Two-faced ions form a promising battery material

Electrolyte molecules that have both positive and negative charges stay in place while lithium ions move among them.

Lithium-ion batteries have seen stunning improvements in their size, weight, cost, and performance. (See PHYSICS TODAY, December 2019, page 20.) But they haven't yet reached their full potential. One of the biggest remaining hurdles has to do with the electrolyte, the material that ferries lithium ions from anode to cathode inside the battery to drive the equal and opposite flow of charge in the external circuit.

Most commercial lithium-ion batteries use organic liquid electrolytes. The liquids are excellent conductors of lithium ions, but they're volatile, flammable, and defenseless against the whisker-like lithium-metal dendrites that can grow between the electrodes and eventually short-circuit the battery. Because safety comes first, battery designers must sacrifice some performance in favor of not having their batteries explode or catch fire.

A solid-state electrolyte could solve those problems. For the past two decades, Jenny Pringle, Maria Forsyth, and colleagues at Deakin University in Melbourne, Australia, have been exploring a class of materials, called organic ionic plastic crystals (OIPCs), that could fit the bill. Now, along with research fellow Faezeh Makhlooghiazad, they've built on that work to create a new type of electrolyte material: an OIPC made of molecules that contain both positively and negatively charged components.[1]

The two-faced ions, called zwitterions (from the German word *Zwitter*, meaning "hermaphrodite"), have the advantage of being unaffected by the electric field produced by the battery's positive and negative electrodes, as shown in figure 1. As a result, they don't compete with the lithium ions flowing through the battery. Although the specific zwitterionic materials studied so far aren't quite suitable for commercial batteries, the diversity of organic molecules means that many more possibilities are available to investigate.

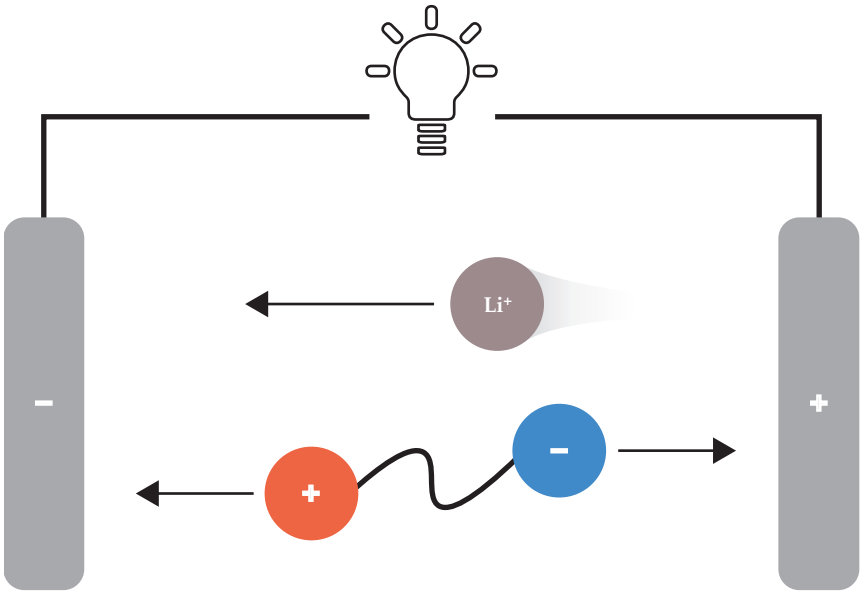

FIGURE 1. INSIDE A BATTERY, working ions, such as lithium, flow between the electrodes to counter the flow of electrons in the external circuit. If the battery electrolyte contains other charged species, they, too, can move under the battery's electric field, compete with the flow of working ions, and compromise performance. But when the electrolyte's positive and negative charges are tethered together in a single molecule, called a zwitterion, the electric forces cancel and the electrolyte molecules stay in place. (Courtesy of Jenny Pringle, adapted by Freddie Pagani.)

Plastic crystals

What kind of solid conducts ions? A perfectly ordered crystal won't do. When every site in a crystal lattice is filled, ions passing through have nowhere to move to. An ionically conductive solid therefore needs to have a disordered structure that's full of lattice dislocations and other defects along which ions can move.

In the 1970s, many researchers worked on designing defect-riddled ceramics with high ionic conductivity. (See the article by John Bates, Jia-Chao Wang, and Nancy Dudney, PHYSICS TODAY, July 1982, page 46.) The idea at the time was to create batteries with liquid electrodes—molten metal and molten salt, say—that needed a solid electrolyte to keep them physically separated.

But rigid ceramic electrolytes work far less well with the solid electrodes of today's lithium-ion batteries. As a battery is charged and discharged, its electrodes slightly expand and contract, so they'd quickly break their electrical contact with a rigid electrolyte. The ideal electrolyte should be solid but also soft enough to deform and accommodate the growing and shrinking of the electrodes.

Toward that end, Pringle, Forsyth, and colleagues embarked on their study of OIPCs.[2] Like other ionic solids, such as sodium chloride, OIPCs are made of regular arrangements of positive and negative ions. Because an OIPC's ions are polyatomic organic molecules, researchers have a lot of leeway to design their shapes and tune their properties.

An OIPC's characteristic plasticity is thought to stem from rotational disorder in the lattice. The molecular ions are rotationally asymmetric, and they needn't all be oriented the same way in their lattice sites. Rotational disorder then gives rise to positional disorder—lattice planes more easily sliding against each other, for example—which endows the mate-

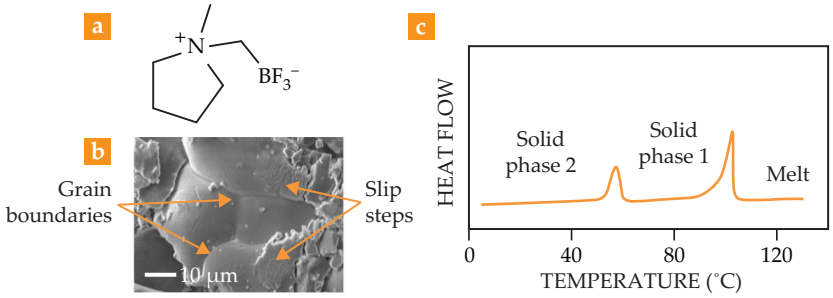

FIGURE 2. MOST ZWITTERIONS form crystalline phases that are unsuitable for solid-state battery electrolytes. But one newly synthesized zwitterion **(a)** exhibits a promising degree of disorder and plasticity. **(b)** An electron micrograph of the material shows small grains rife with defects. **(c)** A differential scanning calorimetry trace reveals a solid–solid phase transition, a known sign of an organic ionic plastic crystal. (Adapted from ref. 1.)

rial with both a network of defects for conducting ions and the malleable, waxy texture needed to maintain contact with the electrodes.

Despite 20 years of research, much about OIPCs is still unknown. The mechanism that connects the rotational and positional disorder is not well understood, and a formula to predict which combinations of ions form OIPCs and which don't is still lacking. "The challenge is in studying the disordered state," explains Pringle. Tools such as x-ray diffraction are well suited to studying crystalline structures, but when the deviation from crystallinity is the very property of interest, they're less useful. Even methods for studying noncrystalline materials, such as solid-state NMR and molecular dynamics simulations, do their best work when a crystal structure exists as a starting point.

Nevertheless, the Deakin researchers have gained some insights into how to identify an OIPC when they've made one. In particular, they've found that the OIPC phase is often associated with a solid–solid phase transition that marks the onset of rotational disorder: Below the transition temperature, the ions are more rotationally ordered; above it, they're more disordered. And phase transitions are easy to recognize with differential scanning calorimetry.

Ideally, the most disordered phase should span the range of battery operating temperatures, from room temperature up to around 100 °C. The ions, therefore, must be prone enough to disorder that they enter the OIPC phase, but not so much that the material melts.

Designing zwitterions

Some classes of OIPCs show promise as electrolytes, but they all share a common weakness. Because they're made of separate positively and negatively charged ions, the constituent ions themselves can migrate through the lattice under the battery's electric field. The migrating ions may compete with the Li^+ conductivity and compromise the electrolyte's performance.

Zwitterions could solve that problem. With positive and negative charges on the same molecule, as sketched in figure 1, they experience no net force under the battery's electric field. They've been explored before in the context of battery electrolytes, but until now only as additives to other electrolyte materials.[3] No one had ever made an electrolyte wholly or even mostly out of zwitterions.

Most known zwitterions, after all, form rigid crystals that don't conduct ions. But the known ones constitute only a tiny fraction of all possible zwitterions. Organic chemists are adept at designing and synthesizing new molecules, but they have a limited kit of tools for adding a negative charge to a molecule that's already positively charged, or vice versa. Almost all zwitterions studied so far for electrochemical applications have their negative charge on an SO_3^- group.

To broaden their horizons, the Deakin researchers turned to colleagues in industry skilled in the chemistry of boron and fluorine. Together, they developed three new zwitterions, including the one in figure 2a that they further explored, with the negative charge on a BF_3^- group. The positive charge, in each case, is spread around a ring of carbon and nitrogen atoms, an arrangement known to lend itself to rotational disorder and OIPC behavior.

The room-temperature micrograph of the zwitterionic material seen in figure 2b already shows promising signs of disorder, with small, irregular grains full of defects. And the calorimetry trace in figure 2c shows the telltale sign of a plastic crystal: a clear transition between two solid phases, tens of degrees below the melting transition.

Even so, the pure zwitterionic material is a poor electrolyte. Its ionic conductivity is less than 10^{-9} S/cm, far below the target of 10^{-4} S/cm for a solid-state electrolyte. But mixing in a small amount of lithium salt—a known trick for optimizing electrolytes—boosts the conductivity all the way to 3×10^{-6} S/cm. That's still not ideal for a real battery, but it's good enough to be tested in a model battery, which could be cycled hundreds of times without the electrolyte breaking down or losing contact with the electrodes.

Aside from the conductivity, the researchers also need to work on the temperature range of the disordered zwitterionic phase. The solid–solid phase transition lies above 50 °C, so the material isn't a plastic crystal at room temperature. But the researchers stress that they're just getting started: This is only the first of a new class of fundamentally different electrolyte materials. Now that they know how to make BF_3^--based zwitterions, they can adapt the synthesis protocol to create new zwitterionic materials and catalog their properties.

"And this isn't just about lithium," notes Pringle. Although Earth's crust has enough accessible lithium to meet humanity's energy-storage needs for the time being, stocks could run out in generations to come, and a different element may be required. Sodium, easily extractable from seawater, is a natural choice. Many OIPCs already conduct sodium ions, and there's every reason to think that a suitably chosen zwitterionic material could do the same.

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References

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2. See, for example, J. M. Pringle et al., *J. Mater. Chem.* **20**, 2056 (2010); H. Zhu et al., *Trends Chem.* **1**, 126 (2019); X. Wang et al., *Adv. Mater.* **32**, 1905219 (2020).
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