Assessing The Safety Of Lithium-Ion Batteries

Lithium-ion batteries are back in the crosshairs after two safety incidents aboard Boeing 787 Dreamliner airplanes in January. Headlines everywhere drew readers to stories about flaming and smoldering batteries. Reports warned of these popular power packs' tendency to overheat and burst into flames. Broadcasts pointed out that fires in portable electronic devices several years ago prompted manufacturers to recall millions of Li-ion laptop batteries.

But these batteries are statistically very reliable. "There's a lot of mythology in the area of lithium-ion battery safety," says Brian M. Barnett, a battery safety specialist at Lexington, Mass.-based technology development firm Tiax. Failure rates for rechargeable Li-ion batteries are on the order of one in 10 million cells, he says. "That's not a reliability problem. It's an exception."

Yet exceptions can still be dangerous. As a result of the enormous number of Li-ion cells manufactured each year—about 4 billion in 2012, according to Barnett—some of those failures can lead to fires and serious safety incidents. Although the probability is tiny, the potential for mishap grows as Li-ion battery use surges. Adding to the concern is the scale issue. Li-ion batteries range from palm-sized or smaller packs weighing an ounce or less to 400-plus-lb electric vehicle batteries, and the larger devices can cause more serious problems if they fail.

Many batteries already feature fuselike structures and several other built-in safety devices. Yet scientists and engineers are working on broader safety strategies that address the characteristics of nearly every battery component. Researchers are tailoring the physical, chemical, electrical, and other properties of the positive and negative electrodes and the materials that electrically insulate them to make them less reactive. They are studying ways to reduce the flammability of the electrolyte solution that carries lithium ions through the battery. And they are designing robust battery management systems that monitor a wide range of battery performance and operating parameters to provide early warning of potential danger.

Khalil Amine, manager of Argonne National Laboratory's Advanced Lithium Battery Technology group, explains that a broad approach is necessary because "safety must be addressed at the full system level."

Li-ion batteries' knack for packing more energy into smaller, lighter units than other common batteries has spurred enormous growth in Li-ion use. Batteries based on this type of chemistry power most of today's cell phones, tablets, laptops, and other portable electronic devices. In the past several years, they have become popular among manufacturers of power tools and other high-current equipment. The low weight and high energy density also make Li-ion batteries attractive for use in hybrid-electric city buses and several lines of electric and hybrid-electric passenger cars. For the same reasons, Boeing chose the batteries for its fuel-efficient Dreamliners.

A potential shortcoming of Li-ion batteries is their flammable electrolyte solutions. Unlike other common types of batteries, in which the electrolytes consist of aqueous solutions of acid or base, the electrolyte in Li-ion cells typically consists of lithium salts in flammable organic solvents such as ethylene carbonate and ethyl methyl carbonate.

Under normal operation, charging the battery causes lithium ions in the electrolyte solution to migrate from the cathode through a micrometer-thin porous polymer separator and insert themselves (intercalate) in the anode. Common cathodes are based on $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, and related oxides. The anode is generally a form of graphite. Charge-balancing electrons also move to the anode but travel through an external circuit in the charger. On discharge, meaning when the battery is used to provide power, the reverse process occurs, and electrons flow through the device being energized.

In rare circumstances, some process could internally or externally short-circuit the battery or subject it to abusive electrical conditions or other trauma. According to Daniel H. Doughty of Battery Safety Consulting in Albuquerque, N.M., those events could generate a lot of heat inside the cell, ignite the liquid, or rapidly raise its vapor pressure until the cell bursts.

In one case in 2011, a battery-powered Chevy Volt car that had been subjected to a severe side-impact and rollover crash test caught fire during subsequent testing several weeks later. The National Highway Traffic Safety Administration found that the fire was likely caused by a coolant leak and minor battery puncture that occurred during the earlier crash test. The agency concluded that electric cars do not pose a greater risk of fire than gasoline-powered vehicles. And General Motors modified the car's design, adding structural reinforcement to better protect the battery pack from damage.

The airplane events involved 63-lb battery units on 787s operated by Japan Airlines (JAL) and All Nippon Airways (ANA). The JAL battery burned as the empty plane sat on the tarmac at Boston's Logan International Airport. The ANA battery smoldered in flight, causing the pilots to make an emergency landing in central Japan. The U.S. National Transportation Safety Board (NTSB) and the Japan Transport Safety Board, respectively, ruled out excess voltage as the cause of the JAL and ANA fires. As of C&EN's press time, the causes of the problems remain unknown and the investigations continue.

Hazardous battery failure, including fires, can be triggered by a number of factors. For example, micrometer-sized metal particles generated during cutting, pressing, grinding, and other manufacturing steps could contaminate the cells. The particles could accumulate and eventually form a short circuit—a conductive contact between the anode and cathode. According to Barnett, experienced manufacturers today use scrupulously clean methods that minimize contamination and therefore that mode of failure.

Overcharging a battery or exposing it to too high voltage by using the wrong charger or one that failed can push the cathode to an unsafe oxidizing state. Doughty explains that under those conditions, the cathode can react with and decompose the electrolyte solution, generating heat and reactive gases such as hydrocarbons. The gases can react further with the cathode, liberating more heat and triggering thermal runaway—uncontrollable heating that can destroy a battery violently.

Overcharging can also drive more lithium from the cathode than can be accommodated via intercalation in the graphite lattice. In that scenario, lithium metal can accumulate (plate) on the anode surface, making it dangerously reactive.

The process could also generate lithium dendrites that grow through microscopic pores in the separator and bring the electrodes into direct electrical contact. That short circuit can cause the cells to discharge rapidly and generate a lot of heat.

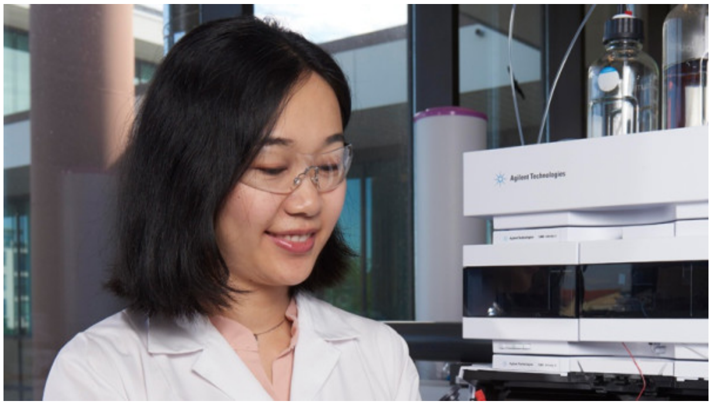
Choosing a safe cathode is one key aspect of battery construction. But there are trade-offs. $LiCoO_2$ cathodes developed in the early 1990s made Li-ion batteries the commercial success they are today. That material remains popular for consumer electronics because it provides relatively high charge capacity. Yet it is less stable than other cathode materials. At elevated temperatures, $LiCoO_2$ liberates oxygen, which can react with organic cell components.

$LiMn_2O_4$ tolerates heat better than $LiCoO_2$, but the manganese-based material's charge capacity is lower, and it too decomposes at high temperature. In contrast, $LiFePO_4$ stands up especially well to thermal abuse due to the strength of phosphorus-oxygen bonds, Amine says. But the operating voltage and energy density on a volume basis are lower than those of $LiCoO_2$.

The film separating the electrodes measures just a few tens of micrometers, but it also can be engineered for cell safety in some applications. Christopher J. Orendorff, a battery safety specialist at Sandia National Laboratories, explains that sandwiching a layer of polyethylene between two layers of polypropylene can provide a degree of protection against mild overheating.

Here's how it works: If the temperature in the cell should start to approach 135 °C, the melting point of polyethylene, that polymer will begin to melt and plug the pores of polypropylene, which has a roughly 30 °C higher melting point. Under favorable conditions, the separator's plugged pores block Li-ion diffusion, which shuts down the cell, letting it cool safely.

To extend the thermal protection range to temperatures above 135 °C, some researchers are working with higher melting point polymers such as polyimides. Entek Membranes, in Lebanon, Ore., follows a similar strategy, embedding a ceramic layer in ultra-high-molecular-weight polyethylene to form a robust higher melting point composite.



Melting-induced material changes lie at the heart of another battery safety innovation. Marta Baginska, Jeffrey S. Moore, Scott R. White, and coworkers at the University of Illinois, Urbana-Champaign, fabricate batteries with embedded microspheres of polyethylene and paraffin wax. Test results from batteries with microsphere-coated anodes and separators show that as the temperature inside the cell approaches the spheres' melting point, the molten material flows and coats the battery surfaces. That response, which the team exploits in related work to make self-healing materials, forms an insulating barrier that shuts down the battery (*Adv. Energy Mater.,* DOI: 10.1002/aenm.201100683).

Formulating electrolyte solutions with phosphates and phosphazenes can reduce flammability. These radical scavengers terminate radical-based combustion reactions, thereby preventing fires. But evaluating the effectiveness of these compounds in realistic battery-failure tests remains challenging. Furthermore, in some cases these additives reduce battery output.

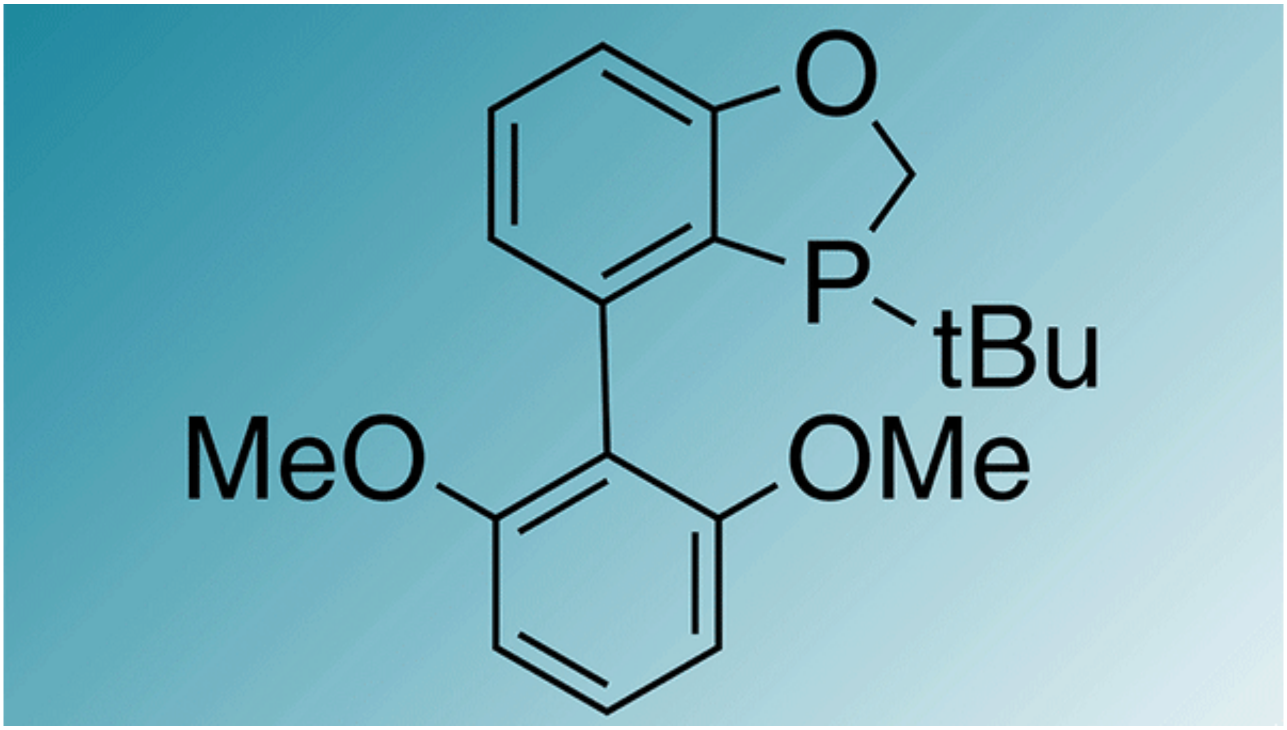
Going a step further, researchers in several labs are studying nonvolatile, nonflammable ionic liquids, fluoroethers, and other highly fluorinated solvents as Li-ion battery electrolytes. The winning solution has not yet emerged from these ongoing studies.

Along the same lines, other researchers are studying Li-ion batteries that contain no liquids at all. These solid-state batteries, which contain inorganic lithium-ion conductors, are inherently nonflammable. According to Ji-Guang (Jason) Zhang of Pacific Northwest National Laboratory, this type of Li-ion battery is very stable and safe and exhibits long cycle life and shelf life. The key drawback is that these cells need to be fabricated via labor-intensive vacuum deposition methods, which are costly.

Protection against overcharging can come in the form of molecules that happily flip-flop electrochemically at a given potential. These so-called redox shuttles, which were first studied decades ago, bounce back and forth readily between oxidized and reduced states at a potential slightly higher than the battery's end-of-charge point.

If the battery charger tries to push the battery beyond that point, that energy is taken up by the shuttles. "They trick the battery and prevent it from being overcharged," Amine says. As long as the shuttles are stable, the battery holds steady at the shuttle's potential. Amine, Zhengcheng Zhang, and Argonne colleagues have evaluated several shuttles including a bis-methoxyethoxy benzene compound designed via quantum calculations. The compound is fully compatible with Li-ion cells and remained stable throughout a 180-shuttle-cycle test (*Energy Environ. Sci.,* DOI: 10.1039/c2ee21977h).

Working in parallel with researchers who focus on the chemistry and materials science issues are others who are designing ever more reliable battery management electronics. Barnett and colleagues at Tiax have developed a sensor system and algorithm that detect changes in battery performance that may signal onset of the early stages of an internal short—a traditionally undetectable situation. He explains that this detection system could be coupled to a control system in an automobile that activates a service maintenance light, broadcasts a warning message, or in an extreme case, disables the battery.



These features are not going to appear in Li-ion batteries tomorrow. As battery specialists point out, new battery designs and materials need to be thoroughly tested under hazardous abuse conditions to properly assess their safety benefits. In addition, those safety-enhancing features cannot reduce the battery’s performance and power output.

Meanwhile, NTSB investigators working on the JAL 787 case continue combing through electrical- and mass-measurement data and various types of imaging results, searching for the cause of the battery fire. “We know the world is waiting for these results and we are working hard to get them,” says NTSB spokesman Peter Knudson. “We are making progress. It’s taking some time, but it’s important we get it right.” Knudson adds that the agency will soon issue safety recommendations based on its findings.

The advanced state of today’s Li-ion battery safety and the broad push to drive safety to even higher levels leaves Battery Safety’s Doughty upbeat about the battery’s transportation prospects. “I’m bullish on Li-ion batteries for electric vehicles,” Doughty says, “provided the required safety analysis is completed rigorously.”