Prospective Materials for Li-ion batteries

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Abstract

Climate change, driven by greenhouse gas emissions, poses significant environmental and economic challenges. As a result there has been increasing interest in renewable energy due to its lack of greenhouse gas emissions unlike fossil fuels. However these sources of energy face issues when it comes to particular energy storage. Lithium-ion batteries, known for their high energy density and rechargeability, are integral for creating a sustainable grid. Most forms of renewable energy are not consistent, for example solar panels don't produce energy at night. Therefore there is a need for an ability to store vast amounts of electricity for future use. In transportation high energy density energy storage is needed to ensure that vehicles can run for long periods of time off of electricity. This paper focuses on understanding what characteristics optimize lithium-ion batteries for commercial electric vehicles, and also addresses issues like cell degradation, dendrite growth, and thermal runaway. By highlighting these hurdles and identifying promising material innovations, this work aims to contribute to the development of safer, more efficient lithium-ion batteries, driving progress toward a sustainable transportation future.

Introduction

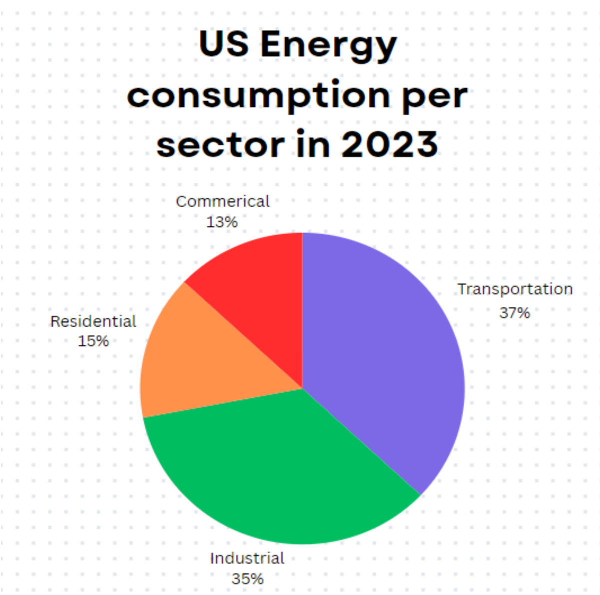


Figure one

Climate change is one of the biggest problems that affect the Earth as of 2024. From 2030 to 2050 climate change will be responsible for 250,000 deaths per year As of 2023, 3.6 billion people live in areas susceptible to climate change. (1)

Fossil fuels are the main cause of climate change. Fossil fuels are made of decomposing plant and animal material and when burned it releases energy that can be converted to electricity. (2) The current sources of fossil fuels from the ground come through fracking, drilling and mining, processes that are linked to air and water pollution. (3) Currently fossil fuels like coal, oil and gas contribute to 75 percent of global greenhouse gasses and 90 percent of all carbon dioxide emissions. (4) In 2023, fossil fuels accounted for 84% of US energy production. (5) The energy created from fossil fuels are used in a variety of sectors: manufacturing, transportation and in powering homes and buildings.

When fossil fuels are burned they emit greenhouse gasses like CO_2, CH_4, and N_2O. These greenhouse gasses join the atmosphere and absorb heat from the sun which raises the Earth's temperature. Rising levels of greenhouse gasses also create climate extremes like droughts and air pollution.(6) The effects of climate change are incredibly destructive and expensive which is why this issue has come to the forefront of global efforts to try and stop it or slow it down.

From the Paris Climate Accords, the global goal for climate emissions is currently to constrain the global average temperature rise to 1.5℃ over pre industrial levels (7) and in 2023 the average global temperature level reached 1.36℃ over pre industrial levels. (8) Transportation as a sector makes up a major portion of the total energy used in the US at 37%, as seen in Figure 1. To mitigate the effects of climate change, investments in new, clean sources of energy are rising. Many types of renewable energy are not dependable for energy production at every time of day, unlike fossil fuels. For example, solar energy cannot be produced at night and wind turbines may produce less energy depending on the season. Due to these issues, energy storage is imperative for development into renewable energy.

Lithium ion batteries provide a solution to the issue of vehicle energy storage. Due to the lithium ion's small atomic weight and radius it is the material that allows for some of the lightest and energy dense batteries with the highest voltage. Its aspect of high energy storage per weight (specific energy, e.g. Wh/kg) is what makes this type of battery particularly appealing for the use of transportation. Gasoline has an energy density of 46 MJ/kg, while lithium ion batteries have an energy density of .3096 MJ/kg to 5.43 MJ/kg. (9,10) While this may seem low, lithium ion batteries have a much higher energy density than other battery types like lead acid batteries which have an energy density of .108 MJ/kg .178 MJ/kg. (11) With the highest energy density amongst reusable batteries, lithium ion batteries are the future of energy conservation.

As of 2019, 15 percent of global greenhouse emissions came from transportation. (12) To reduce the amount of greenhouse gasses released by the transportation industry this paper will aim to cover the best materials for a lithium ion battery in commercial cars.

Background

Redox reactions are reactions where electrons transfer from one material to another. In solutions electron transfer between two ions are only made possible when the energy of the electron at two sites are matched and there is sufficient overlap of the electron orbitals for the actual transfer to occur.(13)

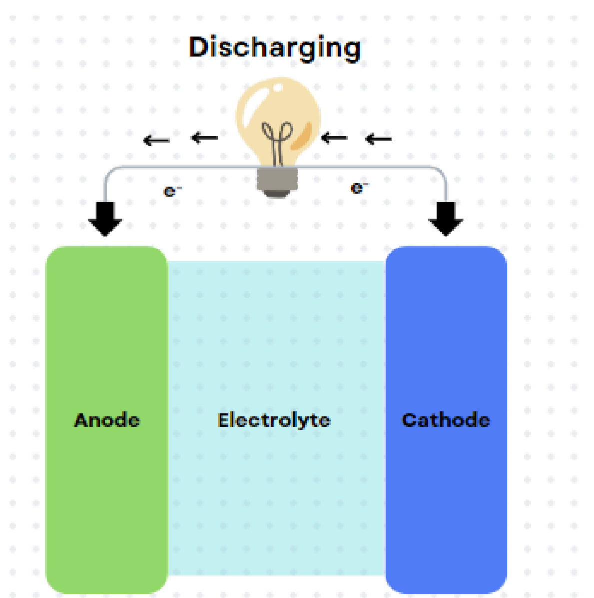


Figure two

A common example of a redox reaction is the rusting of iron. An equation for the redox of iron is

$$4Fe_{(s)} + 3O_{2\,(g)} + 6\,H_2O_{(l)} \rightarrow 4Fe(OH)_{3\,(s)}$$

The anode is the region of the battery where electrons leave during discharging and enter during charging. In our iron equation the anode was the iron.

$$Fe \rightarrow Fe^{3+} + 3e^{-}$$

In a lithium ion battery this is usually graphite or lithium alloyed materials.(12) For lithium ion batteries, anodes must be durable, light weight , low cost and have a voltage match with the cathode material.(13)

The prioritization of cost is attributed to the mass implementation of the anode material for commercial purposes. The light weight property of anode materials is high in demand specifically for transportation purposes. The anode's durability is needed for the battery to survive a variety of environments and temperatures.

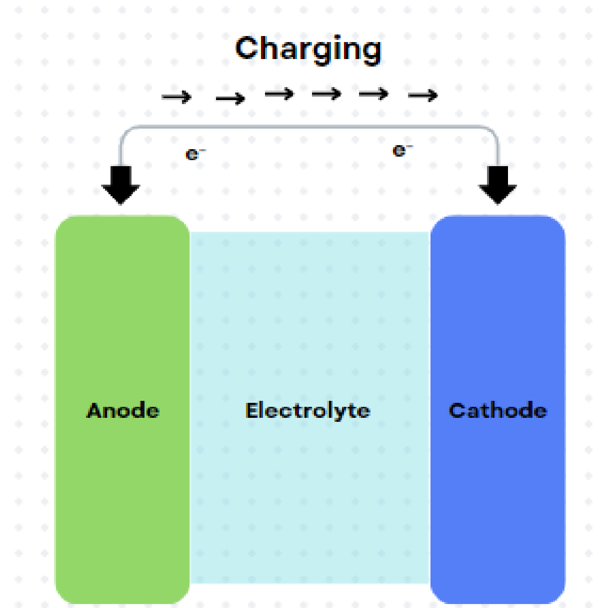


Figure three

Cathodes in batteries are where the electrons are taken in during discharging and leave during charging as seen in figure 2. The cathode has a wide variety of materials available when it comes to lithium ion batteries. In the iron rusting equation the cathode was the oxygen particles.

$$3O_2 + 12e^{-} \rightarrow 6O^{2-}$$

The fundamental elements of any battery are the anode, cathode and electrolyte. During discharging the electrons in a battery are released from the anode to the cathode which is facilitated by the electrolyte as seen on figure 3. While the electron moves through the battery it passes through a device which causes the device to be powered. In typical non rechargeable batteries this is done by utilizing an irreversible reaction that will start when connected. However, the batteries we will be focusing on are rechargeable and function by using a reversible reaction that can support the flow of electrons both ways.

To monitor the efficiency of the battery the theoretical capacity will be used. The theoretical capacity is based on the bonding strength of materials. The stronger the bonds, the less energy released when it breaks due to the stability of the lithium ions in the material. Another important factor in lithium ion batteries is measuring the voltage drops at different charge and discharge points. To do this the voltage of a battery at certain points of charging and discharging we use the Nernst equation.

$$E = E_0 - \frac{RT}{nF} lnQ$$

E is the voltage of the battery at non standard conditions.
E_0 is the voltage of the battery at standard conditions
R is the universal gas constant (8.314 $\frac{J}{mol\ K}$)
T is the temperature in kelvin
n = number of moles of electrons transferred during the redox reaction
F = Faraday constant (approximately 96,485 $\frac{C}{mol}$ l)
Q = ratio of the concentrations of products to reactants

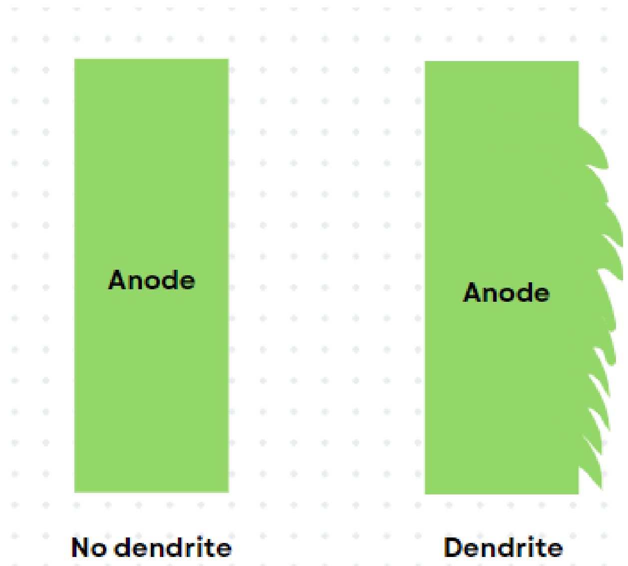


Figure four

The standard state of a battery is defined as when the ratio of products and reactants are equal to one. At standard state E_0 would be equal to E. The nernst equation is typically used to calculate the voltage between two different the two different materials that are used for the anode and cathode.

The Nernst Equation helps predict the energy density in lithium ion batteries which is based on the amount of energy stored per unit mass. This is typically denoted as mAh/g which stands for milliampere-hours per gram. It is a metric used to compare the efficiencies of different lithium batteries. The energy density of the material is an important factor to consider in transportation as a lighter battery is often preferred since transporting a lighter battery takes less energy.

Typical problems

Cell degradation is a major problem facing lithium ion batteries today. It most typically occurs when the electrolyte undergoes degradation at high temperature which leads to the formation of solid byproducts. Cell degradation can also lead to side reactions in the battery. These side reactions are dependent on temperature and cell voltage. (14)

Cell degradation is affected by the SEI. The SEI stands for the solid electrolyte interphase and is created instantaneously as the electrolyte solution interacts with the solid anode. More specifically at higher temperature the (SEI) layer on the anode grows more porous and unstable which results in a faster degradation rate.

Another factor that shortens the lifespan of lithium ion batteries are the higher charging and discharging rates which can shorten the lifetime of a lithium ion battery. As fast charging requires higher currents, it generates more heat leading to an uneven temperature distribution in the battery. This can cause uneven current flow and eventually cause local degradation. (15)

However one of the most pressing problems when it comes to lithium ion batteries is dendrite growth. Dendrites on lithium ion batteries are lithium deposits that plate on the anode. Dendrite growth occurs in lithium ion batteries when the lithium ion density is low and the current is high. Dendrite also forms when the temperatures are low the diffusion rates for lithium ions are lowered which may lead to uneven lithium plating and lithium dendrite growth (*See figure four*).(16)

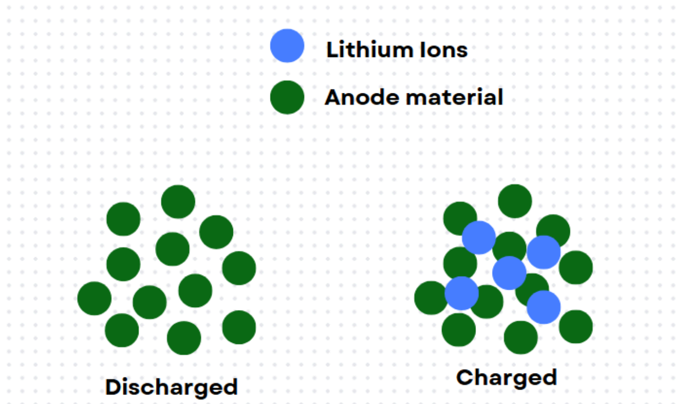


Figure five

Dendrite growth poses a problem for lithium ion batteries as they can reduce the capacity of a lithium ion battery by locking lithium ions in place or can pierce the separator between the anode and the cathode which can lead to a short circuit. (17,18) Some solutions to dendrite growth include investing in solid electrolytes, including additives like fluoroethylene carbonate to stabilize the SEI layer and suppress dendrites. (19, 20) To mitigate the effects of these problems research into new materials for the battery is necessary.

Lithiation/ Delithiation

Lithiation is the process of intercalation of lithium ions into the anode material during charging. Intercalation of lithium ions is the process which during charging the lithium ions will take up positions in the anode with the electrons that pass through from the cathode to the anode through the external circuit. These electrons help hold the lithium anions in place in the anode material by reducing the lithium ion's positive charge and therefore making the ion neutral. During discharging the ions will return to their positions in the cathode in the process of delithiation and the electrons will return back to the cathode through the external circuit which powers your device leading to the cell. (21)

Alloying

During charging lithium ions move from the electrolyte to the anode where it reacts to form an alloy. When the battery discharges, ions move from the alloy and back to the electrolyte. This reaction in lithium ion batteries tends to result in high theoretical capacities but also with various mechanical issues.

Safety

SEI

A dominant factor determining the safety, power capacity, shelf life and cycle life is the SEI of a lithium battery. (22) The SEI provides a buffer layer between the anode and electrolyte which prevents electrolyte degradation and promotes ion transport (*see figure 6*). The thickness of the SEI is integral to maintaining the health of the battery and is controlled by a variety of factors including the cycling frequency. Too much charging and discharging in a short period of time can promote SEI degradation by causing heat in the battery which promotes the SEI layer to decay or grow excessively. (23)

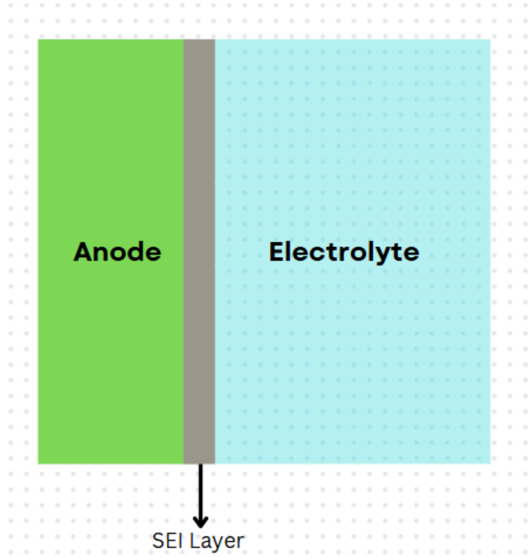


Figure six

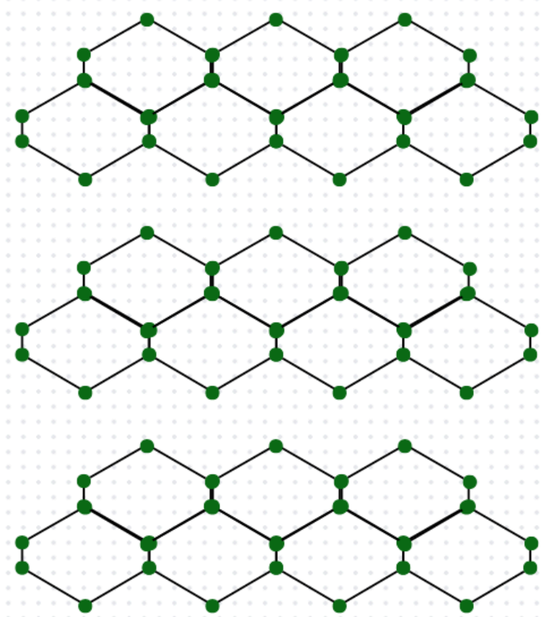
Thermal Runaway

Thermal runaway in lithium-ion batteries is a critical safety issue where an uncontrollable exothermic reaction occurs in a self perpetuating cycle, leading to rapid temperature escalation and potentially resulting in fire or explosion. Lithium fires are especially dangerous due to the high amounts of heat released during combustion, violent reactions with water and it can lead to explosion risk as the lithium fires tend to release gases that can build up in the battery casing and eventually cause an explosion as the pressure gets too high. Thermal runaway begins when the internal temperature of the battery rises beyond a certain threshold, typically due to internal short circuits, overcharging or over-discharging, external heat sources and manufacturing defects.

Anode Materials

The anode is one of the key components of a battery where oxidation (the release of elections during discharging) occurs. The preference of material for the anode of a lithium ion battery is heavily dependent on the structure, the stability, abundance and cost of the anode. (24) In order to keep the cost of the total battery low, a cheaper material for the anode component is preferred. This often correlates to a high abundance of the material. To grade the effectiveness of each battery, theoretical effectiveness will be used. The theoretical capacity of an anode material is based on the amount of lithium ions it can hold per unit mass or volume. The higher the theoretical capacity, the better the material.

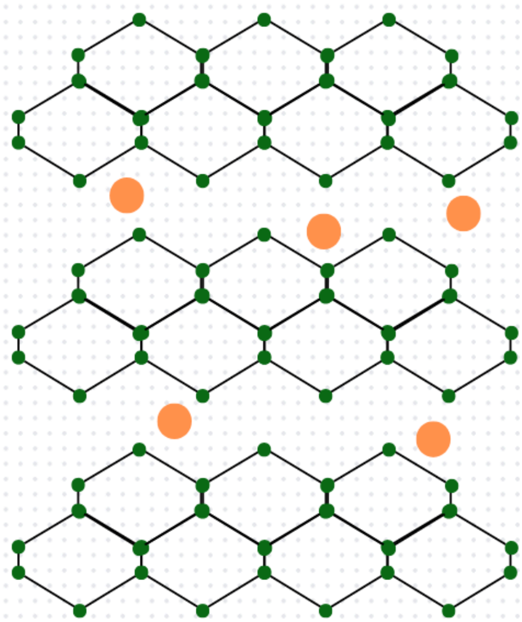
Figure seven



Graphite

Graphite, a form of carbon, is the most common anode used for a lithium ion battery due to its unique layered structure and it is in fact the commercial standard for lithium ion batteries. While carbon has a variety of unique structures that constitute different materials like diamond, the structure of graphite is the most desired due to its unique layers of hexagonal structured molecules. This allows for the intercalation of lithium ions. During lithiation the lithium ions interlace themself in between the layers of graphite (*See figure 7,8*). Graphite is a preferred substance for the anode because of its relative abundance, high electrical conductivity, high power density and its cycle life. Graphite is suitable for a long cycle life due to its ability to maintain its structural integrity over thousands of cycles due to its layered structure. However graphite tends to degrade under high stress from high current rates which can cause side reactions with the electrolyte as the electrolyte decomposes and the products of the decomposition can react with graphite (25). Graphite can also lead to thermal runaway as it reaches higher temperatures, rapid charging and physical stress from slight volumetric changes during charging and discharging, electrical and thermal stress from rapid discharging and charging which can lead to reaction between the anode and the electrolyte which causes heat and in some cases fire and explosions (26). Graphite also has a low theoretical capacity for lithium ion batteries when compared to other anode composites like silicon. Graphite has a theoretical capacity of around 372 mAH/g while other anode materials like silicon have a higher theoretical

Figure eight



capacity at 3579 mAh/g. This is primarily due to the fact that the layered structure of graphite forces one lithium ion to be spaced per six carbon atoms. (27) Due to these problems developments into other anode materials are being researched.

Aluminum

Aluminum anodes are being researched as an alternative to the conventional graphite anode. Aluminum has a theoretical capacity of 2235 mAh/g and works through causing the alloy Li_9Al_4 during lithiation. (28) The current benefits to using aluminum is that it is abundant and has a high theoretical capacity. In comparison to the industry standard, graphite, aluminum are also abundant and therefore low cost.
However, aluminum has a higher energy density than graphite since it can store more lithium ions per gram than graphite can. (29) Some downsides of using pure aluminum as an anode for lithium ion batteries are that they experience volume expansion during the process of introducing lithium atoms to the material which can lead to mechanical stress and poor cycling stability in the battery. (30) Overall, aluminum is a promising new area for development in lithium ion battery anodes but currently has too many technical obstacles for it to be viable currently. However research is being done in the field like with alloying aluminum with other materials or optimizing the electrolyte to improve cycling stability with aluminum.

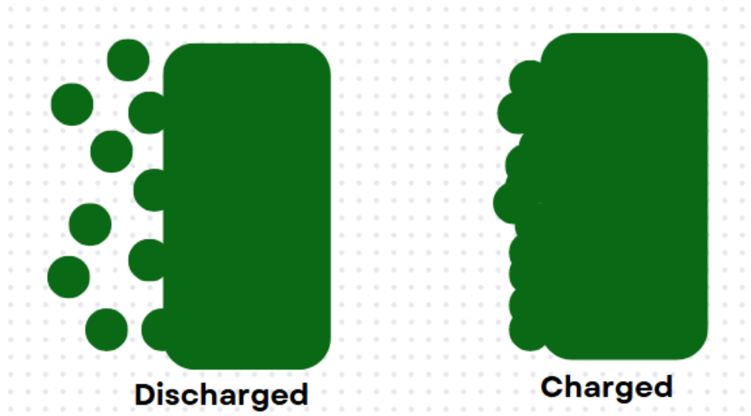


Figure nine

Silicon

Silicon is seen as a possible alternative to Graphite because of its incredibly high theoretical capacity. As mentioned earlier, silicon maintains an incredibly high theoretical capacity of 3579 mAH/g. This is due to the formation of the $Li_{15}Si_4$ during the intercalation process.(31) The high ratio of lithium ions to silicon ions allows for the energy density of the material to be very high. Silicon is also very abundant in the earth's crust with an average of 27.7% of the earth's crust. (32) This means that it would be a relatively low cost alternative for graphite in a lithium ion battery. However silicon still faces issues when it comes to volume expansion as it can increase by almost 300% percent during the process of lithiation. This can lead to a variety of issues like the SEI to rupture which would force the silicon to reform the SEI over and over during discharging this eventually leads to an increase in the internal resistance and a rapid decrease in capacity. (33)

Solid lithium

Solid lithium is considered one of the best anode materials for lithium ion batteries because of its extremely high energy density. Unlike graphite or aluminum, solid lithium anodes instead use the process of stripping and deposition. As the lithium ions get reduced during charging they plate themselves on the solid lithium anode. During discharging the anode gets oxidized and some of the lithium metal turns into ions *(See figure 9)*. A solid lithium anode has a strong theoretical capacity at around 3860 mAH/g.(34) Lithium is a low weight metal which means that its energy density is high. However using solid lithium as an anode is tricky since lithium is highly reactive and would therefore need a lot of safeguard set in the battery to make sure that it does not have any alternate reactions with its surroundings. In addition the repeated cycling of lithium ions with a lithium metal anode could lead to non active lithium as non-even lithium deposition and splitting can lead to some lithium ions to be separated from the rest. Ultimately solid lithium serves the possibility for batteries to have an incredibly high energy density but suffers from technical issues that prevent its implementation. (35)

Cathode Materials

The cathode is the other key component in a battery where reduction (the absorption of elections during discharging) occurs. The preference of material for the cathode of a lithium ion battery is graded on the same criteria as the anode. Just like with the anode we will prioritize energy density with the theoretical capacity and also cost effectiveness. The theoretical capacity of a cathode material is based on the amount of lithium ions it can hold per unit mass or volume. The higher the theoretical capacity, the better the material. Unlike the anode however, the amount of suitable materials for the cathode are varied and therefore there isn't one definite industry standard.

NMC (Nickel- Manganese-Cobalt Oxide)

NMC also known as Nickel-Manganese-Cobalt Oxide is a common cathode material used in a variety of automobiles today. NMC is used for its relatively high energy density and its relatively low cost compared to other expensive cathodes as it uses only a small amount of cobalt. Even with these advantages, NMC faces issues when it comes to stability over repeated cycles. NMC is unique with the nature of its component metals. Nickel provides a high theoretical capacity but a low stability. Manganese provides stability and cobalt provides a buffer to prevent the nickel and manganese from mixing. However NMC does face issues when it comes to safety and its cost. (36) In general the need for higher energy density is causing cathodes with a higher nickel content to be used but these come with downsides. Blends of NMC with a higher nickel content also face problems from thermal runaway and instability caused by dissolving of the transition metal, Li/Ni ion mixing and surface reconstruction. (37) In addition the concerns of where cobalt is sourced is raised as unethical mining procedures that produce cobalt are called into question.(38, 39)

LFP- Lithium-Iron-Phosphate

Lithium Iron Phosphate (LFP) is well regarded for its safety and long life. In addition, in comparison to other cathode materials, LFP is relatively cheap since its component materials are relatively abundant unlike cobalt. In addition iron and phosphate can be more ethically and sustainably mined than cobalt due to their abundance. However LFP does have its downsides with a lower energy density from other cathode materials like NMC but it is more stable. LFP is at a much lower risk for issues like thermal runaway and extreme temperatures or overcharging like with other batteries.(40) Because of its ability to last for a long time and its low energy density, LFP is not as popular as NMC when it comes to vehicle transportation currently but it is growing in use. LFP has its benefits in its lowered cost due to not containing any cobalt and its increased safety from its stability. Some uses for LFP in electric cars are in the Tesla Model three and all BYD electric cars. However, currently instead LFP finds its place amongst stationary energy storage.

Conclusion

Lithium-ion batteries hold a pivotal role in solving the challenges of climate change through the transition to renewable energy, particularly within the energy storage and transportation sectors. This study examined significant developments in anode and cathode materials and underlined how crucial energy density, robustness, and safety are to satisfying the needs of commercial vehicles. While graphite remains the industry standard for anodes, there are many promising alternatives that are burdened by technical challenges such as volume expansion and stability issues. Similar trade-offs occur with cathode materials like NMC and LFP between energy density, cost, and safety. The foundation of lithium-ion technology's future lies in using creative material design and improved production techniques to solve problems like thermal runaway, dendritic growth, and cell deterioration. The advancement of sustainable transportation in the future will depend heavily on ongoing research and development in this area.

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