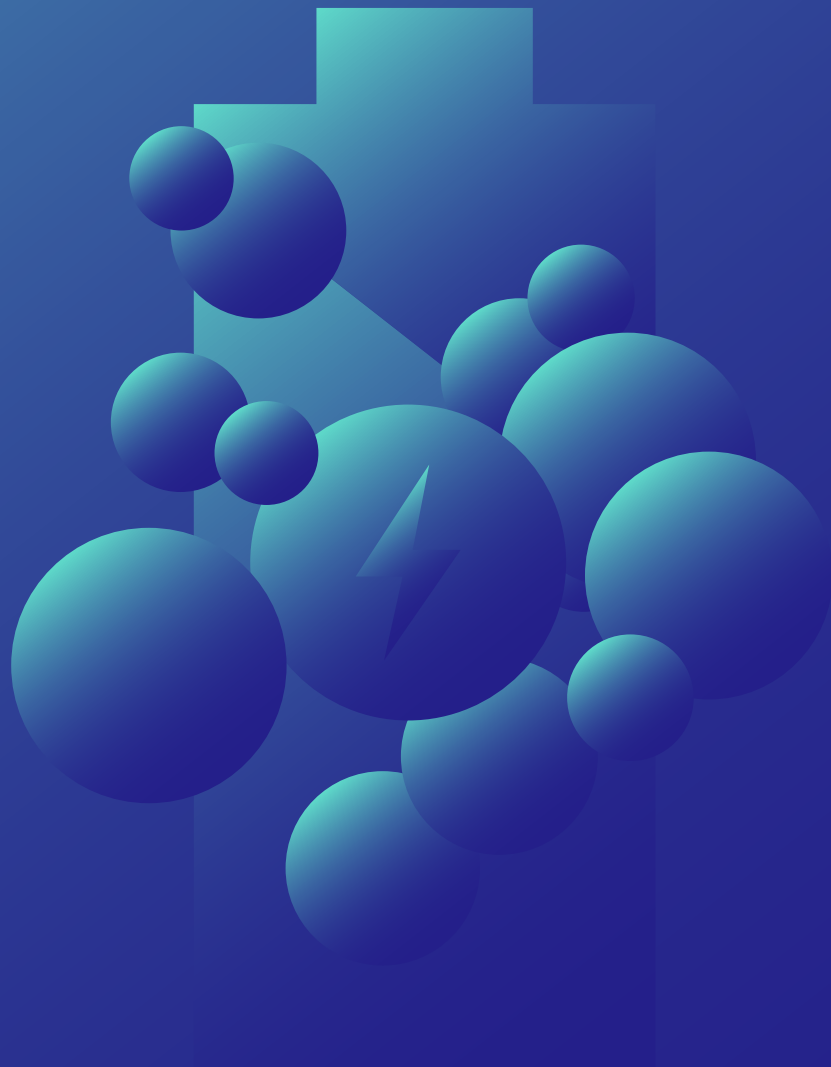


Lithium Batteries



Introduction

There is an ever-growing need for portable energy storage solutions ranging from cell-phone batteries to electric vehicle batteries, and from microbatteries for tiny disposable sensors to lightweight power-packs for flying cars.

Battery technology has been one of the major enablers of mobility innovation over the last 50 years. From medical implants to powered vehicles, every advance made in stored energy density has been accompanied by a sizeable step forward in miniaturization and capability in the broader device market.

Limitations in portable energy storage are one of the biggest reasons that we aren't yet moving around in powered exoskeletons or commuting in flying cars.

In general, the physical size and capability of any device is fundamentally limited by its power source. For portable electronics, the batteries are very often the bulkiest/heaviest component.

Performance Criteria

Improving energy density has been the primary factor driving ongoing battery research. Energy density is typically expressed in units of watt hours, (abbreviated Wh), which is the amount of power (in watts) the battery can deliver for a one-hour period. Energy density is described in two different ways. There is volumetric energy density (expressed in Wh/Liter), where the goal is to have more energy stored in a smaller package volume, such as medical implants or hearing aids. And then there is gravimetric energy density, where the weight of the battery is of primary concern such as in electric vehicles and drones, and expressed in watt-hours per kilogram (Wh/kg). A closely related measure is Capacity (expressed in Amp hours, Ah), representing the discharge current a battery can deliver over time.

Energy density is only one of many factors that might drive selection for a particular application. Also of importance is power density, describing how much electrical current can be delivered by a battery without undesirable effects such as sagging voltage, build-up of heat (which can lead to bursting or fire), or unwanted chemical side-reactions inside the cell. This raises another important factor, safety; both in terms of potential for fire/explosion if the stored energy gets suddenly released, and also in the form of toxicity of the chemical compounds themselves. Toxicity is of concern both during operation, and at end of life when it ends up in a landfill. Other important considerations are the overall cycle-life of a battery, describing how many times it can be discharged and charged before the performance drops below some threshold (usually 80% of the amount of energy it originally stored). Finally, of course, the cost of production and purchase price is a key factor driving battery selection.

Chemistries

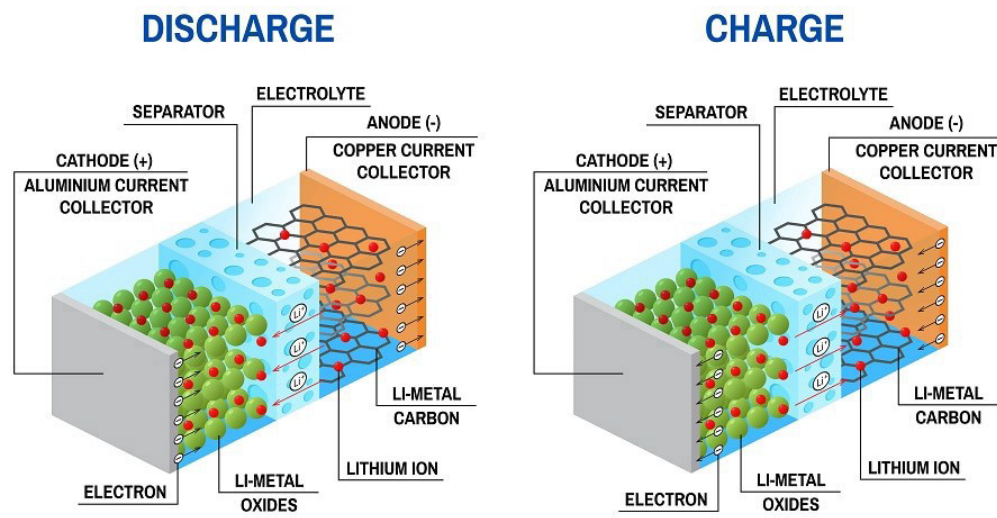
In the search for better battery technology, many different chemistries have been tried. The majority of practical battery technologies involve oxidation/reduction reactions of metals in an acidic or basic electrolyte. The ubiquitous “alkaline” AA and AAA battery derives its power from the reaction between zinc metal and manganese dioxide electrodes in a caustic potassium hydroxide electrolyte. The equally common lead-acid battery reacts lead (Pb) metal and water in a sulfuric-acid electrolyte. It is typical that a chemical battery will contain a significant quantity of reactive metal and a liquid electrolyte, both of which are relatively heavy materials.

It is no surprise that lithium arose as a leading candidate for advanced battery chemistries.

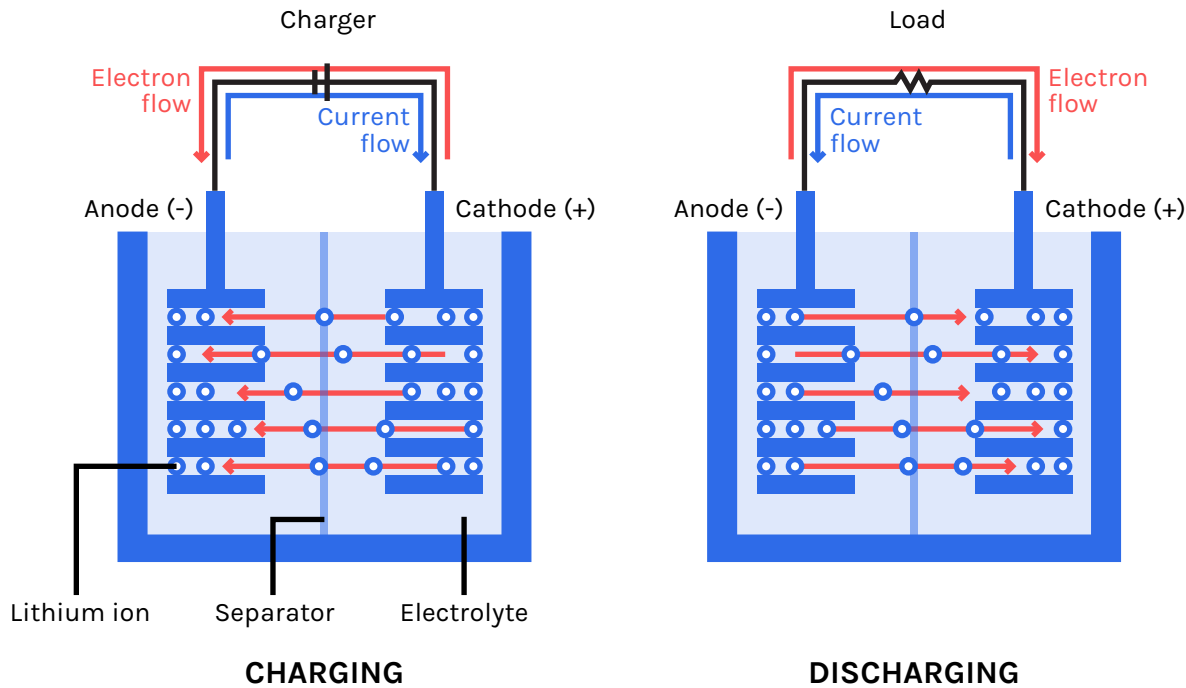
Lithium has the lowest weight of all metals, while having the highest electrochemical potential (voltage) on the periodic table.

Lithium is not only the latest and greatest material in battery science, it's the theoretical best there is.

There are many different Lithium-based chemical reactions that are suitable for encapsulation into battery cells, but all of them share a common mechanical anatomy:



Lithium-ion battery anatomy



Lithium-ion Charging and Discharging Circuit Diagram

Source: greencarcongress.com

Battery Components

Anode

The negative electrode during discharge. Typically a porous carbon graphite sheet that serves like a conductive sponge to loosely bind lithium ions in a process known as intercalation.

Electrolyte

A conductive liquid or gel through which ions are transported as charge carriers. This is typically a strong organic solvent, which is quite flammable if exposed to air, and the source of most battery fires.

Separator

A porous membrane which serves as a spacer, preventing the anode and cathode electrodes from coming into contact, and also acting as a reservoir for the liquid electrolyte. Can be made from plastics, polymers, paper, or more exotic materials. Must allow lithium ions to pass through.

Cathode

A highly-porous metal oxide layer that participates in the chemical reactions of the cell. Lithium ions migrate into this lattice during discharge. This is usually the largest contributor to energy capacity and power density.

Current Collectors

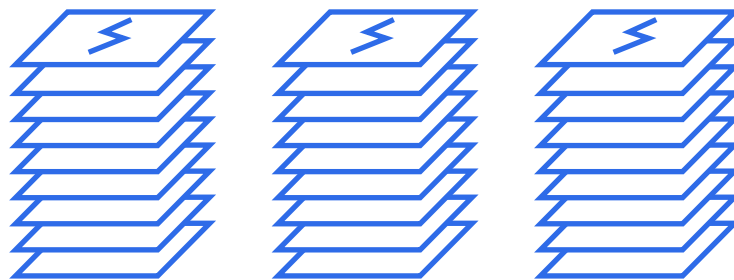
Metal foil applied as a backing to each electrode to conduct electrons into and out of the cell. Copper(Cu) is used on the anode; aluminum(Al) on the cathode. The materials are chosen to be passivated and stable at the potential of each electrode, and do not normally take part in the chemical reactions. Many different metals/materials would work, but Al and Cu are cheap and abundant.

Housing/packaging

The outer enclosure of the battery. Does not participate in reactions, but must be able to withstand elevated temperatures and mechanical effects (expansion, pressure, etc). Contributes to the overall weight and volume of the battery cell.

Advances in any individual cell component can lead to substantial improvements in energy density, safety, power output, or cycle life of the assembled battery cell. Entire materials companies are built around developing and supplying a single one of these

components to the major battery makers. Battery manufacturers can choose the materials for each component (cathode, electrolyte, separator, etc.) to enhance specific qualities desirable for their use-case; however, an enhancement in one property often compromises something else. Thus true advances in any one of these components can lead to new optimal combinations, resulting in substantial gains in overall energy density, safety, power output, and cycle life of the assembled battery cell. However, there are countless material companies pursuing this approach; and getting mass adoption of a particular material can be as much a matter of luck as of actual performance.



Manufacturing Costs

Battery manufacturing is a very capital-intensive undertaking, and very sensitive to economies of scale. For this reason, massive battery plants (so called mega- or giga-factories) have arisen to address this ever-expanding market that is forecasted to grow 1000% between 2018 and 2030. There are over 90 of these megafactories in operation today, with the five largest producers being LG, CATL, BYD, Panasonic, and Tesla.

Assembled lithium battery cells can take many shapes, but the most common form factors are cylindrical, button, prismatic and pouch cells. Each has its own advantages and limitations in terms of cost to produce and specific energy density due to overall shape and enclosure mechanics. Also of concern is how easily each can be integrated into a device compartment and how to prevent heat buildup in and around the battery pack.

Cost of production (expressed in \$/kWh) is a major consideration in evaluating any new battery technology. If a new chemistry, electrode material, or cell construction

doesn't lend itself to factory automation then the new performance gains may not be good enough to justify the increased cost of production.

Most of today's batteries are constructed from layered/laminated materials, often stacked, cut, and conveyed using conventional roll-to-roll processes and equipment adapted from the paper-making industry. So if a new anode or separator material cannot be handled by existing factory equipment (for example if made thinner and thus more prone to tearing) then it might require specialized equipment to be invented and retrofitted onto a production line at great cost to the manufacturer. This is especially true when a new technology will compete with battery cells produced in the megafactories, where massive economies of scale and infrastructure investment have already driven the production costs (and margins) to rock-bottom levels.

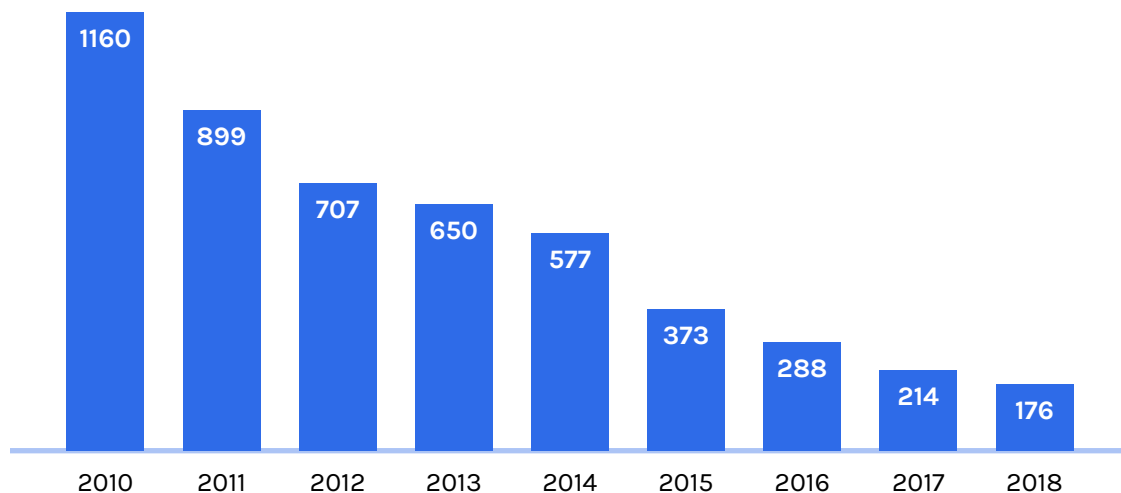
A new technology either needs to be compatible with the existing production infrastructure, or provide such massive performance improvements that it justifies building or retrofitting a megafactory to produce that specific battery type.

However, in these low-margin operations, it becomes very difficult to justify amortizing the large R&D costs necessary for major battery breakthroughs. What we are seeing instead is an incremental evolution of battery materials funded by modest R&D investments. But the number of players pursuing this approach is staggering, with both the major manufacturers and small materials startups seeking to carve out small single % returns in this crowded market.

Lithium-ion battery price survey: volume-weighted average

Source: BloombergNEF

Battery pack price (real 2018 \$/kWh)



This is the primary reason that the battery industry has shown such poor returns to investors in the last decade. Dozens of electrically-superior battery technologies have arisen and died because they couldn't stay ahead of the falling price of existing Lithium-ion battery production. In fact, most of the development work today is aimed at improving the manufacturing processes. It is said that one engineer working to improve the manufacturing process is worth 10 engineers working to improve the battery chemistry technology.

Industry Terms to Know

BOL

Beginning of Life, when a battery enters service and the capacity can be assumed to be near 100% of the nameplate spec.

EOL

End of Life, is defined when the battery degrades to a point where only 70–80% of Beginning-of-Life (BOL) capacity is remaining under nameplate conditions.

DOD

Depth of Discharge. Referring to the amount of energy cycled out of a battery on a given discharge cycle, expressed as % of total capacity (100% = empty, 0% = full)

SOC

State of Charge. The compliment to DOD, indicating the present amount of energy remaining in a battery, expressed as % of total capacity (0% = empty, 100% = full)

C-rate

Charge or discharge. The ratio of current (in Amps, A) into/out of a battery cell as compared to the overall Capacity (in Amp Hours, Ah). A battery being charged at 1C will fully charge from 0 to 100% in 1 hour. At 4C the same battery will charge in 15 minutes. At 0.1C the battery will charge/discharge in 10 hours. Higher C-rates will cause elevated temperature, which can dramatically reduce the lifetime of the cell.

Cycle Life

The total number of charge/discharge cycles a cell can undergo before its total charge capacity degrades to some percent (typically 80%, see EOL above) of the nominal nameplate capacity. Essentially the number of charge/discharge cycles between BOL and EOL.

Primary Cell

A single-use battery (not rechargeable), e.g. AAA batteries

Secondary Cell: a multiple-use battery (can be recharged), e.g. cell phone and laptop batteries

BMS

Battery Management System. Electronic circuitry built into nearly all battery packs that monitors individual cells, monitors and controls charge-rates, prevents over-charging, and acts to prevent thermal run-away events.

Today's State of the Art Technology

The portable battery market today is dominated by Lithium Ion (Li-Ion) chemistry with over 316GWh of battery capacity being produced in 2019. And the demand for Li-ion batteries is projected to surge another 8x from 2019 to 2030, mostly due to the boom in electric vehicles.

There are a number of common Li-Ion chemistries in use today, with the main distinctions between being energy density/capacity, cycle life, safety, and cost. The most common chemistries are listed below and generally refer to the cathode materials.

NMC: Lithium Nickel Manganese Cobalt Oxide

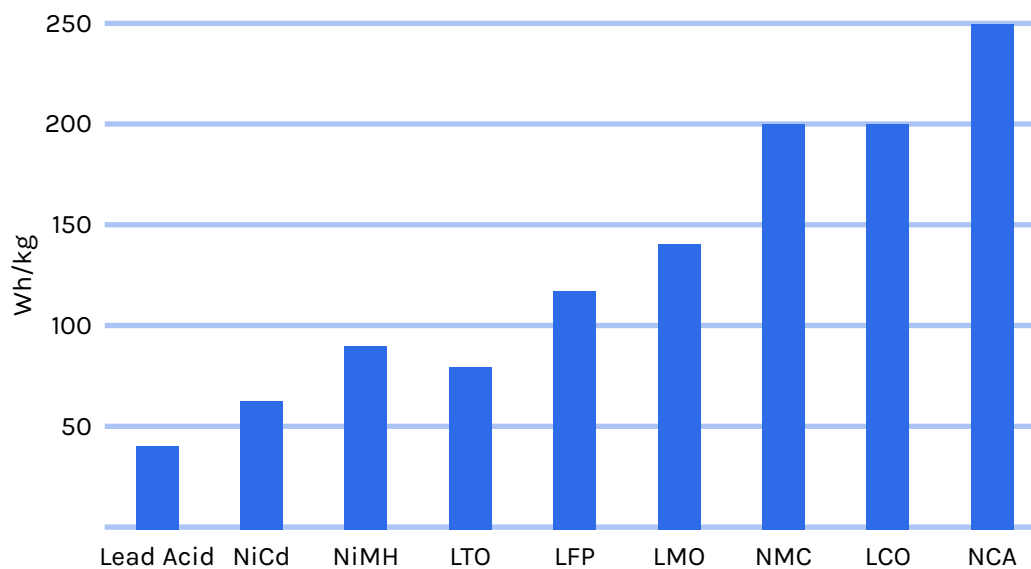
LCO: Lithium Cobalt Oxide

NCA: Lithium Nickel Cobalt Aluminum Oxide

LFP: Lithium Iron Phosphate

LMO: Lithium Manganese Oxide

LTO: Lithium Titanate



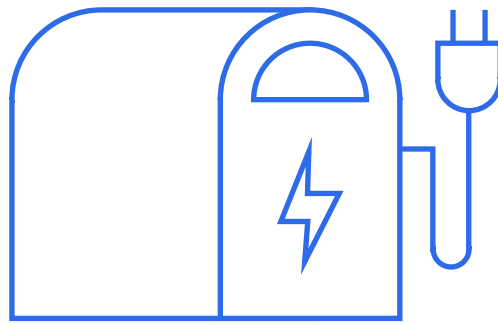
Energy Density by Material

Source: https://batteryuniversity.com/learn/article/types_of_lithium_ion

Cathodes

Many of the biggest advances in energy capacity are expected to come from advances in cathode materials, both composition and structure. The cathode is the largest driver of energy density, as this is where most of the actual chemical reaction takes place (pure metals being converted into metal oxides and back again during charge and discharge).

It can be worthwhile watching for startup companies that are developing new cathode materials. However, as mentioned previously, they must be compatible with existing factory automation equipment, or be enabling at least 2x increases in energy density over the current state of the art cathode materials.



A key metric for evaluating a new battery technology is demonstrated traction with major battery producers. It is not enough to show a promising chemical component in the lab; there must be demand, and ability to produce the material at massive volume.

Cobalt

Cobalt is a common component in cathode materials, and contributes significantly to performance and longevity. However, cobalt supplies on earth are limited to a small number of highly-contested geographical regions; particularly the unstable Congo region of Africa which holds over 55% of the world's supply of this metal.

One of the major pushes in Li-Ion research has been to reduce or eliminate cobalt content in favor of more common metals. The problem is that most alternatives lead to poor performance in Lithium battery chemistries in terms of energy capacity, longevity/cycle life, power delivery, and cost. Lithium iron phosphate (LFP), lithium manganese oxide (LMO) and lithium titanate (LTO) batteries are cobalt-free, but as can be seen in the chart above their energy densities are lower than the cobalt-containing chemistries (denoted by the "C" in the material abbreviations). They may also have other limitations such as shorter cycle-life and lower power density.

LFP is a noteworthy exception here, being cobalt-free while demonstrating 2000+ cycles, which makes it a promising chemistry for vehicles and mobility despite the lower energy density. Essentially, a device maker using this chemistry will require more batteries, but they will be cheaper and last longer.

Silicon Anodes

An advance that is getting a lot of attention is the incorporation of silicon(Si) into the battery anode (traditionally graphite). Silicon-based anode materials can hold as much as 10x more lithium ions than the graphite anodes used commercially today. This 10x sounds impressive, but the anode is only a small fraction of the overall battery assembly, so this technology could lead to overall cell energy capacity gains of 10-50%. However, there is a well-known problem with mechanical swelling of the silicon matrix, expanding (and contracting) to as much as 400% of the original volume as the lithium ions diffuse into and bind with the silicon during charging. This swelling creates a significant mechanical challenge for batteries constructed of many layers of material. There are technologies emerging to compensate for this expansion such as making porous or spongy anode materials that have room to expand within their original volume. Anodes with a small amount of silicon additive have made it into existing commercial products, though the major manufacturers are generally holding these additions as closely guarded trade secrets. Anodes with higher silicon content are in the mid-to-late stages of development, but may not reach the market before better alternatives emerge.

Graphene Anodes

While most anode material today is made from graphite, we are beginning to see the use of graphene, a more highly structured form of carbon that is more thermally stable and electrically conductive. This suggests batteries with graphene-composite anodes could be charged and discharged at much higher C-rates, and thus be more useful for high-power applications.

There are a number of companies exploring silicon-graphite or silicon-graphene composite electrodes, seeking to capture the benefits of both additives. Further, there is research to show that these composite anodes can be charged to higher voltages of 4.2-4.35V, which can yield a 10% increase in energy density over 3.7V cells with plain graphite anodes.

Separator Membrane

The primary role of the separator is to prevent short circuits between the positive and negative electrodes. Thus safety is the major consideration in separator development. Common trends are to make thinner separator films, which will make the layers thinner and thus the battery smaller in volume (and perhaps reduce weight). However, this must be accomplished without sacrificing the separator's ability to keep the electrodes electrically isolated from one another, while still allowing ions to migrate between the electrodes. Some key innovations here are advanced fiber materials that are more thermally stable and able to withstand the tremendous current density and heat, while also being substantially thinner. Also under development are structured

nano-materials that contain and release flame-retardant compounds into the electrolyte in the event of a short circuit, rupture, or high-heat event.

Electrolyte

Most electrolytes in use today are strong organic liquid solvents with high volatility and high flammability, which are necessary to dissolve the high concentrations of lithium ions that serve as the charge carriers within the battery. Much work today is dedicated to trying different solvent chemistries or additives to lessen the potential for a “venting with flame” event, which is the technical term for a ruptured and burning cell, or “rapid disassembly” which is the nice way of saying something exploded. Flame retardant additives are common, but cannot be added at sufficient concentrations to reliably stop all fires without the additives having detrimental effects on battery performance. There is ongoing research to use non-flammable inorganic liquids or ionic liquids as electrolyte, or to do away with the liquid electrolyte all together in favor of a solid-state crystalline electrolyte.

Lithium Metal Batteries

A development push that we are very optimistic about is the commercialization of Lithium-metal batteries. A lithium-metal battery uses a layer of pure lithium metal foil as the anode, where today’s lithium-ion batteries use a carbon graphite anode to bind and store lithium atoms (in a process called intercalation). When a lithium metal battery is charged, lithium ions simply plate out of solution onto the surface of the metal anode; growing in thickness slightly, but much less than the swelling expansion that today’s carbon-based anodes experience as they become lithiated.

This essentially means that the anode can hold a vast abundance of accessible lithium atoms. This would then make the cathode the only limiter on battery capacity. Further, the lithium metal foil is significantly thinner and lighter than graphite, leading to immediate decreases in weight and theoretical improvements of 80% or more in overall gravimetric energy density (already approaching 500Wh/kg in test cells).

Lithium metal anodes have the potential to create a drastic leap forward in energy density of 2x or more, which could single-handedly enable the nascent electric aviation industry, which today is held back by the weight of heavy battery packs.



However, this approach has some significant challenges that must be addressed by any company putting forth a lithium metal anode technology. The primary factor that has hindered the commercialization of rechargeable lithium-metal batteries in the past is the uncontrolled deposition of small needle-like crystals of lithium metal (called dendrites) that grow on the surface of the metal anode during charging. These dendrites can project outward from the anode like a conductive spike, piercing the separator membrane and creating the potential for a short circuit condition and the fiery demise of the battery pack. Much work today is going into surface coatings and electrolyte chemistry to cause a flat, uniform plating of lithium atoms on the surfaces to prevent the growth of these high aspect-ratio dendrites.

Another reason why we have not seen widespread commercialization of lithium metal anode technology is that the lithium metal itself is highly reactive if exposed to air or water. This means it must be handled carefully in production facilities, contributing to infrastructure and cost. And then even after assembly the lithium can heat up and burn if the battery cell is ruptured. This can be solved by modifying the battery chemistry to passivate the surface of the metal through the formation of a Solid Electrolyte Interphase (SEI) layer so it won't react if exposed.

Long View – The Future

Solid-state Batteries

When considering the next 3–5 years of portable power there are a number of promising battery technologies to consider. Solid-state-batteries are getting a lot of press and attention from researchers, and are definitely a technology to watch. The basic premise with these lithium-based cells is that the electrolyte layer consists of a solid material instead of the liquid or polymer-gel electrolytes in use today. This solid layer would allow the use of the lithium metal anode by providing a barrier to problematic dendrite growth, as discussed above.

The solid electrolyte material is also generally non-flammable, whereas almost all of the liquid or gel electrolytes in use today contain chemicals that are flammable if exposed to air. So the big push for solid-state batteries is to enable the theoretical 2.5x increase in energy density over today's Li-ion batteries that can be achieved by incorporating a lithium-metal anode, all while improving the safety. Additionally, the separator layer needed to keep the electrodes separate can be much thinner, (3–4 μ m, vs the 20–30 μ m films in use today), so volumetric energy density should improve. Further, these batteries are expected to have much greater cycle life (theoretically tens of thousands of cycles), better thermal stability at higher temperatures, and

better shelflife than liquid electrolyte batteries. This is especially interesting for electric vehicles, where the holy grail is to produce a battery pack that can undergo 5,000-10,000 cycles and last 20+ years to match the life of the car frame itself.

However, for all of this promise solid-state technologies face many technical challenges that should be considered before making an investment. So far the proposed technologies are very expensive to produce and are generally not compatible with existing production methods. The current methods to produce these solid layers require complex vapor deposition processes, and produce a solid crystalline sheet that is not compatible with the roll-to-roll processes favored by the battery industry today. For this reason, we do not regard them as commercially viable within the next 3 years, though many of the large vehicle manufacturers are investing heavily to try to beat this. Further, these solid layers are often formed from metal oxides and ceramics, which are dense materials and thus lead to heavy battery packs. So this may inherently limit the adoption of this technology for electric aviation and other weight-sensitive applications.

Lithium-Air Batteries

On a longer time horizon, we consider Lithium-oxygen batteries an intriguing possibility. This class of battery derives energy by oxidizing pure lithium metal with a source of oxygen, traditionally in the form of ambient air. Reacting pure lithium with ambient oxygen can result in an electrochemical cell with the highest possible energy density of any metal, yielding theoretical capacities of 11,000 Wh/kg (not counting the weight of the reacted oxygen). This is noteworthy when Li-ion is today topping out at 250 Wh/kg, and Li-metal will theoretically top out around 3,000 Wh/kg. And especially interesting when you consider that liquid gasoline has a maximum energy density of 13,000 Wh/kg, with only 1,700 Wh/kg delivered to the wheels after losses. But a lithium-air battery in this basic configuration is not rechargeable. And significant technological challenges remain before any appreciable cycle-life is expected from batteries built with this technology. These lithium-air or lithium-oxygen batteries are at least 5-10 years away from commercialization, but could disrupt the market with a 10x step-change in energy density, rivaling liquid gasoline in terms of raw energy density.

Conclusion

It is worth mentioning that there are many different use-cases for battery technology, each of them with specific requirements that guide selection. Lithium-based batteries as outlined in this paper will dominate most of the portable-electronics applications. But lithium is a relatively unstable compound, so it may not be the chemistry of choice for applications that require ultra-reliability such as powering medical devices or spacecraft.

And then there is a massive and ever-growing need for stationary energy storage solutions to enable the future of renewable power generation. Many different mechanical and chemical means are being explored to address this market segment. Lithium-based batteries have historically been too expensive per kWh to be competitive in this market. But with continually-falling battery production costs this trend could soon reverse, opening opportunities for investment in grid-scale lithium battery storage systems.