

2019

# Battery University Booklet

ARISTURTLE (HIGH VOLTAGE)

IORDANIS PANAGIOTIDIS

# CONTENTS

1. Basics about Batteries.....	5
1.1. Getting to know the Battery.....	5
1.2. Comparing the Battery with other power sources.....	7
1.3. The Octagon Battery – Battery Requirements.....	9
1.4. Battery definitions and what they mean.....	11
2. Battery types.....	14
2.1. Primary Batteries.....	14
2.1.1. Choices of Primary Batteries.....	15
2.2. Secondary Batteries.....	17
2.2.1. Lead Acid Batteries.....	17
2.2.2. Nickel-based Batteries.....	20
2.2.3. Lithium-ion Batteries.....	21
2.2.3.1. Types of Lithium-ion.....	24
2.2.3.2. Lithium-polymer (LiPo).....	31
2.2.3.3. Cycling Performance of Li-ion.....	32
2.2.4. Supercapacitor.....	33
2.2.5. Other Battery Systems.....	34
2.2.6. Summary Tables.....	35
3. Packaging and Safety.....	38
3.1. Old and new Battery Packaging.....	39
3.1.1. Types of Battery Cells.....	39
3.2. Series and Parallel Battery Configurations.....	43
3.3. Confusion with Voltages.....	47
3.4. Protection Circuits.....	48
3.5. Safety concerns with Li-ion.....	50
3.5.1. What to do when a Battery overheats or catches fire.....	51
3.6. Building a Li-ion Pack.....	52
3.7. Separator.....	53
3.8. Electrolyte.....	54

4. Charge Methods.....	56
4.1. C-Rate.....	56
4.2. Battery Chargers.....	57
4.2.1. Fast and Ultra-fast Chargers.....	59
4.3. Charging Lithium-ion.....	62
4.3.1. Why do old Li-ion Batteries take long to charge?.....	66
4.4. Charging at High and Low Temperatures.....	68
4.5. Summary Table.....	70
5. Discharge Methods.....	71
5.1. Basics about Discharging.....	71
5.2. Discharge Characteristics of Lithium-ion.....	72
5.3. Discharging at High and Low Temperatures.....	76
5.4. How to calculate Battery Runtime.....	77
6. From Birth to Retirement.....	81
6.1. How to Prime Li-ion Batteries.....	81
6.2. How to Store Li-ion Batteries.....	82
6.3. How to Transport Li-ion Batteries.....	83
6.4. How to Recycle Li-ion Batteries.....	84
7. How to Prolong Battery Life.....	85
7.1. General.....	85
7.1.1. How to define Battery Life.....	85
7.1.1.a. How does Rising Internal Resistance affect Battery Performance?.....	86
7.1.1.b. What does Elevated Self Discharge do?.....	88
7.1.1.c. How low can a Battery be Discharged?.....	89
7.1.2. Cell Matching and Balancing.....	90
7.1.3. What causes Cells to Sort?.....	92
7.1.4. Loss of Electrolyte.....	92
7.2. Lithium-ion.....	93
7.2.1. What causes Lithium-ion to Age?.....	93
7.2.2. How to awaken a Sleeping Li-ion.....	99

7.2.3. What causes Li-ion to Die?.....	100
7.2.4. Coulombic and Energy Efficiency.....	105
8. Battery Testing and Monitoring.....	106
8.1. Fundamentals in Battery Testing.....	106
8.2. How to measure Internal Resistance.....	108
8.3. How to measure State-of-Charge.....	111
8.4. How to measure Capacity.....	113
8.5. Testing Lithium-ion Batteries.....	114
8.6. Battery Management System (BMS).....	116
8.7. Battery Test Methods (Summary).....	118

## 1. Basics about Batteries

Although the battery is increasingly promoted as a green energy solution to liberate society from the dependency of fossil fuel, it has not yet matured to assume this vital task. Pushing the boundaries of the battery reminds us of the many limitations by being an electrochemical power source that is slow to fill, holds limited energy, runs for a time like a wind-up toy, and has a short life span of only a few hundred cycles before it becomes a nuisance.

In an age where surprise developments flash before our eyes almost daily, the battery seems slow in maturing. During the last two decades, Li-ion only gained 8 percent capacity per year. This has slowed to 5 percent, but the good news is a cost reduction of 8 percent per year.

Consumers are generally satisfied with battery performance in portable devices, but the electric vehicle (EV) has a higher demand; cost and endurance will determine the long-term success. It's as if the EV sets the threshold for how far the battery can go. Competing against fossil fuel with a net calorific value that is 100 times higher than the battery is a challenge. Conversely, petroleum cannot match the battery, which is clean, quiet, small, and has an immediate start-up with the flick of a switch.

### 1.1. Getting to know the Battery

Nature offers many ways to produce power. Most result through combustion, mechanical movement and photosynthesis, as in a solar cell. Electrical energy generation of the battery develops by an electrochemical reaction between two metals of different affinities. When exposed to acids, a voltage develops between the metals as part of ion transfer; closing the circuit induces a current. The voltage potential become stronger the farther apart the affinity numbers move.

The simplest manifestation of a battery is a lemon. Driving a zinc-plated nail and a copper coin into a lemon creates a voltage, but this quasi battery does not deliver much power. The current delivery system is weak and any electrical load causes the voltage to collapse. The energy does not come from the lemon itself but from the chemical change in dissolving zinc into the acid or lemon juice. Figure 1 illustrates the lemon battery.

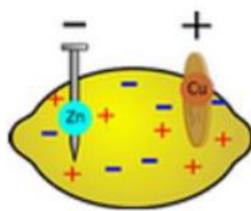


Figure 1: Lemon battery. The experiment is often used for educational purposes. The electrodes are zinc in the form of a galvanized nail and copper in a coin. The lemon juice acts as electrolyte to induce a chemical reaction.

Standard potential of zinc = -0.76

Standard potential of copper = 0.34

Cell potential with conducting path = 1.10V

A battery is rated in ampere-hours (Ah). This specifies how much charge a pack can hold. Like fluid in a container, the energy can be dispensed slowly over a long period of time or rapidly in a short time. The amount of liquid a container holds is analogous to the energy in a battery; how quickly the liquid is dispensed is analogous to power. Multiplying the voltage by the current provides power (W) and multiplying the voltage by capacity (Ah) provides energy (Wh).

An electrochemical battery consists of a cathode, an anode, electrolyte and a separator. When charging, a buildup of positive ions forms at anode/electrolyte interface. This leads electrons moving towards the anode, creating a voltage potential between the cathode and the anode. Release is by a passing current from the anode through an external load and back to the cathode. On charge, the current flows in the other direction. The battery anode is always negative and the cathode positive.

A battery has two separate pathways; one is the electric circuit through which electrons flow, feeding the load, and the other is the path where ions move between the electrodes though the separator that acts as an insulator for electrons. Ions are atoms that have lost or gained electrons and have become electrically charged. The separator electrically isolates the electrodes but allows the movement of ions.

The anode of Li-ion is carbon but the order is reversed with lithium-metal batteries. Here the cathode is carbon and the anode metallic lithium.

Ion flow is made possible with an activator called the electrolyte. In a flooded battery system, the electrolyte moves freely between the inserted electrodes; in a sealed cell, the electrolyte is normally added to the separator in a moistened form. The separator segregates the anode from the cathode, forming an isolator for electrons but allowing ions to pass through.

See: <https://www.youtube.com/watch?v=VxMM4g2Sk8U> (Lithium-ion battery, How does it work?)

## 1.2. Comparing the battery with other power sources

One hears of wonderful improvements in battery technologies, each offering distinct benefits, but none providing a fully satisfactory solution to all of today's energy needs. Though the battery has many advantages over other energy sources, it also has major limitations that need addressing.

### **Energy storage**

Batteries store energy reasonably well and for a long time. Primary batteries (non-rechargeable) hold more energy than secondary (rechargeable) and the self-discharge is lower. Lead-, nickel- and lithium-based batteries need periodic recharges to compensate for lost energy.

### **Specific energy (capacity)**

Compared to fossil fuel, the energy storage capability of the battery is less impressive. The energy by mass of gasoline is over 12,000Wh/kg. In contrast, a modern Li-ion battery only carries about 200Wh/kg; however the battery has the advantage of delivering energy more effectively than a thermal engine.

### **Responsiveness**

Batteries have a large advantage over other power sources by being ready to deliver on short notice – think of the quick action of the camera flash! There is no warm-up, as is the case with the internal combustion engine (ICE); battery power flows within a fraction of a second. In comparison, a jet engine takes several seconds to rev up, a fuel cell requires a few minutes to gain power, and the cold steam engine of a locomotive needs hours to build up steam.

### **Power bandwidth**

Most rechargeable batteries have a wide power bandwidth, meaning that they can effectively handle small and large loads, a quality that is shared with the diesel engine. In comparison, the bandwidth of the fuel cell is narrow and works best within a specific load. So does the jet engine, which operates most efficiently at a defined revolution-per-minute (RPM).

### **Environment**

The battery runs clean and stays reasonably cool. Most sealed cells have no vents, run quietly and do not vibrate. This is in sharp contrast with the ICE and large fuel cells that require compressors and cooling fans. The ICE also needs air intake and provision to exhaust toxic gases.

### **Efficiency**

The battery is highly efficient. Li-ion has 99 percent charge efficiency, and the discharge loss is small. In comparison, the energy efficiency of the fuel cell is 20 to 60 percent, and the ICE is 25 to 30 percent. At optimal air intake speed and temperature, the GE90-115 on the Boeing 777 jetliner achieves an efficiency of 37 percent. The charge efficiency of a battery is connected with the ability to accept charge. See BU-808b: What causes Li-ion to die? under Coulombic Efficiency.

## **Installation**

The sealed battery operates in any position and offers good shock and vibration tolerance. Most ICEs must be positioned in the upright position and mounted on shock-absorbing dampers to reduce vibration. Thermal engines also need an air intake manifold and an exhaust muffler.

## **Operating cost**

Lithium- and nickel-based batteries are best suited for portable devices; lead acid batteries are economical for wheeled mobility and stationary applications. Price and weight make batteries impractical for the electric powertrain in larger vehicles. The cost of drawing energy from a battery is about three times higher than getting it off the AC grid. The calculation includes the cost of the battery, charging it from the grid and budgeting for an eventual replacement.

## **Maintenance**

With the exception of watering of flooded lead batteries and exercising NiCds to prevent “memory,” rechargeable batteries are low maintenance. Service includes cleaning the corrosion buildup on the outside terminals and applying periodic performance checks.

## **Service life**

The rechargeable battery has a relatively short service life and ages even if not in use. The 3- to 5-year lifespan is satisfactory for consumer products, but this is not acceptable for larger batteries. Hybrid and electric vehicle batteries are guaranteed for 8–10 years; the fuel cell delivers 2,000–5,000 hours of service, and depending on temperature, large stationary batteries are good for 5–20 years.

## **Temperature extremes**

Like molasses, cold temperatures slow the electrochemical reaction and batteries do not perform well below freezing. The fuel cell shares the same problem, but the internal combustion engine does well once warmed up. Fast charging must always be done above freezing. Operating at a high temperature provides a performance boost, but this causes rapid aging due to added stress.

## **Charge time**

Here, the battery has an undisputed disadvantage. Lithium- and nickel-based systems take 1–3 hours to charge; lead acid typically takes 14 hours. In comparison, filling up a vehicle with fuel takes only a few minutes. Although some electric vehicles can be charged to 80 percent in less than one hour on a high-power outlet, Li-ion batteries get stressed on ultra-fast charges.

## **Disposal**

Nickel-cadmium and lead acid batteries contain hazardous material and cannot be disposed of in landfills. Nickel-metal-hydride and lithium systems are environmentally friendly and can in small quantities be included with regular household items, but authorities recommend that all batteries be recycled.

## 1.3. The Octagon Battery - Battery Requirements

A battery has some of the most stringent requirements and is on par with complex pharmaceutical products for which one change can have multiple side effects. To make a battery viable as an electric storage device, eight basic requirements must be met and a battery is fittingly called the octagon battery (Figure 1). The eight key elements to a working battery are as follows.



Figure 1: Octagon battery.

*So-called because of the eight critical requirements needed to achieve basic function. Many new arrivals claim to meet or exceed some prerequisites but fail in others, limiting market acceptance.*

*Courtesy of Cadex*

### 1. High specific energy

A key feature in consumer products is long runtime and device manufacturers achieve this by building batteries with high ampere-hour (Ah). The term lithium-ion is synonymous with a high specific energy. This does not mean that all Li-ion batteries have high Ah ratings. While the Energy Cell in an 18650 package can have 250Ah/kg, the same chemistry in a Power Cell is 150Ah/kg or less, and a long-life Li-ion for the powertrain is as low as 60Ah/kg. Furthermore, consumer NiMH has about 90Ah/kg compared to a 45Ah/kg for long-life units in the electric powertrain, 45Ah/kg being almost par with lead acid.

### 2. High specific power

Batteries made for power tools and electric powertrains provide high load capabilities but the specific energy is low.

### 3. Affordable price

Materials, refining processes, manufacturing, quality control and cell matching add cost for battery manufacturing; volume production only assists in part to reduce costs. Single cell use in mobile phones when no cell matching is required also lowers costs.

### 4. Long life

Nowhere is longevity more important than in large, expensive battery packs. If the battery life of the electric car could be extended from the anticipated 8–10 years to 20 years, driving an EV could be justified even if the initial investment is high. Longevity does not depend on battery design alone but also on how the battery is used. Adverse temperature, fast charge times and harsh discharge conditions stress the battery.

## **5. Safety**

Lithium-based batteries can be built with high specific energy, but these systems are often reactive and unstable. Nickel-based Li-ion is such an example, so is metallic lithium. Most manufacturers stopped production of these systems because of safety issues. When used correctly, brand-name Li-ion is very safe.

## **6. Wide operating range**

Batteries perform best at room temperature as cold temperatures slow the electrochemical reaction of all batteries. Li-ion cannot be charged below freezing, and heating blankets are often added to facilitate charging. High heat shortens battery life and compromises safety.

## **7. Toxicity**

Cadmium- and mercury-based batteries have been replaced with alternative metals for environmental reasons. Authorities in Europe are attempting to ban lead acid, but no economical replacement of similar performance is available. Nickel- and lithium-based batteries contain little toxic material, but they still pose a hazard if disposed carelessly.

## **8. Fast charging**

Lithium- and nickel-based batteries should be charged at 1C or slower (See What Is C-Rate) At 1C, a nickel-based battery fully charges in about 90 minutes and Li-ion in 2–3 hours. Lead acid cannot be fast charged and the charge time is 8–16 hours. Fast charge times are possible for nickel and lithium, but the batteries must be built for it, be in good condition and be charged at room temperature. Aged and mismatched cells do not lend themselves to fast charging. Any charge above 1C causes undue stress, especially on the Energy Cell, and this should be avoided. (See BU-401a: Fast and Ultra-fast Chargers.) NiCd is the only battery that accepts ultra-fast charge with minimal stress.

In addition to the eight basic requirements of the octagon battery, a battery must have low self-discharge to allow long storage and provide an instant start-up when needed. All batteries have self-discharge, and the loss increases with temperature and age. Secondary batteries have a higher self-discharge rate than the primary equivalent. A further requirement is a long shelf-life with little performance degradation.

## 1.4. Battery definitions and what they mean

Batteries are specified by three main characteristics: chemistry, voltage and specific energy (capacity). A starter battery also provides cold cranking amps (CCA), which relates to the ability to provide high current at cold temperatures.

### Chemistry

The most common battery chemistries are lead, nickel and lithium, and each system needs a designated charger. Charging a battery on a charger designed for a different chemistry may appear to work at first but might fail to terminate the charge correctly. Observe the chemistry when shipping and disposing of batteries as each chemistry has a different regulatory requirement.

### Voltage

Batteries are marked with nominal voltage; however, the open circuit voltage (OCV) on a fully charged battery is 5–7 percent higher. Chemistry and the number of cells connected in series provide the OCV. The closed circuit voltage (CCV) is the operating voltage. Always check for the correct nominal voltage before connecting a battery.

### Capacity

Capacity represents specific energy in ampere-hours (Ah). Ah is the discharge current a battery can deliver over time. You can install a battery with a higher Ah than specified and get a longer runtime; you can also use a slightly smaller pack and expect a shorter runtime. Chargers have some tolerance as to Ah rating (with same voltage and chemistry); a larger battery will simply take longer to charge than a smaller pack, but the Ah discrepancy should not exceed 25 percent. European starter batteries are marked in Ah; North America uses Reserve Capacity (RC). RC reflects the discharge time in minutes at a 25A discharge.

### Cold cranking amps (CCA)

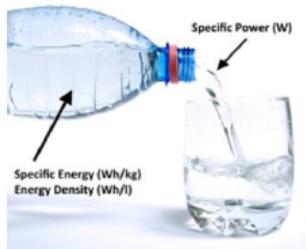
Starter batteries, also known as SLI (starter light ignition) are marked with CCA. The number indicates the current in ampere that the battery can deliver at  $-18^{\circ}\text{C}$  ( $0^{\circ}\text{F}$ ). American and European norms differ slightly.

### Specific energy, energy density

Specific energy, or gravimetric energy density, defines battery capacity in weight (Wh/kg); energy density, or volumetric energy density, reflects volume in liters (Wh/l). Products requiring long runtimes at moderate load are optimized for high specific energy; the ability to deliver high current loads can be ignored.

### Specific power

Specific power, or gravimetric power density, indicates loading capability. Batteries for power tools are made for high specific power and come with reduced specific energy (capacity). Figure 1 illustrates the relationship between specific energy (water in bottle) and specific power (spout opening).



Specific Power Energy Density

Figure 1: Relationship between specific energy and specific power.

The water in the bottle represents specific energy (capacity); the spout pouring the water govern specific power (loading).

AA battery can have high specific energy but poor specific power as is the case with the alkaline battery, or low specific energy but high specific power as with the supercapacitor.

### C-rates

The C-rate specifies the speed a battery is charged or discharged. At 1C, the battery charges and discharges at a current that is on par with the marked Ah rating. At 0.5C, the current is half and the time is doubled, and at 0.1C the current is one-tenth and the time is 10-fold.

### Load

A load defines the current that is drawn from the battery. Internal battery resistance and depleting state-of-charge (SoC) cause the voltage to drop under load, triggering end of discharge. Power relates to current delivery measured in watts (W); energy is the physical work over time measured in watt-hours (Wh).

### Watts and Volt-amps (VA)

Watt is real power that is being metered; VA is the apparent power that is affected by a reactive load. On a purely resistive load, watt and VA readings are alike; a reactive load such as an inductive motor or fluorescent light causes a phase shift between voltage and current that lowers the power factor (pf) from the ideal one (1) to 0.7 or lower. The sizing of electrical wiring and the circuit breakers must be based on VA power.

### State-of-health (SoH)

The three main state-of-health indicators of a battery are:

- Capacity, the ability to store energy
- Internal resistance, the capability to deliver current, and
- Self-discharge, reflecting mechanical integrity and stress-related conditions

Li-ion reveals SoH in capacity. Internals resistance and self-discharge stay low under normal circumstances. SoH is commonly hidden form the user in consumer products; only state-of-charge (SoC) is provided.

SoH is sometimes divided into:

- Absolute state-of-health (ASoH), the ability to store the specified energy when the battery is new
- Relative state-of-health (RSOH), available storage capability when battery is broken in

Note: Unless otherwise mentioned, RSOH refers to SoH.

### **State-of-charge (SoC)**

SoC reflects the battery charge level; a reading battery user is most familiar with. The SoC fuel gauge can create a false sense of security as a good and faded battery show 100 percent when fully charged.

SoC is sometimes divided into:

- Absolute state-of-charge (ASoC), the ability to take the specified charge when the battery is new
- Relative state-of-health (RSOC), available charge level taking capacity fade into account.

Note: Unless otherwise mentioned, RSOC refers to SoC.

### **State-of-function (SoF)**

SoF reflects battery readiness in terms of usable energy by observing state-of-charge in relation to the available capacity. This can be shown with the tri-state fuel gauge in which the usable capacity is reflected as stored energy in the form of charge (RSOH); the part that can be filled as empty and the unusable part that cannot be restored as dud. SoF can also be presented with the fishbowl icon for a battery evaluation at a glance. Tri-state fuel gauges are seldom used in fear of elevated warranty claims. Some devices offer an access code for service personnel to read SoF.

Figure 2 summarizes battery state-of-health and state-of-charger graphically.

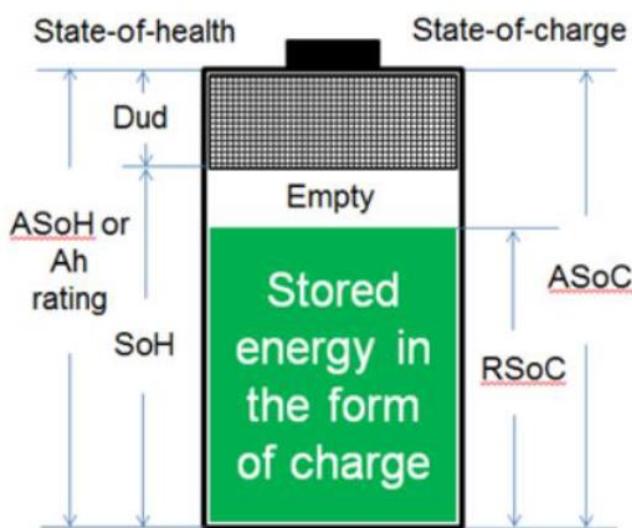


Figure 2: Relationship of battery state-of-health and state of charge.

## 2. Battery types

### 2.1. Primary Batteries

Primary batteries, also known as non-rechargeable batteries, tend to get overshadowed by the media attention secondary or rechargeable batteries receive. However, primaries play an important role, especially when charging is impractical or impossible, such as in military combat, rescue missions and forest-fire services. Regulated under IEC 60086, primary batteries also service pacemakers in heart patients, tire pressure gauges in vehicles, smart meters, intelligent drill bits in mining, animal-tracking, remote light beacons, as well as wristwatches, remote controls, electric keys and children's toys.

#### Pros and Cons of primary batteries

High specific energy, long storage times and instant readiness give primary batteries a unique advantage over other power sources. They can be carried to remote locations and used instantly, even after long storage; they are also readily available and environmentally friendly when disposed. Specific energy only indicates the capacity a battery can hold and does not include power delivery, a weakness with most primary batteries. While most secondary batteries are rated at a 1C discharge current, the capacity on consumer-grade primary batteries is measured with a very low current of 25mA. One of the reasons for low performance under load conditions is the high internal resistance of primary batteries, which causes the voltage to collapse. Resistance determines how well electrical current flows through a material or device and is measured in ohms ( $\Omega$ ). As the battery depletes on discharge, the already elevated resistance increases further. Figure 1 compares the specific energy of lead acid, NiMH and Li-ion as secondary, as well as alkaline and lithium-metal as primary batteries. Figure 2 compares the performance of primary and secondary batteries as "Rated" and "Actual." Rated refers to the specific energy when discharging at a very low current; Actual discharges at 1C, the way most secondary batteries are rated.

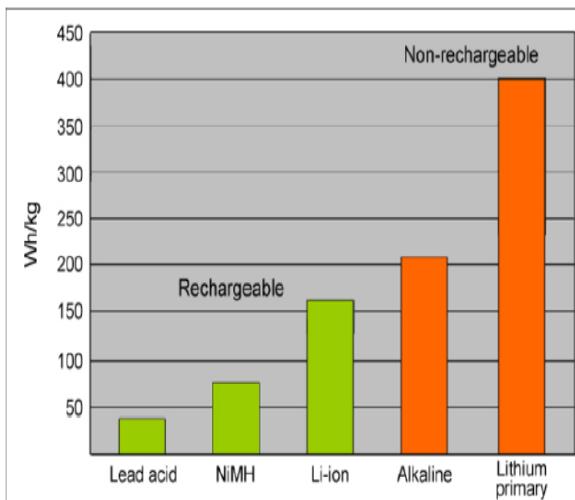


Figure 1: Specific energy comparison of secondary and primary batteries.

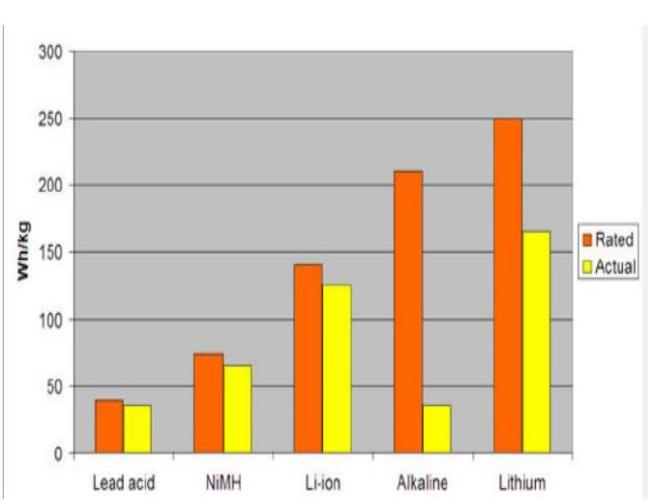


Figure 2: Energy comparison underload.

The most common cell formats for primary batteries are AA and AAA. Table 1 compares common primary batteries available in AA and AAA format (NiCd and NiMH are secondary batteries).

	Zinc-carbon	Alkaline	Lithium (Li-FeS2)	NiCd	NiMH
<b>Capacity AA AAA</b>	400-1,700 ~300	1,800-2,600 800-1,200	2,500-3,400 1,200	600-1,000 300-500	800-2,700 600-1,250
<b>Nominal V</b>	1.50	1.50	1.50	1.20	1.20
<b>Discharge rate</b>	Very low	Low	Medium	Very high	High
<b>Rechargeable</b>	No	No	No	Yes	Yes
<b>Shelf life</b>	1-2 years	7 years	10-15 years	5 years	5 years
<b>Retail AA (2015) AAA</b>	Not in all stores	\$0.75 \$1.00	\$3.00-5.00 \$4.00-5.00	Not in all stores	\$1.60-2.00 \$1.00

Table 1: Summary of batteries available in AA and AAA format

### 2.1.1. Choices of primary batteries

**Zinc-carbon**, also known as carbon-zinc or the Leclanché battery, is one of the earliest and least expensive primary batteries. It delivers 1.5V and often come with consumer devices.

**Alkaline**. Alkaline-manganese, also known as alkaline, is an improved version of the zinc-carbon battery and delivers 1.5V. Alkaline delivers more energy at higher load currents than zinc-carbon. Furthermore, a regular household alkaline provides about 40 percent more energy than the average Li-ion but alkaline is not as strong as Li-ion on loading. Alkaline has very low self-discharge and does not leak electrolyte when depleted as the old zinc-carbon does, but it is not totally leak-proof.

**Lithium iron disulfide** (Li-FeS2) is a newcomer to the primary battery family and offers improved performance compared to alkaline. Lithium batteries normally deliver 3 volts and higher, but Li-FeS2 has 1.5 volts to be compatible with the AA and AAA formats. It has a higher capacity and a lower internal resistance than alkaline. This enables moderate to heavy loads and is ideal for digital cameras. Further advantages are improved low temperature performance, superior leakage resistance and low self-discharge, allowing 15 years of storage at ambient temperatures. The disadvantages of the Li-FeS2 are a higher price and transportation issues due to the lithium metal content in the anode.

**Lithium-thionyl chloride** (LiSOCl<sub>2</sub> or LTC) is one of the most rugged lithium-metal batteries. The ability to withstand high heat and strong vibration enables horizontal drilling, also known as fracking. Some LTC are said to operate from 0°C to 200°C (32°F to 392°F). Other uses are in medical and sensor applications. With a specific energy of over 500Wh/kg, LTC offers twice the capacity of the best Li-ion. The nominal voltage is 3.60V/cell; the end-of-discharge cut-off voltage is 3.00V. The runtime is not based on capacity alone; thermal conditions and load pattern also have an effect. Constant current is more enduring than pulsed load; a

phenomenon that applies to most batteries. Like alkaline, lithium-thionyl chloride has a relatively high resistance and can only be used for moderate discharge loads. If stored for a time, a passivation layer forms between the lithium anode and the carbon-based cathode that dissipates when applying a load. This layer protects the battery by granting low self-discharge and a long shelf life. LTC is one of the most powerful and potent battery chemistries and should only be used by trained workers. For safety reasons, this battery is not used in consumer devices.

**Lithium manganese dioxide** ( $\text{LiMnO}_2$  or Li-M) is similar to LTC but has a lower specific capacity and is safe for public use. The voltage is 3.0–3.30V and the specific energy is about 280Wh/kg. Li-M is economically priced, has a long life and allows moderate loads but can deliver high pulse currents. Operational temperature ranges from -30°C to 60°C (-22°F to 140°F). Typical uses are meter sensing, medical devices, road toll sensors and cameras.

**Lithium sulfur dioxide** ( $\text{LiSo}_2$ ) is a primary battery with a voltage of 2.8V and an energy density up to 330Wh/kg. It offers a wide temperature range of -54°C to 71°C (-65°F to 160°F) with a projected shelf life of 5–10 years at room temperature.  $\text{LiSo}_2$  is inexpensive to make and is commonly used by the military. The Iraqi war used tons of these batteries, but it is giving way to the more superior Li-M.

**Note:** Primary lithium batteries are also known as lithium-metal. The cathode is carbon and the anode holds the active material, the reverse of Li-ion, which features a carbon anode.

Table 2 summarizes the most common primary batteries.

Primary Cell	Alkaline	Lithium iron disulfide ( $\text{LiFeS}_2$ )	Lithium-thionyl chloride ( $\text{LiSOCl}_2$ or LTC)	Lithium manganese dioxide ( $\text{LiMnO}_2$ or Li-M)	Lithium sulfur dioxide ( $\text{LiSo}_2$ )
Specific energy	200Wh/kg	300Wh/kg	500Wh/kg	280Wh/kg	330Wh/kg
Voltage	1.5V	1.5V	3.6–3.9V	3–3.3V	2.8V
Power	Low	Moderate	Excellent	Moderate	Moderate
Passivation	N/A	Moderate	Moderate	Moderate	Moderate
Safety	Good	Good	Precaution	Good	Precaution
Pricing	Low	Economical	Industrial	Economical	Industrial
Shelf life	10 years	15 years	10–20 years	10–20 years	5–10 years
Operating temp	0°C to 60°C	0°C to 60°C	-55°C to 85°C, higher for short time	-30°C to 60°C some enable from -55°C to 90°C	-54°C to 71°C
Usage	Consumer devices	Swaps alkaline for higher power and long runtime	Horizontal drilling, (fracking). Not for consumer use.	Meter sensing, medical devices, road toll sensors, cameras	Defense; being replaced by $\text{LiMnO}_2$

Table 2: Summary table of common primary batteries. Values are estimated.

## 2.2. Secondary Batteries

Rechargeable batteries play an important role in our lives and many daily chores would be unthinkable without the ability to recharge. The most common rechargeable batteries are lead acid, NiCd, NiMH and Li-ion. Here is a brief summary of their characteristics.

- Lead Acid – This is the oldest rechargeable battery system. Lead acid is rugged, forgiving if abused and is economically priced, but it has a low specific energy and limited cycle count. Lead acid is used for wheelchairs, golf cars, personnel carriers, emergency lighting and uninterruptible power supply (UPS). Lead is toxic and cannot be disposed in landfills.
- Nickel-cadmium – Mature and well understood, NiCd is used where long service life, high discharge current and extreme temperatures are required. NiCd is one of the most rugged and enduring batteries; it is the only chemistry that allows ultra-fast charging with minimal stress. Main applications are power tools, medical devices, aviation and UPS. Due to environmental concerns, NiCd is being replaced with other chemistries, but it retains its status in aircraft due to its good safety record.
- Nickel-metal-hydride – Serves as a replacement for NiCd as it has only mild toxic metals and provides higher specific energy. NiMH is used for medical instruments, hybrid cars and industrial applications. NiMH is also available in AA and AAA cells for consumer use.
- Lithium-ion – Li-ion is replacing many applications that were previously served by lead and nickel-based batteries. Due to safety concerns, Li-ion needs a protection circuit. It is more expensive than most other batteries, but high cycle count and low maintenance reduce the cost per cycle over many other chemistries.

### 2.2.1. Lead Acid Batteries

Lead acid was the first rechargeable battery for commercial use. The grid structure of the battery is made from a lead alloy. Pure lead is too soft and would not support itself, so small quantities of other metals are added to get the mechanical strength and improve electrical properties. Although lead is toxic, the 99% recycling rate makes lead acid less environmentally hazardous and these batteries are still in wide use today.

Lead acid	Cathode (positive)	Anode (negative)	Electrolyte
Material	Lead dioxide (chocolate brown)	Gray lead, (spongy when formed)	Sulfuric acid
Full charge	Lead oxide ( $PbO_2$ ), electrons added to positive plate	Lead (Pb), electrons removed from plate	Strong sulfuric acid
Discharged	Lead turns into lead sulfate at the negative electrode, electrons driven from positive plate to negative plate		Weak sulfuric acid (water-like)

There are two basic types of lead acid batteries. The flooded and the sealed batteries. In sealed lead acid batteries, rather than submerging the plates in a liquid, electrolyte is impregnated into a moistened separator, a design that resembles nickel- and lithium-based systems. This enables operating the battery in any physical orientation without leakage. The sealed battery contains less electrolyte than the flooded type and maybe the most significant advantage of this battery type is the ability to combine oxygen and hydrogen to create water and prevent dry out during cycling. Several types of sealed lead acid have emerged and the most common are gel, also known as valve-regulated lead acid (VRLA), and absorbent glass mat (AGM).

### **Pros and Cons of lead acid batteries**

Lead acid is dependable and inexpensive on a cost-per-watt base. There are few other batteries that deliver bulk power as cheaply as lead acid, and this makes the battery cost-effective for automobiles, golf cars, forklifts, marine and uninterruptible power supplies (UPS). Lead acid has a moderate life span, but it is not subject to memory as nickel-based systems are, and the self-discharge is lowest among rechargeable batteries. While NiCd loses approximately 40 percent of their stored energy in three months, lead acid self-discharges the same amount in one year. The lead acid battery works well at high and cold temperatures and is superior to lithium-ion when operating in subzero conditions. Lead acid batteries are rated at a 5-hour (0.2C) and 20-hour (0.05C) discharge rate. The battery performs best when discharged slowly; the capacity readings are substantially higher at a slower discharge than at the 1C-rate. Lead acid can, however, deliver high pulse currents of several C if done for only a few seconds (high specific power). This makes the lead acid well suited as a starter battery, also known as starter-light-ignition (SLI).

But, there are several limitations of lead acid batteries. Lead acid is heavy, has low specific energy and is less durable than nickel- and lithium-based systems when deep cycled. A full discharge causes strain and each discharge/charge cycle permanently robs the battery of a small amount of capacity. This loss is small while the battery is in good operating condition, but the fading increases once the performance drops to half the nominal capacity. This wear-down characteristic applies to all batteries in various degrees. The primary reasons for its relatively short cycle life are grid corrosion on the positive electrode, depletion of the active material and expansion of the positive plates. This aging phenomenon is accelerated at elevated operating temperatures and when drawing high discharge currents.

Charging a lead acid battery is simple, but the correct voltage limits must be observed. Choosing a low voltage limit shelters the battery, but this produces poor performance and causes a buildup of sulfation on the negative plate. A high voltage limit improves performance but forms grid corrosion on the positive plate. While sulfation can be reversed if serviced in time, corrosion is permanent. Lead acid does not lend itself to fast charging and with most types, a full charge takes 14–16 hours. The battery must always be stored at full state-of-charge. Low charge causes sulfation, a condition that robs the battery of performance. Adding carbon on the negative electrode reduces this problem but this lowers the specific energy.

Additional limitations are about flooded lead acid, which requires water refilling and has transportation restrictions.

### **Absorbent Glass Mat (AGM)**

The AGM suspends the electrolyte in a specially designed glass mat. This offers several advantages to lead acid systems. The AGM battery is spill proof through acid encapsulation in matting technology, has very low internal resistance and is capable to deliver high currents on demand and offers a relatively long service life, even when deep cycled. It is maintenance free, provides good electrical reliability and is lighter than the flooded lead acid type. While regular lead acid batteries need a topping charge every six months to prevent the buildup of sulfation, AGM batteries are less prone to sulfation and can sit in storage for longer before a charge becomes necessary. The battery stands up well to low temperatures and has a low self-discharge. Also, it can be charged up to 5 times faster than flooded type and has a better cycle life. However, it has higher manufacturing cost than flooded version, it is sensitive to overcharging, it has low specific energy, suffers from capacity fading and must be stored in charged condition.

### **Gel lead acid**

Mixing sulfuric acid with a silica-gelling agent converts liquid electrolyte into a semi-stiff paste to make the gel maintenance free. A gel battery generally lasts longer than AGM; improved heat transfer to the outside is one reason. (The gel separator moves heat whereas the absorbent glass mat of the AGM acts as insulator.) A further advantage of gel is the dome shaped performance curve that allows the battery to stay in the high performance range during most of its service life before dropping rapidly towards the end of life; AGM, in comparison, fades gradually. Furthermore, it is safe in operation and forgiving if abused. However, it has higher manufacturing cost than AGM, it is sensitive to overcharging (less than AGM) and has moderate specific energy and load current. Finally, as with all lead acid batteries, it must be stored in charged conditions (less critical than flooded).

New lead acid systems try to solve the slow charging problem by adding carbon to this electrode with promising results. Those are, namely, Advanced Lead-carbon, Firefly Energy, Altraverda Bipolar, Axion Power, CSIRO Ultrabattery, EEstor, Enhanced Flooded Battery (EFB).

## 2.2.2. Nickel-based Batteries

For 50 years, portable devices relied almost exclusively on nickel-cadmium (NiCd). This generated a large amount of data, but in the 1990s, nickel-metal-hydride (NiMH) took over the reign to solve the toxicity problem of the otherwise robust NiCd. Many of the characteristics of NiCd were transferred to the NiMH camp, offering a quasi-replacement as these two systems are similar. Because of environmental regulations, NiCd is limited to specialty applications today. Other nickel-based batteries are nickel-iron (NiFe), nickel-zinc (NiZn) and nickel-hydrogen (NiH).

NiMH, NiCd	Cathode (positive)	Anode (negative)	Electrolyte
Material	Nickel oxyhydroxide	NiMH: hydrogen-absorbing alloy NiCd: Cadmium	Potassium hydroxide

### Nickel-cadmium (NiCd)

NiCd is one of the most rugged and forgiving (if abused) battery. It is the only battery that can be ultra-fast charged with little stress and has a long cycling life. Also, it can be stored in a discharged state, but needs priming before use. Other advantages are simple storage and transportation, good low-temperature performance, economical price (the lowest in term of cost per cycle) and availability in a wide range of sizes and performance options.

However, NiCd, and in part also NiMH, have memory effect that causes a loss of capacity if not given a periodic full discharge cycle. The battery appears to remember the previous energy delivered and once a routine has been established, it does not want to give more. Furthermore, it has relatively low specific energy compared with newer systems, high self-discharge (needs recharging after storage) and the low cell voltage of 1.20V requires many cells to achieve high voltage. Finally, cadmium is a toxic metal and cannot be disposed in a landfill.

### Nickel-metal-hydride (NiMH)

NiMH has 30-40 per cent higher capacity and is less prone to memory than a standard NiCd. It can be simply stored and transported, it is environmentally friendly and nickel content makes recycling profitable. Also, it can operate on wide temperature range.

Nickel-metal-hydride is not without drawbacks. The battery is more delicate and trickier to charge than NiCd. With 20 percent self-discharge in the first 24 hours after charge and 10 percent per month thereafter, NiMH ranks among the highest in the class. Modifying the hydride materials lowers the self-discharge and reduces corrosion of the alloy, but this decreases the specific energy. Moreover, it has limited service life and deep charges and overcharges must be avoided.

### 2.2.3. Lithium-ion Batteries

Lithium is the lightest of all metals, has the greatest electrochemical potential and provides the largest specific energy per weight. Rechargeable batteries with lithium metal on the anode could provide extraordinarily high energy densities; however, it was discovered in the mid-1980s that cycling produced unwanted dendrites on the anode. These growth particles penetrate the separator and cause an electrical short. The cell temperature would rise quickly and approach the melting point of lithium, causing thermal runaway, also known as “venting with flame.” The inherent instability of lithium metal, especially during charging, shifted research to a non-metallic solution using lithium ions. In 1991, Sony commercialized the first Li ion, and today this chemistry has become the most promising and fastest growing battery on the market. Although lower in specific energy than lithium-metal, Li ion is safe, provided the voltage and currents limits are being respected.

The key to the superior specific energy is the high cell voltage of 3.60V. Improvements in the active materials and electrolytes have the potential to further boost the energy density. Load characteristics are good and the flat discharge curve offers effective utilization of the stored energy in a desirable and flat voltage spectrum of 3.70–2.80V/cell. Cost reduction, increased specific energy and the absence of toxic material paved the road to make Li-ion the universally accepted battery for portable applications, heavy industries, electric powertrains and satellites.

Li-ion is a low-maintenance battery, an advantage that most other chemistries cannot claim. The battery has no memory and does not need exercising (deliberate full discharge) to keep it in good shape. Self-discharge is less than half that of nickel-based systems and this helps the fuel gauge applications. The nominal cell voltage of 3.60V can directly power mobile phones, tablets and digital cameras, offering simplifications and cost reductions over multi-cell designs. The drawbacks are the need for protection circuits to prevent abuse, as well as high price.

Lithium-ion	Cathode (positive) on aluminum foil	Anode (negative) on copper foil	Electrolyte
<b>Material</b>	Metal oxides derived from cobalt, nickel, manganese, iron, aluminum	Carbon based	Lithium salt in an organic solvent
<b>Full charge</b>	Metal oxide with intercalation structure	Lithium ions migrated to anode.	
<b>Discharged</b>	Lithium ions move back to the positive electrode	Mainly carbon	

Lithium-ion uses a cathode (positive electrode), an anode (negative electrode), electrolyte as conductor and a separator. (The anode of a discharging battery is negative and the cathode positive (see BU-104b: Battery Building Blocks). The cathode is metal oxide that is coated onto an aluminum current collector and the anode consists of porous carbon on a copper current collector. During discharge, the ions flow from the anode to the cathode through the

electrolyte and separator; charge reverses the direction and the ions flow from the cathode to the anode. Figure 1 illustrates the process.

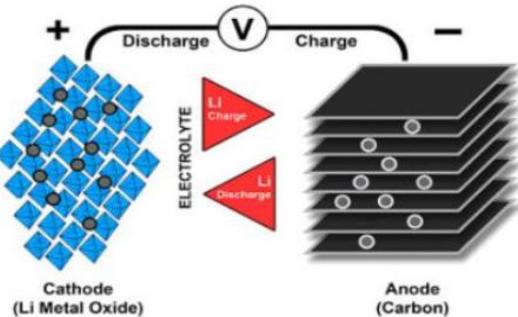


Figure 1: Ion flow in lithium-ion battery.

When the cell charges and discharges, ions shuttle between cathode (positive electrode) and anode (negative electrode). On discharge, the anode undergoes oxidation, or loss of electrons, and the cathode sees a reduction, or a gain of electrons. Charge reverses the movement.

Li ion batteries come in many varieties but all have one thing in common – the “lithium-ion” catchword. Although strikingly similar at first glance, these batteries vary in performance and the choice of active materials gives them unique personalities.

Sony's original lithium-ion battery used coke as the anode (coal product). Since 1997, most Li ion manufacturers, including Sony, shifted to graphite to attain a flatter discharge curve. Graphite is a form of carbon that has long-term cycle stability and is used in lead pencils. It is the most common carbon material, followed by hard and soft carbons. Nanotube carbons have not yet found commercial use in Li-ion as they tend to entangle and affect performance. A future material that promises to enhance the performance of Li-ion is graphene.

Figure 2 illustrates the voltage discharge curve of a modern Li-ion with graphite anode and the early coke version.

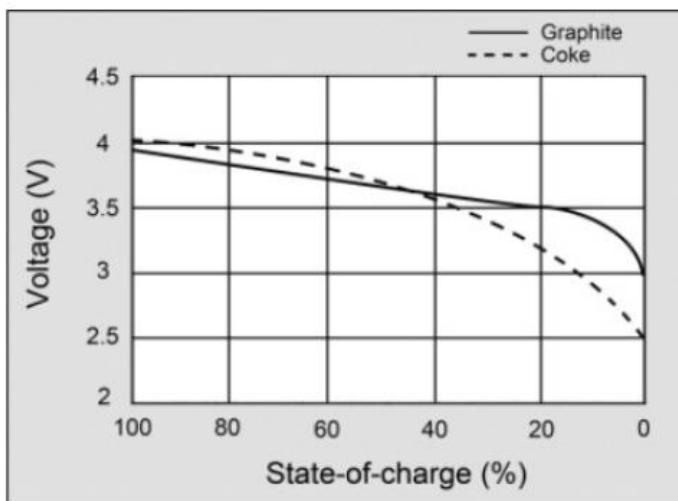


Figure 2: Voltage discharge curve of lithium-ion.

Several additives have been tried, including silicon-based alloys, to enhance the performance of the graphite anode. It takes six carbon (graphite) atoms to bind to a single lithium ion; a single silicon atom can bind to four lithium ions. This means that the silicon anode could theoretically store over 10 times the energy of graphite, but expansion of the anode during charge is a problem. Pure silicone anodes are therefore not practical and only 3–5 percent of silicon is typically added to the anode of a silicon-based to achieve good cycle life.

Using nano-structured lithium-titanate as an anode additive shows promising cycle life, good load capabilities, excellent low-temperature performance and superior safety, but the specific energy is low and the cost is high.

Experimenting with cathode and anode material allows manufacturers to strengthen intrinsic qualities, but one enhancement may compromise another. The so-called “Energy Cell” optimizes the specific energy (capacity) to achieve long runtimes but at lower specific power; the “Power Cell” offers exceptional specific power but at lower capacity. The “Hybrid Cell” is a compromise and offers a little bit of both.

Manufacturers can attain a high specific energy and low cost relatively easily by adding nickel in lieu of the more expensive cobalt, but this makes the cell less stable. While a start-up company may focus on high specific energy and low price to gain quick market acceptance, safety and durability cannot be compromised. Reputable manufacturers place high integrity on safety and longevity. Table 3 summarizes the advantages and limitations of Li-ion.

<b>Advantages</b>	High specific energy and high load capabilities with Power Cells  Long cycle and extend shelf-life; maintenance-free  High capacity, low internal resistance, good coulombic efficiency  Simple charge algorithm and reasonably short charge times  Low self-discharge (less than half that of NiCd and NiMH)
<b>Limitations</b>	Requires protection circuit to prevent thermal runaway if stressed  Degrades at high temperature and when stored at high voltage  No rapid charge possible at freezing temperatures (<0°C, <32°F)  Transportation regulations required when shipping in larger quantities

Table 3: Advantages and limitations of Li-ion batteries

### 2.2.3.1. Types of Lithium-ion

Lithium-ion is named for its active materials; the words are either written in full or shortened by their chemical symbols. A series of letters and numbers strung together can be hard to remember and even harder to pronounce, and battery chemistries are also identified in abbreviated letters.

For example, lithium cobalt oxide, one of the most common Li-ions, has the chemical symbols  $\text{LiCoO}_2$  and the abbreviation LCO. For reasons of simplicity, the short form Li-cobalt can also be used for this battery. Cobalt is the main active material that gives this battery character. Other Li-ion chemistries are given similar short-form names. This section lists six of the most common Li-ions. All readings are average estimates at time of writing.

#### Lithium Cobalt Oxide( $\text{LiCoO}_2$ ) — LCO

Its high specific energy makes Li-cobalt the popular choice for mobile phones, laptops and digital cameras. The battery consists of a cobalt oxide cathode and a graphite carbon anode. The cathode has a layered structure and during discharge, lithium ions move from the anode to the cathode. The flow reverses on charge. Figure 1 illustrates the structure.

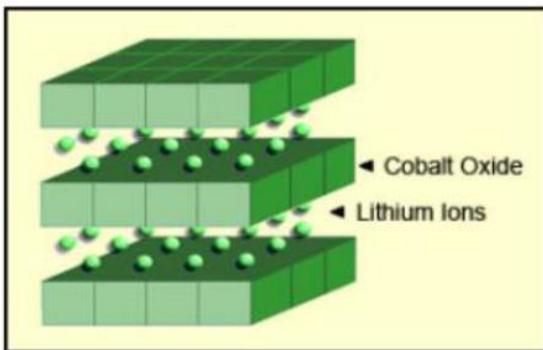


Figure 1: Li-cobalt structure.

The cathode has a layered structure. During discharge the lithium ions move from the anode to the cathode; on charge the flow is from cathode to anode.

Source: Cadex

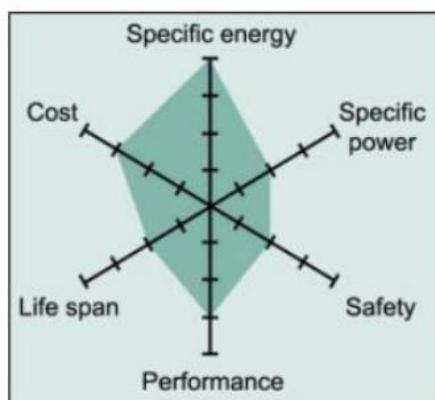
The drawback of Li-cobalt is a relatively short life span, low thermal stability and limited load capabilities (specific power). Like other cobalt-blended Li-ion, Li-cobalt has a graphite anode that limits the cycle life by a changing solid electrolyte interface (SEI), thickening on the anode and lithium plating while fast charging and charging at low temperature. Newer systems include nickel, manganese and/or aluminum to improve longevity, loading capabilities and cost.

Li-cobalt should not be charged and discharged at a current higher than its C-rating. This means that an 18650 cell with 2,400mAh can only be charged and discharged at 2,400mA. Forcing a fast charge or applying a load higher than 2,400mA causes overheating and undue stress. For optimal fast charge, the manufacturer recommends a C-rate of 0.8C or about 2,000mA. (See BU-402: What is C-rate: <https://batteryuniversity.com/learn/>). The mandatory battery protection circuit limits the charge and discharge rate to a safe level of about 1C for

the Energy Cell. (Note: The LCO batteries used by Aristurtle are unique and are manufactured with specifications according to FSAE needs, e.g. high load capabilities)

The hexagonal spider graphic (Figure 2) summarizes the performance of Li-cobalt in terms of specific energy or capacity that relates to runtime; specific power or the ability to deliver high current; safety; performance at hot and cold temperatures; life span reflecting cycle life and longevity; and cost. Other characteristics of interest not shown in the spider webs are toxicity, fast-charge capabilities, self-discharge and shelf life.

The Li-cobalt is losing favor to Li-manganese, but especially NMC and NCA because of the high cost of cobalt and improved performance by blending with other active cathode materials. (See description of the NMC and NCA below.)



**Figure 2: Snapshot of an average Li-cobalt battery.**

Li-cobalt excels on high specific energy but offers only moderate performance specific power, safety and life span.

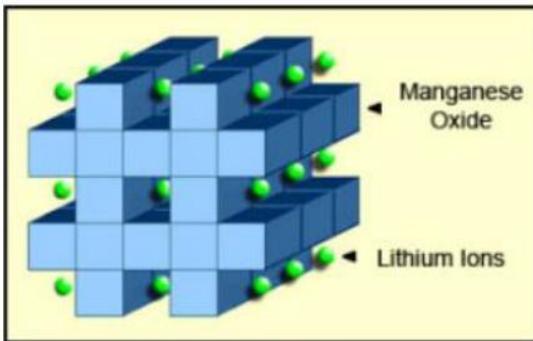
Source: Cadex

### Lithium Manganese Oxide ( $\text{LiMn}_2\text{O}_4$ ) — LMO

Li-ion with manganese spinel was first published in the Materials Research Bulletin in 1983. In 1996, Moli Energy commercialized a Li-ion cell with lithium manganese oxide as cathode material. The architecture forms a three-dimensional spinel structure that improves ion flow on the electrode, which results in lower internal resistance and improved current handling. A further advantage of spinel is high thermal stability and enhanced safety, but the cycle and calendar life are limited.

Low internal cell resistance enables fast charging and high-current discharging. In an 18650 package, Li-manganese can be discharged at currents of 20–30A with moderate heat buildup. It is also possible to apply one-second load pulses of up to 50A. A continuous high load at this current would cause heat buildup and the cell temperature cannot exceed 80°C (176°F). Li-manganese is used for power tools, medical instruments, as well as hybrid and electric vehicles.

Figure 4 illustrates the formation of a three-dimensional crystalline framework on the cathode of a Li-manganese battery. This spinel structure, which is usually composed of diamond shapes connected into a lattice, appears after initial formation.



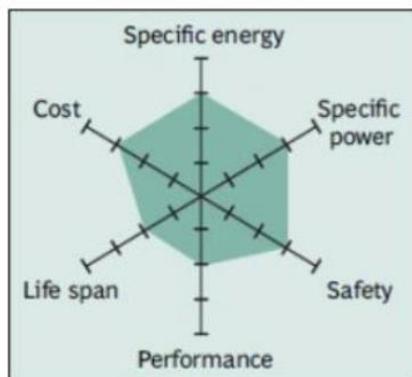
**Figure 4: Li-manganese structure.**

The cathode crystalline formation of lithium manganese oxide has a three-dimensional framework structure that appears after initial formation. Spinel provides low resistance but has a more moderate specific energy than cobalt.

Source: Cadex

Li-manganese has a capacity that is roughly one-third lower than Li-cobalt. Design flexibility allows engineers to maximize the battery for either optimal longevity (life span), maximum load current (specific power) or high capacity (specific energy). For example, the long-life version in the 18650 cell has a moderate capacity of only 1,100mAh; the high-capacity version is 1,500mAh.

Figure 5 shows the spider web of a typical Li-manganese battery. The characteristics appear marginal but newer designs have improved in terms of specific power, safety and life span. Pure Li-manganese batteries are no longer common today; they may only be used for special applications.



**Figure 5: Snapshot of a pure Li-manganese battery.**

Although moderate in overall performance, newer designs of Li-manganese offer improvements in specific power, safety and life span.

Source: Boston Consulting Group

Most Li-manganese batteries blend with lithium nickel manganese cobalt oxide (NMC) to improve the specific energy and prolong the life span. This combination brings out the best in each system, and the LMO (NMC) is chosen for most electric vehicles, such as the Nissan Leaf, Chevy Volt and BMW i3. The LMO part of the battery, which can be about 30 percent, provides high current boost on acceleration; the NMC part gives the long driving range.

Li-ion research gravitates heavily towards combining Li-manganese with cobalt, nickel, manganese and/or aluminum as active cathode material. In some architecture, a small amount of silicon is added to the anode. This provides a 25 percent capacity boost; however,

the gain is commonly connected with a shorter cycle life as silicon grows and shrinks with charge and discharge, causing mechanical stress.

These three active metals, as well as the silicon enhancement can conveniently be chosen to enhance the specific energy (capacity), specific power (load capability) or longevity. While consumer batteries go for high capacity, industrial applications require battery systems that have good loading capabilities, deliver a long life and provide safe and dependable service.

### **Lithium Nickel Manganese Cobalt Oxide ( $\text{LiNiMnCoO}_2$ ) — NMC**

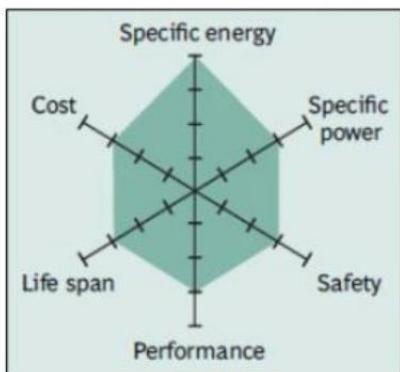
One of the most successful Li-ion systems is a cathode combination of nickel-manganese-cobalt (NMC). Similar to Li-manganese, these systems can be tailored to serve as Energy Cells or Power Cells. For example, NMC in an 18650 cell for moderate load condition has a capacity of about 2,800mAh and can deliver 4A to 5A; NMC in the same cell optimized for specific power has a capacity of only about 2,000mAh but delivers a continuous discharge current of 20A. A silicon-based anode will go to 4,000mAh and higher but at reduced loading capability and shorter cycle life. Silicon added to graphite has the drawback that the anode grows and shrinks with charge and discharge, making the cell mechanically unstable.

The secret of NMC lies in combining nickel and manganese. An analogy of this is table salt in which the main ingredients, sodium and chloride, are toxic on their own but mixing them serves as seasoning salt and food preserver. Nickel is known for its high specific energy but poor stability; manganese has the benefit of forming a spinel structure to achieve low internal resistance but offers a low specific energy. Combining the metals enhances each other strengths.

NMC is the battery of choice for power tools, e-bikes and other electric powertrains. The cathode combination is typically one-third nickel, one-third manganese and one-third cobalt, also known as 1-1-1. This offers a unique blend that also lowers the raw material cost due to reduced cobalt content. Another successful combination is NCM with 5 parts nickel, 3 parts cobalt and 2 parts manganese (5-3-2). Other combinations using various amounts of cathode materials are possible.

Battery manufacturers move away from cobalt systems toward nickel cathodes because of the high cost of cobalt. Nickel-based systems have higher energy density, lower cost, and longer cycle life than the cobalt-based cells but they have a slightly lower voltage.

New electrolytes and additives enable charging to 4.4V/cell and higher to boost capacity. Figure 7 demonstrates the characteristics of the NMC.



**Figure 7: Snapshot of NMC.**

NMC has good overall performance and excels on specific energy. This battery is the preferred candidate for the electric vehicle and has the lowest self-heating rate.

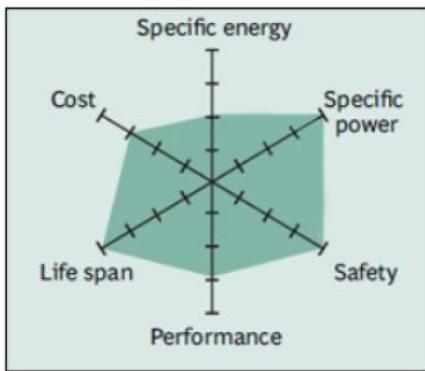
Source: Boston Consulting Group

There is a move towards NMC-blended Li-ion as the system can be built economically and it achieves a good performance. The three active materials of nickel, manganese and cobalt can easily be blended to suit a wide range of applications for automotive and energy storage systems (EES) that need frequent cycling. The NMC family is growing in its diversity.

### Lithium Iron Phosphate(LiFePO<sub>4</sub>) — LFP

In 1996, the University of Texas (and other contributors) discovered phosphate as cathode material for rechargeable lithium batteries. Li-phosphate offers good electrochemical performance with low resistance. This is made possible with nano-scale phosphate cathode material. The key benefits are high current rating and long cycle life, besides good thermal stability, enhanced safety and tolerance if abused.

Li-phosphate is more tolerant to full charge conditions and is less stressed than other lithium-ion systems if kept at high voltage for a prolonged time. (See BU-808: How to Prolong Lithium-based Batteries). As a trade-off, its lower nominal voltage of 3.2V/cell reduces the specific energy below that of cobalt-blended lithium-ion. With most batteries, cold temperature reduces performance and elevated storage temperature shortens the service life, and Li-phosphate is no exception. Li-phosphate has a higher self-discharge than other Li-ion batteries, which can cause balancing issues with aging. This can be mitigated by buying high quality cells and/or using sophisticated control electronics, both of which increase the cost of the pack. Cleanliness in manufacturing is of importance for longevity. There is no tolerance for moisture, lest the battery will only deliver 50 cycles. Figure 9 summarizes the attributes of Li-phosphate.



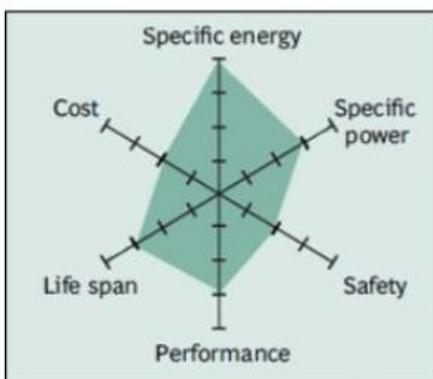
**Figure 9: Snapshot of a typical Li-phosphate battery.**

Li-phosphate has excellent safety and long life span but moderate specific energy and elevated self-discharge.

Source: Cadex

### Lithium Nickel Cobalt Aluminum Oxide ( $\text{LiNiCoAlO}_2$ ) — NCA

Lithium nickel cobalt aluminum oxide battery, or NCA, has been around since 1999 for special applications. It shares similarities with NMC by offering high specific energy, reasonably good specific power and a long life span. Less flattering are safety and cost. Figure 11 summarizes the six key characteristics. NCA is a further development of lithium nickel oxide; adding aluminum gives the chemistry greater stability.



**Figure 11: Snapshot of NCA.**

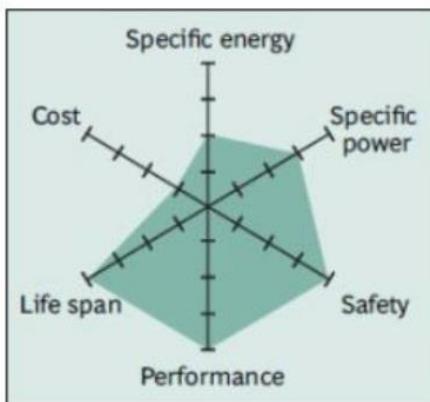
High energy and power densities, as well as good life span, make NCA a candidate for EV powertrains. High cost and marginal safety are negatives.

Source: Cadex

### Lithium Titanate ( $\text{Li}_2\text{TiO}_3$ ) — LTO

Batteries with lithium titanate anodes have been known since the 1980s. Li-titanate replaces the graphite in the anode of a typical lithium-ion battery and the material forms into a spinel structure. The cathode can be lithium manganese oxide or NMC. Li-titanate has a nominal cell voltage of 2.40V, can be fast charged and delivers a high discharge current of 10C, or 10 times the rated capacity. The cycle count is said to be higher than that of a regular Li-ion. Li-titanate is safe, has excellent low-temperature discharge characteristics and obtains a capacity of 80 percent at  $-30^\circ\text{C}$  ( $-22^\circ\text{F}$ ).

LTO (commonly Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) has advantages over the conventional cobalt-blended Li-ion with graphite anode by attaining zero-strain property, no SEI film formation and no lithium plating when fast charging and charging at low temperature. Thermal stability under high temperature is also better than other Li-ion systems; however, the battery is expensive. At only 65Wh/kg, the specific energy is low, rivalling that of NiCd. Li-titanate charges to 2.80V/cell, and the end of discharge is 1.80V/cell. Figure 13 illustrates the characteristics of the Li-titanate battery. Typical uses are electric powertrains, UPS and solar-powered street lighting.

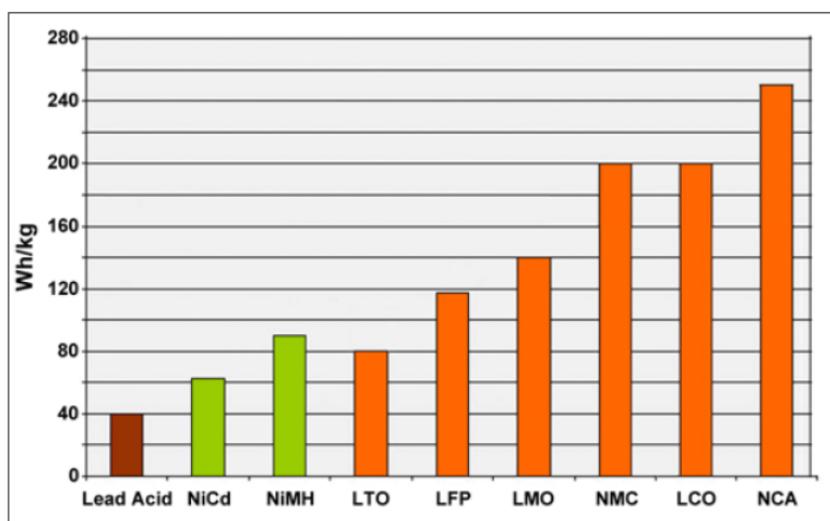


**Figure 13: Snapshot of Li-titanate.**

Li-titanate excels in safety, low-temperature performance and life span. Efforts are being made to improve the specific energy and lower cost.

Source: Boston Consulting Group

Figure 15 compares the specific energy of lead-, nickel- and lithium-based systems. While Li-aluminum (NCA) is the clear winner by storing more capacity than other systems, this only applies to specific energy. In terms of specific power and thermal stability, Li-manganese (LMO) and Li-phosphate (LFP) are superior. Li-titanate (LTO) may have low capacity but this chemistry outlives most other batteries in terms of life span and also has the best cold temperature performance. Moving towards the electric powertrain, safety and cycle life will gain dominance over capacity. (LCO stands for Li-cobalt, the original Li-ion.)



**Figure 15: Typical specific energy of lead-, nickel- and lithium-based batteries.**

NCA enjoys the highest specific energy; however, manganese and phosphate are superior in terms of specific power and thermal stability. Li-titanate has the best life span.

Courtesy of Cadex

### 2.2.3.2. Lithium-polymer (LiPo)

The term polymer is commonly used to describe certain type of lithium-based battery that may or may not be polymer based. These typically include pouch and prismatic cells. While the word “polymer” is perceived as a plastic, polymers range from synthetic plastics to natural biopolymers and proteins that form fundamental biological structures.

Lithium-polymer differs from other battery systems in the type of electrolyte used. The original polymer design dating back to the 1970s used a solid (dry) polymer electrolyte that resembles a plastic-like film. This insulator allows the exchange of ions (electrically charged atoms) and replaces the traditional porous separator that is soaked with electrolyte.

A solid polymer has poor conductivity at room temperature, and the battery must be heated to 60°C (140°F) and higher to enable current flow. Large polymer batteries for stationary applications were installed that needed heating, but these have since disappeared. The much anticipated hype of the “true plastic battery” promised in the early 2000s did not materialize as conductivity could not be attained at ambient temperature.

To make the modern Li-polymer battery conductive at room temperature, gelled electrolyte has been added. Most Li-ion polymer cells today incorporate a micro porous separator with some moisture. Li-polymer can be built on many systems, the likes of Li-cobalt, NMC, Li-phosphate and Li-manganese, and is not considered a unique battery chemistry. The majority of Li-polymer packs are cobalt based; other active material may also be added.

With gelled electrolyte added, what is the difference between a normal Li ion and Li ion polymer? As far as the user is concerned, lithium polymer is essentially the same as lithium-ion. Both systems use identical cathode and anode material and contain a similar amount of electrolyte.

Li-polymer is unique in that a micro porous electrolyte replaces the traditional porous separator. Li-polymer offers slightly higher specific energy and can be made thinner than conventional Li-ion, but the manufacturing cost is said to be higher than cylindrical design. For the purpose of discussion, pouch cells are often identified as being Li-polymer.

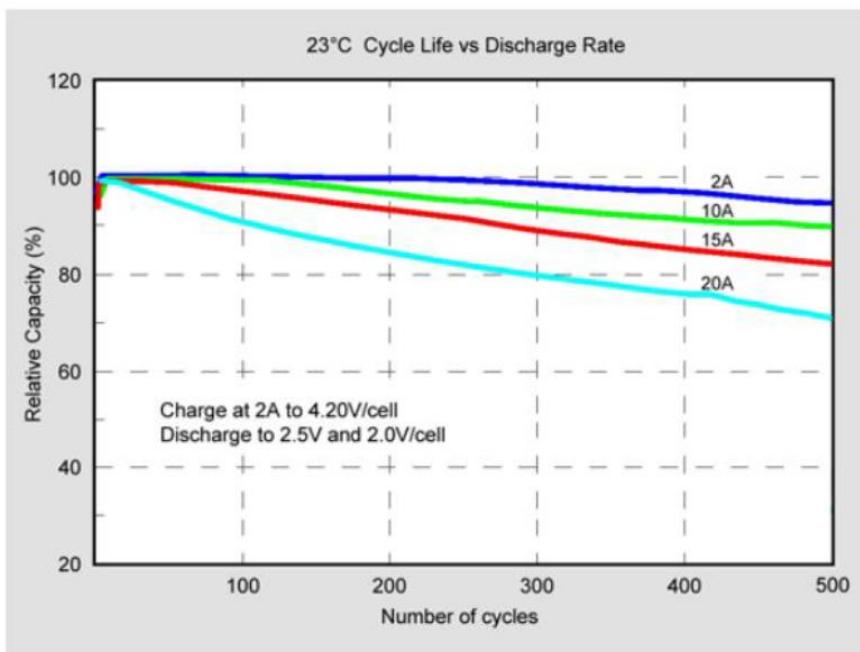
Li-polymer cells also come in a flexible foil-type case that resembles a food package. While a standard Li-ion needs a rigid case to press the electrodes together, Li-polymer uses laminated sheets that do not need compression. A foil-type enclosure reduces the weight by more than 20 percent over the classic hard shell. Thin film technology liberates the design as the battery can be made into any shape, fitting neatly into stylish mobile phones and tablet. Li-polymer can also be made very slim to resemble a credit card (See Pouch Cell.) Light weight and high specific power make Li-polymer the preferred choice for hobbyists.

Charge and discharge characteristics of Li-polymer are identical to other Li-ion systems and do not require a dedicated charger. Safety issues are also similar in that protection circuits are needed. Gas buildup during charge can cause some prismatic and pouch cells to swell, and equipment manufacturers must make allowances for expansion. Li-polymer in a foil package may be less durable than Li-ion in the cylindrical package.

### 2.2.3.3. Cycling Performance of Li-ion

Cadex tested a large volume of lithium ion batteries used in portable communication devices. Figure 4 examines the capacity fade of a modern Li-ion Power Cell at a 2A, 10A, 15A and 20A discharge. Stresses increase with higher load currents, and this also applies to fast charging. (See BU-401a: Ultra-fast charging of Li-ion.)

Li-ion manufacturers seldom specify the rise of internal resistance and self-discharge as a function of cycling. Advancements have been made with electrolyte additives that keep the resistance low through most of the battery life. The self-discharge of Li-ion is normally low but it can increase if misused or if exposed to deep discharges.



**Figure 4: Cycle characteristics of IHR18650C by E-One Moli. (3.6V, 2,000mA). 18650 Power Cell was charged with 2A and discharged at 2, 10, 15 and 20A. The internal resistance and self-discharge are N/A.**

Courtesy of E-One Moli Energy

Batteries tested in a laboratory tend to provide better results than in the field. Elements of stress in everyday use do not always transfer well into a test laboratory. Aging plays a negligible role in a lab because the batteries are cycled over a period of a few months rather than the expected service life of several years. The temperature is often moderate and the batteries are charged under controlled charging condition and with approved chargers. The load signature also plays a role as all batteries were discharged with a DC load. Batteries tend to have a lower cycle life if discharged with pulses. (See BU-501: Basics About Discharging.) Do not overstress a battery as this will shorten the life. If a battery must repeatedly be loaded at peak currents, choose a pack with increased Ah rating.

## 2.2.4. Supercapacitor

The supercapacitor, also known as ultracapacitor or double-layer capacitor, differs from a regular capacitor in that it has very high capacitance. A capacitor stores energy by means of a static charge as opposed to an electrochemical reaction. Applying a voltage differential on the positive and negative plates charges the capacitor. The supercapacitor is used for energy storage undergoing frequent charge and discharge cycles at high current and short duration.

All capacitors have voltage limits and, specifically, the supercapacitor is confined to 2.5–2.7V. Voltages of 2.8V and higher are possible, but at a reduce service life. To get higher voltages, several supercapacitors are connected in series. Serial connection reduces the total capacitance and increases the internal resistance. Strings of more than three capacitors require voltage balancing to prevent any cell from going into over-voltage. Lithium-ion batteries share a similar protection circuit.

The specific energy of the supercapacitor ranges from 1Wh/kg to 30Wh/kg, 10–50 times less than Li-ion. The discharge curve is another disadvantage. Whereas the electrochemical battery delivers a steady voltage in the usable power band, the voltage of the supercapacitor decreases on a linear scale, reducing the usable power spectrum. An optional DC-DC converter helps to recover the energy dwelling in the low voltage band, but this adds costs and introduces loss. A battery with a flat discharge curve, in comparison, delivers 90 to 95 percent of its energy reserve before reaching the voltage threshold.

The charge time of a supercapacitor is 1–10 seconds. The charge characteristic is similar to an electrochemical battery and the charge current is, to a large extent, limited by the charger's current handling capability. The initial charge can be made very fast, and the topping charge will take extra time. Provision must be made to limit the inrush current when charging an empty supercapacitor as it will suck up all it can. The supercapacitor is not subject to overcharge and does not require full-charge detection; the current simply stops flowing when full.

The supercapacitor can be charged and discharged a virtually unlimited number of times. Unlike the electrochemical battery, which has a defined cycle life, there is little wear and tear by cycling a supercapacitor. Age is also kinder to the supercapacitor than a battery. Under normal conditions, a supercapacitor fades from the original 100 percent capacity to 80 percent in 10 years. Applying higher voltages than specified shortens the life. The supercapacitor is forgiving in hot and cold temperatures, an advantage that batteries cannot meet equally well.

The self-discharge of a supercapacitor is substantially higher than that of an electrostatic capacitor and somewhat higher than an electrochemical battery; the organic electrolyte contributes to this. The supercapacitor discharges from 100 to 50 percent in 30 to 40 days. Lead and lithium-based batteries, in comparison, self-discharge about 5 percent per month.

The chemistry of a battery determines the operating voltage; charge and discharge are electrochemical reactions. In comparison, the capacitor is non-electrochemical and the maximum allowable voltage is determined by the type of dielectric material used as separator between the plates. The presence of electrolyte in some capacitors boosts the capacitance and this may cause confusion.

Table 3 compares the supercapacitor with a typical Li-ion.

Function	Supercapacitor	Lithium-ion (general)
Charge time	1–10 seconds	10–60 minutes
Cycle life	1 million or 30,000h	500 and higher
Cell voltage	2.3 to 2.75V	3.6V nominal
Specific energy (Wh/kg)	5 (typical)	120–240
Specific power (W/kg)	Up to 10,000	1,000–3,000
Cost per kWh	\$10,000 (typical)	\$250–\$1,000 (large system)
Service life (industrial)	10–15 years	5 to 10 years
Charge temperature	–40 to 65°C (–40 to 149°F)	0 to 45°C (32° to 113°F)
Discharge temperature	–40 to 65°C (–40 to 149°F)	–20 to 60°C (–4 to 140°F)

Table 3: Performance comparison between supercapacitor and Li-ion.

Source: Maxwell Technologies, Inc.

## 2.2.5. Other Battery Systems

Other battery systems are fuel cells, sodium-sulfur batteries and flow batteries. A fuel cell is an electrochemical device that combines hydrogen fuel with oxygen to produce electricity, heat and water. The fuel cell is similar to a battery in that an electrochemical reaction occurs as long as fuel is available. Sodium-sulfur batteries, also known as sodium beta-alumina battery (NBB), molten salt or high temperature ceramic batteries, come in secondary versions only. The battery is characterized by a ceramic solid electrolyte and liquid electrodes: sodium in the anode and sulfur at the cathode. High conductivity is obtained by heating the stack to a temperature of 270–360°C (518–680°F). Finally, a flow battery is an electrical storage device that is a cross between a conventional battery and a fuel cell. Liquid electrolyte of metallic salts is pumped through a core that consists of a positive and negative electrode, separated by a membrane. The ion exchange that occurs between the cathode and anode generates electricity.

The media promotes wonderful new batteries that promise long runtimes, charge in minutes, are paper-thin and will one day power the electric car. While these experimental batteries produce a voltage, the downsides are seldom mentioned. The typical shortcomings are low load capacity and short cycle life. These batteries are zinc-air (primary and secondary), silver-zinc (primary and secondary) and reusable alkaline.

Most experimental batteries in the lithium family have one thing in common; they use a metallic lithium anode to achieve a higher specific energy than what is possible with the oxidized cathode in lithium-ion, the battery that is in common use today. However, these batteries pose a serious safety risk as the growth of lithium dendrites cause electric shorts leading to thermal runaway conditions. Researchers have also developed an anode structure for Li-ion batteries that is based on silicon-carbon nanocomposite materials. A silicon anode could theoretically store 10 times the energy of a graphite anode, but expansions and shrinkage during charge and discharge make the system unstable. Adding graphite to the

anode is said to achieve a theoretical capacity that is five times that of regular Li-ion with stable performance, however, the cycle life would be limited due to structural problems when inserting and extracting lithium-ion at high volume. Meeting the eight basic requirements of the octagon battery is a challenge. Commercialization appears to dwell on a moving target that is always a decade ahead, but scientists are not giving up. Some of the most promising experimental batteries are lithium-air (Li-air), lithium-metal (Li-metal), solid-state lithium, lithium-sulfur (Li-S), sodium-ion (Na-ion) and lithium-manganese-iron-phosphate (LMFP).

## 2.2.6. Summary Tables

Table 1 compares the characteristics of the four commonly used rechargeable battery systems, showing average performance ratings at time of publication. Li-ion is divided into different types, named by their active materials, which are cobalt, manganese, phosphate and titanate.

Specifications	Lead Acid	NiCd	NiMH	Li-ion <sup>1</sup>		
				Cobalt	Manganese	Phosphate
<b>Specific energy (Wh/kg)</b>	30–50	45–80	60–120	150–250	100–150	90–120
<b>Internal resistance</b>	Very Low	Very low	Low	Moderate	Low	Very low
<b>Cycle life<sup>2</sup> (80% DoD)</b>	200–300	1,000 <sup>3</sup>	300–500 <sup>3</sup>	500–1,000	500–1,000	1,000–2,000
<b>Charge time<sup>4</sup></b>	8–16h	1–2h	2–4h	2–4h	1–2h	1–2h
<b>Overcharge tolerance</b>	High	Moderate	Low	Low. No trickle charge		
<b>Self-discharge/month (room temp)</b>	5%	20% <sup>5</sup>	30% <sup>5</sup>	<5% Protection circuit consumes 3%/month		
<b>Cell voltage (nominal)</b>	2V	1.2V <sup>6</sup>	1.2V <sup>6</sup>	3.6V <sup>7</sup>	3.7V <sup>7</sup>	3.2–3.3V
<b>Charge cutoff voltage (V/cell)</b>	2.40 Float 2.25	Full charge detection by voltage signature		4.20 typical Some go to higher V		3.60
<b>Discharge cutoff voltage (V/cell, 1C)</b>	1.75V	1.00V		2.50–3.00V		2.50V
<b>Peak load current Best result</b>	5C <sup>8</sup> 0.2C	20C 1C	5C 0.5C	2C <1C	>30C <10C	>30C <10C
<b>Charge temperature</b>	–20 to 50°C (~4 to 122°F)	0 to 45°C (32 to 113°F)		0 to 45°C <sup>9</sup> (32 to 113°F)		
<b>Discharge temperature</b>	–20 to 50°C (~4 to 122°F)	–20 to 65°C (~4 to 149°F)		–20 to 60°C (~4 to 140°F)		
<b>Maintenance requirement</b>	3–6 months <sup>10</sup> (toping chg.)	Full discharge every 90 days when in full use		Maintenance-free		
<b>Safety requirements</b>	Thermally stable	Thermally stable, fuse protection		Protection circuit mandatory <sup>11</sup>		
<b>In use since</b>	Late 1800s	1950	1990	1991	1996	1999
<b>Toxicity</b>	Very high	Very high	Low	Low		
<b>Coulombic efficiency<sup>12</sup></b>	~90%	~70% slow charge ~90% fast charge		99%		
<b>Cost</b>	Low	Moderate		High <sup>13</sup>		

Table 1: Characteristics of commonly used rechargeable batteries. The figures are based on average ratings of commercial batteries at time of publication. Specialty batteries with above-average ratings are excluded.

1. Combining cobalt, nickel, manganese and aluminum raises energy density up to 250Wh/kg.
2. Cycle life is based on the depth of discharge (DoD). Shallow DoD prolongs cycle life.
3. Cycle life is based on battery receiving regular maintenance to prevent [memory](#).
4. Ultra-fast charge batteries are made for a special purpose. (See [BU-401a: Fast and Ultra-fast Chargers](#))
5. [Self-discharge](#) is highest immediately after charge. NiCd loses 10% in the first 24 hours, then declines to 10% every 30 days. High temperature and age increase self-discharge.
6. 1.25V is traditional; 1.20V is more common. (See [BU-303: Confusion with Voltages](#).)
7. Manufacturers may rate voltage higher because of low internal resistance (marketing).
8. Capable of high current pulses; needs time to recuperate.
9. Do not charge Li-ion below freezing. (See [BU-410: Charging at High and Low Temperatures](#).)
10. Maintenance may be in the form of equalizing or topping charge\* to prevent sulfation.
11. Protection circuit cuts off below about 2.20V and above 4.30V on most Li-ion; different voltage settings apply for lithium-iron-phosphate.
12. Coulombic efficiency is higher with quicker charge (in part due to self-discharge error).
13. Li-ion may have lower cost-per-cycle than lead acid.

\* Topping charge is applied on a battery that is in service or storage to maintain full charge and to prevent [sulfation](#) on lead acid batteries.

The term lithium-ion points to a family of batteries that shares similarities, but the chemistries can vary greatly. Li-cobalt, Li-manganese, NMC and Li-aluminum are similar in that they deliver high capacity and are used in portable applications. Li-phosphate and Li-titanate have lower voltages and have less capacity, but are very durable. These batteries are mainly found in wheeled and stationary uses. Table 2 summarizes the characteristics of major Li-ion batteries.

Chemistry	Lithium Cobalt Oxide	Lithium Manganese Oxide	Lithium Nickel Manganese Oxide	Lithium Iron Phosphate	Lithium Nickel Cobalt Aluminum Oxide	Lithium Titanate Oxide
Short form	Li-cobalt	Li-manganese	NMC	Li-phosphate	Li-aluminum	Li-titanate
Abbreviation	LiCoO <sub>2</sub> (LCO)	LiMn <sub>2</sub> O <sub>4</sub> (LMO)	LiNiMnCoO <sub>2</sub> (NMC)	LiFePO <sub>4</sub> (LFP)	LiNiCoAlO <sub>2</sub> (NCA)	Li <sub>2</sub> TiO <sub>3</sub> (common) (LTO)
Nominal voltage	3.60V	3.70V (3.80V)	3.60V (3.70V)	3.20, 3.30V	3.60V	2.40V
Full charge	4.20V	4.20V	4.20V (or higher)	3.65V	4.20V	2.85V
Full discharge	3.00V	3.00V	3.00V	2.50V	3.00V	1.80V
Minimal voltage	2.50V	2.50V	2.50V	2.00V	2.50V	1.50V (est.)
Specific Energy	150–200Wh/kg	100–150Wh/kg	150–220Wh/kg	90–120Wh/kg	200–260Wh/kg	70–80Wh/kg

Charge rate	0.7–1C (3h)	0.7–1C (3h)	0.7–1C (3h)	1C (3h)	1C	1C (5C max)
Discharge rate	1C (1h)	1C, 10C possible	1–2C	1C (25C pulse)	1C	10C possible
Cycle life (ideal)	500–1000	300–700	1000–2000	1000–2000	500	3,000–7,000
Thermal runaway	150°C (higher when empty)	250°C (higher when empty)	210°C (higher when empty)	270°C (safe at full charge)	150°C (higher when empty)	One of safest Li-ion batteries
Maintenance	Keep cool; store partially charged; prevent full charge cycles, use moderate charge and discharge currents					
Packaging (typical)	18650, prismatic and pouch cell	prismatic	18650, prismatic and pouch cell	26650, prismatic	18650	prismatic
History	1991 (Sony)	1996	2008	1996	1999	2008
Applications	Mobile phones, tablets, laptops, cameras	Power tools, medical devices, powertrains	E-bikes, medical devices, EVs, industrial	Stationary with high currents and endurance	Medical, industrial, EV (Tesla)	UPS, EV, solar street lighting
Comments	High energy, limited power. Market share has stabilized.	High power, less capacity; safer than Li-cobalt; often mixed with NMC to improve performance.	High capacity and high power. Market share is increasing. Also NCM, CMN, MNC, MCN	Flat discharge voltage, high power low capacity, very safe; elevated self-discharge.	Highest capacity with moderate power. Similar to Li-cobalt.	Long life, fast charge, wide temperature range and safe. Low capacity, expensive.

**Table 2: Summary of most common lithium-ion based batteries.** Experimental and less common lithium-based batteries are not listed. Readings are estimated averages at time of publication.

## 3. Packaging and Safety

### 3.1. Old and new Battery Packaging

Early batteries of the 1700s and 1800s developed in Europe were mostly encased in glass jars. As batteries grew in size, jars shifted to sealed wooden containers and composite materials. In the 1890s, battery manufacturing spread from Europe to the United States and in 1896 the National Carbon Company successfully produced a standard cell for widespread consumer use. With the move to portability, sealed cylindrical cells emerged that led to standards sizes. The International Electrochemical Commission (IEC), a non-governmental standards organization founded in 1906, developed standards for most rechargeable batteries. In around 1917, the National Institute of Standards and Technology formalized the alphabet nomenclature that is still used today.

Standardization included primary cells, mostly in zinc-carbon; alkaline emerged only in the early 1960s. With the growing popularity of the sealed nickel-cadmium in the 1950s and 1960s, new sizes appeared, many of which were derived from the "A" and "C" sizes. Beginning in the 1990s, makers of Li-ion departed from conventional sizes and invented their own standards. A successful standard is the 18650 cylindrical cell. Developed in the early 1990s for lithium-ion, these cells are used in laptops, electric bicycles and even electric vehicles (Tesla). The first two digits of 18650 designate the diameter in millimeters; the next three digits are the length in tenths of millimeters. The 18650 cell is 18mm in diameter and 65.0mm in length. Other sizes are identified with a similar numbering scheme. For example, a prismatic cell carries the number 564656P. It is 5.6mm thick, 46mm wide and 56mm long. P stands for prismatic. Because of the large variety of chemistries and their diversity within, battery cells do not show the chemistry.

Few popular new standards have emerged since the 18650 appeared in ca. 1991. Several battery manufacturers started experimenting using slightly larger diameters with sizes of 20x70mm, 21x70mm and 22x70mm. Panasonic and Tesla decided on the 21x70, so has Samsung, and other manufacturers followed. The "2170" is only slightly larger than the 18650 but has 35% more energy (by volume).

On the prismatic and pouch cell front, new cells are being developed for the electric vehicle (EV) and energy storage systems (ESS). Some of these formats may one day also become readily available similar to the 18650, made in high energy and high power versions, sourced by several manufacturers and sold at a competitive prices. Prismatic and pouch cells currently carry a higher price tag per Wh than the 18650. The EV and ESS markets advance with two distinct philosophies: The use of a large number of small cells produced by an automated process as low cost, as done by Tesla, versus larger cells in the prismatic and pouch formats at a higher price per Wh for now, as done by other EV manufacturers. We have not seen clear winners of either format; time will tell.

#### **Future Cell Formats**

Standardization for Li-ion cell formats is diverse, especially for the electric vehicle. Research teams, including Fraunhofer,\* examine and evaluate various formats and the most promising

cell types until 2025 will be the pouch and the 21700 cylindrical formats. Looking further, experts predict the large-size prismatic Li-ion cell to domineer in the EV battery market. Meanwhile, Samsung and others bet on the prismatic cell, LG gravitates towards the pouch format and Panasonic is most comfortable with the 18650 and 21700 cylindrical cells.

### Safety Concerns with Rechargeable Cells

Off-the-shelf cells have primarily been non-rechargeable and for public use. Typical applications are spares for flashlights, portable entertainment devices and remote controls. Accidental shorting with keys or coins in a jean pocket only causes an alkaline cell to heat up and not catch fire. The voltage collapses on an electrical short because of high internal resistance; removing the short stops the reaction.

Rechargeable cells are normally encapsulated in a for-purpose pack. The exception is the 18650 available as a spare cell for vaping. Looking like a large AA cell, these Li-ion cells can inflict acute injury, even death, if mishandled. If shorted, an unprotected Li-ion cell will vent with flame. Once the jet-like explosion is in progress, removing the short no longer stops the reaction and the cell burns out. Li-ion's ability to deliver high power is a characteristic that must be respected.

The 18650 cell can be made safe with built-in safety circuits. With protection, excessive current shuts the cell down, either momentarily by a heat element or permanently by an electric fuse. But the fused 18650 has the disadvantage of shutting down when high current is needed on purpose, such as vaping. Spare cells for vaping are normally unprotected.

Another cause of fire is low quality no-brand cells. Li-ion batteries are safe if made by a reputable manufacturer. Many aftermarket cells do not have the same rigorous safety checks as brand name products have. Cells can also be damaged by stress related to heat, shock, vibration and incorrect charging or loading.

Underwriters Laboratory (UL) may change the safety regulations by mandating that commercially available cells, like the 18650, cannot be removed by the customer.

\* Fraunhofer is Europe's largest research organization focusing on health, security, communication, energy and the environment.

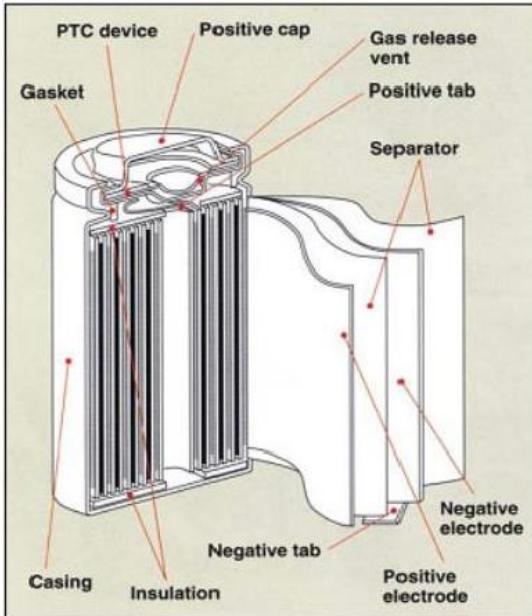
### 3.1.1. Types of Battery Cells

#### Cylindrical Cell

The cylindrical cell continues to be one of the most widely used packaging styles for primary and secondary batteries. The advantages are ease of manufacture and good mechanical stability. The tubular cylinder can withstand high internal pressures without deforming.

Many lithium and nickel-based cylindrical cells include a Positive Thermal Coefficient (PTC) switch, a Charge Interrupt Device (CID) and gas release vent as safety mechanisms.

Figure 1 shows a cross section of a cylindrical cell.



**Figure 1: Cross section of a lithium-ion cylindrical cell.**

The cylindrical cell design has good cycling ability, offers a long calendar life and is economical, but is heavy and has low packaging density due to space cavities.

Source: Sanyo

Typical applications for the cylindrical cell are power tools, medical instruments, laptops and e-bikes. The 18650 illustrated in Figure 2 remains one of the most popular cell packages. Typical applications for the 18650 Li-ion are power tools, medical devices, laptops and e-bikes.

Even though the cylindrical cell does not fully utilize the space by creating air cavities on side-by-side placement, the 18650 has a higher energy density than a prismatic/pouch Li-ion cell. The 3Ah 18650 delivers 248Ah/kg, whereas a modern pouch cell has about 140Ah/kg. The higher energy density of the cylindrical cell compensates for its less ideal stacking abilities and the empty space can always be used for cooling to improve thermal management.

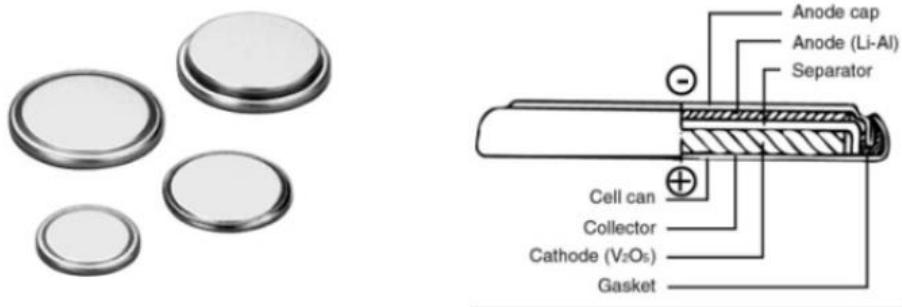


**Figure 2: Popular 18650 lithium-ion cell.**

Cell disintegration cannot always be prevented but propagation can. Cylindrical cells are often spaced apart to stop propagation should one cell take off. Spacing also helps in the thermal management. In addition, a cylindrical design does not change size. In comparison, a 5mm prismatic cell can expand to 8mm with use and allowances must be made.

### Button Cell

The button cell, also known as coin cell, enabled compact design in portable devices of the 1980s. Although small and inexpensive to build, the stacked button cell fell out of favor and gave way to more conventional battery formats. A drawback of the button cell is swelling if charged too rapidly. Button cells have no safety vent and can only be charged at a 10- to 16-hour charge. Most button cells in use today are non-rechargeable and are found in medical implants, watches, hearing aids, car keys and memory backup. Figure 4 illustrates the button cells with a cross section.

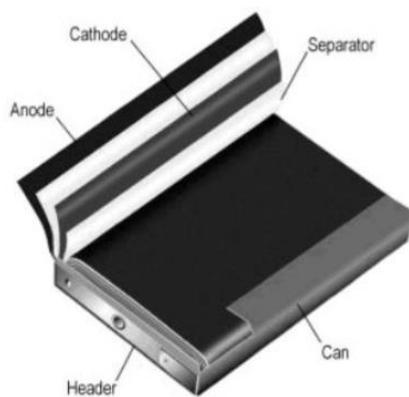


**Figure 4: Button cells** provides small size, most are primary for single-cell use.

Source: Sanyo and Panasonic

### Prismatic Cell

Introduced in the early 1990s, the modern prismatic cell satisfies the demand for thinner sizes. Wrapped in elegant packages resembling a box of chewing gum or a small chocolate bar, prismatic cells make optimal use of space by using the layered approach. Other designs are wound and flattened into a pseudo-prismatic jelly roll. These cells are predominantly found in mobile phones, tablets and low-profile laptops ranging from 800mAh to 4,000mAh. No universal format exists and each manufacturer designs its own. Prismatic cells are also available in large formats. Packaged in welded aluminum housings, the cells deliver capacities of 20–50Ah and are primarily used for electric powertrains in hybrid and electric vehicles. Figure 5 shows the prismatic cell.



**Figure 5: Cross section of a prismatic cell.**

The prismatic cell improves space utilization and allows flexible design but it can be more expensive to manufacture, less efficient in thermal management and have a shorter cycle life than the cylindrical design. Allow for some swelling.

Source: Polystor Energy Corporation

The prismatic cell requires a firm enclosure to achieve compression. Some swelling due to gas buildup is normal, and growth allowance must be made; a 5mm (0.2") cell can grow to 8mm (0.3") after 500 cycles.

## Pouch Cell

In 1995, the pouch cell surprised the battery world with a radical new design. Rather than using a metallic cylinder and glass-to-metal electrical feed-through, conductive foil-tabs were welded to the electrodes and brought to the outside in a fully sealed way. Figure 6 illustrates a pouch cell.

The pouch cell makes most efficient use of space and achieves 90–95 percent packaging efficiency, the highest among battery packs. Eliminating the metal enclosure reduces weight, but the cell needs support and allowance to expand in the battery compartment. The pouch packs are used in consumer, military and automotive applications. No standardized pouch cells exist; each manufacturer designs its own.



Figure 6: The pouch cell.

Pouch packs are commonly Li-polymer. Small cells are popular for portable applications requiring high load currents, such as drones and hobby gadgets. The larger cells in the 40Ah range serve in energy storage systems (ESS) because fewer cells simplify the battery design.

Although easily stackable, provision must be made for swelling. While smaller pouch packs can grow 8–10 percent over 500 cycles, large cells may expand to that size in 5,000 cycles. It is best not to stack pouch cells on top of each other but to lay them flat, side by side or allow extra space in between them. Avoid sharp edges that can stress the pouch cells as they expand.

Extreme swelling is a concern. Users of pouch packs have reported up to 3 percent swelling incidents on a poor batch run. The pressure created can crack the battery cover, and in some cases, break the display and electronic circuit boards. Discontinue using an inflated battery and do not puncture the bloating cell in close proximity to heat or fire. The escaping gases can ignite. Figure 7 shows a swollen pouch cell.



Figure 7: Swollen pouch cell.

Swelling can occur due to gassing. Improvements are being made with newer designs. Large pouch cells designs experience less swelling. The gases contain mainly CO<sub>2</sub> (carbon dioxide) and CO (carbon monoxide).

Source: Cadex

Pouch cells are manufactured by adding a temporary “gasbag” on the side. Gases escape into the gasbag while forming the solid electrolyte interface (SEI) during the first charge. The gasbag is cut off and the pack is resealed as part of the finishing process. Forming a solid SEI is key to good formatting practices. Subsequent charges should produce minimal gases, however, gas generation, also known as gassing, cannot be fully avoided. It is caused by

electrolyte decomposition as part of usage and aging. Stresses, such as overcharging and overheating promote gassing. Ballooning with normal use often hints to a flawed batch.

The technology has matured and prismatic and pouch cells have the potential for greater capacity than the cylindrical format. Large flat packs serve electric powertrains and Energy Storage System (ESS) with good results. The cost per kWh in the prismatic/pouch cell is still higher than with the 18650 cell but this is changing. Flat-cell designs are getting price competitive and battery experts predict a shift towards these cell formats, especially if the same performance criteria of the cylindrical cell can be met.

### **Summary**

With the pouch cell, the manufacturer is attempting to simplify cell manufacturing by replicating the packaging of food. Each format has pros and cons as summarized below.

Cylindrical cell has high specific energy, good mechanical stability and lends itself to automated manufacturing. Cell design allows added safety features that are not possible with other formats (see BU-304b: Making Lithium-ion Safe); it cycles well, offers a long calendar life and is low cost, but it has less than ideal packaging density. The cylindrical cell is commonly used for portable applications.

Prismatic cell are encased in aluminum or steel for stability. Jelly-rolled or stacked, the cell is space-efficient but can be costlier to manufacture than the cylindrical cell. Modern prismatic cells are used in the electric powertrain and energy storage systems.

Pouch cell uses laminated architecture in a bag. It is light and cost-effective but exposure to humidity and high temperature can shorten life. Adding a light stack pressure prolongs longevity by preventing delamination. Swelling of 8–10 percent over 500 cycles must be considered with some cell designs. Large cells work best with light loading and moderate charge times. The pouch cell is growing in popularity and serves similar applications to the prismatic cell.

## **3.2. Series and Parallel Battery Configurations**

Batteries achieve the desired operating voltage by connecting several cells in series; each cell adds its voltage potential to derive at the total terminal voltage. Parallel connection attains higher capacity by adding up the total ampere-hour (Ah).

Some packs may consist of a combination of series and parallel connections. Laptop batteries commonly have four 3.6V Li-ion cells in series to achieve a nominal voltage 14.4V and two in parallel to boost the capacity from 2,400mAh to 4,800mAh. Such a configuration is called 4s2p, meaning four cells in series and two in parallel. Insulating foil between the cells prevents the conductive metallic skin from causing an electrical short.

Most battery chemistries lend themselves to series and parallel connection. It is important to use the same battery type with equal voltage and capacity (Ah) and never to mix different makes and sizes. A weaker cell would cause an imbalance. This is especially critical in a series configuration because a battery is only as strong as the weakest link in the chain.

A weak cell may not fail immediately but will get exhausted more quickly than the strong ones when on a load. On charge, the low cell fills up before the strong ones because there is less to fill and it remains in over-charge longer than the others. On discharge, the weak cell empties first and gets hammered by the stronger brothers. Cells in multi-packs must be matched, especially when used under heavy loads.

### Single Cell Applications

The single-cell configuration is the simplest battery pack; the cell does not need matching and the protection circuit on a small Li-Ion cell can be kept simple. Typical examples are mobile phones and tablets with one 3.60V Li-ion cell.

### Series Connection

Portable equipment needing higher voltages use battery packs with two or more cells connected in series. Figure 2 shows a battery pack with four 3.6V Li-ion cells in series, also known as 4S, to produce 14.4V nominal.



**Figure 2: Series connection of four cells (4s).**

Adding cells in a string increases the voltage; the capacity remains the same.

Courtesy of Cadex

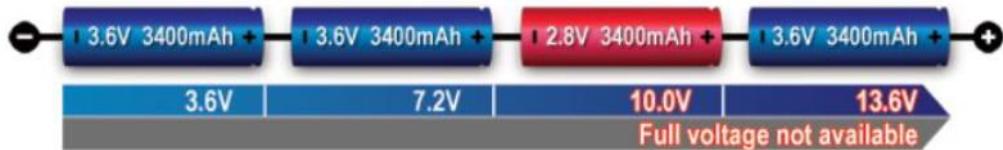
If you need an odd voltage of, say, 9.50 volts, connect five lead acid, eight NiMH or NiCd, or three Li-ion in series. The end battery voltage does not need to be exact as long as it is higher than what the device specifies. A 12V supply might work in lieu of 9.50V. Most battery-operated devices can tolerate some over-voltage; the end-of-discharge voltage must be respected, however.

High-voltage batteries require careful cell matching, especially when drawing heavy loads or when operating at cold temperatures. With multiple cells connected in a string, the possibility of one cell failing is real and this would cause a failure. To prevent this from happening, a solid state switch in some large packs bypasses the failing cell to allow continued current flow, albeit at a lower string voltage.

Cell matching is a challenge when replacing a faulty cell in an aging pack. A new cell has a higher capacity than the others, causing an imbalance. Welded construction adds to the complexity of the repair, and this is why battery packs are commonly replaced as a unit.

High-voltage batteries in electric vehicles, in which a full replacement would be prohibitive, divide the pack into modules, each consisting of a specific number of cells. If one cell fails, only the affected module is replaced. A slight imbalance might occur if the new module is fitted with new cells.

Figure 3 illustrates a battery pack in which “cell 3” produces only 2.8V instead of the full nominal 3.6V. With depressed operating voltage, this battery reaches the end-of-discharge point sooner than a normal pack. The voltage collapses and the device turns off with a “Low Battery” message.



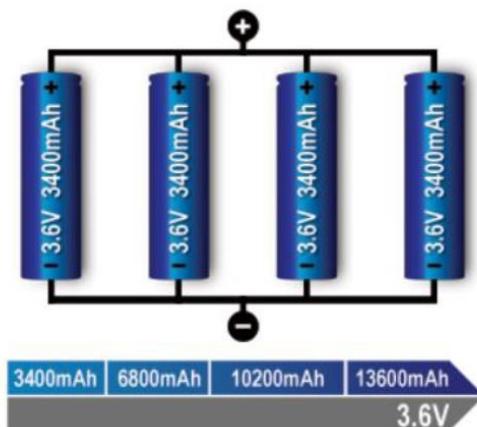
**Figure 3: Series connection with a faulty cell.**

Faulty cell 3 lowers the voltage and cuts the equipment off prematurely.

Courtesy of Cadex

### Parallel Connection

If higher currents are needed and larger cells are not available or do not fit the design constraint, one or more cells can be connected in parallel. Most battery chemistries allow parallel configurations with little side effect. Figure 4 illustrates four cells connected in parallel in a P4 arrangement. The nominal voltage of the illustrated pack remains at 3.60V, but the capacity (Ah) and runtime are increased fourfold.

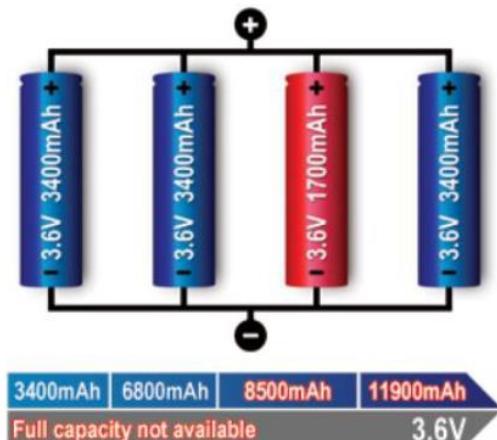


**Figure 4: Parallel connection of four cells (4p).**

With parallel cells, capacity in Ah and runtime increases while the voltage stays the same.

Courtesy of Cadex

A cell that develops high resistance or opens is less critical in a parallel circuit than in a series configuration, but a failing cell will reduce the total load capability. An electrical short, on the other hand, is more serious as the faulty cell drains energy from the other cells, causing a fire hazard. Most so-called electrical shorts are mild and manifest themselves as elevated self-discharge. A total short can occur through reverse polarization or dendrite growth. Large packs often include a fuse that disconnects the failing cell from the parallel circuit if it were to short. Figure 5 illustrates a parallel configuration with one faulty cell.



**Figure 5: Parallel/connection with one faulty cell.**

A weak cell will not affect the voltage but provide a low runtime due to reduced capacity. A shorted cell could cause excessive heat and become a fire hazard. On larger packs a fuse prevents high current by isolating the cell.

Courtesy of Cadex

### Series/parallel Connection

The series/parallel configuration shown in Figure 6 enables design flexibility and achieves the desired voltage and current ratings with a standard cell size. The total power is the sum of voltage times current; a 3.6V (nominal) cell multiplied by 3,400mAh produces 12.24Wh. Four 18650 Energy Cells of 3,400mAh each can be connected in series and parallel as shown to get 7.2V nominal and a total of 48.96Wh. The slim cell allows flexible pack design but a protection circuit is needed.



**Figure 6: Series/ parallel connection of four cells (2s2p).**

This configuration provides maximum design flexibility. Paralleling the cells helps in voltage management.

Courtesy of Cadex

Li-ion lends itself well to series/parallel configurations but the cells need monitoring to stay within voltage and current limits. Integrated circuits (ICs) for various cell combinations are available to supervise up to 13 Li-ion cells. Larger packs need custom circuits, and this applies to e-bike batteries, hybrid cars and the Tesla Model 85 that devours over 7000 18650 cells to make up the 90kWh pack.

### 3.3. Confusion with Voltages

A battery is an electrochemical device that produces a voltage potential when placing metals of different affinities into an acid solution (electrolyte). The open circuit voltage (OCV) that develops as part of an electrochemical reaction varies with the metals and electrolyte used.

Applying a charge or discharge places the battery into the closed circuit voltage (CCV) condition. Charging raises the voltage and discharging lowers it, simulating a rubber band effect. This voltage behavior under a load and charge is governed by the current flow and the internal battery resistance. A low resistance produces low fluctuation under load or charge; a high resistance causes the voltage to swing excessively. Charging and discharging agitates the battery; full voltage stabilization takes up to 24 hours. Temperature also plays a role; a cold temperature lowers the voltage and heat raises it.

Manufacturers rate a battery by assigning a nominal voltage, and with a few exceptions, these voltages follow an agreed convention. The nominal voltage of lithium-ion is 3.60V/cell. Some cell manufacturers mark their Li-ion as 3.70V/cell or higher. This offers a marketing advantage because the higher voltage boosts the watt-hours on paper (voltage multiplied by current equals watts).

How did this higher voltage creep in? The nominal voltage is a function of anode and cathode materials, as well as impedance. Voltage calculations include measuring the mid-way point from a full-charge of 4.20V/cell to the 3.0V/cell cutoff with a 0.5C load. For Li-cobalt the mid-way point is about 3.60V. The same scan done on Li-manganese with a lower internal resistance gives an average voltage of about 3.70V. It should be noted that the higher voltage is often set arbitrarily and does not affect the operation of portable devices or the setting of the chargers. But there are exceptions.

Some Li-ion batteries with LCO architecture feature a surface coating and electrolyte additives that increase the nominal cell voltage and permit higher charge voltages. To get the full capacity, the charge cut-off voltage for these batteries must be set accordingly. Figure 1 shows typical voltage settings.

Nominal cell voltage	Typical end-of-discharge	Max charge voltage	Notes
3.6V	2.8–3.0V	4.2V	Classic nominal voltage of cobalt-based Li-ion battery
3.7V	2.8–3.0V	4.2V	Marketing advantage. Achieved by low internal resistance
3.8V	2.8–3.0V	4.35V	Surface coating and electrolyte additives. Charger must have correct full-charge voltage for added capacity
3.85V	2.8–3.0V	4.4V	Surface coating and electrolyte additives. Charger must have correct full-charge voltage for added capacity

**Figure 1: Voltages of cobalt-based Li-ion batteries.** End-of-charge voltage must be set correctly to achieve the capacity gain.

Battery users want to know if Li-ion cells with higher charge voltages compromise longevity and safety. There is limited information available but what is known is that, yes, these batteries have a shorter cycle life than a regular Li-ion; the calendar life can also be less. Since these batteries are mostly used in consumer products, the longevity can be harmonized with obsolescence, making a shorter battery life acceptable. The benefit is longer a runtime because of the gained Wh (Ah x V). All cells must meet regulatory standards and are safe.

### 3.4. Protection Circuits

Batteries can release high energies and the safety requirements for nickel- and lithium-based batteries and cells for portable applications are harmonized under IEC 62133. The standard came into effect in 2012 to reduce the global risk in transporting, storing and operating batteries.

The most basic safety device in a battery is a fuse that opens on high current. Some fuses open permanently and render the battery useless; others are more forgiving and reset. Figure 1 illustrates the top of an 18650 cell for Li-ion with built-in safety features.

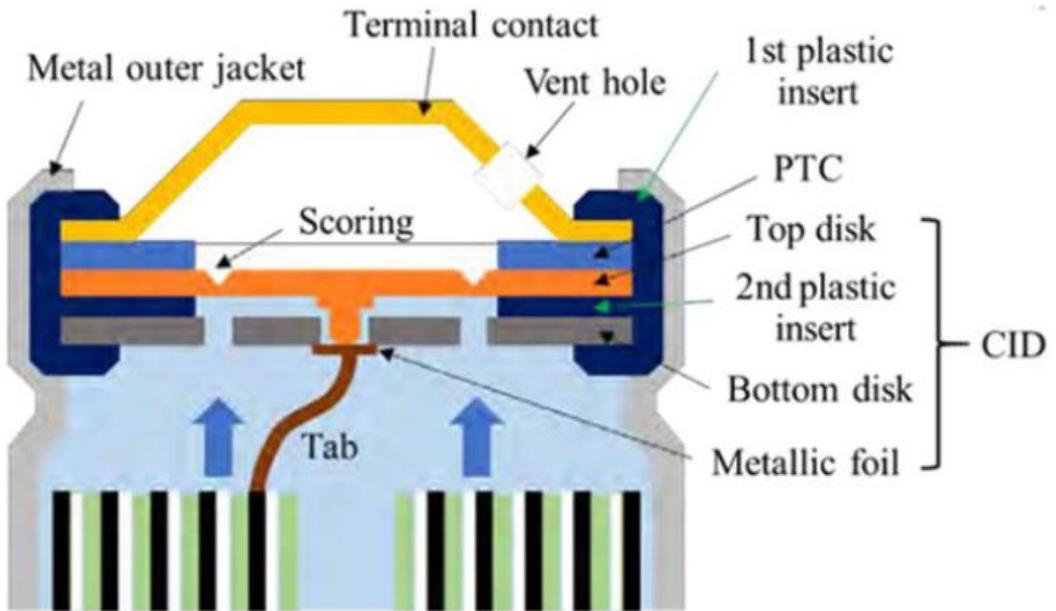
The resistance of the positive thermal coefficient (PTC) (blue) is low during normal operation and increases when the temperature rises above a critical level to reduce current flow. The PTC is reversible and returns to high conductivity when the temperature normalizes.

The current interrupt device (CID) is a fuse-type device that cuts off the electrical circuit permanently when triggered by excessive cell pressure, high temperature, or high voltage, depending on design. In Figure 1, the CID operates by pressure. When the internal pressure increases to about 1,000kPa, the scored top disk (orange) breaks, separates from the metallic foil (brown) and disconnects the current flow. This also allows gas to vent.

The last safety device is the vent that releases gas during an anomaly and can be resealed. However, the pressure of a disintegrating cell can be so large that the gases are unable to escape in an orderly way and venting with flame occurs. In some cases the top of the cell escapes like a bullet from a shotgun. Similar to a nuclear meltdown that cannot be stopped once in progress; a Li-ion battery once in disintegration should be allowed to burn out in a safe place with ventilation.

Protection devices have a residual resistance that causes a slight decrease in overall performance due to a resistive voltage drop. Not all cells have built-in protections and the responsibility for safety in its absence falls to the Battery Management System (BMS).

Further layers of safeguards can include solid-state switches in a circuit that is attached to the battery pack to measure current and voltage and disconnect the circuit if the values are too high. Protection circuits for Li-ion packs are mandatory.



**Figure 1: Typical safety mechanism of the 18650 cell cap.**

PTC (blue) increases resistance by heat to reduce electrical current. The effect is reversible.

CID consists of a top disk (orange) that breaks under pressure and permanently disconnects the current flow.

Source: CALCE (Center for Advanced Life Cycle Engineering)

The PTC and CID work well in a smaller 2- or 3-cell pack with serial and parallel configuration, however, these safety devices are often omitted in larger multi-cell batteries, such as those for power tools, because the shutdown can occur in a cascade format. While some cells may go offline early, the load current causes excess current on the remaining cells. Such overload condition could lead to a thermal runaway before the remaining safety devices activate.

In addition to internal cell safeguards, an external electronic protection circuit prevents any cell from exceeding its maximum voltage on charge. In addition, a fuse cuts the current if the skin temperature of any cell approaches its temperature limit. To prevent the battery from over-discharging, a control circuit cuts off the current path at cut-off voltage.

Each cell in a string needs independent voltage monitoring. The higher the cell count, the more complex the protection circuit becomes. Monitoring two or more cells in parallel to get higher current is less critical than controlling the voltage in a string configuration.

Protection circuits can only shield abuse from the outside, such as an electrical short or faulty charger. If, however, a defect occurs within the cell, such as a contamination of microscopic metal particles, the external protection circuit has little effect and cannot arrest the reaction. Reinforced and self-healing separators are being developed for cells used in electric powertrains, but this makes the batteries large and expensive.

### 3.5. Safety concerns with Li-ion

Safety of lithium-based batteries has attracted much media and legal attention. All batteries carry a safety risk, and battery makers are obligated to meet safety requirements; less reputable firms are known to make shortcuts and it's "buyer beware!"

Lithium-ion is safe but with millions of consumers using batteries, failures are bound to happen. In 2006, a one-in-200,000 breakdown triggered a recall of almost six million lithium-ion packs. Sony, the maker of the lithium-ion cells in question, points out that on rare occasion microscopic metal particles may come into contact with other parts of the battery cell, leading to a short circuit within the cell. Battery manufacturers strive to minimize the presence of metallic particles.

A compromised Li-ion can make its way into the workforce undetected and deteriorate without knowing. Resulting failures are especially critical with the thinning of the separators to increase the specific energy. Cells with ultra-thin separators of  $24\mu\text{m}$  or less are more susceptible to impurities than the older designs with lower Ah ratings. Whereas the 1,350mAh cell in the 18650 package could tolerate a nail penetration test, the high-density 3,400mAh can ignite when performing the same test. New safety standards direct how batteries are used, and the UL1642 Underwriters Laboratories (UL) test no longer mandates nail penetration for safety acceptance of lithium-based batteries.

Li-ion using conventional metal oxides is nearing its theoretical limit on specific energy. Rather than optimizing capacity, battery makers are improving manufacturing methods to enhance safety and increase calendar life. The real problem lies when on rare occasions an electrical short develops inside the cell. The external protection peripherals are ineffective to stop a thermal runaway once in progress. The batteries recalled in 2006 had passed the UL safety requirements — yet they failed under normal use with appropriate protection circuits.

Let's examine the inner workings of the cell more closely. A mild short will only cause elevated self-discharge and the heat buildup is minimal because the discharging power is very low. If enough microscopic metallic particles converge on one spot, a sizable current begins to flow between the electrodes of the cell, and the spot heats up and weakens. As a small water leak in a faulty hydro dam can develop into a torrent and take a structure down, so too can heat buildup damage the insulation layer in a cell and cause an electrical short. The temperature can quickly reach 500C (932F), at which point the cell catches fire or it explodes. This thermal runaway that occurs is known as "venting with flame." "Rapid disassembly" is the preferred term by the battery industry.

Uneven separators can also trigger cell failure. Poor conductivity due to dry areas increases the resistance, which can generate local heat spots that weaken the integrity of the separator. Heat is always an enemy of the battery.

There are two basic types of battery failures. One occurs at a predictable interval-per-million and is connected with a design flaw involving the electrode, separator, electrolyte or processes. These defects often involve a recall to correct a discovered flaw. The more difficult failures are random events that do not point to a design flaw. It may be a stress event like charging at sub-freezing temperature, vibration, or a fluke incident that is comparable to being hit by a meteor.

Incorrect uses of all batteries are excessive vibration, elevated heat and charging Li-ion below freezing. Li-ion and lead acid batteries cannot be fully discharged and must be stored with a remaining charge. While nickel-based batteries can be stored in a fully discharged state with no apparent side effect, Li-ion must not dip below 2V/cell for any length of time. Copper shunts form inside the cells that can lead to elevated self-discharge or a partial electrical short. If recharged, the cells might become unstable, causing excessive heat or showing other anomalies.

Heat combined with a full charge is said to induce more stress to Li-ion than regular cycling. Keep the battery and a device away from sun exposure and store in a cool place at a partial charge. Exceeding the recommended charge current by ultra-fast charging also harms Li-ion. Nickel-cadmium is the only chemistry that accepts ultra-fast charging with minimal stress.

Li-ion batteries that have been exposed to stresses may function normally but they become more sensitive to mechanical abuse. The liability for a failed battery goes to the manufacturer even if the fault may have been caused by improper use and handling. This worries the battery manufacturers and they go the extra mile to make their products safe. Treat the battery as if it were a living organism by preventing excess stress.

Power Cells have a lower Ah rating than Energy Cells and are in general more tolerant and safer if abused.

To sum up, lithium-ion batteries have become very safe and heat-related failures occur rarely when used correctly.

### 3.5.1. What to do when a Battery overheats or catches fire

If a Li-ion battery overheats, hisses or bulges, immediately move the device away from flammable materials and place it on a non-combustible surface. If at all possible, remove the battery and put it outdoors to burn out. Simply disconnecting the battery from charge may not stop its destructive path.

A small Li-ion fire can be handled like any other combustible fire. For best result use a foam extinguisher, CO<sub>2</sub>, ABC dry chemical, powdered graphite, copper powder or soda (sodium carbonate). If the fire occurs in an airplane cabin, the FAA instructs flight attendants to use water or soda pop. Water-based products are most readily available and are appropriate since Li-ion contains very little lithium metal that reacts with water. Water also cools the adjacent area and prevents the fire from spreading. Research laboratories and factories also use water to extinguish Li-ion battery fires.

With the increased use of Li-ion batteries, improved methods to extinguish lithium fires have been developed. The Aqueous Vermiculite Dispersion (AVD) fire extinguishing agent disperses chemically exfoliated vermiculite in the form of a mist that provides advantages over existing products.

A large Li-ion fire, such as in an EV, may need to burn out. Water with copper material can be used, but this may not be available and is costly for fire halls. Increasingly, experts advise using water even with large Li-ion fires. Water lowers combustion temperature but is not recommended for battery fires containing lithium-metal.

When encountering a fire with a lithium-metal battery, only use a Class D fire extinguisher. Lithium-metal contains plenty of lithium that reacts with water and makes the fire worse. As the number of EVs grows, so must the methods to extinguish such fires.

During a thermal runaway, the high heat of the failing cell inside a battery pack may propagate to the next cells, causing them to become thermally unstable also. A chain reaction can occur in which each cell disintegrates on its own timetable. A pack can thus be destroyed in a few seconds or over several hours as each cell is being consumed. To increase safety, packs should include dividers to protect the failing cell from spreading to the neighboring one.

The knowledge on the toxicity of burning electrolyte is limited and toxicity can be higher than with regular combustibles. Ventilate the room and vacate area if smoke and gases are present.

### 3.6. Building a Li-ion Pack

Building a Li-ion battery pack begins by satisfying voltage and runtime requirements, and then taking loading, environmental, size and weight limitations into account. Portable designs for consumer products want a slim profile and the choice is a prismatic or pouch cell. If space allows, a cylindrical cell such as the 18650 often provides the lowest cost and best performance in terms of specific energy, safety and durability.

Most battery packs for medical devices, power tools, e-bikes and even powertrains for electric cars (EV) are based on the 18650. This appears impractical but the small cell works well because it is one of the most mature Li-ion formats available, is produced in high volume and enjoys a low cost per Wh.

The cylindrical cell is not ideal as it leaves empty spaces in a multi-cell configuration. This disadvantage turns into an advantage when considering flexibility and cooling. The Tesla S85 EV uses over 7,000 cells, switched in parallel to boost the current and in series to increase the voltage. Should one cell in series open, the total power loss is minimal; if one in parallel shorts, fuse protection removes this cell from the circuit. Failing cells can thus be eliminated without bringing the battery down.

EV manufacturers are not united on the choice of cell, but there is a trend towards larger formats to reduce supportive electronics that adds 20–25 percent to the finished pack. With a larger cell, however, the electronic components get dearer because of higher current handling. According to 2015 reports, the Tesla S 85 has the lowest cost per kWh using the 18650. Other EVs have larger prismatic cells at higher kWh costs. Table 1 compares the kWh cost.

Make and model	Cell type	Cost per kWh	Specific energy
Tesla S 85, 90kWh (2015)*	18650	\$260/kWh	250Wh/kg
Tesla 48kWh Gen III	18650	\$260/kWh	250Wh/kg
Best practices DoE/AABC)	pouch/prismatic	\$350/kWh	150–180Wh/kg
Nissan Leaf, 30kWh (2016)*	pouch/prismatic	\$455/kWh	80–96Wh/kg
BMW i3	pouch/prismatic	N/A	120Wh/kg

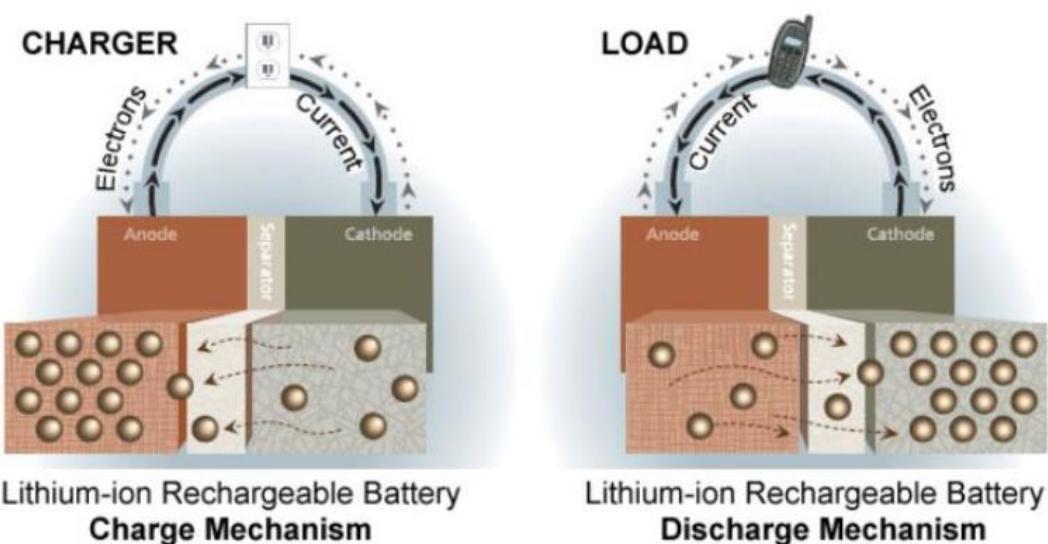
**Table 1: Price comparison of EV batteries.** Mass production allows a low price using the 18650 cell.

\* In 2015/16 Tesla S 85 increased the battery from 85kWh to 90kWh; Nissan Leaf from 25kWh to 30kWh.

### 3.6. Separator

The building blocks of a battery are the cathode and anode, and these two electrodes are isolated by a separator. The separator is moistened with electrolyte and forms a catalyst that promotes the movement of ions from cathode to anode on charge and in reverse on discharge. Ions are atoms that have lost or gained electrons and have become electrically charged. Although ions pass freely between the electrodes, the separator is an isolator with no electrical conductivity.

The small amount of current that may pass through the separator is self-discharge and this is present in all batteries to varying degrees. Self-discharge eventually depletes the charge of a battery during prolonged storage. Figure 1 illustrates the building block of a lithium-ion cell with the separator and ion flow between the electrodes.



**Figure 1. Ion flow through the separator of Li-ion.** Battery separators provide a barrier between the anode (negative) and the cathode (positive) while enabling the exchange of lithium ions from one side to the other.

Source: CELGARD, LLC

Early batteries were flooded, including lead acid and nickel-cadmium. With the development of the sealed nickel-cadmium in 1947 and the maintenance-free lead acid in the 1970s, the electrolyte is absorbed into a porous separator that is compressed against the electrodes to achieve chemical reaction. The tightly wound or stacked separator/electrode arrangement forms a solid mechanical unit that offers similar performance to the flooded type but is smaller and can be installed in any orientation without leakage. The gases created during charge are absorbed and there is no water loss if venting can be prevented.

Early separators were made of rubber, glass fiber mat, cellulose and polyethylene plastic. Wood was the original choice but it deteriorated in the electrolyte. Nickel-based batteries use separators of porous polyolefin films, nylon or cellophane. The absorbed glass mat (AGM) in the sealed lead acid version uses a glass fiber mat as a separator that is soaked in sulfuric acid.

Commercially available Li-ion cells use polyolefin as a separator. This material has excellent mechanical properties, good chemical stability and is low-cost. A polyolefin is a class of polymer that is produced from olefin by polymerizing olefin ethylene. Ethylene comes from a

petrochemical source; polyolefin is made from polyethylene, polypropylene or laminates of both materials. The Li-ion separator must be permeable and the pore size ranges from 30 to 100nm. The recommended porosity is 30–50 percent. This holds enough liquid electrolyte and enables the pores to close should the cell overheat.

On excessive heat, a shut-down occurs by closing the pores of the Li-ion separator through a melting process. The polyethylene (PE) separator melts when the core reaches 130°C (266°F). This stops the transport of ions, effectively shutting the cell down. Without this provision, heat in the failing cell could rise to the thermal runaway threshold and vent with flame.

The separator should be as thin as possible so as to not add dead volume and still provide sufficient tensile strength to prevent stretching during the winding process and offer good stability throughout life. The pores must be uniformly spread on the sheet to ensure even distribution throughout the entire separator area. Furthermore, the separator must be compatible with the electrolyte and allow easy wetting. Dry areas can create hot spots through elevated resistance, leading to cell failure.

Separators are getting thinner. A thickness of 25.4µm is common but some go down to 20µm, 16µm and now even 12µm without significantly compromising the properties of the cell (See: 3.5. Safety Concerns with Li-ion). The separator with electrolyte in modern Li-ion only makes up 3 percent of the cell content.

## 3.8. Electrolyte

Electrolyte serves as catalyst to make a battery conductive by promoting the movement of ions from the cathode to the anode on charge and in reverse on discharge. The electrolyte of a battery consists of soluble salts, acids or other bases in liquid, gelled and dry formats. Electrolyte also comes in a polymer, as used in the solid-state battery, solid ceramic and molten salts, as in the sodium-sulfur battery. Lead acid uses sulfuric acid as electrolyte, while nickel-cadmium (NiCd) and nickel-metal-hydride (NiMH) uses mostly potassium hydroxide.

### Lithium-ion (Li-ion)

Li-ion uses liquid, gel or dry polymer electrolyte. The liquid version is a flammable organic rather than aqueous type, a solution of lithium salts with organic solvents similar to ethylene carbonate. Mixing the solutions with diverse carbonates provides higher conductivity and expands the temperature range. Other salts may be added to reduce gassing and improve high temperature cycling.

Li-ion with gelled electrolytes receives many additives to increase conductivity, so does the lithium-polymer battery. The true dry polymer only becomes conductive at elevated temperatures, and this battery is no longer in commercial use. Additives are also administered to achieve longevity and unique characteristics. The recipe is classified and each manufacturer has its own secret sauce.

The electrolyte should be stable, but this is not the case with Li-ion. A passivation film forms on the anode that is called solid electrolyte interface (SEI). This layer separates the anode from the cathode but allows ions to pass through much like a separator. In essence, the SEI layer must form to enable the battery to work. The film stabilizes the system and gives the Li-ion a

long life but this causes a capacity reduction. Electrolyte oxidation also occurs on the cathode that permanently lowers the capacity.

To prevent the films from becoming too restrictive, additives are mixed with the electrolyte that is consumed during the formation of the SEI layer. It is difficult, if impossible, to trace their presence when doing a forensic evaluation. This keeps proprietary additives a trade secret, both their composition and the amount used.

For most commercial Li-ion, the SEI layer will break down at a cell temperature of 75–90°C (167–194°F). The type of cell and state-of-charge (SoC) affects the breakdown at elevated temperature. A self-heating behavior may occur that can lead to a thermal runaway if not properly cooled. Lab tests done on 18650 cells have shown that such a thermal event can take two days to develop.

The flammability of the Li-ion electrolyte is a further concern and experiments are done to produce non-flammable or reduced flammable electrolytes by additives or developing non-organic ionic liquids. Research is also conducted to operate Li-ion at low temperatures. At time of writing, none of these electrolytes are in wide commercial use.

Drying up or slowly turning the liquid electrolyte into a solid form is one more aging event that lowers the performance of Li-ion. “When the liquid is gone, the batteries are dead,” says Jeff Dahn, specialist in Li-ion batteries and Professor of Physics. Liquidity of the electrolyte is one more state-of-health indicator that relates to all battery chemistries.

## 4. Charge Methods

### 4.1. C-Rate

Charge and discharge rates of a battery are governed by C-rates. The capacity of a battery is commonly rated at 1C, meaning that a fully charged battery rated at 1Ah should provide 1A for one hour. The same battery discharging at 0.5C should provide 500mA for two hours, and at 2C it delivers 2A for 30 minutes. Losses at fast discharges reduce the discharge time and these losses also affect charge times.

A C-rate of 1C is also known as a one-hour discharge; 0.5C or C/2 is a two-hour discharge and 0.2C or C/5 is a 5-hour discharge. Some high-performance batteries can be charged and discharged above 1C with moderate stress. Table 1 illustrates typical times at various C-rates.

C-rate	Time
5C	12 min
2C	30 min
<b>1C</b>	<b>1h</b>
0.5C or C/2	2h
0.2C or C/5	5h
0.1C or C/10	10h
0.05C or C/20	20h

**Table 1: C-rate and service times when charging and discharging batteries of 1Ah (1,000mAh)**

When discharging a battery with a battery analyzer capable of applying different C rates, a higher C rate will produce a lower capacity reading and vice versa. By discharging the 1Ah battery at the faster 2C-rate, or 2A, the battery should ideally deliver the full capacity in 30 minutes. The sum should be the same since the identical amount of energy is dispensed over a shorter time. In reality, internal losses turn some of the energy into heat and lower the resulting capacity to about 95 percent or less. Discharging the same battery at 0.5C, or 500mA over 2 hours, will likely increase the capacity to above 100 percent.

## 4.2. Battery Chargers

A good battery charger provides the base for batteries that are durable and perform well. In a price-sensitive market, chargers often receive low priority and get the “after-thought” status. Battery and charger must go together like a horse and carriage. Prudent planning gives the power source top priority by placing it at the beginning of the project rather than after the hardware is completed, as is a common practice. Engineers are often unaware of the complexity involving the power source, especially when charging under adverse conditions.

Chargers are commonly identified by their charging speed. Consumer products come with a low-cost personal charger that performs well when used as directed. Although batteries operate below freezing, not all chemistries can be charged when cold and most Li-ions fall into this category. Lead- and nickel-based batteries accept charge when cold but at a lower rate.

Some Li-ion chargers (Cadex) include a wake-up feature, or “boost,” to allow recharging if a Li-ion battery has fallen asleep due to over-discharge. A sleep condition can occur when storing the battery in a discharged state in which self-discharge brings the voltage to the cut-off point. A regular charger treats such a battery as unserviceable and the pack is often discarded. Boost applies a small charge current to raise the voltage to between 2.2V/cell and 2.9V/cell to activate the protection circuit, at which point a normal charge commences. Caution is required if a Li-ion has dwelled below 1.5V/cell for a week or longer. Dendrites may have developed that could compromise safety.

Lead- and lithium-based chargers operate on constant current constant voltage (CC/CV). The charge current is constant and the voltage is capped when it reaches a set limit. Reaching the voltage limit, the battery saturates; the current drops until the battery can no longer accept further charge and the fast charge terminates. Each battery has its own low-current threshold.

Nickel-based batteries charge with constant current and the voltage is allowed to rise freely. This can be compared to lifting a weight with a rubber band where the hand advances higher than the load. Full charge detection occurs when observing a slight voltage drop after a steady rise. To safeguard against anomalies, such as shorted or mismatched cells, the charger should include a plateau timer to assure a safe charge termination if no voltage delta is detected.

Temperature sensing should also be added that measures temperature rise over time. Such a method is known as delta temperature over delta time, or  $dT/dt$ , and works well with rapid and fast charge.

A temperature rise is normal with nickel-based batteries, especially when reaching the 70 percent charge level. A decrease in charge efficiency causes this, and the charge current should be lowered to limit stress. When “ready,” the charger switches to trickle charge and the battery must cool down. If the temperature stays above ambient, then the charger is not performing correctly and the battery should be removed because the trickle charge could be too high.

NiCd and NiMH should not be left in the charger unattended for weeks and months. Until required, store the batteries in a cool place and apply a charge before use.

Lithium-based batteries should always stay cool on charge. Discontinue the use of a battery or charger if the temperature rises more than  $10^{\circ}\text{C}$  ( $18^{\circ}\text{F}$ ) above ambient under a normal

charge. Li ion cannot absorb over-charge and does not receive trickle charge when full. It is not necessary to remove Li-ion from the charger; however, if not used for a week or more, it is best to place the pack in a cool place and recharge before use.

### Types of Chargers

The most basic charger was the overnight charger, also known as a slow charger. This goes back to the old nickel-cadmium days where a simple charger applied a fixed charge of about 0.1C (one-tenth of the rated capacity) as long as the battery was connected. Slow chargers have no full-charge detection; the charge stays engaged and a full charge of an empty battery takes 14–16 hours. When fully charged, the slow charger keeps NiCd lukewarm to the touch. Because of its reduced ability to absorb over-charge, NiMH should not be charged on a slow charger. Low-cost consumer chargers charging AAA, AA and C cells often deploy this charge method, so do some children's toys. Remove the batteries when warm.

The rapid charger falls between the slow and fast charger and is used in consumer products. The charge time of an empty pack is 3–6 hours. When full, the charger switches to "ready." Most rapid chargers include temperature sensing to safely charge a faulty battery.

The fast charger offers several advantages and the obvious one is shorter charge times. This demands tighter communication between the charger and battery. At a charge rate of 1C, which a fast charger typically uses, an empty NiCd and NiMH charges in a little more than an hour. As the battery approaches full charge, some nickel-based chargers reduce the current to adjust to the lower charge acceptance. The fully charged battery switches the charger to trickle charge, also known as maintenance charge. Most of today's nickel-based chargers have a reduced trickle charge to also accommodate NiMH.

Li-ion has minimal losses during charge and the coulombic efficiency is better than 99 percent. At 1C, the battery charges to 70 percent state-of-charge (SoC) in less than an hour; the extra time is devoted to the saturation charge. Li-ion does not require the saturation charge as lead acid does; in fact it is better not to fully charge Li-ion — the batteries will last longer but the runtime will be a little less. Of all chargers, Li-ion is the simplest. No trickery applies that promises to improve battery performance as is often claimed by makers of chargers for lead- and nickel-based batteries. Only the rudimentary CC/CV method works.

Lead acid cannot be fast charged and the term "fast-charge" is a misnomer. Most lead acid chargers charge the battery in 14–16 hours; anything slower is a compromise. Lead acid can be charged to 70 percent in about 8 hours; the all-important saturation charge takes up the remaining time. A partial charge is fine provided the lead acid occasionally receives a fully saturated charge to prevent sulfation.

#### 4.2.1. Fast and Ultra-fast Chargers

Nowhere is ultra-fast charging in bigger demand than with the electric vehicle. Charging an EV will always take longer than filling a tank, and the battery will always deliver less energy per weight than fossil fuel. Breaking the rule of law and forcing ultra-fast charging adds stress, even if the battery is designed for such a purpose. We must keep in mind that a battery is sluggish in nature. Like an aging man, its physical condition becomes less ideal with use and age. So is the ability to fast-charge.

One assumes that all charge energy goes into the battery, whether charged slowly, rapidly or by ultra-fast method. Batteries are nonlinear devices and most chemistry accepts a fast charge from empty up to about 50% state-of-charge (SoC) with little losses. NiCd does best and suffers the least amount of strain. Stresses occur in the second half of the charge cycle towards top charge when acceptance of lithium ions in the anode of Li-ion becomes labored. An analogy is irate drivers fighting for the last parking spot in a shopping mall to catch a sale special.

Applying an ultra-fast charge when the battery is empty and then tapering off the current when reaching 50% SoC and higher is called step charging. The laptop industry has been applying step charging for many years. The charge currents must harmonize with the battery type as different battery systems have dissimilar requirements in charge acceptance.

As our bodies work best at 37°C (98°F), so does the transport mechanism improve when a battery is warm. Modern EVs will enable the “pre-charge” feature to prepare the battery temperature for the pending fast-charge while driving.

Whether you own an EV, e-bike, a flying object, a portable device or a hobby gadget, the following conditions must be respected when charging a battery the ultra-fast way:

1. The battery must be designed to accept an ultra-fast charge and must be in good condition. Li-ion can be designed for a fast charge of 10-minutes or so but the specific energy of such a cell will be low.
2. Ultra-fast charging only applies during the first charge phase. The charge current should be lowered after the battery reaches 70 percent state-of-charge (SoC).
3. All cells in the pack must be balanced and have ultra-low resistance. Aging cells often diverge in capacity and resistance, causing mismatch and undue stress on weaker cells.
4. Ultra-fast charging can only be done under moderate temperatures, as low temperature slows the chemical reaction. Unused energy turns into gassing, metal-plating and heat.

A well-designed ultra-fast charger evaluates the condition of the “chemical battery” and makes adjustments according to the ability to receive charge. The charger should also include temperature compensations and other safety features to lower the charge current when certain conditions exist and halt the charge if the battery is under undue stress.

### Limitations to ultra-fast charging Li-ion

The maximum charge current a Li-ion can accept is governed by cell design, and not the cathode material, as is commonly assumed. The goal is to avoid lithium-plating on the anode and to keep the temperature under control. A thin anode with high porosity and small graphite particles enables ultra-fast charging because of the large surface area. Power Cells can be charged and discharged at high currents, but the energy density is low. Energy Cells, in comparison, have a thicker anode and lower porosity and the charge rate should 1C or less. Some hybrid Cells in NCA (nickel-cobalt-aluminum) can be charged above 1C with only moderate stress.

Apply the ultra-fast charge only when necessary. A well-designed ultra-fast charger should have charge-time selection to give the user the option to choose the least stressful charge for the time allotted. Figure 2 compares the cycle life of a typical lithium-ion battery when charged and discharged at 1C, 2C and 3C rates. The longevity can further be prolonged by charging and discharging below 1C; 0.8C is the recommended rate.

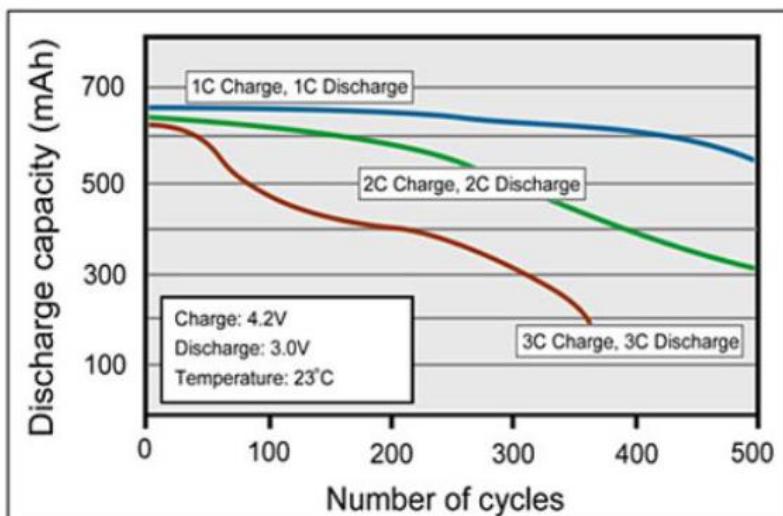


Figure 2: Cycle performance of Li-ion with 1C, 2C and 3C charge and discharge.

Charging and discharging Li-ion above 1C reduces service life. Use a slower charge and discharge if possible. This rule applies to most batteries.

### Lithium deposition

Lithium deposition forms if the charge rate exceeds the ability by which lithium can be intercalated into the negative graphite electrode of Li-ion. A film of metallic lithium forms on the negative electrode that spreads uniformly over the host material or gravitates to one region in planar, mossy or dendritic format. The dendritic form is of concern because it may increase self-discharge that in extreme case can create a short and lead to venting with flame.

Environmental conditions affect the deposition of lithium as follows:

1. Lithium deposit grows when Li-ion is ultra-fast charged at low temperature
2. Deposition develops if Li-ion is ultra-fast charged beyond a given state-of-charge level
3. The buildup is also said to increase as Li-ion cells age due to raised internal resistance.

Consumers demand fast charging at low temperature and this is especially critical with the electric vehicle. Solutions include special electrolyte additives and solvents, optimal negative to positive electrode ratios, and special cell design.

The question is often asked; “Why do ultra-fast chargers charge a battery to only 70 and 80 percent?” This may be done on purpose to reduce stress, but is also caused naturally by a lag between voltage and state-of-charge that amplifies the faster the battery is being charged. This can be compared to a rubber band lifting a heavy weight. The larger the weight, the wider the lag becomes. The ultra-fast charge forces the voltage to the 4.20V/cell ceiling quickly while the battery is only partially charged. Full charge will occur at a slower pace as part of saturation.

Lithium Titanate may be the exception and allow ultra-fast charging without undue stress. This feature will likely be used in future EVs; however, Li-titanate has a lower specific energy than cobalt-blended Li-ion and the battery is expensive.

Nickel-cadmium is another battery chemistry that can be charged in minutes to 70 percent state-of-charge. Like with most batteries, the charge acceptance drops towards full-charge and the charge current must be reduced.

All ultra-fast methods need for high power. An ultra-fast EV charge station draws the equivalent electrical power of five households. Charging a fleet of EVs could dim a city.

Table 3 summarizes the charge characteristics of lead, nickel and lithium-based batteries.

Type	Chemistry	C rate	Time	Temperatures	Charge termination
Slow charger	NiCd Lead acid	0.1C	14h	0°C to 45°C (32°F to 113°F)	Continuous low charge or fixed timer. Subject to overcharge. Remove battery when charged.
Rapid charger	NiCd, NiMH, Li-ion	0.3- 0.5C	3-6h	10°C to 45°C (50°F to 113°F)	Senses battery by voltage, current, temperature and time-out timer.
Fast charger	NiCd, NiMH, Li-ion	1C	1h+	10°C to 45°C (50°F to 113°F)	Same as a rapid charger with faster service.
Ultra-fast charger	Li-ion, NiCd, NiMH	1- 10C	10-60 minutes	10°C to 45°C (50°F to 113°F)	Applies ultra-fast charge to 70% SoC; limited to specialty batteries.

**Table 3: Charger characteristics.** Each chemistry uses a unique charge termination.

### 4.3. Charging Lithium-ion

Charging and discharging batteries is a chemical reaction, but Li-ion is claimed to be the exception. Battery scientists talk about energies flowing in and out of the battery as part of ion movement between anode and cathode. This claim carries merits but if the scientists were totally right, then the battery would live forever. They blame capacity fade on ions getting trapped, but as with all battery systems, internal corrosion and other degenerative effects also known as parasitic reactions on the electrolyte and electrodes till play a role.

The Li ion charger is a voltage-limiting device that is very strict on the correct setting because Li-ion cannot accept overcharge. The so-called miracle charger that promises to prolong battery life and gain extra capacity with pulses and other gimmicks does not exist. Li-ion is a "clean" system and only takes what it can absorb.

#### Charging Cobalt-blended Li-ion

Li-ion with the traditional cathode materials of cobalt, nickel, manganese and aluminum typically charge to 4.20V/cell. The tolerance is  $\pm 50\text{mV}/\text{cell}$ . Some nickel-based varieties charge to 4.10V/cell; high capacity Li-ion may go to 4.30V/cell and higher. Boosting the voltage increases capacity, but going beyond specification stresses the battery and compromises safety. Protection circuits built into the pack do not allow exceeding the set voltage.

Figure 1 shows the voltage and current signature as lithium-ion passes through the stages for constant current and topping charge. Full charge is reached when the current decreases to between 3 and 5 percent of the Ah rating.

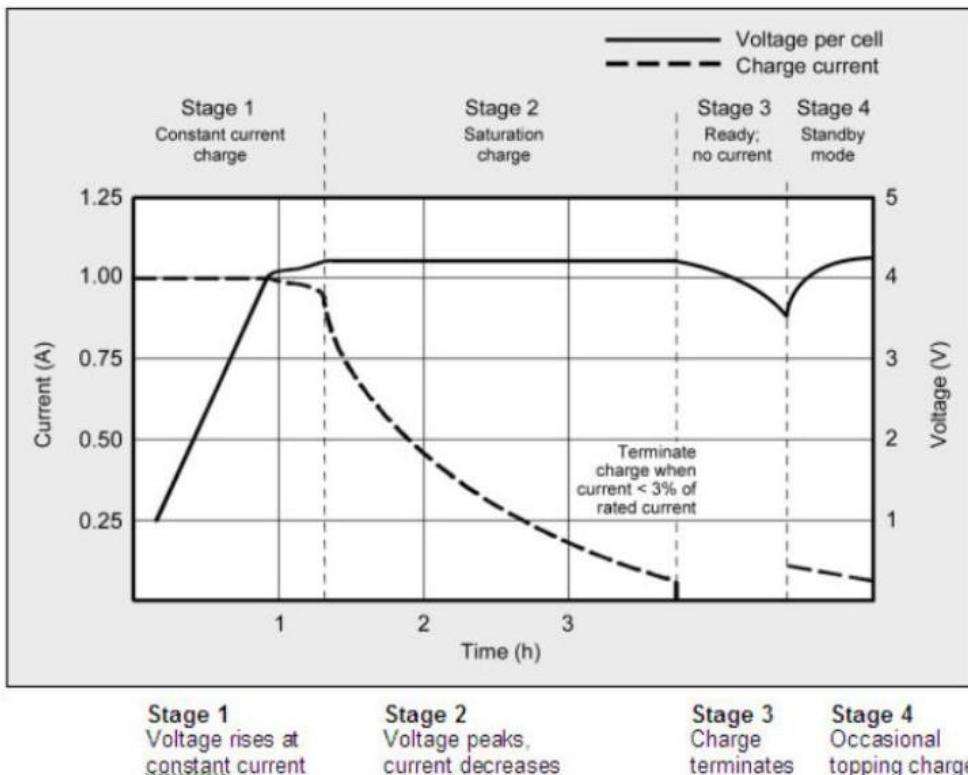


Figure 1: Charge stages of lithium-ion. Li-ion is fully charged when the current drops to a set level. In lieu of trickle charge, some chargers apply a topping charge when the voltage drops.

Courtesy of Cadex

The advised charge rate of an Energy Cell is between 0.5C and 1C; the complete charge time is about 2–3 hours. Manufacturers of these cells recommend charging at 0.8C or less to prolong battery life; however, most Power Cells can take a higher charge C-rate with little stress. Charge efficiency is about 99 percent and the cell remains cool during charge.

Some Li-ion packs may experience a temperature rise of about 5°C (9°F) when reaching full charge. This could be due to the protection circuit and/or elevated internal resistance. Discontinue using the battery or charger if the temperature rises more than 10°C (18°F) under moderate charging speeds.

Full charge occurs when the battery reaches the voltage threshold and the current drops to 3 percent of the rated current. A battery is also considered fully charged if the current levels off and cannot go down further. Elevated self-discharge might be the cause of this condition.

Increasing the charge current does not hasten the full-charge state by much. Although the battery reaches the voltage peak quicker, the saturation charge will take longer accordingly. With higher current, Stage 1 is shorter but the saturation during Stage 2 will take longer. A high current charge will, however, quickly fill the battery to about 70 percent.

Li-ion does not need to be fully charged as is the case with lead acid, nor is it desirable to do so. In fact, it is better not to fully charge because a high voltage stresses the battery. Choosing a lower voltage threshold or eliminating the saturation charge altogether, prolongs battery life but this reduces the runtime. Chargers for consumer products go for maximum capacity and cannot be adjusted; extended service life is perceived less important.

Some lower-cost consumer chargers may use the simplified “charge-and-run” method that charges a lithium-ion battery in one hour or less without going to the Stage 2 saturation charge. “Ready” appears when the battery reaches the voltage threshold at Stage 1. State-of-charge (SoC) at this point is about 85 percent, a level that may be sufficient for many users.

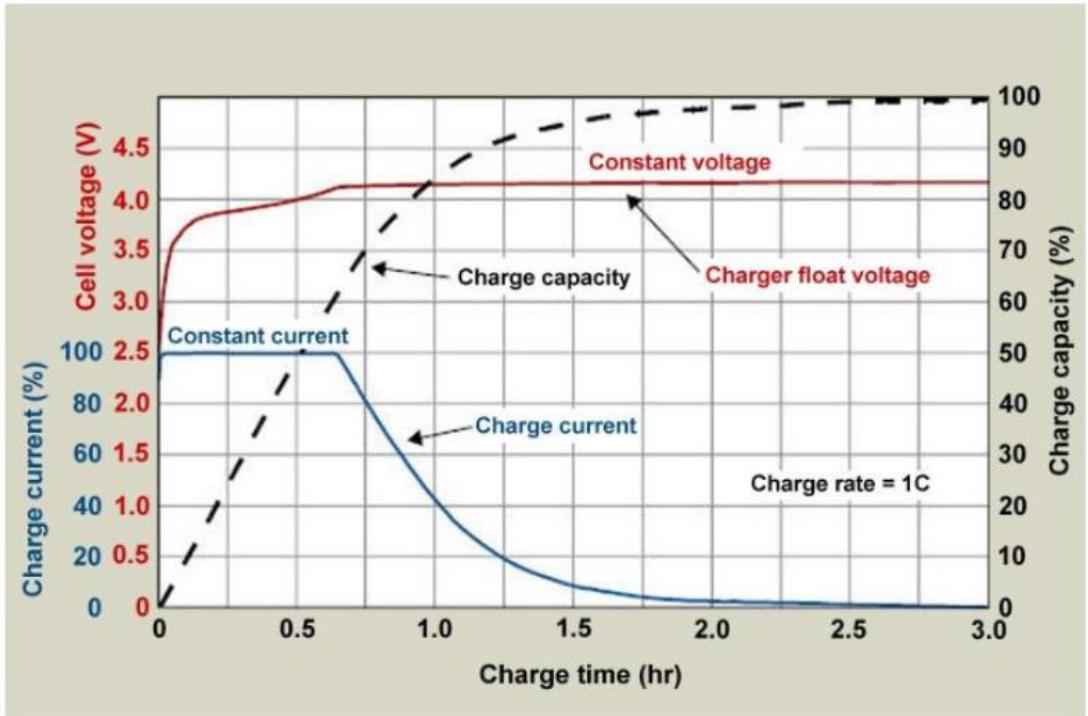
Certain industrial chargers set the charge voltage threshold lower on purpose to prolong battery life. Table 2 illustrates the estimated capacities when charged to different voltage thresholds with and without saturation charge.

Charge V/cell	Capacity at cut-off voltage*	Charge time	Capacity with full saturation
3.80	~40%	120 min	~65%
3.90	~60%	135 min	~75%
4.00	~70%	150 min	~80%
4.10	~80%	165 min	~90%
4.20	~85%	180 min	100%

**Table 2: Typical charge characteristics of lithium-ion.** Adding full saturation at the set voltage boosts the capacity by about 10 percent but adds stress due to high voltage.

\* Readings may vary

When the battery is first put on charge, the voltage shoots up quickly. This behavior can be compared to lifting a weight with a rubber band, causing a lag. The capacity will eventually catch up when the battery is almost fully charged (Figure 3). This charge characteristic is typical of all batteries. The higher the charge current is, the larger the rubber-band effect will be. Cold temperatures or charging a cell with high internal resistance amplifies the effect.



**Figure 3: Volts/capacity vs. time when charging lithium-ion.**

The capacity trails the charge voltage like lifting a heavy weight with a rubber band.

Courtesy of Cadex

Estimating SoC by reading the voltage of a charging battery is impractical; measuring the open circuit voltage (OCV) after the battery has rested for a few hours is a better indicator. As with all batteries, temperature affects the OCV, so does the active material of Li-ion. SoC of smartphones, laptops and other devices is estimated by coulomb counting.

Li-ion cannot absorb overcharge. When fully charged, the charge current must be cut off. A continuous trickle charge would cause plating of metallic lithium and compromise safety. To minimize stress, keep the lithium-ion battery at the peak cut-off as short as possible.

Once the charge is terminated, the battery voltage begins to drop. This eases the voltage stress. Over time, the open circuit voltage will settle to between 3.70V and 3.90V/cell. Note that a Li-ion battery that has received a fully saturated charge will keep the voltage elevated for a longer than one that has not received a saturation charge.

When lithium-ion batteries must be left in the charger for operational readiness, some chargers apply a brief topping charge to compensate for the small self-discharge the battery and its protective circuit consume. The charger may kick in when the open circuit voltage drops to 4.05V/cell and turn off again at 4.20V/cell. Chargers made for operational readiness, or standby mode, often let the battery voltage drop to 4.00V/cell and recharge to only 4.05V/cell instead of the full 4.20V/cell. This reduces voltage-related stress and prolongs battery life.

Some portable devices sit in a charge cradle in the ON position. The current drawn through the device is called the parasitic load and can distort the charge cycle. Battery manufacturers advise against parasitic loads while charging because they induce mini-cycles. This cannot always be avoided and a laptop connected to the AC main is such a case. The battery might be charged to 4.20V/cell and then discharged by the device. The stress level on the battery is high because the cycles occur at the high-voltage threshold, often also at elevated temperature.

A portable device should be turned off during charge. This allows the battery to reach the set voltage threshold and current saturation point unhindered. A parasitic load confuses the charger by depressing the battery voltage and preventing the current in the saturation stage to drop low enough by drawing a leakage current. A battery may be fully charged, but the prevailing conditions will prompt a continued charge, causing stress.

### **Charging Non-cobalt-blended Li-ion**

While the traditional lithium-ion has a nominal cell voltage of 3.60V, Li-phosphate (LiFePO) makes an exception with a nominal cell voltage of 3.20V and charging to 3.65V. Relatively new is the Li-titanate (LTO) with a nominal cell voltage of 2.40V and charging to 2.85V. (See BU-205: Types of Lithium-ion.)

Chargers for these non cobalt-blended Li-ions are not compatible with regular 3.60-volt Li-ion. Provision must be made to identify the systems and provide the correct voltage charging. A 3.60-volt lithium battery in a charger designed for Li-phosphate would not receive sufficient charge; a Li-phosphate in a regular charger would cause overcharge.

### **Overcharging Lithium-ion**

Lithium-ion operates safely within the designated operating voltages; however, the battery becomes unstable if inadvertently charged to a higher than specified voltage. Prolonged charging above 4.30V on a Li-ion designed for 4.20V/cell will plate metallic lithium on the anode. The cathode material becomes an oxidizing agent, loses stability and produces carbon dioxide (CO<sub>2</sub>). The cell pressure rises and if the charge is allowed to continue, the current interrupt device (CID) responsible for cell safety disconnects at 1,000–1,380kPa (145–200psi). Should the pressure rise further, the safety membrane on some Li-ion bursts open at about 3,450kPa (500psi) and the cell might eventually vent with flame.

Venting with flame is connected with elevated temperature. A fully charged battery has a lower thermal runaway temperature and will vent sooner than one that is partially charged. All lithium-based batteries are safer at a lower charge, and this is why authorities will mandate air shipment of Li-ion at 30 percent state-of-charge rather than at full charge.

The threshold for Li-cobalt at full charge is 130–150°C (266–302°F); nickel-manganese-cobalt (NMC) is 170–180°C (338–356°F) and Li-manganese is about 250°C (482°F). Li-phosphate enjoys similar and better temperature stabilities than manganese.

Lithium-ion is not the only battery that poses a safety hazard if overcharged. Lead- and nickel-based batteries are also known to melt down and cause fire if improperly handled. Properly designed charging equipment is paramount for all battery systems and temperature sensing is a reliable watchman.

#### 4.3.1. Why do old Li-ion Batteries take long to charge?

Battery users often ask: "Why does an old Li-ion take so long to charge?" Indeed, when Li-ion gets older, the battery takes its time to charge even if there is little to fill. We call this the "old-man syndrome." Figure 1 illustrates the charge time of a new Li-ion with a capacity of 100 percent against an aged pack delivering only 82 percent. Both take roughly 150 minutes to charge.

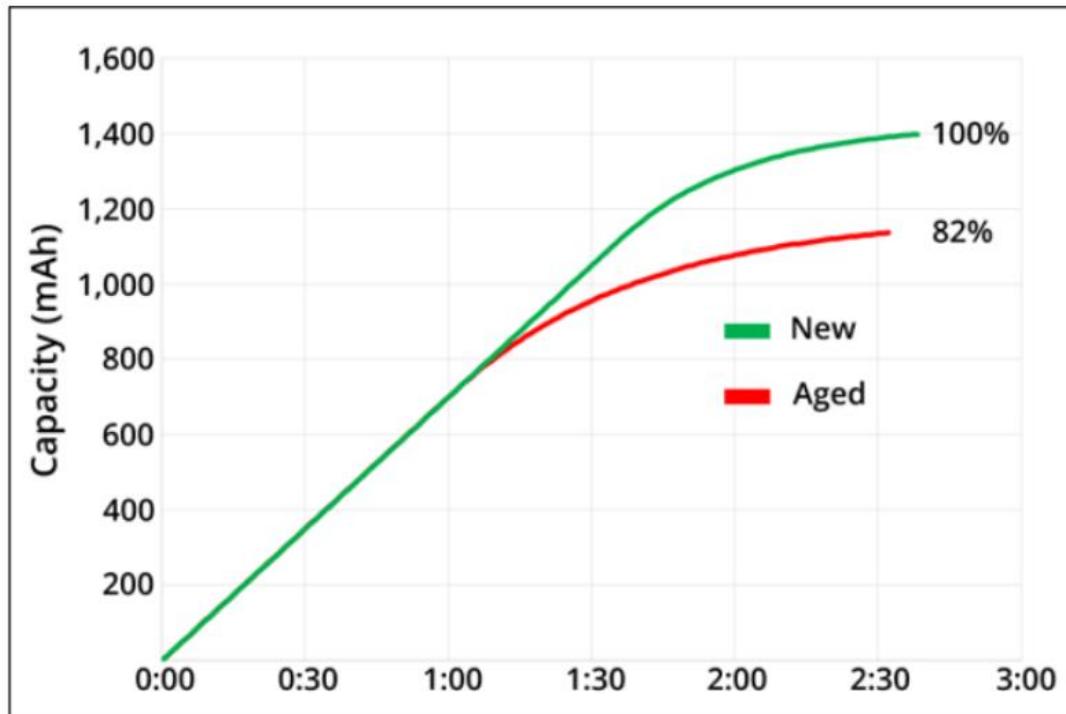


Figure 1: New and aged Li-ion batteries are charged.

Both packs take roughly 150 minutes to charge. The new pack charges to 1,400mAh (100%) while the aged one only goes to 1,150mAh (82%).

Courtesy: Cadex Electronics Inc.

When charging Li-ion, the voltage shoots up similar to lifting a weight with a rubber band. The new pack as demonstrated in Figure 2 is "hungrier" and can take on more "food" before reaching the 4.20V/cell voltage limit compared to the aged Li-ion that hits V Limit in Stage 1 after only about 60 minutes. In terms of a rubber band analogy, the new battery has less slack than to the aged pack and can accept charge longer before going into saturation.

Figure 3 demonstrates the different saturation times in Stage 2 as the current trails from the fully regulated current to about 0.05C to trigger ready mode. The trailing off on a good battery is short and is prolonged on an aged pack. This explains the longer charge time of an older Li-ion with less capacity. An analogy is a young athlete running a sprint with little or no slow-down towards the end, while the old man gets out of breath and begins walking, prolonging the time to reach the goal.

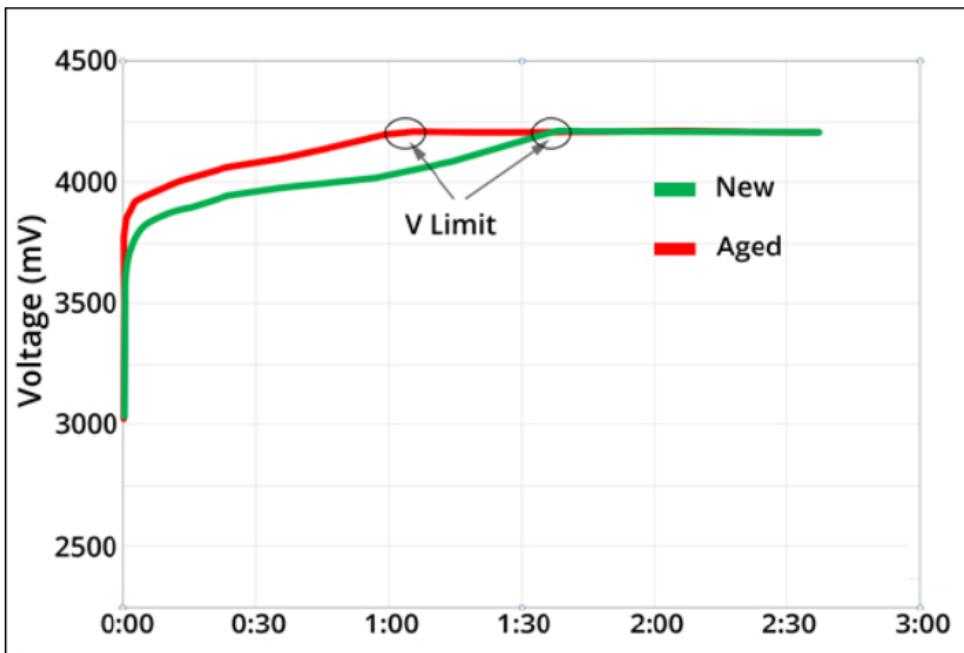


Figure 2: Observing charge times of a new and aged Li-ion in Stage 1.

The new Li-ion takes on full charge for 90 minutes while the aged cell reaches 4.20V/cell in 60 minutes  
Courtesy: Cadex Electronics Inc.

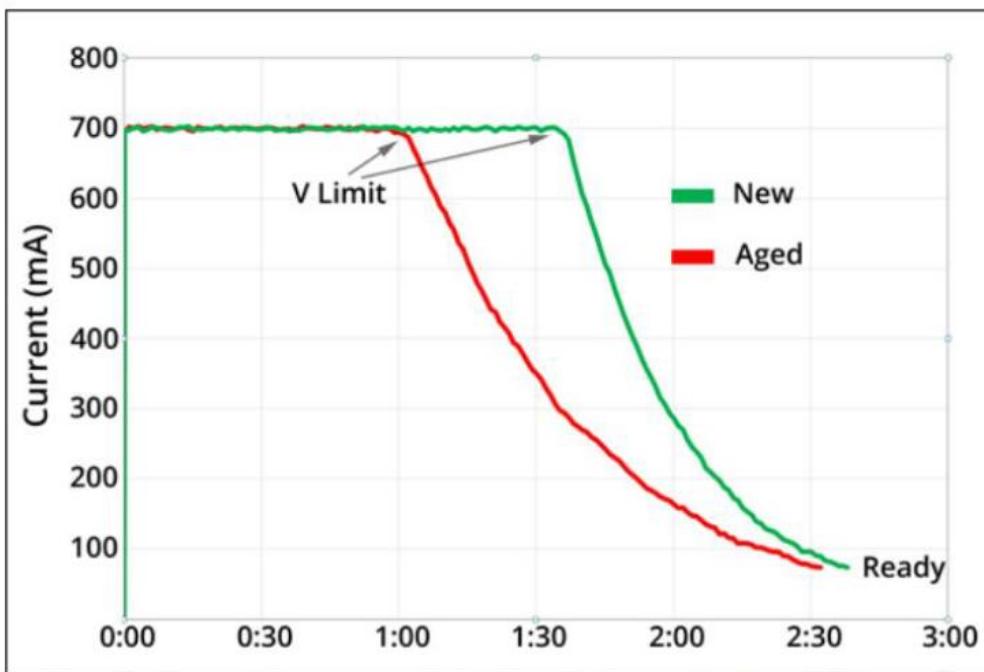


Figure 3: Observing saturation times of new and aged Li-ion in Stage 2 before switching to ready.

The new cell stays in full-charge longer than the old cell and has a shorter current trail.  
Courtesy: Cadex Electronics Inc.

A common aging effect of Li-ion is loss of charge transfer capability. This is caused by the formation of passive materials on the electrodes, which inhibits the flow of free electrons. This reduces the porosity on the electrodes, decreases the surface area, lowers the lower ionic conductivity and raises migration resistance. The aging phenomenon is permanent and cannot be reversed.

The health of a battery is based on these three fundamental attributes:

- Capacity, the ability to store energy. Capacity is the leading health indicator of a battery
- Internal resistance, the ability to deliver current
- Self-discharge, indicator of the mechanical integrity

The charge signature reveals valuable health indicators of Li-ion. A good battery absorbs most of the charge in Stage 1 before reaching 4.20V/cell and the trailing in Stage 2 is short. “Lack of hunger” on a Li-ion can be attributed to a battery being partially charged; exceptionally long trailing times relates to a battery with low capacity, high internal resistance and/or elevated self-discharge.

Algorithms can be developed that compare Stage 1 and Stage 2 based on capacity and state-of-charge. Anomalies, such as low capacity and elevated self-discharge can be identified by setting acceptance thresholds.

#### 4.4. Charging at High and Low Temperatures

Batteries operate over a wide temperature range, but this does not give permission to also charge them at these conditions. The charging process is more delicate than discharging and special care must be taken. Extreme cold and high heat reduce charge acceptance, so the battery must be brought to a moderate temperature before charging.

Older battery technologies, such as lead acid and NiCd, have higher charging tolerances than newer systems. This allows them to charge below freezing but at a reduced charge C-rate. When it comes to cold-charging NiCd is hardier than NiMH. As for Li-ion batteries, no charge is permitted below freezing. They have good performance at higher temperatures, but shorter life.

Li ion can be fast charged from 5°C to 45°C (41 to 113°F). Below 5°C, the charge current should be reduced, and no charging is permitted at freezing temperatures because of the reduced diffusion rates on the anode. During charge, the internal cell resistance causes a slight temperature rise that compensates for some of the cold. The internal resistance of all batteries rises when cold, prolonging charge times noticeably.

Many battery users are unaware that consumer-grade lithium-ion batteries cannot be charged below 0°C (32°F). Although the pack appears to be charging normally, plating of metallic lithium can occur on the anode during a sub-freezing charge. This is permanent and cannot be removed with cycling. Batteries with lithium plating are more vulnerable to failure if exposed to vibration or other stressful conditions.

Advancements are being made to charge Li-ion below freezing temperatures. Charging is indeed possible with most lithium-ion cells but only at very low currents. According to research papers, the allowable charge rate at -30°C (-22°F) is 0.02C. At this low current, the charge time would stretch to over 50 hours, a time that is deemed impractical. There are, however, specialty Li-ions that can charge down to -10°C (14°F) at a reduced rate.

Lithium-ion performs well at elevated temperatures but prolonged exposure to heat reduces longevity. Charging and discharging at elevated temperatures is subject to gas generation that might cause a cylindrical cell to vent and a pouch cell to swell. Many chargers prohibit charging above 50°C (122°F).

Capacity loss at elevated temperature is in direct relationship with state-of-charge (SoC). Figure 5 illustrates the effect of Li-cobalt (LiCoO<sub>2</sub>) that is first cycled at room temperature (RT) and then heated to 130°C (266°F) for 90 minutes and cycled at 20, 50 and 100 percent SoC. There is no noticeable capacity loss at room temperature. At 130°C with a 20 percent SoC, a slight capacity loss is visible over 10 cycles. This loss is higher with a 50 percent SoC and shows a devastating effect when cycled at full charge.

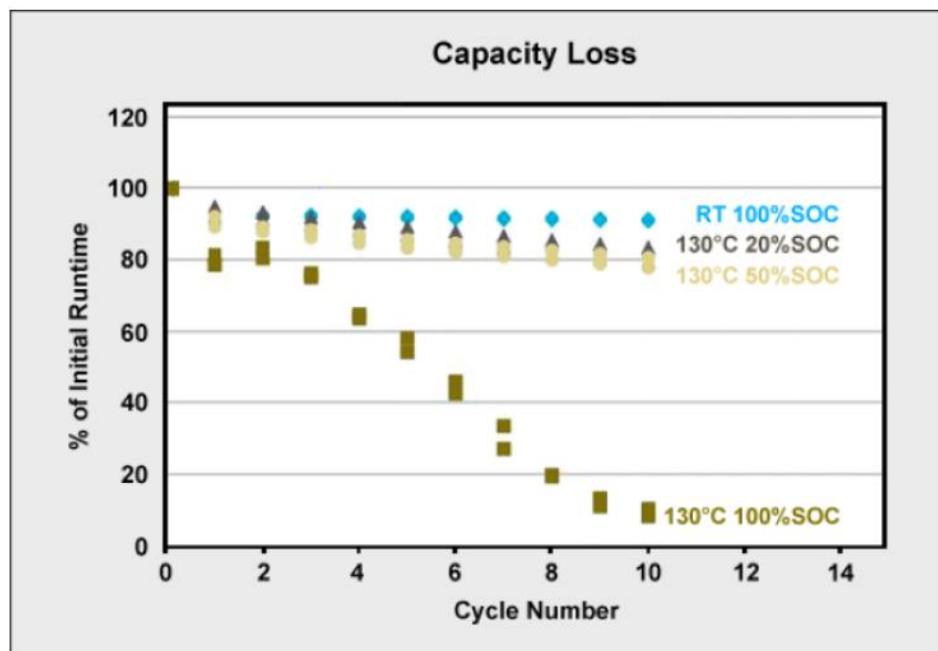


Figure 5: Capacity loss at room temperature (RT) and 130°C for 90 minutes

Sterilization of batteries for surgical power tools should be done at low SoC.

**Test:** LiCoO<sub>2</sub>/Graphite cells were exposed to 130°C for 90 min. at different SoC between each cycle.  
Source: Greatbatch Medical

## 4.5. Summary Table

Folks are eager to learn more about this wonderful portable energy device and one of the most common questions asked is, “What can I do to prolong the life of my battery?” Following table addresses how to care for your batteries to meet their needs. Because of similarities within the different battery families, the table addresses the needs and wants of only the most common systems by keeping in mind that these desires extend to almost all batteries in use.

Frequently asked question	Lead acid (Sealed, flooded)	Nickel-based (NiCd and NiMH)	Lithium-ion (Li-ion, polymer)
How should I prepare a new battery?	Battery comes fully charged. Apply a topping* charge.	Charge 14–16h. Priming may be needed to format	Apply a topping charge before use. No priming needed
Can I damage a battery with incorrect use?	Always store battery fully charged.	Battery is robust. New pack will improve with use.	Keep partially charged. Low charge can turn off protection circuit
Do I need to apply a full charge?	Fully charge every few weeks or months. Continuous low charge causes sulfation.	Partial charge is fine	Partial charge better than a full charge
Can I disrupt the charge cycle?	Partial charge causes no harm when applying periodic fully saturated charges.	Repeat charges can cause heat buildup	Partial charge causes no harm
Should I use up all battery energy before charging?	No, deep discharge wears battery down. Charge more often	Apply scheduled discharges only to prevent memory	Deep discharge wears the battery down
Do I have to worry about “memory”?	No, there is no memory	Discharge NiCd every 1–3 months	No memory
How do I calibrate a “smart” battery?	Not applicable	Apply discharge/charge when the fuel gauge gets inaccurate. Repeat every 1–3 months	
Can I charge with the device on?	Avoid load if possible	Parasitic load can alter full-charge detection and overcharge battery or cause mini-cycles	
Do I remove the battery when full?	Charger switches to float charge	Remove after a few days in charger	Not necessary; charger turns off
How do I store my battery?	Keep cells above 2.10V; topping-charge* every 6 months.	Store in cool place; can be stored fully discharged	Store in cool place partially charged
Does battery heat up on charge?	Gets lukewarm towards end of charge	Warm but must cool down when ready	Must stay cool or slightly warm
How do I charge when cold?	Slow charge (0.1): 0–45°C (32–113°F) Fast charge (0.5–1C): 5–45°C (41–113°F)		Do not charge below freezing
Can I charge at hot temperatures?	Lower threshold by 3mV/°C above 25°C	Battery will not fully charge when hot	Do not charge above 50°C (122°F)

## 5. Discharge Methods

### 5.1. Basics about Discharging

The purpose of a battery is to store energy and release it at a desired time. This section examines discharging under different C-rates and evaluates the depth of discharge to which a battery can safely go. The document also observes different discharge signatures and explores battery life under diverse loading patterns.

The electrochemical battery has the advantage over other energy storage devices in that the energy stays high during most of the charge and then drops rapidly as the charge depletes. The supercapacitor has a linear discharge, and compressed air and a flywheel storage device is the inverse of the battery by delivering the highest power at the beginning. Figures 1, 2 and 3 illustrate the simulated discharge characteristics of stored energy.

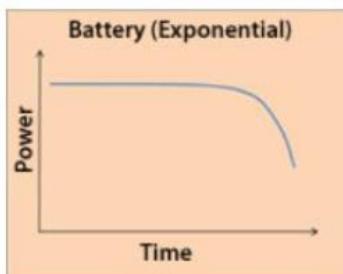


Figure 1: Discharge curve of Battery. Exponential discharge provides steady power to the end.

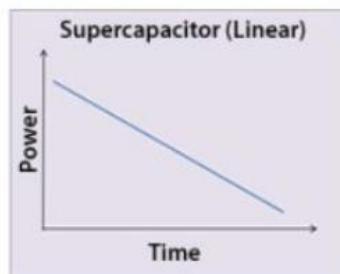


Figure 2: Discharge curve of supercapacitor. Linear discharge prevents the full use of energy.

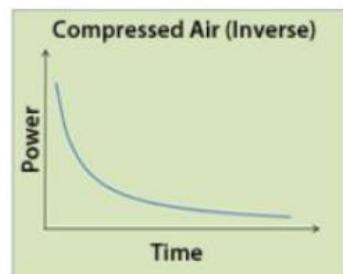


Figure 3: Discharge curve of compressed air. Inverse. Best performance at beginning

Most rechargeable batteries can be overloaded briefly, but this must be kept short. Battery longevity is directly related to the level and duration of the stress inflicted, which includes charge, discharge and temperature.

#### Depth of Discharge

Lead acid discharges to 1.75V/cell; nickel-based system to 1.0V/cell; and most Li-ion to 3.0V/cell. At this level, roughly 95 percent of the energy is spent, and the voltage would drop rapidly if the discharge were to continue. To protect the battery from over-discharging, most devices prevent operation beyond the specified end-of-discharge voltage.

When removing the load after discharge, the voltage of a healthy battery gradually recovers and rises towards the nominal voltage. Differences in the affinity of metals in the electrodes produce this voltage potential even when the battery is empty. A parasitic load or high self-discharge prevents voltage recovery.

A high load current, as would be the case when drilling through concrete with a power tool, lowers the battery voltage and the end-of-discharge voltage threshold is often set lower to prevent premature cutoff. The cutoff voltage should also be lowered when discharging at very cold temperatures, as the battery voltage drops and the internal battery resistance rises. Table 4 shows typical end-of-discharge voltages of various battery chemistries.

End-of-discharge	Li-manganese	Li-phosphate	Lead acid	NiCd/NiMH
Nominal	3.60V/cell	3.20V/cell	2.00V/cell	1.20V/cell
Normal load	3.0–3.3V/cell	2.70V/cell	1.75V/cell	1.00V/cell
Heavy load or low temperature	2.70V/cell	2.45V/cell	1.40V/cell	0.90V/cell

**Table 4: Nominal and recommended end-of-discharge voltages under normal and heavy load.** The lower end-of-discharge voltage on a high load compensates for the greater losses.

### What Constitutes a Discharge Cycle?

A discharge/charge cycle is commonly understood as the full discharge of a charged battery with subsequent recharge, but this is not always the case. Batteries are seldom fully discharged, and manufacturers often use the 80 percent depth-of-discharge (DoD) formula to rate a battery. This means that only 80 percent of the available energy is delivered and 20 percent remains in reserve. Cycling a battery at less than full discharge increases service life, and manufacturers argue that this is closer to a field representation than a full cycle because batteries are commonly recharged with some spare capacity left.

## 5.2. Discharge characteristics of Lithium-ion

The early Li-ion battery was considered fragile and unsuitable for high loads. This has changed, and today lithium-based systems stand shoulder to shoulder with the robust nickel and lead chemistries. Two basic types of Li-ion have emerged: The Energy Cell and the Power Cell.

The performance of these two battery types is characterized by energy storage, also known as capacity, and current delivery, also known as loading or power. Energy and power characteristics are defined by particle size on the electrodes. Larger particles increase the surface area for maximum capacity and fine material decreases it for high power.

Decreasing particle size lowers the presence of electrolyte that fills the voids. The volume of electrolyte within the cell determines battery capacity. Decreasing the particle size reduces the voids between the particles, thereby lowering the electrolyte content. Too little electrolyte reduces ionic mobility and affects performance. Think of a drying felt pen that needs recuperating to keep marking papers.

## Energy Cell

The Li-ion Energy Cell is made for maximum capacity to provide long runtimes. The Panasonic NCR18650B Energy Cell (Figure 1) has high capacity but is less enduring when discharged at 2C. At the discharge cutoff of 3.0V/cell, the 2C discharge produces only about 2.3Ah rather than the specified 3.2Ah. This cell is ideal for portable computing and similar light duties.

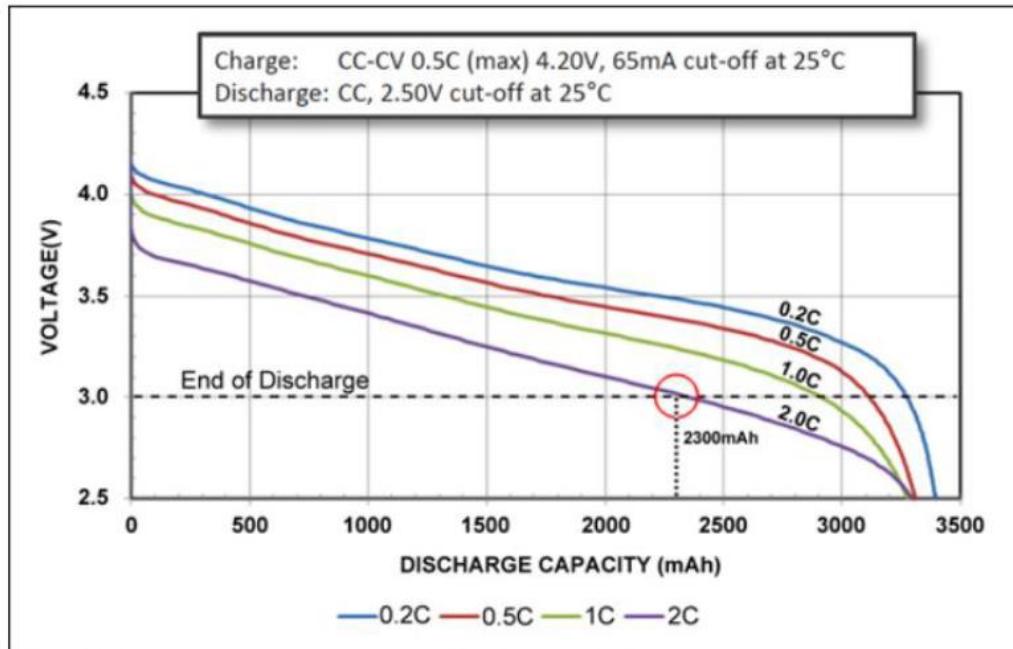


Figure 1: Discharge characteristics of NCR18650B Energy Cell by Panasonic.

The 3,200mAh Energy Cell is discharged at 0.2C, 0.5C, 1C and 2C. The circle at the 3.0V/cell line marks the end-of-discharge point at 2C.

Cold temperature losses:

25°C (77°F) = 100%

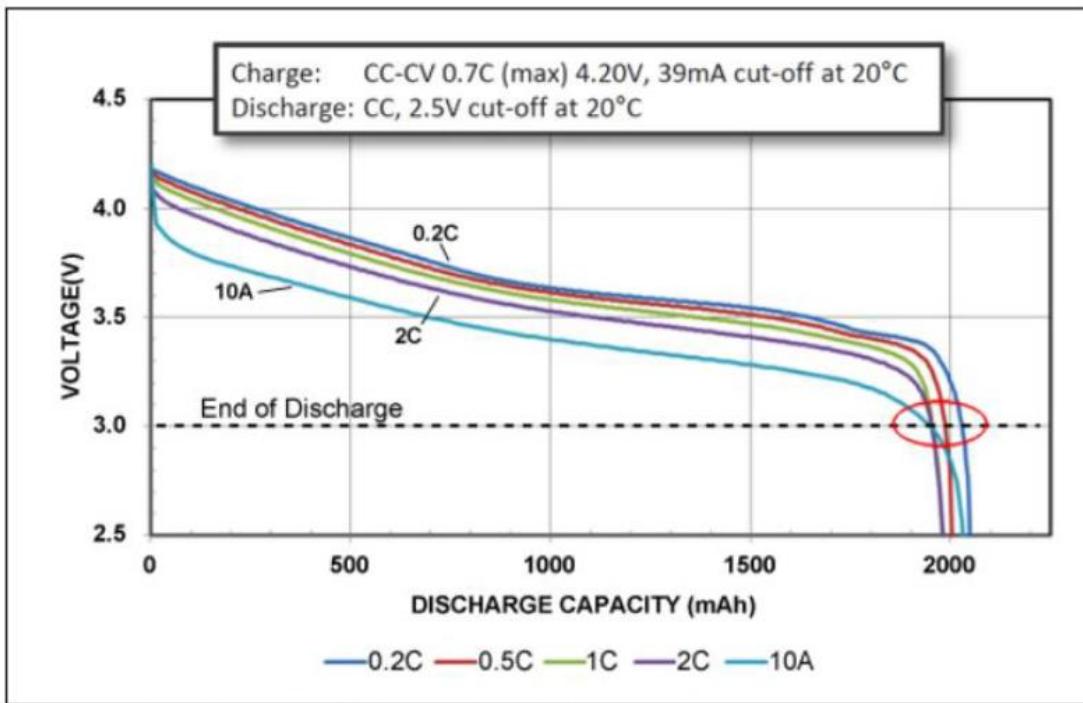
0°C (32°F) = ~83%

-10°C (14°F) = ~66%

-20°C (4°F) = ~53%

## Power Cell

The Panasonic UR18650RX Power Cell (Figure 2) has a moderate capacity but excellent load capabilities. A 10A (5C) discharge has minimal capacity loss at the 3.0V cutoff voltage. This cell works well for applications requiring heavy load current, such as power tools.



**Figure 2: Discharge characteristics of UR18650RX Power Cell by Panasonic.**

The 1950mAh Power Cell is discharged at 0.2C, 0.5C, 1C and 2C and 10A. All reach the 3.0V/cell cut-off line at about 2000mAh. The Power Cell has moderate capacity but delivers high current.

Cold temperature losses:

25°C (77°F) = 100%

0°C (32°F) = ~92%

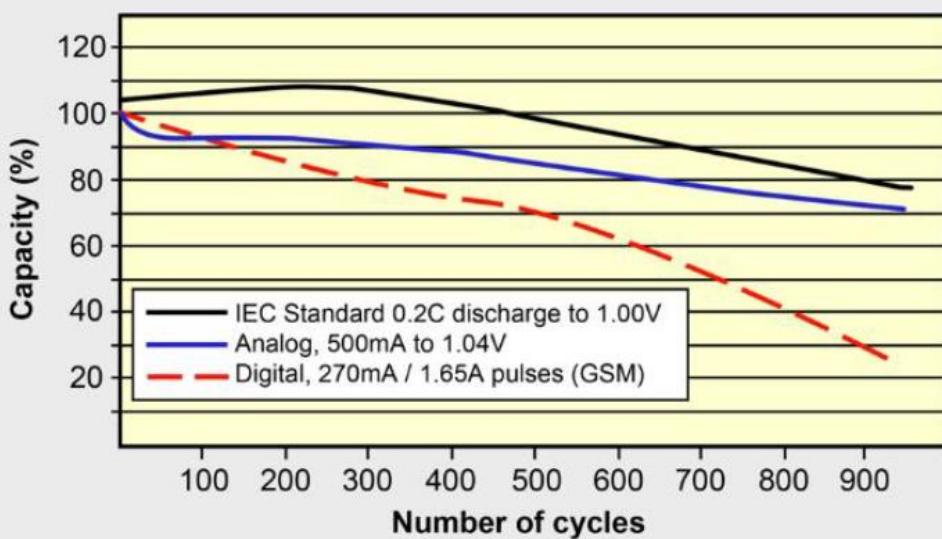
-10°C (14°F) = ~85%

-20°C (4°F) = ~80%

The Power Cell permits a continuous discharge of 10C. This means that an 18650 cell rated at 2,000mAh can provide a continuous load of 20A (30A with Li-phosphate). The superior performance is achieved in part by lowering the internal resistance and by optimizing the surface area of active cell materials. Low resistance enables high current flow with minimal temperature rise. Running at the maximum permissible discharge current, the Li-ion Power Cell heats to about 50°C (122°F); the temperature is limited to 60°C (140°F).

To meet the loading requirements, the pack designer can either use a Power Cell to meet the discharge C-rate requirement or go for the Energy Cell and oversize the pack. The Energy Cell holds about 50 percent more capacity than the Power Cell, but the loading must be reduced. This can be done by oversizing the pack, a method the Tesla EVs use. The battery achieves exceptional runtime but it gets expensive and heavy.

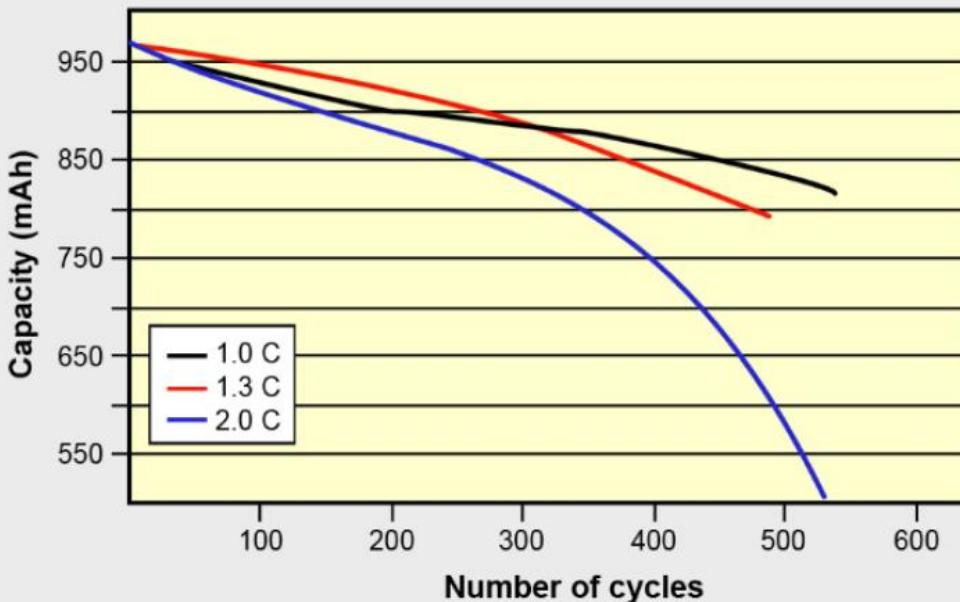
In terms of longevity, a battery prefers moderate current at a constant discharge rather than a pulsed or momentary high load. Figure 4 demonstrates the decreasing capacity of a NiMH battery at different load conditions from a gentle 0.2C DC discharge, an analog discharge to a pulsed discharge. Most batteries follow a similar pattern in terms of load conditions, including Li-ion.



**Figure 4: Cycle life of NiMH under different load conditions.**

NiMH performs best with DC and analog loads; digital loads lower the cycle life. Li-ion behaves similarly.

Figure 5 examines the number of full cycles a Li-ion Energy Cell can endure when discharged at different C-rates. At a 2C discharge, the battery exhibits far higher stress than at 1C, limiting the cycle count to about 450 before the capacity drops to half the level.



**Figure 5: Cycle life of Li-ion Energy Cell at varying discharge levels.**

The wear and tear of all batteries increases with higher loads. Power Cells are more robust than Energy Cells.

Source: Choi et al (2002)

### 5.3. Discharging at High and Low Temperature

Like humans, batteries function best at room temperature. Warming a dying battery in a mobile phone or flashlight in our jeans might provide additional runtime due to improved electrochemical reaction. This is likely also the reason why manufacturers prefer to specify batteries at a toasty 27°C (80°F). Operating a battery at elevated temperatures improves performance but prolonged exposure will shorten life.

All batteries achieve optimum service life if used at 20°C (68°F) or slightly below. If, for example, a battery operates at 30°C (86°F) instead of a more moderate lower room temperature, the cycle life is reduced by 20 percent. At 40°C (104°F), the loss jumps to a whopping 40 percent, and if charged and discharged at 45°C (113°F), the cycle life is only half of what can be expected if used at 20°C (68°F).

The performance of all batteries drops drastically at low temperatures; however, the elevated internal resistance will cause some warming effect by efficiency loss caused by voltage drop when applying a load current. At -20°C (-4°F) most batteries are at about 50 percent performance level. Although NiCd can go down to -40°C (-40°F), the permissible discharge is only 0.2C (5-hour rate). Specialty Li-ion can operate to a temperature of -40°C but only at a reduced discharge rate; charging at this temperature is out of the question. With lead acid there is the danger of the electrolyte freezing, which can crack the enclosure. Lead acid freezes quicker with a low charge when the specific gravity is more like water than when fully charged.

Figure 1 illustrates the discharge voltage of an 18650 Li-ion under various temperatures. A 3A discharge of a 2.8Ah cell represents a C-rate of 1.07C. The reduced capacity at low temperature only applies while the cell is in that condition and will recover in room temperature.

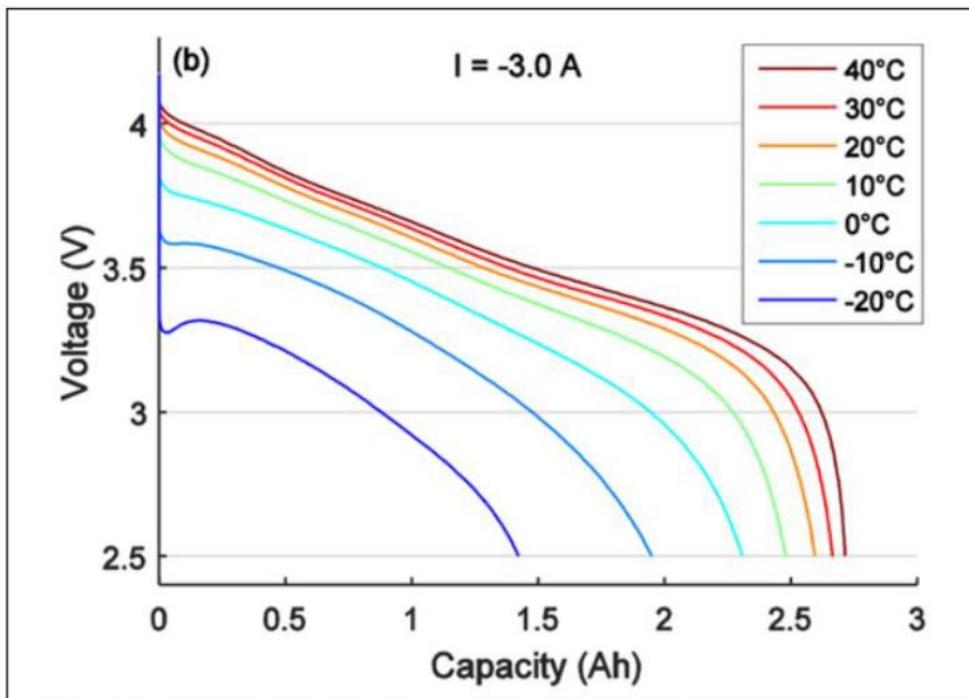


Figure 1: Discharge voltage of an 18650 Li-ion cell at 3A and various temperatures.

Cell type: Panasonic NRC18650PD, 2.8Ah nominal, LiNiCoAlO<sub>2</sub> (NCA)

Source: Technische Universität München (TUM)

Matched cells with identical capacities play an important role when discharging at low temperature and under heavy load. Since the cells in a battery pack can never be perfectly matched, a negative voltage potential can occur across a weaker cell in a multi-cell pack if the discharge is allowed to continue beyond a safe cut-off point. Known as cell reversal, the weak cell gets stressed to the point of developing a permanent electrical short. The larger the cell-count, the greater is the likelihood of cell-reversal under load. Over-discharge at a low temperature and heavy load is a large contributor to battery failure of cordless power tools.

The driving range of an electric vehicle between charges is calculated at ambient temperature. EV drivers are being made aware that frigid temperature reduces the available mileage. This loss is not only caused by heating the cabin electrically but by the inherent slowing of the battery's electrochemical reaction, which reduces the capacity while cold.

## 5.4. How to calculate Battery Runtime

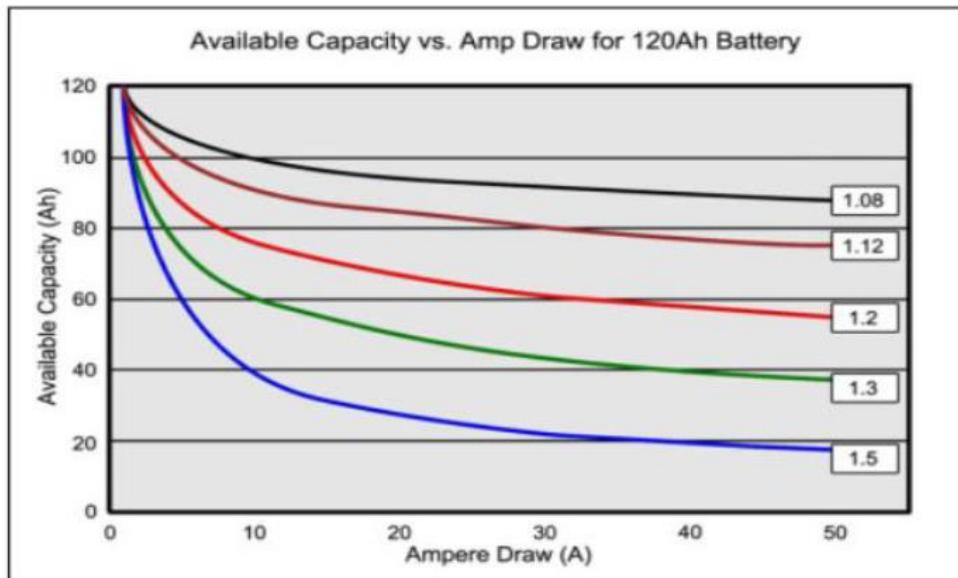
If the battery was a perfect power source and behaved linearly, charge and discharge times could be calculated according to in-and-out flowing currents, also known as coulombic efficiency. What is put in should be available as output in the same amount; a 1-hour charge at 5A should deliver a 1-hour discharge at 5A, or a 5-hour discharge at 1A. This is not possible because of intrinsic losses and the coulombic efficiency is always less than 100 percent. The losses escalate with increasing load, as high discharge currents make the battery less efficient.

### **Peukert Law**

The Peukert Law expresses the efficiency factor of a battery on discharge. W. Peukert, a German scientist (1855–1932), was aware that the available capacity of a battery decreases with increasing discharge rate and he devised a formula to calculate the losses in numbers. The law helps estimate the runtime under different discharge loads.

The Peukert Law takes into account the internal resistance and recovery rate of a battery. A value close to one (1) indicates a well-performing battery with good efficiency and minimal loss; a higher number reflects a less efficient battery. Peukert's law is exponential; the readings for lead acid are between 1.3 and 1.5 and increase with age. Temperature also affects the readings. Figure 1 illustrates the available capacity as a function of amperes drawn with different Peukert ratings.

As example, a 120Ah lead acid battery being discharged at 15A should last 8 hours (120Ah divided by 15A). Inefficiency caused by the Peukert effect reduces the discharge time. To calculate the actual discharge duration, divide the time with the Peukert exponent that in our example is 1.3. Dividing the discharge time by 1.3 reduces the duration from 8h to 6.15h.



**Figure 1: Available capacity of a lead acid battery at Peukert numbers of 1.08–1.50.** A value close to 1 has the smallest losses; higher numbers deliver lower capacities. Peukert values change with battery type age and temperature:

AGM: 1.05–1.15

Gel: 1.10–1.25

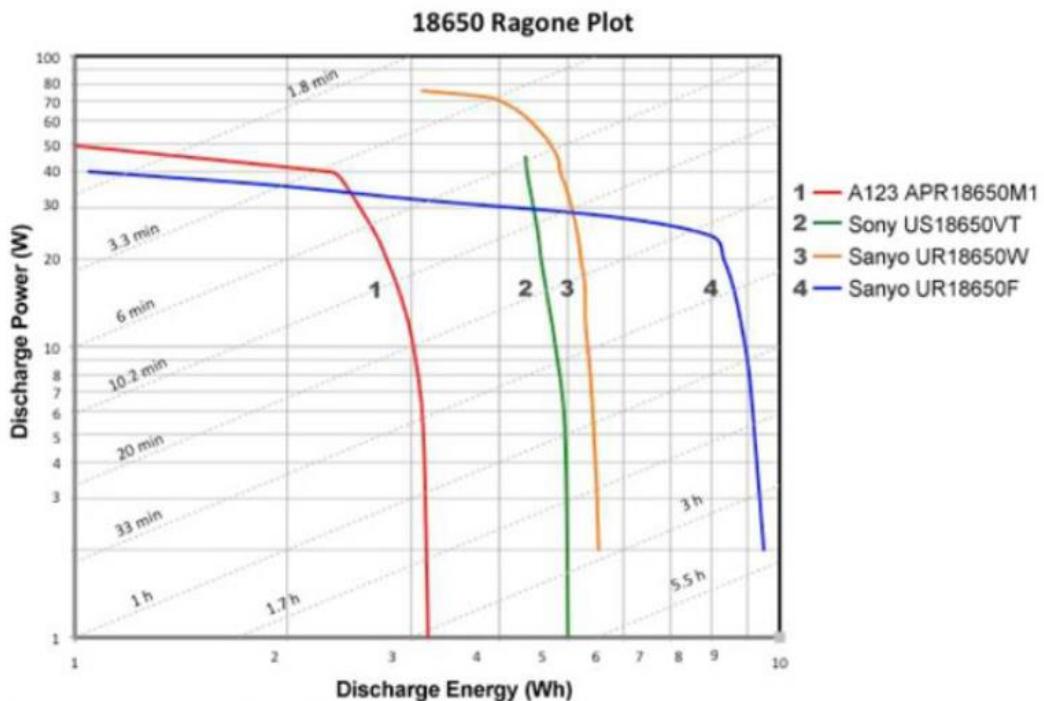
Flooded: 1.20–1.60

Source: Von Wentzel (2008)

### Ragone Plot

Lithium- and nickel-based batteries are commonly evaluated by the Ragone plot. Named after David V. Ragone, the Ragone plot looks at the battery's capacity in watt-hours (Wh) and discharge power in watts (W). The big advantage of the Ragone plot over the Peukert Law is the ability to read the runtime in minutes and hours presented on the diagonal lines on the Ragone graph.

Figure 2 illustrates the Ragone plot of four lithium-ion systems using 18650 cells. The horizontal axis displays energy in watt-hours (Wh) and the vertical axis is power in watts (W). The diagonal lines across the field reveal the length of time the battery cells can deliver energy at given loading conditions. The scale is logarithmic to allow a wide selection of battery sizes. The battery chemistries featured in the chart include lithium-iron phosphate (LFP), lithium-manganese oxide (LMO), and nickel manganese cobalt (NMC).



**Figure 2:** Ragone plot reflects Li-ion 18650 cells.

Four Li-ion systems are compared for discharge power and energy as a function of time. Not all curves are fully drawn out.

**Legend:** The A123 APR18650M1 is a lithium iron phosphate (LiFePO<sub>4</sub>) Power Cell rated at 1,100mAh, delivering a continuous discharge current of 30A. The Sony US18650VT and Sanyo UR18650W are manganese based Li-ion Power Cells of 1,500mAh each, delivering a continuous discharge of 20A. The Sanyo UR18650F is a 2,600mAh Energy Cell for a moderate 5A discharge. This cell provides the highest discharge energy but has the lowest discharge power.

Source: Exponent

The Sanyo UR18650F [4] Energy Cell has the highest specific energy and can run a laptop or e-bike for many hours at a moderate load. The Sanyo UR18650W [3] Power Cell, in comparison, has a lower specific energy but can supply a current of 20A. The A123 [1] in LFP has the lowest specific energy but offers the highest power capability by delivering 30A of continuous current. Specific energy defines the battery capacity in weight (Wh/kg); energy density is given in volume (Wh/l).

The Ragone plot helps in the selection of the optimal Li-ion system to satisfy discharge power while retaining the required runtime. If an application calls for a very high discharge current, the 3.3 minute diagonal line on the chart points to the A123 (Battery 1); it can deliver up to 40 watts of power for 3.3 minutes. The Sanyo F (Battery 4) is slightly lower and delivers about 36 watts. By focusing on discharge time and following the 33 minute discharge line further down, Battery 1 (A123) only delivers 5.8 watts for 33 minutes before the energy is depleted. The higher capacity Battery 4 (Sanyo F) can provide roughly 17 watts for the same time; its limitation is lower power.

A design engineer should note that the Ragone snapshot taken by the battery manufacturers represents a new cell, a condition that is temporary. When calculating power and energy needs, engineers must take into account battery fade caused by cycling and aging. Battery-

operated systems must still function with a battery that will eventually drop to 70 or 80 percent capacity. A further consideration is low temperature as a battery momentarily loses power when cold. The Ragone plot does not take these decreased performance conditions into account.

The design engineer should further develop a battery pack that is durable and does not get stressed during regular use. Stretching load and capacity boundaries to the limit shortens battery life. If repetitive high discharge currents are needed, the pack should be made larger and with the correct choice of cells. An analogy is a truck that is equipped with a large diesel engine instead of a souped-up engine intended for a sports car.

## 6. From Birth to Retirement

### 6.1. How to Prime Li-ion Batteries

Not all rechargeable batteries deliver the rated capacity when new, and they require formatting. While this applies to most battery systems, manufacturers of lithium-ion batteries disagree. They say that Li-ion is ready at birth and does not need priming. Although this may be true, users have reported some capacity gains by cycling after a long storage.

“What’s the difference between formatting and priming?” people ask. Both address capacities that are not optimized and can be improved with cycling. Formatting completes the fabrication process that occurs naturally during use when the battery is being cycled. A typical example is lead- and nickel-based batteries that improve with usage until fully formatted. Priming, on the other hand, is a conditioning cycle that is applied as a service to improve battery performance during usage or after prolonged storage. Priming relates mainly to nickel-based batteries.

Some battery users insist that a passivation layer develops on the cathode of a lithium-ion cell after storage. Also known as interfacial protective film (IPF), this layer is said to restrict ion flow, cause an increase in internal resistance and in the worst case, lead to lithium plating. Charging, and more effectively cycling, is known to dissolve the layer and some battery users claim to have gained extra runtime after the second or third cycle on a smartphone, albeit by a small amount.

Scientists do not fully understand the nature of this layer, and the few published resources on this subject only speculate that performance restoration with cycling is connected to the removal of the passivation layer. Some scientists outright deny the existence of the IPF, saying that the idea is highly speculative and inconsistent with existing studies. Whatever the outcome on the passivation of Li-ion may be, there is no parallel to the “memory” effect with NiCd batteries that require periodic cycling to prevent capacity loss. The symptoms may appear similar but the mechanics are different. Nor can the effect be compared to sulfation of lead acid batteries.

A well-known layer that builds up on the anode is the solid electrolyte solid electrolyte interface (SEI). SEI is an electrical insulation but has sufficient ionic conductivity to allow the battery to function normally. While the SEI layer lowers the capacity, it also protects the battery. Without SEI, Li-ion might not get the longevity that it has.

The SEI layer develops as part of a formation process and manufacturers take great care to do this right, as a batched job can cause permanent capacity loss and a rise in internal resistance. The process includes several cycles, float charges at elevated temperatures and rest periods that can take many weeks to complete. This formation period also provides quality control and assists in cell matching, as well as observing self-discharge by measuring the cell voltage after a rest. High self-discharge hints to impurity as part of a potential manufacturing defect.

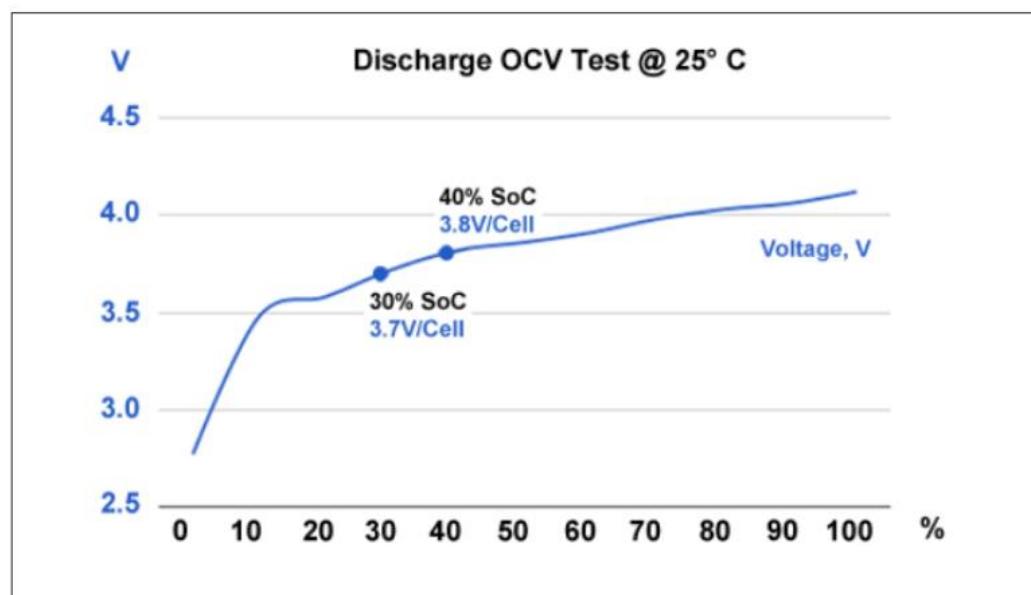
Electrolyte oxidation (EO) also occurs on the cathode. This causes a permanent capacity loss and increases the internal resistance. No remedy exists to remove the layer once formed but electrolyte additives lessen the impact. Keeping Li-ion at a voltage above 4.10V/cell while at

an elevated temperature promotes electrolyte oxidation. Field observation shows that the combination of heat and high voltage can stress Li-ion more than harsh cycling.

Lithium-ion is a very clean system that does not need additional priming once it leaves the factory, nor does it require the level of maintenance that nickel-based batteries do. Additional formatting makes little difference because the maximum capacity is available right from the beginning, (the exception may be a small capacity gain after a long storage). A full discharge does not improve the capacity once the battery has faded — a low capacity signals the end of life. Instructions recommending charging a new Li-ion for 8 hours are written off as “old school,” a left-over from the old nickel battery days.

## 6.2. How to Store Li-ion Batteries

There is virtually no self-discharge below about 4.0V at 20C (68F); storing at 3.7V yields amazing longevity for most Li-ion systems. Finding the exact 40–50 percent SoC level to store Li-ion is not that important. At 40 percent charge, most Li-ion has an OCV of 3.82V/cell at room temperature. To get the correct reading after a charge or discharge, rest the battery for 90 minutes before taking the reading. If this is not practical, overshoot the discharge voltage by 50mV or go 50mV higher on charge. This means discharging to 3.77V/cell or charging to 3.87V/cell at a C-rate of 1C or less. The rubber band effect will settle the voltage at roughly 3.82V. Figure 1 shows the typical discharge voltage of a Li-ion battery.



**Figure 1: Discharge voltage as a function of state-of-charge.** Battery SoC is reflected in OCV. Lithium manganese oxide reads 3.82V at 40% SoC (25°C), and about 3.70V at 30% (shipping requirement). Temperature and previous charge and discharge activities affect the reading. Allow the battery to rest for 90 minutes before taking the reading.

Li-ion cannot dip below 2V/cell for any length of time. Copper shunts form inside the cells that can lead to elevated self-discharge or a partial electrical short. If recharged, the cells might become unstable, causing excessive heat or showing other anomalies. Li-ion batteries that have been under stress may function normally but are more sensitive to mechanical abuse. Liability for incorrect handling should go to the user and not the battery manufacturer.

### Capacity Loss during Storage

Storage induces two forms of losses: Self-discharge that can be refilled with charging before use, and non-recoverable losses that permanently lower the capacity. Table 2 illustrates the remaining capacities of lithium- and nickel-based batteries after one year of storage at various temperatures. Li-ion has higher losses if stored fully charged rather than at a SoC of 40 percent.

Temperature	Lead acid at full charge	Nickel-based at any charge	Lithium-ion (Li-cobalt)	
			40% charge	100% charge
0°C	97%	99%	98%	94%
25°C	90%	97%	96%	80%
40°C	62%	95%	85%	65%
60°C	38% (after 6 months)	70%	75%	60% (after 3 months)

**Table 2: Estimated recoverable capacity when storing a battery for one year.** Elevated temperature hastens permanent capacity loss. Depending on battery type, lithium-ion is also sensitive to charge levels.

### 6.3. How to Transport Li-ion Batteries

Safety prompted authorities to tighten the rules when transporting batteries. Although lithium batteries get the most attention, the Federal Aviation Administration (FAA) says that based on records from 1991 to 2007 it was only a factor in 27 percent of all incidents. Lead acid, NiMH, NiCd and alkaline are also to blame. Reports say that short circuit, a preventable problem that can be solved with better packaging, is the largest problem.

The largest changes in shipping directive are with lithium batteries, and with good reasons. Li-ion is the fastest growing battery chemistry and already in 2009, 3.3 billion Li-ion were transported by air. Safety is an ongoing concern, and an airline-pilot union asked the FAA to ban lithium batteries on passenger aircraft. This came into effect in 2016 and lithium batteries are now shipped in cargo airplanes only.

Since 2008, lithium batteries can no longer be placed in checked baggage; they must be carried onboard. Air travelers are reminded of how many batteries they can carry with a portable device and as spares. Quick access to a fire extinguisher enables putting out a fire in the cabin should one take off. A coffee pot served as the fire extinguishing device for a flaming laptop battery in one reported incident. This is not possible with a burning battery in the cargo hold.

All lithium batteries are considered to be dangerous goods and transporting them requires compliance with Class 9 directives. However, exemptions are made when shipping these batteries in small quantities.

## 6.4. How to recycle Li-ion Batteries

For the first time, lithium-ion has been added to the list of pollutants. This chemistry was classified as only mildly toxic, but their sheer volume requires tighter scrutiny.

Li-ion is reasonably harmless but spent packs should be disposed of properly. This is done less to retrieve valuable metals, as is the case with lead acid, than for environmental reasons, especially with the growing volume used in consumer products. Li-ion contains harmful elements that are at the toxicity level of electronic devices.

With the increasing use of Li-ion, the European Commission report named “Towards the Battery of the future” delivers warnings because of the large number of batteries that will meet end-of-life. In Europe, Li-ion cannot be landfilled because of toxicity and danger of explosion, nor can they be incinerated as the ashes are also toxic in landfill. Of concern is cobalt and agents that bind electrode materials together.

The report no longer brands lead acid as the most toxic battery. Lead acid is the only battery that can be recycled profitably. With almost 100% of lead acid being recycled, the focus shifts to Li-ion because of growing volume and value of retrievable materials.

According to an ATZ report (2018), the 33kWh Li-ion traction battery of the BMW i3 electric vehicle contains 2kg (4.4 lb) cobalt, 6kg (13 lb) lithium, 12kg (26 lb) manganese, 12kg (26 lb) nickel and 35kg (77 lb) graphite. Not all retrieved materials may reach battery-grade quality when recycled but the gained resources can be used for less demanding purposes. Lithium is also used as a lubricant.

The recycling process of Li-ion batteries normally begins with deactivation involving a full discharge to remove the stored energy and prevent a surprise thermal event. The electrolyte can also be frozen to prevent electrochemical reactions during the crushing process. Duesenfeld patented a process that evaporates and recovers the organic solvents of the electrolyte in a vacuum by condensation. This process is said to not produce toxic exhaust gases.

The following steps are divided into mechanical, pyrometallurgical and hydrometallurgical treatments. Mechanical involves crushing the battery cells; pyrometallurgical extracts the metals by thermal treatment; and hydrometallurgy involves aqueous processes.

Once disassembled, sorting separates copper foil, aluminum foil, separator and the coating materials. Nickel, cobalt and copper can be recycled from the cast, but lithium and aluminum remain in the slag. A hydrometallurgical process is necessary to recover lithium. This includes leaching, extraction, crystallization, and precipitation from a liquid solution. Hydrometallurgical treatment is used to recover pure metals, e.g. lithium, gleaned from separated coating materials after mechanical processes or from slag in pyrometallurgical processes.

Recycling Li-ion batteries is not yet profitable must be government subsidized. There is an incentive to recover costly cobalt. No recycling technology exists today that is capable of producing pure enough lithium for a second use in batteries. Lithium for batteries is mined; second hand lithium is used for lubricants, glass, ceramics and other applications.

## 7. How to Prolong Battery Life

### 7.1. General

A battery is a corrosive device that begins to fade the moment it comes off the assembly line. The stubborn behavior of batteries has left many users in awkward situations. Battery-induced failures are common; some are a nuisance but others have serious consequences. Even with the best of care, a battery only lives for a defined number of cycles and time. It shares similarity with a living organism that develops an illness and dies early. Although the manufacturer may specify a given number of discharge/charge cycles, a battery has no distinct life span; the health rests much on environmental conditions and usage patterns.

Lead acid reaches the end of life when the active material has been consumed on the positive grids; nickel-based batteries lose performance because of corrosion. Lithium-ion fades over time when the transfer of ions slows down due to the buildup of layers on the electrodes. Only the supercapacitor should achieve an unlimited number of cycles, but this is not a real battery.

Batteries should receive the same treatment as a critical part in an aircraft, medical device or industrial machine where the wear and tear falls under strict maintenance guidelines. Authorities struggle to implement such guidelines and for good reasons. Generally accepted test procedures have not yet been established for batteries, and even auditors doing quality control shy away from such ruling and only examine the outer appearance; state-of-health is mostly ignored. This allows faded batteries to hide comfortably among their stronger peers. The omission is in part connected with a lack of battery test devices that can reliably assess a battery on the fly.

#### 7.1.1. How to define Battery Life

A portable system works well when the batteries are new but confidence drops after the first packs need replacing due to capacity fade. In time, the battery fleet becomes a jumble of good and bad batteries, and that's when the headache begins. Battery management mandates that all batteries in a fleet are kept at an acceptable capacity level. Packs that fall below a given threshold must be replaced to keep system integrity. Battery failure occurs most often on a heavy traffic day or in an emergency when more than normal service is demanded.

Batteries exhibit human-like qualities and need good nutrition. Care begins by operating at room temperature and discharging them at a moderate current. There is some truth as to why batteries cared for by an individual user outperform those in a fleet; studies can back this up.

Charging is generally well understood, but the “ready” light is misconstrued. Ready does not mean “able.” There is no link to battery performance, nor does the green light promise full runtime. All batteries charge fully, even if weak; “ready” simply means that the battery is full.



The capacity a battery can hold diminishes with age and the charge time shortens with nickel-based batteries and in part also with lead acid, but not necessarily with Li-ion. Lower charge transfer capability that inhibits the flow of free electrons prolongs the charge time with aged Li-ion.

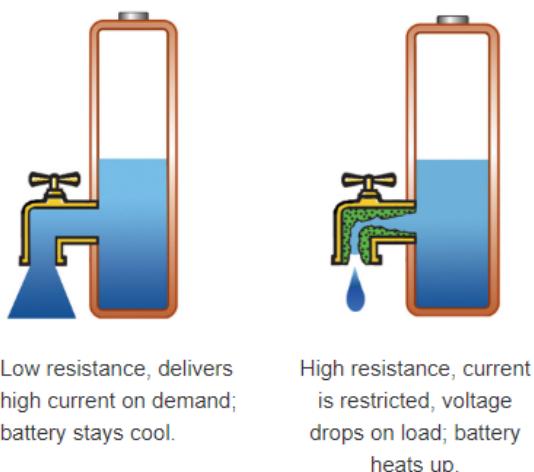
The amount of energy a battery can hold is measured in capacity. Capacity is the leading health indicator that determines runtime and predicts end of battery life when low. A new battery is rated at 100 percent, but few packs in service deliver the full amount: a workable capacity bandwidth is 80–100 percent. A cell or pack should be replaced when the capacity drops to 80 percent.

The service life of a battery is specified in number of cycles. Lithium- and nickel-based batteries deliver between 300 and 500 full discharge/charge cycles before the capacity drops below 80 percent.

Cycling is not the only cause of capacity loss; keeping a battery at elevated temperatures also induces stress. A fully charged Li-ion kept at 40°C (104°F) loses about 35 percent of its capacity in a year without being used. Ultra-fast chargers and harsh discharging is also harmful. This cuts battery life to half, and hobbyists can attest to this.

### 7.1.1.a How does Rising Internal Resistance affect Performance?

Capacity alone is of limited use if the pack cannot deliver the stored energy effectively; a battery also needs low internal resistance. Measured in milliohms ( $m\Omega$ ), resistance is the gatekeeper of the battery; the lower the resistance, the less restriction the pack encounters. This is especially important in heavy loads such as power tools and electric powertrains. High resistance causes the battery to heat up and the voltage to drop under load, triggering an early shutdown. Figure 1 illustrates a battery with low internal resistance in the form of a free-flowing tap against a battery with elevated resistance in which the tap is restricted.



**Figure 1: Effects of internal battery resistance.**

A battery with low internal resistance delivers high current on demand. High resistance causes the battery to heat up and the voltage to drop. The equipment cuts off, leaving energy behind.

Courtesy of Cadex

The internal resistance of Li-ion increases with use and aging but improvements have been made with electrolyte additives to keep the buildup of films on the electrodes under control. With all batteries, SoC affects the internal resistance. Li-ion has higher resistance at full charge and at end of discharge with a big flat low resistance area in the middle.

Two methods are used to read the internal resistance of a battery: Direct current (DC) by measuring the voltage drop at a given current, and alternating current (AC), which takes reactance into account. When measuring a reactive device such as a battery, the resistance values vary greatly between the DC and AC test methods, but neither reading is right or wrong. The DC reading looks at pure resistance ( $R$ ) and provides true results for a DC load such as a heating element. The AC reading includes reactive components and provides impedance ( $Z$ ). Impedance provides realistic results on a digital load such as a mobile phone or an inductive motor.

Figure 2 illustrates the internal resistance of an 18650 Li-ion cell when exposed to 1,000 full cycles at 40°C (104°F). The AC readings in the green frame do not reflect the true resistive state of a battery; DC method provides more reliable performance data with loading.

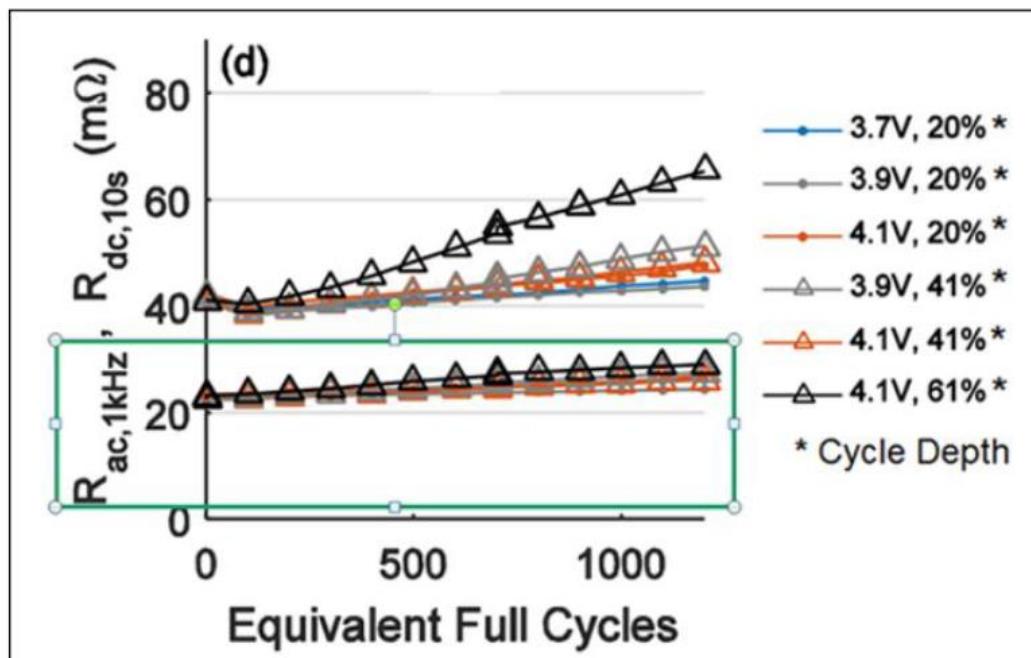


Figure 2: Rise of internal resistances of 18650 Li-ion cell measured with AC and DC methods when cycled.

AC resistance readings in green frame stay low; DC method gives true state.

Source: Technische Universität München (TUM)

### Pack Resistance

The internal resistance of a battery does not consist of the cells alone but also includes the interconnection, fuses, protection circuits and wiring. In most cases these peripherals more than double the internal resistance and can falsify rapid-test methods. Typical readings of a single cell pack for a mobile phone are shown below.

#### Internal Resistance of a Mobile Phone Battery

Cell, single, high capacity prismatic	50mΩ	subject to increase with age
Connection, welded	1mΩ	
PTC, welded to cable, cell	25mΩ	18–30 mΩ according to spec
Protection circuit, PCB	50mΩ	
<b>Total internal resistance</b>	<b>ca. 130mΩ</b>	

### 7.1.1.b. What does Elevated Self Discharge do?

All batteries are affected by self-discharge. Self-discharge is not a manufacturing defect but a battery characteristic; although poor fabrication practices and improper handling can increase the problem. Self-discharge is permanent and cannot be reversed. Figure 1 illustrates self-discharge in the form of leaking fluid.



**Figure 1: Effects of high self-discharge.**

Self-discharge increases with age, cycling and elevated temperature. Discard a battery if the self-discharge reaches 30 percent in 24 hours.

Courtesy of Cadex

The amount of electrical self-discharge varies with battery type and chemistry. The energy loss is asymptotical, meaning that the self-discharge is highest right after charge and then tapers off. Li-ion self-discharges about 5 percent in the first 24 hours and then loses 1–2 percent per month; the protection circuit adds another 3 percent per month. A faulty separator can lead to elevated self-discharge that could develop into a current path, generating heat and, in an extreme case, initiate a thermal breakdown.

The self-discharge of all battery chemistries increases at higher temperature, and the rate typically doubles with every  $10^{\circ}\text{C}$  ( $18^{\circ}\text{F}$ ). A noticeable energy loss occurs if a battery is left in a hot vehicle. High cycle count and aging also increase self-discharge of all systems.

Under normal circumstances the self-discharge of Li-ion is reasonably steady throughout its service life; however, full state-of-charge and elevated temperature cause an increase. These same factors also affect longevity. Furthermore, a fully charged Li-ion is more prone to failure than one that is partially charged. Table 4 shows the self-discharge per month of Li-ion at various temperatures and state-of-charge. The high self-discharge at full state-of-charge and high temperatures comes as a surprise.

State-of-charge	$0^{\circ}\text{C}$ ( $32^{\circ}\text{F}$ )	$25^{\circ}\text{C}$ ( $77^{\circ}\text{F}$ )	$60^{\circ}\text{C}$ ( $140^{\circ}\text{F}$ )
Full charge	6%	20%	35%
40–60% charge	2%	4%	15%

**Table 4: Self-discharge per month of Li-ion at various temperatures and state-of-charge**

Self-discharge increases with rising temperature and higher SoC.

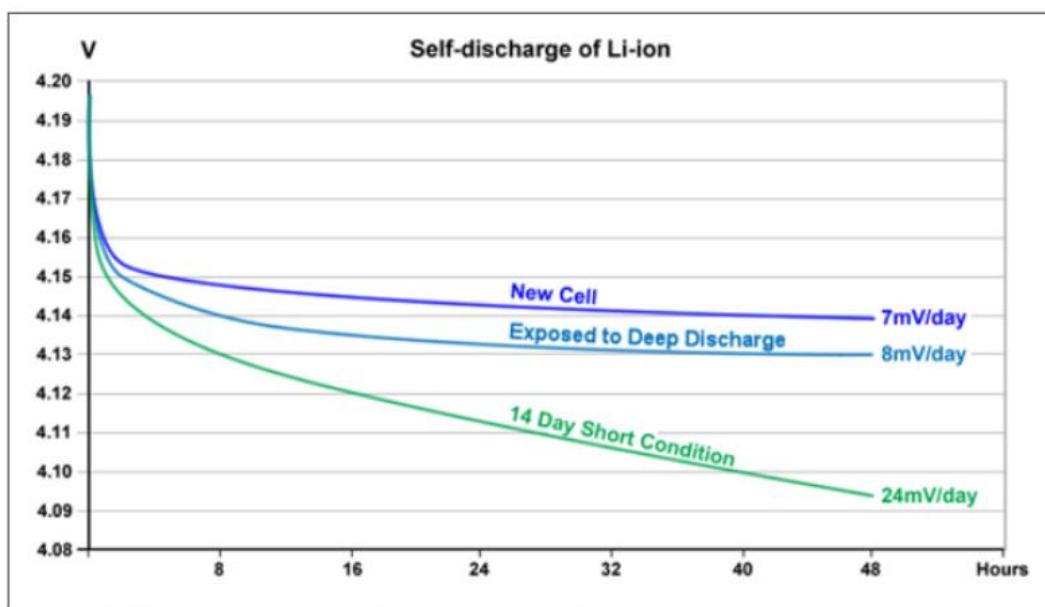
There are reasons why Li-ion is put to sleep when discharging below 2.50V/cell. Copper dendrites grow if the cell is allowed to dwell in a low-voltage state for longer than a week. This results in elevated self-discharge, which could compromise safety.

Self-discharge mechanisms must also be observed in manufacturing. They vary from corrosion to impurities in the electrodes that reflect in self-discharge variations not only from batch to

batch but also from cell to cell. A quality manufacturer checks the self-discharge of each cell and rejects those that fall outside tolerances.

Regular charge and discharge causes an unwanted deposit of lithium metal on the anode (negative electrode) of Li-ion, resulting in capacity loss through a depletion of the lithium inventory and the possibility of creating an internal short circuit. An internal short is often preceded with elevated self-discharge, a field that needs further research to learn what levels of self-discharge would pose a hazard that can lead to a thermal runaway. Unwanted lithium deposition also increases the internal resistance that reduces loading capability.

Figure 5 compares the self-discharge of a new Li-ion cell with a cell that underwent forced deep discharges and one that was fully discharged, shorted for 14 days and then recharged. The cell that was exposed to deep discharges beyond 2.50V/cell shows a slightly higher self-discharge than a new cell. The largest self-discharge is visible with the cell that was stored at zero volts.



**Figure 5: Self-discharge of new and stressed Li-ion cells.** Cells that had been stressed with deep discharges and kept at 0V show a higher self-discharge than a new cell.

Source: TU München

### 7.1.1.c. How Low can a Battery be Discharged?

Not all battery energy can or should be used on discharge; some reserve is almost always left behind on purpose after the equipment cuts off. There are several reasons for this.

Most mobile phones, laptops and other portable devices turn off when the lithium-ion battery reaches 3.00V/cell on discharge. At this point the battery has about 5 percent capacity left. Manufacturers choose this voltage threshold to preserve some energy for housekeeping, as well as to reduce battery stress and allow for some self-discharge if the battery is not immediately recharged. This grace period in empty state can last several months until self-discharge lowers the voltage of Li-ion to about 2.50V/cell, at which point the protection circuit opens and most packs become unserviceable with a regular charger.

To prevent triggering premature cutoff at a high load or cold temperature, some device manufacturers may lower the end-of-discharge voltage. Li-ion in a power tool may discharge the battery to 2.70V/cell instead of 3.00V/cell and Li-phosphate may go to 2.45V/cell instead of 2.70V/cell.

Industrial applications aim to attain maximum service life rather than optimize runtime, as it is done with consumer products. This also applies to the electric powertrain; batteries in a hybrid cars and electric vehicles are seldom fully discharged or charged; most operate between 30 and 80 percent state-of-charge when new. This is the most effective working bandwidth; it also delivers the longest service life. A deep discharge to empty followed a full charge would cause undue stress for the Li-ion.

### 7.1.2. Cell Matching and Balancing

A manufacturer cannot predict the exact capacity when the cell comes off the production line, and this is especially true with lead acid and other batteries that involve manual assembly. Even fully automated cell production in clean rooms causes performance differences. As part of quality control, each cell is measured and segregated into categories according to their capacity levels.

Let's look at what happens to a weak cell that is strung together with stronger cells in a pack. The weak cell holds less capacity and is discharged more quickly than their strong brothers. Going empty first causes their strong brothers to overrun their feeble sibling to the point where a high load can push the weak cell into reverse polarity. Nickel-cadmium can tolerate a reverse voltage of minus 0.2V at a few millamps, but exceeding this will cause a permanent electrical short. On charge, the weak cell reaches full charge first, and then goes into heat-generating overcharge, while the strong brothers still accept charge and stay cool. The weak cell experiences a disadvantage on both charge and discharge; it continues to weaken until giving up the struggle.

The capacity tolerance between cells in an industrial battery should be  $\pm 2.5$  percent. High-voltage packs designed for heavy loads and a wide temperature range should reduce the capacity tolerance further. There is a strong correlation between cell balance and longevity.

Figure 1 illustrates the cycling performance of five aged Li-ion packs as a function of cell match. The cells are connected in a 2P4S arrangement with a center tap, forming two battery sections that in our example are poorly matched. The capacity differences between the two sections are 5, 6, 7 and 12 percent. When cycled, all batteries show large capacity losses over 18 cycles, but the greatest decrease occurs with the pack exhibiting 12 percent capacity mismatch.

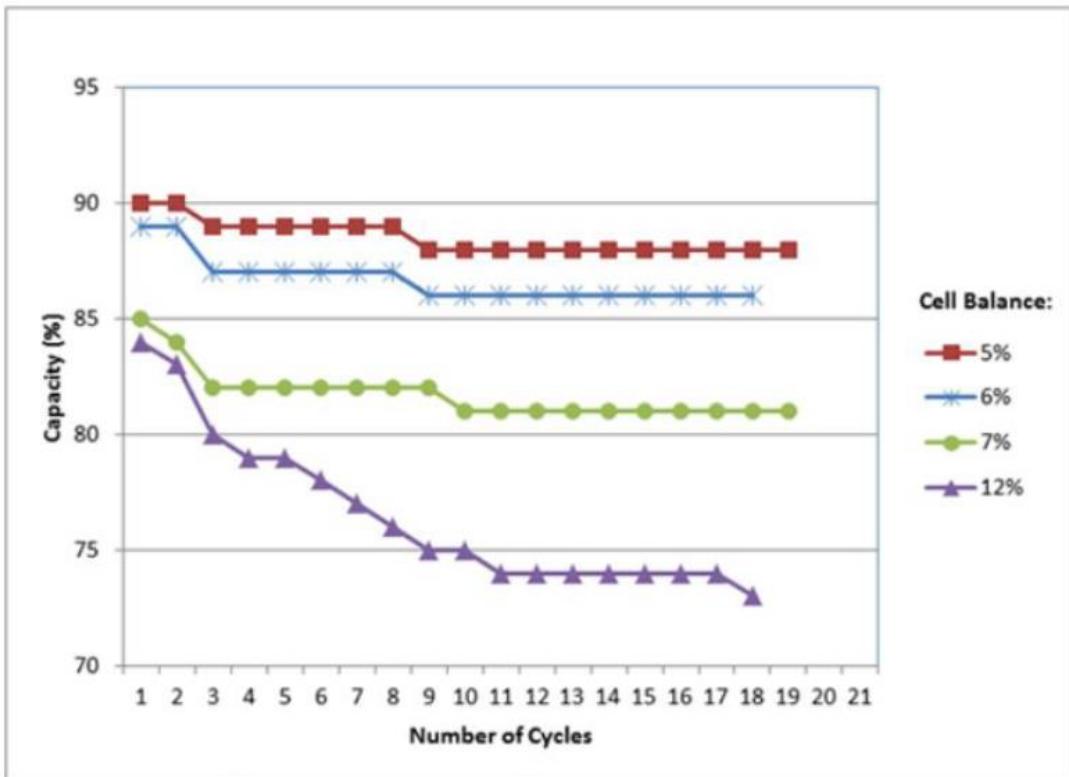


Figure 1: Cycling performance as a function of cell match

Battery packs with well-matched cells perform better than those in which the cell or group of cells differ in serial connection.

Configuration: 5Ah prismatic Li-ion connected in 2P4S (14.8V, 10Ah) with center tap

Quality Li-ion cells have uniform capacity and low self-discharge when new. Adding cell balancing is beneficial especially as the pack ages and the performance of each cell decreases at its own pace. A problem arises when a cell in a string loses capacity or develops elevated self-discharge. This can be attributed to high-temperature spots in a large battery. Low-quality cells may also be prone to unequal aging. Li-phosphate has higher self-discharge than other Li-ion, and this complicates cell balancing.

A battery expert once said: “I have not seen a cell balancing circuit that works.” For multi-cell packs, he suggested using quality Li-ion cells that have been factory-sorted on capacity and voltage. This works well for Li-ion packs up to 24V; packs above 24V should have balancing. Most balancing is passive; active balancing is complex and is only used in very large systems.

Passive balancing bleeds high-voltage cells on a resistor during charge in the 70–80 percent SoC curve; active balancing shuttles the extra charge from higher-voltage cells during discharge to those with a lower voltage. Active balancing is the preferred method for EV batteries, but it requires DC-DC converters. The corrected currents are in the mA range only. Applying a heavy load during acceleration, followed by rapid-charging with regenerative braking requires well-tuned cells in a high-voltage battery to attain the anticipated life. EV batteries in the Tesla, BMW i3 and other EVs employ active balancing to minimize cell stress.

All Li-ion cells require a protection circuit that assures that serially connected cells do not exceed 4.25V/cell (most Li-ion) on charge and that disconnect when the weakest cell drops to 2.80V/cell or lower. The discharge disconnect prevents the stronger cells from pushing the depleted cell into reverse polarity. The protection circuit acts like a guardian angel that shields

the weaker siblings from being bullied by the stronger peers. This may explain why Li-ion packs for power tools last longer than nickel-based batteries without a protection circuit. The protection circuit also safeguards the battery from excessive load current.

### 7.1.3. What causes Cells to Sort?

Manufacturers are at a loss to explain why some cells develop high electrical leakage or a short while still new. The culprit might be foreign particles that contaminate the cells during fabrication, or rough-spots on the plates that damage the delicate separator. Clean rooms, improved quality control at the raw material level and minimal human handling during the manufacturing process have reduced the “mortality rate.”

It is not advised to replace a shorted cell in an aging pack as the new cells will always be stronger than the others. Replacing faulty cells often leads to battery failures within 6 months. It's best not to disturb the cells but allow them to age naturally as an intact family. The exception is replacing a defective cell to salvage a well-functioning pack.

Cobalt-blended Li-ion cells develop fewer leak and electrical shorts than nickel- and lead-based batteries but they can occur, especially with Li-phosphate. For unknown reasons, the cell at the positive end in a string is most likely to short first. Perhaps it gets the most stress while the middle cells enjoy some protection by being buffered.

The mandatory protection circuit for Li-ion packs can only shield the cell from over-voltage, excessive loading and reverse polarity. An electrical short caused by internal cell damage lies outside the safeguard of the protection circuit. Most cell failures occur when the battery has been damaged by shock and vibration, or has been overcharged or overheated. Charging at freezing temperatures can also damage Li-ion without indication of stress to the user. The Sony recall in 2006, when microscopic metal particles came into contact with other parts and the Boeing 787 Dreamliner that called for a redesign of the battery system are examples of when an internal short could not be prevented by a protection circuit. These were certified Li-ion batteries that developed an electrical short during service.

To reduce the risk of an electrical short, Li-ion cells for electric powertrains and demanding industrial applications use a heavy-duty separator. These batteries are larger than those used in consumer products and also have a lower specific energy. Saying that Li-ion has twice the energy density of NiMH can inaccurate. Long-lasting Li-ion cells can have a specific energy as low as 60Wh/kg, which is similar to nickel-cadmium, while some consumer Li-ion can go up to 250Wh/kg.

### 7.1.4. Loss of Electrolyte

A properly designed and correctly charged lithium-ion cell should not generate gases, nor should it lose electrolyte through venting. In spite of what advocates say, lithium-based cells can build up an internal pressure under certain conditions, and a bloated pouch cell is proof of this. (See BU-301a: Types of Battery Cells) Some cells include an electrical switch that opens

if the cell pressure reaches a critical level. Others feature a membrane that releases gases. Many of these safety features are one way only, meaning that once activated, the cell becomes inoperable. This is done for safety reasons.

When overcharged, a battery gases, splitting water in the electrolyte into hydrogen and oxygen. A battery becomes a “water-splitting device” by electrolysis. A parallel is the fuel cell but it does the opposite way, turning oxygen and hydrogen into electricity by producing water. Energy is needed to produce oxygen and hydrogen and the battery gets the energy through overcharging.

## 7.2. Lithium-ion

### 7.2.1. What causes Lithium-ion to Age?

Battery research is focusing on lithium chemistries so much that one could imagine that the battery future lies solely in lithium. There are good reasons to be optimistic as lithium-ion is, in many ways, superior to other chemistries.

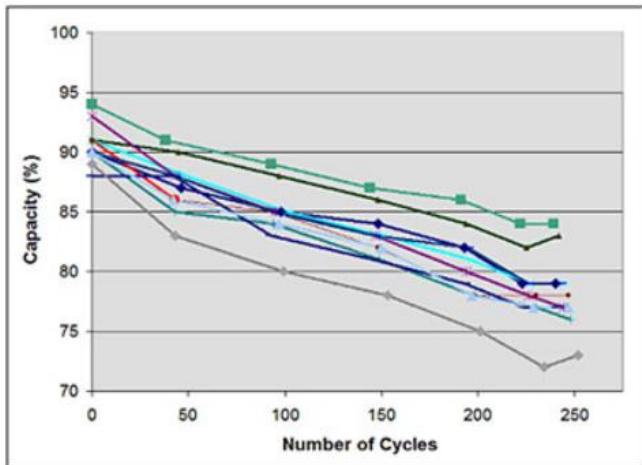
Lithium-ion has not yet fully matured and is still improving. Notable advancements have been made in longevity and safety while the capacity is increasing incrementally. Today, Li-ion meets the expectations of most consumer devices but applications for the EV need further development before this power source will become the accepted norm.

The lithium-ion battery works on ion movement between the positive and negative electrodes. In theory such a mechanism should work forever, but cycling, elevated temperature and aging decrease the performance over time. Manufacturers take a conservative approach and specify the life of Li-ion in most consumer products as being between 300 and 500 discharge/charge cycles.

Evaluating battery life on counting cycles is not conclusive because a discharge may vary in depth and there are no clearly defined standards of what constitutes a cycle (see 5.1: Basics About Discharging). In lieu of cycle count, some device manufacturers suggest battery replacement on a date stamp, but this method does not take usage into account. A battery may fail within the allotted time due to heavy use or unfavorable temperature conditions; however, most packs last considerably longer than what the stamp indicates.

The performance of a battery is measured in capacity, a leading health indicator. Internal resistance and self-discharge also play roles, but these are less significant in predicting the end of battery life with modern Li-ion.

Figure 1 illustrates the capacity drop of 11 Li-polymer batteries that have been cycled at a Cadex laboratory. The 1,500mAh pouch cells for mobile phones were first charged at a current of 1,500mA (1C) to 4.20V/cell and then allowed to saturate to 0.05C (75mA) as part of the full charge saturation. The batteries were then discharged at 1,500mA to 3.0V/cell, and the cycle was repeated. The expected capacity loss of Li-ion batteries was uniform over the delivered 250 cycles and the batteries performed as expected.



**Figure 1: Capacity drop as part of cycling.** Eleven new Li-ion were tested on a Cadex C7400 battery analyzer. All packs started at a capacity of 88–94% and decreased to 73–84% after 250 full discharge cycles. The 1500mAh pouch packs are used in mobile phones.

Courtesy of Cadex

Similar to a mechanical device that wears out faster with heavy use, the depth of discharge (DoD) determines the cycle count of the battery. The smaller the discharge (low DoD), the longer the battery will last. If at all possible, avoid full discharges and charge the battery more often between uses. Partial discharge on Li-ion is fine. There is no memory and the battery does not need periodic full discharge cycles to prolong life.

The following tables indicate stress related capacity losses on cobalt-based lithium-ion. The voltages of lithium iron phosphate and lithium titanate are lower and do not apply to the voltage references given. Table 2, 3 and 4 indicate general aging trends of common cobalt-based Li-ion batteries on depth-of-discharge, temperature and charge levels, while Table 6 further looks at capacity loss when operating within given and discharge bandwidths. The tables do not address ultra fast charging and high load discharges that will shorten battery life. Not all batteries behave the same.

Table 2 estimates the number of discharge/charge cycles Li-ion can deliver at various DoD levels before the battery capacity drops to 70 percent. DoD constitutes a full charge followed by a discharge to the indicated state-of-charge (SoC) level in the table.

Depth of discharge	Discharge cycles	
	NMC	LiPO <sub>4</sub>
100% DoD	~300	~600
80% DoD	~400	~900
60% DoD	~600	~1,500
40% DoD	~1,000	~3,000
20% DoD	~2,000	~9,000
10% DoD	~6,000	~15,000

**Table 2: Cycle life as a function of depth of discharge.\*** A partial discharge reduces stress and prolongs battery life, so does a partial charge. Elevated temperature and high currents also affect cycle life.

**Note:** 100% DoD is a full cycle; 10% is very brief. Cycling in mid-state-of-charge would have best longevity.

Lithium-ion suffers from stress when exposed to heat, so does keeping a cell at a high charge voltage. A battery dwelling above 30°C (86°F) is considered elevated temperature and for most Li-ion a voltage above 4.10V/cell is deemed as high voltage. Exposing the battery to high temperature and dwelling in a full state-of-charge for an extended time can be more stressful than cycling. Table 3 demonstrates capacity loss as a function of temperature and SoC.

Temperature	40% charge	100% charge
0°C	98% (after 1 year)	94% (after 1 year)
25°C	96% (after 1 year)	80% (after 1 year)
40°C	85% (after 1 year)	65% (after 1 year)
60°C	75% (after 1 year)	60% (after 3 months)

**Table 3: Estimated recoverable capacity when storing Li-ion for one year at various temperatures.**  
Elevated temperature hastens permanent capacity loss. Not all Li-ion systems behave the same.

Most Li-ions charge to 4.20V/cell, and every reduction in peak charge voltage of 0.10V/cell is said to double the cycle life. For example, a lithium-ion cell charged to 4.20V/cell typically delivers 300–500 cycles. If charged to only 4.10V/cell, the life can be prolonged to 600–1,000 cycles; 4.0V/cell should deliver 1,200–2,000 and 3.90V/cell should provide 2,400–4,000 cycles.

On the negative side, a lower peak charge voltage reduces the capacity the battery stores. As a simple guideline, every 70mV reduction in charge voltage lowers the overall capacity by 10 percent. Applying the peak charge voltage on a subsequent charge will restore the full capacity.

In terms of longevity, the optimal charge voltage is 3.92V/cell. Battery experts believe that this threshold eliminates all voltage-related stresses; going lower may not gain further benefits but induce other symptoms. Table 4 summarizes the capacity as a function of charge levels. (All values are estimated; Energy Cells with higher voltage thresholds may deviate.)

Charge level * (V/cell)	Discharge cycles	Available stored energy **
[4.30]	[150–250]	[110–115%]
4.25	200–350	105–110%
<b>4.20</b>	<b>300–500</b>	<b>100%</b>
4.15	400–700	90–95%
4.10	600–1,000	85–90%
4.05	850–1,500	80–85%
4.00	1,200–2,000	70–75%
3.90	2,400–4,000	60–65%
3.80	See note	35–40%
3.70	See note	30% and less

**Table 4: Discharge cycles and capacity as a function of charge voltage limit.** Every 0.10V drop below 4.20V/cell doubles the cycle but holds less capacity. Raising the voltage above 4.20V/cell would shorten the life. The readings reflect regular Li-ion charging to 4.20V/cell.

**Guideline:** Every 70mV drop in charge voltage lowers the usable capacity by about 10%.

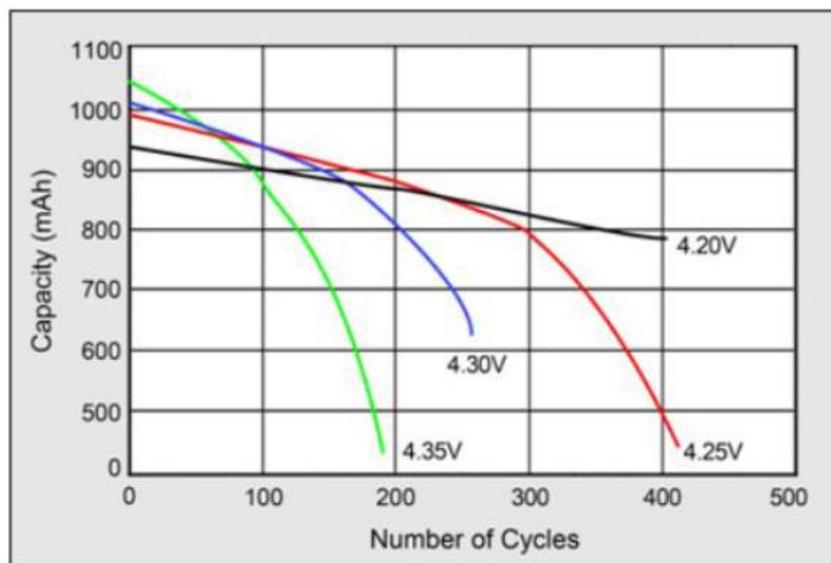
**Note:** Partial charging negates the benefit of Li-ion in terms of high specific energy.

\* Similar life cycles apply for batteries with different voltage levels on full charge.

\*\* Based on a new battery with 100% capacity when charged to the full voltage.

**Experiment:** Chalmers University of Technology, Sweden, reports that using a reduced charge level of 50% SOC increases the lifetime expectancy of the vehicle Li-ion battery by 44–130%.

For safety reasons, many lithium-ions cannot exceed 4.20V/cell. (Some NMC are the exception.) While a higher voltage boosts capacity, exceeding the voltage shortens service life and compromises safety. Figure 5 demonstrates cycle count as a function of charge voltage. At 4.35V, the cycle count of a regular Li-ion is cut in half.

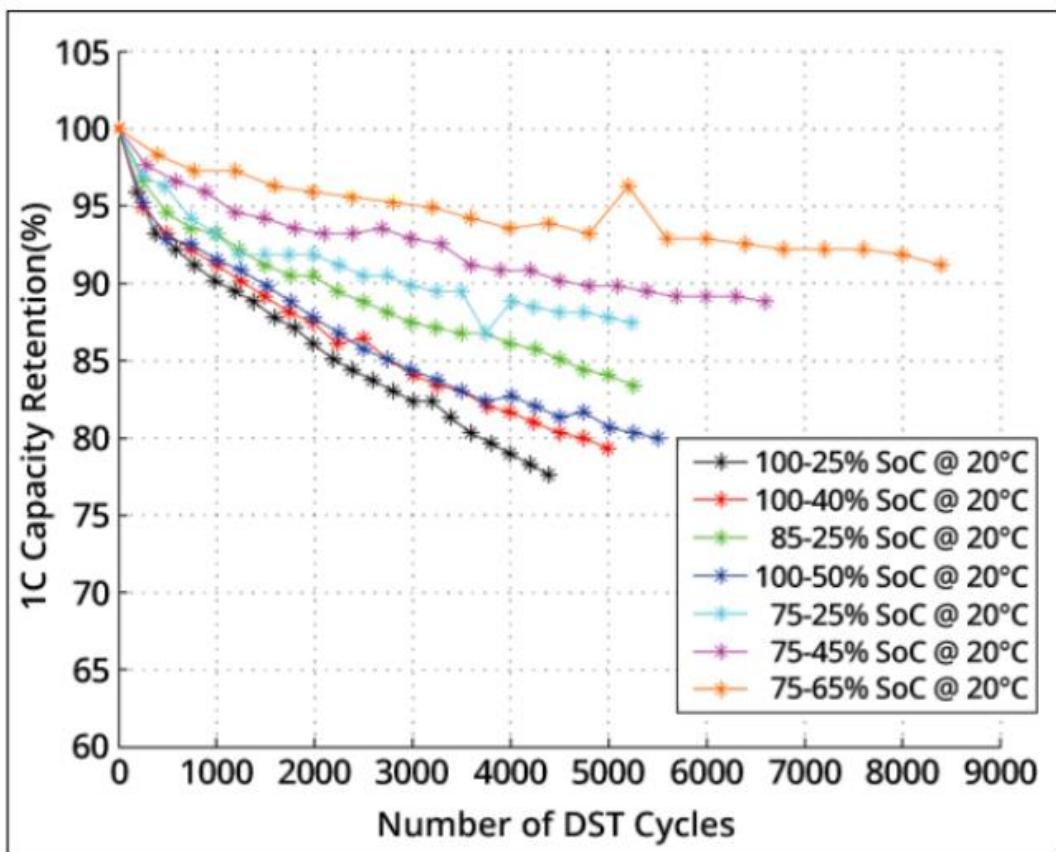


**Figure 5: Effects on cycle life at elevated charge voltages.** Higher charge voltages boost capacity but lowers cycle life and compromises safety.

Source: Choi et al. (2002)

Besides selecting the best-suited voltage thresholds for a given application, a regular Li-ion should not remain at the high-voltage ceiling of 4.20V/cell for an extended time. The Li-ion charger turns off the charge current and the battery voltage reverts to a more natural level. This is like relaxing the muscles after a strenuous exercise.

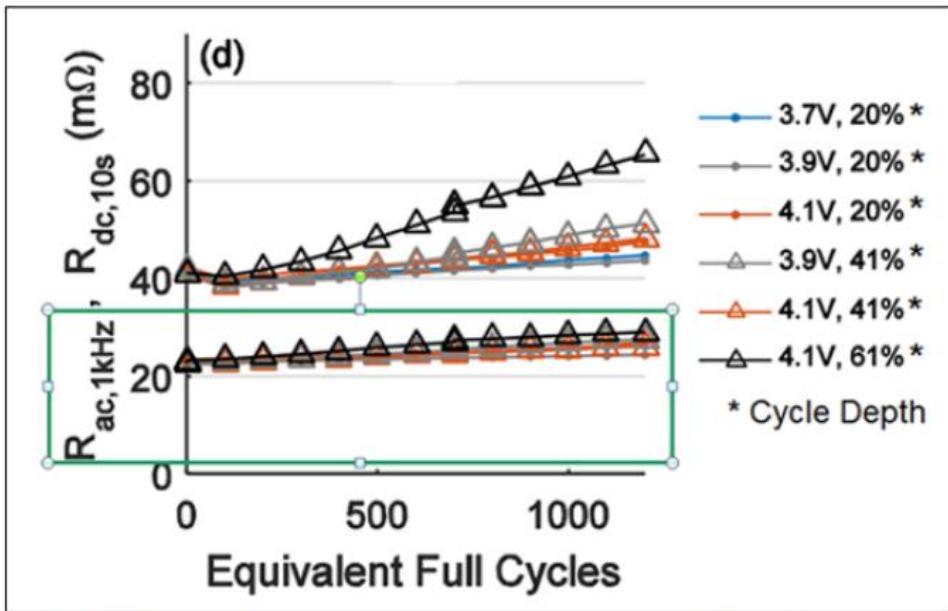
Figure 6 illustrates dynamic stress tests (DST) reflecting capacity loss when cycling Li-ion at various charge and discharge bandwidths. The largest capacity loss occurs when discharging a fully charged Li-ion to 25 percent SoC (black); the loss would be higher if fully discharged. Cycling between 85 and 25 percent (green) provides a longer service life than charging to 100 percent and discharging to 50 percent (dark blue). The smallest capacity loss is attained by charging Li-ion to 75 percent and discharging to 65 percent. This, however, does not fully utilize the battery. High voltages and exposure to elevated temperature is said to degrade the battery quicker than cycling under normal condition.



**Figure 6: Capacity loss as a function of charge and discharge bandwidth.\***

Charging and discharging Li-ion only partially prolongs battery life but reduces utilization.

Increasing the cycle depth also raises the internal resistance of the Li-ion cell. Figure 7 illustrates a sharp rise at a cycle depth of 61 percent measured with the DC resistance method. (See also 7.1.1a: How does Rising Internal Resistance affect Performance?) The resistance increase is permanent.

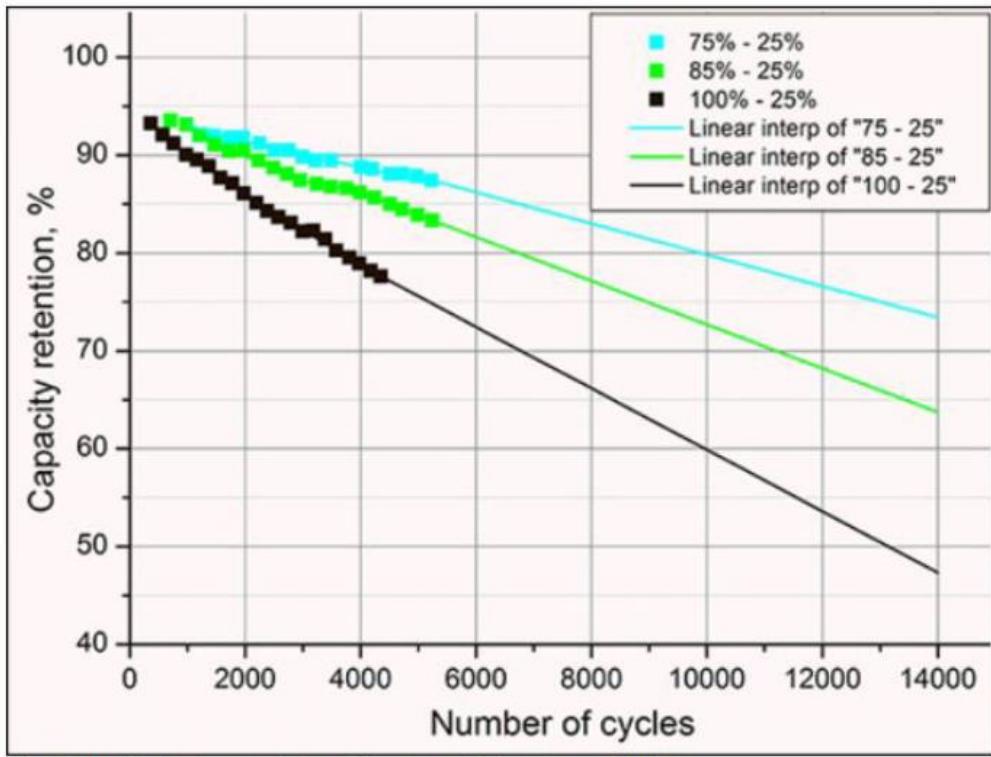


**Figure 7: Sharp rise in internal resistance by increasing cycle depth of Li-ion.**

Note: DC method delivers different internal resistance readings than with the AC method (green frame). For best results, use the DC method to calculate loading.

Source: Technische Universität München (TUM)

Figure 8 extrapolates the data from Figure 6 to expand the predicted cycle life of Li-ion by using an extrapolation program that assumes linear decay of battery capacity with progressive cycling. If this were true, then a Li-ion battery cycled within 75%–25% SoC (blue) would fade to 74% capacity after 14,000 cycles. If this battery were charged to 85% with same depth-of-discharge (green), the capacity would drop to 64% at 14,000 cycles, and with a 100% charge with same DoD (black), the capacity would drop to 48%. For unknown reasons, real-life expectancy tends to be lower than in simulated modeling.



**Figure 8: Predictive modeling of battery life by extrapolation.**

Li-ion batteries are charged to three different SoC levels and the cycle life modelled. Limiting the charge range prolongs battery life but decreases energy delivered. This reflects in increased weight and higher initial cost.

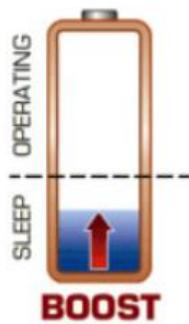
With permission to use. Interpolation/extrapolation by OriginLab.

Battery manufacturers often specify the cycle life of a battery with an 80 DoD. This is practical because batteries should retain some reserve before charge under normal use. The cycle count on DST (dynamic stress test) differs with battery type, charge time, loading protocol and operating temperature. Lab tests often get numbers that are not attainable in the field.

### 7.2.2. How to Awaken a Sleeping Li-ion

Li-ion batteries contain a protection circuit that shields the battery against abuse. This important safeguard also turns the battery off and makes it unusable if over-discharged. Slipping into sleep mode can happen when storing a Li-ion pack in a discharged state for any length of time as self-discharge would gradually deplete the remaining charge. Depending on the manufacturer, the protection circuit of a Li-ion cuts off between 2.2 and 2.9V/cell.

Some battery chargers and analyzers (including Cadex), feature a wake-up feature or “boost” to reactivate and recharge batteries that have fallen asleep. Without this provision, a charger renders these batteries unserviceable and the packs would be discarded. Boost applies a small charge current to activate the protection circuit and if a correct cell voltage can be reached, the charger starts a normal charge. Figure 1 illustrates the “boost” function graphically.



**Figure 1: Sleep mode of a lithium-ion battery.**

Some over-discharged batteries can be "boosted" to life again. Discard the pack if the voltage does not rise to a normal level within a minute while on boost.

Do not boost lithium-based batteries back to life that have dwelled below 1.5V/cell for a week or longer. Copper shunts may have formed inside the cells that can lead to a partial or total electrical short. When recharging, such a cell might become unstable, causing excessive heat or show other anomalies. The Cadex "boost" function halts the charge if the voltage does not rise normally.

When boosting a battery, assure correct polarity. Advanced chargers and battery analyzers will not service a battery if placed in reverse polarity. A sleeping Li-ion does not reveal the voltage, and boosting must be done with awareness. Li-ion is more delicate than other systems and a voltage applied in reverse can cause permanent damage.

Storing lithium-ion batteries presents some uncertainty. On one end, manufacturers recommend keeping them at a state-of-charge of 40–50 percent, and on the other end there is the worry of losing them due to over-discharge. (See 6.2: How to Store Batteries) There is ample bandwidth between these criteria and if in doubt, keep the battery at a higher charge in a cool place.

### 7.2.3. What causes Li-ion to Die?

The ultimate focus of maximizing the energy density of Li-ion shifted in 2006 when Li-ion unexpectedly disassembled in consumer products and millions of packs were recalled. Safety gained attention and batteries became safer. With the advent of the electric vehicle (EV), longevity is moving to the forefront and experts have begun exploring why batteries fail.

While a 3-year battery life with 500 cycles is acceptable for laptops and mobile phones, the mandated 8-year life of an EV battery seems long at first. However, it still makes an EV buyer cringe when learning that a replacement battery carries the price of a compact car with an internal combustion engine. If the life of the battery could be extended to, say, 20 years, then driving an EV would be justified even if the initial investment is high.

Manufacturers of electric vehicles choose battery systems that are optimized for longevity rather than high specific energy. These batteries are normally larger and heavier than those used in consumer goods.

Batteries chosen for an electric powertrain go through strenuous life cycle testing and Nissan selected a manganese-based Li-ion for the Leaf EV because of solid performance. To beat the clock, the test protocol mandated a rapid charge of 1.5C (less than 1 hour) and a discharge of 2.5C (20 minutes) under a temperature of 60°C (140°F). Under these harsh conditions, a

heavy-duty battery is expected to lose 10 percent after 500 cycles, which represents 1–2 years of driving. This emulates driving an EV through the heat of a biblical hell, leaving rubber marks from aggressive driving, and still coming out with a battery that boasts 90 percent capacity.

In spite of the careful selection and extensive testing, the owners of the Nissan Leaf realized a capacity loss of 27.5 percent after 1–2 years of ownership, and this without aggressive driving. Why then would the Leaf under sheltered conditions drop the capacity by so much?

To get a better understanding of what causes irreversible capacity loss in Li-ion batteries, the Center for Automotive Research at the Ohio State University in collaboration with Oak Ridge National Laboratory and the National Institute of Standards and Technology performed forensic tests by dissecting failed batteries to find suspected problem areas on the electrodes.

Unrolling a 1.5-meter-long (5 feet) strip of metal tape representing the anode and cathode coated with oxide revealed that the finely structured nanomaterials had coarsened. Further studies revealed that the lithium ions responsible for shuttling electric charge between the electrodes had diminished on the cathode and had permanently lodged on the anode. This resulted in the cathode having a lower lithium concentration than a new cell, a phenomenon that is irreversible.

### Coulombic Efficiency

Professor Jeff Dahn and his team at Dalhousie University in Halifax studied the longevity of Li-ion by examining coulombic efficiency (CE). CE defines the completeness by which electrons are transferred in an electrochemical system during charge and discharge. The higher the efficiency, the less stress there is on the battery and the longer it should live.

During charge, lithium gravitates to the graphite anode (negative electrode) and the voltage potential changes. Removing the lithium again during discharge does not reset the battery fully. A film called solid electrolyte interface (SEI) consisting of lithium atoms forms on the surface of the anode. Composed of lithium oxide and lithium carbonate, the SEI layer grows as the battery cycles. The film gets thicker and eventually forms a barrier that obstructs interaction with graphite.

The cathode (positive electrode) develops a similar restrictive layer known as electrolyte oxidation. Dr. Dahn stresses that a voltage above 4.10V/cell at elevated temperature causes this, a demise that can be more harmful than cycling a battery. The longer the battery stays in a high voltage, the faster the degradation occurs.

The buildup can result in a sudden capacity loss that is difficult to predict by testing the duration of a battery through cycling alone. This phenomenon had been known for some years and measuring the coulombic efficiency can verify these effects in a more scientific and systematic manner than mere cycling.

Similar to an EV, Li-ion in satellites must also endure a lifespan of 8 years and more. To achieve this, the cells are charged to only 3.90V/cell and lower. An interesting discovery was made by NASA in that Li-ion dwelling above 4.10V/cell tend to decompose due to electrolyte oxidation on the cathode, while those charged to lower voltages lose capacity due to the SEI buildup on the anode.

NASA reports that once Li-ion passes the 8 year mark after having delivered about 40,000 cycles in a satellite, cell deterioration caused by this phenomenon progresses quickly.

Charging to 3.92V/cell appears to provide the best compromise in term of maximum longevity, but this reduces the capacity to only about 60 percent.

Coulombic efficiency is capable of measuring both changes: the lithium lost due to SEI growth on the anode and electrolyte oxidation at the cathode. The results can be used to rank the life expectancy of a battery by quantifying the parasitic reaction.

The CE of a perfect battery would be 1.000. If this were the case, Dr. Dahn says, the Li-ion battery would last for ever. An excellent coulombic efficiency is 0.9999, a level that some lithium cobalt oxides (LCO) reach. By far the best Li-ion in terms of CE is lithium titanate (LTO); it has a potential to deliver 10,000 cycles. The negatives are high cost and relatively low specific energy.

The coulombic efficiency readings vary with temperature and charge rate, also known as C-rate. As the cycle time gets longer, self-discharge comes into play and CE drops (gets worse). Electrolyte oxidation at the cathode, in part, causes this self-discharge. Li-ion loses about 2 percent per month at 0°C (32°F) with a state-of-charge of 50 percent and up to 35 percent at 60°C (140°F) when fully charged.

Table 1 provides data for the most common Li-ion systems. For simplicity reasons, CE is described as excellent, good, moderate and poor taken at 30°C (86°F).

Chemical name	Material	Coulombic efficiency <sup>1</sup>	Notes
Lithium Cobalt Oxide <sup>2</sup> (LCO)	LiCoO <sub>2</sub> (60% Co)	Good, only slight drop at 50–60°C	High capacity, limited power; fragile. Mobile phone, laptop
Lithium Manganese Oxide <sup>2</sup> (LMO)	LiMn <sub>2</sub> O <sub>4</sub>	Poor, CE is low, drops further at 40°C	High capacity, high power, tolerant to abuse.  Power tools, e-bikes, EV, medical, UPS
Lithium Iron Phosphate <sup>2</sup> (LFP)	LiFePO <sub>4</sub>	Moderate, CE drops at 50–60°C	
Lithium Nickel Manganese Cobalt Oxide <sup>2</sup> NMC	LiNiMnCoO <sub>2</sub> (10–20% Co)	Good, small drop at 60°C	
Lithium Nickel Cobalt Aluminum Oxide <sup>2</sup> (NCA)	LiNiCoAlO <sub>2</sub> (9% Co)	N/A	Electric powertrain (Tesla Model S), grid storage
Lithium Titanate <sup>3</sup> (LTO)	Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	Excellent	Very durable but expensive and low specific energy

**Table 1: Most commonly used Li-ion with coulombic efficiency rated as excellent, good, moderate and poor.** Battery manufacturers may one day specify CE in a number.

<sup>1</sup> Taken at C/20 (0.05C) and 30°C (86°F). (20h charge & discharge); <sup>2</sup> Cathode material; <sup>3</sup> Anode material

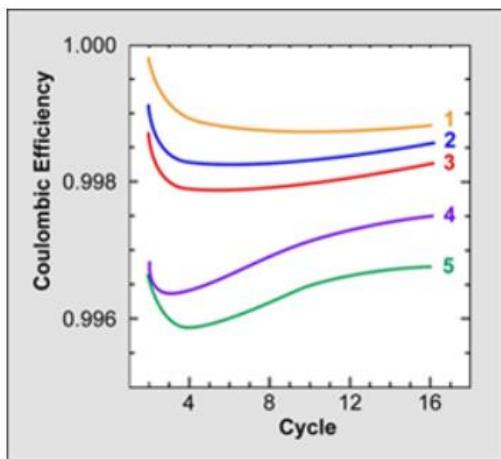
### Additives and the effects on Coulombic Efficiency

Lithium-ion has improved and much credit goes to electrolyte additives. Each cell has several additives and manufacturers keep the combinations a secret. Additives lower internal resistance by reducing corrosion, decreasing gassing, speeding up manufacturing by fine-tuning the wetting process, and improving low and high temperature performance. Adding 1–

2 percent vinylene carbonate improves SEI on the anode, limits electrolyte oxidation at the cathode and enhances the CE readings. (See also 3.8: Electrolyte)

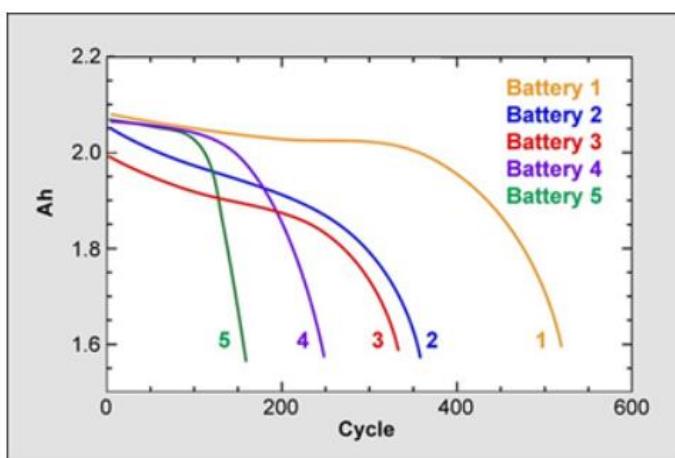
Additives make up less than 10 percent of the electrolyte and the chemicals are consumed in the formation of the SEI layer. Folks ask, "Can additives interact with each other?" The answer is, "Absolutely." Using coulombic efficiency allows the discovery of possible interferences in weeks rather than having to wait for years for symptoms to develop.

To examine the correlation between CE and longevity, Dalhousie University worked with battery manufacturers, including E-One Moli. Dalhousie identified five batteries of interest, each with its own architecture and additives. Figure 2 shows the coulombic efficiency of these five samples with values ranging from 0.9960 to 0.9995. Figure 3 demonstrates the test results when cycled to death. To Dalhousie's anticipation and satisfaction, CE harmonized well with the cycle count. Batteries with high CE lasted the longest; those with low CE values were the first to die.



**Figure 2: Coulombic efficiency.** Five experimental batteries were tested for coulombic efficiency. A higher CE provides a longer life.

Courtesy of the Dalhousie University

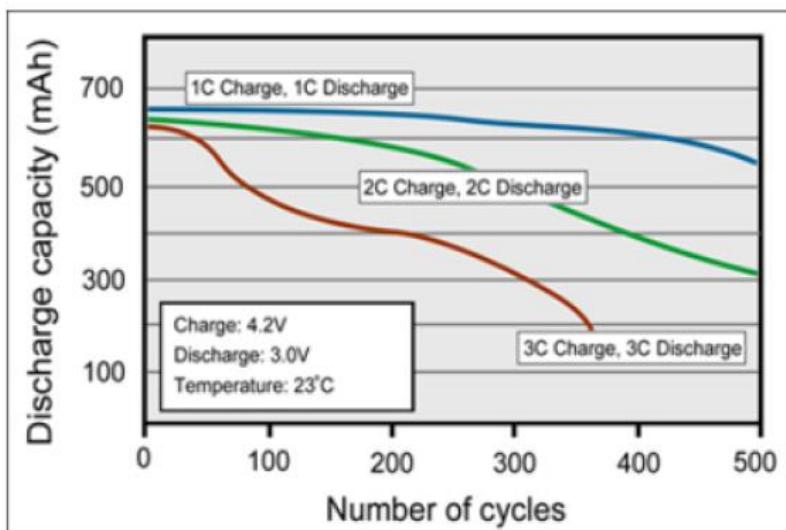


**Figure 3: Relationship of coulombic efficiency and cycle life.** High CE values live the longest; low values die first.

Courtesy of the Dalhousie University

Battery wear and tear also includes structural degradation that can be captured with traditional cycle testing. Dr. Dahn calls this type of testing the “sausage machine.” While measuring coulombic efficiency assists in battery development by giving a snapshot assessment of additives; the old sausage machine does the verification thereafter.

Figure 4 demonstrates capacity loss caused by the structural degradation of an older Li-ion when cycled at a 1C, 2C and 3C. The elevated capacity loss at higher C-rates may be lithium plating at the anode caused by rapid charging.



**Figure 4: Cycle performance of Li-ion with 1C, 2C and 3C charge and discharge.**

Moderate charge and discharge currents reduce structural degradation. This applies to most battery chemistries.

### Capacity degradation in Electro Powertrains

When choosing batteries for the powertrains, manufacturers of electric vehicles come to different conclusions. Tesla cars use the 18650 cell because the cell is readily available and has a low price. This was a strange choice for the Tesla Roadster, the first EV by Tesla, as the cell was designed for portable devices such as laptops and medical and military devices. Perhaps unknown to Elon Musk, the founder of Tesla Motors, cobalt-blended lithium-ion has a high CE reading that adds to longevity in the way the battery is being used in that application.

The newer Tesla models use the same concept and to reduce stress, Tesla “super-sizes” the pack. The battery is so large that it operates at a C-rate of only 0.25C (C/4), even at highway speed. This allows Tesla to focus on high energy density for maximum runtime; power density becomes less important. The negative of super-sizing is increased energy consumption due to a heavier vehicle and a higher battery price. (For more information on EV battery choices see BU-1003: Electric Vehicle.)

### Summary

The manganese-based Li-ion batteries chosen for the Nissan Leaf and other EVs have excellent lab results. What may have been overlooked in the Nissan Leaf test is the damage that is being done when keeping the battery at high voltage and elevated temperature. As the coulombic efficiency tests reveal, these two conditions can cause more damage than cycling.

The four suspected renegades responsible for capacity loss and the eventual end-of-life of the Li-ion battery are:

1. Mechanical degradation of electrodes or loss of stack pressure in pouch-type cells. Careful cell design and correct electrolyte additives minimize this cause. (See Figure 4.)
2. Growth of solid electrolyte interface (SEI) on the anode. A barrier forms that obstructs the interaction with graphite, resulting in an increase of internal resistance. SEI is seen as a cause for capacity loss in most graphite-based Li-ion when keeping the charge voltage below 3.92V/cell. Electrolyte additives reduce some of the effect.
3. Formation of electrolyte oxidation (EO) at the cathode that may lead to a sudden capacity loss. Keeping the cells at a voltage above 4.10V/cell and at an elevated temperature promotes this phenomenon.
4. Lithium-plating on the surface of the anode caused by high charging rates. (Elevated capacity loss at higher C-rates in Figure 4 might be caused by this.)

#### 7.2.4. Coulombic and Energy Efficiency

All batteries have losses. The energy retrieved after a charge is always less than what had been put in. Parasitic reaction that occurs within the electrochemistry of the cell prevents the efficiency from reaching 100 percent. Ultra-fast charging and heavy loading also reduces the energy efficiency. This also contributes to battery strain by reducing cycle life.

Battery efficiency is gaining interest. This is especially critical with large battery systems in electric vehicles, energy storage systems (ESS) and satellites. The efficiency factor is commonly measured by coulombic efficiency.

##### **Coulombic Efficiency**

Coulombic efficiency (CE), also called faradaic efficiency or current efficiency, describes the charge efficiency by which electrons are transferred in batteries. CE is the ratio of the total charge extracted from the battery to the total charge put into the battery over a full cycle.

Li-ion has one of the highest CE ratings in rechargeable batteries. It offers an efficiency that exceeds 99 percent. This, however, is only possible when charged at a moderate current and at cool temperatures. Ultra-fast charging lowers the CE because of losses due to charge acceptance and heat, so also does a very slow charge in which self-discharge comes into play. See BU-808b: What Causes Li-ion to Die.

The coulombic efficiency of Li-ion improves with cycling. To prove this, Panasonic, E-one Moli, Sony, LG and Samsung Li-ion batteries in 18650 cell format were cycled. Some cells began with a coulombic efficiency of 99.1 percent and improved to 99.5 percent with 15 cycles. Some started at 99.5 percent and reached 99.9 percent with 30 cycles. The consistency on repeat tests was high, reflecting in Li-ion being a very stable battery system.

Lead acid comes in lower at a CE of about 90 percent, and nickel-based batteries are generally lower yet. With fast charge, NiCd and NiMH may reach 90 percent but a slow charge reduces this to about 70 percent. Lower charge acceptance when above 70 percent state-of-charge

and self-discharge that increases when the battery gets warm toward the end of charge are contributing factors for the low CE. Best efficiencies of all batteries are attained in mid-range state-of-charge of 30 to 70 percent. All battery systems provide unique CE values that vary with charge rates and temperature. Age also plays a role.

### **Voltaic efficiency**

Voltaic efficiency is another way to measure battery efficiency, which represents the ratio of the average discharge voltage to the average charge voltage. Losses occur because the charging voltage is always higher than the rated voltage to activate the chemical reaction within the battery.

### **Energy Efficiency**

While the coulombic efficiency of lithium-ion is normally better than 99 percent, the energy efficiency of the same battery has a lower number and relates to the charge and discharge C-rate. With a 20-hour charge rate of 0.05C, the energy efficiency is a high 99 percent. This drops to about 97 percent at 0.5C and decreases further at 1C. In the real world, the Tesla Roadster is said to have an energy efficiency of 86 percent. Ultra-fast charging on newer EVs will have a negative effect on energy efficiency, as well as the battery life.

## **8. Battery Testing and Monitoring**

### **8.1. Fundamentals in Battery Testing**

No practical method exists to quantify all conditions of a battery in a short, comprehensive test. State-of-health (SoH) cannot be measured per se, it can only be estimated to various degrees of accuracy based on available symptoms. If the symptoms are vague or not present, a reliable measurement is not possible. When testing a battery, three SoH indicators must be evaluated:

1. Capacity, the ability to store energy
2. Internal resistance, the capability to deliver current, and
3. Self-discharge, reflecting mechanical integrity and stress-related conditions

Batteries come in many conditions and a charge can easily mask a symptom allowing a weak battery to perform well. Likewise, a strong battery with low charge shares similarities with a pack that exhibits capacity loss. Battery characteristics are also swayed by a recent charge, discharge or long storage. These mood swings must be clearly identified when testing batteries.

The leading health indicator of a battery is capacity, a measurement that represents energy storage. A new battery should deliver 100 percent of the rated capacity. This means a 5Ah pack should deliver five amperes for 1 hour. If the battery quits after 30 minutes, then the capacity is only 50 percent. Capacity also supports warranty obligations with a replacement due when falling below 80 percent. Most importantly, capacity defines end of battery life.

Manufacturers base device specifications on a new battery. This state is temporary and does not represent a battery in real-life situations because fading begins from the day it is made. The decrease in performance only becomes visible once the shine of a new device has worn off and daily routines are being taken for granted. An analogy is an aging man whose endurance begins to wear off after the most productive years.

Many batteries and portable devices include a fuel gauge that shows the remaining energy. A full charge always shows 100 percent, whether the battery is new or faded. This creates a false sense of security by anticipating that a faded battery showing fully charged will deliver the same runtime as a new one. Batteries with fuel gauges only indicate SoC and not the capacity.

It is really difficult to test batteries. Battery rapid-test methods seem to dwell in medieval times, and this is especially evident when comparing advancements on other fronts. We don't even have a reliable method to estimate state-of-charge, which is based mostly on voltage and coulomb counting. Assessing capacity, the leading health indicator of a battery, dwells further behind. Measuring the open circuit voltage and checking the internal resistance do not provide conclusive evidence of battery state-of-health.

The battery user may ask, "Why is the industry lagging so far behind?" The answer is simple: "Battery diagnostics are complex." As there is no single analytical device to assess the health of a person, nor are instruments available that can quickly and reliably check the state-of-health of a battery.

A dead battery is easy to check and all testers are 100 percent accurate. The challenge comes in evaluating a battery in the 80–100 percent performance range while on duty. Regulators struggle to introduce battery test procedures. This is mostly due to the unavailability of suitable technology that can assess a battery on the fly. The battery is labeled "uncontrollable" for good reason; this gives it immunity.

The battery world devotes much effort on the super battery, but this improved battery is incomplete without being able to check performance while in service. Improving performance and reliability does not rest in a better battery alone, but in tracking the performance as it ages.

Professor Mark Orazem compares the complexity of testing batteries with the Indian tale in which blind men touch an elephant to learn what it is (Figure 3). Because each man only feels a part of the body, disagreements arise among them. Battery testing is complex even for the sighted man but progress is being made. Better technologies will eventually immerge.



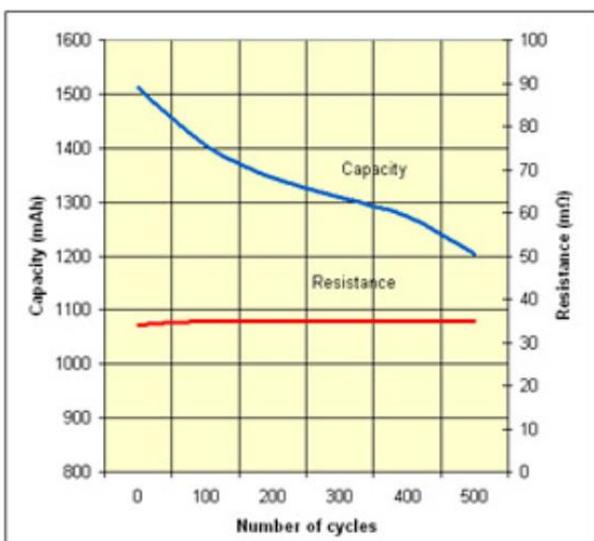
Figure 3: Indian tale reflecting the complexity of estimating battery state-of-health.

Story of blind men trying to figure out an elephant through touch. The tale provides insight into the relativity and opaqueness of a subject matter, such as a battery.

## 8.2. How to measure Internal Resistance

The internal resistance provides valuable information about a battery as high reading hints at end-of-life. This is especially true with nickel-based systems. Resistance measurement is not the only performance indicator as the value between batches of lead acid batteries can vary by 5–10 percent, especially with stationary units. Because of this wide tolerance, the resistance method works best when comparing the readings of a given battery from birth to retirement. Service crews are asked to take a snapshot of each cell or monoblock at time of installation and then measure the subtle changes as the cells age.

There is a notion that internal resistance is related to capacity, but this is false. The resistance of modern lead acid and lithium-ion batteries stays flat through most of the service life. Better electrolyte additives have reduced internal corrosion issues that affect the resistance. This corrosion is also known as parasitic reactions on the electrolyte and electrodes. Figure 1 shows capacity fade with cycling in relation to the internal resistance of Li-ion cells.



**Figure 1: Relationship between capacity and resistance as part of cycling.** Resistance does not reveal the state-of-health of a battery and often stays flat with use and aging.

Cycle test on Li-ion batteries at 1C:

Charge: 1,500mA to 4.2V, 25°C

Discharge: 1,500 to 2.75V, 25°C

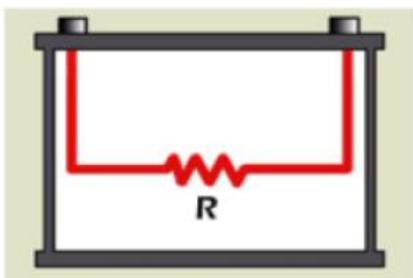
Courtesy of Cadex

### DC Load Method

The ohmic measurement is one of the oldest and most reliable test methods. The battery receives a brief discharge for a second or longer. The load current for a small battery is 1A or less; for a starter battery it might be 50A or more. A voltmeter measures the open circuit voltage (OCV) with no load, followed by the second reading with a load; Ohm's law calculates the resistance value (voltage difference divided by current equals resistance).

DC load measurements work well to check large stationary batteries, and the ohmic readings of the device are very accurate and repeatable. High-end test instruments claim resistance readings in the 10 micro-ohm range. Many garages use the carbon pile to measure starter batteries and an experienced mechanic gets a reasonably good assessment of the battery.

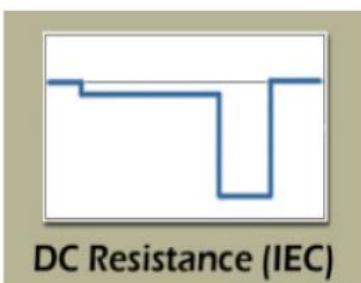
The DC load method has limitations in that it blends R1 and R2 of the Randles model into one combined resistor and ignores the capacitor (see Figure 3). “C” is an important component of a battery that represents 1.5 farads per 100Ah capacity. In essence, the DC method sees the battery as a resistor and can only provide ohmic references. In addition, the DC load method gets similar readings from a good battery that is partially charged and a marginal battery that is fully charged. State-of-charge and capacity estimations are not possible.



**Figure 3: DC load method.** The true integrity of the Randles model cannot be seen. R1 and R2 appear as one ohmic value.

Courtesy of Cadex

The two-tier DC load method offers an alternative method by applying two sequential discharge loads of different currents and time durations. The battery first discharges at a low current for 10 seconds, followed by a higher current for 3 seconds (see Figure 4); the Ohm's law calculates the resistance values. Evaluating the voltage signature under the two load conditions offers additional information about the battery, but the values are strictly resistive and do not reveal SoC or capacity estimations. The load test is the preferred method for batteries that power DC loads.

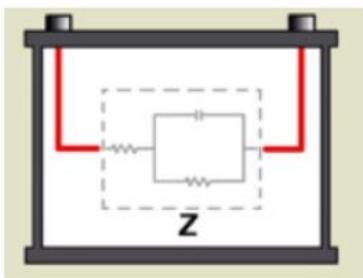


**Figure 4: Two-tier DC load.** The two-tier DC load follows the IEC 61951-1:2005 standards and provides lifelike test conditions for many DC battery applications.

Courtesy of Cadex

### AC Conductance

Conductance measurement to evaluate starter batteries was first reported by Keith Champlin in 1975 by demonstrating a linear correlation between load test and conductance. When injecting a frequency of about 90 hertz, capacitive and inductive reactance converge with a 70–90Ah lead acid battery, resulting in a negligible voltage lag that minimizes the reactance. (This frequency rises with a smaller battery and drops with a large pack.) The single-frequency method (Figure 5) sees the components of the Randles model as one complex impedance called the modulus of Z.

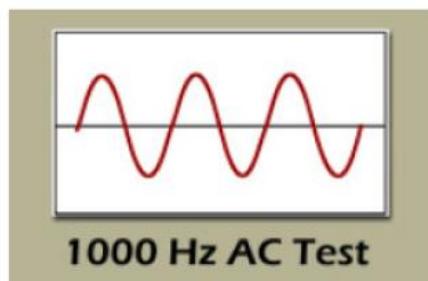


**Figure 5: AC conductance method.** The individual components of the Randles model are molten together and cannot be distinguished.

Courtesy of Cadex

The 1,000-hertz (Hz) ohm test is another common method. A 1,000Hz signal excites the battery and Ohm's law calculates the resistance. Note that the AC method shows different values to the DC method when measuring a reactive resistance, and both readings are correct.

For example, Li-ion in an 18650 cell produces about 36mOhm with a 1,000Hz AC signal and roughly 110mOhm with a DC load. Since both readings are valid, yet far apart, the user must consider the application. The pulse DC load method provides valuable readings for a DC application such as a heating element or an incandescent light, while the 1,000Hz method better reflects the performance requirements of a digital load, such as portable computing and mobile phones that rely to a large extent on the capacitive characteristics of a battery. Figure 6 illustrates the 1,000Hz-method.

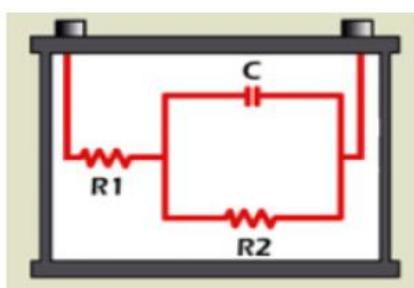


**Figure 6: 1000-hertz method.** The 1000-hertz provides reactive resistance readings. This has been the preferred method for taking impedance snapshots of batteries powering digital devices.

Courtesy of Cadex

### Electrochemical Impedance Spectroscopy (EIS)

Research laboratories have been using EIS for many years to evaluate battery characteristics. High equipment cost, slow test times and the need for trained professionals to decipher the large volume of data have limited this technology to laboratory environments. EIS reads R1, R2 and C values in the Randles model (Figure 7); however, correlating the data into CCA and capacity estimations requires complex modeling.



**Figure 7: Spectro™ method.** R1, R2 and C are measured separately, which enables state-of-charge and capacity measurements.

Courtesy of Cadex

### 3. How to measure State-of-Charge

#### Voltage Method

Measuring state-of-charge by voltage is simple, but it can be inaccurate because cell materials and temperature affect the voltage. The most blatant error of the voltage-based SoC occurs when disturbing a battery with a charge or discharge. The resulting agitation distorts the voltage and it no longer represents a correct SoC reference. To get accurate readings, the battery needs to rest in the open circuit state for at least four hours; battery manufacturers recommend 24 hours for lead acid. This makes the voltage-based SoC method impractical for a battery in active duty.

Each battery chemistry delivers its own unique discharge signature. While voltage-based SoC works reasonably well for a lead acid battery that has rested, the flat discharge curve of nickel- and lithium-based batteries renders the voltage method impracticable.

The discharge voltage curves of Li-manganese, Li-phosphate and NMC are very flat, and 80 percent of the stored energy remains in the flat voltage profile. While this characteristic is desirable as an energy source, it presents a challenge for voltage-based fuel gauging as it only indicates full charge and low charge; the important middle section cannot be estimated accurately. Figure 1 reveals the flat voltage profile of Li-phosphate (LiFePO<sub>4</sub>) batteries.

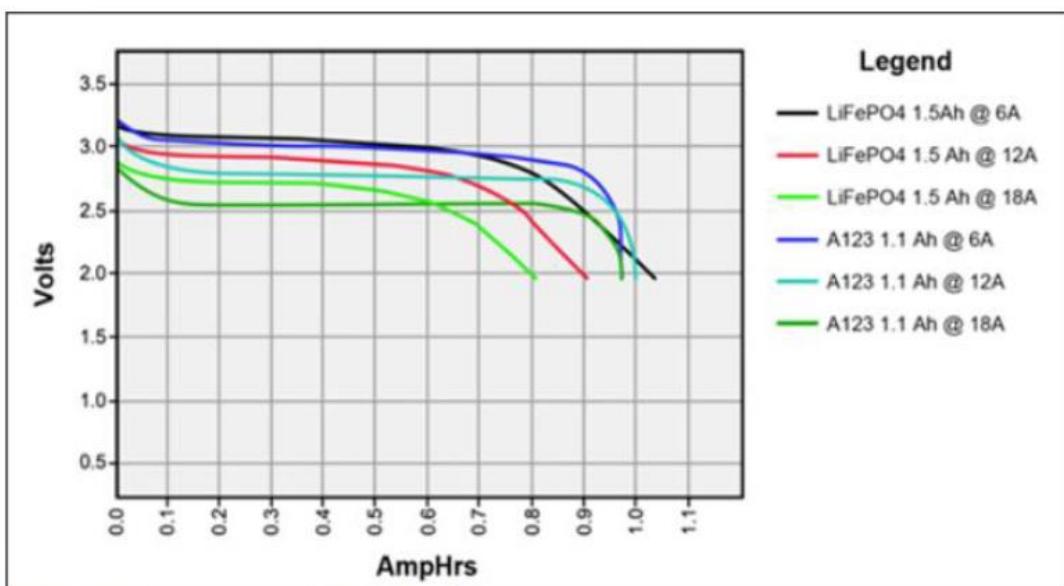


Figure 1: Discharge voltage of lithium iron phosphate.

Li-phosphate has a very flat discharge profile, making voltage estimations for SoC estimation difficult.

In spite of inaccuracies, most SoC measurements rely in part or completely on voltage because of simplicity. Voltage-based SoC is popular in wheelchairs, scooters and golf cars. Some innovative BMS (battery management systems) use the rest periods to adjust the SoC readings as part of a “learn” function.

## Coulomb Counting

Laptops, medical equipment and other professional portable devices use coulomb counting to estimate SoC by measuring the in-and-out-flowing current. Ampere-second (As) is used for both charge and discharge.

While this is an elegant solution to a challenging issue, losses reduce the total energy delivered, and what's available at the end is always less than what had been put in. In spite of this, coulomb counting works well, especially with Li-ion that offer high coulombic efficiency and low self-discharge. Improvements have been made by also taking aging and temperature-based self-discharge into consideration.

Makers of advanced BMS claim high accuracies but real life often shows otherwise. Much of the make-believe is hidden behind a fancy readout. Smartphones may show a 100 percent charge when the battery is only 90 percent charged. Design engineers say that the SoC readings on new EV batteries can be off by 15 percent. There are reported cases where EV drivers ran out of charge with a 25 percent SoC reading still on the fuel gauge.

## Impedance Spectroscopy

Battery state-of-charge can also be estimated with impedance spectroscopy using the Spectro™ complex modeling method. This allows taking SoC readings with a steady parasitic load of 30A. Voltage polarization and surface charge do not affect the reading as SoC is measured independently of voltage. This opens applications in automotive manufacturing where some batteries are discharged longer than others during testing and debugging and need charging before transit. Measuring SoC by impedance spectroscopy can also be used for load leveling systems where a battery is continuously under charge and discharge.

Measuring SoC independently of voltage also supports dock arrivals and showrooms. Opening the car door applies a parasitic load of about 20A that agitates the battery and falsifies voltage-based SoC measurement. The Spectro™ method helps to identify a low-charge battery from one with a genuine defect.

SoC measurement by impedance spectroscopy is restricted to a new battery with a known good capacity; capacity must be nailed down and have a non-varying value. While SoC readings are possible with a steady load, the battery cannot be on charge during the test.

Figure 4 demonstrates the test results of impedance spectroscopy after a parasitic load of 50A is removed from the battery. As expected, the open terminal voltage rises as part of recovery but the Spectro™ readings remains stable. Steady SoC results are also observed after removing charge during when the voltage normalizes as part of polarization.

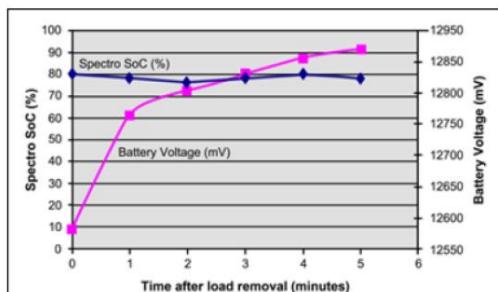


Figure 4: Relationship of voltage and measurements taken by impedance spectroscopy after removing a load.

Battery is recovering after removing a load. Spectro SoC readings remain stable as the voltage rises.

## 8.4. How to measure Capacity

Capacity is the leading health indicator of a battery, but estimating it on the fly is complex. The traditional charge/discharge/charge cycle is still the most dependable method to measure battery capacity. While portable batteries can be cycled relatively quickly, a full cycle on large lead acid batteries is not practical for capacity measurement.

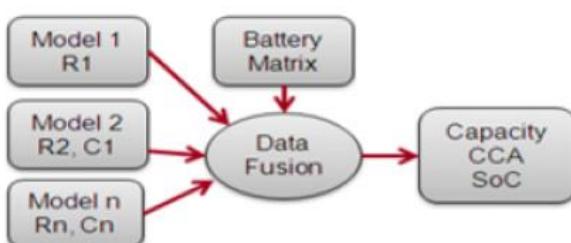
### Discharge Method

One would assume that capacity measurement by discharge is the most accurate method, but this is not always the case, especially with lead acid batteries. Even when using highly accurate equipment in a temperature controlled environment and following established charge and discharge standards, variations between identical tests occur. This is not fully understood except to realize that batteries are electrochemical devices that have human-like qualities. Our IQ level also varies depending on the time of day and other conditions. Lithium- and nickel-based chemistries provide more consistent discharge results than lead acid.

### Non-invasive Method

Spectro™ (by Cadex) uses multi-model electrochemical impedance spectroscopy (EIS) that checks battery health in seconds with a scanning process. The non-invasive technology combines EIS with complex modeling to estimate capacity, CCA and SoC with the help of matrices, also known as look-up tables. Here is how it works:

A sinusoidal signal of multiple frequencies is injected into the battery at a few millivolts. After digital filtering, the extracted signal forms a Nyquist plot onto which various electro-chemical models are superimposed. Spectro™ selects the best matching models; non-fitting replicas are rejected. Data fusion then correlates the values of the key parameters to derive at capacity and CCA estimations. Figure 2 illustrates the patented process in a simplified way.



**Figure 2 Spectro™ combines EIS with complex modeling to estimate battery capacity and improve CCA measurements.** A sinusoidal signal produces a Nyquist plot; data fusion correlates the values of the key parameters to estimate capacity and CCA.

US patent 7,072,871; Courtesy of Cadex

### How does the Spectro™ Rapid-tester work?

Spectro uses multi-model electro-chemical impedance spectroscopy (Spectro™). This is a further development of electro-chemical impedance spectroscopy (EIS), a technology that has been in use for many years. The non-invasive test scans the battery with multiple frequencies to generate a Nyquist plot. The Nyquist information is filtered and superimposed onto electrochemical models to derive battery state-of-health (SoH). Nyquist analysis is suitable to test lead acid and Li-ion batteries.

## 8.5. Testing Lithium-ion Batteries

With the large number of lithium-ion batteries in use and the applications growing, a functional rapid-testing method is becoming a necessity. Several attempts have been tried, including measuring internal resistance, and the results have been mixed. Additives keep the internal resistance of modern Li-ion low throughout most of the life, making ohmic test unreliable.

Electrochemical dynamic response, the method QuickSort™ uses, measures the mobility of ion flow between the electrodes. Based on time domain analysis by applying brief load pulses, the response time on attack and recovery is measured; an algorithm computes the results and compares them against a set of parameters. As seen in Figure 1, a good battery resists the attack and recovers quickly whereas the impact of a weaker battery is larger and the recovery is slower. Figure 1 illustrates the concept of the technology.

Lithium-ion batteries have different diffusion rates. In terms of electrochemical dynamic response, Li-ion polymer with gelled electrolyte is found to be faster than standard Li-ion and needs modified parameters to achieve accuracy. Unique active materials and additives that are kept top secret by battery manufacturers complicate the test procedure.

Cadex devoted much effort to testing small single Li-ion cell in mobile phones. The objective is to also test larger Li-ion in multi-cell configuration, over a broad range of state-of-charge, which involves combining time domain test with frequency domain.

When scanning a battery from kilohertz down to millihertz in frequency domain mode, the high frequency range called migration reveals the resistive qualities of a battery that present a bird's-eye view of the landscape. However, the unique characteristics of Li-ion lie in the mid frequency range called charge transfer and the low range dubbed diffusion. Batteries with faded capacity suffer from low charge transfer and slow active Li-ion diffusion.

Evaluating batteries at sub one-hertz frequency would require prolonged test times. At one millihertz, for example, one cycle takes 1,000 seconds, or 16 minutes, and several data points are required to complete the analysis. Rapid-tests should only last a few seconds and not longer than 5 minutes. With clever software simulation, the duration can be shortened to fall within the desired short test time.

In Figure 2, a good battery and a faded battery are scanned from 0.1Hz to 1kHz. The difference in impedance ( $-\text{Imp} - Z$ ) is strongest between 1Hz and 10Hz. It should be noted that capturing resistive readings alone has limited value as state-of-charge (SoC) and temperature also affect the signature and muddle SoH references. Furthermore, different Li-ion architectures and how the battery has aged also affect the results. Natural aging produces a different signature than artificial aging and the reason for this discrepancy is not fully understood.

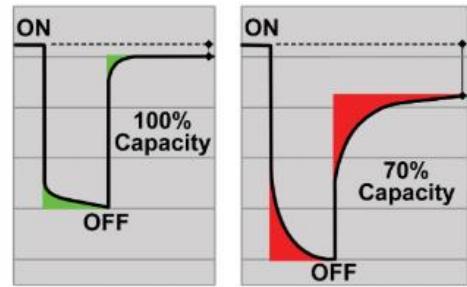
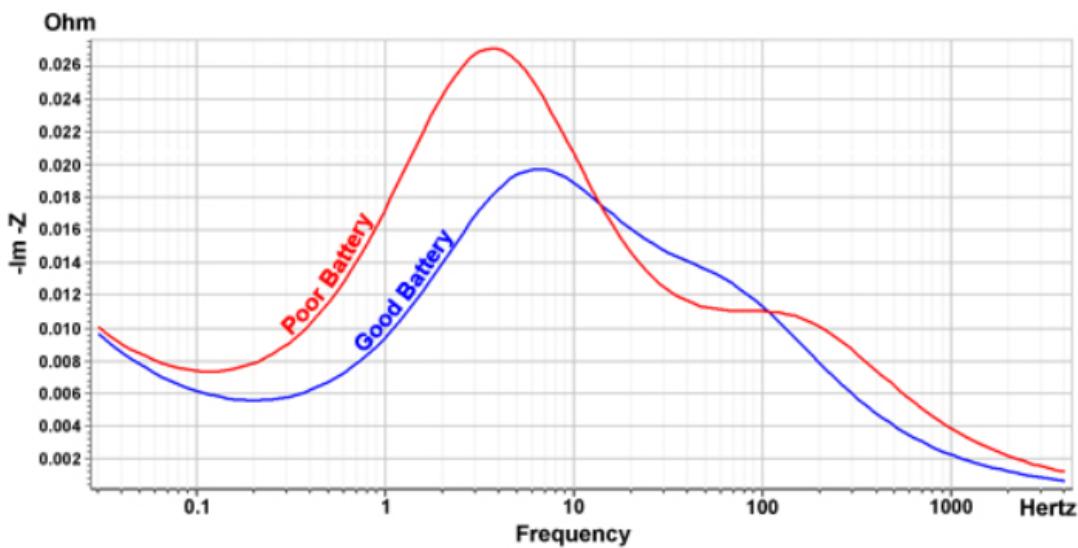


Figure 1:  
Electrochemical dynamic response.



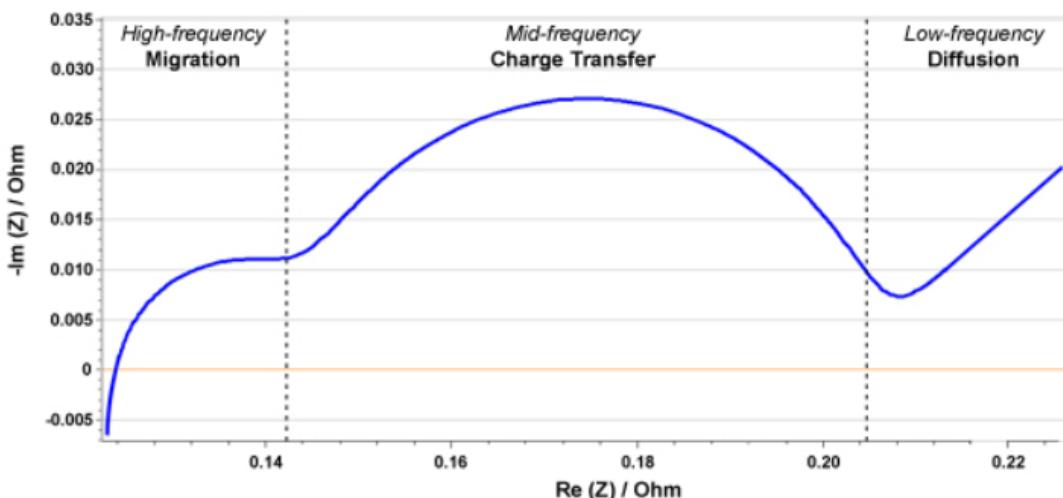
**Figure 2: Frequency scan of good and weak mobile phone batteries.**

Impedance variances are most visible below 10Hz. The horizontal scale is logarithmic to condense the frequency range.

Courtesy of Cadex

Test results captured by frequency domain are best represented by the Nyquist plot. Invented by Harry Nyquist (1889–1976) while at Bell Laboratories; a Nyquist plot presents the frequency response of a linear systems displaying both amplitude and phase angle on a single plot using frequency as parameter. The horizontal x axis of a Nyquist plot reveals the real Ohm impedance while the vertical y axis represents the imaginary impedance.

Figure 3 divides the scanned battery results as delivered by the Nyquist plot into migration, charge transfer and diffusion. Migration derived at high frequency on the left provides resistive characteristics of a battery; the all-important charge transfer in the middle forms a semi-circle that represents the kinetics of the battery; and the low frequency part on the right represents diffusion.



**Figure 3: The Nyquist plot is divided into high, mid and low frequency sections.**

The mid-frequency semi-circle represents battery characteristics best. Larger batteries require lower frequencies.

Courtesy of Cadex

## **Summary**

No rapid-test can evaluate all battery symptoms and there are always outliers that defy the test protocol. Correct prediction should be 9 out of 10. QuickSort™ (by Cadex) exceeds this requirement with most Li-ion packs for mobile phones, but this technology only tests single-cell packs up to 1,500mAh. New technologies in development promise to test larger Li-ion packs, but this may extend the test to a few minutes to accommodate low frequency sampling.

Capacity is the gate keeper to battery health, and rapid-test technologies with capacity estimation also enhance battery management systems (BMS). Such rapid-test technologies can be included in chargers to evaluate the integrity of the battery with each charge by giving the green ready light only if the set target capacity is met; low capacity batteries are shown the backdoor. This provides quality control without adding an extra layer of overhead.

## **8.6. Battery Management System (BMS)**

The purpose of a BMS is to:

1. Provide battery safety and longevity, a must-have for Li-ion.
2. Reveal state-of-function in the form of state-of-charge and state-of-health (capacity)
3. Prompt caution and service. This could be high temperature, cell imbalance or calibration.
4. Indicate end-of-life when the capacity falls below the user-set target threshold.

Not all BMS offer all these features. The most basic functions are battery protection and showing state-of-charge (SoC).

While SoC is helpful, the readout is incomplete without also tracking the capacity as the battery fades. The user may be accustomed to a battery that delivers full capacity, but this condition is temporary and cannot be maintained. Capacity is the primary indicator of battery state-of-health (SoH) and should be part of the battery management system (BMS). Knowing SoC and SoH provides state-of-function (SoF), the ultimate confidence of readiness, but technology to provide this information in an effective way is being improved.

Building a better BMS is a challenge when considering that we still lack a dependable method to read state-of-charge, the most basic measure of a battery. Reading the remaining energy in a battery is more complex than dispensing liquid fuel. While a fuel tank has a fixed dimension and delivers fuel which can be measured with great accuracy, an electrochemical storage system reduces its size and the in- and out-flowing coulombs cannot be assessed with great accuracy as the battery ages.

The BMS also provides protection when charging and discharging; it disconnects the battery if set limits are exceeded or if a failure occurs. Established BMS standards are the SMBus (System Management Bus) used for mostly portable applications, as well as the CAN Bus (Controller Area Network) and the simpler LIN Bus (Local Interconnect Network) for automotive use.

Stationary batteries were among the first to include supervisory systems and the most basic is voltage monitoring of individual cells. Some systems also include cell temperature and current measurement. Recording a slight difference in cell temperature hints to a problem, and measuring the voltage drop of each cell at a given load reveals cell resistance. Dry-out, corrosion, plate separation, and other malfunctions can thus be identified.

Although the BMS is effective in detecting anomalies; capacity fade, the most predictable health indicator, is difficult to estimate because voltage and internal resistance are commonly not affected. The ability to read capacity fade from 100 to 70 percent would be valuable, but most BMS cannot do this effectively and the battery might be given a clean bill of health even if the capacity has dropped to 50 percent. Most BMS only respond to anomalies that lie outside capacity estimation, such as voltage differences among cells caused by cell imbalances and a change in internal resistance.

Some industrial and medical device manufacturers use a date stamp to determine the end of battery life, others observe the cycle count. While counting cycles may be simplistic, no convention exists that defines a cycle and some systems simply call it a cycle when the battery is charged. Date-stamping has similar shortcomings in that it promotes premature replacement of batteries that are seldom used, while the heavy hitters may stay in service too long. To reduce risk of failure, authorities mandate early replacement, and a two-year service life is common. Prolonged storage will give the batteries a very short working life.

Let's look at how a BMS works, note the shortcomings and examine up-and-coming technologies that could change the way batteries are monitored.

A BMS takes the imprint of the "chemical battery" during charging and discharge and establishes the "digital battery" that communicates with the user. Figure 1 illustrates the battery components consisting of stored energy, the empty portion that can be refilled and the inactive part that is permanently lost. Rated capacity refers to the manufacturer's specified capacity in Ah (ampere-hours) that is only valid when the battery is new; available capacity designates the true energy storage capability derived by deducting the inactive part. State-of-charge (SoC) refers to the stored energy, which also includes the inactive part.

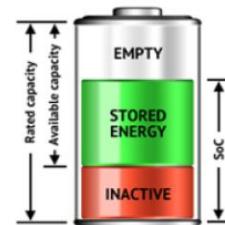


Figure 1: Three parts of a battery

A BMS is programmed to a rated capacity and it measures the in-and-outflowing coulombs that relate to the available capacity. As the capacity drops, the coulomb count decreases and this discrepancy enables capacity estimation. The most accurate readings are possible when counting the coulombs from a fully discharged battery during a complete charge or discharging a fully charged battery to the cut-off point. Such clean starts are seldom possible and real-life capacity estimations get muddled over time.

A BMS sets flags when receiving a full discharge and charge. During a rest period, an advanced BMS may also calculate SoC on hand of the stable open circuit voltage and begin counting the coulombs during charge and discharge from that vantage point. Some BMS also look at voltage recovery after removing a load to estimate SoC and/or SoH.

### Adding Capacity Estimation in BMS

Figure 3 shows a BMS with common sensing points to which the ability to measure capacity has been added. Spectro™ stands for electrochemical impedance spectroscopy (EIS) with complex modeling. This converts a simple battery sensor to the state-of-function (SoF) level.

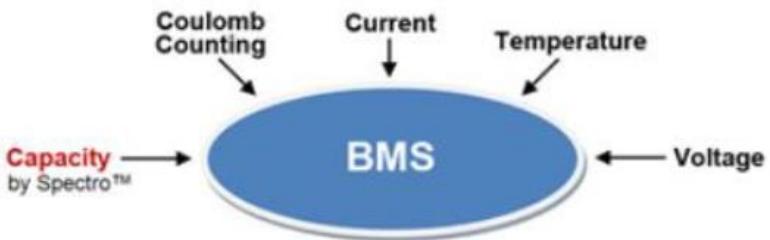


Figure 3: Spectro-BMS™ adds capacity as key element to estimate battery state-of-health.

Knowing SoF improves battery validation, but some device manufacturers refuse to reveal capacity readings to a consumer that are less than 100 percent, especially during the warranty period. To conceal unwanted information, the data can be made code-accessible for service personnel use only.

Consumer concerns put aside, SoF signifies a momentous improvement to BMS in terms of battery reliability as it tracks capacity fade and calculates the true runtime on the available energy. Capacity-based BMS will also predict eventual replacement, an issue that cannot be fully satisfied with current BMS technologies. Future BMS will combine the information of the “digital battery” with that of the “chemical battery” to provide reliable SoF data through advanced learn algorithms.

## 8.7. Battery Test Methods (Summary)

A battery resembles a living organism that cannot be measured; only estimated by diagnostics similar to a doctor examining a patient. The accuracy of rapid-testing varies according to symptoms that change with state-of-charge (SoC), agitation after charge and discharge, temperature and storage. A rapid-test must distinguish between a good battery that is partially charged and a weak pack that is fully charged. Both will deliver similar runtimes in the hands of the user but have different performance levels.

A widely used performance analysis is coulomb counting in which in-and-out-flowing energies are measured. Coulomb counting goes back 250 years when Charles-Augustin de Coulomb first established the “Coulomb Rule.” Elegant in concept, coulomb counting has its own problem by losing accuracy when the battery is randomly charged and discharged. State-of-health (SoH) estimation by a digital solution is incomplete without including the chemical battery.

The leading health indicator of a battery is capacity. Capacity represents energy storage, a quality that gradually and permanently fades with use. Other characteristics responsible for SoH are internal resistance that governs load current and self-discharge that examines

mechanical integrity. All three characteristics must be met to give a battery a clean bill of health.

Estimating the capacity of the chemical battery on the fly is most complex. This involves algorithms and matrices that serve as lookup tables similar to letter or face recognition. Modern rapid-test methods move towards advanced machine learning in capturing the many moods of a battery.

Here is a summary of simple to complex test methods to examine batteries.

**Voltage** Reveals SoC. Capacity estimation is not possible.

**Ohmic test** Measures internal battery resistance to verify loading characteristics and to identify fault conditions. Resistance readings do not correlate with capacity. The ohmic test is also known as an impedance test ( $Z$ ).

**Full cycle** Reads the capacity of the chemical battery with a charge/discharge/charge cycle. The results are accurate but a battery must often be removed from service and the testing times take hours.

**Rapid-test** Most rapid-test methods are based on time domain or frequency domain. Time domain excites the battery with pulses to observe ion-flow of Li-ion batteries. Frequency domain scans the battery with multiple frequencies to generate a Nyquist plot for analysis. Both methods require complex algorithms with parameters or matrices that serve as lookup tables.

**BMS** Battery Management Systems estimate SoC by monitoring voltage, current and temperature. Some BMS for Li-ion also counts coulombs. A BMS can identify a battery defect but is unable to estimate capacity accurately.

**Coulomb counting** Reads in-and out flowing current. The smart battery stores the data in the Full Charge Capacity (FCC) register that can be accessed but the readings can be inaccurate if the battery is not calibrated. A full cycle corrects the tracking error.

**Battery parser** A new method to estimate capacity during charge. A proprietary filtering algorithm establishes the precise SoC; coulomb counting estimates battery capacity.

### Rapid-test Methods

No single test can capture all health indicators of a battery. Many rapid-test devices look only at voltage and internal resistance. While capacity loss of a fading NiCd or NiMH may correlate with rising internal resistance, this relationship is less evident with lithium- and lead-based batteries. Advertising capacity estimation with a tester that only measures voltage and internal resistance can be misleading. It confuses the industry into believing that complex results are attainable with simplistic methods. Resistance-based instruments will indeed identify a dying or dead battery; but so does the user.

A battery is a reactive device and the method by which resistance measurements are taken matters. A DC measurement looks at pure resistive values while AC includes reactive components that provide additional information. Figure 1 represents the impedance of a good and faded Li-ion battery when scanned with AC from 0.1Hz to 1kHz. The strongest variances

in impedance (-Imp -Z) are observed on the low frequency scale ranging between 1Hz and 10Hz.

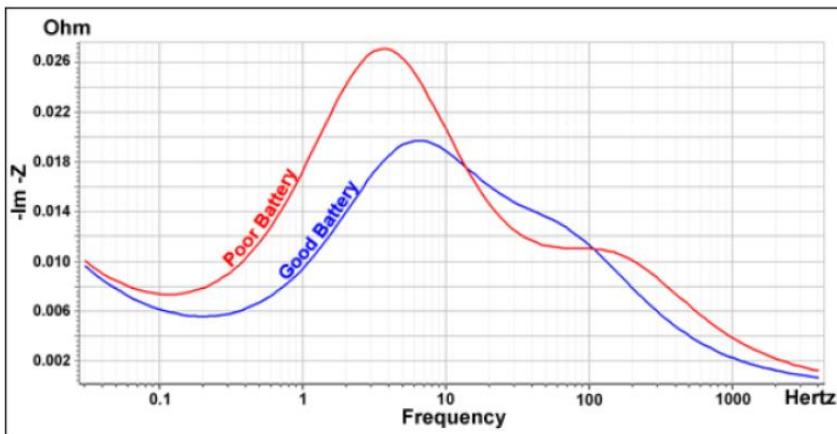


Figure 1: Frequency scans of a good and weak mobile phone battery.

Impedance variances are most visible below 10Hz. The horizontal scale is logarithmic to condense the frequency range.

Source: Cadex Electronics

It should be noted that resistive readings alone are inconclusive. No size fits all and the signatures vary with battery size and type. The results are further skewed by SoC levels, agitation and temperature. Cadex laboratories further discovered differences in how batteries are aged. What is most puzzling is why natural aging produces dissimilar signatures than artificial aging done in environmental chambers with fixed test regimes. This human-like behavior shares similarities with longevities people experience living in different global regions.

Cadex is pioneering in several rapid-test methods. These are Quick-sort Model Specific, Electrochemical Dynamic Response and Electrochemical Impedance Spectroscopy (EIS).

### Quick-sort Model Specific (QSMS)

QSMS observes difference in resistive values when assessing a battery with DC and AC methods. For example, the resistance of Li-ion in an 18650 cell is about 110mOhm with DC measurement and roughly 36mOhm with a 1,000Hz AC signal. The variance between the two readings provides performance information when compared with battery-specific parameters that are stored in a lookup table.

The algorithm is relatively simple and the test time is short, but the logistics of creating the parameters derived from good, marginal and poor batteries adds to complexity. QSMS is one of several rapid-test methods that Cadex has developed to classify mobile phone batteries on the fly.

### Electrochemical Dynamic Response (EDR)

EDR measures the mobility of ion-flow between electrodes by applying load pulses and evaluating the response time on attack and recovery. The recovery times are compared with stored parameters relating to battery performance. Figure 2 demonstrates a good battery that is firm and has a quick recovery against a weak battery that shows softness and has a sluggish recovery.

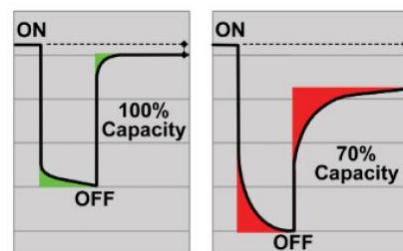


Figure 2: Electrochemical dynamic response.

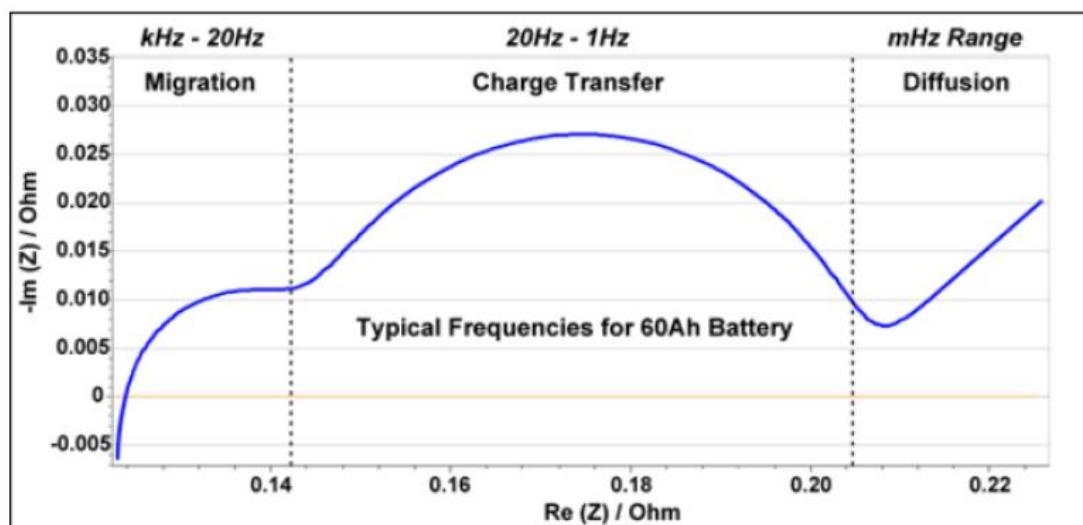
The diffusion coefficient of Li-ion differs according to active material and electrolyte additives used. EDR was developed by Cadex to rapid-test a broad range of mobile phone batteries. The technology is now being developed to test larger batteries.

### **Electrochemical Impedance Spectroscopy (EIS)**

EIS moves rapid-testing to a higher complexity level by scanning a battery with multiple frequencies to generate a Nyquist plot. The Nyquist information is superimposed onto electrochemical models that enable the estimation of capacity, CCA and SoC non-invasively. The typical test time is 15 seconds.

The Nyquist plot is named after Harry Nyquist (1889–1976), a former engineer at Bell Laboratories. It presents the frequency response of a linear system by displaying both amplitude and phase angle on a single plot using frequency as parameter. The horizontal x axis reveals the real Ohm impedance while the vertical y axis represents the imaginary impedance. Scientists predict that battery diagnostics is gravitating toward EIS technology by combining test results with complex modeling.

Figure 3 illustrates the three domains of the Nyquist plot entitled migration on the high frequency end, charge transfer in mid-range, and diffusion on the low frequency scale.



**Figure 3: The Nyquist plot is divided into high, mid and low frequency sections.**

The mid-frequency semi-circle represents battery characteristics best. Larger batteries require lower frequencies.

Source: Cadex

When scanning a battery from kilohertz to millihertz, the Migration field reveals resistive qualities of a battery that represents a bird's-eye view of the landscape. Valuable characteristics are found in the mid frequency range called Charge Transfer. This all-important domain forms a semi-circle representing the kinetics of the battery that provide SoH references. The low range dubbed Diffusion includes additional information relating to capacity but this requires long test times. Battery size directs the frequency; the larger the battery in ampere-hours, the lower the applied frequency becomes.

A rapid-test should last from a few seconds to no more than 5 minutes, but applying ultra-low frequencies prolongs time. For example, at one millihertz (mHz), one cycle takes 1,000

seconds, or 16 minutes, and several data points are required to complete the analysis. Test durations can often be shortened with clever software simulation.

### Battery Parser

The term “parser” has been in use in computer technology to describe receiving and sorting instructional data. Cadex uses this term to define battery capacity by establishing the precise SoC with a proprietary algorithm (patent pending) and then counting the coulombs that “fill” the available space of the battery. The charge period must be long enough to attain good readings.

The battery parser uses advanced machine learning, algorithms that will make its way into modern battery chargers to provide quality control in batteries. This integration will promote the charger into a supervisory system with no added logistics and little extra cost. Diagnostic battery chargers make battery performance transparent by removing the “black box” syndrome, a problem that has haunted battery users for centuries.

Table 1 summarizes test procedures with the most common battery systems. Lead acid and Li-ion share communalities in keeping low resistance under normal condition. Exceptions are heat fail and mechanical faults that raise the internal resistance and a battery replacement ahead of time. Nickel-cadmium and nickel-metal-hydride, and in part also the primary battery, reveal the end-of-life.

Test Method		Lead acid	Nickel-based	Li-ion	Primary battery
A N A L O G	Voltage	Estimates SoC in open circuit condition. Temperature and active materials within a battery system may cause slight voltage variations. Performance evaluation is not possible.			
	Ohmic test	Identifies heat fail and other defects; cannot do capacity estimation	Correlation exists between resistance and capacity	Low capacity may not affect resistance	Resistance relates to SoC; unique for each battery type
	Full Cycle	Use sparingly on large batteries	Recommended for small batteries		N/A
	Rapid-test	Time domain checks resistance, ion flow; Frequency domain reads capacity	Internal resistance correlates in part with SoH.	High efficiency enables time and frequency domain	Resistance check with lookup table for diverse batteries possible
	BMS	Voltage, current and temperature sense to monitor battery	Not practical due to inefficiencies	High efficiency enables coulomb counting	SoC by voltage
D I G I T A L	Coulomb counting	Low charge and discharge efficiency makes this impractical	Not suitable due to low efficiency and high self-discharge	Good for most Li-ion. LiFePO has high self-discharge	Used for critical applications with good results
	Read-and-charge (RAC)	Not practical because of low charge and discharge efficiency, high self-discharge		Enabled by high efficiency	N/A
	SOLI (State-of-life-indicator)	Estimates battery life based on delivered energy. A new battery starts at 100%. Drawing energy consumes the coulomb allotment, prompting battery replacement when zero. Can be applied to all batteries.			

Table 1: Battery test methods for common battery chemistries. Lead acid and Li-ion share communalities by keeping low resistance under normal condition; nickel-based and primary batteries reveal end-of-life by elevated internal resistance.