SUSTAINABLE ENERGY STORAGE

A Deep Dive into Advanced Materials for Next-Gen Batteries

MATERION

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The last decade has witnessed the beginnings of a global transition to decarbonized energy; the next decade expects to see that transition accelerate rapidly. A pivotal facet of this transition will be the development and subsequent mass production of more advanced batteries, including batteries for demanding mobile applications like passenger electric vehicles (EV). Batteries are agnostic in how the electricity to charge them is generated. Aside from eliminating harmful tailpipe emissions of internal combustion engine (ICE) vehicles, the ultimate promise of advanced batteries is the role they can play in a decarbonized energy eco-system, storing energy from non-carbon dioxide (CO_2) emitting power sources such as photovoltaic (PV), wind, hydro-electric and nuclear. This storage capability is especially critical for emerging economies in India, Africa, and Southeast Asia with growing energy and transportation demands (Abdul-Manan et al., 2022; The International Council On Clean Transportation, 2021).

BETTER BATTERIES

Advances in EV batteries and their manufacture are needed in four critical areas to increase public adoption:

1) Advancement in gravimetric and volumetric energy densities
2) Faster charging rates leading to reduced charging times
3) Longer battery lifetime with safe operation
4) Sustainable manufacturing

Performance advancements in energy densities, faster-charging rates, and longer battery lifetime with safe operation are routinely mentioned in discussions about mobile battery improvements needed to accelerate consumer adoption. Recently, the need for more sustainable manufacturing and supply chains has gained attention and become a critical aspect of this growing industry.

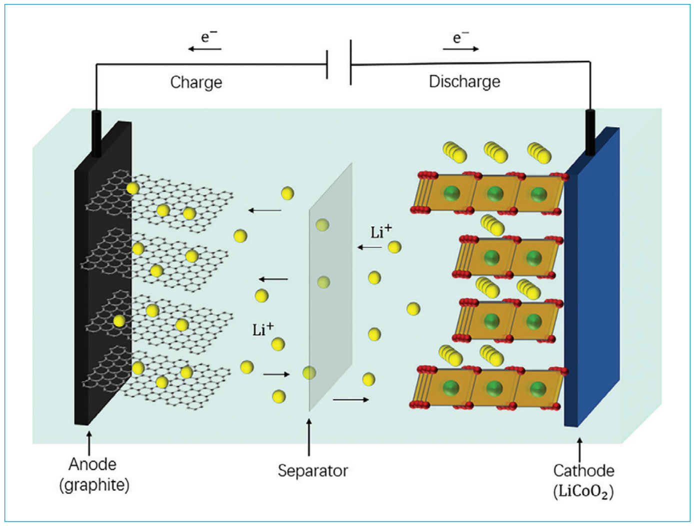

Figure 1 - Schematic of a Li-ion battery (Cheng et al., 2021).

In its simplest form, current Lithium-ion batteries (LIB) consist of a cathode(+) and an anode(–) material separated by a thin, porous polymer film soaked in an organic liquid electrolyte solution (Figure 1). The battery works by shuttling the Li ions, which are solvated in an electrolyte solution, back and forth between the anode and cathode through the polymer separator pores. During a charge cycle, Li ions move from the cathode to anode and then back to the cathode upon the discharge process. From this basic arrangement, the current industry roadmap to improving lithium (Li) battery performance characteristics depends heavily on implementing new and better anode materials. It's here that near-term progress in higher energy density and faster charge rate batteries are needed to entice more drivers towards electric vehicles.

Current LIB designs use graphite as their anode, having gone virtually unchanged in this respect since the first commercial cells entered the market in 1991. The use of graphite as the anode has been a remarkable success in advancing energy storage technology and was even recognized as part of the 2019 Nobel Prize for Chemistry. The key attribute is the ability of graphite to reversibly intercalate Li atoms between the 2D layers of sp^2 hybridized carbon sheets at a favorable voltage. Three decades later, however, graphite has become the primary bottleneck in terms of improved storage capacity and charging rates[1]. Graphite's specific capacity is constrained to 372 mAhr/g as it takes six carbon atoms to accommodate just one Li atom. Due to graphite's 2D layered crystal structure, the charging rate of Li into the carbon layers is limited by the anisotropy. Li can only enter and flow in graphite in two dimensions as opposed to three. These aspects make graphite a primary limiting factor in today's lithium battery performance.

Several promising alternatives to graphite have emerged as potentially viable for next-generation commercial anodes. Herein, we aim to summarize some of the more promising approaches to breaking through the limits imposed by the graphite anode.

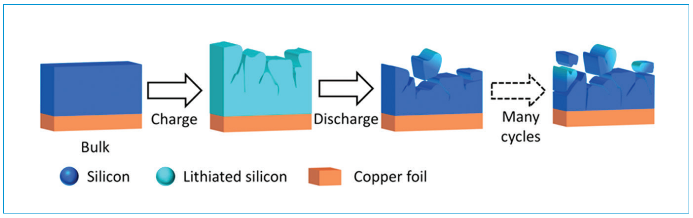

Figure 2 - Visualization of Si anode expansion/contraction cracking from Lithiation/De-Lithiation process. (González, Yang, & Liu, 2017)

One widely researched material for next-generation battery anodes is silicon (Si). Elemental silicon can serve as a Li-ion anode by taking up a theoretical maximum of nearly four Li atoms to one Si atom in its crystal structure and providing more favorable electrochemical potentials, giving it a theoretical gravimetric capacity of 3600mAhr/g[2]. This capacity gives Si a substantial advantage over traditional graphite anodes, in terms of greater energy storage capacity per unit weight and volume. Silicon also allows for higher charging rates, as it can take up Li into its structure in three dimensions, as opposed to two-dimensional intercalation in graphite. The performance improvements associated with Si anodes could translate into a 20 percent greater EV range and 10-20 minute charging times (Lee, J., Oh, G., Jung, H.-Y., & Hwang, J.-Y., 2023). An increase in EV range from 250 to 300 miles without needing a larger, more expensive battery would be a potential tipping point for consumers. The 300-mile range is what some believe is the minimum target required for greater commercial adoption in the EV auto market. While the price for EVs using Si anode batteries remains to be understood, the performance claims could certainly entice more consumers concerned with range and charging times.

Si anodes also present technical challenges that must be addressed. When Si takes up Li into its structure during charging, it expands greatly in volume (up to 400 percent) and then contracts when Li leaves during discharge or use. This volume change leads to particles and cracking (Figure 2), which in turn severs electron conduction pathways, causing a rapid decrease in charge capacity. This fundamental material science problem is being addressed through approaches such as the design of novel silicon nano structures, as well as Si composites, conductive additives, and/or matrixes. Si nanowires, for example, are one-dimensional structures that can expand and contract along their radial axis limiting the stress and strain that would cause cracking in common micro-particle designs (Figure 3). Despite the progress achieved from these advanced material architectures, developers are still working to solve the issues of loss of capacity and battery lifetime. Throughout many charge/discharge cycles, irreversible lithium losses (Li et al., 2023) degrade the electronic conduction pathways observed with the current collector. While Tesla is believed to currently use ~5-6wt% silicon-based additive blended with graphite in the anode of its batteries ("Tesla tweaks its battery chemistry," 2015), Mercedes Benz has announced the rollout of its new G series EVs, in 2025, using high silicon content anodes (Johnson, 2023).

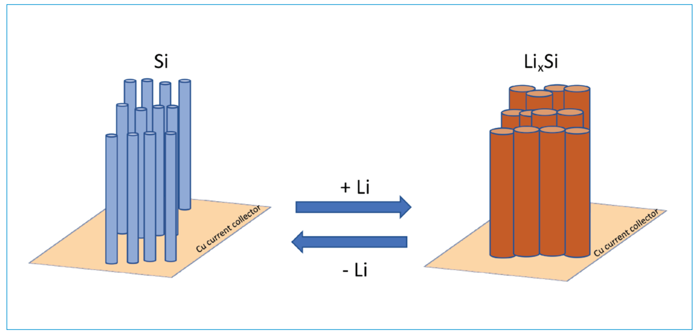

Figure 3 - Diagram of Si nano wire lithiation

Another general class of new Li-ion anodes is transition metal oxides. These materials function by using a transition metal ion shuttling between oxidation states much like cathode materials, but at a much lower relative energy potential. During charging, the metal atoms accept an electron with the concomitant uptake of Li^+ into the structure to balance the charge (Figure 4). When the cell discharges, the metal ions oxidize giving up electrons and releasing Li^+ back into the electrolyte. Some examples of these materials include Lithium Niobate ($LiNbO_3$), Lithium Titanate ($Li_4Ti_5O_{12}$), and Lithium Vanadate (Li_3VO_4). These materials benefit from safer operating voltages and are chemically robust giving them long lifecycles even under fast charging and extreme temperature conditions.

$$Li_4Ti^{V}{}_5O_{12} + Li \rightarrow Li_5Ti^{IV}{}_5O_{12} \quad E = 1.55V \text{ vs } Li/Li^+$$

Figure 4 - Lithiation reaction of LTO anode.

A shortcoming of these materials is that they typically have lower energy storage capacities compared to graphite, despite their superior stability. They also require conductive additives due to low electronic conductivities. Batteries employing these materials are more likely to find commercialization in heavy industrial vehicles where range isn't critical, but stability and high power are required under harsh operating conditions throughout the lifetime of the battery. It is less likely that these transitional metal oxide anode materials will be applied in the passenger EV market as those benefits come at the expense of lower range and higher upfront cost.

[1] It should be mentioned that cathode material advancements are still vital to overall cost, sustainability, and supply chain stability. Cell makers actively seek to reduce or eliminate Co and Ni content in cathode materials to reduce costs and supply chain issues. The cathode currently makes up to 51% of a LIB battery cost while the anode makes up only 12% Breaking Down the Cost of an EV Battery Cell (visualcapitalist.com)

[2] *Si in its pure form has a 3600mAhr/g capacity based on the reaction 4Li+1Si → Li4Si. Capacity is reduced in a practical Si anode based on the need for additives like polymers, carbon black or carbon nano tubes and void space. Even then, a battery's charge carrying capacity is dictated by the cathode. Translated, this means that even with a theoretically 10X higher Li capacity anode like Si, it does not give the battery 10X electrical storage capacity, but it does allow for using 10X less anode material which reduces the weight and volume of the overall battery.

A so-called "holy grail" of anode materials is pure lithium metal. Pure lithium stores more energy compared to silicon or graphite and does not require other additives. However, lithium is unable to be used in conventional cell battery designs for stability and safety reasons. Lithium anodes are not compatible with existing rechargeable Li-ion battery cells thus far, due to their tendency to be consumed into its solid electrolyte interphase (SEI) layer and to form dendrites that cause shorting and the potential for dangerous thermal runaway events (i.e., explosions).

One material engineering approach to use Li metal as anodes requires solid electrolyte/separator technology. Solid-state separator batteries use Li-ion conductive solid materials in place of standard porous polymers infused with organic liquid electrolytes; Li transport between the anode and cathode is facilitated by the solid-state separator which also provides the necessary electrical insulation. During the charging cycles in a solid electrolyte separator, Li ions travel from the cathode material through the solid and are electroplated at the anode as Li metal. Upon discharge, the Li metal is "stripped" releasing its electrons into the circuit to perform work, with its corresponding Li-ion traveling back through the solid separator and intercalating back into the cathode material. Several inorganic compounds exhibiting fast Li ion conduction as well as requisite mechanical strength are candidates for solid-state separator applications given those properties. These compounds include lithium lanthanum zirconium oxide (LLZO) garnet, lithium aluminum titanium phosphate (LATP), lithium-phosphorous sulfides, and lithium/metal chloride compounds, such as Lithium Zirconium Chloride (Li_2ZrCl_6).

Some key characteristics of these materials include wide electronic band-gaps and 3-D structures that are rigid while still allowing Li ions to easily hop from one lattice site to the next. They must also be strong and durable to prevent penetration by lithium dendrites. Finally, the processability of the materials into a battery plays a role as well. Some of these materials have low melting points, including lithium metal and certain lithium metal halides, allowing them to be easily melted when processed into a cell, while others with very high melting points require ceramic processing techniques that are challenging for producing consistent, ultra-thin and uniform separators.

Cells using the solid separator technology with lithium metal anodes offer the largest potential for gains in passenger EV performance. Toyota has announced a target of 2027- 2028 for the introduction of an EV with an all-solid-state Li battery with a range of 745 miles and charge times from 0 to 80 percent in 10 minutes (Bentley, 2023). Other groups developing solid-state battery cells have offered similar improvements in both range and charging times (Motavalli, 2022).

SAFETY IS CRITICAL

Solid-state lithium battery technology lowers the risks of catastrophic fires. Lithium-ion battery fires are typically caused by an internal defect or penetrating damage from an external impact. Each can lead to short circuits between the positive and negative electrodes causing a "thermal runaway" reaction, where the heat created by the short circuit cascades, eventually igniting the battery materials.

During the first wave of lithium battery commercialization in the 1980s, Canadian firm Moli Energy developed a rechargeable battery that used a lithium metal anode and a solid polymer separator that was prone to shorts from Li metal electroplating into dendrite tree-like structures during charging cycles. These dendrites could penetrate the polymer separator, causing short circuits and fires in early cell phone batteries. Ultimately, these rechargeable batteries were recalled, resulting in a "black eye" for the lithium-ion battery technology; battery makers were forced to turn to the graphite lithium intercalation anode, combined with an organic liquid electrolyte system for enhanced safety.

Ceramic solid-state separators can significantly reduce these risks due to their high shear modulus relative to Li allowing it to block the propagation of electroplated dendrites through their layers. Although dendrites can still form in these cells – where defects occur – they pose a much lower risk of fire because of the thermal insulating properties of the solid-state separators and the low content of flammable organic electrolytes and additives (Sandia National Laboratories, 2022).

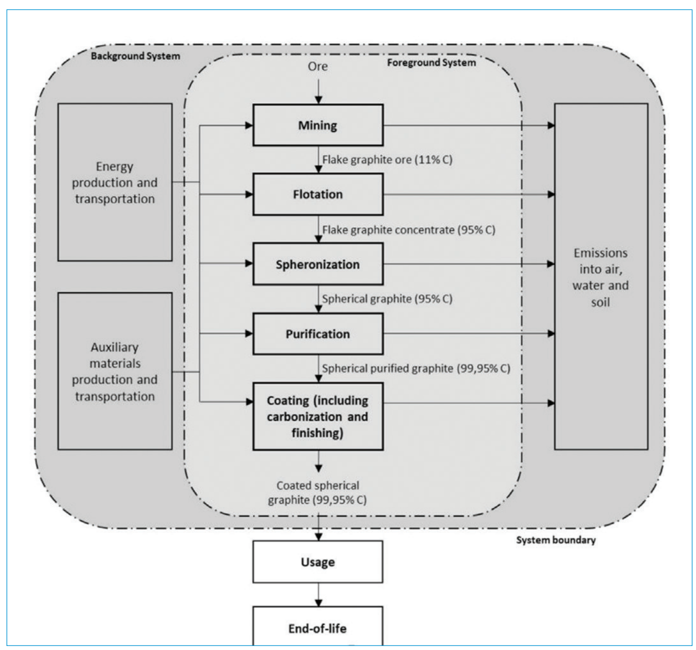

Figure 5 - Process flow of graphite production for anode. (Engels et al., 2022)

SUSTAINABILITY

While LIB cathode raw materials like nickel, cobalt, and the ubiquitous lithium often get attention for their extraction and sustainability prospects, the prevalent anode material in LIB, graphite, contributes a surprisingly significant carbon footprint to the overall environmental footprint of cell manufacturing. Graphite anodes in lithium-ion batteries currently consist of a blend of natural and synthetic graphite. Natural graphite (sometimes referred to as "flake"), obtained through mining is crushed and then processed with large quantities of acid to remove trace metal impurities before being annealed at 1500°C to create spherical particles of carbon (Engels et al., 2022). Synthetic graphite is produced from coke, a petroleum by-product, and requires heating to an excess of 3000°C to form the graphite structure. Both processes are energy and material-intensive. However, studies indicate that natural graphite has a higher overall environmental impact.

The use of energy-intensive and high carbon footprint graphite threatens to offset some of the environmental benefits of transitioning from internal combustion engine transportation to battery-powered, electrified transit. Further confounding the issue for graphite anodes is the recycling processes are similarly demanding of chemical and energy resources (Irene et al., 2021).

In terms of availability, silicon benefits from being the most abundant element in the Earth's crust allowing for a simplified supply chain and the potential for lower costs. Supply challenges (Kuo, 2023) related to geopolitics, scarcity, and further mining become moot. Battery-grade Si starts from naturally occurring silicon dioxide (SiO_2), which still requires energy input for conversion to elemental Si and purification to achieve a battery grade. Reduction can be done through the melt reduction with magnesium (Mg) metal in relatively high yields.

$$2Mg + SiO_2 \rightarrow Si + 2MgO$$

Figure 6 - Magnesium reduction of SiO_2 to Si metal

Mg metal itself is made by energy-intensive electroreduction of Mg salts. When manufactured into the active anode material, the Si is typically mixed with carbon-based additives requiring further energy input. One Si anode production facility is addressing the energy needs by using hydroelectric power with an advertised target of producing material with a 30 percent smaller overall CO_2 footprint when compared with synthetic graphite (Stephens, 2023).

Employing Li metal anodes could ultimately have the greatest impact on advancing Li battery sustainability. Solid-state batteries using Li anodes could result in a 29 to 36 percent reduction in overall carbon footprint according to some estimates (Carey, 2022). The elements and other materials used in the manufacture of solid separators and electrolytes, including Zirconium, Lanthanum, Sulfur, Phosphorus, Aluminum, and Titanium are abundant and available in a diverse global supply chain.

What's Next?

Li-ion battery performance and price have made giant strides in vehicle electrification over the past several years bringing EVs into the reach of more drivers. However, the technology still has a performance gap to close. Advances made by researchers in lithium batteries in the 21st century have made widely adopted electrified transportation a realistic technological objective by the coming decade. There, of course, remain major hurdles in improving performance and scaling up the production of new materials, battery designs and architectures. These challenges are formidable and no single material, technology, or company will be able to solve them alone. Collaborations allowing for the cross-pollination of novel technology with chemical processing and manufacturing know-how are essential for the industry to solve the battery challenges. At Materion, we've been solving inorganic material challenges for cutting-edge applications, including batteries, since the 1960s. As a true technology partner, we work closely with customers who need a supplier with the capabilities to produce unique materials with the right properties, including high-purity, defined particle sizes, and preferred morphologies. Materion has demonstrated the ability to collaborate closely with customers and assist in making their products commercially successful.

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