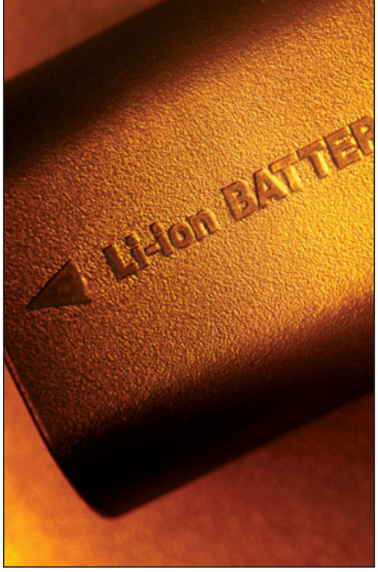

The consequences of rare failures scale with the energy stored and put a premium on designing for safety.

Pushing the frontiers of lithium-ion batteries raises safety questions

By **Arthur L. Robinson**
Feature Editor **M. Stanley Whittingham**

At Underwriters Laboratories, where researchers develop standards and testing procedures for batteries, J. Thomas Chapin, vice president of research, sees a surge in the production of lithium-ion batteries. Billions of lithium-ion cells are being manufactured monthly, a figure that will more than double with massive new facilities under construction or planned in the United States and Korea. “If failures occur in the wrong place, the consequences can be serious,” Chapin said, some as severe as the January 2013 incidents on Boeing 787 Dreamliners that grounded the entire 787 fleet until a fix was in hand. The recent publicity about hoverboard fires further raises the public impression that lithium-ion batteries are not as safe as they could be, despite their impressively low failure rate.

Lithium-ion batteries with their high energy density, long lifetime, and comparatively affordable cost have been driving a portable electrical power revolution in consumer electronics, industrial equipment, and medical instrumentation. But packing a lot of energy into a small volume is also what makes them dangerous if they are not treated with respect, said Mike Wentz, who oversees the transportation of dangerous goods for American Airlines, which, along with other airlines, will only carry lithium-ion batteries that have been properly declared by the shipper. The trend toward larger batteries presents new safety issues, added Christopher Orendorff, manager of Power Sources R&D at Sandia National Laboratories. “New failure modes become evident in large-scale batteries, and it is critically important to find robust materials and to engineer safety into the batteries,” he said.

Depending on the current and voltage required, a rechargeable battery may comprise a single cell or up to many thousands of cells. The prototypical lithium-ion battery cell starts with a lithium–cobalt–oxygen cathode ($LiCoO_2$), which has a layered structure in which lithium ions lie between the cobalt–oxygen planes. Similarly, the anode is graphite, another layered material, with lithium again intercalated between graphene planes. For high lithium-ion mobility, electrode wettability, and electrochemical compatibility with the electrodes and performance requirements, the electrolyte is a non- aqueous liquid mixture of organic solvents and salts, such as alkyl carbonates and $LiPF_6$. To electrically isolate the electrodes from each other but allow the lithium ions to pass through, there is a 50-µm-thick porous separator sheet made of a polyolefin, such as polyethylene.

There is no single solution to improving the safety of lithium-ion batteries, observers say. Safety starts with the materials in the battery cell, but continues with cell design, control systems to mitigate battery failures, battery manufacture, testing and certification, and ends with their use. Shortcomings at any stage can result in battery failure. A short-circuit in the cell, which can have many causes, can raise the temperature, causing fully charged layered oxides to release oxygen, which reacts with the electrolyte, causing further heating. Thermal runaway results when heat is generated faster than it can be dissipated, leading to ever-higher pressure until the cell bursts, releasing flammable gases that ignite on contact with oxygen in the air.

Researchers continue to investigate safer cathode materials. For example, groups led by Jeff Dahn of Dalhousie University and Stan Whittingham of Binghamton University have characterized the relative safety of some commonly studied cathode materials by the onset temperature of strong reactions between the cathode and electrolyte—the higher the temperature, the better. Among the layered oxides, a standard $LiCoO_2$ sample was the most reactive of all the samples; switching from $LiCoO_2$ to a higher-capacity $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) compound did not lead to significant safety compromises; but a $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) compound with an energy capacity comparable to that of $LiCoO_2$ offered the best safety properties of the oxides. In contrast, the olivine $LiFePO_4$ does not release any oxygen and so is inherently safer but stores only about half the energy of a layered oxide cell. Moreover, the carbon anode and electrolyte solvent are still combustible. $VOPO_4$, a promising olivine alternative, also does not release any oxygen, but this needs more study. Whittingham concluded, “Researchers have a challenge here, and a number of research centers are studying the limits that the layered oxides can be pushed to, while still retaining a long lifetime and today’s safety.”

The selection of cathode material is far from the whole story. Dahn pointed out, for example, that minimizing the surface area where the electrolyte contacts the cathode can reduce the danger. “Designing a surface area that is large enough for the cell to deliver

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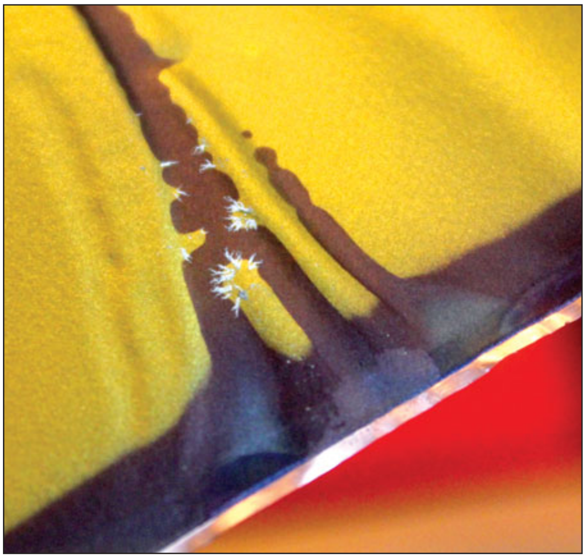
the desired performance but small enough to curtail dangerous reactions at high temperature is an example of the importance and complexity of careful design when the macroscopic behavior of a battery results from its active materials’ microscopic compositions, including shape, size, and their multidimensional distributions,” said Bor Yann Liaw of the University of Hawai‘i at Mānoa. “We use empirical correlations to translate materials properties into a design, but we don’t have techniques to characterize how safe the battery design actually is.”

The cathode is not the only materials component that contributes to the safety of the battery. Pure lithium is not used in any liquid electrolyte cell because of its propensity to form dendrites on electrodeposition that can short the cell and cause thermal runaway. The presently used graphite anodes are protected from reaction with the electrolyte by a passivating solid-electrolyte interface or SEI layer on its surface. Breakdown of this film is a safety issue. If a safe anode could be found that does not require such a film, the manufacturing cost would also be reduced, as today’s cells must be pre-cycled to form the film. Alternatives to carbon, such as silicon and tin, are being studied, as they can store double the capacity per unit volume. However, during the charge–discharge cycle, the anode volume change can be as large as 100%, which does not help the lifetime. Moreover, said Dahn, there is little evidence to date showing that silicon reacts significantly less than graphite with the electrolyte.

Orendorff pointed out that what ignites following cell bursting is electrolyte solvent vapor, so it makes sense to look for less reactive or outright non-flammable electrolytes that still maintain or even enhance the high-performance characteristics that led to the choice of organic electrolytes in the first place. At the University of Rhode Island, for example, battery researcher Brett Lucht is working on additives that lead to the formation of an SEI layer at the cathode, thus decreasing reactions with the electrolyte there, while fortunately also increasing the operating potential and hence the energy density, a win-win scenario if it works. At Sandia, Orendorff’s group is also looking at electrolyte salts that discourage solvent decomposition. One problem with all additives is that too much of a good thing reduces performance. Progress with alternative electrolytes, including so-called ionic liquids, is farther down the learning curve with no clear idea yet how to simultaneously meet safety, performance, and cost goals.



Troublesome whiskers. Lithium dendrites (white whiskers) can grow on the anode (yellow coating) of a lithium-ion battery cell when the battery is improperly operated, contributing to an internal short circuit and an uncontrolled temperature rise (thermal runaway), a dramatic buildup of gas pressure in the cell, cell rupture, and venting of flammable gases to the cell exterior, where they can ignite. Courtesy of J. Thomas Chapin, Underwriters Laboratories, Inc.

Then there is the separator. It may seem to be a mainly passive element in the battery, but maintaining its integrity is essential to both performance and safety, as the thermal-runaway scenario illustrates. But polyolefin separators begin melting at relatively low temperatures, closing some of the pores that allow lithium ions to pass through. One approach that has been successful is a composite structure consisting of ceramic coatings on the separator. Orendorff cites a commercial example comprising a trilayer membrane with two layers of ceramic (SiO_2/Al_2O_3) on either side of a porous polyethylene terephthalate (PET) film, which raises the melting point from 130°C, a temperature where electrolyte–electrode reactions begin, to 220°C or higher. “Ceramic-coated separators have made a big difference,” said Dahn.

Several factors beyond materials, cell chemistry, and design can affect lithium-ion cell and battery safety. In its November 2014 report (NTSB/AIR-14/01) on the Boeing 787 incident at Boston’s Logan International Airport, for example, the US National Safety Transportation Board not only blamed thermal runaway but put equal emphasis on manufacturing, testing, inspection, and documentation shortcomings for the fires. Chapin added, “These factors, individually or in combination, increase safety failures when the cells or batteries are subjected to impact, indentation, puncture, overcharging, over-discharging, operation outside of stated temperature limits, or using after-market chargers.”

When all is said and done, even the best-designed batteries can fail. “The goal is to stop failure propagation from cell to cell,” said Dan Doughty, founder of Battery Safety Consulting, Inc. Soft failure is an often-used term for this process. Ways to accomplish soft failures include auxiliary systems to monitor the battery state and limit failures as they are detected, as well as development of comprehensive standards and methods for testing before certification. But engineers and testers need to know what the systems should look for and respond to. To this end, Underwriters Laboratories and Sandia, for example, engage in reverse engineering of failed batteries down to the microscale so that researchers can determine the root causes of the failures. Investment is still needed to develop methodologies and tools to feed these findings into safer cell designs. Liaw is working with industry to tackle the problem of bridging the gap between the microscopic and macroscopic, but he said, “we are still far from being able to do that.” ☐