

# 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 (See BU-701 How to Prime Batteries)

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(See BU-808: How to Prolong Lithium-based Batteries)

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 1.000,000. 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. (See BU-205: Types of Lithium-ion.)

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
<b>Lithium Cobalt Oxide<sup>2</sup></b> (LCO)	LiCoO <sub>2</sub> (60% Co)	Good, only slight drop at 50–60°C	High capacity, limited power; fragile. Mobile phone, laptop
<b>Lithium Manganese Oxide<sup>2</sup></b> (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.
<b>Lithium Iron Phosphate<sup>2</sup></b> (LFP)	LiFePO <sub>4</sub>	Moderate, CE drops at 50–60°C	Power tools, e-bikes, EV, medical, UPS
<b>Lithium Nickel Manganese Cobalt Oxide<sup>2</sup></b> NMC	LiNiMnCoO <sub>2</sub> (10–20% Co)	Good, small drop at 60°C	
<b>Lithium Nickel Cobalt Aluminum Oxide<sup>2</sup></b> (NCA)	LiNiCoAlO <sub>2</sub> (9% Co)	N/A	Electric powertrain (Tesla Model S), grid storage
<b>Lithium Titanate<sup>3</sup></b> (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

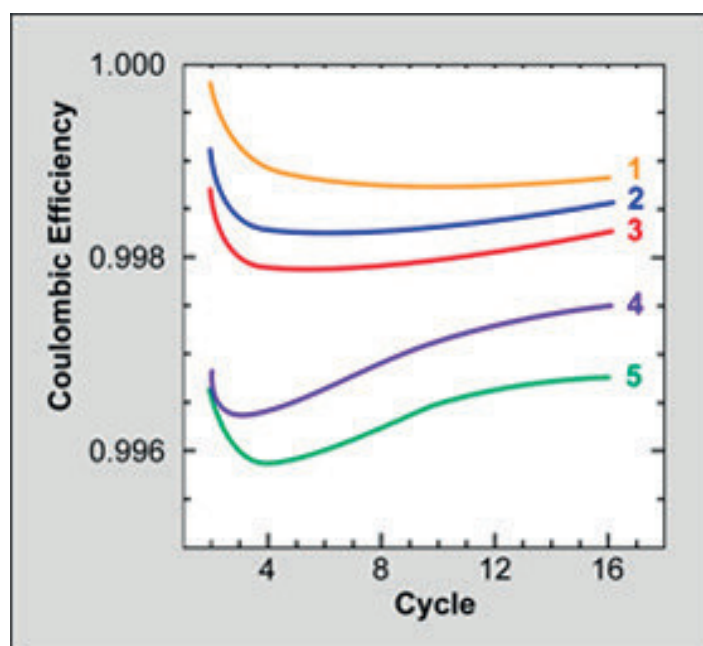
## Additives and the effects on Coulombic Efficiency

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 BU-307: 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.” A battery behaves like a living organism and, as a patient taking multiple medications must inform the doctor before additional pills can be prescribed, similar conditions exist with a battery. Using coulombic efficiency allows the discovery of possible interferences in weeks rather than having to wait for years for symptoms to develop.

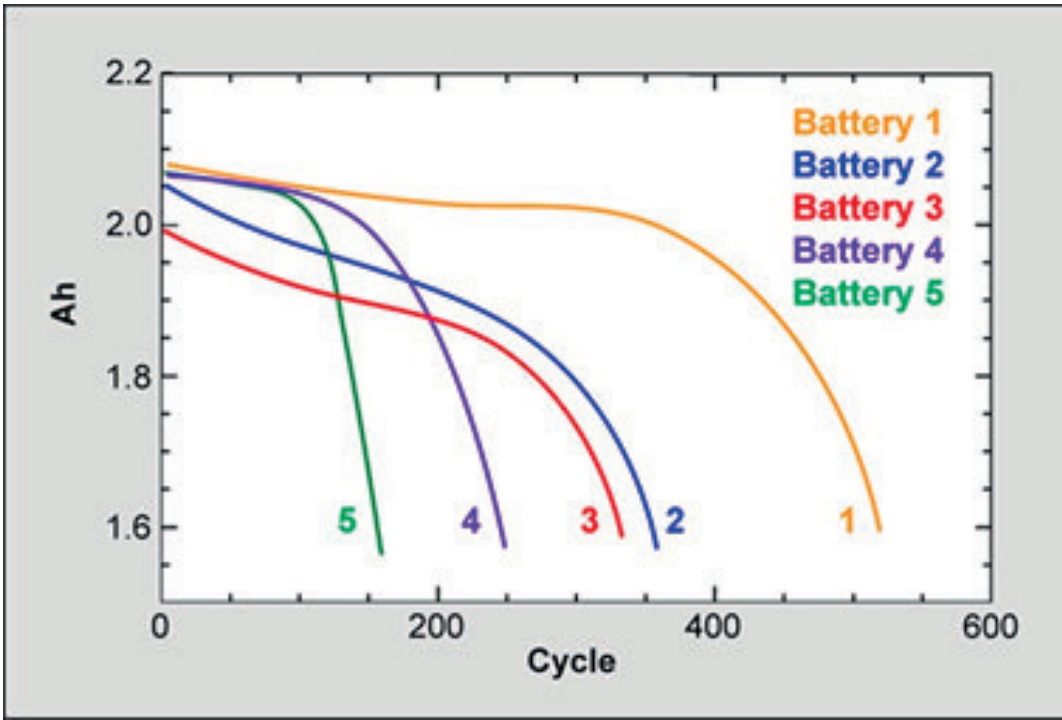
To examine the correlation between CE and longevity, Dalhousie University worked with battery manufacturers, including E-One Moli. While a university can carefully document ingredients, cell manufacturers keep these as top secret. The test bed consisted of 160 cells, four of each type. E-One Moli provided 80 cells with their own secret sauce; Dalhousie specified the other 80 electrolyte samples.

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 <sup>[1]</sup>

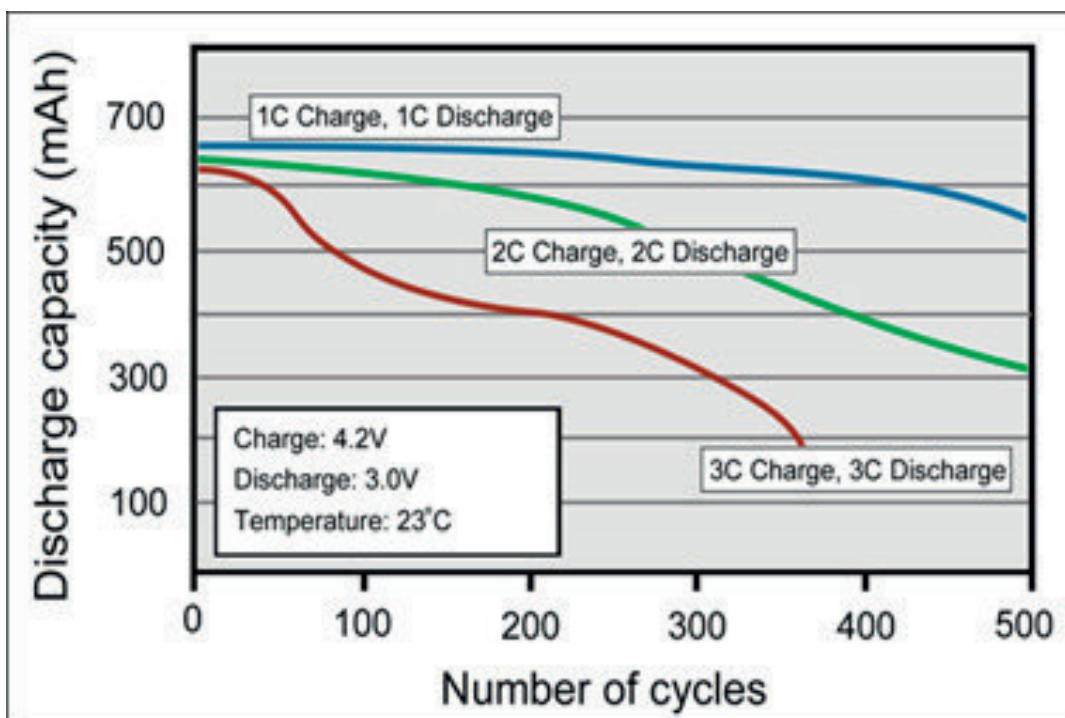
Five experimental batteries were tested for Coulombic efficiency. A higher CE provides a longer life.



**Figure 3:** Relationship of Coulombic efficiency and cycle life <sup>[1]</sup>  
 High CE values live the longest; low values die first.

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 (See BU-401a: Fast and Ultra-fast chargers)



**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

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.

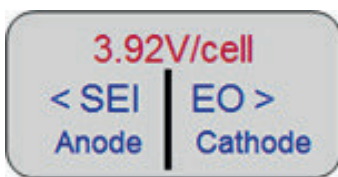
The newer Tesla models use the same concept and to reduce stress, Tesla “super-sizes” the pack. The battery is so large that it operates at a C-rate of only 0.25C (C/4), even at highway speed. This allows Tesla to focus on high energy density for maximum runtime; power density becomes less important. 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. Figure 5 demonstrates SEI and EO as a function of voltage.
- 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.)



*Figure 5: A cell voltage of 3.92V appears neutral lower voltages add to SEI, higher to EO.*

## References

[1] Courtesy of the Dalhousie University

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