Could “disordered rock salts” bring order to next-gen lithium batteries?

Enlarge / Ordered rock crystals, courtesy of a salt mine.

reader comments

37 with 24 posters participating, including story author

Share this story

Better batteries are a critical enabling technology for everything from your gadgets all the way up to the stability of an increasingly renewable grid. But most of the obvious ways of squeezing more capacity into a battery have been tried, and they all run straight into problems. While there may be ways to solve those problems, they’re going to need a lot of work to overcome those hurdles.

Earlier this week, a paper covers a new electrode material that seems to avoid the problems that have plagued other approaches to expanding battery capacity. And it’s a remarkably simple material: a variation on the same structure that’s formed by crystals of table salt. While it’s far from being ready to throw in a battery, the early data definitely indicate it’s worth looking into further.

Lithium density

Lithium-ion batteries, as their name implies, involve shuffling lithium between the cathode and the anode of the battery. The consequence of this is that both of the

electrodes will end up needing to store lithium atoms. So most ideas for next-generation batteries involve finding electrode materials that do so more effectively.

The simplest of these is probably to use an electrode that's lithium metal. That works from a chemical perspective, as long as the reactive lithium is properly protected. But there are problems from a physical perspective: there's nothing at the electrode to structure the lithium once it comes back during a charge/discharge cycle. So the metal that re-forms tends to be uneven and spiky, and it will eventually punch through the membrane that separates the two electrodes.

An approach that works for the other electrode is to simply react the lithium with oxygen, storing it as a lithium oxide. Again, there are structural issues here with how the oxide forms. But most of the problems are chemical, as plenty of side-reactions occur—some of them with the other components of the battery—that quickly cause the capacity to drop.

So, other researchers have been focused on electrode materials that can store a lot more lithium. Various sulfur materials work, but they also tend to react in ways that reduce the capacity of the battery. Silicon is closer to chemically inert in batteries, but stuffing so much lithium into it causes it to expand dramatically (a problem with sulfur-based electrodes, too). As a result, it tends to physically break the battery unless there's some way to control this expansion.

So far, there hasn't been much discussion of materials that solve both the chemical and structural issues. But that's exactly what disordered rock salts seem to promise.

Disorderly conduct-ion

So, what exactly is a disordered rock salt? They're best understood by starting with orderly rock salts, and they're represented by crystals of sodium chloride. In these crystals,

the sodium and chloride ions form regular, orderly structures. You can think of these as a series of things like cubes or pyramids, with ions at each of the corners of the shape. This structure leaves little in the way of open space, as the ions are packed tightly and every available corner has one in it.

Disordered rock crystals have the same sort of ordered structure to their relatives but simply don't pack ions into every possible location of that structure. The precise sites that lack ions can vary, which is why they're called "disordered"—their notional structure is very ordered, but it's filled in somewhat chaotically.

So, what does this have to do with batteries? Disordered rock salts can form with some of these spaces filled by lithium ions. And it's possible to stuff some additional lithium ions into the spots within the crystal that might otherwise be unoccupied in its disordered form.

Charge and discharge

For this work, a large US-based collaboration used a material built from a combination of lithium, vanadium, and oxygen. The crystal framework has the formula V_2O5, with a variable number of lithium ions incorporated. To figure out just how many, the researchers made some of the material and charged and discharged it. Next, they imaged the material using a combination of X-ray and neutron diffraction, as well as electron microscopy. They also built a dynamic chemical model of the charge/discharge process.

As expected, the charge and discharge cycle involved shifting lithium ions into and back out of the structure. At maximum charging, the material can hold nearly five lithium ions for each V_2O5 unit. When fully emptied of lithium, it dropped to just under three lithium ions for each unit of V_2O5. Critically, since it's fitting into a very ordered structure,

the added lithium doesn’t change it much—it only expands by a total of 5.9 percent.

The process of loading and unloading lithium isn’t a static process of slotting the new ions into place. Instead, lithium will preferentially occupy some locations in the crystal, but shift to others as additional lithium ions move in and change the charge environment. In addition, the vanadium ions can change their oxidation state during this process as well.

An actual battery

The interesting thing about this shifting of charges is that it’s remarkably easy to get some of the charges back out. When the researchers built a battery using it, they found that about 40 percent of its total capacity could be discharged in just 20 seconds. And the total capacity was only slightly less than that reported for batteries that use a pure lithium-metal electrode.

Best yet, it was stable. After 1,000 charge/discharge cycles—that’s nearly three years of daily charging—it still had 87 percent of its original capacity. And they’ve sent one through 6,000 cycles and found it was still working.

The big problem with the material right now is that the Li_xV_2O5 doesn’t conduct well, meaning that the harvesting of charges needed for a functional battery doesn’t work very efficiently. The researchers suggest that it will be necessary to either dope the material with something more conductive or disrupt the rock salt with some sort of conductive material.

But that seems to be a smaller challenge than those faced by many of the alternative materials that have been considered as battery electrodes. Of course, other problems may pop up when trying to figure out how to produce something like this at scale. But the initial results suggest that someone will undoubtedly try to find out what those problems might be.

Nature, 2020. DOI: 10.1038/s41586-020-2637-6 (About DOIs).

https://arstechnica.com/?p=1703786