ANALYTICAL CHEMISTRY

Burning Batteries

Hazardous failures of lithium-ion batteries are uncommon, yet researchers strive to minimize dangers

by ***Mitch Jacoby***

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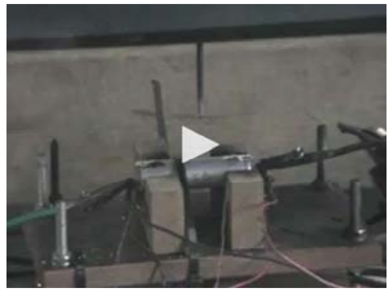
Y**ou hardly notice** them when everything's going well. Most of the time, lithium-ion batteries go about their business quietly, providing the power needed to drive today's feature-rich cell phones, laptop computers, other electronic devices, and a growing array of high-end power tools.

But once in a while, things go awry. And when they do, lithium-ion batteries can dump the energy they contain rapidly, dangerously, even explosively. Highly publicized incidents of laptop computers and cell phones spontaneously bursting into flames have focused the attention of electronics consumers worldwide on the safety of these lightweight and energy-packed batteries. The events have also raised questions about the suitability of these batteries for automotive applications. In addition, these incidents have driven researchers in industry and academia alike to redouble their efforts in the search for safer materials, components, and designs for lithium-ion batteries.

GET THE POINT!



Credit: Enerdel

When subjected to an industry-standard nail-puncture abuse test, which is designed to determine how a battery responds as it is being destroyed, two types of commercial lithium-ion batteries (top and middle) violently spew flaming material. In contrast, Enerdel's novel lithium-titanate-based battery safely tolerates the destructive abuse. (bottom)

The safety of lithium-ion batteries rose to center stage in 2006 when computer and battery manufacturers recalled millions of rechargeable laptop batteries. The massive recalls, and the laptop fires that triggered them, grabbed headlines everywhere.

News of the fires, for example, prompted a few foreign airlines to temporarily prohibit the use of lithium-ion batteries on their flights. In the U.S., however, neither the **Federal Aviation Administration** nor the Transportation Security Administration judged that imposing such a ban was warranted.

The battery fires and related events caused other ripple effects. Suddenly, photos of mangled laptops accompanied by stories telling how the computers or other electronic devices spontaneously spewed smoke or burst into flame began popping up all over the Internet. Lithium-ion batteries seemed to be failing disastrously and frequently. As it turns out, some of the accounts and photos were credible. But others were believed to be the work of pranksters who staged these accidents.

A case in point was a story about two weeks ago in South Korea of a **cell phone disaster** that cost a quarry worker his life when the device exploded without warning in his shirt pocket. At least that's how the story was widely reported in the worldwide press at the time. The next day, South Korea's leading daily newspaper, *Chosun Ilbo*, reported a different version of events, but that story hasn't spread as quickly as the original.

The day-after story noted that another quarry worker confessed to having killed his coworker accidentally by backing up over the man with a hydraulic drill rig. The equipment operator then lied about the circumstances of the coworker's death to cover up his negligence. The results of a medical exam suggest that the melted cell phone found in the dead man's pocket could not have caused the massive injuries he sustained. Police are investigating whether the force of the accident caused the phone battery to burn or whether it was deliberately set on fire to mislead authorities. Either way, the sensational version was a hoax.

The explosive battery failures and the widespread attention they've attracted have also led to an entirely different type of effect: a positive one. They have prodded battery manufacturers and others who work in the field to begin discussing battery safety issues more openly, which is something the industry has historically been reluctant to do.

The battery industry acknowledges that lithium-ion batteries have safety issues that need to be addressed, says Brian M. Barnett, vice president of technology at **Tiax**, a technology development company based in Cambridge, Mass. But traditionally, manufacturers have avoided talking publicly about that topic any more than they absolutely had to for fear of giving the impression that their products are prone to safety problems. "But lately, there has been progress," Barnett says.

Underscoring the point, Barnett notes that just a few years ago he was unable to organize battery safety symposia at scientific meetings, because, as he puts it, "no one was interested in talking about safety." Things are changing now.

In October, the **Electrochemical Society** hosted a well-attended battery-safety session at its international meeting in Washington, D.C. The "Battery Safety and Abuse Tolerance" symposium, which Barnett coorganized, featured technical presentations on several topics, including new computational methods for probing battery failures and properties of novel materials for electrodes and other battery components. Scientists from several countries, including representatives of industry, academia, and national laboratories, presented research results.

Credit: Enerdel

One fact that emerged is that it's tough to get solid statistics on the number of lithium-ion batteries that apparently explode or catch fire without having been set off by abusive actions. Unprovoked battery explosions are known as "field failures," and industry experts say such events are rare. They estimate that between one in 1 million and one in 10 million lithium-ion batteries fail that way.

Credit: Enerdel

SEEING IS BELIEVING?

[+]Enlarge

Stories and photos of exploding laptop batteries garner major media coverage. But don't believe everything you see. Experts point out that the appearance and location of the battery (on the keyboard) and the lack of damage to the computer casing suggest this photo is likely a hoax. (Copyright 2006 Stewart. Reprinted under the Creative Commons Attribution 2.0 License. Image accessed on Nov. 28, 2007; originally published here: flickr.com/photos/stewart/248442701)

Not only are the statistics of field failures difficult to pin down, but the fundamental mechanisms that trigger the hazardous events are also challenging to elucidate. For one thing, field failures are difficult to reproduce and study in a lab because they happen so infrequently. Those kinds of failures stand in contrast to failures of abuse-tolerance tests, in which batteries are methodically subjected to damaging treatments such as "baking," overcharging, crushing, or puncturing to assess a battery's response to deliberate and sometimes destructive abuse.

Another difficulty in analyzing the causes of spontaneous failures is that batteries that fail in the field come from lots that have already passed abuse and reliability tests, and they appear to have worked normally for a while. Those batteries simply don't give researchers a clue that trouble is brewing inside of them. Furthermore, when one of them catches fire or explodes, not enough battery material may be left behind to determine what went wrong.

Nonetheless, researchers have some ideas regarding the nature of the failure mechanism. According to **M. Stanley Whittingham**, a chemistry professor at the State University of New York (SUNY), Binghamton, the trouble is thought to begin with tiny metal particles in the vicinity of an ultrathin separator membrane that provides electrical insulation between the battery's cathode and anode. A statement from Sony, one of the largest manufacturers of lithium-ion batteries, explains that the microscopic particles are impurities that find their way into the cells during manufacture of the battery housings. Sony has taken steps to reduce the level of these impurities but has not completely eliminated them or the problems they can cause.

UNDER PRESSURE

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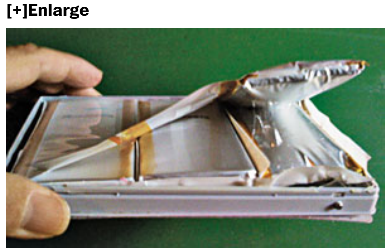

Credit: M. Stanley Whittingham, SUNY Binghamton

This commercial laptop lithium-ion battery is shown exploding in slow motion. Decomposition reactions inside some of the battery's cells can generate enough pressure over a period of a few weeks to rupture the battery casing.

Ordinarily, lithium ions travel through the separator from one electrode to the other during charging and discharging cycles, and electrons travel through an external circuit. However, if a metal particle pierces the separator, or if the particles accumulate (plate) onto an electrode and form dendrites that grow through microscopic pores in the separator, the electrodes come into direct electrical contact. That short circuit can cause the cells to discharge rapidly, leading to significant heat generation.

It doesn't take much to trigger that process. Using computer simulation methods, Barnett, Suresh Sriramulu, and their coworkers found that a low-power electrical short circuit mediated by a metal particle measuring just 100 µm in diameter can cause the temperature in the vicinity of the particle to rise well in excess of 200 °C within about one second. In that time, while the temperature inside the cell is soaring, the external surfaces of the battery can remain at room temperature, Barnett says.

The sequence of events from that point on can vary from case to case and has not been determined with certainty. The short circuit could initiate a process by which the battery fails benignly and simply stops working with no additional external signs of trouble. In other cases, an undesirable and as yet unidentified reaction can cause pressure to build up in the cells and slowly destroy the battery pack.

That's just what happened to Whittingham's laptop battery. Recently, the SUNY chemist found that his Macintosh computer would not lie flat on his desk due to a small bulge in the battery pack, a complaint voiced by other Mac users. Cautiously, Whittingham removed the battery and placed it in a fume hood, where it continued to expand for several days until the battery casing cracked open. Whittingham is now considering ways to analyze the battery safely.

At other times, batteries fail violently. Given that lithium-ion cells contain a flammable electrolyte solution consisting of lithium salts in organic solvents such as ethylene carbonate and ethyl methyl carbonate, the heat generated from an internal electrical short could, under some circumstances, ignite the liquid or rapidly raise its vapor pressure until the cell bursts. Likewise, the cathode and anode surfaces can support unwanted reactions or begin to decompose under conditions that lead to thermal runaway, the onset of an unstoppable and potentially violent chain reaction.

AFTERMATH OF ABUSE

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These commercial lithium-ion cells (the size of AA batteries) spewed flaming material when they were destroyed by puncturing a hole through them in standard abuse tests. Videos of the tests, which are done to determine how safely a battery responds to destructive abuse

An approach to better battery safety is designing components such as electrodes from new materials that stand up to abusive conditions more readily than the ones used at present. Most of today's lithium-ion batteries make use of a lithium-intercalated carbon (LiC_6) anode and a cathode made of a metal oxide such as $LiCoO_2$ or mixed oxides containing lithium, cobalt, nickel, and manganese.

One safety shortcoming of today's common lithium-ion cells is that upon overcharging or even moderate temperature excursions, the cathodes are prone to releasing oxygen, which can accelerate combustion of flammable electrolytes and other battery materials. Cathodes based on lithium iron phosphate ($LiFePO_4$) offer enhanced safety in that regard, because oxygen is tied up more tightly in the phosphate group than it is in the commonly used oxide materials. $LiFePO_4$-based batteries have recently been commercialized by **A123 Systems**, Watertown, Mass., for use in high-end cordless power tools.

Oxygen-related safety issues with common cathode materials and potentially dangerous reactions on carbon-based anodes have prompted researchers in several labs to explore a new battery design combining a $LiMn_2O_4$ cathode, which minimizes oxygen release, and a lithium titanate ($Li_4Ti_5O_{12}$) anode.

WHITTINGHAM

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According to Naoki Ota, chief operating officer at **EnerDel**, an Indianapolis-based company that's commercializing the batteries for use in electric vehicles, the new titanate anode sidesteps a common problem with carbon anodes. Electrolyte solution reacts on the surface of common carbon anodes and forms a passivating layer that's essential to good battery performance, he explains. If temperatures at the anode reach roughly 70 °C, however, that layer begins to decompose and a fresh layer forms on the carbon surface via an exothermic reaction that raises the temperature further. The rapid formation and decomposition of the surface film can trigger an explosive chain reaction, he says. The titanate anode does not form that passivating film.

Credit: Mitch Jacoby/C&EN

Other researchers are also studying the titanate-based system. For example, at **Illinois Institute of Technology**, Chicago, postdoc Humberto Joachin, chemical engineering professor Jai Prakash, and their coworkers have found on the basis of thermal analysis methods that the titanate and manganese oxide-based electrodes generate less heat during charging and discharging than do conventional materials. And at **Argonne National Laboratory**, Ilias Belharouak, Khalil Amine, and their coworkers have probed the electrochemical, thermal, and safety profile of the titanate and manganese oxide-based system with an assortment of techniques. Overall the group finds that the system yields good electrochemical performance and resists explosion and thermal runaway (J. Electrochem. Soc. 2007, 154, A1083). "It could turn out to be one of the safest lithium-ion battery systems," Belharouak says.

PROBING BATTERIES

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Credit: Humberto Joachin, Ill. Inst. Technology

At Illinois Institute of Technology's electrochemistry lab, Shabab Amiruddin (left) and Joachin prepare calorimetry experiments to probe thermal properties of novel battery electrode materials.

Similar efforts are under way to find durable and heat-resistant substitutes for other battery components. For example, manufacturers are developing new types of separators made from polymers that are more likely than conventional separators to remain intact at higher temperatures, thereby preventing or delaying the onset of electrical shorts in the event of a rise in temperature. Likewise, some scientists are studying the possibility of substituting today's flammable electrolytes with nonflammable ionic liquids. That approach has achieved only limited success thus far.

Despite widespread media coverage of lithium-ion battery disasters, the rate at which these lightweight power systems fail hazardously remains low. Nonetheless, with the spotlight shining brightly on the potential hazards of these extremely popular devices, researchers continue to search for ways to make these batteries ever safer.

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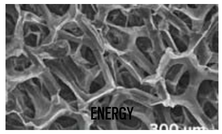

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