A battery material charges via an unexpected mechanism

Time-resolved x-ray diffraction experiments help to explain why lithium iron phosphate cathodes work so well.

Rechargeable batteries are ubiquitous in consumer electronics, and they're becoming more widely used in hybrid and electric vehicles. But the performance of today's batteries falls short of what's necessary for future applications. In particular, for battery-powered vehicles to compete with gasoline-powered ones, it will be necessary to increase not only the energy that can be stored for a given battery weight but also the power that can be delivered—that is, the speed at which the battery can be charged or discharged.

Lithium-based batteries lead the way on those fronts because of lithium's low atomic weight and the ease with which it gives up its valence electron. (See the article by Hector Abruña, Yasuyuki Kiya, and Jay Henderson in PHYSICS TODAY, December 2008, page 43.) When a lithium-ion battery is charged or discharged, Li^+ ions move between the electrodes inside the battery, and electrons flow in the external circuit. The two electrodes thus must be made of different materials that can store and release Li atoms readily and reversibly.

In one attractive cathode material, lithium iron phosphate, Li moves into and out of voids in the $FePO_4$ lattice. The lattice expands and contracts slightly but doesn't change its overall shape. In the lab, $LiFePO_4$ electrodes have been made to charge and discharge at astonishing speeds, equivalent to fully charging a battery in 10–20 seconds.[1] Batteries with $LiFePO_4$ cathodes have been commercialized for use in electronics and vehicles.

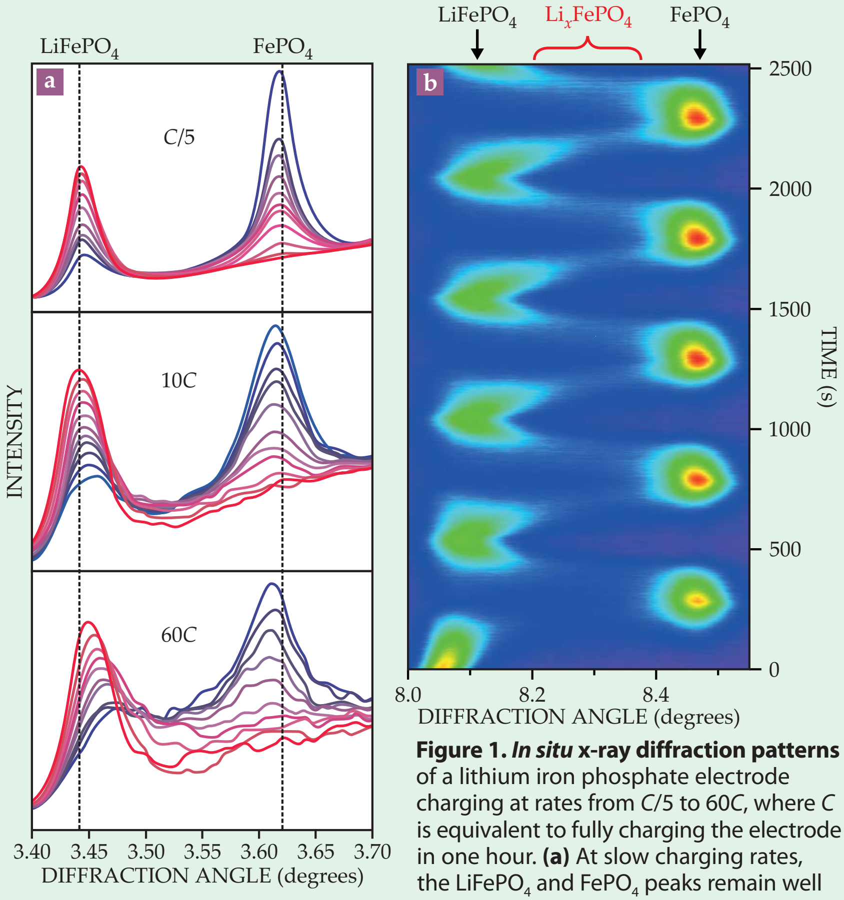

Figure 1. *In situ* x-ray diffraction patterns of a lithium iron phosphate electrode charging at rates from *C*/5 to 60*C*, where *C* is equivalent to fully charging the electrode in one hour. **(a)** At slow charging rates, the $LiFePO_4$ and $FePO_4$ peaks remain well separated; at faster rates, the diffraction signal is smeared between them. (Adapted from ref. 3.) **(b)** Cycling of an electrode at 10*C* shows the continuous evolution of the diffraction profile. (Adapted from ref. 2.)

But the material's success has come despite some apparent disadvantages. Both the lithiated and delithiated forms of the material are very poor conductors of ions and electrons; making an electrode out of $LiFePO_4$ nanoparticles dispersed in a conducting matrix goes a long way toward surmounting that hurdle. What's more, both calculations and experiments show that $LiFePO_4$ is a two-phase material: A partially charged electrode at equilibrium phase-segregates into regions of almost pure $LiFePO_4$ and $FePO_4$, and intermediate phases of Li_xFePO_4 are thermodynamically unstable. That phase separation should limit the rate at which Li can be inserted or removed; understanding why the electrodes can nevertheless operate at high rates has been a major puzzle for materials scientists.

Now two independent groups, one led by Clare Grey[2] (Cambridge University in the UK) and the other by Marnix Wagemaker[3] (Delft University of Technology in the Netherlands), have taken a step closer to solving it. Both groups, working at synchrotron facilities, used time-resolved x-ray diffraction to study the structure of $LiFePO_4$ electrodes as they were being charged and discharged. At fast enough charging rates, they observed not only peaks corresponding to $LiFePO_4$ and $FePO_4$ but also a continuous signal in between, indicative of a region of thermodynamically disfavored but kinetically accessible Li_xFePO_4.

Particle by particle

Although the study of $LiFePO_4$ as an electrode material[4] dates back to 1997, the first big breakthrough in understanding its charging mechanism came just over a decade later, when Claude Delmas and colleagues proposed their "domino cascade" model.[5] Diffraction measurements on electrodes in different states of lithiation revealed, as expected, that as the $LiFePO_4$ diffraction peaks shrank, the corresponding $FePO_4$ peaks grew, with no signal in between. But unexpectedly, there was little change in the widths of those peaks, which are related to the sizes of the $LiFePO_4$ and $FePO_4$ domains.

Because the electrode was made of nanoparticles, Delmas and colleagues concluded that the domains were the particles themselves. That is, no particles contained both $LiFePO_4$ and $FePO_4$; once a particle began the transition from one to the other, it completed that transition quickly.

But Delmas and colleagues made their measurements *ex situ*—on electrodes that weren't in the process of being charged—so they had no direct observation of the mechanism of that single-particle transformation. They suggested that a rapidly moving interface could propagate from one side of the particle to the other—like a cascade of dominos—driven by the elastic energy of the strained crystal lattices at the $LiFePO_4$–$FePO_4$ interface.

A plethora of other models have since been proposed[6] describing different ways a sharp interface might propagate. In 2011 MIT's Gerbrand Ceder and colleagues were the first to propose a mechanism[7] involving a continuously changing composition Li_xFePO_4, with x varying smoothly between 0 and 1. But experimentally testing any of those theories is easier said than done. Directly observing single transitioning nanoparticles requires extraordinary spatial and temporal resolution.

Fast charging

Grey and Wagemaker both tried to observe the transition at the single-particle level, but both eventually gave up, at least temporarily. Instead, they adopted the strategy of looking at many-particle electrodes charging at high rates, to force as many nanoparticles as possible to transition simultaneously. Wagemaker and his group studied a wide range of charging rates—from $C/5$ to $60C$, where C is the rate that would fully charge or discharge an electrode in one hour—and Grey and her group used rates of $5C$ to $20C$.

During a slow charge, as in the top panel of figure 1a, the $LiFePO_4$ and $FePO_4$ peaks remained well separated and didn't change appreciably in width or position, just as Delmas and colleagues had seen. At higher rates, as in the bottom two panels of figure 1a, the two main peaks are still there, because most of the nanoparticles are still either $LiFePO_4$ or $FePO_4$, but they become broadened and distorted, and a continuous signal arises between them. Figure 1b shows Grey and company's observation (using a different x-ray wavelength) of the same phenomena in an electrode that they repeatedly charged and discharged at $10C$.

But a continuous signal between the $LiFePO_4$ and $FePO_4$ peaks doesn't necessarily imply a continuously changing nanoparticle composition. Diffraction angles depend, first and foremost, on the crystal lattice constants; an apparent lattice constant in between those of equilibrium $LiFePO_4$ and $FePO_4$ could arise for various reasons. For example, on either side of a sharp interface between lithiated and delithiated phases, lattice strain could produce a small region of intermediate lattice constant.

When presenting their x-ray diffraction data to other colleagues in the field, Grey and her student Hao Liu found themselves fielding challenges to prove that what they were seeing wasn't the effect of an interface strain or other mechanism. "We got our data more than a year ago," says Grey, "and since then we've been working hard to rule out every other possibility."

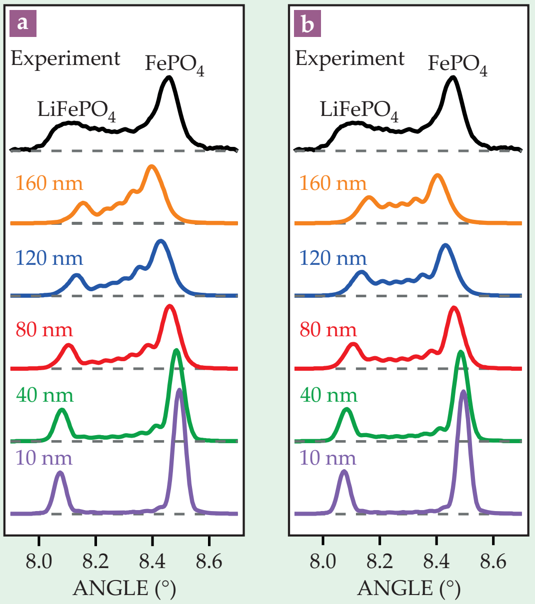

Figure 2. Simulated diffraction profiles of a 186-nm nanoparticle with a strained $LiFePO_4$–$FePO_4$ interface, with the lattice strain spread over thicknesses of 10 nm to 160 nm, and the lithium composition changing either **(a)** abruptly or **(b)** continuously across the interface. Only when the interface thickness encompasses most of the particle do the simulated profiles resemble the experimental one (shown in black). (Adapted from ref. 2.)

Figure 2 shows some of Liu's calculations of the diffraction profiles that would arise from a strained interface in a 186-nm-diameter particle. Liu repeated the calculation for different interface thicknesses over which the lattice strain might be spread, and he considered that the Li composition might change abruptly at the interface (figure 2a) or gradually across it (figure 2b). For the most realistic interface thickness, 10 nm, the simulations show discrete diffraction peaks and don't match the experimental profiles at all. The simulations don't start to resemble the experimental data until the interface thickness exceeds 100 nm, which is more than half of the width of the particle.

A kinetic approach

How general are those observations? Diffraction data point to a Li_xFePO_4 transition mechanism at high charging rates, but is the mechanism the same when the electrodes are charged more slowly? Wagemaker and colleagues are getting closer to making time-resolved measurements at the single-particle level, which will elucidate how the mechanism changes, if at all, under different conditions.

And what about other materials? Batteries with $LiFePO_4$ cathodes are advantageous for their ability to operate at high rates. But their operating voltage is relatively low, and so, therefore, is their energy-storage capacity. Other two-phase materials, such as those based on manganese instead of iron, allow higher operating voltages. Can they, too, be coaxed into a continuous-composition transition mechanism? Doing so would require researchers to look beyond the range of thermodynamically favorable structures and focus on lowering the kinetic barrier to metastable phases—an approach that's contrary to what most battery researchers are doing now. Says Ceder, "This puts a whole new perspective on trying to understand the kinetics of phase transformations."

Johanna Miller

References

1. B. Kang, G. Ceder, *Nature* **458**, 190 (2009).
2. H. Liu et al., *Science* **344**, 1252817 (2014).
3. X. Zhang et al., *Nano Lett.* **14**, 2279 (2014).
4. A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* **144**, 1188 (1997).
5. C. Delmas et al., *Nat. Mater.* **7**, 665 (2008).
6. R. Malik, A. Abdellahi, G. Ceder, *J. Electrochem. Soc.* **160**, A3179 (2013).
7. R. Malik, F. Zhou, G. Ceder, *Nat. Mater.* **10**, 587 (2011).