

COMMENT

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Top electric cars can now travel more than 500 kilometres on a single charge, but their lithium-ion batteries remain inefficient.

Track batteries degrading in real time

Monitor deforming electrodes to speed development of renewable-energy storage, write **Liqiang Mai, Mengyu Yan and Yunlong Zhao.**

Energy storage is the main bottleneck for clean electricity, transport and portable electronics. Electrochemical devices such as lithium-ion batteries are most promising. These hold and release energy through reversible reactions in their electrodes. They are compact, safe and efficient — ideal for electric vehicles. Improved lithium-ion batteries have extended the mileage of electric cars from about 150 kilometres in 2012 to more than 500 km today, for Tesla's Model S 100D. Yet lithium-ion batteries remain expensive (US\$250 per kilowatt-hour¹) and of limited efficiency

(200–250 watt-hours per kilogram)^{2,3}.

Degradation of electrodes is the main problem. But this is hard to address. The electrochemical processes involved are complicated and poorly understood. They depend, for example, on the behaviour of the electrode materials (typically involving compounds such as lithium iron phosphate and lithium nickel manganese cobalt oxide) and the liquid or solid electrolytes that transfer charge.

To learn more about why electrodes deteriorate, researchers must find fresh ways to track electrochemical processes in

real time. Microscopes and spectroscopic instruments are expensive and restricted in what they can see, and using them requires specialist training. What's more, they normally operate at temperatures and pressures far from the ambient ones at which the batteries are used. This means that results and conclusions could be inaccurate.

Government, academia and industry need to share facilities, know-how and funding to develop techniques for tracking the structures and chemistry of battery electrodes. By learning more about how electrodes deform and the reactions they undergo, we can ▶

► develop the efficient and cheap batteries that the world sorely needs.

BLACK BOX

A running lithium-ion battery is a black box. Researchers open it to check the state of the materials inside during charging or discharging, or after a series of cycles. But this gives just a glimpse of the story. Electrochemical processes evolve quickly, and many products of the reactions break down in air, or even in inert gases (such as argon). Some of these products react with oxygen or carbon dioxide. So opening the box might alter the composition of the materials within it⁴.

Electrochemical processes need to be tracked while the system is closed. We started to do this in 2008, when we developed a device with a silicon nanowire electrode that could track flows of charge and changes in the structure of the nanowire while the battery was operating⁵. As the battery was charged and discharged repeatedly, lithium was progressively incorporated into the electrode, causing it to lose its crystalline structure and weakening its conductivity.

About the same time, Jianyu Huang and his team used a transmission electron microscope to monitor a tin dioxide nanowire electrode⁶. It swelled and elongated as it was charged, because lithium was being drawn into the electrode, changing its internal stresses. Non-crystalline lithium oxide, was created; and because this does not conduct, the electrode eventually failed.

Since then, researchers have investigated other electrode materials, including metal oxides, sulfides, fluorides, silicon, metals and composites. They have used various forms of spectroscopy (including X-ray technologies, nuclear magnetic resonance, Raman spectroscopy and infrared spectroscopy) as well as probe techniques (such as atomic-force microscopy)^{7,8}.

The materials' electrochemical reactions and degradation mechanisms have become clearer. And potential solutions have been suggested, including making electrode architectures less prone to deforming⁹ and implanting lithium ions in the electrode materials in advance¹⁰. But there is still a long way to go.

One problem is that each method captures only part of what is going on. For example, X-ray diffraction monitors the entire electrode and cannot spot interactions between particles and electrolytes on electrode surfaces. Combined approaches offer a possible solution: crystallography and spectroscopy, for instance, could gather detailed information about the interior and surface of the electrodes, respectively. But more comprehensive methods are also needed.

All these techniques operate in conditions that are far from realistic — at low pressures or without electrolytes, for example. And



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Repeatedly charging and discharging lithium-ion batteries weakens the electrodes' conductivity.

the processes could damage the samples. So results in the lab might not be representative.

Techniques for monitoring that offer higher spatial and temporal resolution would open up new ways to study electrochemical interfaces and reaction kinetics. Such techniques are hindered by three further problems. First, the instruments described above are too expensive for a single research group to make and redesign. Second, microscopes and other probing techniques require expertise across many areas, from nanofabrication to optics and electrochemistry. This necessitates large teams of highly paid specialists, adding to the cost and complexity of projects. And, third, academic incentives favour original research rather than efforts to perfect existing technology.

NEXT STEPS

More coordination across disciplines and between universities is needed to develop imaging, modelling and testing technologies. This will speed the development of monitoring techniques such as *in situ* X-ray and Raman spectroscopy, as well as the commercialization of electrodes and batteries based on nanomaterials. For example, Wuhan University of Technology in China and Harvard University in Cambridge, Massachusetts, are collaborating on designing innovative devices^{3,5}.

Opening up large facilities to academic institutions would also help. The Shanghai Synchrotron Radiation Facility in China, for instance, and the Stanford Synchrotron Radiation Lightsource at the SLAC National Accelerator Laboratory in California are already shared in this way. Joint programmes might, for example, tell us how lithium ions move and how the valences of elements evolve. Governments or companies could fund such programmes.

Better links with industry are vital. For example, companies that build electron microscopes could send their engineers to work in academic labs for a period to help solve technical problems. This would reduce innovation costs, overcome technical

hurdles faster and speed commercialization.

The pioneering work of Huang⁶ prompted one such collaboration to commercialize a transmission electron microscope for performing electrochemical experiments *in situ*. Now, start-up companies (such as Protochips, based in Morrisville, North Carolina) have sprung up to sell accessories for it. And China's National Key Technology Research and Development Program supports a number of joint projects by universities, research institutes and enterprises on advanced battery technologies, including lithium-sulfur and lithium-air devices.

Efforts such as these are a step in the right direction, helping us to develop the technologies and skills needed to create the next generation of batteries. ■

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