Why fast charging reduces the capacity of a car battery

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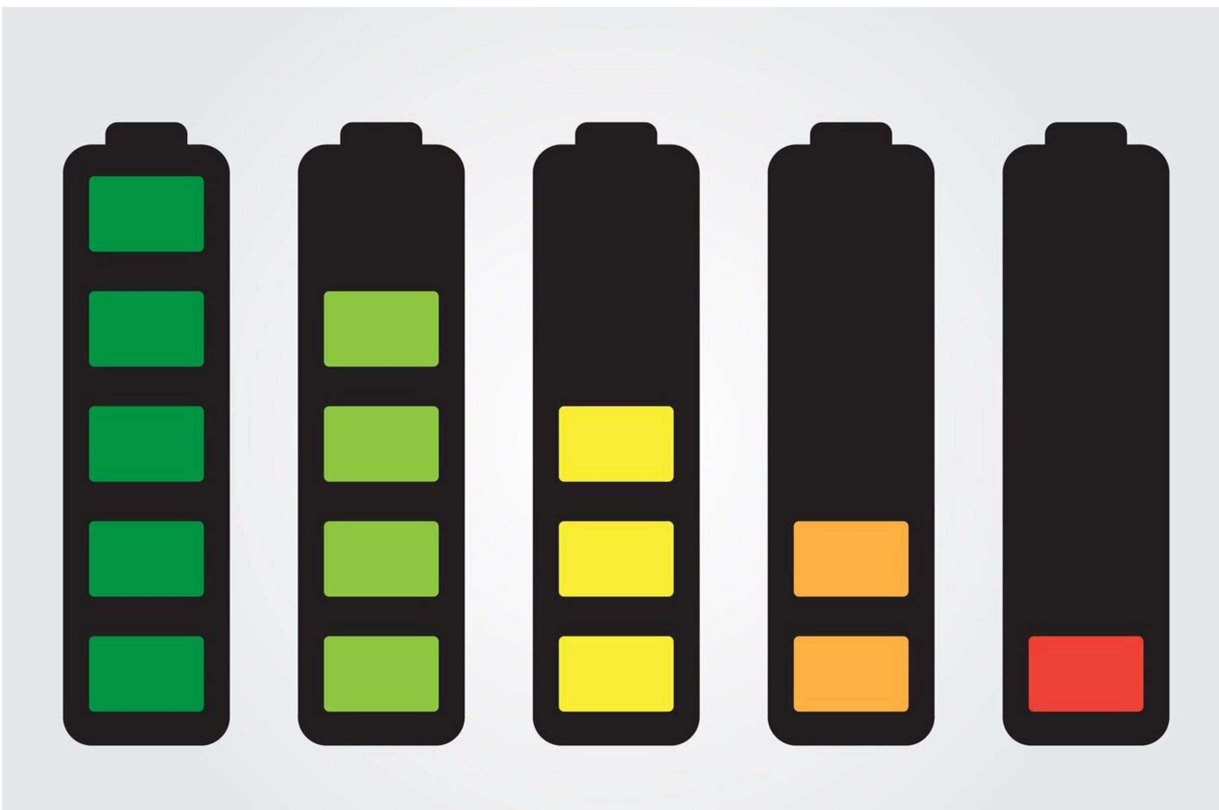

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When lithium ions are forced rapidly through a battery, they might get stuck and turn into lithium metal, no longer able to move through the battery.

Imagine being able to refuel your electric car while stopping for a quick snack or refill your phone while brushing your teeth.

"Fast charging is kind of the Holy Grail. It is what everyone who owns a lithium ion battery based device wants to be able to do," says Senior Engineer David Wragg from Centre for Materials Science and Nanotechnology at the University of Oslo.

Inside the battery, however, there is a lot of complicated chemistry that can be sensitive to how fast it is charged. Things can go wrong.

"Capacity loss is the most critical one," Wragg says to Titan.uio.no.

"It is possible to make batteries with very high capacity that might allow you to drive your electric car 1000 km, but after you've charged and discharged it a few times, you would lose about half of that capacity and range.

All rechargeable batteries deteriorate over time, but this negative effect is extra strong when the battery is subjected to fast charging. Wragg is one of the researchers behind a study that shows why.

They have been able to see that the lithium ions, which are so important for the capacity of a battery, are converted into pure lithium metal and are no longer useful. And most importantly: this effect is greatly enhanced by fast charging.

The battery is like a rocking chair

On one side of the battery is the anode, and on the other side is the cathode. Both of these electrodes can store electrons and ions. Between them is a separator and a liquid electrolyte that helps the ions from one side to the other.

Ions and electrons move from one side of the battery to the other when you use the current stored there and back again when you recharge it.

"They call this the rocking chair mechanism, where you rock the irons and the electrons from one side to the other. "

"When they're fresh and they're working perfectly, batteries can store a certain amount of ions, and that's the total capacity of the system," Wragg says.

When the ions, which used to move back and forth, turn into metal, they are no longer able to move through the battery. The ions are charged and can be lured back and forth. The metal atoms are neutral, and can not be tempted in either direction.

"Once lithium is turned into metal it's not really accessible for the electrochemical reaction anymore. This capacity is completely lost," Wragg says.

This happens in all rechargeable lithium-ion batteries when you have charged them many enough times. But why does it get worse when you charge fast?

Bottlenecks during fast charging

During fast charging, the same number of ions move through the system, but much faster. All ions must find their place in the anode in a much shorter time.

"When you charge at double speed, you have to move the same amount of ions and electrons in half the time," Wragg says.

If you charge four or six times as fast, it will naturally be even more difficult.

"It is difficult because there are certain limits on the chemistry that is going on when the you try put lithium ions into a solid electrode material really fast," Wragg says.

The anodes, which receive ions during charging, are made of graphite, which is formed of thin layers of carbon. The anode consists of several million such layers.

"Empty graphite is like a deck of cards and the lithium ions are like tiny balls getting pushed into the spaces between the cards. The problem is that you can get bottlenecks as you try to push the lithium ions between the layers in the graphite.

"You keep pushing ions in, but unless the ions that are already between the layers can push deeper into the stack there's no space for new ions to get into. When you charge the battery really fast, the lithium doesn't spread through the whole graphite electrode at all. It just gets stuck close to the electrolyte, where the anode and the cathode are separated."

It is especially here, in these bottlenecks, that the charged ions become neutral atoms and accumulate in tiny lumps of metal. The ions do not move further, at the same time as energy is applied. This excess energy may be what changes an ion into a neutral and stable atom.

"It is called lithium plating. That is when lithium ions, instead of staying in the ionic form, turn into lithium metal. This has been known for quite a long time, but it's not really been observed in a working battery before," Wragg says.

This, however, Wragg and his colleagues have managed to do. Using X-rays, they scanned batteries every 25 milliseconds, over and over again while rapidly charging at different rates. This gave them huge amounts of data about what is happening right down to the atomic level.

"We could actually see the lithium plating building up. During fast charging we could see the amount of lithium increasing really fast. Our theory is that it has something to do with this bottleneck of lithium ions. We see a lot of lithium ions close to the separator and this is also where we see the lithium plating," Wragg says.

"The most likely thing is you get these lithium ions building up and they just can't get to the graphite anymore. They get stuck there and there's a lot of heat, a lot of energy being put into them, and so they get reduced to lithium metal."

They saw how the graphite layers closest to the other electrode were very rich in lithium, while deeper into it there was almost no lithium at all. It got worse the faster they charged.

"The faster you push it, the faster the plating occurs," Wragg says.

The future: nanotubes and graphene?

The study is by no means the end of fast charging. It just means that researchers must find new and better solutions.

"The key thing from this is for people who make batteries to try and work out ways to improve the lithium transport so that when you're charging fast, there's more chance for the lithium to actually get through to the whole of the graphite anode," Wragg says.

Researchers around the world are looking for new materials and methods that can make batteries withstand fast charging better.

"For example, there are a lot of people using carbon nanotubes. Carbon nanotube is what you get if you take one of the cards and curl it around into a tube. It's like a graphite that's been formed into tubes rather than a bit flat."

Wragg and colleagues at the University of Oslo are working with graphene, single sheets of graphite, in the anode.

"Graphite has been known for hundreds of years. Graphene and carbon nanotubes have been known for about 30 years, so it takes time."

So far, none of these innovations have appeared in commercial batteries.

"But it will happen, no doubt," Wragg says.

More information: Donal P. Finegan et al, Spatial dynamics of lithiation and lithium plating during high-rate operation of graphite electrodes, *Energy & Environmental Science* (2020). DOI: 10.1039/d0ee01191f

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