

Lithium-ion Battery Technology

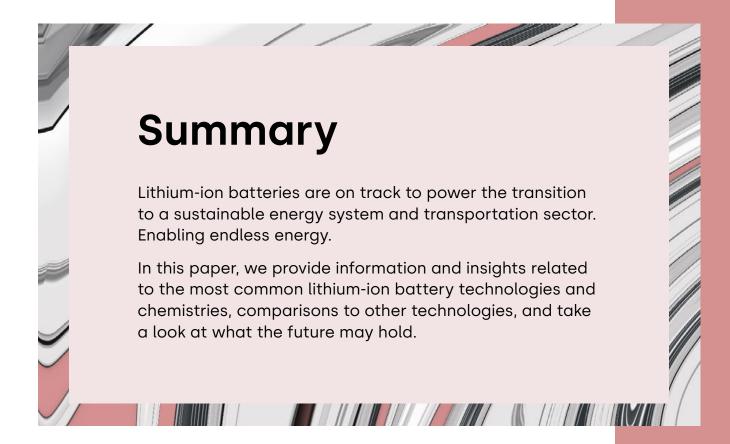
Chemistries, Comparisons, and Future Outlook





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Introduction

In a world where we've become dependent on batteries, constantly carrying around one in our pocket or purse, it may come as a surprise that batteries will likely become even more important in the future. This is due to the electrification of the energy system, to enable it to handle larger amounts of renewables, as well as the electrification of the transportation sector. Most of these changes are being powered by lithium-ion batteries, which offer an unrivaled combination of energy density, cycle life and cost competitiveness.

In this paper, Polarium describes the most common lithium-ion battery technologies and compare them to conventional lead-acid battery technology. We also take a look at technologies that could replace the lithium battery in the future, in the so-called post-lithium era.





Lithium-ion Battery Chemistries

Lithium-ion batteries (LIBs), or Li-ion batteries, has been the fastest-growing battery technology in recent years. LIBs typically have very high energy density, long cycle life, and low self-discharge. LIBs are used for portable consumer products, such as smartphones and laptop computers, and for electric powertrains in vehicles. They are also becoming increasingly common in energy storage applications.

Lithium is the lightest metallic element in the periodic table (atomic number 3) and has the highest electronegativity (-3.05 V compared to the standard hydrogen electrode) of all elements, making it very favorable to use for batteries.

Li-ion batteries is a family of battery chemistries with several different electrode materials (chemistries) with their own advantages and disadvantages. As with all batteries, a lithium-ion battery consists of one positive electrode and one negative electrode. The material and composition of both electrodes can be varied to obtain the desired properties. The positive electrode is sometimes referred to as the cathode and the negative electrode as the anode. In between the electrodes is the electrolyte, which conducts ions between the two electrodes. The electrolyte is often situated inside a porous plastic separator to prevent electronic contact between the electrodes. Because of the high operating voltage of lithium-ion batteries, aqueous electrolytes (i.e., water-based), which are used for most conventional rechargeable battery technologies, cannot be used and an organic electrolyte is used instead. Figure 1 shows a generalized evolution of the gravimetric energy density (based on weight) for Nickel-based and Iron-based battery cells.





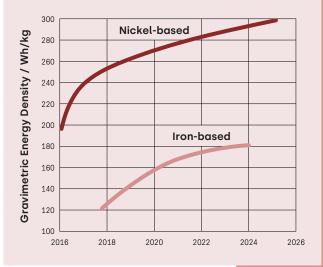
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Number of cycles to the fraction of remaining capacity versus rated capacity (also called state of health, SOH), is the most common way to compare the degradation. However, given the information presented in **Figure 1**, this metric is flawed because one cycle for Nickel-based battery cells provide approximately double the energy compared to one cycle for Iron-based battery cells. The industry is therefore trying to move towards discussing energy throughput as the comparative metric instead, thus comparing lifetime cycled energy instead of simply the number of charges/discharges.

LIBs normally have a nominal voltage of about 3.2-3.7 V/cell, depending on the chemistry.

Figure 1: Generalized evolution of gravimetric energy density for Nickel-based and Iron-based battery cells.









Form Factors

There are three main form factors used for lithium-ion batteries: cylindrical, prismatic and pouch, see Figure 2.

A cylindrical cell, as the name suggests, is a cylinder. There are a number of standardized diameters and heights used for cylindrical cells, with the two most common for LIBs being 18mm in diameter and 65 mm in height (the 18650 cell), and 21 mm in diameter and 70 mm in height (the 21700 cell). New formats set for launch include the 4680 cell with 46 mm diameter and 80 mm height that also includes major internal design changes to further optimize performance. Cylindrical cells are small (≤6 Ah) compared to the other form factors. The cylinder is normally made of nickel-plated steel, with the negative electrode being connected to the can. The electrode materials inside are wound into a spiral (known as a jellyroll). A cylinder is a very favorable and robust shape, which has positive effects on for example, cell swelling and cycle life. This is due to its ability to evenly distribute internal forces preventing swelling, without the need for an external mechanical structure to provide a clamping force.

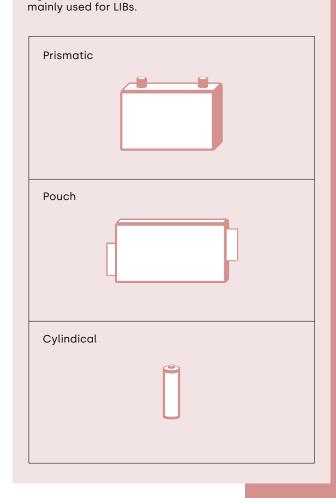


Figure 2: Sketch of the different cell form factors

Prismatic cells have a cuboid shape and are generally large (≥50 Ah), to take advantage of the cost benefits of the form factor. Contrary to cylindrical cells, there are large number of prismatic cell sizes. Cell dimensions are often tailored to specific uses. The can is usually made of aluminum. The electrode materials inside the cells can either be wound (similar to a cylindrical cell) or stacked. Stacked cells have become more common in recent years.

Pouch cells have a lot in common with prismatic cells, having a cuboid shape and generally being large. The electrode materials are normally stacked, as in modern prismatic cells and sealed inside a pouch made of laminated aluminum foil.

Larger cells are generally more cost-optimized, simply due to having less overhead in terms of terminals, cell can, etc. However, larger cells also lead to an increased safety risk in the event of cell failure. Smaller cells provide a redundancy in case of cell failure. The loss of one cell in a cell with several parallel strings does not have a major performance impact. However, the loss of one cell in a battery consisting of one large cell and no parallel connections would cause that battery to stop functioning.

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Positive Electrodes (Cathodes)

When comparing different lithium-ion battery chemistries, it is often only the positive electrode that is discussed, because in most cases the negative electrode is more or less fixed (and consist of graphite/carbon).

Nickel-based Chemistries

Nickel-based chemistries are primarily represented by lithium nickel manganese cobalt oxide (NMC), LiNi_xMn_yCo_zO₂ (where x,y,z = e.g., 1,1,1; 5,3,2; 6,2,2; or 8,1,1), and lithium nickel cobalt aluminum oxide (NCA), LiNi_xCo_yAl_zO₂ (where e.g., x = 0.8, y = 0.15, and z = 0.05).

NMC can be optimized for energy, power, or cycle life applications, depending on requirements. The trend in recent years has been to increase the nickel content of NMC to increase its energy density and decrease the use of the conflict material cobalt, closing the gap to NCA. However, the higher nickel content has made cells less stable and put extra pressure on the safety of systems. A simplified schematic on the properties of NMC depending on the fractions of nickel, manganese and cobalt is shown in Figure 3.

NMC have similar properties to NCA, especially with the high Nickel-NMC variants introduced recently. NCA has the highest energy density of all currently commercialized positive electrode materials. NMC with varying amounts of nickel, manganese, and cobalt. Nickel Capacity Cvcle life Safety Cobalt Manganese NICKEL NUGGET

Figure 3: Simplified schematic of the properties of

Because NMC and NCA contain several valuable metals, recycling is favorable and increasingly widely available. As lithium-ion battery recycling becomes more available, the recycling value of NMC and NCA will likely increase in the future i.e., the raw materials extracted from recycling will be worth more than the cost of the recycling process.

Energy density of NMC batteries has increased rapidly in recent years. Since 2015, the energy density of a state-of-the-art cell has increased from approximately 150 Wh/kg to approximately 270 Wh/kg in 2020. Market indications show that energy densities of NMC cells could reach close to 300 Wh/kg before 2025.

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A typical 100 Ah 48 V NMC battery module with 19" width and 4 U height weighs approximately 35 kg (~135 Wh/kg). For a 200 Ah 48 V NMC battery module with a 23" width and 2 U height., the typical weight is approximately 55 kg (~180 Wh/kg).

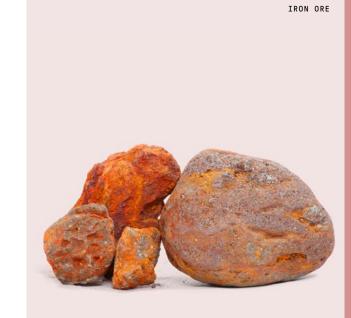
To maximize the lifetime of NMC or NCA batteries, it is recommended to use a limited depth-of-discharge (DOD) and lower the maximum state-of-charge (SOC). Nickel-based cells can have significantly higher cycle life at, for example, DOD of 80% compared to a DOD of 100%. Because of this, in combination with the recycling value, nickel-based cells provide the lowest total cost of ownership (TCO) of all lithium-ion battery chemistries.

Typical nominal voltage of NMC and NCA is 3.6-3.7 V/cell when paired with a graphite negative electrode.

Iron-based Chemistries

Iron-based chemistries, most commonly Lithium Iron Phosphate (LFP), LiFePO₄, is characterized by low initial capital cost (for large prismatic/pouch cells), high intrinsic safety, and the use of readily available iron instead of the rare metals used in the other positive electrode materials. However, it has lower energy density and operating voltage compared to NMC and NCA, as well as higher self-discharge. Its use in Li-ion batteries was discovered by Nobel prize winner John B. Goodenough's research group in 1996.

Recycling of LFP based batteries is generally worse than for other Li-ion chemistries, as it contains no valuable metals. This will likely result in that LFP batteries will continue to have negative value, i.e., cost money, to recycle even in the future.



In terms of cycle life LFP is the chemistry which in general can handle most cycles to end-of-life (EOL) when comparing at DOD of 100%. However, considerable progress has been made in recent years, and in terms of energy throughput (i.e., lifetime cumulative cycled kWh) many NMC cells outperform LFP. Contrary to NMC, reducing the DOD for LFP cells does not result in a large gain in cycle life.

LFP has a very flat open circuit voltage profile (open circuit voltage as a function of SOC). This results in very stable output voltage but makes cell balancing and SOC determination more difficult, sometimes requiring periodic equalization charging to 100% of SOC to recalibrate the SOC algorithm.



V:

As mentioned above, LFP batteries usually have a higher self-discharge rate compared to NMC/NCA which makes it less suitable for applications with long stand-by or storage times.

A typical 100 Ah 48 V LFP battery module with 19" width and 4 U height weighs approximately 43 kg (~110 Wh/kg). For a 200 Ah 48 V LFP battery module with a 19" width and 6 U height, the typical weight is approximately 75 kg (~130 Wh/kg).

Typical nominal voltage is 3.2 V/cell when paired with a graphite negative electrode.

Negative Electrodes (Anodes)

Graphite

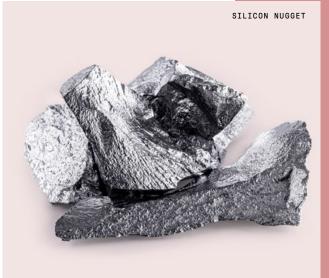
Graphite is the most used negative electrode for lithium-ion batteries. It provides a good cycle life with high energy density. It has an electrode potential close to that of metallic lithium, creating a risk of forming short-circuiting lithium-metal dendrites during charging, especially during low temperatures and at high rates. A mix of natural (mined) and synthetic (produced from other carbon-containing compounds) graphite is usually used to achieve optimal electrode properties.

During the formation stage of the battery production, a solid-electrolyte interface (SEI) is formed, that passivates the otherwise aggressive environment of the electrode to ensure a long life.

Silicon

Silicon has a theoretical capacity 10 times higher than graphite. However, due to poor cycle life properties caused by large volume expansion during cycling the use of pure silicon electrodes is not currently feasible. Instead, graphite electrodes are doped with nanoparticles of silicon to increase their energy density. Typical doping fractions range from 1-20% silicon. Silicon electrodes provide a slightly lower cell voltage compared to graphite, having the effect that LIBs containing silicon will have more capacity at lower voltages (<3 V for NMC batteries, where pure graphite NMC batteries are considered fully discharged).







Safety Considerations

The high energy density of lithium-ion batteries carries a certain safety risk. This is worsened by the fact that organic electrolytes used are highly combustible. A general rule of thumb is that a lithium-ion battery cell contains about 5-10 times more chemical energy than electrical energy. The means that a 1 kWh battery can release 6-11 kWh (20-40 MJ) of energy during a safety event, i.e., thermal runaway. It is therefore of the utmost importance to avoid any abuse conditions that can trigger such events, e.g., over-temperature, overcharge, over discharge, and short-circuit.

The intrinsic safety hazards of lithium-ion batteries are mitigated by having a robust design, protecting it from mechanical damage, and by using a battery management system (BMS) which prevents hazardous conditions such as overcharge and short-circuit.

Safety certification of LIBs is extremely important, because of the inherent hazards of the chemistry. For industrial applications, such as telecom or stationary energy storage, cells should be certified to UL 1642 in North America and IEC 62619 for Europe and many other countries around the world. Systems are certified to UL 1973 in North America and IEC 62619 in Europe/rest of the world. For larger energy storage systems, UL 9540 and IEC 62933-5-2 are required to ensure appropriate safety and performance.

Another important part of LIB certification is functional safety. Functional safety is the part of the system safety concept that depends on automatic protection based on measured inputs or component failures. E.g., the failure of voltage sensor or a too high discharge current must not result in a hazardous situation. Regardless of operating mode or environmental conditions, hardware and software shall operate safely and as intended. The functional safety is handled by the BMS.

Quality, especially for cells and BMS electronics, also has a high impact on safety. Higher quality results in lowered risk of failure, higher capabilities to detect failures before hazardous situations occur, and more possibilities to mitigate danger when a hazardous situation occurs.





Lead-acid Batteries (LABs vs LIBs)

Rechargeable, or secondary, batteries play an important role in our life and many daily chores would be unthinkable without the ability to recharge an empty battery. Since its introduction in 1991 lithium-ion batteries has been conquering more and more markets and applications. However, the most common rechargeable battery chemistry is still lead-acid batteries (LABs).

The LAB was invented in 1859 and has been the dominating rechargeable battery chemistry since at least the beginning of the 20th century. However, its low gravimetric energy density of about 30 Wh/kg at cell level makes it impractical for mobile applications (about 1/10 compared to state-of-theart LIBs on cell level). In practice this translates to that a lithium-ion battery module with the same performance (rated voltage and capacity) as a corresponding lead-acid battery, has a weight of approximately 1/5 of the lead battery and takes up approximately 1/3 of the volume.

In hindsight, it may be argued that the very commercial success of the LABs hindered its technological development. Rather than trying to push its low energy density towards its theoretical maximum of ~180 Wh/kg, the industry exploited the fact that LABs worked well enough in its diverse range of applications. Lead is abundantly available in the earth's crust as galena, lead sulfide, and lead mines are commonplace in many countries. Today, due to reduced lead dependency as an additive to gasoline and paints, and extensive LAB recycling infrastructure, reliance on mined lead materials has diminished considerably. More than 95% of all new lead products rely on recycled lead as their source material.

Dependency for the capacity on the discharge rate is another differentiator for LABs and LIBs, as LABs have a significantly stronger relationship between capacity and discharge current. This means that at higher currents, LABs will deliver less capacity than their rated capacity. For LIBs, dependency is quite low. For example, for LABs the capacity at 1 C compared to C/10 might be 60% but for LIBs this figure is generally more than 95%.

LABs are often optimized for their intended use, for example, cyclic use, high temperature, or float life. However, LABs optimized for cyclic use or float life cannot compete with the cycle or float life of LIBs, meaning that LABs need to be replaced more often than LIBs.

LABs have a nominal voltage of 2.0 V/cell. A 48 V, 100 Ah lead-acid battery string weighs approximately 135 kg (28 Wh/kg).

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Future Chemistries

The promise of the next super battery replacing lithium-ion batteries often makes the headlines. However, there are often several difficult problems that need to be solved before commercialization. In the section, a few of the most notable future chemistries or developments will be discussed briefly.

Solid State Batteries

Solid-state batteries are effectively an evolution of the lithium-ion battery. Liquid electrolyte of today's LIBs is replaced by a solid-state material, such as a ceramic. The biggest benefit of this change is that it reduces the safety risks associated with LIBs as fuel the make them burn so well is effectively removed.

However, discussions regarding solid-state batteries are often accompanied with the replacement of the negative electrode, today usually comprised of graphite, with pure metallic lithium. This replacement would result in a large boost in energy density. However, the introduction of lithium metal electrodes is challenging. Mainly due to risk of forming short-circuiting dendrites as well as lifetime issues.

There exist solid-state lithium batteries today, but they are mainly utilizing polymeric electrolytes that are required to operate at high temperatures to achieve optimal performance.

Lithium-sulfur

Lithium-sulfur is a rechargeable battery chemistry in which the positive electrode consists of elemental Sulfur, and the negative electrode of metallic lithium. It is most known for offering a large increased energy density compared to LIBs, potentially above 500 Wh/kg. At its fully charged state the positive electrode consists of pure Sulfur (S), and the negative electrode pure metallic Lithium (Li) and has a cell voltage of about 2.15 V. In the discharged states, poly-sulfides are formed that are dissolved in the electrolyte, eventually resulting in Li₂S when fully discharged.

The main issues are related to lifetime, associated with a massive volume expansion during discharging, as well as performance since Sulfur has an extremely low electronic conductivity.

Sodium-ion Batteries

Sodium-ion batteries (NIBs) are analogues to lithium-ion batteries where the lithium ion (Li+) is replaced by sodium ions (Na+), having the same basic cell construction, and working principle. The main benefits of sodium-ion batteries are associated with the fact that Sodium is significantly more naturally



abundant than Lithium, resulting in a potentially large reduction in cost. State-of-the-art NIBs have an energy density of about 100 Wh/kg, with a nominal voltage of slightly less than 3 V.

NIBs provide superior safety properties compared to LIBs. This is partly due to aluminum being used as the current collector for the negative electrode, removing risks associated with over discharge. Furthermore, increased amounts of propylene carbonate can be used in the electrolyte to reduce flammability.

While graphite cannot be used as a negative electrode for sodium-ion batteries due to difficulties in storing the larger sodium ion, other carbon-based materials work well, (e.g., hard carbon). As with LIBs, metal oxides (e.g., $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$) are the most common positive electrode material for NIBs.

NIBs can be designed to function with aqueous electrolytes at the cost of lowered voltage and energy density. For high energy-density NIBs, organic carbonate solvents are normally used as for LIBs.



Abbreviations

- BMS Battery management system
- DOD Depth of discharge
- EOL End of life
- LAB Lead-acid battery
- LFP Lithium Iron Phosphate
- LIB Lithium-ion battery (Li-ion battery)
- NCA Lithium Nickel Cobalt Aluminum Oxide
- NIB Sodium-ion Battery (Na-ion battery)
- NMC Lithium Nickel Manganese Cobalt Oxide
- SEI Solid-electrolyte interface
- SOC State of charge



About Polarium

Polarium is a Swedish company dedicated to providing the best performing, safe and sustainable energy storage solutions built on lithium-ion technology for the telecom, commercial, and industrial segments. The company was founded in 2015 with the purpose to empower a smart and sustainable world with the help of energy storage.

We are driven by innovation and cutting-edge technology, resulting in advanced technology made easy to use. Our energy storage solutions are superior in quality, recyclable, certified and designed with the highest safety in mind. The embedded intelligence of our lithium batteries puts you in charge and minimizes maintenance.

Our headquarters and R&D center are situated in Sweden and we have manufacturing in Mexico and Vietnam. Through our global sales channels and representations, we serve customers worldwide.

Today, our market-leading solutions are in use on all continents and in all climate zones – from the Equator to the Arctic – enabling our customers to move away from lead acid batteries and fossil fuels to long-lasting, smart, and recyclable lithium batteries – reducing costs as well as environmental impact.



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