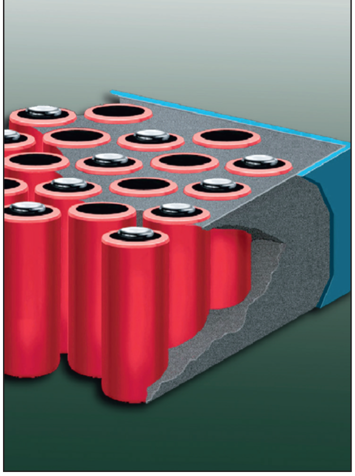

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Manufacturing Li-ion batteries for safety and performance

By **Angela Saini**
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In the spring of 2017, on a flight between Beijing and Melbourne, an unlucky passenger was left with burns to her face when the lithium (Li)-ion battery in her wireless headphones caught fire. Covered in the international press, the incident was the latest in a string of headlines about combusting gadgets blamed on failing batteries. Airlines are now banning suspect devices entirely, and Samsung was recently forced to recall millions of Galaxy Note 7 smartphones because of fears around overheating and fire. In 2016, half a million hoverboards were similarly recalled because of the risk of fire. Given the ubiquity of Li-ion batteries, manufacturers have naturally come under pressure to improve safety.

When Li-ion batteries were introduced to consumers in the early 1990s, people were unprepared for such incidents. Although defect rates are extremely low (in September 2016, when Samsung recalled its Galaxy Note 7, it had registered 35 reports of battery problems, of 2.5 million phones in circulation), the problem appears more significant because of the hundreds of millions of Li-ion cells now in use around the world and the spectacular nature of their failure when it happens. Leaking alkaline batteries are problematic; even one exploding Li-ion battery is newsworthy.

The benefit of the Li-ion cell lies in its high energy and power density, which has given manufacturers scope to produce high-performance gadgets that are also very small. But this, in turn, can pose a problem. If compromised, the separator between the cathode and anode can allow a short circuit and overheating. The electrolyte is not only highly flammable, but reaches such high temperatures when it combusts that it can cause even an aluminum casing to melt; this is a dangerous combination. A decomposing cell also produces vast amounts of oxygen. This creates the conditions for thermal runaway, potentially transforming a device into something short of a small explosive. Single cells may reach temperatures as high as 700°C during thermal runaway.

"Any number of defects or outside variables can act as a trigger mechanism to start a fire," said Said Al-Hallaj, adjunct professor in the Department of Chemical Engineering at the University of Illinois at Chicago. One common cause of failure is lithium deposition on the graphite anode when a cell is charged too quickly. Dendritic growth may then penetrate the separator, causing a short. Other causes of failure include physical deformation of the battery, mechanical intrusion, and overheating.

The demand to improve device performance, expand the variety of applications, and reduce the size of personal gadgets is placing further pressures on safety. "As cell companies race to pack more energy into a smaller volume, you see some compromises to the thickness of safety barriers inside the cell, further increasing risk," said Al-Hallaj.

For instance, separators are being made thinner to increase the energy density of batteries. "This increases the possibility of the electrodes shorting," said Venkat Srinivasan, director of the Collaborative Center for Energy Storage Science at Argonne National Laboratory. As manufacturers move to use silicon-based anodes, because they also allow for large increases in energy density, the problem becomes more acute. "As we start to use silicon-based anodes, which undergo significant volume expansion, the chance of the separator integrity being compromised increases as the anode pushes against the separator."

According to Srinivasan, there are many possible approaches to improving cell safety. One is to use electrodes that are inherently at less risk of thermal runaway. "For example, lithium iron phosphate is not as susceptible to oxygen release, so it tends to be safer," he said. The drawback, however, is that lithium iron phosphate batteries have a lower energy density than many of the higher-volatility options. One type, the BYD iron phosphate cell, developed and used by the Chinese automobile manufacturer, BYD Company Ltd, is stable even at temperatures up to 600°C. BYD builds electric cars, buses, trucks, forklifts, and grid-scale energy-storage systems all with fire-safe lithium iron phosphate. Traditional ultrahigh-energy-density, lithium cobalt oxide-based Li-ion batteries, however, tend to be used in single-cell products such as cordless and mobile phones and small handheld devices.

"Using ceramic separators can help prevent physical shorting between electrodes. And understanding metal deposition and dendrite formation can help mitigate shorting from lithium-plating during fast charge conditions. Electrolytes that are not flammable can also go a long way in making batteries safer. We need overcharge protection that is built into cells, and we need redundant safety systems at all levels," said Srinivasan.

Yet-Ming Chiang, professor of materials science and engineering at the Massachusetts Institute of Technology,

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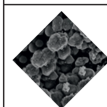
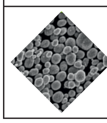
notes that separators are approaching 10 micrometers in thickness, and electrodes are also getting thinner, causing aluminum and copper current collectors to be only about 100 micrometers apart. His research team has developed a new kind of electrode architecture that reduces the tortuosity of the pore network in the cell electrode, allowing thicker, higher-capacity electrodes to be used, while still having acceptable charge and discharge rates. Thicker electrodes allow for better separation of cathode and anode.

24M Technologies, which produces a cell that is more tolerant to abuse due to a thick semisolid electrode, took another approach to the same problem. "Both methods give you an electrode that has several times the capacity per area of typical lithium-ion electrodes," said Chiang.

Safety profiles of some common lithium-ion battery types

Cathode Chemistry	Energy Density	Acceptable Operating Temperatures	Safety Profile
 Lithium Cobalt Oxide	240 to 280 Wh/kg	0 to 50°C	Decomposes rapidly above 180°C and releases high volume of oxygen
 Lithium Iron Phosphate	180 to 220 Wh/kg	–30 to 60°C	Stable at 270°C and as high as 600°C depending on the chemistry. No oxygen release.
 Lithium Nickel Manganese Cobalt Oxide	220 to 240 Wh/kg	–5 to 50°C	Decomposes above around 210°C and releases high volumes of oxygen

Sources: BYD, Sandia National Laboratories, and Incell International Academy.

Beyond this, are solid electrolytes a promising safety solution in the future? "The use of solid electrolytes could remove the flammable liquid electrolytes that are currently used, while also enabling higher energy density by allowing use of lithium metal electrodes," said Chiang. "However, in our investigations of the mechanisms by which solid inorganic electrolytes resist lithium dendrite penetration, we are finding that this is not as simple a fix as one might think."

For electric vehicles that use packs of cells, the additional challenge for manufacturers is how to isolate a fire within one cell to prevent it from spreading to others. A further burden is consumer demand for faster charging. As efforts accelerate to build grid-scale storage using Li-ion batteries, there are also concerns that failure rates of one in several million cannot be tolerated, because such storage devices would employ potentially billions of cells.

In an effort to stop a fire in a pack of cells from spreading, Al-Hallaj helped invent a novel composite that can be combined with graphite for use in battery packs, which absorbs heat by melting. Manufactured by AllCell Technologies, this system aims to prevent propagation when one cell in the pack enters thermal runaway by bringing down the surrounding temperature around the unaffected cells to safe levels.

While it is clear that measures can be taken to improve safety, the challenge for manufacturers may be striking a tradeoff between this and the commercial drive for high performance, low weight, and low cost. "Manufacturers encounter multiple contradictory demands when engineering a lithium-ion battery," said Heather Barkholtz, who researches the safety and reliability of Li-ion batteries at Sandia National Laboratories. "Previously, safety was only improved as a direct response to a hazard or incident. Presently, manufacturers are proactively designing batteries with a focus on safety. Advances in chemistry, packaging, design, and controls have all been implemented within commercial battery storage systems."

According to George Crabtree, director of the Joint Center for Energy Storage Research at Argonne National Laboratory, manufacturers could do much more to mitigate safety concerns. "Recent incidents with phones and hoverboards show that manufacturers have been too willing to compromise safety for cost or energy density," he said. What compounds the problem is that regulations vary from country to country. "Manufacturers are capable of designing and manufacturing batteries with far lower risk of fire or explosion. Risk is tied to design and manufacturing practices, not to random chance. Minimum safety standards need to be set for each battery use."

A commercially scaled alternative to the Li-ion battery seems unlikely in the next decade, with more than 100 GWh in worldwide manufacturing capacity in service today. "Research and development scientists throughout the world are working on non-flammable electrolytes, safer separators, and chemistries beyond lithium ion that could be safer. Right now, there's no silver bullet, said Al-Hallaj.

According to Chiang, "Lithium ion batteries and their derivatives are here to stay. No currently envisioned approach gives the same level of energy density without any risk."

Ultimately, it is not only consumer pressure, but also smarter regulation that will improve the safety of Li-ion technology. In China, where the majority of these batteries are produced, new standards were brought into effect in 2015, giving the country some of the most advanced thermal standards in the world. This immediately resulted in the banning of several highly volatile chemistries, including lithium nickel cobalt aluminum and lithium nickel cobalt manganese, both of which are still in common use in the United States. China has also cracked down on the export of counterfeit and noncompliant Li-ion cells, which are often feared to be unsafe. While these types of regulations may be a headache for manufacturers, they are also a sign that some governments and industries are taking safety seriously. □

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