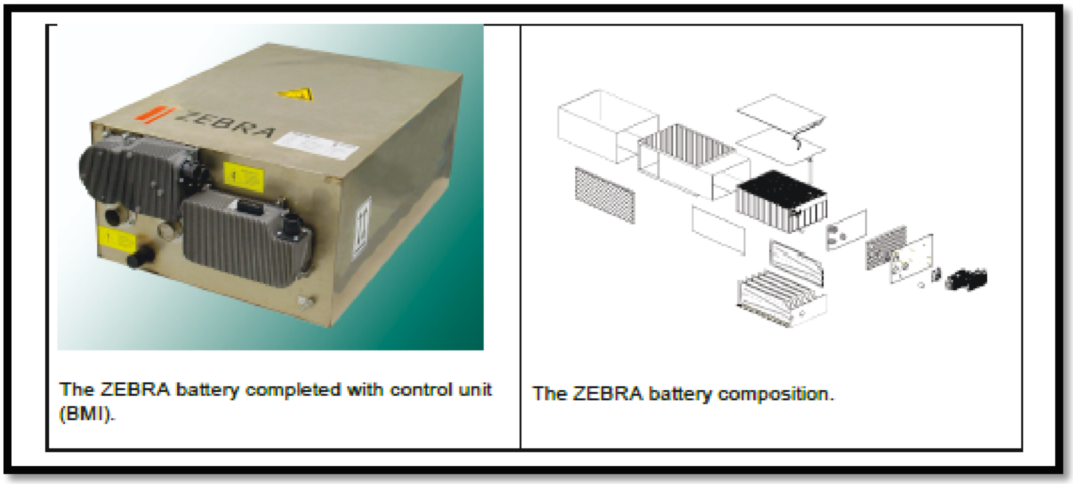
The positive electrode and the current collector are located inside the ceramic electrolyte tube. The porous solid cathode of $NiCl_2$ is impregnated with a Na+ ion conductive salt ($NaAlCl_4$), which provides conductivity between the inside wall of the separator and the reaction zone. The negative electrode (the sodium) is located between the ceramic and the cell case, which is also the negative pole of the cell. A metal-ceramic seal closes the cell hermetically.

The ß"-alumina ceramic conducts sodium ions and is adequately conductive at higher temperatures. Its properties and shape determine the resistance and therefore the efficiency of a cell. The cell and battery operate at temperatures between 250°C and 350 °C.

Each single cell in the charged state contains sodium as the negative electrode and nickel chloride as the positive electrode. The sodium reacts with the nickel chloride on discharging to form sodium chloride (common salt) and nickel. The process takes place in the reverse direction on charging.

As the positive electrode (nickel chloride or common salt and nickel) is used as a solid electrode, a second liquid electrolyte (sodium aluminum chloride) provides the ion conducting properties inside the positive electrode. Neither of the electrolytes is involved in the cell reactions, but they are only used for conducting sodium ions.

Sodium ions resulting from the oxidation of sodium at the negative electrode are transported through the solid sodium β-alumina electrolyte to the $NiCl_2$ by a secondary electrolyte (a eutectic mixture of NaCl and $AlCl_3$). For most of the discharge, the system functions as a Na-$NiCl_2$ cell. If a high current pulse is applied to the cell and the working voltage falls below 2.35 V, the iron reaction augments the main nickel reaction: both discharges in parallel. This occurs at the front of the electrode and the cell therefore has its minimum resistance. When the working voltage recovers above 2.35 V, the iron produced is then re-oxidized to $FeCl_2$ by the remaining nickel chloride and the $FeCl_2$ is then available for the next high current discharge.



The ZEBRA battery completed with control unit (BMI).

The ZEBRA battery composition.

Figure 31 ZEBRA® Battery

The ZEBRA® battery is controlled by the Battery Management Interface (BMI). The BMI, an electronic device with integrated main circuit breakers, is the "brain" of the battery system and provides temperature control, SOC measurement, measurement of isolation resistance between "plus", "minus" and "ground." The BMI also monitors current and voltage limits, maintains life-data-memory, controls the charge, and provides CAN communication with the system.

According to the manufacturer of ZEBRA® batteries, their halide system may last thousands of cycles before requiring replacement, based on such factors as the DOD and discharge power rates. Replacement may be due to increases in internal resistance. ZEBRA® claims that their initial testing indicates potential capability of over 2000 discharges to 80% DOD.

However, there are still some problems with premature intermittent degradation during cycling at 80% DOD this is caused by relatively high impedance of the positive electrode.

Nickel metal is the most expensive material in the ZEBRA® battery. The percolating network of Ni particles are responsible for providing electronic conductivity within the cathode. Therefore, an excess amount of Ni is used to guarantee the formation of the above network. However, microstructure investigations have revealed that not all Ni particles are active in the cell reaction as during large numbers of cycles; some of them form individually within the cathode while they are surrounded with only ionic conductors. The inactive Ni particles increase the internal resistance of the cell and therefore, cause capacity loss. It has been observed that a mixed conductive electrolyte could allow the individual Ni particles to participate in the reactions and thus, prevent the capacity loss caused by gaps in the Ni backbone.

Because of the solid electrode, the sodium battery does not self-discharge and may be capable of 15 plus years of operation on float. The battery may be cooled to ambient temperature, freezing the sodium electrode and the liquid electrolyte in either a charged or uncharged state. In the frozen state the Sodium Battery may have a near indefinite shelf life.

According to ZEBRA®, their $Na/NiCl_2$ batteries have been successfully demonstrated in electric vehicles and sodium-metal halide battery technology has shown promise in hybrid locomotive applications. Compared to VRLA batteries, the ZEBRA® battery has about 4 times the energy per weight and 2 times the energy per volume.

The $Na/NiCl_2$ system is attractive for electric traction applications due to its power limitations. These cells can be designed to deliver up to 500 Ah. If the cell electrolyte fails, Sodium (Na) will react with the secondary electrolyte to short circuit the cell. The system can tolerate short circuiting, which does not cause complete failure of the battery. As a result, the $Na/NiCl_2$ system is safer than the Na/S system. ZEBRA® claims that their halide system requires very little maintenance and no emissions under any operational condition. Operating temperatures of 250 to 350°C (518–662°F), lead to issues with thermal management and safety, and place more stringent requirements on the rest of the battery components. Even with special insulation, heating consumes 14 percent of the battery's energy per day, which results in the equivalent of an 18 percent self-discharge. A ZEBRA® battery should be either on charge or in use. Halide cells fail safely when over-discharged. It takes 3–4 days to cool down; reheating requires about two days depending on the SOC at time of shutdown. Common failures are electrical shorts due to corrosion and dendrite growth, which increases self-discharge.

When not in use, ZEBRA® batteries are typically required to be left on charge, in order to be ready for use when needed. If shut down, the reheating process lasts 24 hours, and then a normal charge process of 6 to 8 hours is required for a full charge. This is a major issue for electric vehicle customers who may not use their vehicle every day or forget to put the vehicle on charge. It is also inefficient as it consumes energy when not in use.

Based on internal data from ZEBRA, calendar life was reported as 11 years. The determination was based on measuring mean cell resistance.

The operating temperature influences the performance and aging of Zebra® cells. Based on experimental investigations, Zebra® cells were cycled at 260°C and 350°C. It is hypothesized that the formation of AlF_3 on the surface of the β'' alumina electrolyte contributes to the failure of cells at low temperatures. A mechanism based on the overcharge reaction is proposed for the formation of this phase. At 350°C, a significant capacity loss is observed with cycle life. Nickel particle growth was found to be the cause of this phenomenon.

The power of $Na/NiCl_2$ technology is limited because the temperature rise must not go beyond specified limits, otherwise degradation and system life will be dramatically reduced. The temperature must return to these normal operational levels while the battery is charging.[42]

Table 15 provides a summary of benefits and limitations / risks for Na / $NiCl_2$ Salt.

Table 15 $Na/NiCl_2$ Molten Salt Summary

Benefits	Limitations / Risks
• High energy density (5 times higher than Lead acid) • Tolerant of internal short circuits • Typical cell failure is short circuit which does not cause complete failure of the battery • Low cost materials • Excellent columbic efficiency • Maintenance Free • Battery: Broad operating temperature range • Withstand abuse testing such as over heat, overcharge, external short circuit, drop test and crash test	• High internal resistance • Molten sodium electrode • Labor intensive assembly • Battery requires thermal management (heating and cooling) to ensure the battery remains within the operating limits • 10% to 15% of the energy is used to heat the battery • Slow charge time especially after the battery is let to cool down • Battery needs to be hotter (>330°C) to run high power (2C rate) • Complicated (quoted by customers) mode of operation • Some possible sensitivity to Shock and Vibe (needs to be confirmed) that may lead to cracks in the ceramic separator • A typical failure mode is a slow short through a crack in the ceramic separator. • Need for electronic control – in case of bigger defect or mechanical failure (bigger crack, case rapture, etc.) the electronics disconnects the battery and in some cases can deplete the energy.

3.7.1 Health Hazard Identification of $Na/NiCl_2$ batteries

Sodium/metal halide cells are housed within a temperature-controlled, double-walled, sealed, vacuum-insulated battery case. This battery case or enclosure protects the outside environment from the effects of mishaps within, and protects internal battery components from hazards outside.[43] If the battery case is penetrated, its insulating and containment functions will be compromised, and if the penetration is severe enough, the cells contained inside will be ruptured.

Even though $Na/NiCl_2$ batteries are hermetically sealed and vacuum packed, it is feasible for the battery to suffer severe mechanical damages or short circuit and failure of the battery, leading to emission of potentially corrosive and/or toxic substances for inhalation, ingestion and contact, possible generation of flammable gas, and eventually fire. The following Table 16 identifies hazardous components for $Na/NiCl_2$ batteries:[44, 45]

Table 16 Composition Information on Components as reported by ZEBRA®

Components	CAS Number	Amount % by weight	TLV (mg/m^3)
Nickel (as metallic Ni)	7440-02-0	9*-13	1.5
Sodium (Na)	7440-23-5	2-5*	Not defined
Nickel Chloride ($NiCl_2$)	7718-54-9	5-13*	0.05
Sodium fluoride	7681-49-4	< 0,5	2.5
Aluminum	7429-90-5	< 0,1	10
Nickel Sulphide (as Ni_3S_2)	12035-72-2	< 0,7**	0.1 (as Ni)
Sodium Iodide	7681-82-5	< 0,1	10 3 inhalable dust
Sodium Aluminum Chloride ($NaAlCl_4$)	7784-16-9	13	2 (as Al) 7,5 (C) as HCl (decomp)
Ceramic fibers	42844-00-6	0,5	0,2 ff/cm3

*% Present during charged state

Source: ZEBRA® Batteries, Switzerland

** Theoretical maximum % generated during battery use

3.7.2 *Recycling Na/$NiCl_2$ Batteries*

INMETCO has successfully recycled >20 MT loads of ZEBRA® cells by adding them to their standard submerged arc smelting furnace and producing nickel with remelt alloy, which is used in the stainless steel industry. The ceramic and the salt contained in the cells are collected and sold as a replacement for limestone used in road construction – resulting in complete recycling of the batteries. While the capability to recycle cells has been demonstrated, collecting cells at the end of life is a known limitation in the recycling process. In the case of ZEBRA® batteries, European customers are required to return old ZEBRA® batteries. After removal of the BMS, the cells are packaged and shipped to the recycling location. Another issue in recycling ZEBRA® batteries is the cost of collection, transport and processing. The net worth of the nickel in the battery pack ensures that the entire recycle process is cost neutral.

3.8 Li-ion Batteries

Li-ion batteries are common in portable electronic devices due to their high energy density, lack of memory effect, and discharge rate capabilities. Li-ion batteries are a relatively new technology which was first marketed in the early 1990s. Research and development work on Li-ion batteries is ongoing to further improve safety and increase capacity, charge/discharge rate, and lifetime. Some key features of lithium-ion batteries as compared to other battery technologies are:

- Light weight compared to other rechargeable battery chemistries
- Very high energy and power density
- Excellent charge retention
- Excellent cycle and calendar life

- Do not contain toxic heavy metals

Li-ion batteries are said to be an energy storage system for the future and have become indispensable, especially in electro mobility. As noted above, li-ion batteries have more energy density, power density and cell voltage output compared to other batteries. As a result, these batteries are well suited for the power and energy demands of hybrid diesel-electric battery locomotive applications. JR East (Japan Railroad East) engineers and Hitachi engineers have used Li-ion batteries for their version of HDEB locomotives to capture regenerative braking energy. Shimada et al. (2010) mention that Hitachi is working on the development of energy-saving systems for rolling stock that use Li-ion batteries to reduce the environmental impact of railway systems.[46] Kadhim (2009), however, states that Li-ion batteries are very sensitive to overcharging or over discharging with the potential of fire. As a result, an accurate charge/discharge BMS is required for Li-ion batteries to prevent hybrid system failure. As noted previously, the use of an accurate BMS for any HDEB locomotive application is required due to the significant number of cells utilized, the high voltage required, and the harsh charge and discharge environment of an HDEB locomotive application.

Unlike other battery technologies, lithium-ion batteries represent a family of battery chemistries that employs various combinations of positive and negative materials. Each combination has distinct advantages and disadvantages in terms of safety, performance, and cost, among other parameters. The most common technologies for energy storage applications are lithium-nickel-cobalt-aluminum oxide (NCA), lithium iron phosphate (LFP), lithium-nickel-manganese-cobalt oxide (NMC), lithium-manganese spinel (LMO) and lithium-titanium-oxide (LTO). An energy density chart of various Li-ion chemistries is shown in Figure 32.

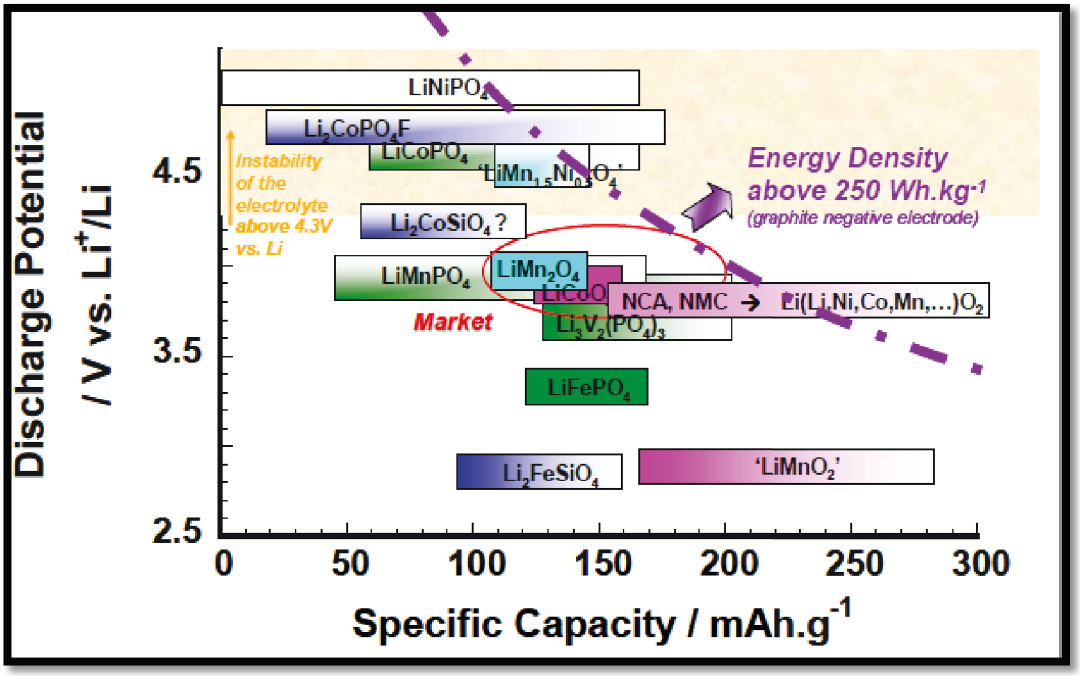
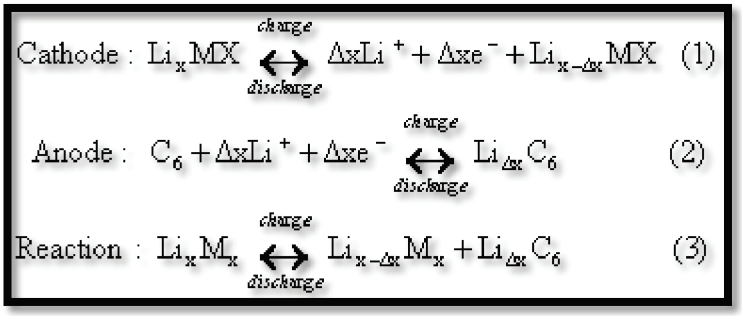


Figure 32 Energy Density Chart

Graphite is by far the most common material for the negative electrode in lithium-ion cells, but some other technologies are under development. Lithium titanate ($Li_4Ti_5O_{12}$) offers very high cycle life, faster charging, and better safety than graphite, but at a much lower energy density and higher cost. These batteries are starting to become available commercially, mainly for electric vehicles and grid energy storage applications.

In li-ion batteries, carbon material is used in the anodes and a metal oxide (MX) material containing lithium is used in the cathodes; lithium ions migrate between the two electrodes via an organic electrolyte. By designing these batteries in accordance with the reversible capacity of the carbon material, lithium does not exist in a metallic state during the charging or discharging processes. To differentiate these batteries from those which use metallic lithium or lithium alloy in the anode, this system is designated as a Li-ion rechargeable battery.

As noted above, the charging and discharging of Li-ion batteries occurs when lithium ions migrate between the cathodes and anodes as well as the exchange of electrons through intercalation and de-intercalation. More specifically, during charging, lithium is deintercalation from cathodes consisting of a lithium-containing compound (MX), and the inter-layers of carbon in anodes are doped with lithium. Conversely, during discharge, lithium is deintercalation from between the carbon layers in anodes, and the compound layers in cathodes are doped with lithium. Reactions occurring in lithium ion rechargeable batteries are shown in the following figures.[47]



$$\text{Cathode}: \mathrm{Li}_x\mathrm{MX} \underset{\textit{discharge}}{\overset{\textit{charge}}{\longleftrightarrow}} \Delta x\mathrm{Li}^+ + \Delta x e^- + \mathrm{Li}_{x-\Delta x}\mathrm{MX} \quad (1)$$

$$\text{Anode}: \mathrm{C}_6 + \Delta x\mathrm{Li}^+ + \Delta x e^- \underset{\textit{discharge}}{\overset{\textit{charge}}{\longleftrightarrow}} \mathrm{Li}_{\Delta x}\mathrm{C}_6 \quad (2)$$

$$\text{Reaction}: \mathrm{Li}_x\mathrm{M}_x \underset{\textit{discharge}}{\overset{\textit{charge}}{\longleftrightarrow}} \mathrm{Li}_{x-\Delta x}\mathrm{M}_x + \mathrm{Li}_{\Delta x}\mathrm{C}_6 \quad (3)$$

Figure 33 Li-ion Chemical Reactions

As with other rechargeable battery chemistries, Li-ion battery performance (power and energy) is affected by cold temperature operation, due to poor ion transport. Charging li-ion batteries is more challenging in cold temperatures since lithium dendrites can grow within the cell, reduce the life of the battery, and compromise safety[47].

During hot temperature operation, li-ion batteries generate side reactions, which lead to faster degradation. Once the battery reaches a very high temperature, the potential for thermal runaway is increased. Prolonged exposure to heat also reduces battery life.

Charging should be performed between 5ºC and 45ºC. At temperatures from 0°C to 5°C charging is possible, but the charge current should be reduced. High temperatures during charging may lead to battery degradation and charging at temperatures above 45°C will degrade battery performance.[48]

Battery Cycle Life is defined as the number of complete charge - discharge cycles a battery can perform before its nominal capacity falls below 80% of its initial rated capacity. For lithium-ion batteries, a charge-discharge capacity fade is due to the loss of active lithium ions resulting from a solvent reduction reaction. There is a rise of the surface film resistance at the anode due to this parasitic reaction. Improvements in cycle life continue with ongoing advancements in the evolution of Li-ion technology. The key factors affecting cycle life are charge rate (CR), depth of discharge (DOD), end of charge voltage (EOCV), and the cycling temperature conditions[1]. The following charts detail the impact level involving such factors.

Based on A-123 data,[49] Lithium Iron Phosphate (LFP) cells were put on a 100 percent depth-of-discharge (DOD) test at 23 degrees Celsius at a 1C/1C charge/discharge rate. After more than 7,000 full DOD cycles, the cells were shown to have approximately 80 percent of their initial capacity remaining. To put this in perspective, if a battery is fully changed and discharged once per day, 7,000 cycles is equivalent to approximately 19 years.

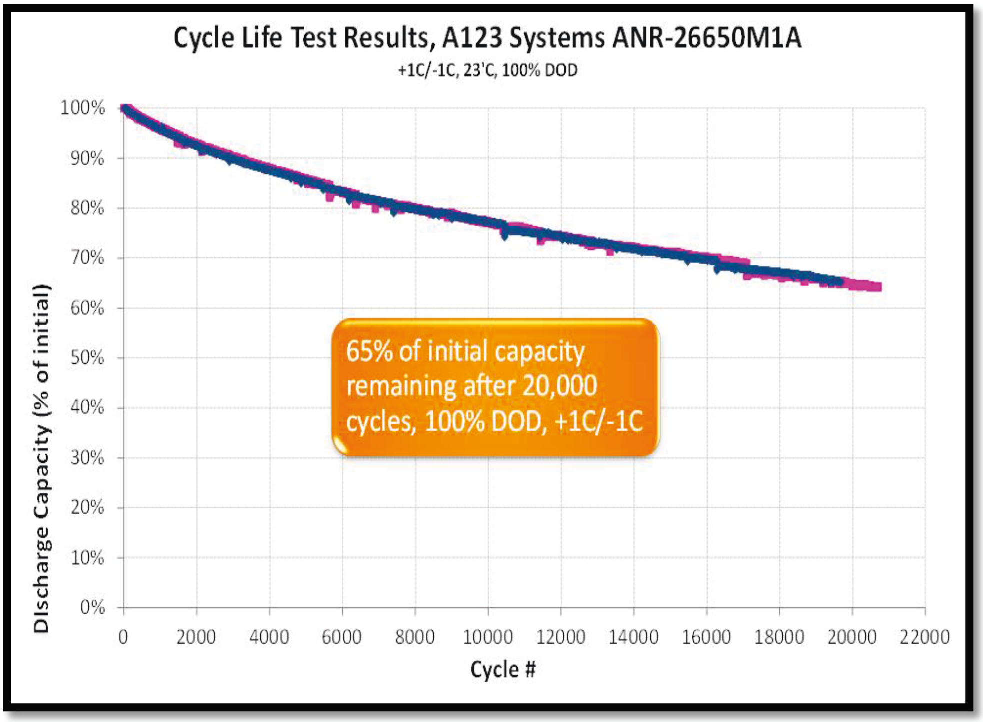


Figure 34 Nominal Cycling Rate Vs Discharge Capacity

The following chart examines the number of full cycles in a Lithium Metal Oxide battery can endure when discharged at different C-rates.[50] As would be expected, at a 2C discharge, the battery exhibits higher stress than at 1C, limiting the cycle count to about 450 before the capacity drops to half level.

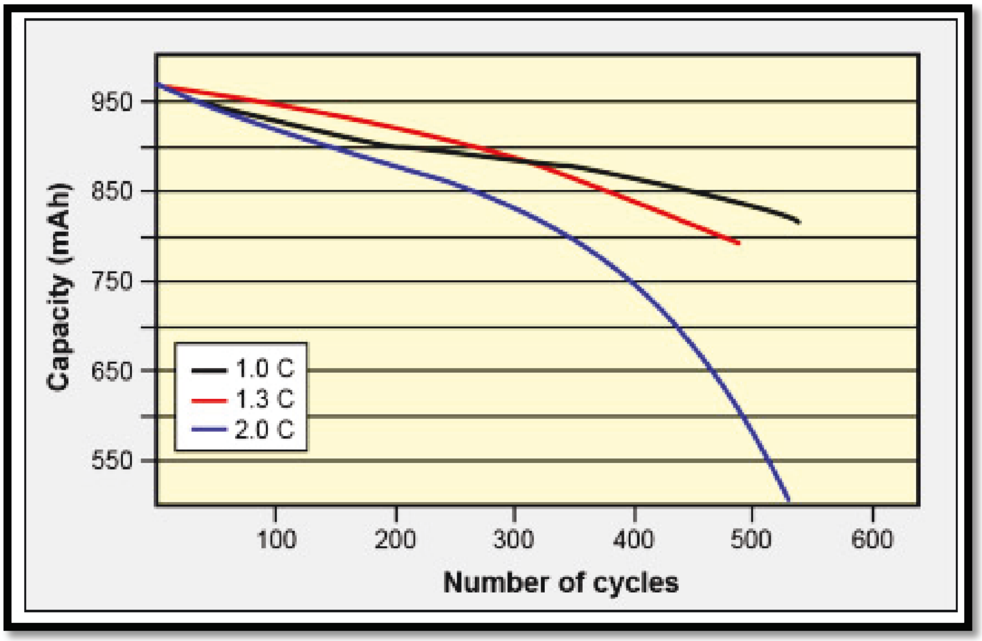


Figure 35 Cycle Life Behavior of Lithium Metal Oxide Battery with Varying Rate of Discharge

For safety reasons, many Li-ion cells cannot exceed 4.20V/cell. (The exception is the high energy-density NMC cells that charge to 4.30V/cell.) While a higher voltage boosts capacity of the battery, exceeding the voltage shortens service life and compromises safety. Figure 36 demonstrates cycle count as a function of charge voltage. At 4.35V, the cycle count of a regular li-ion cell is cut in half, with the higher charge voltages boosting capacity but lowering cycle life and compromising safety.

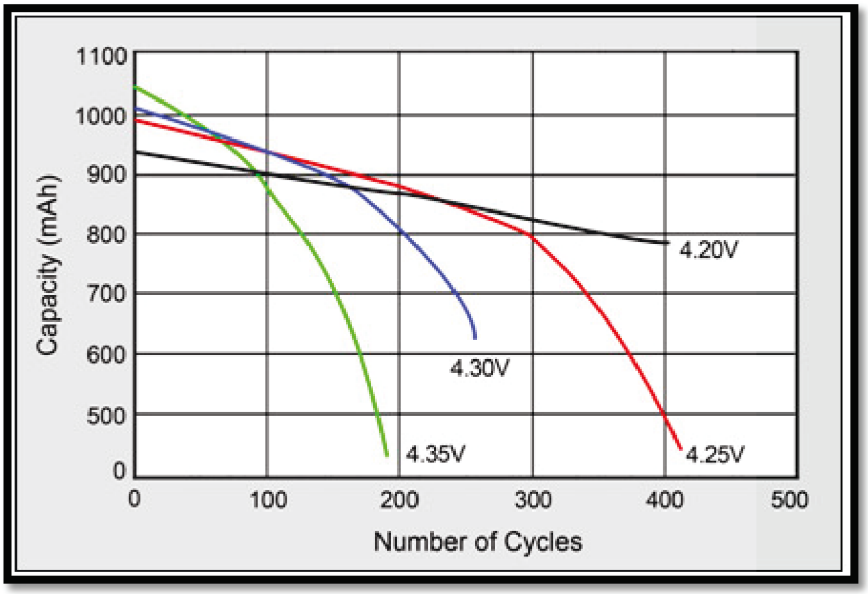


Figure 36 Charge Voltage Vs Cycle Life[51]

In addition to selecting the best-suited voltage thresholds for a given application, a regular li-ion battery should not remain at the high-voltage ceiling of 4.20V/cell for an extended period of time. When fully charged, the battery charger should stop providing additional energy and allow the battery voltage to revert to a more natural level. Although a properly functioning li-ion charger will terminate charging when the battery is full, some chargers apply a topping charge if the battery terminal voltage drops to a given level. As a result, it is important that the charger is matched to the li-ion battery chemistry being utilized to reduce the potential for overcharging of the system.

Battery life for most of the li-ion technology is influenced by the charging rate. The only lithium technology not affected by charging rate is LTO technology. Because of the titanate anode, LTO cells will accept recharge at a much higher rate than other li-ion technologies without any harmful effects. For any cell being discharged beyond its design limits, a capacity reduction occurs because the transformation of the active chemicals cannot keep pace with the current drawn. This may be accompanied by changes in the morphology of the electrode crystals such as cracking or crystal growth, which adversely affects the internal impedance of the cell. At the same time, maintaining the higher voltages needed for fast charging can lead to breakdown of the electrolyte, which will also result in capacity loss.

Figure 37 provides a basic comparison between lithium-ion chemistries with respect to cost, safety, specific energy, specific power, life span and overall performance. The further the polygon extends from the center of the axes, the better the performance for that specific characteristic.

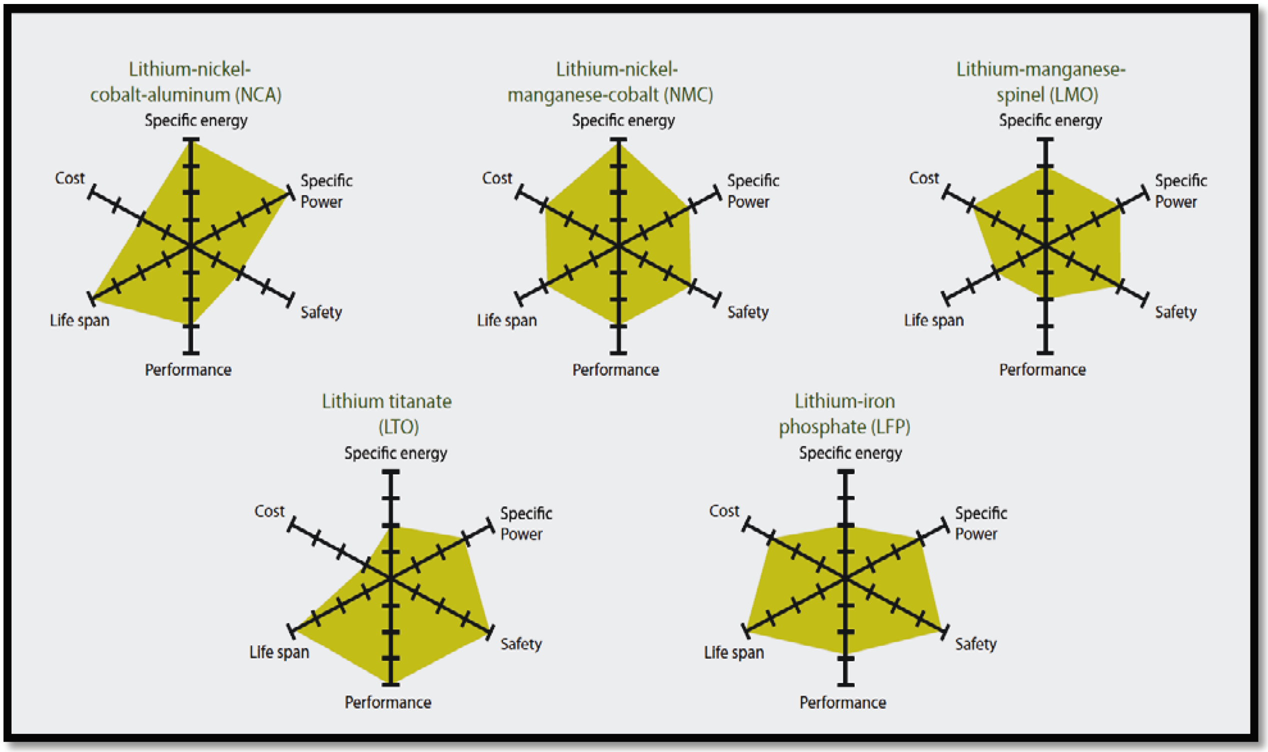


Figure 37 Basic Comparison Between Li-ion Chemistries[52]

Storage temperature, as well as end of charge voltage with and without trickle charging, are major factors that impact the calendar life of lithium-ion batteries. Storage at high temperature reduces battery life, as does storage while fully charged, since the electrodes degrade faster when fully charged. To prevent this degradation while still allowing for some self-discharge in storage, many manufacturers recommend storing li-ion batteries at 40-50% of charge capacity.

Like all batteries, li-ion batteries will self-discharge during storage and must be periodically charged; the rate of self-discharge is generally about 2 to 5 percent per month. An additional 2 to 5 percent can be consumed by the current needed to operate the monitoring electronics built into the battery pack. The battery can be permanently damaged if allowed to discharge below the recommended minimum voltage.

Figure 38 details NCA batteries tested at two different temperatures (5°C and 35°C), two different end-of-charge voltages (4.0 V and 4.2 V) and two different types of charging conditions (float and open) for duration of 7 months.

Irreversible capacity loss is calculated as follows:

{(Initial Capacity - Actual Capacity)/ (Initial Capacity)} 100*

Temperature and storage voltage shows a significant impact on calendar life of lithium-ion system.

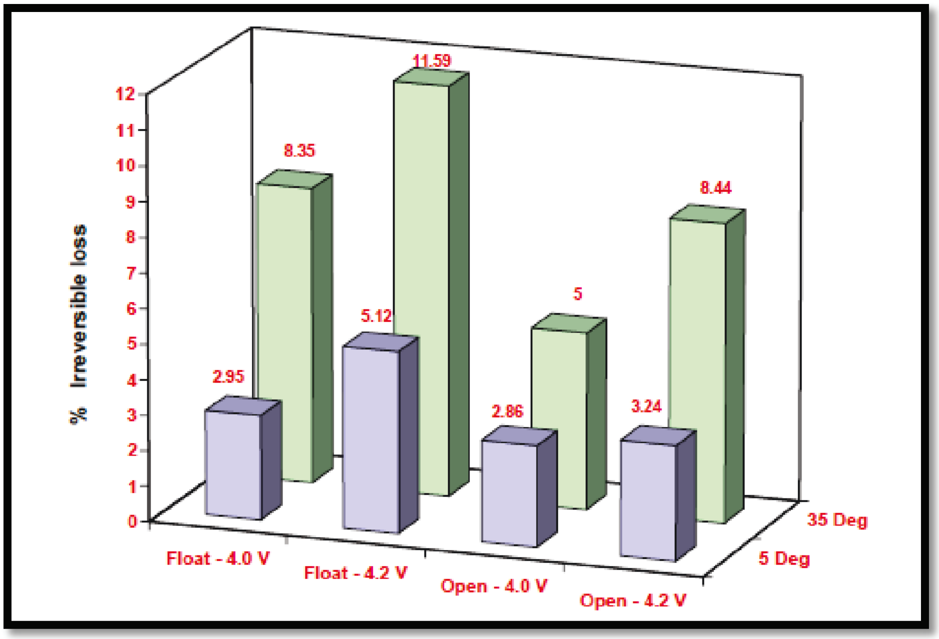


Figure 38 NCA Storage at Different Float Voltages

Aging of lithium-ion batteries is caused by multiple phenomena related to both cycling and calendar age. Battery degradation is accelerated with the DOD of cycling, elevated temperature, and elevated voltage exposure, among other factors. The degradation is due to the growth of a resistive film layer at the electrode surface. As the layer grows, cyclable lithium is consumed from the system, reducing battery capacity. Among li-ion chemistries, the nickel cobalt aluminum (NCA) chemistry has graceful aging characteristics, and is expected to achieve 8 or more years of life when sized appropriately for a specific application.

At the battery terminals, the observable effects of degradation are an increase in resistance and a reduction in capacity. These two effects can be correlated with power and energy loss that cause battery EOL in an application. Mechanisms for resistance growth include loss of electrical conduction paths in the electrodes, fracture and isolation of electrode sites, growth of film layers at the electrode surface, and degradation of electrolyte. Mechanisms for capacity loss include fracture, isolation, and chemical degradation of electrode material, as well as loss of cyclable lithium from the system as a result of side reactions within the cell.

While all batteries can present safety hazards if used improperly, li-ion batteries are sensitive to proper handling and treatment. Li-ion batteries can vent electrolyte, catch fire, or explode if significantly overcharged, overheated, or short-circuited. Li-ion electrolytes use flammable organic solvents, unlike the water-based electrolytes in SLA, NiCd, and NiMH batteries. When a Li-ion battery catches fire, it can be extinguished with water or standard dry chemical fire extinguishers.

Li-ion batteries require careful attention to safety. For a safe and long-lasting product, li-ion-specific safety issues must be taken into account in product design. There are a number of early failure symptoms which identify lithium-ion battery packs that are likely to suffer thermal runaway failures:

- Excessive cell voltage drop during extended rest periods.
- Long taper-current charging times consistent with dissipation of charge current in a micro-shorts.
- Cell heating during cell charging, particularly near the end of charging.

- Cell providing noisy voltage readings during charging and discharging, indicating the formation of transient soft-shorts.
- Cell charge/discharge inefficiency change.

Safety risks for lithium-ion battery systems can be mitigated by incorporating safety devices into cells, modules, and battery packs to protect against the abnormal conditions noted above. In order to manage the consequences of heat and gas generation, many lithium-ion battery manufacturers have incorporated the following features into their systems:

- No metallic lithium – Free of highly active lithium metal.
- Each cell is hermetically sealed – Eliminates out gassing.
- Thermally stable positive active materials and electrolyte additives were used to avoid thermal run away conditions.
- Graphite material were used to avoid exfoliation (crystalline structure damage) during cycling.
- Selection of optimum binders, mix formulation, and robust electrode processing technology to avoid separation of active materials from conductive networks.
- Each cell carries a mechanical vent as part of cell assembly to release the pressure prior to thermal run away conditions.
- The current interrupt device (CID) protects against over-current that breaks the internal electrical connection when internal pressure reaches a set value.
- Positive temperature coefficient disks.
- Implementing a shut-down separator (activates ~130-140°C) between anode and cathode prevents ionic conduction if cell internal temperature exceeds a certain limit, thus preventing the cell charge/discharge process from continuing.
- Each cell design is qualified in accordance with UL-1642 and IEC requirements.
- Current limiting devices are assembled as part of each battery module.
- Modules and batteries meet DOT requirements for packaging integrity, transportation shock, vibration and drop testing

Table 17, Table 18, Table 19, and Table 20 provides a summary of benefits and limitations / risks for Li-ion technologies.

Table 17 Lithium-Ion Technology Lithium Nickel Cobalt Aluminum Oxide (NCA) Summary

Benefits	Limitations / Risks
• Sloping discharge curve – Open circuit voltage ○ Simplifies SOC electronics by aiding cell balancing. • High pulse rate charge acceptance • Higher specific power/energy density compared to all other commercial available battery technologies; results in lower volume and weight. • Excellent discharge cyclic life compared to	• High temperature/flammable gases possible during cell failures. Flammable organic solvent • Hybrid Loco Energy System Management design must account for the following: ○ Li-ion batteries should never be depleted to below their minimum voltage ○ Thermal management may need to be employed for charging at temperatures below 0°C and usage above 50°C. • Higher systems cost compared to all other

Benefits	Limitations / Risks
all other commercial available battery technologies • Excellent charge/discharge efficiency • Excellent RT calendar life / Low self-discharge • No service maintenance due to state of health electronics • No Toxic Metals	commercial available battery technologies with the exception of large format LTO cells. • BMS Requirement • Storage ○ Li-ion packs should be stored at intermediate SOC to optimize life. ○ State of health electronics tend to drain Li-ion packs; therefore, recharge is required for extended periods of storage. ○ Does not tolerate being left completely discharged during storage • Restrictions placed on air and ground transportation • Failure mechanism – gradual and slow impedance growth during cycle and calendar life

Table 18 Li-ion Technology Lithium Nickel Manganese Cobalt oxide (NMC) Summary

Benefits	Limitations / Risks
• Lower temperatures as compared NCA technology during cell failures • Higher specific power/energy density compared to all other commercial available battery technologies; results in lower volume and weight. • Excellent discharge cyclic life compared to all other commercial available battery technologies except for other li-ion technologies • Sloping discharge curve – Open circuit voltage ○ Simplifies SOC electronics by aiding cell balancing Sloping discharge curve • High current charge/discharge capability • Higher specific power/energy density compared to all other commercial available battery technologies except for NCA • Lower cost compared to NCA li-ion : • Excellent RT calendar life / Low self-discharge • No service maintenance due to state of health electronics • No toxic metals	• High temperature/flammable gases possible during cell failures; lower temperatures than NCA. • Hybrid loco energy system management design must account for the following: ○ Li-ion batteries should never be depleted to below their minimum voltage ○ Thermal management may need to be employed for charging at temperatures below 0°C and usage above 50°C. • Higher systems cost compared to all other commercial available battery technologies. • BMS Requirement • Storage ○ Li-ion packs should be stored at intermediate SOC to optimize life. ○ State of Health electronics tend to drain li-ion packs; therefore, recharge is required for extended periods of storage. ○ Does not tolerate being left completely discharged during storage • Restrictions placed on air and ground transportation • Immature technology • Failure mechanism – gradual impedance growth and capacity loss

Table 19 Li-ion Technology Lithium Iron Phosphate (LFP) Summary

Benefits	Limitations / Risks
• Lower temperatures as compared NCA and NMC technology during cell failures ○ Doesn't evolve O2 to aid fueling flames during cell failures • Excellent abusive over-discharge tolerance as compared to NCA and NMC. • Higher specific power/energy density compared to all other commercial available battery technologies; results in lower volume and weight. • Excellent charge/discharge efficiency • Higher current recharge rate up to 4C • Excellent regenerative load acceptance. • Highest specific power compared to all other commercial available battery technologies except for NCA and NMC • Lower cost compared to NCA and NMC li-ion in the long term. • Excellent discharge cyclic life compared to all other commercial available battery technologies • Excellent RT calendar life when to all other commercial available battery technologies except for li-ion • No service maintenance due to state of health electronics • No Toxic Metals	• High temperature/flammable gases possible during cell failures though lower than NCA and NMC. • Hybrid loco energy system management design must account for the following: ○ Li-ion packs should be stored at intermediate SOC to optimize life. ○ Thermal management may need to be employed for charging at temperatures below 0°C and usage above 50°C. • Many suppliers of LFPs have low discharge rate capability (Less maturity processing) • Lower specific energy (Wh/Kg) when compared to NCA and NMC li-ion technologies • Lower high temperature cycling compared to other li-ion technologies. • Flat Discharge Plateau ○ More complex electronics - requires columbic counting in BMS • BMS Requirement • Poor low temperature performance as compared to all other commercially available li-ion technologies • Storage ○ Li-ion packs should be stored ~ 40% charge. ○ State of Health electronics tend to drain li-ion packs; therefore, recharge is required for extended periods of storage. ○ Limited tolerance for being left completely discharged during storage • Restrictions placed on air transportation • Immature Technology and expensive LFP synthesis process increases the final material cost • Failure mechanism – gradual capacity loss

Table 20 Li-ion Technology Lithium Titanate Oxide (LTO) Summary

Benefits	Limitations / Risks
• Superior cyclic life compared to all other commercial available battery technologies. • Lowest temperatures as compared to all other li-ion chemistries during cell failures. ○ Spinel Structure anode (Stable) • Only li-ion chemistry that can be shorted to 0 volts without damage. • Highest charge rate and efficiency of all battery technologies • Excellent abusive over-discharge tolerance as compared to all li-ion chemistries • Higher specific power/energy density compared to all other commercial available battery technologies; results in lower volume and weight. • Active material not required form Solid Electrolyte Interface (SEI) formation at the anode. • Safety (Cell venting/rapid disassembly) ○ Internal short circuit reaction on the LTO anode is three order of magnitude lower than graphite anode • Long storage life – recoverable capacity loss. • Good low temperature performance • No service maintenance due to state of health electronics • No toxic metals • Recoverable from short duration to low discharge voltages above 0 volts. • Sloping discharge curve – Open circuit voltage • Simplifies SOC electronics by aids cell balancing Sloping discharge curve	• Higher cell cost based on materials as compared with other li ion technologies • Hybrid loco energy system management design must account for the following: ○ Thermal management may need to be employed for usage above 50°C. • Lower specific energy as compared to NCA and NMC • Storage ○ Li-ion packs should be stored at intermediate SOC to optimize life. ○ State of health electronics tends to drain li-ion packs; therefore, recharge is required for extended periods of storage. • BMS Requirement • Immature Technology • Failure Mechanism – Impedance growth over time

3.8.1 Health Hazard Identification of Li-ion batteries

The chemicals and metals in lithium-ion batteries are contained in a sealed can. The contents will not be exposed to the outside unless the battery leaks, is exposed to high temperatures that result in a venting of the cell, or the cell is mechanically, physically, or electrically abused.

A damaged battery will generate hazards due to the corrosive and flammable properties of the electrolyte and the gas released from the cell, including volatile organic substances with flammable properties.[53]

The positive electrode of a Li-ion cell varies based on the selection of chemistry. This typically includes lithiated oxides such as manganese oxide (LMO), nickel-cobalt-aluminum oxide (NCA), nickel-manganese-cobalt oxide, or cobalt oxide (NMC); or iron phosphate (LFP) as the positive material. The negative electrode is a carbon based electrode or lithiated titanium oxide (LTO), which can store lithium-ion. Most of the lithium ion batteries use one molar concentration of lithium hexafluoro phosphate ($LiPF_6$) as electrolyte salt dissolved in multiple organic solvents. These solvents are flammable. Toxic gases in lithium ion battery smoke are listed below:[54]

1. Carbon Monoxide (CO)
2. Hydrogen Fluoride (HF)
3. Phosphorus Trifluoride (PF_3)
4. Phosphorus Pentafluoride (PF_5)
5. Phosphorous Oxyfluoride (POF_3)

The chemical risks associated with the direct exposure to the substances contained in the battery are given in Table 21.

Table 21 Li-ion Composition Information on Ingredients

Components	CAS Number	Amount % by weight	OSHA PEL (mg/m³)
Lithium Nickel Manganese Cobalt Oxide	346417-97-8	< 30	None
Lithium Cobalt Nickel Aluminum Oxide	193214-24-3	< 30	None
Lithium Cobalt Oxide	12190-79-3	< 30	0.02
Other Lithium Metal Oxide	NA	< 30	None
Lithium Metal Phosphate	15365-14-7	< 30	3.5
Carbon/Graphite	7440-44-0	< 25	3.5
Lithium Hexaflurophosphate - Salt	21324-40-3	<35	None
Ethylene Carbonate- Solvent	96-49-1	<35	None
Diethyl Carbonate – Solvent	105-58-8	<35	None
Dimethyl Carbonate - Solvent	616-38-6	<35	None
Copper	7440-50-8	<10	1
Aluminum	7429-90-5	< 10	15 Total Dust 5 Respirable

3.8.2 Recycling Li-ion Batteries

Several companies recycle lithium-ion batteries: Recycling Coordinators Incorporated (Akron, Ohio), Retriev (Trail, British Columbia), and Umicore (Raleigh, NC). Each company has its own unique recycling process. Recycling Coordinators Inc. and Retriev convert spent li-ion batteries into feed stocks that are sent to Glencore, a smelter located in Sudbury, Ontario, Canada, for recovering cobalt, copper, and nickel. Umicore sends spent li-ion batteries collected in North America to its recycling process located in Hoboken, Belgium.

As noted previously, 99 percent of lead acid batteries are recycled and over 50 percent of the lead supply comes from recycled batteries. While becoming more common throughout the industrial and consumer markets, lithium ion batteries are not being recycled widely. The increase of lithium demand is very large while analyses of Lithium's geological resource base indicate that there is insufficient lithium available in the Earth's crust to sustain electric vehicle manufacturing in the required volume, based solely on li-ion batteries.[55] Recycling can dramatically reduce the amount of new lithium that is required.[56] Having a recycling infrastructure in place will ease concerns that the increased deployment of vehicles that use Li-ion batteries could lead to a shortage of lithium carbonate and a dependence on countries such as China, Russia, and Bolivia, which control the bulk of global lithium reserves.[57]

With the multitude of lithium ion battery chemistries being used to produce lithium ion batteries, it is important to develop a simple and environmentally acceptable recycling process. One of the major objectives of recycling is to extract useful elements such as Co, Ni, Mn, Li, and Fe from mixed cathode materials, and then utilize the recycled materials to synthesize active materials for new batteries.[58] Presently, the cathode materials widely used commercial lithium ion batteries include $LiCoO_2$ (LCO), $LiMn_2O_4$ (LMO), $NiCoAlO_2$ (NCA), $LiNiMnCoO_2$ (NMC) and $LiFePO_4$ (LFP).

4. Modeling a Locomotive Battery

Some of the most important goals which led to developing a battery system for use in an HDEB locomotive were to improve locomotive efficiencies and reduce environmental pollution. To achieve this objective, the battery system must be able to capture as much regenerative energy as possible and then deliver that energy to supplement the traction loads. By utilizing validated models, the life of a battery system, given specific input parameters and operating environments, was simulated, with a focus on the regenerative braking energy that could be recovered and the traction loads provided to the main generator. The modeling answers the threshold question of whether the battery is able to provide reasonable traction loads to the locomotive based on the regenerative braking energy available, and also represents a first step in establishing optimization sequences for a battery system.

4.1 Input Parameters and Assumptions

The key parameters and assumptions for the empirical based MATLAB® model simulation exercise were load profile, temperature environment, cooling type, service life (7–10 year target), and voltage range (750V, plus or minus 50). While the load profile was considered fixed, the amount of regenerative braking load absorbed by the battery was varied to achieve the target service life. This model allowed the battery system to absorb regenerative braking energy if the battery SOC was less than 100%, and allowed the battery to supplement the traction loads if the SOC was greater than 40%.

Two different load profiles were evaluated; Route A and B. Each route had unique regenerative and traction energy that operated over different durations. For the balance of time to equal 7 days, the duration differences required forced air cooling during operation and natural convection to atmospheric conditions. These parameters are addressed in this section.

An existing 790V battery system was chosen for the modeling exercise. The battery system consists of Super Iron Phosphate cells (VL30PFe) cells in a series configuration to yield the 790V nominal voltage; specifically, 240 VL30PFe cells connected in series. In order to achieve the capacity needed to recapture an arbitrary target of 60% of the regenerative braking loads, twenty of the 790V modules had to be placed in parallel. This configuration is not optimized; the locomotive and battery system level trade studies would need to be refined before optimization can take place.

4.2 Route A Model Results

First, the analysis was run with an appropriate route for a new battery and specific output parameters that determine the expected battery life in years. Next, the model inputs for cell State of Health (SOH) were changed and the model was run again to validate that the battery system satisfies the voltage and current of the locomotive at the EOL of the battery system.

Figure 39 shows the model's load profile A, which illustrates the power at the motor as a function of time. The negative values represent regenerative breaking loads and the positive values represent traction loads. In order to predict the life of the battery system, Route A was performed for 2.52 days continuously per the figure below, and then permitted to rest without loads for the remainder of a 7 day period (4.48 days). This profile was repeated every 7 days for the life expectancy of the battery system. This load profile does not reflect typical locomotive operations but represents an extreme case of operation for battery technology due to the long periods of rest.

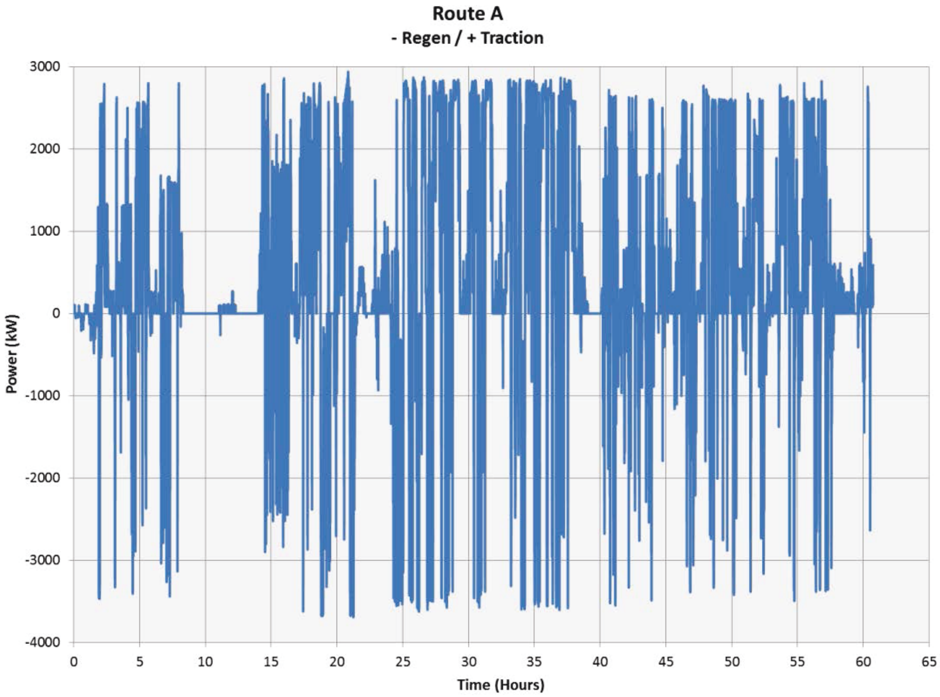


Figure 39 Load Profile - Route A

During the first 2.52 days, while the battery was simulated with the Route A profile, the model assumed that the battery system was cooled using conditioned forced air. In order to complete the week, (4.48 days) the locomotive and battery system were exposed to cyclic temperatures representing summer conditions (see Figure 40). The summer conditions were taken from the National Oceanic and Atmospheric Administration database for a typical Midwestern city in the year 2010.

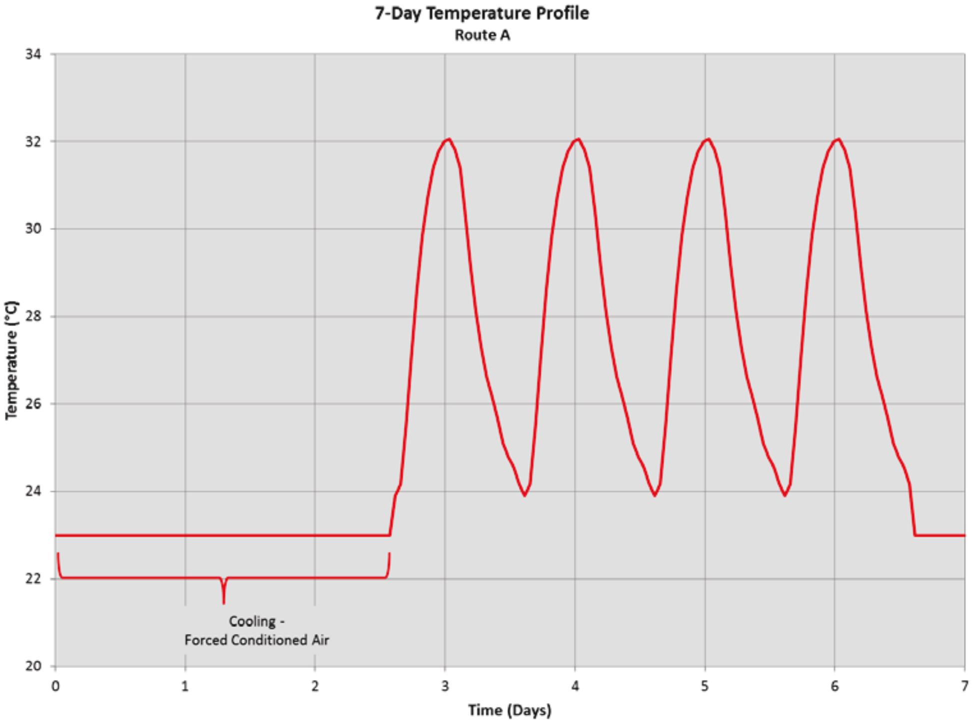


Figure 40 Summer Temperature Profile - Route A

By subjecting the system to four seasons from the same source as above, the life expectancy of the battery system can be improved by ~13 to 15%. The profile used for the four seasons is shown in Figure 41.

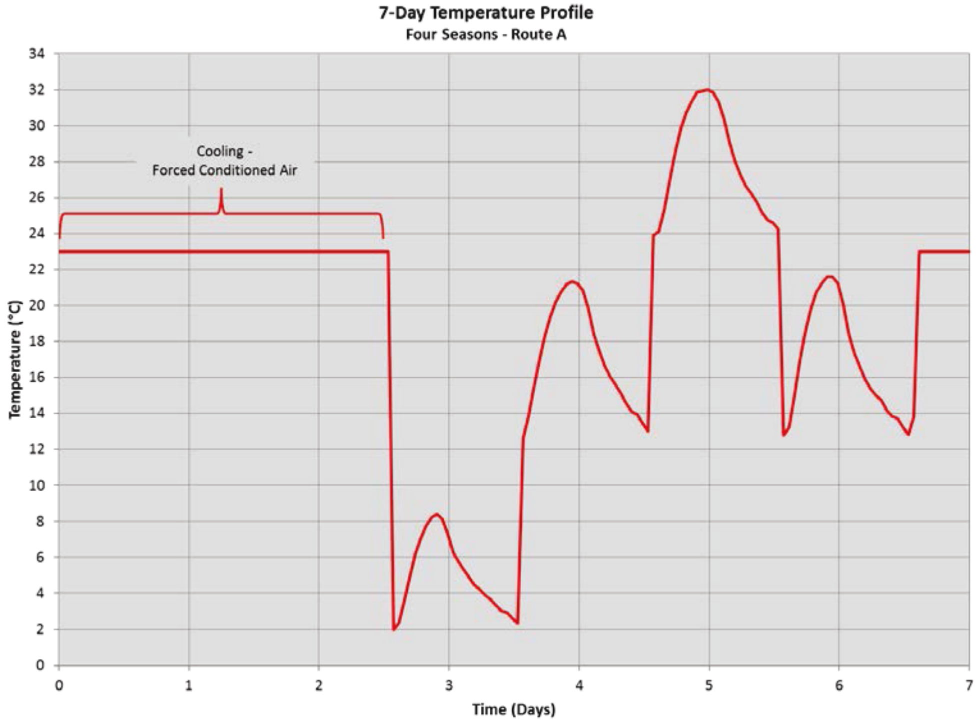


Figure 41 Four Seasons Profile - Route A

4.2.1 Route A Initial Run for New Battery

The initial run of a Beginning of Life (BOL) battery model yielded the following currents and voltages into and out of the battery, refer to Figure 42 for the plot of the voltage and current.

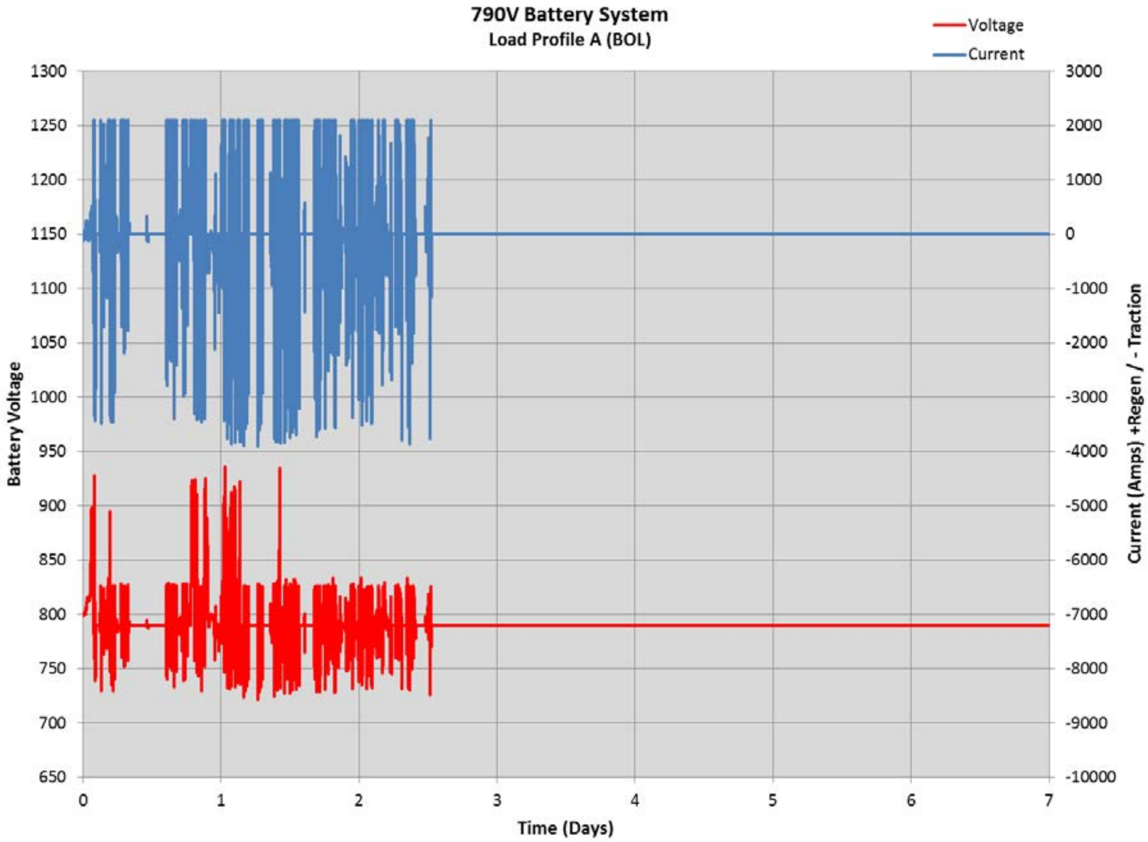


Figure 42 BOL Battery Voltage and Current - Route A

The battery temperature and battery SOC during this 7 day period is shown in Figure 43. The last 4 days are subjected to ambient conditions. It should be noted that this profile runs 365 days a year; and as mentioned earlier, a more realistic and less severe temperature profile would have been generated if this model was run for all four seasons (see Figure 41).

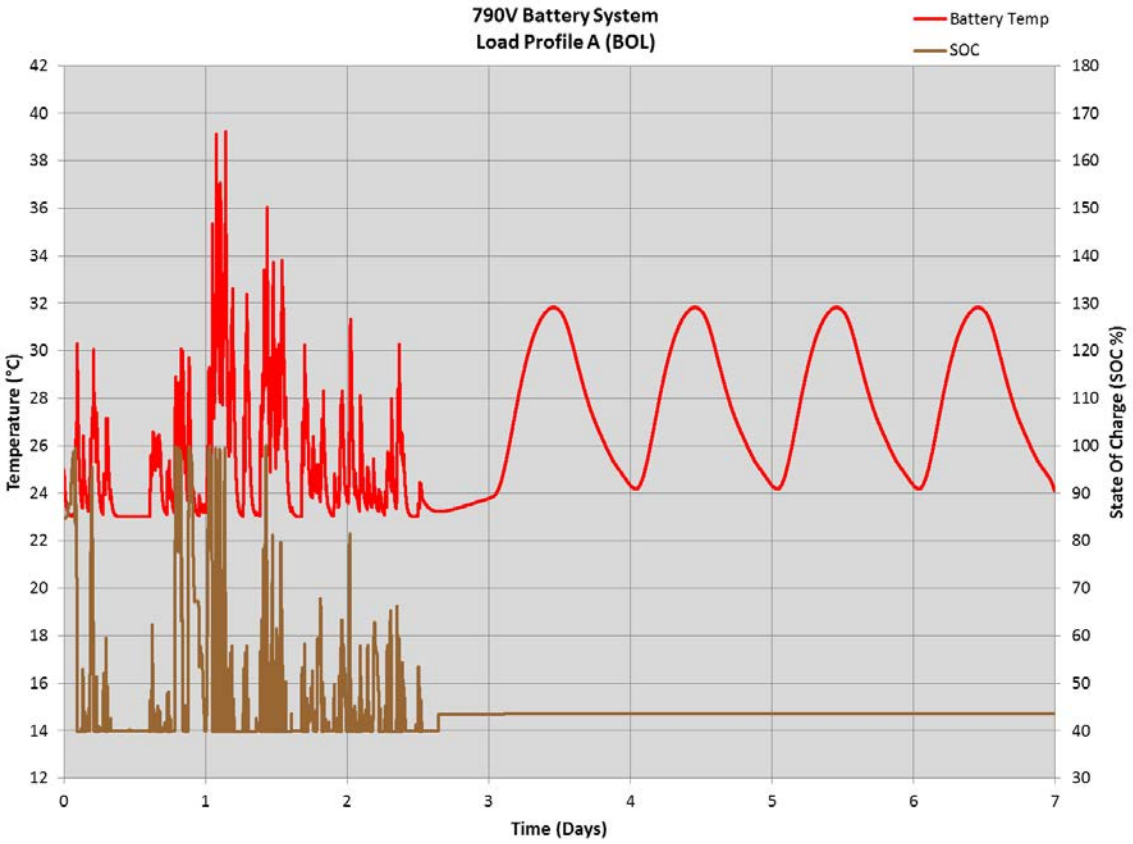


Figure 43 BOL Battery Temperature and SOC - Route A

By utilizing data produced from the Route A profile (Figure 39) and the summer temperature profile (Figure 40) the projected life for the battery is:

- 8.5 years for the capacity needs of Route A.
- 8.5 years for the power needs, based on changes in resistance.

In order to validate the accuracy of the prediction, the profile must be conducted utilizing battery parameters representing EOL.

4.2.2 Route A Final Run for EOL Battery Validate Life

A final run of the EOL battery model is required to validate that the modeled battery system can support all the loads for the duration predicted. The successful EOL model current and voltage results are shown in Figure 44.

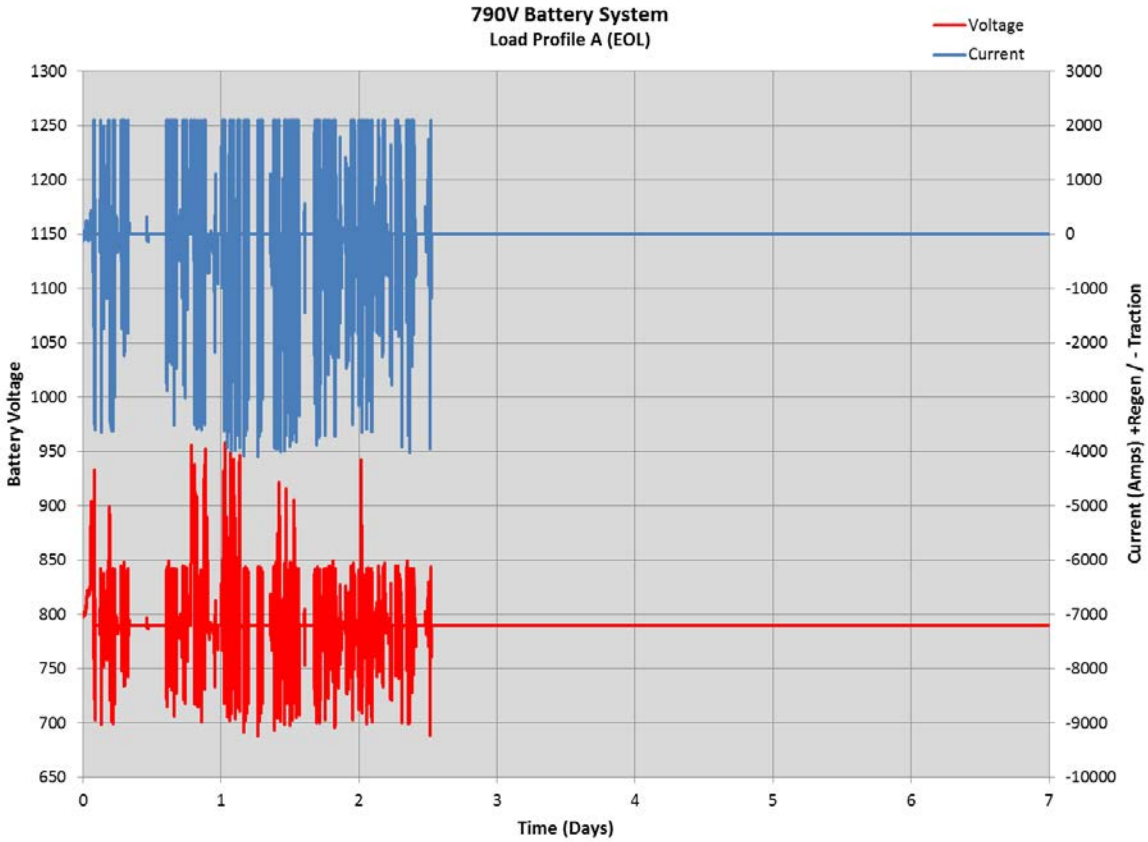


Figure 44 EOL Battery Voltage and Current - Route A

When one compares Figure 42 and Figure 44, the effects of increased battery impedance and lower capacity are evident. In the BOL battery, the currents were lower, resulting in the voltage that stays above 720V; the EOL battery has voltages slightly higher than 680V while satisfying traction power. The impact of this increased current is shown in the increased temperature reached on the EOL battery, reference the battery temperature and battery SOC plot shown in Figure 45.

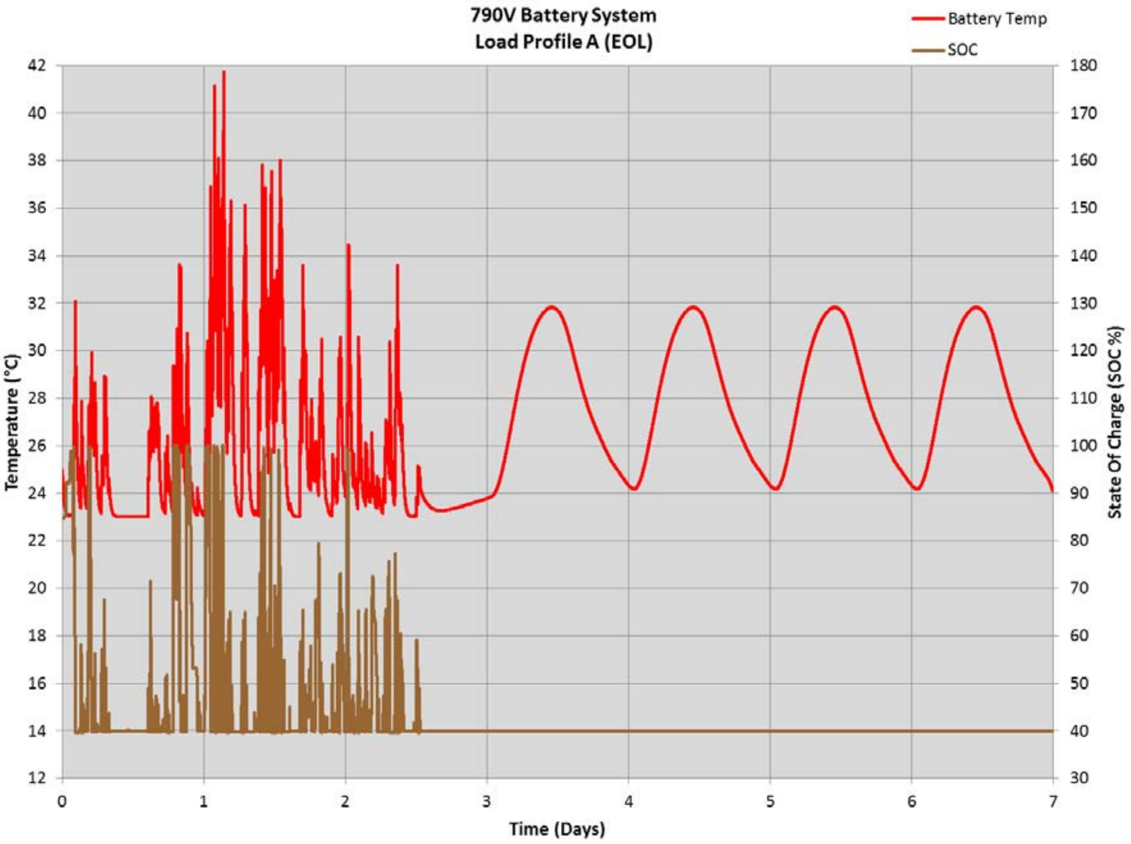


Figure 45 EOL Battery Temperature and SOC - Route A

4.2.3 Route A Regenerative Energy Captured and Traction Loads Supplemented

The improved efficiency and cost savings of a specific battery system is difficult to quantify from examining the battery system side alone. The only data that can be stated with certainty are the amount of total regenerative braking energy that can be absorbed and the traction energy that can be provided. The model indicated that the battery system was able to support the hotel and low speed traction loads while the train moved through the congested rail yard (the duration for this instance was approximately 1.7 hours). Since low speed travel and idle time on a locomotive increases pollution and fuel cost, the overall system design could be optimized to ensure that the battery retains some of its recaptured regenerative energy to allow the battery to support hotel and traction loads at known congested areas/yards, such as in the Route A example. For the battery system evaluated, the model demonstrated the ability for the BOL battery system to absorb approximately 63.3% of the energy generated on Route A and supplemented the traction energy needed by approximately 18.8% (Figure 46). At EOL the model indicated that the battery system absorbed approximately 58.7% of the energy generated on Route A and supplemented the traction energy by 16.9% (Figure 47).

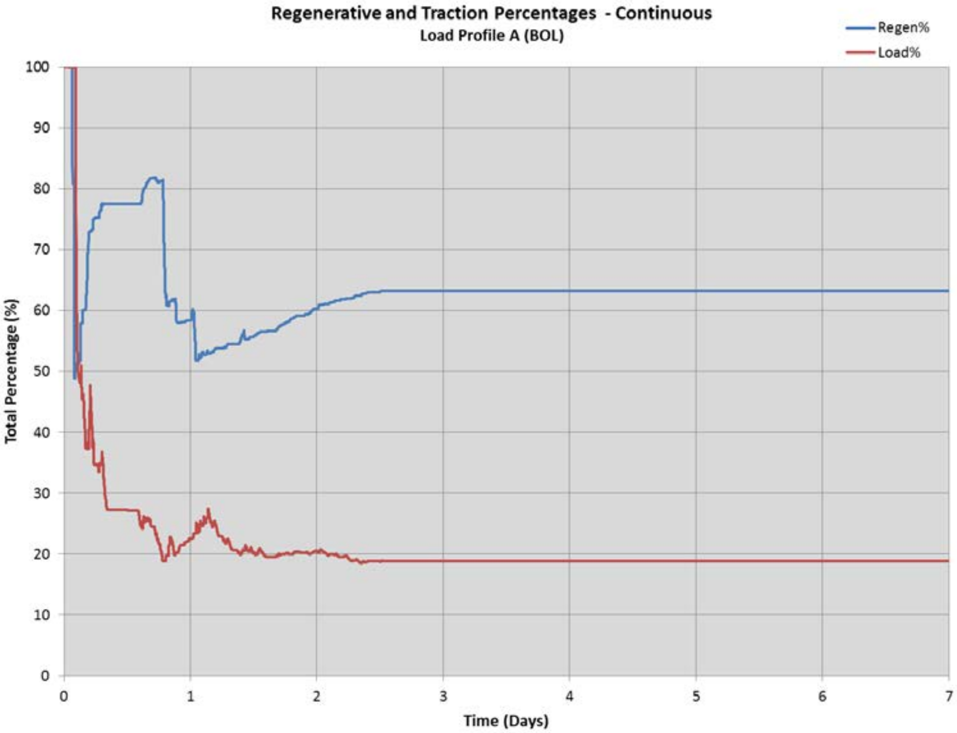


Figure 46 BOL Energy Absorbed / Supplemented - Route A

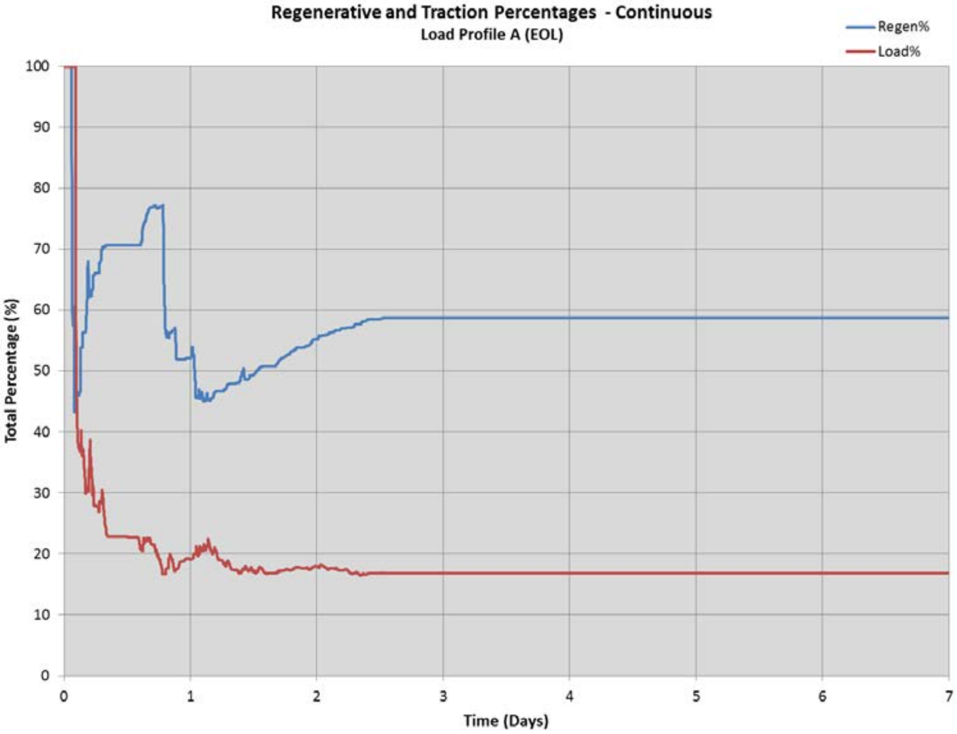


Figure 47 EOL Energy Absorbed / Supplemented - Route A

4.3 Route B Model Results

The Route B load profile for the model is shown in Figure 48, which illustrates the power being seen at the motor as a function of time. The negative values represent regenerative breaking loads and the positive values represent traction loads.

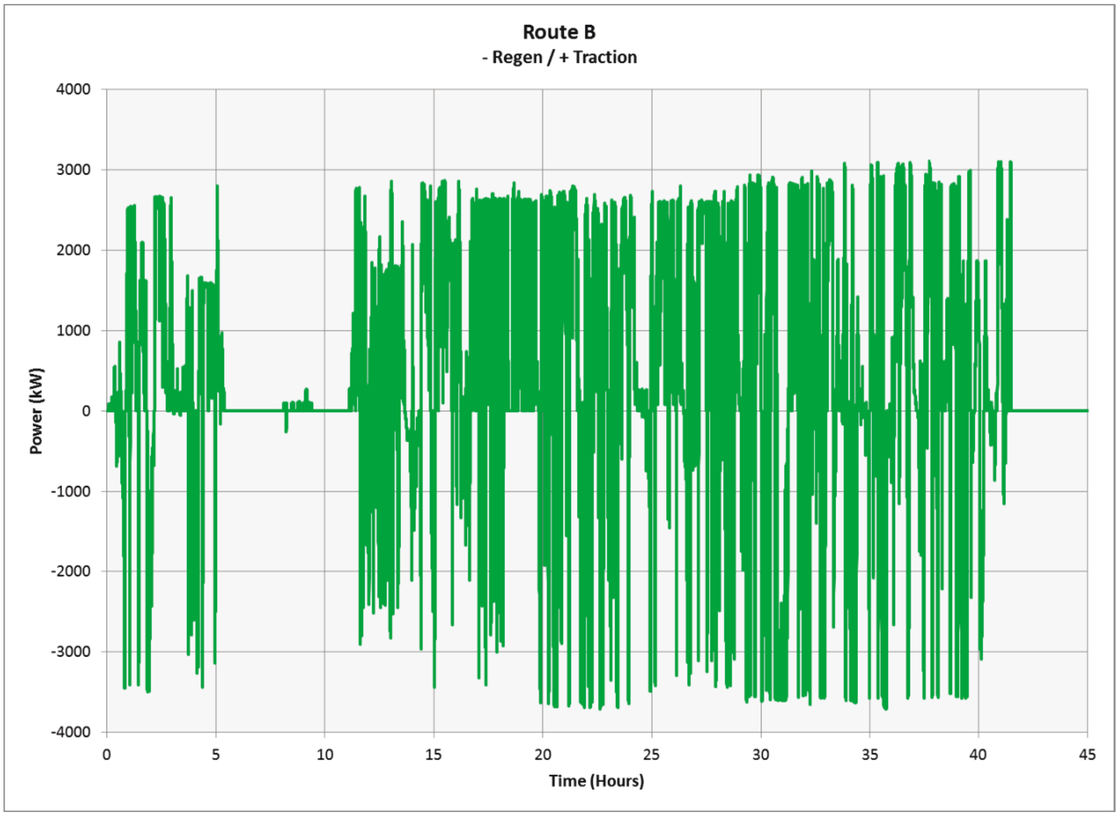


Figure 48 Load Profile - Route B

As noted above, the model must simulate an entire year of environmental conditions in order to predict the life of the battery system, Route B operated for 1.73 days continuously per the figure above, after which the locomotive is permitted to rest without loads for the balance of a 7 day period (5.27 days). This was not representative of typical locomotive operation but represented an extreme case for battery technology due to the long periods of rest. This profile was repeated every 7 days for the life expectancy of the battery system. Utilizing a summer profile that was similar to Route A resulted in five seasons of summer instead of the typical four seasons in one year (Figure 49).

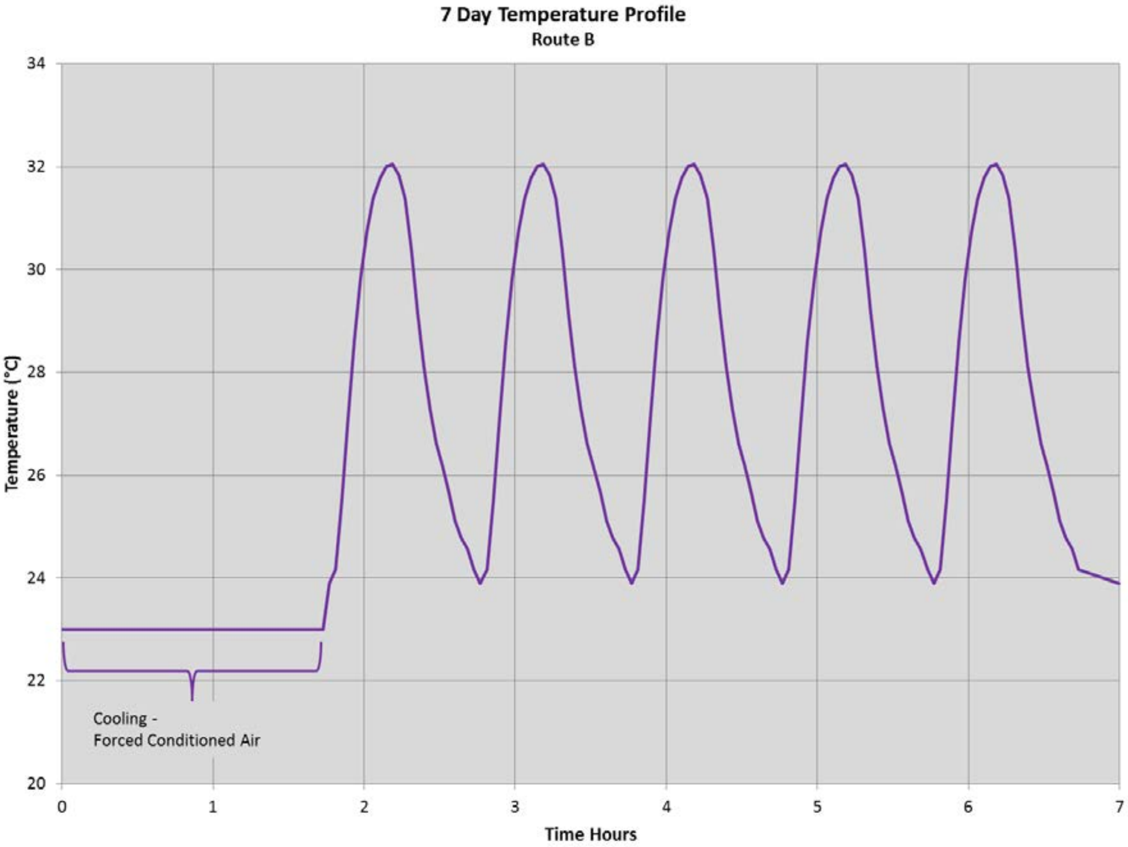


Figure 49 Temperature Profile - Route B

In an effort to represent exposure to only four summers, the durations were changed. The same temperature values from the National Oceanic and Atmospheric Administration database were used. The model indicated a reduction of life expectancy of the battery system because high temperature exposure was increased. By rescaling the duration, the model provided a direct comparison to four normal seasons versus using four summers. Route B's temperature profile is provided in Figure 50.

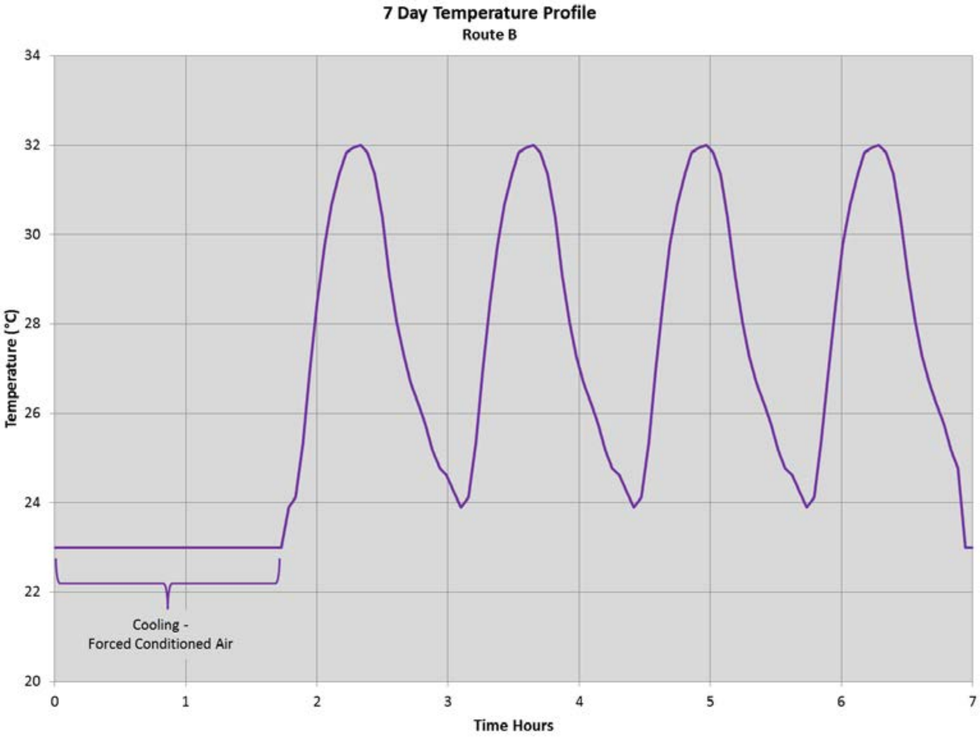


Figure 50 Summer Temperature Profile - Route B

By subjecting the system to four seasons, the life expectancy of the battery system can be improved by ~16 to 18%. The profile used for the four seasons is in Figure 51.

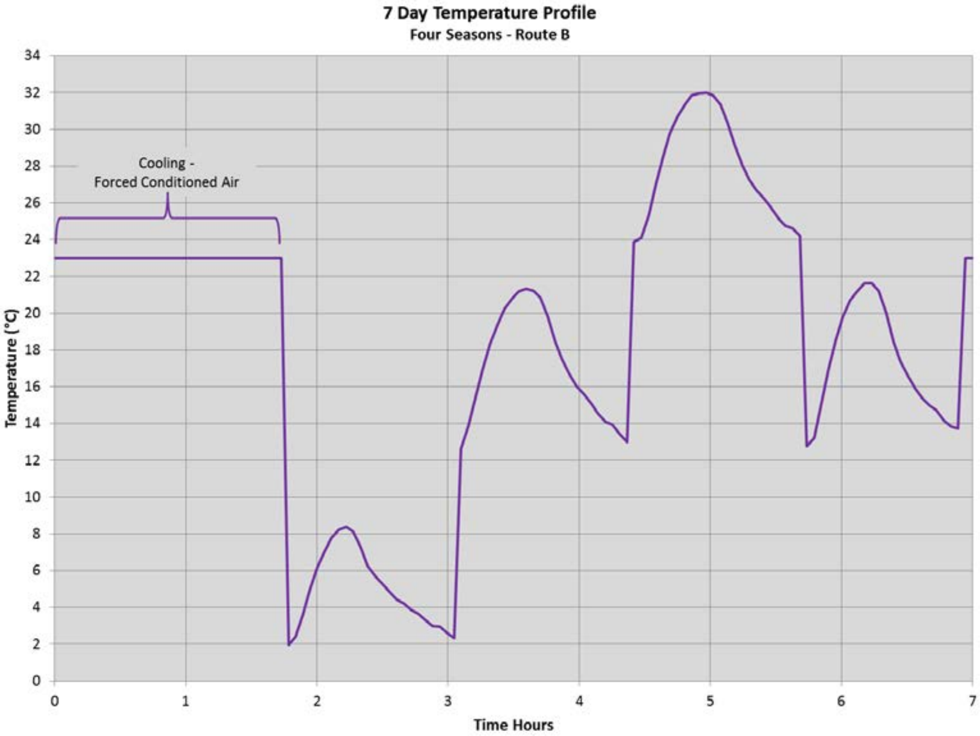


Figure 51 Four Seasons Temperature Profile - Route B

4.3.1 Route B Initial Run for New Battery

The initial run of the Beginning of Life (BOL) battery model yielded the following currents and voltages into and out of the battery (Figure 52).

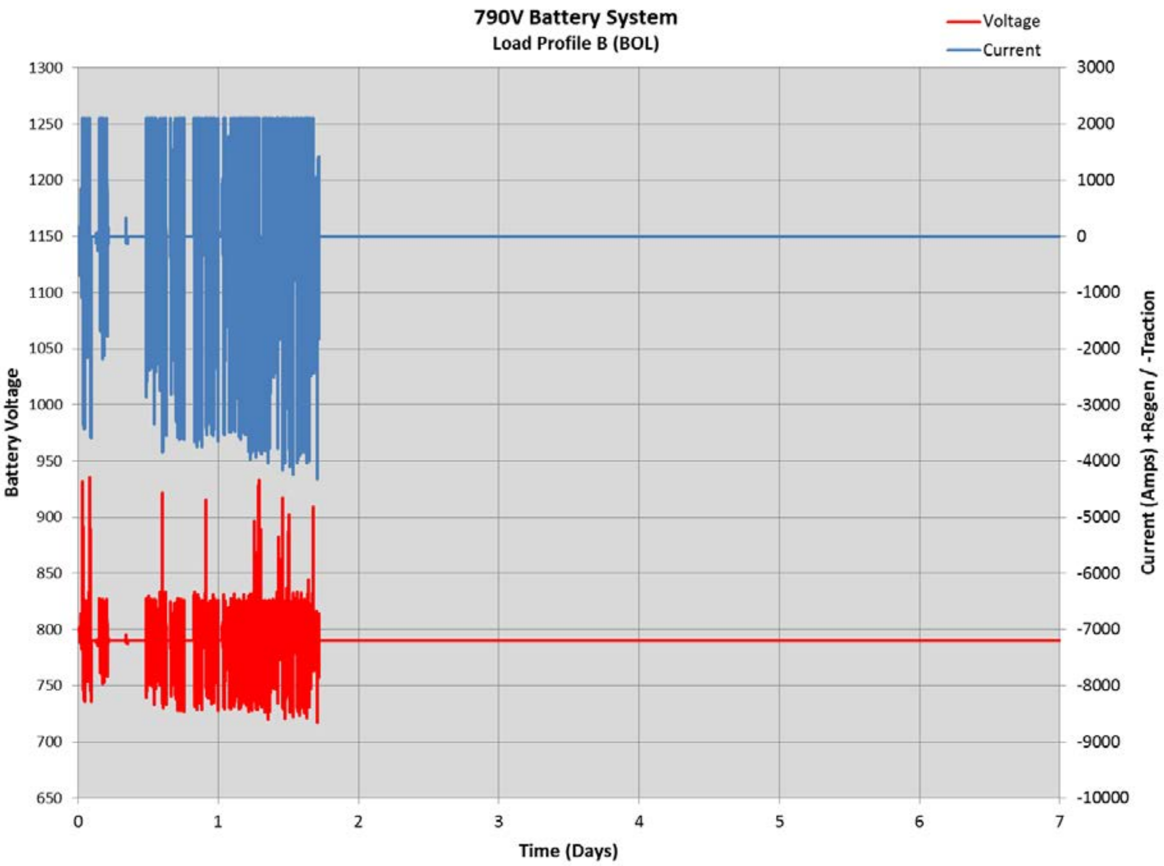


Figure 52 BOL Battery Voltage and Current - Route B

Figure 53 shows the battery temperature and battery SOC during this 7 day period. The last 5 days are subjected to four cycles of summer conditions. It should be noted that this profile runs 365 days a year; and as mentioned earlier, a more realistic and less severe temperature profile would have been to run the model for all four seasons as shown in Figure 51.

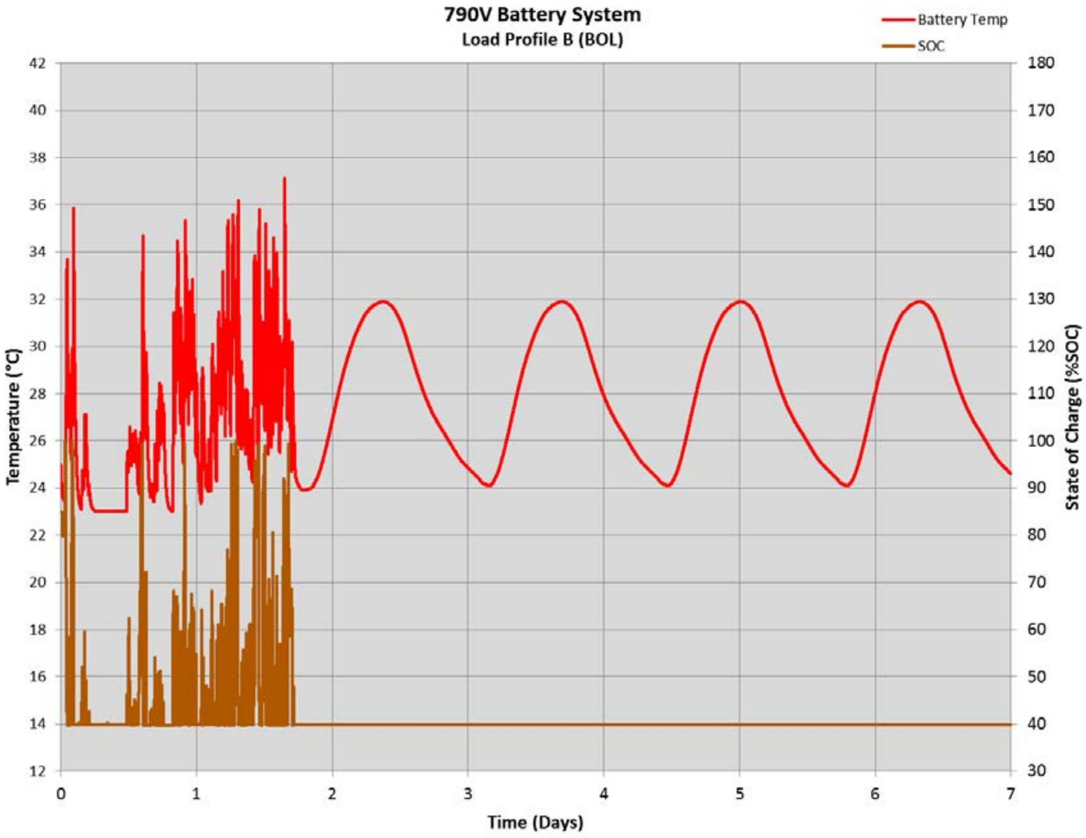


Figure 53 BOL Battery Temperature and SOC - Route B

By utilizing data produced from the Route B profile (Figure 48), and the model and temperature profile (Figure 50), the projected life for the battery is:

- 7.8 years for the capacity needs of Route B.
- 7.7 years for the power needs, based on changes in resistance.

In order to validate the prediction, the profile must be conducted utilizing battery parameters representing EOL.

4.3.2 Route B Final Run for EOL Battery Validate Life

The final run of the EOL battery model yielded the following currents and voltages into and out of the battery. The plot of the voltage and current is shown in Figure 54.

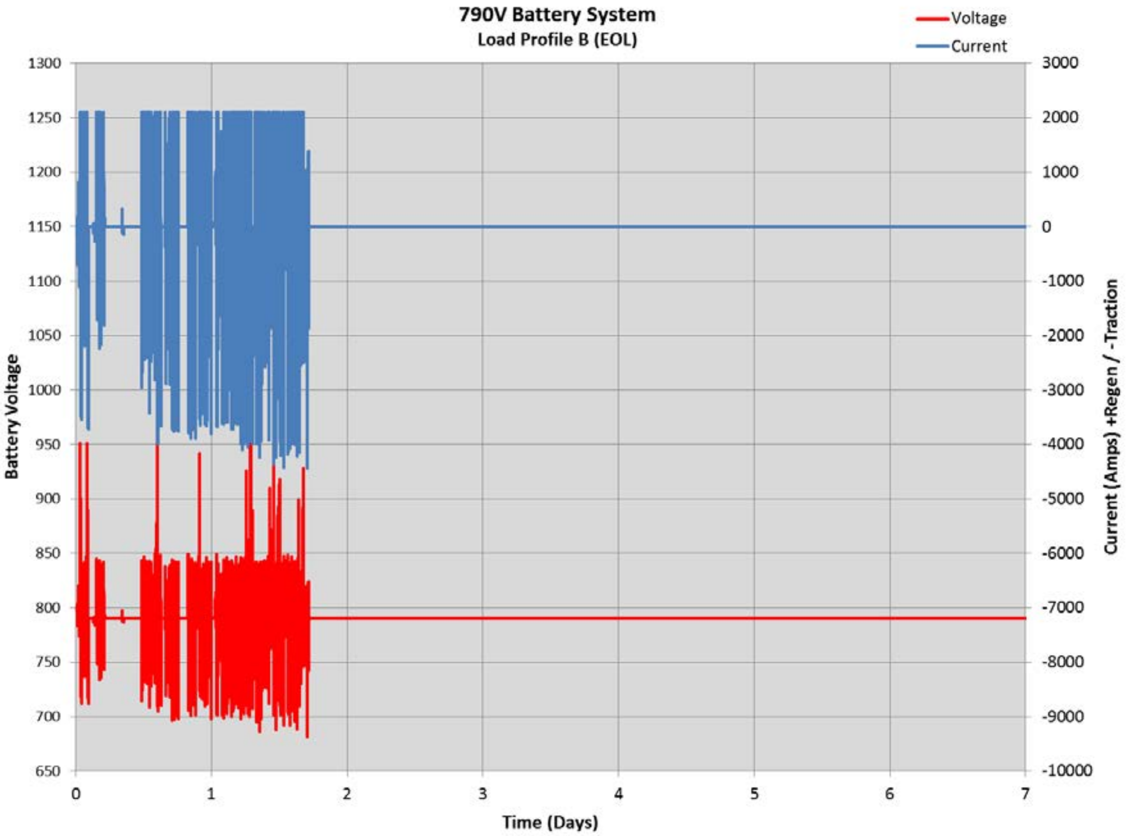


Figure 54 EOL Battery Voltage and Current - Route B

When Figure 52 and Figure 54 are compared, the effects of increased battery impedance and lower capacity can be observed. In the BOL battery, the currents are lower resulting in the voltage that stays above 717V; the EOL battery has voltages slightly higher than 681V while satisfying the traction power. The impact of this increased current is shown in the increased temperature reached on the EOL battery. (reference the battery temperature and battery SOC plot shown in Figure 55).

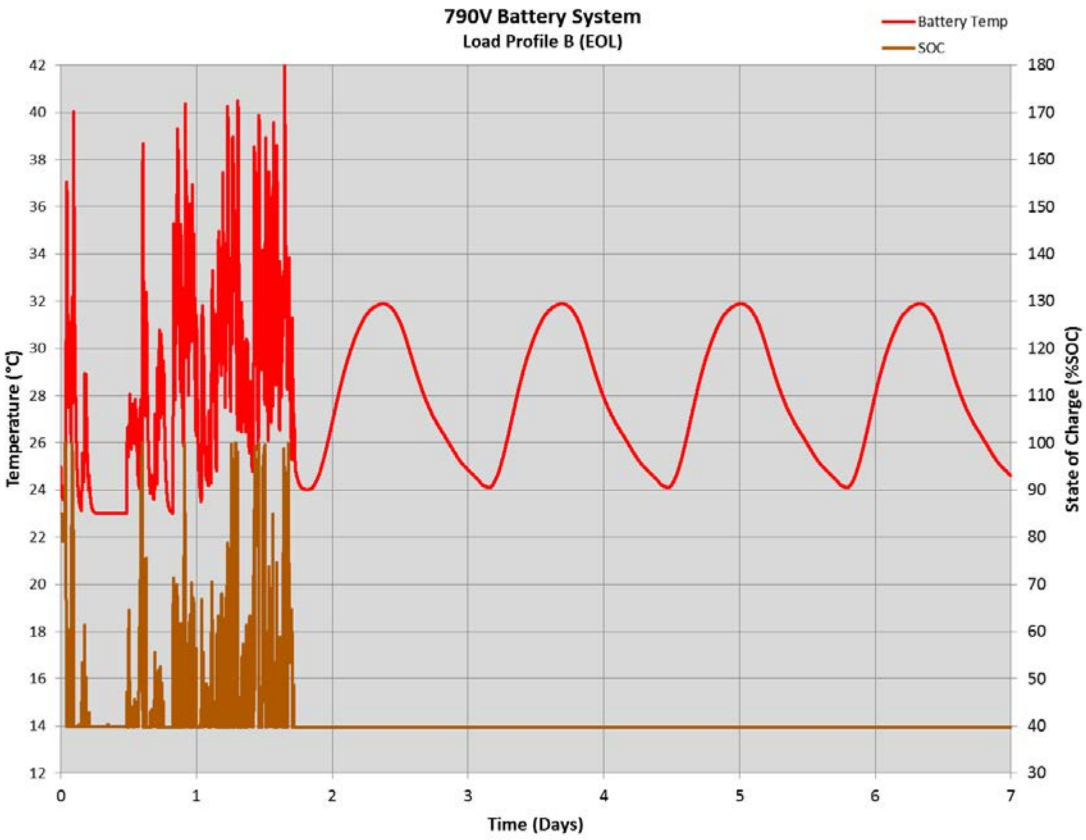


Figure 55 EOL Battery Temperature and SOC – Route B

4.3.3 Route B Regenerative Energy Captured and Traction Loads Supplemented

As mentioned above, improved efficiency and cost savings of a specific battery system is difficult to determine by examining the battery system side alone. The only parameters that are certain are the amount of total regenerative breaking energy that can be absorbed and the traction energy that can be provided. The model indicated that the battery system was able to support the hotel and low speed traction loads while the train moved through the congested rail yard; the duration for this instance was approximately 1.13 hours. Since low speed travel and idle time on a locomotive increases pollution and fuel cost, further optimization could be incorporated in the overall system design to ensure the battery retains some of its recaptured regenerative energy to allow the battery to support hotel and traction loads at known congested areas/yards, such as in the Route B example. For the battery system evaluated, the model demonstrated the ability for the BOL battery system to absorb approximately 61.0% of the energy generated on Route B and supplemented the traction energy needed by approximately 23.1% (Figure 56). At EOL the model indicated that the battery system absorbed approximately 60.0% of the energy generated on Route B and supplemented the traction energy by 21.8% (Figure 57).

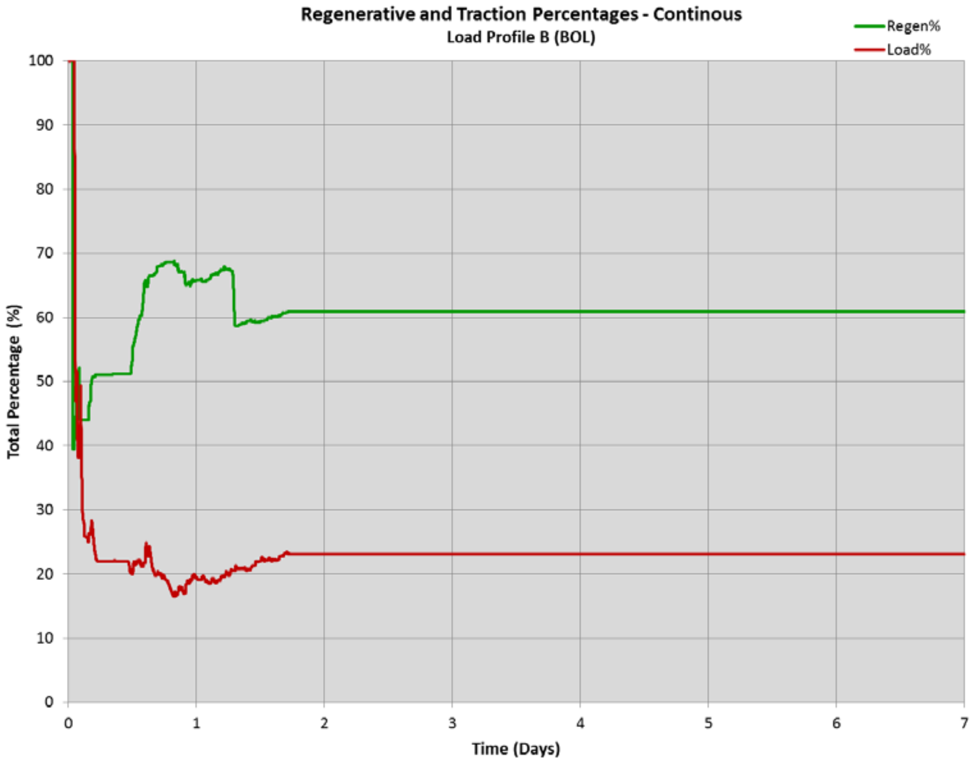


Figure 56 BOL Energy Absorbed / Supplemented - Route B

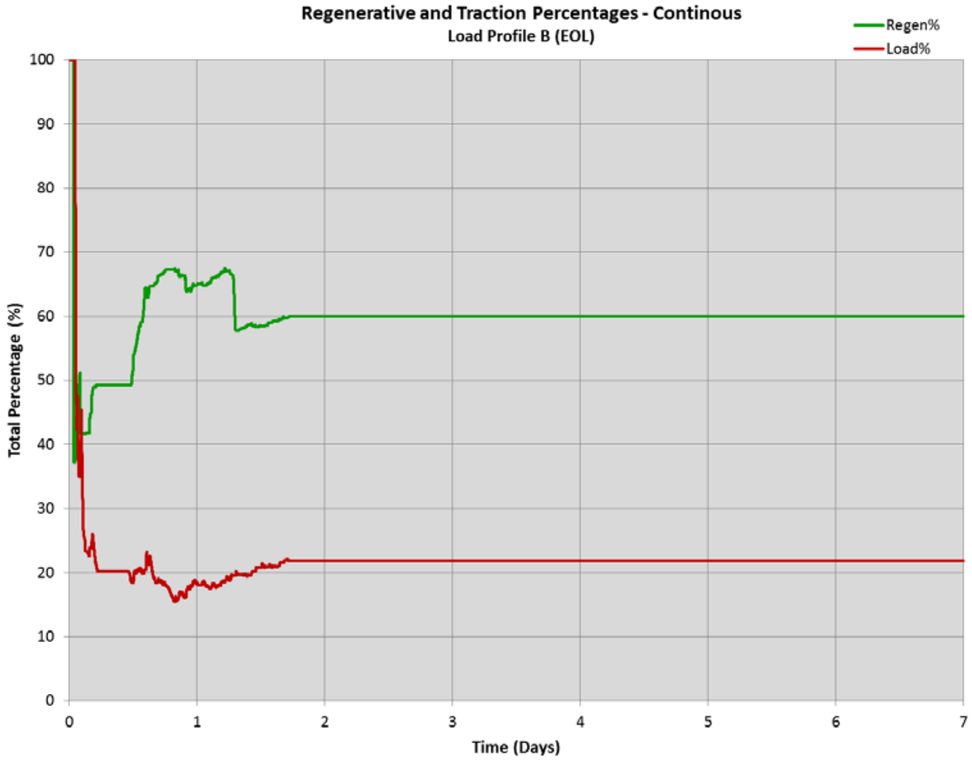


Figure 57 EOL Energy Absorbed / Supplemented - Route B

As previously mentioned, further optimization is required via trade studies of locomotive and battery systems parameters to determine an optimum system design. The model had to be limited in the amount of regenerative braking the battery could absorb because the model assumed that the regenerative braking energy was constant current charging. In reality, a great deal of this energy would be pulse types charging. Such pulse charging would result in higher charge rates (more energy absorbed) for the battery and therefore more energy available for traction loads. This constant current charging assumption for the model also affects the battery life prediction. Further study and modeling is needed to determine how a battery system will operate when the charge energy is not constant current.

While reducing the size of the engine on the locomotive may not be practical, the model demonstrates the ability of the battery to provide a meaningful supplement to the overall traction loads for both Routes A and B (18.8-23.1%) and allows the train to run in all-electric mode during the transiting of congested rail yards. All-electric operation could significantly reduce rail yard pollution levels and provide significant fuel savings.

5. System Cost Discussions

Cost represents the most significant factor in determining market success.[59] The system cost for an HDEB locomotive battery includes the initial cost, life of the battery system, replacement cost to meet the required duration, maintenance costs or savings, and reduction in wear and tear to other systems. The voltage and capacity requirements needed to support the regenerative and traction loads of an HDEB locomotive dictate that electronics are required for any battery technology. Parameters such as battery state of health and cell balancing would be managed by the required electronics, which also provides an additional layer of thermal runaway protection.

While the cost breakdown of the electronics depends on the needed level of complexity, the HDEB locomotive system needs are similar to what is found in wayside energy storage for electric commuter rail applications. An approximation of the cost breakdown for a typical lithium-ion grid-connected system is shown in Figure 58.

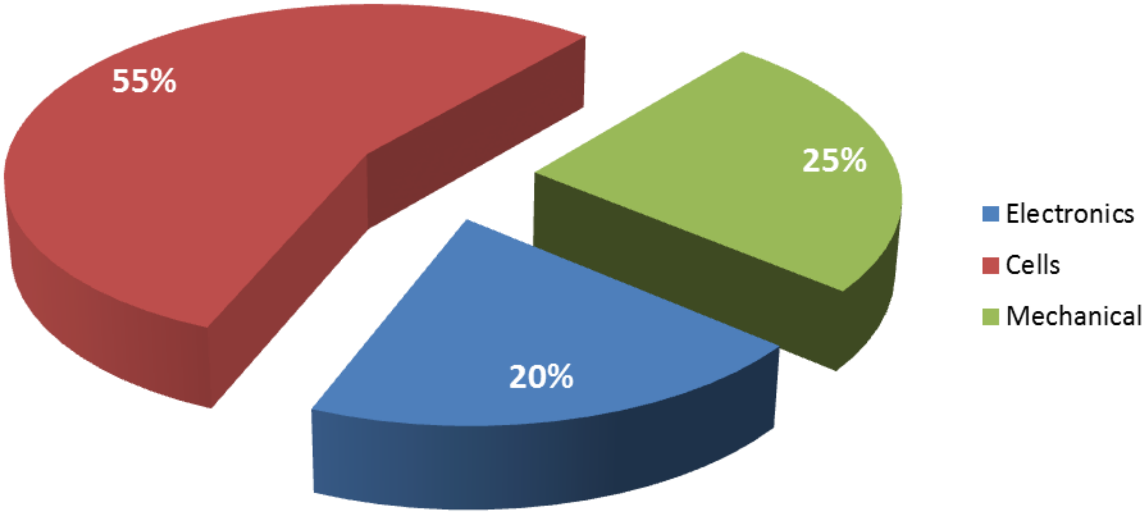


Figure 58 Typical Li-ion System Cost Percentages

A key aspect of cost is based on the quantities of cell chemistries in the market.[60] This is reflected in the data presented this year in Figure 59 on the estimated demand for rechargeable chemistries in the HEV, ESS, EV, and portable markets. The data reveals the anticipated mega-watt-hours for each calendar year. As lithium technologies usage continues to increase, the cost of materials and process will continue to decrease.[60] Further, li-ion battery technology is displacing NiMH technology in multiple markets, with the potential for an increase in NiMH cost due to lower future production volume.

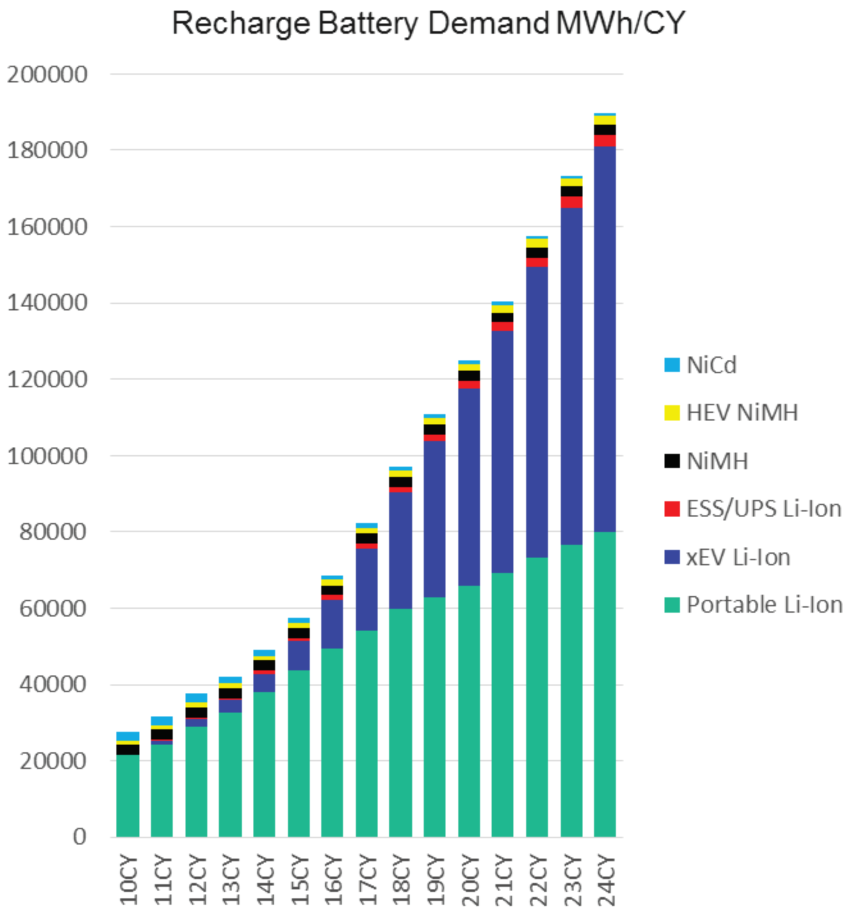


Figure 59 Rechargeable Demand for Calendar Year [61]

The actual cost of a HDEB locomotive battery system can be linked to actual production and raw material costs. Of the technologies discussed in this report, only VRLA, NiCd, and standard NiMH technologies have well-known production costs. Table 22 provides dollar rankings from $ to $$$$$ for costs and † to †††††† for least to greatest for cycle life.

Table 22 Cost Benefit Table

Technology	Initial Costs	Life Cycle Cost	Electronic / Protections	Cycle Life
VRLA	$	$$$$$	$$$$	†
Pb-Carbon	$$	$$$$	$$$$	††
NiCd	$$	$$$$	$$$$	††
NiMH	$$$	$$$$	$$$	†††
BiPolar NiMH	$$$	Unknown	$$$$	Unknown
Ni SuperCap	$$	$$$	$$	†††††

Technology	Initial Costs	Life Cycle Cost	Electronic / Protections	Cycle Life
$Na/NiCl_2$	$$$$$	$$$	$$$$	†††
NCA	$$$$	$$	$$$$	†††††
NMC	$$$$	$$	$$$$	††††
LFP	$$$$	$$	$$$	††††
LTO	$$$$	$	$$	††††††

When a battery technology is being chosen, life cycle cost is an important factor to consider. As discussed above, certain battery chemistries have limited cycle life and therefore need to be replaced multiple times over the seven to 10-year life of an HDEB locomotive battery system. For example, VRLA batteries offer a low initial cost solution, which has been utilized previously in locomotive applications. The limitations of VRLA technology, however, lead to a short operational life and the need for frequent maintenance and replacement of cells. As a result, the life cycle cost for a VRLA system is significantly higher. NiMH technology, a common technology utilized in hybrid electric vehicles, has a higher initial cost but is better suited for the HDEB locomotive application. The technology does have limitations and the batteries must be replaced over the seven to 10-year timeframe, as indicated in the table. Lithium-ion technology, with its various chemistries, represents a higher initial-cost option. However, the cycle life and performance of lithium-ion allow for limited maintenance and no replacement need over the 7-to-10-year performance period for the HDEB locomotive battery system.

6. Battery Safety in the Rail Environment

Various protection mechanisms are often employed with high power or high energy battery systems. These mechanisms range from internal cell safety separators to fuses, contactors, and carefully controlled charging algorithms and monitoring systems. Regardless of the systems used to manage safety, there is need for an inherently safe chemistry when batteries are subject to harsh conditions or when battery systems are placed in sensitive areas. Abuse conditions can always occur in which the various safety mechanisms may not be able to prevent a thermal runway. Global systems safety of any large battery system can only be ensured at the system and application level. As a result, large battery systems use the operating system to coordinate the safety controls with user needs, including power and energy availability or cooling systems control.

All energy storage systems are associated with electrical, mechanical, and chemical risks, and unexpected environmental conditions or defaults can lead to an accidental or uncontrolled energy release. Depending on the environmental stress conditions, these risks can eventually create dangerous consequences, referred to as potential hazards.

When a battery is in operation, it generates heat due to Joule heating, which is the energy loss from the flow of current through the internal resistance of the battery (whether it is being charged or discharged). If the battery is discharging, the total energy within the system is fixed and the temperature rise will be limited by the available energy of the battery. However, this can still cause very high localized temperatures even in low power batteries. No such automatic limit applies while charging, as there is nothing to stop the user from continuing to pump electrical energy into the battery after it has become fully charged. Battery designers strive to keep the internal resistance of the cells as low as possible to minimize the heat losses or heat generation within the battery, but even if cell resistances are as low as 1 mΩ the heating can be substantial.

Any battery system may be driven into thermal runway if it is severely over-charged for a prolonged period of time (due to factors such as faulty separators resulting from aging, rough handling of the battery, excessive vibration, and high-temperature).

While safety measures are especially critical for larger multi-cell batteries, two main objectives are shown as fundamental to all efforts in battery safety:

- Propagation of “Thermal Runaway” from cell-battery to cell-battery, which leads to a cascading failure of a battery module or pack, cannot be allowed to occur.
- The failure rate of cell-batteries that leads to thermal runaway will need to become extremely rare.

Cell and battery failures modes can be categorized into two main areas:

(1) **Non-energetic** – Benign failures such as include loss of capacity, increase in internal impedance (loss of power capability), activation of permanent disabling current limiting devices, closing the pores of shutdown separator, electrical fuse, electrolyte leakage, cell dry-out, and cell swelling.

(2) **Energetic** – This class of failures involves thermal runway. Cell thermal runaway refers to rapid self-heating of a cell due to the exothermic chemical reaction of the highly oxidizing positive electrode and the highly reducing negative electrode; it can occur with batteries of any chemistry. In a thermal runway reaction, a cell rapidly releases its stored energy. The more energy a cell has stored, the more energetic a thermal runaway reaction will be. Since lithium-ion batteries have very high energy-densities compared with other battery systems, thermal runaway reactions for lithium-ion batteries can be very energetic. The flammable electrolyte also contributes to the intensity of the thermal runaway reaction in Li-ion batteries.

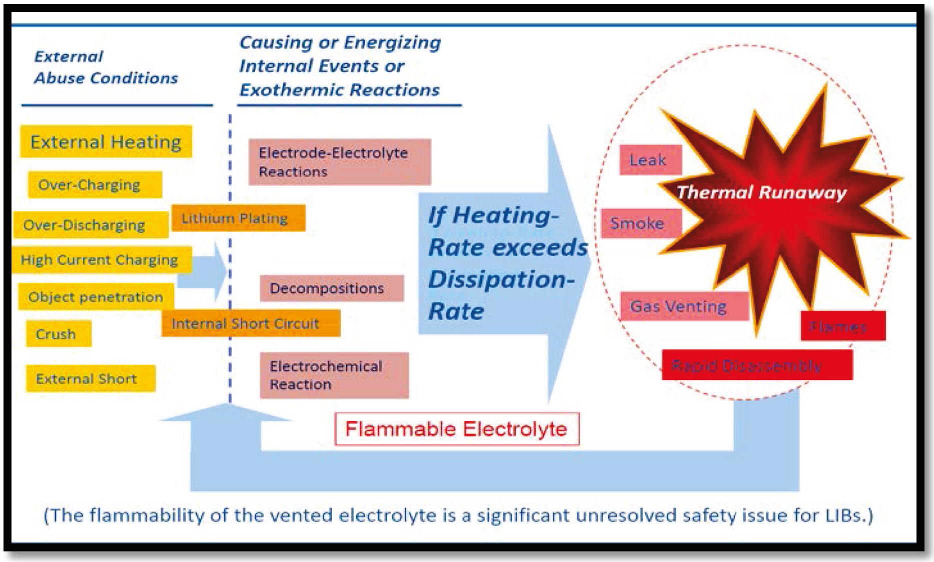


Figure 60 Schematic Representation of Li-ion Thermal Runaway

Figure 60 describes how a battery can be led into thermal runaway and cause safety events. It shows what happens during the over-charging external abuse condition and describes how it affects the positive electrode of the battery cell. The normal charging process transfers lithium ions from the positive to the negative and, if continued past the normal end point, the positive active material continues to increase its SOC. Active materials may become delithiated to the point of instability, generating lithium plating, causing decomposition of electrolyte, initiating exothermic reaction leading into severe thermal runaway condition as shown in Figure 57.

6.1 VRLA Batteries

It is not normal to experience thermal runaway in well maintained VRLA batteries, but runaway is a serious concern when the VRLA is used in float service applications.

Thermal runaway occurs in VRLA batteries when the rate of internal heat generation exceeds the heat that is being dissipated into the ambient condition. Once such a situation continues as the temperature increases, the cells would start the process of “dry-out” because the water in the electrolyte vaporizes and the battery vent steams. As the temperatures increases, the plastic case will soften at 100°C, and then rupture and melt around 160°C.

As the VRLA battery charges, some resistive heat is generated because charging current flows through the resistive components of the cell. However, the major portion of the internal heating results from the exothermic reaction at the negative plate where the oxygen from the positive plate reacts with the lead and sulfuric acid to form lead sulfate and water. Approximately 90% of the current supplied to the battery during float charging is used to facilitate this oxygen recombination cycle.

The oxygen recombination process is negligible in the freed liquid electrolyte (VLA, vented lead-acid) cell because the oxygen gas generated at the positive plate can percolate up through the electrolyte to the environment instead of being redirected by an AGM separator or gel and diffused to the negative plate. Consequently the vented liquid electrolyte lead-acid cell does not exhibit oxygen recombination; thus, it emits oxygen and hydrogen at low float voltage, draws less float current, and generates less heat than does a VRLA cell.

6.1.1 Conditions Conductive to Thermal Runaway

The conditions that cause batteries to undergo thermal runaway can significantly increase the heat generated within the battery or minimize its ability to dissipate internally generated heat to the environment. These would include (singly or in combination):

- Too-high float charging voltage which resulted in:
    1. Elevated float charging current
    2. Accelerated gassing and dry-out
    3. Increased oxygen recombination rate and resulting heating
- Too-high recharge current resulting in increase of battery temperature above ambient
- Imbalance that can occurs in larger quantities of cell strings
- Long term temperature raise due to repetitive cycling as stated in # 2
- As the battery operates at a high temperature environment, these results can be anticipated:
    1. Poor Heat Dissipation
    2. Increase in grid corrosion rate
    3. Increase in float current acceptance
    4. Generate gassing and electrolyte dry out
    5. Increased level of oxygen recombination rate and into heating
    6. Increase solubility of conductive compounds
- Improper battery enclosure design impacting heat transfer

Thermal runaway can be a catastrophic failure of the battery system. Attention should be given in areas such as system design, proper installation and operation.

6.2 NiCd batteries

When vented NiCd batteries are overcharged, compartments and charging rooms are needed to remove the hydrogen gas that is generated. If the cells are allowed to overcharge and the cells are dried out as a result, hazardous conditions such as thermal runaway can occur.

A NiCd battery can overheat due to excess current while the NiCd battery is under a high cell voltage charge. The battery typically has a very low internal resistance, but if the heat generated by the overcharge accumulates quicker than the heat can be expelled, then the resistance of the battery will go down as the internal temperature increases. The reduction in impedance allows more current and increased overcharge. The battery will experience increases in its internal temperature until the battery is destroyed.

6.3 NiMH batteries

NiMH chemistry is very sensitive to high temperatures. Testing has shown that continuous exposure to 45°C will reduce the cycle life by 60 percent. High rate charging, which is an exothermic reaction in NiMH systems, makes thermal management and cooling of these batteries essential.

NiMH batteries require a highly developed battery management system with temperature as one main control variable. These battery management systems must operate in real time to prevent NiMH cells from undergoing thermal runaway. The system may also optimize the charging and discharging cycles and control overloading effects.

Typically, NiMH batteries suffer abuse when they are overcharged and over-discharged. The batteries can suffer severe damage if precautions are not taken to avoid those conditions. The battery to handle abusive conditions and limit severe and permanent effects, the cell undergoes different chemical reactions, such as oxygen recombination.

When over-discharge occurs, the net result is no reaction but heat and some pressure are generated in the cell. Tolerating over-discharge is very important for large series strings of NiMH batteries, since capacity mismatches may allow some cells to be over discharged. For overcharge, heat generation also occurs and the heat generation from the reaction equals the energy input, which occurs at the expense of increasing the stored charge in the battery. If the rate of charge exceeds the rate of recombination, then an increase in cell pressure will result.

6.4 Molten Salt System (ZEBRA®)

ZEBRA® cells are housed within a temperature-controlled, double-walled, sealed, vacuum-insulated battery case. This enclosure protects the outside environment from the effects of failures within and protects internal battery components from hazards outside. Penetrating the casing can compromise its insulating and containment functions and, if severe enough, rupture the cells inside.

Cell failure is separated into two distinct categories: incidents where the cell casing or seals are ruptured and incidents where the cell exterior remains intact. Cases where cells fail with intact cell casings lead to relatively straightforward consequences. The β-alumina tube fractures, and relatively inconsequential amounts of heat are released, but no toxic or otherwise harmful substances are released into either the battery case or outside of it.

If cell rupture occurs, it is potentially much more severe, given the reactive nature of sodium and, to a lesser degree, the chlorinated nickel that may be present in the positive electrode. Most or all of the sodium is “consumed” in the resulting reaction between it and the melt, leaving little or none to escape or otherwise impose hazards outside of the cell. Should some sodium escape the cell it quickly reacts with the oxygen inside of the battery casing, given the high operating temperature of the battery. In 2 years of abuse testing, according to ZEBRA®, no releases of sodium from the battery casing have been observed.

When the charge voltage continues to be applied to a fully charged cell, the overcharge reaction increases the risk of removing Na ions from liquid $NaAlCl_4$. In case of having failed cells in parallel strings of cells in a battery, the voltage of the failed one can be balanced by overcharging the remaining cells in that string.

During over discharge, all the nickel chloride has been de-chlorinated and any further discharging leads to a chemical reaction that converts liquids to chemically stable solids (NaCl and Aluminum). No gasses are produced and the reaction delivers only 2/3 of the overall energy as heat. Sodium tetrachloroaluminate ($NaAlCl_4$) vigorously reacts with sodium if agitated with it, but, in practical cells, it resides in the porous structure of the positive electrode. This reduces the reaction rate and reduces heat generation.

Aluminum, besides being non-hazardous and non-reactive, is electrically conductive and solid at the operating temperature range. As a result, when a β”-alumina fracture takes place in a sodium nickel chloride cell, the aluminum resulting from the ensuing reaction creates a physical barrier that prevents further reaction. This prevents additional release of the potentially available electrochemical energy (resulting in a lower than potentially possible temperature rise), but electrical conductivity between the cathode and the anode is allowed, which effectively shorts the cell. The impedance remains very close to the value of an operating cell.

By design, a failed cell should never reach a temperature could cause adjacent cells in the cell pack to fail in a cascading manner.

When a ZEBRA® battery loses its thermal management system, the "freezing" of cells can occur but does not constitute an event having issues. Reducing the temperature of a ZEBRA® cell results in an increase in internal resistance (due to the characteristics of β"-alumina) until the freezing point of the liquid electrolyte is reached, at which point the cell stops operating.

ZEBRA® batteries are designed with recessed terminals, which eliminate the across-the-terminal shorts that occur in traditional lead acid battery configurations. However, assuming that a short circuit between the terminals did develop, or an accident or other event resulted in short circuiting of individual cells, the expected result would be a rapid discharge, accompanied by significant heat release. Short circuiting of ZEBRA® cells usually does not lead to cell failure.

Safety tests have shown that an internal electric short of the entire battery (a worst case scenario) could boost the internal temperature of the battery to 800°–1000°C. However, even under these circumstances, the shell and insulation protects the battery exterior from high temperature. In such a case, the battery would be expected to remain closed and intact, but to emit aluminum hydroxide and trace amounts of hydrogen chloride in vapor form.

6.5 Li-ion batteries

Lithium-ion batteries that are made with phosphate as the cathode are thought to be safer than other lithium-ion batteries, since phosphates are not prone to thermal runway and will not burn even after the battery suffers abuse. Batteries made from $LiFePO_4$ (LFP) technology have good shelf life, long cycle life and are maintenance free. LFP batteries are environment friendly as compared to $LiCoO_2$, $LiMn_2O_4$ and NCA. Also, LFP batteries can work within a temperature range of -20C to 70C.

Li-ion safety is ensured by a combination of prevention, mitigation and protection systems:

- An application hazard analysis is necessary to adapt the design of a Li-ion battery system for each specific application.
- Protections are required at all levels: cell, module, and battery. Lithium-ion batteries are equipped with electronic protections, mechanical design, and electric design incorporating the necessary redundancies in the risk control chain to ensure the reliability of the safety functions.

All lithium-ion batteries are equipped with individual electronic protections to avoid electrical misuse (minimum and maximum voltage protection, current protection, and so on). Their mechanical design makes them resistant to shocks and vibrations and can be used safely in a large range of temperatures (typically between -20°C and +60°C).

Lithium-ion batteries and systems are designed to mitigate potential hazards. For example, the battery design safely manages fume exhausts with specific vents, and large systems have thermal protections that limit fire propagation.

The global approach to hazard management has made the lithium-ion battery one of the safest energy storage systems. Billions of electrical and electronic items are powered by lithium-ion batteries and are used worldwide on a daily basis.

Understanding the root causes of potential Li-ion hazards will allow the users to define a specific and reliable method of risk management. The materials used in lithium-ion batteries are completely stable up to 80°C. At high temperatures, the protective passivation layer called Solid-Electrolyte-Interface (SEI or protective layer) starts a progressive dissolution in the electrolyte, becoming significant at 120-130°C. The electrolyte further reacts with the least protected surface of graphite, generating some heat. This phenomenon varies based on the choice of electrode components. Lithium Metal Oxides can decompose at high temperatures and generate heat, while LFP will not. The following chart details the thermal stability of components used in a lithium-ion battery. A positive number shows the released energy for exothermic reactions and SEI breakdown.

Table 23 Thermal Stability of Internal Components

Temperature, °C	Reaction Identified	Energy (J/gram)	Comment
120-130	Passivation layer	200-350	Layer breaks Solubilisation starts below 100°C
130-140	PE Separator Melts	-90	Endothermic
160-170	PP Separator Melts	-190	Endothermic
200	Solvent-$LiPF_6$	300	Slow kinetic
200-230	Positive Material Decomposition	1000	Oxygen emission reacts with solvents
240-250	LiC_6 + Binder	300-500	-
240-250	LiC_6 + Electrolyte	1000-1500	-

The consequences of the heat evolution depend on the environment of the cells. When the cells are in an environment where heat can be transferred, the exothermic reactions will stabilize and failed cells are able to progressively cool down. If the heat cannot be transferred away from the cells, or even worse, if the battery is located in a heated environment, the battery temperature will increase and attain a status where new reactions can initiate, contributing more heat. Thermal runaway reactions that involve the separator, electrolyte, and positive anode might be ignited with the increase in temperature: consequently, the rate of heating accelerates from less than a 1°C/minute to >100°C/minute as shown in Figures 61 and 62.

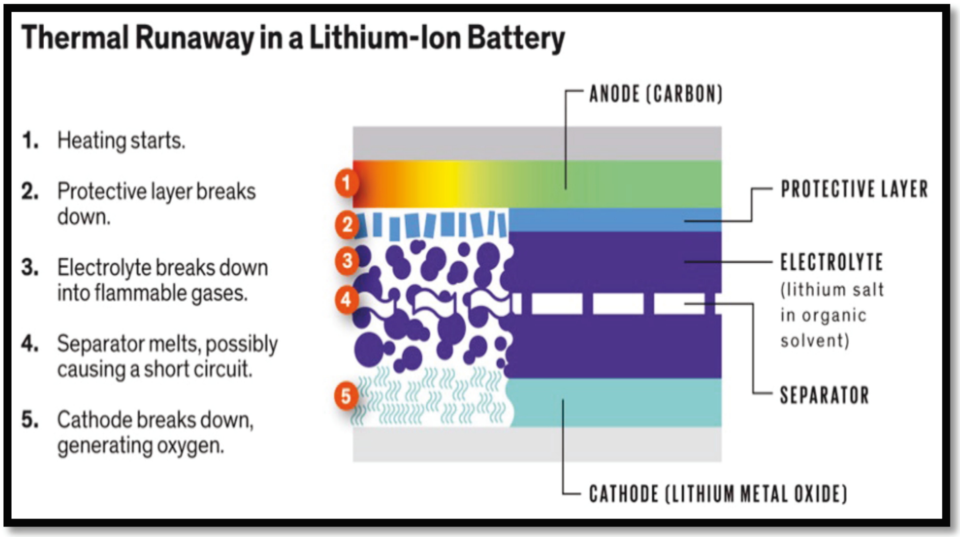


Figure 61 Thermal Runaway in a Li-ion Battery

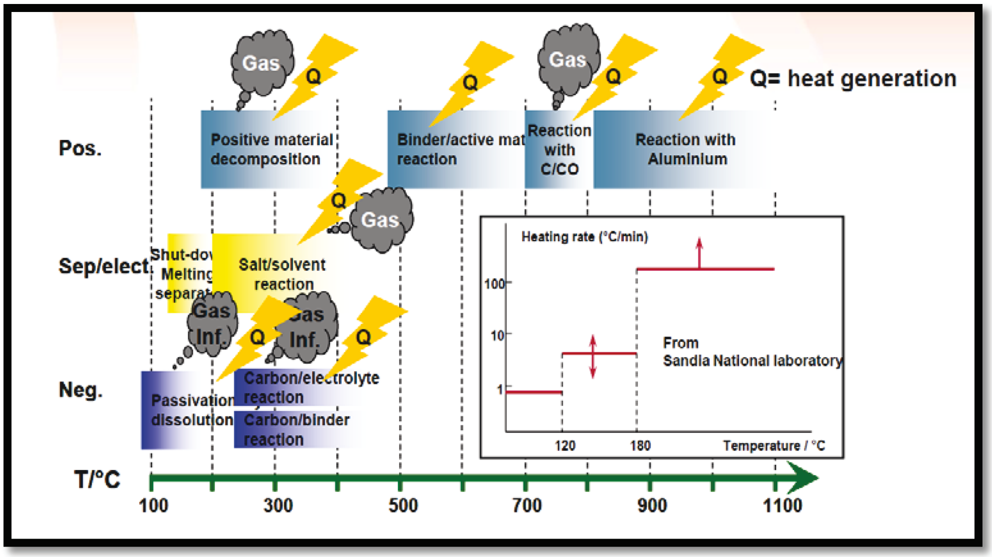
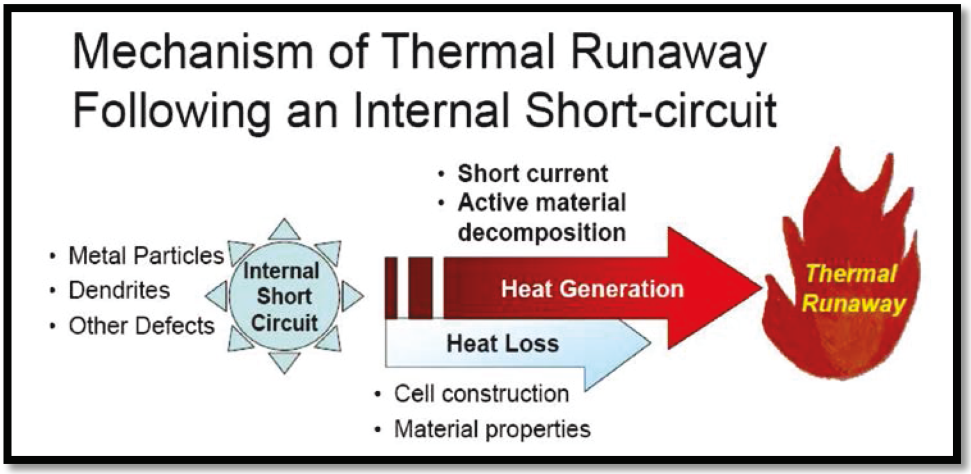


Figure 62 Thermal Runaway Contributors

Preliminary findings of the Boeing Dreamliner battery failure investigation by NTSB stated that the Li-ion battery experienced a thermal runaway when the failure of one battery cell cascaded to other neighboring cells within the battery assembly. The initial thermal runaway was determined to be an internal short circuit of a cell and the mechanism is explained in the following chart:



Mechanism of Thermal Runaway Following an Internal Short-circuit

- Metal Particles
- Dendrites
- Other Defects

- Short current
- Active material decomposition

- Cell construction
- Material properties

Figure 63 Thermal Runaway Mechanism

Based on NTSB findings, the high heat of the failing cell may propagate to the next cells and cause them to become thermally unstable. A chain reaction can occur in which each cell disintegrates on its own timetable. As each cell is being consumed one by one, a pack can be destroyed in a few seconds or over several hours. To increase safety, packs should include dividers to protect the failing cell from spreading to the neighboring one. In the Tesla Roadster car, for example, each cell is encased in its own metal compartment. In a typical lithium-ion battery pack, the following points outline the thermal propagation analysis conducted for a specific application (Reference NASA-JSC):

1. Convection negligible in space
2. Conduction dominates at T<500°C
3. Radiation exponentially increases with temperature

4. Radiant barrier prevents propagation
5. Increasing spacing between cells significantly decreases heat transfer
6. Fire due to electrolyte venting in the presence of high temperatures can cause significant propagation

6.6 Battery Safety Summary

Specific environmental conditions are often used to test and characterize the stability of an energy storage system, defining the frontier between the acceptable conditions of use and the abusive conditions. In case of accidental abusive conditions or defaults producing some potential hazard, mitigations measures can be taken to avoid the consequences of such a failure. Based on this information, energy storage systems can be designed with appropriate means for risk prevention and mitigation of the consequences, while controlling to eliminate hazardous events during normal usage.

For applications with high power or high energy needs, such as an HDEB locomotive, thermal runaway risks are a risk for any battery technology. The management of risk is critical to guarantee safe use of batteries in such a demanding application.

As a result, safety must be a fundamental function of an HDEB locomotive battery system. The occurrence of an energetic failure and its consequences must be minimized by employing prevention, protection and mitigation systems:

- Prevention and protection systems are incorporated into the system's electronics, mechanical design, and electric design. They include the necessary redundancies that ensure the reliability of the safety system, including current and voltage control, state of charge monitoring, and temperature management.
- Mitigation systems reduce the consequences of defaults or abuse, e.g. internal shorts, temperature elevation, excess current, and mechanical damage, through the usage of safety vents, heat protection or evacuation systems, and container ruggedization.

In addition, the following elements should be factored into the optimization of an HDEB locomotive battery system, including the particular cell format (cylindrical, prismatic, pouch, etc.), cell configuration within a module and within the battery, cooling and/or heating, protection under abusive conditions, thermal runaway propagation prevention, and critical electronics such as the battery management systems (BMS).

7. Conclusion

Based on the load profiles provided for this study, HDEB locomotives require high voltage systems with sufficient recharge capabilities to accept and absorb the regenerative braking energy produced by the locomotive. In addition, a high power system is needed to support the traction loads. The complexity and size of the systems, in terms of the number of batteries, also require that a battery management system be used for battery balancing and state of health (SOH) to ensure individual batteries or cells do not go into thermal runaway.

As seen in the "Green Goat" project, VRLA technology is not suitable for HDEB locomotive applications. Although lead-carbon technology has been shown to provide benefits in the shallow cycling environment of the "Green Goat," Sandia National Lab testing indicates that carbon enhanced VRLA batteries degrade during higher operating temperature (~10 to 15° C above ambient), exhibiting reduced pulse power capability, and a reduced number of partial state of charge cycles versus traditional VRLA batteries in terms of the cell aging process.

Nickel supercapacitors provide extremely high power, but limited energy. The ability to accept high regenerative braking loads, as well as offer significant power to supplement the locomotive traction loads are significant benefits of nickel supercapacitors. This technology, however, is better suited for short duration power applications such as engine starting, rather than a HDEB locomotive.

Molten sodium metal-halide batteries are not well suited for HDEB locomotive applications, given the high operating temperature of the system, the need to charge the system when not in use, and the 24-hour restart period, followed by the initial charge period to reactivate a dormant battery system. Also, when molten sodium metal-halide battery systems are used for high-power applications, the operating temperature of the system is increased and system life is reduced.

NiMH batteries have been the predominant choice for EV and HEV applications, since NiMH batteries provide reliable operation and high energy density at a relatively low cost compared to lithium-ion (Li-ion) technology. With cost reductions of Li-ion battery systems and the increased energy and power needs of EV and HEV applications, the automotive sector is moving away from NiMH systems in favor of Li-ion. In addition, recycling NiMH batteries is difficult and not cost-effective, with suitable industrial recycling processes still under development. Further, NiMH batteries rely on rare earth elements, which are increasingly difficult to source. As a result of these factors, NiMH technology is not suitable for longer-term HDEB locomotive applications.

This study confirmed the potential benefits of a HDEB locomotive and suggests that LFP and LTO technologies would be best able to meet the needs of a HDEB locomotive. These Li-ion technologies can accept high levels of regenerative braking energy; have a high cycle life, long calendar life, and a lower life-cycle cost; and, provide a balanced solution for both the charge and discharge needs of the locomotive. Further, LFP and LTO technologies demonstrate stable impedance over time, making these batteries well suited for power applications such as a HDEB locomotive, in which the end of life is driven by voltage regulation. In terms of safety, LFP and LTO technologies are considered to be the safest within the family of Li-ion chemistries, with lower energy density than NCA technology, balancing the need for safe operation of a high power system in a railroad environment.

JR East engineers and Hitachi engineers used Li-ion batteries to capture regenerative braking energy for their hybrid locomotives. Shimada et al. (2010)[62] noted that Hitachi is developing an energy-saving system for rolling stock using Li-ion batteries to reduce the environmental impact of railway systems.

A key finding of the study, found by modeling a battery system, indicated that the battery was able to provide a significant supplement to the traction loads for both Routes A and B (18.8-23.1%), while also allowing the train to run in all-electric mode during the transiting of congested rail yards. The model also revealed that 58.7 to 63.3% of the generative loads were absorbed instead of being wasted via resistive loads. As noted previously, the option for all-electric operation in congested areas could significantly reduce localized pollution levels from mobile sources and provide significant fuel savings.

In reviewing the cost of a battery system, this study concluded that life cycle cost is a key consideration for any technology to be utilized in an HDEB locomotive, since the system must be operational for 7 to 10 years. When considering maintenance and replacement costs, Li-ion and NiMH technologies become far more cost effective over this longer timeperiod because these technologies meet the 7- to 10-year performance metric. Further, the displacement of NiMH technology in the EV and HEV marketplace is reducing the cost of Li-ion battery systems due to increased production volume.

We recommend that a demonstration project be developed. It should include further optimization of the battery system for a HDEB locomotive to determine the optimum system design and demonstrate the specific benefits of a HDEB locomotive for use in Class I railroad service.

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Appendix A. Battery Comparison Table

Battery Chemistry	Benefits	Limitations / Risks
VRLA Pb-Acid	• Exhibit low self-discharge. • Fully recyclable with many recyclers. • Low cost compared to other technologies due to large production volumes and low cost raw materials. • Safety valve/flame arrested. • Mature technology, high volume production capacity at low cost fully established. • High volume recycling and collection systems in place in North America and Europe. • Simple installation. • Higher weight per Kw to help in traction. • Recombination reaction to minimize the escape of H2 and O2 and water consumption. • Low maintenance. • Simple charge algorithm – constant voltage float charging.	• Does not tolerate being left completely discharged during storage; must be charged to prevent permanent damage. • Environmentally unfriendly. • Limited performance at higher rates and lower temperature extremes due diffusion rate of the acid ions. • Low cycle life relative to other battery types. • Battery life severely curtailed with deep discharges. Typical starter battery, minimal depth of discharge used or battery capacity degrades quickly. • Water is consumed during corrosion of the positive electrode grids (current collecting supports). • Slower to recharge than other battery types leads to poor handling of Brake Energy Regeneration (BER) and Integrated Stop-Start (ISS). • Transportation restrictions on flooded lead acid. • Failure mechanism (sudden death) - Grid/plate corrosion sulfation—results in limiting the capacity, rate, and cycle life; ultimately loss of physical and electrical contact. • Grid/plate corrosion is increased with prolong high temperature exposure. Calendar life highly influenced by temperature. • Poor low temperature performance to most other battery technologies. • EU REACH regulations jeopardize long-term usage of lead in industrial application. • Battery management would be required to ensure the cells/modules are not allowed to be reversed.

Battery Chemistry	Benefits	Limitations / Risks
VRLA Pb-Acid with Absorbed Glass Mat (AGM)	• Exhibit low self-discharge. • Fully recyclable with many recyclers. • Low cost compared to other technologies due to large production volumes and low cost raw materials. • Safety valve/flame arrested. • Mature technology. • Recombination reaction to minimize the escape of H2 and O2 and water consumption. • Low maintenance. • Simple charge algorithm – constant voltage float charging. • Highly compressible mats that provides padded protection around plates to absorb shock and vibration. • Wider operational temperature range than other SLA batteries. • Improved high power applications. • Better cyclic life and charge acceptance compared to other SLA technologies. • No transportation restrictions.	• Does not tolerate being left completely discharged during storage; must be boost charged to prevent permanent damage. • Environmentally unfriendly. • Prolong high temperature exposure increases Grid/plate corrosion. • Limited performance at higher rates and lower temperature extremes due diffusion rate of the acid ions. • Thermal runaway can occur with improper charging. • Relatively low cycle life to other battery technologies. • Water is consumed during corrosion of the positive electrode grids (current collecting supports). • Slower to recharge than other battery types leads to poor handling of Brake Energy Regeneration (BER) and Integrated Stop-Start (ISS). • Failure mechanism (sudden death) - Grid/plate corrosion sulfation—results in limiting the capacity, rate, and cycle life; ultimately loss of physical and electrical contact. • Grid/plate corrosion is increased with prolong high temperature exposure. • EU REACH regulations jeopardize long-term usage of lead in industrial application. • Battery management would be required to ensure the cells/modules are not allowed to be reversed.

Battery Chemistry	Benefits	Limitations / Risks
Pb Carbon (Carbon as additives)	• Advantages of increased surface area of the negative active material (NAM): ○ Low current density; ○ Low polarization; ○ Improves charge acceptance and efficiency. • Highly compressible mats that provides padded protection around plates to absorb shock and vibration. • Sulfation process is significantly reduced (carbon appears to enhance nucleation and retard recrystallization of lead sulfate). • Improve battery cycle life dramatically to other Pb-acid technologies. • Require minimal modification of existing industrial-scale manufacturing processes. • Offer a potential low-cost, high-performance energy storage solution. • Mature technology. • Fully recyclable access to many recyclers. • Simple installation. • Best cycle life of traditional Pb-acid.	• Researchers do not yet fully understand the characteristics of carbon that are beneficial or detrimental to lead-acid batteries. • Battery management system may be required. • Low energy density performance to most other battery technologies. • Failure mechanism (sudden death) - Grid/plate corrosion; ultimately loss of physical and electrical contact. • Not suited to absorb large amounts of regenerative energy. • Higher cost as compared to other lead-acid technologies due to manufacturing process. • Failure mechanism (sudden death) - Grid/plate corrosion sulfation (less than other lead-acid technologies)—results in limiting the capacity, rate, and cycle life; ultimately loss of physical and electrical contact.

Battery Chemistry	**Benefits**	**Limitations / Risks**
Pb-Carbon Battery / Capacitor Hybrid	• High cycle life. • Unlike other Pb-acid technology, can be cycled at partial SOC's. • Lighter weight than other Pb-acid technologies yet the available energy is much less. • Improved high power capability compared to other Pb-acid technologies. • Fully recyclable. • Low maintenance compared to other Pb-acid other Pb-acid technologies. • Good power over wide temperature range (-20°C to +50°C). • Virtual elimination of sulfation. • Fast recharge capability. • Handle the regenerative energy. • Minimal negative electrode corrosion (sulfation process). • Charge profile characteristics: ○ Forces balancing multiple battery strings and internal cells ○ Simplifies SOC electronics	• Low specific energy as compared to other battery technologies with the exception of Ni-Cap. • Require BMS at system level. • Failure mechanism (sudden death) - Positive Grid/plate corrosion - results in limiting the capacity, rate, and cycle life; ultimately loss of physical and electrical contact.
NiCd	• Good cycle life. • Long storage life – recoverable capacity loss. • Rapid charge capability. • Mature technology. • Good low temperature discharge performance. • Simple installation.	• Low volumetric and gravimetric energy density compared to Li-ion. • Environmentally unfriendly. • Failure mechanism—Dendrite Growth. • Raw material cost more expensive than most other battery technologies. • EU REACH regulations jeopardize long-term usage of NiCd

Battery Chemistry	Benefits	Limitations / Risks
	• Low maintenance. • High cycle life. • Fully recyclable. • Simple charge algorithm – constant voltage float charging.	in industrial application. • Battery management would be required to ensure the cells/modules are not allowed to be reversed.

Battery Chemistry	Benefits	Limitations / Risks
NiMH	• Higher capacity than NiCd batteries. • Sealed construction and no maintenance required. • Cadmium free (Environmentally friendly). • Rapid discharge capability. • Long cycle life. • Matured technology. • Moderate cost. • No regulatory control for transportation. • Long storage life—recoverable capacity loss. • Mature technology. • Maintenance free. • Fully recyclable.	• Lower power capability than NiCd batteries. • High self-discharge. • Performance degrades if stored/operated at high temperatures. • More expensive than NiCd. • Raw material cost more expensive than most other battery technologies. • Deep discharge at high current reduces the service life. • Battery and thermal management system required. • Significantly reduced life due to high temperature exposure. • Complex charge algorithm needed; tight charge voltage and current control. • Materials controlled/restricted by countries with rare earth metals could limit support/availability.
Bipolar Nickel Metal Hydride	• Efficient packing. • Reduction of collector losses. • Higher power and capacity than NiCd and other NiMH batteries. • Sealed construction and no maintenance required. • Cadmium free (environmentally friendly). • Rapid charge/discharge capability. • Long cycle life. • Matured technology. • Moderate cost. • No regulatory control for transportation. • Long storage life—recoverable capacity loss. • Mature technology.	• Electrolyte leakage. • Dealing with gas pressure. • Lower power capability than NiCd batteries. • High self-discharge. • Performance degrades if stored/operated at high temperatures. • More expensive than NiCd and other NiMH batteries. • Raw material cost more expensive than most other battery technologies. • Deep discharge at high current reduces the service life. • Battery and thermal management system required. • Significantly reduced life due to high temperature exposure. • Complex charge algorithm needed; tight charge voltage and

Battery Chemistry	Benefits	Limitations / Risks
	• Maintenance free • Fully recyclable.	current control. • Materials controlled/restricted by countries with rare earth metals could limit support/availability.
Na/NiCl2 Molten Salt	• High energy density (five times higher than Lead acid). • Tolerant of internal short circuits. • Typical cell failure is short circuit which does not cause complete failure of the battery. • Low cost materials. • Excellent columbic efficiency. • Maintenance free. • Battery: Broad operating temperature range. • Withstand abuse testing such as over heat, overcharge, external short circuit, drop test and crash test.	• High internal resistance. • Molten sodium electrode. • Labor intensive assembly. • Battery requires thermal management (heating and cooling) to ensure the battery remains within the operating limits. • 10% to 15% of the energy is used to heat the battery. • Slow charge time especially after the battery is let to cool down. • Battery needs to be hotter (>330oC) to run high power (2C rate). • Complicated (quoted by customers) mode of operation. • Some possible sensitivity to shock and vibe (needs to be confirmed) that may lead to cracks in the ceramic separator. • A typical failure mode is a slow short through a crack in the ceramic separator. • Need for electronic control – in case of bigger defect or mechanical failure (bigger crack, case rapture, etc.) the electronics disconnects the battery and in some cases can deplete the energy.

Battery Chemistry	Benefits	Limitations / Risks
Ni-Supercapacitor	• High specific power and efficiency. • Efficient and fast charge acceptance. • Low resistance. • Quick response. • No balancing electronics. • Excellent calendar life and cycle life. • High specific power even at low temperature: ○ Good low temperature performance -40C. • No maintenance. • Produce no hazard substances.	• Low specific energy (Wh/Kg). • Very low energy storage density leading to very high capital costs for large scale applications. • High self-discharge. • Quick voltage variation. • High cost/unit energy. • Typical run time: 1 second to 1 minute. • Heavier and bulkier than conventional batteries. • Low voltage cells leading to larger system for higher voltages. • Vertical orientation only. • Failure mechanism—gradual capacitance loss and resistance growth.
Li-ion (NCA)	• Sloping discharge curve—open circuit voltage: ○ Simplifies SOC electronics by aiding cell balancing. • High pulse rate charge acceptance. • Higher specific power/energy density compared to all other commercial available battery technologies; results in lower volume and weight. • Excellent discharge cyclic life compared to all other commercial available battery technologies. • Excellent charge/discharge efficiency. • Excellent RT calendar life/low self-discharge • No service maintenance due to state of health electronics. • No toxic metals.	• High temperature/flammable gases possible during cell failures. Flammable organic solvent. • Hybrid Loco Energy System Management design must account for the following: ○ Li-ion batteries should never be depleted to below their minimum voltage. ○ Thermal management may need to be employed for charging at temperatures below 0°C and usage above 50°C. • Higher systems cost compared to all other commercial available battery technologies with the exception of large format LTO cells. • BMS requirement.

Battery Chemistry	Benefits	Limitations / Risks
		• Storage: ○ Li-ion packs should be stored at intermediate SOC to optimize life. ○ State of Health electronics tend to drain Li-ion packs; therefore, recharge is required for extended periods of storage. ○ Does not tolerate being left completely discharged during storage. • Restrictions placed on air and ground transportation. • Failure mechanism—gradual and slow impedance growth during cycle and calendar life.
Li-ion (NMC)	• Lower temperatures as compared NCA technology during cell failures. • Higher specific power/energy density compared to all other commercial available battery technologies; results in lower volume and weight. • Excellent discharge cyclic life compared to all other commercial available battery technologies except for other Li-ion technologies. • Sloping discharge curve—open circuit voltage: ○ Simplifies SOC electronics by aiding cell balancing Sloping discharge curve. • High current charge/discharge capability. • Higher specific power/energy density compared to all other commercial available battery technologies except for NCA. • Lower cost compared to NCA Li-ion. • Excellent RT calendar life/low self-discharge	• High temperature/flammable gases possible during cell failures; lower temperatures than NCA. • Hybrid Loco Energy System Management design must account for the following: ○ Li-ion batteries should never be depleted to below their minimum voltage. ○ Thermal management may need to be employed for charging at temperatures below 0°C and usage above 50°C. • Higher systems cost compared to all other commercial available battery technologies. • BMS Requirement. • Storage: ○ Li-ion packs should be stored at intermediate SOC to optimize life. ○ State of Health electronics tend to drain Li-ion packs; therefore, recharge is required for extended periods of storage.

Battery Chemistry	**Benefits**	**Limitations / Risks**
	• No service maintenance due to state of health electronics. • No toxic metals.	○ Does not tolerate being left completely discharged during storage. • Restrictions placed on air and ground transportation. • Immature technology. • Failure mechanism – gradual impedance growth and capacity loss.
Li-ion (LFP)	• Lower temperatures as compared NCA and NMC technology during cell failures: ○ Doesn't evolve O2 to aid fueling flames during cell failures. • Excellent abusive over-discharge tolerance as compared to NCA and NMC. • Higher specific power/energy density compared to all other commercial available battery technologies; results in lower volume and weight. • Excellent charge/discharge efficiency. • Higher current recharge rate up to 4C. • Excellent regenerative load acceptance. • Highest specific power compared to all other commercial available battery technologies except for NCA and NMC. • Lower cost compared to NCA and NMC Li-ion in the long term. • Excellent discharge cyclic life compared to all other commercial available battery technologies. • Excellent RT calendar life when to all other commercial available battery technologies except for li-ion. • No service maintenance due to state of health electronics.	• High temperature/flammable gases possible during cell failures though lower than NCA and NMC. • Hybrid Loco Energy System Management design must account for the following: ○ Li-ion packs should be stored at intermediate SOC to optimize life. ○ Thermal management may need to be employed for charging at temperatures below 0°C and usage above 50°C. • Many suppliers of LFPs have low discharge rate capability (less maturity processing). • Lower specific energy (Wh/Kg) when compared to NCA and NMC Li-ion technologies. • Lower high temperature cycling compared to other Li-ion technologies. • Flat Discharge Plateau: ○ More complex electronics - requires columbic counting in BMS. • BMS requirement. • Poor low temperature performance as compared to all other commercially available Li-ion technologies. • Storage: ○ Li-ion packs should be stored ~ 40% charge.

Battery Chemistry	**Benefits**	**Limitations / Risks**
	• No toxic metals.	○ State of Health electronics tend to drain Li-ion packs; therefore, recharge is required for extended periods of storage. ○ Limited tolerance for being left completely discharged during storage. • Restrictions placed on air transportation. • Immature technology and expensive LFP synthesis process increases the final material cost. • Failure mechanism—gradual capacity loss.
Li-ion (LTO)	• Superior cyclic life compared to all other commercial available battery technologies. • Lowest temperatures as compared to all other Li-ion chemistries during cell failures. ○ Spinel Structure anode (Stable). • Only Li-ion chemistry that can be shorted to 0 volts without damage. • Highest charge rate and efficiency of all battery technologies. • Excellent abusive over-discharge tolerance as compared to all Li-ion chemistries. • Higher specific power/energy density compared to all other commercial available battery technologies; results in lower volume and weight. • Active material not required form Solid Electrolyte Interface (SEI) formation at the anode. • Safety (Cell venting/rapid disassembly): ○ Internal short circuit reaction on the LTO anode is three order of magnitude lower than graphite anode.	• Higher cell cost based on materials as compared with other Li Ion technologies. • Hybrid Loco Energy System Management design must account for the following: ○ Thermal management may need to be employed for usage above 50°C. • Lower specific energy as compared to NCA and NMC. • Storage: ○ Li-ion packs should be stored at intermediate SOC to optimize life. ○ State of Health electronics tend to drain Li-ion packs; therefore, recharge is required for extended periods of storage. • BMS requirement. • Immature technology. • Failure Mechanism—Impedance growth over time.

Battery Chemistry	Benefits	Limitations / Risks
	- Long storage life—recoverable capacity loss. - Good low temperature performance. - No service maintenance due to state of health electronics. - No toxic metals. - Recoverable from short duration to low discharge voltages above 0 volts. - Sloping discharge curve—open circuit voltage. - Simplifies SOC electronics by aids cell balancing Sloping discharge curve.	

Abbreviations and Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
AGM	Absorbed Glass Mat
Ah	Ampere Hour
BER	Brake Energy Regeneration
BMS	Battery Management System
BOL	Beginning of Life
CAN	Controller Area Network
CAS	Chemical Abstracts Service
CD	Charge Depleting
CS	Charge Sustaining
DOD	Depth of Discharge
DOT	Department of Transportation
DE	Diesel-Electric
EINECS	European Inventory of Existing Chemical Substances
EPA	Environmental Protection Agency
EODV	End of Discharge Voltage
EOL	End of Life
EU	European Union
EUCAR	European Council for Automotive R&D
EV	Electric Vehicle
FRA	Federal Railroad Administration
GE	General Electric
HDEB	Hybrid Diesel-Electric Battery
HEV	Hybrid Electric Vehicle
HPPC	Hybrid Pulse Power Characterization
IARC	International Agency for Research on Cancer
ICE	Internal Combustion Engine
ISS	Integrated Stop-Start
JR East	East Japan Railway
KOH	Potassium Hydroxide
LFP	Lithium Ferrophosphate
LTO	Lithium Titanate

MPV	Mid-Point Voltage
MSDS	Material Safety Data Sheets
MT	Metric Tons
NASA-JSC	National Aeronautics and Space Administration- Johnson Space Center
NCA	Nickel Cobalt Aluminum
NMC	Nickel Manganese Aluminum
NREL	National Renewable Energy Laboratory
NS	Norfolk Southern
NTP	National Toxicology Program
NTSB	National Transportation Safety Board
OKO	Öko-Institut
OSHA	Occupational Safety and Health Administration
PBC	Lead Carbon
PEL	Permissible Exposure Limits
PNGV	Partnership for Next Generation Vehicle
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RHOLAB	Reliable Highly Optimized Lead-Acid Battery
RMS	Root Mean Square
SLA	Sealed Lead Acid
SEI	Solid Electrolyte Interface
SOC	State of Charge
SOH	State of Health
TLV	Threshold Limit Value
tpa	Metric tons per annum
URL	Uniform Resource Locator
UTU	United Transportation Union
VRLA	Valve Regulated Lead Acid
WEELs	Workplace Environmental Exposure Levels