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Batteries of the Future III: Making Lithium-Ion Batteries Safer

Allan Chen, a_chen@lbl.gov



Recent years have seen highly publicized incidents of PCs and other electronic devices bursting into flame because of overheating batteries, resulting in massive recalls.

The BATT Program—Batteries for Advanced Transportation Technologies—is a \$6 million program of the Department of Energy's Office of FreedomCAR and Vehicle Technologies, which is developing a new generation of batteries for use in electric, hybrid-electric, and plug-in hybrid-electric vehicles. Berkeley Lab's Environmental Energy Technologies Division (EETD) assists DOE in managing BATT Program research at Berkeley Lab and other national labs, universities, and private companies.

In recent years battery failures in laptops and cell phones—many overheating, some bursting into flame—have drawn attention to one of the biggest problems posed by lithium-ion (Li-ion) batteries: overcharging can lead to battery failure and chemical leakages from the battery pack, and sometimes fire and personal injury.

"Electrolyte material in these batteries is highly energetic," says EETD's Guoying Chen. "It consists of lithium salts

dissolved in organic solvents, and it's flammable. Often, overcharging these batteries is what causes the problem. As the battery heats up it swells, and it can burst into flame."

A lithium-ion battery consists of a cathode layer, an anode layer, and a separator between. When the battery is charging, positively charged lithium ions move through a liquid electrolyte from the cathode to the anode, and in the opposite direction when the battery is discharging. The electrolyte is a lithium salt, dissolved in organic solvents. When the batteries are overcharged, the cathodes tend to release oxygen gas. Oxygen plus the flammable solvent and heat can cause battery fires.

At present, improving Li-ion batteries for plug-in hybrid vehicles (PHEVs) is the electrochemistry research frontier. Batteries based on lithium-ion chemistry hold great promise for PHEVs. They are lighter than current batteries based on nickel metal hydride and lead acid. And because their energy density is higher, they can boost both the range and power of PHEVs.

Batteries that meet the Department of Energy's program goals could make PHEVs sufficiently economical to succeed in the marketplace. But before this can happen, researchers need to develop technologies to improve safety.

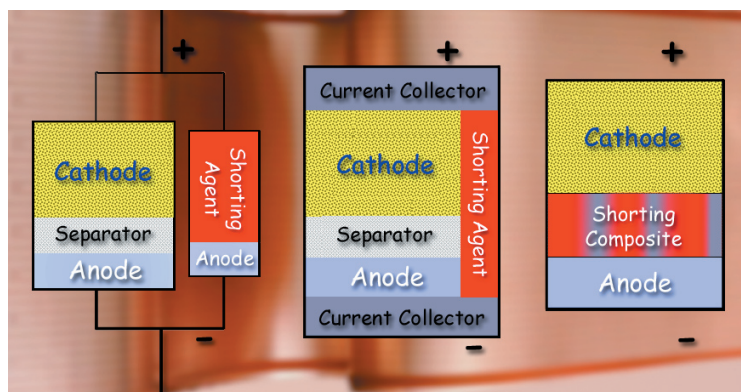
"The current industry solution is to use an electronic circuit to monitor the battery's voltage and shut it off when it reaches its proper charge," says Chen. "The problem with this approach is that in a plug-in vehicle, 30 to 40 batteries would be connected in a series. Monitoring each battery with an electronic device raises the cost and weight of the battery pack substantially. And a single failure of any of the monitoring devices could cause one battery to leak or catch fire, rendering the entire battery pack unusable."

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A shorting agent caps the charge

With a reliable, inexpensive method of protecting Li-ion batteries from overcharging as their goal, Chen and EETD's Thomas Richardson have studied several promising approaches. In one, they found materials that could serve as “shorting agents.” Added to the battery as an additional component, the shorting agent redirects the flow of electrical current inside the battery when it becomes fully charged.

A shorting agent prevents overcharging by acting as a cap on how high the battery voltage can rise. As the battery approaches full charge the agent, which is resistive during normal operation, becomes conductive. When the agent becomes sufficiently conductive it carries the charging current (thus “shorting” the circuit), and no net charge goes to the battery.



Polymer “shorting agents” can redirect the flow of current when a battery is fully charged. Reversible shorting agents can be used outside the cell (left), as an extra internal component of the cell (middle), or as a composite in the separator between anode and cathode (right).

The shorting agent has to be reversible—as the battery discharges, it has to become resistive again—and this back-and-forth reaction must take place with no degradation for as long as the battery lasts.

“We started looking at different classes of electroactive polymers,” says Chen. “These are long-chained materials that are insulating when neutrally charged. When you oxidize or reduce them, they become conducting almost like a metal.”

They found that a polymer called poly 3-butylthiophene, P3BT, was a shorting agent with the ability to prevent the battery cell from overcharging. The

material could be placed in a number of different configurations: within the layer that separates the anode from the cathode, as a distinct internal component of the battery, or as a completely external component to the battery. The latter approach proved to be inexpensive and lightweight, and did not interfere with the battery chemistry.

Electroactive polymers comprise a large family of compounds with various backbone structures that can be oxidized or reduced at a wide range of potentials. With the right choice of polymer and configuration, the approach could provide overcharge protection at any voltage, giving battery engineers the option of designing batteries at different voltages for diverse applications—they can choose the battery chemistry and system configuration that they need.

Electroactive polymers also have the advantage of improving the performance of Li-ion batteries in cold climates. These batteries don't function well in the cold because the electrolyte, already low in viscosity, solidifies, and the lithium charges can't move around as freely as they do at room temperature. Chen and Richardson found polymers that continue to provide overcharge protection in spite of the cold. The Department of Energy is now working with a battery manufacturer to commercialize the electroactive polymer technology.

Inherently safer materials

The research team is also pursuing another approach to overcharge protection: making electrodes out of materials that are inherently safer because they are less prone to overcharge. Currently they are studying lithium iron phosphate, LiFePO_4 , for use as the cathode material. This material differs from current experimental lithium battery chemistries at Berkeley Lab, which are mostly compounds of lithium, manganese, nickel, and cobalt.

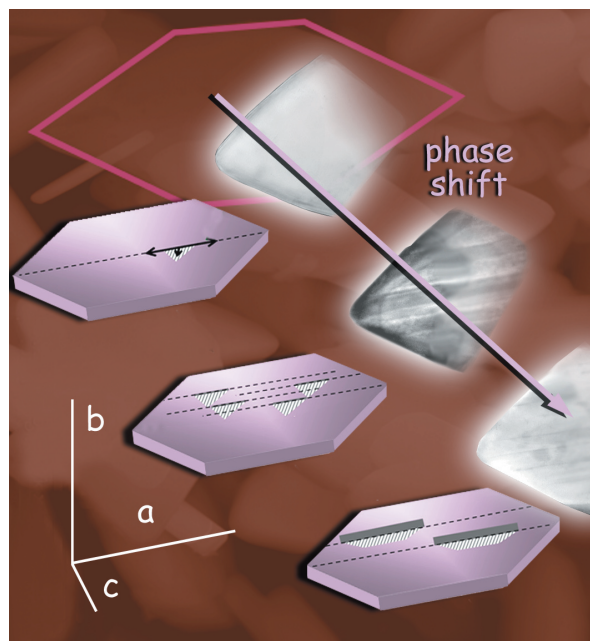
In lithium iron phosphate, strong chemical bonds between the phosphorus and oxygen, known as covalent bonds, reduce the tendency of the cathode to release oxygen gas. Iron and phosphate are also cheaper

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than manganese and cobalt, and batteries made with this material show longer shelf-life, a larger number of charging cycles, and greater stability. And they have a high charge capacity, ideal for the plug-in hybrid application.

However, the material's electronic and ionic conductivities need to be improved before battery manufacturers can use it as an electrode material. "The work we are doing is to understand the physical mechanism of how it conducts charge, which allows us to design the material to have higher conductivity," says Chen.

Lithium iron phosphate's crystal structure changes when the lithium ion becomes mobile, leaving behind an iron phosphate matrix; the physical nature of this change is poorly understood. To make more conductive electrodes, scientists need to understand what is holding back the material's conductance.



As lithium ions move out of a hexagonal lithium iron phosphate crystal, the material undergoes a phase shift to iron phosphate in the ac plane. Since ions flow only in the b direction, the ideal particle shape is a plate of lithium iron phosphate as thin as possible.

Chen and Richardson's conclusion: "The ideal particle shape is small thin plates of LiFePO₄, as thin as possible, to minimize the distance of Li movement. Adding a thin carbon coating to the material to create a good electrical contact on the ac plane will increase its conductivity further."

This work not only suggests a way to manufacture more conductive cathodes out of LiFePO₄, it also challenges current scientific thinking on the nature of phase transitions in the crystal. The existing theoretical model of the phase transition requires that the crystals display isotropy, a regular crystalline structure in all directions. But Chen and Richardson have shown that domains separated by a boundary zone form within the crystal. To explain their experimental observations they developed a model that incorporates anisotropy (crystalline structure that is different along different planes or axes) and domains within crystals of LiFePO₄.

Chen and Richardson are continuing to study ways of improving the safety, lifetimes, and charge capacity of battery materials. They are now applying similar observational techniques to lithium magnesium solid solutions, a candidate for use as anodes in Li-ion batteries. This material seems to suppress the formation of "dendrites" in the anode material, a surface roughness that reduces the life and number of cycles of batteries.

In their lab, Chen and Richardson grew extremely pure, uniform, high-quality crystals of lithium iron phosphate. Transmission electron microscope images of these pure LiFePO₄ crystals revealed regular hexagonal plates. The researchers studied the physical and chemical changes of the crystal structure during phase transitions, using advanced techniques such as Raman scattering, x-ray diffraction, and Fourier transform infrared spectroscopy, carried out with the assistance of EETD scientist Robert Kostecki.

When lithium ions are removed from the LiFePO₄ crystal, the material undergoes a phase transition to FePO₄. Electron microscope images reveal a boundary where the phase transition is taking place. Chen and Richardson found that the phase transition progresses along the face of the flat hexagonal crystal (called the ac plane); this is the "electroactive" part of the crystal, which supplies the lithium ions for conducting the battery's electric charge. The thickness of the crystal, called its b axis, is the only direction in which the lithium ions move.

In round particles of LiFePO₄, only 33 percent of the area consists of the ac plane of these crystals; in the pure crystal plates Chen and Richardson grew in the lab, up to 85 percent is ac plane.

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Additional information

More about the BATT Program is at <http://berc.lbl.gov/BATT/BATT.html>.

More about the Department of Energy's FreedomCAR and Vehicle Technologies Program is at http://www1.eere.energy.gov/vehiclesandfuels/technologies/energy_storage/index.html.

More about how DOE's goals for batteries will help electric vehicles succeed in the marketplace (**Batteries of the Future I**) is at <http://www.lbl.gov/Science-Articles/Archive/sabl/2007/Feb/future-batteries-I.html>.

More about methods of analyzing the chemistry of advanced batteries (**Batteries of the Future II**) is at <http://www.lbl.gov/Science-Articles/Archive/sabl/2007/Feb/future-batteries-II.html>.