



Before Li-metal batteries can be commercially viable, ways must be found to increase the life cycle and prevent premature failure.

There's a lithium battery in your future

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Battery technology has come a long way since September 1899, when Ferdinand Porsche's electric powered car won its first road race. The "Egger-Lohner electric C.2 Phaeton" carried a Tudor brand lead-acid battery that weighed 500 kg and propelled the 1350-kg vehicle with 3 hp (2.2 kW for 3–5 h) for 80 km.

Under the hood of today's commercial fully electric vehicles is usually a rechargeable lithium-ion (Li-ion) battery pack. The Tesla Model 3, ranked by *Business Insider* as the best-selling electric vehicle for the first half of 2019, can put out 258 hp with a 50 kWh battery (standard model, range = 220 miles). The Nissan Leaf, also in the top 10, is rated at 147 hp with 40 kWh battery (standard model, range = 150 miles). Those cars and their many competitors have battery cells with energy densities ranging from 150 to 250 Wh/kg, where energy density refers to how much energy a cell can store with respect to its mass. Developing ways to increase energy density is a goal for many researchers in electrical engineering, chemistry, and materials science.

To spur work toward the goal of developing batteries with higher energy density, the US Department of Energy (DOE) created a research consortium in 2016 called "Battery500." The program is designed to develop and demonstrate batteries with an energy density of 500 Wh/kg, or approximately twice that of today's Li-ion cells. The DOE believes that a smaller, lighter, longer-lasting, and less expensive battery could power the next generation of electric vehicles and, perhaps, advance large-scale stationary grid energy-storage systems.

When a Li-ion battery discharges, the anode releases Li^+ ions through the electrolyte carrier to the cathode. That movement creates free electrons in the anode that can then flow through and power cell phones, computers, cars, or other devices. When the battery is plugged in to charge, lithium ions are then released from the cathode and return to the anode.

M. Stanley Whittingham, 2019 Nobel Laureate in chemistry, developed the first lithium battery in 1976. He used a metallic lithium anode as the Li-ion source. Shortly thereafter, Nobel Laureate John B. Goodenough developed a cobalt oxide cathode that made use of the Li-metal battery's exceptional performance. But the high reactivity and flammability of the reaction products in lithium batteries made it unsuitable for commercial use. Finally, Nobel Laureate Akira Yoshina introduced the graphite anode with a Li-ion source from an intercalated metal oxide cathode. The graphite anode isolates the lithium as a stable compound, which solved the reactivity problem of early metal anodes. That develop-

ment led to the lightweight, rechargeable Li-ion batteries that have been on shelves since 1991 and received recognition this year from the Royal Swedish Academy of Sciences.

Pioneers of rechargeable Li battery technologies include several other key figures: Rachid Yazami was the first to suggest graphite intercalated with lithium ions as a replacement for Li-metal anodes. Turning to graphite as the anode created the Li-ion battery revolution. The first Li-ion batteries lost 90% of their specific capacity compared to their Li-metal counterparts but gained excellent cycle life, stability, and safety features.

In 1979, Emanuel Peled established the model that exists in all Li-metal and Li-ion batteries. The solid-electrolyte interphase (SEI) is an electronically insulating and ionically conducting passivation layer that forms between electrode and electrolyte, acting as a solid electrolyte and adding stability. At the same time, SEI growth consumes active materials and leads to capacity fading and poor power density. The SEI has long been considered an important but poorly understood component of rechargeable Li-ion batteries.

Nearly three decades ago, Jean-Marie Tarascon and Dominique Guyomard discovered the electrolyte solutions that enabled the development of practical Li-ion batteries. These solutions are based on highly reactive alkyl carbonate solvents and the reactive and moderately unstable salt LiPF_6 . The salt's reactivity proved vital in the solution's suitability. As Peled had explained several years before, the components' reactivity made them compatible with most relevant Li-ion electrode materials. Vigorous surface reactions between electrode and electrolyte formed the protective surface films that behaved as near-perfect SEI. The SEI blocks the active electrodes electronically, thus avoiding side reactions, but allows Li ions to pass through effectively. That behavior clinched the long cycle life and stability of Li-ion batteries.

During the past 25 years, the energy density of Li-ion batteries has steadily increased while their cost has decreased, going as low as USD\$200 per kWh. Replacing the heavy, traditional graphite anodes with lighter metallic lithium could further increase the cell's energy density. Jun Liu, director of the Battery500 consortium, said that today's Li-ion batteries are nearing their maximum achievable energy density limit in the current configuration. However, members of the consortium hope to double that limit by focusing on rechargeable batteries with metallic lithium anodes.

A major problem with Li-metal batteries is their low Coulombic efficiency, meaning that the cells undergo a limited number

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of charge-discharge cycles before they fail. As the battery cycles, it gradually depletes its stores of active lithium and electrolytes. Before Li-metal batteries can be commercially viable, ways must be found to increase the life cycle and prevent premature failure.

Liu is a strong believer in a multidiscipline engineering approach to solve these and other problems. “In materials research, one component doesn’t translate into a real system. You can have an electrolyte with certain exceptional properties, but how does it work in a real world battery system? We need to understand real performance requirements,” he said.

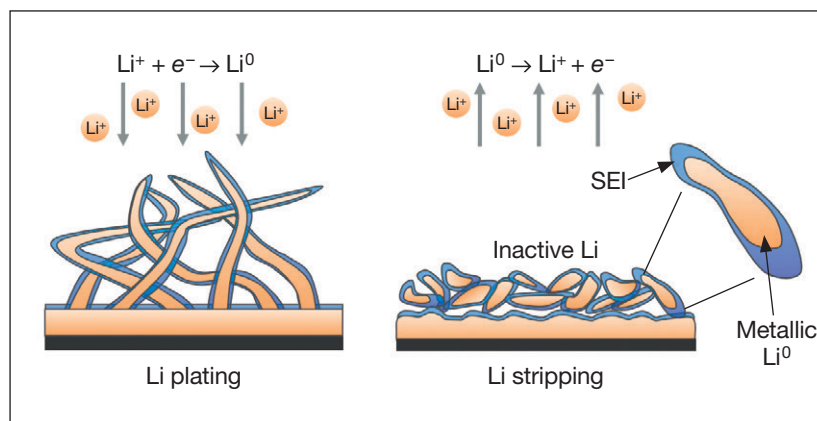
In the first phase of cycling in a Li-metal battery, positive lithium ions in the electrolyte join with electrons and deposit on the fresh lithium anode. Irregular deposition can lead to long fingers or “dendrites” of lithium extending into the electrolyte and to the cathode, resulting in a short circuit. Most work on preventing dendrite formation has been with idealized cells with Li foils. However, dendrite growth has rarely been observed in real cells. Rather, horizontal, interwoven whisker-like deposits develop, leading Liu to note, “We need to know why the battery fails in a real cell with real cycling.”

Another culprit for failure is the SEI that forms from chemical reaction between electrodes and electrolytes. The SEI thickens as cycling continues, which researchers attribute to fractures in the anode. The key to understanding the cycle life involves differentiating lithium ions that are the building blocks of the SEI layer from electrochemically inactive metallic lithium trapped by the SEI. Y. Shirley Meng, professor of nanoengineering and materials science at the University of California, San Diego, has developed a technique to perform such differentiation.

In the second phase of battery cycling, lithium metal from the anode dissolves into the electrolyte to form lithium ions. If dissolution first occurs at the base of a whisker-like deposit, the top part of the whisker will disconnect from the anode and become trapped in the SEI layer. Without the electrical connection to the anode, the unreacted lithium can no longer be used through the battery. Depletion of unreacted lithium is responsible for lowering the cell’s cycling life.

Meng and her colleagues made this discovery by measuring how much unreacted lithium metal gets trapped as inactive lithium. They added water to a sealed flask containing inactive lithium. The remaining lithium reacted with the water to produce hydrogen gas. By measuring how much gas was produced, researchers could calculate the amount of trapped, unreacted lithium metal. They found that unreacted metallic lithium was the main inactive ingredient, while lithium ions from the SEI stayed low. “If we can quantify where the inactive lithium in batteries comes from, then we can strategize to mitigate the problems,” said Meng.

Another avenue of research is focused on developing new electrolytes that improve lithium cycling. Different electrolytes lead to different morphologies of deposited lithium. “The field is moving toward electrolyte science,” said Meng. New solid



During plating in a Li-metal battery, Li^+ deposits on fresh Li in a whisker-like morphology (left). During stripping, Li dissolves in the electrolyte to become Li^+ (right). If dissolution initiates at the base of the whiskers, the top part will disconnect and become electrochemically inactive. Credit: Y. Shirley Meng and Chengcheng Fang.

electrolytes can also protect the Li metal from reacting with the electrolyte and the environment. But Liu pointed out that even if a solid-state electrolyte has good conductivity, it’s “difficult to implement it into a real battery today. And that’s not even considering the cost of doing this.”

Jeff Dahn, of Dalhousie University, has been working on lithium batteries for 40 years. He pointed out that for Li-metal batteries to transition from laboratory to the real-world market, they will still have to displace the established and mass-produced Li-ion technology. “Even if you come up with a new technology that might be cheap and reliable, at first you’d be selling it at a price point that’s way above the existing technology,” he said.

Moreover, “you can build a wonderful car with the Li-ion batteries we have today. But the purchase price of the car is high.” Dahn and his colleagues are investigating several ways to reduce the price and improve the already-good lifetime of Li-ion cells. One technique makes use of the fact that most electric vehicles use Li-ion batteries with a cathode that includes cobalt. But this transition metal is expensive. The community is trying to reduce cobalt utilization while maintaining energy density and lifetime. In one recent study, Hongyang Li and others from Dahn’s team found that cells with a high concentration of nickel—a relatively cheap and abundant metal—do not sacrifice performance when cobalt content is reduced or even eliminated.

Jessie Harlow and others from Dahn’s laboratory recently published a range of testing results on moderate-energy-density Li-ion cells, which may be like ones used in today’s commercial electric vehicles. Those cells retained 90–100% of their capacity over at least 4000 full cycles—a similar level of use compared to what a consumer vehicle would undergo over a 30-year period. In contrast, data on many commercially available batteries show significant capacity loss after less than 500 full cycles. By completing the time-consuming task of establishing a baseline of what is possible with today’s Li-ion chemistries, Dahn and co-workers have provided a valuable benchmark to which battery researchers can compare new developments. □