Tortuous paths hamper ion transport

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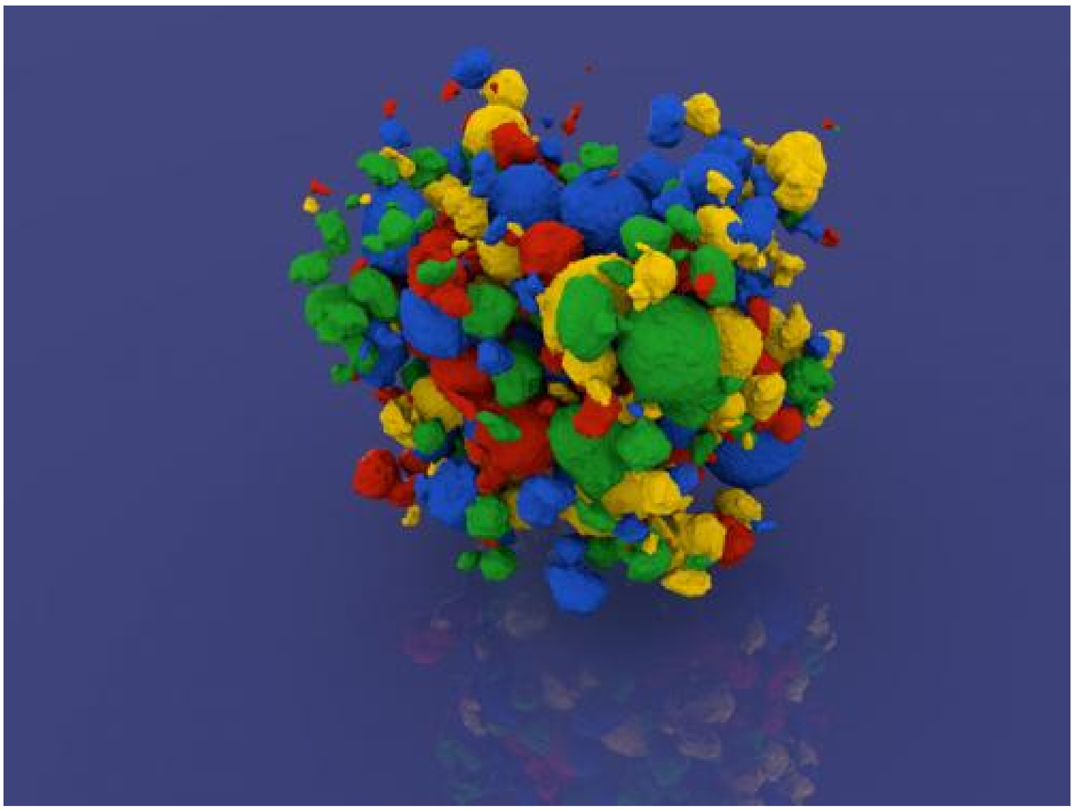

Electrodes of Lithium ion batteries are composed of various particles of different shapes and sizes. These particles have a strong influence on how fast ions flow through the electrode. Credit: Martin Ebner / ETH Zurich

(Phys.org) —ETH-Zurich researchers use x-ray tomography to screen lithium ion battery electrodes and can reconstruct the microstructure in high resolution. This helps to understand the discharging and charging process better and develop optimised electrodes.

Mobile phone batteries that last longer, car batteries that enable you to drive further, storage that accumulates a lot of energy from wind and solar generators: many applications require better batteries. The research essentially focuses on three aspects here: researchers want to increase the energy density – in other words store more energy in a smaller battery. They are also looking to improve the discharging and charging speed by changing and controlling the material, shape and size of the electrochemically active particles and the structure of the battery electrodes in a targeted fashion. And scientists are working on the durability of the battery in general by trying to understand the degradation mechanisms that shorten the life of batteries. Martin Ebner, a doctoral student from the group headed by Vanessa Wood, a professor at the Department of Information Technology and Electrical Engineering , has been examining the issue of the discharging and charging speed. In order to understand what influences it, he has been researching the microstructure of the electrodes of commercially available and home-made lithium ion batteries. Knowing this also enables us to understand the charging and discharging mechanism better and endeavour to produce optimised electrodes with more efficient batteries in mind.

Hard-to reach microstructure scanned

"Until now, the microstructure has been neglected in battery research because it was difficult to access experimentally," says Ebner. He has managed able to fill this gap with the aid of synchrotron radiation x-ray tomography and Professor Marco Stampanoni's group, which specialises in working with this particular radiation.

"This radiation, which can be produced at the Swiss Light Source at the Paul Scherrer Institute, is very bright and spectrally pure. This allows many high-resolution experiments in a short space of time," says Ebner. It only took around five minutes to study a sample on the TOMCAT beamline as opposed to up to five hours on conventional devices. This meant that Ebner could x-ray many electrode material samples produced under different conditions.

Using the hundreds of gigabytes of data that the x-ray tomography generated, the electroengineer was ultimately able to reconstruct the three-dimensional electrode structure. His paper was recently published in the journal *Advance Energy Materials* and the raw data of the sixteen cathodes studied deposited in a freely accessible open-source database.

Small particles on boundary layer

The computer reconstructions reveal that the electrodes comprise numerous particles of different shapes and sizes. While smaller particles appear on the edge of the cathode, larger ones are mostly present in the interior. Moreover, Ebner was also able to demonstrate that some particles can break under very high pressure during production. While this does not have much of an impact on the electrochemistry of the battery, it needs to be taken into consideration when simulating it on the computer, he stresses.

The size, distribution and configuration of the particles, however, have a major influence on a battery's discharging and charging speed. Smaller particles form a compact structure while the structure in large particles tends to be looser and thus provide more pore space. The porosity of the material ultimately determines the battery's energy density and the speed at which the lithium ions surge through the electrodes during charging or discharging.

The flow behaviour of the lithium ions can be described by what is known as tortuosity – the value that indicates the degree of a structure's twistedness. To put it simply, the more twisted the path of the ions through the electrode, the more slowly the battery is charged or discharged and the greater the tortuosity.

Graphite plates hamper ion flow

While round to potato-shaped particles mostly have a positive influence on flow, plate-like ones such as those in the anode, the negative pole, provide unfavourable conditions for rapid charge transport. A lithium battery's anode is mostly made of graphite. This highly conductive material consists of wafer-thin plates that lie on top of one another like roof tiles. Depending on the direction from which the ions hit the graphite plates, the tortuosity can be very high. In order to flow around the tiles, long paths are required, which vastly reduces the discharging and charging speed. Lengthwise, however, the lithium ions cross the graphite without any major detours. The analyses reveal that graphite electrodes already exhibit direction-dependent differences in path length of over 300 per cent with a porosity of forty per cent.

The tortuosity of graphite electrodes might be improved through the use of round graphite particles. The drawback here is that up to seventy per cent of the valuable raw material is wasted during production – one reason why many battery manufacturers still use plate-shaped graphite as an anode material.

Optimising established technique

Lithium ion batteries have been in use with more or less the same base materials since the 1980s. The materials can be processed industrially in large quantities and alternatives that are commonly found as raw materials on Earth are gradually catching on. In the long run, researchers want to understand how the microstructure of the electrodes is formed and how you can influence it positively. One idea is to rely on the self-organisation of the materials used. However, the criterion is and will remain whether the method is feasible and affordable for industry. "We mustn't forget that a battery is a mass product that needs to be producible in large quantities," says Ebner.

More information: Ebner, M. et al. X-Ray Tomography of Porous, Transition Metal Oxide Based Lithium Ion Battery Electrodes. *Advanced Energy Materials* 2013. Article first published online: 13 MAR 2013. DOI: 10.1002/aenm.201200932

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