

Fill 'er Up with . . . Lithium

By Dana Mackenzie

From Pennsylvania Avenue to Wall Street, green car technology has been hot in recent months. In August, the U.S. Department of Energy awarded \$2.4 billion in grants for “advanced battery and electric drive” projects. In September, A123 Systems, a company that makes lithium-ion batteries for electric cars and other applications, had a very successful initial public stock offering. For drivers who want to reduce their dependence on fossil fuels, the electric future seems to be coming closer.

If and when the electric or hybrid cars of tomorrow replace the gas guzzlers of today, it's a good bet that they will owe some of their capabilities to mathematics. “Batteries have been a very empirical field of research until recently, with not very many mathematical models,” says Martin Bazant, a mathematician in the chemical engineering department at the Massachusetts Institute of Technology. But Bazant and others are now working on mathematical models that are keeping pace with and might even anticipate new technology.

Bazant's model takes into account, for the first time, the fine-scaled, anisotropic structure of the electrodes in a lithium-ion battery. It predicts new kinds of behavior, such as the formation of waves of lithium ions within the electrodes. Researchers have seen pattern formation of this kind in other composite materials, but never before in batteries.

Perhaps most intriguing, Bazant believes that his model has a chance of explaining the ultra-fast charging and discharging observed for a new electrode material developed by his MIT collaborator Gerbrand Ceder and others. The material, as described by Ceder in a recent paper in *Nature*, is able to discharge a hundred times faster than the present generation of lithium-ion batteries. Faster discharge times would lead to speedier response in an electric car engine. Until now, pokey acceleration has been one of the sacrifices that hybrid and electric vehicles have had to make.

“If we can understand the dynamics of lithium transport, hopefully we can design better microstructures,” Bazant says. “At present, those structures, their size and shape, are designed very empirically. I would like to move in the direction of rational design.”

Rechargeable Batteries 101

A lithium-ion battery has three parts: an anode, a cathode, and a separator—a barrier that allows positively charged lithium ions, but not electrons, to pass through. When the battery is connected to an electrical circuit, the lithium ions flow from the anode to the cathode through the separator, and electrons, unable to flow through the separator, have to flow around the circuit. When the battery is recharging, the flows are reversed, in a process that is often compared to a rocking chair.

That much is well understood. The advanced technology enters in the design of the electrodes, and especially the cathode. The cathode material, the main feature that differentiates the various kinds of lithium-ion batteries, is a mix of carbon black, metal oxide particles, and a liquid electrolyte that fills the gaps (Figure 1). (By contrast, the anode is usually just made of graphite.) Particle diameters, typically tens of microns in first-generation lithium-ion batteries, have shrunk to tenths of a micron as production techniques have improved.

The key feature of both graphite and the metal oxide is a layered crystalline structure that allows lithium ions (the smallest positively charged ion there is, except for hydrogen) to slip between the layers. Ultimately, it's the difference in electric potential between the lithium in the metal oxide and the lithium in the graphite that produces a voltage difference between the anode and the cathode.

Lithium-ion batteries were invented by John Goodenough of the University of Texas, the recipient of the 2009 Enrico Fermi Award from the Department of Energy. The first type of lithium-ion battery to go into commercial production, in 1991, had cobalt oxide as the cathode material. The development of these cobalt oxide lithium-ion batteries is the main reason cell phones have shrunk from the size of a brick to the size of a couple packs of chewing gum. Goodenough didn't stop there, however; in 1996, he patented a new kind of lithium-ion battery that replaces cobalt oxide with iron phosphate. The new batteries seem to be more powerful and also less prone to catching fire, both of which are important considerations for automotive applications.

Meanwhile, John Newman, a chemical engineer at the University of California at Berkeley, developed a widely accepted model of the flow of lithium in a lithium-ion battery. “He literally wrote the book,” Bazant says admiringly. The book, *Electrochemical Systems*, can be found on the bookshelf of any battery researcher today.

Catching the Wave

Newman's model has two drawbacks, however. First, it treats the cathode material as an isotropic medium, meaning that lithium ions flow through it equally well in all directions. This was an excellent approximation for the cobalt oxide batteries of the early 1990s, when Newman developed the model, but it does not apply at all to iron phosphate, which is strongly anisotropic. Second, Newman's model contains a number of parameters that have to be measured experimentally. “Newman's equations do very successfully what the field wanted,” says Stephen Harris, a physical chemist

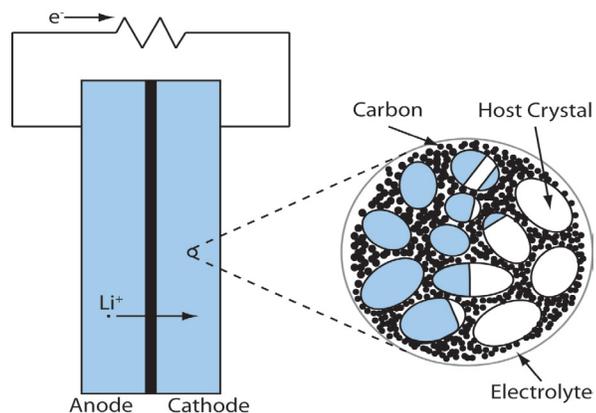


Figure 1. During discharge in a lithium-ion battery, lithium ions move across a separator (black) from the anode to the cathode. At the same time, electrons (which cannot pass through the separator) are forced to go through an external circuit. During recharging, both directions of flow are reversed. The cathode is typically a composite material consisting of crystalline host particles, carbon powder, and a liquid electrolyte. When the host crystals are made of iron phosphate, Bazant's group predicts that the lithium will insert itself into the host particles in a wavelike pattern. Here, fully lithiated regions are shown in blue, and unlithiated regions in white. Figures courtesy of Martin Bazant and Todd Ferguson.

at General Motors. The model “tells you how thick and how porous the electrodes should be. If you want to predict the performance of the battery, his model tells you. But it contains a number of empirical bits, such as diffusion coefficients.” As Troy Farrell, a mathematician at Queensland University in Australia says, “Newman’s model makes no apologies for the diffusion coefficients or the transport parameters. At the end of the day, he says, I’ll just measure those quantities anyway.”

In iron phosphate electrodes, the materials are not uniform, and it is not clear that their properties can be described by bulk averages over large volumes. Iron phosphate is strongly “phase-separating”: The crystal prefers to have either no lithium or a full layer of lithium ions sandwiched between the iron phosphate layers (see Figure 2). From a mathematician’s point of view, then, the lithium concentration c likes to be either 0 or 1, and there is a strong energy penalty (proportional to the square of the gradient $|\nabla c|^2$) at the interface between the two phases.

Within the sheets of lithium, the ions preferentially travel in only one direction, customarily labeled as the y -axis. Thus, when lithium ions fill up an iron phosphate particle, they do so in the manner of people filling up an auditorium—filling along the first row until it is filled, then along the next row, and so on. This process does not at all resemble the uniform diffusion process described by Newman’s equations, in which the spectators would filter in uniformly in all directions from the edges of the auditorium.

Bazant knew about the Cahn–Hilliard equation, which was developed in the 1950s to describe another kind of phase-separating material, metal alloys. In the Cahn–Hilliard approach, the energy of a crystal is described as an integral:

$$\iiint_V \left[f(c) + \frac{1}{2} (\nabla c)^t K (\nabla c) \right] dV.$$

The first term in the integral represents the bulk free energy of the crystal, which is minimized when $c = 0$ or 1 , and the second term represents the gradient penalty. The crystal has two distinct phases, one with concentration $c = 0$, the other with concentration $c = 1$. Systems with an energy formula of this kind usually evolve to a state with large regions of one phase or the other, separated by interfaces that try to become as compact as possible. Most importantly, the Cahn–Hilliard equation allows for the formation of traveling waves.

“Newman’s model has no discussion of phase separation,” Bazant says. “The assumption is that it’s all diffusion and reaction, and the reaction rates are described by the Butler–Volmer equation. Using the potential from the Cahn–Hilliard equation leads to a completely different reaction rate, which depends on the gradient of the concentration. That turns out to be the key, both physically and mathematically, to the prediction of intercalation waves that propagate transversely to the lattice planes.”

Defects in the iron phosphate particles (which can be crystal defects but can also be locations on the surface with reduced lithium flux) can slow the lithium waves as they sweep through the particles, degrading the performance of the battery (see Figure 3). A defect forces the wave to bend around it, which costs energy (because the interface between phases gets longer). Too many defects can block the waves altogether. Bazant’s model could thus allow theoretical predictions of how a battery will degrade over time.

New Hypotheses

Bazant’s student Damian Burch also noticed that if one particle in the cathode happens to get ahead of its neighbors in the charging process, it will tend to suck lithium away from them and get even further ahead. Thus, while smooth intercalation waves are seen inside

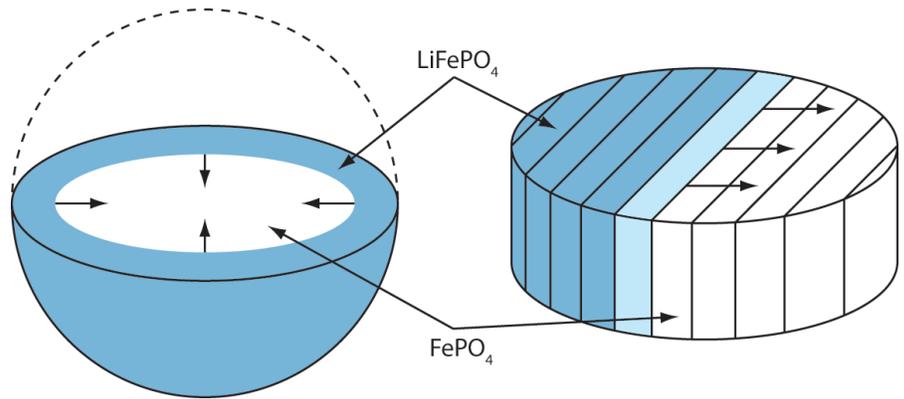


Figure 2. Two possible modes of lithium intercalation in a phase-separating host crystal. Left, the prevailing model assumes that lithium diffuses into the host crystal uniformly from all directions. Right, Bazant’s model predicts “intercalation waves” that propagate one layer at a time through an iron phosphate crystal. Fully lithiated (LiFePO_4) layers are shown in blue, layers with no lithium (FePO_4) in white; the light blue layer is partly lithiated (Li_xFePO_4 , $x < 1$).

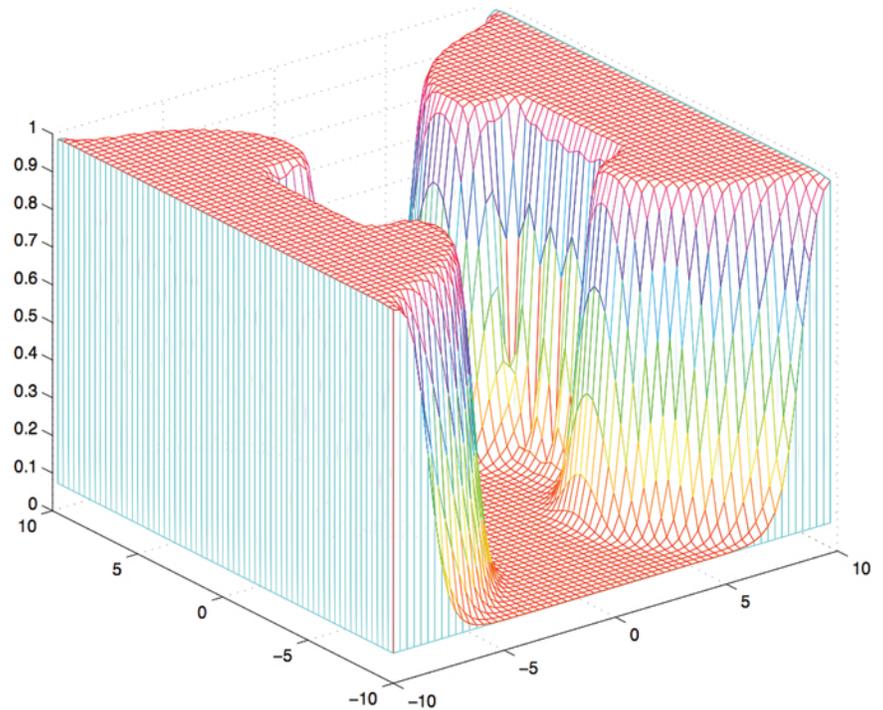


Figure 3. Simulation of a lithium insertion wave bending around a crystal defect. Here the density of lithium is shown on the vertical axis (1 = fully lithiated). The defect is the square region in the center, and the wave is moving from both sides toward the center. From D. Burch, G. Singh, G. Ceder, and M.Z. Bazant, “Phase-transformation wave dynamics in LiFePO_4 ,” *Solid State Phenomena*, 139 (2008), 95–100.

each particle at the nanometer scale, the larger (micrometer-scale) picture is a “mosaic” of lithiated particles surrounded by unlithiated ones. Harris, of General Motors, recently confirmed this “mosaic instability” experimentally in graphite. “It’s really nice when you have the theory before the experiment,” he says.

Bazant hypothesizes that lithiation waves may also account for the fast-discharging phenomenon. Ceder, Bazant’s collaborator at MIT, showed experimentally that the discharging process goes much faster if the iron phosphate particles are coated by a thin phosphate layer. This was a very strange finding, because the phosphate layer is not itself very conductive. (Goodenough’s group at Texas had shown earlier that a coating of graphite, which is conductive, would result in a modest improvement in discharging times.) Bazant believes that the surface of an iron phosphate particle may act like a defect, which slows the propagation of an intercalation wave. The phosphate coating may somehow allow the lithium and the intercalation wave to pass through unimpeded. This hypothesis is unpublished and unproven, but, as Bazant says, “There’s no other explanation at present.”

It will be important for economic reasons to explain the fast-discharging phenomenon, because battery design is a contentious field with millions of dollars at stake. In 1997, Goodenough’s group licensed the iron phosphate technology to Hydro-Quebec in Canada, which has filed a patent infringement suit against A123 Systems, a company that was founded by engineers from MIT.

“I’d like to think that the science can be separated from the commercial applications,” Bazant says. “I don’t play favorites—I want the truth.”

“Bazant gets behaviors that are very interesting and that correspond well to the material science properties,” says Farrell, of Queensland University. “As a modeler that’s very exciting to me. The challenge is for other groups to comment critically and integrate his work into their own structural models.”

Farrell believes that mathematical models connecting the atomic scale to the particle scale, and the particle scale to the full-battery scale, will become increasingly important as new materials are developed. “At the Electrochemical Society meetings I see paper after paper of people trying different chemical structures,” he says. “I definitely don’t believe that lithium–iron phosphate is the end of the story.”

Dana Mackenzie writes from Santa Cruz, California.